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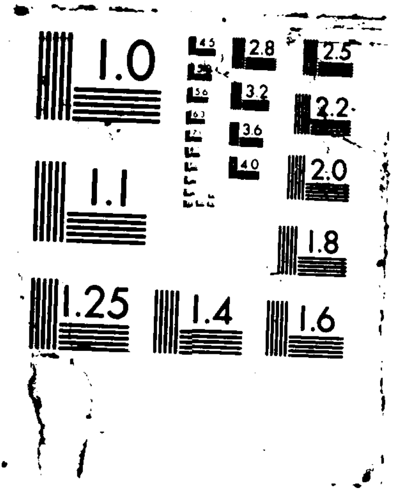
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Completed Project Summary

Title: A New Approach to Highly Fluorinated Lubricants

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Publications:

"Polyether Compounds and their Preparation", R.D. Chambers, U.K. Patent Application No. 86.12983 (1986).

"Model Compounds in the Preparation of Fluorinated Ethers", R.D. Chambers, P.T. Telford, and M.W.H. West, manuscript in preparation for the Journal of Fluorine Chemistry.

"Modification of Polyethers, using Fluorinated Alkenes", R.D. Chambers, P.T. Telford, and M.W.H. West, manuscript in preparation for J.C.S. Perkin Trans. 1.

"New Routes to Highly Fluorinated Ethers", Ph.D. thesis, University of Durham, 1986 (Restricted access for six years).

Abstract of Objectives and Accomplishments:

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A NEW APPROACH TO HIGHLY FLUORINATED LUBRICANTS

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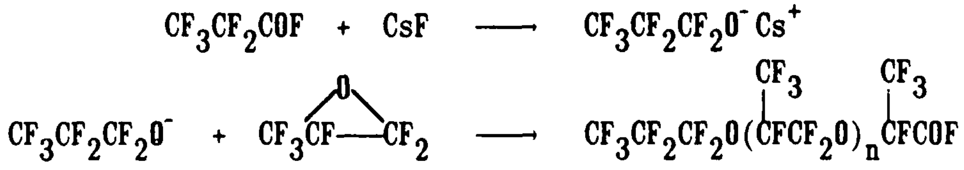
Introduction

Perfluorinated polyethers constitute an important class of materials that demonstrate exceptional chemical and thermal stability,[1] amongst organic liquids, and some of these materials show good lubricant properties.[2] Consequently, such materials are of especial interest to the U.S.A.F. as lubricants in agressive environments and, particularly, as potential liquid lubricants for high temperature/high-efficiency aero engines.

The aim of this project is to explore new approaches to the synthesis of perfluorinated ethers because the main problem that limits the wider application of industrially available materials is their high cost, which is an inevitable consequence of the limited methodology available. [illegible] These approaches are essentially:

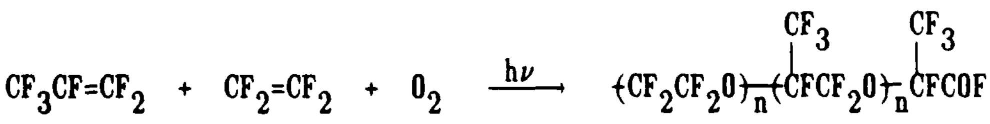
1. Polymerisation of Perfluoro-epoxides[3] ('Krytox' fluids, Du-Pont Co.)



$$CF_3CF_2COF + CsF \longrightarrow CF_3CF_2CF_2O^-Cs^+$$

$$CF_3CF_2CF_2O^- + CF_3CF{-}CF_2 \text{ (epoxide)} \longrightarrow CF_3CF_2CF_2O(\overset{CF_3}{|}\!\!\!\!CFCF_2O)_n\overset{CF_3}{|}\!\!\!\!CFCOF$$

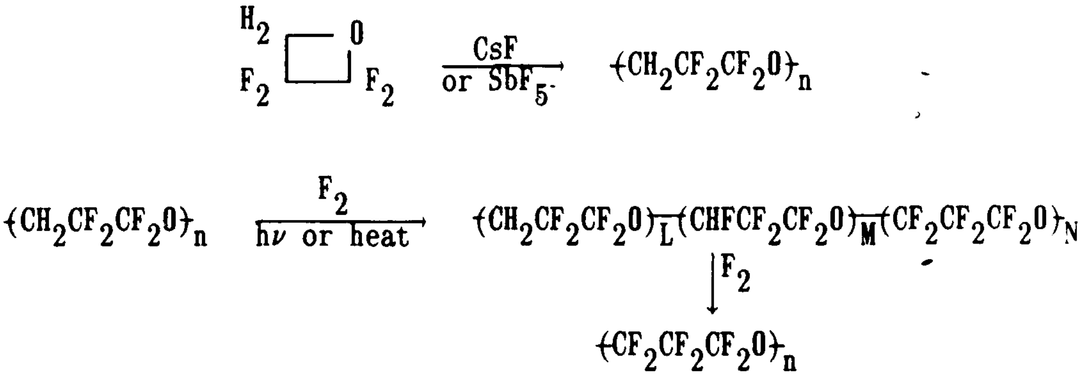
2. Photochemical Oxidation/Polymerisation of F-Alkenes[4] ('Fomblin' fluids, Montefluos Co.)



$$CF_3CF{=}CF_2 + CF_2{=}CF_2 + O_2 \xrightarrow{h\nu} (CF_2CF_2O)_n(\overset{CF_3}{CF}CF_2O)_n\overset{CF_3}{CF}COF$$

(Each of the above approaches are followed by end-group stabilisation.)

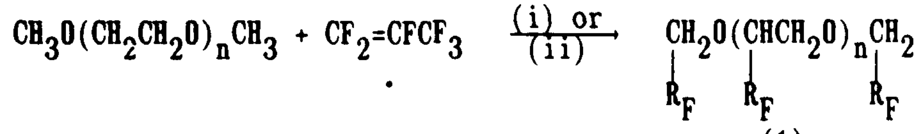
3. Polymerisation of a Fluorinated Oxetane, followed by Direct Fluorination[5] ('Demnum' fluids, Daikin Co.)



$$(CH_2CF_2CF_2O)_n \xrightarrow[h\nu \text{ or heat}]{F_2} (CH_2CF_2CF_2O)_L(CHFCF_2CF_2O)_M(CF_2CF_2CF_2O)_N \xrightarrow{F_2} (CF_2CF_2CF_2O)_n$$

The present project involves the development of a two-stage approach to perfluoropolyethers based on modification of polyethers of known molecular-weight range. A severe disadvantage of existing methodology, outlined above, is that each approach involves a polymerisation stage with a consequent range of molecular-weight in the product. If this could be avoided, as in the present approach, then it would have very considerable advantage. Two stages are involved in the present approach: (A) involving addition of a perfluoroalkene to a polyether and (B) development of fluorination techniques for fluorination of the product polyadducts (1) from (A).

(A) e.g.



