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REACTIONS OF TETRAFLUOROETHENE OLIGOMERS. PART XIII .  
REACTIONS OF A PERFLUORINATED DIHYDROFURAN; PERFLUORO-4-  
ETHYL-2,3,4,5-TETRAMETHYL-4,5-DIHYDROFURAN

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SUMMARY

The perfluorinated dihydrofuran, perfluoro-4-ethyl-2,3,4,5-tetramethyl-4,5-dihydrofuran PFDHF (1), prepared from tetrafluoroethene pentamer, was reacted with a range of nucleophiles. The type of product formed was found to be dependant upon the nucleophile used. Attack with oxygen, sulphur and carbon nucleophiles was found to occur at the 2-position, whereas nitrogen nucleophiles were found to attack at either the 2-position or the exocyclic 3-position.

INTRODUCTION

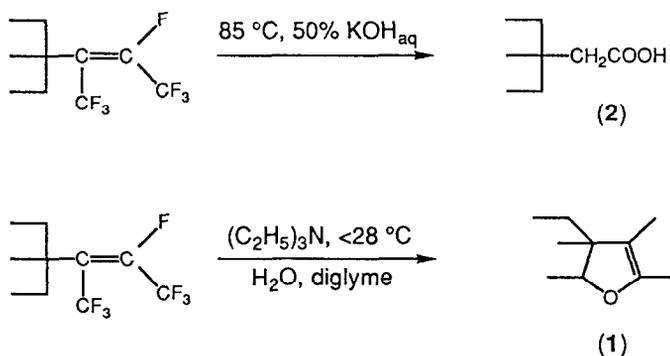
Perfluoro-4-ethyl-2,3,4,5-tetramethyl-4,5-dihydrofuran(1), (PFDHF), prepared initially by Chambers [1], was obtained [2] from the reaction of tetrafluoroethene pentamer with aqueous triethylamine employing diglyme as a phase-transfer solvent under conditions of vigorous phase mixing. We now report the reactions of this compound with a range of nucleophiles.

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## RESULTS AND DISCUSSION

(1) was prepared in large quantities (50-100g) from the reaction of TFE pentamer with triethylamine/water. The reaction of TFE pentamer with hydroxide ion can lead to various products depending upon the base employed and the reaction conditions. Thus use of  $\text{KOH}_{\text{aq}}$  as base at  $85\text{ }^{\circ}\text{C}$  led to the formation of 4,4,5,5,5-pentafluoro-3-pentafluoroethyl-3-trifluoromethylpentanoic acid (2), pentamer acid, Scheme 1 [ 3].

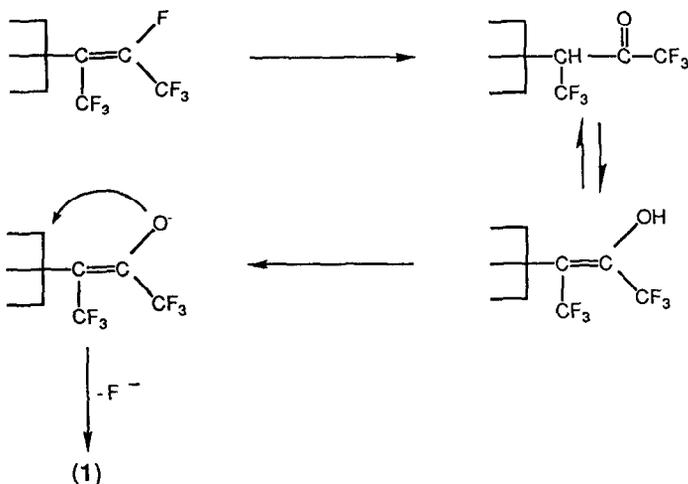


Scheme 1.

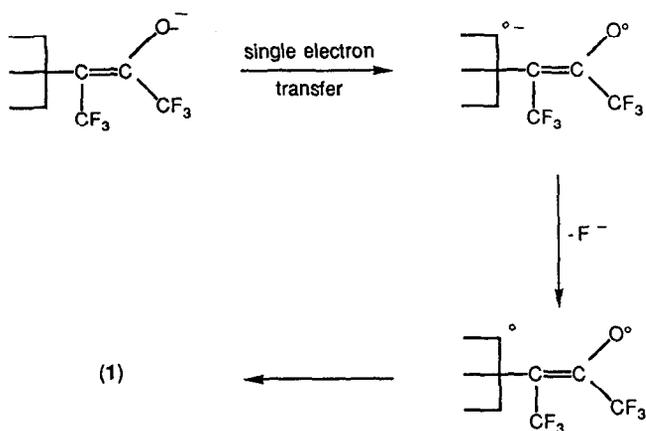
However, use of triethylamine as base, diglyme as a phase transfer agent and Monoflor 31 as a surfactant under vigorous phase mixing conditions gave 61% of (1) after distillation.

