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FLUOROCYCLOPENTANES—IV[1]

THE FLUORINATION OF CYCLOPENTANE WITH COBALT TRIFLUORIDE

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Abstract—The fluorination of cyclopentane with cobalt trifluoride gives the following polyfluorocyclopentanes: C_5F_{10}, C_5F_9H, all four $C_5F_8H_2$ isomers, all the six $C_5F_7H_3$ isomers, five of the six $C_5F_6H_4$ isomers and 1H,2,H4H/3H,5H-pentafluorocyclopentane. The fluorination is believed to take place *via* this last compound and its 1H,2H,3H/4H,5H-isomer. A number of possible mechanistic features of cobalt trifluoride fluorination are discussed. Polyfluoropentanes (ca. 5%) are also produced in the fluorination; they probably arise from impurities in the cyclopentane.

IN PART 1 of this series,[2] we described the fluorination of cyclopentadiene with cobalt trifluoride and we isolated several of the lower-boiling products [perfluorocyclopentane, nonafluorocyclopentane, the 1H,2H/-, 1H,3H/-, 1H/2H- and 1H/3H-octafluorocyclopentanes, and 1H,3H/2H-heptafluorocyclopentane]. We also synthesized all three 1H:2H:3H-heptafluorocyclopentanes by chlorine addition to 3H-heptafluorocyclopentene, followed by reduction with LAH. In Part III,[1] we described the preparation and proof of structure of the three 1H:2H:4H-heptafluorocyclopentanes from 4H-heptafluorocyclopentene, and the preparation of five of the six possible 1H:2H:3H:4H-hexafluorocyclopentanes [the 1H,2H,3H,4H/-isomer was missing] from 3H/4H- and 3H,4H/-hexafluorocyclopentene. The structures of only three [the 1H,3H/2H,4H-, 1H,2H,4H/3H-, and 1H,2H,3H/4H-isomers] were proved conclusively.[1] We now report a complete study of the fluorination of cyclopentane with cobalt trifluoride as part of our programme[3] on the scope and mechanism of fluorination with transition metal fluorides. All the polyfluorocyclopentanes isolated previously, either from fluoro-olefinic intermediates or from the cyclopentadiene fluorination, were among the products. This study has been carried out in a similar degree of detail to that reported previously[3,4] on the fluorination of benzene by cobalt trifluoride.

RESULTS

The compounds produced by fluorination of 95% cyclopentane with cobalt trifluoride at 170–200° can be divided into two groups; the polyfluorocyclopentanes $C_5H_nF_{10-n}$ [n = 0–5], and the polyfluoropentanes, $C_5H_nF_{12-n}$ [n = 2–5]. The latter compounds (only about 6% of the total products) could have arisen either by ring-opening, since cyclopentane is known[5] to give a fair yield of perfluoropentane as well as perfluorocyclopentane, on being treated with cobalt trifluoride at 300–325°, or

[1] Part III. J. Burdon, T. M. Hodgins, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 2382 (1965).
[2] R. Heitzman, R. Stephens, C. R. Patrick and J. C. Tatlow, *J. Chem. Soc.* 281 (1963).
[3] J. C. Tatlow and M. Stacey, *Advances in Fluorine Chemistry* **1**, 166 (1960).
[4] E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 159 (1959), and earlier papers in this series.
[5] E. J. Barber, L. L. Berger and G. H. Cady, *J. Amer. Chem. Soc.* 73, 4241 (1951).

from impurities in the commercial (95%) cyclopentane which was used in the fluorinations. PMR indicated that the impurity contained a methyl-group and therefore could well have been n-pentane. The polyfluoropentanes therefore appear to contribute little to this study of the fluorination of cyclopentane and their structures have not been investigated in any detail; mere proof that a compound was not a cyclopentane was all that was attempted in most cases.

