resent a new and efficient asymmetric synthetic approach to various physiologically active 1α-hydroxyvitamin D_3 steroids via Lythgoe-type coupling (eq 1).[12]

Finally, the successful stereochemical outcome and the mildness of the 2 + 4 cycloaddition in Scheme I producing stable bicyclic lactone endo diastereomer **5** almost exclusively represent another valuable example of how electronically matched electron-poor pyrone dienes and electron-rich vinyl ether dienophiles can be useful in effective synthesis of complex organic molecules.[6] We are working to make Scheme I even more efficient (e.g., by use of a catalytic amount of a cheap Lewis acid).

Acknowledgment. We thank the NIH (GM-30052) for financial support, Rhône-Poulenc for a graduate fellowship to J.-C.C., and the NSF for a graduate fellowship to T. E.N.A.

Supplementary Material Available: Full experimental details and spectral data for compounds **4-9** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(12) For recent examples of linking chiron (-)-1 with various C,D-ring units, see: (a) Dauben, W. G.; Ollmann, R. R., Jr.; Funhoff, A. S.; Leung, S. S.; Norman, A. W., Bishop, J. E. *Tetrahedron Lett.* **1991**, *32*, 4643. (b) Uskoković, M. R. et al. In *Vitamin D. Gene Regulation, Structure-Function Analysis and Clinical Application*; Norman, A. W., Bouillon, R., Thomasset, M., Eds.; W. de Gruyter: Berlin, 1991; p 139.

Articles

Addition of Phenols to Perfluorovinyl Ethers. Protonation and Halogenation of Carbanionic Intermediates†,‡

Andrew E. Feiring* and Edward R. Wonchoba

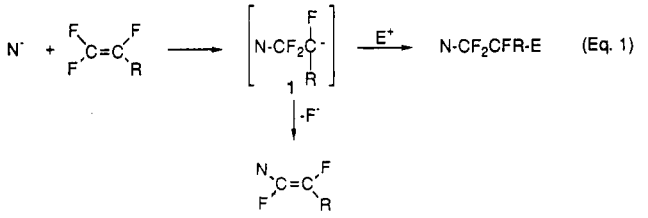
Du Pont Central Research & Development, Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

Received August 6, 1992

Fluorinated ethers $ArOCF_2CFHOR_f$ are obtained in good yield by base-catalyzed addition of phenols to perfluoroalkyl vinyl ethers, $CF_2{=}CFOR_f$ (R_f = C_3F_7, $C_3F_7OCF(CF_3)CF_2$, $CH_3O_2CCF_2CF_2OCF(CF_3)CF_2$). Reaction of sodium phenoxides with fluorinated vinyl ethers and hexachloroethane affords chlorinated ethers $ArOCF_2CFClOR_f$. Treatment of $BrCF_2CFBrOC_3F_7$ with sodium phenoxide in the presence of $CF_2{=}CFOC_3F_7$ gives $PhOCF_2CFBrOC_3F_7$ in high yield at room temperature, probably by an anionic chain mechanism. Sodium phenoxide reacts cleanly with $CF_2{=}CFOC_3F_7$ in the absence of an electrophile to give a 1:1 cis-trans mixture of olefins $PhOCF{=}CFOC_3F_7$. NMR chemical shifts of the OCF_2CFHOR_f group proton shows an unusually large solvent dependence.

Introduction

Additions of nucleophiles to fluorinated olefins are among the best known reactions in organofluorine chemistry.[1] The initially formed carbanion[2] **1** (eq 1) can be



(Eq. 1)

trapped by electrophiles or isolated as the substituted fluoroolefin after loss of fluoride ion. The product mixture depends on the fluoroolefin, nucleophile and the reaction conditions, and complex mixtures are often formed especially since the product fluoroolefin may also react with the nucleophile. The electrophile is typically a proton, although a variety of other trapping agents, such as carbon dioxide,[3] dimethyl carbonate,[4] and positive halogen sources[5,6] have been employed.

Nucleophilic additions to tetrafluoroethylene, chlorotrifluoroethylene, and larger perfluorinated olefins have been widely investigated, but relatively little has been reported[7] on additions to the perfluorinated vinyl ethers **2**. In the course of developing synthetic approaches to novel fluorinated monomers and polymers,[8] we have in-

† Contribution No. 6316.

