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SYNTHESIS OF PERFLUORINATED ETHERS BY AN IMPROVED SOLUTION PHASE DIRECT FLUORINATION PROCESS

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SUMMARY

We have developed schemes to make perfluorinated ethers that cover a wide range of molecular weights and boiling points. We describe a relationship that can be used to predict the boiling points of perfluoro polyethers; this is used to assist in the combination of reagents for synthesizing a target having particular physical properties such as boiling point, etc. Our first scheme is to build molecular weight by condensing polyols with fluoro-olefins such as TFE and HFP. These intermediates are then fluorinated by a simple solution phase, batch, photo-assisted direct fluorination to give high yields of isomerically pure perfluorinated ethers. In a second scheme we use ethylene oxide to fine-tune the molecular weight of the polyol, and the weight of these can be extended by reaction with an appropriate fluoro-olefin. These intermediates can be fluorinated using our batch fluorinator to make new perfluorinated ethers of a specific molecular weight and boiling point.

INTRODUCTION

Perfluoropolyethers possess excellent chemical and thermal stability which ensures a wide field of application for these compounds as heat transfer media, sealing liquids, lubricants under extreme chemical conditions, additives for oils and greases, turbine propellents and hydraulic liquids. They exhibit low dielectric constants, high breakdown voltages and low loss factors in alternating fields which makes them

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particularly suited for applications in the electrical area. In the electronics industry, for example, perfluoropolyethers are particularly useful in vapor phase soldering or as convection cooling liquids in transformers or similar devices. Their excellent dissolving power for oxygen and carbon dioxide enables them to be used as oxygen conveyers in heart-lung machines and also directly as blood substitutes in living organisms. These products also find applications in many spheres of nuclear and chemical engineering. Because of their outstanding chemical resistance, they are superior to the polypropylene oxide fluids which hitherto dominated these application fields, especially at temperatures above 200°C. Currently available vapor phase soldering fluids can be relatively expensive to manufacture, and they may release toxic vapors at their decomposition temperatures. In addition, some have a high solubility in soldering rosin which requires expensive reclamation and reduces fluid life.

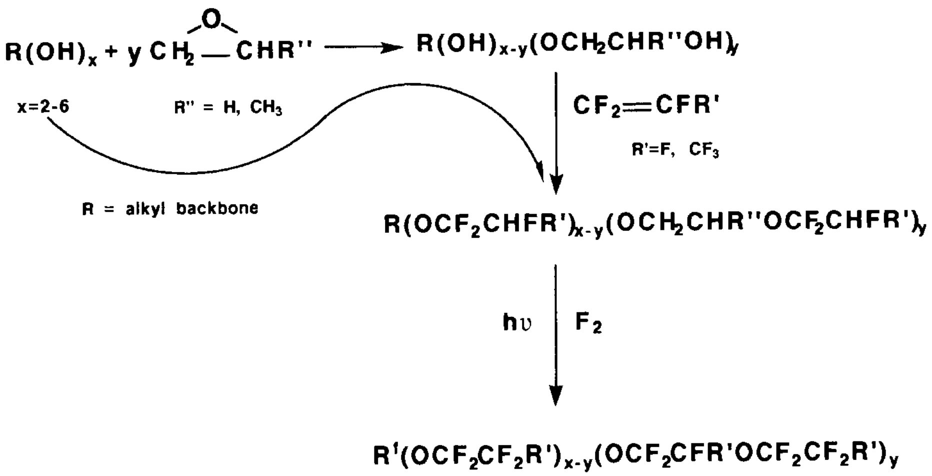
It is well known that fluorination of hydrocarbons requires very low initial temperatures, low initial concentrations of fluorine, long reaction times, or highly specialized equipment to prevent uncontrolled reactions and formation of unwanted by–products. Remedies for these difficulties have been offered by Lagow who uses a cryogenic reactor having a number of temperature zones which enable the gradual perfluorination of a hydrocarbon as the substrate moves through the reactor [1]. Reaction times in this process are typically very long. Adcock has described an aerosol fluorination reactor in which the substrate is deposited on an aerosol of sodium fluoride produced at high temperatures [2]. The substrate is then exposed to fluorine along a thermal gradient and is optionally sent through a photochemical reactor zone to form the perfluorinated product. The process requires specialized equipment, uses large quantities of sodium fluoride, and is difficult to scale up. Scherer, et al., recently described a liquid phase fluorination process in which F-hexane (FC-72) and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) are in combination as the reaction medium or solvent for the substrate in liquid phase photofluorination [3]. This combination broadens the substrate spectrum applicable to this method from partially fluorinated substrates to non-fluorinated substrates. The fluorine is maintained in stoichiometric excess at all times. The compound to be fluorinated is metered into the reactor slowly with vigorous stirring to maintain a low concentration relative to fluorine, and to ensure that efficient heat dispersal occurs. Prior to Scherer's work, a number of other publications have appeared in recent years utilizing solution phase direct fluorination for the syntheses of fluorinated and perfluorinated compounds [4].

In this paper we describe a convenient, simple, easily scalable, and cost-effective method for preparing perfluoropolyethers using an improved method of photo-assisted solution phase direct fluorination.

RESULTS AND DISCUSSION

Our method of solution phase direct fluorination involves partially fluorinated intermediates rather than non-fluorinated intermediates. Whereas direct fluorination of hydrocarbons proceeds in an uncontrolled manner unless precautions are taken, the fluorination of partially fluorinated materials proceeds much more smoothly with reduced degradation of the substrate and reduced formation of oligomeric and polymeric by-products. The desired product is obtained in a shorter period of time resulting in higher productivity. As a result less fluorine, an expensive reactant, is used resulting in a substantial economic benefit.

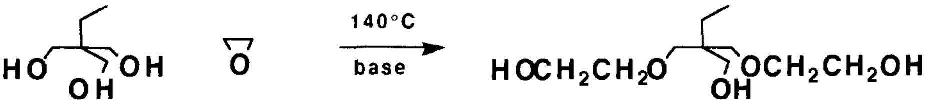
Our reaction sequence to make a wide range of perfluorinated ethers is shown below.



