Synthesis of Trifluorovinyl Ethers Incorporating Functionalized Hydrocarbon Ether Groups: Insight into the Mechanism of Trifluorovinyl Ether Formation from Trimethylsilyl 2-Alkoxy-2,3,3,3-tetrafluoropropionates

Robert D. Lousenberg[†] and Molly S. Shoichet*[,†,†]

Departments of Chemistry and of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario M5S 3E5, Canada

Received July 18, 1997[⊗]

Novel trifluorovinyl ethers (TFVEs, $ROCF{=}CF_2$), where R is an oligoether, were synthesized from the corresponding sodium alkoxide and hexafluoropropene oxide. The sodium alkoxide ring opened hexafluoropropene oxide at the more highly substituted carbon (C2) to give the 2-alkoxy-2,3,3,3-tetrafluoropropionic acid ester incorporating 2 equiv of the alcohol, $ROCF(CF_3)CO_2R$. Hydrolysis of the ester and reaction of the resulting sodium 2-alkoxy-2,3,3,3-tetrafluoropropionate with chlorotrimethylsilane gave the trimethylsilyl 2-alkoxy-2,3,3,3-tetrafluoropropionate, $ROCF(CF_3)CO_2Si(CH_3)_3$. Gas phase vacuum thermolysis of the trimethylsilyl ester at 140−150 °C gave the corresponding TFVEs in 55−63% yields. Thus, 1-[2-(ethoxyethoxy)ethoxy]-1,2,2-trifluoroethene and 1-[2-(2-*tert*-butoxyethoxy)ethoxy]-1,2,2-trifluoroethene were synthesized from 2-(2-ethoxyethoxy)-ethanol and 2-(2-*tert*-butoxyethoxy)ethanol, respectively. Interestingly, thermolysis of sodium or potassium 2-alkoxy-2,3,3,3-tetrafluoropropionates resulted in negligible to low yields of TFVEs.[1] For example, thermolysis of sodium 2-[2-(ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate gave a trifluoroacetate ester, 2-(2-ethoxyethoxy)ethyl trifluoroacetate. Variable temperature ^{19}F NMR spectroscopy of trimethylsilyl 2-[2-(ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate suggests that an equilibrium exists between two structural conformations of these trimethylsilyl esters: one in which there is an intramolecular "interaction" of silicon with fluorine and one in which there is no silicon−fluorine interaction. This interaction may affect the outcome of the trimethylsilyl ester thermolysis.

Introduction

Fluoropolymers, such as poly(tetrafluoroethylene) or poly(tetrafluoroethylene-*co*-hexafluoropropylene), are difficult to process, insoluble in common organic solvents, and chemically inert, requiring highly reactive species for surface modification.[2] Perfluorinated ether groups on trifluorovinyl ethers (TFVEs) have been shown to improve the processability of the resulting polymer.[3] Incorporating a hydrocarbon ether group into the fluoromonomer will likely further improve the processability of the resulting polymers; however, no one has yet synthesized (or polymerized) the hydrocarbon TFVEs described herein.

Two new TFVEs were synthesized for copolymerization with tetrafluoroethylene, promising polymers with improved processability and solubility in common organic solvents over existing fluoropolymers. To facilitate further chemical modification, one of the TFVEs was designed to have a terminal hydroxyl group (synthesized protected as the *tert*-butylalkoxy). Unlike the existing chemically inert fluoropolymers, the hydroxyl TFVE provides a site for covalent bonding of numerous functional groups. For example, an acrylate group may be covalently attached to the hydroxyl group for applications in the paint formulation industry.[4] For biomaterial applications, fluoropolymers have been found to be relatively biologically inert yet still adsorb proteins. A TFVE having an oligo-ethylene oxide pendant group was synthesized to render the polymer less protein adsorptive.[5]

TFVEs have been previously synthesized by two principal synthetic routes which do not involve the use of elemental fluorine, chlorine, or hydrogen fluoride. For example, 1-methoxy-1,1,2-trifluoroethene was prepared[6] by the reaction of sodium methoxide with tetrafluoroethylene. This reaction was expanded to include ethoxide-, isopropoxide-, and *tert*-butoxide-substituted TFVEs.[7] While straightforward in approach, this method required high-pressure reaction equipment to achieve high tetrafluoroethylene pressures and long reaction times (and in one instance an explosion was reported).[7]

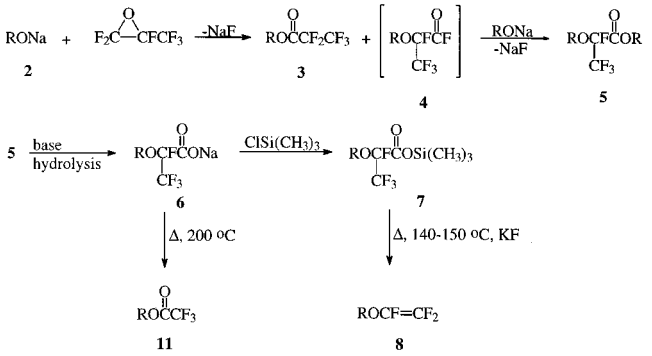
An alternate synthesis of TFVEs (i.e., (perfluoroalkoxy)-1,1,2-trifluoroethene) involved the reaction of a perfluoro acid fluoride[8,9] or perfluoro ketone[8,10] with hexafluoropropene oxide (HFPO) in the presence of an alkali metal fluoride (e.g., potassium or cesium fluoride) to yield the 2-(perfluoroalkoxy)-2,3,3,3-tetrafluoropropionyl fluoride intermediate. Thermolysis of either this

