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Synthesis of hydrofluoroethers (HFEs) as alternatives to CFCs

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Abstract

A facile synthetic route for the preparation of a series of hydrofluoroethers (HFEs) was developed. This route was based on two key reactions. The first reaction involved the alcoholysis of various fluoroalcohols with *p*-toluenesulfonyl chloride in a sodium hydroxide solution, while the second involved the Williamson ether syntheses of the desired HFEs from the corresponding tosylates using sodium methoxide in methanol. As a result, a range of HFEs were synthesized using this mild and efficient method.

Keywords: hydrofluoroethers • alcoholysis • Williamson ether synthesis

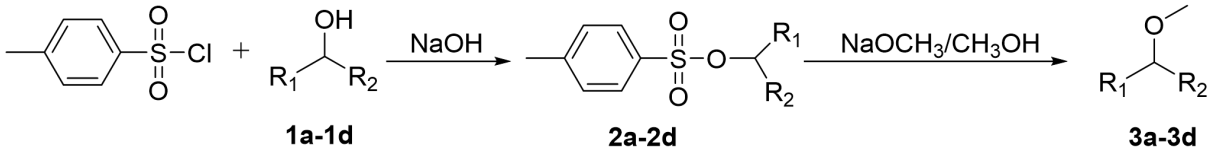
1. Introduction

Owing to the implementation of the Montreal Protocol, the use of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) has been discontinued due to their high ozone depletion potentials (ODP) and high global warming potentials (GWP). Thus, as a potential

substitute for CFCs and HCFCs, hydrofluoroethers (HFEs) have recently been considered, as they exhibit no ozone depletion potential and have relatively short atmospheric lifetimes [1–3].

To date, HFEs have been synthesized via two key methods. The first of these methods involves the fluorination of ethers with reagents such as F_2, HF, or metal fluorides (e.g., SbF_5, CoF_3, or MnF_3) [4–7]. However, the use of such fluorinating reagents has a number of disadvantages. For example, F_2 exhibits a particularly high reactivity but poor selectivity towards the target product, while the use of metal fluoride reagents is limited due to their high costs. The second route towards HFEs involves the fluorinated block method, i.e., the addition reaction between hydrofluoroolefins (HFOs) and alcohols, an elimination reaction between alkyl halides and alcohols, and the alkylation of fluorinated carbonyl compounds [8–19]. However, the above methods also have a number of disadvantages. More specifically, although the preparation of HFEs by the addition of alcohols and olefins using relatively mild reaction conditions and a simple separation method is convenient, strong bases are required as catalysts, thereby resulting in a number of post-processing problems. In addition, the elimination reaction between alkyl halides and alcohols requires harsh reaction conditions and tends to provide the desired products in low yields. Furthermore, although the generation of HFEs through the alkylation of fluorinated carbonyl compounds gives good yields, this method requires the use of expensive raw materials.

Thus, we herein report the development of a facile synthetic route for the preparation of a series of HFEs from fluoroalcohols (Scheme 1). This process contains two key steps, namely esterification of the fluoroalcohol (**1**) by *p*-toluenesulfonyl chloride (TsCl) to generate the intermediate tosylate (**2**) [20,21], and subsequent reaction of this tosylate with $NaOCH_3$ in methanol to produce the desired HFE (**3**). The reaction parameters for the preparation of a range of HFEs are also optimized.



a:R_1=CF_3CH-, R_2=H
b:R_1=CF_2HCH-, R_2=H
c:R_1=CF_2HCF_2CH-, R_2=H
d:R_1=R_2=-CF_3

Scheme 1. The proposed two-step route for the preparation of HFEs.

2. Results and discussion

The synthesis of a range of HFEs (**3a–3d**) from various fluoroalcohols (**1a–1d**) was investigated as outlined in Scheme 1, during which optimization of the reaction temperature, stoichiometry, and sodium hydroxide concentration was carried out. Each stage in the reaction will now be examined individually.