Scheme 1.

Advantages of this method are that 1) some fluorine is added to the final product in the form of relatively inexpensive fluoroolefins (TFE and HFP), 2) the starting materials for our direct fluorination step and our final products have well defined structures and molecular weights; we observe no C-C bond cleavage using our mild conditions, and 3) the partially fluorinated ethers are more robust in the direct fluorination step than the fully protonated analogue.

This overall method gives us two ways to control the molecular weight of the final product 1) by alkoxylation of a commercially available polyol with either ethylene oxide or propylene oxide and 2) by using TFE or HFP as the fluoroolefin. An example of using ethylene oxide to extend a polyol is shown in Scheme 2.



Average composition by NMR

Scheme 2.

The partially fluorinated intermediates are obtained by reacting a commercially available polyalcohol or extended polyalcohol (*vide supra*) with a fluorinated olefin in the presence of a base in a polar aprotic solvent, such as N,N-dimethylformamide as described by England, et al. [5] (Scheme 3).

$$R(OH)_x + xCF_2{=}CFR' \xrightarrow[DMF]{30\text{-}80^\circ C} R(OCF_2CHFR')_x$$

$x = 2\text{-}6$ $\quad$ $R' = F, CF_3$

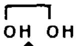
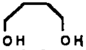
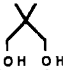
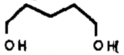
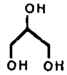
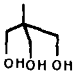
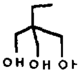
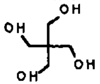
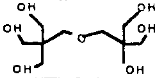
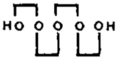
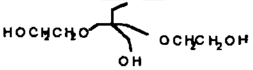
Scheme 3.

The yields for these reactions varied from 33 to 85% (unoptimized), and the OH^-/base ratio used was anywhere from 3-16. A list of the tetrafluoroethyl ethers we have prepared are shown in Table 1.

The partially fluorinated ethers prepared by the method shown in Scheme 3 using TFE as the fluoro-olefin are more easily prepared than the HFP analogues. The HFP reactions were plagued by side reactions believed to arise from HF elimination of the partially fluorinated ether under the basic conditions. Insertion of the resulting olefins into OH bonds of another polyol molecule could give a number of byproducts. NMR data for some fluoroethers is shown in Tables 2 and 3.

TABLE 1

TFE Adducts of Polyols

Polyol	% Yield (%purity)^a	BP (mm Hg)^b
	33(94)	91(55)
	50(95)	95(20)
	48(94)	106(55)
	34(94)	110(50)
	85(95)	127(70)
	19(87)	126(50)
	24(94)	140(50)
	50(98)	123(20)
	78(98)	162(10)
	50(91)	165(10)
	40(99.5)	181(27)
	-	170(15)

a Product yield based on polyol. Value in parentheses is % purity of distilled product (assessed from GC area%).

b. Boiling point (°C) at pressure (mm Hg) indicated in parentheses.

Our attempts to add TFE to the following polyols were unsuccessful, possibly due to steric or solubility effects: erythritol, xylitol, sorbitol [6], and inositol. The perfluorinated TFE adducts of these polyols would be particularly interesting since they are predicted to have boiling points of 168°C, 207°C, 239°C, and 233°C, respectively (*vide infra*).

Our fluorination method uses a simple Teflon® FEP reactor connected to a stainless steel head using a compression clamp that encircled the entire reactor (see Fig.1). The reactor was made from a 1 L bottle with the top cut off. Our UV source is a simple Sylvania UV sunlamp commonly found in the hardware store [7]. The outside of the reactor is shrouded with aluminum foil to contain the UV irradiation and to prevent condensation on the reactor surface with the aid of a nitrogen blanket.

TABLE 2

NMR Data for Fluorocthers[a]

Formula	^1H Chemical Shifts (Coupling Constants)
$(HCF_2CF_2OCH_2)_2$	3.35 (s, 4), 5.02 (t of t, 2JHF=53.4 Hz, J_{HF}=3.0 Hz,1. 9H)
$HCF_2CF_2O(CH_2)_3OCF_2CF_2H$	1.24 (quinet, 3JHH=6.1Hz, 1.9H), 3.48 (t, 3JHH=6.2 Hz, 4.1H), 5.00(t of t, JHF=53.0 Hz, 3JHF=2.6 Hz, 2.0 H)
$(HCF_2CF_2OCH_2)_2C(CH_3)_2$	0.55 (s,6H), 3.37 (s, 4H), 5.00 (t of t, JHF= 2.7 Hz, 3JHF= 53.1H,
$HCH_2CF_2O(CH_2)_4OCF_2CF_2H$	1.14(m, 3.7 H, 3.43(m, 4.0 H), 5.08(t of t, J_{HF}=53.2Hz, J_{HF}=2 . 7
$HCF_2CF_2O(CH_2)_5OCF_2CF_2H$	0.93(m, 2.0 H), 1.10(m, 4.0 H), 3.47(t, $^3J_{HH}$= 6.4Hz, 4.2 H), 5.11 (t of t, J_{HF}= 53.2 Hz, J_{HF}= 2.7 Hz, 2.1H)
$HCF_2CF_2(OCH_2CH_2)_4OCF_2CF_2H$	3.18(m), 3.31(m, integral w/3.18 = 12.1H), 3.67(m, 4.1 H), 5.11 (t of t, J_{HF}=53.1 Hz, J_{HF}= 3.0 Hz, 2.0 H)
$HCF_2CF_2(OCH_2CH_2)_5OCF_2CF_2H$	3.23(m, 4H), 3.35(m), 3.42(s) last two sets of resonances
$(HCF_2CF_2OCH_2)_2CHOCF_2CF_2H$	3.51 (d, $^3J_{HH}$=4.9 Hz, 4.5 H), 4.02 (quintet, J_{HH}= 4.9 Hz, 1.0 H), 4.96
$(HCF_2CF_2OCH_2)_3CCH_3$	0.58 (s, 3H), 3.43 (s, 7.1 H), 4.98 (t of t, J_{HF} = 53.0 Hz, $^3J_{HF}$ = 2.6
$(HCF_2CF_2OCH_2)_3CC_2H_5$	0.48 (t, $^3J_{HH}$ =7.6 Hz, 3.0 H), 1.08 (q, $^3J_{HH}$= 7.5 Hz, 2.0 H), 3.50 (s,
$(HCF_2CF_2OCH_2)_4C$	3.55 (s, 8.1 H), 4.93 (t of t, $^2J_{HF}$= 53.0 Hz, $^3J_{HF}$= 2.3 Hz, 4.0 H)
$[(HCF_2CF_2OCH_2)_3CCH_2]_2O$	2.95 (s, 4 H), 3.70 (s, 12.4 H), 5.02 (t of t, $^2J_{HF}$= 53.0 Hz, $^3J_{HF}$= 1.9

