Journal of Fluorine Chemistry, 29 (1985) 323–339

Received: December 8, 1984; accepted: April 22, 1985

FREE RADICAL CHEMISTRY. PART 5. [1] A NEW APPROACH TO THE SYNTHESIS OF PERFLUORINATED ETHERS

RICHARD D. CHAMBERS, BRIAN GRIEVSON

Department of Chemistry, University Science Laboratories, South Road,
Durham, DH1 3LE (U.K.)

FREDERICK G. DRAKESMITH

Electricity Council Research Laboratories, Capenhurst, Chester CH1 6ES (U.K.)

and RICHARD L. POWELL

I.C.I. p.l.c., Mond Division, Runcorn, Cheshire WA7 4QD (U.K.)

SUMMARY

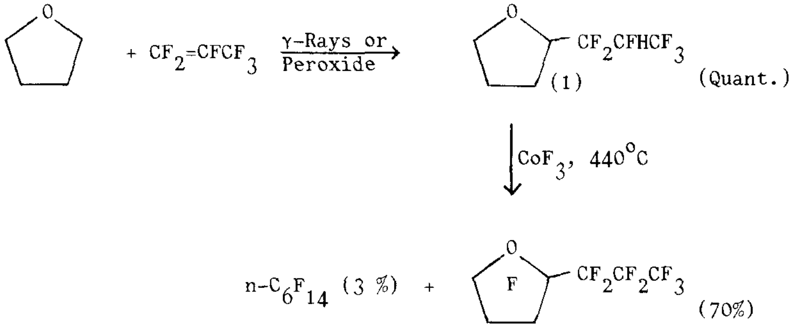
Fluorinations of the free-radical adducts of fluorinated alkenes, to ethers, over cobalt trifluoride are described and perfluorinated ethers are obtained at temperatures in excess of 400°C. The effect of structure on the formation of perfluoroethers is outlined.

RESULTS AND DISCUSSION

Volatile perfluorinated ethers are of considerable interest as inert fluids [2,3] etc. and previous methods for the synthesis of this class of compounds have usually involved electrochemical fluorination [2]. This process is, of course, only available in a very limited number of laboratories and, furthermore, yields are often very low. Fluorination of ethers, using cobalt fluorides, has been investigated by other workers [e.g. 4-10] but any perfluorinated ethers obtained are in very low yields and associated with a complex product mixture, arising from fragmentation and partial fluorination.

0022-1139/85/$3.30

In earlier papers [11], we described some investigations of free-radical additions of hydrocarbon derivatives to fluorinated alkenes and the adducts provide potential starting materials for investigating new routes to perfluorinated compounds. As part of this investigation we established [12] that the adduct of dimethylether to perfluorocyclobutene may be further fluorinated with cobalt trifluoride and relatively high recovery of polyfluoroethers, without significant fragmentation, was recorded. We have now conducted extensive studies on the further fluorination of a range of adducts to fluorinated alkenes, including the use of extremes of temperature. Consequently, we have made the surprising discovery that these adducts can be converted to perfluoroethers and that remarkably high yields may be obtained in some cases, with minimal fragmentation at the extreme temperatures required to effect complete fluorination. Therefore, the process exemplified below, starting with hexafluoropropene and oxolane, provides a new and realistic laboratory route to the synthesis of perfluoroethers.



The variation in product composition from the fluorination of (1), over cobalt trifluoride, with increasing temperature is shown in Table 1 and the persistance of partly fluorinated material in the product, until extremes of temperature are reached may be noted. Plotted in Figure 1 is the extent of fluorination, with temperature, for three different adducts to hexafluoropropene and the convergence in each case illustrates the need for temperatures in excess of 400°C, to effect complete fluorination. It is reasonable to conclude, therefore, that all adducts will require temperatures in this region and the fact that the products withstand these very aggressive conditions is, in itself, a testimony to the remarkable inertness of these compounds.

TABLE 1

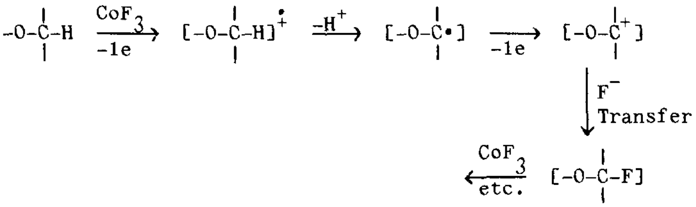
Extent of cobalt trifluoride fluorination of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane at various temperatures

Temperature (^oC)	% Composition of Product[†]					% Fluorination
	% $C_7F_{14}O$	% $C_7F_{13}HO$	% $C_7F_{12}H_2O$	% $C_7F_{11}H_3O$	% $C_7F_{14-n}H_nO$, n = 4-8	
110	trace	1.3	3.7	24.3	71.1	45.5
180	trace	1.5	7.5	69.8	21.2	54.8
240	0.4	1.2	14.8	63.7	19.7	62.2
270	2.8	20.9	29.2	42.9	2.4	71.0
355	31.6	46.3	14.2	7.8	-	87.6
440	96 + n-C_6F_{14} (4%)	trace	-	-	-	100

[†] Determined by a combination of g.l.c. (using a gas-density detector) and *g.l.c./mass spectrometry*. *In a* number of cases, components were isolated by g.l.c. and confirmed by elemental analysis, (see also Fig. 1).