[†] Department of Chemistry.
[†] Department of Chemical Engineering and Applied Chemistry.
[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

(1) Pellerite, M. J. *J. Fluor. Chem.* **1990**, *49*, 43−6.
(2) Shoichet, M. S.; McCarthy, T. J. *Macromolecules* **1991**, *24*, 982−6.
(3) Feiring, A. E. In *Organofluorine Chemistry: Principles and Commercial Applications*; (Banks, R. E., Tatlow, J. C., Smart, B. E., Eds.; Plenum Press: New York, 1994, Chapter 15.
(4) Reisch, M. S. *Chem. Eng. News* **1996**, Oct. 14, 44−67.
(5) Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 10714−21.
(6) Dixon, S. U.S. Patent 2917548, 1959.
(7) Okuhara, K.; Baba, H.; Kojima, R. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 532−5.
(8) Fritz, C. G.; Moore, E. P., Jr.; Selman, S. U.S. Patent 3114778, 1963.
(9) Moore, E. P., Jr.; Milian, A. S., Jr.; Eleuterio, H. S. U.S. Patent 3250808, 1966.
(10) Selman, S. U.S. Patent 3274239, 1966.

S0022-3263(97)01319-4 CCC: $14.00

Scheme 1



intermediate in the vapor phase over a metal oxide or the alkali metal salt of the corresponding carboxylic acid yielded the TFVE.[8,11] Thermolysis of the acid fluoride intermediate was a "fair yielding step at best";[12] however, the yield was improved by using 3-chloroperfluoropropene oxide, instead of HFPO, producing a 2-(perfluoroalkoxy)-3-chloro-2,3,3-trifluoropropionyl fluoride intermediate.[13] The latter was reported to react with sodium carbonate at temperatures between ambient and 80 °C to form a TFVE in very high yields. 3-Chloroperfluoropropene oxide is not commercially available.

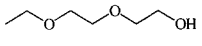
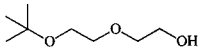
Herein we describe the first reported syntheses of alkoxy TFVEs by thermolysis of trimethylsilyl esters of 2-*alkoxy*-2,3,3,3-tetrafluoropropionates. Previous attempts to synthesize hydrocarbon-substituted TFVEs by thermolysis of 2-alkoxy-2,3,3,3-tetrafluoropropionate salts gave unanticipated chemistry with negligible to low yields of TFVE depending on the hydrocarbon substituent and counterion.[1] To date, fluoro/perfluorinated TFVEs have been synthesized in high yields by thermolysis of trimethylsilyl 2-*fluoro*alkoxy-2,3,3,3-tetrafluoropropionates in the presence of potassium fluoride.[12] Substituted acid fluorides have also been successfully converted to the TFVEs;[12,14,15] however, unlike the TFVEs described herein, published examples were prepared from highly fluorinated or perfluorinated acid fluorides or ketones. Fluorine or trifluoromethyl substitution appears to stabilize a fluoroalkoxide intermediate which then reacts with HFPO.[16]

Results

The overall synthetic route and reaction yields are summarized in the Scheme 1 and Table 1, respectively. Two equivalents of the sodium alkoxide react with HFPO to yield the ester **5**, which is converted to the sodium carboxylate salt **6** and then to the trimethylsilyl ester[17] **7** prior to thermolysis to the desired TFVE **8**. Conversion of the alkoxy ester to the trimethylsilyl ester is critical to the success of this synthesis as will be described.

The sodium alkoxide **2** was prepared (but not isolated) by reaction of the appropriate alcohol **1** with sodium hydride. The sodium alkoxide was required for reaction with HFPO because, unlike lower alcohols (i.e., methanol, ethanol) which react readily with HFPO, higher alcohols

Table 1. Yields (%) for the Series of Reactions of a Sodium Alkoxide with HFPO To Produce the Desired TFVEs 8a,b

Entry	1 ROH	3 (%)	5 (%)	7 (%)	8 (%)
a		12 (22[a])	78 (68[a])	78	55
b		14	71.5	69	63

[a] Reaction started at −78 °C.

are significantly less reactive.[18] 2-(2-*tert*-Butoxyethoxy)ethanol,**1b**, was first prepared by reacting diethylene glycol with 1 equiv of isobutene in the presence of Amberlyst 15 resin in methylene chloride.[19] The monoether was obtained in 70% yield (96% purity by gas chromatography, GC) following vacuum distillation. A negligible amount of the bis(2-*tert*-butoxyethyl) ether was formed.

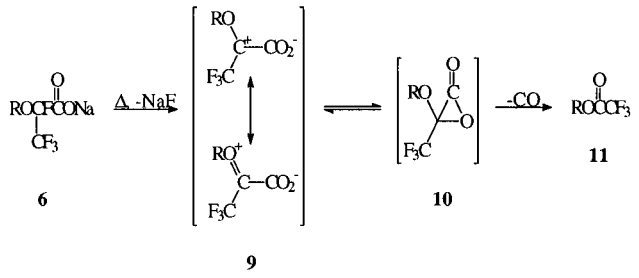
The reaction of the sodium alkoxide **2** with 0.59−0.75 equiv of HFPO in anhydrous ethylene glycol dimethyl ether (DME) was exothermic, resulting in the formation of an ester, **5**, and an alkyl perfluoropropionate, **3**. **5** contains two equivalents of the alcohol per equivalent of HFPO (cf. Scheme 1). Ring opening of HFPO at the more highly substituted carbon (C2) is favored by the electron-withdrawing trifluoromethyl (CF_3) group.[18] The mechanism likely involves formation of an acid fluoride intermediate, **4**, which reacts with a second equivalent of the alkoxide **2** to form **5**.

