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Synthesis of Perfluorovinyl Ether Monomers[1]

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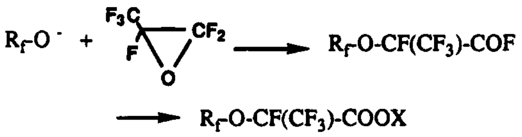
Introduction

Perfluorovinyl ethers ($R_fOCF{=}CF_2$) are an important class of commercial monomers that are used to modify crystallinity in fluoroplastics[2,3] or are a principal component in fluoroelastomers.[3] There are only a few known methods to prepare perfluorinated vinyl ethers, which include the thermal elimination of perfluorosulfinic acids[4] and the dehalogenation of dichloro ethers made from perfluoroalkyl hypofluorites with dichloroolefins.[5] The pyrolysis of a perfluorocarboxylic acid or its metal salt (eq 1) is probably the most direct and widely used

$$R_fYCF(CF_3)COOX \xrightarrow{\Delta} R_fYCF{=}CF_2 \quad (1)$$

(X = H, alkali metals; Y = O, NR_f')

method.[6,7] The acid precursors are generally prepared from fluoroalkoxide salts and hexafluoropropylene oxide (eq 2). This approach also can be used for the syntheses of (perfluorovinyl)amines.[8]



(2)

However, the preparation of perfluoroalkoxide salts can be cumbersome, and their reaction with hexafluoropropylene oxide (HFPO) often results in side products (for example, HFPO oligomers and isomeric ring opening products[9]) in addition to the desired compound. Thus, we have developed a new process for the synthesis of perfluorovinyl ethers that avoids these complications by using tetrafluoroethylene instead of HFPO. This new method involves the sequence in eqs 3−6.

$$R_fCH_2ONa + CF_2{=}CF_2 \rightarrow R_fCH_2OCF{=}CF_2 \quad (3)$$

$$R_fCH_2OCF{=}CF_2 + Cl_2 \rightarrow R_fCH_2OCFClCF_2Cl \quad (4)$$

$$R_fCH_2OCFClCF_2Cl + F_2 \rightarrow R_fCF_2OCFClCF_2Cl \quad (5)$$

$$R_fCF_2OCFClCF_2Cl \rightarrow R_fCF_2OCF{=}CF_2 \quad (6)$$

Results and Discussion

1,1-Dihydrofluoroalkyl trifluorovinyl ethers $R_fCH_2OCF{=}CF_2$ are easily prepared from fluoroalkoxide salts and tetrafluoroethylene.[10] These vinyl ethers themselves are interesting, reactive monomers that readily copolymerize with tetrafluoroethylene to give polymers whose chemical and thermal stability is limited by the presence of the geminal hydrogens.[11] The best way to avoid this weak point is to substitute these hydrogens with fluorine atoms by a postfluorination technique. This is accomplished by using fluorine radicals generated from F_2. Any similar fluorination technique to replace the hydrogens in $R_fCH_2OCF{=}CF_2$ obviously would first require protection of the vinyl ether double bond and, after treatment with fluorine, easy regeneration of the double bond. Epoxidation or bromination would not be suitable since both epoxides[12] and the C−Br bond[13] are attacked by elemental fluorine, but chlorination might be since the C−Cl bond can survive at least the relatively mild conditions of electrophilic fluorination with F_2.[14] Although it was far from certain that this bond would endure the extreme conditions associated with radical fluorinations, there did not seem to be any other practical alternatives so the use of the vicinal dichloro moiety was examined as a universal protecting group for fluoroolefins. The vinyl ethers were chlorinated by treating them with Cl_2 at 5−15 °C in the absence of solvent (eq 4). The reactions went smoothly under these mild conditions to afford the dichloro adducts in high yields.

