Journal of Fluorine Chemistry, 49 (1990) 409–419

Received February 9, 1990, accepted May 15, 1990

FREE-RADICAL CHEMISTRY. PART 8[1]. ELECTROCHEMICAL FLUORINATION OF PARTLY FLUORINATED ETHERS

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SUMMARY

Free-radical additions of hexafluoropropene to cyclic ethers may be carried out to achieve mono- or di-adducts and mixtures of isomers of di-adducts are formed. These adducts may be fluorinated, using electrochemical fluorination, to give the corresponding perfluoro-ethers and, in some cases, with surprising efficiency. Adducts of acyclic ethers are less efficiently fluorinated.

INTRODUCTION

Perfluorinated ethers are increasingly useful as inert fluids but synthetic methods for these compounds are limited. Electrochemical fluorination (ECF) has been the most used method for synthesis, so far, but we established that partly fluorinated derivatives may be fluorinated using cobalt trifluoride, with great reduction in fragmentation over that obtained with unfluorinated material [2]. Consequently, we have investigated the effect of partial fluorination of ethers on the products of ECF. Sanders and Blöchl [3] have shown that partial fluorination is beneficial in electrochemical fluorination of hydrocarbons.

0022-1139/90/$3 50

RESULTS AND DISCUSSION

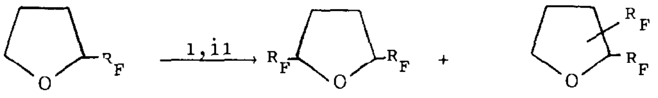
The overall process envisaged involves free-radical addition of a fluorinated alkene (hexafluoropropene has been used throughout), followed by further fluorination of the resultant adducts.

$$\text{-}CH_2\text{-}O\text{-}CH_2\text{-} \;+\; CF_2{=}CFCF_3 \;\xrightarrow[\text{etc.}]{In^{\cdot}}\; \underset{(1)}{\text{-}CH_2\text{-}O\text{-}CHR_F\text{-}}$$

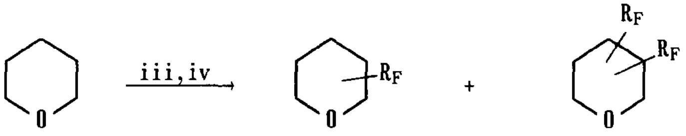
$$\text{where } R_F = CF_2CFHCF_3 \qquad\qquad + \;\underset{(2)}{\text{-}CHR_F\text{-}O\text{-}CHR_F\text{-}}$$

Various mono-adducts (1) have been described previously [4,5] and di-adducts (2) were obtained by further reaction of adducts (1) with hexafluoropropene at elevated temperatures. Di-adducts (2) were obtained readily, directly from diethylether, but this occurs via an intramolecular hydrogen-transfer process [5] but most other systems preferentially give mono-adducts (1). The much greater difficulty observed in effecting further free-radical additions to (1) may be attributed to polar-effects of the polyfluoroalkyl group in the derived radical (1a,b) where the R_F reduces the ability of oxygen to donate (1b). Hexafluoropropene is, of course, an electrophilic alkene and reaction occurs preferentially with nucleophilic radicals. Surprisingly, oxane (5) gave a mixture of isomeric mono-adducts (6a-c), rather than (6a) alone but, on reflection, the observed ratio of isomers may be accounted for on the basis of inductive electron-withdrawal by oxygen, which would of course fall off from 2- to 4-positions, and the stabilising donor ability of oxygen, as illustrated by (1a,b), which has an opposing activating effect at the 2-position. Obviously, the latter dominates and is even more effective in a five-membered ring [4], which accounts for the formation of only one isomer (3).

$$(1) \;\xrightarrow{In^{\cdot}}\; \underset{(1a)}{\text{-}\dot{C}H\text{-}\ddot{O}\text{-}CHR_F\text{-}} \;\longleftrightarrow\; \underset{(1b)}{\text{-}\overset{-}{\ddot{C}}H\text{-}\overset{+\cdot}{O}\text{-}CHR_F}$$



(3) (4a) (*ca.* 9:1) (4b)



(5) (6) (3.5:1) (6d)

a, 2-(10.2);
b, 3-(1);
c, 4-(1.4).

i, C_3F_6 (2.25 molar excess), 140°C, D.T.B.P.; ii, 65% conversion; iii, C_3F_6 (2.8 molar excess), 140°C, D.T.B.P.; iv, 67% yield of adducts.

