THE FLUORINATION OF BUTANE OVER COBALT TRIFLUORIDE*

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SUMMARY

The fluorination of butane over cobalt trifluoride has given a complex mixture of partially fluorinated compounds: 51 of these have been identified, comprising over 99% of the products. Most were polyfluorobutanes but 1-2% were polyfluoro-2-methylpropanes. The reaction has no synthetic utility. There was some selectivity in the fluorination: secondary C-H was converted into C-F more easily then primary, and the ease of replacement of a particular H was reduced by geminal and vicinal fluorines. A computer model of the fluorination was only partially successful, perhaps because the fluorination proceeded in part by simple F for H replacement and in part via alkenes: the model only allowed for the former.

INTRODUCTION

Although there is a reasonably satisfactory mechanism for the fluorination of aromatic substrates [1] over high-valency transition metal fluorides (CoF₃, MnF₃, etc), the fluorination of aliphatic compounds is neither so well studied nor so well understood. In the aromatic area, the positions of residual hydrogens and double bonds can be rationalized [1], but in the aliphatic there is not much data to go on. The only well-studied cases are those of ethane [2], ethene [2], and

Dedicated to Emeritus Professor W.K.R. Musgrave on the occasion of his 70th birthday.

2-methylpropane [3]: the distribution of hydrogens in the partially fluorinated products was almost random in the first two cases. and in the last tertiary H was replaced by F about 10 times faster than primary H was. More recently [4]. it has become clear that extensive skeletal rearrangements can occur during the fluorination of saturated aliphatics: for example, octane over cobalt trifluoride gave only about 50% of straight-chain perfluoro-octane, the rest being perfluorinated branched-chain Cg-isomers or Cg-cyclic compounds.

In the hope of developing a usable mechanism for the fluorination of aliphatics we have investigated the partial fluorination of butane over cobalt trifluoride. This case is potentially more complex than that of 2-methylpropane because the number of possible partially fluorinated butanes is much greater (88 as compared to 40, counting optical pairs as one). This turned out to be the case: we have identified about 40 partially fluorinated butanes in the cobalt trifluoride product as compared with only 20 partially fluorinated 2-methylpropanes [3].

RESULTS

The crude fluorination mixture was separated by fractional distillation into 16 fractions (Table 6). The major peaks from many of these fractions were then separated by preparative-scale glc and were then identified (many were still mixtures - see Table 7) by a straightforward combination of spectroscopic and chemical methods. In addition, careful examination of ¹⁹F and ¹H nmr spectra of each fraction enabled many minor components to be identified. This is summarized in Table 1, where the approximate percentage of each compound in the reaction mixture, and an assessment of the confidence with which its structure can be claimed (see later) are also presented. The overall composition was calculated from the compositions of the individual distillation fractions as determined by nmr (fractions D-P) or glc (fractions A-C): it should only be regarded as approximate and in any case would change if a different temperature of fluorination were employed.

The major problem in identification is the great complexity of the reaction mixture. Even those components which were single peaks on glc normally contained at best very small amounts of minor components, amounts

TABLE 1	
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Compound	Compound No.	Distillation fraction ^a in which present	How Identified ^b	Identification category ^C	% in reaction mixture ^d
		amount			
CF3CF2CF2CF3	1	A	Sep(A)	a	0.2
CF3CF2CF2CF2H	2	Α	Z Sep(B)	b	4.8
CF3CF2CFHCF3	3	А	5	b	3.1
CF3CF2CF2CFH2	4	с	Sep(C)	a	1.7
CF3CF2CFHCF2H	5	С	Sep(C)	a	3.0
CF3CFHCF2CF2H	6	Е	Sep(D)	a	11.4
CF2HCF2CF2CF2H	7	G	Sep(G)	a	5.6
CF3CF2CH2CF3	8	В	Sep(C)	a	1.0
CF3CFHCFHCF3(m)	9	В	Synth(C)	b	2.0
CF ₃ CFHCFHCF ₃ (±)	10	E	Synth(E)	е	1.8
CF3CF2CFHCFH2	11	F	F	f	0.2
CF3CFHCF2CFH2	12	F	G	b	3.4
CF2HCF2CF2CFH2	13	J	Sep(I)	a	5.5
CF3CFHCFHCF2H-Ae	14	н	Sep(H)	с	2.4
CF3CFHCFHCF2H-Be	15	Н	Sep(H)	с	2.5
CF2HCF2CFHCF2H	16	I	Synth(I)	a	14.0
CF3CH2CF2CF2H	17	F	G	с	1.9
CF3CFHCH2CF3	18	С	Sep(C)	с	0.7
CF2HCF2CF2CH3	19	F	F	e	1.7
CF3CFHCFHCFH2	20	м	м	g	0.2
CF2HCF2CFHCFH2	21	м	Sep(L)	e	1.2
CF3CH2CF2CFH2	22	н	н	f	0.4
CF2HCFHCF2CFH2	23	м	Sep(L)	b	6.6
CFH2CF2CF2CFH2	24	м	M	đ	3.0
CF2HCF2CH2CF2H	25	К	J	f	0.7
CF3CH2CFHCF2H	26	I	I	f	0.5
CF2HCFHCFHCF2H-A	e 27	L	Sep(L)	b	4.6
CF2HCFHCFHCF2H-B	e 28	N	Sep(N)	a	3.9
CF2HCFHCF2CH3	29	К	J	g	0.4

Compounds Identified in the CoF3/butane Reaction

(continued overleaf)

TABLE	1	(cont.)

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CFH2CF2CF2CH3	30	G	G	d	2.1
CF2HCFHCFHCFH2-A	e ₃₁	Р	(Sep(P)	b	1.3
CF2HCFHCFHCFH2-B	e 32	Р	J	b	1.3
CFH2CF2CFHCFH2	33	0	Sep(0)	b	2.5
CF2HCH2CF2CFH2	34	0	0	е	0.8
CF2HCFHCH2CF2H	35	Р	0	f	0.5
CFH2CFHCFHCFH2-A	e 36	Р	Sep(P)	b	0.4
CFH2CFHCFHCFH2-B	e 37	Р	}	b	0.4
CH3CF2CFHCH3	38	F	F	f	0.6
(CF ₃) ₃ CF	39(1) ^f	Α	Sep(A)	gg	tr.
CF ₃ CF(CF ₂ H) ₂	40(7)	D	D	f	0.1
CF ₃ CF(CF ₂ H)CFH ₂	41(8)	F	F	f	0.3
(CF3)2CHCFH2	42(8a)	F	F	g	tr.
(CF ₂ H) ₃ CF	43(12a)	Н	I	f	0.4
CF3CH(CF2H)2	44(13)	Н	Н	f	0.1
CF3CH(CF2H)CFH2	45(14a)	J	J	f	tr.
(CF ₂ H) ₂ CFCFH ₂	46(12)	I	I	f	0.4
CF3CF(CH3)CFH2	47(8b)	F	F	g	tr.
CF ₂ HCF(CFH ₂) ₂	48(16)	M	М	f	0.1
$CF_2HCF(CFH_2)CH_3$	49(14)	К	L	f	0.1
h	50(17/18)	0	0	f	0.1
h	51(17/18)	0	0	f	0.1

a See Table 6. ^b Sep = Separated by prep-scale glc from the distillation fraction in parenthesis and then identified either by comparison of its ir spectrum with that of an authentic specimen or by nmr analysis. Synth = synthesised and then identified in the fraction in parehthesis either by ir or nmr. A single letter (F.G, etc) indicates that the compound was identified in that distillation fraction by picking out and analysing its nmr signals from the nmr signals of the whole fraction. C a = compound **isola**ted in >90% purity: b = compound present as 40-90% of some mixture (either a distillation fraction or a glc cut of a distillation fraction); compound then identified by picking out its nmr signals from those of the mixture: c = as b, but 30-40%: d = as b, but 20-30%; e = as b, but 10-20%; f = as b, but <10%; g = as f, but either only one nmr peak (CF3 or CH3) visible (20,29) or signals very weak (42,47) (In cases b-f. some signals were usually obscured by those of other compounds - see Table 4). d Obtained from the compositions of the individual fractions: these

TABLE 1 (footnotes cont.)

were analysed either by glc (A,B,C) or nmr (the remainder). ^e See text for A.B. ^f The numbers in parentheses (1,8a,etc.) refer to the compound numbers given to polyfluoro-2-methylpropanes in ref. 3. ^g Identified in a mixture with compound 1 solely on the basis of the ir peak at 1000 cm⁻¹ [5]. ^h these two compounds were identical to compounds 17 and 18 of ref. 3: they were not there identified but are undoubtedly polyfluoro-2-methylpropanes.

which were insufficient to affect elemental analyses (for example, a small amount of 19, $CF_2HCF_2CF_2CH_3$, was revealed when an apparently pure sample of 6, $CF_3CFHCF_2CF_2H$, which is a major product, was dehydrofluorinated): at worst some single peaks contained several major components in addition to minor ones (Table 7).

