Functionalisation of Secondary and Tertiary Hydrofluorocarbons by Electro-oxidation in Fluorosulphuric Acid: Novel Route to Perfluoroketones and Tertiary Alcohols†

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Aliphatic and alicyclic secondary and tertiary hydrofluorocarbons are indirectly electro-oxidised in fluorosulphuric acid. Thus, 2*H*-heptafluoropropane and undecafluorocyclohexane are transformed into the corresponding perfluorosulphates. Pyrolysis of these latter compounds over caesium fluoride afforded the corresponding ketones. This method constitutes a novel route to perfluoro ketones particularly hexafluoroacetone. Tertiary hydroperfluoroalkanes are less reactive than secondary compounds *vis-à-vis* electro-oxidation. Nevertheless, the reaction of 1*H*-undecafluoronorbornane with the peroxide $(FSO_3)_2$, followed by hydrolysis of the ester so obtained, yielded perfluoronorbornan-1-ol.

Perfluoroketones $(R_F)_2CO$ are a class of compounds of considerable interest in organofluorine chemistry. A characteristic example of the class is hexafluoroacetone, in which the CF_3 groups, by virtue of their strong inductive effect, intensify the electrophilicity of the carbonyl group and consequently influence its reactivity in typical CO reactions.[1,2]

Hexafluoroacetone is the starting point for the preparation of many fluorocarbon derivatives and has many important commercial applications, such as the preparation of hexafluoropropan-2-ol,[3] heterocyclic compounds containing gem CF_3 groups (many of which have interesting biological activity),[4–7] co-polymers with acrylates and perfluoro-epoxides,[8] and other high performance polymers.

Notwithstanding the interest and diversity of these applications, hexafluoroacetone is difficult to obtain. Several laboratory syntheses have been developed, such as the oxidation of $(CF_3)_2C{=}CF_2$ with $KMnO_4$,[9] the isomerisation of hexafluoropropene oxide (HFPO) with suitable catalysts,[10,11] the oxidation of $(CF_3)_2CS$ with nitrogen oxides[12] or by direct oxidation of hexafluoropropene with oxygen in the presence of AlF_3.[13]

The exchange reaction between hexachloroacetone and HF in the presence of basic oxides of chromium,[14,15] remains at present the only reasonable process for industrial production.

$$CCl_3COCCl_3 \xrightarrow[200-300\,^{\circ}C]{HF,Cr^{3+}} CF_3COCF_3$$

However, the toxicity of the intermediate chlorofluoro compounds and the difficulty of removal of excess of HF has led to studies on new methods for the preparation of this ketone and its homologues.

It has recently been shown[16,17] that the indirect anodic oxidation in fluorosulphuric acid of fluorocarbon derivatives of the type R_FCF_2X (X = H, CO_2H, SO_3H, CH_2OH, Br), which are not directly oxidisable, leads to fluorosulphates of the type $R_FCF_2OSO_2F$ which are precursors of fluorocarboxylic acids, *e.g.*

$$\begin{array}{ccc} CF_3(CF_2)_5H & \xrightarrow[HSO_3F]{-2e} & CF_3(CF_2)_5OSO_2F \\ & & \downarrow{\scriptstyle +H_2O}\ \ {\scriptstyle -HSO_3F} \\ CF_3(CF_2)_4CO_2H & \xleftarrow{-2HF} & [CF_3(CF_2)_5OH] \end{array}$$

Extension of this method to secondary hydrides should lead to perfluoro ketones,

$$\begin{array}{ccc} (R_F)_2CFH & \xrightarrow[HSO_3F]{-2e} & (R_F)_2COSO_2F \\ & & \downarrow{\scriptstyle +H_2SO_3F}\ \ {\scriptstyle -HSO_3F} \\ (R_F)_2CO & \xleftarrow[-HF]{} & [(R_F)_2CFOH] \end{array}$$

in particular $R_F = CF_3$ should give hexafluoroacetone.

We have already shown that secondary bromoperfluoroalkanes, in contrast to their primary analogues, are not reactive.[17] However, given the greater reactivity of hydrofluorocarbons, it may be possible to functionalise secondary hydrides by anodic oxidation in HSO_3F. As a logical extension of this work, we have further demonstrated the oxidation of a tertiary hydride to stable alcohol.

