Journal of Fluorine Chemistry, 10 (1977) 523 – 540

Received: August 18, 1977

THE FLUORINATION OF 2-METHYLPROPANE OVER COBALT TRIFLUORIDE

JAMES BURDON, THOMAS N. HUCKERBY and ROBERT STEPHENS

Chemistry Department, The University of Birmingham, P.O. Box 363,
Birmingham B15 2TT (Great Britain)

SUMMARY

2-Methylpropane has been fluorinated over cobalt trifluoride at 140-200°C to give a mixture of at least 30 components, of which 22 have been identified with some certainty and five, more tentatively; this represents well over 95% of the reaction mixture. About 95% of the identified products were polyfluoro(2-methylpropanes); the rest were polyfluorobutanes. The fluorination was not completely random; there was a clear preference (by some 10 times greater than chance) for compounds in which the tertiary hydrogen had been replaced by fluorine. A scheme for the fluorination pathway is proposed. Attempts to dehydrofluorinate 1H,3H-pentafluoro-2-fluoromethylpropane failed.

INTRODUCTION

Ethane is only saturated aliphatic hydrocarbon whose partial fluorination by high-valency transition metal fluorides has been studied thoroughly [1]; the replacement of hydrogen by fluorine was largely random with both cobalt trifluoride and potassium tetrafluorocobaltate, and the products were almost all polyfluoroethanes with very little C-C bond cleavage.

In the saturated alicycles, cyclopentane and cobalt trifluoride gave a complex mixture of polyfluorocyclopentanes [2] in which the regioselectivity of the fluorination was low (except that there were no compounds containing CH_2-groups), but the stereoselectivity was high. Bicyclo[2,2,1] heptane [3], bicyclo[2,2,2] octane and its derivatives [4], and bicyclo[3,2,1] octane [4] have also been fluorinated over cobalt trifluoride; in the first two cases there was a marked preference against replacing the bridgehead hydrogens; a

Table 1

Summary of Fractional Distillation

Fraction	Weight (g)	b. range (°C)	Main Components[a]
A	51.5	15.7-18.6	1,3,4,5
B	50.9	18.6-28.1	3,4,5
C	33.5	28.1-34.3	4,5,7,8
D	78.5	34.3-38.6	7,8
E	29.7	38.6-41.7	7,8,9
F	40.2	41.7-44.0	8,9
G	48.6	44.0-53.3	8,9,11,12,12a
H	23.3	53.3-54.6	11,12,12a
I	29.1	54.6-55.4	12,12a
J	29.4	55.4-55.8	12,12a
K	61.8	55.8-56.4	12,12a
L	43.2	56.4-58.7	12,14
M	21.3	58.7-65.2	12,14,16
N	12.8	65.2-69.5	14,16
O	22.0	69.5-70.0	14,16
P	47.9	> 70.0[b]	16,17,18,19

[a] Dominant components underlined. Every fraction contained minor amounts of other components - for example, K contained traces of 13 and 14 in addition to 12 and 12a; trace amounts of unidentified compounds were also commonly present - see Text. See Schemes 1 and 2 for formulae of compounds.

[b] Pot residue.

considerable amount of rearrangement, probably *via* carbenium ion intermediates, occurred with both bicyclo-octanes. Rearrangement, again presumably of carbenium ions, has also been noted [5] in the fluorination of 2,2-dimethylpropane, when only perfluoro(2-methylbutane) was isolated, and in the fluorination of medium rings (> C_7) [6], when perfluorinated smaller rings were among the products.

In this paper we report the fluorination of a second aliphatic hydrocarbon, 2-methylpropane, and in a subsequent paper [7] we will describe a similar study on butane.

RESULTS

The fluorination was carried out in the usual way [1-8] in the range 140-200°C; as expected the extent of fluorination increased with temperature. Glc showed 19 peaks and the relative amounts are shown in Table 2. [The method of analysis - peak area ratios - is only approximate and so the figures in the Table should be taken only as rough guides to the true composition]. Separation by fractional distillation (Table 1) and preparative-scale glc gave nine compounds (1, 3, 4, 5, 7, 8, 12, 16, and 19 - see Scheme 1 for formulae) in a pure state. All were polyfluoro(2-methylpropanes) and their structures were determined quite straightforwardly from elementary analyses, mass spectra, and, mainly, NMR spectra; chemical shift data and geminal H-F couplings were quite sufficient for identification, although, as noted in Table 3, other regularities were also present. The shift ranges observed were in complete accord with literature data [9] as were the geminal H-F couplings. Table 4 lists the NMR parameters for all the polyfluoro(2-methylpropanes) which have been identified with some certainty. Many of the spectra showed evidence of second-order coupling (beyond the AB type): this has been ignored in analysing the spectra which have been assumed to be first-order except for AB situations. This may introduce slight errors in the coupling constants, but it in no way affects the structural assignments.

Further evidence for the structures of 12 and 16 was obtained by their partial fluorination; in each case the expected products were formed.