2.1. Synthesis of tosylated intermediates 2a–2d

The influence of reaction temperature, stoichiometry, and sodium hydroxide concentration on the alcoholysis of fluoroalcohols (**1a–1d**) with TsCl was initially examined and the results are presented in Tables 1–3.

As indicated in Table 1, the yields of all tosylate intermediates **2a–2d** increased upon increasing the reaction temperature from 0 to 20 °C, but decreased upon increasing the temperature further to 30 °C. We expect that this was due to hydrolysis of the intermediates at higher temperatures, and so an optimal temperature of 20 °C was selected for subsequent experiments.

Table 1. Effect of reaction temperature on the yields of tosylate intermediates 2a–2d[a]

Temperature (°C)	yield of **2a** (%)[b]	yield of **2b** (%)[b]	yield of **2c** (%)[b]	yield of **2d** (%)[b]
0	85.1	87.2	81.5	76.4
10	87.9	91.8	86.1	83.2
20	96.1	97.3	94.1	95.1
30	91.1	90.2	89.4	85.9

[a]Reaction conditions: Molar ratio of TsCl to **1a–1d** = 1:1; NaOH concentration = 20 wt%; reaction time = 2 h.

[b]The yields of intermediates **2a–2d** were determined by GC versus a calibrated internal standard.

We then investigated the effect of the molar ratio of TsCl to the starting fluoroalcohols (**1a–1d**), as outlined in Table 2. In this case, an increase in the molar ratio from 1:1 to 1.1:1 (TsCl:**1**) produced significantly enhanced yields of **2a–2d**; however, further increases to 1.2:1 and 1.3:1 had only a minor effect on the obtained yields. Thus, a TsCl to fluoroalcohol ratio of 1.1:1 was selected for further experiments.

Table 2. Effect of TsCl:fluoroalcohol ratio on the yields of intermediates 2a–2d[a]

TsCl:**1a–1d**	yield of **2a** (%)[b]	yield of **2b** (%)[b]	yield of **2c** (%)[b]	yield of **2d** (%)[b]
1:1	83.2	88.8	82.1	76.9
1.1:1	96.1	97.3	94.1	95.1
1.2:1	96.2	97.9	95.3	95.2
1.3:1	97.1	96.9	95.4	96.3

[a]Reaction conditions: Reaction temperature = 20 °C; NaOH concentration = 20 wt%; reaction time = 2 h.

[b]The yields of intermediates **2a–2d** were determined by GC versus a calibrated internal standard.

Finally, we examined the effect of NaOH concentration of the yields of intermediates **2a–2d**. As indicated in Table 3, an increase in the NaOH concentration from 10 to 20 wt% produced a slight increase in yield for all intermediates. However, at a higher NaOH concentration of 25 wt%, the corresponding yields decreased once again, likely due to the hydrolysis of these intermediates at high NaOH concentrations. We therefore selected the NaOH concentration of 20 wt% as the optimal condition for this reaction.

Table 3. Effect of NaOH concentration on the yields of intermediates 2a–2d[a]

NaOH (wt%)	yield of **2a** (%)[b]	yield of **2b** (%)[b]	yield of **2c** (%)[b]	yield of **2d** (%)[b]
10	95.1	96.7	91.3	88.2
15	96.3	97.1	91.3	93.5
20	96.1	97.3	94.1	95.1
25	90.4	89.4	87.2	84.1

[a]Reaction conditions: Molar ratio of TsCl to **1a–1d** = 1.1:1; reaction temperature 20 °C; reaction time = 2 h.

[b]The yields of intermediates **2a–2d** were determined by GC versus a calibrated internal standard.

Thus, based on the above results, we could conclude that the optimal conditions for the initial transformation were as follows: reaction temperature = 20 °C, TsCl:fluoroalcohol molar ratio = 1.1:1, NaOH concentration = 20 wt%, and reaction time = 2 h.

2.2. Synthesis of HFE products 3a–3d

With the required tosylated intermediates **2a–2d** in hand, we moved on to examine the effect of reaction temperature, reaction solvent, and stoichiometry on the subsequent Williamson ether syntheses of HFEs **3a–3d** in the presence of $NaOCH_3$.