The first part of this paper describes the electrochemical studies and the second part is concerned with the preparation of the ketones and the alcohol.

Results and Discussion

Anodic Oxidation and Formation of Fluorosulphates.—As examples of secondary perfluorohydrides we chose 2*H*-heptafluoropropane as a model for aliphatic compounds and undecafluorocyclohexane as an alicyclic example.

1*H*-Perfluoronorbornane (**1**) was chosen as a tertiary hydride because of the potential biological interest on the resulting alcohol (**3**).[18]

Initial tests on the anodic oxidation of these compounds under the conditions used for primary compounds failed. We have already shown[16] that the reactions proceed *via* the intermediate peroxide FSO_2OOSO_2F, itself formed *in situ via* the oxidation of HSO_3F [Equation (1)] which then reacts by hydrogen removal [Equation (2)].

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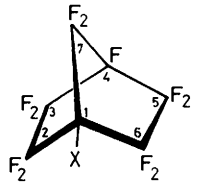
Table 1. Reaction of the peroxide FSO_2OOSO_2F on hydroperfluorocarbons

Substrate	Product	Temp. (°C)	Time (h)	Yield *(%)
$(CF_3)_2CFH$	$(CF_3)_2CFOSO_2F$	40	1	5[a]
		60	3	98[b]
$C_6F_{11}H$	$C_6F_{11}OSO_2F$	45	1	5[a]
		50	30	95[b]
$\overline{\underline{CHCF_2CF_2CFCF_2CF_2}}$ $\underline{CF_2}$	$FO_2SO\overline{\underline{CCF_2CF_2CFCF_2CF_2}}$ $\underline{CF_2}$	60	1	5[a]
		60	15	70[b]

* By ^{19}F n.m.r. [a] In n.m.r. tube. [b] Preparative scale.



(**1**) X = H
(**2**) X = OSO_2F
(**3**) X = OH

$$2^{-}OSO_2F \xrightarrow{-2e} FSO_2OOSO_2F \quad (1)$$

$$R_FH + FSO_2OOSO_2F \longrightarrow R_FOSO_2F + HOSO_2F \quad (2)$$

Thus it was decided to study the reaction of preformed peroxide with our substrates before a detailed study of their electrolysis.

(*a*) *Peroxide Reaction.*—The method of choice for this study was variable temperature ^{19}F n.m.r. spectroscopy. This allowed us eventually to find suitable conditions to carry out preparative scale reactions and to isolate and identify the products. These results, summarised in Table 1, clearly show that the order of reactivity is secondary > tertiary and both are much less reactive than the primary hydrides, which react rapidly at room temperature.[16] This is in accord with the order obtained from the reactions of polyfluorohalogenoalkanes with $(FSO_3)_2$[17] or FSO_3Cl.[19] This is in keeping with the known order of the electronegativities of perfluoroalkyl chains[20–22] $(CF_3)_3C > (CF_3)_2CF > CF_3CF_2 > CF_3$.

The polarity of the C–H bond in perfluorohydroalkanes should increase from primary to tertiary compounds. Further, in accord with literature results,[23] the increase in bond polarity should disfavour the homolytic fission of the C–H bond.

It may not be possible either to neglect the steric interactions which also play a part in the reactivity of hydrofluoroalkanes. In effect the increased branching around the C–H bond makes the approach of the substrate radical more difficult.

In all of the cases we have studied, the fluorosulphates are the sole products isolated. There is no evidence of dimers being formed.

Although the fluorosulphate from 2*H*-heptafluoropropane is known [from $(CF_3)_2CO$ by reaction with SO_2Cl_2 and KF],[24] the other derivatives from $C_6F_{11}H$ and 1*H*-perfluoronorbornane are novel. They were fully characterised by ^{19}F n.m.r., i.r., and mass spectroscopy and by elemental analysis.

It should be noted that a CIDNP effect is observed in the ^{19}F spectrum during the formation of the fluorosulphate from 2*H*-heptafluoropropane. This effect is characterised by an emission signal for the fluorine α to the OSO_2F group at 141.9 p.p.m.