The fluorination products were initially separated by fractional distillation, and the various fractions were separated into the individual components by GLC. Table 1 lists all the polyfluorocyclopentanes which we have isolated from the fluorination of cyclopentane, together with their percentage abundances in the fluorination mixture; these percentages were substantially reproducible. Fluorination at higher or lower temperatures would, of course, alter these relative percentages in favour of the more and less highly fluorinated products, respectively, and so the figures in Table 1 should only be taken as a guide.

All except two of the polyfluorocyclopentanes were known compounds. 1H,2H/3H,4H-Hexafluorocyclopentane had been isolated in trace amounts before[1] but its structure had not been proved. Mild fluorination of it over cobalt trifluoride, a technique we have employed many times[1-4] for structural determinations, gave only two heptafluorocyclopentanes, the 1H,2H/3H- and 1H,2H/4H-isomers, thus proving the 1H,2H/3H,4H-structure, and confirming the earlier tentative identification.[1] The other unknown product was completely new. It analysed as $C_5H_5F_5$ and mild fluorination afforded two hexafluorocyclopentanes, the 1H,3H/2H,4H- and 1H,4H/2H,3H-isomers, thus showing that it was 1H,2H,4H/3H,5H-pentafluorocyclopentane, the only $C_5H_5F_5$ isomer we have obtained in all our studies on polyfluorocyclopentanes. This pentafluoroisomer was isolated in bulk from a fraction which contained several other components by treating the fraction with aqueous alkali. The other components were dehydrofluorinated into low-boiling olefins, while the pentafluoro-isomer was largely unchanged. The pentafluoro-isomer is much more resistant to dehydrofluorination than the other components presumably because all its hydrogen atoms are flanked by >CFH groups only. The other components were hexafluorocyclopentanes and therefore had more acidic hydrogen atoms (flanked by a $>CF_2$ group). Elimination of hydrogen fluoride from fluorocyclopentanes is discussed in more detail in Part III.[1]

A very small amount of perfluorocyclopentene was isolated from the fluorination; as polyfluorocyclo-alkanes are known[6] to lose hydrogen fluoride and yield olefins on being passed over sodium fluoride at 300°, an analogous dehydrofluorination of nonafluorocyclopentane during the fluorination could well have occurred.

No polyfluorocyclopentanes which possess two hydrogens on the same carbon atom have been isolated in a pure state; mass-spectrometry of one of the components gave a $—CF_2—CH_2—$ fragment and proton resonance spectroscopy of the same component indicated that it was a mixture and that it contained about 10% of a $—CF_2CH_2CF_2$-grouping, with >CHF and $—CHF_2$ as the major hydrogen-containing groups. The CH_2-containing component, which was present in extremely small amounts (<0·1%), could have been linear or cyclic; it is, however, the only compound which we have detected which might possibly be a 1H,1H-polyfluorocyclopentane.

[6] T. Rimmington, R. Stephens and J. C. Tatlow, unpublished; D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 3035 (1964).

For the reasons given previously, the polyfluoropentanes have not been investigated very closely. The major one appeared to be a 1H,2H,3H,4H,5H-heptafluoropentane from its elemental analysis and proton magnetic resonance spectrum. Since gas chromatography indicated that this substance was clearly a mixture, this structural assignment is very tentative. A most significant reaction of this compound, from the point of view of the fluorination of cyclopentane, was mild fluorination over cobalt trifluoride. Thirteen components were produced, none of which were known polyfluorocyclopentanes, and most of which had been isolated (all must, of course, be