a. Spectra were recorded in 5 mm tubes using C_6D_6 solvent on a Bruker 250, Varian 300, or Varian 400 MHz instrument. Chemical shifts were measured relative to an internal TMS standard.

TABLE 3

^{19}F NMR Data For Fluoroethers[a]

$HCF_2CF_2(OCH_2CH_2)_4OCF_2CF_2H$	-91.52 (m, 2F), -136.5 (d ot t, $^2J_{HF}$= 52.8 Hz, J_{FF}= 5.7 Hz, 2F)
$HCF_2CF_2O(CH_2)_5OCF_2CF_2H$	-91.31 (s, 2F), -136.39 (d of t), $^2J_{HF}$= 53.0 Hz, $^3J_{FF}$= 5.4 Hz, 2F)
$(HCF_2CF_2OCH_2)_3CC_2H_5$	-92.24 (m, 2F), -136.62 (d of t, $^2J_{HF}$= 53.3 Hz, $^3J_{FF}$= 4.8 Hz, 2F)
$[(HCF_2CF_2OCH_2)_3CCH_2]_2O$	-92.25 (s, 2F), -136.66 (d, $^2J_{HF}$= 53.2 Hz, 2F)

a. Spectra were recorded in 5 mm tubes using C_6D_6 solvent on a Varian 300 or Varian 400 MHz instrument. Chemical shifts were measured relative to external CFC-11 standard.

Internal copper cooling coils were used to maintain a low reactor temperature (usually -15°C), and the cooling fluid (CFC-11) was cycled on and off by a temperature controller that monitored the internal reactor temperature. The salient feature of our simple reactor is the Teflon® baffling made from 1/8" flat Teflon® stock. Owing to low polarizability, F_2 has a low solubility in all solvents; for optimum F_2 utilization, we found that baffles, a Teflon® (or Monel®) impeller on a Monel® shaft with Teflon® bearing, and an overhead stirrer operating at 600 rpm are essential.

This combination increases the contact time of the F_2 gas with the fluorinated solvent (CFC-11, CFC-113, or Krytox®); bubbles of gas seem to be suspended in the liquid owing to the turbulent currents in the reactor using this setup. A Teflon®-coated stir bar is far less efficient.

We dissolved our fluorinated ether intermediates in an inert solvent such as CFC-11 ($CFCl_3$), CFC-113, Krytox® heptamer ($CF_3CF_2CF_2O$-[$CF(CF_3)CF_2O$]$_5$-CF_2CF_3), or direct fluorination products of our reactions. Typically, the concentration of substrate varied from .2 to 2% (w/w). The solution is cooled to a temperature between -10°C and -78°C. The agitation is begun, and the solution is purged with nitrogen to displace dissolved oxygen in the solvent and solute.

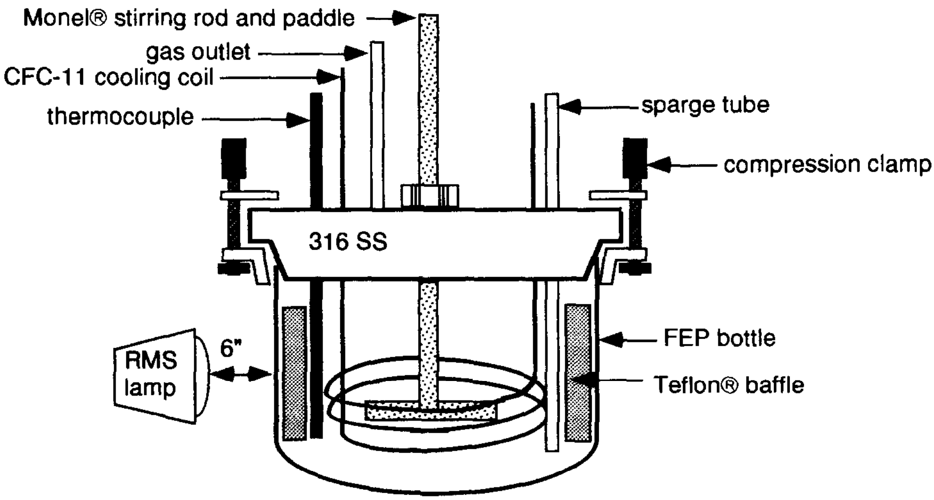


Fig.1. Direct Fluorination Reactor.

The concentration of the fluorine in the feed gas is gradually increased from 5% by volume to 50% by volume over the course of one to five hours. The timing of the reaction sequence is determined by the amount of hydrogen present in the substrate. If the substrate has greater than about 3% hydrogen by weight, then the increase in the fluorine concentration in the feed gas must occur over the course of about three hours. If the substrate contains 0.5% hydrogen by weight or less, then the concentration of fluorine can be increased more quickly. After the concentration of fluorine-containing feed gas reaches 50% by volume, the fluorine concentration in the feed gas remains constant thereafter for an additional two to five hours until the reaction is complete. The feed gas is passed continuously through the reactor during the reaction, and gas leaving the reactor is passed through sodium fluoride and alumina or carbon scrubbers to remove the HF and fluorine, respectively, in the effluent gas.