Results of fluorination of a variety of mono- and di-adducts [11] of fluorinated alkenes to various ethers are contained in Table 2 and it is clear that yields from cyclic systems are generally higher than for acyclic systems. Ethoxy- and n-propoxy-groups are most efficiently fluorinated while methoxy-groups are associated with greater fragmentation, probably associated with the opportunity for loss of COF_2 i.e. a very stable fragment.

The overall effect of polyfluoroalkyl, in increasing the efficiency of reaction of partly fluorinated ethers with cobalt trifluoride, raises the interesting question of the basis of the effect. It is now reasonably well established that cobalt fluorides react via a one-electron oxidative process [13,14] and, translated to ethers, this could be summarised as shown below:



$$\begin{tikzcd} -O-\overset{|}{\underset{|}{C}}-H \arrow[r, "CoF_3", "-1e"'] & {[-O-\overset{|}{\underset{|}{C}}-H]^{+\bullet}} \arrow[r, "-H^+"] & {[-O-\overset{|}{\underset{|}{C}}\bullet]} \arrow[r, "", "-1e"'] & {[-O-\overset{|}{\underset{|}{C}}^+]} \arrow[d, "F^-\ Transfer"] \\ & & \arrow[r, phantom, ""] & {[-O-\overset{|}{\underset{|}{C}}-F]} \arrow[l, "CoF_3", "etc."'] \end{tikzcd}$$

In agreement with this is the fact that sites adjacent to O are the more readily fluorinated. This is illustrated by the observation that dioxane derivatives are more easily fluorinated than oxolane derivatives (see Figure 1) and here, of course, all of the ring sites are adjacent to oxygen. Since oxygen, as a potential donor, encourages oxidative fluorination then, conversely, electron withdrawing groups inhibit the process and, correspondingly, moderate the fluorination. It would seem, therefore, that this simple effect is the basis of the increased efficiency of fluorination of the ether/fluorinated alkene adducts, in comparison with direct reaction with the corresponding ethers.

EXPERIMENTAL

The radical induced addition products of ethers to fluoro-alkenes, used as starting materials were prepared as outlined in previous papers [11]. Quantitative analyses by glc were carried out on a Varian Aerograph Model 920 equipped with a gas density balance detector, using a column packed with di-isodecyl phthalate (20%) on chromosorb P. Preparative glc were carried out on a similar instrument equipped with a cold-trap for

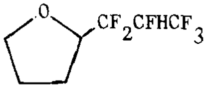
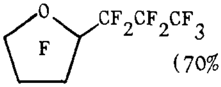
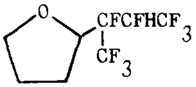
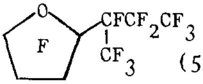
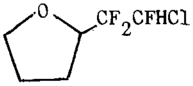
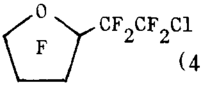
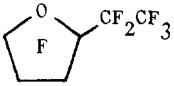
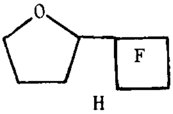
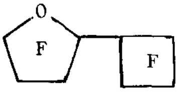
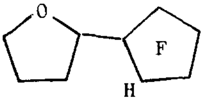
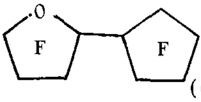
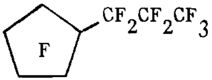
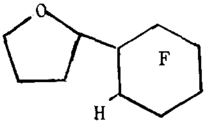
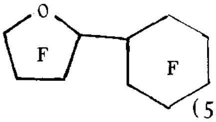
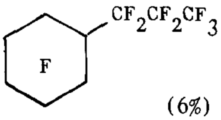
TABLE 2

$$R'\text{-}OCHR''(R_f) \xrightarrow[440^{\circ}C]{CoF_3/CaF_2} R'_FOCFR''_F(R_F) + \text{By-products}$$

(Adduct) (Perfluoroether)

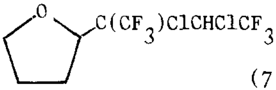
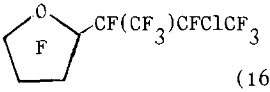
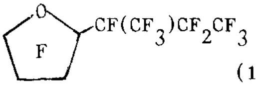
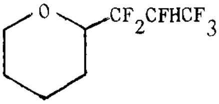
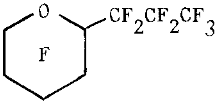
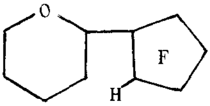
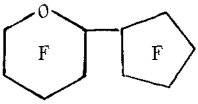
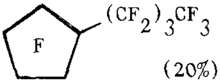
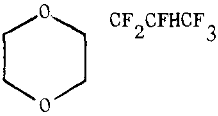
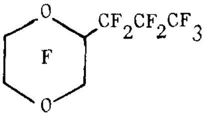
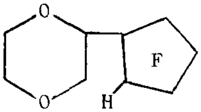
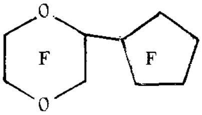
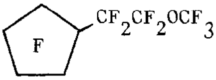
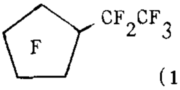
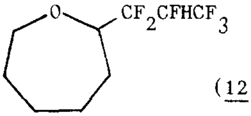
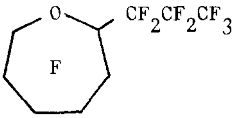
R', R" = alkyl R_F, R'_F, R''_F = perfluoroalkyl

