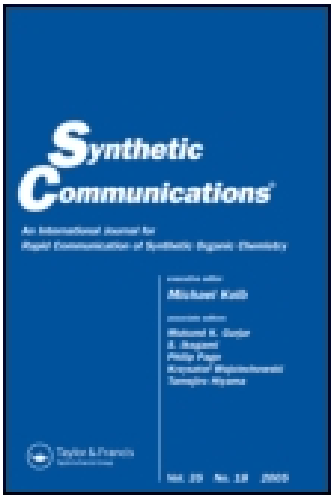

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DIRECT PERFLUORINATION OF AN ACID-SENSITIVE GLYCOL ETHER AS PRECURSOR FOR PERFLUORO(2-(METHOXYMETHOXY)ETHYL VINYL ETHER)

Hongle Liu,[1] Xusong Pan,[1] Lihua Yuan,[1] Shuliang Zou,[1] Peishen Li,[1] Wei Wang,[1] Youzhou He,[1] Wen Feng,[1] Xiaoyong Yang,[2] Kai Luo,[2] and Yong Wu[2]

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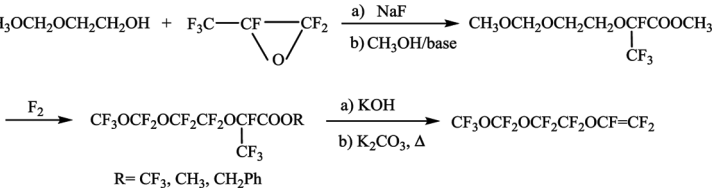
GRAPHICAL ABSTRACT



Abstract *A four-step approach to perfluoro(2-(methoxymethoxy)ethyl vinyl ether) **5** from an acid-sensitive glycol ether **3** by liquid-phase direct fluorination (DF) has been described. The perfluoro precursor was achieved by control of the gradient increase of temperature (−20 °C to 15 °C) and addition of sodium fluoride. Improved workup with benzyl alcohol provided a convenient method for purification and a practical means for tracing the progress of fluorination.*

Keywords Acid-sensitive glycol ether; fluorination; perfluoro-vinyl ether

INTRODUCTION

Perfluorocarbon vinyl ethers are important compounds for use as monomers for preparing lubricants,[1] fluoroelastomers[2,3] and other thermally and chemically resistant materials especially in medical and electronic applications.[4] Various strategies have been developed for the synthesis of perfluorinated compounds, including

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the use of perfluorinated acyl fluoride R_fCOF and hexafluoropropylene oxide,[5] utilization of perfluoroalkyl-hypofluorites R_fOF as intermediates,[6] and application of the bis(fluoroxy)difluoromethane (BDM) chemistry starting from $CF_2(OF)_2$.[7]

One of the most commonly applied processes to prepare perfluorovinyl ethers involves synthesis of a hydrocarbon precursor, fluorination, conversion of the perfluorinated intermediate to its carboxylic acid metal salt (or acyl fluoride), and pyrolysis[8] to its perfluorovinyl ether. The fluorinated starting materials used in the synthetic approaches were usually prepared by either direct fluorination (DF)[9] or electrochemical fluorinaton (ECF). Among the documented perfluorocarbon vinyl ethers $R_fOCF{=}CF_2$(R_f = perfluoroalkyl, perfluoroaromatic, or derivative moiety containing ether linkage),[5–8,10–13] the compound with the formula of $CF_3O(CF_2O)_n$-R_f-$OCF{=}CF_2$ (R_f = perfluoroalkyl) is more intriguing because of the high density of ether linkages (the lower C/O ratio) embedded along the molecule chain and absence of branches. For example, fluoroelastomers with a lower Tg could be prepared from polymerization of this monomer.[1]