Literature [5] infrared spectra sufficed for the identification of several compounds present as virtually pure single glc peaks (compounds 1 and 7) or as simple mixtures (2.3). Re-synthesis of 27 and 28 [6] enabled 28 to be identified by ir [it is the main (>90%) component of glc peak XIII (Table 7)] and 27 by finding most of its nmr peaks in a mixture with 21 and 23 (glc peak XII). 9, 10, and 16 have been synthesised unambiguously:

 $CF_{3}CC_{2}=CC_{2}CF_{3} \xrightarrow{CoF_{3}} CF_{3}CFC_{2}CFC_{2}CF_{3} \xrightarrow{\text{LiAlH}_{4}} CF_{3}CFHCFHCF_{3}$ (9 and 10)

 $CF_{2}HCF_{2}CF=CF_{2} \xrightarrow{CI_{2}/h\nu} CF_{2}HCF_{2}CFCICF_{2}CF \xrightarrow{LiAlH_{4}} CF_{2}HCF_{2}CFHCF_{2}HCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}CFHCF_{2}HCF_{2}HCF_{2}CFHCF_{2}HCF_{2}HCF_{2}CFHCF_{2}HCF$

9 and 16 were major components of single glc peaks (V and XI) and 10 was identified by picking out all its 19 _{F nmr} signals in distillation fraction E. 9 was distinguished from 10 by dehydrofluorination with KOH: it reacted about 2-3 times slower, and assuming trans-periplanar elimation it is therefore most plausibly the meso-isomer:









more stable (unreactive) less stable (→ alkene)

9

10

The ¹H and ¹⁹F spectra of compound 4 are described in the literature [7]: glc peak IV contained a spectrum with essentially the same parameters. Compound 8 is recorded in the literature [8] and the chemical shifts are included in Table 4. There are also mentions [9] of compounds 6, 9 or 10, 11 and 12, but without physical properties or spectral details. One of 9 or 10 has been reported [10]: the nmr chemical shifts (no couplings given) agree best with those given here for 10, although there is clearly something amiss with the proton shift. Compounds 22 and 26 have also been synthesised [11]: there is good agreement between our parameters and those reported. Compound 38 has also been detected [12] as a minor component in a complex reaction mixture; no physical or spectral properties were given.

The remaining compounds (with the exception of the polyfluoro-2-methylpropanes - see later) are completely new. All were identified by nur spectrocopy; this usually necessitated picking out the relevant nmr signals from those presented by a mixture. This was not a problem when all the signals were visible. However, with the minor components some signals were commonly obscured by those of major components: this was almost invariably true of 1 H signals from CHF, CH₂F and CHF₂ because their chemical shift range is so narrow. The essence of the problem is apparent from Table 4 where some minor components have several signals unrecorded. The two worst examples are compounds 20 (CF3CFHCFHCFH2) and 29 (CF2HCFHCF2CH3) and we have recorded these to make the point that even in such cases all is not lost. With 20 the CFa signal is the only one visible. It is in the correct place (Table 2) (76.7) for CF3-CFH: it is split into a doublet (J-1.5Hz) of doublet (6Hz) of triplets (10Hz), and these couplings are typical (Table 2) of CF_3 with an F on 4, CF_3 with an H on 2, and CF_3 with Fs on 2 and 3, respectively. We do not pretend that this is conclusive - but it is difficult to suggest what else the compound might be. There is, of course, the question of <u>threo</u> or <u>erythro</u> - but that is beyond speculation with the evidence available.

The second example of a very speculative assignment is compound 29 $(CF_2HCFHCF_2CH_3)$ where only the CH₃ signal was observed: this was in the expected position for a CH₃CF₂. There was a small doublet (J = 2.9Hz) coupling in addition to the larger CH₃CF₂ triplet (19.5Hz): the doublet must be a J₄ H-F coupling. There are no unassigned CF₃ or CFH₂ peaks in the spectrum of fraction J and we have given the structure as 29 even though the CF₂H signal is not visible: in fraction J the CF₂H region contained many strong signals from major components whereas the CF₃ and CFH₂ regions did not, thus making it most probable that the missing signal was indeed a CF₂H.

Having given some details of the two most speculative structural assignments just to show what can be done, we leave the remaining unknowns (~5 - each in <0.1% in the reaction mixture) unassigned, even though it is possible to write down structures for them as with 20 and 29. and with similar confidence.

The reassuring feature of structural determination of polyfluorobutanes by nmr is the consistancy of the parameters (Table 2): literature data are also in complete accord with our values. The most useful group for identification purposes is the CF₃: the parameter ranges are relatively narrow, there is no overlap with other types of signal (as there is between C-CF₂-C and C-CF₂H), and no second-order coupling (these can vary from simple AB cases - any CF₂ in the same molecule as a CFH can present as an AB - to more complex situations). CH₃ and CH₂ are also very valuable because they are relatively uncommon. The least useful are CF<u>H</u>, CF₂H, and CF<u>H</u>₂ because overlapping with signals from other compounds is almost certain when mixtures are involved.

Two unusual structures $(30 - CFH_2CF_2CF_2CH_3 - and 38 - CH_3CF_2CFHCH_3)$ have been firmly established by homo- and hetero-nuclear decoupling studies.

TABLE 2

Group	¹⁹ F shift range ^a	1 H shift range ($ au$)
CF3-CF2	81.5-83.9	-
<u>CF</u> 3-CFH	74.9-81.2	_
<u>CF</u> 3-CH2	62.0-65.2	-
CF2H-CF2	134.2-144.2 ^b	
<u>CF2H</u> -CFH	130.6-134.1	3.97-4.26
<u>CF2H</u> -CH2	114.5-117.9	
CFH2-CF2	235.0-244.1	5.17-5.5
<u>CFH</u> 2-CFH	233.8-237.6	5.1
-CF2-	105.4-132.4 ^C	-
-CFH-	189.5-220.5 ^d	5.05-5.6
CH3-CF2	-	8.26-8.30
<u>CH</u> 3-CFH	_	8.64
-CH2-	-	7.18-7.8

Chemical Shift (19 F and 1 H) and Coupling Constant Ranges in Polyfluorobutanes

^a In ppm upfield from CFCl₃. ^b If centres of AB spectra are taken instead of chemical shifts of individual fluorines, the range is 136.8-139.2. ^c The lowest field signals occur when there is a neighbouring CH₂ or CH₃: without these groups, the range is 121.9-132.4. ^d As for \underline{c} ; range would be 203.2-220.5.

System	Coupling range <u>e</u> (Hz)	System	Coupling range ^e (Hz)
CF ₂ H(gem)	51.0-55.3	C <u>F</u> 2H-C-C-CF	0-2.8
CFH ₂ (gem)	45.7-47.4	C <u>F</u> H2-CF2	14.0-15.0
CFH(gem)	44.3-45.5	с <u>ғ</u> н2-с <u>ғ</u> н	20.4-24.8
		(continued overleaf)

CF3-CF2	~0	CEH2-CFH	11.3-15.8
CF3-C <u>F</u> H	9.9-10.6	CEH2-C-CF	4.5-5.7
CF3-CF <u>H</u>	5.6-6.5	C <u>F</u> H ₂ -C-C-CF	1.2-2.8
CF3-CH2	9.4-10.4	С <u></u> FH ₂ -С-СН	1.8-2.1
CF3-C-CF	9.4-11.1 ^f	CH_3-CF_2	18.9-19.5
CF3-C-C-CF	0-2.6	CH3-C <u>F</u> H	24.1
C <u>F</u> 2H-CF2	<4-5.7 ^g	СН3-СF <u>Н</u>	6.3
C <u>F</u> 2H-C <u>F</u> H	8-12.6	CH3-C-CF	0-2.9
C <u>F</u> 2H-CF <u>H</u>	10-12.6	CH3-C-C-CF	0-1.5
C <u>F</u> 2H-CH2	15.7-16.3	CH2F-CF	2.8-12.8
C <u>F2</u> H-C-C <u>F</u> H	<4-10.2 ^g	CHF2-CF	2.8-8.4
С <u>F</u> 2H-C-CF2	5.8-9.5	CHF2-CH	3.6-4.6

^e Some couplings were unobtainable and some of those given are probably composite values rather the simple couplings implied; in both cases this is due to second-order effects, particularly with couplings involving $C\underline{F}_2H$ and $-CF_2-$. ^f Compounds 18 and 26 had 7.4Hz and 7.3Hz for this coupling. ^g Bottom of range may be zero - not clear because of second-order effects.