R_f = polyfluoroalkyl

Adduct		Perfluoroether (yield)	By-products (yield)
	(1)	 (70%)	n-C_6F_{14} (3%)
	(2)	 (53%)	
	(3)	 (45%) +  (12%)	
	(4)	 (64%)	
	(5)	 (65%)	 (11%)
	(6)	 (51%)	 (6%)

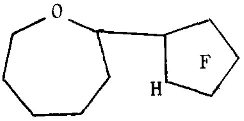
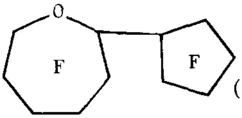
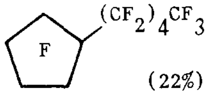
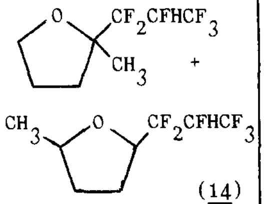
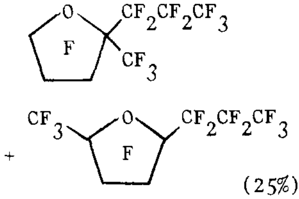
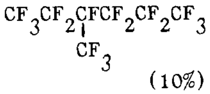
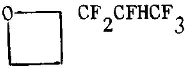
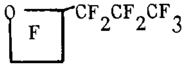
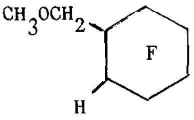
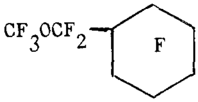
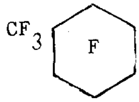
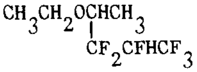
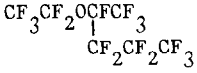
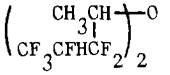
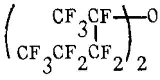
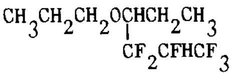
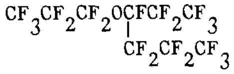
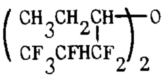
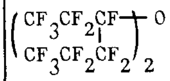
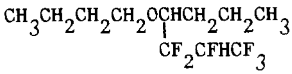
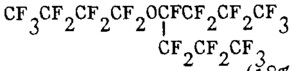
(continued overleaf)

TABLE 2 (cont.)

Adduct	Perfluoroether (yield)	By-products (yield)
 (7)	 (16%) +  (15%)	
 (8)	 (62%)	
 (9)	 (31%)	 (20%)
 (10)	 (68%)	
 (11)	 (17%) +  (8%)	 (10%)
 (12)	 (45%)	$n\text{-}C_8F_{18}$ (12%)

(continued on facing page)

TABLE 2 (cont.)

Adduct		Perfluoroether (yield)		By-products (yield)	
	(13)		(20%)		(22%)
Isomer Mixture 	(14)		(25%)	 $CF_3CF_2\underset{\substack{\vert\\CF_3}}{C}FCF_2CF_2CF_3$	(10%)
	(15)		(8%)	$n\text{-}C_5F_{12}$ $n\text{-}C_6F_{14}$	(3%) (10%)
$CH_3OCH_2CF_2CFHCF_3$	(16)	$CF_3O(CF_2)_3CF_3$	(36%)	$n\text{-}C_4F_{10}$	(44%)
	(17)		(16%)		(9%)
 $CH_3CH_2O\underset{\substack{\vert\\CF_2CFHCF_3}}{C}HCH_3$	(18)	 $CF_3CF_2O\underset{\substack{\vert\\CF_2CF_2CF_3}}{C}FCF_3$	(43%)	$n\text{-}C_5F_{12}$	(10%)
 $\left(CH_3\underset{\substack{\vert\\CF_3CFHCF_2}}{C}H\right)_2O$	(19)	 $\left(CF_3\underset{\substack{\vert\\CF_3CF_2CF_2}}{C}F\right)_2O$	(41%)	$n\text{-}C_5F_{12}$	(9%)
 $CH_3CH_2CH_2O\underset{\substack{\vert\\CF_2CFHCF_3}}{C}HCH_2CH_3$	(20)	 $CF_3CF_2CF_2O\underset{\substack{\vert\\CF_2CF_2CF_3}}{C}FCF_2CF_3$	(32%)		
 $\left(CH_3CH_2\underset{\substack{\vert\\CF_3CFHCF_2}}{C}H\right)_2O$	(21)	 $\left(CF_3CF_2\underset{\substack{\vert\\CF_3CF_2CF_2}}{C}F\right)_2O$	(12%)	$n\text{-}C_6F_{14}$	(30%)
 $CH_3CH_2CH_2CH_2O\underset{\substack{\vert\\CF_2CFHCF_3}}{C}HCH_2CH_2CH_3$	(22)	 $CF_3CF_2CF_2CF_2O\underset{\substack{\vert\\CF_2CF_2CF_3}}{C}FCF_2CF_2CF_3$	(18%)	$n\text{-}C_7F_{16}$	(10%)

sample collection. Boiling points were determined by the Siwoloboff method. Fluorine nmr spectra were recorded on a Varian EM360L spectrometer operating at 56.46 MHz and chemical shifts are quoted relative to trichlorofluoromethane. Mass spectra were recorded on an A.E.I. MS9 spectrometer and glc/ms were recorded on a V.G. Micromass 12B spectrometer fitted with a Pye 104 gas chromatograph.

