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FLUORO-OLEFIN CHEMISTRY PART 20 [1]. REACTION OF HEXAFLUOROPROPENE WITH ALCOHOLS

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SUMMARY

Reaction of hexafluoropropene (HFP) with a series of alcohols under thermal, photochemical or peroxide-initiated conditions affords the 1:1 adducts $CF_3CHFCF_2CR^1R^2OH$ (R^1 = H, R^2 = H, Me, Pr^n or CF_3; R^1 = Me, R^2 = Me or Et) in high yield via a radical chain mechanism. Adducts are not formed with the alcohols $(CF_3)_2CHOH$ and $CF_3CHFCF_2CH_2OH$. Other 1:1 adducts of structure $CHF_2CF(CF_3)CH_2OH$ and $CH_3(C_2H_3CF_2CHFCF_3)CH_2OH$ are formed as minor products in the methanol and n-butanol reactions, respectively.

INTRODUCTION

The insertion of HFP under thermal or, in certain cases, photochemical conditions into C-H bonds of alkanes [2,3], trifluoromethylalkanes [4], alkylbenzenes [5,6], alkenes [7] and halogenoalkanes [8] has been investigated in this Department; C-Cl bond insertion has also been observed with the di- and tri- chloroethanes [8].

A radical-chain mechanism initiated by excited fluoro-olefin has been proposed (Scheme 1).

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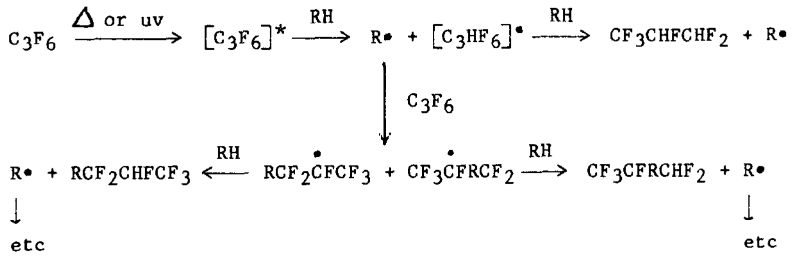


SCHEME 1

In a continuation of this investigation the reactions of HFP with various alcohols under thermal, photochemical and peroxide-initiated conditions have been carried out.

RESULTS AND DISCUSSION

The results obtained are shown in Table 1.

$CF_3CHFCF_2CR^1R^2OH$

(I)

a; $R^1 = R^2 = H$

b; $R^1 = H$, $R^2 = Me$

c; $R^1 = R^2 = Me$

d; $R^1 = Me$, $R^2 = Et$

e, $R^1 = H$, $R^2 = Pr^n$

f; $R^1 = H$, $R^2 = CF_3$

$CHF_2CF(CF_3)CH_2OH$

(II)

$CF_3CHFCF_2CHMeCH_2CH_2OH$

(III)

$CF_3CHFCF_2CHEtCH_2OH$

(IV)

From Table 1 it can be seen that high yields of the 1:1 adducts (I) were formed in all the reactions except that involving the alcohol $(CF_3)_2CHOH$, but that photochemical and peroxide-initiated conditions gave somewhat higher yields than thermal conditions. In the products of the thermal and photochemical reactions small amounts of the hexafluoropropane, $CF_3CHFCHF_2$, were detected which is consistent with the mechanism shown (Scheme 1).