There are several methods available for total hydrogen substitution by fluorine. Lagow has described the fluorination of selected hydrocarbon compounds using elemental fluorine wherein both temperature and fluorine concentration are gradually increased.[15] Adcock developed another process termed "aerosol fluorination", in which the substrate was deposited on solid NaF and then reacted with fluorine.[16] It should be noted that the only heteroatoms these substrates contained were oxygen, and in few cases also a tertiary nitrogen. We decided to try an approach based on treating the substrates with relatively concentrated fluorine under irradiation.[17]

To minimize the chances of fragmentation, the reaction was conducted in a solvent. Although dilution somewhat decreases the chances for radical chain reactions, it helps

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(1) Contribution No. 6826.

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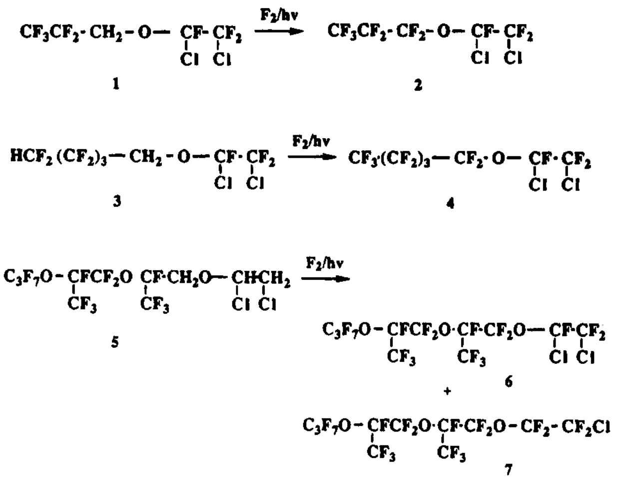
Scheme 1

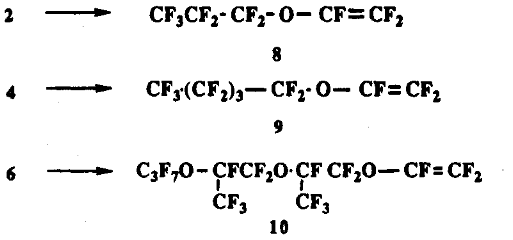


to absorb part of the energy released when hydrogen atoms are replaced by fluorine. The choice of solvent is not a trivial matter, however. Hydrogen-containing solvents obviously are not suitable, but even halogenated ones such as Freon 11 (CF_3Cl) or 113 (CF_2Cl-$CFCl_2$), which usually are stable to fluorine, can react violently with this element when irradiated at temperatures near 0 °C. Two perfluorinated solvents which proved safe and suitable for radical fluorination were perfluoro 2-butyltetrahydrofuran (FC-75) and hexafluoropropylene oxide (HFPO) oligomers (Krytox).[18] These solvents can be recovered and reused for the reactions without any complications.

When the dichloro ether derivative **1** was treated with F_2 under irradiation, one of its geminal hydrogens was easily substituted by fluorine, but the second one required a longer time and an excess of F_2, as evidenced by GC/MS monitoring of the reaction. It is difficult to accurately assess the yield of such reactions based on the amount of fluorine used, however. There are many factors, such as the reactor shape, the contact time between the gas bubbles and the reaction mixture, and the UV transmission efficiency of the reaction vessel made from either Teflon or quartz. Roughly 3−4 mol/equiv was enough to replace the first hydrogen, while an additional 5−6 mol/equiv was required to complete the reaction. The yield of the perfluoro derivative **2** based on **1** was 70%. The ω-hydrogen in **3** did not change the reaction course and was replaced simultaneously with one of the ether geminal hydrogens to eventually give the perfluoro-1,2-dichloroethyl butyl ether **4**. The dichloro ether **5** with its multiple hydrogens presented a more complicated case, the major challenge being the replacement of the primary or secondary hydrogens geminal to the chlorine atom without affecting the C—Cl bond. Two compounds were isolated from the fluorination reaction. The major one (60% yield) indeed was the desired perfluorinated product **6**, but it was accompanied by the minor product **7** (15% yield) missing the secondary chlorine atom (Scheme 1).

