# *The preparation and reactions of cyclic organic fluorine-containing compounds*

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DURHAM COLLEGES IN THE UNIVERSITY OF DURHAM

A THESIS

entitled

# THE PREPARATION AND REACTIONS OF CYCLIC ORGANIC FLUORINE-CONTAINING COMPOUNDS

submitted by

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A candidate for the degree of Doctor of Philosophy.

1963.

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# SUMMARY

## The Preparation and Reactions of Cyclic Organic Fluorine-containing Compounds.

### PART I. Chlorofluorination and Fluorination of Hexachlorobenzene and Dehalogenation of the Products.

The liquid phase reaction of hexachlorobenzene and chlorine trifluoride at 240°C, gave good yields of the perchlorofluorocyclohexenes, of general formula $C_6Cl_nF_{10-n}$, n = 3-6, and a small amount of tetrachlorotetrafluorocyclohexadiene. The retention of the -CCl=CCl- structure in these cyclohexenes sterically hindered further addition, but a large excess of chlorine trifluoride gave the perchlorofluorocyclohexanes, of general formula $C_6Cl_xF_{12-x}$, x = 3-7. The composition of the product was only slightly changed when catalysts were used.

Passage of these compounds over heated iron gauze, at 200-300°C, gave all the possible perchlorofluorobenzenes. The identification of the isomeric perchlorofluorobenzenes in the dehalogenation of the perchlorofluorocyclohexenes, shed some light on the structure of the parent cyclohexene, and hence on the mechanism of the chlorofluorination.

The liquid phase reaction of hexachlorobenzene and fluorine at room temperature, in 1,1,2-trichlorotrifluoroethane, gave excellent yields of the perchlorofluorocyclohexanes, of general formula $C_6Cl_xF_{12-x}$, x = 4-7. Passage of this mixture over heated iron filings, at 330°C, gave mainly hexafluorobenzene, chloropentafluorobenzene and dichlorotetrafluorobenzene.

## PART II. Some Reactions of Chloropentafluorobenzene.

Chloropentafluorobenzene was prepared by the dehalogenation of the perchlorofluorocyclohexanes, obtained by the fluorination of hexachlorobenzene (see Part I).

The nucleophilic reactions between chloropentafluorobenzene and sodium methoxide in methanol, ammonia in ethanol, and hydrazine monohydrate in ethanol were investigated. Nucleophilic replacement of a fluorine atom by the $OCH_3^-$, $NH_2^-$ and $NHNH_2^-$ nucleophiles occurred.

Both the ortho and para positional isomers were formed; these were separated by preparative scale vapour phase chromatography, and identified by a chlorine and fluorine analysis, and N.M.R. spectroscopy. The isomer distribution of the substituted chlorotetrafluorobenzene did not alter with different nucleophiles.

A further reaction of chloropentafluorobenzene, where the chlorine atom was eliminated, was the Ullmann reaction; this gave a good yield of decafluorodiphenyl.

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# PART I

# CHLOROFLUORINATION AND FLUORINATION OF HEXACHLOROBENZENE AND DEHALOGENATION OF THE PRODUCTS.

## Chapter 1

## HISTORICAL INTRODUCTION

A natural reaction for the preparation of chlorofluorocyclohexanes, -cyclohexenes and -cyclohexadienes containing no hydrogen, is the fluorination of hexachlorobenzene. The exhaustive chlorofluorination of benzene and the fluorination of chlorobenzenes produce only the fully saturated compounds, which are also prepared by the chlorination of perfluorobenzene, perfluorocyclohexene and perfluorocyclohexadiene.

## Fluorination of Hexachlorobenzene.

These fluorinations can be mainly divided into two groups, firstly the reaction with fluorine and halogen fluorides, and secondly the reaction with heavy metal fluorides. The first group is concerned with the action of elemental fluorine, bromine trifluoride and sulphur tetrafluoride on hexachlorobenzene. The second group deals with the vapour phase reactions using cerium tetrafluoride, plumbic fluoride and cobaltic fluoride and the lower temperature reaction with antimony pentafluoride.

### Hexachlorobenzene and Fluorine.

Bigelow and Pearson[1] reported the isolation of hexachlorotetrafluorocyclohexene and hexachlorohexafluorocyclohexane in small quantities by the reaction of hexachlorobenzene, as a suspension in carbon tetrachloride, with elemental fluorine. When the solid had disappeared into solution, the solvent was removed leaving an oil. This was further fluorinated at 0°C in a copper vessel.

$$C_6Cl_6 + F_2 \longrightarrow C_6Cl_6F_4 + C_6Cl_6F_6$$

The amount of known product isolated was only a very small percentage of the fluorinated product. Later Fukuhara and Bigelow[2] reacted hexachlorobenzene with fluorine in the vapour phase, using a copper gauze catalyst. The heavy yellow oil produced was reduced with iron and glacial acetic acid, and on fractionation yielded twelve definite chemical individuals. The properties of these were reported, but no structures were assigned, and although further investigation was carried out, there is no report of this work in the literature.

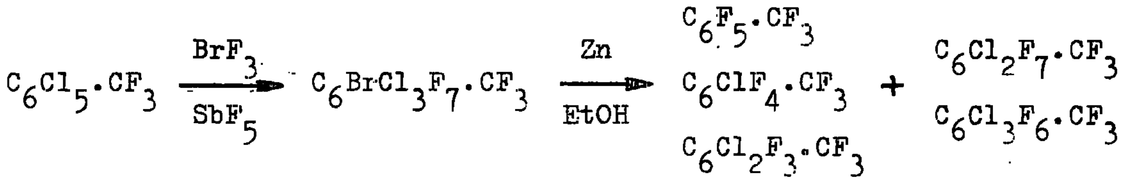
## Hexachlorobenzene and Bromine Trifluoride.

McBee, Lindgren and Ligett[3,4,5] reacted hexachlorobenzene and bromine trifluoride in a stirred nickel tube, the hexachlorobenzene was added in small amounts and the tube heated to 150°C; the vessel was cooled before each further addition. The mixture of products from this reaction corresponded to the approximate molecular formula $C_6Br_2Cl_4F_6$. This was further fluorinated with antimony pentafluoride at 100°C, and a solid product formed of approximate molecular formula $C_6BrCl_4F_7$.

$$C_6Cl_6 + BrF_3 \xrightarrow{150^\circ C} C_6Br_2Cl_4F_6 + SbF_5 \xrightarrow{100^\circ C} C_6BrCl_4F_7$$

Again no attempt was made to realize its constitution and it was dehalogenated using zinc and ethanol[6], giving the aromatic compounds $C_6F_6$ and $C_6ClF_5$, and the cyclic unsaturated compounds $C_6F_8$, $C_6ClF_7$, $C_6Cl_2F_6$, $C_6Cl_3F_5$, and $C_6Cl_2F_8$, $C_6Cl_3F_7$. The physical properties were reported, but there was no attempt to find their configurations.

A similar fluorination process was reported on trifluoromethylpentachlorobenzene[3,4,7], which gave an approximate molecular formula of $C_6BrCl_3F_7.CF_3$ on treatment with a bromine trifluoride and antimony pentafluoride. Dehalogenation with zinc and ethanol gave a mixture of chlorofluorobenzenes and -cyclohexenes.



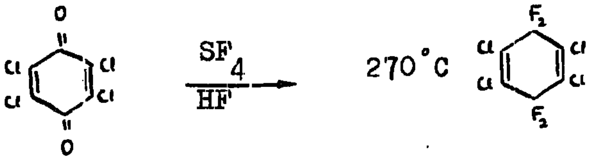
$$C_6Cl_5.CF_3 \xrightarrow[SbF_5]{BrF_3} C_6BrCl_3F_7.CF_3 \xrightarrow[EtOH]{Zn} \begin{matrix} C_6F_5.CF_3 \\ C_6ClF_4.CF_3 \\ C_6Cl_2F_3.CF_3 \end{matrix} + \begin{matrix} C_6Cl_2F_7.CF_3 \\ C_6Cl_3F_6.CF_3 \end{matrix}$$

Florin and coworkers[8] repeated the above work and stressed the importance of the temperature control throughout the reaction, and the necessity of small additions of hexachlorobenzene. An attempt was made to fluorinate the initial products of this reaction with chlorine trifluoride, however explosions occurred and the reaction was not pursued.

Hexabromobenzene was found to react with both iodine pentafluoride and bromine trifluoride, to give the fully saturated hexabromohexafluorocyclohexane, and the unsaturated hexabromotetrafluorocyclohexene.

## Hexachlorobenzene and Sulphur Tetrafluoride.

Smith and coworkers[9] working with sulphur tetrafluoride fluorinated hexachlorobenzene at 200-400°C and obtained cyclic $C_6Cl_2F_8$ and $C_6Cl_3F_9$. He also fluorinated chloranil[10], using sulphur tetrafluoride and hydrogen fluoride at 270°C, and isolated the pure 1,2,4,5-tetrachlorotetrafluorocyclohexa-1,4-diene in a 75% yield.

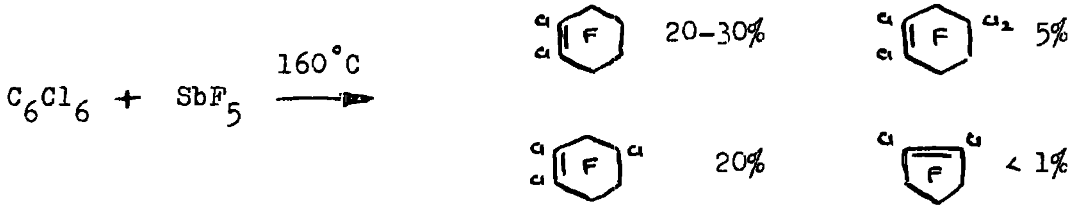


Hexachlorobenzene and Antimony Pentafluoride.

This reaction was first reported by McBee et al.[11], who heated hexachlorobenzene and antimony pentafluoride to 125°C and obtained 1,2-dichlorooctafluorocyclohexene in up to 60% yields. Later work[12] revealed that at 150°C the yield was increased to 87%. Trifluoromethylpentachlorobenzene was also treated with antimony pentafluoride at 150°C, this yielded the unsaturated 1,2-dichlorooctafluorocyclohexene and 1-chlorononafluorocyclohexene. If the temperature was raised (up to 300°C), and the reaction time prolonged, a further product was produced, the saturated $C_6Cl_3F_9$.

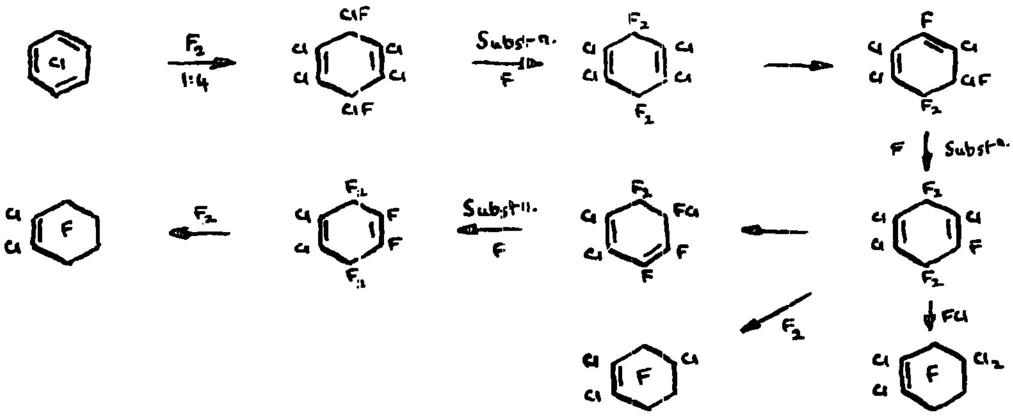
Stilmar[13] on heating hexachlorobenzene with antimony pentafluoride at 250°C, reported the isolation of a chlorofluorobenzene $C_6Cl_2F_4$, together with the unsaturated cyclic $C_6Cl_2F_6$, prolonged reaction gave the fully saturated cyclic $C_6F_{12}$, $C_6ClF_{11}$ and $C_6Cl_2F_{10}$. This is the only report of an aromatic compound found in this reaction and although an analysis was quoted, no physical data were given.

Recent work on this reaction has been carried out by Leffler[14], who reacted hexachlorobenzene with antimony pentafluoride at 160°C. A careful control of the temperature was maintained, as an exothermic reaction occurred at 160°C which resulted in loss of some of the product. The structure determinations were made by infra red and N.M.R. measurements and the products were shown to be 1,2-dichlorooctafluorocyclohexene, 1,2,4-trichloroheptafluorocyclohexene, 1,2,4,4-tetrachlorohexafluorocyclohexene and 1,2-dichlorohexafluorocyclopentene.



The infra red spectra of these compounds all had a single strong, absorbtion band at 6.15µ, which was assigned to the -CCl=CCl- grouping, N.M.R. measurements showed that only the pure, single isomers were present.

The mechanism put forward consisted of 1,4 addition of fluorine and substitution of allylic chlorine by fluorine. The diene, so formed, rearranges and further substitution takes place. Finally, addition of fluorine or chlorine monofluoride, from the antimony dichlorotrifluoride produced in the latter part of the reaction, occurs to give the cyclic monoenes.



## Hexachlorobenzene and Metallic Fluorides.

The high temperatures necessary for these reactions results in the formation of the fully saturated compounds being formed, no unsaturated material has been isolated except in very mild reaction conditions.

The reaction between hexachlorobenzene and cobaltic fluoride, investigated in these laboratories by Johncock and Musgrave[15,16], produced a large range of chlorofluorocyclohexanes. The hexachlorobenzene was vapourized, and passed over cobaltic fluoride at 350°C, in a cylindrical stirred reactor, to give good yields of the cyclohexanes of general formula $C_6Cl_nF_{12-n}$, n=1-6.

McBee and coworkers[17] used a static reactor to fluorinate hexachlorobenzene with cerium tetrafluoride at 275°C. Cyclic $C_6Cl_3F_9$ was obtained in good yields; recycling the product produced the fully fluorinated cyclic $C_6F_{12}$. Lindgren and McBee similarly fluorinated hexachlorobenzene with plumbic fluoride at 300°C to give cyclic $C_6Cl_3F_9$ in 8% yield.

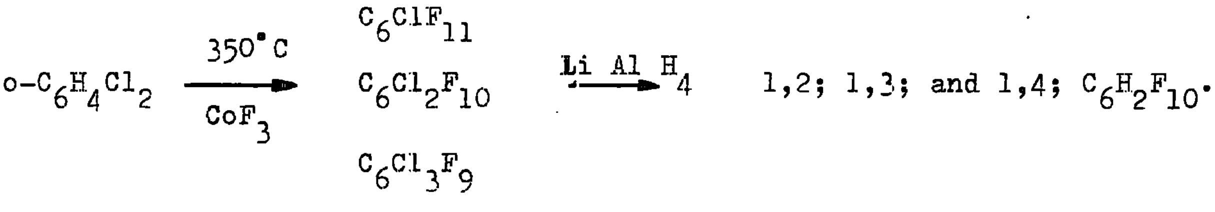
## Fluorination and Chlorofluorination of Benzenes.

Benzene has been reacted with chlorine trifluoride by Musgrave and coworkers[19,20]. The chlorine trifluoride, diluted with nitrogen, and the vapourized benzene, were passed into a reaction vessel packed with copper clippings at 260°C. Perchlorofluorocyclohexanes of the general formula $C_6Cl_nF_{12-n}$, where n=1-4, were produced, however these formed complex mixtures with the hydrochlorofluorocyclohexanes, and isolation was impossible.

A wide variety of aromatic compounds have been reacted with elemental fluorine[1,2,21-28,72,73]. Normally a controlled reaction will ensue at 0°C, and if the material is a solid, in carbon tetrachloride solution. Addition, substitution, fragmentation and polymerization all take place giving a wide variety of products.

The fluorination of O-dichlorobenzene has been carried out by Lindgren and McBee[18] in America, and Tatlow and Worthington[29] in Birmingham. The former used six static reactors in series, and the dichlorobenzene was recycled three times through the reactors, at temperatures from 118°C-323°C. The fluorinating agents used, were firstly argentic fluoride, and secondly manganic fluoride; both produced reasonable yields of cyclic $C_6ClF_{11}$ and $C_6Cl_2F_{10}$.

Tatlow and Worthington used a single stirred reactor at 350°C, with cobalt trifluoride as the fluorinating agent. The product was shown to contain cyclic $C_6ClF_{11}$, $C_6Cl_2F_{10}$ and $C_6Cl_3F_9$. The existance of a trichloro- compound indicated that the liberated chlorine could re-enter the organic molecule. Further proof of this[30] was shown with the cyclic $C_6Cl_2F_{10}$, which was a mixture of isomers. These on reduction gave the seperable dihydrodecafluorocyclohexanes.



$$o\text{-}C_6H_4Cl_2 \xrightarrow[CoF_3]{350^\circ C} \begin{matrix} C_6ClF_{11} \\ C_6Cl_2F_{10} \\ C_6Cl_3F_9 \end{matrix} \xrightarrow{LiAlH_4} 1,2;\ 1,3;\ \text{and}\ 1,4;\ C_6H_2F_{10}.$$

Chlorobenzene was fluorinated similarly by these workers, and gave cyclic $C_6ClF_{11}$ in 14% yield.

## Chlorination of Perfluoro- Compounds.

This method although extremely limited gives compounds of known configuration.

Brice and Simons[31] added chlorine to perfluorocyclohexene to give 62% of 1,2-dichlorodecafluorocyclohexane; this work was repeated by Tatlow and Worthington[29], who used liquid chlorine in a sealed tube heated by a mercury-vapour lamp. A later paper by Smith and Tatlow[32] indicated that the reaction occurred by cis addition. This was proved by reduction with lithium aluminium hydride to give the dihydro-compound, and then examination of the products on dehydrofluorination.

Further work by Tatlow[33,34] showed that chlorine added to perfluorocyclohexa-1,3-diene and perfluorobenzene, to give 1,2,3,4-tetrachlorooctafluorocyclohexane, and 1,2,3,4,5,6-hexachlorohexafluorocyclohexane respectively.

## The Preparation of Fluorine - Containing Aromatic Compounds.

### The Schiemann Reaction.

The first step towards the interest shown in fluoroaromatic compounds was taken by Balz and Schiemann[35] in 1927. Aniline was diazotized to form phenyl diazonium chloride. This on treatment with fluoroboric acid gave an insoluble precipitate of phenyl diazonium fluoroborate, which was filtered off, and carefully decomposed by heat to form fluorobenzene.

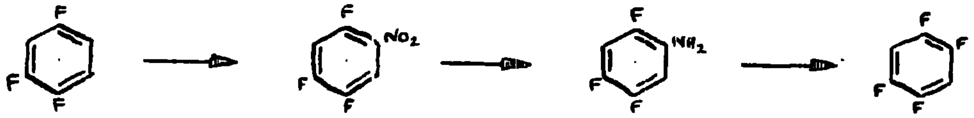
$$C_6H_5NH_2 + NaNO_2/HCl \xrightarrow{0^\circ C} C_6H_5\overset{+}{N}{\equiv}N \cdot \overset{-}{Cl}$$

$$C_6H_5\overset{+}{N}{\equiv}N \cdot \overset{-}{Cl} + HBF_4 \longrightarrow C_6H_5\overset{+}{N}{\equiv}N \cdot \overset{-}{BF_4} \text{ (ppt.)}$$

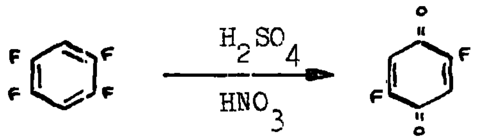
$$C_6H_5\overset{+}{N}{\equiv}N \cdot \overset{-}{BF_4} \xrightarrow[\text{Heat}]{} C_6H_5F + N_2 + BF_3.$$

This is now a standard method for the introduction of fluorine into an aromatic system[35,37], and yields of up to 90% have been obtained.

The amount of fluorine, however, that can be introduced into benzene in this way is limited. Finger[38-41] found that fluorine can be introduced in a stepwise manner. Thus fluorobenzene can be nitrated and then reduced to form the amine, this on diazotization and treatment with fluoroboric acid, gives the phenyl diazonium fluoroborate; which gives the difluorobenzene on careful heating. This was repeated to give tri- and tetrafluorobenzenes.



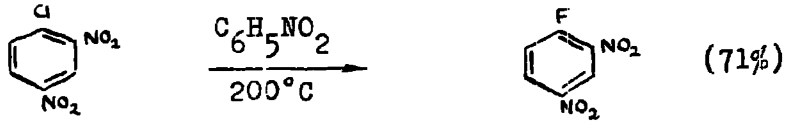
A large number of substituted fluorobenzenes have been isolated in this manner. When the 1,2,4,5-tetrafluorobenzene was nitrated, oxydation occurred, and instead of the nitro-compound being isolated, fluorine was eliminated, and a difluoroquinone was formed.



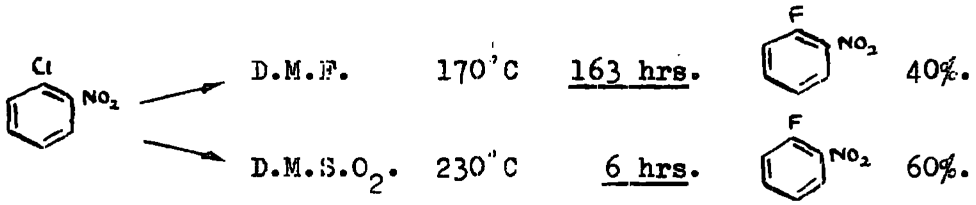
Thus pentafluoro- and perfluorobenzenes have to be synthesised by different methods.

## General Methods of Fluorination.

The fluorination of aromatic compounds using vigorous reagents such as the metallic fluorides[42] or halogen fluorides gives in most cases the fully saturated compounds. However, alkali metal fluorides can replace halogen atoms in the nucleus, if these are suitably activated. Thus Gottlieb[43], and later Cook and Saunders[44], replaced chlorine in chlorodinitrobenzene using potassium fluoride.



Finger and Kruse[45] extended this method of fluorination to the mononitrohalogenobenzenes and using dimethylformamide (D.M.F.) or dimethylsulphoxide as solvent obtained reasonable yields of the corresponding fluoro- compound. These yields were increased when dimethyl sulphone (D.M.S.O$_2$.)[46] was used as the solvent.



The fluorination of benzene, in carbon tetrachloride, with chlorine trifluoride at 0°C gave fluorobenzene in quite good yields[47,48]. Better yields were isolated when cobalt fluoride was used as a catalyst. Similar work was reported with benzotrifluoride, toluene, and chlorobenzene, when the main reaction was again one of substitution. The chlorofluorination of benzene in the vapour phase (250°C)[19], yielded some p-chlorofluorobenzene, although it could not be isolated from a complicated mixture of saturated compounds.

The electrochemical fluorination[49] of aromatic hydrocarbons and halogenohydrocarbons is limited due to their insolubility in hydrogen fluoride. Even on agitation of the cell contents, the yields of fluorine compounds are extremely low, although some polymeric compounds are formed. Aromatic amines and heterocyclic bases are soluble, but normally saturation occurs.

## Dehydrofluorination.

A useful method for the preperation of fluorobenzenes is the dehydrofluorination of alicyclic fluorine-containing compounds, using aqueous potassium hydroxide. This method is used for both pentafluoro- and perfluorobenzenes, as well as the lower members of the series. Thus octafluorocyclohexane[50-52], obtained from the fluorination of benzene[53], was refluxed with 18N aqueous potassium hydroxide for four hours and gave a 45% yield of pentafluorobenzene. Similar treatment of 1,2,4-trihydrononafluorocyclohexane[34] gave perfluorobenzene as well as a mixture of polyfluorocyclohexenes and -cyclohexadienes.

Other reactions with hydrofluorocyclohexanes have produced polyfluorocyclohexenes and -cyclohexadienes. A similar dehydrofluorination reaction takes place using anion exchange resins[59].

## Perfluorobenzene.

Perfluorobenzene was first isolated by McBee[3], by treatment of hexachlorobenzene with bromine trifluoride and antimony pentafluoride, and consequent dehalogenation with zinc dust and ethanol. Chloropentafluorobenzene was also produced, but like perfluorobenzene the overall yield was low (about 3% ). When trifluoromethylpentachlorobenzene was treated similarly, very much better yields of perfluorotoluene and trifluoromethylchlorotetrafluorobenzene were obtained.

$$\begin{array}{lcll} C_6Cl_5{\cdot}CF_3 & \longrightarrow & C_6F_5{\cdot}CF_3 & (10\%) \\ & & C_6ClF_4{\cdot}CF_3 & (20\%) \\ & & C_6Cl_2F_3{\cdot}CF_3 & (12\%) \end{array}$$

Pentachloroheptafluorocyclohexane has been dehalogenated[60] with zinc dust and refluxing n-butyl alcohol, and yielded perfluorobenzene (65%) and chloropentafluorobenzene (7 %). Tetrachlorooctafluorocyclohexane similarly yielded perfluorobenzene (20%), octafluorocyclohexa-1,4-diene (20%) and chloroheptafluorocyclohexadiene (10%).

The first production of perfluorobenzene in good overall yields was reported in 1955 by Desirant[61]. She pyrolysed tribromofluoromethane at 640°C in a platinum tube, and obtained yields up to 45%.

$$6CBr_3F \xrightarrow[640^\circ C]{\text{Pt. Tube.}} C_6F_6 + 9Br_2$$

Conditions for the pyrolysis were latter improved[62,63], and Wall and coworkers using an elevated pressure of four atmospheres at 540°C obtained a 55% yield. Haszeldine repeated this work[64], and found that in a sizeable reaction the amount of bromine evolved caused some difficulty. Pyrolysis of 1-chloro, 1,2-difluoroethylene[65] avoided this difficulty, but at 600°C using a platinum tube, only 14% of perfluorobenzene was obtained.

$$CClF = CHF \xrightarrow[Pt.]{600^\circ C} C_6F_6 \; . \; (14\%).$$

Investigation into the pyrolysis of the easily obtained dibromo- and dichlorofluoromethanes by Haszeldine and coworkers[66] again gave low yields of perfluorobenzene. (Normally 5-10%, although a yield of 33% was recorded). Conditions used with a platinum tube were 600-800°C, and contact times of 0.4-20 seconds.

$$6CHFX_2 \longrightarrow C_6F_6 + 3X_2 + 6HX.$$

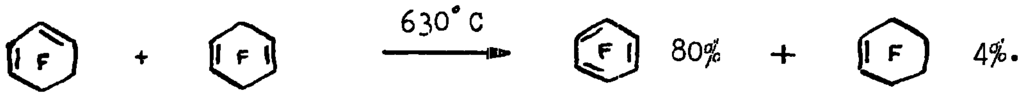
$$(X = Cl \text{ or } Br)$$

Perhaps the best method, so far described in the literature for the preparation of perfluorobenzene, is the dehalogenation of polyfluorocyclohexanes, -cyclohexenes and -cyclohexadienes, using the method described below.

Dehalogenation using Reduced Metal Surfaces.

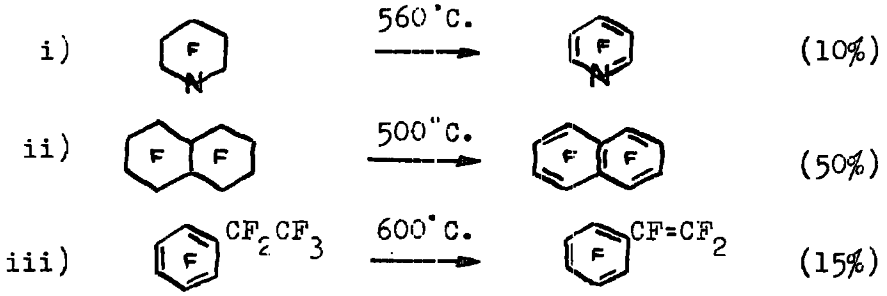
Until recently the interest in saturated cyclic fluorine-containing compounds has only been in the study of their physical properties. Now, however, they are extremely important precursors for a wide range of aromatic compounds.