TABLE I

Reaction of HFP with alcohols

	Alcohol		C_3F_6		Conditions		C_3F_6 recov.	1:1 Adducts	
	g	mmol	g	mmol	(°C)	(days)	(%)	(%)*	
MeOH	1.09	34.2	1.71	11.4	280	4	2	(Ia)	(85)
								(II)	(4)
	1.92	60.0	3.00	20.0	*ca.* 40^{a}	4	10	(Ia)	(95)
								(II)	(2)
	1.92	60.0	3.00	20.0	150^{b}	0.83	0.2	(Ia)	(93)
								(II)	(2)
EtOH	1.75	38.0	1.83	12.2	280	4	46	(Ib)	(79)
	3.46	75.2	3.42	22.8	*ca.* 40^{a}	4	45	(Ib)	(92)
	2.07	45.0	6.75	45.0	150^{b}	0.83	30	(Ib)	(86)
$Pr^{i}OH$	1.95	32.5	1.72	11.5	280	4	44	(Ic)	(86)
	4.20	70.0	3.60	24.0	*ca.* 40^{a}	4	2	(Ic)	(95)
	2.70	45.0	6.75	45.0	150^{b}	0.83	2	(Ic)	(89)
$Bu^{i}OH$	2.59	35.0	1.62	10.8	280	4	62	(Id)	(91)
	5.06	68.4	3.42	22.8	*ca.* 40^{a}	3	1.5	(Id)	(97)
$Bu^{n}OH$	26.0	351	17.6	117	*ca.* 40^{a}	5	53	(Ie)	(94)
								(III) or (IV)	(4)
CF_3CH_2OH	14.8	148	7.20	48.0	320	0.7	43	(If)	(95)
$(CF_3)_2CHOH$	4.03	24.0	1.20	8.0	355	5	100	-	-
(Ia)	4.37	24.0	1.20	8.0	385	1.5	98.5	-	-

* Based on HFP consumed. [a] Photochemical experiments.

[b] Peroxide-initiated experiments using $Bu^{t}{}_2O_2$ (0.5 g).

The benzoyl peroxide-initiated reaction of methanol with HFP has been reported previously [9] to afford adduct (Ia) (90% yield, 70-75% conversion). In contrast to this result a second 1:1 adduct (II) (2-4%) was isolated from all the methanol reactions reported in the present work including that initiated by di-t-butyl peroxide. This minor adduct is formed via $\dot{C}H_2OH$ radical attack on the central carbon atom of HFP (see Scheme 1), but corresponding adducts were not detected in the reactions involving the higher alcohols. In these latter reactions the intermediate radicals $R\dot{C}HOH$ and $R^1R^2\dot{C}OH$ have greater steric bulk and are less electrophilic than the $\dot{C}H_2OH$ radical and would therefore be expected to attack the central carbon atom of HFP to a lesser extent.

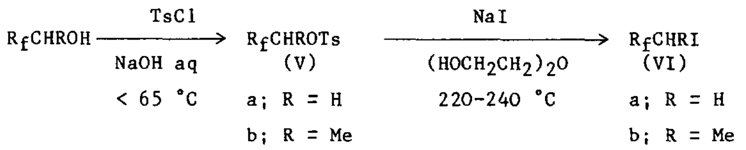
The 1:1 adducts (Ib), (Id), (Ie) and (If) were each isolated as mixtures of two diastereoisomers in the ratios 52:48, 55:45, 55:45, and 50:50, respectively.

Only in the reaction involving n-butanol was evidence obtained for a 1:1 adduct formed other than via abstraction of an α-hydrogen atom from the alcohol. The n.m.r. spectra of the 1:1 adduct fraction showed that it was a ca. 96:4 mixture of adduct (Ie) and a second adduct (as a 50:50 mixture of two diastereoisomers) with bands at δ_F (TFA ref) + 2.0 (6F, $2CF_3$), -42.2 (2F, CF_2), -47.8 (2F, CF_2) and -138.0 (1F, $CH\underline{F}$) and δ_H (C_6H_6 ref) -3.35 (2H, CH_2OH) and -4.70 (1H, $R_fC\underline{H}$) p.p.m.; the ^{19}F absorption of the CHF group in one of the diastereoisomers and the ^1H absorptions of the CH_3, CH_2 and CHF groups were masked by the corresponding absorptions of the major adduct (Ie). The second 1:1 adduct is therefore of structure (III) or (IV).

Although the thermal reaction of HFP with the alcohol CF_3CH_2OH gave adduct (If), the reaction of HFP with compound (Ia) under comparable conditions was unsuccessful. This observation indicates that replacement of a CF_3 group in the alcohol by the more bulky CF_3CHFCF_2 group sterically hinders abstraction of an α-hydrogen atom thus preventing adduct formation.

The alcohol $(CF_3)_2CHOH$ also did not undergo thermal reaction with HFP presumably because the presence of two adjacent strongly electron-withdrawing CF_3 groups deactivated the alcohol towards abstraction of the single α-hydrogen atom.