Some dehydrofluorinations helped to confirm a few of the structural assignments.

$$CF_{2}HCFHCF_{2}CFH_{2} (23) + CF_{2}HCFHCF_{2}H (27) + CF_{2}HCF_{2}H (27) + CF_{2}HCF_{2}$$

CF2HCF2CF2CFH2 (13) KOH (Z)-CF2HCF2CF=CFH

The nmr spectra of the polyfluorobutenes are recorded in Table 5: all are in accord with expectation. Z and E isomers were distinguished by the typically large (~120Hz) J_{FF} -coupling shown by a <u>trans</u>-CF=CF group or the large J_{HF} of a <u>trans</u>-CH=CF (~30Hz) [14].

This leaves compounds 39-51. All are polyfluoro-2-methylpropanes and all had been obtained previously [3] from a $(CH_3)_3CH/CoF_3$ reaction. They were identified in the present work by comparison of ^{19}F nmr signals: since these are quite complex, they serve as reasonable fingerprints. Nevertheless such identifications, while certain in some cases, must be regarded as tentative in others.

Four pairs of compounds (14,15; 27,28; 31,32; 36,37) have been designated 'A' or 'B' in Table 1. All are pairs of stereoisomers and we have not attempted to distinguish them.

Table 1 gives an assessment of the certainty with which a structure has been established. This is based on the argument that the smaller the amount of a substance there is in a mixture, the less likely it is that the identity of the compound has been established.

In summary, we have identified 51 compounds, with varying degrees of certainty, in the butane/CoF₃ reaction mixture: they comprise over 99% of it. About five compounds remain unidentified (their presence is clear from otherwise unattributed CF₃, CFH₂, or CH₃ signals in several distillation fractions): none are present in greater amount than 0.1% of the reaction mixture. It is extremely unlikely that we have missed any significant component because this would require <u>all</u> of its peaks to be obscured by those of other components without distorting any of them.

DISCUSSION

It is surely obvious that the fluorination of butane over cobalt trifluoride is virtually valueless for preparative purposes. In

extremis, a case might be made for $CF_3CFHCF_2CF_2H$ (6), $CF_2HCF_2CF_2CF_2H$ (7), and $CF_2HCF_2CFHCF_2H$ (16) but the need would have to be very great (6 and 7 have, in fact, been tested as anaesthetics [15] and were prepared for that purpose by the fluorination route described in this paper. The same point arose in the fluorination of 2-methylpropane [3] and even with ethane [2], although the production of CFH_2CFH_2 from the latter might just be viable.

With higher alighatics, the preparative utility of cobalt trifluoride fluorination for partially fluorinated compounds is likely to be even less, since substantial skeletal rearrangements can occur as well [4].

This contrasts with aromatic fluorination: with benzene, for example. cobalt trifluoride provides a viable route to $C_6F_{11}H$ and to some of the $C_6F_{10}H_2$ and $C_6F_9H_3$ isomers [16].

Any interest in the butane fluorination therefore lies in the information it provides on the mechanism of CoF_3 /aliphatics fluorination. Two points will be addressed in this paper:

- (1) is the replacement of hydrogen by fluorine random?

The first point requires some discussion of 'random'. It could mean: (i) is every hydrogen in every molecule from $C_{4}H_{10}$ to $C_{4}F_{9}H$ equally likely to be replaced by fluorine? (ii) Are all hydrogens in all molecules with the same number of fluorines (e.g. all the H's in all the $C_4F_5H_5$ isomers) equally reactive? (iii) Are all hydrogens in the same molecule (e.g. the three types of H in CF2HCF2CFHCF2H) equally reactive? (iv) Are hydrogens in all CF2H groups, say, equally reactive, irrespective of the number of fluorines in the rest of the molecule? Random fluorination as defined by (i) clearly does not occur, since if it did significant amounts of compounds containing one or two fluorines would be present, and none are: even compounds with three or four fluorines only comprise 1.4% of the Cases (ii)-(iv) are related and, while random reaction mixture. fluorination according to these definitions also does not occur, as will be shown later, accepting them is not badly wrong.

We have written a computer program (see Appendix) which can model a fluorination pattern in which H's are replaced one at a time by F's without the intervention of alkenes. That is :-

 $C_{4}H_{m}F_{n} \xrightarrow{C_{4}H_{m-1}F_{n}} c_{4}H_{m-1}F_{n+1}$ $C_{4}H_{m-1}F_{n}^{+}$

(n=10-m)

The model contains five disposable parameters:

- (i) the reactivity ratio between a single H in a \mbox{CH}_2 to a single H in a \mbox{CH}_3 :
- (ii) the amount by which the reactivity of an H in a CH_2 (or CH_3) is reduced (or increased) by introducing a geminal F (e.g. the reactivity of one H in a CH_2 as compared with the H in a CHF);
- (iii) the amount by which the reactivity of an H is reduced (or increased) by the introduction of a vicinal F (e.g. the reactivity of CH_3CH_2 as compared with CH_3CH_F);
- (iv) and (v) two parameters to allow for the ease with which a compound might be released from the surface of the cobalt trifluoride and so appear in the products.

TABLE 3

Comparison between Observed and Calculated^a Isomer Distributions in Partially Fluorinated Butanes

Compound ^b	*	C	Compound <u>b</u>	\$ا	c
	Observed	Calc.		Observed	Calc.
Nonafluorobutanes	3				
2	60	50	3	40	50
Octafluorobutanes	3				
4	4	3	7	21	23
5	11	16	8	4	2
6	43	47	9+10	14	8
Heptafluorobutane	98				
CF3CF2CF2CH3	<u>d</u>	0	14+15	16	17

(continued overleaf)

TABLE	3	(cont.))
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11	1	1	16	46	51
12	11	11	17	6	7
13	18	10	18	2	1
CF3CF2CH2CF2H	d	1			
Hexafluorobutane	s				
CF3CF2CFHCH3	d	0	23	36	35
CF3CFHCF2CH3	d	1	24	11	3
19	7	0	CF3CFHCH2CF2H	d	1
CF3CF2CH2CFH2	d	0	25	3	8
20	1	4	26	2	2
21	9	11	27+28	28	29
22	2	5	CF3CH2CH2CF3	d	0
Pentafluorobutan	es				
29	4	5	33	30	24
30	24	1	34	9	18
31+32	30	40	35	6	8
е					
Tetrafluorobutan	es				
36+37	100	44	CFH2CF2CH2CH2F	đ	10
CF2HCH2CF2CH3	d	9	CFH2CF2CFHCH3	d	10
CF2HCH2CFHCFH2	d	18	f		
Trifluorobutanes					
38	100	3	CFH ₂ CFHCFHCH ₃	d	34
СF2HCH2CFHCH3	đ	7	CFH2CFHCH2CFH2	d	36
CFH2CH2CF2CH3	d	19	ğ		

a See Appendix. b See Table 1 for identities of numbered compounds. C The figures are %, with each set of isomers being treated separately (e.g.: the sum of all the $C_{4}F_{7}H_{3}$ isomers = 100; the sum of all the $C_{4}F_{8}H_{2}$ isomers = 100; etc). d Not detected. e No other isomer detected and none predicted to occur to >2%. f As e, but none >4%. g No other isomers detected or predicted. The best set of parameters gives the results shown in Table 3. With notable exceptions (to be discussed later), the fit between the observed data and the calculated is quite reasonable given the likely errors involved. Since some of these sets of isomers only comprise a small amount of the reaction mixture (e.g. the $C_4F_5H_5$ at 8.9%), and since even the major isomer of a set may occur to only a small extent (e.g. the major $C_4F_5H_5$ (33) at 2.5%), then expressing the results in the way we have that is each set of isomers at 100% (footnote <u>c</u> of Table 3) - magnifies any errors. Add to this the difficulty of measuring the many small quantities accurately, then apparently large differences between 'calculated' and 'observed' can be quite acceptable as a test of the model.