General procedure for fluorinations with cobalt trifluoride

The apparatus for fluorination with cobalt trifluoride [15] consisted of a nickel tube equipped with inlet and outlet ports and nickel paddles attached to a rod situated along the centre of the tube and rotated by an electric motor. A mixture of cobalt trifluoride (150 g) and calcium difluoride (150 g) was contained in the tube and heated to the required temperature, using an electric heating tape wrapped around the tube, with continual stirring. Dry nitrogen (50 ml/min.) was passed through the reactor for 10 mins. prior to use. Starting materials were dropped into the reactor at a rate of 1 ml/10 mins. in a nitrogen flow (50 ml/min.). After all the compound for fluorination was added, the reactor was flushed with nitrogen for 15 mins. Products were collected in a trap cooled with liquid air, which was detached from the reactor and left to warm up in an efficient fume cupboard. Anhydrous sodium carbonate or sodium fluoride was added to remove hydrogen fluoride and the product pipetted out or transferred out under vacuum. Pure samples of the product components were isolated by preparative glc.

After fluorination, the cobalt fluoride system was regenerated by passing fluorine gas, from a fluorine cell, via a copper pipe through the heated reactor (> 300°C), until fluorine was detected at the outlet, using starch/iodide paper (white to blue).

Fluorination of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (1)

(a) At 440°C

Adduct (1) (1.93 g, 8.7 mmol) was passed over cobalt trifluoride at 440°C, according to the general procedure outlined above, to give a product (2.27 g) containing perfluoro-2-propyloxolane (2.18 g, 70%) [16], b.p. 79°C, and perfluorohexane (0.09 g, 3%).

(b) At lower temperatures

Adduct (1) was passed over cobalt trifluoride to give products as listed in Table 3.

TABLE 3

Adduct (1)	Temp. (°C)	Product
(2.82 g, 13 mmol)	355	(3.24 g)
(3.55 g, 16 mmol)	270	(3.69 g)
(5.10 g, 23 mmol)	240	(5.67 g)
(2.40 g, 11 mmol)	180	(1.66 g)
(1.75 g, 8 mmol)	110	(0.7 g)

The products were analysed by glc/ms to determine the extent of fluorination of each component as listed in Table 1. These assignments were confirmed by elemental and spectroscopic analysis of some components isolated by preparative scale glc.

Fluorination of 2,2,3,4,4,4-hexafluoro-1-methyl butyl ethyl ether (18)

(a) At 440°C

Adduct (18) (0.56 g, 2.6 mmol) gave a product (0.56 g) containing perfluoro-1-methyl butyl ethyl ether (nc) (0.44 g, 43%), b.p. 78°C (Found: C, 20.0; F, 74.5. $C_7F_{16}O$ requires: C, 20.8%; F, 75.2%); δ_F 82.0 (m) and 84.8 (t, J 11 Hz) (6F, $2\underline{CF_3}CF_2$), 89.3 (2F, m, CF_2O), 90.7 (3F, m, $\underline{CF_3}CF$), 124.8 (2F, m, CF_2), 127.4, 130.3 (2F, AB, J 288 Hz, $\underline{CF_2}CF$), 142.8 (1F, m, CF); m/z 335 (M^+-CF_3, 0.5%), 119 (100), 69 (50), and perfluoropentane (0.10 g, 10%).

(b) At lower temperatures

Adduct (18) gave products as listed in Table 4.

TABLE 4

Adduct (18)	Temp. (°C)	Product
(3.02 g, 14 mmol)	410	(2.07 g)
(2.47 g, 11 mmol)	320	(1.95 g)
(1.55 g, 7 mmol)	240	(1.4 g)

The products were analysed by glc/ms according to the method outlined for the oxolane adduct (1) and the results are shown in the Figure.

Fluorination of 2-(1,1,2,3,3,3-hexafluoropropyl)-1,4-dioxane (10)

(a) At 440°C

Adduct (10) (2.17 g, 9 mmol) gave a product (2.55 g) containing perfluoropropyl-1,4-dioxane (nc) (2.37 g, 68%), b.p. 90°C (Found: C, 21.6; F, 66.9. $C_7F_{14}O_2$ requires: C, 22.0; F, 69.6%); δ_F 79.3 to 98.0 (6F, overlapping m, $3CF_2O$), 84.0 (3F, m, CF_3), 124.3, 127.5 (4F, m, $2CF_2$), 131.7 (1F, m, CF); m/z 363 (M^+-F, 0.3%), 131 (46), 119 (61), 100 (100), 69 (31).

(b) At lower temperatures

Adduct (10) gave products as listed in Table 5.

TABLE 5

Adduct (10)	Temp. (°C)	Product
(3.71 g, 16 mmol)	370	(3.97 g)
(3.37 g, 14 mmol)	240	(3.62 g)
(2.89 g, 12 mmol)	130	(1.58 g)

The products were analysed by glc/ms according to the method outlined for the oxolane adduct (1) and the results shown in the Figure were obtained.

Fluorination of 2,2,3,4,4,4-hexafluorobutyl methyl ether (16) at 440°C

Adduct (16) (2.04 g, 10.4 mmol) gave a gaseous product (2.57 g) containing perfluorobutyl methyl ether (nc) (1.14 g, 36%), m/z 219 (M^+-CF_3O, 7%), 135 ($C_2F_5O^+$, 17), 69 (100), and perfluorobutane (1.40 g, 44%).

