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Syntheses of a Perfluoroethanesulfonyl Fluoride Vinyl Ether

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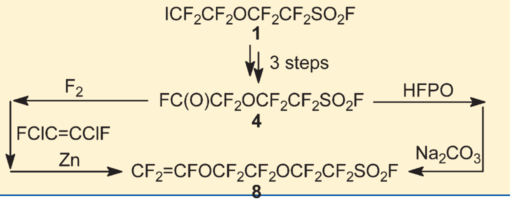
S *Supporting Information*

ABSTRACT: The target monomer, perfluoroethanesulfonyl fluoride vinyl ether **8**, was obtained from the starting material, iodoperfluoroethanesulfonyl fluoride **1**, through the intermediate, acyl fluoride **4**. Two different synthetic routes were utilized in the conversion of **4** to **8**.



Perfluoroalkyl trifluorovinyl ethers, such as $CF_2{=}CFOCF_3$, were initially synthesized through two different synthetic routes. In one route, perfluoroalkyl hypofluorites, such as CF_3OF,[1] were added to FClC=CClF to give saturated ether intermediates. The saturated ether intermediates were dechlorinated with zinc to afford the corresponding trifluorovinyl ethers.[2] In another route, perfluoroalkyl acyl fluorides, including carbonyl fluoride, were reacted with hexafluoropropylene oxide (HFPO) to form perfluoroalkoxy acyl fluorides. The resulting perfluoroalkoxy acyl fluorides were then pyrolyzed at high temperatures in the presence of an inorganic salt to afford dehalocarbonylated products, perfluoroalkyl trifluorovinyl ethers.[3] Pyrolysis could be carried out in a batch mode[3b] or in a flow system.[3c] Through these two synthetic routes, two important functional monomers, $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and $CF_2{=}CFOCF_2CF_2SO_2F$, have been synthesized.[4]

As part of a program for the development of new fuel cell membranes, the synthesis of the monomer **8**, $CF_2{=}CFOCF_2CF_2OCF_2CF_2SO_2F$, was of interest. Although monomer **8** was mentioned in previous ion-exchange membrane[5a] and recent fuel cell membrane[5b,c] applications, no method of preparation for the compound has been reported.

In this research, iodoperfluoroethanesulfonyl fluoride **1** was used as the starting material. It was reported that when **1** was treated with 50% oleum at elevated temperature, the corresponding acyl fluoride **4** was obtained.[6] Due to the unavailability of 50% oleum, 26% oleum was prepared and used with the starting material **1** (eq 1).

$$\underset{\mathbf{1}}{ICF_2CF_2OCF_2CF_2SO_2F} \xrightarrow[\text{70 °C, 7 days; 88\%}]{\text{26\% Oleum}} \underset{\mathbf{2}}{HOC(O)CF_2OCF_2CF_2SO_2F} \qquad (1)$$

Instead of the desired acyl fluoride **4**, the carboxylic acid **2**[7] was obtained in 88% yield. To obtain **4**, **2** was converted to the corresponding acyl chloride **3**[6] using thionyl chloride with DMF as a catalyst (eq 2).

$$\mathbf{2} \xrightarrow[\text{65 °C, overnight}]{SOCl_2\text{, DMF}} \underset{\mathbf{3}}{ClC(O)CF_2OCF_2CF_2SO_2F} \qquad (2)$$

The excess $SOCl_2$ could not be completely separated from the desired acyl chloride **3** at this step. After distillation, the resulting mixture was converted to the corresponding acyl fluoride **4** and thionyl fluoride SOF_2 using antimony trifluoride in the presence of chlorine.[8] The reaction was carried out in a stainless steel reactor. Distillation gave **4** in 95% yield based on **2** (eq 3).

$$\mathbf{3} \xrightarrow[\text{85 °C, 7 days}]{SbF_3\text{, }Cl_2} \underset{\mathbf{4}}{FC(O)CF_2OCF_2CF_2SO_2F} \qquad (3)$$