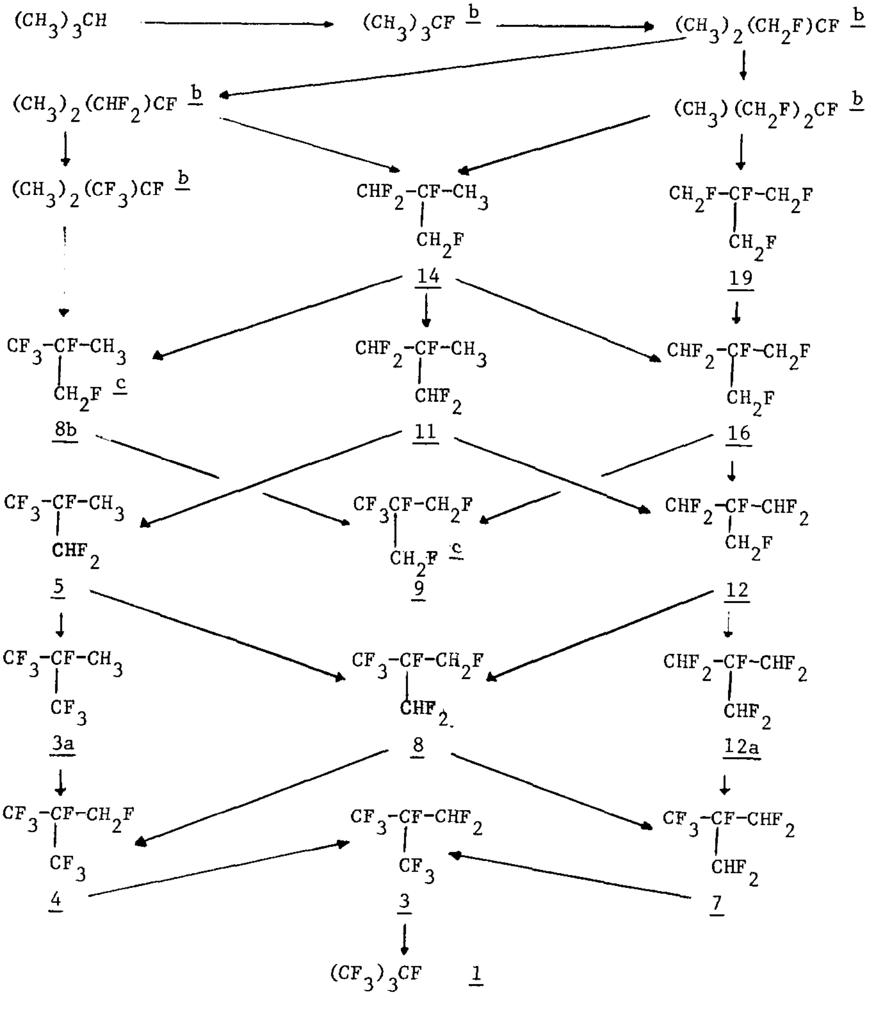
Six other polyfluoro(2-methylpropanes) (3a, 11, 12a, 13, 14, and 14a) have been almost certainly identified correctly from NMR data obtained on the distillation Fractions A-P (Table 1). These six compounds could not be obtained in a pure state because their boiling-points and glc retention times were too close to those of more predominant components. There is perhaps a doubt about the structure of 14a, since two of the expected NMR signals were obscured by those of other components. It should be noted that 13 and 14a each contain a tertiary C-H group. This apparently leads to ^{19}F NMR shifts for CF_3 and CF_2H groups which lie below the ranges quoted; in 13 the

Table 2. Composition of Fluorination Mixture

Compound No. or name [a]	% present [b]
1,2	tr. [c]
3	2
3a	tr.
4	2
5	4
6	tr.
7	5
8	14
8a, 8b	tr.
9	4
10	tr.
11	3
12	24
12a	16
13	2
14	6
14a	tr.
15	1
16	15
17	1
18	1
19	tr.
2*H*-nonafluorobutane	tr.
2*H*,2*H*-octafluorobutane	tr.
1*H*,4*H*-octafluorobutane	tr.
1*H*,3*H*-octafluorobutane	tr.
1*H*,1*H*,4*H*-heptafluorobutane	tr.
1*H*,2*H*,4*H*-heptafluorobutane	tr.

[a] See Schemes 1 and 2 for formulae. Compounds are numbered in order of glc retention time (dinonyl phthalate on Celite). [b] From glc peak area ratios (katharometer detector) in the total crude fluorination product. Compounds 3a, 12a, and 14a had the same retention times as 3, 12, and 14: their relative amounts were determined from the ^{19}F nmr spectra of the fractions which contained them (Table 1). 8a and 8b may or may not have the same retention times as 8 (see text). The polyfluorofluorobutanes, other than 10 (see text), were determined from the ^{19}F nmr spectra alone. [c] tr = trace (<0.5%)

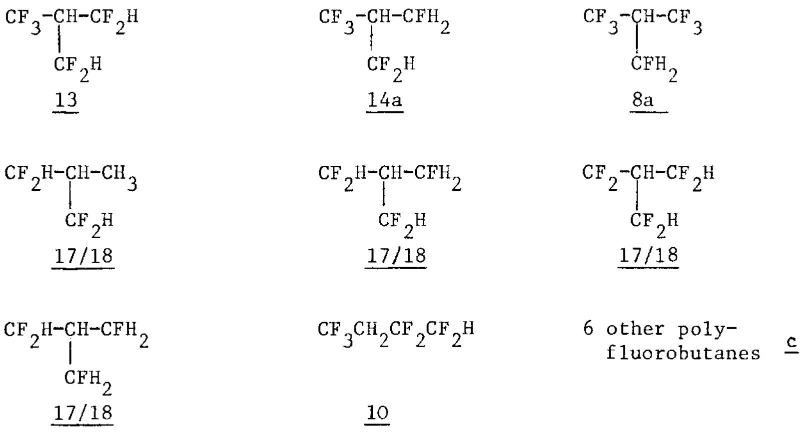
Scheme 1 Possible Pathways in the Fluorination of Isobutane over Cobalt Trifluoride [a]



---

[a] Compounds are numbered in order of glc retention time. Other numbered compounds are identified in scheme 2: compound 2, 6, and 15 have not been identified at all. [b] Not found in fluorination mixture. [c] Presence in fluorination mixture very uncertain: see text for further discussion.