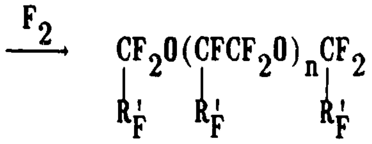
$$CH_3O(CH_2CH_2O)_nCH_3 + CF_2{=}CFCF_3 \xrightarrow[(ii)]{(i)\text{ or}} \underset{R_F}{CH_2}O(\underset{R_F}{CH}CH_2O)_n\underset{R_F}{CH_2}$$

(1)

(where $R_F = CF_2CFHCF_3$)

(i) = Peroxide, heat (ii) = γ ray initiation

(B) (1)



$$\xrightarrow{F_2} \underset{R_F'}{CF_2}O(\underset{R_F'}{CF}CF_2O)_n\underset{R_F'}{CF_2}$$

(where $R_F' = CF_2CF_2CF_3$)

Model Compound Studies

The first phase of the work was to explore the use of model compounds, in order to develop technique. This is more effective than working directly on high molecular-weight material because of the obviously easier identification procedures involved.

Free-Radical Additions of F-Propene to Ethers

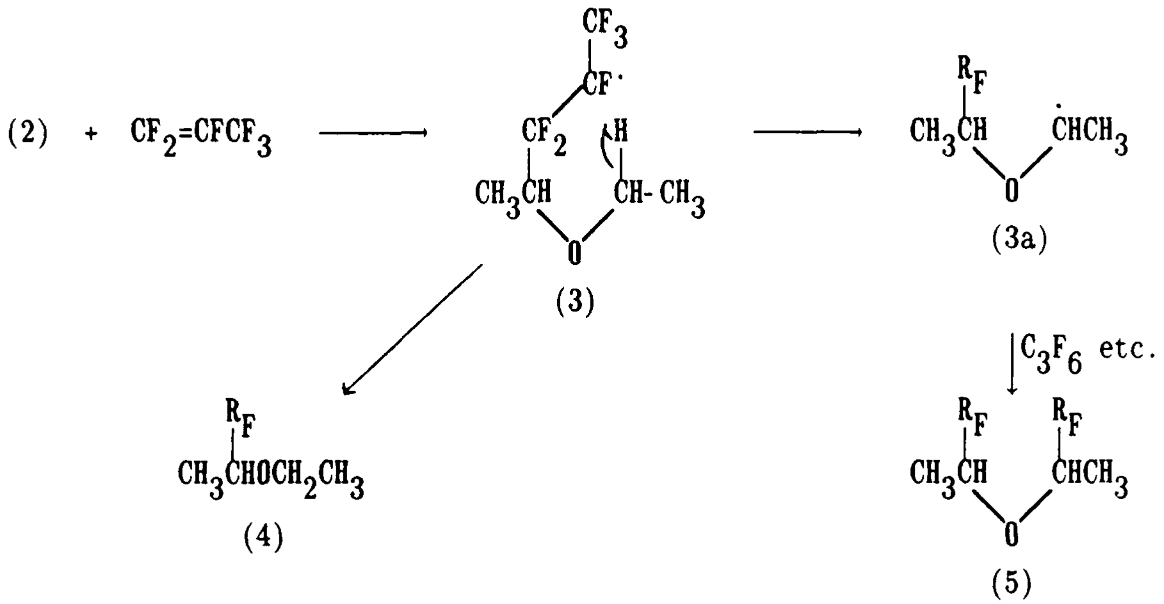
The normal radical-chain process is involved in addition of ethers to e.g. F-propene but there are two features to stress.[6] First, a radical derived from an ether is stabilised by interaction with the non-bonding electron-pair on oxygen.

$$\text{e.g.}\quad (CH_3CH_2)_2O \xrightarrow{In^{\cdot}} \underset{(2)}{CH_3\dot{C}H\text{-}\ddot{O}\text{-}CH_2CH_3} \longleftrightarrow \underset{(2a)}{CH_3\overset{-}{\ddot{C}}H\text{-}\overset{+}{\dot{O}}\text{-}CH_2CH_3}$$

(where $In^{\cdot}$ = initiating radical.)

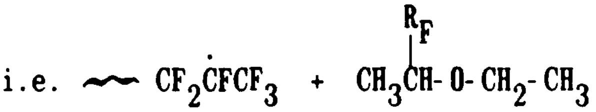
As a consequence of this interaction these radicals are quite <u>nucleophilic</u> in character and, consequently, are extremely reactive towards F-alkenes which are, of course, <u>electrophilic</u> in character.

The second feature to stress is the fact that, after addition to the fluorinated alkene, the intermediate radical (3) is ideally orientated for a 1-5 transfer of a hydrogen atom. Therefore, the di-adduct (5) is produced in competition with the mono-adduct (4). The fact that this intramolecular process occurs follows from the fact that the mono-adduct (4) is not easily converted to (5) under conditions where (5) may be obtained in good yield when starting from the diethylether.



(R_F = CF_2CFHCF_3)

This latter observation highlights a third factor which affects additions of ethers to F-alkenes i.e. the influence of electron-withdrawing substituents. We have already drawn attention to the fact that (2) is especially reactive because the radical is nucleophilic. However, the converse effect applies on the reactivity of the chain-propagating radical (7) with an ether that is partly fluorinated. The propagating radical (7) is



$$\text{i.e.} \sim\!\sim CF_2\dot{C}FCF_3 + CH_3\overset{R_F}{\overset{|}{C}}H\text{-}O\text{-}CH_2\text{-}CH_3$$

(7) (4)

electrophilic in character and the ether adduct (4) is made more electrophilic by introduction of the polyfluoroalkyl group. Hence, this combination is less reactive than a system which involves diethylether itself. Entropy factors, of course, favour the intramolecular hydrogen transfer in (3).

The points outlined above are highly relevant to the additions that follow and additions of F-propene to a variety of model compounds are now described.

A comparison of terminal methoxy and ethoxy derivatives revealed a very clear difference in reactivity. The ethoxy derivatives showed a preference for attack at the ethoxy group and this usually led to a greater degree of addition of F-propene units than with methoxy compounds. This undoubtedly stems from the easier hydrogen abstraction from secondary ethoxy sites, followed then by the intramolecular hydrogen transfer processes like that illustrated in (3).

$$CH_3OCH_2CH_2OCH_3 + C_3F_6 \xrightarrow{(i)} \underset{(30\%)}{R_FCH_2OCH_2OCH_3} + \underset{(60\%)}{CH_3OCHR_FCH_3OCH_3}$$

$R_F = CF_2CFHCF_3$; (i), γ-ray initiator, 20°C

$$\underset{(8)}{CH_3CH_2OCH_2CH_2OCH_2CH_3} + C_3F_6 \xrightarrow{(i)} \underset{(9)}{CH_3CH_2OCHR_FCH_2OCH_2CH_3}\ (14\%)\ [5\%]$$

$$+ \underset{(10)}{CH_3CHR_FOCH_2CH_2OCH_2CH_3}\ (48\%)\ [16\%]$$

$$\left.\begin{array}{l} + \underset{(11)}{CH_3CHR_FOCHR_FCH_2OCH_2CH_3} \\ + \underset{(12)}{CH_3CHR_FOCH_2CHR_FOCH_2CH_3}\text{(Minor)} \end{array}\right\}\ \begin{array}{c} (27\%) \\ {[22\%]} \end{array}$$

$$+ \underset{(13)}{CH_3CHR_FOCH_2CH_2OCHR_FCH_3}\ (11\%)\ [16\%]$$

$$+ \underset{(14)}{CH_3CHR_FOCHR_FCH_2OCHR_FCH_3}\ [14\%]$$

Ether: C_3F_6 3:1 (% yields), 1:2 [% yields]