Compound **4** was then used to prepare monomer **8**. In the first synthetic route, the acyl fluoride **4** was converted to the hypofluorite **5** by direct fluorination with F_2 in the presence of CsF.[9] The reaction was carried out on a small scale (ca. 4.00 mmol) at low temperature in a 150 mL Monel reactor (eq 4).

$$\mathbf{4} \xrightarrow[\text{−60 °C, 36 h; 89\%}]{F_2\text{, CsF}} \underset{\mathbf{5}}{FOCF_2CF_2OCF_2CF_2SO_2F} \qquad (4)$$

Compound **5** (CAUTION! **5** can undergo explosive decomposition at 22 °C) was isolated at low temperature in 89% yield and used immediately in the next step. The decomposition of **5** at room temperature proceeded as follows (eq 5).

$$\mathbf{5} \xrightarrow[\text{100\%}]{\text{rt, 1 h}} COF_2 + CF_3OCF_2CF_2SO_2F \qquad (5)$$

Hypofluorite **5** was combined with 1,2-dichlorodifluoroethylene at low temperature to form the ether intermediate **6** in 73% yield (eq 6).

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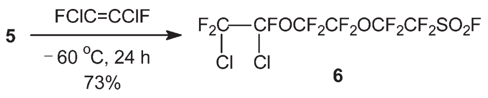


$$\mathbf{5}\xrightarrow[-60\ ^\circ C,\ 24\ h;\ 73\%]{FClC{=}CClF} F_2\underset{Cl}{C}-\underset{Cl}{C}FOCF_2CF_2OCF_2CF_2SO_2F\ \ \mathbf{6} \qquad (6)$$

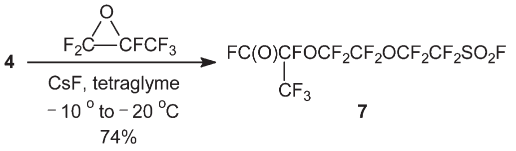
Compound **6** was then dechlorinated with zinc in NMP[10] to afford the final vinyl ether monomer **8** in 82% yield (eq 7).

$$\mathbf{6}\xrightarrow[60\ ^\circ C,\ overnight;\ 82\%]{Zn,\ NMP} F_2C{=}CFOCF_2CF_2OCF_2CF_2SO_2F\ \ \mathbf{8} \qquad (7)$$

In the second synthetic route to **8**, acyl fluoride **4** was mixed with hexafluoropropylene oxide (HFPO) in a solvent with CsF as a catalyst to form acyl fluoride **7**. Compound **7** was converted to the sodium carboxylate with Na_2CO_3, followed by pyrolysis to afford the desired vinyl ether **8**.

Initially, monoglyme and diglyme were tried as solvents for the formation of **7**. After distillation, **7** (containing some of the solvent used) was treated with Na_2CO_3 in the same solvent in a batch mode. After the sodium carboxylate was formed at 70 °C, the solvent was removed under reduced pressure. However, the complete removal of the solvent at this temperature was difficult to achieve. Therefore, the desired vinyl ether **8** obtained in the following step by pyrolysis at 200 −220 °C contained small amounts of the solvent.

Subsequent use of tetraglyme in the reactions (eq 8) resulted in pure **7** after distillation in modest yield (74%).



$$\mathbf{4}\xrightarrow[CsF,\ tetraglyme;\ -10\ ^\circ\ to\ -20\ ^\circ C;\ 74\%]{F_2C\overset{O}{—}CFCF_3} FC(O)\underset{CF_3}{C}FOCF_2CF_2OCF_2CF_2SO_2F\ \ \mathbf{7} \qquad (8)$$

To obtain **8** in higher yield, a flow system for the pyrolysis was employed. Acyl fluoride **7** was vaporized and carried through Na_2CO_3 column by dry nitrogen. Pyrolysis of **7** followed by distillation gave **8** in a 63% yield (eq 9).