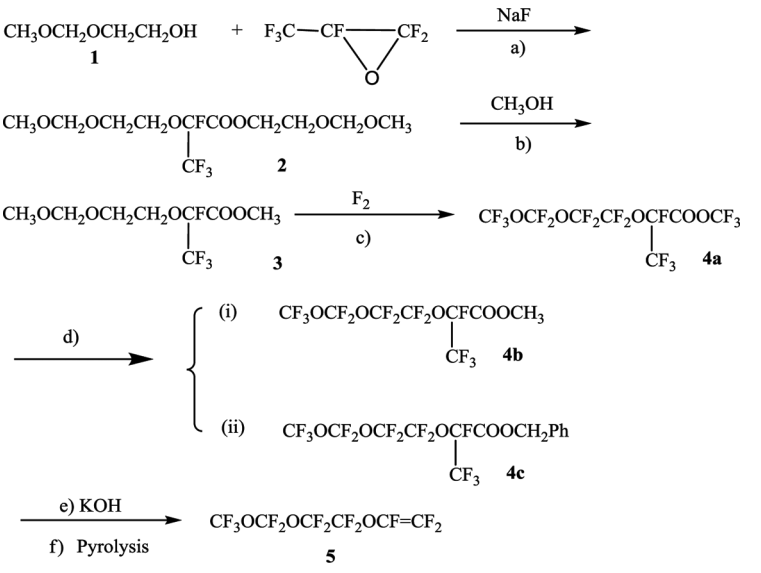
Although a perfluorinated acyl fluoride containing one 2-alkoxy propionate moiety, such as $CF_3OCF_2OCF_2CF_2OCF(CF_3)COF$, could be pyrolyzed to afford the perfluorovinyl ether, the preparation of the acyl fluoride precursor involved photo-oxidation of perfluoroolefins, such as tetrafluoroethylene or hexafluropropene,[13,14] or electrochemical fluorination of the hydrocarbon carboxylic acid analogs. The potential danger and handling of intermediates in the reaction,[15] as well as transportation of a huge amount of perfluo-olefins such as tetrafluoroethylene, made the process somewhat cumbersome and impractical in some regions for large-scale production. In spite of the new approaches,[6,7] a simple and improved process is still in demand for preparing these perfluorovinyl ethers.

The difficulty in directly fluorinating vinyl ethers containing the CH_3OCH_2O-(MOM) group is the high sensitivity of the MOM group in the reaction environment. Herein we report the successful direct fluorination of the acid-sensitive glycol ether **3** in gas–liquid (F_2/Freon 113) media with gradient increase of temperature for preparing the precursor of perfluoro(2-(methoxymethoxy)ethyl vinyl ether) **5**.

RESULTS AND DISCUSSION

The monoprotected glycol **1** was readily prepared according to the reported procedure.[16] Reaction of **1** with hexafluoropropylene oxide (HFPO) in the presence of NaF proceeded smoothly to the ester **2** in 70% yield. Transesterification efficiently converted **2** into the partially fluorinated methly ester **3** in good yield (90%) with metal alkoxide or metal salt of alcohol, such as NaOH or MeONa. Preferably the use of MeONa could facilitate the reaction and bring the reaction to completion in a shorter time (<8 h) compared to NaOH (ca. 20 h). Conversion of **2** to **3** in step b (Scheme 1) is worthwhile for more cost-effective fluorination in the next step. Fluorination of **3** in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) was performed using fluorine diluted with nitrogen (10%). Although the use of this fluorinated solvent is regulated because of enviromental concerns, we temporarily utilize it on a laboratory scale for convenience because it is still much more cheaply available than other fluorinated solvents.