Tatlow and coworkers[67] discovered in 1959 that if perfluorocyclohexadiene was passed over a clean nickel surface, at 400-600°C, defluorination occurred to give perfluorobenzene.



Similarly perfluoro- or hydrofluorocyclohexanes passed over a clean nickel surface at 400-600°C, defluorinated or dehydrofluorinated to give perfluorobenzene and hydrofluorobenzenes. It was also found that other metals could replace nickel as the dehalogenating agent, of these iron gauze was the most convenient. The metal surface must be regenerated after each reaction by passing hydrogen through the reactor at 500°C.

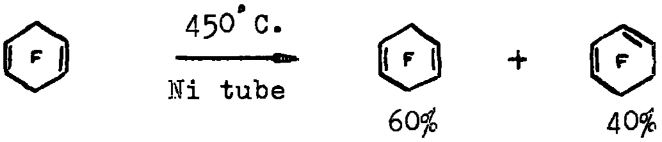
Many aromatic fluorine compounds have now been prepared by this method[16,68-74]. The versility of this reaction is seen in the formation of perfluoropyridine from perfluoropiperidine[71,72], perfluoronapthalene from perfluorodecalin[67,73], and also the formation of perfluorostyrene from pentafluoroethylpentafluorobenzene[74], the defluorination occurring in the side chain.



Although little is known about the exact process of dehalogenation of these saturated compounds, the formation of the aromatic material must depend on its greater stability to the reaction conditions. Work at Birmingham and Durham suggests that for every compound there should be a certain temperature and reaction time, that will produce the best yield of aromatic material. This will vary with the geometry of the dehalogenation reactor, the type of packing, and also the age and previous treatment of the packing.

In the defluorination of polyfluorocyclohexanes and -cyclohexenes[68], it was found that no polyfluorocyclohexadienes were isolated. It would seem that these compounds are extremely unstable in the reaction conditions used. In fact the octafluorocyclohexadienes were defluorinated at temperatures between 400°C and 450°C to give excellent yields of perfluorobenzene (up to 90%). Temperatures of 550°C or more were required to defluorinate decafluorocyclohexene and dodecafluorocyclohexane.

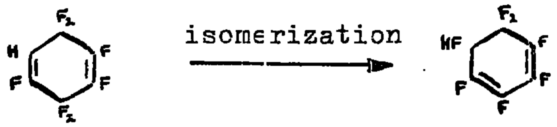
It was found by Tatlow and coworkers[69] that polyfluorocyclohexadienes isomerize at temperatures varying between 250°C and 600°C, to give a mixture of 1,3- and 1,4-dienes.



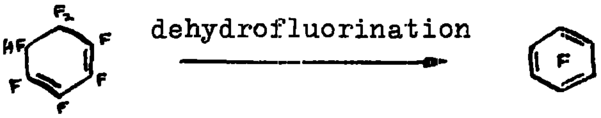
The compositions of these mixtures were not greatly dependant on either the temperature, or the contact time; and it was probable that they were close to equilibrium compositions. It was also found that the -dienes disproportionate, thus perfluorocyclohexadiene, under certain conditions, disproportionated to perfluorobenzene and perfluorocyclohexene.

The dehalogenation of the mixed 1,3- and 1,4-hydroheptafluorocyclohexadienes[68] is extremely interesting, as it was found that the composition of the product changed due to isomerization competing with the dehalogenation. This variation of the composition was influenced by the distribution of temperature along the reactor. Thus if the temperature of the inlet side was reduced, the easier reaction, isomerization, took place and produced compounds with the hydrogen attached to a saturated carbon atom.

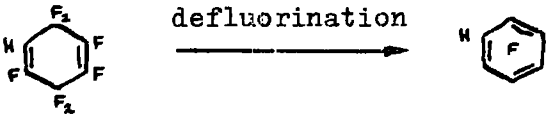
i.e.



This lost hydrogen fluoride and produced perfluorobenzene.



If the inlet temperature was raised defluorination took place immediately and a larger proportion of pentafluorobenzene was produced.



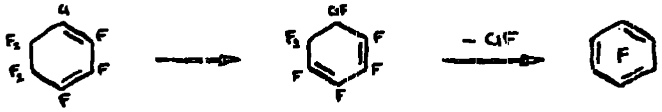
Further proof of this competition was obtained by passing two successive samples, of the mixed 1,3- and 1,4-hydroheptafluorocyclohexadienes, through the dehalogenator without regenerating the iron. The first sample gave perfluorobenzene (40%) and pentafluorobenzene (60%), the second sample, perfluorobenzene (60%), pentafluorobenzene (40%). The second sample had more time to isomerize before defluorination occurred, and thus more perfluorobenzene was produced.

i) $C_6HF_7 \xrightarrow[460^\circ C.]{} C_6F_6$ (37%) + $C_6HF_5$ (63%)

ii) $C_6HF_7 \xrightarrow{\text{Fe gauze.}} C_6F_6$ (61%) + $C_6HF_5$ (39%)

Dehalogenation of polyfluorocyclohexanes and -cyclohexenes must go stepwise to the diene stage. The diene will either disproportionate to an aromatic compound and a cyclohexene, dehalogenate solely to the aromatic state, or isomerization will occur to give another diene; this in turn can either dehalogenate or disproportionate.

Work in these laboratories on the dehalogenation of chlorine-containing fluorocyclohexanes[16,75], at 430°C, showed that chlorine was preferentially elliminated, and no chloroaromatic compounds were isolated; although some unsaturated chlorine-containing compounds were present. The absence of these compounds was again explained by the rearrangement of the cyclodiene, and elimination of chlorine or chlorine monofluoride.



The dehalogenation process therefore seems to be fairly straight forward, although some peculiar results have been obtained by Tatlow. In the defluorination of hydroheptafluorocyclohexadiene[68], some tetrafluorobenzene was isolated, the hydrogen absorbed by the packing during the regeneration, re-entered the molecule at some stage of the dehalogenation process. It was also found that after renewal of the packing, erratic results were obtained until the metal had 'aged'.

## Polymerization and Further Pyrolysis Reactions.

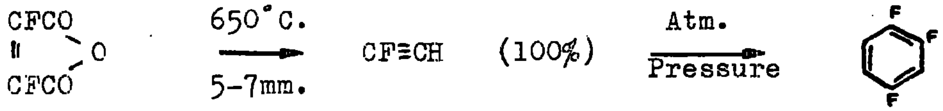
In the previously described methods of production of highly fluorinated aromatic compounds, there is a marked absence of reactive groupings in the molecule.

Wall and coworkers[76] noticed that in the production of perfluorobenzene, by the pyrolysis of tribromofluoromethane, a 5% impurity of bromopentafluorobenzene was present. With the intention of increasing this yield, they copyrolysed a variety of bromomethanes with tribromofluoromethane. The most successful was the copyrolysis with tribromomethane, at 540°C, and 4 atmospheres pressure. Good yields of perfluorobenzene and bromopentafluorobenzene were obtained, dibromotetrafluorobenzene was isolated in small yields.

$$CBr_3F + CHBr_3 \longrightarrow C_6F_6 + C_6BrF_5 + C_6Br_2F_4$$

Bromopentafluorobenzene is an extremely useful intermediate in the preparation of a wide range of substituted pentafluorobenzenes[52,77-79], as the Grignard reagent is readily made.

Some interesting polymerization reactions have been carried out with fluoroacetylene compounds. Fluoroacetylene[80], prepared by the pyrolysis of fluoromaleic anhydride, polymerized on standing to give 1,2,4-trifluorobenzene.



Perfluoroacetylene[81] did not polymerize although perfluoro, 2-butyne[82] gave hexakistrifluoromethylbenzene.

## Perchlorofluorobenzenes.

The isolation of perchlorofluorobenzenes has been reported by the fluorination of hexachlorobenzene, both with elemental fluorine[83,84], and antimony pentafluoride[13]. It seems extremely doubtful however, from further work on the fluorination of hexachlorobenzene (see page 1 ), that substitution could occur before addition, to give an aromatic fluorine compound in any quantity.

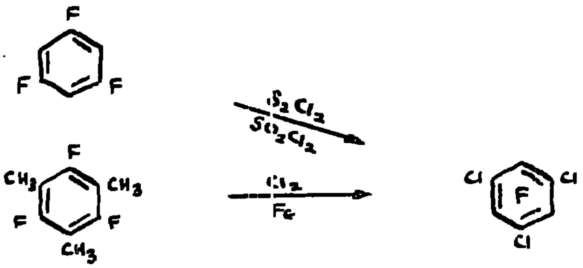
Chloropentafluorobenzene was made by McBee[3] by treatment of hexachlorobenzene with bromine trifluoride and antimony pentafluoride and consequent dehalogenation using zinc dust and ethanol. The yield was low although dehalogenation of cyclic $C_6Cl_4F_8$[6,60], with zinc dust and alcohol, improves the yield slightly.

Pentafluorobenzene can be iodinated and brominated to form the iodo- and bromopentafluorobenzene [52]. Mobbs[85] using the same tecnique obtained a 20% yield of chlorofluorobenzene.

$$C_6HF_5 \ + \ Cl_2 \ \xrightarrow[AlCl_3]{H_2S_2O_7} \ C_6ClF_5 \quad 20\%.$$

The chlorine was bubbled into a solution of pentafluorobenzene, dissolved in fuming sulphuric acid, with aluminium trichloride present as a catalyst.

The symmetrical 1,3,5-trichlorotrifluorobenzene was prepared by Finger[39,41]; 1,3,5-trifluorobenzene was chlorinated using sulphur monochloride and sulphuryl chloride. The chlorination of 1,3,5-trifluoromesytilene, using chlorine and iron catalyst also gave 1,3,5-trichlorotrifluorobenzene.



Low Yields.

A wide variety of fluorohalobenzenes have been reported by Vorozhtsov and coworkers[86]. These were prepared by chlorination and bromination of fluorobenzenes. The preparation of perchlorofluorobenzenes was also reported. The appropriate fluorobenzene was brominated in the presence of aluminium, the perbromofluorobenzene was then treated with chlorine, in U.V. light for 5-6 hours.

73%.

The more lightly chlorinated perchlorofluorobenzenes have been prepared very recently, in reasonable yields, by Parshall[87]. He reacted 1,2,4,5-tetrachlorotetrafluorocyclohexa-1,4-diene with potassium fluoride at elevated temperatures. The -diene is conveniently made as mentioned earlier by the action of sulphur tetrafluoride on chloranil.

The overall yields of perchlorofluorobenzenes are best at 600°C, below this temperature full aromatization does not occur, and above, the overall yield decreases rapidly.

| | |
|---|---|
| $C_6F_6$ | 5%. |
| $C_6ClF_5$ | 11%. |
| $C_6Cl_2F_4$ | 9%. |
| $C_6Cl_3F_3$ | 4%. |

Another reaction producing these lightly chlorinated benzenes, was reported by Maynard[83], who reacted potassium flueride with hexachlorobenzene using n-methylpyrrolidone as solvent.

$$\mathrm{KF} + \mathrm{C_6Cl_6} \xrightarrow[\text{pyrrolidone.}]{\text{n-methyl-}} \begin{array}{ll} \mathrm{C_6Cl_3F_3} & 23\%. \\ \mathrm{C_6Cl_2F_4} & 34\%. \\ \mathrm{C_6ClF_5} & \text{small.} \end{array}$$

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# Chapter 2.

# DISCUSSION OF EXPERIMENTAL WORK

# FLUORINATION OF HEXACHLOROBENZENE.

## Preparation of Cyclic Fluorine Compounds Suitable for Dehalogenation.

The vapour phase reaction of chlorine trifluoride and benzene, carried out in these laboratories by Musgrave and Banks[19,20], gave a complicated mixture of hydrochlorofluorocyclohexanes that were extremely difficult to separate. The main difficulty was the retention of hydrogen within the molecule, giving a large number of hydrogen substituted cyclohexanes. This was partially remedied by using a lower nitrogen dilution rate and increasing the chlorine trifluoride, benzene ratio. This complex mixture could not be separated by distillation, although distillation fractions, which contained azeotropic mixtures of cyclohexanes, were dehalogenated. Mobbs[19], using the relatively new technique of passing the vapours over iron gauze at an elevated temperature[69], found that perfluorobenzene (overall yield 5%), pentafluorobenzene (7%), and some fluorobenzenes containing more hydrogen, were produced. Although the starting material (benzene) is readily accessible, the low yields of the dehalogenated products do not make it an attractive route to highly fluorinated aromatic compounds.

In order to eliminate the hydrogen from the cyclohexanes, work was carried out by Johncock[16] on the reaction between hexachlorobenzene and cobalt trifluoride. In the vapour phase reaction, using a modification of the reactor used by Massingham[89], good yields of the highly fluorinated perchlorofluorocyclohexanes were obtained.

$$C_6Cl_6 + CoF_3 \longrightarrow C_6Cl_xF_{12-x} + CoF_2 \quad x=1-6$$

$$CoF_2 + ClF_3 \longrightarrow CoF_3$$

This reaction involved the regeneration of the cobalt fluoride after each run, by passing chlorine trifluoride over the fluorinating agent[90]. This regeneration was somewhat laborious, as well as considerable corrosion occurring within the reactor. The average amount of hexachlorobenzene that could be reacted in each run was 100 gms.

These perchlorofluorocyclohexanes were again dehalogenated by Mobbs[16], to give good yields of perfluorobenzene. This is a very much more attractive route to perfluorobenzene. However it was thought that if the more highly chlorinated perchlorofluorocyclohexanes could be formed, on dehalogenation some of the chlorine would remain within the aromatic product; and thus provide a reactive point within the molecule.

The reaction between chlorine trifluoride and hexachlorobenzene should provide such a mixture of perchlorofluorocyclohexanes, and this work is reported in the first part of this chapter.

## Reaction of Hexachlorobenzene with Chlorine Trifluoride.
## (Molar Ratio 1:1½)

An exploratory run was carried out using carbon tetrachloride as a solvent, at room temperature. The chlorine trifluoride, diluted with nitrogen was passed into a stirred slurry of hexachlorobenzene. The only reaction that ensued was the fluorination of the solvent.

The reaction of molten hexachlorobenzene at 240°C. with chlorine trifluoride proceeded reasonably smoothly to give good yields of perchlorofluorocyclohexenes, $C_6Cl_nF_{10-n}$ where $n=3-6$, tetrachlorotetrafluorocyclohexadiene and unreacted hexachlorobenzene (see table 1).

The rate of chlorine trifluoride addition and nitrogen dilution were controlled such that ignition did not occur. In the initial stages of the reaction, sublimation of the hexachlorobenzene often caused blockages in the air condenser.

Analytical V.P.C. showed that in subsequent chlorofluorinations, the distribution of the products although not identical, was fairly consistant. In each reaction about thirteen products were formed; six of these were isolated and identified. These were separated by distillation and finally purified by preparative scale vapour phase chromatography.

Infra red spectra and N.M.R. measurements showed these perchlorofluorocyclohexenes to be mixtures of isomers. These isomers could not be separated by distillation, or by vapour phase chromatography on packings so far used in these laboratories. Other workers[15,29,30] have shown that the perchlorofluorocyclohexanes, formed by the fluorination of chlorobenzenes with metallic fluorides, similarly cannot be separated by distillation or chromatography. The physical properties of these cyclohexenes, i.e. boiling point and refractive index, show the normal gradation

TABLE I. Products from Chlorofluorination of Hexachlorobenzene.

| Products | $C_6Cl_6$ $1\frac{1}{2}$ $ClF_3$ | $C_6Cl_6$ 3 $ClF_3$ | $C_6Cl_6$ 7 $ClF_3$ | $C_6Cl_6$ 3 $ClF_3$ $FeCl_3$ | $C_6Cl_6$ 3 $ClF_3$ $CoF_2$ | $C_6Cl_6$ 3 $ClF_3$ Limited $BF_3$ | $C_6Cl_6$ 3 $ClF_3$ Excess $BF_3$ | $C_6Cl_6$ 3 $F_2$ |
|---|---|---|---|---|---|---|---|---|
| $C_6Cl_3F_7$ | 2% | 1% | - | 4% | Trace | - | 2% | - |
| $C_6Cl_4F_6$ | 10% | 5% | - | 14% | 2% | 2% | 10% | - |
| $C_6Cl_5F_5$ | 30% | 15% | - | 6% | 2% | 12% | 15% | - |
| $C_6Cl_6F_4$ | 35% | 10% | - | - | - | 18% | 2% | - |
| $C_6Cl_3F_9$ | - | Trace | Trace | Trace | - | - | Trace | - |
| $C_6Cl_4F_8$ | - | 4% | 10% | 8% | 3% | 3% | 4% | 5% |
| $C_6Cl_5F_7$ | - | 15% | 25% | 16% | 5% | 14% | 17% | 24% |
| $C_6Cl_6F_6$ | - | 20% | 15% | 5% | 13% | 30% | 25% | 36% |
| $C_6Cl_7F_5$ | - | 10% | 2% | - | 4% | 15% | - | 22% |
| $C_6Cl_6$ | 10%* | - |  | - | - | - | - | 3% |
| Others | $C_6Cl_4F_4$ 4% | - |  | - | - | - | - |  |
| Total Yield | 81% | 80% | 52% | 53% | 29% | 94% | 80% | 90% |

* Before correction.

on replacement of a fluorine atom by a chlorine atom.

## Infra Red Spectra.

The infra red spectra of these compounds are extremely interesting as they shed some light on the nature of the existing double bond. The characteristic absorbtion due to the double bond occurs from 1600 $cm^{-1}$ to 1770 $cm^{-1}$. The -CCl=CCl- grouping giving an absorbtion in the 1645-1618 $cm^{-1}$ region, -CF=CCl- at 1700-1678 $cm^{-1}$, and -CF=CF- at 1757-1733 $cm^{-1}$. The reaction of antimony pentafluoride and hexachlorobenzene described by Leffler[14] gave perchlorofluorocyclohexenes, which contained only the -CCl=CCl- structure. The cyclohexenes, prepared from the action of chlorine trifluroide on hexachlorobenzene, contain mainly this structure, however the presence of both -CCl=CF- and -CF=CF- groupings can also be detected. The latter structures are more prevalent in the highly fluorinated cyclohexenes. From the size of the absorbtion peaks, a rough idea of the percentage of each structure present in each cyclohexene, can be deduced. (see table 2).

Table 2. Nature of Double Bond from I.R. Spectra.

| Product | % yield | % $-\overset{Cl}{C}=\overset{Cl}{C}-$ | % $-\overset{F}{C}=\overset{Cl}{C}-$ | % $-\overset{F}{C}=\overset{F}{C}-$ |
|---|---|---|---|---|
| $C_6Cl_3F_7$ | 2 | 35 | 55 | 10 |
| $C_6Cl_4F_6$ | 10 | 50 | 45 | 5 |
| $C_6Cl_5F_5$ | 30 | 65 | 30 | 5 |
| $C_6Cl_6F_4$ | 35 | 95 | 0 | 5 |
| $C_6Cl_4F_4$ | 4 | 100 | - | - |

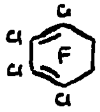
It can be seen that where there is more chlorine in the compound, the percentage of the -CCl=CCl- grouping is considerably more, i.e. $C_6Cl_5F_5$ and $C_6Cl_6F_4$. These two compounds are the major components, and looking at the table, it can be seen that 80% of the product has the -CCl=CCl- structure.

Infra red spectra of the perchlorofluorocyclohexenes are recorded on page 137.

## Tetrachlorotetrafluorocyclohexadiene.

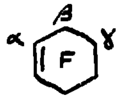
The cyclic $C_6Cl_4F_4$ isolated in this reaction in 4% yield was shown by N.M.R. measurements to contain only one type of fluorine. Both 1,2,4,5-tetrachlorotetrafluorocyclohexa-1,4-diene (I) and 1,2,3,4-tetrachlorotetrafluorocyclohexa-1,3-diene (II) fulfil this requirement, however from a study of the fluorine shift, (I) can be seen to be the correct structure.

(I)



(II)

(III)



(IV)

(V)

Comparison of the $F^{\gamma}$ shifts (from trifluoroacetic acid) in (III) and (IV) showed that replacement of fluorine by chlorine in the double bond had no effect on the $\gamma$-fluorine nucleus. A similar comparison of the $F^{\beta}$ shifts showed that a shift occurred to low field of -8.7 p.p.m. This shift is due to a direct interaction between the chlorine and fluorine nuclei and can be observed in many other molecules to shift the resonance of the fluorine to low field. This ortho effect of a chlorine atom is additive; thus the shift of the $\beta$-fluorine nuclei in (I) would be expected to be approximately 17.5 p.p.m. to low field of that in (V). The difference between the $\beta$-fluorine nuclei in (II) and (V) would be ~ 9 p.p.m. The observed shift between $C_6Cl_4F_4$ and (V) was 21.26 p.p.m. indicating that (I) was the correct structure.

The infra red spectrum, (No. 8, page 140) contains a single absorbtion peak at 1645 $cm^{-1}$. This indicates that the structure is a 1,4-diene, as a 1,3-diene normally has a doublet in this region.

The most conclusive evidence that this compound is I is obtained from a study of the ultra violet spectrum of I and III (1,2-dichlorooctafluorocyclohexene). As I contains two -CCl=CCl- groupings which are not conjugated, the extinction coefficient would be expected to be twice the value for III. Also the maximum absorbtion $\lambda_{max}$ should occur at the same point as the $\lambda_{max}$ for III. This is in fact what happens.

| | $\epsilon$ | $\lambda_{max}$ |
|---|---|---|
| $C_6Cl_4F_4$ | 13,140 | 208 mμ |
| $C_6Cl_2F_8$ (III) | 5,659 | 213.5 mμ |

If the cyclic $C_6Cl_4F_4$ was a conjugated diene, the maximum absorbtion $\lambda_{max}$, would be shifted to the 255-265 mμ region[91].

## Reaction of Hexachlorobenzene with Chlorine Trifluoride.

## (Molar Ratio 1:3)

This reaction was very similar to the previous reaction, but as the cyclohexenes produced in the initial reaction were liquids, the further fluorination was carried out at a lower temperature (100°C). The product, which again was a liquid contained a mixture of perchlorofluorocyclohexanes and -cyclohexenes, (see table 1).

$C_6Cl_xF_{12-x}$ where $x = 3-7$

$C_6Cl_nF_{10-n}$ where $n = 3-6$

The compounds with the same number of chlorine atoms had very similar boiling points and their retention times using vapour phase chromatography were very close, making isolation of the products very difficult.

### Boiling Points.°C.

$C_6Cl_4F_6$:- 178.5. $C_6Cl_5F_5$:- 208.5. $C_6Cl_6F_4$:- 242.5.

$C_6Cl_4F_8$:- 175.5. $C_6Cl_5F_7$:- 207.5. $C_6Cl_6F_6$:- 248.0.

The compounds were isolated in pairs by distillation as previously described. Each "pair" was then separated into the cyclohexane and cyclohexene by chromatography; although for a pure sample to be obtained, the product had to be recycled.

This reaction was used as a control reaction, to compare with the products from the catalysed reactions of chlorine trifluoride and hexachlorobenzene, which are mentioned later. The production of the cyclohexane and cyclohexene compounds, shows the effect of both saturation and fluorination, with the least number of experiments.

## Reaction of Hexachlorobenzene and Chlorine Trifluoride.

### (Molar Ratio 1:7)

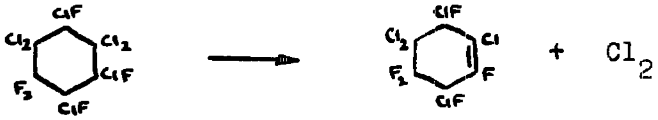
After the initial mixture of cyclohexenes had been prepared, the temperature was again lowered to 100°C. and the further fluorination carried out. The full saturation of this remaining double bond required seven moles of chlorine trifluoride to one mole of hexachlorobenzene. The total yield of the perchlorofluorocyclohexanes, $C_6Cl_xF_{12-x}$ where $x=3-7$, was just over 50%, (see table 1, page 30). These cyclohexanes contain more chlorine than the products from the cobalt trifluoride, hexachlorobenzene reaction[16], but the yield was lower. The amount of chlorine trifluoride used in the reaction was about the same as that required to regenerate the cobalt difluoride.

The perchlorofluorocyclohexanes were separated by distillation and vapour phase chromatography, and identified by analysis. Cyclic $C_6Cl_3F_9$, $C_6Cl_4F_8$ and $C_6Cl_5F_7$, prepared from the cobalt trifluoride, hexachlorobenzene reaction, were available for comparisons of infra red spectra, and retention times using vapour phase chromatography.

The heptachloropentafluorocyclohexane could not be purified by preparative scale V.P.C. as dehalogenation occurred on the column. This is quite understandable, as the temperature used had to be high (260°C), and cyclic $C_6Cl_7F_5$ must contain a gem dichloro grouping. This must be unstable, as cyclic $C_6Cl_5F_5$ was isolated as the dehalogenation product.

The infra red spectrum of this compound showed that the double bond present was mainly of the -CF=CCl- structure (absorbtion at 1686 $cm^{-1}$). This shows that the instability of the cyclic $C_6Cl_7F_5$ is not due to two adjacent gem dichloro groups.

i.e.



## The Influence of Catalysts on the Reaction between Hexachlorobenzene and Chlorine Trifluoride.

It was thought that in the chlorofluorination of hexachlorobenzene, Lewis acid catalysts would aid both fluorination, and saturation of the cyclic monoenes. A 1:3 molar ratio of hexachlorobenzene to chlorine trifluoride was used, for reasons already explained. The products were identified by analytical scale V.P.C., and in the case of ferric chloride and coblat fluoride, the product was distilled and the main components isolated by preparative scale V.P.C., and identified by infra red spectroscopy.

There was some difficulty in the addition of ferric chloride, as sublimation occurred at the temperature required for initial chlorofluorination (240°C). This was overcome by addition, after the temperature was dropped to 100°C., halfway through the experiment. Both cobalt fluoride and boron trifluoride were added at the beginning. Aluminium trichloride was found to be of no use as a catalyst, as it turned the liquid monoenes into a thick paste. This could not be effectively stirred, and the chlorine trifluoride ignited, causing considerable decomposition. The results of these reactions (see table 1, page 30), may be summarized as follows:-

<u>Ferric Chloride</u>. More fluorination occurred both in the saturated and unsaturated compounds, although the percentage of saturated

material in the product is lower. The overall yield (53%) was considerably reduced.

Cobalt Fluoride. The overall yield was very poor (29%). Saturation was much more prevalent, only 13% of the product was present as unsaturated material.

Boron Trifluoride. Small amounts of boron trifluoride gave an extremely good yield (94%). The product contained more of the highly chlorinated material, both saturated and unsaturated, i.e. $C_6Cl_6F_6$ 30%, $C_6Cl_6F_4$ 18%, compared with the uncatalysed reaction $C_6Cl_6F_6$ 20%, $C_6Cl_6F_4$ 10%.

Large amounts of boron trifluoride did not alter the overall yields of the reaction, although the unsaturated material contained more of the highly fluorinated compounds.