The mechanism of the reaction remains a source of some controversy, with two schools of thought prevailing. The first, originally invoked by Chambers[4], proposes initial attack by hydroxyl ion on TFE pentamer to give the enol in equilibrium with the ketone. Under the basic reaction conditions this then undergoes an intramolecular nucleophilic displacement of fluoride ion by the enolate  $\text{O}^-$  to give the cyclised product, Scheme 2.

The chief objection to this proposed mechanism is that displacement of a methylene fluoride ion by  $\text{RO}^-$  is not commonplace[5]. Thus, as an alternative mechanism, we propose the involvement of single electron transfer (Scheme 3), in which the enolate



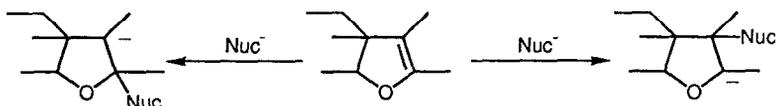
Scheme 2.



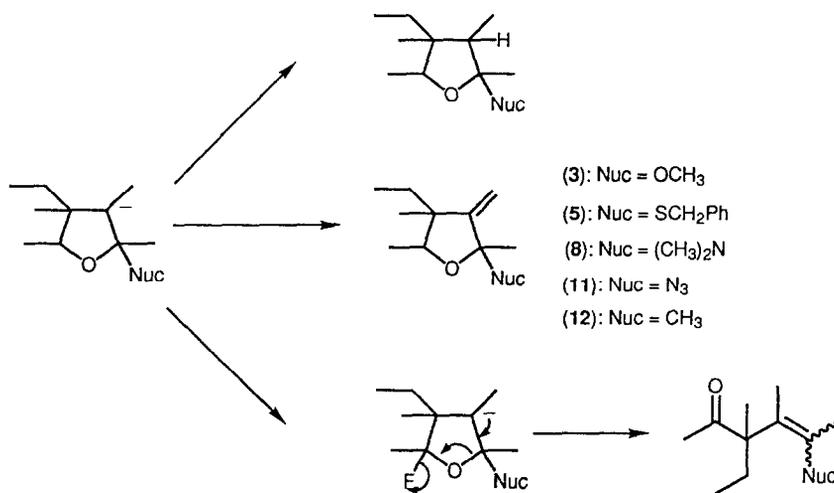
Scheme 3.

oxygen is assumed to donate an electron to the  $\text{CF}_2$  carbon, which undergoes loss of fluoride ion followed by radical recombination to give (1). Although we have no direct evidence for such a mechanism there is now considerable literature precedent for the involvement of SET in a number of similar reactions [6]. The merit of our proposal is that it does at least overcome the lack of precedent for direct displacement of fluoride from a difluoromethylene group.

Nucleophiles could possibly attack (1) at either the 2- or 3- position (Scheme 4). However, a consideration of the relative stabilities of the intermediate anions which would result showed that attack at the 2-position was to be expected. Attack at the 3-position would lead to an intermediate which would, on electronic grounds be less favourable due to the destabilising effect of the oxygen lone pair on a negative charge  $\alpha$ - to it. Whereas attack at the 2- position would give an intermediate where the negative charge would be relatively stabilised by the adjacent  $\text{CF}_3$  group ( Scheme 4 ).



Scheme 4.



Scheme 5.

Steric factors may also be expected to be important, since the approach of  $\text{Nuc}^-$  to the 3-position is likely to be hindered by the  $\text{CF}_3$  and  $\text{C}_2\text{F}_5$  groups at the 4-position.

In principle, three fates are possible for the intermediate anion (Scheme 5):

- 1) Protonation, either by abstraction from solvent or from  $\text{NucH}$ .
- 2) Loss of fluoride ion by an  $\text{S}_{\text{N}}2'$  process-i.e. loss of fluoride ion from the trifluoromethyl group which was originally allylic to give the exocyclic double bond.
- 3) Loss of fluoride ion from the 5-position by a ring-opening reaction leading to an  $\beta,\gamma$ -unsaturated ketone.

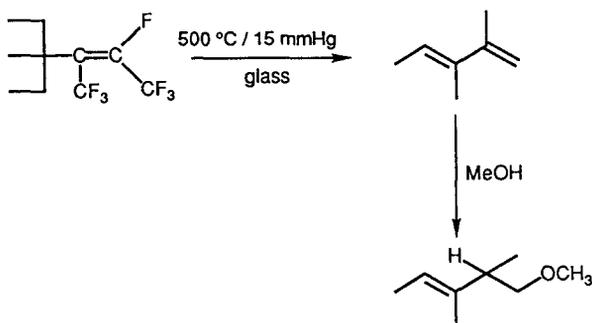
### Reaction with methanol/methoxide ion

When (1) was mixed with methanol in the absence of base or solvents and stirred at room temperature for forty eight hours, no reaction took place and (1) was recovered in quantitative yield.

