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HEXAFLUORO- AND PERCHLOROFLUORO-BENZENES* FROM PERCHLOROFLUORO-CYCLOHEXANES AND -CYCLOHEXENES†

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Abstract—Liquid phase halogenation of hexachlorobenzene by chlorine trifluoride appears to proceed by a series of additions and vinylic and allylic substitutions, until all of the hexachlorobenzene is converted into chlorofluoro-cyclohexenes, $C_6F_nCl_{10-n}$ (where n is mainly 4, 5 and 6). A very large excess of chlorine trifluoride gives chlorofluoro-cyclohexanes, $C_6F_nCl_{12-n}$ (where n is mainly 5, 6 and 7). Aromatisation of the cyclohexenes at 200°–300° gives all possible chlorofluorobenzenes while aromatisation of the cyclohexanes at 250°–300° gives mainly chloropentafluorobenzene and dichlorotetrafluorobenzene, with some hexafluorobenzene and trichlorotrifluorobenzene. At the low temperatures which are used for aromatisation there is little opportunity for rearrangement within the molecule and this results in the retention of chlorine atoms in the aromatic products.

The distribution of isomers of the aromatic products sheds some light on the structures of the chlorofluorocyclohexenes and -cyclohexanes from which they are derived, and hence on the mechanism of halogenation.

IN EARLIER communications, the preparation of fluorinated derivatives of benzene by the action of chlorine trifluoride on benzene itself has been described. In the liquid phase[1] this resulted in aromatic products containing little fluorine while, in the vapour phase,[2] saturated chlorofluorocyclohexanes and chlorofluorohydrocyclohexanes were obtained which lost chlorine preferentially on dehalogenation to give mainly hexa- and penta-fluorobenzenes.[3] The presence of even a small amount of hydrogen in these saturated cyclohexanes enforced the use of vigorous dehalogenation conditions and low yields resulted. In order to avoid the presence of hydrogen altogether it was decided to use hexachlorobenzene as the starting material and, because of its high boiling point, carry out the reaction with chlorine trifluoride in the liquid phase at 240°. It was found that halogenation to give a mixture of chlorofluorocyclohexenes occurred easily if a fifty per cent excess of chlorine trifluoride was used and the product was mainly hexachlorotetrafluoro- and pentachloropentafluoro-cyclohexenes together with smaller amounts of tetrachlorohexafluoro- and trichloroheptafluorocyclohexenes and tetrachlorotetrafluorocyclohexadiene. Apart from the diene these were all mixtures of isomers but the diene was shown, by nuclear magnetic resonance and U.V.

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* For the sake of brevity the prefix "Per" is assumed in the rest of the script since none of the cyclic compounds described contain hydrogen.

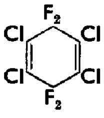
† Presented in part at *The Second International Symposium on Fluorine Chemistry* Estes Park, Colorado, July (1962).

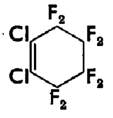
[1] J. F. Ellis and W. K. R. Musgrave, *J. Chem. Soc.* 3608 (1950); 1063 (1953).

[2] R. E. Banks, P. Johncock, R. H. Mobbs and W. K. R. Musgrave, *Ind. Eng. Chem. Proc. Des. & Dev.* **1**, 262 (1962).

[3] P. Johncock, R. H. Mobbs and W. K. R. Musgrave, *Ind. Eng. Chem. Proc. Des. & Dev.* **1**, 267 (1962).

spectroscopic measurements, to be pure 1,2,4,5-tetrachloro-tetrafluoro-cyclohexa-1,4-diene. (I)


I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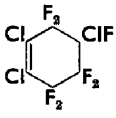
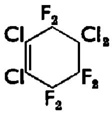
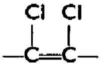

III


IV

Examination of the I.R. spectra of the products indicated a tendency as shown in Table 1, for the retention of the structure



$$\overset{Cl}{\underset{|}{}}\ \overset{Cl}{\underset{|}{}}\\ -C{=}C-$$

in each ring system, and only in the later stages of the chlorofluorination are these chlorine atoms replaced by fluorine. This tendency has been shown even more strongly in the reaction between antimony pentafluoride and hexachlorobenzene when the main products (II, III and IV) retain this structure throughout the fluorination.[4]