‡ Presented in part at the 13th International Symposium on Fluorine Chemistry, Bochum, Germany, Sept 1991.

(1) Hudlicky, M. *Chemistry of Organic Fluorine Compounds*, 2nd ed., Ellis Horwood; Chichester, 1976; pp 285-290, 407-410. Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973; pp 148-170.

(2) Koch, H. F.; Kielbania, A. J., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 729.

(3) Krespan, C. G.; Van-Catledge, F. A.; Smart, B. E. *J. Am. Chem. Soc.* **1984**, *106*, 5544.

(4) Wiley, D. W. US Patent 2 988 537, 1961.

(5) Krespan, C. G.; Smart, B. E. US Patent 4 922 038, 1990; *Chem. Abstr.* **1990**, *113*, 97028.

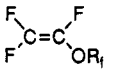
(6) Eleev, A. F.; Vasil'ev, N. V.; Sokol'skii, G. A. *J. Org. Chem. USSR* **1985**, *21*, 250. Smart, B. E.; Middleton, W. J.; Farnham, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 4905.

(7) Fuss, A.; Koch, V. *Synthesis* **1990**, 604. Fuss, A.; Hintzer, K. Ger. Offen. DE 3 828 063, 1990. Fuss, A.; Hintzer, K. Ger. Offen DE 3 828 064, 1990. Meazza, G.; Bettarini, F.; Massardo, P.; Caprioli, V. Eup. Pat. Appl. EP 0 293 943, 1988.

(8) Percec, V.; Tomazos, D.; Feiring, A. E. *Polymer* **1991**, *32*, 1897. Rodenhouse, R.; Percec, V.; Feiring, A. E. *J. Polym. Sci., Polym. Lett.* -1990, *28*, 345. Feiring, A. E.; Auman, B. C.; Wonchoba, E. R. Submitted to *Macromolecules*.

0022-3263/92/1957-7014$03.00/0

vestigated the addition of phenols[9] to perfluorinated vinyl ethers **2a–c**. We find that either addition or substitution products can be isolated in excellent yields under suitable conditions, even from the ester vinyl ether[10] **2c** which contains a potentially interfering functional group. In addition, we find that the intermediate carbanions can readily be trapped by sources of positive chlorine or bromine.



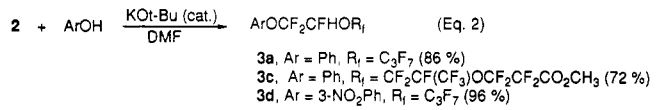
2a, $R_f = C_3F_7$

2b, $R_f = CF_2CF(CF_3)OC_3F_7$

2c, $R_f = CF_2CF(CF_3)OCF_2CF_2CO_2CH_3$

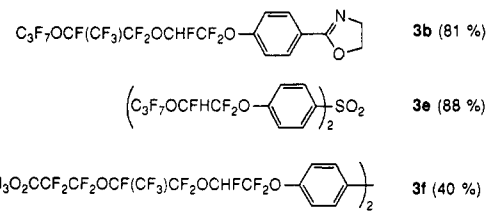
Results

Addition of the perfluorovinyl ethers **2a–c** to phenols in DMF containing a catalytic amount of potassium *tert*-butoxide at room temperature resulted in formation of the mono- or bis-addition products **3a–f** in good to excellent isolated yields (eq 2). Other basic catalysts, such



2 + ArOH $\xrightarrow[DMF]{KOt\text{-}Bu\ (cat.)}$ $ArOCF_2CFHOR_f$ (Eq. 2)

3a, Ar = Ph, $R_f = C_3F_7$ (86 %)
3c, Ar = Ph, $R_f = CF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ (72 %)
3d, Ar = 3-NO_2Ph, $R_f = C_3F_7$ (96 %)



3b (81 %)

3e (88 %)

3f (40 %)

as sodium hydride, could also be employed. Proton and fluorine NMR spectra of the crude reaction mixtures indicated formation of only addition products under these conditions; the relatively low isolated yields of **3c** and **3f** are due to hydrolysis of the sensitive ester function during workup. In other work,[8] direct reduction of the crude ester to the corresponding alcohol and purification of the hydrolytically stable alcohol often gave better overall yields.