Part of the main path (but see later) of fluorination then becomes (the steps shown before compounds 36 + 37 are speculative and are not part of the model):



Scheme 1

There are, of course, other compounds on the full main path (or CH₂ groups would not appear in any products), and it is quite possible that, particularly in the later stages of the fluorination, radicals could go directly to fluoro-compounds ($R + CoF_3 \rightarrow RF + CoF_2$) without the intervention of carbocations.

However, there are a set of compounds for which the model fails very badly.

They are:

		Observed	<u>Calc.</u>
CH3CF2CFHCH3	(38)	100	3
CFH ₂ CF ₂ CF ₂ CH ₃	(30)	24	1
CF2HCF2CF2CH3	(19)	7	0
CFH2CF2CF2CFH2	(24)	11	3

These compounds are clearly structurally related. Other compounds which share the same structural pattern are $CFH_2CF_2CFHCFH_2$ (33; observed 30, predicted 24) and $CFH_2CF_2CF_2CF_2H$ (13, 18 <u>vs</u> 10) but since these are predicted to occur in quite significant amounts. It is not obvious, given the crudity of the model, that they are present in anomalously large amounts. It is also just possible that $CH_3CFHCF_2CFH_2$, which could be a member of the anomalous set, occurs in Fraction H (there are CH_3 and CFH_2 signals at the expected positions showing the expected couplings): if this were so, then the compound would also be present in anomalously large amount - about 20% compared to the calculated 10%.

One can only speculate why this set of compounds is present. Perhaps early in the fluorination alkenes might form:

 $\begin{array}{ccc} CH_3CH_2CH^+CH_3 & \xrightarrow{-H^+} & CH_3CH=CHCH_3 & \xrightarrow{COF_3} & \longrightarrow & CH_3CFHCFHCH_3 \\ (See Scheme 1) & & & & & \\ \end{array}$

 $\xrightarrow{-HF} CH_3CH=CFCH_3 \xrightarrow{CoF_3} CH_3CFHCF_2CH_3 (38)$

Simple F for H replacement 33,30,etc.

Scheme 2

This sequence cannot be the only one - compounds with CH_2 groups are quite common (~6.5% of the total reaction product): furthermore, starting the model calculations with 38 gives predictions for the amounts of many of the more highly fluorinated products which are very far from those observed, whatever the choice of parameters in the model. If the anomalously large amounts of the compounds which could be formed by

Compound	Compound				hemical	Shifts				Coupling
	No.	-	~	ø	4	ы	9	2	æ	Constants (Hz) ^C
1 2 3 4 5 CF3CF2CFH2	4	81.5	128.4	124.5	p	5.23				J ₁₃ = 9.3(Lit. 9.4); J ₁₄ = 2.6
	Lit.[7]	81.0	127.7	123.7	242.3	5.33				(2.7); J ₃₆ = 12.0(12.0); J ₄₅ = 46.0(46.6)
1 2,3 45 6 7 CP ₃ CF ₂ CFHCF ₂ H	сл	83.6	124.6	130.6	218.0	5.6	130.4	4.05		J14 = 11.1; J16 = 1.4; J23 =
: ;										294 ; $J_24 = 8.3$; $J_{25} = 5.7$; J_{26}
										$= 9.5; J_{34} = 15.5; J_{35} = 12.1;$
										$J_{36} = 7.2; J_{45} = 45.5; J_{47} =$
										$6.6; J_57 = 4.3; J_67 = 53.7$
1 23 4 5,67										
CF3CFHCF2CF2H	9	74.9	216.1	5.0	130.2	136.3	141.9	4.19		$J_{12} = J_{14} = 10.9; J_{13} = 6.5;$
										$J_{23} = 45.0; J_{56} = 308; J_{57} =$
										$51.0; J_{67} = 53.0$
123 re.ure.re.re.u	Ű	6 0 0 1	0							
ur Znur Zur Zur Zu		7.001	÷. UO	1.161						$12 \approx 3c$
	Lit.[7]	137.3	3.98	130.5						

 $^{19}\mathrm{F}$ and $^{1}\mathrm{H}$ NMR Spectra^a of Polyfluorobutanes

TABLE 4

1 2 3 4 CF3CF2CH2CF3	8	q	þ	7.47	p				J13 = 0.7; J23 = 16.2; J24 =
	Lit.[8]	86.3	113.8		61.9				^J 34 = 9.5
1 23 CF3CFHCF3 (meso)	9 0	78.1	211.4	5.53					J ₂₃ ≈ 51. The 78.1 signal shows apparent triplet (9.4Hz) and doublet (6.1Hz) couplings.
1 23 CF3CFHCFHCF3 (±)	10 Lit.[10]	77.8 75.6	220.5 221.3	5.28 4.25					The -CFHCFH- segment forms an AA'XX' sub-spectrum with J _{AX} = 45.1; J _{AX} ' = 22.6; J _{AA} = 2.6; J _{XX} = 1.5. The 77.8 signal shows apparent triplet (9.4Hz) and
1 2,3 45 67 CF3CF4CFH2	11	83.9	125.1	131.1	208.6	ب	237.2	ų	doublet (6.0Hz) couplings J14 = 10.1: J16 ≈ 2: J23 =294 J67 = 46.2
1 234.5 67 CF3CFHCF2CFH2	12	75.2	215.4	¢.	119.4	125.6	239.8	فين	J12 = J14 = J15 = 10.3; J13 = 5.9: J16 = 2.1; J23 = 44.3; = 288; J46 = J56 = 14.6; Je7 = 46
									(continued overleaf)

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1 2 3 4 56 CF2HCF2CF2CFH2	13	138.2	4.04	132.4	125.2	243.5	5.31			$J_{12} = 52.5; J_{13} = 5.7; J_{14} = 8.7; J_{15} = 2.8; J_{23} = 5.3; J_{35} = 5.7; J_{45} = 15.0; J_{46} = 12.4$ $J_{56} = 46.0$
1 23 45 6 7 CF ₃ CFHCFHCF ₂ H (A)	14	77.1	216.8	ŝ	213.4	2 1	131.7	4.0		J12 = J14 = 10.3; J13 = 5.6; J23 = J45 = 45; J67 = 54.1
1 23 45 6 7 CF3CFHCFHCF2H (B)	15	7.77	220.5	ž	220.5	ر م	133.6	4.0		J12 = 9.9; J13 = 5.8; J14 = 11.0; J16 = 2.0; J26 = J46 = J56 = 10.2; J67 = 53.6
1,23 4 56 7 8 CF2HCF2CFHCF2H	16	134.2	144.2	4.1	130.0	219.9	5.2	130.7	4.0	J12 = 310; J13 = 52.2; J23 = 53.5; J45 ≈ J57 ≈ 9; J56 = 44.6 J78 ≈ 52
1 2 3 4 5 CF3CH2CF2CF2H	17	62.0	7.18	116.2	136.8	4.26				J12 = J13 = 9.4: J14 = 1.8: J23 = 15.4: J35 = 2.8: J45 = 53.5

TABLE 4 (cont.)