Scheme 2 Other[a] Products and Possible[b] Products from the Fluorination of Isobutane over Cobalt Trifluoride



$CF_3-\underset{\underset{CF_2H}{|}}{CH}-CF_2H$ 13

$CF_3-\underset{\underset{CF_2H}{|}}{CH}-CFH_2$ 14a

$CF_3-\underset{\underset{CFH_2}{|}}{CH}-CF_3$ 8a

$CF_2H-\underset{\underset{CF_2H}{|}}{CH}-CH_3$ 17/18

$CF_2H-\underset{\underset{CF_2H}{|}}{CH}-CFH_2$ 17/18

$CF_2-\underset{\underset{CF_2H}{|}}{CH}-CF_2H$ 17/18

$CF_2H-\underset{\underset{CFH_2}{|}}{CH}-CFH_2$ 17/18

$CF_3CH_2CF_2CF_2H$ 10

6 other poly- fluorobutanes[c]

[a] See Scheme 1 for remaining products [2,6, and 15 have not been identified at all]. [b] The identities of 8a, 17, and 18 are very uncertain and the text should be consulted on this point and for further discussion of compounds 10 and 14a. [c] See Table 2.

CF_3 absorbed at 64.5 ppm and the CF_2H at 122.6; in 14a the CF_3 was at 66.7 and the CF_2H at 124.

There is a possible problem in equating a peak on the glc trace of a particular Fraction with a set of signals in the ^{19}F NMR spectrum of the same Fraction. For compounds 3a, 11, 12a, 13, 14, and 14a, however, this difficulty did not materialize. 3a had the same glc retention time as 3 but it was the only significant impurity in it; 12a, which had the same retention time as 12, was in much too large an amount in Fractions H-K for there to be any confusion; for 11, 13 and 14, the size of each of their glc peaks rose and fell in parallel with the NMR signals attributed to them in the relevant Fractions; and with 14a, the glc trace for Fraction K, for example, showed a peak at the position for compound 14, although the ^{19}F NMR spectrum showed clearly that no 14 was present.

Seven polyfluorobutanes also belong to the "almost certainly identified" category. They were picked out from the ^{19}F NMR spectra of the crude distillation Fractions A-P by matching signals with their known [7] spectra.

2H-nona- and 2H,2H-octa-fluorobutane were identified in Fraction B, 1H,1H,4H- and 1H,2H,4H-heptafluorobutane in Fraction J, and the others and compound 10 (scheme 2) in Fraction F. None of the polyfluorobutanes were present in more than trace amounts and their total quantity, even including possible unidentified compounds, cannot be more than 5%.

The problem referred to above, that of equating peaks on a glc trace with ^{19}F NMR signals, has not been solved for compounds 8a, 8b, 9, 10, and 1H,3H- and 1H,4H-octafluorobutane. In Fraction F, which is typical, the relative sizes of peaks 9 and 10 (at least 2:1) on the glc trace did not correspond to any pair of sets of peaks in the ^{19}F NMR spectrum: there was no set of signals of a minor component of Fraction F [the major compound (∿ 85%) was 8] which was twice as big as any of the others; furthermore, there was a peak with the same retention time as 11, and yet there was no 11 present according to NMR. It is clear, therefore, that the minor components of Fraction F do not have boiling points that parallel their glc retention times. We have not, therefore, been able to equate peaks 9 and 10 on the glc trace with sets of signals in the NMR spectra and hence with structures. What we have done is to arbitrarily assign a polyfluoro(2-methylpropane)-with-tertiary-F structure to peak 9 merely because it is the major component of the possible contenders (8a, 8b, 9, and 10, and 1H,3H-, and 1H,4H-octafluorobutane) in the fluorination mixture. We have assigned the 1H,3H,3H-heptafluorobutane structure to peak 10, again rather arbitrarily because this butane appears to be the second biggest component, according to ^{19}F NMR, of about the correct boiling point.

Up to this point, some 90-95% of the crude fluorination mixture has been identified: it must be frankly admitted that our remarks on the structures of the components remaining (8a, 8b, 9, 17, and 18) about which we have any evidence at all is highly speculative. [Structure 10 does not come into this category. It is undoubtedly present - its ^{19}F NMR signals were quite clear - but it is not at all certain that the structure given in scheme 2 should be equated with peak 10 on the glc] The difficulty arises because these compounds are in such small amounts in any Fraction: Fraction F, for example, contains, according to its ^{19}F NMR spectrum, 80-90% of 8, 3-4% 10, 4-5% 8a, 2-3% each of 1H,3H- and 1H,4H-octafluorobutane, about 1% each of 9 and an unknown, and about 0.5% each of 8b and at least one other unknown. [The labels 8a and 8b are merely a convenience - the compounds may not have the same retention times as 8]. The only ^{19}F NMR signals for 8a, 8b, and 9 that could be clearly seen were those from the

CF_3-groups; the others were obscured by signals from 8 or were expected to be weak (CF) or broad and weak ($C\underline{F}H_2$). It is possible, by following trends in the ^{19}F NMR chemical shifts and the coupling constants of the polyfluoro(2-methyl)propanes of established structure (Table 3) to predict the parameters for the compounds assigned the structures 8a, 8b, and 9.