Fluorination of 1,2,3,3,4,4,5,5,6,6-decafluoro-1-methoxymethylcyclohexane (17) at 440°C

Adduct (17) (1.87 g, 6.1 mmol) gave a product (1.05 g) containing perfluoromethoxy methylcyclohexane (nc) (0.40 g, 16%), δ_F 58.7 (3F, m, CF_3O), 73.0 (2F, m, CF_2O), 119.1 to 148.7 (10F, overlapping AB, $5CF_2$), and 189.7 (1F, m, CF), m/z 332 (M^+-CF_3O, 4%), 135 (29), 69 (100) and perfluoromethylcyclohexane (0.22 g, 9%).

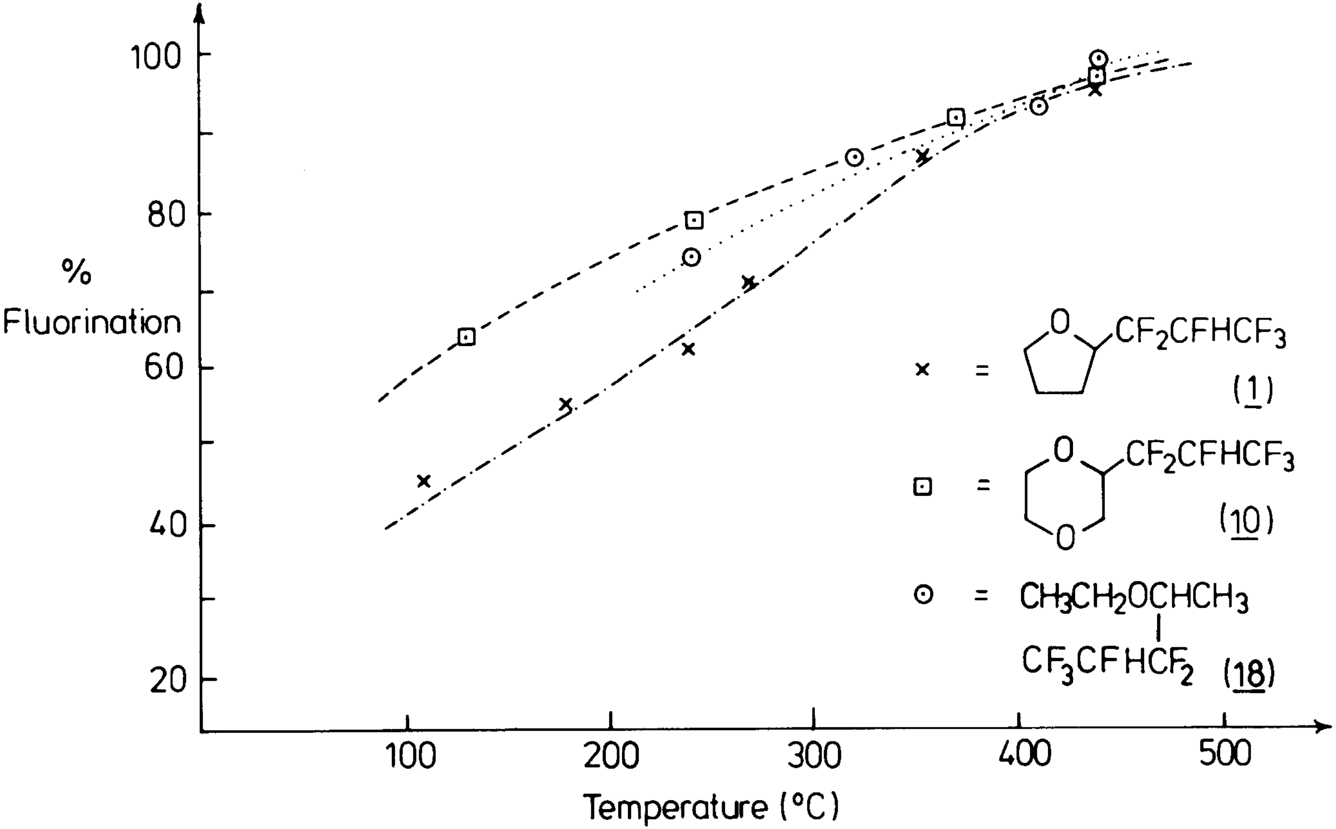


Fig 1. Graph of Extent of Fluorination against Temperature for Compounds (1), (10) and (18).

Fluorination of di(1-methyl-2,2,3,4,4,4-hexafluorobutyl)ether (19) at 440°C

Adduct (19) (2.07 g, 5.5 mmol) gave a product (1.68 g) containing perfluorodi(1-methylbutyl)ether (1.25 g, 41%), b.p. 136°C (Found: C, 22.0; F, 72.5. $C_{10}F_{22}O$ requires: C, 21.7; F, 75.4%), δ_F 80.0 and 81.3 (6F, m, $2\underline{CF_3}CF$), 84.2 (6F, t, J 11 Hz, $2\underline{CF_3}CF_2$), 122.8 (4F, m, $2\underline{CF_2}CF$), 127.5 and 128.2 (4F, m, $\underline{CF_2}\,CF_3$), 136.8 (2F, m, 2CF), m/z 485 (M^+-CF_3, 2%), 269 (43), 181 (34), 119 (51), 69 (100), and perfluoropentane (0.27 g, 9%).