We were able to conclude from these experiments that the order of reactivity of various sites is:

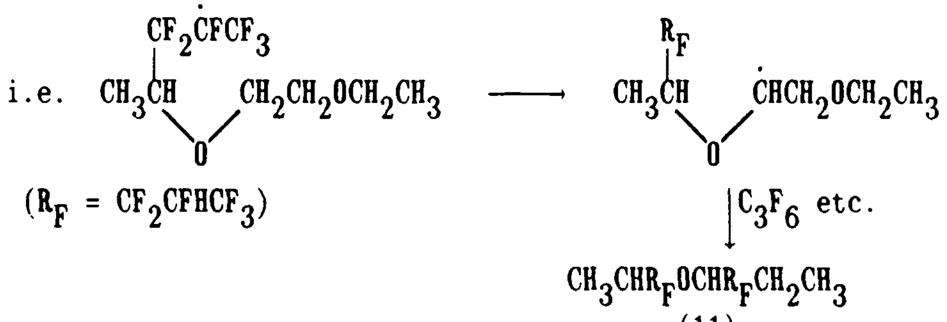
$$CH_3CH_2O- > -OCH_2CH_2O- > CH_3O$$

Consequently, we concluded that the use of ethoxy end-groups would be particularly useful in higher molecular-weight ethers, both to make certain that end group are reactive and that the maximum number of additions to F-propene takes place.

It is important to stress that in no case have we observed the addition of two F-propene units <u>to the same carbon site</u>.

$$\text{i.e.}\quad -CH_2-O-CH_2CH_2 + C_3F_6 \quad \not\longrightarrow \quad -C(R_F)_2-O-CH_2CH_2-$$

The fact that compound (11) is a major product derived from (8) follows from the intramolecular transfer mechanism.



i.e.

$(R_F = CF_2CFHCF_3)$

C_3F_6 etc.

$CH_3CHR_FOCHR_FCH_2CH_3$

(11)

Similarly, the formation of isomer (11) in considerable preference to (12), may be explained on the same basis. As we increase the ratio of F-propene, then the extent of addition increases and the tri-adduct (14) is formed with excess alkene. It may be obtained as the major product if a considerable excess of F-propene is employed.

The importance of polar effects is illustrated by the fact the the mono-adduct (10) may be converted to (13) and (14) but (9) is relatively inert to further attack. Clearly, the presence of polyfluoroalkyl groups is deactivating unless they are sufficiently remote. Again, formation of (14) from (10) must involve the intramolecular process.

$$\underset{(10)}{CH_3CH_2OCH_2CH_2OCHR_FCH_3} + C_3F_6 \xrightarrow{i} \underset{(13)}{CH_3CHR_FOCH_2CH_2OCHR_FCH_3} \quad (43\%)$$

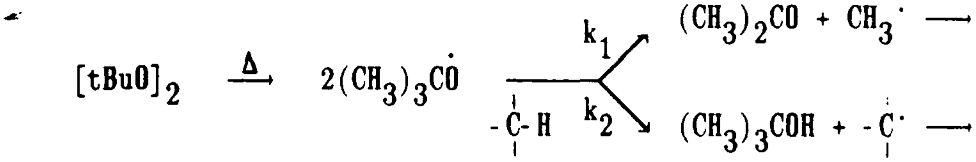
$$(R_F = CF_2CFHCF_3) \qquad + \underset{(14)}{CH_3CHR_FOCHR_FCH_2OCHR_FCH_3} \quad (21\%)$$

$$(i),\ \gamma\text{-rays},\ 20^oC$$

$$\text{cf.}\quad \underset{(9)}{CH_3CH_2OCHR_FCH_2OCH_2CH_3} + C_3F_6 \xrightarrow{i} \underset{(11)}{CH_3CH_2OCHR_FCH_2OCHR_FCH_3} \quad (2\%)$$

Acetone-Butanol Ratios

We have found previously, that acetone-butanol ratios formed in the decomposition of di-tertbutyl peroxide, in the presence of various substrates is a valuable approach to assessing reactivities to relatively electrophilic radicals.[6]



$$[tBuO]_2 \xrightarrow{\Delta} 2(CH_3)_3C\dot{O} \xrightarrow[-\overset{|}{\underset{|}{C}}-H]{} \begin{cases} \xrightarrow{k_1} (CH_3)_2CO + CH_3^{\cdot} \longrightarrow \\ \xrightarrow{k_2} (CH_3)_3COH + -\overset{|}{\underset{|}{C}}^{\cdot} \longrightarrow \end{cases}$$

The ratios represent $k_1 : k_2$ and comparisons for different substrates reveal differences in k_2. Low ratios indicate easier hydrogen abstraction and the ratios contained in TABLE 1 demonstrate how it becomes progressively more difficult to abstract hydrogen, with increasing numbers of perfluoroalkyl groups present.

TABLE 1. Acetone:Butanol ratios (140°C)

Substrate[†]	Ratio
$[CH_3CH_2OCH_2]_2$ (8)	0.1
$CH_3CH_2OCH_2CH_2OCHR_FCH_3$ (10)	0.9
$CH_3CH_2OCH_2CHR_FOCH_2CH_3$ (9)	1.9
$CH_3CH_2OCH_2CHR_FOCHR_FCH_3$ (11)	2.5
$[CH_3CHR_FOCH_2]_2$ (13)	75
$CH_3CHR_FOCH_2CHR_FOCHR_FCH_3$	No BuOH detected

[†] $R_F = CH_2CFHCF_3$

Additions of diethylether and other ethers to a variety of F-alkenes and -cycloalkenes are summarised in TABLE 2. Additions to diethylether reveal that fluoro-ethenes prefer to participate in telomerisation reactions, rather than intramolecular hydrogen transfer, which would have given di-adducts i.e. $(CH_3CHR_F)_2O$. Perfluorocyclo-pentane and -cyclohexane give substantial amounts of the di-adducts whereas only a low yield of di-adduct is obtained with perfluorocyclobutene, indicating that ring size of the cyclic F-alkene has a significant effect on hydrogen-transfer.