Compounds bearing MOM groups are known to be sensitive to acid and subject to fast decomposition in strongly acidic media.[17] However, the decomposition



Scheme 1. Reagents and conditions: (a) NaF (1.1 equiv), 20 °C; (b) MeOH, MeONa, reflux, 20 h; (c) F_2, Freon113, flow rate: 200 ml/min; (d) (i) MeOH, (ii) benzyl alcohol; (e) KOH, H_2O, MeOH; and (f) K_2CO_3, 220–250 °C.

may be slowed down at lower temperature. Thus, fluorination of the starting material **3** with F_2 was first performed at 0 °C under a flow of 10% F_2 for a period of time and then subject to quenching with MeOH. Our first few attempts failed to obtain any detectable methyl ester of product **4b** (entry 1, in Table 1) because of serious breakdown. Instead, low-boiling-point species (<50 °C) appeared as the major product. As temperature was lowered to −20 °C, together with intermittent addition of NaF to absorb the released HF,[18] the loss due to decomposition from

Table 1. Effect of temperature, reaction time, and NaF on fluorination of **3** (0.1 mol)

Entry	Temperature (°C)	Time (h)	NaF (mol)	Yield (%)[a]
1	0	20	1.3	n.d.
2	0–5	20	1.0	1.5
3	0–5	40	1.3	3.0
4	0–5	60	1.5	2.2
5	−10 to 10	20	1.3	10.5
6	−10 to 10	40	1.5	11.7
7	−10 to 10	60	1.0	9.6
8	−20 to 15	20	1.5	19.4
9	−20 to 15	40	1.0	19.8
10	−20 to 15	60	1.3	19.9

[a]Yield was based on methyl ester **4b** obtained from addition of methanol to **4a** and determined by the distilled fraction. Identity of each fraction was confirmed by ^{1}H NMR characterization.

deprotection of MOM groups was considerably reduced, but the conversion to fluorinated species was very poor.

Inspired by the Exfluor–Lagow's process for fluorination of selected hydrocarbon compounds wherein both temperature and fluorine concentration are gradually increased,[19] we probed the gradient increase of reaction temperature, but maintained the F_2 concentration (10%) at a flow rate of 200 mL/min. The effect of temperature, sodium fluoride and reaction time on the yield of product was examined, and the results are summarized in Table 1.

Among the three temperature ranges, 0 to 5 °C, −10 to 10 °C, and −20 to 15 °C, the fluorination starting from −20 °C demonstrated a great improvement in yield (ca. 20%, entries 8–10). At the higher temperature range of 0 to 5 °C, the conversion of **3** was remarkably poor (entries 2–4). When the temperature was set to −10 to 10 °C, a mixture consisting of partially fluorinated products and side products was obtained, leading to a yield of less than 10% (entries 5–7). It should be noted that a temperature greater than 5 °C was necessary in the last stage of the reaction to reach perfluorination. However, we observed a considerable decrease in yield if the temperature was more than 25 °C at a later stage of the reaction. Longer reaction time exerted little effect on the yield (entries 8–10) at −20 to 15 °C. Addition of benzene at 5 to 15 °C had no marked effect upon the reaction, which was supposed to be effective in generating a great concentration of fluorine radicals.[20] The presence of excess NaF and intermittent addition to the system was critical for the amelioration of yield and diminution of decomposition of MOM groups in **3**. Although addition of more NaF could alleviate the decomposition, a 1:1.3 ratio was found to be appropriate, considering the efficient stirring in the reactor.

It was well known that the replacement of hydrogen atoms adjacent to the carbon atoms by fluorine atoms increases the C-C bond strength and makes the molecule more stable. Therefore, the acid-sensitive MOM group becomes more stable when part of the hydrogens was replaced by fluorine atoms with progress of the fluorination. This was realized by careful control of the gradient increase of temperature starting from low temperature and providing surroundings that are favorable to the stability of the intermediates. The greatest loss in the fluorination process that occurs at the start of the reaction was minimized when the substrate has very few fluorine atoms.[21] Thus, the desired product **4b** was successfully obtained in ca. 20% yield under the optimized condition (−20 to 15 °C, 1.3 mol NaF, and 40 h).