As an example of a "prediction," consider the CF_3-group of structure 9: when the CF_2H group in 7 is changed to a CFH_2 in 8, the chemical shift (see Table 4 for data) of the CF_3-group changes by + 1.8 ppm (+ 2.2 if the 3 → 4 change is used); therefore, carrying out the same change on compound 8 (to produce structure 9) should cause the CF_3-group to shift by the same amount - from 76.7 ppm to 78.5 or 78.9 - say 79. This CF_3 signal should (Table 2) also be a quartet J ∿ 7.5 Hz. There is, in fact, just such a signal [a quartet (J ∿ 7.5 Hz) at 79 ppm] in Fraction F. Furthermore, the CFH_2-group of structure 9 is predicted to be a triplet at about 242 ppm - there is a weak triplet in Fraction F at 242.6 - and the CF to resonate at 188-192 ppm; this is not visible but it could be obscured by the CF of 8. For structure 8b, a triplet (J ∿ 7.5 Hz) at 83 ppm is predicted - Fraction F has such a signal at 82 ppm - but there are no signals observable at the other predicted positions, perhaps because of the very small (∿ 0.5%) amount of this compound present. For structure 8a, the CF_3-group is predicted to be a triplet (J ∿ 7.5 Hz) at 67 ppm [that is, below the range for CF_3-CF signals and akin to the CF_3-CH signals of compounds 13 and 14a] (observed, in Fraction F, a triplet (J ∿ 8.5 Hz) at 67.1 ppm) and the CFH_2 a triplet at about 235 ppm (a very weak signal at about 233 ppm is present in Fraction F): there are also weak signals in the ^1H spectrum of Fraction F at ∿ 7.0 τ and 8.5 τ which can be attributed to CH and CH_3 signals.

Peaks 17 and 18 are only present in Fraction P, and their glc retention times are too close to that of 16 for separation. There were two CF_2H-signals of approximately equal intensity (this excludes 15 from consideration as glc indicated that it was present in less than half the amounts of 17 or 18, which were about equal) in the ^{19}F NMR spectrum of Fraction P at 123.7 and 122.5 ppm: the predicted positions for four of the possible structures for 17 and 18 (see Scheme 2) are about 125 ppm. It should be noted that these figures lie about 10 ppm below the range given for $C\underline{F}_2H$-CF signals (Table 3); this is typical of $C\underline{F}_2H$-CH compounds, if this feature of 13 and 14a can be relied upon. There is also a weak triplet (J ∿ 45-50 Hz) at 234.7 ppm (approximately as expected for some of the 17/18 structures of Scheme 2) and in the ^1H spectrum there are weak signals in the CH and

Table 3

Chemical Shift (^{19}F and ^{1}H) and Coupling Constant Ranges in Polyfluoro(2-methylpropane)

Group	^{19}F shift range [a]	^{1}H shift range (τ)
CF_3	74.3-80.9 [b]	-
CF_2H	131.2-139.0 [b]	3.90-4.16
CFH_2	237.7-248.7	5.17-5.44
CF	173.1-202.1	-
CH_3	-	8.25-8.64

[a] In ppm upfield from $CFCl_3$. [b] Compounds 13 and 14a absorb some 10 ppm below these ranges - See Table 4 and text.

System	Coupling Range (Hz)	System	Coupling Range (Hz)
CF_2H (gem)	52.0-54.4	$C\underline{F}H_2$-CF	11.4-12.5
CFH_2 (gem)	46.4-48.4	CH_3-CF	21.5-22.4
CF_3-CF	6.6-7.9	$C\underline{H_2}F$-CF	16.5-20.7
$C\underline{F_2}H$-CF	6.1-9.0	$C\underline{H}F_2$-CF	4.0-6.5
CF_3-C-CF	7.4-9.4	HC-C-CH	< 1-1.0
$C\underline{F_2}H$-C-CF	< 1-3.5	FC-C-CH	< 1-2.2

CH_3 regions. However, even if none of the structures given for 17 and 18 are correct, it is probable that there are two compounds present in Fraction P which have tertiary hydrogens, just because two of the observed CF_2H groups have chemical shifts below the usual range.

Peaks 2, 6, and 15 remain wholly unidentified, although the first two have about the same retention times as decafluorobutane and 2-methylpropane, respectively. There are, in fact, a number of other unidentified compounds in the fluorination mixture, none in greater amount than 0.1%. All the distillation Fractions A-P showed a few extremely weak unassigned signals in their ^{19}F NMR spectra (see, for example, the composition of Fraction F detailed earlier).

We have also attempted, unsuccessfully, to dehydrofluorinate 1H,3H-pentafluoro-2-fluoromethylpropane (12). No reaction occurred with sodium fluoride at 405°C and at 475°C there was some general degradation; with methyl-lithium and with refluxing 10 M potassium hydroxide, no reaction occurred; and with molten potassium hydroxide at 210°C, there was some degradation but no simple dehydrofluorination products were found. All this is in accord with the known [7,10] difficulty of dehydrofluorination when CF_2H or CFH_2 groups are involved, and is presumably associated with the low acidity of hydrogen in these groups [11].

DISCUSSION

It should be clear from the previous section that the fluorination of 2-methylpropane over cobalt trifluoride is of no great preparative value, except perhaps for decafluoro- and nonafluoro-(2-methyl)propane where conditions could probably be adjusted to give quite good yields of these easily separable products. The reaction mixture is basically too complex as far as the other products are concerned, but no doubt the method would have to be employed for most of them if they were really wanted since there is no other procedure available.

The other point we wish to discuss is the mechanistic one: some years ago we [12] published a theory of fluorination for high-valency transition metal fluorides which serves well for aromatic substrates but which, while it should apply to aliphatics, has not been developed or extensively tested, except for compounds containing heteroatoms or functional groups [10,13].