As indicated in Table 4, an increase in the reaction temperature from 10 to 25 °C produced higher yields of the target HFEs, although no further increases were observed upon increasing the temperature from 25 to 65 °C. These results indicate that the effect of temperature was insignificant in the reaction between a strongly nucleophilic methoxy anion and a good tosyl leaving group. We therefore selected a temperature of 25 °C for subsequent reactions.

Table 4. Effect of reaction temperature on the yields of HFEs 3a–3d[a]

temperature (°C)	yield of **3a** (%)[b]	yield of **3b** (%)[b]	yield of **3c** (%)[b]	yield of **3d** (%)[b]
10	75.1	69.8	72.2	78.1
25	79.2	74.1	76.3	80.7
45	80.2	73.3	75.1	79.9
65	81.1	75.3	75.9	81.1

[a]Reaction conditions: Molar ratio of $NaOCH_3$ to **2a–2d** = 1.2:1; reaction solvent = methanol; reaction time = 4 h.

[b]The yields of HFEs **3a–3d** were determined by GC versus a calibrated internal standard.

We then examined the effect of the reaction solvent on this transformation, as outlined in Table 5. At a reaction temperature of 25 °C, methanol gave higher yields of **3a–3d** than ethanol. However, the reaction was unsuccessful in polar aprotic solvents, such as acetonitrile and dichloromethane, likely due to the poor solubility of $NaOCH_3$ in these solvents.

Table 5. Effect of reaction solvent on the yields of HFEs 3a–3d[a]

solvent	yield of **3a** (%)[b]	yield of **3b** (%)[b]	yield of **3c** (%)[b]	yield of **3d** (%)[b]
methanol	79.2	74.1	76.3	80.7
ethanol	75.4	72.6	70.7	77.3
dichloromethane	0	0	0	0
acetonitrile	0	0	0	0

[a]Reaction conditions: Molar ratio of $NaOCH_3$ to **2a–2d** = 1.2:1; reaction temperature = 25 °C; reaction time = 4 h.

[b]The yields of HFEs **3a–3d** were determined by GC versus a calibrated internal standard.

Finally, we investigated the effect of the reaction stoichiometry (i.e., the $NaOCH_3$: **2a–2d** molar ratio) on the yields of HFEs **3a–3d**. As shown in Table 6, increased yields were obtained upon increasing the molar ratio from 1:1 to 1.2:1, although no significant increase was observed at higher molar ratios. We therefore selected a molar ratio of 1.2:1 as the optimal condition for this reaction.

Table 6. Influence of NaOCH3:2a–2d molar ratio on the yields of HFEs 3a–3d[a]

$NaOCH_3$:**2a–2d**	yield of **3a** (%)[b]	yield of **3b** (%)[b]	yield of **3c** (%)[b]	yield of **3d** (%)[b]
1:1	58.4	63.2	59.3	67.1
1.1:1	66.2	71.2	68.4	75.2
1.2:1	79.2	74.1	76.3	80.7
1.3:1	80.1	74.3	77.2	80.4

[a]Reaction conditions: Reaction solvent = methanol; reaction temperature = 25 °C; reaction time = 4 h.

[b]The yields of HFEs **3a–3d** were determined by GC versus a calibrated internal standard.

Based on the above results, we could therefore conclude that the optimal conditions for the Williamson ether syntheses of HFEs **3a–3d** from tosylated intermediates **2a–2d** were as

follows: reaction temperature = 25 °C, $NaOCH_3$:**2a–2d** molar ratio = 1.2:1, reaction solvent = methanol, and reaction time = 4 h.