TABLE 1. NATURE OF DOUBLE BONDS IN CHLOROFLUOROCYCLOHEXENES

Mixture of isomers	% $\overset{Cl}{C}{=}\overset{Cl}{C}$ Abs. band 1626 cm^{-1}	% $\overset{Cl}{C}{=}\overset{F}{C}$ Abs. band 1695 cm^{-1}	% $\overset{F}{C}{=}\overset{F}{C}$ Abs. band 1754 cm^{-1}
$C_6F_7Cl_3$	35	55	10
$C_6F_6Cl_4$	50	45	5
$C_6F_5Cl_5$	65	30	5
$C_6F_4Cl_6$	95	0	5
$C_6F_4Cl_4$ (I)	100		

The complete saturation of the product to give a mixture of chlorofluorocyclohexanes required prolonged treatment with a four hundred per cent excess of chlorine trifluoride. It resulted in considerable decomposition and gave mainly those products containing 6, 7 and 8 fluorine atoms, the overall yield being 52 per cent whereas the overall yield of chlorofluorocyclohexenes was over 80 per cent.

A few experiments were carried out in which boron trifluoride, ferric chloride or cobalt difluoride were added to the reaction mixture. In these experiments only a one hundred per cent excess of chlorine trifluoride was used in order to determine in the minimum number of experiments the effect of the catalysts on the proportions of both cyclohexenes and cyclohexanes. It can be seen from Table 7 that cobaltous fluoride encouraged saturation but also encouraged decomposition; ferric chloride increased the proportion of more highly fluorinated product but also encouraged decomposition, while boron trifluoride gave results which, whilst somewhat better, differed so little from those obtained without a catalyst that it was not thought worthwhile to continue to use it.

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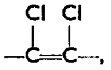
[4] Leffler, *J. Org. Chem.* **24,** 1132, 2074 (1959); E. T. McBee, J. D. Park, Wiseman and Bachman, *Ind. Eng. Chem.* **39,** 415, 1947.

The chlorofluorocyclohexenes were aromatized as previously described by Gething *et al.*[5] and by workers in this laboratory,[3] by passing their vapours over heated iron gauze but it was found that the temperatures required were much lower than those needed to aromatize the less highly chlorinated chlorofluorocyclohexanes obtained from the action of chlorine trifluoride on benzene in the vapour phase;[3] indeed, if the higher temperature (430°) were used, very little product was obtained. The products also were different because the chlorine no longer reacted preferentially and a mixture of all possible chlorofluoro-benzenes was obtained in each case, as shown in Table 2. The percentage distribution of isomers of the aromatic compounds was determined by nuclear magnetic resonance spectroscopy since it is impossible to separate isomeric chlorofluorobenzenes by gas chromatography with any of our stationary phases. This is also the case for isomeric chlorofluorocyclohex-anes and -enes.

The reason for the retention of chlorine in the aromatic products is indicated by the last three results quoted in Table 2. These three compounds, dichloro-octafluorocyclohexene, trichloroheptafluorocyclohexene and tetrachlorotetrafluorocyclohexadiene were the only pure isomers to be aromatized and it is significant that:

(i) in the absence of a third chlorine atom which would allow easy formation of a diene, the dichloro-octafluorocyclohexene decomposes at 360° rather than undergo defluorination or isomerization which would place one of its chlorine atoms in a suitable position for forming a diene; i.e., even at this temperature, isomerization can not occur at the monoene stage and higher temperatures simply cause greater decomposition.

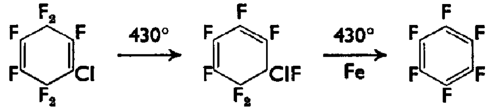
(ii) while it is evident from the products from the trichloroheptafluorocyclohexene and tetrachlorotetrafluorocyclohexadiene that migration of chlorine atoms occurs to a slight extent, in the major product (80–90 per cent of the whole) the grouping



$$-\overset{\text{Cl}}{\overset{|}{\text{C}}}=\overset{\text{Cl}}{\overset{|}{\text{C}}}-,$$

present in the starting cyclohexene, has been retained. This must mean that at the low aromatization temperatures used, isomerization of the -cyclohexadiene intermediates occurs to only a slight extent.