This effect is identical with that we have already described and analysed for the reaction of R_FCF_2H derivatives with $(FSO_3)_2$,[16] using Kaptein's rule[25] for the analysis. The *g* factor of $(CF_3)_2CF^{\bullet}$ is 2.0033,[26] somewhat lower than that for $FSO_3^{\bullet}$ 2.0108.[27,28] The electron to fluorine coupling constant is positive at 67.46G.[26] This permits us to deduce that the mechanism for the formation of the fluorosulphates is *via* a radical pair combination between $FSO_3^{\bullet}$ and $(CF_3)_2CF^{\bullet}$.

$$FSO_2OOSO_2F \rightleftharpoons 2\,{}^{\bullet}OSO_2F$$

$$(CF_3)_2CFH + {}^{\bullet}OSO_2F \longrightarrow (CF_3)_2CF^{\bullet} + HOSO_2F$$

$$(CF_3)_2CF^{\bullet} + {}^{\bullet}OSO_2F \longrightarrow \overline{(CF_3)_2CF^{\bullet\bullet}OSO_2F}^{F} \longrightarrow (CF_3)_2CFOSO_2F$$

$$2(CF_3)_2CF^{\bullet} \longrightarrow\!\!\!\!\!\!\times\; (CF_3)_2CFCF(CF_3)_2$$

The absence of dimerisation is explained by the fact that $(CF_3)_2CF^{\bullet}$ is formed in the presence of an excess of $FSO_3^{\bullet}$ (a quite stable radical) and the former is thus more likely to meet $FSO_3^{\bullet}$ that another $(CF_3)_2CF^{\bullet}$ radical. This presupposes that the slow step in the reaction is hydrogen abstraction from R_FH. This is in agreement with the observed differences in reactivities from $(R_F)_3CH$, $(R_F)_2CFH$, and R_FCF_2H.

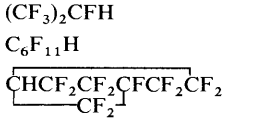
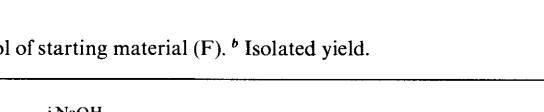
These positive results now allow us to establish conditions for the synthesis of R_FOSO_2F by the indirect electro-oxidation of $(R_F)_2CFH$ and $(R_F)_3CH$ in HSO_3F by means of *in situ* generation of $FSO_3^{\bullet}$.

(*b*) *Electro-oxidation.*—Given the physical properties of the substrates and products, indirect electro-oxidations are subject to a number of technological constraints (see Experimental section). The results we obtained are shown in Table 2.

These results show that the yields of the desired products are rather less than with the peroxide reaction, particularly for the norbornane. In contrast, the yield of the major by-product $(FSO_2)_2O$ increases with temperature. This was not observed before, since the peroxide was prepared at low temperature. A further problem may be an as yet undetected secondary reaction in the electro-oxidation at higher temperature.

Synthesis of Ketones and Tertiary Alcohols.—We have shown previously[16] that hydrolysis of primary perfluoroalkyl fluorosulphates affords carboxylic acids. We have now repeated this method with secondary esters in the hope of obtaining ketones. Thus, reaction of $(CF_3)_2CFOSO_2F$ with aqueous sodium hydroxide gave on acidification hexafluoroacetone hydrate [Equation (3)].

Table 2. Electro-oxidation of hydrofluorocarbons in fluorosulphuric acid

Substrate	Product	Temp. (°C)	n^a/F mol^{-1}	Yield[b] (%)
$(CF_3)_2CFH$	$(CF_3)_2CFOSO_2F$	50	4	43
$C_6F_{11}H$	$C_6F_{11}OSO_2F$	60	4.2	42.5
		80	4.2	6

[a] Current per mol of starting material (F). [b] Isolated yield.