Effect of Temperature

Additions of F-propene to $(EtOCH_2)_2$ were investigated with gamma-rays at 20°C and with $(tBuO)_2$ at 140°C and the following conclusions were drawn from the results: (a) initial radical attack on the ether is less selective at the higher temperature but still favours the ethyl end-groups and (b) the

TABLE 2. Free-Radical Additions of F-Alkenes and -Cycloalkenes to Ethers (γ-ray Initiation, 20°C)

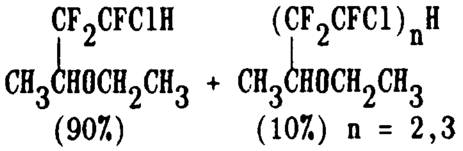
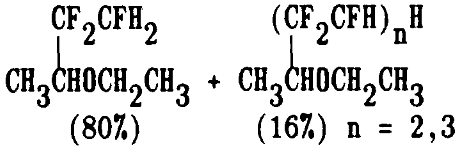
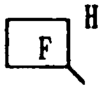
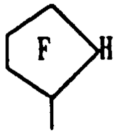
Reactants	Products (Yield)
$Et_2O + CF_2{=}CFCF_3$	$CH_3CHR_FOCH_2CH_3 + (CH_3CHR_F)_2O$ (57%) (43%) ($R_F = CF_2CFHCF_3$)
$Et_2O + CF_2{=}CFCl$	 $\underset{(90\%)}{CH_3\overset{CF_2CFClH}{CH}OCH_2CH_3} + \underset{(10\%)}{CH_3\overset{(CF_2CFCl)_nH}{CH}OCH_2CH_3}$ $n = 2,3$
$Et_2O + CF_2{=}CFH$	 $\underset{(80\%)}{CH_3\overset{CF_2CFH_2}{CH}OCH_2CH_3} + \underset{(16\%)}{CH_3\overset{(CF_2CFH)_nH}{CH}OCH_2CH_3}$ $n = 2,3$
Et_2O + 	$CH_3CHR_FOCH_2CH_3 + (CH_3CHR_F)_2O$ R_F =  (90%) (5%)
Et_2O + 	R_F =  (60%) (27%)
Et_2O + 	R_F =  (40%) (40%)
$(EtOCH_2)_2$ + 	$EtOCH_2CH_2OCHR_FCH_3$ $+ EtOCH_2CHR_FOEt$ } (50%) + Di-adducts (16%)

TABLE 2 continued

$(EtOCH_2)_2$ + 	$EtOCH_2CH_2OCHR_FCH_3$ + $EtOCH_2CHR_FOEt$ (33%) + $CH_3CHR_FOCHR_FOEt$ (20%) + $(CH_3CHR_FOCH_2)_2$ (14%) + $(CH_3CHR_FOCH_2CHR_FOCHR_FCH_3$ (6%)
$Et(OCH_2CH_2)_3OEt$ + CF_2=$CFCF_3$	Mono-adducts (24%) Di- " (33%) Tri- " (34%) Tetra- " (8%)
$(CH_3OCH_2)_2$ + CF_2=CF_2 [a]	$CH_3OCHR_FCH_2OCH_3$ (53%) + $R_FCH_2OCH_2CH_2OCH_3$ (18%) + Telomeric products (31%) (R_F = CF_2CF_2H)

[a] Initiated by $(tBuO)_2$, 140°C.

1,5-hydrogen transfer process, although still significant, is no in competition with a step-wise process that can occur at higher temperatures.

General Conclusions

These model compound studies provide a sound basis of understanding for corresponding polyether modification, which is described in the next section.

Adducts to Polyethers

Remarkably, modification of polyethers by free-radical additions of fluorinated alkenes have not been reported. To maximise reactivity, we prepared di-ethyl derivatives using a range of commercially available polyethyleneglycols.

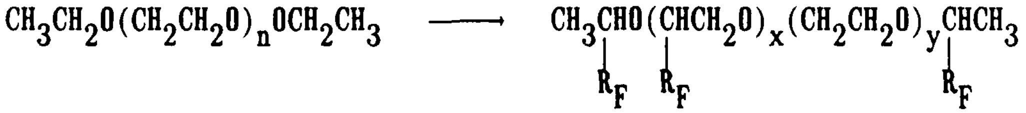
$$\begin{tikzcd}
HO(CH_2CH_2O)_nH + NaH \arrow[r, "Toluene"] & NaO(CH_2CH_2O)_{n-1}CH_2CH_2ONa \arrow[d, "EtI"] \\
 & EtO(CH_2CH_2O)_nEt
\end{tikzcd}$$

TABLE 3

Glycol [Abbreviation]	Glyme [Abbreviation]	M.Wt. of Glyme	Yield (%
$HO(CH_2CH_2O)_{8-9}H$ [PEG 400]	$EtO(CH_2CH_2O)_{8-9}Et$ [DEPEG 400]	~456	74
$HO(CH_2CH_2O)_{13}H$ [PEG 600]	$EtO(CH_2CH_2O)_{13}Et$ [DEPEG 600]	~656	69
$HO(CH_2CH_2O)_{45}H$ [PEG 2000]	$EtO(CH_2CH_2O)_{45}Et$ [DEPEG 2000]	~2056	66

Free-radical additions of F-propene to the glymes was carried out using ditertiarybutylperoxide or gamma-rays as initiator and the products showed considerable incorporation of F-propene into the polyether backbone (see Table 4). The degree of incorporation was determined by adding a known weight reference compound (trifluoromethylbenzene) to a sample of the adduct and then comparing H-1 and F-19 n.m.r. spectra.

The ethyl end-groups are substituted, as anticipated, and then incorporation into the backbone occurs. These poly-adducts are discussed in terms of a general structure (15) but, beyond establishing from n.m.r. data, that the end-groups are substituted, we have no way at this stage of determining the distribution of the fluorinated groups along the backbone. However, from our model-compound studies described earlier, we may assume that not more than one addition takes place per CH_2CH_2O group. Scale-up of these reactions has also been successfully achieved.



$$CH_3CH_2O(CH_2CH_2O)_nOCH_2CH_3 \longrightarrow CH_3\underset{R_F}{CH}O(\underset{R_F}{CH}CH_2O)_x(CH_2CH_2O)_y\underset{R_F}{CH}CH_3$$

$R_F = CF_2CFHCF_3$ (15)

i.e. $n = x + y$

TABLE 4. Adducts from Glymes and F-Propene [see structure (15)]

Glyme	X	Y	Yield (%)	M.Wt. (Calc.)
DEPEG 400	4-5	4.5-3.5	86	~1431
DEPEG 600	9-10	4-3	84	~2306
DEPEG 2000	18	27	80	~5056

We have reacted the initial product from DEPEG 600 with more F-propene in considerable excess and obtained the product where x = 13 and we have also demonstrated that products from DEPEG 2000 can also be reacted further.

Diethyl derivatives of polytetrahydrofuran were reacted with F-propene in a similar way and it is very noticeable that this system leads to considerably increased incorporation of hexafluoropropene. This undoubtedly arises because the OCH_2 units are separated by a larger number of units so that, on introduction of a polyfluoroalkyl group, the deactivating influence $-OCHR_FCH_2CH_2CH_2-O-$ is much attenuated in comparison with glycol units i.e. $-OCHR_FCH_2O-$ which, as we have seen, are considerably deactivated towards further attack.

$$CH_3CH_2[O(CH_2)_4]_{14}OCH_2CH_3 \xrightarrow{i} CH_3CHR_F[OCHR_F(CH_2)_2CHR_F]_x[OCHR_F(CH_2)_3]_yOCHR_FCH_3$$

i, $CF_2{=}CFCF_3$, benzoyl peroxide, 90% (17) ca. 20R_F groups incorporated

($R_F = CF_2CFHCF_3$)

Structure (17) is also an average formula because we have little information on the distribution of R_F groups along the chain except to know that the end-groups are substituted. However, by adding further F-propene to the product it is possible to obtain a product where virtually each site adjacent to oxygen has been modified to an $OCHR_F$ unit.