However, use of diglyme as solvent and anhydrous sodium carbonate as base gave good yields (86%, 12% starting material recovered) of the mono-methoxylated product, 3-difluoromethylene-5-fluoro-2-methoxy-4-pentafluoroethyl-2,4,5-tris(trifluoromethyl)-tetrahydrofuran (3), from its  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^1\text{H}$  N.M.R. spectra.

No products resulting from further attack of methoxide upon the exocyclic double bond were observed. Attempts to force the reaction by using more vigorous conditions proved unsuccessful, with an inseparable mixture of products being formed. Nor was any product resulting from addition of methanol across the double bond detected, which was surprising, since perfluoro-2,3-dimethylpenta-1,3-diene (prepared by the pyrolysis of TFE pentamer[7]) reacted with methanol in the absence of base or solvent to give 1,1,1,2,5,5-hexafluoro-5-methoxy-3,4-bis(trifluoromethyl)pent-2-ene (Scheme 6), *i.e.* the product resulting from addition across one of the double bonds only: that containing the  $\text{C}=\text{CF}_2$  group [8].

Similar results are not unprecedented in the perfluoro-olefin field, since the addition of methanol to TFE tetramer[1] and pentamer[9] have been found to give products containing the  $\text{C}=\text{CF}_2$  group, although these have often undergone facile rearrangement to more stable isomers, depending on the base employed.



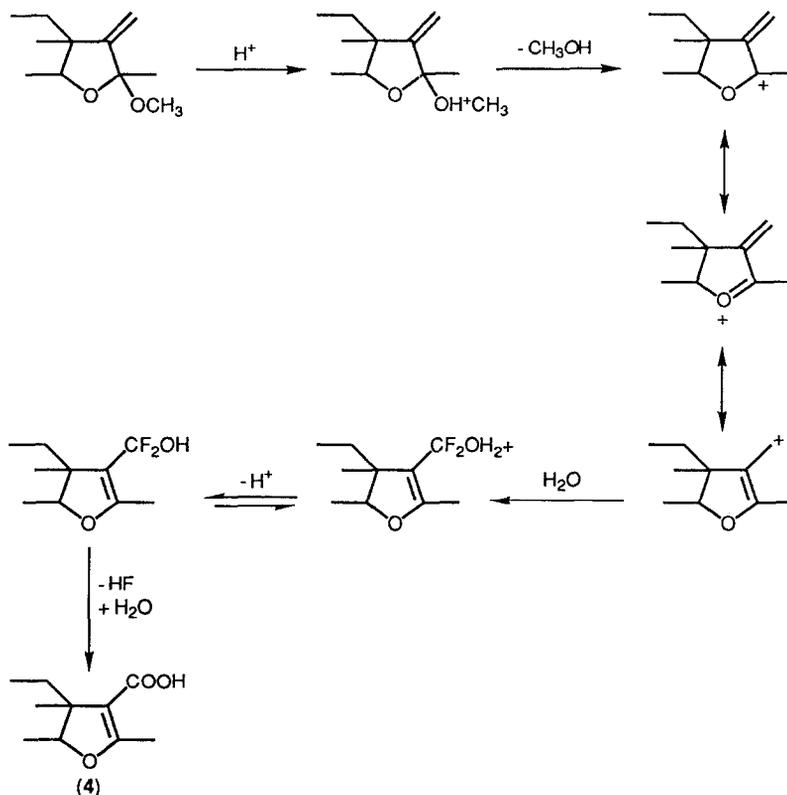
Scheme 6.

Further proof of structure was sought by chemical methods. Thus treatment of (3) with concentrated sulphuric acid in a sealed Carius tube at  $190\text{ }^\circ\text{C}$  for twenty four hours gave a white solid on cooling which was recrystallised from hexane to give perfluoro-4-

ethyl-2,4,5-tris(trifluoromethyl)-4,5-dihydrofuran-3-carboxylic acid(4). The mechanism presumably involves initial protonation followed by loss of methanol, followed by hydration of the intermediate carbocation (Scheme 7).