1 23 4 5 CF ₃ CFHCH ₂ CF ₃	18	81.2	200.8	сц.	7.45	65.2				J12 = 10.6; J13 = 5.8; J23 ≈ 45 J25 = 7.4; J45 ≈ 10.0
1 2 3 4 5 CF2HCF2CF2CH3	19	137.0	4.08	132.3	108.0	8.26				J15 = 51.5: J13 = 5.6; J14 = 7.6: J23 = 5.5: J35 ≈ 1.2: J45 = 19.5
1 23 45 67 CP3CPHCFHCFH2	20	76.7	فس	G (ن ب	ŝ	с н	ŝ.		J12 = J14 = 10: J13 = 6: J16 ≈ 1.5
1,23 4 56 78 CF2HCF2CFHCFH2	21	137.3	141.3	я ц	130	209.3	4 -1	237	6 ⊷.	J12 = 315: J13 ≈ J23 ≈ 54
1 2 3 45 CF3CH2CF2CFH2	22 Lit.[11]	62.9 62.7	7.18 7.5	107.5 106.7- 108.5	235.0 231	f 6.0				$J_{12} = 10.2(Lit. 9); J_{13} = 9.6$ $(9.4); J_{14} = 2.0; J_{23} = 14.4$ $(13); J_{24} = 2.1(2); J_{34} = 14.4;$ $J_{12} = 2 & 8. J_{12} = 4.6 & 6.47 & 3)$
1 2 345,6 78 CF2HCFHCF2CFH2	23	130.3	3.99	217.5	مب	119.3	124.5	239.8	5.46	$J_{12} = 53.5; J_{13} \approx J_{15} \approx J_{16} \approx 8$ $J_{23} = 8.4; J_{24} = 3.6; J_{35} = J_{45}$ $=J_{57} = 14.6; J_{58} \approx 7; J_{78} = 46$
										(continued overleaf)

TABLE 4 (cont.)								
12 3 CFH2CF2CF2CFH2	24 ^e	243.9	ولينا	125.7				$J_{12} = 45.7$
123456								
cF_hcF_cH_cF_h	25	136.5	e.	115.2	7.46	114.5	6 -4	$J_{12} = 53.4; J_{15} = 1.9; J_{34} = J_{45} = 15.9; J_{35} = 5.8; J_{46} = 4.8$
1 2 34 5 6 CF ₃ CH ₂ CFHCF ₂ H	26	65.1	7.5	201.5	f	133.85	Ţ	J12 = 10.4(Lit. 11); J13 = 7.3:
	Lit.[11]	65.0	8.0	202.0	5.6	131.4, 134.4	4 .6	J35 = J45 = 12.6(12.2): J56 = 53.6(48)
1 2 34 CP2HCFHCFPCF2H (A)	27 ^e	131.9	4.07	220.4	5.22			$J_{12} = 55; J_{34} + J_{36} = 41$
1 2 34 CF ₂ HCFHCFHCF ₂ H (B)	28	132.7	4.04	216.8	5. 3			J12 = 53; J34 * 45
1 2 34 5 6 CF2HCFHCF2CH3	29	đ,	4 4	μų	ŝ	¥4	8.3	J36 = 2.9; J56 = 19.5
12 3 4 5 CFH ₂ CF ₂ CF ₂ CH ₃	30h	244.1	4.27	125.3	108.2	8.28		J ₁ 2 = 46.2; J ₁ 3 = 14.1; J ₁ 4 = 4.5; J ₁ 5 ≈ 1; J ₂ 3 = 12.8; J ₃ 4
								$= 13; J_{35} = 1.5; J_{45} = 19.2$

(continued overleaf)

TABLE 4 (cont.)									
12 34 CFH2CFHCFH2FH2 (A)	36	233.8	ູ ະ ະ ເ	206.6	-5.1			$J_{12} = 47.3; J_{13} = 24.8; J_{1}$ 10.2; $J_{34} \approx 45-50$	
12 34 CFH2CFHCFH2 (B)	37	237.6	ະ ເ	203.2	-5.1			$J_{12} = 46.8$: $J_{13} = 20.7$: J_{1} . 14.7: $J_{34} \approx 45-50$	॥ प
1 2,3 45 6 СН ₃ сг ₂ сгнсн ₃	38 ^h	8.41	102.9	107.9	189.3	4 4 1	8 . 64	$J_{12} = J_{13} = 18.9; J_{14} = 2.$ $J_{23} = 255; J_{24} = 7.6; J_{25};$ $J_{26} \approx J_{36} \approx 1; J_{34} = 8.8;$ $8.5; J_{46} = 24.1; J_{56} = 6.3$	4; = 5.6 J35 =
a Run on a Perkin compounds or CC44 on the τ scale; second-order feat the central C-C b neccessarily zero signals; (ii) stro broad, incomplete by larger or over the aid of homo- the aid of homo- attributed.	-Elmer R1. solution remaining remaining tremaining ired (bey hured (bey hured (bey huresolv ly-resolv ly-resolv ly-resolv ly-resolv sind heterv imost eque	2B [at 6 s. Deco figures ond the ertheles ave been d-order ed hump. ignal. o-nuclea	MMEZ(1H upling are 19 are 19 simple s all h omitte d No d No g Uppe g Uppe r decou ts: it	<pre>() or 56 experime F shifts AB situe ave beer d when (ent; and t measur t masur t half c pling.</pre>	4MHz(19] 4MHz(19] s in ppm ation), i a analyst 1 (ii) the 1 (i) the 1 (iii) s ed. e of AB spe i These efore no	<pre>%)] or i > carrio upfield particu ed as ij celevan' se many Spectru ; two co ot entin</pre>	A Varian XL100 ed out on the X l from internal larly those of they were fir they were fir they were fir signals are o couplings are couplings are im very markedl lower half ob ompounds were i vely certain th	[1000HHz(1H) or 94.1(^{19}F)] on neat L100. b Figures <10 are ¹ H shift CFC\$2. ^C Many spectra show some compounds which are symmetrical al compounds which are symmetrical al st order. Omitted J-values are i bscured by stronger or overlappin present in a signal that it become y second-order. ^f Signal obscurve y second-order. ^f Signal obscurve scured. ^h Spectrum analysed with nseparable (see Experimental) and e signals have been correctly	t ts bout s s h

Compound			hemical	Shifts	٩	-	Coupling Constants ^C
	_	2	ę	4	5	9	(Hz)
12 3 4 5 (Z)-CFH=CFCF ₂ CF ₃ ^e	156.0	3.57	152.5	123.7	85.0		$J_{12} = 70.6; J_{23} = 13.5; J_{34} \approx 19$
1.2 3 4 5 6 CF2≡CFCF2CF2H ^f	91.6	108.1	141.1	123.1	137.3	4.60	J12 = 58.3; J13 = 39.0; J14 = 5.4; J23 = 116.5; J24 = 26.8; J25 = 3.3; J34 = 14.7; J35 = J45 =
							3.8; J₄6 = 3.0; J ₅₆ = 53.2
12 3 4 5 6 (Z)-CFH=CFCF ₂ CF ₂ H ^f	157.0	3.88h	158.2	124.8	138.3	4.88 ^h	J12 = 69.2; J13 = 8.2; J23 = 15.0; J56 = 53
							(continued overleaf)

TABLE 5

1 2 3 4 5 (E)-CF2HCF=CFCF3E	σ	4.00h	IJ	U	σ		$J_{12} = 51.3; J_{23} = 12.6; J_{24} = 3.5$
1 2 3 4 5 (Z)-CF ₂ HCF=CFCF ₃ ^f	120.7	3.99 ^h	149.3	151.3	57.9		J12 ≈ 50; J13 = 19.8; J14 = 12.4; J15 = 4.5; J23 =16.0; J24 ≈ 1; J34 ≈ 1.5; J35 ≈ 8; J45 = 12.3
(z)-cfh=cfcf2cfh2 ^e	158.5	3.10	156.5	117.8	263.3	5.39	$J_{12} = 69.4$; $J_{13} = 7.6$; $J_{14} \approx 1$; $J_{23} = 15.4$; $J_{24} \approx 1$; $J_{34} = 15.7$; $J_{35} = 2.5$; $J_{36} = 1.4$; $J_{45} = 19.3$; $J_{46} = 11.2$; $J_{56} = 46.3$
1 2 3 4 5 6 (Z)-CF2HCF=CHCF2H ^e	126.4	3.46	124.0	4.33	114.5	3.92	J12 = 52.8; J13 = 16.4; J23 = 7; J34 = 32.7; J45 = J46 = 7: J56 = 54.2
123456 CF2HCF=CFCFH2f (Z or E)	IJ	4.03 ^h	q	Ţ	Ţ	4.71	$J_{12} \approx 52.1; J_{23} = 11.5; J_{46} = 21.9; J_{56} = 47.5$
a, b, d As Table 4. ^h External TMS.	c Omitt	ed valu	es are 1	not nec	essarily	zero.	^e CC≉₄ solution. ^f C ₆ F ₆ solution. ^g Neat.

TABLE 5 (cont.)