The use of ferric chloride and cobalt fluoride lowered the yields considerably, and had no real advantage over the uncatalysed reactions. The cyclohexanes may be formed more quickly by using cobalt fluoride as a catalyst, however low yields are obtained. The use of boron trifluoride, in limited amounts, gave enhanced yields, and prevented ignition of the hexachlorobenzene throughout the experiment. If the preparation of these compounds were required in large amounts, it would be advantageous to use boron trifluoride as a catalyst.

# Theoretical Considerations.

## Introduction.

The perchlorofluorocyclohexenes formed in the chlorofluorination of hexachlorobenzene have been shown to be mixtures of isomers which cannot be separated. The N.M.R. spectra of the cyclohexenes were too complicated to give any data on their configuration, although the infra red spectra did show the nature of the double bond, (see table 2, page 31).

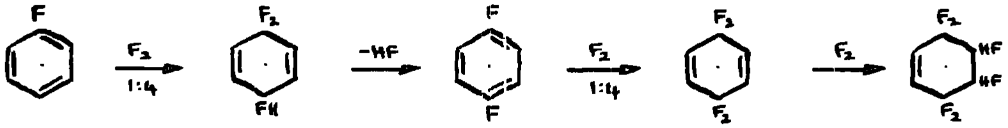
It is obvious that these isomers can be formed by a number of different routes. These would involve, firstly, the addition of fluorine and chlorine monofluoride across a double bond; in the case of a conjugated diene both 1,2 and 1,4 addition can occur. Secondly, both vinylic and allylic substitution of chlorine can occur, similarly although less likely fluorine may be substituted by chlorine.

It is also possible that at the elevated temperature of the reaction, isomerization of the dienes, formed after the initial addition, may occur. Also the more unstable dienes may dehalogenate, or more likely dechlorinate. Finally it must be born in mind that although addition occurs easily with the aromatic and diene compounds there is a marked resistance to further addition to the cyclohexenes so formed.

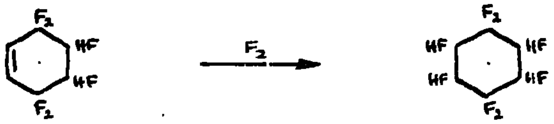
## Initial Attack in the General Fluorination of Benzenes.

Initial addition of fluorine, or chlorine monofluoride, can either occur in the 1,2 or the 1,4 positions. From a survey of the literature it seems likely that the 1,4 addition is more probable.

It has been shown in the fluorination of benzene using cobalt trifluoride[92] that the initial addition occurs in the 1,4 position. The products isolated from this reaction are mainly 1,2,4,5-tetrahydrooctafluorocyclohexane, and 1,2,4-trihydrononafluorocyclohexane. These products are also formed in the fluorination of fluorobenzene, which is probably an intermediate in the former reaction. The explanation for the production of only these hydrofluorocyclohexanes is that 1,4 addition must occur. If 1,2 addition occurs a 1,2,3,4-tetrahydrooctafluorocyclohexane would be formed.



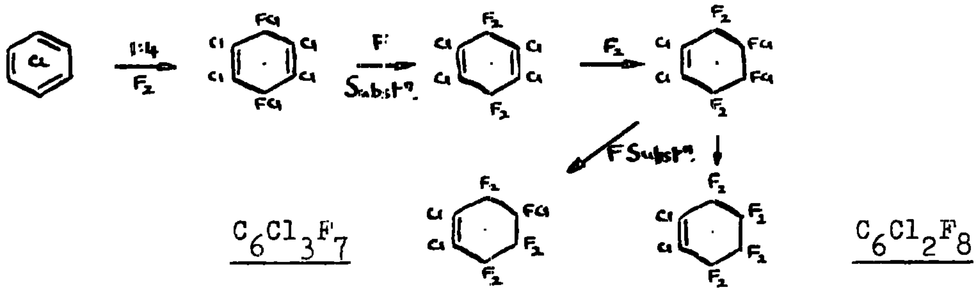
Stage 2 can easily dehydrofluorinate, whereas stage 4 cannot, therefore addition of fluorine occurs.



Similarly, 1,4 addition of fluorine was postulated by Leffler[14], to explain the mechanism of the reaction between hexachlorobenzene and antimony pentafluoride (see page 5). However no evidence was shown for this assumption.

His mechanism also suggested that rearrangement of the cyclohexadienes occurred; and although it is quite likely that a temperature was reached where rearrangement could occur, no evidence for this was given. The products he obtained can be explained more simply without this rearrangement, if we assume that antimony pentafluoride is a good reagent for the substitution of fluorine. This assumption has been verified in the literature[93,94].

Thus:-



$C_6Cl_3F_7$ $C_6Cl_2F_8$

It is also well known that in the halogenation of 1,3 butadiene, the main product is the 1,4-dihalobut-2-ene.

$$CH_2 = CH - CH = CH_2 \xrightarrow{Br_2} CH_2Br - CH = CH - CH_2Br$$

In the vapour phase chlorofluorination of benzene at 260°C, in a reactor packed with copper clippings, it has been suggested that chlorine trifluoride dissociates into fluorine radicals and chlorine monofluoride[20].

$$ClF_3 \longrightarrow ClF + 2F^{\cdot} \quad .....(1)$$

The chlorine monofluoride then dissociates into fluorine and chlorine radicals.

$$ClF \longrightarrow F^{\cdot} + Cl^{\cdot} \qquad \Delta H = 60 \text{ K cals/mole.}$$

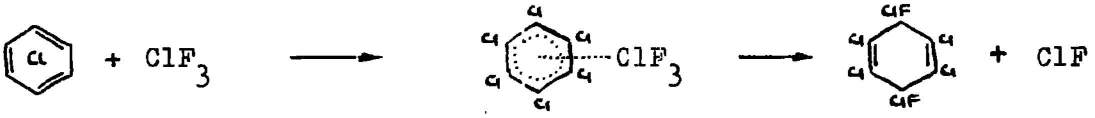
$$F_2 \longrightarrow F^{\cdot} + F^{\cdot} \qquad \Delta H = 38 \text{ K cals/mole.}$$

These radicals add across double bonds, and replace hydrogen with fluorine and chlorine. This seems likely, although the initial stage (1) raises some doubts, as chlorine trifluoride is prepared by heating fluorine and chlorine monofluoride together at temperatures of over 200°C.

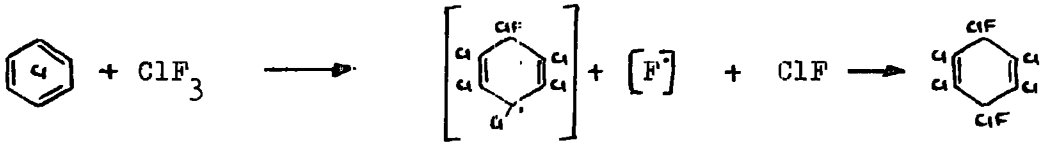
## Initial Attack in the Chlorofluorination of Hexachlorobenzene.

The mechanism of the above reaction cannot be compared with the reaction of chlorine trifluoride with hexachlorobenzene. If radical attack occurred in a similar manner, the reaction would not stop at the cyclohexene stage, but go on to the fully saturated cyclohexane. Again if free radical attack does occur, the products should be similar to those obtained from the reaction between hexachlorobenzene and elemental fluorine. However no cyclohexene has been isolated at any stage in this reaction (see page 51).

It is most likely that chlorine trifluoride, itself, interacts with hexachlorobenzene to give the addition compound. There is no evidence to indicate whether this attack is ionic or free radical.



However, if a free radical attack does occur the fluorine radical produced must immediately be used in the addition.

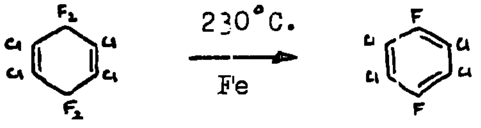


It should be noted that after addition of fluorine has occurred, a molecule of chlorine monofluoride is produced. Similarly if the interaction of chlorine trifluoride with hexachlorobenzene adds a molecule of chlorine monofluoride, a molecule of fluorine is produced. However if fluorine is produced, it will form free radicals (see page 53 ); but it is known that the reaction does not involve the large scale radical attack by fluorine. Thus it seems most likely that in the addition reaction of chlorine trifluoride, chlorine monofluoride is liberated and two atoms of fluorine are added across the double bond. Chlorine monofluoride has a much higher bond dissociation energy, i.e. 22 K. cals/mole more. It seems unlikely that this dissociates to give free radicals, which would again fully saturate the cyclohexenes.

This initial addition of fluorine must occur mainly in the 1,4 position, as the 1,2,4,5-tetrachlorotetrafluorocyclohexa-1,4-diene was isolated uncontaminated with the 1,3 isomer. It is known that these isomers would have the same retention time using vapour phase chromatography. Therefore if any of this isomer was present, indicating 1,2 addition, it would have been isolated as well.

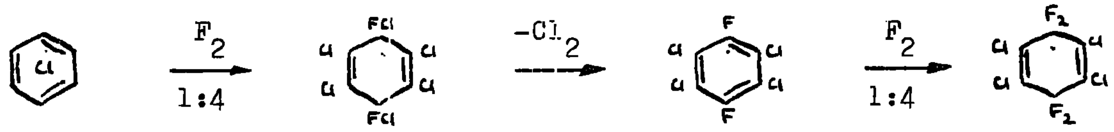
Rearrangement and Dehalogenation.

The isolation of cyclic $C_6Cl_4F_4$ as a pure isomer, indicates that rearrangement of the cyclic dienes does not occur. If rearrangement did occur within the reaction, it is highly improbable that a pure isomer could have been isolated. Other evidence in the dehalogenation of the perchlorofluorocyclohexenes (see page 61 ), also points to the fact that the amount of rearrangement that occurs, at this temperature is very limited.



47% + $C_6Cl_3F_3$ 6%.

Although it is doubtful that the dienes rearrange, it is quite possible that they dehalogenate. Cyclohexadienes are generally known to dehalogenate at temperatures well below that required for the cyclohexenes[67,68,69]. Thus cyclic $C_6Cl_4F_4$ was aromatized, using the iron gauze dehalogenator, without a trace of starting material present in the product, at 230°C. This is the same temperature as used in the chlorofluorination reaction. Thus we can imagine such a reaction occurring:-



<u>Addition to the Cyclohexene.</u>

Further addition of fluorine or chlorine monofluoride to the cyclohexadiene must occur to give the cyclohexene. The addition of fluorine will be as before, i.e. as the chlorine trifluoride molecule, and not as elemental fluorine. The addition of chlorine monofluoride will be more prevalent in the latter stages of the reaction, as it will build up after the addition of fluorine from chlorine trifluoride.

Further addition to the monoene is hindered due to steric considerations, although saturation does occur with prolonged passage of chlorine trifluoride. However the resistance of this bond to addition can be seen by the large excess of chlorine trifluoride required for complete saturation.

It can be seen from figs. (a) and (b), (page 44) that the chlorine atoms 2 and 3 cause considerable crowding in the monoene (a),

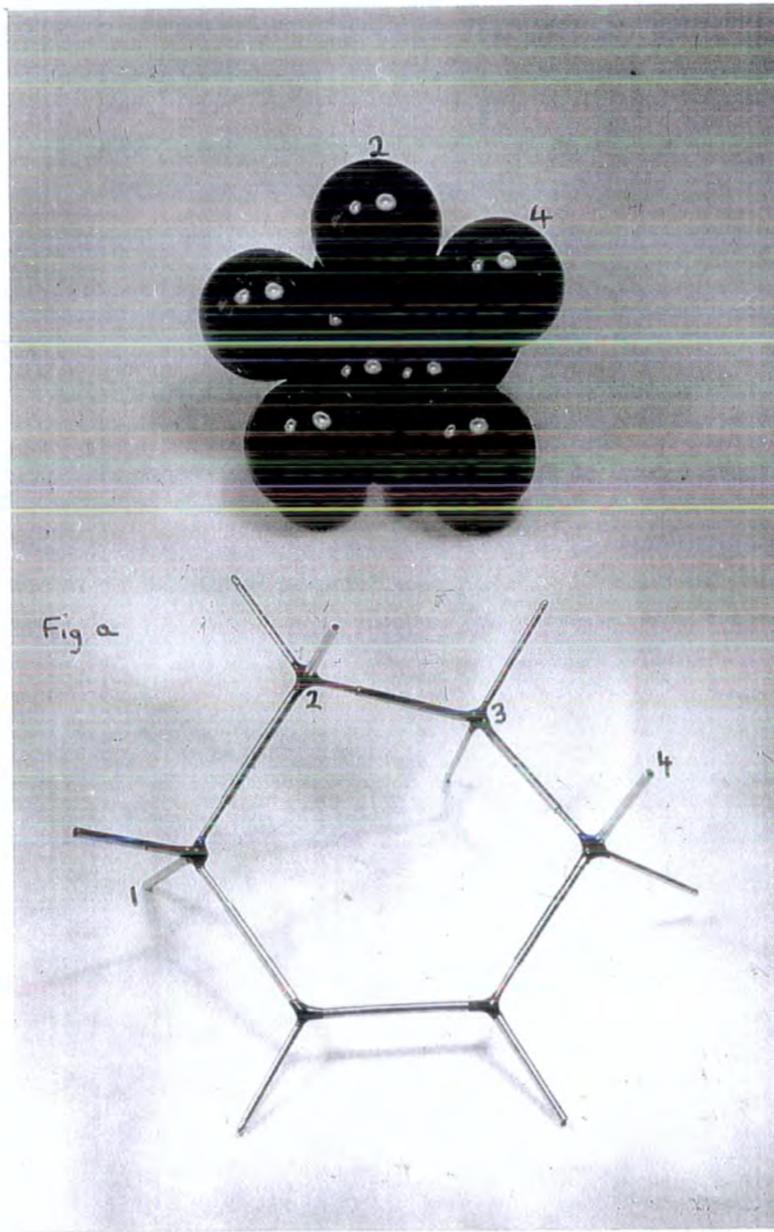


Fig a

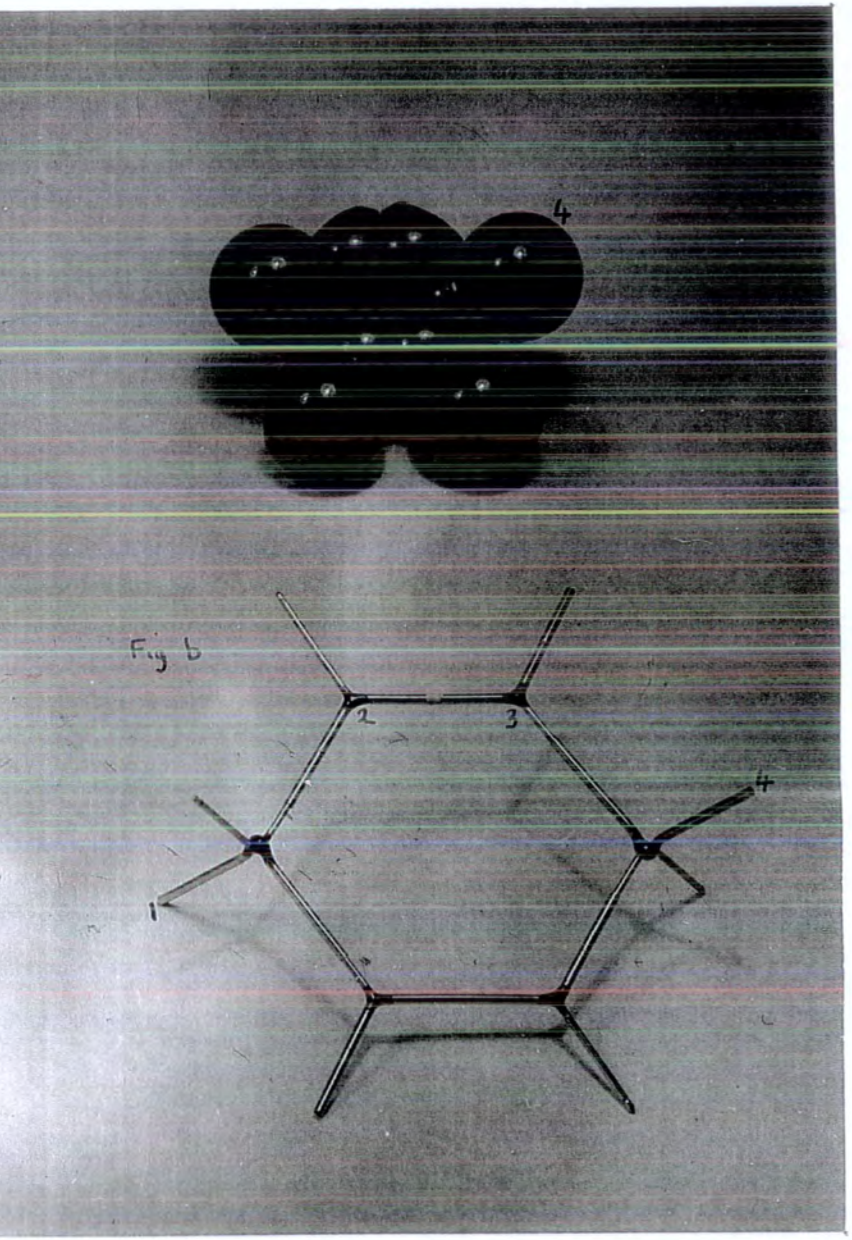


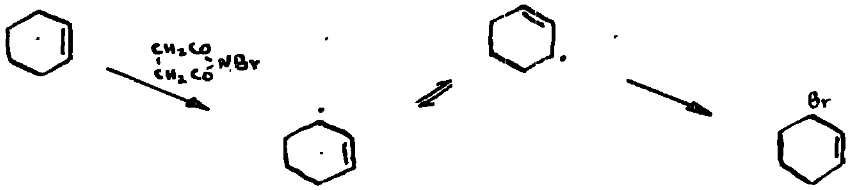
Fig b

as they are directed from the carbon atoms 2 and 3, towards the double bond; whereas in the diene (b) they are directed away. It can also be seen that chlorines 1 and 4 are closer to the vertical in the monoene (a), than in the diene (b); they must therefore shield the double bond more.

Thus the approach of a large molecule, such as chlorine trifluoride or antimony pentafluoride, towards a double bond is considerably easier in the diene stage, than in the monoene stage.

Allylic and Vinylic Substitution.

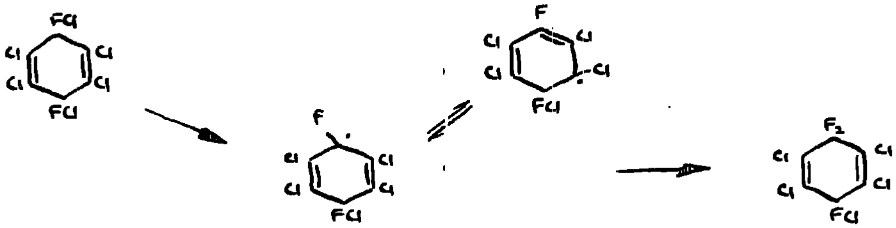
Throughout the reaction both allylic and vinylic substitution can occur. The greater reactivity of an allylic grouping to substitution, is due to the extra stability of the ionic or free radical intermediate. Thus in a free radical substitution, the extra stability is caused by the fact that the electron can be shared over the molecule. In the bromination of cyclohexene with n-bromosuccinimide, which has been shown to occur via a free radical mechanism, we have:-



Consequent bromination occurring in the allylic position.

In the substitution of allylic chlorine in the chlorofluorodienes, extra stability may be gained by the ability of the intermediate formed to rearrange.

i.e.

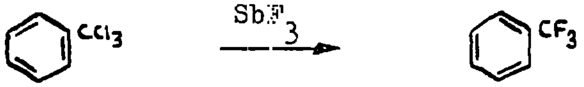


Although the last step probably does not form the substituted 1,3 diene, as no evidence is found for such a diene, it may still help in the stability of the intermediate.

The evidence that is available to point to the difference in susceptibility of vinylic and allylic substitution in this reaction, is that 80% of the reaction product contains the $-CCl=CCl-$ structure; indicating that vinylic substitution does not occur very readily.

Henne[93] has shown quite conclusively that allylic chlorine is substituted by fluorine far more readily than vinylic chlorine.

1) $CCl_2 = CCl - CCl_3 \xrightarrow{SbF_3} CCl_2 = CCl - CF_3$ 100%.

2)  60%.

The second reaction is so vigorous that 40% decomposition occurs.

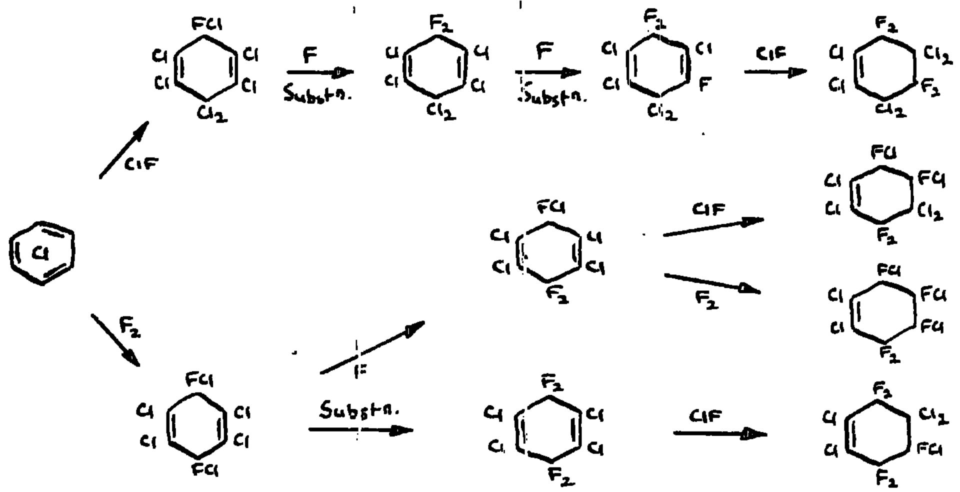
Only recently have reports indicated that fluorination of chlorine can occur in the vinylic position[95].

A General Reaction Scheme.

Although to postulate a detailed mechanism on the evidence put forward is impossible, a general reaction scheme can be put forward. This shows the initial 1,4 addition of fluorine, the growing importance of chlorine monofluoride as the reaction progresses, the disability of the cyclohexadienes to rearrange, allylic chlorine substitution and formation of the 1,2,4,5-tetrachlorotetrafluoro-1,4-diene as an intermediate.

It is difficult, at first sight, to find which isomers are present in the highest proportion in each cyclohexene. It is, however, possible to discover the exact configuration of the aromatic compounds present in the dehalogenated product.

This is done by N.M.R. measurements (see page 60 , table IV ). Thus if we know the aromatic compounds present, and also the mechanism of the dehalogenation process (see page 61 ); it is possible to predict which isomers are present in each cyclohexene, (see page 65 ).



As the reaction scheme is extremely general, the production of $C_6Cl_5F_5$ and $C_6Cl_6F_4$ only, is indicated, (this is 80% of the product). It can easily be seen that $C_6Cl_4F_6$ and $C_6Cl_3F_7$ will be formed by further fluorination.

## The Liquid Phase Reaction between Fluorine and Hexachlorobenzene.

The most interesting property of the perchlorofluorocyclohexanes, -cyclohexenes and -cyclohexadienes is their ability to dehalogenate, in good yields, into highly fluorinated aromatic compounds. Perhaps the most important of these are perfluorobenzene and chloropentafluorobenzene.

Although the liquid phase reaction between chlorine trifluoride and hexachlorobenzene gave both the unsaturated compounds $C_6Cl_nF_{10-n}$, where $n = 3$-$6$, and the saturated compounds $C_6Cl_xF_{12-x}$, where $x = 3$-$7$; good yields of the highly fluorinated aromatic compounds are only obtained with the latter. The perchlorofluorocyclohexenes retain the $-CCl=CCl-$ grouping after dehalogenation, to give aromatic compounds with rather more chlorine present than is desired.

The perchlorofluorocyclohexanes, although obtained in moderate yields (50%) from the chlorofluorination of hexachlorobenzene, require, for full saturation, rather a large amount of chlorine trifluoride, (7 moles for 1 mole of hexachlorobenzene). The cyclohexanes, obtained from the fluorination of hexachlorobenzene with cobalt trifluoride[16], are much more highly fluorinated and do not, on dehalogenation, retain a chlorine atom[19]. Thus for production of chloropentafluorobenzene, the above methods are not entirely adequate.

In order to obtain perchlorofluorocyclohexanes suitable for dehalogenation to give chloropentafluorobenzene, an obvious choice, after using chlorine trifluoride on hexachlorobenzene, is to use elemental fluorine on hexachlorobenzene. This reaction has already been investigated by Bancroft and Whearty[83,84] in 1931, and by Bigelow[12] in 1934 and 1938. Both investigations met with little success, although Bigelow reported the isolation of cyclic $C_6Cl_6F_6$ and $C_6Cl_6F_4$; however these represented only a small amount of the product.

Fluorination of Hexachlorobenzene.

Several exploratory reactions without the use of a solvent proved to be of no value. The choice of the solvent for this reaction was governed by two factors. Firstly it must affect the course of the fluorination as little as possible; secondly it must be easily removed from the products. The actual solvent power was not taken into consideration, as a slurry of hexachlorobenzene was perfectly adequate for fluorination.

The two solvents available were 1,1,2-trichlorotrifluoroethane (Isceon 113), and carbon tetrachloride. Both solvents would be removed from the reaction vessel, by fluorination, during the reaction.

1) $C_2Cl_3F_3$ b.p. 48°C. $\longrightarrow$ $C_2Cl_2F_4$ b.p. 3°C.

2) $CCl_4$ b.p. 76°C. $\longrightarrow$ $CCl_3F$ b.p. 20°C. $\longrightarrow$ $CCl_2F_2$ b.p. -28°C.

Isceon 113 was chosen as less fluorination of the solvent is required to remove it from the vessel.

Both the solvent and the hexachlorobenzene are fluorinated simultaniously. As the resultant mixture of cyclohexanes is a liquid paste, which can conveniently be further fluorinated without the addition of solvent, the removal of the solvent by fluorination is a distinct advantage.

It is important that the reaction should be carried out in the fume cupboard, for if a condenser was used on the outlet side, violent explosions occurred. This could be due to either fluorine oxides, or uncontrolled fluorination in the gaseous state. Most of the early literature on fluorination reactions with elemental fluorine, stress the importance of keeping the vapour phase present to a minimum.

The amount of fluorine passed into the reaction mixture was calculated to saturate fully the benzene nucleus, and also to fluorinate the solvent.

1) $C_6Cl_6 + 3F_2 \longrightarrow C_6Cl_6F_6$

2) $C_2Cl_3F_3 + \frac{1}{2}F_2 \longrightarrow C_2Cl_2F_4$

Some of the solvent will evaporate from the vessel without being fluorinated, but this is counteracted by the fluorine which passes through unreacted. The product was identified by analytical scale V.P.C. This showed the presence of the perchlorofluorocyclohexanes $C_6Cl_xF_{12-x}$, where x = 4-7. See table 3.

Table 3.

| Reaction | Product % | | | | Total |
|---|---|---|---|---|---|
| | $C_6Cl_4F_8$ | $C_6Cl_5F_7$ | $C_6Cl_6F_6$ | $C_6Cl_7F_5$ | Yield % |
| $C_6Cl_6/3F_2$ | 5 | 24 | 36 | 22 | 90[a] |
| $C_6Cl_6/7\frac{1}{2}F_2$ | 16 | 21 | 15 | 3 | 59[b] |

a. including 3% $C_6Cl_6$ b. including 4% $C_6Cl_3F_9$.