The 1:1 adducts (Ia) and (Ib) were converted into their tosylates (Va) (80%) and (Vb) (67%) and thence into the corresponding iodides (VIa) (71%) and (VIb) (36%), a method which has been reported [10] for the conversion of the alcohol $CF_3CF_2CH_2OH$ into the iodide $CF_3CF_2CF_2CH_2I$, i.e. where R_f = CF_3CHFCF_2.



$$\mathrm{R_fCHROH} \xrightarrow[\substack{\text{NaOH aq}\\ <65\ ^\circ\text{C}}]{\text{TsCl}} \underset{\substack{\text{(V)}\\ \text{a; R = H}\\ \text{b; R = Me}}}{\mathrm{R_fCHROTs}} \xrightarrow[\substack{(\mathrm{HOCH_2CH_2})_2\mathrm{O}\\ 220\text{-}240\ ^\circ\text{C}}]{\text{NaI}} \underset{\substack{\text{(VI)}\\ \text{a; R = H}\\ \text{b; R = Me}}}{\mathrm{R_fCHRI}}$$

Adduct (Ia) was also converted into the chloride $CF_3CHFCF_2CH_2Cl$ (87%) by treatment with thionyl chloride under reflux in the presence of pyridine.

EXPERIMENTAL

General techniques

Thermal and peroxide-initiated reactions were carried out in Pyrex ampoules (*ca.* 300 cm^3), while photochemical reactions employed silica ampoules (*ca.* 300 cm^3) which were shaken at a distance of 14 cm from a Hanovia 500 W medium-pressure lamp.

G.l.c. was carried out on a Pye 104 instrument and analytical work employed Phasesep Q columns (4 m, 80-100 °C) for non-condensable gases, Phasesep Q columns (4 m, 150 °C) for HFP and 1,1,1,2,3,3-hexafluoropropane, DNP columns (2m, 25-60 °C) for 1,1,1,2,3,3-hexafluorobutane and acetone, and SE30 columns (2m, 100-150 °C) for adduct fractions. Preparative-scale g.l.c. used columns as indicated in the text.

I.r., n.m.r. (shifts to *high* field of references designated negative) and mass spectroscopic analyses, respectively, were carried out with a Perkin-Elmer spectrophotometer model 257, a Perkin-Elmer R10 instrument (^{19}F at 56.46 and ^{1}H at 60 MHz), and a G.E.C.-A.E.I. MS902 spectrometer (electron beam energy 70 eV). The ^{19}F n.m.r. reference was ext. CF_3CO_2H.

Reactions of HFP (Amounts of reactants used given in Table 1)

(1) With methanol

(a) Under thermal conditions

A mixture of HFP and methanol heated at 280 °C (4 days) *in vacuo* gave (i) unchanged HFP (0.03 g, 0.20 mmol, 2% recovered) and a mixture of 1*H*,2*H*-hexafluoropropane and other gaseous products (0.53 mmol), (ii) unchanged methanol (0.62 g, 19.4 mmol, 57% recovered), (iii) a fraction (1.90 g), b.p. 108-113 °C, which was separated by g.l.c. (2 m SE30 at 100 °C) into its two major components identified as 2,2,3,4,4,4-hexafluorobutan-1-ol (Ia) (1.72 g, 9.5 mmol, 85%) (Found: C, 26.6; H, 2.4%. Calc. for $C_4H_4F_6O$: C, 26.4; H, 2.2%), b.p. 113 °C (lit., 112 °C) [9], $\lambda_{max.}$ 2.94 µm (O-H str.), *m/e* 182 (0.8%, *M*$^+$) and 31 (100%, CH_3O^+) and 2,3,3-trifluoro-2-trifluoromethyl-propan-1-ol (II) (0.09 g, 0.5 mmol, 4%), *m/e* 182 (3.6%, M^+), 51 (27%, CHF_2^+) and 31 (100%, CH_3O^+), δ_F +2.8 (3F, CF_3), -56.2 (2F, CHF_2, J_{HF} gem. 52.0 Hz), and -107.3 (1F, CF), δ_H (TMS ref.) +3.62 (1H, OH), +3.93 (2H, CH_2), and +5.60 (1H, CHF_2, J_{FH} gem. 52.0 Hz), and (iv) higher-boiling material (*ca.* 0.2 g).