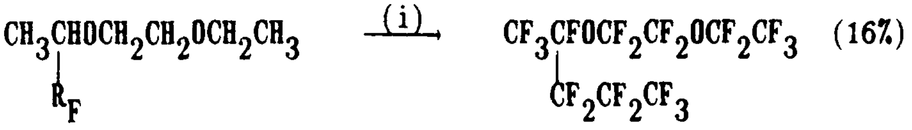
This process is quite remarkable because we are using the polyether backbone to introduce quite dramatically large quantities of F-alkene and it is certain that these products will become industrially significant in their own right.

Fluorination of Adducts

(a) Cobalt Trifluoride

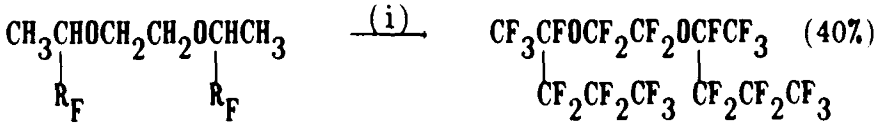
Although mass-spectrometry and n.m.r. were very useful, an additional and helpful tool of characterisation of the model compounds was conversion to the corresponding perfluorinated ether, by passing over cobalt trifluoride. Note that, in the absence of perfluoroalkyl groups in the system to be fluorinated, extensive fragmentation occurs. In earlier work from this laboratory, we have demonstrated the value of perfluoroalkyl groups being present.[7]

In this way, various perfluoroethers were characterised, thus demonstrating the structures of the corresponding precursor adducts. This is made possible because of the easier interpretation of F-19 n.m.r. spectra than corresponding H-1 spectra of the precursor adducts.

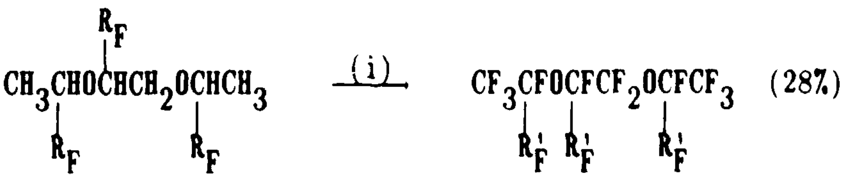


$$CH_3\underset{R_F}{CH}OCH_2CH_2OCH_2CH_3 \xrightarrow{(i)} CF_3\underset{CF_2CF_2CF_3}{CF}OCF_2CF_2OCF_2CF_3 \quad (16\%)$$

($R_F = CF_2CFHCF_3$) (i) CoF_3, 440°C

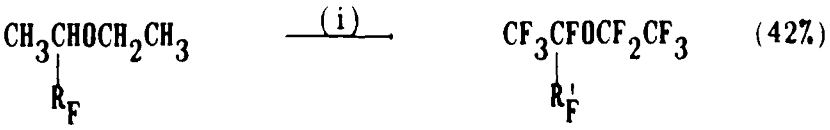


$$CH_3\underset{R_F}{CH}OCH_2CH_2O\underset{R_F}{CH}CH_3 \xrightarrow{(i)} CF_3\underset{CF_2CF_2CF_3}{CF}OCF_2CF_2O\underset{CF_2CF_2CF_3}{CF}CF_3 \quad (40\%)$$

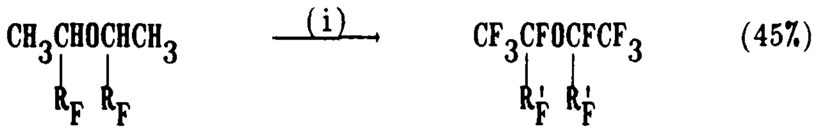


$$CH_3\underset{R_F}{CH}O\overset{R_F}{C}HCH_2O\underset{R_F}{CH}CH_3 \xrightarrow{(i)} CF_3\underset{R'_F}{CF}O\underset{R'_F}{CF}CF_2O\underset{R'_F}{CF}CF_3 \quad (28\%)$$

($R'_F = CF_2CF_2CF_3$)



$$CH_3\underset{R_F}{CH}OCH_2CH_3 \xrightarrow{(i)} CF_3\underset{R'_F}{CF}OCF_2CF_3 \quad (42\%)$$



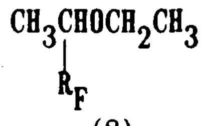
$$\underset{R_F\ \ R_F}{CH_3CHOCHCH_3} \xrightarrow{(i)} \underset{R'_F\ \ R'_F}{CF_3CFOCFCF_3} \quad (45\%)$$

(b) Direct Fluorinations

Clearly, cobalt trifluoride cannot be used to fluorinated high molecular-weight material using conventional technology. Therefore, we have developed direct fluorination for this purpose. A 10 amp fluorine generator was built, to provide 100% F_2 and concentrations in nitrogen above 50%. We have also employed 50% F_2 in N_2, that is commercially available in cylinders. For safety reasons we have avoided 100% F_2 in large-scale cylinders.

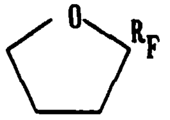
Reactivity of Simple Adducts towards Fluorine

We here used some simple 1:1 adducts (8)-(10) and treated these with fluorine, diluted with nitrogen, and cooled to -80°C. However, we found it difficult to control the fluorination of these materials without ignition, especially if these materials were present in the vapour phase.

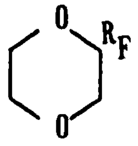


$$\underset{R_F}{CH_3CHOCH_2CH_3}$$

(8)



(9)



(10)

(R_F = CF_2CFHCF_3)

In contast, however, di-adducts showed remarkable stability to fluorine. For example, we have now found that the di-adduct (11) will react smoothly with fluorine at 20°C, Therefore, using a very simple procedure, of passing fluorine/nitrogen into a column of the liquid then extensive fluorination may be obtained, as indicated.

$$CH_3\underset{\underset{R_F}{|}}{CH}O\underset{\underset{R_F}{|}}{CH}CH_3 \xrightarrow[(ii)]{(i)} C_{10}F_{16}H_6O \quad \text{(40\% fluorination)}$$

$(R_F = CF_2CFHCF_3)$

(11)

(i), 25% F_2/N_2 20°C-60°C (5 h) (ii), 50% F_2/N_2 20°C-60°C (5 h)

These are not optimised conditions and it now seems clear that the process may be completed quickly at the higher temperature. The only losses are not due to fragmentation but to the volatility of the starting material and products.