In the fluorination of ethane over cobalt trifluoride [1], replacement of hydrogen was largely random. This is not the case with 2-methylpropane; there was a marked preference, which went well beyond statistical expectation, for replacing the tertiary hydrogen by fluorine. This is most easily illustrated by compound 13. If replacement of hydrogen by fluorine were entirely random at all stages of the fluorination, then the ratio 13:16 would be 1:1; it is, in fact about 1:8. From this and other examples, we conclude that tertiary hydrogen replacement occurs about ten times more readily than would be expected on chance alone. This is, of course, consistent with either radical or carbenium ion involvement in fluorination.

ble 4

^{19}F and ^{1}H NMR Spectra [a] of Polyfluoroisobutanes

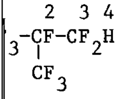
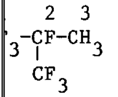
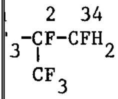
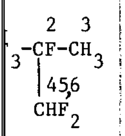
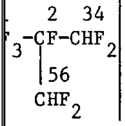
Compound	Compound No.	Chemical Shifts [b]							Coupling Constants (Hz) [c]
		1	2	3	4	5	6	7	
$\overset{1}{F_3})_3\overset{2}{CF}$	1	75.1	189.4						$J_{12}=6.6$
 $_3-\underset{\vert\;CF_3}{\overset{2}{CF}}-\overset{3}{CF_2}\overset{4}{H}$	3	74.3	191.9	133.1	3.96				$J_{12}=7.2$; $J_{13}=9.1$; $J_{23}=7.4$; $J_{24}=5.0$; $J_{34}=52.5$
 $_3-\underset{\vert\;CF_3}{\overset{2}{CF}}-\overset{3}{CH_3}$	3a	79.8	178.2	8.25					$J_{12}=7.1$; $J_{13}=1.2$; $J_{23}=22.1$
 $_3-\underset{\vert\;CF_3}{\overset{2}{CF}}-\overset{34}{CFH_2}$	4	76.5	190.7	243.0	5.19				$J_{12}=6.9$; $J_{13}=9.4$; $J_{14}\sim1.0$; $J_{23}=12.4$; $J_{24}=16.5$; $J_{34}=46.4$
 $_3-\underset{\vert\;\overset{456}{CHF_2}}{\overset{2}{CF}}-\overset{3}{CH_3}$	5 [d]	80.8	178.1	8.42	4.16	131.2	136.6		$J_{12}=6.8$; $J_{13}\sim1.0$; $J_{15}=9.1$; $J_{16}=5.7$; $J_{23}=22.4$; $J_{24}=4.0$; $J_{25}=4.8$; $J_{26}=11.4$; $J_{35}\sim J_{36}\sim1.5$; $J_{45}=53.2$; $J_{46}=54.4$; $J_{56}=310.5$
 $_3-\underset{\vert\;\overset{56}{CHF_2}}{\overset{2}{CF}}-\overset{34}{CHF_2}$	7 [d]	74.9	198.0	3.90	134.6				$J_{12}=7.5$; $J_{14}=8.8$; $J_{24}=8.2$; $J_{34}=53.3$; $J_{23}\sim6.5$

Table 4 (Contd.)

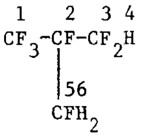
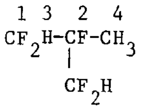
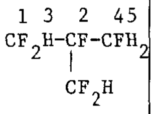
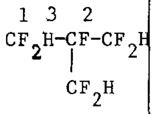
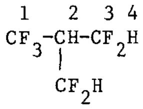
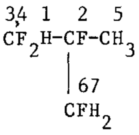
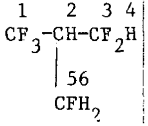
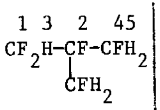
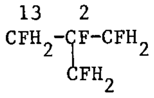
 $\overset{1}{\mathrm{CF_3}}\text{-}\underset{\substack{\mid\,56\\ \mathrm{CFH_2}}}{\overset{2}{\mathrm{CF}}}\text{-}\overset{3}{\mathrm{CF_2}}\overset{4}{\mathrm{H}}$	8 [d]	76.7	192.9	135.6	5.17	246.7	3.92		$J_{12}=J_{13}=J_{15}=7.9$; $J_{14}\sim1.0$; $J_{16}\sim1.1$; $J_{23}\sim J_{25}\sim7$; $J_{24}=5.6$; $J_{26}=18.2$; $J_{34}=46.7$; $J_{35}=3.5$; $J_{36}\sim J_{45}\sim J_{46}\sim1.1$; $J_{56}=53.1$
 $\overset{1}{\mathrm{CF_2}}\overset{3}{\mathrm{H}}\text{-}\underset{\substack{\mid\\ \mathrm{CF_2H}}}{\overset{2}{\mathrm{CF}}}\text{-}\overset{4}{\mathrm{CH_3}}$	11	138.0	184.0	[e]	8.53				$J_{12}\sim J_{23}\sim7.5$; $J_{13}\sim50$; $J_{14}=1.3$; $J_{24}=21.7$
 $\overset{1}{\mathrm{CF_2}}\overset{3}{\mathrm{H}}\text{-}\underset{\substack{\mid\\ \mathrm{CF_2H}}}{\overset{2}{\mathrm{CF}}}\text{-}\overset{45}{\mathrm{CFH_2}}$	12 [d]	135.7	193.8	4.00	248.7	5.23			$J_{12}=7.0$; $J_{13}=52.0$; $J_{14}=2.5$; $J_{15}=1.4$; $J_{23}=5.6$; $J_{24}=11.5$; $J_{25}=19.5$; $J_{45}=46.5$
 $\overset{1}{\mathrm{CF_2}}\overset{3}{\mathrm{H}}\text{-}\underset{\substack{\mid\\ \mathrm{CF_2H}}}{\overset{2}{\mathrm{CF}}}\text{-}\mathrm{CF_2H}$	12a [d]	135.1	202.1	3.90					$J_{12}=7.9$; $J_{13}=53.0$; $J_{23}=6.5$
 $\overset{1}{\mathrm{CF_3}}\text{-}\underset{\substack{\mid\\ \mathrm{CF_2H}}}{\overset{2}{\mathrm{CH}}}\text{-}\overset{3}{\mathrm{CF_2}}\overset{4}{\mathrm{H}}$	13	64.5	6.93	122.6	[e]				$J_{12}=J_{13}=8.1$; $J_{23}=12.9$; $J_{24}=3.6$; $J_{34}=52.3$
 $\overset{3,4}{\mathrm{CF_2}}\overset{1}{\mathrm{H}}\text{-}\underset{\substack{\mid\,67\\ \mathrm{CFH_2}}}{\overset{2}{\mathrm{CF}}}\text{-}\overset{5}{\mathrm{CH_3}}$	14 [d]	[e]	173.1	132.6	139.0	8.64	237.7	[e]	J_{12}-[f]; $J_{13}=J_{14}=54.0$; J_{23}-[f]; $J_{24}=9.0$; $J_{25}=21.5$; $J_{26}=11.7$; J_{27}-[f]; $J_{34}=302.0$; $J_{35}\sim J_{45}\sim1.0$; $J_{56}=2.2$; $J_{67}=52.5$
 $\overset{1}{\mathrm{CF_3}}\text{-}\underset{\substack{\mid\,56\\ \mathrm{CFH_2}}}{\overset{2}{\mathrm{CH}}}\text{-}\overset{3}{\mathrm{CF_2}}\overset{4}{\mathrm{H}}$	14a	66.7	$\sim$7.4	124.0	[e]	243.5	[e]		$J_{12}=J_{13}=J_{15}=7.9$; J_{23}-[f]; J_{24},J_{25},J_{26}-[e] $J_{34}\sim50$; $J_{56}\sim50$