(b) Under photochemical conditions

A mixture of HFP and methanol, sealed *in vacuo* in a silica ampoule and irradiated (4 days), gave (i) unchanged HFP (0.30 g, 2.0 mmol, 10% recovered) contaminated with 1*H*,2*H*-hexafluoropropane (trace), (ii) unchanged methanol (1.33 g, 41.6 mmol, 69% recovered), (iii) a mixture of 1:1 adducts (Ia) (3.11 g, 1.71 mmol, 95%) and (II) (0.06 g, 0.36 mmol, 2%), and (iv) higher-boiling material (0.10 g).

(c) Under peroxide-irritated conditions

A mixture of HFP, methanol and di-t-butyl peroxide, heated *in vacuo* at 150 °C (20 h), gave (i) a mixture of carbon monoxide and methane (0.06 g, 3.5 mmol), (ii) a gaseous fraction (0.13 g, 1.1 mmol) which consisted of unchanged HFP (*ca.* 0.04 mmol, 0.2% recovered), 1,1,1,2,3,3-hexafluorobutane, acetone and three unidentified components, (iii) a liquid (4.92) which consisted of 1,1,2,3,3-hexafluorobutane, acetone, unchanged methanol, 2-methylpropan-2-ol, and the 1:1 adducts (Ia) and (II) (3.40 g, 18.7 mmol, 95%) in the ratio 100:2 (^{19}F n.m.r.), and (iv) higher-boiling material (0.28 g).

(2) With ethanol

(a) Under thermal conditions

A mixture of HFP and ethanol, heated *in vacuo* at 280 °C (96 h), gave (i) non-condensable gaseous material (1.2 mmol), (ii) unchanged HFP (0.83 g, 5.56 mmol, 46% recovered) contaminated with 1*H*,2*H*-hexafluoropropane (< 1%), (iii) unchanged ethanol (1.39 g, 30.3 mmol, 80% recovered), and (iv) a mixture (1.33 g) containing 3,3,4,5,5,5-hexafluoropentan-2-ol (1.03 g, 5.25 mmol, 79%).

(b) Under photochemical conditions

A mixture of HFP and ethanol, irradiated *in vacuo* (96 h), gave (i) unchanged HFP (1.52 g, 10.16 mmol, 45% recovered) contaminated with 1*H*,2*H*-hexafluoropropane, (ii) unchanged ethanol (2.84 g, 61.8 mmol, 82% recovered), and (iii) a liquid mixture (2.43 g) from which the major component was separated by g.l.c. (2 m SE30 at 120 °C) and identified as 3,3,4,5,5,5- hexafluoropentan-2-ol (Ib) (2.28 g, 11.63 mmol, 92%) (Found: C, 30.7; H, 3.3%. $C_5H_6F_6O$ requires C, 30.6; H, 3.1%), b.p. 120-122 °C, $\lambda_{max.}$ 2.95 μm (O-H str.), *m/e* 181 (3.2%, $C_4H_3F_6O^+$), 69 (19.8%, CF_3^+), and 45 (100%, $C_2H_5O^+$) as a pair of diastereoisomers in the ratio 52:48 (^{19}F n.m.r.).

(c) Under peroxide-initiated conditions

A mixture of HFP, ethanol and di-t-butyl peroxide, heated *in vacuo* at 150 °C (20 h), gave (i) carbon monoxide and methane (0.05 g, 2.1 mmol), (ii) unchanged HFP (2.03 g, 13.5 mmol, 30% recovered), (iii) a liquid mixture (7.23 g) which was analysed (g.l.c.) and fractionated to afford adduct (Ib) (5.32 g, 27.1 mmol, 86%) together with 1,1,1,2,3,3-hexafluorobutane, acetone, unchanged ethanol, and 2-methylpropan-2-ol and a high-boiling residue (0.4 g).

(3) With propan-2-ol

(a) Under thermal conditions

A mixture of HFP and propan-2-ol, heated *in vacuo* at 280 °C (96 h), gave (i) a non-condensable gas (1.0 mmol) (ii) unchanged HFP (0.76 g, 5.08 mmol, 44% recovered) contaminated with 1*H*,2*H*-hexafluoropropane, (ii) unchanged propan-2-ol (1.53 g, 25.5 mmol, 78% recovered), (iii) 3,3,4,5,5,5-hexafluoro-2-methylpentan-2-ol (Ic) (1.16 g, 5.52 mmol, 86%), and (iv) higher-boiling material (0.1 g).