Scheme 2 are added then <u>about</u> 10-25% of the fluorination could have proceeded down this path. This estimate only refers to compounds with three or more hydrogens, since those with less could be formed by either the Scheme 1 or the Scheme 2 route.

Alkenes could alternatively be formed in the <u>early</u> stages in the fluorination by HF elimination, either thermally or by fluoride ion catalysed elimination:

CH₃CH₂CHFCH₃ → CH₃CH=CHCH₃

Alkene-forming processes could only occur early in a fluorination. since it is known [17] that highly fluorinated compounds do not give alkenes over cobalt trifluoride (but they can do over KCoF₄). It is quite possible that alkene formation is, in fact, dominant at early stages in the fluorination. By invoking but-1-ene as well as but-2-ene, CH₃CH₂CF₂CFH₂ and CH₃CH₂CFHCF₂H could form in a way similar to compound 38 (see Schemes 1 and 2). Indeed, starting with a judiciously chosen mixture of 38. CH₃CH₂CF₂CFH₂, CH₃CH₂CFHCF₂H, and CH₃CFHCFHCFH₂, and using the parameters of our single-F-for-H model, the final composition of the fluorination mixture can be simulated quite well.

There are a few compounds where the amount predicted is much greater than the amount observed. Most of these (20, 22, 25, 34) are present in only small quantities and so the observed figures are particularly susceptible to error. Only two, compounds 31 and 32, are present in substantial amount (Taken together, 2.6% of mixture. Calc. for 31+32; 40% of $C_{4}H_{5}F_{5}$ isomers; obs. 30%). However, if the anomalous compound 30(CH₃CF₂CF₂CFH₂) is omitted from the $C_{4}H_{5}F_{5}$ set then the observed' figure for 31 and 32 rises to 39%. If this correction is made to all the pentafluoro-isomers the amount of 33 (CFH₂CF₂CFHCFH₂) also rises to 39% compared to the observed 24%; if, as discussed above, some of 33 arises from the "anomalous" route (i.e. from 38, CH₃CF₂CFHCH₃), then this fits in rather well.

Table 3 also lists predicted values for some compounds which have <u>not</u> been isolated. With the hepta-, hexa, and penta-fluorobutanes, these are all <2%. With the tetra- and tri-fluoro, the figures are higher; for the tetrafluoro, the major isomer 'predicted but not isolated' is expected to occur in less than half the amount of the isomers which were isolated,

and since these only comprise 0.8%. then the lack of detection is not too surprising. The only trifluoro-isomer detected is the anomalous one (38) discussed previously.

The other point we wish to discuss is skeletal rearrangement. In the butane case about 1-2% of the products are fluorinated 2-methylpropanes: a similar amount of fluorinated butanes occurred [3] in the fluorination of 2-methylpropane (in the original paper [3] we estimated that this amount was about 5%, but a reassessment of the results suggests that 1-2% is more accurate). Some of these 'rearrangement' products must be due to there being some 2-methylpropane in the butane feedstock, and <u>vice-versa</u> (although both samples were purchased as >99.5% pure): the amount of true rearrangement is therefore about 1%, starting with either C_4 -isomer.

Why is this amount so small? Lewis acid catalysed rearrangement of either C₄-hydrocarbon results in an equilibrium mixture of about 40% butane and 60% 2-methylpropane at 200^oC [18]. This is clearly not happening over CoF₃. However, if the rearrangements involve carbocations, then for either C₄-isomer to rearrange to the other, a primary carbocation would have to form: since these are much higher in energy than either secondary or tertiary ions, then rearrangements are inevitably slow, so slow that they cannot, it seems, compete with fluorination:

Primary carbocations can be avoided with longer chain alkanes than C4 by invoking protonated cyclopropanes, and extensive rearrangements do, in fact, occur during fluorination (e.g. hexane ~25%; octane ~50% [4]). The C₄-isomers cannot avoid primary carbocations if they are to rearrange - not even if protonated cyclopropanes are invoked. Lewis acid catalysed isomerisation between butane and 2-methylpentane only occurs because there is no other competing process - such as fluorination - and so the slow reactions via primary carbocations take place.

EXPERIMENTAL

Fluorination of Butane

Butane (890 g) was fluorinated in 9 portions by passage over a stirred bed of CoF_3 (10 kg) in a reactor of the type described before [16] at

140-230°C. Residual products were swept from the reactor with $N_2(20 \text{ dm}^3/\text{h})$ for 2.5h through a trap containing NaF pellets (to remove HF) and collected in a trap cooled in liquid air. The combined products (1921 g) were dried over P_2O_5 and distilled through a vacuum-jacketed column (1.2 m long) packed with Dixon-gauze nickel spirals; fractions taken are recorded in Table 6.

TABLE 6

Fraction	Wt(g)	b.range (^o C)	Compounds ^a in Fraction
A	57.6	<16.4	1, <u>2</u> , <u>3</u> , 9 (39)
В	101.4	16.4-24.6	<u>2</u> , <u>3</u> , <u>8</u> , <u>9</u> (18)
С	104.2	24.6-32.2	(2),(3), <u>4</u> , <u>5</u> ,6,8,9,18
D	50.0	32.2-33.6	4, <u>5</u> , <u>6</u> ,(9),18, (40)
E	151.6	33.6-35.7	<u>6</u> ,10,(18),(19)
F	128.9	35.7-42.8	6,7,10,(11), <u>12</u> ,17,19,38,
			(41),(42),(47)
G	149.6	42.8-46.6	<u>7</u> ,(10),12,(14),(15),17, <u>30</u> ,
			(38),(41)
Н	131.8	46.6-55.0	7,(12),13, <u>14,15</u> ,16,22,(26),
			30,(43)(44),(46)
I	162.8	55.0-57.2	13,(14),(15), <u>16</u> ,(25),(26),(29),
			(43),(44),(46)
J	112.6	57.2-57.9	<u>13, 16, (25), (26), 27, (29), (43),</u>
			(45),(46)
К	43.8	57.9-64.0	<u>13,16</u> ,23,25,(26), <u>27</u> ,(29),(45),
			(49)
L	96.9	64.0-66.7	21, <u>23</u> ,24,(25), <u>27</u> ,(29),(49)
м	245.0	66.7-69.2	(20),21, <u>23</u> , <u>24</u> ,27,28,(48)
N	39.4	69.2-71.2	23, <u>24,28</u> ,33,(34),(48),(50),(51)
0	70.8	71.2-75.0	24, <u>28,33</u> ,34,35,(50),(51)
P	72.8	>75.0 ^b	<u>31,32</u> ,33,34,35,36,37,(50),(51)

Summary of Fractional Distillation

^a See Table 1 for formulae corresponding to compound numbers. An underlined compound is present to >20% in a particular fraction: a compound in parenthesis is present to <3%. ^b Pot residue.

Separation of Distillation Practions by Gfc

Five columns were employed: unit 1 - 35 mm dia x 5.5 m, packed with dinonyl phthalate on Celite (1 : 2); unit 2 - as unit 1 but 75 mm dia.; unit 3 - as unit 1 but packed with Kel-F oil on Celite (1 : 4); unit 4 - 15 mm dia x 2 m, packed as unit 1; unit 5 - a Pye 104 instrument, column 1 cm dia x 2 m, packed as unit 1.

All were used with N₂ carrier gas and katharometer detection. With each separation, the unit no., the N₂ flow-rate (dm^3/h) (units 1-4) or inlet pressure (psi) (unit 5), and the temp. (^oC) are stated, in that order.

<u>Fraction A</u> (13.0 g) was separated (1;9.25;58) into (i) perfluorobutane (6.35 g), containing a little (<10%) perfluoro-2-methylpropane as evidenced by an ir peak at 1000 cm⁻¹, identified by ir [5] and (ii) a mixture of nonafluorobutanes (0.4 g).

<u>Fraction B</u> The three main peaks of B (25.9 g) were separated (2;40; 57); the first and third (4.75 g) were rejected and the second (18.2 g) was shown by ir [5] to be an approximately 3:2 mixture of $1\underline{H}$ - and $2\underline{H}$ -nonafluorobutanes (2,3).