It has been demonstrated quite conclusively by Tatlow *et al.*[5,6] that polyfluorocyclohexadienes will isomerize at temperatures of 260° and, in the dechlorination of chlorofluorocyclohexanes[3] containing small numbers (1 to 4) of chlorine atoms at 430°, we have postulated that isomerism must again take place in order to explain the exclusive formation of hexafluorobenzene



It is evident that at temperatures up to 315° this allylic rearrangement does not occur in the case of the chlorofluoro-cyclohexadienes. Thus we can assume that the structures

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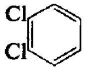
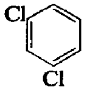
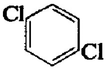
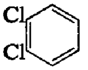
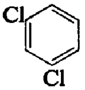
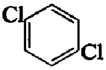
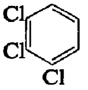
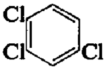
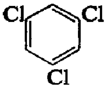
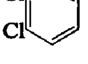
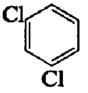
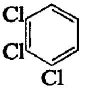
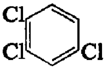
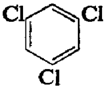
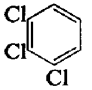
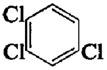
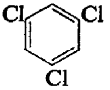
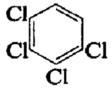
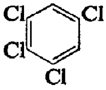
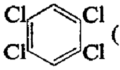
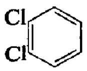
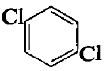
[5] R. Gething, C. R. Patrick, M. Stacey and J. C. Tatlow, *Nature, Lond.* **183**, 588 (1959).

[6] P. L. Coe, C. R. Patrick and J. C. Tatlow, *Tetrahedron* **9**, 240 (1960).

TABLE 2. AROMATISATION OF CHLOROFLUOROCYCLOHEXENES

Cyclohexene	Temp of reaction (°C)	Total yield (%)	Yields of products (%) and distribution of isomers (%)[a]
$C_6F_7Cl_3$	315	73	C_6F_6(11), C_6F_5Cl(27), $C_6F_3Cl_3$(5), $C_6F_4Cl_2$(30);  (59),  (19),  (22)
$C_6F_6Cl_4$	260	84	C_6F_6(5), C_6F_5Cl(32), $C_6F_2Cl_4$(2) $C_6F_4Cl_2$(33);  (50),  (25),  (25) $C_6F_3Cl_3$(12);  (6),  (90),  (4)
$C_6F_5Cl_5$	260	83	C_6F_5Cl(3), $C_6F_2Cl_4$(3), C_6FCl_5(1), $C_6F_4Cl_2$(58);  (74),  (15),  (11) $C_6F_3Cl_3$(18);  (13),  (83),  (4)
$C_6F_4Cl_6$	300	85	$C_6F_4Cl_2$(6), C_6FCl_5(16), $C_6F_3Cl_3$(30);  (14),  (83),  (3) $C_6F_2Cl_4$(33);  (20),  (57),  (23)
$C_6F_4Cl_4$	230	56	$C_6F_3Cl_3$(6), C_6FCl_5(3), $C_6F_2Cl_4$(47);  (100)
$C_6F_7Cl_3$[b]	315	79	C_6F_6(7), C_6F_5Cl(15), $C_6F_3Cl_3$(3), $C_6F_4Cl_2$(54);  (97),  (3)
$C_6F_8Cl_2$[b]	360	45	$C_6F_8Cl_2$(43)