$$\mathbf{7}\xrightarrow[200\ ^\circ\ to\ 210\ ^\circ C;\ 63\%]{Na_2CO_3}\mathbf{8} \qquad (9)$$

In summary, oleum (26%) converts the iodoperfluoroalkyl compound **1** into carboxylic acid **2**, which requires two additional steps to obtain the desired acyl fluoride **4**. The desired monomer **8** is then obtained by two synthetic routes. In the first route, the hypofluorite method results in good yields, but is limited in a batch scale by the instability of the hypofluorite **5**. In the second route, acyl fluoride **4** is converted to acyl fluoride **7** with HFPO in tetraglyme. The flow pyrolysis of **7** over Na_2CO_3 gave modest yields of monomer **8**, which could probably be improved by optimization. However, we believe that the yield is limited by the $-SO_2F$ functional group reacting with Na_2CO_3.

EXPERIMENTAL SECTION

Synthesis of 2. Into a three-necked round-bottom flask (1 L) was added 20% fuming sulfuric acid (500 g). SO_3 (40 g) was then slowly added into the flask with stirring to form an oleum (25.9%). A water-cooled condenser with a balloon on the top, a pressure-equalizing addition funnel, and a glass stopper were fitted to the flask. Iodide **1** (100 g, 0.235 mol) was added dropwise through the additional funnel into the oleum with stirring. The reaction mixture was stirred at room temperature overnight and then heated at 70 °C with stirring. The progress of the reaction was monitored by ^{19}F NMR. After 7 days, the reaction was complete. The reaction mixture was slowly poured onto ice to form an aqueous solution which was extracted twice with diethyl ether. The combined ether layer was washed with sodium bisulfite ($NaHSO_3 + Na_2S_2O_5$) aqueous solution and dried with anhydrous Na_2SO_4. The solvent was removed by rotary evaporation. Carboxylic acid **2** (61.3 g, 0.208 mol, 88.5%) was obtained after vacuum distillation: ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) 45.1 (m, 1F), −78.3 (m, 2F), −82.2 (m, 2F), −112.4 (m, 2F).

Synthesis of 3. Into carboxylic acid **2** (61.3 g, 0.208 mol) was slowly added $SOCl_2$ (66.1 g, 0.555 mol) with stirring, followed by the addition of anhydrous DMF (1 mL). The reaction mixture was then stirred at room temperature under N_2 protection for 1 h before it was heated at 65 °C overnight. The completion of the reaction was confirmed by ^{19}F NMR. The distillation of the reaction mixture under vacuum gave the desired acyl chloride **3** containing $SOCl_2$ (total 84.7 g): ^{19}F NMR (282 MHz, neat) δ (ppm) 45.3 (m, 1F), −76.6 (m, 2F), −81.8 (m, 2F), −112.4 (m, 2F).

Synthesis of 4. Freshly sublimed SbF_3 (213 g, 1.19 mol) was added into a 300 mL stainless steel reactor inside a drybox. The reactor was evacuated, and Cl_2 (11.2 g, 0.158 mol) was condensed into the reactor cooled with liquid nitrogen. The reactor was then heated at 80 °C for 1 h before it was cooled with liquid nitrogen again. Acyl chloride **3** containing $SOCl_2$ (total 84.7 g) was then vacuum transferred into the reactor. The closed reactor was warmed to room temperature and then heated at 85 °C for 7 days on a shaker. After the reactor was cooled to 22 °C, the pressure (SOF_2) was released through an oil bubbler, followed by distillation to remove the residue of SOF_2 and to isolate the acyl fluoride **4** (58.6 g, 0.198 mol, 95.2% based on carboxylic acid **2**): ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) 45.5 (m, 1F), 14.6 (m, 1F), −76.7 (m, 2F), −82.0 (m, 2F), −112.5 (m, 2F); IR (gas phase, 5 Torr) ν (cm^{-1}) 1895 (s, $\nu_{C=O}$), 1474 (s, $\nu_{S=O}$), 1349 (s), 1218 (s), 1157 (s), 1035 (s), 807 (s), 612 (m).