Table 4 (Contd.)

 1 3 2 45 $CF_2H-CF(CFH_2)-CFH_2$	16 [d]	136.2	187.3	4.05	245.2	5.30	J_{12}=6.1; J_{13}=52.5; J_{23}=5.5; J_{24}=12.0; J_{25}=20.7; J_{34}=1.4; J_{45}=48.0
 13 2 $CFH_2-CF(CFH_2)-CFH_2$	19 [d]	240.6	181.9	5.44			J_{12}=12.5; J_{13}=48.4; J_{23}=17.9

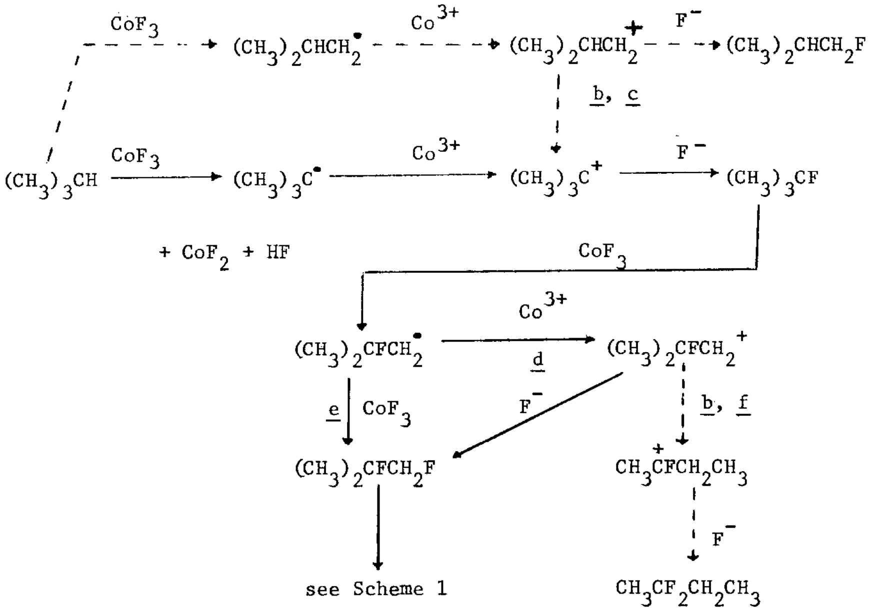
[a] Run on either a Perkin-Elmer R10 or a Perkin-Elmer R12B at 60 MHz (^1H) or 56.4 MHz (^{19}F) on neat compounds or CCl_4 solutions. See text for discussion and data on compounds <u>8a</u>, <u>8b</u>, <u>9</u>, <u>17</u>, and <u>18</u>. [b] Figures <10 are ^1H shifts on τ scale; remaining figures are ^{19}F shifts in p.p.m. upfield from internal $CFCl_3$. [c] Couplings <1.0 Hz not recorded. The symbol ∿ indicates an approximate value due to the broad, incompletely resolved, nature of the relevant signal, or to the partial obscuring of a signal by another stronger one, or to the weakness of a signal in the case of a minor component. [d] In these cases there are clear signs of second-order effects (beyond the simple AB situation): nevertheless the spectra have been analysed as if they were first order. [e] Peak hidden by stronger peak. [f] The broad, incompletely resolved, nature of the relevant signal prevented measurement.

There are other trends away from randomness of fluorination, but these are less marked: there is a tendency for the more symmetrically fluorinated compounds to occur more abundantly than chance expectation - the compounds on the right-hand side of Scheme 1 are favoured (by about two-fold) over those on the left. Compound 19 is an exception to this; random fluorination would give a 14:19 ratio of 2:1; in fact it is of the order of 10:1.