Reaction of the vinyl ethers with sodium phenoxides in the presence of hexachloroethane at room temperature in DMF gave the corresponding chlorinated products **4**, again in excellent yield (eq 3). Only traces of the corresponding

$$ArONa + CCl_3CCl_3 + \mathbf{2} \rightarrow ArOCF_2CFClOR_f \quad \text{(Eq. 3)}$$

4a, Ar = Ph, $R_f = C_3F_7$ (99%)
4b, Ar = Ph, $R_f = CF_2CF(CF_3)OC_3F_7$ (92%)
4c, Ar = Ph, $R_f = CF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ (78%)
4d, Ar = 3-NO_2Ph, $R_f = C_3F_7$ (89%)

protonated derivatives **3** and no olefinic products (see below) were detected. Hexachloroethane has previously been used as a source of positive chlorine for reaction with fluorinated carbanions,[5] and the expected byproduct tetrachloroethylene was readily detected by glpc. Neither carbon tetrachloride nor *N*-chlorosuccinimide gave satisfactory results under these conditions.

Although the hydrofluoro ethers **3** are generally stable compounds (**3e** was unchanged after stirring for days in concentrated sulfuric acid or in refluxing triethylamine), **3a** could be converted in high yield to **4a** on treatment with potassium *tert*-butoxide and hexachloroethane in DMF at room temperature (eq 4).

$$\mathbf{3a} + CCl_3CCl_3 + KOC(CH_3)_3 \rightarrow \mathbf{4a}\ (94\%) \quad \text{(Eq. 4)}$$

The brominated derivative **5** was previously prepared in 45% yield by reaction of potassium phenoxide with the dibromo adduct **6** of **2a** in diglyme at 112 °C.[11] In our hands, reaction of sodium phenoxide with **6** in DMF at room temperature gave **5** in 34% yield. The same reaction in the presence of 10 mol % olefin **2a** gave **5** in 90% isolated yield (eq 5). The product **5** could also be obtained

$$PhONa + \underset{\mathbf{6}}{BrCF_2CFBrOC_3F_7} \xrightarrow[25\ °C]{DMF} \underset{\mathbf{5}}{PhOCF_2CFBrOC_3F_7} \quad \text{(Eq. 5)}$$

no **2a**: 34%
10 mol % **2a**: 90%

$$PhONa + \mathbf{2a} + BrCF_2CF_2Br \xrightarrow[25\ °C]{DMF} \mathbf{5}\ (92\%) \quad \text{(Eq. 6)}$$

in 92% yield by reaction of the phenoxide with **2a** in the presence of 1,2-dibromotetrafluoroethane as the Br^+ source (eq 6).

Although the major focus of this work was on preparation of saturated derivatives, reaction of **2a** with sodium phenoxide in the absence of an electrophile was briefly examined. Under these conditions, the vinyl ethers **7** (approximately 1:1 cis–trans mixture) were produced in good yield using THF as solvent. Olefins **7** together with **2a** and a coupled product were previously obtained by reduction of **5** with zinc.[11]

$$PhONa + \mathbf{2a} \xrightarrow[25\ °C]{THF} \underset{\mathbf{7}\ (80\%)}{PhOCF{=}CFOC_3F_7} \quad \text{(Eq. 7)}$$

Discussion

The high yields obtained from additions of phenols to perfluorovinyl ethers suggest that the intermediate carbanion **1** (N = PhO, R = OR_f) is relatively resistant to β-elimination of fluoride ion, allowing the carbanion to be efficiently trapped by proton or positive halogen sources. Conformation of the carbanion has been suggested[3] as the cause for slow elimination from **1**. Addition–elimination to form olefin **7** can occur quite efficiently, however, in the absence of an electrophile. Stability of the product **7** under the reaction conditions allows it to be isolated in high yield.[12]

Addition of phenol to the ester vinyl ether **2c** appears to occur selectively on the double bond rather than on the reactive fluorinated carbonyl function. However, attack by phenoxide on the ester group may be a reversible process, while addition to the olefin may be irreversible, accounting for the apparent chemoselectivity.