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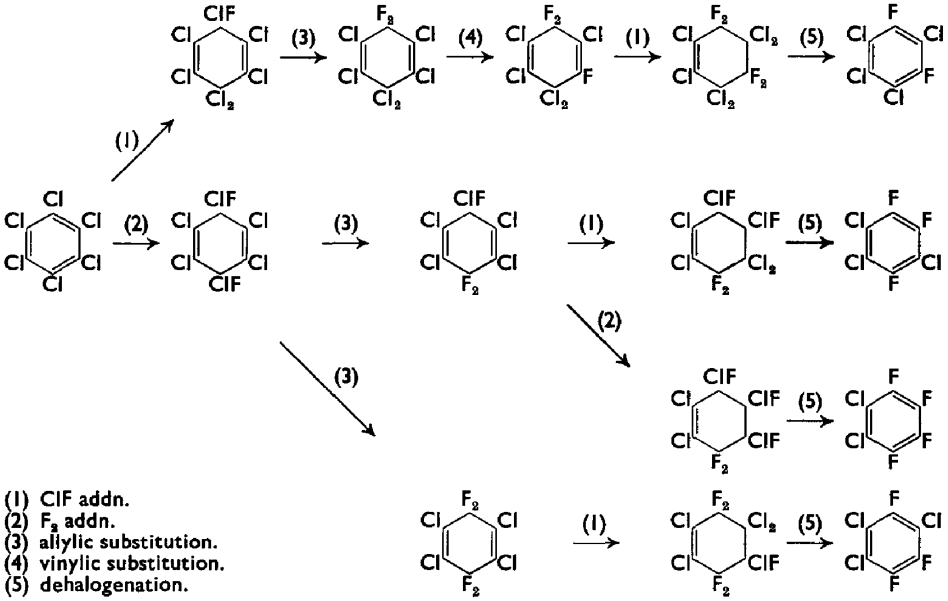
[a] Only the positions of the chlorine atoms are shown, fluorine atoms occupy the other positions in the ring.

[b] Pure isomers (II and III) obtained from the action of SbF_5 on C_6Cl_6.

of the aromatic compounds reflect the structures of the cyclohexenes from which they are derived i.e. the remaining chlorine atoms are those which were associated with the double bond in the original cyclohexene or formed part of a *gem*-dichloro group. In the light of this it would also appear to be a reasonable assumption that little or no isomerization occurs during the halogenation of the intermediate cyclic olefins since this also is carried out at a comparatively low temperature (240°). Choosing as examples the major products $C_6F_4Cl_6$ and $C_6F_5Cl_5$ which gave on aromatization mainly $C_6F_2Cl_4$, $C_6F_3Cl_3$ and $C_6F_4Cl_2$ (see Table 2) a possible mechanism for chlorofluorination which involves only addition of fluorine or chlorine monofluoride and allylic or vinylic substitution will be as follows:



While it is perfectly evident that the chlorofluorination process is more complex than this scheme indicates, we think that it accounts for the major facts brought out in the present investigation.

Although the overall effect of the addition processes is the addition of either two atoms of fluorine or one of fluorine and one of chlorine to the ring systems, it must be remembered that the attacking reagent is either chlorine trifluoride or chlorine monofluoride (formed from chlorine trifluoride as a result of reaction with hexachlorobenzene). It can not be elemental fluorine since this reacts with hexachlorobenzene very much more readily than does chlorine trifluoride to give saturated products.[7] Even at intermediate stages in the latter reaction only saturated material and unchanged hexachlorobenzene can be isolated. It is evident that the chlorofluorocyclohexenes are difficult to saturate when chlorine trifluoride is used because of its larger size. A comparison of models of chlorofluorocyclohexenes with those of chlorofluorocyclohexadienes shows that the double bonds of the latter are easily approached even by a large reagent whereas the former are very much more sterically hindered.

[7] G. M. Brooke, R. D. Chambers, J. Heyes and W. K. R. Musgrave, *Proc. Chem. Soc.* (in press).

The aromatization of the chlorofluorocyclohexanes, obtained by using a large excess of chlorine trifluoride, which contain much more chlorine than those isolated from the vapour-phase fluorination of hexachlorobenzene by cobalt trifluoride, also had to be carried out at temperatures lower than that used for the more lightly chlorinated compounds. The retention of up to four chlorine atoms in the aromatic molecules, as shown in Table 3, again illustrates the presence of gem-dichloro groups in the cyclohexanes and the reluctance to undergo allylic rearrangement of the cyclohexenes and -hexadienes. When a sample of pentachloroheptafluorocyclohexane was aromatized under the conditions (430°) previously used for chlorofluorocyclohexanes containing less chlorine, the aromatic product was wholly hexafluorobenzene (13% yield). This illustrates the greater ease with which isomerization, resulting in elimination of more chlorine, of the intermediates occurs at the higher temperature. When the time of contact between the organic material and the iron gauze was halved, the product was a mixture of two parts hexafluorobenzene and one part pentafluoromonochlorobenzene.