3. Conclusions

We herein reported a novel and facile synthetic route for the preparation of hydrofluoroethers (HFEs) from a range of substituted fluoroalcohols. In the initial stage of this transformation, the alcoholysis of these fluoroalcohols with *p*-toluenesulfonyl chloride (TsCl) in a 20 wt% sodium hydroxide solution produced the desired tosylated intermediates in yields >94% at 20 °C over 2 h when a TsCl to fluoroalcohol molar ratio of 1.1:1 was employed. In the subsequent Williamson ether syntheses of the desired HFEs from the tosylated intermediates, product yields >74% were obtained in methanol at 25 °C over 4 h when a $NaOCH_3$ to tosylated intermediate molar ratio of 1.2:1 was employed. We could therefore conclude that a highly efficient method for the synthesis of a range of HFEs under mild conditions has been developed. This result is of particular importance for replacing ozone-depleting and global warming-promoting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) with the more environmentally friendly HFEs. The research for the flammability, the environmental safety and the synthesis of the Freon alternatives will continue in our work. It will provide more technical support for the application and popularization of the substitute.

4. Experimental

4.1. Chemicals

1,1,1,3,3,3-Hexafluoropropan-2-ol (HFiP) (>99.7%) was purchased from Sinochem Lantian Co., Ltd. (China). 2,2,2-Trifluoroethan-1-ol (99.0%), 2,2-difluoroethan-1-ol (>99.0%), 2,2,3,3-tetrafluoropropan-1-ol (>99.0%), *p*-toluenesulfonyl chloride (TsCl, >99.0%), deuterated chloroform ($CDCl_3$, 99.8 atom%) and sodium methoxide (99.0%) was purchased from Aladdin Co., Ltd. (China).

4.2. Instruments and apparatus

Mass spectrometry was carried out on a GC-MS-7890B/ 5977A instrument (Agilent) using the following column temperature program: 60 °C for 5 min, heat to 220 °C at a rate of 10 °C/min, hold for 8 min. The temperatures of the injection port and the hydrogen flame

ionization detector (FID) were maintained at 240 °C, and the He carrier gas was introduced at a rate of 10 mL/min.

Gas chromatography was carried out on a GC-2014C instrument (Shimadzu) equipped with a DB-VRX capillary column (i.d. 0.32 mm; length 60 m; J & W Scientific Inc.), and the column temperature program employed was as follows: 60 °C for 5 min, heat to 220 °C at a rate of 10 °C/min, hold for 8 min. The temperatures of the injection port and the hydrogen FID were maintained at 240 °C, and the He carrier gas was introduced at a rate of 10 mL/min.

All ^{13}C NMR, ^{1}H NMR, and ^{19}F NMR spectra of the intermediates and products were recorded on a Bruker AVANCE HD 600 MHz NMR spectrometer in $CDCl_3$ at 25 °C.

4.3. General methods

4.3.1. Preparation of intermediates 2a–2d

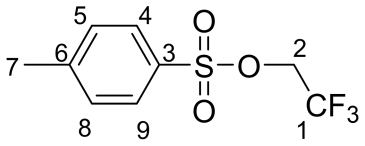
TsCl and the desired fluoroalcohol (**1a–1d**, 1 mol, TsCl : fluoroalcohol ratio = 1:1, 1.1:1, 1.2:1, or 1.3:1) were placed in a 500 mL three-necked round-bottomed flask equipped with a thermometer and an agitating device. The flask was dipped into an oil bath and heated to the desired reaction temperature (0, 10, 20, or 30 °C). Following the dropwise addition of a sodium hydroxide solution (10, 15, 20, or 25 wt%), the resulting mixture was stirred for 2 h at the previously defined temperature. After this time, the reaction mixture was allowed to separate, and the organic phase was washed with brine (3 × 50 mL) prior to drying in a vacuum oven to give the desired intermediates **2a–2d**. Results of the optimization reactions can be found in Tables 1–3.

4.3.2. Preparation of HFEs 3a–3d

$NaOCH_3$ and the synthesized intermediate (**2a–2d**, 0.5 mol, $NaOCH_3$: intermediate ratio = 1:1, 1.1:1, 1.2:1, or 1.3:1) were placed in a 500 mL three-necked round-bottomed flask equipped with a thermometer and an agitating device. After the addition of the desired organic solvent (methanol, ethanol, dichloromethane, or acetonitrile, 200 mL), the reaction mixture was stirred for 4 h at the desired temperature. The desired products **3a–3d** were then obtained by distillation. Results of the optimization reactions can be found in Tables 4–6.