For comparison of these results with the chlorofluoroination of hexachlorobenzene, see page 30 table 1.

This mixture of perchlorofluorocyclohexanes, without separation, is extremely suitable for the preparation of perfluorobenzene and chloropentafluorobenzene, by dehalogentation, (see page 80 ). The overall yield of 90% is very good, and the method gave easily reproducible results even with large amounts of starting material. The largest amount fluorinated in these laboratories was 400 gms. of hexachlorobenzene, giving 516 gms. of perchlorofluorocyclohexanes.

Both analytical scale V.P.C. and an infra red spectrum of the product, showed that no unsaturated material was present. More important, a similar analysis of a sample removed halfway through the reaction, showed that only perchlorofluorocyclohexanes and unreacted starting material were present.

## Further Fluorination of the Perchlorofluorocyclohexanes.

The product from the above reaction was further fluorinated, to see if substitution occurred easily, giving more highly fluorinated cyclohexanes. These would, on dehalogenation, give higher yields of perfluorobenzene.

The fluorination was tried out at room temperature, 100°C. and 200°C. At each stage the amount of fluorine passed into the vessel was sufficient to react with the cyclic $C_6Cl_6F_6$, and produce cyclic $C_6Cl_3F_9$.

$$C_6Cl_6F_6 + 1\tfrac{1}{2}F_2 \longrightarrow C_6Cl_3F_9.$$

However very little fluorination occurred, and after the third stage, the mixture was shown to contain cyclohexanes of general formula $C_6Cl_xF_{12-x}$, where x = 3-7. The average constitution was $C_6Cl_5F_7$. See table 3.

$$C_6Cl_6F_6 + 4\tfrac{1}{2}F_2 \longrightarrow C_6Cl_5F_7.$$

It seems that although fluorine is a very effective reagent for the saturation of double bonds, it is not a good reagent for the substitution of chlorine. If a better yield of the more highly fluorinated cyclohexanes is required, the chlorofluorocyclohexanes, (of average constitution $C_6Cl_6F_6$) could be treated with antimony pentafluoride. This, as already stated is a very effective reagent for the substitution of chlorine by fluorine[93].

## Theoretical Considerations.

### Introduction.

In the reaction of hexachlorobenzene with fluorine, no unsaturated material was found in the reaction product, or indeed at the halfway stage. The report by Bigelow[1,2] of the isolation of cyclic $C_6Cl_6F_4$ is dubious, it is far more likely to be cyclic $C_6Cl_7F_5$.

Bigelow identified this compound by an analysis and a molecular weight determination. The chlorine and fluorine analysis of $C_6Cl_5F_7$ and $C_6Cl_6F_4$ are very close, and wrong identification could arise from this.

| | $C_6Cl_6F_4$ | $C_6Cl_7F_5$ |
|---|---|---|
| Chlorine % | 59.0 | 59.7 |
| Fluorine % | 21.05 | 22.9 |

Similarly, Bigelow's method of molecular weight determination was rather inaccurate, as shown by the molecular weight determination of $C_6Cl_6F_6$, which was 11% low. Bigelow also reported that $C_6Cl_6F_4$ boils at higher temperatures than $C_6Cl_6F_6$, and had a melting point of 113°C.

It has been found that the boiling point of $C_6Cl_6F_4$, isolated from the chlorofluorination of hexachlorobenzene, is very similar to $C_6Cl_6F_6$ and is a liquid. The $C_6Cl_7F_5$ has a boiling point higher than the boiling point of $C_6Cl_6F_6$, and a melting point of 105-110°C.

| | $C_6Cl_6F_4$ | $C_6Cl_6F_6$ | $C_6Cl_7F_5$ |
|---|---|---|---|
| Boiling point ° C:- | 242.5 | 248.0 | 270-273 |

## General Principals.

The full saturation of hexachlorobenzene is in agreement with the generally accepted view that reactions with elemental fluorine proceed by a chain mechanism involving free radicals[96]. The ease of fluorine radical attack is due to the low bond dissociation energy of fluorine (1).

These reactions are normally initiated either by heat or radiation, as the degree of dissociation at room temperature is extremely low (2).

$$F_2 \longrightarrow 2F^{\bullet} \qquad \Delta H = 38 \text{ K cals/mole} \qquad (1)$$

$$F_2 \rightleftharpoons 2F^{\bullet} \qquad K = 10^{-20} \qquad (2)$$

In the fluorine attack of hydrocarbons, the activation energy required for hydrogen abstraction by the fluorine radical is low, and even this low degree of dissociation is suitable for the initiation of a chain reaction.

$$RH + F^{\cdot} \longrightarrow R^{\cdot} + HF \quad \Delta H = -34 \text{ K cals/mole}$$

$$R^{\cdot} + F_2 \longrightarrow RF + F^{\cdot} \quad \text{etc.}$$

The activation energy required for chlorine abstraction by the fluorine radical is obviously higher than that required for hydrogen abstraction; as reactions of fluorine with fully chlorinated compounds proceed with considerably less vigour[97, 98, 99] than similar reactions with hydrocarbons. Because of the higher activation energy required in the abstraction of chlorine, it seems unlikely that the fluorination is initiated by this step.

It is more likely that initiation occurs by addition to the double bond:-

$$>C = C< + F^{\cdot} \longrightarrow >CF - \underset{\cdot}{C}<$$

$$>CF - \underset{\cdot}{C}< + F_2 \longrightarrow >CF - CF< + F^{\cdot} \quad \text{etc.}$$

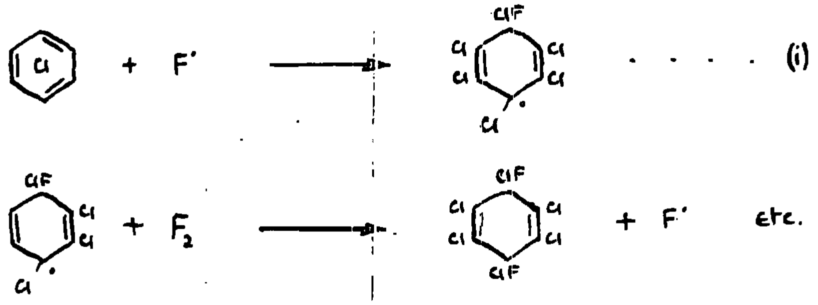
The degree of dissociation of fluorine at room temperature being sufficient to enable this to occur. Although Miller[100-102] has suggested that fluorine molecules will react with olefins.

$$>C = C< + F_2 \longrightarrow >CF - \underset{\cdot}{C}< + F^{\cdot}$$

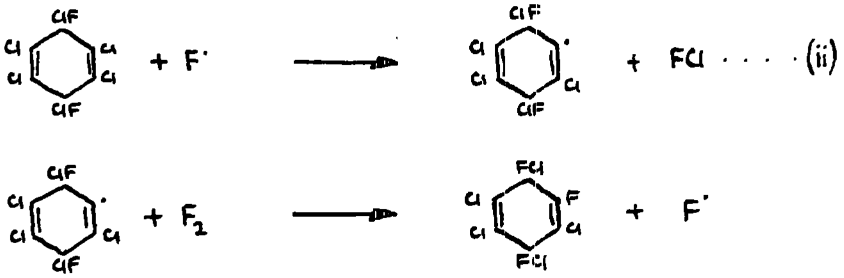
This can be supported both thermodynamically and practically. Thus tetrachloroethylene and chlorine do not react at -7 °C., however if a trace of fluorine is used, an 85% yield of hexachloroethane is obtained.

## Hexachlorobenzene and Fluorine.

The first stage of the fluorination of hexachlorobenzene is the initiation of a free radical chain reaction, by addition to a double bond.



The next step is either further saturation (i) or chlorine abstraction (ii)

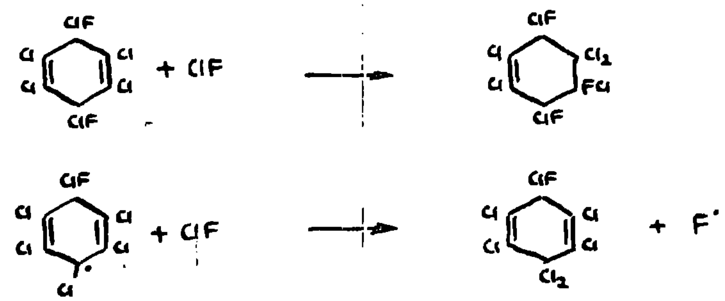


Abstraction of chlorine must occur to quite a reasonable extent, as both cyclic $C_6Cl_4F_8$ and $C_6Cl_5F_7$ were isolated. It must be noticed that chlorine abstraction of both the cyclic compounds (ii), and the solvent (iii), gives rise to a molecule of chlorine monofluoride.

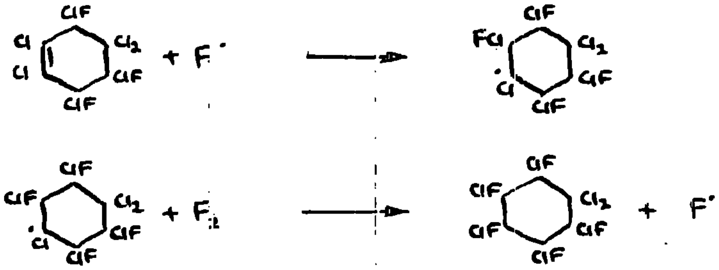
$$CF_2ClCFCl_2 + F^{\cdot} \longrightarrow CF_2Cl\dot{C}FCl + FCl \quad ...(iii)$$

$$CF_2Cl\dot{C}FCl + F_2 \longrightarrow CF_2ClCF_2Cl + F^{\cdot}$$

The chlorine monofluoride will either add across a double bond, as described in the reaction of chlorine trifluoride and hexachlorobenzene, or it can be attacked by a radical.



Unlike the reaction between hexachlorobenzene and chlorine trifluoride, the cyclohexene is susceptible to further attack, to form the fully saturated cyclohexane.



As no unsaturated material was isolated, it must be more susceptible to radical attack than the starting material, hexachlorobenzene.

## DEHALOGENATION

In the dehalogenation of fully saturated cyclic compounds at elevated temperatures, using the iron gauze technique, no aromatic compound has been isolated which contains a reactive group within the molecule. The dehalogenation of polychlorofluorocyclohexanes, carried out in these laboratories,[19] using this method, gave perfluoro- and hydrofluorobenzenes.

1) $C_6H_6 + ClF_3 \longrightarrow C_6H_xCl_yF_z \qquad (x + y + z = 12)$

$C_6H_xCl_yF_z \xrightarrow[500^\circ C]{Fe} C_6H_xF_{6-x} \qquad (x = 0\text{–}3)$

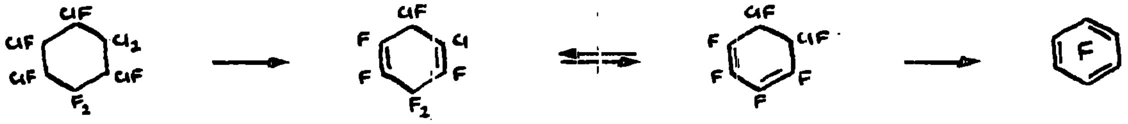
2) $C_6Cl_6 + CoF_3 \longrightarrow C_6Cl_nF_{12-n} \qquad (n = 1\text{–}5)$

$C_6Cl_nF_{12-n} \xrightarrow[430^\circ C]{Fe} C_6F_6$

No chlorine containing fluoro-aromatic compound was isolated. This was disappointing, as both bromine and iodine provide reactive centers in fluoro-aromatic compounds, and it was thought that chlorine may similarly provide such a grouping. Although the chlorine atoms in these polychlorofluorocyclohexanes are preferentially eliminated, a more heavily chlorinated cyclohexane could aromatize to give chlorofluorobenzenes.

It is unlikely that these lightly chlorinated cyclohexanes, obtained from the reaction between cobalt trifluoride and hexachlorobenzene, contain a gem dichloro grouping. This was shown by the reduction of cyclic $C_6Cl_2F_{10}$ with lithium aluminium hydride;[15] no 1,1-dihydrodecafluorocyclohexane was isolated, although the 1,2-, 1,3-

and 1,4-dihydro- isomers were present. However the presence of a gem dichloro grouping, will not necessarily give a chloro-aromatic compound on dehalogenation. Rearrangement of the intermediate diene can occur, if the temperature is sufficiently high.



The perchlorofluorocyclohexanes, -cyclohexenes and -cyclohexadienes formed in the fluorination of hexachlorobenzene with chlorine trifluoride and fluorine (see before), contain considerably more chlorine, which is probably present, in part, as gem dichloro groupings. Due to the structure of these cyclohexenes, and the fact that dehalogenation can be carried out at much lower temperatures, (thus preventing rearrangement of the cyclic diene), the aromatic compounds formed, contain chlorine.

## Dehalogenation of Perchlorofluorocyclohexenes and Tetrachlorotetrafluorocyclohexadiene.

It was found from preliminary dehalogenations on the mixture of perchlorofluorocyclohexenes, produced from the action of chlorine trifluoride and hexachlorobenzene, that the temperature of the dehalogenator must not be too high as decomposition occurred. This was also found with the more lightly chlorinated cyclohexanes, obtained from the reaction of cobalt trifluoride and hexachlorobenzene. Thus as more chlorine entered the compound, the amount of product, obtained on dehalogenation at 430°C, decreased.

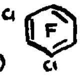
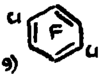
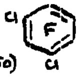
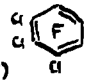
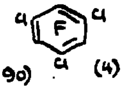
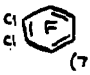
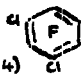
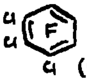
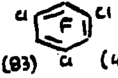
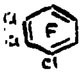
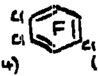
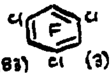
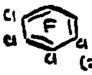
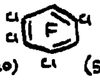
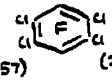
$$C_6Cl_4F_8 \longrightarrow C_6F_6 \quad 70\%$$

$$C_6Cl_5F_7 \longrightarrow C_6F_6 \quad 45\%$$

The temperature used to dehalogenate the perchlorofluorocyclohexenes was fixed at 50°C above the boiling point. However if full aromatization did not occur at this temperature (i.e. with cyclic $C_6Cl_3F_7$ and $C_6Cl_4F_6$), the temperature was raised until full aromatization occurred.

The same amount of starting material must be used for each dehalogenation, if the distribution of the various isomers formed, are going to be compared with each other (see page 73). Table 4 shows the distribution of the products obtained from dehalogenating 5 gms. of each cyclohexene. The aromatic products that were present in a reasonable yield were separated by preparative scale V.P.C., and the isomer ratio obtained by N.M.R. measurements.

Table IV. Aromatization of Perchlorofluorocyclohexenes and -hexadiene.

| Reactant | Temp. of reaction °C | Total Yield % | Product (%) and Distribution of Isomers. |
|---|---|---|---|
| $C_6Cl_3F_7$ | 315 | 73 | $C_6F_6$(11) $C_6ClF_5$(27) $C_6Cl_3F_3$(5)<br>$C_6Cl_2F_4$(30)  (59)  (19)  (22) |
| $C_6Cl_4F_6$ | 260 | 84 | $C_6F_6$(5) $C_6ClF_5$(32) $C_6Cl_4F_2$(2·5)<br>$C_6Cl_2F_4$(33) $C_6Cl_3F_3$(12)<br> (50)  (25)  (25)  (6)  (90)  (4) |
| $C_6Cl_5F_5$ | 260 | 83 | $C_6ClF_5$(3) $C_6Cl_4F_2$(3) $C_6Cl_5F$(1)<br>$C_6Cl_2F_4$(58) $C_6Cl_3F_3$(18)<br> (74)  (15)  (11)  (13)  (83)  (4) |
| $C_6Cl_6F_4$ | 300 | 85 | $C_6Cl_2F_4$(6) $C_6Cl_5F$(16)<br>$C_6Cl_3F_3$(30) $C_6Cl_4F_2$(33)<br> (14)  (83)  (3)  (20)  (57)  (23) |
| $C_6Cl_4F_4$<br> | 230 | 56 | $C_6Cl_3F_3$(6) $C_6Cl_4F_2$(47) $C_6FCl_5$(3)<br> (100) |
| * $C_6Cl_3F_7$<br> | 315 | 83 | $C_6F_6$(7) $C_6ClF_5$(15) $C_6Cl_3F_3$(3)<br>$C_6Cl_2F_8$(53·5)  (97)  (3) |
| * $C_6Cl_2F_8$<br> | Decomposes before dehalogenating. | | |

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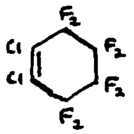
* Obtained from the reaction of antimony pentafluoride and hexachlorobenzene.

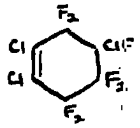
## Theoretical Considerations.

In the majority of these dehalogenation reactions, although the exact nature of the product can be found, the structure of the reactant is unknown. In order to be able to obtain a knowledge of the dehalogenation process, a study must be made of reactions where both reactant and products have known configurations. Three reactants of a suitable and known configuration were available, (the reactant must necessarily be a perchlorofluorocyclohexene or -diene).

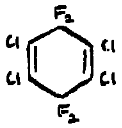
Two of these were the main products from the reaction between antimony pentafluoride and hexachlorobenzene, 1,2-dichlorooctafluorocyclohexene(I) and 1,2,4-trichloroheptafluorocyclohexene(II). The third reactant was 1,2,4,5-tetrachlorotetrafluorocyclohexa-1,4-diene(III), prepared in the chlorofluorination of hexachlorobenzene.



I



II

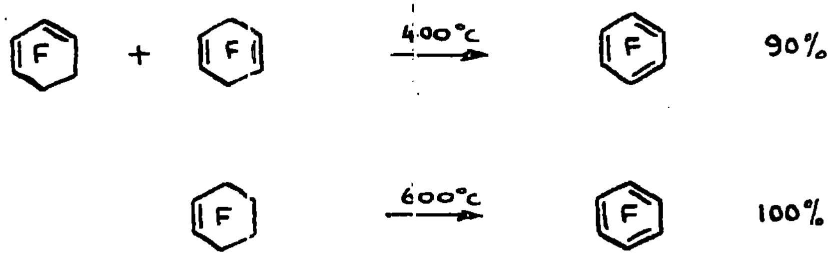


III

## Decomposition and Dehalogenation.

In the dehalogenation of 1,2-dichlorooctafluorocyclohexene, it was found that decomposition occurred before a temperature was reached high enough for defluorination to occur. Other workers[68] have found that to defluorinate perfluorocyclohexene a temperature of 550°C is required, but no decomposition occurred. It seems that the inclusion of a chlorine in the cyclohexene, lowers its stability towards high temperatures. Thus at 360°C, 1,2-dichlorooctafluorocyclohexene decomposed.

However as 1,2,4-trichloroheptafluorocyclohexene dehalogenated, at lower temperatures, without decomposition. The presence of a chlorine atom on a saturated carbon atom must facilitate the dehalogenation. Thus dehalogenation must take place by removal of chlorine monofluoride to form the cyclohexadiene, and this defluorinates to the aromatic product. The perfluorocyclohexadienes defluorinate at temperatures about 100°C below the temperature required to defluorinate perfluorocyclohexene.[68]



It appears that this must similarly be so in the perchlorofluoro-series

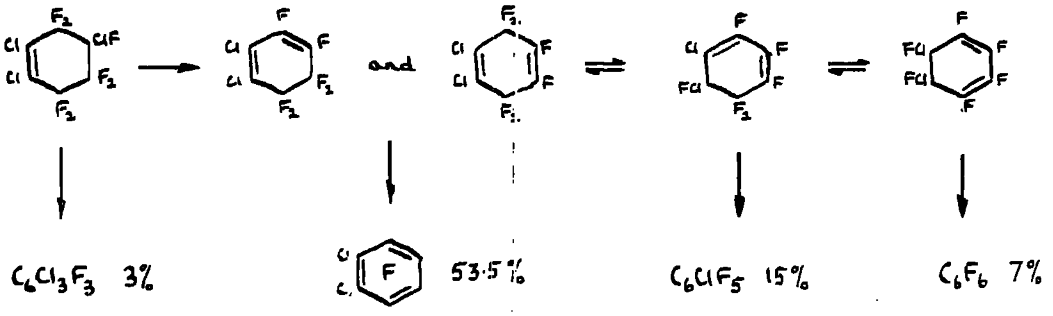
It has been established in the dehalogenation of the fully saturated perchlorofluorocyclohexanes, prepared from the action of cobalt trifluoride on hexachlorobenzene, that the elimination of chlorine is preferred; this is also seen throughout all these experiments.

## Rearrangement.

It is extremely important to find out if rearrangement occurs within the molecule during the process of dehalogenation, as has been suggested in the defluorination and dehydrofluorination of cyclic $C_6F_8$, $C_6F_7H$, etc. (see page 15).

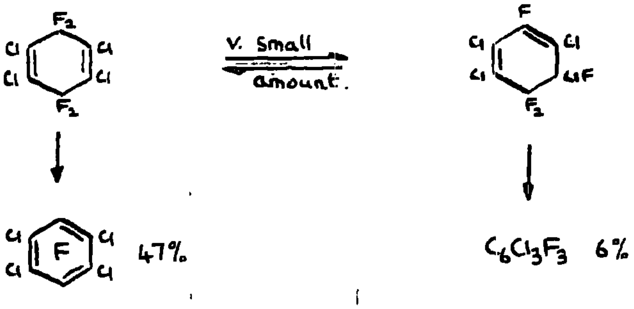
From the initial reaction with 1,2-dichlorooctafluorocyclohexene, it is evident that rearrangement of the cyclohexene does not occur, raising the temperature of the reactor simply causes greater decomposition.

Full aromatization of 1,2,4-trichloroheptafluorocyclohexene did not take place until the temperature was raised to 315°C, the products from this reaction are shown in Table IV. The main product was 1,2-dichlorotetrafluorobenzene, the two chlorine atoms present in the cyclohexene remaining at the end of the double bond. However both perfluorobenzene and chloropentafluorobenzene were formed. This indicates that rearrangement must occur, although only to a limited extent. i.e.



Only 3% of the cyclic $C_6Cl_3F_3$ was isolated, again indicating that the chlorine atom attached to a saturated carbon atom, which also contains a fluorine atom, is preferentially eliminated.

The temperature used for this reaction was 315°C, this was the highest used for all the perchlorofluorocyclohexenes. It would seem, therefore, that isomerization would be less prevalent in the other dehalogenations. This is shown in the dehalogenation of cyclic $C_6Cl_4F_4$; at 230°C the main product was 1,2,4,5-tetrachlorodifluorobenzene, only 6% of $C_6Cl_3F_3$ was isolated.



The total overall yield was low, probably due to the fact that the dehalogenation was carried out at a temperature little above the boiling point of the product, some of which must have remained inside the reactor.

At temperatures higher than those used in these dehalogenations, more rearrangement will occur, and the more highly fluorinated compounds will be produced. However the overall yield will decrease, as more decomposition will occur.

In the dehalogenation of perfluorocyclohexadiene, disproportionation takes place.

$$C_6F_8 \xrightarrow{450^\circ C} C_6F_6 \ \ 80\% \ + \ C_6F_{10} \ \ 4\%$$

However this happens to only a very limited extent, and no indication of such a reaction is shown in the dehalogenation of the chlorofluorocyclohexenes.

## Discussion.

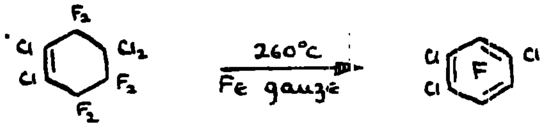
Thus the structure of the aromatic product reflects the structure of the parent cyclohexene. The chlorine present in the aromatic compound must have been present either in the double bond, or associated with a gem dichloro grouping. The position of the double bond in the cyclohexene is shown by two adjacent chlorine atoms. The other chlorines present in the aromatic compound show the position of gem dichloro groupings.

## Dehalogenation of Perchlorofluorocyclohexenes.

Trichloroheptafluorocyclohexene and tetrachlorohexafluorocyclohexene, obtained from the reaction between chlorine trifluoride and hexachlorobenzene, are mixtures of isomers which contain both the -CCl=CCl- and the -CF=CCl- structures, (shown by infra red data, see Table 2). They are only formed in low yields, and it is impossible to obtain the structure of the parent cyclohexene from a study of their dehalogenation products.

However it can be seen that the products, from the dehalogenation of $C_6Cl_3F_7$, are more highly fluorinated than those from the 1,2,4-isomer. This confirms the infra red evidence of the existance of the -CF=CCl- grouping.

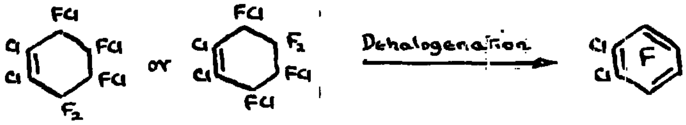
Also in the dehalogenation of $C_6Cl_4F_6$ the structure of the cyclohexene, which dehalogenates to 1,2,4-trichlorotrifluorobenzene, is easily found.



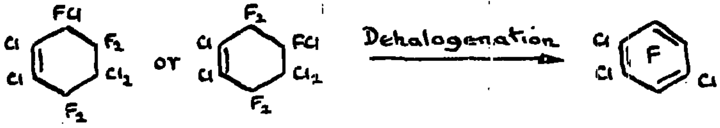
The major products from the chlorofluorination of hexachlorobenzene are cyclic $C_6Cl_5F_5$ (30%) and $C_6Cl_6F_4$ (35%). These are composed mainly of isomers containing the -CCl=CCl- grouping (see Table 2), and from a study of their dehalogenation products, a general picture of the parent cyclohexenes can be obtained.

Pentachloropentafluorocyclohexene.

The main component of the dehalogenated product is dichlorotetrafluorobenzene (58%), most of which is the 1,2- isomer. Thus three chlorine atoms are eliminated from the cyclohexene, where they must have been present as >CFCl groupings. The removal of one fluorine atom shows that a gem difluoro grouping was also present.

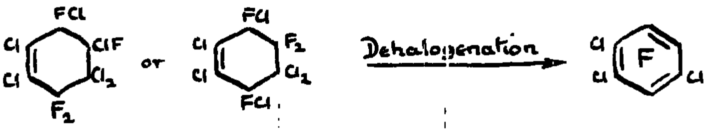


The dehalogenation product also contains 18% of the 1,2,4-trichlorotrifluorobenzene. This, by similar reasoning, must have come from:-

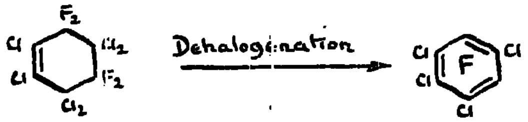


## Hexachlorotetrafluorocyclohexene.

The main components of the dehalogenation product are cyclic $C_6Cl_3F_3$ 30% and $C_6Cl_4F_2$ (33%). The former is composed of 83% of 1,2,4-trichlorotrifluorobenzene, and the latter of 57% of 1,2,3,5-tetrachlorodifluorobenzene. Again similar reasoning shows:-



and



## Dehalogenation of Mixed Perchlorofluoro-cyclohexanes and -cyclohexenes.

Partial saturation of the perchlorofluorocyclohexenes, with chlorine trifluoride, occurs fairly readily to give a mixture of the cyclohexenes and cyclohexanes, (see page 33). These were separated by distillation into pairs, each pair contains the cyclohexane and cyclohexene with the same number of chlorine atoms. Each pair was dehalogenated at 50°C above its boiling point. The results are shown in Table 5, 5 gms. being used in each dehalogenation.