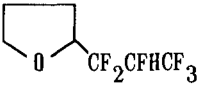
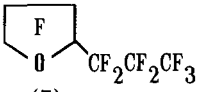
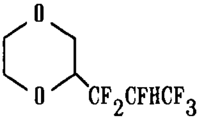
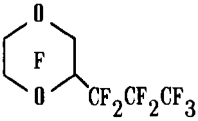
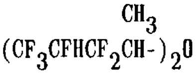
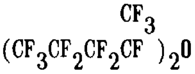
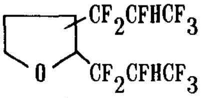
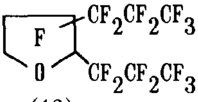
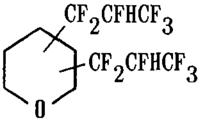
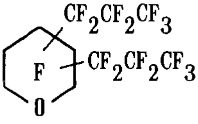
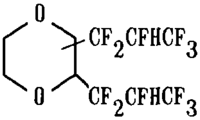
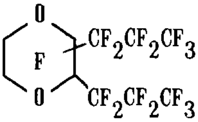
Electrochemical fluorinations of the adducts were carried out using apparatus that has been described previously [6] and electrolysis was continued for a minimum of 110% of the required current. No attempt was made to optimise conditions and material was collected from the bottom of the cell, without determining how much remained in solution. Therefore the quantities recovered represent minimum yields. Volatile materials from the cell were collected but were insufficient to warrant investigation.

The results are summarised in Table 1 and the following conclusions may be drawn. (a) Surprisingly good yields are obtained from cyclic systems and indicate that partial fluorination of the starting material does indeed increase the efficiency of the process. (b) Acyclic systems are less efficiently fluorinated. (c) Mono- and di-adducts react with similar efficiencies. (d) Comparatively little fragmentation occurs with any of these adducts. (e) A relatively efficient process could be developed by a combination of optimisation of the conditions together with continuous usage (to saturate the hydrogen fluoride).

EXPERIMENTAL

The electrochemical fluorination experiments were carried out using apparatus developed in the University of Duisburg. The cell (1170 ml) consisted of a conical stainless steel body with an outlet valve at the bottom and it was surrounded by a cooling jacket. A transparent tube, fitted to the outside of the cell, enabled constant monitoring of the liquid colour and level in the cell. Electrodes consisted of a pack of nickel plates and possessed a total surface area of 3588 cm^2: they were

TABLE 1

Starting material	(g)	Product	total recovered organic material (g)	Yield (%)
<u>mono-adduct</u>:				
 (3)	(101)	 (7)	83.5	50
 (8)	(89.5)	 (9)	34.9	16
<u>di-adducts</u>				
 $(CF_3CFHCF_2\overset{CH_3}{CH}\text{-})_2O$ (10)	(89.6)	 $(CF_3CF_2CF_2\overset{CF_3}{CF})_2O$ (11)	32.5	8
 (4a), (4b)	(102.0) (100.0)	 (12)	70.0 82.7	45
 (6d)	(50.0)	 (13)	30.5	36
 (14)	(65.0)	 (15)	36.5	27

fitted to the lid and were isolated from it with a PTFE gasket. The lid itself, was screwed onto the body and also sealed with a PTFE gasket. A metal condenser was fitted to the top of the cell, together with facilities for introduction of starting material. From the top of the metal condenser, FEP tubing was used to connect two PE-cold traps (ca. 200 ml) cooled with dry ice. A third trap was fitted with a saturated solution of sodium thiosulphate and a fourth trap contained ca. 15% potassium iodide solution. Current was supplied by a direct current (DC) generator which had additional facilities to count the ampere minutes during electrolysis. The potential difference was measured by a voltmeter across the electrode connections on top of the cell and was regulated manually. Within limits of ca. ±0.3 V, the potential difference chosen remained constant and, consequently, the current changed accordingly once the conductivity within the cell had changed. Within the first hours of every run, care was taken that the current did not exceed a limit of ca. 12 A.