<u>Fraction C</u> (32.0 g) was separated (2;45;52) into (i) 2<u>H</u>. 2<u>H</u>-octafluoropropane (8, 0.7 g) b.p. 18° C (bp [20] 18° C); (ii) 1<u>H</u>, 1<u>H</u>-octafluorobutane (4, 5.2 g) b.p. $27-28^{\circ}$ C; a mixture (6.3 g, <u>ca</u>. 2:1) of 2<u>H</u>, 3<u>H</u>-octafluorobutane (9) and 2<u>H</u>,2<u>H</u>,3<u>H</u>-heptafluorobutane (18). identified by ir (see later) and nmr; (iv) 1H,2H-<u>octafluorobutane</u> nc (5, 8.6 g), b.p. $30-31^{\circ}$ C, ms peaks at (m/e) $183(M^{+}-19)$ and 83 (CF₂HCFH⁺), but no peak at 101 (CF₃CFH,⁺); (v) 1H,3H-<u>octafluorobutane</u> nc (6, 2.7 g), b.p. 34-34.5°C, ms peaks at (m/e) $183(M^{+}-19)$, 101 (CF₃CFH⁺ or CF₂HCF₂⁺) and 95 (C₃F₃H₂⁺).

Peak No	Main Components ^b , ^c	Peak No	Main Components ^b ,C
I	1	X	14(E),15(E),13(L)
II	2,3	XI	16(E),24(L)
III	8	XII	27(E),21(L),23(L)
IV	4	XIII	28
Vd	9(E),18(L)	XIV	33
VI	5	XV	35
VII VIII	6(E),19(L) 10(E),12,17,30(L)	XVI XVII } e	31,32
IX	7	$\begin{bmatrix} XVIII \\ XIX \end{bmatrix} e$	36,37

Compositions of Ggc Peaks a

As displayed on a Pye 104 instrument (5 mm dia x 3.5m column packed with dinonyl phthalate on Celite (1:5), N₂ pressure 15 psi, temp. 60°C).
b Only major components are listed. See text for minor ones. ^C Where more than one compound is listed beside a peak number. all had approximately the same retention time; 'E' indicates a compound concentrated mainly in the relatively lower-boiling distillation fractions in which it occurs, and 'L' one concentrated in the relatively higher.
d A peak appeared between V and VI in some fractions: it was butane.
e Although displayed as distinct peaks, these compounds were not separated.

<u>Fraction G</u> (35.0 g) gave (2;68;52) two main peaks: (i) a mixture (9.7 g) of four (nmr analysis) components (10,12,17,30); (ii) a mixture (3.7 g) of (i) and (iii); and (iii) $1\underline{H}, 4\underline{H}$ -octafluorobutane (7, 11.9 g), b.p. $44^{\circ}C$ (Lit. [19] $43^{\circ}C$), identified by ir [5].

<u>Fraction H</u> (41.0 g) separated (2:47:69) into (i) a mixture (<u>ca</u> 1:2:2. 6.8 g) of compounds 13, 14, and 15; and (ii) a mixture (25.5 g) of several other compounds, 16 being the major. <u>Fraction I</u> contained two major peaks. Separation (2;47;69) of 80.0 g gave (i) impure compound 13 (9.1 g); (ii) a mixture (16.3 g) of (i) and (iii); and (iii) impure compound 16 (39.7 g). Re-separation of (i) gave 1<u>H</u>,1<u>H</u>,4<u>H</u>-heptafluorobutane (13) of <u>ca</u>. 90% purity. b.p. 53-54^oC: re-separation of (iii) gave pure 1H,2H,4H-heptafluorobutane nc (16), b.p. 57-58^oC (Found: C,26.5; H,1.7. C4H₃F₇ requires C,26.1; H,1.6%), ms peaks at 165 (M⁺-19), 101(CF₂HCF₂⁺), 95(C₃H₂F₃⁺), and 83(CF₂HCFH⁺).

<u>Fraction L</u> This consisted mainly of one peak. This was separated (2;42;68) from 30.0 g as a mixture (<u>ca</u>. 1:1, 26.8 g) of mainly 1<u>H</u>,2<u>H</u>,3<u>H</u>,4<u>H</u>-hexafluorobutane-A (27) and 1<u>H</u>,1<u>H</u>,3<u>H</u>,4<u>H</u>-hexafluorobutane (23), (a small proportion of 1<u>H</u>,1<u>H</u>,2<u>H</u>,4<u>H</u>-hexafluorobutane (21) was detected by nmr), b.p. 64^oC, with an ir spectrum consistent with the presence of 27 (synthesised as described in the literature [6]) (Found: C,29.1; H,2.4. C₄H₄F₆ requires C,28.9; H,2.4**%**).

<u>Fraction N</u> (23.7 g) separated (2;68;71) into (i) several small peaks (9.1 g), and (ii) $1\underline{H}, 2\underline{H}, 3\underline{H}, 4\underline{H}$ -hexafluorobutane-B (28, 10.0 g) b.p. $71-72^{0}$ C, identified by ir.

<u>Fraction 0</u> This contained two major peaks. Separation of a small sample (<u>ca</u>. 0.5 g) (unit 4) gave (i) $1\underline{H}, 2\underline{H}, 3\underline{H}, 4\underline{H}$ -hexafluorobutane-B (28), and (ii) 1,2,2,3,4-pentafluorobutane (33) in about 80-90% purity.

<u>Fraction P</u> (28.4 g) was separated (2;69;103) into (i) several minor peaks (4.5 g); (ii) two peaks which were too close to be fully separated (21.5 g, in 1:1 proportion) - they were the 1,1,2,3,4-pentafluorobutane isomers 31 and 32 - b.p. 90° C (Found: C, 32.5; H,3.1. C₄H₅F₅ requires C,32.4; H,3.4%), ms peaks at 129 (M⁺-19:v.small), 83(C₂H₂F₃⁺), 65(C₂H₃F₂⁺) and 59(C₃H₄F⁺).

A further separation (5,15 psi,95) of 3.50 g in seven portions gave: (i) all peaks contained in (i) and (ii) above (2.44 g); and (ii) two overlapping peaks which were isolated as a 1:1 mixture (0.12 g) of the 1,2,3,4-tetrafluorobutane isomers 36 and 37, b.p. 110° C, ms peaks at 111 (M⁺-19 : v.small), $65(C_2H_3F_2^+)$ and $59(C_3H_4F^+)$.

2.3-Dichlorohexafluorobut-2-ene (80.7 g) was fluorinated in the usual way over $CoF_3(6 \text{ kg})$ at 230-240^oC. The product (78.5 g) showed one main peak on glc. Separation (unit 2) gave the mixed isomers of the title compound (54.2).

Reduction of 2,3-Dichloro-octafluorobutane

The dichloro-compound (13.7 g) was added dropwise over 100 min to a stirred suspension of lithium aluminium hydride (4.2 g) in ether (50 cm³) at 0°C. After 2h stirring, sulphuric acid (70%, 30 cm³) was added dropwise. The most volatile contents of the reaction flask were distilled into a cooled (-78°C) receiver and were then separated by glc (2;4.6;62) to give (in addition to the longer retained ether): (i) meso-2H,3H-<u>octafluorobutane</u> nc (9, 2.8 g), b.p. 25°C, top ms peak at 183(M⁺-19), and (ii) a mixture (1:1) of compound 10 and ether which was re-separated (3;10;54) to yield pure (\pm)-2H,3H-<u>octafluorobutane</u> nc (10, 2.8 g), b.p. 41°C, top ms peak at 183(M⁺-19).

Competitive Dehydrofluorination of the 2H, 3H-octafluorobutane Isomers

A mixture (2:1 of 9 and 10, 0.45 g) was passed in a stream of N_2 over 1h through molten KOH (26 g) at 225°C. The product (0.05 g), collected at -180°C. consisted (glc) of the starting isomers, but in 5:1 ratio. Isomer 9 therefore dehydrofluorinates about 2-3 times slower than isomer 10.

1.2-Dichloro-4H-heptafluorobutane

 $4\underline{H}$ -Heptafluorobut-1-ene [21] (7.5 g) and chlorine (2.9 g) were irradiated in a 30 cm sealed glass tube by two 20 watt fluorescent lamps (20 cm distant) for 1.5h. Distillation of the product gave $\underline{1,2-dichloro-4}H$ -heptafluorobutane nc (9.7 g), b.p. 80-82°C (Found : C, 18.9; H,0.5; Cf, 27.7; F,53.1. $C_4HCf_2F_7$ requires C,19.0; H,0.4; Cf.28.0; F,52.6%). This compound is mentioned in a Russian patent [22], but apparently without any properties being given.