Two possible reaction pathways lead to the formation of the alkyl perfluoropropionate **3**: (1) the alkoxide **2** may attack at the least hindered carbon (C1) of HFPO with elimination of a fluoride ion followed by rearrangement to give **3**, or more likely, (2) a fluoride ion may react with HFPO at C2 to give the perfluoropropionyl fluoride which reacts with the alkoxide to give **3**. While HFPO has been shown to be stable to fluoride ion attack in *tert*-butyl alcohol, potassium *tert*-butoxide has been shown to react with HFPO in *tert*-butyl alcohol at 20 °C to form *tert*-butyl perfluoropropionate exclusively.[20] This suggests that nucleophilic attack occurs at C1 due to steric hindrance at C2. However, HFPO has also been shown to react with cesium fluoride to form perfluoropropionyl fluoride in ethers.[21] In the experiments described herein, the relative amount of **5** vs **3** produced was controlled by temperature. For example, a reaction started at −78 °C yielded 40 mol % (or 22% yield) of **3a**, whereas one started at 0 °C yielded 18 mol % (or 12% yield) of **3a**. At higher temperatures, formation of **5** and thus alkoxide attack at C2 were favored.

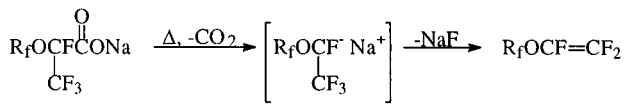
The ester **5** was hydrolyzed to the sodium salt **6** (but not isolated) in aqueous tetrahydrofuran (THF) with approximately 1.1−1.2 equiv of sodium hydroxide. THF and water (and the majority of byproduct alcohol **1**) were removed from the flask. The sodium carboxylate salt,

(11) Anderson, D. G.; Selman, S. U.S. Patent 3326984, 1967.
(12) Farnham, W. B. U.S. Patent 5391796, 1995.
(13) Ezzell, B. R.; Carl, W. P.; Mod, W. A. U.S. Patent 4515989, 1985.
(14) Pattison, D. B. U.S. Patent 3311658, 1967.
(15) Ezzell, B. R.; Carl, W. P.; Mod, W. A. U.S. Patent 4337211, 1982.
(16) Millauer, H.; Schwertfeger, W.; Siegemund, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 161−79.
(17) Yur'ev, Y. K.; Belyakova, Z. V. *Rus. Chem. Rev.* **1960**, *29* (7), 383−94.
(18) Sianesi, D.; Pasetti, A.; Tarli, F. *J. Org. Chem.* **1966**, *23*, 2312−6.
(19) Imaizumi, M.; Yasuda, M. German U.S. Patent 2450667, 1974; *Chem. Abstr. 83*, P178305e.
(20) Bekker, R. A.; Asratyan, G. V.; Dyatkin, B. L.; Knunyants, I. L. *Tetrahedron* **1974**, *39*, 3539−44.
(21) Moore, E. P., Jr. U.S. Patent 3322826, 1967.

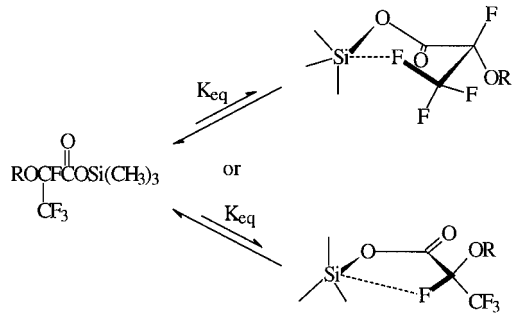
Scheme 2



Scheme 3



Scheme 4



dissolved in anhydrous diethyl ether, reacted with trimethylsilyl chloride (TMSCl) to produce the trimethylsilyl ester **7**. The sodium salt **6** is sensitive to acidic conditions, while **7** is susceptible to hydrolysis. To remove acidic species introduced from TMSCl and ensure complete dryness, sodium hydride was added before the addition of TMSCl to avoid conversion of **6** or **7** to the corresponding acid.

For purposes of characterization, pure sodium carboxylate salt **6a** was obtained in near-quantitative yields by reaction of **7a** with an equivalent of sodium hydroxide in aqueous THF. (Otherwise, **6a** was prepared, but not isolated, from the ester **5a** prior to thermolysis.) Thermolysis of **6a**, at 200 °C, resulted in the formation of a complex mixture of products. The yield was approximately 27% by mass and consisted primarily of the trifluoroacetate ester **11a** as identified by GC analysis. The trifluoroacetate ester **11a** was isolated by vacuum fractional distillation and further characterized by HRMS.

The trimethylsilyl ester **7** was injected at a constant rate onto the evacuated preheated column as described in the Experimental Section. Although the thermolysis reaction is exothermic, the reaction column was heated to between 140 and 150 °C to both maintain volatility of and ensure efficient passage of the trimethylsilyl ester through the column. GC analysis of the crude thermolysis product indicated that it consisted primarily of TFVE, fluorotrimethylsilane, and a small amount of the trifluoroacetate ester **11** (2−7% as determined by GC). The fluorotrimethylsilane and residual carbon dioxide were removed using an aspirator vacuum. TFVE **8** was further purified by vacuum fractional distillation with yields of 55−63% from the silyl ester.