Formation of the chlorinated and brominated products **4** and **5** involves the now well-known process of electrophilic attack by carbanions on halogen in highly halogenated molecules.[13] Hexachloroethane is an efficient reagent

(9) Additions of phenols (and alcohols) to other fluorinated olefins are well-known. For examples, see: Tarrant, P.; Brown, H. C. *J. Am. Chem. Soc.* **1951**, *73*, 5831. England, D. C.; Melby, L. R.; Dietrich, M. A.; Lindsey, R. V., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 5116. Crawford, J. W. C. *J. Chem. Soc. C* **1967**, 2395.

(10) England, D. C. Ger. Offen DE 2 817 366, 1978.

(11) Kim, A. Ch.; Glazkov, A. A.; Ignatenko, A. V.; Krukovskii, S. P.; Ponomarenko, V. A. *Bull. Acad. Sci. USSR, Ser. Chem.* **1984**, *33*, 2118.

(12) Compare, for example, the synthesis of $PhOCF{=}CF_2$ from PhONa and $CF_2{=}CF_2$ which gives significant amounts of $PhOCF_2CF_2H$, $PhOCF{=}CFOPh$, and other products in addition to the desired olefin: Pummer, W. J.; Wall, L. A. *SPE Trans.* **1963**, 220. Zaitseva, E. L.; Nikanorova, E. A.; Monakhova, A. T.; Yakubovich, A. Ya. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 981.

Scheme I

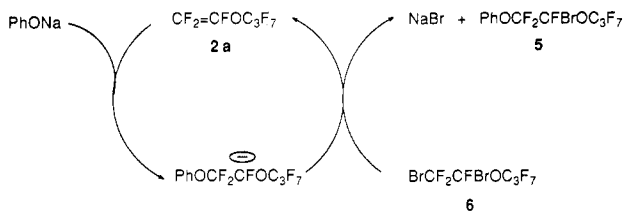
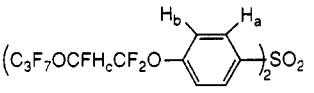


Table I. Proton Chemical Shifts as a Function of Solvent



solvent	δ_{Ha}	δ_{Hb}	δ_{Hc}
C_6D_6	7.64	6.76	5.36
CCl_2FCF_2Cl	7.96	7.27	6.03
CD_2Cl_2	7.99	7.36	6.16
CD_3CN	8.03	7.43	6.60
CD_3OD	8.09	7.45	6.93
$(CD_3)_2CO$	8.16	7.54	7.04
$(CD_3)_2SO$	8.13	7.52	7.46

for transfer of Cl^+ since the tetrachloroethylene byproduct is relatively inert. For bromination of the carbanion, 1,2-dibromotetrafluoroethane works efficiently, although its presumed byproduct tetrafluoroethylene (TFE) could also react with phenoxide.[12] No such products were detected, perhaps because the volatile TFE readily escapes from the reaction mixture. A more convenient procedure involves use of the dibromo adduct **6** of the olefin as the brominating agent since the byproduct is now the vinyl ether itself. The key to rapid reaction is addition of small quantities of the olefin at the start to initiate the anionic chain process (Scheme I). The results suggest that initiation in the absence of olefin (presumably by attack of phenoxide on the secondary bromine) is slow relative to propagation.

In examining the proton NMR spectra of compounds **3**, we noted that the chemical shift of the proton in the $-CF_2CHFO-$ unit shows unusually strong solvent dependence, shifting by about 2.1 ppm from benzene to DMSO (Table I). This shift is similar in direction and a bit larger in magnitude than the solvent shift observed for the chloroform proton.[14] This strong interaction with solvent may help account for our qualitative observation of high solubility of the ether derivatives in a variety of organic solvents.

More generally, the stability, ease of synthesis, and solubility of these fluorinated ethers make them attractive precursors to new fluorinated monomers. A number of these applications are reported elsewhere.[8]

Experimental Section

Materials. Vinyl ethers **2a–c** were obtained from Du Pont. 1,2-Dibromo-3-oxaperfluorohexane was prepared by a literature procedure.[11] Other materials were commercially available and used as received.