Fluorination of 1-ethyl-2,2,3,4,4,4-hexafluorobutyl propyl ether (20) at 440°C

Adduct (20) (0.33 g, 1.3 mmol) gave a product (0.24 g) containing perfluoro-1-ethylbutyl propyl ether (nc) (0.16 g, 32%), b.p. 127°C (Found: C, 20.8; F, 75.3. $C_9F_{20}O$ requires: C, 21.4; F, 75.4%), δ_F 83.5 (2F, m, CF_2O), 84.0, 85.0 and 85.4 (9F, m, $3CF_3$), 122.3, 125.7, 128.2, 132.5 (8F, m, $4CF_2$) and 141.7 (1F, m, CF); m/z 385 (M^+-C_2F_5, 0.7%), 169 (100), 69 (51).

Fluorination of di(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)ether (21) at 440°C

Adduct (21) (1.77 g, 4.4 mmol) gave a product (1.15 g) containing perfluoro-di(1-ethyl butyl)ether (nc) (0.35 g, 12%), b.p. 162°C (Found: C, 21.9; F, 74.0. $C_{12}F_{26}O$ requires: C, 22.0; F, 75.5%), δ_F 83.5 and 84.8 (12F, m, $4CF_3$), 120.7 and 123.7 (8F, m, $4\underline{CF_2}CF$), 128.0 (4F, m, $2\underline{CF_2}CF_2$) and 130.8 (2F, m, CF); m/z 535 (M^+-C_2F_5, 0.9%), 319 (31), 231 (34), 169 (61), 119 (75), 69 (100), and perfluorohexane (0.86, 30%).

Fluorination of 1-propyl-2,2,3,4,4,4-hexafluorobutyl butyl ether (22) at 440°C

Adduct (22) (0.56 g, 2 mmol) gave a product (0.35 g) containing perfluoro-1-propylbutyl butyl ether (nc) (0.22 g, 18%), b.p. 149°C (Found: C, 21.1; F, 75.9. $C_{11}F_{24}O$ requires: C, 21.8; F, 75.5%), δ_F 82.0 (2F, m, CF_2O), 84.5 (9F, m, $3CF_3$), 121.5 (4F, m, $\underline{CF_2}CF$), 128.0 (6F, m, $3CF_2$), 129.0 (2F, m, $CF_2\underline{CF_2}CF_2$), 140.3 (1F, m, CF), m/z 435 (M^+-C_3F_7, 0.9%), 369 (11), 281 (11), 219 (95), 69 (100) and perfluoroheptane (0.12 g, 10%).

Fluorination of 2-(1,1,2,3,3,3-hexafluoropropyl)oxetane (15) at 440°C

Adduct (15) (2.22 g, 10.7 mmol) gave a gaseous product (0.71 g) containing perfluoro-2-propyl oxetane (nc) (0.27 g, 8%); m/z 250 (M^+-CF_2O, 0.4%), 197 (2, C_4F_7O), 169 (36), 131 (100), 119 (64), 100 (99), 69 (81), perfluoropentane (0.10 g, 3%) and perfluorohexane (0.34 g, 10%). The intense peak at 100 (C_2F_4) is highly characteristic of cyclic F-ethers.

Fluorination of 2-(1-trifluoromethyl-1,2,3,3,3-pentafluoropropyl)oxolane (2) at 440°C

Adduct (2) (2.03 g, 7.5 mmol) gave a product (1.96 g) containing perfluoro-2-(1-methylpropyl)oxolane (nc) (1.65 g, 53%), b.p. 101°C (Found: C, 23.3; F, 76.0. $C_8F_{16}O$ requires: C, 23.1; F, 73.1%), δ_F 73.3, 74.5 (3F, m, $\underline{CF_3}CF$), 83.8 (3F, m, $\underline{CF_3}CF_2$), 85.5, 86.8, 87.7, 89.5, 90.0, 92.0 (2F, overlapping m, CF_2O), 117.8 (3F, m, CFO and $\underline{CF_2}CF_3$) 126.2 to 142.5 (4F, overlapping AB, 2 ring CF_2), 185.3 (1F, m, CF); m/z 397 (M^+-F, 4.4%), 259 (11), 231 (12), 197 (18), 181 (27), 169 (91), 150 (100), 100 (76), 69 (75).

Fluorination of 2-(2-chloro-1,1,2-trifluoroethyl)oxolane (3) at 440°C

Adduct (3) (1.68 g, 8.9 mmol) gave a product (2.11 g) containing perfluoro-2-(2-chloro ethyl)oxolane (nc) (1.34 g, 45%), b.p. 82°C (Found: C, 22.4; F, 62.5; Cl, 11.6. $C_6ClF_{11}O$ requires: C, 21.7; F, 62.9; Cl, 10.7%), δ_F 70.5 (2F, m, CF_2Cl), 85.2, 87.4 (2F, AB, J 136 Hz, CF_2O), 125.2 (1F, m, CF), 119.8, 124.7 (AB, J 282 Hz), 129.0, 139.4 (AB, J 260 Hz) and 131.3 (m) (6F, 2 ring CF_2, $\underline{CF_2}CF_2Cl$), m/z 313 (M^+-F, 0.4%), 297 (57), 197 (68), 169 (100), 150 (38), 100 (51), 87 (20), 85 (60), and perfluoroethyloxolone [16] (0.35 g, 12%), b.p. 54°C.