Discussion

Vacuum thermolysis of sodium 2-[2-(2-ethoxyethoxy)-ethoxy]-2,3,3,3-tetrafluoropropionate, **6a**, resulted in the formation of a trifluoroacetate ester, 2-(2-ethoxyethoxy)-ethyltrifluoroacetate, **11a**. Sodium or potassium carboxylate salts, similar to those described herein, have also been shown to yield the trifluoroacetate esters as the major product after thermolysis.[1] A unimolecular reaction pathway was proposed, similar to that shown in Scheme 2: sodium fluoride, eliminated α to the carbonyl, results in a zwitterionic intermediate which can exist in either open-chain, **9**, or cyclic, **10**, forms. Loss of carbon monoxide from **10** results in the observed trifluoroacetate ester **11**. The alkoxy substituent, which is relatively electron-rich compared to a fluoroalkoxy substituent, may also stabilize the zwitterion **9** through resonance with the positive charge on the ether oxygen.

In contrast to the mechanism described for the formation of the undesirable trifluoroacetate ester **11** from **6**, it is generally accepted that salts of 2-*fluoro*alkoxy-2,3,3,3-tetrafluoropropionates decarboxylate to form an intermediate carbanion which eliminates fluoride ion at the *β*-position to form the desired olefin (Scheme 3).[13] For example, salts of 2-(fluoroalkoxy)-3-chloro-2,3,3-trifluoropropionates decarboxylate with loss of chloride ion to form the olefin at temperatures between ambient and 80 °C[11] and thus require dramatically less energy (with respect to what we observed) when a better leaving group (i.e., chloride) replaces fluoride.

The ^{19}F NMR spectrum of **7** lends insight into the thermolysis mechanism of trimethylsilyl esters to the desired TFVEs. The ^{19}F NMR spectrum of **7a** in deuterated chloroform, for example, was expected to have a simple AX3 pattern. However, two sets of peaks were observed as follows: (1) a doublet at −81.6 ppm and a relatively broader singlet at −131.7 ppm with an integration ratio of 3:1, attributed to CF_3 and CF, respectively, and (2) a less intense doublet at −82.0 ppm and a broad, considerably less intense, singlet at −131.2 ppm also with an integration ratio of 3:1. Comparing this ^{19}F NMR spectrum to those of preceding intermediates, reaction byproducts, and potential decomposition products of **7a** (i.e., the corresponding acid), it was determined that the second set of peaks could also be attributed to the CF_3 and CF of **7a**. A similar ^{19}F NMR spectrum was observed for **7b**.

In order to justify the assignment of the two sets of peaks to the same fluorine atoms, an equilibrium between two different forms of **7** is proposed as follows: (1) a conformation where there is no silicon−fluorine interaction and (2) a conformation with an intramolecular interaction between silicon and fluorine (cf. Scheme 4). The two possible interaction conformations that can be rationalized include those of either CF or CF_3 fluorine with silicon through either a five- or six-membered ring, respectively. The driving forces for the interaction conformation may include the high silicon−fluorine bond energy (43 kJ/mol) and the stability of the five- or six-membered ring. The interaction conformation is disfavored by the resultant steric crowding of the trimethylsilyl methyl groups in the interaction conformation which may decrease entropy. The ^{19}F NMR spectrum suggests a CF fluorine−silicon interaction (or a five-membered ring) because both peaks attributed to CF_3 are doublets.

To support the proposed equilibrium, the effect of temperature on relative NMR peak areas was studied. ^{19}F NMR spectra were collected for **7a** over a temperature range of −30 °C (243 K) to 94 °C (367 K), the temperature

being limited only by the boiling point of the NMR solvent (deuterated chloroform). Assuming that the less intense set of peaks represents the interaction conformation, the small to large peak area ratio[22] may be expected to increase with increasing temperature if the equilibrium (as described in Scheme 4) is endothermic. As the temperature increases the equilibrium constant (K_{eq}) shifts to the right.

As shown in Figure 1, a van't Hoff plot of ln K_{eq} versus $1/T$ appears linear (R^2 is 0.988); ln K_{eq} decreases as $1/T$ increases, or K_{eq} increases with increasing temperature. Assuming a similar equilibrium exists in the gas phase as exists in the deuterated chloroform, K_{eq} is estimated at 0.10 for thermolysis temperatures. The standard enthalpy for the equilibrium described in Scheme 4 was calculated from the slope in Figure 1, $\Delta H° = 3.0 \pm 0.1$ kJ mol^{-1}, and the standard entropy from the intercept, $\Delta S° = -12.1 \pm 0.4$ J mol^{-1} K^{-1}. The enthalpy and entropy data indicate that entropy dominates K_{eq} at temperatures higher than 250 K.

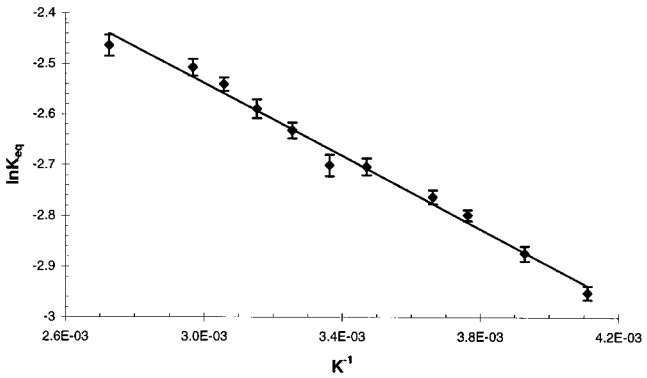


Figure 1. Plot of ln K_{eq} vs $^1/_T$ for the equilibium defined in Scheme 4 for trimethylsily ester **7a** ($R^2 = 0.988$). From the slope, $\Delta H° = 3.0 \pm 0.1$ kJ mol^{-1}. From the intercept, $\Delta S° = -12.1 \pm 0.4$ J mol^{-1} K^{-1} .