The formation of compound **4b** was revealed by ^{1}H NMR, providing only one signal at 3.98 ppm. This is further substantiated with ^{19}F NMR spectrum. The result from atmospheric pressure chemical ionization–mass spectrometry (APCI-MS, negtive mode) afforded a signal at 424.91, which is in good agreement with the calculated value of 424.97.

Because the perfluorinated product **4a** is unstable in moisture,[22] it is difficult to trace the perfluorination directly. Usually, the reaction was monitored by the formation of **4b** via quenching **4a** with methanol. Nevertheless, the overlapping of the signal from methyl ester of **4b** with that of methanol around 3.98 ppm would hinder the accurate assignment and mislead the analysis. We found an efficient means to detect the formation of **4a** by converting **4a** to **4c** with benzyl alcohol. In the ^{1}H NMR spectrum of **4c**, there are two signals at 7.40 ppm (multiplet) and 5.38 ppm (singlet) in $CDCl_3$, which are quite distinct from other signals. Moreover, the benzyl

alcohol could be readily removed by either distillation or filtering through a pad of silica gel, rendering the purification of its corresponding benzyl ester simple and straightforward. It is noteworthy that an increased yield (32%) was achieved when benzyl alcohol was used to quench the reaction. The difference in fluorination between the methyl ester and the benzyl ester was ascribed to the loss during the purification process. Further improvement is possible if a combination of such factors as temperature range, F_2 concentration, and solvents are thoroughly taken into account. Thus, benzyl alcohol could be utilized not only as a more convenient indicator for the progress of the reaction by displaying the two characteristic signals, but also as a purification method for the perfluorinated mixture.

The chemical shift in ^{19}F NMR was in full accord with the structure of **4c** compared to that of **4b**. Furthermore, the result from high-resolution mass spectroscopy (HRMS, ESI, negative mode) disclosed a signal at 501.0008 (calc. 501.0008), which unambiguously proved the formation of the perfluorinated precursor (**4c**).

In conclusion, the liquid-phase direct fluorination of an acid-sensitive partially fluorinated glycol ether **3** for perfluoro(2-(methoxymethoxy) ethyl vinyl ether **5** was achieved in four steps. The key fluorinated precursor **4b** was obtained in ca. 20% yield under the optimized condition with the gradient change of temperature (−20 to 15 °C) and intermittent addition of NaF. Benzyl alcohol derivative **4c** was useful both as an indicator for tracing the progress of fluorination and as a convenient precursor for purification. We expect that this method may also be applicable to the synthesis of other partially fluorinated esters intolerable to strong acidic media.

EXPERIMENTAL

Ethylene glycol, anhydrous methanol, and potassium bicarbonate are commercially available substances. Benzyl alcohol was dried over Na_2SO_4 before use. NaF was dried in vacuum at 250 °C. Boiling points were measured by distillation. The NMR spectra were recorded on a Bruker ACF 400 spectrometer (tetramethylsilane as internal standard for ^1H, and trichlorofluoromethane for ^{19}F). ^{19}F NMR spectra were observed at 376 MHz with fluorotrichloromethane as standard. HRMS were obtained on a Jeol SX-102A coupled to HP-5890 with a 60-m capillary column (J&W DB-1 or DB-1301). Elemental fluorine was provided by Zhong Lan Chenguang Research Institute of Chemical Industry, China. Elemental fluorine is a highly toxic and corrosive gas and may explode when it meets organics in the vapor phase. Extreme care must be taken when handling it! The hydrogen fluoride (bp 19.5 °C) evolved during the reaction is also highly corrosive and must be absorbed by a base, such as NaOH. The fluorination was carried out in low-temperature circulating baths purchased from Chengdu Jinniu Refrigeration Co., China, with ethanol as cooling agent, and the temperature was determined by a digital thermometer.

2-(Methoxymethoxy)ethanol (1)

Compound **1** was prepared according to the reported procedure.[16] The chemical shift of this compound in ^1H NMR spectrum is in agreement with the reported values.