TABLE 1. COMPOUNDS IDENTIFIED IN THE FLUORINATION PRODUCTS OF CYCLOPENTANE

Compound	% of Fluorination Mixture
Cyclopentane	4·5
Decafluorocyclopentane	11·5
Nonafluorocyclopentane	11·4
Octafluorocyclopentene	0·2
1H/2H-Octafluorocyclopentane	10·3
1H,2H/-Octafluorocyclopentane	1·5
1H/3H-Octafluorocyclopentane	17·5
1H,3H/-Octafluorocyclopentane	7·2
1H,2H/3H-Heptafluorocyclopentane	3·3
1H,3H/2H-Heptafluorocyclopentane	5·1
1H,2H,3H/-Heptafluorocyclopentane	<0·1
1H,2H/4H-Heptafluorocyclopentane	2·3
1H,4H/2H-Heptafluorocyclopentane	12·5
1H,2H,4H/-Heptafluorocyclopentane	0·3
1H,2H,3H/4H-Hexafluorocyclopentane	0·2
1H,2H,4H/3H-Hexafluorocyclopentane	1·4
1H,4H/2H,3H-Hexafluorocyclopentane	1·8
1H,3H/2H,4H-Hexafluorocyclopentane	2·3
1H,2H/3H,4H-Hexafluorocyclopentane	0·3
1H,2H,4H/3H,5H-Pentafluorocyclopentane	0·5
Mixed Polyfluoropentanes	5·6
High-boiling material	0·3
1H,1H-Octafluorocyclopentane (?)	<0·1

present) from lower-boiling fractions of the reaction product from the fluorination of cyclopentane; indeed, all the polyfluoropentanes isolated from the cyclopentane fluorination with gas-chromatographic retention times shorter than the $C_5H_5F_7$-isomer were present in the products of fluorination of this compound. Two of the supposed polyfluoropentanes also contained CF_2H-groups, according to proton magnetic resonance spectroscopy, indicating that, whatever their structure, they were not polyfluorocyclopentanes and were not therefore pertinent to the fluorination of cyclopentane. One other 1H,2H,3H,4H,5H-heptafluoropentane, whose structure was also assigned by nuclear magnetic resonance spectroscopy was isolated from the cyclopentane fluorination mixture; it was present in too small an amount to fluorinate. Only two gas-chromatographic peaks remain completely unidentified; both were high-boiling (>120°) and both were present to an extent of <0·05% of the reaction mixture. We consider it unlikely that we have not detected any compound comprising >0·5% of the total fluorination mixture, even if such a compound had the

same boiling point and gas-chromatographic retention time as one of the major products.

DISCUSSION

A plausible, though not rigorous, explanation of the almost complete absence of polyfluorocyclopentanes with $>CH_2$ groups is that the cobalt trifluoride fluorination of cyclopentane proceeds *via* some or all of the four possible 1H:2H:3H:4H:5H-pentafluorocyclopentanes. In fact only two, the 1H,2H,3H/4H,5H- and 1H,2H,4H/-3H,5H-isomers, are necessary to explain all the more highly fluorinated products actually formed, and the latter has been isolated from the fluorination mixture. We previously observed[1] that the mild fluorination of a partially fluorinated cyclopentane appeared to take place so that the hydrogens which are on that side of the ring plane where most of the hydrogens are situated, are replaced by fluorine more often than statistical expectation. For example, 1H,2H/3H-heptafluorocyclopentane gave[1] only 1H/3H- and 1H/2H-octafluorocyclopentane and none of the 1H,2H/-isomer. Application of this observation to the formation of the $C_5H_5F_5$ isomers from cyclopentane would suggest that the necessary 1H,2H,3H/4H,5H- and 1H,2H,4H/3H,5H-isomers should be formed preferentially. Of course, isolation alone does not prove that the latter compound is, in fact, an intermediate in the fluorination; it would have been isolated had it been easy to form but difficult to fluorinate. Its fluorination was not, however, slow and furthermore, the pattern of products was similar, by gas-chromatography, to that given by cyclopentane itself. We therefore suggest that 1H,2H,4H/3H,5H-pentafluorocyclopentane is a major intermediate in the fluorination of cyclopentane. Its further fluorination would be expected, according to the argument advanced above, to take the course indicated in Fig. 1.