The presence of polyfluorobutanes suggest that some rearrangement has occurred. This might not be so; their amount is small - no more than 5% of the reaction product - and it is possible that the starting 2-methylpropane contained some butane. Rearrangement is, of course, quite likely if fluorination over cobalt trifluoride does give rise to carbenium ions; there is certainly evidence for carbenium ion rearrangements during fluorination, as was mentioned in the Introduction, and the relevant rearrangement step (f in Scheme 3) would certainly be expected to be energetically feasible since carbenium ions with α-fluorines are more stable than their β-isomers [14]. Such a rearrangement would probably have to occur early in the fluorination if it were to occur at all (this seems to be the case with bicyclo[2,2,2] octane [4]), either because the oxidation step (d in Scheme 3) from radical to cation becomes less and less favourable relative to quenching of the radical with CoF_3 (step e) because the inductive effect of the substituents raises the radical oxidation potential, or because migratory aptitude falls in the order $CH_3 > CH_2F > CHF_2 > CF_3$ (there is, in fact, no literature evidence for the migration of any of these groups except CH_3).

The structures of the polyfluorobutanes identified in the fluorination product is of no help in understanding any possible rearrangements since only those whose ^{19}F NMR signals did not, by chance, happen to lie under the much stronger signals of the polyfluoro(2-methylpropanes) could possibly be identified.

At this stage in our studies we favour the general mechanism outlined in Schemes 1 and 3 for the main fluorination sequence and for polyfluorobutane formation. Rearrangement only occurs early in the fluorination, and perhaps carbenium ion formation also, for the reasons given earlier; this may account for what, at first sight, seems a smaller extent of rearrangement than might have been expected. Replacement of tertiary hydrogen is favoured over primary because t-butyl radicals are more stable than iso-butyl; in any case, hydrogen migration from isobutyl carbenium ions to give the t-butyl ions, which is well-known, could occur (step c, Scheme 3 Possible Early Stages [a] in the Fluorination of 2-Methylpropane



[a] ——→ = Main route; - - - - - → = minor route

[b] Rearrangement. [c-f] See text.

Scheme 3) early in the fluorination and bring back the minor sequence to the major one.

There is a possibility that polyfluoro(2-methylpropenes) may be intermediates in the fluorination; they could be formed by loss of a proton from a suitable polyfluoro(t-butyl) ion. In the ethane fluorination [1], we rejected polyfluoroethenes as major intermediates, and since there is no evidence for the presence of olefins in the present fluorination, we do so here in the later stages of the fluorination, although we do recognize that pyrolytic elimination of hydrogen fluoride from lightly fluorinated *t*-butyl fluorides is a possibility.

EXPERIMENTAL

Fluorination of Iso-butane

Iso-butane (370 g) was fluorinated in four portions by passage over a stirred bed of cobalt trifluoride (10 kg) in a reactor of the type described before [8] at 140-200°C. Residual products were swept from the reactor with nitrogen (25 dm^3/h) and all (793 g from the four runs) were collected in a copper trap cooled to -78°C; they were washed with ice-water, dried (P_2O_5), treated with sodium fluoride (to remove any residual hydrogen fluoride), and then filtered through a glass wool plug.

The combined products (698 g) were distilled through a vacuum-jacketed column (4' long) packed with Dixon gauge spirals; fractions taken are recorded in Table 1.

Separation of Distillation Fractions by Glc

Separations were carried out either on Column A [6 m x 35 mm, dinonyl phthalate on Celite (1:2)] or column B [2 m x 15 mm dinonyl phthalate on Celite (1:2)]; temp. and N_2 carrier-gas flow-rate are stated in each case.

Fraction A (5.1 g) was separated (B, 34-35°C, 3.2 dm^3/h) in four portions to give: perfluoro-isobutane (0.25 g, *1*, i.r. [15]); 1*H*-2-*trifluoromethylhexafluoropropane* nc (1.2 g, *3*), mass spec. peaks at ($^m/e$) 220 (M^+, v.weak), 201 (M^+-19), 131 ($C_3F_5^+$), 113 ($C_3HF_4^+$), 69 (CF_3^+), and 51 (CF_2H^+, base peak) [^{19}F NMR showed this to contain a minor impurity, *3a*, - see text]; 1*H*,1*H*-2-trifluoromethylpentafluoropropane (0.3 g, *4*, i.r.); and 1,1,2-trifluoro-2-trifluoromethylpropane (0.1 g, *5*, i.r.).

Fraction B (7.25 g) was separated (B, 38-39°C, 5.2 dm^3/h) in five portions to give: 1*H*-2-trifluoromethylhexafluoropropane (2.8 g, *3*, i.r.); 1*H*,1*H*-2-*trifluoromethylpentafluoropropane* nc (1.1 g, *4*), mass spec. peaks at ($^m/e$) 202 (M^+, v.weak), 183 (M^+-19), 114 ($C_3H_2F_4^+$) 113 ($C_3HF_4^+$), 69 (CF_3^+, base peak), 33 (CFH_2^+); and 1,1,2-*trifluoro*-2-*trifluoromethylpropane* nc (1.6 g, *5*); mass spec. peaks at ($^m/e$) 166 (M^+ v.weak), 115 ($C_3H_3F_4^+$), 97 ($C_3H_4F_3^+$, equal base peak), 96 ($C_3H_3F_3^+$, equal base peak), 95 ($C_3H_2F_3^+$; equal base peak), 77 ($C_3H_3F_2^+$), 69 (CF_3^+), 65 ($C_2H_3F_2^+$), and 51 (CF_2H^+).

Fraction D (1.4 g), in two portions (B, 48°C, 6 dm^3/h), gave 1H,3H-2-*trifluoromethylpentafluoropropane* nc (0.5 g, *7*) as major component; mass spec. shows ions at ($^m/e$) 202 (M^+, v.small), 183 (M-19), 113 ($C_3HF_4^+$), 82 ($C_2HF_3^+$), 69 (CF_3^+), and 51 (CF_2H^+, base peak).