The trimethylsilyl ester **7** is necessary for successful thermolysis to the desired TFVE **8**; however, it is not clear that the proposed interaction conformation at thermolysis temperatures contributes significantly to the overall success. The proposed silicon−fluorine interaction may serve to weaken the silicon−oxygen bond, thereby facilitating decarboxylation in a similar way that alkali metal 2-methoxy-2,3,3,3-tetrafluoropropionates are more easily decarboxylated with weaker metal−oxygen bonds.[23] However, the concentration of the interaction conformation is relatively low (estimated at 9% from Figure 1) compared to the noninteraction conformation at thermolysis temperatures. On contact with the potassium fluoride catalyst, the trimethylsilyl ester is desilylated. Given that potassium carboxylates yield the undesired trifluoroacetate esters **11**, it is likely that decarboxylation is well advanced before a potassium−oxygen bond can form. The potassium fluoride catalyst is necessary because, in its absence, most of the trimethylsilyl ester is recovered while a small amount (~12 mol %) of the undesirable trifluoroacetate ester is formed. This observation further supports the proposed thermolysis mechanism.

(22) The CF_3 ^{19}F NMR signals were used for the van't Hoff plot to obtain the best signal to noise resolution. The TMS ester was distilled twice to >99% purity as determined by GC.

(23) Rozov, L. A.; Ramig, K. *Tetrahedron Lett.* **1994**, *35*, 4501−4.

Conclusion

Two new trifluorovinyl ethers incorporating hydrocarbon oligoether groups were synthesized by a new method from hexafluoropropene oxide and the appropriate sodium alkoxide. Conversion of the sodium (or potassium) carboxylate to the trimethylsilyl ester prior to thermolysis was essential for successful preparation of the desired TFVE. Without conversion to the trimethylsilyl ester, the undesired trifluoroacetate ester was formed. The thermolysis mechanism was investigated in order to gain insight into the importance of the silyl ester. ^{19}F NMR spectra indicate that either a five or six-membered ring exists between silicon and either CF or CF_3 fluorine. This interaction may influence the thermolysis mechanism.

Experimental Section

The reagents and solvents were purchased from Aldrich Chemical Co. (Millwaukee, WI) and used as received unless otherwise stated. Anhydrous diethyl ether and Celite 545 were purchased from Fisher Scientific (Toronto, Canada). Dry sodium hydride was prepared prior to use from a 60% dispersion in mineral oil by dispersion in pentane followed by filtration through a medium porosity glass frit funnel (four times) and then dried under nitrogen. Hexafluoropropene oxide (HFPO, 97%) was purchased from PCR Chemicals (Gainesville, FL) and used as received.

Compounds were characterized by gas chromatography (HP 6890, Hewlett Packard, Ontario) using a Restek Rtx-5 column (Chromatographic Specialties, Ontario; 0.530 mm × 15 m with a 1.2 μm film thickness) with FID detector, helium carrier gas (35 cm/s), and a split ratio of ~25:1. A typical temperature profile held the initial temperature at 80 °C for 1 min, then ramped the temperature to 230 °C at 15 °C/min, and finally held the temperature at 230 °C for 4 min.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were taken on a 200 MHz Varian Gemini spectrometer using tetramethylsilane as an external reference standard and deuterated chloroform as the solvent. Fluorine (^{19}F NMR) spectra were taken on a 300 MHz Varian Gemini spectrometer using fluorotrichloromethane as an external reference standard and deuterated chloroform as the solvent. Mass spectra were obtained on a Micromass 70-250S (double-focusing) mass spectrometer, arrayed with a HP 5890 gas chromatograph (capillary column: J&W Scientific, DB-5ms, 30 m, 0.25 mm). High-resolution data were obtained at 10 000 (10% valley) resolution. $2\sigma = 5.7$ ppm based on 27 measurements of the molecular ion of cholesterol.

The gas phase thermolysis apparatus consisted of a 1.9 cm × 43 cm borosilicate glass tube with B24 female inlet and B24 male outlet ground glass joints. A 1.3 cm × 2.3 m 400 W heating tape was wrapped along the middle 35 cm and insulated with multiple layers of glass insulation tape. Sample and nitrogen carrier gas were introduced via needles through a septum. A B24/B14 reducer to vacuum side arm adapter and a receiver flask were attached to the outlet. The tube was packed with 40 g of approximately 3 mm diameter borosilicate glass beads held in place by Vigreaux type indentations in the tube, 1.3 cm above the outlet. Suspended on the glass beads was approximately 2−3 g of potassium fluoride. The temperature was maintained by a temperature controller connected to a hose clamp thermocouple mounted on the outside of the heating tape and under the insulation. The internal temperature was monitored using a thermocouple mounted in the center of the tube through a port located halfway along the tube length.