TABLE 3. THE AROMATIZATION OF CHLOROFLUOROCYCLOHEXANES

Cyclohexane	Temp of reaction (°C)	Products and yield (%)
$C_6F_7Cl_5$	260	C_6F_6(21), C_6F_5Cl(29), $C_6F_4Cl_2$(8), $C_6F_7Cl_3$(14)
$C_6F_7Cl_5$	430	C_6F_6(13)
$C_6F_7Cl_5$[a]	430	C_6F_6(13), C_6F_5Cl(6)
$C_6F_6Cl_6$	300	C_6F_6(2), C_6F_5Cl(39), $C_6F_4Cl_2$(33), $C_6F_3Cl_3$(2)
$C_6F_5Cl_7$	330	C_6F_5Cl(11), $C_6F_4Cl_2$(46), $C_6F_3Cl_3$(11), $C_6F_2Cl_4$(3)
$C_6F_7Cl_5$[b]	260	C_6F_6(60), C_6F_5Cl(20), $C_6F_4Cl_2$(3·5)

[a] Contact time with catalyst halved.

[b] From action of CoF_3 on C_6Cl_6.

TABLE 4. CORRELATION OF INFRARED SPECTRA OF CHLOROFLUOROBENZENES

	Skeletal vibrations (cm^{-1})	C—F Stretching (cm^{-1})		C—Cl Stretching (cm^{-1})
C_6ClF_5 (liquid film)	1522, **1508**	1101, 1096, 1009, 981		880
1,2-$C_6Cl_2F_4$ (liquid film)	**1493**, **1473**, 1458	1052, 962, 926	[893]	855, 840, 807
1,3,5-$C_6Cl_3F_3$ (KI disc)	**1464**, **1445**	1075, 1064		800, 793, 787
1,2,4-$C_6Cl_3F_3$ (liquid film)	**1471**, **1437**	1088, 965	[890, 852]	803, 784
1,2,3,5-$C_6Cl_4F_2$ (KBr disc)	1449, **1444**, **1422**, 1389	—	[877]	813, 787, 740, 730
1,2,4,5-$Cl_6Cl_4F_2$ (KBr disc)	1473, **1443**, **1393**, 1370, 1350	—	[893, 877]	735
C_6Cl_5F (KI disc)	**1411**, **1372**, 1351 [1266]	1111—1020 (broad)		805, 769, 724
C_6Cl_6 (KI disc)	**1348**, **1300**	—		696

The higher yield of hexafluorobenzene from the sample of pentachloroheptafluorocyclohexane obtained by using cobalt trifluoride as the fluorinating agent[3] indicates, in our view, that this different fluorination procedure results in a greater tendency to simple addition and hence far fewer gem dichloro groups.

Infrared spectra of chlorofluorobenzenes

Strong bands in the spectra of the chlorofluorobenzenes which we have isolated and also of 1,3,5-trichlorofluorobenzene are given in Table 4. These spectra are sufficiently simple to enable the assignment to be made of three principal regions which are associated with skeletal ring vibrations, C—F stretching, and C—Cl stretching. Those bands which are difficult to assign unambiguously are enclosed in brackets. Surprisingly, absorption in the C—F region is very weak in 1,2,3,5- and 1,2,4,5-tetrachlorodifluorobenzene.

The strongest absorption in the region 1400–1500 for chlorofluorobenzenes is a doublet, except for C_6ClF_5 which shows a singlet. These absorptions are indicated by bold type and it can be seen that a steady shift to lower frequency occurs with increasing substitution of fluorine by chlorine. It is therefore reasonable that the position of such a doublet could be used to deduce the number of chlorine atoms in an unknown chlorofluorobenzene.

EXPERIMENTAL

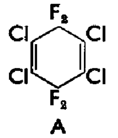
Chlorofluorocyclohexenes

Chlorine trifluoride (55 g, 0·6 M) diluted with nitrogen (5 l/hr for first hour and 2½ l/hr thereafter) was passed into molten (240°) hexachlorobenzene (100 g, 0·35 M) at the rate of 20–25 g/hr for the first hour and then at 10–15 g/hr. The mixture was stirred vigorously and a wide air-condenser prevented removal of hexachlorobenzene which tended to sublime in the early stages. The reaction proceeded smoothly and with only slight decomposition. After passing nitrogen alone for about 30 min to remove the last traces of chlorine trifluoride, the liquid product was diluted with ether, filtered to remove carbon, washed with N·NaOH, water, dried and the ether distilled. The product was distilled through a 20-plate concentric-tube column and then each fraction was purified by preparative scale gas chromatography using silicone elastomer as the stationary phase. The percentage composition of the product was determined from the chromatographic results and is based on the amount of hexachlorobenzene used up (90%). Results are shown in Table 5.