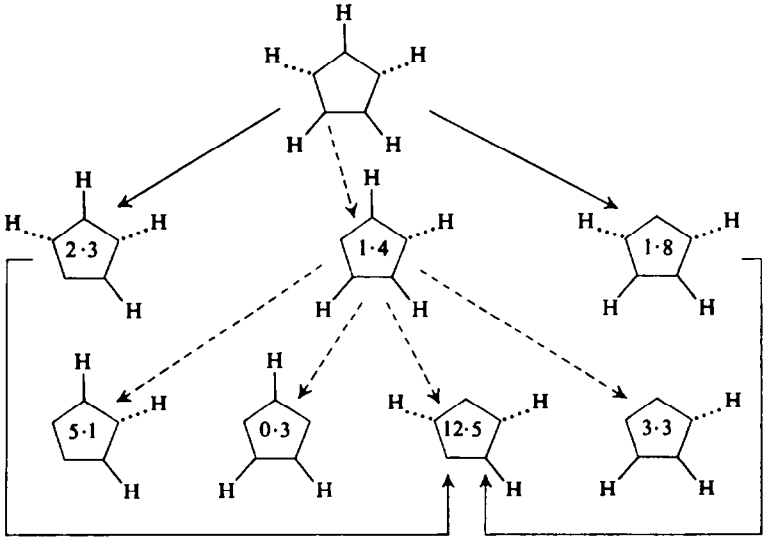

FIG. 1.* The Fluorination of 1H,2H,4H/3H,5H-Pentafluorocyclopentane. The figures inside the cyclopentane rings are percentage abundances in the fluorination of cyclopentane

——→ predicted primary (most favoured) fluorination paths.
— — —→ predicted secondary fluorination paths.
· · · · · · · → predicted tertiary fluorination paths.

* All unmarked substituents on the cyclopentanes in this Figure are fluorines. Thick lines indicate bonds above the plane of the ring and dotted lines, bonds below it.

The percentage abundances agree with those predicated on the basis of the rule that the most easily replaced hydrogens are those on the side of the ring plane where most of the hydrogens are. A similar pattern can be written out for 1H,2H,3H/4H,5H-pentafluorocyclopentane:

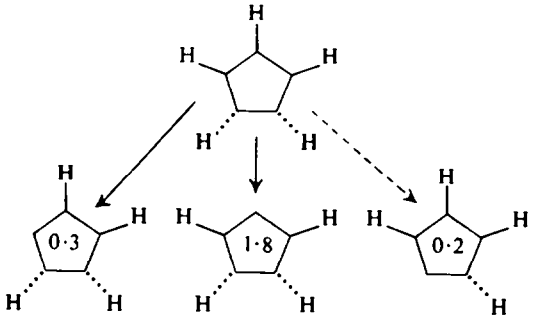

FIG. 2

Since these percentages are lower than those of the analogous compounds (with the exception of the 1H,4H/2H,3H-compound which is common to both) obtained from the other $C_5H_5F_5$-isomer, then this would appear to be a less common route for the fluorination of cyclopentane to take.

There is another feature of the cyclopentane fluorination to which we wish to draw attention. Although a considerable amount (~5%) of unreacted cyclopentane was among the products, we have found no C_5H_9F, $C_5H_8F_2$, $C_5H_7F_3$ or $C_5H_6F_4$ isomers. It seems extremely unlikely that we would have missed all of these had they been present in even minute amounts. Many of them would be expected to have gas-chromatographic retention times and b.ps (cyclopentyl fluoride[7] has b.p. 49°) less than some of the $C_5H_4F_6$ and $C_5H_5F_5$ compounds that we, in fact, isolated; it is well-known that the b.p. of an alkane first increases as fluorine substituents are introduced and then begins to decrease again as the last few hydrogens are replaced by fluorine. Gas-chromatographic retention times follow the same pattern.

A similar phenomenon has been observed[8] in the cobalt trifluoride fluorination of benzene; benzene is often recovered in far greater amounts than are fluorobenzene and *p*-difluorobenzene which have been suggested[3] as the primary fluorination products.