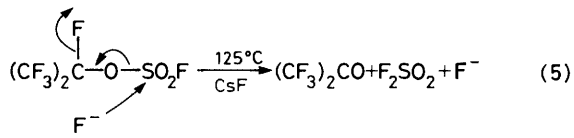
$$(CF_3)_2CFOSO_2F \xrightarrow[\text{ii,HCl}]{\text{i,NaOH}} (CF_3)_2CFOH \xrightarrow[(n+1)H_2O]{-HF} (CF_3)_2C(OH)_2nH_2O \quad (3)$$

This hydrate is then dehydrated over phosphoric anhydride to yield anhydrous hexafluoroacetone $(CF_3)_2CO$. However the yields are poor due to the subsequent formation of sodium trifluorocarboxylate in an already described haloform cleavage step of hexafluoroacetone hydrate[29,30] according to Equation (4).

$$(CF_3)_2C(OH)_2 + 4NaOH \longrightarrow CF_3CO_2Na + 3NaF + CO + H_2O \quad (4)$$

This method was not satisfactory and we next investigated an alternative approach which had been used previously.[19,31] We found that pyrolysis of the fluorosulphate over KF and CsF afforded the desired ketone, identified by ^{19}F n.m.r.,[32] in 50% overall yield.

The mechanism of the reaction involves the fission of the S–O bond, as discussed previously[33] [Equation (5)].



(5)

In the same way $C_6F_{11}OSO_2F$ over CsF gave perfluorocyclohexanone, identical with that previously prepared.[34] The yield is somewhat lower than that for hexafluoroacetone partly due to fluoride ion-mediated decomposition of the ketone at the temperature of preparation. This could possibly be overcome by using flash vacuum pyrolysis methods, but we have not yet investigated this possibility.

The tertiary alcohol, perfluorobicyclo[2.2.1]heptan-1-ol (**3**) was readily obtained by the hydrolysis method above, since the competing haloform reaction can no longer take place. This alcohol has been prepared previously[38] from diazoperfluorobicyclo[2.2.1]heptane but was not totally characterised by ^{19}F n.m.r. and mass spectroscopy and elemental analysis.

Conclusion.—Although secondary hydroperfluoroalkanes are electro-oxidised with more difficulty than corresponding primary compounds, the reaction can be performed with the appropriate conditions. The hydrolysis of the fluorosulphates obtained in such electro-oxidations is not an efficient method for obtaining the corresponding perfluorinated ketones. However, those ketones are easily obtained, non-hydrated, by pyrolysis over caesium fluoride.

The combination of the two methods constitutes an efficient alternative route for the preparation of perfluoroketones.

On the other hand, tertiary derivatives, less reactive than secondary analogues, are transformed by electrolysis only in poor yields. However, the corresponding fluorosulphates can be obtained from the reaction of the initially preformed peroxide $(FSO_3)_2$. Although this method is more difficult to be carried out, it may lead, after a simple alkaline hydrolysis, to new tertiary alcohols, such as perfluoronorbornan-1-ol.

Experimental

^{19}F N.m.r. spectra were obtained with a VARIAN EM 360 and a variable temperature EM 390 spectrometers with $CFCl_3$ or CF_3CO_2H (CF_3CO_2H = 76.5 p.p.m.) as external reference. Upfield ^{19}F are quoted as positive. I.r. spectra were obtained with a PERKIN-ELMER 225 spectrometer. Electrolyses were performed with a TACUSSEL PRT-1X potentiostat coupled with a TACUSSEL IG-5N current integrator. Mass spectra were obtained with a JEOL JMS D100 spectrometer (ionisation current 100A, ionisation energy 70 eV).

Materials.—2-Iodoheptafluoropropane was provided by ATOCHEM. Fluorosulphuric acid was obtained from Fluka and was redistilled before use.

2*H*-Heptafluoropropane was prepared by the reaction of $(CF_3)_2CFI$ with KOH in acetone[35] or together with $C_6F_{11}H$ by pyrolysis of $(CF_3)_2CFC_6F_{11}$ in the presence of toluene.[36]

1*H*-Perfluorobicyclo[2.2.1]heptane (**1**) was obtained by fluorination of norbornadiene with CoF_3.[37]

$(FSO_3)_2$ was prepared by the electro-oxidation at a platinum electrode of FSO_3H in a divided cell and was distilled under a dynamic vacuum as it was formed, by the method of Dudley.[39] It was then redistilled under reduced pressure.