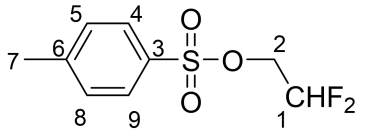
4.4. Analytical results for the intermediates and the HFEs

4.4.1. 2,2,2-Trifluoroethyl tosylate (2a)



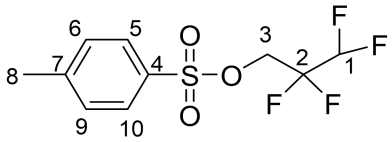
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.43 (d, 3H, CH_3), 3.78 (q, 2H, J = 8.7 Hz, CH_2), 7.48 (d, 2H, J = 8.1 Hz, CH), 7.76 (d, 2H, J = 8.2 Hz, CH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.3 (s, C-7), 60.8 (s, C-2), 120.2 (q, J = 278.4 Hz, C-1), 124.0 (s, C-4 and C-9), 130.5 (s, C-5 and C-8), 140.3 (s, C-6), 144.6 (s, C-3). ^{19}F NMR (565 MHz, $CDCl_3$): δ −77.54 (t, 3F, J = 7.6 Hz, CF_3).

4.4.2. 2,2-Difluoroethyl tosylate (2b)



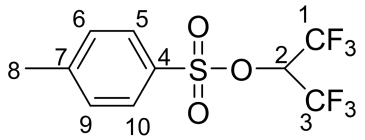
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 3.82 (t, J = 14.8 Hz, 2H, CH_2), 5.86 (t, 1H, J = 55.6 Hz, CHF_2), 7.46 (d, 2H, J = 8.1 Hz, CH), 7.74 (d, 2H, J = 8.2 Hz, CH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.6 (s, C-7), 62.8 (m, C-2), 114.8 (t, J = 240.5 Hz, C-1), 128.6 (s, C-4 and C-9), 130.8 (s, C-5 and C-8), 140.2 (s, C-6), 144.2 (s, C-3). ^{19}F NMR (565MHz, $CDCl_3$): δ −128.12 (m, 2F, CF_2H).

4.4.3. 2,2,3,3-Tetrafluoropropyl tosylate (2c)



^{1}H NMR (600 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 3.96 (t, 2H, J = 13.3 Hz, CH_2), 5.92 (m, 1H, CF_2H), 7.46 (d, 2H, J = 8.1 Hz, CH), 7.74 (d, 2H, J = 8.1 Hz, CH). ^{13}C NMR (150M Hz, $CDCl_3$): δ 21.2 (s, C-8), 59.8 (t, J = 27.8 Hz, C-3), 109.2 (tt, J_1 = 249 Hz, J_2 = 36.3 Hz, C-2), 115.2 (tt, J_1 = 248.7 Hz, J_2 = 27.5 Hz, C-1), 128.4 (s, C-5 and C-10), 130.6 (s, C-6 and C-9), 140.2 (s, C-7), 144.4 (s, C-4). ^{19}F NMR (565 MHz, $CDCl_3$): δ −127.13 (d, 2F, J = 3.0 Hz, CF_2), −138.92 (d, 2F, J = 53.2 Hz, CF_2H).

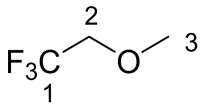
4.4.4. 1,1,1,3,3,3-Hexafluoropropan-2-yl tosylate (2d)



^{1}H NMR (600 MHz, $CDCl_3$): δ 2.48 (s, 3H, CH_3), 5.27 (m, 1H, CH), 7.39 (d, 2H, J = 8.1 Hz, CH), 7.83 (d, 2H, J = 8.2 Hz, CH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.8 (s, C-8), 71.9 (m, C-2), 120.8 (m, C-1 and C-3), 128.2 (s, C-5 and C-10), 130.2 (s, C-6 and C-9), 131.9 (s, C-7), 146.6 (s, C-4). ^{19}F NMR

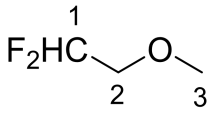
(565 MHz, $CDCl_3$): δ −73.15 (d, 6F, J = 6.0 Hz, CF_3).