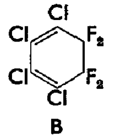
Dichloro-octafluorocyclohexene(II) and trichloroheptafluorocyclohexene(III) from the action of SbF_5 on C_6Cl_6 were supplied by the Imperial Smelting Corporation Ltd. After purification by large-scale gas chromatography they analysed as follows: Found F. 51·3, Cl. 24·3; $C_6F_8Cl_2$ requires F 51·5, Cl. 24·1%; Found F. 42·9, Cl. 34·6; $C_6F_7Cl_3$ requires F 42·7, Cl. 34·2%).

The structure of tetrachlorotetrafluorocyclohexadiene

Spectral data for this compound prove conclusively that it is isomer A



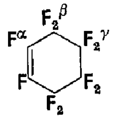
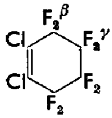
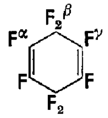
A



B

The I.R. spectrum showed a single peak at 1645 cm^{-1} whereas two peaks would be expected for (B). The U.V. spectrum distinguished between (A) and (B) by showing a single band λ_{max} 208 mμ (methanol), ϵ 13·140; since $C_6Cl_2F_8$, (D), showed a band λ_{max} 213 mμ (methanol), ϵ 5,659. These maxima are very close and the ϵ value for $C_6Cl_4F_4$ is approximately twice that of (D); this situation would not obtain if $C_6Cl_4F_4$ was a conjugated diene.

The ^{19}F. N.M.R. spectrum shows a single, sharp peak at $\phi = 93{\cdot}87$ p.p.m., measured from an internal reference of 10% $CFCl_3$ and the shift from CF_3COOH is 15·29 p.p.m. Both (A) and (B) would be expected to give a single resonance peak, but the value of the chemical shift favours (A). This can be seen from a comparison of the following chemical shift values.

	Compound	Shift from CF_3COOH (external)
(C)		F^{α} 74·6 F^{β} 40·9 F^{γ} 55·6
(D)		F^{β} 32·16 F^{γ} 55·77
(E)		F^{α} 80·9 F^{β} 36·55

Comparing the shifts of (C) and (D) it is apparent that replacement of F by Cl on the double bond does not alter the chemical shifts of the F^{γ} nucleus. On electronegativity grounds, replacement of F by Cl should increase the value of the chemical shift of the F^{β} nucleus, however, the observed change is a shift to low field of −8·7 p.p.m. This is a result of a direct interaction between the F and Cl nuclei which is observed in many other molecules to shift the resonance of the F nucleus to low field. To a first approximation the "ortho effect" of a Cl atom is additive, hence the shift of the F^{β} nuclei in (A) would be expected to be approximately 17·5 p.p.m. to low field of that in (E); the difference between the F^{β} nuclei in (B) and (E) would be approximately 9 p.p.m. The observed shift between F^{β} nuclei in $C_6Cl_4F_4$ and (E) is 21·26 p.p.m., thus indicating that (A) is the correct structure.

TABLE 5. CHLOROFLUOROCYCLOHEXENES FROM HEXACHLOROBENZENE AND CHLORINE TRIFLUORIDE

Boiling range of fractions (°C)	Main components	% yield	b.p.	Mol wt.	n_D(°C)	Analysis Calc. (%) F	Cl	Found (%) F	Cl
142–145	$C_6F_7Cl_3$	2	148	323	1·4050(20) 1·4006(30)	42·7	34·2	42·5	34·2
175–180	$C_6F_6Cl_4$	10	178·5	334	1·4367(20) 1·4327(30)	34·7	43·3	34·0	43·1
	$C_6F_4Cl_4$[a]	4	m.p. 46·5	295		26·2	49·0	26·0	49·8
205–209	$C_6F_5Cl_5$	30	208·5	352	1·4699(20)	27·6	51·5	27·4	51·7
245–248	$C_6F_4Cl_6$	35	242·5	360	1·4998(20)	21·1	59·0	20·9	59·3
273–283	C_6Cl_6	10	m.p. & mixed m.p. 227[b]			—	74·7	1·4	74·0

[a] Isolated as pure isomer (I); Smith *et al.*[8] give m.p. 46°.