We suggest, therefore, as a working hypothesis, that in the cobalt trifluoride fluorination of a hydrocarbon, the hydrocarbon either remains in the vapour phase and is recovered unchanged, or it becomes attached in some way to the solid cobalt trifluoride. If it becomes attached it is not released until fluorination has proceeded to a considerable extent; in the cyclopentane case to the $C_5H_5F_5$ stage. This suggestion, and the previous one about which hydrogens were most easily replaced, will require considerably more investigation before they can be regarded as anything like established. Such investigations are hampered by the heterogeneous nature of the fluorination reaction. It will also be necessary to determine relative rates of fluorination of all postulated intermediates in a reaction sequence and to determine the relative amounts of the products formed in each stage of such a fluorination. This last

[7] M. T. Rogers and J. D. Roberts, *J. Amer. Chem. Soc.* **68**, 843 (1946).

[8] A. K. Barbour, H. D. Mackenzie, M. Stacey and J. C. Tatlow, *J. Appl. Chem.* **4**, 341 and 347 (1954).

requirement is difficult since the fluorination of a fluorocyclopentane (say $C_5H_6F_5$) is hard to stop entirely at the next stage ($C_5H_4F_6$).

EXPERIMENTAL

Fluorination of cyclopentane

Cyclopentane (commercial grade, 95% pure; 170 g) was added dropwise over 3–4 hr to a stirred bed of CoF_3 (6·5 Kg) (the apparatus has been described previously[1,2]) at 180–200°. The products were collected in a cooled (−78°) trap, the residual amount being swept from the apparatus with N_2 (20 l/hr) for 2 hr. The contents of the trap were washed with cold (0°) water and then cold $NaHCO_3$aq. Final yields of mixed polyfluorocyclopentanes were 300–330 g.

Combined polyfluorocyclopentanes (3076 g) from ten fluorination were fractionally distilled from P_2O_5 (20 g) through a vacuum-jacketed glass column (120 cm × 1 cm) packed with Dixon iron gauze spirals ($\frac{1}{16}$" × $\frac{1}{16}$"); the fractions taken and their wts are given in Table 2.

TABLE 2

Fraction No.	Wt (g)	Boiling-range (°C)
1	374	17·0–22·8
2	97	22·8–29·5
3	310	29·5–32·0
4	71	32·0–48·0
5	181	48·0–51·5
6	199	51·5–56·8
7	436	56·8–60·1
8	104	60·1–65·5
9	155	65·5–66·7
10	133	66·7–69·0
11	150	69·0–76·0
12	313	76·0–80·0
13	162	80·0–85·4
14	86	85·4–94·2
15	40	94·2–97·5
16	53	99·1–104
17	54	104–105
18	43	105–125[a]
19	30	>125

[a] This fraction was obtained by distillation through a column 1′ long.

Separation of fractions 1–19

The separations were all accomplished by GLC; five columns were employed. Column A was 4·8 m × 75 mm diam, columns B and C, 4·8 m × 35 mm diam and columns D and E, 2 m × 12 mm diam. Columns A, B and D were packed with dinonyl phthalate on Celite and columns C and E with silicone gum on Celite. N_2 was used as the carrier gas and its flow-rate and the column temp are stated in each case. Most of the products were identified by IR spectroscopy.[1,2]

Fraction 1. Separation (B, 14 l/hr, 100°) of a sample (5·5 g) gave perfluorocyclopentane (2·7 g; IR) and cyclopentane (0·3 g; IR).

Fraction 2. Separation (B, 12 l/hr, 100°) of a sample (3·3 g) gave perfluorocyclopentane (0·1 g; IR), perfluorocyclopentene (0·1 g; IR), nonafluorocyclopentane (1·7 g; IR), and cyclopentane (0·2 g; IR).

Fraction 3. A sample (5·5 g) gave (B, 12 l/hr, 100°) 1H,2H-decafluoropentane (I; trace), nonafluorocyclopentane (3·2 g; IR), and cyclopentane (0·8 g; IR). The decafluoropentane identification is very tentative; mass-spectroscopy showed major mass peaks at 169 (C_2F_7), 82 (CF_2—CFH) and 51

(CF_2H); the compound had the same gas-chromatographic retention time as one of the products of fluorination of $C_5H_8F_7$.