**Table V.** Dehalogenation of cyclohexanes and cyclohexenes.

| Reactant. | Ratio. | Temp. of Reaction °C. | % of Product. |
|---|---|---|---|
| $C_6Cl_4F_6$ | 1 | 230°C | $C_6F_6$ (2%) $C_6ClF_5$ (10%) $C_6Cl_2F_4$ (12%) $C_6Cl_3F_3$ (20%) |
| $C_6Cl_4F_8$ | 1 | | $C_6Cl_4F_2$ (10%) $C_6Cl_3F_7$ (10%) Starting Material (20%) |
| $C_6Cl_5F_5$ | 1 | 260°C | $C_6F_6$ (17%) $C_6ClF_5$ (21%) $C_6Cl_2F_4$ (35%) $C_6Cl_3F_3$ (24%) |
| $C_6Cl_5F_7$ | 1 | | $C_6Cl_4F_2$ (2%) |
| $C_6Cl_6F_4$ | 1 | 300°C | $C_6F_6$ (2%) $C_6ClF_5$(25%) $C_6Cl_2F_4$ (35%) $C_6Cl_3F_3$ (30%) |
| $C_6Cl_6F_6$ | 2 | | $C_6F_2Cl_4$ (7%) |

No direct comparisons can be obtained from these results as:-

i) $C_6Cl_4F_6/C_6Cl_4F_8$ contains only 54% of aromatic material.

ii) The ratios of cyclohexene/cyclohexane are different.

However it can be seen that the inclusion of a fully saturated compound gives more highly fluorinated products. However the aromatic compounds are spread over a wide range, i.e. from $C_6F_6$ to $C_6Cl_4F_2$, and there is no preponderance of any one chlorofluorobenzene.

## Dehalogenation of Perchlorofluorocyclohexanes.

The full saturation of hexachlorobenzene with chlorine trifluoride, gave compounds of molecular formula $C_6Cl_xF_{12-x}$ where x = 5, 6 and 7. They were prepared by using a fourfold excess of chlorine trifluoride, and were obtained in a 50% yield. These cyclohexanes were separated by distillation, and dehalogenated under a variety of conditions. (See Table 6a). In each dehalogenation 5 gms. of starting material were used.

When the temperature for dehalogenation was 50°C above the boiling point of the reactant, good yields of aromatic material were obtained. The good yields of chloropentafluoro- and dichlorotetrafluorobenzenes were encouraging, although the low yield of perfluorobenzene was disappointing.

Table 6a. Dehalogenation of Perchlorofluorocyclohexanes

| Reactant | Temp. °C | Flow Rate $N_2$ ccs/min. | Introduction Rate mins/gm. | Total Yield % | Product |
|---|---|---|---|---|---|
| $C_6Cl_5F_7$ | 260 | 60 | 4 | 72 | $C_6F_6$ 21% $C_6ClF_5$ 29% $C_6Cl_2F_4$ 8% $C_6Cl_3F_7$ 14% |
| $C_6Cl_5F_7$ | 430 | 60 | 4 | 19 | $C_6F_6$ 13% $C_6ClF_5$ 6% |
| $C_6Cl_5F_7$* | 430 | 30 | 9 | 12 | $C_6F_6$ 12% (20% of product non-aromatic) |
| $C_6Cl_6F_6$ | 300 | 60 | 4 | 76 | $C_6F_6$ 2% $C_6ClF_5$ 38·5% $C_6Cl_2F_4$ 33·5% $C_6Cl_3F_3$ 2% |
| $C_6Cl_6F_6$* | 425 | 30 | 9 | - | $C_6F_6$ 0·1% (80% of product non-aromatic) |
| $C_6Cl_7F_5$ | 330 | 60 | 4 | 71 | $C_6ClF_5$ 11% $C_6Cl_2F_4$ 46% $C_6Cl_3F_3$ 11% $C_6Cl_4F_2$ 3% |
| $C_6Cl_7F_5$* | 430 | 30 | 9 | - | 0·1 gms. (all non-aromatic) |

* These conditions are identical with the dehalogenations of perchlorofluorocyclohexanes (obtained by the reaction of hexachlorobenzene and cobalt fluoride) carried out by Mobbs.[16]

## Pentachloroheptafluorocyclohexane.

When the temperature of the dehalogenation of $C_6Cl_5F_7$ was raised from 260°C to 430°C, the overall yield of aromatic material dropped considerably, from 72% to 19%. However the more heavily chlorinated aromatic product had disappeared. This is obviously due to isomerization of the diene occurring, giving more elimination of the chlorine.

In the dehalogenation of $C_6Cl_5F_7$,[19] obtained from the reaction of hexachlorobenzene and cobalt fluoride, the nitrogen dilution rate was 30 ccs/min. and the introduction rate was one gram every nine minutes. The product from this reaction contained perfluorobenzene, in a 43% yield, and a small amount of an unidentified compound. This compound was thought to be a chlorofluorodiene, however this is unlikely as cyclodienes have been found to dehalogenate very much more readily than the cyclohexanes. It is far more likely to be a perchlorofluorocyclohexene.

Dehalogenation of $C_6Cl_5F_7$ (obtained from the reaction of hexachlorobenzene and chlorine trifluoride), under similar conditions gave perfluorobenzene 12%, and a small amount of material having a similar retention time, on analytical V.P.C., to that mentioned above.

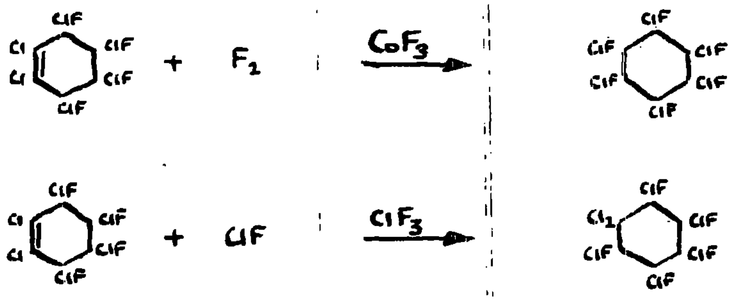
Hexachlorohexafluorocyclohexane, dehalogenated under similar conditions, gave an extremely low yield of perfluorobenzene, and heptachloropentafluorocyclohexane gave none at all. The same impurity was present in both these products.

It can be seen from these experiments that the perchlorofluorocyclohexanes, or their intermediates in the dehalogenation process, become less stable to high temperatures, as their chlorine content is increased.

## Structures of Perchlorofluorocyclohexanes.

From a comparison of the dehalogenation products of $C_6Cl_5F_7$ ($C_6Cl_6/CoF_3$) and $C_6Cl_5F_7$ ($C_6Cl_6/ClF_3$), it is possible to see the main difference in their structures. Thus $C_6Cl_5F_7$ ($C_6Cl_6/CoF_3$) gave much less of the chlorofluoroaromatic product than $C_6Cl_5F_7$ ($C_6Cl_6/ClF_3$). See Table 6b. As rearrangement does not occur at this temperature (260°C), this indicates that there are more gem dichloro groupings present in the $C_6Cl_5F_7$ ($C_6Cl_6/ClF_3$). Other evidence pointing to the presence of gem dichloro groupings in the chlorofluorination product of hexachlorobenzene, is seen in the dehalogenation of $C_6Cl_7F_5$, where $C_6Cl_3F_3$ was isolated. This indicates the presence of three such groupings.

The presence of more gem dichloro groups, in this product, is to be expected. Cobalt fluoride will only add fluorine to double bonds, whereas chlorine trifluoride can add both fluorine and chlorine monofluoride.



The difference in the two types of perchlorofluorocyclohexanes explains the difference in the yields of perfluorobenzene, when $C_6Cl_5F_7$ is dehalogenated at 430°C.

$$C_6Cl_5F_7\ (C_6Cl_6/CoF_3) \longrightarrow C_6F_6\quad 43\%$$

$$C_6Cl_5F_7\ (C_6Cl_6/ClF_3) \longrightarrow C_6F_6\quad 12\%$$

The cyclohexanes containing more gem dichloro groupings, or the more highly chlorinated intermediates formed during the dehalogenation, must be more readily decomposed at elevated temperatures.

## Size of Sample to be Dehalogenated.

It has been noticed in the dehalogenations of the perchlorofluorocyclohexanes, -cyclohexenes and -cyclohexadiene, that the size of the sample will influence the distribution of the products. Thus if a large amount of material is dehalogenated, the product contains compounds with considerably more chlorine present, than if a small amount had been dehalogenated. This is obviously due to the fact that the freshly reduced iron is selective in the dehalogenation, removing mainly chlorine and chlorine monofluoride.

i.e.

However as the surface of the iron gauze becomes coated with iron halides, the selectivity is decreased.

i.e.

Table 6b. Dehalogenation of $C_6Cl_5F_7$

| Amount | Product % $C_6F_6$ | $C_6ClF_5$ | $C_6Cl_2F_4$ | $C_6Cl_3F_7$ | Others |
|---|---|---|---|---|---|
| I) 2.5 gms.* | 70 | 25 | 5 | - | - |
| II) 2.5 gms. | 40 | 40 | 10 | 10 | - |
| III) 5 gms. | 35 | 35 | 10 | 20 | - |
| IV) 10 gms. | 20 | 20 | 5 | 40 | St.Mat. 10<br>$C_6Cl_4F_6$ 5 |

* Cyclic $C_6Cl_5F_7$ obtained from the reaction of hexachlorobenzene and cobalt fluoride.

All dehalogenations were carried out at 260°C, with a nitrogen flow rate of 60 ccs/min. and an introduction rate of 1 gm. in 4 minutes.

This effect is demonstrated in Table 6b, where $C_6Cl_5F_7$ was dehalogenated, using different sample sizes but keeping the conditions exactly the same. As the sample size is increased, the yield of perfluoro- and chloropentafluorobenzene decreases and the yield of $C_6Cl_3F_7$ increases.

This dehalogenation technique is therefore very limited in the large scale preparation of the more highly fluorinated chlorofluorobenzenes. If the size of the sample to be dehalogenated is increased above 5.0 gms, the more highly chlorinated compounds are produced in increasing yields.

The perchlorofluorocyclohexanes, ($C_6Cl_xF_{12-x}$ where x = 4-7), obtained in excellent yields from the reaction of elemental fluorine and hexachlorobenzene, were dehalogenated without being separated. The results are shown in Table 6c.

Table 6c.

| | Amount gms. | Yield % | Product % |
|---|---|---|---|
| I) | 5 | 61 | $C_6F_6$ 14%, $C_6ClF_5$ 28%, $C_6Cl_2F_4$ 14%, $C_6Cl_3F_3$ 5% |
| II) | 20 | 73 | $C_6F_6$ 19%, $C_6ClF_5$ 21%, $C_6Cl_2F_4$ 16%, $C_6Cl_3F_3$ 11% $C_6Cl_4F_2$ 5%, $C_6Cl_5F$ 1% |

The high temperature of 330°C had to be used, as the boiling point of $C_6Cl_7F_5$ is 280°C. This would naturally cause some decomposition, which explains the lower overall yield obtained. The yields of the more highly fluorinated aromatic compounds are, however, an improvement on the dehalogenated products of the cyclohexanes, obtained by the chlorofluorination of hexachlorobenzene. This is probably due to the slightly elevated temperature, enabling more rearrangement to occur, and thus eliminating more chlorine.

## A New Technique of Dehalogenation.

The method of dehalogenation described above suffers from two serious faults. Firstly the amount of material that can be dehalogenated, without the regeneration of the iron gauze, is very low. As this regeneration uses large amounts of hydrogen, the preparation of aromatic material, by this method, is both costly and time consuming. Secondly, a variation in the reaction conditions, i.e. size of sample, introduction rate, will cause a different distribution of products.

It was suggested that these difficulties could be avoided, if the vapourized reactant could be passed through a large amount of iron filings. Consequently a stirred "cobalt fluoride" reactor (see page 128) was filled with 3 k.g. of coarse iron filings.

The perchlorofluorocyclohexanes obtained from the reaction of elemental fluorine and hexachlorobenzene, were dehalogenated, without separation, using this method. (See Table 7a). The temperature of the reactor, for all the dehalogenations, was 330°C., and the nitrogen flow rate was 60 ccs/min.

Table 7a. Dehalogenation Using Iron Filings.

| Amount | Introduction rate mins/gm. | Yield % | Product |
|---|---|---|---|
| 1) 5 gms. | 4 | 43.5 | $C_6F_6$ 14% $C_6ClF_5$ 18%<br>$C_6Cl_2F_4$ 9.5% $C_6Cl_3F_3$ 2% |
| 2) 10 gms. | 4 | 47 | $C_6F_6$ 15% $C_6ClF_5$ 20%<br>$C_6Cl_2F_4$ 10% $C_6Cl_3F_3$ 2% |
| 3) 20 gms. | 4 | 50.5 | $C_6F_6$ 16% $C_6ClF_5$ 21%<br>$C_6Cl_2F_4$ 11% $C_6Cl_3F_3$ 2.5% |
| 4) 20 gms. | 2 | 50 | $C_6F_6$ 13% $C_6ClF_5$ 21%<br>$C_6Cl_2F_4$ 11% $C_6Cl_3F_3$ 5% |
| 5) 20 gms. | 1 | 55 | $C_6F_6$ 15% $C_6ClF_5$ 21%<br>$C_6Cl_2F_4$ 13% $C_6Cl_3F_3$ 6% |

The results show quite conclusively that both variation of the introduction rate, and sample size, does not alter the product distribution. When samples of 5, 10 and 20 gms. were introduced, (all at 4 mins. /gm.), the difference in the amounts of perfluorobenzene, is at the most 3%.

The overall yield of 50% is lower compared with the dehalogenation using iron gauze (70%). However the difference lies in the more highly chlorinated compounds, which is not so important.

When the introduction rate was changed from 4 mins./gm. to 2 mins./gm., and then to 1 min./gm.; the yield of aromatic material rose slightly, but the product distribution did not change. However the amount of non-aromatic material increased. Thus when the introduction rate was increased from 2 mins./gm. to 1 min./gm. the amount of impurity present increased from 15% to 20%.

Erratic results were obtained when the first 15-30 gms. of material were dehalogenated. This is generally found when using a new metal surface. After 700 gms. of material had been passed through the reactor, it was found that both the amount of more highly chlorinated benzenes, and the amount of non-aromatic impurities, were increasing. The iron filings must be covered with iron halides, thus deactivating the surface. The filings were removed and replaced by 5 Kg. of fine iron filings. Table 7b shows the difference in the products from using fine and coarse iron filings.

Again it can be seen quite conclusively that the fine iron filings are a vast improvement. The yield increases from 50% to 65%, and this increase is with the perfluoro- and chloropentafluorobenzenes, exactly where it is wanted. The amount of non-aromatic material present was very much less, and after 1000 gms. of material had been dehalogenated, although the packing showed slight signs of deteriation, good yields were still obtained.

Table 7b.

| | Reactant | Yield | Fine or coarse filings | Product |
|---|---|---|---|---|
| 1) | $C_6Cl_6/3F_2$ | 50 | coarse | $C_6F_6$ 13% $C_6ClF_5$ 21% $C_6Cl_2F_4$ 11%<br>$C_6Cl_3F_3$% |
| 2) | $C_6Cl_6/7\frac{1}{2}F_2$ | 56 | coarse | $C_6F_6$ 29% $C_6ClF_5$ 23% $C_6Cl_2F_4$ 4% |
| 3) | $C_6Cl_6/3ClF_3$* | 62 | coarse | $C_6F_6$ 8% $C_6ClF_5$ 22% $C_6Cl_2F_4$ 20%<br>$C_6Cl_3F_3$ 9% $C_6Cl_4F_2$ 3% |
| 4) | $C_6Cl_6/3F_2$ | 64 | fine | $C_6F_6$ 22% $C_6ClF_5$ 27% $C_6Cl_2F_4$ 12.5%<br>$C_6Cl_3F_3$ 3% |
| 5) | $C_6Cl_6/3F_2$‡ | 62.5 | fine | $C_6F_6$ 18% $C_6ClF_5$ 26.5% $C_6Cl_2F_4$ 15%<br>$C_6Cl_3F_3$ 3% |

* For comparison an average molecular weight of 380 was taken.

‡ After 1 Kg. had been dehalogenated.

The mixture of perchlorofluorocyclohexanes and -cyclohexenes, obtained from the chlorofluorination of hexachlorobenzene, was also dehalogenated under similar conditions. The overall yield of aromatic material was good, and could be increased, as the coarse filings were used. However the yield of perfluorobenzene was poor, compared with the products from the dehalogenated cyclohexanes, obtained from the straight fluorination of hexachlorobenzene. The increased yield comes from the more highly chlorinated aromatic product.

The second reaction in Table 7b shows the dehalogenation of the cyclohexanes obtained from the prolonged action of fluorine on hexachlorobenzene. (Average molecular constitution $C_6Cl_5F_7$). This gives good yields of perfluoro- and chloropentafluorobenzenes, which could be increased if the fine iron filings were used. However these cyclohexanes are only produced in 64.5% yield from hexachlorobenzene.

## Preparation of Perfluorobenzene and Chloropentafluorobenzene.

The dehalogenation of the perchlorofluorocyclohexanes, obtained from the reaction between hexachlorobenzene and fluorine, is probably the best method for the production of perfluorobenzene. Both perfluorobenzene (20% overall yield) and chloropentafluorobenzene (25% overall yield), obtained in this reaction, can be used as precursors to fluoro-aromatic compounds. Chloropentafluorobenzene (similar to the iodo- and bromo-analogues) has been shown in these laboratories to form a Grignard reagent.[103]

$$C_6ClF_5 + Mg \xrightarrow{Et_2O} C_6F_5MgCl.$$

The advantages in this method of preparation are given below:-

i) The starting material, hexachlorobenzene, is readily accessible and relatively cheap. The fluorination to the cyclohexane stage (average molecular formula $C_6Cl_6F_6$), only requires theoretical amounts of fluorine, to give excellent yields (90%). Some fluorine is lost, however, in the fluorination of the solvent.

ii) Both the fluorination and dehalogenation steps can be carried out on a large scale.

iii) Provided that a source of fluorine and a cobalt fluoride reactor are available, these compounds can be made quickly, cheaply, very simply and in good yields.

iv) The advantage in using the chlorofluorocyclohexanes as the precursor to these aromatic compounds, is that the chlorine and not the fluorine is eliminated. There is, therefore, little wastage of fluorine.

$$C_6Cl_6 + 3F_2 \longrightarrow C_6Cl_6F_6 \longrightarrow C_6F_6 + C_6ClF_5.$$

v) Chloropentafluorobenzene is produced. This provides a reactive grouping in the perfluoro- nucleus.

It was found that changing from coarse filings to fine filings, in the dehalogenation step, increased the yield of aromatic material by 15%. A further increase may be found if the packing was changed to iron powder. The iron powder would lend itself to a more simple method of replacement; i.e. the powder could be blown out, and new powder replaced in a similar manner.

# Chapter 3.

# EXPERIMENTAL WORK

# FLUORINATION OF HEXACHLOROBENZENE.

## The Liquid Phase Reaction between Chlorine Trifluoride and Hexachlorobenzene.

Hexachlorobenzene was reacted in the liquid phase, with chlorine trifluoride, diluted with nitrogen, and produced a chlorofluorocyclohexadiene, $C_6Cl_4F_4$, Chlorofluorocyclohexenes (of general formula $C_6Cl_nF_{10-n}$ n=3-6), and chlorofluorocyclohexanes (of general formula $C_6Cl_xF_{12-x}$ x=3-7).

The products were separated by distillation and preparative scale vapour phase chromatography, and analysed for chlorine and fluorine. Their identity was confirmed by analytical vapour phase chromatography, (Griffen and George Mk. II a.); infra red spectroscopy, (Grubb Parsons G.S. IIa. ); molecular weight determination, (Victor Meyer method.); and refractive index, (Bellingham and Stanley Abbe type refractometer.).

The hexachlorobenzene used was technical grade, made by British Drug Houses; the chlorine trifluoride was supplied in 1000gm. cylinders from I.C.I.; and the fluorine was generated from an I.C.I. fluorine cell capable of a ten amp. load.

### Exploratory Run.

Hexachlorobenzene (100gms. 0.35 M.) was placed in a one litre, mild steel pot, with carbon tetrachloride (500mls). This was mechanically stirred, and the chlorine trifluroide, diluted with nitrogen, bubbled into the slurry at room temperature.

Chlorine trifluoride addition rate was 25gms/hr.; nitrogen flow rate was 10 litres/hr.

The reaction was continued for three and a half hours, a total of 84 gms. (0.9 M), of chlorine trifluoride being added. The product was washed once with sodium hydroxide solution (0.5 N), and twice with water. The solid was filtered off and dried to give hexachlorobenzene (84 gms.). This was confirmed by melting point (226°C.) and mixed melting point (227°C.). The infra red spectrum was identical with authentic hexachlorobenzene.

The filtrate was dried (anhydrous $MgSO_4$) and distilled to give carbon tetrachloride (290 mls.), b.p. 76°C., leaving a residue of hexachlorobenzene (10 gms.).

### Reaction of Hexachlorobenzene with Chlorine Trifluoride.
### (Molar Ratio 1:1½).

Hexachlorobenzene (100 gms., 0.35 M.) was placed in a three necked 250 cc. flask and heated to 240°C. using an isomantle, the chlorine trifluoride, diluted with nitrogen, was led into the vessel by a gas lead dipping below the molten, stirred, hexachlorobenzene. A wide air condenser prevented the subliming hexachlorobenzene from leaving the apparatus, and a heating tape prevented blockage in the condenser (see fig. i). A trap cooled in water to collect any low boiling product, and a bubbler (using carbon tetrachloride), were connected to the end of the air condenser.

Chlorine trifluoride was introduced at 20-25 gms/hr., and the nitrogen flow rate was 5 litres/hr., for the first hour; the chlorine

CHLOROFLUORINATION
APPARATUS.

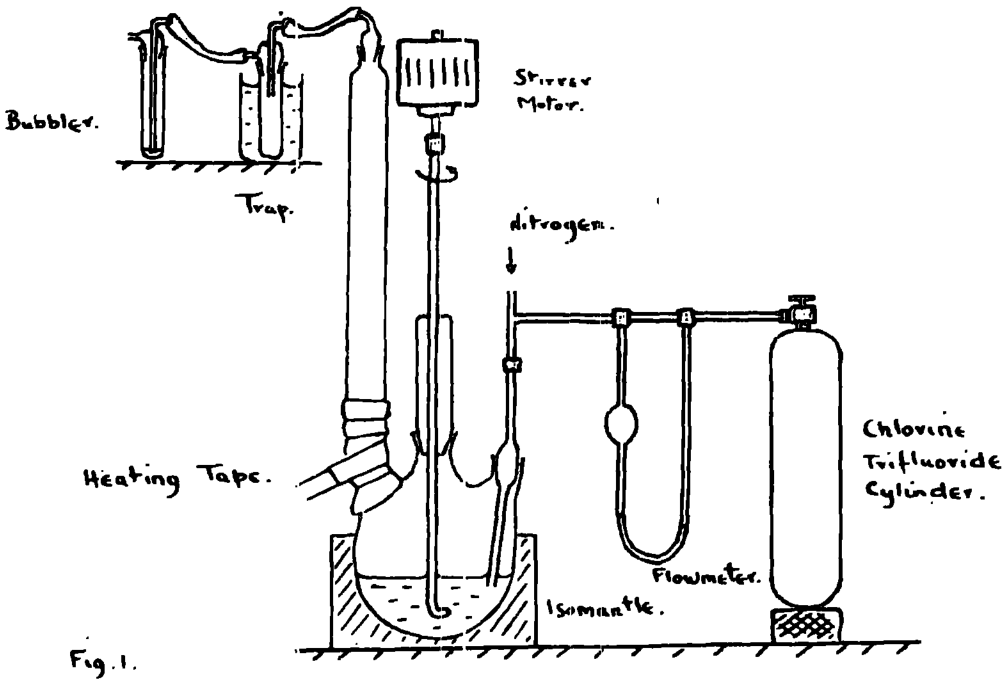


Fig. 1.

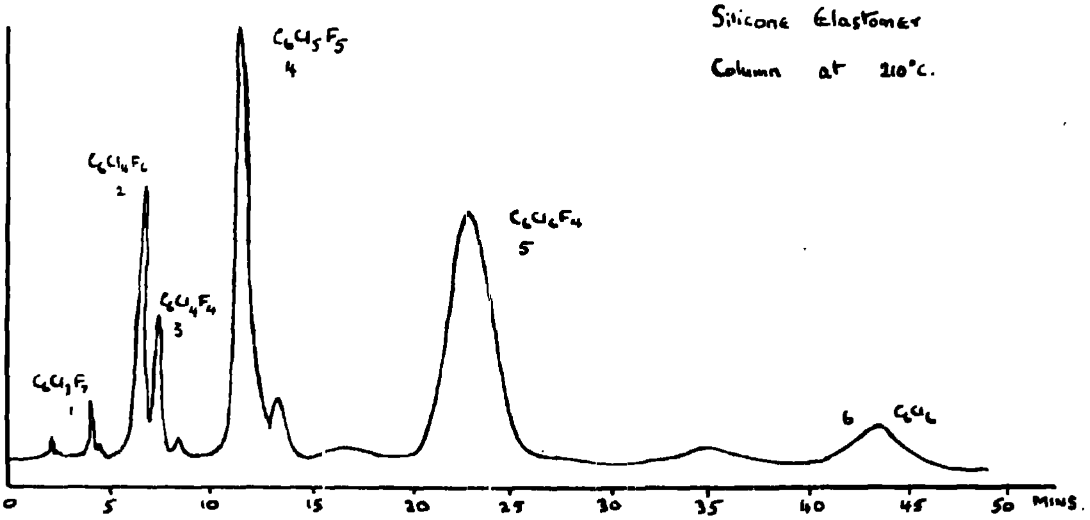


Fig. 11. Reaction product of $C_6Cl_6$ and $ClF_3$. (Molar ratio 1 : 1½).

trifluoride flow rate was then cut to 10-15 gms/hr., and the nitrogen flow rate to 2.5-3.0 litres/hr. The reaction was stopped after 56 gms. of chlorine trifluoride (0.60 M) had been added, the nitrogen was stopped after a further half hour.

Ignition of the chlorine trifluoride occurred during the reaction, this caused decomposition of the hexachlorobenzene and resulted in carbon contamination of the product. When this occurred the chlorine trifluoride addition was stopped, and the system swept with nitrogen before passing more chlorine trifluoride.

The reaction product, which was a liquid, was diluted with ether, and filtered to remove carbon using hyflosupercell (Johns Manderville & Co.Ltd.) as the filtration pad. The etherial solution was washed with sodium hydroxide solution (N) and then with water, dried (anhydrous $MgSO_4$), and the ether distilled. The product was distilled, without a distillation column, to give an oily colourless liquid (85 gms.), with a pungent smell.

This reaction was repeated seven times, using varying amounts of hexachlorobenzene and chlorine trifluoride. Details are given in table 8.

Table 8.

| | Wt. $C_6Cl_6$ gms. | Temp. °C. | Wt. $ClF_3$ gms. | Time of Reaction, hrs. | Product, gms. |
|---|---|---|---|---|---|
| 1. | 100 | 240 | 56 | 4 | 85 |
| 2. | 100 | 240* | 55 | $3\frac{3}{4}$ | 90 |
| 3. | 100 | 250 | 62 | $4\frac{1}{2}$ | 92 |
| 4. | 100 | 240 | 56 | 3 | 72 |
| 5. | 200 | 240 | 121 | 7 | 178 |
| 6. | 250 | 240 | 128 | 10 | 193 |
| 7. | 125 | 240 | 80 | $3\frac{1}{2}$ | 138 |

* The temperature was lowered gradually throughout the reaction to 150°C.