### Reaction with benzyl thiol

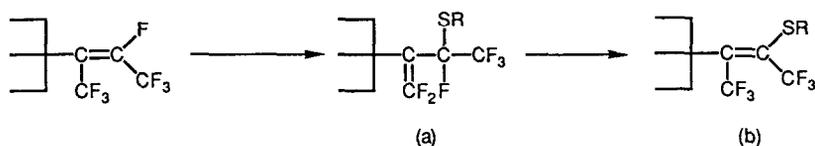
When (1) was stirred with one equivalent of triethylamine and one equivalent of benzyl thiol, 2-benzylthio-3-difluoromethylene-4-pentafluoroethyl-2,4,5-tristrifluoromethyl-4,5-dihydrofuran (5) was obtained in 85% yield.  $^{19}\text{F}$  N.M.R. spectroscopy indicated the formation of two diastereoisomeric pairs of compounds. (1) is chiral at C-4, although the absolute stereochemistry or ratio of enantiomers is unknown. This was the only reaction in this series that was observed to give a diastereomeric mixture of products, however attempts to separate the 2-R and 2-S diastereomers by g.l.c. or h.p.l.c. proved unsuccessful. The structure was confirmed by  $^{13}\text{C}$  N.M.R. spectroscopy which showed the exocyclic C-3 carbon as an unresolved doublet of doublets at 156.0 ppm



Scheme 7.

Note that this shift is similar to that of (3) (157.2 ppm), supporting the proposed attack at the 2-position rather than at the exocyclic methylene position.

Chen *et al.* [10] (Scheme 8) have found that TFE pentamer reacts with sulphur nucleophiles in the presence of triethylamine at -30 °C to -60 °C to give 3-difluoromethylene-1,1,1,2,5,5,6,6,6-nonafluoro-4-pentafluoroethyl-2-thio-4-trifluoromethylhexane (a) as the kinetically controlled product, although at higher temperatures the amount of isomeric 1,1,1,5,5,6,6,6-octafluoro-4-pentafluoroethyl-2-thio-3,4-bistrifluoromethylhex-2-ene (b) obtained, increased. This indicates the moderate stability of a C=CF<sub>2</sub> group to further nucleophilic attack. No products resulting from attack on the C=CF<sub>2</sub> group in (a) followed by 'inwards' elimination were detected by Chen. Indeed, the reason for the instability of (a) to rearrangement can be attributed to the availability of a fluorine atom  $\alpha$ - to the thiophenol group, which is obviously unavailable in (5).



Scheme 8.

### Reaction with nitrogen nucleophiles

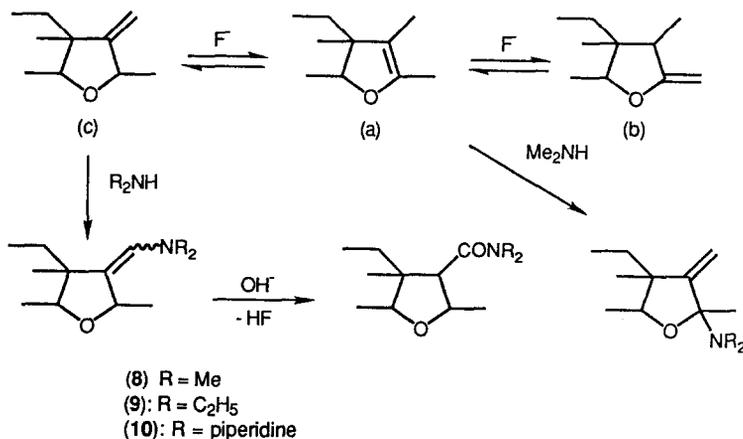
#### Reaction with primary amines, ammonia and hydrazines

(1) was reacted with ethylamine, n-propylamine and cyclohexylamine. However, all such reactions, even at low temperatures gave complex inseparable mixtures of products. It would appear, therefore, that the first formed product (presumably similar to (3) and (5)) underwent further rapid nucleophilic attack, possibly involving a ketenimine intermediate.

Similarly, with ammonia and hydrazines, complex inseparable product mixtures were isolated.

### Reaction with secondary amines

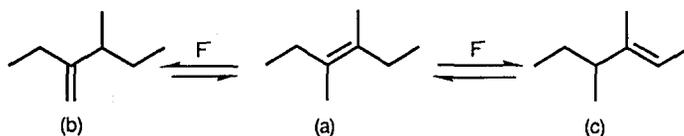
The reaction of (1) with secondary amines was found to be dependent upon the amine used (Scheme 9). Thus, when (1) was reacted with dimethylamine, the product arising from amine attack at the 2-position with loss of fluoride ion from the trifluoromethyl group which in the original structure was allylic, was observed; 3-difluoromethylene-2-dimethylamino-5-fluoro-4-pentafluoroethyl-2,4,5-tris(trifluoromethyl)tetrahydrofuran (8) was obtained in 76% yield. However, when either diethylamine or piperidine were used, the 3-amido compounds, 3-(*N,N*-diethylamido)-5-fluoro-4-pentafluoroethyl-2,4,5-tris(trifluoromethyl)-4,5-dihydrofuran (9) and 3-(piperidino)-5-fluoro-4-pentafluoroethyl-2,4,5-tris(trifluoromethyl)-4,5-dihydrofuran (10) were obtained in 64% and 79% respectively.