Fraction 4. This fraction (5·2 g) gave (B, 12 l/hr, 100°) 1H,2H-decafluoropentane (I; trace, IR), a polyfluoropentane (II; trace), nonafluorocyclopentane (0·8 g; IR), a mixture (0·2 g), 1H/2H-octafluorocyclopentane (2·5 g; IR), and cyclopentane (0·7 g; IR). Mass-spectroscopy of the mixture showed a mass peak at 64 ($—CF_2—CH_2—$); the ^1H NMR spectrum showed a quintet (J = 12·7 c/s; each peak was ca. 6 c/s broad) at 2·7 ppm (downfield from tetramethylsilane as external reference). The quintet was only $\frac{1}{10}$th the intensity of the remaining peaks in the spectrum, which consisted of a complex set of multiplets in the 4·2–6·8 ppm region, one of which was a triplet (J = 55 c/s) ($—CF_2H$). The polyfluoropentane (II) and the mixture had the same gas-chromatographic retention times as two (II and III) of the fluorination products of $C_5H_8F_7$; the IR spectrum of the mixture was very similar to that of fluorination product (III).

Fraction 5. A sample (8·1 g) of this fraction gave (B, 12 l/hr, 97°) the same mixture as fraction 4 (trace; IR), 1H/2H-octafluorocyclopentane (5·1 g; IR), and 1H/3H-octafluorocyclopentane (trace; IR).

Fraction 6. Separation (A, 44 l/hr, 66°) of a sample (100 g) gave the same mixture as fraction 4 and 5 (12·2 g; IR), 1H/2H-octafluorocyclopentane (31·7 g; IR), and 1H/3H-octafluorocyclopentane (31·3 g; IR).

Fraction 7. Analytical gas-chromatography indicated that this fraction contained mainly (~95%) 1H/3H-octafluorocyclopentane with trace amounts of 1H,3H/2H-heptafluoro- and 1H,3H/-octafluorocyclopentane.

Fraction 8. A sample (62·2 g) was separated (A, 48 l/hr, 70°) into polyfluoropentane (IV; 6·6 g; IR), 1H/3H-octafluorocyclopentane (11·3 g; IR), 1H,3H/2H-heptafluorocyclopentane (11·4 g; IR), and 1H,3H/-octafluorocyclopentane (20·4 g; IR). The ^1H NMR spectrum of IV showed a triplet (J = 55 c/s) at 5·85 ppm ($—CF_2H$), and other complex multiplets centred at 5 ppm.

Fraction 9. Separation (A, 44 l/hr, 66°) of a sample (23·9 g) gave V (0·4 g; IR), 1H,3H/2H-heptafluorocyclopentane (6·0 g; IR), and 1H,3H/-octafluorocyclopentane (11·8; IR). The ^1H NMR spectrum of V showed a triplet (J = 53 c/s) at 5·65 ppm (CF_2H), and other complex multiplets centred at 4·8 ppm.

Fraction 10. Polyfluoropentane (V; 1·8 g; IR), 1H,3H/2H-heptafluorocyclopentane containing ca. 20% VI and VII (7·4 g; IR), 1H,3H/-octafluorocyclopentane (7·9 g; IR), and 1H,4H/2H-heptafluorocyclopentane (0·3 g; IR) were isolated (A, 50 l/hr, 78°) from a sample (23·1 g) of this fraction.

Fraction 11. A sample (24·3 g) was separated (A, 54 l/hr, 82°) to yield V (0·3 g; IR), a mixture of VI and VII containing ca. 20% of 1H,3H/2H-heptafluorocyclopentane (10·0 g; IR), 1H,3H/-octafluorocyclopentane (0·1 g; IR), 1H,4H/2H-heptafluorocyclopentane (9·9 g; IR), and 1H,2H/-octafluorocyclopentane (0·2 g; IR). The ^1H NMR spectrum of the mixed polyfluoropentanes showed a broad doublet (J = ca. 50 c/s) at 4·6 ppm.