Further treatment of the mixture $C_{10}F_{16}H_6O$, with 100% fluorine, gave further fluorination but, remarkably, only 75% fluorination could be achieved at temperatures up to 100°C. The chemical resistance of even these partly fluorinated compounds is, therefore, quite outstanding.

$$C_{10}F_{16}H_6O \xrightarrow{(iii)} C_{10}F_{19}H_3O \ (14\%), \quad C_{10}F_{18}H_4O \ (20\%), \quad C_{10}F_{17}H_5O \ (26\%)$$

(iii) 100% F_2 20-50°C (10 h)

$$C_{10}F_{16}H_6O \xrightarrow{(iv)} C_{10}F_{20}H_2O, \quad C_{10}F_{19}H_3O$$

(iv) 100% F_2 20-100°C (8 h)

Sealed-Tube Fluorination

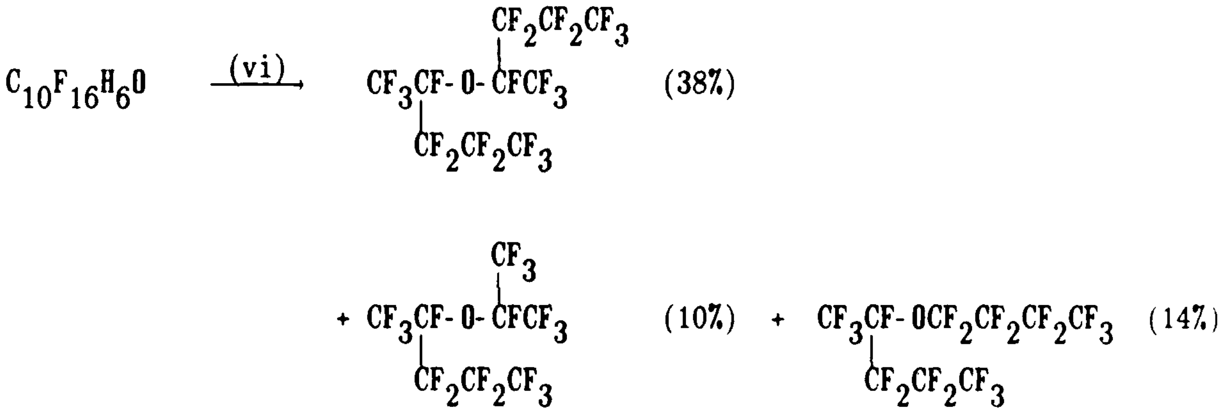
At these higher temperatures, loss by evaporation is considerable (this is not, of course, a problem with the high molecular-weight materials) and we therefore condensed fluorine into a steel tube containing the $C_{10}F_{16}H_6O$ mixture.

$$C_{10}F_{16}H_6O \xrightarrow{(v)} C_{10}F_{20}H_2O \ (13\%), \quad C_{10}F_{19}H_3O \ (20\%), \quad C_{10}F_{18}H_4O \ (25\%)$$

(v) 100% F_2, sealed tube 20°C (10 h)

Remarkably, the system not only survived this treatment but, also, fluorination was still not complete. This was, however, completed by using the same sealed tube procedure, and a temperature of 40°C.

It is a clear illustration of the stability of these compounds, that such simple and drastic procedures may be applied to such effect. The recorded yields are not optimised at all and, no doubt, much higher yields may be obtained with more development. However, the virtue of this approach, of introducing polyfluoroalkyl groups through fluorinated alkenes prior to fluorination lies in the simplicity of the conditions required for the subsequent stages of fluorination.



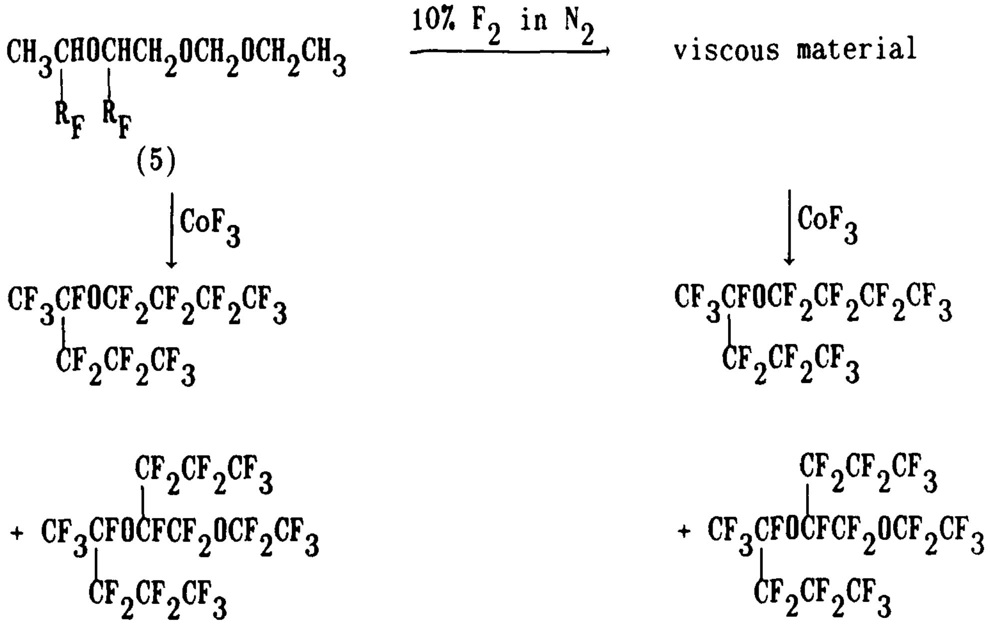
$$C_{10}F_{16}H_6O \xrightarrow{(vi)} CF_3\underset{\substack{|\\ CF_2CF_2CF_3}}{CF}\text{-}O\text{-}\overset{\substack{CF_2CF_2CF_3\\ |}}{C}FCF_3 \quad (38\%)$$

$$+\ CF_3\underset{\substack{|\\ CF_2CF_2CF_3}}{CF}\text{-}O\text{-}\overset{\substack{CF_3\\ |}}{C}FCF_3 \quad (10\%) \quad +\ CF_3\underset{\substack{|\\ CF_2CF_2CF_3}}{CF}\text{-}OCF_2CF_2CF_2CF_3 \quad (14\%)$$

(vi) 100% F_2, sealed tube 40°C (24 h).

Viscosity of Intermediate Stages

In the course of these fluorinations of adducts, we have observed that a stage is often reached where the medium becomes exceedingly viscous. At first, we deduced that fluorine-induced coupling of ethers was occurring (this would have been an interesting phenomena). However, we took these partly fluorinated, viscous materials, in some cases and subjected them to fluorination over cobalt trifluoride. In each case, the perfluoroether which corresponds to the original adduct was obtained, demonstrating that <u>no</u> coupling or change in the carbon-oxygen skeleton had occurred.



$$CH_3\underset{R_F}{\underset{|}{C}}HO\underset{R_F}{\underset{|}{C}}HCH_2OCH_2OCH_2CH_3 \xrightarrow{10\%\ F_2\ \text{in}\ N_2} \text{viscous material}$$

(5)

$$\downarrow CoF_3 \qquad\qquad\qquad\qquad \downarrow CoF_3$$

$$CF_3\underset{CF_2CF_2CF_3}{\underset{|}{C}}FOCF_2CF_2CF_2CF_3 \qquad\qquad CF_3\underset{CF_2CF_2CF_3}{\underset{|}{C}}FOCF_2CF_2CF_2CF_3$$

$$+\ CF_3\underset{CF_2CF_2CF_3}{\underset{|}{C}}FO\overset{CF_2CF_2CF_3}{\overset{|}{C}}FCF_2OCF_2CF_3 \qquad\qquad +\ CF_3\underset{CF_2CF_2CF_3}{\underset{|}{C}}FO\overset{CF_2CF_2CF_3}{\overset{|}{C}}FCF_2OCF_2CF_3$$

We may assume, therefore, that this dramatic change in viscosity, on partial fluorination, is a consequence of increased intermolecular hydrogen-bonding. Needless to say, the corresponding perfluoroethers are mobile ligands.