Scheme 9.

The reactions to give (9) and (10) were rationalised to take place via a rearrangement of (1), due to fluoride ion in the form of alkylammonium fluoride or due to an effect of the amine being investigated, and that (c) reacted with the amine faster than (a) or (b) (Scheme 9).

That dimethylamine gave a product resulting from attack at the 2-position was best accounted for by assuming that dimethylamine hydrofluoride did not promote the equilibrium of (a) to (b) or (c). Chambers [11] has reported similar results from his studies on the reaction of TFE tetramer with amines, in which he found that methylamine gave products resulting from (a), whereas ethylamine gave products consistent with reaction with (a), (b) and (c), (Scheme 10).



Scheme 10.

$^{19}\text{F}$  N.M.R. spectroscopy of a mixture of (1) and triethylamine in petroleum ether failed to show the presence of any isomers other than (a), (Scheme 9). Also, since benzyl thiol in the presence of triethylamine had been shown to give only products resulting from attack at the 2-position (when triethylamine hydrofluoride would have been present), we can assume, in these particular cases, that triethylamine hydrofluoride is an insufficiently strong source of fluoride ion to effect the isomerisation, and that isomerisation of (1) is dependent not on the triethylamine present, but upon the nature of the primary or secondary amine. Further evidence for similar effects has recently been found in the reaction of some unsaturated fluoroketones [12].

#### Reaction of (1) with sodium azide

Reaction of (1) with sodium azide using a selection of solvent systems (acetonitrile, Arcton 113, diethyl ether, petroleum ether and mixtures thereof) gave only a complex mixture of products, from which a small amount (19%) of the azido substitution product 2-

azido-3-difluoromethylene-5-fluoro-4-pentafluoroethyl-2,4,5-tristrifluoromethyltetrahydrofuran (**11**) was obtained. The low yields may be due to azirine formation [13], many examples of which are known to be heat-sensitive, decomposing extensively upon distillation or semi-preparative g.l.c. purification.

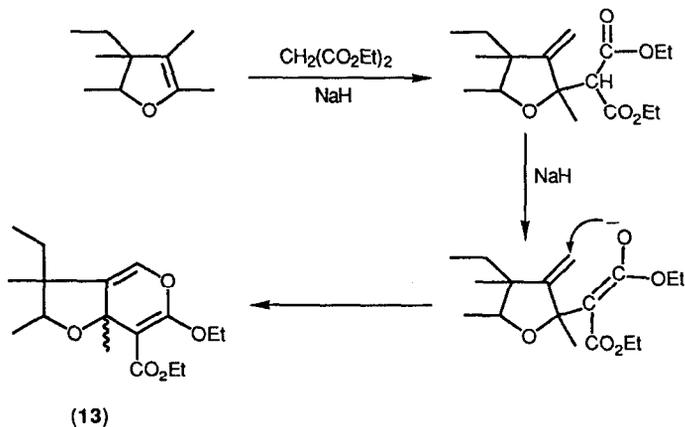
### Reaction of (1) with carbon nucleophiles

#### Reaction with organometallic reagents

When (**1**) was reacted with a freshly prepared solution of methyl lithium in ether/petroleum ether at  $-78^{\circ}\text{C}$ , 3-difluoromethylene-5-fluoro-2-methyl-4-pentafluoroethyl-2,4,5-tristrifluoromethyltetrahydrofuran (**12**) was obtained in 67% yield as a waxy white low melting point solid. No reaction was observed with phenylmagnesium bromide. Ishikawa [14] observed that perfluoro-2-methyl-2-pentene reacted readily with alkyl Grignard reagents but not with aryl ones, and that the product distribution was found to be dependent upon the nature of the reaction conditions and the particular organometallic used, although perfluoro-2-methyl-3-alkyl-1-pentene was usually the major product. Chambers [15] obtained perfluoro-2-ethyl-3,3-dimethyl-1-pentene as the major product in 23% yield from the reaction of perfluoro-3,4-dimethylhex-3-ene with ethyl- and methyl lithium, and no products resulting from further attack on this compound.