The Reduction of 1,2-Dichloro-4H-heptafluorobutane

The dichloro-compound (2.5 g) in ether (20 cm^3) was added dropwise with stirring to a cooled (-65°C) solution of lithium aluminium hydride (0.75 g) in ether (50 cm^3) . After 2h at -65°C , the mixture was allowed to warm to room temperature and sulphuric acid $(60\%, 20 \text{ cm}^3)$ was added. The ether layer was separated, dried (MgSO₄) and fractionally distilled (15 cm column packed with glass helices) to remove the ether. The residue (<u>ca</u> 0.5 cm³) was separated by glc (unit 4) to yield (i) ether and (ii) a small amount (<u>ca</u> 0.1 g) of 1<u>H</u>, 2<u>H</u>, 4<u>H</u>-heptafluorobutane (16), identical by ir with the substance separated from fraction I.

Attempts to carry out the reduction at higher temperature or in THF lead to more complex products which could have arisen by initial alkene formation and then reaction of this with $LiAlH_4$.

Dehydrofluorination Experiments

(a) Mixture of 1H- and 2H-Nonafluorobutane (2 and 3)

The mixture (12.0 g) (from Fraction B), potassium hydroxide (22 g) and water (24 cm³) were shaken together in a sealed tube for 23 days at room temperature. The organic layer was separated (2;43;62) into (i) octafluorobut-2-ene (1.9 g) identified by ir, and (ii) 1<u>H</u>-nonafluorobutane (2.2 g).

(b) <u>1H,2H-Octafluorobutane</u> (5)

This compound (3.2 g) was passed through molten KOH (30 g) at 220° C over 40 min and the products (1.6 g) collected at -180° C. Separation (4;5.5;29) gave the major component, (Z)-1<u>H</u>-heptafluorobut-1-ene, ir peaks at 3110 and 1734 cm⁻¹.

(c) 1H, 3H-Octafluorobutane (6)

This (19.0 g) was treated as in (a), but for 10h at 100° C. Separation (1;13;67) gave (i) unknown (0.8 g): (ii) (Z)-1<u>H</u>-heptafluorobutane (1.0 g), ir peak at 1725 cm⁻¹; (iii) (E)-1<u>H</u>-heptafluorobutane (1.3 g), ir peak at 1720 cm⁻¹; and (iv) 1<u>H</u>,1<u>H</u>,4<u>H</u>-hexafluorobutane (19, 0.2 g).

(d) <u>1H,1H,4H-Heptafluorobutane (13)</u>

This butane (5.1 g) was treated as in (b) to give a product (4.2 g) containing one major and one minor component. Separation (3;5.5.56) gave (i) $(Z)-1\underline{H},4\underline{H}$ -hexafluorobut-1-ene (0.4 g), ir peaks at 3110, 2970, and 1734 cm⁻¹; and (ii) starting material (2.1 g).

(e) Mixture of 1H,2H,3H,4H-A-(27) and 1H,1H,3H,4H-(23)-Hexafluorobutanes

This mixture (10.1 g, <u>ca</u> 1:1 from Fraction L) was treated as in (a), but for 44h. The product (7.2 g) was separated (1;13;57) into: (i) unknown (0.2 g); (ii) (Z)-1<u>H</u>,4<u>H</u>,4<u>H</u>-pentafluorobut-1-ene (0.3 g),ir peaks at 3120, 2950, and 1732 cm⁻¹; (iii) (Z)-1<u>H</u>,2<u>H</u>,4<u>H</u>-pentafluorobut-2-ene (2.1 g), ir peak at 1720 cm⁻¹, ms peaks at 146(M⁺), 127(M-19), 95(CFCHCF₂H⁺ or CHCFCF₂H⁺), 82(CF₂HCF⁺), and 51(CF₂H⁺); and (iv) Z or E 1<u>H</u>,1<u>H</u>,4<u>H</u>-pentafluorobut-2-ene (0.3 g), ir peak at 1725 cm⁻¹.

APPENDIX

A Computor Program for Modelling Fluorination

Each hydrogen in a fluorocarbon is given a reactivity of either 1 (each H in a CH₃ or a CFH₂ or a CF₂H) or <u>n</u> (each H in a CH₂ or a CFH): this is modified by multiplying by <u>g</u> for each geminal fluorine and <u>v</u> for each vicinal. For example, each hydrogen in the CFH₂ group of a CFH₂CF₂-molety is assigned a reactivity of gv^2 .

In a molecule, the total reactivity is the sum of the individual reactivities. For example, $CFH_2CF_2CFHCF_2H$ has reactivity $2gv^2 + ngv^4 + g^2v$. The amount of a compound found in the final product depends on the amount formed and on the balance between its reactivity and the liklihood

of its release from the cobalt trifluoride surface. We have modelled release by assuming that it depends only on the number of fluorines in a molecule and not on their distribution. In our notation, each fluorine has the same $\underline{R}\underline{I}$ value, so that all pentafluorobutanes, for example, have the same release factor, $5R\underline{I}$.

If an amount A(i) of a compound is formed, then this is distributed between further fluorination and release from the cobalt trifluoride (and hence appearance in the product):

Amt. of i in product = $\underbrace{N \cdot R!}_{[reactivity(i)]^p + N.R!} X A(i)$

where N = no. of fluorines in i, and <u>p</u> is a disposable parameter (reactivity is taken to the power <u>p</u>) which helps to balance reactivity against release. In the case of $CFH_2CF_2CFHCF_2H$ (23) for example:

Amt. of 23 in product =
$$5 \cdot R I$$
 X Amt. of 23 formed
 $(2gv^2 + ngv^4 + g^2v)^p + 5 \cdot R I$

For CF2HCFHCFHCF2H (27 and 28):

Amt. of 27 + 28 in = ______X Amt. of 27 + 28 formed
product
$$(2g^2v + 2ngv^2)P + 5 \cdot Rt$$

So, even though the release factors are the same for 23 and for the pair 27 and 28, the amounts in the product would not be equal, even if the amounts formed were equal, because the reactivities differ.

The amount fluorinated to a given isomer is, in this model, obviously given by (In the case of the $CFH_2CF_2CFHCF_2H(23)$ ---> $CF_2HCF_2CFHCF_2H(16)$ conversion):

Amt. of 16 formed = $2gv^2$ X Amt. of 23 formed from 23 $(2gv^2 + ngv^4 + g^2v)^p + 5 \cdot Rf$

The amounts of each hexafluoro-isomer, for example, produced from all possible pentafluoro-isomers and released into the product are then summed and the result expressed as a percentage of the total amount of hexafluoro-isomers released.

The best fit was obtained by trial and error by adjusting $\underline{n}, \underline{g}, \underline{v}, \underline{R}, \underline{\ell}$, and <u>p</u>: this gave $\underline{n} = 2$; $\underline{g} = 0.25$; $\underline{v} = 0.4$; $\underline{R}, \underline{\ell} = 1$; and $\underline{p} = 3$. The results are given in Table 3. They are not very sensitive to $\underline{R}, \underline{\ell}$ and \underline{p} , and variations of \underline{g} and \underline{v} between 0.2 and 0.7 do not produce large disparities between "predicted" and "observed". They are more sensitive to \underline{n} ; increasing it from 2 to 5, for example, gave ridiculous predictions.

A similar program has been constructed for the fluorination of 2-methylpropane [3]: best values here were $\underline{n} = 10$; $\underline{g} = 0.5$; $\underline{v} = 0.5$; $\mathbb{R}^{g} = 100$; $\underline{p} = 3$. Here again there was an anomalous compound: there was much more CH₃(CF₂H)CFCFH₂ (compound 14 of reference 3) than predicted, relative to (CFH₂)₃CF (19 of ref. 3).

It is quite reasonable to argue that the probability of release of a fluorohydrocarbon from the cobalt trifluoride surface should depend on the types of fluorine (or hydrogen) in a molecule and not merely their number; for example, a $CF_{2}H$ group should contribute a different factor from two CFH_2 groups towards the probability of release. Nevertheless we have not allowed for this in the model because we feel that five disposable parameters are quite enough: more (one each for CH_3 , CH_2F , CHF_2 , CF_3 , CH_2 , CFH, and CF_2) would be unreasonable.

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