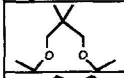
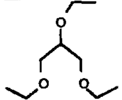
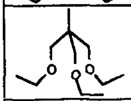
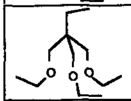
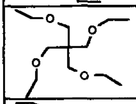
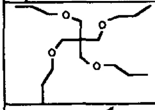
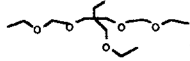
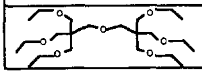
In the later stages of the reaction, it becomes progressively more difficult to replace all of the hydrogen substituents of the intermediate with fluorine atoms. By irradiating the reaction solution with ultraviolet radiation, it is possible to achieve a significantly higher degree of fluorine substitution. It is important that the irradiation be initiated at an appropriate time in the fluorination sequence otherwise the intermediate may be subjected to degradative attack due to the high reactivity of the fluorine atoms generated by the influence of the ultraviolet light. It is important to achieve an appropriate balance between the concentration of fluorine in the feed gas and the degree of completion of the reaction and irradiating the reaction solution with an ultraviolet source while increasing the concentration of fluorine in the feed gas from 28% by volume to 50% by volume and maintaining the irradiation until the reaction is complete.

The temperature of the reaction was dictated by the number of hydrogens to be replaced by fluorine in the substrate, the vapor pressure of the substrate, and the vapor pressure and potential reactivity of the solvent. Normally, the temperature of the solution is adjusted to between the freezing point of the solvent and that temperature which corresponds to a solvent vapor pressure of no more than 100 mm Hg. For example, with CFC-113 we did not exceed -15°C, since calculations show that at this temperature a pressure inside of the reactor reaches 115 PSI during spontaneous vapor phase explosions owing to the CFC-113 and substrate converting in entirety to CF_4 and HF. *These vapor phase explosions only occurred if the F_2 flow was continued beyond the end point of the reaction, and under these conditions, the reactor never ruptured. When they occurred, a flash of light could be seen coming from inside the reactor, a loud thump could be heard, and the reactor would slightly lift above the jack stand it was resting on.*

Table 4 shows some of the perfluorinated ethers made using this process.

TABLE 4

Perfluorinated Ethers Made Via Solution Direct Fluorination

Structure	GC Yield	Mol. Wt.	BP°C
	~100%	370.1	76*
	~100%	420.1	91*◆
	89%	470.1	106*+
	75%	520.1	108++
	32%	520.1	120*
	86%	536.1	114
	71%	636.1	153
	78%	686.1	163
	99%**	752.1	169
	49%#	952.5	219
 ##	49%#	921.4	218-220
	67%	1250	256

* Calculated boiling point (vide infra).
◆ obtained in 36% yield in [8].
+ obtained in 37% yield in [8] reported 96°C boiling point.
++ obtained in 38% yield in [8]; reported 85°C boiling point.
** This compound was made via electrochemical fluorination of the same partially fluorinated intermediate [9] in < 40% yield and by direct fluorination of the full hydrogen analogue using a low temperature cryogenic reactor in 25% yield [10].
# Isolated yield.
Probably an isomeric mixture.

The structures of these compounds were confirmed by NMR and GCMS. Table 5 shows ^{19}NMR data for perfluoroethers shown in Table 4.

TABLE 5

^{19}F NMR DATA FOR PERFLUOROETHERS

GLYCEROL-TFE ADDUCT $(CF_3CF_2OCF_2)_2CF(OCF_2CF_3)$

A C D F E B

A	B	C	D	E	F
-87.2(6F,b)	-87.1(3F,b)	-88.4(4F,b)	-81.9(4F)	-85.2(2F,b),	-144.6(1F,t+,23.6Hz)

2,2-DIMETHYL-1,3-PROPANEDIOL-TFE ADDUCT $(CF_3CF_2OCF_2)_2(CF_3)_2C$

A C D B

A	B	C	D
-87.3(6F)	-63.5(6F,pentet,J_{F-F}=11.2 Hz)	-88.5(4F,m)	-66.7 (4F,m)

2-METHYL,2-HYDROXYMETHYL-1,3-PROPANEDIOL-TFE ADDUCT

$(CF_3CF_2OCF_2)_3C(CF_3)$

A C D B

A	B	C	D
-87.1(9F,s)	-62.8(3F,heptet,J_{F-F}=11.2 Hz)	-88.3(6F,s),	-65.9(6F,m)

2-ETHYL,2-HYDROXYMETHYL-1,3-PROPANEDIOL-TFE ADDUCT

$(CF_3CF_2OCF_2)_3C(CF_2CF_3)$

A C D B E

A	B	C	D	E
-87.0(9F,s)	-77.3(3F,t,J_{F-F}=10.8 Hz),	-88.2(6F,s),	-63.1(5F?,m)	-106.7(2F,m,J_{F-F}=12 Hz)

PENTAERYTHRITOL-TFE $(CF_3CF_2OCF_2)_4C$

A C D

A	C	D
-87.0(12F,s),	-88.1(8F),	-65.1(8F)

DIPENTAERYTHRITOL-TFE $(CF_3CF_2OCF_2)_3CCF_2OCF_2C(CF_3CF_2OCF_2)_3$

A C D B

A	B	C	D
-86.9(18F,b),	-64.0(4F,b),	-88.0(12F,b),	-64.9(~10F,b)

2-ETHYL,2-HYDROXYMETHYL-1,3-PROPANEDIOL-BIS ETHYLENE OXIDE-TFE ADDUCT

$(CF_3CF_2OCF_2CF_2OCF_2)_2(CF_3CF_2OCF_2)CCF_2CF_3$

A B B B D A B D B E

A	B	C	D	E
-89.3 (m) -89.5 (m) 10.9F	-79.6 (2.5F,q,J_{FF}=10.5Hz)	-90.7(16.9F,m)	-65.5 (6F,br)	-09.1(2F,m,J_{FF}=10.8Hz)

As mentioned above, we are able to predict with the fair degree of accuracy, the boiling point of perfluoroethers. This was accomplished by plotting the reported boiling points for known perfluorinated ethers versus their molecular weight [11]. The data was then fit to a simple third order polynomial and is shown in Fig.2.