#### Reaction with diethyl malonate

When (**1**) was reacted with diethyl malonate and two equivalents of sodium hydride in dry petroleum ether, the heterocyclic compound 7-carboethoxy-6-ethoxy-2,3,7a-tristrifluoromethyl-2H,3H-furo[3,2-c]pyran (**13**) was obtained in 54% yield (Scheme 11). The reaction was assumed to follow the expected path with initial C-alkylation at the 2-position, followed by removal of the second methylene proton and subsequent O-alkylation of the  $\text{C}=\text{CF}_2$  group to give the fused six-membered ring. All attempts to isolate the open-chain compound failed, which was not unexpected due to the increased acidity of the second methylene proton relative to those in diethyl malonate. Similar types of reactions have been noted by others [16] in the reactions of perfluoro-3,4-dimethylhex-3-ene with diethyl malonate, acetylacetone and ethyl acetoacetate to give a series of pyrans.



Scheme 11.

## EXPERIMENTAL

**Preparation of Perfluoro-4-ethyl-2,3,4,5-tetramethyl-4,5-dihydrofuran (PFDHF)** - In a 500 cm<sup>3</sup> round-bottomed flask fitted with reflux condenser, thermometer, dropping funnel and vibrostirrer paddle was placed TFE pentamer (150g), diglyme (15g), water (6g) and Monoflor 31 (0.3g) as an emulsification aid. The mixture was vibrostirred vigorously and to it was added triethylamine (63g), dropwise, at a rate which maintained the internal temperature below 28 °C during the addition. After the addition of the triethylamine was complete, the emulsion was allowed to stir for a further eighteen hours at room temperature. The contents of the flask were then distilled directly and the fraction boiling between 80 and 100 °C was collected as two layers. The lower fluorocarbon layer was separated, washed with dilute aq. hydrochloric acid (2x20 cm<sup>3</sup>) and dried (magnesium sulphate). Distillation gave 87g (61%) of a colourless liquid, b.p. 124 °C, which was identified by comparison with the spectra of an authentic sample.

Reactions of PFDHF(a) with methanol

PFDHF (1) (3.0g, 6.3 mmol.) was stirred with methanol (0.2g, 6.3 mmol) and anhydrous sodium carbonate (0.7g) in diglyme (10 cm<sup>3</sup>) at room temperature. After forty eight hours the reaction mixture was filtered and poured into water, whereupon a lower fluorocarbon layer separated out to give 2.35g of a colourless oil, a small amount of which was purified by semi-preparative scale glc (diisodecyl phthalate on celite, 30' column, 145 °C, 25 p.s.i.) to give (3). b.p. 133°C (nc) [Found: C, 26.7; H, 0.65; F, 65.9% C<sub>10</sub>H<sub>3</sub>F<sub>17</sub>O<sub>2</sub> requires C, 26.9; H, 0.62; F 65.9% M (mass spec) 471 (M-F) ].

(3), (2.0g) was sealed in a Carius tube with conc. sulphuric acid (2 cm<sup>3</sup>) and heated for twenty four hours at 190 °C with gentle rocking. After this time the tube was cooled in liquid air and the contents poured cautiously with vigorous stirring into ice/water (50g). A lower fluorocarbon layer settled out as an oil, slowly solidifying overnight. The solid was filtered off, dried and recrystallised from hexanes to give colourless needles of (4) (0.85g, 46%), m.p 65-66 °C (nc) M.S. gave M<sup>+</sup>= 454, (M-OH)<sup>+</sup>= 437, (M-C<sub>2</sub>F<sub>5</sub>)<sup>+</sup>=335. [Found: C, 26.4; H, 0.2 % C<sub>10</sub>HF<sub>17</sub>O<sub>3</sub> requires C, 26.45; H, 0.29 % ].

(b) with benzyl thiol

PFDHF (1) (10.0g, 20.9 mmol) was stirred in dry petroleum ether (40 cm<sup>3</sup>) together with dry triethylamine (2.11g, 20.9 mmol) for ten minutes. To this was added benzyl thiol (2.59g, 20.9 mmol) in petroleum ether (15 cm<sup>3</sup>), dropwise. Stirring was continued for forty eight hours at room temperature in a sealed flask. After this time, the solid triethylamine hydrofluoride was filtered off, and the organic phase washed with dilute sulphuric acid (10 cm<sup>3</sup>) and water (10 cm<sup>3</sup>) and dried (magnesium sulphate). Removal of solvent gave 10.24g of a pale yellow oil, distillation of which gave (5) as a colourless oil b.p. 75-78 °C/0.03 mmHg (9.95g, 85%) (nc). A small fraction was further purified to analytical purity by hplc (25 cm x 1/2" Spherisorb column, hexane as eluent). M.S. gave M<sup>+</sup>= 582, (M-SCH<sub>2</sub>Ph)<sup>+</sup>=459. [ Found: C, 35.4; H, 1.2; S, 5.51 % C<sub>17</sub>H<sub>7</sub>F<sub>17</sub>OS requires C, 35.07; H, 1.20; S, 5.51% ] .