The dechlorination step on compounds **2**, **4**, and **6** to produce the corresponding perfluorovinyl ethers **8**, **9**, and **10** was easily accomplished with zinc dust in DMF solvent (Scheme 2).

Scheme 2



Conclusion

Our approach establishes a versatile and easy method to synthesize perfluorovinyl ethers from readily available starting materials having the general formula R_fCH_2-$OCX{=}CYZ$ (X, Y, Z = H, F), with those derived from fluorinated alcohols and tetrafluoroethylene (X, Y, Z = F) being especially preferred. The discovery that fluorinated double bonds can be simply chlorinated to protect them during photochemical fluorination was key to the success of the new method. The new process can be used to make perfluorovinyl ethers with either short or long perfluoroalkyl groups.

Experimental Section

^{1}H NMR spectra were recorded with a GEQE plus instrument at 300 MHz with $CDCl_3$ as solvent and Me_4Si as internal standard. The ^{19}F NMR spectra were measured with the NIC 1180E instrument at 188.2 MHz and GEQE plus at 283.1 MHz and are reported in parts per million upfield from $CFCl_3$, which also served as internal standard. Mass spectra were measured with a VG micromass 7070H instrument. GC was done using a Hewlett-Packard 5890 with a 25-m × 0.2-mm HP1 crosslinked methyl silicon capillary column, operating at 60−250 °C. Elementary analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. Pentafluoropropanol, 2,2,3,3,4,4,5,5-octafluoropentan-1-ol, and hexafluoropropylene oxide trimer (perfluoro-2,5-dimethyl-3,6-dioxanonanoyl fluoride) were obtained from PCR Inc.

General Procedure for Working with Fluorine. Caution: Molecular fluorine is a strong oxidizer and a very toxic and corrosive material. An appropriate vacuum line made from copper or monel in a well-ventilated area should be constructed for working with this element, and the experimenter should be familiar with the precautions necessary for the safe handling of fluorine.[19] The reactions themselves were carried out in either transparent Teflon or quartz vessels.

1,1-Dihydropentafluoropropyl Trifluorovinyl Ether[10] ($C_2F_5CH_2OCF{=}CF_2$). NaH (60% oil suspension, 48 g, 1.2 mol) was suspended in anhydrous 1,4-dioxane (600 mL) in a round-bottomed flask. Pentafluoropropanol (135 g, 0.9 mol) was added slowly while the pot was kept at 15−20 °C with external cooling. After addition was completed, the mixture was stirred at ambient temperature for 1−2 h. The pentafluoropropanol salt solution was then transferred into a 1-L autoclave, sealed, and heated for 20 h at 100 °C. The autoclave was cooled, evacuated, and pressured with tetrafluoroethylene (TFE) to 300 psi. The reaction was allowed to proceed for 40 h at 30−35 °C while the TFE pressure was maintained at 300 psi.

The product mixture was dumped into ice−water, and the organic layer was separated, washed with water twice, and then distilled to afford the desired product (128 g, 62% yield) as a clear, colorless liquid: bp 87−88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.36 (t, J = 12.4 Hz); ^{19}F NMR (188.24 MHz, $CFCl_3$) −84.2 (3F), −125.1 (t, J = 12.4 Hz, 2F), −120.8, −121.1, −121.3, −121.6 (4d, 1F), −126.6, −127.1, −127.2, -127.7 (4s, 1F), −137.8, −138.1, −138.3, −138.7 (4s, 1F). Anal. Calcd for $C_5H_2F_8O$: C, 26.10; H, 0.88; F, 66.06. Found: C, 25.98; H, 0.86; F, 65.90.

1,1,5-Trihydrooctafluoropentyl Trifluorovinyl Ether ($H(CF_2)_4CH_2OCF{=}CF_2$). The alcohol sodium salt was prepared

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[18] Several oligomers by this name with different molecular weights are commercially available from DuPont Co.