Fraction 12. Analytical gas chromatography indicated that this fraction consisted only of 1H,4H/2H-heptafluorocyclopentane (85%) and 1H, 2H/-octafluorocyclopentane (15%).

Fraction 13. A sample (29·8 g) separated (A, 44 l/hr, 85°) into a mixture (15·8 g; 7:3 by IR) of 1H,3H/2H,4H-hexafluorocyclopentane and 1H,4H/2H-heptafluorocyclopentane (the authentic compounds have very similar gas-chromatographic retention times) and 1H, 2H/3H-heptafluorocyclopentane (9·8 g; IR).

Fraction 14. Separation (A, 58 l/hr, 92°) of a sample (25·8 g) gave a mixture (9·9 g; 9:1 by IR) of 1H, 2H/3H-heptafluorocyclopentane and the heptafluoropentane (X), and 1H,2H/4H-heptafluorocyclopentane (10·6 g; IR). Two very small peaks, which were present in too small a quantity to isolate, showed before the mixture peak. Their retention times were different from those of the known polyfluorocyclopentanes and about the same as those of VIII and IX.

Fraction 15. Separation (A, 44 l/hr, 98°) of a sample (12·5 g) yielded X (5·8 g), b.p. 94°. (Found: C, 29·9; H, 2·0. Calc. for $C_5H_5F_7$: C, 30·3; H, 2·5%) and 1H,2H/4H-heptafluorocyclopentane (4·4 g; IR). The heptafluoropentane peak was broad and non-symmetric, implying a mixture;

it ^{1}H NMR spectrum showed a triplet (J = 54 c/s) at 5·9 ppm and a doublet (J = 45 c/s) at 5·0 ppm in approximate intensity ratio 2:3; each of these peaks was further split into complex multiplets.

Fraction 16. This fraction (5·7 g) yielded (B, 21 l/hr, 100°) X (0·5 g; IR), 1H,2H/4H-heptafluorocyclopentane (0·1 g) and a mixture (3·0 g). The mixture (40 μl) was separated (E, 5 l/hr, 36°) to yield 1H,2H,4H/3H- and 1H,4H/2H,3H-hexafluorocyclopentane (IR); the two components were present in approximately equal amounts, together with a much smaller amount of 1H,2H,4H/3H,5H-pentafluorocyclopentane, which was not isolated.

Fraction 17. Separation (B, 21 l/hr, 100°) of a sample (5·7 g) gave two mixtures. The first (0·5 g) appeared to contain (IR and GLC) X, 1H,2H/4H-heptafluorocyclopentane and the next mixture; the second (3·1 g) was further separated (80 μl, E, 5 l/hr, 36°) into 1H,2H,4H/3H-hexafluorocyclopentane (IR), 1H,4H/2H,3H-hexafluorocyclopentane (IR) and 1H,2H,4H/3H,5H-pentafluorocyclopentane (IR) [the GLC peak areas were in the approximate ratios 2:3:1, respectively].

Fraction 18. This fraction (6·0 g) yielded (C, 22 l/hr, 50°) a mixture (3·2 g), 1H,2H/3H,4H-*hexafluorocyclopentane* (1·2 g) b.p. 118–119°, m.p. ca. 20°. (Found: C, 33·8; H, 2·3. $C_5H_4F_6$ requires: C, 33·7; H, 2·3%). [This compound had an IR spectrum identical with that of a compound previously isolated in trace amounts only and suggested to have this structure], and 1H,2H,3H/4H-hexafluorocyclopentane (0·6 g; IR). The mixture (1·0 g) was separated (D, 5·5 l/hr, 100°) in three portions into a new mixture (0·5 g), almost the same by IR with the second mixture of fraction 17, polyfluoropentane (0·05 g) and 1H,2H,4H/-heptafluorocyclopentane (0·3 g). The ^{1}H NMR spectrum of the polyfluoropentane showed a triplet (J = 54 c/s) at 6·0 ppm and a doublet (J = 45 c/s) at 4·8 ppm in approximate intensity ratio 2:3; each peak was a complex multiplet; the ^{19}F spectrum showed three multiplets centred at 55·5, 140·2 and 142·6 (in ppm upfield from trifluoroacetic acid as internal reference) in approximate intensity ratio 4:2:1. Three very small peaks (<2% of the fraction) were present in this fraction in addition to those described above; the longest retained had the same gas-chromatographic retention time as 1H,2H,3H/-heptafluorocyclopentane.