2-(2-*tert*-Butoxyethoxy)ethanol (1b). To a dry 500 mL, 3-neck round bottom flask that was fitted with a dry ice/acetone condenser under a static nitrogen purge were added 30.0 g (283 mmol) of diethylene glycol, 250 mL of methylene chloride, and 7.0 g of Amberlyst 15 resin. With magnetic stirring, 19.0 g (337 mmol) of isobutene was slowly added and the reaction mixture was maintained at 30 °C. After 7 h, GC

analysis indicated that 90% of the diethylene glycol had been converted to 2-(2-*tert*-butoxyethoxy)ethanol and that very little (<1%) had been converted to bis(2-*tert*-butoxyethyl) ether. The reaction was stopped by removal of the Amberlyst 15 resin by gravity filtration. The solvent was removed by rotary evaporation leaving a clear, oily liquid. 2-(2-*tert*-Butoxyethoxy)ethanol (32.1 g, 70% yield, >96% purity by GC) was isolated by vacuum fractional distillation (~0.05 mmHg, bp 36−37 °C). ^{1}H NMR: δ 3.8−3.5 (m, 8H, CH_2), 3.0 (br s, 1H, OH), 1.2 (s, 9H, $C(CH_3)_3$).

2-(2-Ethoxyethoxy)ethyl 2-[2-(2-Ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (5a). To a dry 500 mL, 3-neck round bottom flask that was fitted with a 50 mL pressure-equalizing addition funnel, mechanical stirrer, and dry ice/acetone condenser under a nitrogen purge was added 3.6 g (150 mmol) of dry sodium hydride. Approximately 200 mL of anhydrous ethylene glycol dimethyl ether (DME) was added by cannula to the flask. The reaction flask was cooled to ~0 °C, and the dispersion stirred while 20.0 g (149 mmol) of 2-(2-ethoxyethoxy)ethanol was slowly added. In forming the alkoxide, hydrogen gas evolved and the resulting cloudy white solution was stirred for 1 h. The addition funnel was replaced with a septum through which 14.6 g (88.0 mmol) of HFPO was slowly added using a transfer needle. Since the reaction was very exothermic, care was taken to maintain the temperature at or below 30 °C. A cloudy, pale yellow reaction mixture resulted and was stirred for an additional 3 h at room temperature. The reaction mixture was filtered through 1 cm of Celite 545 on a coarse porosity glass frit funnel (to separate sodium fluoride), and the supernatant was rotary evaporated, leaving a yellow, oily liquid that was vacuum distilled using a 10 cm Vigreaux column. Two fractions were isolated; the first fraction (bp 43−45 °C, 0.05 mmHg) was identified as the byproduct ester, 2-(2-ethoxyethoxy)ethyl perfluoropropionate (yield 3.8 g, 13%), and the second fraction (bp 112−114 °C, 0.04 mmHg) was identified as the desired product, 2-(2-ethoxyethoxy)ethyl 2-[2-(2-ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (yield 22.8 g, 78%, >97% purity by GC). ^{19}F NMR: δ −81.7 (d, CF_3), −132.0 (br m, CF). ^{1}H NMR: δ 4.5 (m, 2H, CO_2CH_2), 3.95 (m, 2H, $CFOCH_2$), 3.7−3.45 (m, 16H, OCH_2), 1.2 (t, 6H, CH_3). HRMS: $(MH)^+$ calcd 395.1693, obsd 395.1705.

2-(2-*tert*-Butoxyethoxy)ethyl 2-[2-(2-*tert*-Butoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (5b). To a dry 500 mL, 3-neck round bottom flask that was fitted with a 50 mL pressure-equalizing addition funnel, mechanical stirrer, and dry ice/acetone condenser under a nitrogen purge was added 3.3 g (140 mmol) of dry sodium hydride. Approximately 200 mL of anhydrous DME was added by cannula to the flask. 2-(2-*tert*-Butoxyethoxy)ethanol (22.0 g or 136 mmol) was slowly added to the cooled reaction flask (~0 °C) to form the alkoxide with evolution of hydrogen gas. The resulting cloudy white reaction mixture was stirred for 1 h to ensure complete formation of the alkoxide. The addition funnel was replaced with a septum through which 17.0 g (102 mmol) of HFPO was slowly added using a transfer needle and during which the reaction mixture was maintained below 30 °C. The slightly cloudy, pale yellow reaction mixture that resulted was stirred for an additional 3 h. The reaction mixture was filtered through 1 cm of Celite 545 on a coarse porosity glass frit funnel (to separate sodium fluoride), and the supernatant was removed by rotary evaporation, leaving a yellow, oily liquid. The crude product was vacuum distilled using a short path distillation apparatus. Two fractions were isolated, the first fraction (bp 53−56 °C, 0.05 mmHg, yield 4.3 g, 14%) was identified by GC as a mixture of unreacted alcohol (0.3 g) and byproduct ester 2-(2-*tert*-butoxyethoxy)ethyl perfluoropropionate (yield 4 g, 13%), and the second fraction (bp 132−134 °C, 0.04 mmHg) was identified as the desired product, 2-(2-*tert*-butoxyethoxy)ethyl 2-[2-(2-*tert*-butoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (yield 21.8 g, 71.5%, >99% purity by GC). ^{19}F NMR: δ −81.7 (d, CF_3), −132.0 (br m, CF). ^{1}H NMR: δ 4.5 (m, 2H, CO_2CH_2), 3.95 (m, 2H, $CFOCH_2$), 3.8−3.4 (m, 12H, OCH_2), 1.2 (s, 18H, $C(CH_3)_3$). HRMS: $(M-CH_3)^+$ calcd 435.2006, obsd 435.1988.