[19] *Specialty Gas Material Data Sheet on Fluorine*; Air Products and Chemicals, Inc.: Allentown, PA, 1986.

from NaH (60% oil suspension, 32 g, 0.8 mol) and 2,2,3,3,4,4,5,5-octafluoropentan-1-ol (139.2 g, 0.6 mol) in anhydrous ether solvent (600 mL) in a 1-L autoclave. The reactor was cooled and evacuated, and TFE was charged into the reactor. The reaction was allowed to proceed 24 h at 50 °C while the TFE pressure was maintained at 350 psi during the process. After similar workup and distillation, the title compound was obtained as a clear liquid: bp 56−57 °C at 60 mm; yield 115 g (61.4%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (tt, *J* = 54.6 Hz, 5.4 Hz, 1H), 4.39 (t, *J* = 12.6 Hz, 2H); ^{19}F NMR (188.24 MHz, $CFCl_3$) −121.4 (br, 2F), −125.7 (s, 2F), −130.4 (s, 2F), −137.7 (d, *J* = 55 Hz, 2F), −121.2 (m, 1F), −127.0 (m, 1F), −138.3 (m, 1F). Anal. Calcd for $C_7H_3F_{11}O$: C, 26.94; H, 0.97; F, 66.96. Found: C, 26.70; H, 0.93; F, 66.60.

1,1-Dihydro-2,5-bis(trifluoromethyl)-3,6-dioxa-2,4,4,5,7,7,8,8,9,9,9-Undecafluorononyl Vinyl Ether ($C_3F_7OCF(CF_3)CF_2OCF(CF_3)CH_2OCH{=}CH_2$).[20] This compound was prepared from hexafluoropropylene oxide trimer. The alcohol substrate ($C_3F_7OCF(CF_3)CF_2OCF(CF_3)CH_2OH$) (96.4 g, 0.2 mol), vinyl acetate (86 g, 1.0 mol), and mercuric acetate (0.5 g) were mixed at 0 °C with vigorous stirring. Concentrated sulfuric acid (25−50 μL) was added and the reaction was allowed to proceed for 6−8 h at 0−10 °C. Potassium carbonate (3 g) was added to terminate the reaction, the product mixture was fractionally distilled, and the product boiling between 30 and 100 °C at 20 mmHg was collected. Potassium hydroxide (12 g) was added to destroy the residual vinyl acetate in the distillate. A second distillation gave the desired vinyl ether 30 g (30%) as a clear, colorless liquid: bp 148−152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.46 (m, 1H), 4.28 (dm, *J* = 15 Hz, 1H), 4.20 (m, 3H); ^{19}F NMR (188.24 MHz, $CFCl_3$) −80.7 (m, br, 3F), −82.1 (m, 3F), −83.4 (m, 3F), −79.3 to −85.3 (m, 4F), −130.3 (s, 2F), −134.2 (m, 1F), −145.8 (m, 1F); MS *m/e* 508.

1,1-Dihydropentafluoropropyl 1,2-Dichlorotrifluoroethyl Ether ($C_2F_5CH_2OCFClCF_2Cl$) (1). Neat 1,1-dihydropentafluoropropyl trifluorovinyl ether (75 g, 0.326 mol) from above was chlorinated with chlorine gas (bubbling into the substrate through a gas inlet tube) at 10−15 °C. The reaction was monitored by gas chromatography and was stopped when the conversion of the starting material was complete. The product was purified by distillation and afforded **1** as a clear, colorless liquid: bp 95−96 °C; yield 86 g (88%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.44 (m); ^{19}F NMR (188.24 MHz, $CFCl_3$) −69.6 (d, *J* = 6.2 Hz, 2F), −74.8 (s, br, 1F), −84.2 (s, 3F), −123.9 (t, *J* = 11.8 Hz, 2F); mass *m/e* 215 $[(M - CF_2Cl)^+]$, 281 $[(M - F)^+]$, 265 $[(M - Cl)^+]$. Anal. Calcd for $C_5H_2Cl_2F_8O$: C, 19.95; H, 0.67; F, 50.50. Found: C, 19.95; H, 0.65; F, 50.60.