A typical run gave a vapour phase chromatogram as shown in fig.ii; this shows five major components and some eight minor components. The compounds isolated and characterized have been given a peak number to aid identification.

The products from runs 1-4 were combined, and distilled using a concentric tube column, with a heating jacket. This apparatus was set up to give a maximum platage of 18 using a mixture of n-heptane and methylcyclohexane, following the method of Bromiley and Quiggle.[104] The refractive index of the still pot and the distillate, were found after equilibrium had been attained. The plateage of the column was then read off from the table of refractive index against theoretical plates, which was constructed by Lecky and Ewell.[105]

The details of the distillation are shown in table 9. and fig. iii.

Table 9. Distillation 1.

| Fraction No. | Boiling Range °C. | Size of Fraction gms. | Containing Components No. |
|---|---|---|---|
| 1 | 142-145 | 3.7 | 1. |
| 2 | 175-180 | 31.6 | 2,3. |
| 3 | 205-209 | 107.5 | 4. |
| 4 | 245-248 | 101.0 | 5. |
| 5 | 273-283 | 36.0 | 6. |

Residue 5.0 gms. Intermediate fractions 49 gms. Recovery 96%.

## Fractional Distillation of the Reaction Product from Hexachlorobenzene and Chlorine Trifluoride (Molar Ratio 1:1½).

Fraction 1. This contained mainly component 1. A.S.V.P.C.[a] using a T.C.P.[b] column, showed it to have a coincident retention time with $C_6Cl_3F_7$ obtained from the hexachlorobenzene, antimony pentafluoride reaction.[14] 3.75 gms. of fraction 1 gave 2.1 gms. of component 1. (P.S.V.P.C.[c] T.C.P. column at 150°C; P.D.[d] 40 cms. of Hg; nitrogen 200 ccs/min.).

Molecular weight, found: 323, calc. for $C_6Cl_3F_7$: 311.5.

B.p. 148°C. Leffler[14] gave 140°C., McBee[3] 145.5°C. $n_D^{20}$ 1.4050,

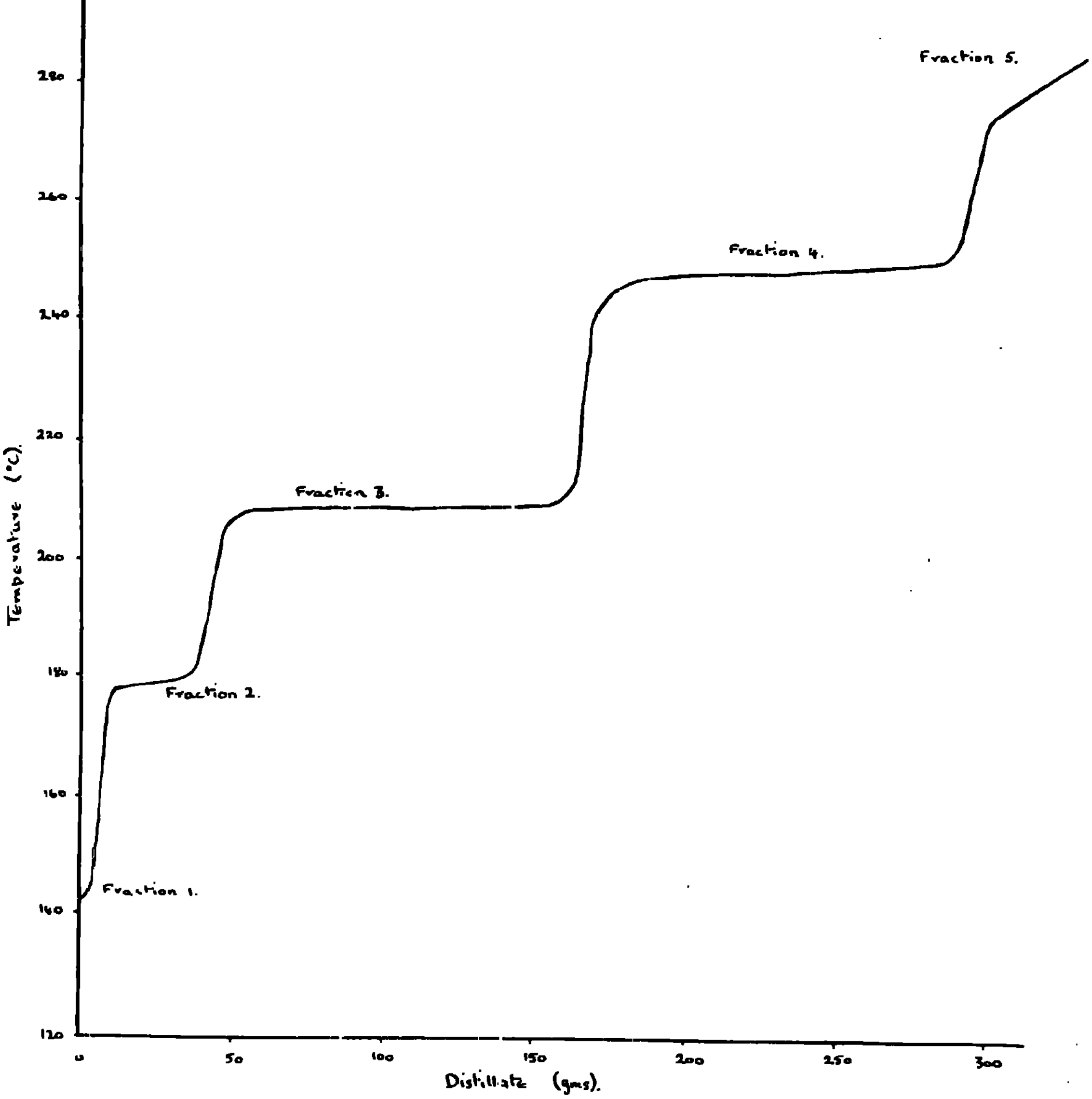
[a] Analytical scale vapour phase chromatography.

[b] Tri cresyl phosphate.

[c] Preparative scale vapour phase chromatography.

[d] Pressure difference.

Fig iii. Distillation curve for 339 gms of reaction product from Chlorofluorination of Hexachlorobenzene.
Column: 15 plate.
Pressure: 1 Atmosphere.



$n_D^{30}$ 1.4006. Leffler gave $n_D^{30}$ 1.3995, McBee $n_D^{20}$ 1.4013.
Analysis gave: Cl, 34.2, F, 42.5%; calc. for $C_6Cl_3F_7$: Cl, 34.2, F, 42.7%.
An infra red spectrum of component 1 (No. 3. see page 138) showed strong absorbtion at 1633 $cm^{-1}$ and 1693 $cm^{-1}$, which indicated the presence of the unsaturated structures -CCl=CCl- and -CF=CCl- . The former structure is present in 1,2,4-trichloroheptafluorocyclohexene,[14] and an infra red spectrum of this (No. 2) indicated that some of this compound is present in component 1.

Fraction 2. This contained about 60% of component 2, and 30% of component 3. 20.0 gms. of fraction 2 gave 7.0 gms. of component 2, and 2.3 gms of component 3. (P.S.V.P.C. Si.El.[a] column at 175°C; P.D. 30 cms. Hg; nitrogen 175 ccs/min.; recycled once).
Component 2. Molecular weight, found: 334, calc. for $C_6Cl_4F_6$: 328. B.p. 178.5°C. Leffler[14] gave 95°C/63 mm. $n_D^{20}$ 1.4367, $n_D^{30}$ 1.4327. Leffler gave $n_D^{30}$ 1.4313.
Analysis gave: Cl, 43.1, F, 34.0%; calc. for $C_6Cl_4F_6$: Cl, 43.3, F, 34.7%.
The infra red spectrum of component 2 (No. 5) showed strong absorbtions at 1637 $cm^{-1}$ and 1695 $cm^{-1}$, which indicated the presence of the structures -CCl=CCl- and -CF=CCl- .
Component 3. Molecular weight, found: 295, calc. for $C_6Cl_4F_4$: 290. M.p. 46.5°C. Smith et al.[10] gives 46.0°C.
Analysis gave: Cl, 49.8, F, 26.0%; calc. for $C_6Cl_4F_4$: Cl, 49.0, F, 26.2%.

[a] Silicone elastomer.

The infra red spectrum of component 3 (No. 8) had a strong absorbtion at 1642 $cm^{-1}$, consistant with the -CCl=CCl- grouping, the spectrum was simple which indicated a symmetrical molecule. This was shown by N.M.R. to be 1,2,4,5-tetrachlorotetrafluorocyclohexa-1,4-diene. An ultra violet spectrum in methanol, using an Optica C.F.4. spectrophotometer, gave: $\lambda_{max}$ 208mμ, log e 4.119. (0.01024 gms/litre).

Fraction 3. This contained mainly component 4. 10.0 gms. of fraction 3 gave 4.3. gms. of component 4. (P.S.V.P.C. Si.El. column at 200°C; P.D. 35 cms. Hg; nitrogen 175 ccs/min.; recycled once).
Molecular weight, found: 352, calc. for $C_6Cl_5F_5$: 344.5.
B.p. 208.5°C. $n_D^{20}$ 1.4699.
Analysis gave: Cl, 51.7, F, 27.3%; calc. for $C_6Cl_5F_5$: Cl, 51.5, F, 27.6%.
The infra red spectrum (No. 6) showed strong absorbtion at 1623 $cm^{-1}$, and weak absorbtion at 1690 $cm^{-1}$; this indicates a preponderance of the -CCl=CCl- grouping.

Fraction 4. This contained mainly component 5. 10.0 gms. of fraction 4 gave 2.8. gms. of component 5. (P.S.V.P.C. Si.El. column at 230°C; P.D. 40 cms. Hg; nitrogen 200 ccs/min.; recycled twice).
Molecular weight, found: 360, calc. for $C_6Cl_6F_4$: 361.
B.p. 242.5°C. $n_D^{20}$ 1.4998.
Analysis gave: Cl, 59.8, F, 21.7%; calc. for $C_6Cl_6F_4$; Cl, 59.0, F, 21.1%.
The infra red spectrum (No. 7) showed strong absorbtion at 1620 $cm^{-1}$,

and no absorbtion in the 1690 cm$^{-1}$ region; this indicates that component 5 contained none of the -CF=CCl- structure, but that the unsaturation was caused only by the -CCl=CCl- grouping.

Fraction 5. This was a suspension containing mainly component 6, A.S.V.P.C., using a silicone elastomer column, showed it to have a coincident retention time with hexachlorobenzene. 0.5 gms. were isolated after twice recrystalizing from diethyl ether.
M.p. 227°C; mixed m.p. with hexachlorobenzene: 227°C.
Analysis gave: Cl, 74.0, F, 1.4%; calc. for $C_6Cl_6$: Cl, 74.7%.
The infra red spectrum (No. 20 see page 45) had absorbtions at 1348, 1300 and 696 cm$^{-1}$, identical with hexachlorobenzene.

All molecular weights were determined by the Victor Meyer method, which gave results with standards that were consistantly 2-3% high.

### Reaction of Hexachlorobenzene with Chlorine Trifluoride.
### (Molar Ratio 1:3).

Hexachlorobenzene (100 gms., 0.35 M) was reacted with chlorine trifluoride (55 gms., 0.6 M) at 240°C, using the same conditions and apparatus as stated before. After this stage the temperature was lowered to 100°C, and chlorine trifluoride, (45 gms., 0.5 M) diluted with nitrogen (3 litres/hr.), was passed into the reaction vessel for two hours. The resulting liquid was diluted with ether (50 mls.), filtered, washed and dried as before. After an ether distillation, the product was distilled to give a colourless liquid

(95 gms.)

A vapour phase chromatogram of a typical reaction is shown in fig. iv. The compounds indicated by the numbers 1,2,4 and 5, have the same retention times, using A.S.V.P.C. under varying conditions, as those mentioned before; i.e. $C_6Cl_3F_7$, $C_6Cl_4F_6$, $C_6Cl_5F_5$ and $C_6Cl_6F_4$ respectively. In order to isolate these compounds for definite identification, and also to determine the nature of the compounds closely associated with each one (shown in fig. iv by the peak number and suffix a); a sufficient quantity of reaction product was obtained for a fractionation. See table 10.

Table 10.

| wt. of $C_6Cl_6$ gms. | wt. of $ClF_3$ gms. | Time of Reaction hrs. | Product gms. |
|---|---|---|---|
| 100 | 100 | $4\frac{1}{2}$ | 95 |
| 100 | 103 | 5 | 98 |
| 250 | 256 | 11 | 244 |

The products from the above reactions were combined and distilled, using the concentric tube column previously described. The temperature range and the weight of each fraction is given in table 11.

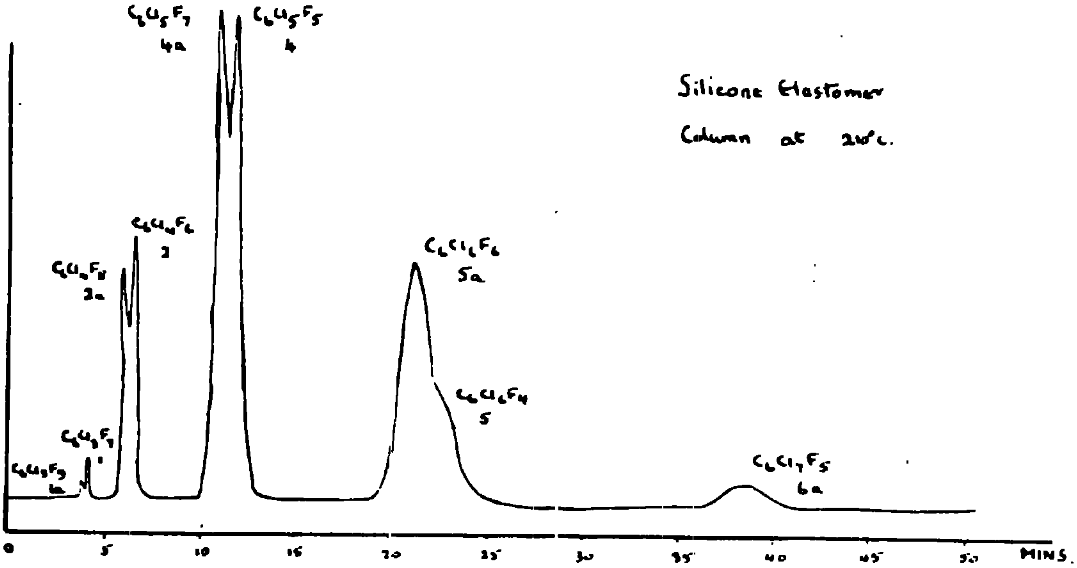


Fig IV. Reaction product of $C_6Cl_6$, and $ClF_3$. (Molar ratio 1·3).

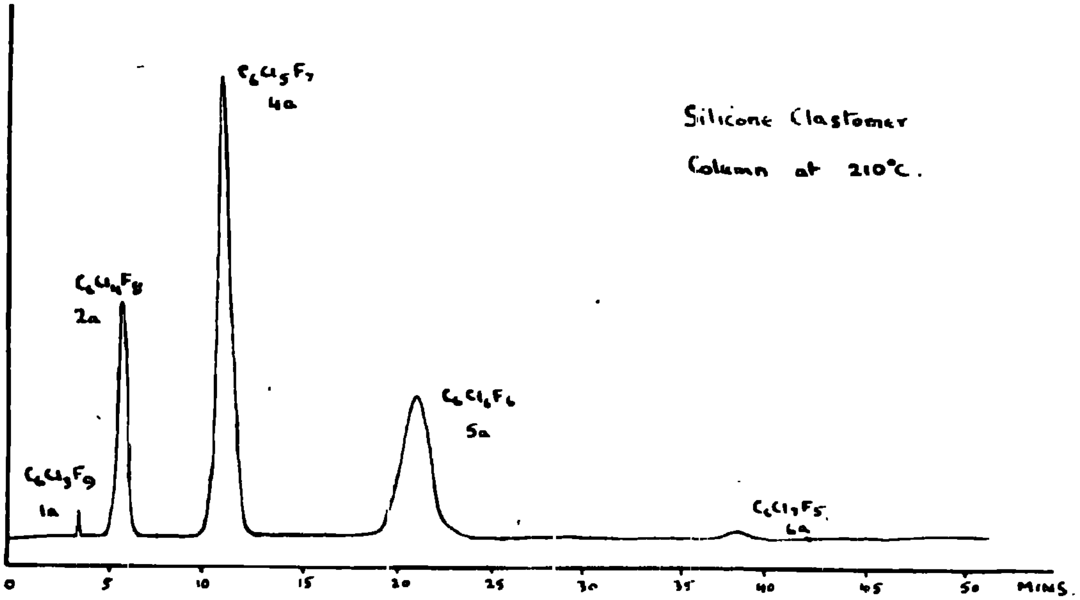


Fig V. Reaction product of $C_6Cl_6$ and $ClF_3$. (Molar ratio 1:7).

Table 11. Distillation 2.

| Fraction No. | Boiling Range°C. | Size of Fraction gms. | Containing Component Nos. | Constitution. |
|---|---|---|---|---|
| 1 | 177-178 | 15 | 2, 2a | 1:1 |
| 2 | 207-208 | 60 | 4, 4a | 1:1 |
| 3 | 240-243 | 50 | 5, 5a | 1:2 |
| 4 | 270-273 | 44 | 6a | - |

Residue 3 gms. Intermediate Fractions 250 gms. Recovery 96%.

Each distillation fraction contained two components, both having similar boiling points and retention times. P.S.V.P.C. was used to obtain a pure specimen of each component, and in each seperation, the component had to be recycled at least once. The amount of each component isolated was small, however the infra red spectrum was obtained, and compared with standard compounds. These were :-

i) the perchlorofluorocyclohexenes, obtained from the reaction between hexachlorobenzene and chlorine trifluoride, with a molar ratio of $1:1\frac{1}{2}$;

ii) the perchlorofluorocyclohexanes, obtained from a similar reaction, with a molar ratio of 1:7.

Fraction 1. This contained 50% of component 2 and 50% of component 2a. Pure specimens were isolated. (P.S.V.P.C. Si.El. column at 180°C; P.D. 30 cms. Hg; nitrogen 175 ccs/min.; recycled once). Infra red spectra and A.S.V.P.C. showed component 2 to be $C_6Cl_4F_6$, and component 2a to be $C_6Cl_4F_8$.

Fraction 2. This contained 50% of component 4 and 50% of component 4a. Pure specimens were isolated. (P.S.V.P.C. Si.El. column at 195°C; P.D. 40 cms. Hg; nitrogen 200 ccs/min.; recycled twice). Infra red spectra and A.S.V.P.C. showed component 4 to be $C_6Cl_5F_5$, and component 4a to be $C_6Cl_5F_7$.

Fraction 3. This contained 30% of component 5 and 60% of component 5a. Pure specimens were isolated. (P.S.V.P.C. Si.El. column at 235°C; P.D. 40 cms. Hg; nitrogen 200 ccs/min.; recycled twice). Infra red spectra and A.S.V.P.C. showed component 5 to be $C_6Cl_6F_4$, and component 5a to be $C_6Cl_6F_6$.

Fraction 4. This contained component 6a. A pure specimen could not be isolated as dehalogenation occurred on the column. An infra red spectrum and A.S.V.P.C. showed component 6a to be $C_6Cl_7F_5$.

## Reaction of Hexachlorobenzene with Chlorine Trifluoride.
## (Molar Ratio 1:7)

Hexachlorobenzene (100 gms., 0.35 M) was reacted with chlorine trifluoride (55 gms., 0.6 M) at 240°C, using the same conditions and apparatus as stated before. The temperature was then lowered to 100°C, and chlorine trifluoride (184 gms., 2.0 M) diluted with nitrogen (2.5 litres/hr.), was passed into the reaction vessel for eighteen hours. The product was dissolved in ether (50 mls.), filtered, washed and dried as before. After an ether distillation, the product was distilled to give a white solid (62 gms.).

This reaction was repeated three times. Details are given in table 12.

Table 12.

| wt. of $C_6Cl_6$ gms. | wt. of $ClF_3$ gms. | Time of Reaction hrs. | Product gms. |
|---|---|---|---|
| 100 | 239 | 20 | 62 |
| 125 | 300 | 27 | 84 |
| 125 | 296 | 27 | 79 |

A vapour phase chromatogram of a typical reaction is shown in fig. v. The products from the above reactions were combined, and distilled using the concentric tube column previously described. The details of the distillation are shown in table 13.

Table 13. Distillation 3.

| Fraction No. | Boiling Range ° C. | Size of Fraction gms. | Containing Component No. |
|---|---|---|---|
| 1 | 0-150 | 1.5 | 1a |
| 2 | 173-176 | 10 | 2a |
| 3 | 204-208 | 40 | 4a |
| 4 | 247-250 | 25 | 5a |
| 5 | 265-275 | 5 | 6a |

Residue 3.0 gms. Intermediate Fractions 91 gms. Recovery 80%.

Fraction 1. This contained mainly component 1a. 1.5 gms. of fraction 1 gave 0.6 gms. of component 1a. (P.S.V.P.C. Si.El. column at 147°C; P.D. 30 cms. Hg; nitrogen 175 ccs/min.). A.S.V.P.C. indicated component 1a to be $C_6Cl_3F_9$.

B.p. 142°C. Tatlow and Worthington[29] gave 141°C.

Analysis gave: Cl, 31.0, F, 48.5%; calc. for $C_6Cl_3F_9$: Cl, 30.4, F, 48.9%.

Fraction 2. This contained mainly component 2a. 3.0 gms. of fraction 2 gave 2.1 gms. of component 2a. (P.S.V.P.C. Si.El. column at 165°C; P.D. 40 cms. Hg; nitrogen 200 ccs/min.). An infra red spectrum (No. 9. see page 141), and A.S.V.P.C. indicated component 2a to be $C_6Cl_4F_8$.

B.p. 175.5°C. Johncock[15] gave 174.0°C.

Analysis gave: Cl, 39.6, F, 41.0%; calc. for $C_6Cl_4F_8$: Cl, 38.8, F, 41.5%.

Fraction 3. This contained mainly component 4a. 5.3 gms. of fraction 3 gave 3.7 gms. of component 4a. (P.S.V.P.C. Si.El. column at 190°C; P.D. 40 cms. Hg; nitrogen 175 ccs/min.). An infra red spectrum (No. 10), and A.S.V.P.C. indicated component 4a to be $C_6Cl_5F_7$.

B.p. 207.5°C; m.p. 74-76°C. Johncock[15] gave b.p. 209°C.

Analysis gave: Cl, 46.1, F, 34.5%; calc. for $C_6Cl_5F_7$: Cl, 46.4, F, 34.8%.

Fraction 4. This contained mainly component 5a. 5.0 gms. of fraction 4 gave 1.7 gms. of component 5a. (P.S.V.P.C. Si.El. column at 230°C; P.D. 50 cms. Hg; nitrogen 150 ccs/min.; recycled once).

B.p. 248°C; m.p. 103-105°C. Godsel et.al.[34] gave b.p. 137°C/30 mm.

m.p. 101-102°C.

Analysis gave: C, 17.9, Cl, 52.9, F, 27.6%; calc. for $C_6Cl_6F_6$:
C, 18.05, Cl, 52.1, F, 27.9%.

An infra red spectrum (No. 11) showed no unsaturation.

Fraction 5. This contained mainly component 6a. Purification by P.S.V.P.C. was ineffective due to dehalogentaion of the compound on the Silicone Elastomer column.

B.p. 270-273°C; m.p. 105-110°C.

Analysis of fraction 5 gave: Cl, 55.3, F, 22.9%; calc. for $C_6Cl_7F_5$:
Cl, 59.7, F, 22.9%.

An infra red spectrum (No. 12) showed no unsaturation.

The impurity caused by dehalogenation of component 6a was separated. (P.S.V.P.C. Si.El. column at 245°C; P.D. 50 cms. Hg; nitrogen 150 ccs/min.). An infra red spectrum and A.S.V.P.C. showed it to be $C_6Cl_5F_5$; the spectrum showed strong absorbtion at 1695 $cm^{-1}$, which indicated the presence of the -CF=CCl- grouping.

Samples of $C_6Cl_3F_9$, $C_6Cl_4F_8$ and $C_6Cl_5F_7$, prepared by the reaction of hexachlorobenzene and cobalt fluoride,[15] were available for infra red spectrum and A.S.V.P.C. comparisons.

## The Influence of Catalysts on the Reaction between Hexachlorobenzene and Chlorine Trifluoride.

### a) Ferric Chloride.

Several reactions between hexachlorobenzene and chlorine trifluoride, using ferric chloride as catalyst, were investigated. Conditions were the same as those described before, the ferric chloride being introduced at the beginning. It was found however, that due to sublimation, ferric chloride could not be used at 240°C. Since this temperature was necessary for the start of the reaction, the catalyst must be introduced at a later stage.

Hexachlorobenzene (100 gms., 0.35 M) was reacted with chlorine trifluoride (55 gms., 0.6 M) at 240°C, using the same conditions and apparatus as previously described, (see page 84 ). The temperature was then lowered to 100°C, and ferric chloride (10 gms., 0.06 M) added. Chlorine trifluoride (45 gms., 0.5 M), diluted with nitrogen (3 litres/hr.), was passed into the reaction vessel for two hours. The product was diluted with ether, and the carbon filtered off. After washing as before, the product was dried and the ether distilled. Finally the product was distilled to give 68 gms. of a colourless liquid. The vapour phase chromatogram is shown in fig. vi. The product was distilled using the concentric tube column previously described (see page 87 ). The details of the distillation are shown in table 14.

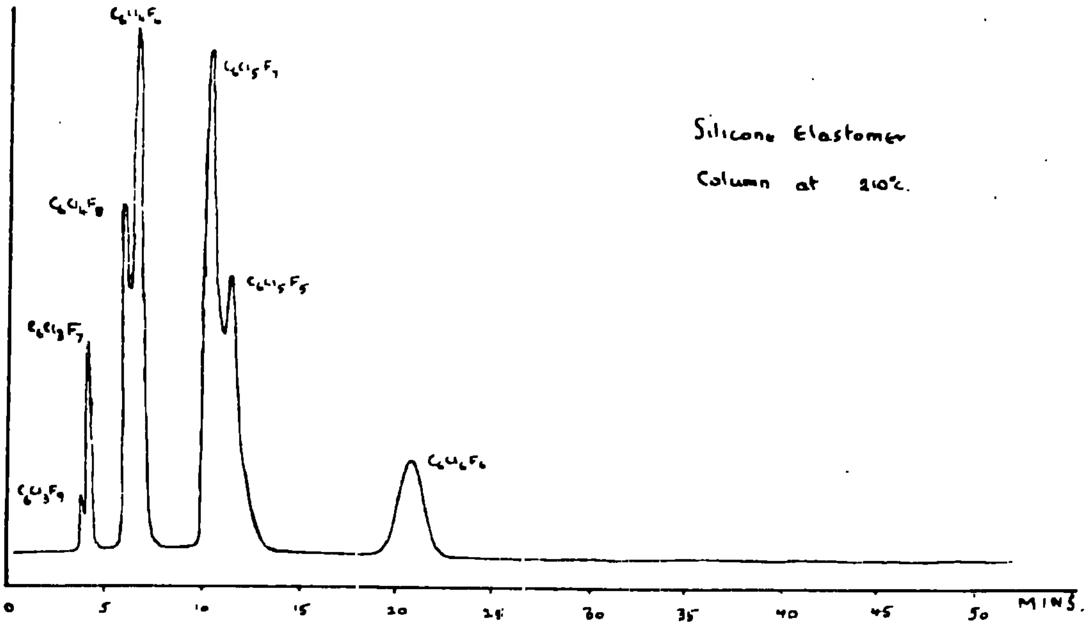


Fig vi Reaction product of $C_6Cl_6$ and $ClF_3$ - Ferric Chloride catalyst.