10-Fluoro-10-(trifluoromethyl)-2,4,7,8,11,14,16-heptaoxaheptadecane (2)

2-(Methoxymethoxy)ethanol **(1)** 120 g (1.13 mol) and NaF 71 g (1.70 mol) were added to a 250-mL, two-necked flask equipped with a condenser linked to a cold trap. While stirring at room temperature, hexafluoropropylene oxide (HFPO) was bubbled via one neck into the reaction mixture. The reaction was monitored by gas chromatography (GC) and was completed when the product reached a constant percentage. The mixture was washed with water, ethyl acetate, dried over Na_2SO_4, and distilled to afford product **2** (135 g, 0.40 mol) in a yield of 72.4%. Bp 80 °C/0.2 kPa. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.37 (s, 6H, CH_3O–), 3.76 (t, $J = 4.8$ Hz, 2H, $-C\mathbf{H}_2CH_2OCF$–), 3.81 (t, $J = 4.8$ Hz, 2H, $-COOCH_2C\mathbf{H}_2O$–), 3.93–4.02 (m, 2H, $-CH_2C\mathbf{H}_2OCF$–), 4.51 (t, $J = 4.8$ Hz, 2H, $-COOC\mathbf{H}_2CH_2O$–), 4.64 (s, 2H, $-OC\mathbf{H}_2OCH_3$), 4.65 (s, 2H, $CH_3OC\mathbf{H}_2O$–). HRMS (ESI$^+$) 361.0866 ($M + Na^+$); calculated: 361.0886.

5-Fluoro-5-(trifluoromethyl)-2,3,6,9,11-pentaoxadodecanemethyl (3)

Methanol 710 mL (17.8 mol) and CH_3ONa 5.78 g (0.107 mol) were added to a 2-L, two-necked, round-bottomed flask, and the mixture was stirred at room temperature until the base was dissolved. The ester **2** (300 g, 0.89 mol) was added, and the mixture was refluxed for 48 h. The solvent was removed, and the resulting slurry was washed with water and extracted with ethyl acetate. After drying over Na_2SO_4, the solvent was removed and distilled under reduced pressure to provide the compound **3** (224 g, 0.85 mol) in a yield of 95%. Bp 75 °C/1.0 kPa. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.37 (s, 3H, CH_3OCH_2O–), 3.760 (t, $J = 4.8$ Hz, 2H, $-OC\mathbf{H}_2CH_2O$–), 3.89–4.02 (m, 2H, $-OCH_2C\mathbf{H}_2O$–), 3.941 (s, 3H, $-COOC\mathbf{H}_3$), 4.653 (s, 2H, $-OC\mathbf{H}_2O$–). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −81.24 (d, $J = 3.76$ Hz, 3F, $-CF_3$), −131.88 [q, $J = 3.76$ Hz, 1F, $-CF(CF_3)$–]. HRMS (ESI$^+$) 287.0505 ($M+Na^+$); calculated: 287.0519.

2-(2-(Difluoro(trifluoromethoxy)methoxy)-1,1,2,2-tetrafluoroethoxy)-2,3,3,3-tetrafluoropropanoate (4b)

R113 500 mL, NaF 44 g (1.24 mol), and compound **3** (25 g, 0.095 mol) were charged into a 1-L autoclave made of stainless steel equipped with a condenser. The mixture was stirred and cooled down to −20 °C. At the gas outlet of the autoclave, the condenser was maintained at −20 °C. Nitrogen gas was blown into the system for 1 h, and then fluorine gas diluted to 10% with nitrogen gas was blown into the mixture at a flow rate of 200 mL/min at atmospheric pressure. The temperature was raised gradiently from −20 to 15 °C at intervals of 5 °C and maintained at each temperature for ca. 5 h, while NaF was added portionwise and intermittently. Then, nitrogen gas was supplied for 1.5 h to remove residual F_2 and volatile materials, followed by the addition of methanol (150 mL). Workup by removal of the solvents, neutralization with Na_2CO_3, drying over Na_2SO_4, and fine distillation (bp 56 °C/0.5 kPa) afforded the methyl ester **4b** (10.1 g) in a yield of 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.97 (s, 3H, $-COOCH_3$). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −53.75 (d, $J = 30.1$ Hz, 2 F, $-OCF_2O$–), −56.94 (d, $J = 18.8$ Hz, 3F,