As a general procedure electrodes were conditioned prior to the experiments, when the cell had not been in immediate use. This was achieved by electrolysing commercial hydrogen fluoride until the current had reached a constant level. Then the cell was refilled with anhydrous hydrogen fluoride. In practice, a constant low-conductivity indicated the end of the drying process and a value of ca. $\leq$ 1 A, over a period of six hours, was considered sufficiently low to indicate that the hydrogen fluoride had been dried adequately. After the new hydrogen fluoride had been dried, the cell was charged with the material to be electrolysed. Electrolysis was maintained until a minimum of 110% of the current calculated for complete fluorination had been passed. Volatile products were collected in cold traps and organic material, which separated from the hydrogen fluoride, was run from the bottom of the cell. After being separated from cell sludge and excess hydrogen fluoride, the organic material was neutralised with anhydrous potassium fluoride and then analysed. Conductivity additives were not necessary; the current density was always between 20 and 30 mA/cm^2.

Electrochemical Fluorinations

Di-(2,2,3,4,4,4-hexafluoro-1-methyl-butyl)ether (10). A solution of (10) (89.6 g, 0.24 mol) in hydrogen fluoride (960 g) was electrolysed by application of a potential difference of 5.5 V at a cell temperature of

0°C. The reaction was terminated after 46 h, 35 min when 145.22 Ah (113% of the theoretical needed current) had been passed. Only minor amounts of volatile material were collected but not investigated. Analysis of the recovered organic material by gc-ms (32.5 g) gave perfluoro-di-(1-methylbutyl)ether (11) (32% of the recovered organic material by glc) and was found identical with previously characterised material [7]. Some 62% of the recovered organic material was found to be a complex mixture of partly fluorinated material and was not investigated further.

2-(2H-hexafluoropropyl)oxolane (3). A solution of (3) (101.0 g, 0.455 mol) in electrochemical dried hydrogen fluoride (898 g) was electrolysed by application of a cell voltage of 4.5 V at 0°C cell temperature for 69 h, 17 min (144% of the theoretically needed current). Some volatiles (*ca.* 7 g) were collected in cold traps but not investigated. Recovered organic material (83.5 g; 50%) was worked up as described previously and gave perfluoro-2-propyl-oxolane (7), (83.5 g, 50%); bp. 79°C; (Found: C, 22.8; F, 73.0; M^+ 366. $C_7F_{14}O$ requires C, 22.95; F, 72.7%; M, 366) [2].

2,x-bis-(2H-hexafluoropropyl)oxolane (x = 3, 4, 5) (4a)

Run A. - A solution of (4a) (102 g, 0.274 mol) in hydrogen fluoride (1000 g) was electrolysed at a potential difference of 5.5 V, at 5-6°C. Volatile material (< 0.5 g) was not investigated. Initial glc analysis of the recovered organic material (70 g) showed it to be of very similar composition to the recovered organic material from run B.

Run B. - The hydrogen fluoride used in run A was retained. Then (4a) (100 g, 0.296 mol) was electrolysed at 5.5 V, at 0°C. Volatiles (< 0.5 g) were trapped but not investigated further. Initial glc analysis of the recovered organic material (82.7 g) showed that it was a very similar composition to run A and so the products were combined. Preparative glc (column 10% silicone elastomer 30, 70°C) of this combined material gave perfluoro-2,x-dipropyloxolane (x = 3, 4, 5) (12) (85% of the recovered organic material by glc); bp. 123°C; (Found: C, 23.5; F, 73.9; M^+, 516. $C_{10}F_{20}O$ requires C, 23.3; F, 73.6%; M, 516). Other minor products were detected by glc but only compound (7) (13% of recovered organic material by glc) was positively identified, by comparison with previously characterised material.

x,y-bis-(2H-hexafluoropropyl)oxane (x = 2, 3; y = 3, 4, 5, 6) (6d). A solution of a mixture of isomers (6d) (50 g, 0.13 mol) in hydrogen fluoride (800 g) was electrolysed at 5.5 V and at 0°C. Volatile products were not obtained in this experiment. Work up was carried out as described above and separation, using preparative scale glc (column 10% silicone elastomer 30, 70°C) of a sample of the recovered organic material (30.5 g) gave perfluoro-x,y-dipropyl-oxane (x = 2, 3; y = 3, 4, 5, 6) (13) (87% of recovered organic material by glc); (Found: C, 23.0; F, 74.4; M^+, 566. $C_{11}F_{22}O$ requires C, 23.3; F, 73.85%; M, 566). Isomers of perfluoro-x-propyl-oxane (x = 2, 3, 4) (10% of recovered organic material by glc) was identified by means of mass spectral data (Found: M^+, 416. $C_8F_{16}O$ requires M, 416) and this material obviously results from breakdown.