(b) Under photochemical conditions

A mixture of HFP and the alcohol, irradiated *in vacuo* (96 h), gave (i) unchanged HFP (*ca* 0.08 g, 0.5 mmol, 2% recovered) contaminated with 1*H*,2*H*-hexafluoropropane (trace), and (ii) a liquid mixture (7.55 g) which was analysed by g.l.c. and fractionated to afford unchanged propan-2-ol (2.77 g, 46.1 mmol, 60% recovered), 3,3,4,5,5,5-hexafluoro-2-methylpentan-2-ol (Ic) (4.68 g, 22.32 mmol, 95%) (Found: C, 33.9; H, 3.5%. $C_6H_8F_6O$ requires C, 34.3; H, 3.8%), b.p. 128 °C, λ_{max} 2.92 μm (O-H str.), and (iv) higher-boiling material (0.1 g).

(c) Under peroxide initiated conditions

A mixture of HFP, the alcohol and di-t-butyl peroxide, heated *in vacuo* at 150 °C (20 h), gave (i) carbon monoxide and methane (0.07 g, 4.1 mmol), (ii) unchanged HFP (0.17 g, 1.1 mmol, 2% recovered), (iii) a mixture (1.15 g) of acetone, 1,1,1,2,3,3-hexafluorobutane, unchanged propan-2-ol, and 2-methylpropane-2-ol, (iii) adduct (Ic) (8.2 g, 39.0 mmol, 89%), and (iv) higher-boiling material (0.20 g).

(4) With butan-2-ol

(a) Under thermal conditions

A mixture of HFP and butan-2-ol, heated *in vacuo* at 280 °C (96 h), gave (i) non-condensable gas (0.3 mmol), (ii) a mixture of unchanged HFP (1.0 g, 6.65 mmol, 62% recovered), 1*H*,2*H*-hexafluoropropane (trace), and other gaseous products (0.24 g, 4.2 mmol), and (iii) a liquid mixture (2.77 g) which was analysed by g.l.c. and fractionated to give unchanged butan-2-ol (1.62 g, 21.9 mmol, 63% recovered), 4,4,5,6,6,6-hexafluoro-3-methylhexan-3-ol (Id) (0.85 g, 3.78 mmol, 91%) (Found: C, 37.8; H, 4.6%. $C_7H_{10}F_6O$ requires C, 37.5; H, 4.5%), b.p. 157-158 °C, λ_{max} 2.90 μm (O-H str.), *m/e* 209 (10.2%, $C_6H_7F_6O^+$), 195 (41.9%, $C_5H_5F_6O^+$), 155 (21.5%, $C_6H_{10}F_3O^+$), and 73 (100%, $C_4H_9O^+$) as a pair of diastereoisomers in the ratio 55:45 (^{19}F n.m.r.), and higher-boiling material (0.3 g).

(b) Under photochemical conditions

A mixture of HFP and the alcohol irradiated *in vacuo* (72 h), gave (i) carbon monoxide and methane (0.12 g, 5.4 mmol), (ii) unchanged HFP (0.05 g, 0.3 mmol, 1.5% recovered) contaminated with 1*H*,2*H*-hexafluoropropane (trace), (iii) unchanged butan-2-ol (3.09 g, 41.7 mmol, 61% recovered), (iv) adduct (Id) (4.88 g, 21.8 mmol, 97%), and (v) unidentified products (0.24 g).

(5) With butan-1-ol under photochemical conditions

A mixture of HFP and butan-1-ol, irradiated *in vacuo* (120 h), gave (i) non-condensable gas (1.1 mmol), (ii) unchanged HFP (9.36 g, 62.4 mmol, 53% recovered) contaminated with 1*H*,2*H*-hexafluoropropane (< 1%), and (iii) a liquid mixture which was analysed by g.l.c. and fractionated to give unchanged butan-1-ol (18.7 g, 246 mmol, 70% recovered), a mixture of 1:1 adducts (12.0 g, 553.5 mmol, 98%) (Found: C, 37.7; H, 4.8%. $C_7H_{10}F_6O$ requires C, 37.5; H, 4.5%), b.p. 56-58 °C at 18 mmHg, $\lambda_{max.}$ 3.05 μm (O-H str.), *m/e* 224 (1.3%, M^+), and other products (*ca.* 1.5 g). The n.m.r. spectra of the 1:1 adduct mixture showed that it consisted of 1,1,2,3,3-hexafluoroheptan-4-ol (Ie) (11.5 g, 51.3 mmol, 94%) as a pair of diastereoisomers in the ratio 55:45 and another 1:1 adduct of structure $CH_3(C_2H_3CF_2CHFCF_3)CH_2OH$ (0.5 g, 22.1 mmol, 4%) as a pair of diastereoisomers.