Trimethylsilyl 2-[2-(2-Ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (7a). To a 300 mL, round bottom flask equipped with condenser and thermocouple side port were added 26.9 g (68.2 mmol) of 2-(2-ethoxyethoxy)ethyl 2-[2-(2-ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate and 175 mL of THF. Sodium hydroxide (3.4 g or 85 mmol) and 6.1 mL (340 mmol) of deionized water were added to the flask with magnetic stirring and maintained at 40 °C for 3 h during which the translucent reaction mixture became slightly yellow. GC analysis of a sample indicated that the ester was converted to the 2-[2-(2-ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionic acid sodium salt. Most of the THF and water were removed from the reaction mixture by rotary evaporation. Any remaining water and most of the 2-(2-ethoxyethoxy)ethanol (~80%) were removed by short path vacuum distillation (~0.05 mmHg, stillpot temperature < 100 °C). After the reaction pot cooled to ambient temperature, approximately 125 mL of diethyl ether was added by cannula into the flask. The sodium salt dissolved with magnetic stirring to give a translucent, light amber solution. Sodium hydride (0.8 g or 30 mmol) was added to the flask. With ice bath cooling, 15.0 g (138 mmol) of trimethylsilyl chloride was slowly added to the flask during which a slight exotherm and sodium chloride precipitation were observed. After 3 h of stirring at room temperature, the reaction mixture was filtered through 1 cm of Celite 545 on a medium porosity glass frit funnel. Most of the diethyl ether was removed by rotary evaporation. The crude product was vacuum distilled using a 4 in. Vigreaux column from which three fractions were isolated; the first fraction (bp 28−30 °C, 0.06 mmHg) was identified as 2-(2-ethoxyethoxy)ethanol, the second fraction (bp 38−40 °C, 0.06 mmHg) was identified as 2-(2-ethoxyethoxy)ethyl trimethylsilyl ether, and the third fraction (bp 56−57 °C, 0.04 mmHg) was identified as the desired product, trimethylsilyl 2-[2-(2-ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (yield 18.6 g, 78%, >97% purity by GC). ^{19}F NMR (20 °C): δ −81.6 and −82.0 (d, CF_3), −131.2 and −131.7 (br s, CF). ^{1}H NMR: δ 3.9 (m, 2H, $CFOCH_2$), 3.8−3.45 (m, 6H, OCH_2), 1.2 (t, 3H, CH_3), 0.4 and 0.15 (s, 9H, $Si(CH_3)_3$). HRMS: $(M-H)^+$ calcd 349.1094, obsd 349.1086.

Trimethylsilyl 2-[2-(2-*tert*-Butoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (7b). To a 300 mL, round bottom flask equipped with a condenser and thermocouple side port were added 20.0 g (44.4 mmol) of 2-(2-*tert*-butoxyethoxy)ethyl 2-[2-(2-*tert*-butoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate and 130 mL of THF. Sodium hydroxide (2.11 g or 52.8 mmol) and 4.0 mL (220 mmol) of deionized water were added to the reaction flask with magnetic stirring and maintained at 40 °C overnight during which a translucent, pale yellow solution resulted. GC analysis of a sample indicated that the ester was converted to the sodium salt. Most of the THF and water were removed from the reaction mixture by rotaryevaporation. The remaining water and most of the 2-(2-*tert*-butoxyethoxy)ethanol (~70%) were removed by short path vacuum distillation (~0.05 mmHg, stillpot temperature < 100 °C). After the reaction pot cooled to ambient temperature, approximately 125 mL of diethyl ether was added by cannula into the flask. The sodium salt dissolved with magnetic stirring to give a translucent, yellow solution; 0.5 g (21 mmol) of sodium hydride was added to the reaction flask with evolution of a small amount of hydrogen gas; 10.0 g (92.0 mmol) of trimethylsilyl chloride was slowly added to the flask during which a slight exotherm and sodium chloride precipitation were observed. After 3 h of stirring at room temperature, the mixture was filtered through 1 cm of Celite 545 on a coarse porosity glass frit funnel. Most of the diethyl ether was removed by rotary evaporation. The crude product was vacuum distilled using a 10 cm Vigreaux column from which two fractions were isolated; the first fraction (bp 45−48 °C, 0.04 mmHg, yield 2.3 g) was identified as 2-(2-*tert*-butoxyethoxy)ethyltrimethylsilyl ether, and the second fraction (bp 71−73 °C, 0.04 mmHg) was identified as the desired product, trimethylsilyl 2-[2-(2-*tert*-butoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (yield 10.8 g, 69%, >96% purity by GC). ^{19}F NMR (ambient temperature): δ −81.6 and −82.0 (d, CF_3), −130.6 and −131.7 (br s, CF). ^{1}H NMR: δ 3.9 (m, 2H, $CFOCH_2$), 3.75−3.45 (m, 6H, OCH_2), 1.3 and 1.2 (s, 9H,

$C(CH_3)_3$), 0.4 and 0.15 (s, 9H, $Si(CH_3)_3$). HRMS: $(M - CH_3)^+$ calcd 363.1251, obsd 363.1237.