Reaction of $(CF_3)_2CFH$ *with* $(FSO_3)_2$.—The peroxide (3.60 g, 0.018 mol) was distilled into FSO_3H (10 cm^3) in a thermostat bath at −50 °C under an atmosphere of dry nitrogen. To the stirred mixture, $(CF_3)_2CFH$ (3 g, 18 mmol) was added by distillation and the reaction flask was fitted with a solid CO_2 condenser. Two aliquots (0.5 cm^3) were sealed into two n.m.r. tubes. One was used as a reference and the other used to study the n.m.r. changes with increasing temperature from −50 °C to +50 °C.

The reaction mixture and the reference tube were kept at 40 °C until all the starting material had disappeared (^{19}F n.m.r.). The products were distilled from the mixture under reduced pressure (20 mmHg) into a trap at −78 °C. The condensate was washed with iced water, separated, dried ($MgSO_4$), and distilled to give heptafluoropropan-2-yl fluorosulphate (3.6 g, 13.4 mmol), b.p. 48 °C (75%). The ^{19}F n.m.r. spectrum shows shifts identical with those previously reported:[24] Φ_F +80 (6 F, dd, *J* 2.06 and 2.87 Hz, CF_3), +141.7 (1 F, md, *J* 2.06 and 9.1 Hz, FC), and −50 (1 F, md, *J* 2.87 and 9.1 Hz, FS).

Reaction of $C_6F_{11}H$ *with* $(FSO_3)_2$.—Undecafluorocyclohexane (28.2 g, 0.10 mol) was distilled by vacuum transfer into a solution of $(FSO_3)_2$ (20 g, 0.10 mol) in FSO_3H (50 cm^3). As

described above, two (0.5 cm^3) aliquots were taken. The reaction mixture and its reference were kept at 50 °C for 30 h. When the reaction was complete, separation as above by distillation *in vacuo* (1.0 mmHg) afforded on redistillation undecafluorocyclohexyl fluorosulphate (28 g, 0.074 mol), b.p. 108 °C (74%) (Found: C, 18.5; F, 60.3. $C_6F_{12}SO_3$ requires C, *18.9*; F, 60%); $\nu_{max.}$ 9.75, 1 230, 1 250, 1 290, 1 310, and 1 480 cm^{-1}; Φ_F 121.6—139 [11 F, m, *J* 9 and 5 Hz, $(CF_2)_5$ and CF], −53.5 (1 F, m, *J* 9 and 5 Hz, FS); *m/z* 380 (M^+), 361 (M^+ − F), 281 (M^+ − OSO_3F), and 259 (M^+ − C_3F_5).

Reaction of 1H-*Perfluorobicyclo*[2.2.1]*heptane* (**1**) *with* $(FSO_3)_2$.—In a similar experiment to the above, 1*H*-perfluorobicyclo[2.2.1]heptane (18.3 g 62 mmol) and $(FSO_3)_2$ (15.8 g, 80 mmol) afforded after reaction at 65 °C for 48 h perfluorobicyclo[2.2.1]heptyl fluorosulphate (**2**) (16.4 g, 42 mmol), b.p. 60 °C/50 mmHg (67%) (Found: C, 20.9; F, 58. $C_7F_{12}SO_3$ requires C, 21.4; F, 58.2%); $\nu_{max.}$ 950, 965, 980, 1 235, 1 270, and 1 480 cm^{-1}; Φ_F 117.4 (4 F, md, *J* 8.5 Hz, 2,6-F), 123.3 (4 F, m, 3,5-F), 113.3 (2 F, m, 7-F), 228.6 (1 F, m, 4-F), −50.7 (1 F, m, *J* 8.5 Hz, SF); *m/z* 392 (M^+), 373 (M^+ − F), and 243 (M^+ − CF_2OSO_3F).