Synthesis of 3a,d. Perfluoropropyl vinyl ether **2a** (14.98 g, 0.056 mol) was added at room temperature to a solution of 5.2 (0.055 mol) of phenol and 0.59 g (0.0053 mol) of potassium *tert*-butoxide in 100 mL of DMF. The solution was stirred overnight and then poured into 100 mL of ice–water containing 2 mL of concentrated hydrochloric acid and extracted with 2 × 100 mL of ether. The combined ether extracts were washed with water, dried over anhydrous magnesium sulfate, filtered, and distilled through an 8-in. spinning band column. After ether was removed at atmospheric pressure, the residue was distilled giving 17 g (86%) of **3a**: bp 93–97 °C at 60 mm (lit.[11] bp 45 °C at 3 mm); ^1H NMR (δ, $CDCl_3$) 6.05 (1 H, dt), 7.2–7.4 (5 H, m); ^{19}F NMR (δ, $CDCl_3$) −81.8 (3 F), −84.8 to −87.9 (4 F), −130.3 (2 F), −145.1 (1 F, CFH).

3d was prepared from 3-nitrophenol in similar fashion and isolated in 96% yield by Kugelrohr distillation at a pot temperature of 85–91 °C and 0.5 mm: ^1H NMR (δ, $CDCl_3$) 6.15 (1 H, dt), 7.63 (2 H, m), 8.09 (1 H, s), 8.20 (1 H, m).

Anal. Calcd for $C_{11}H_5F_{19}NO_4$: C, 32.61; H, 1.24; N, 3.46; F, 46.89. Found: C, 32.86; H, 1.37; N, 3.19; F, 45.86, 46.13.

Synthesis of 3b. Vinyl ether **2b** (15.25 g, 0.035 mol) was added over 15 min to a solution of 2-(4-hydroxyphenyl)oxazoline (4.90 g, 0.03 mol) and potassium *tert*-butoxide (0.6 g, 0.005 mol) in 100 mL of DMF and 15 mL of THF. The solution was stirred for 40 h at room temperature and then poured into 250 mL of water and extracted with 3 × 75 mL of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. The residue was distilled in a Kugelrohr apparatus at a bath temperature of 120–135 °C and 0.5 mm to give 14.46 g (81%) of **3b**: ^1H NMR (δ, $CDCl_3$) 4.08 (2 H, t), 4.43 (2 H, t), 6.05 (1 H, dt), 7.22 (2 H, d), 7.98 (2 H, d); ^{19}F NMR (δ, $CDCl_3$) −80.56 (3 F), −81.86 (3 F), −82.0 to −87.3 (6 F), −130.16 (2 F), −145.13 (1 F, CFH), −145.57 (1 F).

Anal. Calcd for $C_{17}H_9F_{16}NO_4$: C, 34.30; H, 1.52; N, 2.35. Found: C, 34.56; H, 1.57; N, 2.85.

Synthesis of 3e. Vinyl ether **2a** (16.5 g, 0.062 mol) was added at room temperature to a solution of bis(4-hydroxyphenyl)sulfone (4.7 g, 0.0188 mol) and potassium *tert*-butoxide (0.42 g, 0.0038 mol) in 35 mL of DMF. No reaction was evident, so about 10 mL of THF was added to facilitate solution. An immediate eoxtherm warmed the solution to 38 °C. The solution was stirred overnight at room temperature and poured into 300 mL of water. A lower layer was separated, and the aqueous solution was extracted with 2 × 30 mL of methylene chloride. The combined organic phases were washed with water and 1 N aqueous sodium hydroxide, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator. The residue was distilled in a Kugelrohr apparatus at a bath temperature of 153–158 °C and 0.1 mm to give 12.96 g (88%) of **3e**: ^1H NMR (δ, CD_2Cl_2) 6.19 (1 H, dt), 7.39 (4 H, d), 8.02 (4 H, d); ^{19}F NMR (δ, CD_2Cl_2) −81.6 (6 F), −84.8 to −87.7 (8 F), −129.96 (4 F), −144.9 (2 F, CFH).

Anal. Calcd for $C_{22}H_{10}F_{20}O_6S$: C, 33.77; H, 1.29; F, 48.57; S, 4.10. Found: C, 33.54; H, 1.26; F, 48.45; S, 4.66.