Fraction 19. Simple distillation of this fraction gave a very viscous distillate (10 g), b.p. 125–275° and a residue (20 g) which was presumably phosphoric acid. The distillate has not been investigated.

Isolation of 1H,2H,4H/3H,5H-*pentafluorocyclopentane*

Fraction 16 (9·4 g) was shaken with KOHaq (10 g in 20 ml) for 24 hr at 20°. The lower organic layer was separated (B, 20 l/hr, 100°) into 1H,4H/5H-pentafluorocyclopentane (4·2 g; IR), a mixture (0·2 g) of two components which was not investigated and 1H,2H,4H/3H,5H-*pentafluorocyclopentane* (1·6 g), b.p. 109–110°. (Found: C, 37·7; H, 3·1. $C_5H_5F_5$ requires: C, 37·5; H, 3·1%) The ^{19}F NMR spectrum showed three multiplets centred at 119·6, 122·5 and 135·9 ppm in intensity ratio 1:2:2:; it has previously[9] been found that, in polyfluorocyclohexanes, $>CF_2$ groups absorb well downfield of 100 ppm and > CFH groups well above.

Fluorination of 1H,2H,4H/3H,5H-*pentafluorocyclopentane*

This compound (3·1 g) was introduced over 30 min into a small stirred CoF_3-reactor[1] at 180°. The reactor was swept with N_2 for 2 hr more, and the products were collected in a trap cooled in liquid air and then washed with water. Separation (D, 5 l/hr, 86°) of a sample (0·8 g in two portions) of the products (1·8 g) gave nonafluorocyclopentane (trace) 1H/2H-octafluorocyclopentane (0·1 g), 1H/3H-octafluorocyclopentane (0·1 g), 1H,3H/2H-heptafluorocyclopentane (0·1 g), 1H,3H/-octafluorocyclopentane (trace), 1H,3H/2H,4H-hexafluorocyclopentane (0·1 g), 1H,4H/2H-hepta, fluorocyclopentane (0·25 g), 1H, 2H/3H-heptafluorocyclopentane containing ca. 10% 1H,2H/-octafluorocyclopentane (trace) and a mixture of 1H,4H/2H,3H-hexafluorocyclopentane and starting material (trace); all the products were identified by IR.

Fluorination of 1H,2H/3H,4H-*hexafluorocyclopentane*

This compound (2·7 g) was treated as in the previous experiment to yield crude fluorination products (1·5 g), which were separated (B, 21 l/hr, 100°) into perfluorocyclopentane (trace), nonafluorocyclopentane (0·2 g), 1H/2H-octafluorocyclopentane (0·1 g), 1H/3H-octafluorocyclopentane

[9] J. Homer and L. F. Thomas, *Trans Faraday Soc.* **59**, 2431 (1963).

(0·3 g), 1H,2H/3H-heptafluorocyclopentane containing ca. 30% 1H,2H/-octafluorocyclopentane (0·2 g), and 1H,2H/4H-heptafluorocyclopentane (0·3 g); all identified by IR.

Fluorination of the heptafluoropentane, b.p. 94°

The compound (4·2 g) was fluorinated as described above. Analytical gas chromatography showed that the products (3·2 g) contained at least 13 components, of which components (numbered in order of retention time) V, VII and VIII were the major ones, followed by components VI and IX; components I–IV were very minor. Specimens of components III–IX were isolated (C, 15 l/hr, 100°).

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