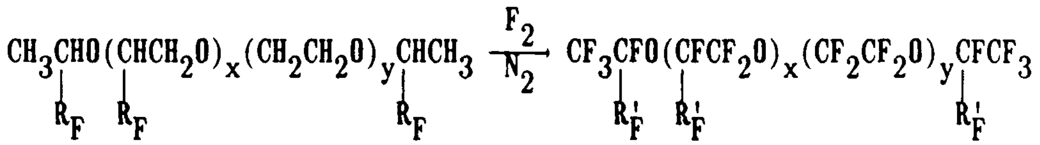
<u>Fluorination of Higher Molecular-Weight Materials</u>

These studies have been carried out in two stages:

(i) Bubbling F_2/N_2 mixtures through the adducts, <u>without any elaborate procedures</u>. It is a remarkable feature of these systems that this direct fluorination can be carried out in quite simple apparatus, that can therefore be scaled up. Generally, the concentration of fluorine is increased in the following sequence

25% F_2/N_2 at 20°C
25% F_2/N_2 at 50°C
50% F_2/N_2 at 50°C

(ii) Final removal of remaining hydrogen was completed by exposing to 100% F_2 in a sealed system. Significant effort is being expended to understand the factors affecting the outcome of this stage, including the effect of pressure.



$$\mathrm{CH_3\underset{R_F}{\underset{|}{C}}HO(\underset{R_F}{\underset{|}{C}}HCH_2O)_x(CH_2CH_2O)_y\underset{R_F}{\underset{|}{C}}HCH_3 \xrightarrow[N_2]{F_2} CF_3\underset{R'_F}{\underset{|}{C}}FO(\underset{R'_F}{\underset{|}{C}}FCF_2O)_x(CF_2CF_2O)_y\underset{R'_F}{\underset{|}{C}}FCF_3}$$

$R_F = CF_2CFHCF_3$ $R'_F = CF_2CF_2CF_3$

Adduct	x	y	Yield of[b] Perfluoroether (%)	Anticipated Average M.Wt.
DEPEG 400	4/5	4-5/3-4	31	2230
DEP 600	9/10	4/3	27	3410
DEP 2000	18	27	34	~8500

[b]-This stage has not been carried out on a large scale and handling losses are therefore exaggerated.

In each case, the final product was examined carefully by F.T. ^{1}H-n.m.r. and no significant amount of H could be detected, confirming that a perfluoropolyether had been obtained. Thus, we have now demonstrated that the technique can be applied equally to materials of a wide range of molecular-weight but the virtue, is the fact that products of high molecular-weight may be obtained, if the appropriate starting material is used. (We have yet to measure molecular weights of the final products.)

We have been exploring more recently, larger-scale reactions in which the materials are fluorinated at atmospheric pressure, and at significantly higher temperatures. Fully fluorinated fluids are obtained and, at this stage, structural elucidation is still under way.

Conclusions

1. Modification of polyethers by simple free-radical reactions with fluorinated alkenes occurs extensively and a range of opportunities for industry is opened by these new materials.
2. Preliminary work on direct fluorination of model adducts and subsequently, adducts of polyethers demonstrate that perfluorinated fluids may be obtained this way.
3. These studies are opening an alternative approach to some new perfluorinated polyether which could provide valuable materials to complement existing high-performance oils.

Experimental

The following are examples which illustrate the general procedures used in the addition, oxidative fluorination and direct fluorination reactions.

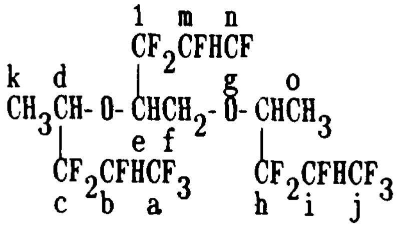
All yields are based on g.l.c. analysis using a gas density balance detector. Column packings for this instrument are as follows: K = 20% Krytox (a commercial perfluoropolyether mixture; A = di-isodecylphthalate 30%; DNP = 10% di-nonylphthalate; 5% SE30 = 5% silicone elastomer.

NMR data: all shifts quoted are; ^{19}F upfield from $CFCl_3$; ^{1}H downfield from TMS. For multiplicity of NMR: S = singlet, D = doublet, T = triplet, M = multiplet.

Free-Radical Addition of Ethyl Glyme to Hexafluoropropene

Technique

Ethyl glyme (5.9 g, 0.05 mol) and hexafluoropropene (17.1 g, 0.114 mol) were irradiated on a Co^{60} source (60 hrs, 200 Krads hr^{-1}). The liquid products (16.5 g) were distilled using conventional apparatus to yield the adducts 4a (5%) b.p.$_{40}$ 79°C; 4b (16%) b.p.$_{40}$ 90°C; 5a,5b (22%) b.p.$_{10}$ 94°C; 5c (16%) b.p.$_{6}$ 106°C; all previously characterised[8] and in addition the tri-adducts, 6, (13%).



$$\underset{\substack{|\\CF_2CFHCF_3}}{CH_3CH}\text{-}O\text{-}\overset{\substack{CF_2CFHCF\\|}}{CH}CH_2\text{-}O\text{-}\underset{\substack{|\\CF_2CFHCF_3}}{CH}CH_3$$

1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-6-[1,1,2,3,3,3,-hexafluoro-propyl]-5,8-dioxadodecane (Found C, 31.7; H, 2.46; F, 60.6%; $C_{15}F_{18}H_{14}O_2$ requires C, 31.96; H, 2.45; F, 60.2%).

^{19}F NMR

	Multiplicity	Shift	JHz	Rel. Intensity	Assignment
	M	73.1		3	a,j,n
	M	121.7		2	c,h,l
	M	214.3		1	b,i,m
^{1}H NMR					
	M	1.55		6	o,k
	M	4.07		5	e,f,d,g
	D of M	5.29	35	3	b,i,

m/z (chemical ionisation, isobutane +ve) 569 (M^+, 2.2%), 373 (2.0), 223 (1.5), 97 (1.5), 85 (4.8), 81 (3.8), 79 (2.9), 69 (9.6).