1,1,5-Trihydrooctafluoropentyl 1,2-Dichlorotrifluoroethyl Ether [$H(CF_2)_4CH_2OCFClCF_2Cl$] (3). 1,1,5-Trihydrooctafluoropentyl trifluorovinyl ether (50 g. 0.16 mol) from above was chlorinated with chlorine gas at 10−15 °C. The reaction was monitored by gas chromatography and was stopped when the conversion of the starting material was complete. The product was purified by distillation and afforded **3** as a clear, colorless liquid: bp 108−110 °C/50 mm; yield 34 g (56%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.06 (tt, *J* = 52 Hz, 4.8 Hz, 1H), 4.48 (m, 2H); ^{19}F NMR (188.24 MHz, $CFCl_3$) −69.6 (d, *J* = 5.8 Hz, 2F), −74.6 (s, br, 1F), −120.1 (t, *J* = 11.6 Hz, 2F), −125.5 (s, 2F), −130.3 (d, *J* = 3.0 Hz, 2F), −137.6 (dt, *J* = 52 Hz, 2.7 Hz, 2F); MS *m/e* 346.9692 $[(M - Cl)^+]$ (calcd 346.9587). Anal. Calcd for $C_7H_3Cl_2F_{11}O$: C, 21.95; H, 0.79; Cl, 18.51. Found: C, 21.91; H, 0.59; Cl, 18.03.

1,1-Dihydro-2,5-bis(trifluoromethyl)-3,6-dioxa-2,4,4,5,7,7,8,8,9,9,9-undecafluorononyl 1,2-Dichloroethyl Ether [$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CH_2OCHClCH_2Cl$] (5). 1,1-Dihydro-2,5-bis(trifluoromethyl)-3,6-dioxa-2,4,4,5,7,7,8,8,9,9,9-undecafluorononyl vinyl ether (16 g. 0.0315 mol) was chlorinated with chlorine gas at 10−15 °C as described in the above examples. After workup and distillation, **5** was isolated as a colorless liquid: bp 91−93 °C/10 mm; yield 16 g (88%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58 (m, 1H), 4.43 (t, *J* = 11.4 Hz, 1H), 4.08 (m, 1H), 3.82 (m, 2H); ^{19}F NMR (188.24 MHz, $CFCl_3$) −80.6 (s, br, 3F), −82.0 (t, *J* = 8.0 Hz, 3F), −83.2 (2s, 3F), −79.2 to −85.2 (m, 4F), −130.2 (d, *J* = 0.5 Hz, 2F), −134.3 (2m, 1F), −145.6 (m, 1F); MS *m/e* 576.9342 $[(M - H)^+]$ (calcd 576.9344). Anal. Calcd for $C_{11}H_5Cl_2F_{17}O_3$: C, 22.82; H, 0.87; Cl, 12.25; F, 55.78. Found: C, 22.84; H, 0.74; Cl, 12.15; F, 55.87.

General Fluorination Procedure. Mixtures of 25−30% F_2 diluted with nitrogen were used in this work. The gas mixtures were prepared in a secondary container before the reaction was started. The appropriate substrate was dissolved either in perfluoro 2-butyl-THF (FC-75, 3M Co.) or in Krytox GPL 100 (a fluorinated oil, DuPont) which also contained about 5 g of pulverized NaF to absorb the released HF. The reaction mixture was cooled to −10 °C, stirred with the aid of a vibromixer, and irradiated with a 450-W medium-pressure mercury lamp. The reactions were monitored by GC/MS and were brought to completion. Because of the volatility of some derivatives, especially **1** and **2**, a dry ice condenser was attached to the reactor just before the outlet of the F_2/N_2 mixture. The unused fluorine was trapped by passing it through a soda lime trap. After the reaction was completed, the mixture was poured into water and washed with bicarbonate until neutral. The organic layer was separated, dried over $MgSO_4$, and then distilled either under atmospheric or reduced pressure.