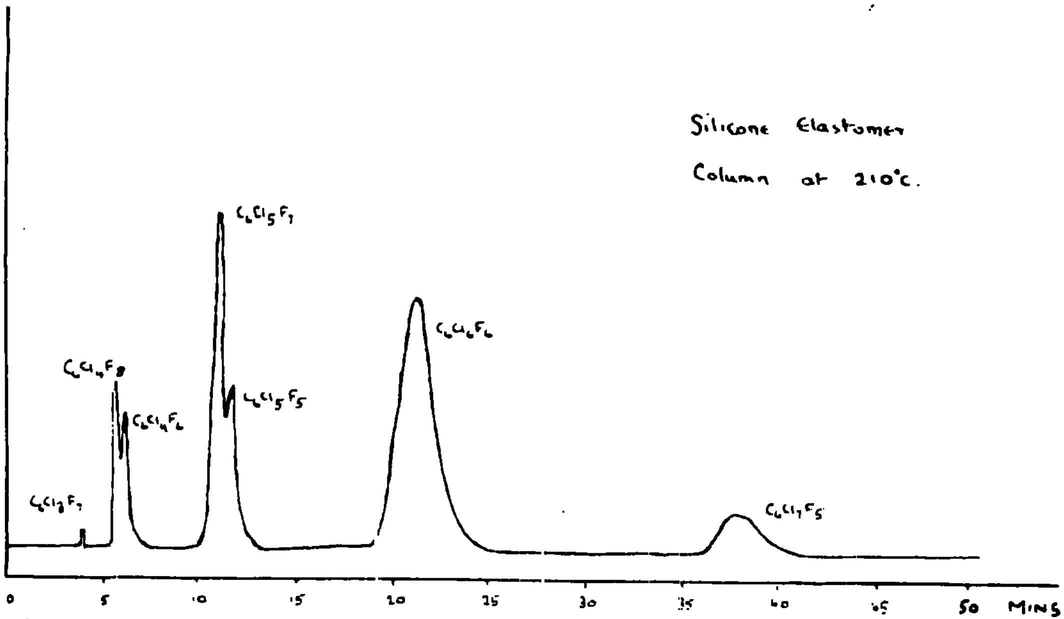


Fig vii Reaction product of $C_6Cl_6$ and $ClF_3$. Cobalt Fluoride catalyst.

Table 14. Distillation 4.

| Fraction No. | Boiling Range ° C. | Size of Fraction gms. | Components |
|---|---|---|---|
| 1 | 140-160 | 5 | $C_6Cl_3F_7$, ($C_6Cl_3F_9$ Trace) |
| 2 | 175-178 | 13 | $C_6Cl_4F_6$, $C_6Cl_4F_8$ |
| 3 | 198-208 | 20 | $C_6Cl_5F_5$, $C_6Cl_5F_7$ |
| 4 | 247-252 | 4 | $C_6Cl_6F_6$ |

Residue 1 gm. Intermediate Fractions 23 gms. Recovery 96%.

The compounds in fractions 2-4 were purified by P.S.V.P.C. The conditions for this were identical to those used for the purification of the compounds in the fractions from distillation 2 (see page 95). The compounds were identified by comparison of their infra red spectra, and their retention times (using A.S.V.P.C.), with compounds from the uncatalysed reactions.

Fraction 1. This contained mainly component 1. A pure specimen was separated. (P.S.V.P.C. Si.El. column at 145°C; P.D. 30 cms. Hg; nitrogen 200 ccs/min.). The infra red spectrum was identical with $C_6Cl_3F_7$ produced in the uncatalysed reaction. Retention times using A.S.V.P.C. showed fraction 1 contained mainly $C_6Cl_3F_7$, but a trace of $C_6Cl_3F_9$ was also present.

b) Cobalt Fluoride.

Cobalt difluoride (15 gms., 0.15 M) and hexachlorobenzene

(100 gms., 0.35 M) were heated to 240°C and reacted with chlorine trifluoride (55 gms., 0.6 M) using the same conditions and apparatus as previously described (see page 84). The temperature was then lowered to 100°C and a further 45 gms. of chlorine trifluoride (0.5 M), diluted with nitrogen (3 litres/hr.), were passed into the vessel for two hours. The product was worked up as before, and gave 45 gms. of a white solid. The vapour phase chromatogram is shown in fig. vii. The product was distilled using the concentric tube column previously described; the details are given in table 15.

Table 15. Distillation 5.

| Fraction No. | Boiling Range ° C. | Size of Fraction. gms. | Components. |
|---|---|---|---|
| 1 | 140-174 | 2.7 | $C_6Cl_3F_7$ (Trace) |
| 2 | 174-180 | 3.1 | $C_6Cl_4F_6$, $C_6Cl_4F_8$ |
| 3 | 208.5 | 7.5 | $C_6Cl_5F_5$, $C_6Cl_5F_7$ |
| 4 | 239.0 | 11.7 | $C_6Cl_6F_6$ |
| 5 | 265-270 | 4.0 | $C_6Cl_7F_5$ |

Residue 1 gm. Intermediate fractions 12 gms. Recovery 92%.

The compounds in fractions 2-4 were purified by P.S.V.P.C. The conditions for this were identical to those used for the purification of the compounds in the fractions from distillation 2 (see page 95). The compounds were identified by comparison of their infra red spectra and their retention times (using A.S.V.P.C.), with compounds from the uncatalysed reactions. Trichloroheptafluorocyclohexene was identified by A.S.V.P.C. only, as insufficient was present to isolate a pure sample for an infra red spectrum.

c) Boron Trifluoride.

The effect as a catalyst of both limited and excess amounts of boron trifluoride was investigated. In both cases boron trifluoride was added to the reaction vessel as a gas, mixed with the chlorine trifluoride and nitrogen. The flow rate was kept constant throughout the experiment.

i) Limited Amount of Boron Trifluoride. Hexachlorobenzene (100 gms., 0.35 M) was heated to 240°C and reacted with chlorine trifluoride (55 gms., 0.6 M) using the same apparatus and conditions as before (see page 84 ). The temperature was then lowered to 100°C and a further 50 gms. of chlorine trifluoride (0.55 M) were passed into the reaction vessel for two hours. 7.5 gms. of boron trifluoride (0.1 M) were used giving 122 gms. of a colourless liquid.

ii) Excess Amount of Boron Trifluoride. Hexachlorobenzene (100 gms., 0.35 M) was heated to 240°C and reacted with chlorine trifluoride (56 gms., 0.6 M) using the previously described apparatus and conditions. The temperature was then lowered to 100°C and a further 44 gms. of chlorine trifluoride (0.5 M) were passed into the reaction vessel for two hours. 342 gms. of boron trifluoride (5 M) were used giving 95 gms. of a colourless liquid.

The compounds from the above reactions were identified by

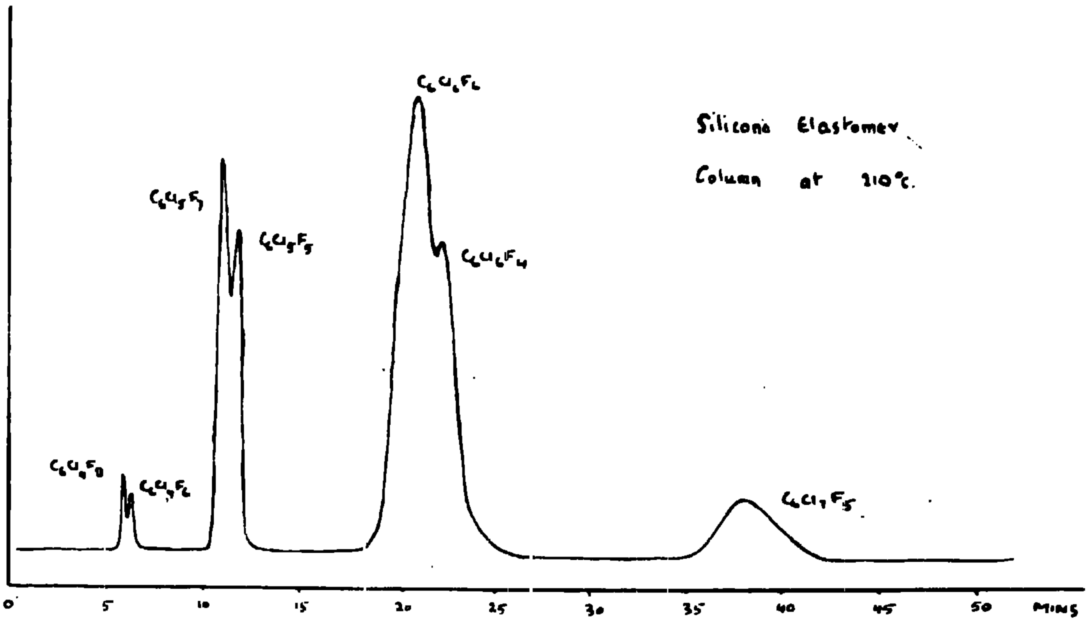
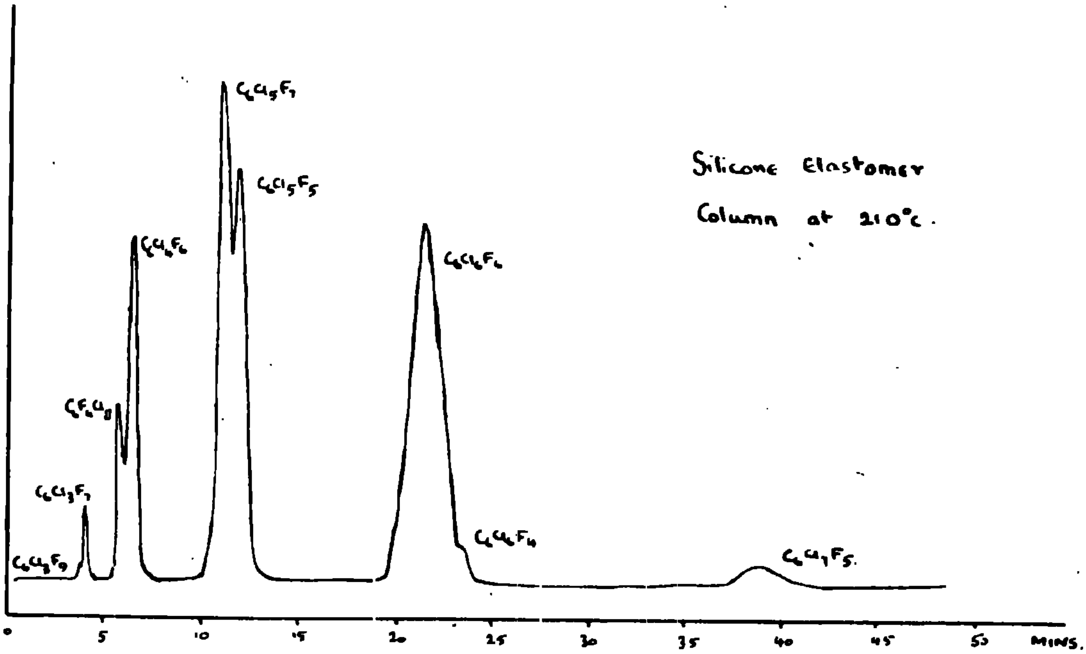


Fig viii. Reaction product of $C_6Cl_6$ and $ClF_3$. Limited Boron Trifluoride catalyst.



1. Fig ix. Reaction product of $C_6Cl_6$ and $ClF_3$. Excess Boron Trifluoride catalyst.

comparison of their retention times (using A.S.V.P.C.), with compounds from the uncatalysed reactions. The vapour phase chromatograms are shown in figs. viii and ix.

### d) Aluminium Trichloride.

The initial temperature necessary for the chlorofluorination of hexachlorobenzene was too high for the addition of this catalyst, as sublimation occurred. However, as with ferric chloride, the catalyst could be added when the temperature was lowered to 100°C. Aluminium trichloride was added to a mixture of perchlorofluorocyclohexenes at room temperature, on heating to 70°C, an exothermic reaction appeared to take place leaving a thick paste, which could not be successfully stirred. This resulted in ignition of the chlorine trifluoride and further reaction was impossible.

A mixture of perchlorofluorocyclohexenes (25 gms.) was heated to 170°C with aluminium trichloride (5 gms., 0.04 M), this formed a thick paste which remained on cooling. The organic product was removed with alcohol (40 ccs.), dried (anhydrous $MgSO_4$), and the alcohol distilled off to give 15 gms. of starting material. (A.S.V.P.C. Si.El. column at 210°C).

## The Liquid Phase Reaction between Fluorine and Hexachlorobenzene.

### Fluorine Generator

The general appearance of the generator is shown in figs. x and xi. It consisted of an electrolyte container mounted on

Fig X.

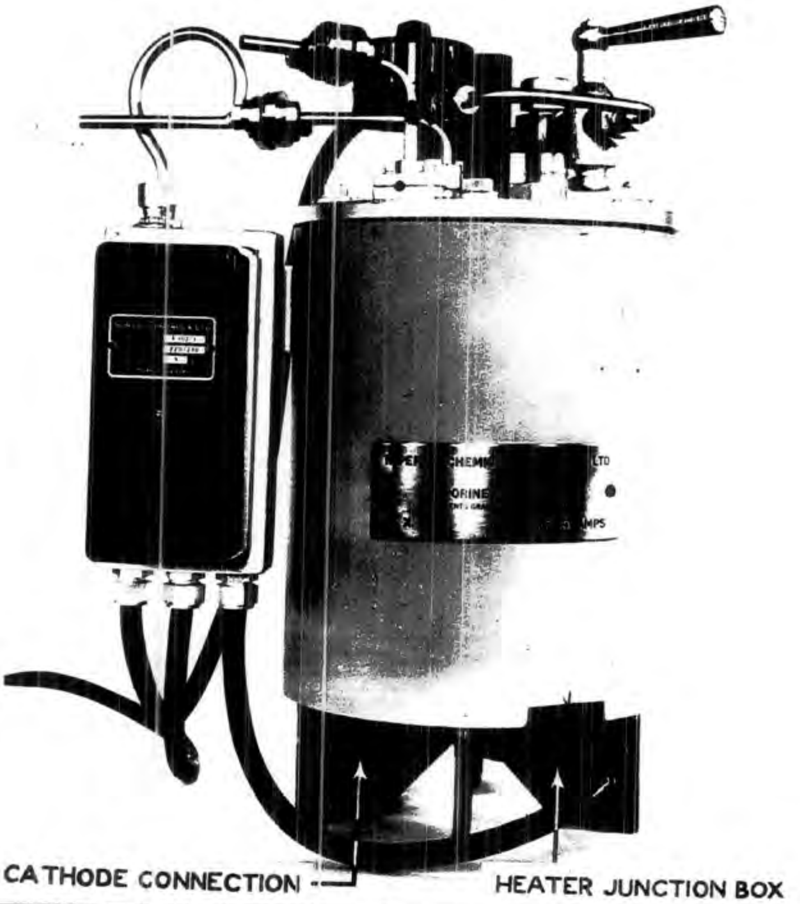
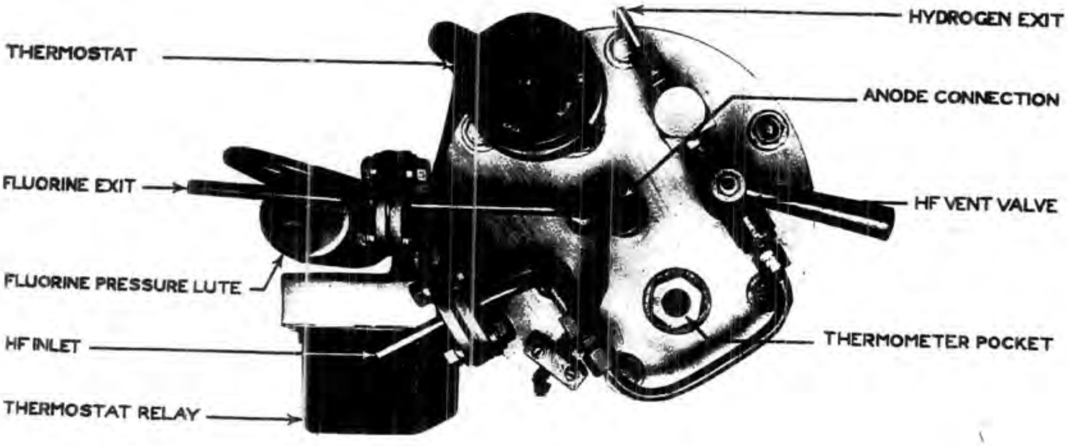

CATHODE CONNECTION
HEATER JUNCTION BOX

Fig XI.


HYDROGEN EXIT
THERMOSTAT
ANODE CONNECTION
FLUORINE EXIT
HF VENT VALVE
FLUORINE PRESSURE LUTE
HF INLET
THERMOMETER POCKET
THERMOSTAT RELAY

cooling fins, one of which acted as the cathode connection. The anode connection was made to an insulated plug on the top of the generator, the top being insulated from the body of the generator. Both the fluorine outlet and the hydrogen fluoride inlet tubes were insulated, as was the hydrogen outlet tube which was made from alkathene.

A pressure lute was fitted on the fluorine outlet to prevent pressures, within the cell, of greater than 2 ins. of water. The hydrogen exit contained a cross piece fitted with an access plug, which was used for sampling, and for finding the electrolyte level. Hydrogen fluoride was added through a dip pipe (HF inlet) which was connected, through a valve (HF vent valve), to the hydrogen exit. The container was fitted with thermostatically controlled heating units, and contained pockets in the top for a thermostatic control, and a thermometer. The generator was supplied with the electrolyte, which had the approximate composition KF.2HF. It had a maximum fluroine output of 6.5 gms/hr. (4 litres/hr.), running at the maximum load of 10 amps.

## Operation of Fluorine Generator.

The electrolyte was kept molten at all times as freezing would cause damage to the anode. The thermostatic control was adjusted to give a temperature of 82±5°C. A power pack provided a variable D.C. voltage of 4-10 volts, at 2-10 amps., for the anode. For production of fluorine the anode current was switched on at 2-3 amps., and after two minutes adjusted to any desired value up to 10 amps.

As fluorine and hydrogen were produced, the amount of hydrogen fluoride in the electrolyte, and therefore the volume of the electrolyte, decreased. The electrolyte composition must be maintained within the range 40-42% of hydrogen fluoride (by weight), and thus it was necessary to add anhydrous hydrogen fluoride at intervals. The level of the electrolyte, and thus the percentage of hydrogen fluoride was found by using a dip stick. This was introduced at the crosspiece of the hydrogen exit. A true reading could only be obtained when the generator was producing fluorine, because when the generator was stopped, the anode tended to absorb the electrolyte.

The amount of hydrogen fluoride in the electrolyte was checked every 1000 amp. hours. About 1 gm. of electrolyte was taken and dissolved in 100 mls. of boiling water, and titrated against normal sodium hydroxide, using phenol phthalein as indicator. When the hydrogen fluoride concentration fell from 42% to 40% the level of the electrolyte fell by 0.25 ins., thus it was possible to determine the hydrogen fluoride concentration by use of the dip stick. These levels were used for an everyday guide to the hydrogen fluoride content of the electrolyte.

When anhydrous hydrogen fluoride was added the generator was always producing fluorine. The cylinder used, which was maintained at 25-35°C, was connected to the hydrogen fluoride inlet tube. When a steady stream of hydrogen fluoride issued from the end of the hydrogen exit tube, the hydrogen fluoride vent valve was closed. The course of the addition was followed by frequent measurements of the electrolyte level, and was normally completed in twenty minutes. The vent valve was then opened and the hydrogen fluoride addition stopped. The rate of addition was such that the generator temperature did not rise above 90°C.

The pressure lute was checked monthly to see that the cell was operating at the correct pressure. A full and accurate record of all operations was kept in the log book provided. A face shield and rubber gloves were worn when working on the generator and the hydrogen fluoride supply.

## Reaction of Fluorine with Hexachlorobenzene.

Several exploratory reactions between hexachlorobenzene and fluorine were investigated before a satisfactory method was found. The direct reaction, with no solvent present, resulted in ignition of the fluorine, both at 240°C, when the hexachlorobenzene is molten, and at room temperature. Different rates of addition of fluorine and nitrogen were investigated, but ignition occurred unless the rate of fluorine addition was below 2 gms/hr., which was considered too low. The use of a solvent was next investigated. Hexachlorobenzene in a slurry of carbon tetrachloride, at room temperature, exploded soon after addition of fluorine began, however 1,1,2-trichlorotrifluoroethane proved to be a most successful solvent.

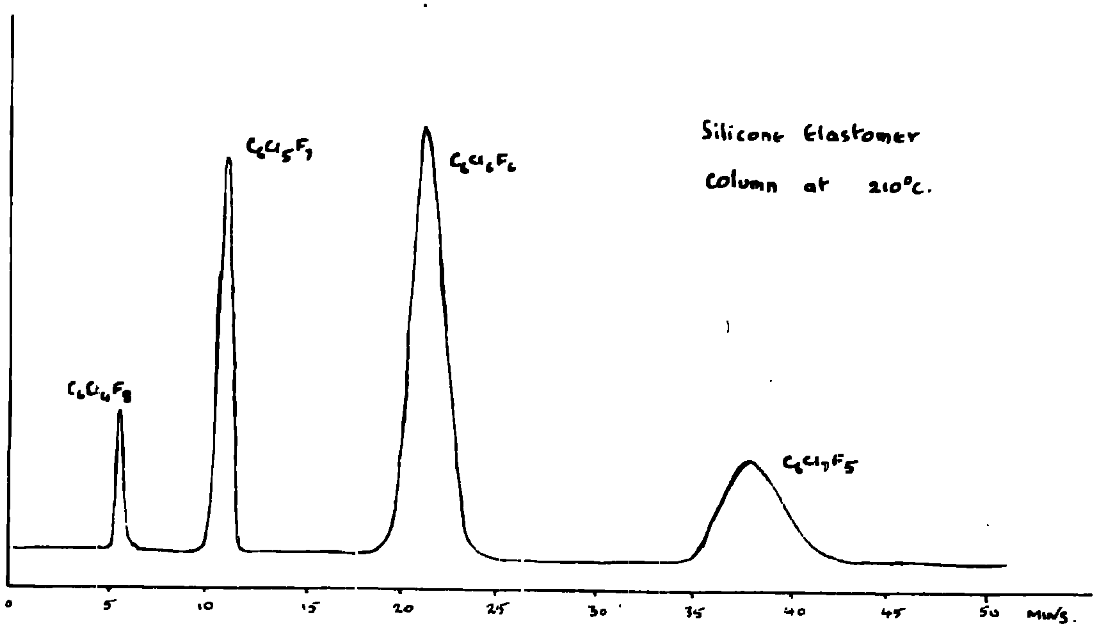
Hexachlorobenzene (200 gms., 0.7 M) was placed in a three necked 500 cc. flask with 1,1,2-trichlorotrifluoroethane (250 mls., 2 M). This was stirred into a slurry and reacted at room temperature with fluorine (125 gms., 3.3 M), diluted with nitrogen (3 litres/hr.). The fluorine was added for 32 hours at 3.9 gms/hr. The solvent (b.p. 48°C) was conveniently fluorinated to dichlorotetrafluoroethane (b.p. 3°C) which was led to a fume disposal unit. The solvent tended to evaporate from the vessel during the reaction, however any form of condenser caused explosions. As the reaction was carried out in a fumes cupboard the exit from the vessel was left open. 256 gms. of product, a white pastey liquid, gave a vapour phase chromatogram as shown in fig. xii.

Table 16.

| | Wt. of $C_6Cl_6$ gms. | Vol. of solvent mls. | Wt. of $F_2$ gms. | Time of Reaction hrs. | Product. gms. |
|---|---|---|---|---|---|
| 1. | 200 | 250 | 125 | 32 | 256 |
| 2. | 200 | 250 | 144 | 37 | 267 |
| 3. | 400 | 500 | 272 | 49 | 510 |
| 4. | 400 | 500 | 292 | 45 | 516 |

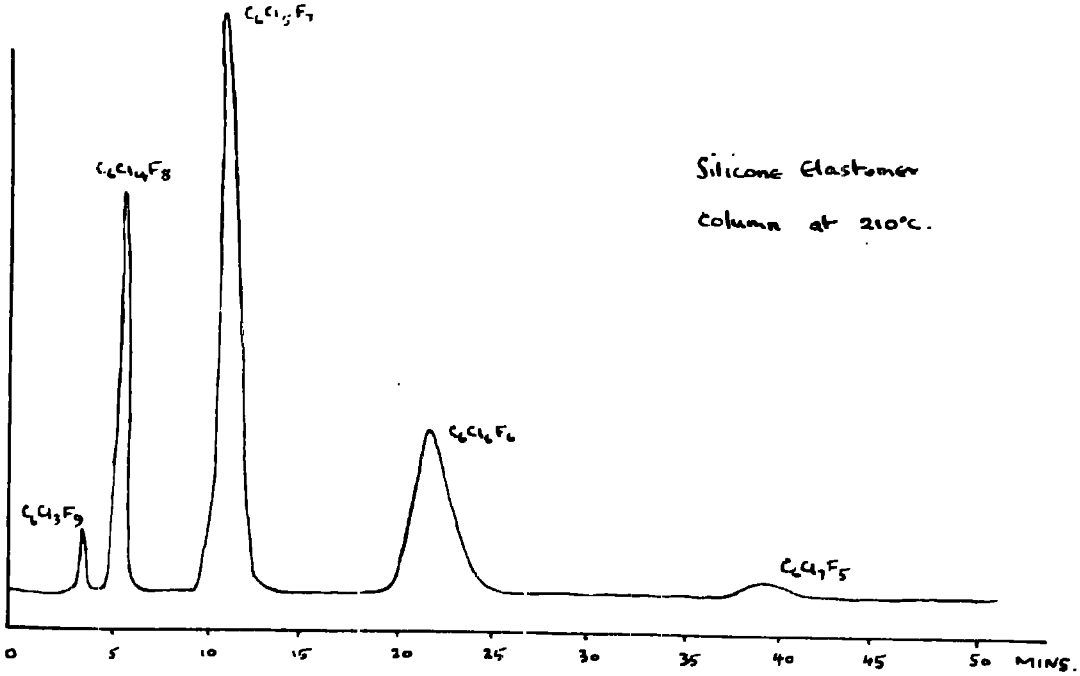
An infra red spectrum of the product showed no absorbtion from 5.5-6.5μ which indicated that no unsaturated material was present.

Analysis gave: Cl, 54.9, F, 27.6%; calc. for $C_6Cl_6F_6$: Cl, 52.1, F, 27.9%.



Silicone Elastomer column at 210°C.

Fig XII Reaction product of $C_6Cl_6$ and $F_2$.



Silicone Elastomer column at 210°C.

Fig XIII Further reaction of $F_2$ on the above mixture.

The product contained mainly $C_6Cl_5F_7$, $C_6Cl_6F_6$, $C_6Cl_7F_5$ and some $C_6Cl_4F_8$. These were identified by comparison of their retention times (using A.S.V.P.C.), with compounds obtained from the reaction between hexachlorobenzene and chlorine trifluoride.

An infra red spectrum of a sample taken half way through the reaction, indicated that no unsaturated compounds were present, except the starting material. This was verified by A.S.V.P.C.