4.4.5. 1,1,1-Trifluoro-2-methoxyethane (3a)



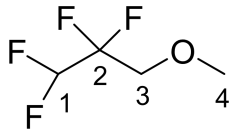
Colorless liquid, b. p. 29.7–31.5 °C (760 mmHg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.51 (s, 3H, CH_3), 3.77 (q, 2H, J = 8.8 Hz, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): δ 60.2 (s, C-3), 69.8 (s, C-2), 124.2 (q, J = 279.6 Hz, C-1). ^{19}F NMR (565 MHz, $CDCl_3$): δ −74.35 (t, 3F, J = 8.8 Hz, CF_3). GC-MS, 70 eV, *m/z* (rel. int.): 114 (1) $[M]^+$, 95 (3) $[M\text{-}F]^+$, 83 (23) $[M-OCH_3]^+$, 69 (21) $[M-CH_2OCH_3]^+$, 45 (100) $[M-CF_3]^+$.

4.4.6. 1,1-Difluoro-2-methoxyethane (3b)



Colorless liquid, b. p. 48.1–49.5 °C (760 mmHg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.44 (s, 3H, CH_3), 3.76 (t, 2H, J = 14.8 Hz, CH_2), 5.82 (t, 1H, J = 55.6 Hz, CF_2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 59.8 (s, C-3), 62.1 (m, C-2), 114.8 (t, J = 240.5 Hz, C-1). ^{19}F NMR (565 MHz, $CDCl_3$): δ −126.24 (m, 2F, CF_2H). GC-MS, 70 eV, *m/z* (rel. int.): 96 (3) $[M]^+$, 77 (18) $[M\text{-}F]^+$, 65 (7) $[M-OCH_3]^+$, 45 (100) $[M-CF_2H]^+$.

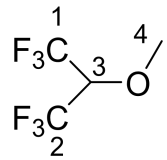
4.4.7. 1,1,2,2-Tetrafluoro-3-methoxypropane (3c)



Colorless liquid, b. p. 57.1–58.6 °C (760 mmHg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.46 (s, 3H, CH_3), 3.92 (t, 2H, J = 13.8 Hz, CH_2), 5.96 (m, 1H, CF_2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 59.4 (s, C-4), 60.8 (t, J = 27.8 Hz, C-3), 109.8 (tt, J_1 = 246.8 Hz, J_2 = 34.2 Hz, C-2), 114.6 (tt, J_1 = 244.8 Hz, J_2 = 31.2 Hz, C-1). ^{19}F NMR (565 MHz, $CDCl_3$): δ −125.3 (d, 2F, J = 3.0 Hz,

CF_2), −136.1 (d, 2F, J = 53.2 Hz, CF_2H). GC-MS, 70 eV, *m/z* (rel. int.): 146 (2) $[M]^+$, 127 (15) $[M\text{-}F]^+$, 115 (2) $[M-OCH_3]^+$, 131 (3) $[M-CH_3]^+$, 95 (100) $[M-CF_2H]^+$.

4.4.8. 1,1,1,3,3,3-Hexafluoro-2-methoxypropane (3d)



Colorless liquid, b. p. 50.1–51.5 °C (760 mmHg). ^1H NMR (600 MHz, $CDCl_3$): δ 3.73 (s, 3H, CH_3), 3.93 (m, 1H, CH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 62.5 (s, C-4), 77.8 (m, C-3), 121.1 (m, C-1 and C-2). ^{19}F NMR (565 MHz, $CDCl_3$): δ −74.37 (d, 6F, J = 6.0 Hz, CF_3). GC-MS, 70 eV, *m/z* (rel. int.): 182 (4) $[M]^+$, 163 (15) $[M-F]^+$, 151 (1) $[M-OCH_3]^+$, 113 (100) $[M-CF_3]^+$.

Acknowledgments

We thank Shengnan and Lijiao for their help and comments in using GC-MS and NMR.

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