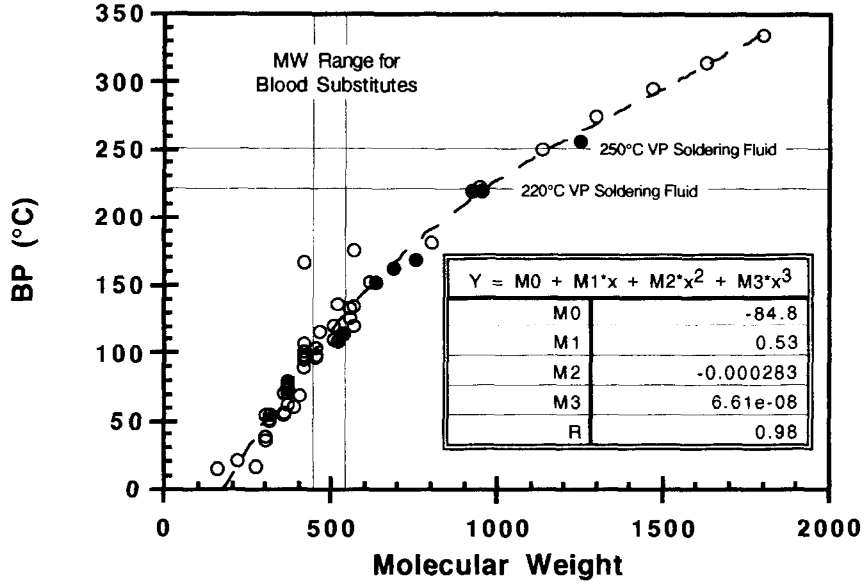


Fig.2. Boiling Points of Perfluorinated Ethers.

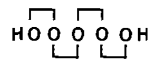
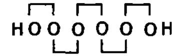
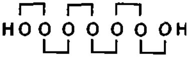
The filled circles are for the ethers reported in Table 4.

The two points that are above the fitted line are the perfluorinated analogues of 2-ethyl-tetrahydropyran and 2-propyl-tetrahydropyran. This is consistent with other perfluorinated compounds that contain rings and have higher than predicted boiling points. The need to be able to predict the boiling points for target compounds is shown by the narrow range of molecular weights that is reported to be suitable for blood substitutes [12], and the need for specific boiling point ranges for the vapor phase soldering process (215-225°C and 245-255°C) [13]. The plot shown above is similar to one reported by Bargigia, et al, for fewer compounds [14].

Table 4 shows three diols that were used to successfully make the partially fluorinated ethers, but did not successfully perfluorinate using our conditions.

TABLE 6

Unsuccessful Perfluorination of Ethers (TFE Adducts)

Ether	Yield (%)$^+$	BP°C(mm)	Calc.BP°C(F-Prod.)
	40	181(27)	172
	61	170(5)	199
	55	153(1)	224

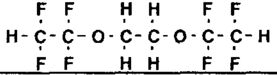
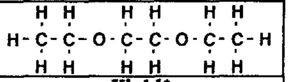
$^+$ Yield for TFE insertion reaction.

We suspected that the failure to successfully perfluorinate the products of the TFE insertion reactions for the diols shown in Table 6 is because very few ether linkages contain an α-CF_2 group. This is unlike the substrates shown in Table 4, where most of the ether linkages contain an α-CF_2 group making the oxygen atom less susceptible to electrophilic attack by HF which is produced in the fluorination reaction. During the fluorination of the substrates shown in Table 6, the starting material was converted to low molecular weight fragments that were swept out of the reactor by humidification of the nitrogen diluent and were not identified.

The importance of having some fluorine in the substrate prior to direct fluorination is shown in Table 7.

TABLE 7

Effect of Fluorine in the Direct Fluorination Substrate

Substrate →	 $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$	 $HCH_2CH_2OCH_2CH_2OCH_2CH_2H$
	Yield*	**Yield***
w/NaF	~100%	75%
No NaF	86%	32%

* GC yield of $CF_3CF_2OCF_2CF_2OCF_2CF_3$ based on starting material.

For both substrates, we used identical reaction conditions and 2.0 molecular equivalents of F_2 per hydrogen in the substrate. In the absence of added NaF (our normal reaction conditions), we obtained nearly three times the yield of the perfluorinated product $CF_3CF_2OCF_2CF_2OCF_2CF_3$ for the substrate that was partially fluorinated. In the presence of added NaF to aborb HF liberated by the direct fluorination reaction, we saw a modest increase in the yield of the desired product for the fluorination of ethylene glycol diethyl ether, suggesting that the α-CF_2 groups of the partially fluorinated substrate are protecting the oxygen atoms by inductive withdrawal of electron density making them less basic and less susceptible to HF cleavage. While effective with the above substrates, added NaF had no discernible effect on the fluorination of $HCF_2CF_2(OCH_2CH_2)_nOCF_2CF_2H$, where n=4-6, the substrates shown in Table 6.

To further explore the effect of HF on the direct fluorination reaction, we co-fed HF vapor and F_2 during the fluorination reaction. This is of commercial significance since HF is always an impurity in F_2, the level of which is determined by the grade of F_2 or the degree of costly HF removal that is used in the electrolysis of HF to make F_2.

TABLE 8

Effect of Added HF on the Yield of $(CF_3CF_2OCF_2)_4C$ in Direct Fluorination Reaction

Starting Material: $(HCF_2CF_2OCH_2)_4C$

In CFC-113:		
	$\%F_2$#	GC Yield*
	100	91
	97.9	86
	96	71
In Krytox®:		
	$\%F_2$#	GC Yield*
	100	99

100% fluorine was diluted with HF to give value shown in this column. This diluted fluorine was then diluted with N_2 according to our normal fluorination schedule (see Experimental).