Fluorination of 2-(1,2,3,3,4,4-hexafluorocyclobutyl)oxolane (4) at 440°C

Adduct (4) (2.32 g, 9.9 mmol) gave a product (2.98 g) containing perfluoro-2-cyclobutyloxolane (nc) (2.41 g, 64%) (Found: C, 23.9; F, 73.3. $C_8F_{14}O$ requires: C, 25.4; F, 70.4%), δ_F 84.3, 88.5 (2F, AB, J 132 Hz, CF_2O), 120.7 (1F, m, CFO), 124.0 to 140.2 (10F, overlapping AB, $5CF_2$), 191.7 (1F, m, CF); m/z 359 (M^+-F, 0.9%), 259 (22), 150 (18), 100 (100), 69 (14), and an unidentified decomposition product (0.45 g).

Fluorination of 2-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)oxolane (5) at 440°C

Adduct (5) (1.87 g, 6.6 mmol) gave a product (2.22 g) containing perfluoro-2-cyclopentyl oxolane (nc) (1.83 g, 65%), b.p. 117°C (Found: C, 24.7; F, 76.0. $C_9F_{16}O$ requires: C, 25.2; F, 71.0%), δ_F 85.7, 87.6 (2F, AB, J 130 Hz, CF_2O), 118.0 (1F, m, CFO), 121.7 to 140.8 (12F, overlapping AB, $6CF_2$), 184.0 (1F, m, CF); m/z 409 (M^+-F, 6%), 243 (20), 193 (23), 169 (31), 150 (100), 100 (70), 69 (28), and perfluoropropylcyclopentane (0.31 g, 11%).

Fluorination of 2-(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)oxolane (6) at 440°C

Adduct (6) (2.42 g, 7.2 mmol) gave a product (2.73 g) containing perfluoro-2-cyclohexyloxolane (nc) (1.76 g, 51%), b.p. 136°C (Found: C, 24.9; F, 71.9. $C_{10}F_{18}O$ requires: C, 25.1; F, 71.6%); δ_F 83.3, 87.7 (2F, AB, J 136 Hz, CF_2O), 113.7 to 147.7 (15F, overlapping AB, CFO and $7CF_2$), 186.7 (1F, m, CF); m/z 459 (M^+-F, 7%), 243 (11), 193 (12), 169 (49), 150 (100), 100 (61), 69 (28), and perfluoropropylcyclohexane (0.21 g, 6%).

Fluorination of 2-(1,2-dichloro-1-trifluoromethyl-3,3,3-trifluoropropyl)-oxolane (7) at 440°C

Adduct (7) (2.78 g, 9.1 mmol) gave a product (1.86 g) containing perfluoro-2-(2-chloro-1-methylpropyl)oxolane (nc), (0.63 g, 16%), δ_F 70.7 to 96.2 (8F, overlapping m, CF_2O and $2CF_3$), 106.7 to 141.7 (6F, overlapping AB, $2CF_2$, CFO and CFCl), 175, 184.7 (1F, m, CF); m/z 363 (M^+-CF_3, 1.3%), 318 (23), 247 (12), 150 (39), 131 (94), 69 (100), perfluoro-2-(1-methylpropyl)oxolane (0.59 g, 15%) and many unidentified compounds (total 0.71 g).

Fluorination of 2-(1,1,2,3,3,3-hexafluoropropyl)oxane (8) at 440°C

Adduct (8) (1.49 g, 6.3 mmol) gave a product (1.96 g) containing perfluoro-2-propyloxane (1.62 g, 62%) [17] δ_F 81.2, 95.0 (2F, AB, J 164 Hz, CF_2O), 84.5 (3F, m, CF_3), 117.7 to 146.8 (11F, overlapping AB, CFO, $5CF_2$).

Fluorination of 2-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)oxane (9) at 440°C

Adduct (9) (3.06 g, 10.3 mmol) gave a product (3.59 g) containing perfluoro-2-cyclopentyloxane (nc) (1.52 g, 31%), b.p. 134°C (Found: C, 23.1; F, 72.1. $C_{10}F_{18}O$ requires: C, 25.1; F, 71.6%); δ_F 79.4, 93.5 (2F, AB, J 160 Hz, CF_2O), 116.8 to 145.2 (15F, overlapping AB, CFO, $7CF_2$), 184.0 (1F, m, CF); m/z 459 (M^+-F, 3%), 343 (8), 219 (10), 131 (65), 100 (100), perfluorobutylcyclopentane (0.98 g, 20%), and other unidentified decomposition products (0.84 g, 17%).

Fluorination of 2-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-1,4-dioxane (11) at 440°C

Adduct (11) (2.80 g, 9.3 mmol) gave a product (1.82 g) containing perfluoro-2-cyclopentyl-1,4-dioxane (nc) (0.70 g, 17%), b.p. 125°C (Found: C, 23.9; F, 67.7. $C_9F_{16}O_2$ requires: C, 24.3; F, 68.5%); δ_F 78.2 to 97.8 (6F, overlapping AB, $3CF_2O$), 121.2 to 140.2 (9F, overlapping AB, CFO, $4CF_2$), 185.5 (1F, m, CF); m/z 331 (M^+-$C_2F_3O_2$, 2%), 312 (2), 193 (19), 119 (22), 100 (100), perfluoro-2-cyclopentylethyl methyl ether (nc) (0.33 g, 8%), b.p. 101°C; δ_F 58.8 (3F, m, CF_3O), 88.3 (2F, m, CF_2O), 122.2 to 138.0 (10F, overlapping AB, $5CF_2$), 188.0 (1F, m, CF); m/z 331 (M^+-CF_3O, 7%), 181 (10), 135 (38), 69 (100), perfluoroethylcyclopentane (0.41 g, 10%), and other decomposition products (0.41 g, 10%).