(6) With 2,2,2-trifluoroethanol under thermal conditions

A mixture of HFP and the alcohol, heated *in vacuo* at 320 °C (112 h), gave (i) hydrogen (2.0 mmol), (ii) unchanged HFP (3.11 g, 20.7 mmol, 43% recovered) contaminated with a small amount of 1*H*,2*H*-hexafluoropropane, (iii) a liquid mixture (18.58 g) which was separated into its two components by g.l.c. (2 m PEG 20M at 120 °C) identified as unchanged 2,2,2-trifluoroethanol (12.10 g, 121 mmol, 82% recovered) and 1,1,1,3,3,4,5,5,5-monafluoropentan-2-ol (If) (6.48 g, 25.9 mmol, 95%) (Found: C, 23.9; H, 1.3%. $C_5H_3F_9O$ requires C, 24.0; H, 1.2%), and (iv) a tarry residue (0.30 g).

(7) With 1,1,1,3,3,3-hexafluoropropan-2-ol under thermal conditions

A mixture of HFP and the alcohol heated *in vacuo* at 355 °C (120 h), gave unchanged HFP (100% recovered) and unchanged alcohol (98% recovered).

(8) With 2,2,3,4,4,4-hexafluorobutan-1-ol under thermal conditions

A mixture of HFP and the alcohol, heated *in vacuo* at 385 °C (36 h), gave unchanged HFP (1.18 g, 7.86 mmol, 98.5% recovered) unchanged alcohol (3.36 g, 18.5 mmol, 77% recovered), and a mixture (0.95 g) which contained at least seven components as shown by g.l.c. (2 m PEG 20M at 140 °C).

Reactions of the 1:1 adducts

(a) Preparation of 1,1,1,2,3,3-hexafluoro-4-iodobutane (VIa)

To a mixture of adduct (Ia) (2.90 g, 15.7 mmol), *p*-toluenesulphonyl chloride (3.17 g, 16.6 mmol) and water (5.4 cm^3) was added a solution of sodium hydroxide (0.72 g, 18.0 mmol) in water (2.9 cm^3) at such a rate to maintain the reaction temperature below 65 °C. The mixture was stirred until neutral and the product 2,2,3,4,4,4-hexafluorobutyl-*p*-toluenesulphonate (Va) 4.20 g, 12.5 mmol, 80%) was isolated by extraction with petroleum ether (b.p. 40-60 °C, 3 x 25 cm^3).

A mixture of the sulphonate (3.40 g, 10.1 mmol), sodium iodide (1.51 g, 10.1 mmol) and diethylene glycol (3 cm^3), heated at 220 °C (2 h), gave 1,1,1,2,3,3-hexafluoro-4-iodobutane (2.10 g, 7.1 mmol, 71%) (Found: C, 16.6; H, 1.2%. $C_4H_3F_6I$ requires C, 16.4; H, 1.0%), b.p. 111 °C, *m/e* 292 (100%, M^+), 191 (50.2%, $CF_2CH_2I^+$), 141 (19.1%, CH_2I^+), and 69 (26.3%, CF_3^+).

(b) Preparation of 1-chloro-2,2,3,4,4,4-hexafluorobutane

A mixture of adduct (Ia) (9.99 g, 54.9 mmol), thionyl chloride (12.00 g, 0.101 mmol) and pyridine (0.1 cm^3) was heated under reflux (10 h). The resulting material was distilled and the fraction (9.06 g), b.p. 66-74 °C, was washed with a solution of sodium bicarbonate (8.0 g) in water (100 cm^3). The lower layer was separated and dried (Na_2SO_4) to afford 1-chloro-2,2,3,4,4,4-hexafluorobutane (7.22 g, 35.2 mmol, 87%) (Found: C, 24.1; H, 1.5; Cl, 17.7; F, 56.8%. $C_4H_3ClF_6$ requires C, 24.0; H, 1.5; Cl, 17.8; F, 57.1%), b.p. 70 °C, *m/e* 200/202 (1.8%, M^+) 99/101 (100%, $CF_2CH_2Cl^+$) and 69 (72.5%, CF_3^+).