Fluorination of Compound 1. A cold solution (−10 °C) of **1** (15.0 g, 0.05 mol) in Krytox was prepared, NaF (5 g) was added, and the reaction was performed as described above. The crude reaction mixture contained only solvent and a single product and was distilled at 78−80 °C to give the perfluoro derivative **2**; 11.8 g (70% yield). No protons were detectable in the ^{1}H NMR: ^{19}F NMR −71.5 (s, br, 2F), −77.5 (narrow m, 1F), −82 (t, *J* = 7 Hz, 3F), −85.5 (m, 2F), −130.7 (narrow m, 2F); MS *m/e* 300.9476 $[(M - Cl)^+]$ (calcd 300.9477), 168.9773 $[(CF_3CF_2CF_2)^+]$ (calcd 168.9888), 150.9251 $[(CFClCF_2Cl)^+]$ (calcd 150.9329). Anal. Calcd for $C_5F_{10}Cl_2O$: C, 17.82; F, 56.38. Found: C, 17.57; F, 56.38.

Fluorination of Compound 3. A cold solution (−10 °C) of **3** (9.3 g, 0.0243 mol) in Krytox was prepared, NaF (5 g) was added, and the reaction was performed as described above. Again the crude reaction mixture contained only solvent and a single product. It was distilled at 92−98 °C at 80 mmHg to afford **4** (7.25 g, 70% yield). No protons were detectable in ^{1}H NMR: ^{19}F NMR −71.27 (narrow m, 2F), −77.17 (narrow m, 1F), −81.3 (narrow m, 3F), −84.75 (m, 2F), −123.55 and −126.17 (two narrow m, each 2F), −126.79 (narrow m, 2F); MS *m/e* 400.9407 $[(M - Cl)^+]$ (calcd 400.9414), 350.9456 $[(M - CF_2Cl)^+]$ (calcd 350.9446), 150.8693 $[(CFClCF2Cl)^+]$ (calcd 150.9329), 84.9684 $[(CF_2Cl)^+]$ (calcd 84.9657). Anal. Calcd for $C_7F_{14}Cl_2O$: C, 19.24; F, 60.87. Found: C, 19.03; F, 61.35.

Fluorination of Compound 5. A cold solution (−10 °C) of **5** (12 g, 0.0207 mol) in FC-75 was prepared, NaF (5 g) was added, and the reaction was performed as described above. The crude reaction mixture contained only solvent and two products in a ratio of 4:1. The solvent was first distilled, followed by the products at 80−100 °C at 120 mmHg. The fractions containing the products were distilled again on a spinning band column. The first fractions (99−105 °C/120 mm) proved to be a mixture of the two products, but the latter one (118 °C/115 mm) was the pure major derivative **6** (60% yield): ^{19}F NMR −71.47 (narrow m, 2F), −77.3 (narrow m, 1F), −79.9 to −85.7 (multiplets for 3 CF_3 and 3 CF_2O groups, 15F), −130.3 (br, s, 2F), −145.4 to −146.1 (m, 2F); MS *m/e* 335 $[(C_3F_7OCF(CF_3)CF_2)^+]$, 285 $[(C_3F_7OCFCF_3)^+]$, 217 $[(CF_2OCFClCF_2Cl)^+]$, 151 $[(CFClCF_2Cl)^+]$. Anal. Calcd for $C_{11}F_{22}Cl_2O_3$: C, 19.75; F, 62.48; Cl, 10.60. Found: C, 19.54; F, 61.62; Cl, 10.34. The minor product obtained in 15% yield could not be analytically purified, but its MS confirmed structure **7**. The most illuminative peaks are at *m/e* 85 $[(CF_2Cl)^+]$, 135 $[(CF_2CF_2Cl)^+]$, 201 $[(CF_2OCF_2CF_2Cl)^+]$, 379 $[((ClCF_2CF_2OCF_2CF(CF_3)OCF_2CF) - F)^+]$.