^1H NMR chemical shifts as a function of solvent were measured by dissolving carefully weighed 0.050-g amounts into NMR tubes and diluting with 1.0 mL of the appropriate solvent containing small amounts of TMS. Measured chemical shifts are shown in Table I.

Synthesis of 3c. To a solution of 4.71 g (0.05 mol) of phenol in 100 mL of DMF was added 1.12 g (0.01 mol) of potassium *tert*-butoxide. Vinyl ether **2c** (24.1 g, 0.057 mol) was added dropwise over 0.5 h at 22–24 °C. The resulting solution was stirred for 4.5 h at room temperature and then poured into 500 mL of ice–water containing 4 mL of concentrated hydrochloric acid. A lower layer was separated, and the upper aqueous solution was extracted with 2 × 30 mL of methylene chloride. The combined organic layers were washed with 50 mL of ice–water, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator at 12 mm to give 28.06 g of residue. Kugelrohr distillation at 0.5 mm and 113–124 °C gave, after a small forerun, 18.5 g (72%) of **3c**: ^1H NMR (δ, $CDCl_3$) 3.93 (s, 3 H), 6.06 (doubled triplet, 1 H), 7.20 (d, 2 H), 7.28 (m, 1 H), 7.38 (m, 2 H); ^{19}F NMR (δ, $CDCl_3$) −80.5 (3 F), −82.6 to −87.6 (6 F), −121.7 (2 F), −144.98 (1 F), −145.57 (1 F).

Anal. Calcd for $C_{15}H_9F_{13}O_5$: C, 34.90; H, 1.76; F, 47.85. Found: C, 34.93; H, 1.78; F, 46.22, 46.74.

Synthesis of 3f. 4,4′-Biphenol (9.31 g, 0.05 mol) was added to a suspension of 0.2 g (0.0083 mol) of sodium hydride in 90 mL of DMF. The clear solution was transferred to an addition funnel and added dropwise over 5.5 h to a solution of 50 g (0.118 mol)

(13) Li, X.; Pan, H.; Jian, X. *Huaxue Xuebao* **1984**, *42*, 297; *Chem. Abstr.* **1984**, *101*, 54178. Li, X.-y., L.; Pan, H.-q.; Jiang, X.-k. *Tetrahedron Lett.* **1984**, *25*, 4937. Li, X.-Y.; Pan, H.-q.; Fu, W.-m.; Jiang, X.-k. *J. Fluorine Chem.* **1986**, *31*, 213. Li, X.-Y.; Jiang, X.-k.; Pan, H.-q.; Hu, J.-s.; Fu, W.-m. *Pure Appl. Chem.* **1987**, *59*, 1015. Wakselman, C.; Kaziz, C. *J. Fluorine Chem.* **1986**, *33*, 347.

(14) Lichter, R. L.; Roberts, J. D. *J. Phys. Chem.* **1970**, *74*, 912.

of **2c** in 100 mL of anhydrous THF at 23–27 °C. The resulting solution was stirred at room temperature for 5 days and then poured in 1 L of ice–water. The aqueous mixture was saturated with sodium chloride and extracted with ether. The ether was dried over anhydrous sodium sulfate and concentrated on a rotary evaporator to 57.9 g of oil. The oil was chromatographed over silica gel and eluted with 1:6 ethyl acetate–hexane. The collected material was distilled in a Kugelrohr apparatus at 190 °C and 0.2 mm of pressure to give 20.4 g of the bis-adduct **3f**: ^{1}H NMR (δ, CD_2Cl_2) 3.95 (s, 6 H), 6.15 (doubled triplet, 2 H), 7.4 (q, 8 H); ^{19}F NMR (δ, CD_2Cl_2) −80.5 (6 F, CF_3), −82.5 to −88.0 (12 F, CF_2's), −122.0 (4 F, CF_2), −144.9 (2 F; CFH), −145.6 (2 F, CF).

Anal. Calcd for $C_{30}H_{16}F_{26}O_{10}$: C, 34.97; H, 1.57; F, 47.94. Found: C, 34.84; H, 1.52; F, 47.66.