CF_3O–), −81.91 [d, $J = 3.76$ Hz, 3F, −$CF(CF_3)$–], −84.40 (dd, $J = 127.8$ Hz, $J =$ 18.8 Hz, 2 F, −OCF_2CF_2O–), −90.14 (d, $J = 18.8$ Hz, 2 F, −OCF_2CF_2O–), −131.63 to −131.67) [m, 1 F, −$CF(CF_3)$–]. APCI-MS (negtive mode) spectrum at 424.91 $(M\text{-}H)^-$, calculated: 424.97.

Benzyl 2-(2-(Difluoro(trifluoromethoxy)methoxy)-1,1,2,2-tetrafluoroethoxy)-2,3,3,3-tetrafluoropropanoate (4c)

The direct fluorination of compound **3** was carried out in the same manner as before except for the addition of 51.3 g (0.475 mol) of benzyl alcohol, and 15.2 g of the desired product **4c** was obtained in a yield of 32%. Bp 78 °C/0.5 kPa. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39 (s, 5H, C_6H_5–), 5.38 (t, 2H, −CH_2O–). ^{19}F NMR (376 MHz,$CDCl_3$) δ (ppm): −53.75 (d, $J = 30.1$ Hz, 2 F, −OCF_2O–), −56.94 (d, $J = 18.8$ Hz, 3F, CF_3O–), −81.91 [d, $J = 3.76$ Hz, 3F, −$CF(CF_3)$–], −84.40 (dd, $J = 127.8$, 18.8 Hz, 2 F, −OCF_2CF_2O–), −90.14 (d, $J = 18.8$ Hz, 2 F, −OCF_2CF_2O–), −131.63 to −131.67 [m, 1 F, −$CF(CF_3)$–]. HRMS ($APCI^+$): 503.0164 $(M + H)^+$, calculated: 503.0164.

1-(2-(Difluoro(trifluoromethoxy)methoxy)-1,1,2,2-tetrafluoroethoxy)-1,2,2-trifluoroethene (5)

A 1-L, three-necked, round-bottomed flask was charged with compound **4b** (35 g, 0.082 mol), potassium hydroxide 5.6 g (82%, 0.082 mol) dissolved in water (0.5 mL), and methanol (40 mL). The mixture was stirred under reflux for 8 h. Evaporation of methanol and evacuation of water provided a potassium salt, which was then mixed thoroughly with potassium carbonate 1.23 g (9 mmol) and sand. After drying at 90 °C in vacuum until a constant weight was reached, the mixture was heated to about 220 °C in a tubular reactor. The pyrolysis afforded a distillate with a boiling point of 60 °C. The distillate was washed with water and dried with anhydrous sodium sulfate to give the title compound **5** (17.1 g, 0.049 mol) in a yield of 60%. Bp 61–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): no signal. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −53.7 (s, 2 F, −OCF_2O–), −57.25 to −58.64 (m, 3F, CF_3O–), −83.37 to −84.82 (m, 2 F, −OCF_2CF_2O–), −87.56 to −88.95 (m, 2 F, −OCF_2CF_2O–), −135.28 (d, $J = 3.76$ Hz, Hz, 1 F, −$CF{=}\mathbf{CF_2}$), −140.85 to −141.97 (m, 1 F, −$CF{=}\mathbf{CF_2}$), −143.16 to −145.35 (m, 1 F, −$\mathbf{C}F{=}CF_2$). APCI-MS spectrum 346.17, calculated: 346.96 (M-H).

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