Fraction F (3.9 g), separated (B, 47°C, 5.9 dm^3/h) in four portions, gave a pure sample of 1,1,2,3-tetrafluoro-2-trifluoromethylpropane nc (1.3 g, 8), mass spec. peaks at $(^m/e)$ 184 (M^+ v.weak), 165 (M-19), 114 ($C_3H_2F_4^+$), 113 ($C_3HF_4^+$), 95 ($C_3H_2F_3^+$), 69 (CF_3^+), 64 ($C_2H_2F_2^+$), 51 (CF_2H^+), and 33 (CFH_2^+).

Fraction L (10.25 g) gave (A, 86-87°C, 50 dm^3/h) a pure sample of 1H,3H-pentafluoro-2-fluoromethylpropane nc (4.1 g, 12) (Found: C, 27.9; H, 2.1. $C_4H_4F_6$ requires C, 28.9; H, 2.6%); mass spec. showed peaks at 166 (M^+ v.weak), 96 ($C_3H_3F_3^+$), 95 ($C_3H_2F_3^+$), 77 ($C_3H_3F_2^+$), 51 (CF_2H^+, base peak), and 33 (CFH_2^+).

Fraction P (10.1 g) was separated (B, 94°, 7.5 dm^3/h) in eight portions, and only two components could be isolated in a pure or near pure state. These were (i) a slightly impure sample of 1,1,2,3-tetrafluoro-2-fluoromethylpropane nc (6.0 g, 16) (Found: C, 32.5; H, 3.6 $C_4H_5F_5$ requires C, 32.4; H, 3.4%), with the mass spec. showing no peaks corresponding to M^+ or $(M-19)^+$; and (ii) 1H,3H-2-difluoromethylpentafluoropropane nc (0.3 g, 19) (Found: C, 36.7; H, 5.0. $C_4H_6F_4$ requires C, 36.9; H, 4.6%), with no peaks in the mass spec. corresponding to M^+ or $(M-19)^+$.

Re-fluorination of 1H,3H-pentafluoro-2-fluoromethylpropane (12)

This compound (2.8 g), in a stream of nitrogen (1.3 dm^3/h), was fluorinated at 215°C over cobalt trifluoride (150 g) in the usual way. The product (3.15 g) was separated (B, 58°, 2.8 dm^3/h) to give perfluoroisobutane (trace, 1), 1H-2-trifluoromethylhexafluoropropane (0.6 g, 3), 1H,1H-2-trifluoromethylpentafluoropropane (trace, 4), 1H,3H-2-trifluoro methylpentafluoropropane (0.4 g, 7), 1,1,2,3-tetrafluoro-2-trifluoromethylpropane (trace, 8), and starting material (0.25 g), all identified by i.r.

Re-fluorination of 1,1,2,3-Tetrafluoro-2-fluoromethylpropane (16)

This compound (3.4 g), ca. 80-90% pure (impurities were approximately equal amounts of compounds 12, 14, 15, 17, and 18) was fluorinated at 145°. The product (3.4 g) contained (glc peak area ratios) 1H,3H-pentafluoro-2-fluoromethylpropane (12, 43% - but this may include compound 12a), 1,1,2,3-tetrafluoro-2-trifluoromethylpropane (8, 7%), starting material (30%), and other peaks (each < 5%).

ACKNOWLEDGEMENTS

One of us (TNH) thanks the SRC for a maintenance award.

REFERENCES

1 J. Burdon, J.R. Knights, I.W. Parsons, and J.C. Tatlow, Tetrahedron (1976) 32, 1041.

[redacted] R. Stephens, and J.C. Tatlow, Tetrahedron (1966) 22, 43.

3 S.F. Campbell, R. Stephens, and J.C. Tatlow, Tetrahedron (1965) 21, 2997.

4 J. Battersby, R. Stephens, and J.C. Tatlow, Tetrahedron Let. (1970), 5041; W.B. Hollyhead, R. Stephens, J.C. Tatlow, and W.T. Westwood, Tetrahedron (1969) 25, 1777.

5 E.J. Barber, L.L. Burger, and G.H. Cady, J. Amer. Chem. Soc. (1951) 73, 4241

6 J.A. Oliver, R. Stephens, and J.C. Tatlow, J. Fluorine Chem. (1975) 6, 19.

7 J. Burdon, S.T. Ezmirly, T.N. Huckerby, and R. Stephens, to be publishe

8 M. Stacey and J.C. Tatlow, Adv. Fluorine Chem. (1960) 1, 166.

9 J.M. Emsley, J. Feeney, and L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2, Chap. 11, Pergamon, Oxford, 1966; J. Burdon, G.E. Chivers, E.F. Mooney, and J.C. Tatlow, J. Chem. Soc. (C) (1969) 1739.

10 M. Brandwood, P.L. Coe, C.S. Ely, and J.C. Tatlow, J. Fluorine Chem. (1975) 5, 521.

11 S. Andreades, J. Amer. Chem. Soc. (1964) 86, 2003.

12 J. Burdon, I.W. Parsons, and J.C. Tatlow, Tetrahedron (1972) 28, 43; J. Burdon and I.W. Parsons, Tetrahedron (1975) 31, 2401.

13 J. Burdon, J.R. Knights, I.W. Parsons, and J.C. Tatlow, J. Chem. Soc., Perk. I (1976) 1930; J. Burdon and I.W. Parsons, Tetrahedron (1971) 27, 4533; R.D. Bagnall, P.L. Coe, and J.C. Tatlow, J. Fluorine Chem. (1973/74) 3, 329; J. Chem. Soc., Perk. I (1972).

14 D.T. Clark and D.M.J. Lilley, Chem. Comm. (1970) 603.

15 American Petroleum Institute, Project 44, Carnegie Institute of Technology (1959).