Synthesis of 4a,d. Vinyl ether **2a** (14.6 g, 0.055 mol) was added dropwise over 0.5 h to a solution of 6.39 g (0.055 mol) of sodium phenoxide and 13.1 g (0.056 mol) of hexachloroethane in 100 mL of DMF at 25–29 °C. The mixture was stirred overnight at room temperature. It was poured into 200 mL of ice–water containing 2 mL of concentrated hydrochloric acid and extracted with 2 × 100 mL of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. The residue was distilled through an 8-in. column to give 21.6 g (99%) of **4a**: bp 106–107 °C at 52 mm; ^{1}H NMR (δ, $CDCl_3$) 7.2–7.4 (5 H, m); ^{19}F NMR (δ, $CDCl_3$) −80.4 (1 F, CFCl), −81.68 (3 F), −85.2 (AB quartet, 2 F), −87.1 (2 F), −130.5 (2 F).

Anal. Calcd for $C_{11}H_5O_2ClF_{10}$: C, 33.28; H, 1.28; F, 48.15; Cl, 8.98. Found: C, 33.13; H, 1.17; F, 47.70; Cl, 9.39.

In similar fashion **4d** was prepared from sodium 3-nitrophenoxide and isolated in 89% yield by Kugelrohr distillation at a pot temperature of 85–95 °C and 0.5 mm: ^{1}H NMR (δ, $CDCl_3$) 7.63 (2 H, m), 8.10 (1 H, s), 8.23 (1 H, m).

Anal. Calcd for $C_{11}H_4NO_4ClF_{10}$: C, 30.05; H, 0.92; N, 3.12; Cl, 8.06. Found: C, 29.79; H, 0.82; N, 3.54; Cl, 8.39.

Conversion of 3a to 4a. Potassium *tert*-butoxide (4.85 g, 0.043 mol) was added in small portions over 0.5 h to a solution of **3a** (15.6 g, 0.043 mol) and hexachloroethane (10.23 g, 0.043 mol) in 35 mL of DMF at room temperature. The resulting white suspension was stirred overnight at room temperature. Workup as above gave 15.9 g (94%) of **4a**.

Synthesis of 4b. The perfluorovinyl ether **2b** (19.4 g, 0.045 mol) was added over 0.5 h to a solution of 5.23 g (0.045 mol) of sodium phenoxide and 10.78 g (0.046 mol) of hexachloroethane in 100 mL of DMF at room temperature. The resulting mixture was stirred overnight. It was poured into ice–water containing 2 mL of concentrated hydrochloric acid and extracted with 2 × 200 mL of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. The residue was distilled through an 8-in. spinning band column to give 23.4 g (92%) of oil: bp 101–102 °C at 13 mm; ^{1}H NMR (δ, $CDCl_3$) 7.2–7.4 (5 H, m); ^{19}F NMR (δ, $CDCl_3$) −80.3 (1 F, CFCl), −80.5 (3 F, CF_3), −81.9 (3 F, CF_3), −87.2 (2 F), −82 to −86 (4 F, $2CF_2$), −130.2 (2 F), −146.1 (1 F, *t*-F).

Anal. Calcd for $C_{14}H_5O_3ClF_{16}$: C, 29.99; H, 0.89; F, 54.22; Cl, 6.32. Found: C, 29.34, H, 0.83; F, 53.77; Cl, 6.72.

Synthesis of 4c. Sodium phenoxide (7.54 g, 0.065 mol) was added over 1.5 h at room temperature to a solution of 34.6 g (0.072 mol) of **2c** and 20.85 g (0.085 mol) of hexachloroethane in 100 mL of DMAC. The resulting mixture was stirred overnight at room temperature. The mixture was poured into 200 mL of ice–water containing 3 mL of concentrated hydrochloric acid. A lower layer was separated, and the aqueous phase was extracted with 50 mL of methylene chloride. The combined organic phases were washed with water, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator at a bath temperature of 100 °C and 12 mm. The residue was distilled through an 8-in. spinning band column giving 27.9 g (78%) of product: bp 88 °C at 0.5 mm; ^{1}H NMR (δ, $CDCl_3$) 3.93 (s, 3 H), 7.20 (d, 2 H), 7.28 (m, 1 H), 7.38 (m, 2 H); ^{19}F NMR (δ, $CDCl_3$) −80.0 (1 F, CFCl), −80.3 (3 F), −82.5 to −87.6 (8 F), −146.1 (1 F).