Two further fractions were obtained (i) b.p. 74-80 °C, which was identified as unchanged thionyl chloride (5.03 g, 44.6 mmol, 44% recovered) and (ii) b.p. 80-117 °C (2.92 g) which, after treatment with aqueous sodium bicarbonate, afforded unchanged adduct (Ia) (2.61 g, 14.3 mmol, 14% recovered).

TABLE 2

N.m.r. spectral data for compounds of type $RCF_AF_BCHFCF_3$

R	Isomer ratio	^{19}F (p.p.m.)			$\underline{J}$(Hz)			^1H (p.p.m.)
		CF_3	F_A	F_B	CHF	AB	HF_{gem}	(TMS ref)
CH_2OH		+3.8	-41.0	-45.0	-136.8	273	43.0	+3.70(CH_2),+4.24(OH), +4.78(CHF)
CHMeOH	52	+1.9	-46.4	-50.6	-142.2	282	42.9	-1.61(CHF),-2.58(OH),
	48	+2.0	-50.4	-56.4	-140.2	293	42.7	-2.65(CH),-5.44(CH_3)$^+$
CMe_2OH		+2.7	-46.9	-51.1	-133.4	280	43.8	-1.47(CHF),-3.28(OH), -5.36($2CH_3$)$^+$
CMeEtOH	55	+3.4	-47.8§		-129.6	-	43.0	+0.88(CH_3),+1.24(CH_3)
	45	+3.0	-45.2§		-130.6	-	44.5	+1.62(CH_2),+2.69(OH), +5.12(CHF)
$CHPr^nOH$	55	+2.6	-48.9	-53.1	-136.8	268	44.0	-1.53(CHF),-2.0(OH),
	45	+2.6	-43.1	-47.5	-133.8	273	45.4	-3.09(CH),-5.12(CH_2), -5.73(CH_3)$^+$
CF_3CHOH	50	+2.9	-40.1	-42.6	-135.5	280	44.0	+3.75(OH),+4.45(CH),
	50	+2.9	-43.9	-46.4	-137.5	286	44.0	+5.05(CHF)
CH_2Cl		+2.0	-37.2	-39.8	-138.5	276	43.0	+3.80(CH_2),+5.05(CHF)
CH_2I		+3.4	-25.1	-29.4	-135.4	267	42.6	-1.35(CHF),-2.86(CH_2)'
CHMeI	50	+4.4	-32.2§		-135.0	-	43.0	-1.30(CHF),-2.15(CH),
	50	+4.4	-41.4§		-136.0	-	44.0	-4.53(CH_3)$^+$

$^+$ C_6H_6 external ref. § Complex multiplets, probably AB systems in which $\delta_A \simeq \delta_B$ and therefore outer bands not observed.

(c) Preparation of 1,1,1,2,3,3-hexafluoro-4-iodopentane (VIb)

To a mixture of adduct (Ib) (2.84 g, 14.5 mmol), *p*-toluenesulphonyl chloride (2.93 g, 15.3 mmol) and water (5 cm^3) heated to 50 °C, was added a solution of sodium hydroxide (0.66 g, 16.5 mmol) in water (2.7 cm^3) over ten minutes. The resultant mixture was stirred until neutral and 2-(3,3,4,5,5,5-hexafluoropentyl)-*p*-toluenesulphonate (Vb) (2.93 g, 8.4 mmol, 67%) isolated by extraction with petroleum ether (b.p. 40-60 °C, 3 x 25 cm^3).

A mixture of the sulphonate (2.56 g, 7.3 mmol), sodium iodide (1.10 g, 7.3 mmol), and diethylene glycol (3 cm^3), heated at 240 °C (1 h) gave 1,1,1,2,3,3-hexafluoro-4-iodopentane (0.80 g, 2.6 mmol, 36%) (Found: C, 19.9; H, 1.8%; $C_5H_5F_6I$ requires C, 19.6; H, 1.6%), b.p. 127-129 °C, *m/e* 306 (72.0 %, M^+) and 77 (100%, $C_3H_3F_2^+$) as a pair of diastereoisomers.

The n.m.r. spectra of compounds of type RCF_2CHFCF_3 are given in Table 2.

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