Perfluoro(propyl vinyl) Ether ($CF_3CF_2CF_2OCF{=}CF_2$)[21] (8). Zinc dust (3.27 g, 0.05 mol) was suspended in *N,N*-dimethylformamide (DMF) (20 mL), activated with bromine (0.1 mL), and heated at 50 °C. The dichloro ether **2** (8.43 g, 0.025 mol) was added slowly. After the mixture was stirred for 6 h at 50 °C, the volatile product from the reaction mixture was distilled and collected. A second distillation gave **8** as a clear, colorless liquid: bp 33 °C (lit.[21] bp 35−36 °C); yield 3.6 g (54%); ^{19}F NMR (188.24 MHz, $CFCl_3$) −81.9 (s, 3F), −86.6 (s, 2F), −113.5, −113.7, −113.8, −114.0 (4s, 1F), −121.7, −122.0,

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(20) Ohmori, K.; Tomihashi, N.; Inukai, H.; Nakai, K. U.S. Pat. 4,568,773, 1986.

(21) Fritz, C. G.; Selman, S. U.S. Pat. 3,291,843, 1966.

−122.1, −122.4 (4s, 1F), −130.2 (s, 2F), −135.4, −135.6, −135.8, −136.0 (4t, $J = 8.8$ Hz, 1F).

Perfluoro(pentyl vinyl) Ether [$CF_3(CF_2)_3CF_2OCF{=}CF_2$] (9). Zinc dust (1.31 g, 0.02 mol) was suspended in *N,N*-dimethylformamide (DMF) (10 mL), activated with bromine (0.1 mL), and heated at 50 °C. The dichloro ether **4** (4.37 g, 0.01 mol) was added slowly. After addition, the pot temperature was raised to 80−85 °C. The reaction was allowed to proceed for 3 h, and the volatile product was distilled and collected. Compound **9** was obtained as a clear, colorless liquid: bp 36 °C/220 mm; yield 2.5 g (68.3%); ^{19}F NMR (188.24 MHz, $CFCl_3$) −81.4 (t, $J = 9.8$ Hz, 3F), −85.3 (s, br, 2F), −113.3, −113.5, −113.6, −113.9 (4s, 1F), −121.5, −121.6, −121.8, −121.9 (4s, 1F), −123.6 (m, 2F), −125.9 (d, $J = 9.8$ Hz, 2F), −126.8 (m, 2F), −135.3, −135.5, −135.7, −135.9 (4t, $J = 8.8$ Hz, 1F); mass *m/e* for [$(M - CF{=}CF_2)^+$] calcd 284.9774, found 284.9825. Anal. Calcd for $C_7F_{14}O$: C, 22.97; F, 72.66. Found: C, 22.47; F, 72.21.

Perfluoro[2,5-bis(trifluoromethyl)-3,6-dioxadecyl vinyl] Ether ($C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF{=}CF_2$) (10). Zinc dust (0.72 g, 0.011 mol) was suspended in a mixed solvent of *N,N*-dimethylformamide (DMF) (5 mL) and anhydrous 1,4-dioxane (2.5 mL), activated with bromine (0.1 mL), and heated at 50 °C. Ether **6** (2.5 g, 3.74 mmol) was added slowly. After addition, the reaction mixture was heated at 120−130 °C for 8 h. After cooling, the bottom product layer was separated and distilled to afford the pure **10** as a clear, colorless liquid: bp 85 °C/80 mm; yield 1.1 g (49.2%); ^{19}F NMR (188.24 MHz, $CFCl_3$) −80.6 (m, 6F), −82.1 (m, 3F), −79.8 to −86.1 (m, 6F), −113.6, −113.8, −113.9, −114.1 (4m, 1F), −121.9, −122.3, −122.4, −122.7 (4s, br, 1F), −130.3 (s, 2F), −135.8, −136.1, −136.2, −136.5 (4m, 1F), −145.6 (m, 2F); mass for [M^+] calcd 597.9496, found 597.9499. Anal. Calcd for $C_{11}F_{22}O_3$: C, 22.08; F, 69.90. Found: C, 21.79; F, 69.90.