Anal. Calcd for $C_{15}H_8F_{13}ClO_5$: C, 32.77; H, 1.45; F, 44.85; Cl, 6.44. Found: C, 33.13; H, 1.45; F, 44.83; Cl, 6.49.

Synthesis of 5. To a solution of 0.79 g (0.003 mol) of **2a** and 12.78 g (0.030 mol) of $BrCF_2CFBrOC_3F_7$ in 25 mL of DMF, cooled in an ice–water bath, was added 3.83 g (0.033 mol) of sodium phenoxide over 0.5 h. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. It was poured into ice–water and extracted with 100 mL of ether. The ether extract was washed with 2 × 25 mL water, dried over anhydrous magnesium sulfate, and concentrated to an oil. A Kugelrohr distillation with a bath temperature of 60–100 °C and 50 mm pressure gave 14.5 g (90%) of product (lit.[11] bp 118 °C at 50 mm): H NMR (δ, $CDCl_3$) 7.2–7.4 (5 H, m); ^{19}F NMR (δ, $CDCl_3$) −80.3 (1 F, CFBr), −81.61 (3 F), −86.2 (AB quartet, 2 F), −85.6 (AB quartet, 2 F), −130.44 (2 F).

An identical experiment, using 0.33 mol of $BrCF_2CFBrOC_3F_7$ in place of the dibromide and **2a**, gave **5** in 34% yield.

The same product was isolated in 92% yield by addition of sodium phenoxide (4.65 g, 0.04 mol) to a 0 °C solution of **2a** (13.3 g, 0.05 mol) and 1,2-dibromotetrafluoroethane (16.9 g, 0.065 mol) in 40 mL of DMF, followed by stirring overnight at room temperature and workup as above.

Synthesis of 7. Perfluoropropyl vinyl ether (64.7 g, 0.24 mol) was added over 15 min to a suspension of 35.6 g (0.31 mol) of sodium phenoxide in 180 mL of anhydrous THF which was cooled in an ice–water bath. The mixture was allowed to warm to room temperature, at which point an exotherm increased the temperature to about 50 °C. The mixture was stirred overnight at room temperature and poured into ice–water containing 20 mL of concentrated hydrochloric acid. The aqueous solution was extracted with 2 × 100 mL of methylene chloride, and the combined extracts were dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator to an oil. Kugelrohr distillation at a bath temperature of 106–110 °C and 80 mm gave 65.9 g (80%) of product: ^{1}H NMR (δ, $CDCl_3$) 7.0–7.4 (5 H, m); ^{19}F NMR (δ, $CDCl_3$) −81.82 (3 F, CF_3), −86.05 (2 F, CF_2), −130.49 (2 F, OCF_2), −114.79 and −124.16 (d, J = 49.4 Hz, *cis*-CF=CF–), −123.40 and −130.44 (d, J = 112.1 Hz, *trans*-CF=CF–). From the integrals of the vinyl fluorines, the cis–trans ratio is 1:1.

Registry No. **2a**, 1623-05-8; **2b**, 1644-11-7; **2c**, 63863-43-4; **3a**, 95454-42-5; **3b**, 144373-63-7; **3c**, 144373-64-8; **3d**, 144373-65-9; **3e**, 144373-66-0; **3f**, 144373-67-1; **4a**, 144373-62-6; **4b**, 144373-68-2; **4c**, 144373-69-3; **4d**, 144385-03-5; **5**, 95472-47-2; **6**, 95454-41-4; *cis*-**7**, 95454-43-6; *trans*-**7**, 95454-46-9; PhOH, 108-95-2; *m*-$NO_2C_6H_4OH$, 554-84-7; $(p\text{-}OHC_6H_4)_2SO_2$, 80-09-1; $(p\text{-}OHC_6H_4)_2$, 92-88-6; NaOPh, 139-02-6; *m*-$NO_2C_6H_4ONa$, 3019-85-0; 2-(4-hydroxyphenyl)oxazoline, 81428-58-2.