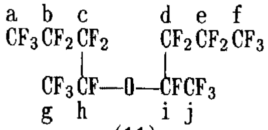
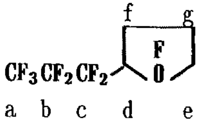
2-(2H-hexafluoropropyl)-1,4-dioxane (8). A solution of (8) (89.5 g, 0.376 mol) in hydrogen fluoride (835 g) was electrolysed at 4.75 V and at 0°C. The reaction was terminated after 45 h 57 min when 208.88 Ah (129.5% of the theoretically needed current had been passed. Volatile material (23.0 g) was collected in cold traps but not identified, although carbonyl absorptions were evident in the gas phase ir spectrum therefore, indicating some ring-opening. Analysis of the organic material recovered from the cell (34.9 g) gave perfluoro-2-propyl-1,4-dioxane (9) (66% of the recovered organic material by glc), identified by comparison with a previously characterised sample [7].

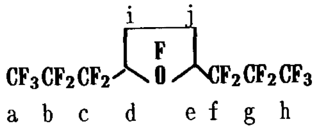
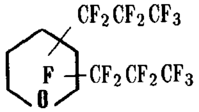
2,x-bis-(2H-hexafluoropropyl)-1,4-dioxane (x = 3, 5, 6) (14). A solution of (14) (65 g, 0.167 mol) in hydrogen fluoride (800 g) was electrolysed for 24 h 17 min when 92.29 Ah (128.5% of the theoretically needed current) had been passed, at 5.5 V, and at 0°C. No volatiles were collected. Analysis of the recovered organic material (36.5 g) gave perfluoro-2,x-dipropyl-1,4-dioxane (x = 3, 5, 6) (15) (66.5% of the recovered organic material by glc) identified by comparison with previously characterised material [7].

N.M.R. data

The data for compounds described in the Experimental section are recorded in Table 2 and assignments are given where possible. Shifts are measured using $CFCl_3$ as external standard, with negative values being to

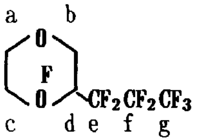
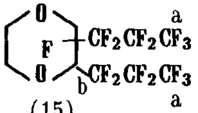
TABLE 2

		Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
 (11)	^{19}F	-79.60 -80.97	s s }		6	g,j
		-83.83	s		6	a,f
		-126.19	m		8	b,c, d,e
		-136.16 -136.93	s s }		2	h,i
 (7)	^{19}F	-83.82	s		3	a
		-84.88 -87.33	A of AB B of AB	J= 132 J= 129 }	2	e
		-126.6	m		8	b,c, f,g
		-138.89 -139.98	s s }		1	d

 (12)	^{19}F	-83.99	s	6	a,h
		-126.03	m	12	b,c, f,g, i,j
		-133.08 -134.17 -134.76 -135.86	s s s s	2	d,e
 (13)	^{19}F	-83.5 -83.9	s		CF_3
		-70.3 - -83.0	m		$O\text{-}CF_2$
		-115.4 - -144.7	m		$CF_2/OCFR_F$
		-179.3 - -190.3	m		CF

(continued)

TABLE 2 (cont.)

		Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assign-ment
 (9)	^{19}F	-83.4	s		3	g
		-84.7	m		5	d,e,f
		-126.6	m		6	a,b,c
 (15)	^{19}F	-83.9	s		3	a
		-81.5	m		2	$O-CF_2$
		-127.3	m		5	$CF_2/CF(b)$

high field. An interesting feature of the spectra is the appearance of more than one signal, when chiral sites occur e.g. in compound (7). When more than one chiral centre occurs e.g. (12) then, obviously, further complexity arises.

ACKNOWLEDGEMENT

We thank the E.E.C. for a twinning grant.

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