[b] After one recrystallisation from ether.

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[8] W. C. Smith, C. W. Tullock, E. L. Muetterties, W. R. Hasek, F. S. Fawcett, V. A. Engelhardt and D. D. Coffman, *J. Amer. Chem. Soc.* **81**, 3165 (1959).

Chlorofluorocyclohexanes

The procedure described for the production of chlorofluorocyclohexenes was repeated but, after chlorine trifluoride (55 g) had been added to the hexachlorobenzene (100 g) the temp was lowered to 100° and more chlorine trifluoride (184 g, 2·0 M) diluted with N_2 (2·5 l/hr) was added over 18 hr. The product was worked up as before and the identities of all except $C_6F_6Cl_6$ and $C_6Cl_5F_7$ were confirmed by comparison, using gas chromatography, with the corresponding compound prepared from hexachlorobenzene and cobalt fluoride as previously described.

TABLE 6. CHLOROFLUOROCYCLOHEXANES\FROM HEXACHLOROBENZENE AND CHLORINE TRIFLUORIDE

Boiling range of fraction	Main components	% yield	b.p. °C	m.p. °C	Calc. (%) F	Calc. (%) Cl	Found (%) F	Found (%) Cl
0–150°	$C_6F_9Cl_3$	Trace	142		48·9	30·4	48·5	31·0
173–176	$C_6F_8Cl_4$	10	175·5		41·5	38·8	41·2	39·1
204–208	$C_6F_7Cl_5$	25	207·5	74–76	34·8	46·4	34·5	46·1
247–250	$C_6F_6Cl_6$	15	248	103–105	27·9	52·1	27·6	52·9[a]
265–275	$C_6F_5Cl_7$[b]	2	270–273	105–110	22·9	59·7	22·9	55·3

[a] requires C = 18·05%; found C = 17·9%.

[b] undergoes dehalogenation during chromatography.

Chlorofluorination in the presence of catalysts

These experiments were conducted as previously described except that a total of 3 moles of chlorine trifluoride per mole of hexachlorobenzene was used. The temp was maintained at 240° until 1½ moles of chlorine trifluoride per mole of hexachlorobenzene had been added and then reduced to 100° while a further 1½ moles were introduced. The cobaltous fluoride was added to the reaction mixture at the start; the ferric chloride, because it sublimes out of the reaction mixture at 240°, was added only at the stage when the temp is lowered to 100°; and the boron trifluoride was passed into the mixture at a steady rate throughout the process together with the chlorine trifluoride and nitrogen. The products (Table 7) were distilled as before, the cyclohexenes and cyclohexanes with the same numbers of chlorine atoms distilling together, and the composition and identity of the fractions determined by analytical gas chromatography using silicone elastomer as the stationary phase. Identities were confirmed by I.R. spectra.

TABLE 7. CATALYSED CHLOROFLUORINATIONS OF HEXACHLOROBENZENE
(In all cases 100 g C_6Cl_6 were used)

Catalyst (g)	Total yield, %	% $C_6F_7Cl_3$	% $C_6F_6Cl_4$	% $C_4F_5Cl_5$	% $C_4F_4Cl_6$	% $C_6F_9Cl_3$	% $C_6F_8Cl_4$	% $C_6F_7Cl_5$	% $C_6F_2Cl_6$	% $C_6F_5Cl_7$
None	80	1	5	15	10	Trace	4	15	20	10
CoF_2(15)	29	Trace	2	2	—	—	3	5	13	4
$FeCl_3$(10)	53	4	14	6	—	Trace	8	16	5	—
BF_3(7·5)	94	—	2	12	18	—	3	14	30	15
BF_3(352)	80	2	10	15	2	Trace	4	17	25	5

*Dehalogenation of chlorofluorocyclohexenes and chlorofluorocyclohexa-*1,4*-diene*