Synthesis of 5. Dry CsF (15.0 g, 98.7 mmol) was added into a 150 mL Monel reactor inside a drybox. The reactor was then evacuated, and acyl fluoride **4** (1.18 g, 3.99 mmol) was transferred through the vacuum line into the reactor cooled to −196 °C. Fluorine (20.0 mmol) was then transferred into the reactor. The reactor was kept at −60 °C for 36 h. The excess fluorine was then removed at −196 °C through a soda lime column by pumping under vacuum. The crude product inside the reactor was then subjected to vacuum fractionation through traps cooled to −60, −120, and −196 °C. The product from both −60 and −120 °C trap was vacuum transferred into a 50 mL stainless steel reactor cooled with liquid nitrogen to give hypofluorite **5** (1.19 g, 3.56 mmol, 89.2%): ^{19}F NMR (282 MHz, CCl_4, ca. −20 °C) δ (ppm) 142.5 (m, 1F), 45.1 (m, 1F), −55.5 (m, 2F), −82.8 (m, 1F), −83.5 (m, 1F), −84.8 (m, 1F), −97.6 (m, 1F), −113.3 (m, 2F); IR (gas phase, 5 Torr) ν (cm^{-1}) 1474 (s, $\nu_{S=O}$), 1253 (s), 1221 (s), 1161 (s), 1084 (m), 995 (m), 898 (m, ν_{O-F}), 809 (s), 755 (w), 607 (m).

Synthesis of 6. 1,2-Dichlorodifluoroethylene (0.475 g, 3.57 mmol) was condensed into the 50 mL stainless steel reactor containing hypofluorite **5** (1.19 g, 3.56 mmol) cooled to −196 °C. The reactor was warmed and kept at −60 °C for 24 h. Vacuum fractionation through traps at −60, −120, and −196 °C gave **6** (1.22 g, 2.61 mmol, 73.3%) in the −60 °C trap: ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) 45.3 (m, 1F), −71.2 (m, 2F), −77.2 (m, 1F), −82.6 (m, 2F), −88.4 (m, 0.5F), −88.9 (m, 2F), −89.9 (m, 1F), −90.4 (m, 0.5F), −112.8 (m, 2F); IR (gas phase, 5 Torr) ν (cm^{-1}) 1473(s, $\nu_{S=O}$), 1252 (s), 1219 (s), 1162 (s), 1139 (s), 1027 (w), 803 (w), 607 (w).

Synthesis of 8 from 6. Activated Zn (0.775 g, 11.8 mmol) was added into a 100 mL one-piece glass reactor inside a drybox, and dry NMP (5 mL) was injected into the reactor. The reactor was cooled to −196 °C and evacuated. The ether intermediate **6** (1.11 g, 2.37

mmol) was vacuum transferred into the reactor, and the mixture was heated at 60 °C overnight. After being cooled to 22 °C, the reaction mixture was vacuum fractionated through traps at −75, −115, and −196 °C. **8** (0.779 g, 1.96 mmol, 82.7%) was obtained in the −75 °C trap: ^{19}F NMR (282 MHz, CDCl$_3$) δ (ppm) 45.3 (m, 1F), −82.5 (m, 2F), −88.1 (m, 2F), −90.6 (2d, ^5J = 4.7 Hz, ^5J = 4.7 Hz, 2F), −112.7 (m, 2F), −113.5 (dd, ^3J = 83.4 Hz, ^3J = 66.7 Hz, F), −121.7 (ddt, ^2J = 112.0 Hz, ^3J = 83.4 Hz, ^5J = 4.7 Hz, F), −135.7 (ddt, ^2J = 112.0 Hz, ^3J = 66.7 Hz, ^5J = 4.7 Hz, F); IR (gas phase, 5 Torr) ν (cm^{-1}) 1841 (w, $\nu_{C=C}$), 1474 (s, $\nu_{S=O}$), 1344 (s), 1293 (s), 1251 (s), 1219 (s), 1177 (s), 1158 (s), 1097 (m), 994 (m), 808 (m), 757 (w), 609 (m).