* GC yield for the formation of $(CF_3CF_2OCF_2)_4C$.

Having only 4% HF in the F_2 has a dramatic effect on the yield of the perfluorinated ether. Presumably, the remainder of the products are fragments from HF cleavage. These are not observed in the GC of the product. Hence, to obtain the highest yield from a direct fluorination process, the lowest concentration of HF in the fluorine is desired. This effect may account for the relatively high yields of ethers that are reported for a process involving Adcock's aerosol reactor where the substrate is deposited on NaF, which could scavenge HF from the direct fluorination process. The result in Krytox® heptamer shown in the table above also suggests that perfluorinated ethers are better solvents for the direct fluorination process, owing to their high gas solubility and inertness.

EXPERIMENTAL

All TFE reactions were carried out at high pressures; they were accomplished by simply charging a 400 mL bomb with the polyol, solvent, and base, purging it with nitrogen at -78°C and placing the cold bomb in the barricade. TFE was added in 50 psig increments until no more uptake occurred, and the reaction is exothermic. Work-up consisted of pouring into ether, and distilling usually under vacuum.

Elemental fluorine is a powerful oxidant and will react (violently in most cases) with virtually all compounds under certain conditions. It should be used with extreme caution following the usual safety precautions [15]. Fluorine was obtained from Air Products and used as received in 1A cylinders. Fluorine was mixed with nitrogen using Teledyne Hastings Mass Flow Controllers (CST-50MG or CST-10MG). All lines for carrying the fluorine were constructed of either 316 SS or Teflon® FEP 1/4" tubing. CFC-11, CFC-113 (Microfree - 99.9995%), TFE, HFP, ethylene oxide, and Krytox® were obtained from Dupont. The polyols were obtained from Aldrich and used as received.

Preparation of Pentaerythritol Tetrakis(1,1,2,2-tetrafluoroethyl ether)

Following the procedure above, pentaerythritol (17.02 g, 0.125 mole), potassium hydroxide (1.75 g, 0.0312 mole), and N,N-dimethylformamide (125 mL) were reacted with 51.5 g (0.515 mole) of TFE at a final temperature of 50C. The product was separated from the crude reaction product by extraction into an ether phase as above. The ethereal solution was dried over sodium sulfate and vacuum distilled. The product (52.31 g, 78% yield) was collected at 125C (10 mm Hg) and was judged to be 98% pure by gas chromatography.

Preparation of F-Pentaerythritol Tetrakis(1,1,2,2-tetrafluoroethyl ether)

Pentaerythritol tetrakis(1,1,2,2-tetrafluoroethyl ether) prepared as above (5.0g, 9.32 mole) was added to CFC-113 (370mL) in an FEP reactor. The solution was cooled to -15°C and fluorine diluted with nitrogen was added according to the following schedule: 4.8% - 30 min, 11.8% - 30 min, 28.6% - 20 min, 40% - 20 min, 50% - 130 min. At the end of the reaction the ratio of F_2 added to each H in the substrate was 1.5. When the F_2 concentration reached 50%, a UV flood lamp positioned outside of the reactor body and directed at the reaction was turned on for the remainder of the experiment. In three experiments a total of 11.0 grams of pentaerythritol tetrakis(1,1,2,2-tetrafluoroethyl ether) was fluorinated. The collective product, F-pentaerythritol tetraethyl ether, was isolated in 71% yield (11.0 gm, bp 169°C); it was analyzed by GCMS and 19F NMR.

Fluorination of Product from the Reaction Ethylene Glycol with Tetrafluoroethylene

Some of the product (1.0 gm, .0038 mol) from an ethylene glycol and TFE reaction (E47854-56) was added to CFC-113 (370 ml) in an FEP reactor. The solution was cooled to -15C and fluorine diluted with nitrogen was added according to the following schedule (the values in parentheses are the volume percentages of fluorine in the nitrogen carrier): 4.8% (5 sccm/100 sccm) - 20 min, 16.7% (10 sccm/50 sccm) - 20 min, 33.3% (10 sccm/20 sccm) - 20 min, and 50% (10 sccm/10 sccm) - 63 min. At the end of the reaction the ratio of F_2 added to each H in the substrate was 2.0. When the F_2 concentration reached 33.3%, a UV flood lamp positioned outside of the reactor body and directed at the reaction was turned on for the remainder of the experiment. The product, F-ethylene glycol diethylether was obtained in 85% yield by GC analysis.

Fluorination of Ethylene Glycol Diethyl Ether

A commercial sample of ethylene glycol diethyl ether (.45 gm, .0038 mol) was added to CFC- 113 (370 ml) in an FEP reactor. The solution was cooled to -15°C and fluorine diluted with nitrogen was added according to the following schedule: 4.8% (5 sccm/100 sccm) - 20 min, 16.7% (10 sccm/50 sccm) - 20 min, 33.3% (10 sccm/20 sccm) - 20 min, and 50% (10 sccm/10 sccm) - 209 min. At the end of the reaction the ratio of F_2 added to each H in the substrate was 2.0. When the F_2 concentration reached 33.3%, a UV flood lamp positioned outside of the reactor body and directed at the reaction was turned on for the remainder of the experiment. The product, F-ethylene glycol diethylether was obtained in 43% yield by GC analysis.

Fluorination of 2-ethyl-2-hydroxymethyl-1,3-propanediol Tri(1,1,2,2-tetrafluoroethyl ether)

A sample of 2-ethyl-2-hydroxymethyl-1,3-propanediol tri(1,1,2,2-tetrafluoroethyl ether) (5.0g, .01152 mole), prepared by a method similar to that for pentaerythritol tetrakis(1,1,2,2-tetrafluoroethyl ether) described above, was added to CFC-113 (370mL) in an FEP reactor. The solution was cooled to -15°C and fluorine diluted with nitrogen was added according to the following schedule: 5 sccm (4.8%) - 20 min, 10 sccm (11.8%) - 20 min, 20 sccm (28.6%) - 20 min, 20 sccm (40%) - 20 min, 20 sccm (50%) - 279 min. At the end of the reaction the ratio of F_2 added to each H in the substrate was 1.71. When the F_2 concentration reached 28.6%, a UV flood lamp positioned outside of the reactor body and directed at the reaction was turned on for the remainder of the experiment. In two experiments a total of 10.0 grams of 2-ethyl-2-hydroxymethyl-1,3-propanediol tri(1,1,2,2-tetrafluoroethyl ether) was fluorinated. The collective perfluorinated product (10.8 gm., .0157 mol) was isolated in 66% yield.