The organic material was flash-distilled at the rate of 5 g in 20 min on a stream of nitrogen (60 ml/min) over a tightly packed roll of iron gauze which filled a mild steel tube 44″ long and 2″ diam. Electrical strip-heaters along the whole tube maintained a constant temp in the central 20″ during the course of a run. The temp of each section of the reactor was determined by means of thermocouples welded to the top of the reactor body which was contained in an aluminium box and insulated by fire-bricks. The metal halide formed on the surface of the gauze was removed by passing hydrogen (20 l/hr for 5–8 hr) at 500°, after each run. The residual hydrogen was removed by purging with nitrogen. The products were collected in traps cooled in liquid air immediately on leaving the reactor and separated as shown in Table 2 using preparative scale gas chromatography (stationary phase, silicone elastomer). The first sample of each compound was identified by analysis for chlorine and fluorine (see Table 8) and by I.R. spectroscopy (see earlier). Subsequent samples were identified by gas chromatographic comparison of peak maxima and by I.R. spectra. The percentage composition of the isomers of the chlorofluorobenzenes were determined by nuclear magnetic resonance spectroscopy.

TABLE 8. PHYSICAL PROPERTIES OF CHLOROFLUOROBENZENES

						Analysis (%)			
				Mol.	Wt.	Found		Calc.	
Cpd.	b.p.°	m.p.°	n_D^{20}	Found	Calc.	F	Cl	F	Cl
C_6F_6	79·0°	—	1·3765	—	—	61·5	—	61·3	—
C_6F_5Cl	117·5°	—	1·4188	206	203	47·2	17·5	46·9	17·5
$C_6F_4Cl_2$	150·5°	—	1·4659	230	219	35·2	32·8	34·7	32·5
$C_6F_3Cl_3$	—	23·5	—	245	236	25·0	44·6	24·2	45·2
$C_6F_2Cl_4$	—	62	—	—	—	14·3	56·3	15·1	56·3
C_6FCl_5	—	134	—	—	—	7·1	66·1	7·1	66·1

NMR *data for chlorofluorobenzenes*

The spectra were recorded by a Varian V4300B spectrometer operating at a frequency of 56·4 Mc/s. The chemical shifts, δ, were measured relative to an external reference sample of trifluoroacetic acid, and are quoted in parts per million. A positive value of δ means that the signal from the sample is at higher applied fields than the reference signal. The percentage composition of the isomers of the chlorofluorobenzenes was determined by comparing the areas under the peaks arising from the separate isomers. The areas were estimated either graphically or by weighing the cut out spectra. A detailed account of the analysis of the spectra is to be published eleswhere.

$C_6F_2Cl_4$

Each isomer gives a single, sharp peak. The chemical shifts are: 1,3 difluoro, $\delta = +29·2$; 1,4 difluoro, $\delta = +31·3$; 1,2 difluoro, $\delta = +51·0$.

$C_6F_3Cl_3$

1,3,5 trifluoro isomer gives a single peak at $\delta = +34·2$;

1,2,3 trifluoro isomer shows an A_2X type of spectrum with the A part a doublet centred on $\delta = +51·7$, and the B part a 1:2:1 triplet centred on $\delta = +76·8$.

1,3,4 trifluoro isomer shows an APX type of spectrum with the A part a doublet at $\delta = +112·7$, the P part is a doublet centred on $\delta = +132·5$, and the X part is a pair of doublets centred on $\delta = +134·2$.

$C_6F_4Cl_2$

1,2,4,5 tetrafluoro isomer gives a single peak at $\delta = +71·1$.

1,2,3,4 tetrafluoro isomer has a AA′BB′ type of spectrum with the A part centred on $\delta = +66·9$, and the B part on $\delta = +86·7$.

1,2,3,5 tetrafluoro isomer shows a A_2PX type of spectrum with the A part a pair of doublets centred on $\delta = +56·5$ the P part of the spectrum is a pair of 1:2:1 triplets at $\delta = +40·2$ and the X part is a 1:2:1 triplet of doublets at $\delta = +82·5$.

Dehalogenation of chlorofluorocyclohexanes

The reaction conditions were exactly as described for the chlorofluoro-cyclohexenes, the optimum temperatures for each of the cyclohexanes being as shown in Table 3.

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