(c) with dimethylamine

To (1) (3.0g, 6.28 mmol) in petroleum ether was added dry triethylamine (0.63g, 6.28 mmol). The solution was cooled to 0 °C in an ice/water bath and dimethylamine

(0.42g, 9.42 mmol) in petroleum ether was added dropwise over a period of twenty minutes. The temperature was maintained at 0 °C for a further five hours, and then allowed to gradually rise to room temperature and stir for a further sixteen hours. The solid ammonium fluorides were filtered off and the solvent removed by evaporation to give (8) (2.40g, 76%) as a pale green oil. A small sample was purified by semi-preparative scale glc (Sigum on Universal B, 30' column, 15 p.s.i., 160 °C) to give pure (8) as a colourless crystalline solid m.p. 104-106 °C (nc) [ Found: C,30.2; H,2.1%  $C_{11}H_6F_{17}NO$  requires C,28.6; H,1.2% ].

(d) with diethylamine

To (1) (1.38g, 2.89 mmol) in petroleum ether (25 cm<sup>3</sup>) was added dry triethylamine (0.30g, 2.97 mmol). The mixture was cooled to 0 °C and diethylamine (0.21g, 2.89 mmol) in petroleum ether (10 cm<sup>3</sup>) was added dropwise over five minutes. The contents were allowed to stir at room temperature for a further eighteen hours, followed by removal of the solid precipitate by filtration. The organic phase was washed with dilute sulphuric acid (10 cm<sup>3</sup>) and dried (magnesium sulphate). Removal of solvent by evaporation gave (9) as a yellow oil (0.94g, 64%) (nc). Purification was effected by semi-preparative scale glc (OV1 on Gas Chrom Q, 30' column, 150 °C, 25 psi.). M.S. gave  $M^+=509$ ,  $(M-F)^+=490$ ,  $(M-N(C_2H_5)_2)^+=437$ ,  $(M-(F+N(C_2H_5)_2))^+=390$ .

(e) with piperidine

(1) (5.0g, 10 mmol) was dissolved in petroleum ether and piperidine (3.5g, 41mmol) was added dropwise with stirring. An instant white precipitate formed. Stirring was continued for five hours at room temperature, followed by removal of the solid material by filtration. The filtrate was washed with water (2 x 10 cm<sup>3</sup>) and dried (magnesium sulphate). Removal of solvent by evaporation gave an orange oil (5.1g). Vacuum distillation gave a fraction boiling at 77-87 °C/0.5 mmHg. Column chromatography of this fraction gave (10) as a colourless liquid (4.1g, 79%)(nc) [Found: C,33.9; H, 2.6 ; N, 2.4%  $C_{15}H_{11}F_{16}NO_2$  requires C, 34.6; H,2.0; N,2.7% ].

(f) with sodium azide

To (1) (3.0g, 6.3 mmol) dissolved in Arcton 113 (15 cm<sup>3</sup>) containing TDA-1 (0.2 cm<sup>3</sup>) as a phase-transfer catalyst, was added sodium azide (0.5g, 7.7 mmol) and the resulting suspension was stirred at room temperature for twenty one hours. Solid material was filtered off and the solvent evaporated to give 2.61g of a multi-component mixture (by glc), containing at least four major components in addition to a large amount of starting

material. Partial separation of one of these components was achieved by semi-preparative scale glc (diisodecyl phthalate on celite, 30' column, 145 °C, 25 psi.) to give 19% of (11) (impure).

(g) with lithium methyl

To a mixture of petroleum ether (25 cm<sup>3</sup>) and dry ether (5 cm<sup>3</sup>) was added lithium metal (0.2g) followed by methyl iodide (1.42g, 1.2 equivalents) in ether (10 cm<sup>3</sup>), dropwise. After the addition was complete the contents were heated to 40 °C for one hour and then cooled to -78 °C under nitrogen. (1) (5.0g, 10 mmol) in petroleum ether (10 cm<sup>3</sup>) was added rapidly to the stirred solution. The contents were stirred at -78 °C for one half hour and then warmed to room temperature and finally heated at 50 °C for sixteen hours. After cooling, the contents were worked up with 4 M aq. HCl in the normal manner and extracted with petroleum ether (2 x 15 cm<sup>3</sup>), washed with water (2 x 10 cm<sup>3</sup>) and dried (magnesium sulphate). Removal of solvent by evaporation gave an oil, glc analysis (dinonylphthalate on celite, 60 °C, 10 psi.) of which showed 10% starting material and 67% of one other major component. Isolation by semi-preparative scale glc (dinonylphthalate on celite 30-60 mesh, 60 °C, 10 psi.) gave (12) as a waxy white solid, m.p. 30 °C (nc). M.S. gave (M-HF)<sup>+</sup>=454, (M-CF<sub>3</sub>)<sup>+</sup>=405. [ Found: C,28.1; H,0.6; F,68.0 % C<sub>11</sub>H<sub>3</sub>F<sub>17</sub>O requires C,27.8 ; H,0.6; F,68.1% ]