Fluorination of 2-(1,1,2,3,3,3-hexafluoropropyl)oxepane (12) at 440°C

Adduct (12) (1.63 g, 6.5 mmol) gave a product (1.98 g) containing perfluoro-2-propyloxepane (nc) (1.37 g, 45%), b.p. 124°C (Found: C, 22.6; F, 76.9. $C_9F_{18}O$ requires: C, 23.2; F, 73.4%); δ_F 82.0 (2F, m, CF_2O), 84.3 (3F, t, J 11 Hz, CF_3), 123.3 to 136.3 (13F, overlapping AB, CF and $6CF_2$); m/z 447 (M^+-F, 0.5%), 281 (9), 181 (18), 169 (27), 131 (100), 119 (22), 100 (14), 69 (81), and perfluoro-octane (0.36 g, 12%).

Fluorination of 2-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)oxepane (13) at 440°C

Adduct (13) (1.81 g, 5.8 mmol) gave a product (2.25 g) containing perfluoro-2-cyclopentyloxepane (nc) (0.61 g, 20%), b.p. 158°C (Found: C, 24.3.

$C_{11}F_{20}O$ requires: C, 25.0%); δ_F 81.3 (2F, m, CF_2O), 122.2 to 141.0 (17F, overlapping AB, CFO and $8CF_2$), 183.7 (1F, m, CF); m/z 509 (M^+-F, 1%), 343 (4), 131 (100), 69 (29), and perfluoropentylcyclopentane (0.67 g, 22%).

Fluorination of an isomer mixture (52:48) of 2- and 5-methyl-2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (14) at 440°C

Adduct mixture (14) (1.63 g, 6.9 mmol) gave a product (1.9 g) containing perfluoro-2-methyl-5-propyloxolane (0.72 g, 25%) [18], b.p. 94°C, perfluoro-2-methyl-2-propyloxolane (nc) (0.52 g, 18%), b.p. 101°C (Found: C, 22.8. $C_8F_{16}O$ requires: C, 23.1%); δ_F 73.8 (3F, m, CF_3), 82.1 and 88.0 (2F, AB, J 141 Hz, CF_2O), 83.8 (3F, m, $\underline{CF_3}CF_2$), 115.5, 118.7, 120.3, 126.0 (m) and 129.1, 133.0 (AB, J 248 Hz) (8F, $4CF_2$); m/z 397 (M^+-F, 6%), 247 (37), 181 (23), 169 (73), 69 (100), and perfluoro-3-methylhexane (0.29 g, 10%).

ACKNOWLEDGEMENT

We thank the Science and Engineering Research Council, for a Co-operative Award Fellowship, and the Electricity Council and I.C.I. p.l.c., Mond Division, for co-operating in this award.

REFERENCES

1 Part 4. R.D. Chambers, B. Grievson and N.M. Kelly, J. Chem. Soc., Perkin Trans. I, submitted for publication.

2 T. Abe and S. Nagase, in R.E. Banks (Ed.), 'Preparation, Properties and Industrial Applications of Organofluorine Compounds', Ellis Horwood, Chichester, (1982), ch. 1, p. 28.

3 D.S.L. Slinn and S.W. Green, ch. 2, see ref. 2.

4 M. Brandwood, P.L. Coe, C.S. Ely and J.C. Tatlow, J. Fluorine Chem., 5 (1975) 521.

5 J. Burdon, G.E. Chivers, E.F. Mooney and J.C. Tatlow, J. Chem. Soc. (C), (1969) 1739.

6 I.W. Parsons, P.M. Smith and J.C. Tatlow, J. Fluorine Chem., 1 (1971) 141.

7 J. Burdon and I.W. Parsons, Tetrahedron, 27 (1971) 4533.

8 R.D. Bagnall, W. Bell and K. Pearson, J. Fluorine Chem., 9 (1977) 359.

9 A.B. Clayton, R. Stevens and J.C. Tatlow, J. Chem. Soc., (1965) 7370.

10 R.D. Bagnall, W. Bell and K. Pearson, J. Fluorine Chem., 11 (1978) 93.

11 See ref. 1 and earlier parts of the series.

12 R.D. Chambers, N.M. Kelly, W.K.R. Musgrave, W.G.M. Jones and R.W. Rendell, J. Fluorine Chem., 16 (1980) 351.

13 J. Burdon, I.W. Parsons and J.C. Tatlow, Tetrahedron, 28 (1972) 43.

14 R.D. Chambers, D.T. Clark, T.F. Holmes, W.K.R. Musgrave and I. Ritchie, J. Chem. Soc., Perkin Trans. I, (1974) 114.

15 R.D. Fowler, W.B. Burford, J.M. Hamilton, R.G. Sweet, C.E. Weber, J.S. Kasper and I. Litant, in C. Slesser and S.R. Schram, (Eds.), 'Preparation, Properties and Technology of Fluorine and Organic Fluoro-Compounds', McGraw-Hill, New York, (1951), p. 349.

16 T. Abe, S. Nagase and H. Baba, Japan Kokai., (1975) 123658; Chem. Abs., 85 (1976) 32820p.

17 J.H. Simons, U.S. Patent, (1950) 2 519 983.

18 T. Abe, E. Hayashi, H. Baba, K. Kazuo and S. Nagase, J. Fluorine Chem., 15 (1980) 353.