Fluorination of Product from the Reaction of Pentaerythritol with Hexafluoropropylene

Some of the product (15.0 gm, .0204 mol) from a pentaerythritol and HFP reaction (E53510-27-2) was added to Freon® 113 (370 ml) in an FEP reactor. The solution was cooled to -15C and fluorine diluted with nitrogen was added according to the following schedule: 4.8% (5 sccm/100 sccm) - 20 min, 11.8% (10 sccm/75 sccm) - 20 min, 28.6% (20 sccm/50 sccm) - 20 min, 40% (20 sccm/30 sccm) - 10 min, 50% (30 sccm/30 sccm) - 280 min, and 50% (20 sccm/20 sccm) - 51 min. At the end of the reaction the ratio of F_2 added to each H in the substrate was 1.75. When the F_2 concentration reached 28.6%, a UV flood lamp positioned outside of the reactor body and directed at the reaction was turned on for the remainder of the experiment. A total of 49.3 gm of material was fluorinated in five batches and the collective product, F-pentaerythritol tetrapropyl ether, was isolated in 46% yield (29.2 gm, bp 219°C).

Preparation of Dipentaerythritol Hexakis(1,1,2,2-tetrafluoroethyl ether)

A 400 mL "Hastelloy" C bomb was charged with dipentaerythritol (21.19 gm, 0.0833 mole), potassium hydroxide (9.35 gm, 0.167 mole), and N,N-dimethylformamide (150 mL). The bomb was sealed, cooled to -78°C in a dry ice-acetone bath and purged three times with nitrogen. The bomb was then removed from the bath and secured in a reaction barricade. The bomb was agitated by shaking and then pressurized with 50 psig of tetrafluoroethylene (TFE). The pressure rapidly dropped; TFE was added in 50 psig increments until a total of 51.0 g had been added. The reactor was then warmed to 50°C for two hours. The bomb was vented, purged with nitrogen, and the reaction mixture poured into a separatory funnel. The mixture was extracted with 150 mL of water and 75 mL of diethyl ether. The organic layer was washed two more times with water (100mL) and then dried over anhydrous sodium sulfate. The ethereal extract was concentrated in vacuum and distilled (10 mm Hg). Three fractions were collected; the third fraction collected at 203°C, weighed 32.1 g and was judged to be 91% pure by gas chromatography (50% yield based on dipentaerythritol added).

Fluorination of Dipentaerythritol Hexakis(1,1,2,2-tetrafluoroethyl ether)

Dipentaerythritol hexakis(1,1,2,2-tetrafluoroethyl ether) prepared as above (5.0g, 5.85 mole) was added to CFC-113 (370mL) in an FEP reactor (see Figure). The solution was cooled to -15°C and fluorine diluted with nitrogen was added according to the following schedule: 4.8% - 20 min, 11.8% - 20 min, 28.6% - 20 min, 40% - 20 min, 50% - 256 min. At the end of the reaction the ratio of F_2 added to each H in the substrate was 1.71. When the F_2 concentration reached 28.6%, a UV flood lamp positioned outside of the reactor body and directed at the reaction was turned on for the remainder of the experiment. This was repeated six times and the collective product, F-dipentaerythritol hexaethyl ether, was isolated in 67% yield (29.3g bp 255-256°C); it was analyzed by GCMS and 19F NMR.

Preparation of Perfluoro-tris(ethyl ether) of 2-ethyl-2-hydroxymethyl-1,3-propanediol bis(ethylene oxide) adduct

Step 1. Preparation of the Bis(ethylene oxide) Adduct of 2-Ethyl-2-hydroxymethyl-1,3-propanediol

The triol was prepared by the reaction of ethylene oxide with neat 2-ethyl-2-hydroxymethyl-1,3-propanediol. A four-necked flask was fitted with a gas inlet tube, a gas outlet, a thermometer, and a mechanical stirrer. The gas inlet tube was connected to a cylinder of ethylene oxide with a nitrogen purge tee, a rotometer, a check valve, and a suck-back trap between the ethylene oxide cylinder and the gas inlet tube. The cylinder of ethylene oxide rested on an electronic balance. The reaction flask was charged with

200 g (1.49 mol) of 2-ethyl-2-hydroxymethyl-1,3-propanediol. The flask was placed in an electric heating mantle and the contents of the flask heated to 140C with a continuous purge of nitrogen through the gas inlet tube for 30 minutes with stirring to sparge out any water and oxygen in the reactor. The reaction flask was cooled to 100°C. Sodium hydride (0.4 g, 0.0083 mol, 50% dispersion in paraffin) was added to the flask, and the reaction was stirred for 30 minutes. The reaction was then reheated to 140°C and 140 g (3.18 mol) of ethylene oxide was bubbled into the reaction over the course of about 2.5 hours. Nitrogen was co-fed with the ethylene oxide such that the volumetric ratio of nitrogen to ethylene oxide was about 1:1. At the conclusion of the addition, nitrogen was purged through the reaction and 0.89 g (0.015 mol) of acetic acid was added to neutralize the catalyst. 340 g of product were recovered. 325 g of the product were charged to a flask set up for a standard vacuum distillation. A forecut was collected at 70-158°C at a pressure of 3 mm Hg. This material was discarded. 131 g of product, amounting to a yield of 40.3%, was collected at 181-194°C at a pressure of 2 mm Hg. The pot residue was discarded. The 1H NMR spectrum of the product integrated correctly for a bis(ethylene oxide) adduct of 2-ethyl-2-hydroxymethyl-1,3-propanediol as an average composition: CD_3OD solvent: 4.84 (s, 3.3H, OH);3.65,3.57 (m, 5.6H, $-CH_2-$); 3.48 (m, 5.2H, $-CH_2-$); 3.36 (m, 3.3H, $-CH_2-$); 1.37 (m, 2.0H, $-C\underline{H_2}CH_3$); 0.87 (t, $^3J_{HH}$=7.5Hz; 3.0H, $-CH_2C\underline{H_3}$). This material was used for reaction step 2.