(h) with diethylmalonate

Sodium hydride (1.00g, 41.7 mmol) in petroleum ether (30 cm<sup>3</sup>) was cooled to 0 °C., diethyl malonate (3.35g, 20.9 mmol) was added dropwise over one half hour followed by two drops of the phase-transfer catalyst TDA-1. The mixture was stirred at 0 °C for one hour and at room temperature for a further two hours, under nitrogen. After this time, the suspension was cooled to 0 °C and (1) (10.0g, 20.9 mmol) in petroleum ether (50 cm<sup>3</sup>) was added in one portion and stirred at 0 °C for three hours, and at room temperature for a further eighteen hours. The solution was washed with 10% ammonium chloride solution (30cm<sup>3</sup>), and water (3 x 50 cm<sup>3</sup>). The organic phase was separated and dried (magnesium sulphate) and the solvent removed by evaporation to give a green oil. Flash column chromatography (chloroform/hexane 1:1 on silica gel) gave (13) as a colourless oil (6.81g, 54%). b.p. 68-75°(nc) M.S./E.I. gave (M-OC<sub>2</sub>H<sub>5</sub>)<sup>+</sup>=553; M.S./C.I. gave (M+H)<sup>+</sup>=599, (M+NH<sub>4</sub>)<sup>+</sup>=614. [Found C,34.3; H, 1.6% C<sub>16</sub>H<sub>10</sub>F<sub>13</sub>O<sub>5</sub> requires C,34.1; H,1.68% ]

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- 14 N. Ishikawa, S. Butler and M. Maruta, *Bull. Soc. Chem. Jpn.*, **54** (1981) 3084.
- 15 R.D. Chambers, J.R. Kirk and A.A. Lindley, *J. Chem. Soc., Perkin Trans. 1* (1983) 1235.
- 16 R.D. Chambers, J.R. Kirk and A.A. Lindley, *J. Chem. Soc., Perkin Trans. 1* (1983) 1239 and ref. [11].

N.M.R.Spectral Data

All spectra were run in CDCl<sub>3</sub> using either a Perkin-Elmer R12B or Varian XL100 machine operating at 60 or 100 MHz for protons and 56.4 or 94 MHz for fluorine. TMS and CFC1<sub>3</sub> were used as references.

## N.M.R.Data for all new compounds

Compound	$^1\text{H}$	Assignment	$^{19}\text{F}$	Assignment
			55.0	c
			65.1	f
			67.2	e
			75.6	d
			77.1	a
			102.1	b
			113.6	g
	3.6	OMe	62.5	e
			64.0	d
			64.5	c
			75.2	d
			77.1	g
			77.6	a
			104.4	b
			106.0	h
	12.15	COOH	63.5	c
			65.9	e
			75.5	d
			76.6	a
			111	b
			112.5	f
	1.2	CH <sub>2</sub>	62.6	c
	3.4	CH <sub>3</sub>	69	e
			72.4	a
			80	d
			104	b
			115.2	f
	1.6	6H	62.6	c
	3.4	4H	69.2	e
			69.3	d
			77.4	a
			106.1	b
			115.9	f

## N.M.R.Data for all new compounds

Compound	$^1\text{H}$	Assignment	$^{19}\text{F}$	Assignment
	1.83	$\text{CH}_3$	61	d
			64.1	c
			65.1	e
			76.5	g
			76.9	a
			78.4	f
			101.6	h
103.2	b			
	2.56	$\text{CH}_3$	60.9	e
			63.5	d
			63.6	c
			70	h
			76.3	a
			78.8	g
			101	f
104.7	b			
			60.5	e
			62.3	d
			64.7	c
			66.3	g
			74.8	f
			77	a
			101	b
		113.7	h	
	1.31/1.35 4.31/4.38	$\text{CH}_3$ $\text{CH}_2$	59.1	d
			63.3	c
			69.7	i
			72.2	a
			78.0	f
			105.2	b
	4.11 7.28 $^{13}\text{C}$ 156 1C	$\text{CH}_2$ Ar $=\text{CF}_2$	59.1	e
			61.7	d
			63.3	c
			72.2	g
			76.7	a
			76.7	f
100.5	h			
104.4	b			