Indirect Electro-oxidation of $(CF_3)_2CFH$.—Into a 100 cm^3 KelF divided electrolytic cell, with a porous PTFE membrane 3 mm thick with a porosity of 200—400 μm and using platinum electrodes, was introduced $(CF_3)_2CFH$ (12 g, 71 mmol) and FSO_3H/FSO_3K (0.2M) (40 cm^3) at −25 °C. The reaction mixture was electrolysed at constant current (100 mA) at 50 °C with magnetic stirring, using a condenseur cooled to −70 °C. After the passage of 27 000 C, the reaction was complete (electrical yield 50%). The products were distilled from the reaction mixture *in vacuo* to give a mixture (15 g) of heptafluoropropan-2-yl fluorosulphate (75%) and the anhydride; the mixture when stirred with water for 12 h gave, after separation and distillation, the fluorosulphate (8 g, 43%).

Electro-oxidation of $C_6F_{11}H$.—In a similar experiment to that described above, $C_6F_{11}H$ (6.8 g, 24 mmol) and FSO_3H/FSO_3K (0.2M; 25 cm^3) containing $CF_3SO_3CF_3$ (1 cm^3) (used to wash the sublimed $C_6F_{11}H$ from the condenser but which is inert to the reaction conditions), afforded after passage of 198 000 C, undecafluorocyclohexyl fluorosulphate (3.86 g, 42.5%) identical with an authentic sample.

Electro-oxidation of 1H-*Perfluorobicyclo*[2.2.1]*heptane* (**1**).—In a similar experiment to that described above but at 80 °C, the heptane (7 g) afforded the corresponding fluorosulphate (**2**) (0.6 g, 6%).

Preparation of Hexafluoroacetone.—(*a*) *By hydrolysis.* Heptafluoropropan-2-yl fluorosulphate (2 g, 7 mmol) was added to a solution of KOH (2 g) in water (5 cm^3) at 0 °C. When the exothermic reaction had subsided, the mixture was acidified and continuously extracted with ether. Concentration of the ether layer gave a solution which was shown by ^{19}F n.m.r. spectroscopy to be a mixture of hexafluoroacetone hydrate and trifluoroacetic acid. The mixture was not further purified.

(*b*) *By pyrolysis.* The fluorosulphate (5.3 g, 20 mmol) was added under nitrogen to caesium fluoride (17.6 g) previously dried at 150 °C *in vacuo* for 12 h. The mixture was heated at 125 °C with passage of a slow stream of nitrogen and the volatile material formed was trapped at −80 °C. Distillation in a low temperature still afforded SO_2F_2, b.p. −55 °C and hexafluoroacetone (1.6 g, 10 mmol), b.p. −27 °C (50%) identified by ^{19}F n.m.r.[32] and i.r. spectroscopy.

Preparation of Perfluorocyclohexanone.—Undecafluorocyclohexyl sulphate (3 g) and caesium fluoride (3 g) were heated together in a stream of nitrogen; the volatile products were collected in traps at −45 and −80 °C. The product in the latter trap was identified as SO_2F_2 and that in the former was redistilled to give perfluorocyclohexanone (0.88 g, 40%) identical with an authentic sample.

Preparation of Perfluorobicyclo[2.2.2]*heptan*-1-*ol* (**3**).—Perfluorobicyclo[2.2.1]heptyl fluorosulphate (**2**) (9.2 g, 23 mmol) was stirrred and heated to 70 °C with sodium hydroxide (2.9 g) in water (25 cm^3) until a single phase was formed. Acidification afforded a lower layer (7.7 g) which was combined with the product from ether extraction of the aqueous layer (2 g), dried (P_2O_5), and vacuum sublimed to give perfluorobicyclo[2.2.1]heptan-1-ol (**3**) (6 g, 19 mmol, 84%), m.p. 112 °C (Found: C, 27.0; H, 0.3; F, 67.6. $C_7HF_{11}O$ requires C, 27.1; H, 0.3; F, 67.4%); Φ_F 123.6 (4 F, m, 2,6-F), 124.2 (4 F, m, 3,5-F), 131.9 (2 F, m, 7-F), and 226.6 (1 F, m, 4-F); δ_H 4.8 (1 H); *m/z* 310 (M^+), 291 (M^+ − F), 290 (M^+ − HF), 271 (M^+ − COH), and 243 (M^+ − CF_2OH).

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