Synthesis of 7. Dry CsF (10.0 g, 65.8 mmol) was added into a 1 L Ace thread flask inside a drybox. Tetraglyme (120 mL, sodium dried) was then added. The flask was cooled to −196 °C and evacuated. Acyl fluoride **4** (55.8 g, 0.188 mol) was vacuum transferred into the flask. The flask was then maintained at −10 to −20 °C, and hexafluoropropylene oxide (HFPO) (97%, 33.9 g, 0.198 mol, 1.05 equiv) was slowly introduced into the flask with stirring at pressures ranging from 400 to 700 Torr over 3 h. After the desired amount of HFPO had been added (total pressure drop 3631 Torr in 1.01 L of volume), the reaction mixture was stirred for another 8 h at 22 °C. The crude product was distilled out of the flask under dynamic vacuum and collected in a two-necked flask cooled with liquid nitrogen. Upon slow warming to room temperature, the crude product was transferred into a 100 mL flask and subjected to further distillation at atmospheric pressure. Acyl fluoride (**7**) (64.4 g, 0.139 mol, 73.9%) was obtained: bp 118 °C; ^{19}F NMR (282 MHz, CDCl$_3$) δ (ppm) 45.2 (m, 1F), 26.4 (m, 1F), −82.3 (m, 3F), −82.6 (m, 2F), −84.3 (dd, ^2J = 145.3 Hz, ^4J = 19.7 Hz, 1F), −88.4 (m, 2F), −91.4 (dt, ^2J = 145.3 Hz, ^5J = 6.5 Hz, 1F), −112.8 (m, 2F), −131.2 (d, ^4J = 19.7 Hz, 1F).

Synthesis of 8 from 7. Granular Na$_2$CO$_3$ (160 g, predried at 160 °C under vacuum) and glass beads (160 g) were well mixed and packed into a column (50 cm long, 2.5 cm inner diameter) inside a drybox. The column was fitted with a pressure-equalizing addition funnel at the top and a two-necked 250 mL flask at the bottom. A flow of dry nitrogen (90 mL/min) was maintained down through the column. The column was heated at 260 °C for 1 h and then kept between 200 and 210 °C. Acyl fluoride **7** (22.5 g, 48.7 mmol) was added dropwise into the column through the finely controlled addition funnel over 3 h. The crude product was collected in the flask cooled to −10 to −20 °C. The final product **8** (12.2 g, 30.8 mmol, 63.2%) was obtained after distillation at atmospheric pressure: bp 107 °C; HRMS of hydrolyzed **8** m/z [M − F + ONa + Na]$^+$ 438.9077, calcd (C$_6$O$_5$F$_{11}$SNa$_2$) 438.9081; ^{19}F NMR (282 MHz, CDCl$_3$) δ (ppm) 45.3 (m, 1F), −82.5 (m, 2F), −88.1 (m, 2F), −90.6 (2d, ^5J = 5.6 Hz, ^5J = 5.6 Hz, 2F), −112.7 (m, 2F), −113.6 (dd, ^3J = 83.3 Hz, ^3J = 66.4 Hz, 1F), −121.8 (ddt, ^2J = 112.2 Hz, ^3J = 83.7 Hz, ^5J = 5.2 Hz, 1F), −135.7 (ddt, ^2J = 112.2 Hz, ^3J = 65.6 Hz, ^5J = 5.2 Hz, 1F).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. IR and ^{19}F NMR spectra for selected compounds and LCMS analysis for the final product. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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