Step 2. Preparation of the Tris[(1,1,2,2-tetrafluoro)-ethyl ether] of 2-ethyl-hydroxymethyl-1,3- propanediol-bis(ethylene oxide) adduct

Bis(ethylene oxide) adduct of 2-ethyl-hydroxy-methyl-1,3-propanediol (73.36 g, 0.33 mol), powdered potassium hydroxide (5.6 g, 0.1 mol), and N,N-dimethylformamide (100 ml, 94.4 g) were placed in a 400 ml "Hastelloy" C bomb. The bomb was sealed, cooled to -78°C, evacuated, and purged with nitrogen three times. The bomb was placed in a barricade, connected to a source of tetrafluoroethylene (TFE), and agitated by shaking. TFE was added to the bomb in 50 psig increments until 100 g (1.0 mol) had been added. During the course of the addition the temperature of the reaction increased to about 30°C. The temperature was increased to 50°C and held at that temperature for 2 hours. The bomb was cooled, vented, and purged with nitrogen. The contents of the bomb were poured into a jar. The reaction mixture consisted of a clear, amber upper layer over a cloudy, white suspension in a lower layer.

The reaction mixture was treated with 100 ml of water and the aqueous and organic layers separated. The yellowish organic layer was then dried over anhydrous sodium sulfate. The 1H NMR spectrum of the dried product was consistent with that of a tris(tetrafluoroethylene) adduct of the starting triol. The product had a Brookfield viscosity of 35 cp at ambient temperature; the density was 1.378 g/ml. The product was then distilled at 15 mm Hg to afford four fractions with the following boiling point ranges: 140-162°C (17.06 g), 162-178°C (51.69 g), 178-180°C (54.11 g), 170°C (10.67 g). The pot residue, which was discarded, weighed 1.68 g. The 1H NMR analysis of the four fractions suggested than on average each fraction contained 0.65, 1.35, 2.25 and 3.0 ethylene oxide units, respectively, for an average of 1.75 ethylene oxide units per mole. This corresponds to a 77% yield of distillable material. The third fraction was used for the next step. The ^{1}H NMR spectrum for the third fraction is as follows (C_6D_6 solvent): 5.12 (t of m, $^2J_{HF}$=53.1 Hz), 5.04 (t of m, $^2J_{HF}$=53.1 Hz) together these two sets of peaks integrate as 3.1H; 3.92 (s), 3.86 (s), 3.74 (s), 3.68 (m), 3.20 (m), 3.09 (m), 3.04 (s), 2.92 (s) this set of peaks collectively integrates as 15 H; 1.41 (q, $^3J_{HH}$=7.6Hz), 1.30 (q, $^3J_{HH}$=7.6Hz) together these two sets of peaks integrate as 2.0 H; 0.78 (t, $^3J_{HH}$=7.6Hz), 0.67 (t, $^3J_{HH}$=7.6Hz) together these two sets of peaks integrate as 3.0 H.

Step 3. Perfluorination of the Tris[(1,1,2,2-tetrafluoro)ethyl ether] of 2-ethyl-hydroxy- methyl-1,3-propanediol-bis(ethylene oxide) adduct

Tris(1,1,2,2-tetrafluoro)ethyl ether of the bis(ethylene oxide) adduct of 2-ethyl-hydroxymethyl-1,3-propanediol (5.0 g, 9.57 mmol) was added to CFC-113 (370 ml) in an FEP reactor. The solution was cooled to -15°C and purged with nitrogen at 100 sccm for half an hour. Fluorine diluted with nitrogen was added to the reaction at flow rates and for the time periods indicated in the following schedule (the values in parentheses are the volume percentages of fluorine in the nitrogen carrier): 5 sccm (4.8%) - 20 min., 10 sccm (11.8%) - 20 min., 20 sccm (28.6%) - 20 min., 20 sccm (40%) - 20 min., and 20 sccm (50%) - 326 min. When the F_2 concentration in the nitrogen reached 28.6%, a UV flood lamp positioned outside the reactor body and directed at the reaction mixture, was turned on for the remainder of the experiment. At the end of the reaction, the molar ratio of fluorine to hydrogen in the substrate was 1.5. The perfluorinated product was isolated by vacuum distillation (7.77g, yield 49%). The boiling point was 218-220°C.

Direct Fluorination of Pentaerythritol Tetrakis(1,1,2,2-tetrafluoroethyl)ether

5.00 g (0.0093 mole) of $C(CH_2OCF_2CHF_2)_4$ and 250 mL of Krytox® heptamer were placed in the "Teflon" reactor. The reactor was sealed and purged with nitrogen at 100 sccm for 4 h. The contents of the reactor were then cooled to -3°C and two molar equivalents of fluorine were added to the reactor as volume percentages of fluorine in the nitrogen carrier): 5 sccm (4.8%) - 30 min., 10 sccm (11.8%) - 30 min., 20 sccm (28.6%) - 20 min., 20 sccm (40%) - 20 min., and 20 sccm (50%) - 210 min. The UV sunlamp was turned on after fluorine had been flowing for 1 h; this caused the temperature in the reactor to rise about 10°C. After the fluorine addition was complete, the reactor was purged with nitrogen for 0.5 h. 500 microliters of CFC-113 were then added to the reactor as an internal standard. Analysis of the product by GC indicated a 95% yield of F-pentaerythritol tetraethyl ether at 100% conversion of the starting material.

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