Addition of Diethyl Diglyme to Hexafluoropropene

Technique

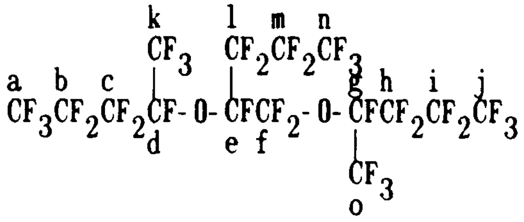
Diethyl diglyme (4.05 g, 0.025 mol) was placed in a nickel tube fitted with a valve and degassed using freeze thaw cycles under vacuum. Hexafluoropropene (14.66 g, 0.098 mol) was transferred, under vacuum, into the tube and the valve closed. The tube was then irradiated on the Co^{60} source for 72 hrs. (200 Krads hr^{-1}). The tube was cooled (liquid air) opened to a vacuum and hexafluoropropene (4.48 g, 0.029 mol) recovered by allowing the tube to warm. The liquid products (12.9 g) containing eleven components (g.l.c. col. K 180°C) were distilled using conventional apparatus to give isomer mixtures, determined by chemical ionisation mass spectrometry/capillary g.l.c. techniques and consistent NMR data, mono-adducts, $C_{11}H_{18}F_6O_3$ (24%) $b.p._5$ 80-90°C; di-adducts, $C_{14}H_{18}F_{12}O_3$ (33%) $b.p._5$ 100-110°C; tri-adducts, $C_{17}H_{18}F_{18}O_3$ (34%) $b.p._{0.01}$ 68°C; tetra-adducts, $C_{20}F_{24}H_{18}O_3$ (8%) $b.p._{0.01}$ > 100°C.

Oxidative Fluorinations Using CoF_3

Fluorination of (6) $CH_3CH(R_F)OCH(R_F)CH_2OCH(R_F)CH_3$ ($R_F = CF_2CFHCF_3$)

Technique

The adduct (6) (1.58 g, 2.78 mmol) was passed over a cobalt trifluoride bed at 440°C in the usual manner.[9] The product mixture (1.12 g), containing five volatile and one less volatile components (g.l.c., col. A, 72%) was separated using preparative scale g.l.c. The less volatile component was characterised as perfluoro-4,9-dimethyl-6-propyl-5,8-dioxadodecane (28%) b.p. 198°C (Found C, 21.7; F, 74.32%. $C_{15}F_{32}O_2$ requires C, 21.9; F, 74.14%)



$CF_3CF_2CF_2CF(CF_3)-O-CF(CF_2CF_2CF_3)CF_2-O-CF(CF_3)CF_2CF_2CF_3$

Multiplicity	Shift	JHz	Rel. Intensity	Assignment
M	79.6		2	f
M	79		3	k,o
M	81.3		3	
T of M	84	10.4	9	a,n,j
M	122		6	h,l,c
M	127.8		6	b,m,i
M	135.2		2	d,e
M	143.5		1	g

Fluorinations Using Elemental Fluorine

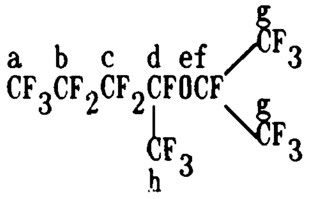
Direct fluorination of di-(1-methyl-2,2,3,4,4,4-hexafluorobutyl)ether

Technique

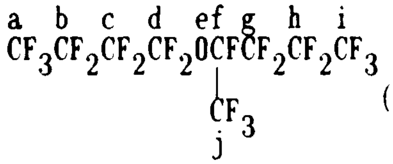
Di-(1-methyl-2,2,3,4,4,4-hexafluorobutyl)ether (4.7 g, 12.6 mmol) was placed in the reactor vessel and the system flushed with nitrogen for 20 minutes. Nitrogen was shut off and a mixture of 25% fluorine in nitrogen was passed through the adduct at 20°C for two hours, then at 60°C for three hours. Further fluorination was then effected using a 50% mixture of fluorine in nitrogen; this was bubbled through the partially fluorinated mixture at 20°C for 2 hours then 60°C for three hours. The liquid products (4.25 g), containing 14 components (g.l.c. 5% SE30 102°C), were not separated due to the complexity of the mixture. Using g.l.c./mass spectrometry mass maxing techniques it was possible to determine the molecular weights of the components:- $C_{10}F_{15}H_7O$ (6%); $C_{10}F_{16}H_6O$ (50%); $C_{10}F_{17}H_5O$ (25%).

Direct Fluorination of the Mixture ca$C_{10}F_{16}H_6O$ Using a Sealed System Technique Technique

The mixture (0.59 g, 1.32 mmol) was contained in a passified 70 ml nickel tube fitted with a monel valve and then degassed using freeze thaw cycles under vacuum. Fluorine (0.86 g, 22.7 mmol) was condensed into the tube by cooling in liquid nitrogen. The tube was allowed to warm to room temperature for eight hours before heating to 40°C for twenty-four hours. The system was then cooled to 20°C, vented and the liquid products (0.44 g) recovered. The product mixture, containing four components (g.l.c. col. A 45°C), was separated using preparative scale g.l.c. techniques to give:- perfluoropentane (4%); perfluoro-[1-methyl-butyl]isopropyl ether (10.5%),



^{19}F NMR	Multiplicity	Shift	Rel. Intensity	Assignment
	M	81.5	3	a
	M	83.5	3	h
	M	85	6	g
	M	124.6	2	c
	M	129	2	b
	M	137.5	1	d
	M	143.6	1	f

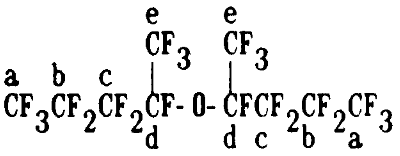


$$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}O\underset{\underset{j}{CF_3}}{\overset{ef}{CF}}\overset{g}{CF_2}\overset{h}{CF_2}\overset{i}{CF_3}$$

(14%) b.p. 118°C

<u>Perfluoro(1-methyl-butyl)butyl ether</u> (Found C, 21.43; F, 74.8%. $C_9F_{20}O$ requires C, 21.43; F, 75.39%).

^{19}F NMR	Multiplicity	Shift	Rel. Intensity	Assignment
	M	81.6	3	j
	M	83.2	2	d
	M	84.2	6	a, i
	M	123.8	2	c
	M	128.3 129	6	b,g,h
	M	143	1	f



$$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\underset{d}{\overset{\overset{e}{CF_3}}{C}}F-O-\underset{d}{\overset{\overset{e}{CF_3}}{C}}F\underset{c}{C}F_2\underset{b}{C}F_2\underset{a}{C}F_3$$

(38%) b.p. 135°C (lit.[4] 136°C)

Perfluoro di-1-methyl-butyl ether (Found C, 21.4; F, 75.8% calculated for $C_{10}F_{22}O$; C, 21.66; F, 75.45%).

^{19}F NMR	Multiplicity	Shift	JHz	Rel. Intensity	Assignment
	M	80		6	e
	M	81.6			
	T of M	84.7		6	a
	M	118.6		4	c
	M	127.5			
	M	128.6		4	b
	M	137.6		2	d

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