1-[2-(2-Ethoxyethoxy)ethoxy]-1,2,2-trifluoroethene (8a). Trimethylsilyl 2-[2-(2-ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (9.30 g or 26.5 mmol) was injected onto the preheated thermolysis column (140 °C, ~50 mL/min N_2 flow, ~0.2 mmHg) at a rate of ~0.2 mL/min using a 10 mL Gastight syringe and syringe pump. The thermolysis was exothermic, and the column temperature increased to ~160 °C during the injection. The product was collected for an additional 1 h after the injection was completed in a receiver flask cooled with liquid nitrogen; 7.8 g of an oily, pale yellow liquid product was collected. The crude product was fractionally distilled to give 3.58 g (63% yield, 95% purity by GC) of a product identified as 1-[2-(2-ethoxyethoxy)ethoxy]-1,2,2-trifluoroethene (bp 22 °C, 0.15 mmHg). ^{19}F NMR: δ −123.4 (dd, 1F, J = 56, 104 Hz, CF), −130.2 (dd, 1F, J = 104, 108 Hz, CF), −135.1 (dd, 1F, J = 56, 108 Hz, CF). ^{1}H NMR: δ 4.15 (m, 2H, $CFOCH_2$), 3.75 (t, 2H, OCH_2), 3.7−3.45 (m, 6H, OCH_2), 1.2 (t, 3H, CH_3).

1-[2-(2-*tert*-Butoxyethoxy)ethoxy]-1,2,2-trifluoroethene (8b). Trimethylsilyl 2-[2-(2-*tert*-butoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (11.8 g or 31.3 mmol) was injected onto the preheated thermolysis column (150 °C, ~50 mL/min N_2 flow, ~0.2 mmHg) at a rate of ~0.2 mL/min using a 10 mL Gastight syringe and syringe pump. The thermolysis was exothermic, and the column temperature increased to ~170 °C during the injection. The product was collected in a receiver flask cooled with liquid nitrogen for an additional 1 h after the injection was completed. An oily, pale yellow liquid product (8.72 g) was collected. The crude product was fractionally distilled to give 4.2 g (55% yield, 95% purity by GC) of a product identified as 1-[2-(2-*tert*-Butoxyethoxy)ethoxy]-1,2,2-trifluoroethene (bp 26 °C, 0.15 mmHg). ^{19}F NMR: δ −123.5 (dd, 1F, J = 56, 104 Hz, CF), −130.3 (dd, 1F, J = 104, 108 Hz, CF), −135.1 (dd, 1F, J = 56, 108 Hz, CF). ^{1}H NMR: δ = 4.15 (m, 2H, $CFOCH_2$), 3.75 (t, 2H, OCH_2), 3.65−3.45 (m, 4H, OCH_2), 1.2 (s, 9H, $C(CH_3)_3$), HRMS: $(M - CH_3)^+$ calcd 227.0895, obsd 227.0892.

Sodium 2-[2-(2-Ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate (6). To a 300 mL round bottom flask were added 9.33 g (26.6 mmol) of trimethylsilyl 2-[2-(2-ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate and 85 mL of THF. With magnetic stirring, 1.22 g (30.5 mmol) of sodium hydroxide followed by 2.52 mL (140 mmol) of deionized water were added to the reaction flask. After 1 h of stirring at room temperature, the reaction mixture was filtered through 1 cm of Celite 545 on a medium porosity frit funnel. Residual suspended small particulates were separated by centrifugation. Most of the THF and water were removed by rotary evaporation, and final purification was done in a vacuum oven at 40 °C for 2 h to give a very viscous, pale yellow liquid. The yield of sodium 2-[2-(2-ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate was 7.58 g (95%). ^{19}F NMR: δ −81.9 (br s, CF_3), −131.8 (br s, CF). ^{1}H NMR: δ 4.2−3.4 (br m, 10H, OCH_2), 1.2 (m, 3H, CH_3).

2-(2-Ethoxyethoxy)ethyl Trifluoroacetate (11a). To a 300 mL round bottom flask equipped with condenser and thermocouple side port were added 30.4 g (77.1 mmol) of 2-(2-ethoxyethoxy)ethyl 2-[2-(2-ethoxyethoxy)ethoxy]-2,3,3,3-tetrafluoropropionate and 175 mL of THF. Sodium hydroxide (4.06 g or 102 mmol) and 7.13 mL (396 mmol) of deionized water were added to the flask with magnetic stirring and maintained at 40 °C for 3 h during which the reaction mixture became slightly yellow. The reaction mixture was filtered through 1 cm of Celite 545 on a coarse porosity glass frit funnel. The majority of the THF and water were removed by rotary evaporation. Most (92%) of the byproduct, 2-(2-ethoxyethoxy)ethanol, was removed by short path vacuum distillation (mantle temperature ~ 120 °C). The temperature of the heating mantle was increased to 200 °C, and the resulting thermolysis product was collected in a receiver flask cooled by liquid nitrogen. An oily, pale yellow liquid was obtained (8.2 g or 27%, w/w, based on the starting ester). GC analysis of a sample indicated that it was a complex mixture with one predominant (~50%) low-boiling component. By vacuum fractional distillation (bp 25 °C, 0.07 mmHg, 87% purity by GC), 3.3 g of a product was isolated and identified as 2-(2-ethoxyethoxy)ethyl trifluoroacetate. ^{19}F NMR: δ −75.3 (s, CF_3). ^{1}H NMR: δ 4.5 (t, 2H, $C(O)CH_2$), 3.8 (t, 2H, OCH_2), 3.6−3.45 (m, 6H, OCH_2), 1.2 (t, 3H, CH_3). HRMS: $(MH)^+$ calcd 231.0844, obsd 231.0822.

Acknowledgment. The authors gratefully acknowledge partial financial assistance from NSERC, the University of Toronto, and DuPont Canada.

Supporting Information Available: ^{1}H and ^{19}F NMR spectra of both monomers **8a**,**b** (4 pages). This material is contained in 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.

JO971319D