## Further Fluorination of Perchlorofluorocyclohexanes.

The above reaction product (128 gms. of average constitution $C_6Cl_6F_6$) was reacted with fluorine (20 gms., 0.5 M), diluted with nitrogen (2½ litres/hr.), for 5 hours at room temperature. A.S.V.P.C. showed that the product had not changed. The above reaction was repeated at 100°C, and the constitution of this product had changed to $C_6Cl_{5.5}F_{6.5}$. Further addition of fluorine (20 gms., 0.5 M) at 200°C. gave 84 gms. of the product, which was shown by A.S.V.P.C. (see fig. xiii) to have an average constitution of $C_6Cl_5F_7$. The yield of $C_6Cl_5F_7$ based on the conversion of $C_6Cl_6F_6$ was 68.5%.

# DEHALOGENATIONS BY HEATED IRON.

## Apparatus.

The general appearance of the dehalogenator is shown in fig. xiv. A steel tube, 44" long and 2" in diameter, was packed with a tightly wound roll of iron gauze (approx. 1250 gms.). The inlet of the reactor was sealed by using a steel disc which contained a $\frac{5}{16}$" copper inlet tube, and a 2" inset aluminium washer. This was bolted to a steel ring which was hard soldered a short distance from the end of the reactor. The sharpened ends of the reactor embedded into the aluminium, forming a perfect seal. The apparatus was then tested for leaks by sealing one end and evacuating the system. The pressure was checked after thirty minutes.

The reactor was placed in an aluminium box lined with firebricks, the ends supported the tube, which was heated by using three rod-like 1 kw. heating elements. These were placed underneath the reactor and were also supported by the ends of the box. Each heater was individually controlled by a simmerstat. The temperature was measured by using three chromel-alumel thermo couples cemented to the tube in the positions shown in fig. xiv. Along the major part of the reactor the temperature was controlled to within 15°C.

The copper tubing at the inlet and the outlet of the reactor was heated using heating tapes, the connections of this tubing with glass apparatus were made with silicone rubber. The emergent gases were condensed in a trap cooled in liquid air.

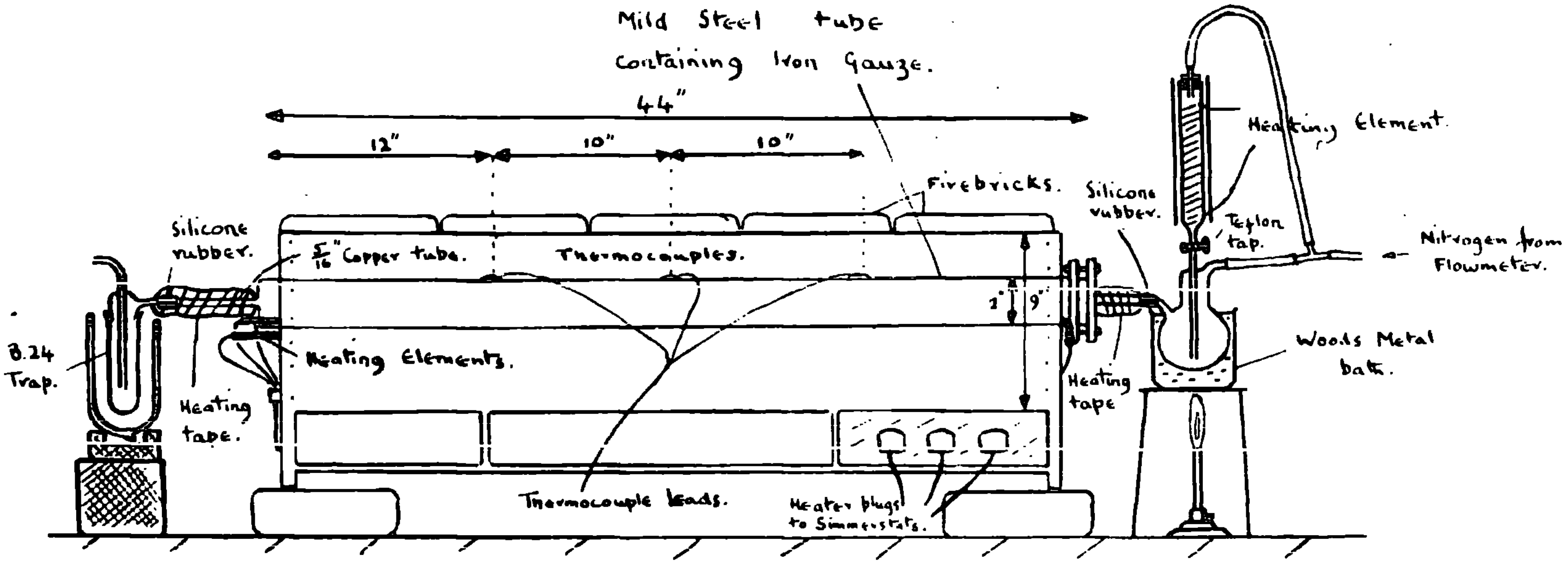


Fig xiv. IRON GAUZE DEHALOGENATOR.

## Experimental Procedure.

Samples were introduced using the system shown in fig. xiv. The dropping funnel was wound with electrical heating ribbon and surrounded by a glass jacket. This enabled a solid to be melted and introduced at the desired rate. A teflon tap was used so that it could be flame heated, and thus prevent any solidification occuring in the bore of the tap.

The reactor was set at the desired temperature, and purged with nitrogen, at a flow rate of about three litres/hour, for one hour before a run, the nitrogen was then set at the desired rate.

A weighed sample was placed in the graduated dropping funnel, and the Woods metal bath heated to a temperature about 50°C above the boiling point of the sample. The liquid was then dropped in at a steady rate. A weighed trap, connected at the outlet end of the reactor, was cooled in liquid air to collect the product. Emergent nitrogen from the trap was collected over water; this checked the flow rate, and gave an immediate indication if a leak occurred or the trap blocked. The nitrogen flow was continued for ninety minutes after the addition of the sample was completed.

The volume of the tube with the gauze was 1500 ccs., and therefore the contact time for nitrogen, at a flow rate of 60 ccs/min., would be 25 minutes. However white fumes often appeared 10 minutes after the addition of the sample and continued up to one hour after. Thus the vapour must expand through the reactor under its own vapour pressure

The iron gauze was regenerated after each dehalogenation by passing hydrogen over it at 500°C, until no fumes of hydrogen fluoride showed in the emergent gases. This normally took 4-8 hours at a flow rate of 20 litres of hydrogen/hour.

## Dehalogenation of Perchlorofluorocyclohexenes and Tetrachlorotetrafluorocyclohexadiene.

Perchlorofluorocyclohexenes of the general formula $C_6Cl_xF_{10-x}$ (x=3-6), prepared by the action of chlorine trifluoride on hexachlorobenzene, were dehalogenated using the method previously described. It was important for the comparison of the dehalogenation products of two different cyclohexenes that the same amount of starting material was used. If different amounts of the same material were dehalogenated, a different product ratio was produced.

The products were analysed by analytical scale V.P.C., and the major compounds from each dehalogentaion were separated by preparative scale V.P.C., and an infra red spectrum was obtained. The spectrum and the retention time (by A.S.V.P.C.) were compared with standards which had been identified by molecular weight determinations, refractive index, and chlorine and fluorine analysis.

Isomers of aromatic compounds present in the dehalogenated product had similar retention times and could not be separated by vapour phase chromatography. The isomer ratio was measured by N.M.R.

## Exploratory Runs.

The product from the chlorofluorination of hexachlorobenzene, containing all the perchlorofluorocyclohexenes, was dehalogenated at varying temperatures.

At 430°C. almost complete decomposition occurred.

At 330°C. 10 gms. of starting material gave 2.5 gms. of product.

A.S.V.P.C. showed that no starting material was present.

At 300°C. 10 gms. of starting material gave 4.3 gms. of product.

A.S.V.P.C. showed that no starting material was present.

It was inconvenient to lower the reaction temperature further, as both the product and the starting material would remain within the reactor. The reactor temperature was normally set 50°C. above the boiling point of the compound to be dehalogenated. If full dehalogenation did not take place, the temperature was raised until no starting material was present in the product.

## Trichloroheptafluorocyclohexene.

4 gms. were dehalogenated in 16 minutes (introduction time). Reactor temperature 315°C; nitrogen 60 ccs/min. 1.95 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 11%, $C_6ClF_5$ 27%, $C_6Cl_2F_4$ 30%, $C_6Cl_3F_3$ 5%, total yield 73%. Pure specimens of $C_6ClF_5$ and $C_6Cl_2F_4$ were separated. (P.S.V.P.C. Si.El. column at 135°C; P.D. 25 cms. Hg; nitrogen 180 ccs/min.). Infra red spectra confirmed their identity. $C_6Cl_2F_4$ was shown by N.M.R. to be a mixture of isomers. (see table iv page 60).

## Tetrachlorohexafluorocyclohexene.

5 gms. were dehalogenated in 20 minutes. Reactor temperature

260°C; nitrogen 60 ccs/min. Two runs gave 5.95 gms. of product. which were shown by A.S.V.P.C. to be $C_6F_6$ 5%, $C_6ClF_5$ 32%, $C_6Cl_2F_4$ 33%, $C_6Cl_3F_3$ 12%, $C_6Cl_4F_2$ 2%, total yield 84%. Pure specimens of $C_6ClF_5$, $C_6Cl_2F_4$ and $C_6Cl_3F_3$ were separated. (P.S.V.P.C. Si.El. column at 150°C; P.D. 30 cms. Hg; nitrogen 200 ccs/min.).

Chloropentafluorobenzene. Molecular weight, found: 206; calc. for $C_6ClF_5$: 202.5. B.p. 117.5°C. $n_D^{20}$ 1.4188.

Analysis gave: Cl, 17.5, F, 47.2%; calc. for $C_6ClF_5$: Cl, 17.5, F, 46.9%.

For infra red spectrum see page 143 (No. 14). Infra red spectra confirmed the identity of $C_6Cl_2F_4$ and $C_6Cl_3F_3$, and N.M.R. showed that both were mixtures of isomers (table iv).

Pentachloropentafluorocyclohexene.

5 gms. were dehalogenated in 20 minutes. Reactor temperature 260°C; nitrogen 60 ccs/min. 2.75 gms. of product were shown by A.S.V.P.C. to be $C_6ClF_5$ 3%, $C_6Cl_2F_4$ 58%, $C_6Cl_3F_3$ 18%, $C_6Cl_4F_2$ 3%, $C_6Cl_5F$ 1%, total yield 83%. Pure specimens of $C_6Cl_2F_4$ and $C_6Cl_3F_3$ were separated. (P.S.V.P.C. Si.El. column at 160°C; P.D. 35 cms. Hg; nitrogen 175 ccs/min.).

Trichlorotrifluorobenzene. Molecular weight, found: 245, calc. for $C_6Cl_3F_3$: 235.5°C. M.p. 23.5°C.

Analysis gave: Cl, 44.6, F, 25.0%; calc. for $C_6Cl_3F_3$: Cl, 45.2, F, 24.2%.

For infra red spectrum see page 144 (No. 17). An infra red spectrum confirmed the identity of $C_6Cl_2F_4$ and N.M.R. showed that both $C_6Cl_2F_4$ and $C_6Cl_3F_3$ were mixtures of isomers (table iv).

26.5 gms. were dehalogenated in 106 minutes. Reactor temperature 255°C; nitrogen 60 ccs/min. 16.0 gms. of product were shown by A.S.V.P.C. to be $C_6ClF_5$ 2%, $C_6Cl_2F_4$ 35%, $C_6Cl_3F_3$ 35%, $C_6Cl_4F_2$ 8%, $C_6Cl_5F$ 5%, total yield 85%. Pure specimens of $C_6Cl_2F_4$, $C_6Cl_3F_3$ and $C_6Cl_4F_2$ were separated. (P.S.V.P.C. Si.Grease column at 200°C; P.D. 25 cms. Hg; nitrogen 200 ccs/min., recycled once). Infra red spectra confirmed their identity.

### Hexachlorotetrafluorocyclohexene.

5 gms. were dehalogenated in 20 minutes. Reactor temperature 295°C; nitrogen 60 ccs/min. Three runs gave 6.95 gms. of product which were shown by A.S.V.P.C. to be $C_6Cl_2F_4$ 6%, $C_6Cl_3F_3$ 30%, $C_6Cl_4F_2$ 33%, $C_6Cl_5F$ 16%, total yield 85%. Pure specimens of $C_6Cl_3F_3$, $C_6Cl_4F_2$ and $C_6Cl_5F$ were separated. (P.S.V.P.C. Si.El. column at 205°C; P.D. 45 cms. Hg; nitrogen 200 ccs/min.).

Tetrachlorodifluorobenzene. M.p. 62°C.

Analysis gave: Cl, 56.3, F, 14.3%; calc. for $C_6Cl_4F_2$: Cl, 56.3, F, 15.1%.

For infra red spectrum of 1,2,4,5- isomer, see page 144 (No. 16).

Pentachlorofluorobenzene. M.p. 134°C.

Analysis gave: Cl, 66.1, F, 7.1%; calc. for $C_6Cl_5F$: Cl, 66.1, F, 7.1%.

For infra red spectrum see page 145 (No. 19). An infra red spectrum confirmed the identity of $C_6Cl_3F_3$ and N.M.R. showed that both $C_6Cl_3F_3$

and $C_6Cl_4F_2$ were mixtures of isomers (table iv)

30 gms. were dehalogenated in 120 minutes. Reactor temperature 295°C; nitrogen 60 ccs/min. 17.0 gms. of product were shown by A.S.V.P.C. to be $C_6Cl_2F_4$ 1%, $C_6Cl_3F_3$ 7%, $C_6Cl_4F_2$ 10%, $C_6Cl_5F$ 40%, $C_6Cl_6$ 16%, total yield 74%. Pure specimens of $C_6Cl_4F_2$, $C_6Cl_5F$ and $C_6Cl_6$ were separated. (P.S.V.P.C. Si.El. column at 235°C; P.D. 50 cms. Hg; nitrogen 150 ccs/min.). Infra red spectra confirmed their identity.

## Tetrachlorotetrafluorocyclohexadiene.

2.35 gms. were dehalogenated in 10 minutes. Reactor temperature 230°C; nitrogen 60 ccs/min. 1.15 gms. of product were shown by A.S.V.P.C. to be $C_6Cl_3F_3$ 6%, $C_6Cl_4F_2$ 47%, $C_6Cl_5F$ 3%, total yield 56%. The infra red spectrum (No. 16) confirmed the identity of $C_6Cl_4F_2$, and N.M.R. showed that it contained 100% of the 1,4-tetrachlorodifluorobenzene.

## Dehalogenation of 1,2-Dichlorooctafluorocyclohexene and 1,2,4-Trichloroheptafluorocyclohexene.

The fluorination of hexachlorobenzene with antimony pentafluoride[14] gave the pure perchlorofluorocyclohexenes 1,2-dichlorooctafluorocyclohexene and 1,2,4-trichloroheptafluorocyclohexene. These were separated. (P.S.V.P.C. Si.El. column at 130°C; P.D. 30 cms. Hg; nitrogen 200 ccs/min.).

$C_6Cl_2F_8$. 13.0 gms. Analysis gave: Cl, 24.3, F, 51.3%. calc. for $C_6Cl_2F_8$: Cl, 24.1, F, 51.5%. For infra red spectrum see page 137 (No.1).

$C_6Cl_3F_7$. 11 gms. Analysis gave: Cl, 34.2, F, 42.7%; calc. for $C_6Cl_3F_7$: Cl, 34.6, F, 42.9%. For infra red spectrum see page 137 (No.2).

Exploratory Runs.

The product from the above reaction, which contained $C_6Cl_2F_8$ 52%, $C_6Cl_3F_7$ 40% and $C_6Cl_4F_6$ 8%, was dehalogenated with an introduction rate of 5 gms. in 20 minutes and a nitrogen flow rate of 60 ccs/min.

i) Reactor temperature 200°C. 4.15 gms. of product shown by A.S.V.P.C. to be all starting material.

ii) Reactor temperature 260°C. 4.0 gms. of product shown by A.S.V.P.C. to be mainly $C_6Cl_2F_8$ with some $C_6Cl_3F_7$, $C_6F_6$, $C_6ClF_5$, $C_6Cl_2F_4$ and $C_6Cl_3F_3$.

iii) Reactor temperature 315°C. 3.2 gms. of product shown by A.S.V.P.C. to be mainly $C_6Cl_2F_8$ and $C_6Cl_2F_4$ with some $C_6F_6$, $C_6ClF_5$ and $C_6Cl_3F_3$.

iv) Reactor temperature 370°C. 2.5 gms. of product shown by A.S.V.P.C. to be identical to reaction iii, see above.

v) Reactor temperature 395°C. 0.2 gms. of product shown by A.S.V.P.C. to be mainly $C_6Cl_2F_8$.

vi) Reactor temperature 435°C. Total decomposition occurred.

1,2-Dichlorooctafluorocyclohexene.

5 gms. were dehalogenated in 20 minutes. Reactor temperature 360°C; nitrogen 60 ccs/min. 2.25 gms. of product were shown by A.S.V.P.C. to be $C_6Cl_2F_8$ 43%; $C_6F_6$, $C_6ClF_5$, $C_6Cl_2F_4$ (trace of each), total yield 43%. An infra red spectrum confirmed the identity of

1,2-dichlorooctafluorocyclohexene.

## 1,2,4-Trichloroheptafluorocyclohexene.

4 gms. were dehalogenated in 16 minutes. Reactor temperature 315°C; nitrogen 60 ccs/min. 2.30 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 7%, $C_6ClF_5$ 15%, $C_6Cl_2F_4$ 53%, $C_6Cl_3F_3$ 3%, total yield 78%. A pure specimen of $C_6Cl_2F_4$ was separated. (P.S.V.P.C. Si.El. column at 135°C; P.D. 25 cms. Hg; nitrogen 180 ccs/min.).
Dichlorotetrafluorobenzene. Molecular weight, found: 230, calc. for $C_6Cl_2F_4$: 219. B.p. 150.0°C. $n_D^{20}$ 1.4659.
Analysis gave: Cl, 32.8, F, 35.2%; calc. for $C_6Cl_2F_4$: Cl, 32.5, F, 34.7%.
For infra red spectrum see page 143 (No. 15). This was shown by N.M.R. to be 1,2-dichlorotetrafluorobenzene.

## Dehalogenation of mixed Perchlorofluorocyclohexenes and Perchlorofluorocyclohexanes.

The product from the reaction between hexachlorobenzene and chlorine trifluoride (molar ratio 1:3) contained a mixture of cyclohexenes and cyclohexanes (see page 91).

The compounds with the same number of chlorine atoms per molecule, i.e. $C_6Cl_5F_5$ and $C_6Cl_5F_7$, could not be separated by distillation, as their boiling points were very near each other. Thus the individual "pairs" were dehalogenated.

### Tetrachlorohexafluorocyclohexene and Tetrachlorooctafluorocyclohexane.

5gms. were dehalogenated in 20 minutes. Reactor temperature 230°C; nitrogen 60 ccs/min. 2.8 gms. of product were shown by A.S.V.P.C. to contain $C_6F_6$ 2%, $C_6ClF_5$ 10%, $C_6Cl_2F_4$ 12%, $C_6Cl_3F_3$ 20%, $C_6Cl_4F_2$ 10%, starting material 20%, $C_6Cl_3F_7$ 10%, impurity 16%. (% of product).

### Pentachloropentafluorocyclohexene and Pentachloroheptafluorocyclohexane.

5 gms. were dehalogenated in 20 minutes. Reactor temperature 260°C; nitrogen 60 ccs/min. 2.5 gms. of product were shown by A.S.V.P.C. to contain $C_6F_6$ 17%, $C_6ClF_5$ 21%, $C_6Cl_2F_4$ 35%, $C_6Cl_3F_3$ 24%, $C_6Cl_4F_2$ 2%.

### Hexachlorotetrafluorocyclohexene and Hexachlorohexafluorocyclohexane.

5 gms. were dehalogenated in 20 minutes. Reactor temperature 300°C; nitrogen 60 ccs/min. 2.37 gms. of product were shown by A.S.V.P.C. to contain $C_6F_5$ 3%, $C_6ClF_5$ 25%, $C_6Cl_2F_4$ 35%, $C_6Cl_3F_3$ 30%, $C_6Cl_4F_2$ 7%.

### Dehalogenation of Perchlorofluorocyclohexanes.

The product from the reaction between hexachlorobenzene and chlorine trifluoride (molar ratio 1:7) contained the fully saturated perchlorofluorocyclohexanes. These were separated by distillation.

The conditions were varied in each separate dehalogenation, in order to understand the dehalogenation process more fully. Pentachloroheptafluorocyclohexane obtained from the vapour phase reaction of hexachlorobenzene, with cobalt trifluoride, was also dehalogenated.

### Pentachloroheptafluorocyclohexane.

i) 2.5 gms. (obtained from $C_6Cl_6/CoF_3$) were dehalogenated in 10 minutes. Reactor temperature 260°C; nitrogen 60 ccs/min. 1.05 gms. of product were shown by A.S.V.P.C. to be $C_6C_6$ 60%, $C_6ClF_5$ 20%, $C_6Cl_2F_4$ 3.5%, total yield 83.5%.

ii) 2.5 gms. (obtained from $C_6Cl_6/ClF_3$) were dehalogenated in 10 minutes. Reactor temperature 260°C; nitrogen 60 ccs/min. 0.9 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 30%, $C_6ClF_5$ 25%, $C_6Cl_2F_4$ 8%, $C_6Cl_3F_7$ 3.5%, total yield 66.5%.

iii) 5 gms. were dehalogenated in 20 minutes. Reactor temperature 260°C; nitrogen 60 ccs/min. 2.1 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 21%, $C_6ClF_5$ 29%, $C_6Cl_2F_4$ 8%, $C_6Cl_3F_7$ 14%, total yield 72%. Pure samples of $C_6F_6$ and $C_6ClF_5$ were separated. (P.S.V.P.C. Si.El. column at 130°C; P.D. 25 cms. Hg; nitrogen 175 ccs/min). Infra red spectra confirmed their identity.

iv) 10 gms. were dehalogenated in 40 minutes. Reactor temperature 260°C; nitrogen 60 ccs/min. 5.85 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 24%, $C_6ClF_5$ 22%, $C_6Cl_2F_4$ 5%, $C_6Cl_3F_7$ 28.5%, $C_6Cl_4F_6$ 3.5%, starting material 10%, total yield 93%. Pure samples of $C_6F_6$, $C_6ClF_5$ and $C_6Cl_3F_7$ were separated. (P.S.V.P.C. Si.El. column at 140°C; P.D. 30 cms. Hg; nitrogen 150 ccs/min.)

Infra red spectra of $C_6F_6$ and $C_6ClF_5$ confirmed their identity. Trichloroheptafluorocyclohexene. Molecular weight, found: 317,

calc. for $C_6Cl_3F_7$: 311.5. B.p. 149°C. $n_D^{20}$ 1.4022.
Analysis gave: Cl, 34.2, F, 42.9%; calc. for $C_6Cl_3F_7$: Cl, 34.2, F, 42.7%.
The infra red spectrum of $C_6Cl_3F_7$, see page 138 (No. 4), showed no absorbtion in the 1640 $cm^{-1}$ region, which corresponds with the cyclohexenes produced in the hexachlorobenzene, chlorine trifluoride reaction. However absorbtions near this region occurred at 1687 $cm^{-1}$ and 1724 $cm^{-1}$ which correspond with the -CCl=CF- and -CF=CF- structures.

v) 4.75 gms. were dehalogenated in 20 minutes. Reactor temperature 430°C; nitrogen 60 ccs/min. 0.5 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 13%, $C_6ClF_5$ 6%, total yield 19%.

vi) 5 gms. were dehalogenated in 45 minutes. Reactor temperature 430°C; nitrogen 30 ccs/min. (Identical conditions used by Mobbs[16] in dehalogenation of perchlorofluorocyclohexanes obtained from the reaction between hexachlorobenzene and cobalt trifluoride). 0.4 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ (80% of product), and two compounds having the same retention times as the impurities in the dehalogenation of $C_6Cl_3F_9$ under similar conditions.[16]

Hexachlorohexafluorocyclohexane.

i) 5 gms. were dehalogenated in 20 minutes. Reactor temperature 300°C; nitrogen 60 ccs/min. 2.0 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 2%, $C_6ClF_5$ 38.5%, $C_6Cl_2F_4$ 33.5%, $C_6Cl_3F_3$ 2%, total yield 76%. Pure samples of $C_6ClF_5$ and $C_6Cl_2F_4$ were separated

(P.S.V.P.C. Si.El. column at 145°C; P.D. 30 cms. Hg; nitrogen 175 ccs/min.). Infra red spectra confirmed their identities.

ii) 5 gms. were dehalogenated in 45 minutes. Reactor temperature 425°C; nitrogen 30 ccs/min. 0.1 gms. of product were shown by A.S.V.P.C. to contain $C_6F_6$ (20% of product), and two compounds, in equal proportions, having the same retention times as the impurities in the dehalogenation of $C_6Cl_3F_9$ under similar conditions.[16]

Heptachloropentafluorocyclohexane.

i) 5 gms. were dehalogenated in 20 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 2.0 gms. of product were shown by A.S.V.P.C. to be $C_6ClF_5$ 11%, $C_6Cl_2F_4$ 46%, $C_6Cl_3F_3$ 11%, $C_6Cl_4F_2$ 3%, total yield 71%. A pure sample of $C_6Cl_2F_4$ was separated. (P.S.V.P.C. Si.El. column at 155°C; P.D. 30 cms. Hg; nitrogen 200 ccs/min.) An infra red spectrum confirmed its identity.

ii) 5 gms. were dehalogenated in 45 minutes. Reactor temperature 430°C; nitrogen 30 ccs/min. 0.05 gms. of product were shown by A.S.V.P.C. to contain only the two compounds having the same retention times as the impurities in the dehalogenation of $C_6Cl_3F_9$ under similar conditions.[16]

## Dehalogenation of mixed Perchlorofluorocyclohexanes from the Reaction between Fluorine and Hexachlorobenzene.

All dehalogenations were carried out on the crude mixture of cyclohexanes obtained from the liquid phase reaction between fluorine and hexachlorobenzene. This had an average constitution of $C_6Cl_6F_6$.

i) 5 gms. were dehalogenated in 20 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 1.6 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 14%*, $C_6ClF_5$ 28%, $C_6Cl_2F_4$ 14%, $C_6Cl_3F_3$ 5%, total aromatic yield 61%.

ii) 20 gms. were dehalogenated in 80 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 8.7 gms. of product were shown by A.S.V.P.C. to contain $C_6F_6$ 19%, $C_6ClF_5$ 21%, $C_6Cl_2F_4$ 16%, $C_6Cl_3F_3$ 11%, $C_6Cl_4F_2$ 5%, $C_6Cl_5F$ 1%, impurities 10%, total aromatic product 73%.

## A New Method of Dehalogenation.

The previously described dehalogenation process was inadequate as a source of highly fluorinated chlorobenzenes. The regeneration of the iron gauze, which took 4-8 hours, made the preparation too laborious. If large amounts of material were dehalogenated (i.e. greater than 10 gms.), a larger proportion of the more highly chlorinated benzenes were formed.

### Apparatus.

The apparatus was a cobalt fluoride reactor, similar to that described by Barbour and others,[106] and consisted of a steel cylinder, 32" long and 2½" internal diameter, filled with iron filings. Both the inlet and the outlet ends consisted of heated towers, 10" high, one 1" in diameter, the other 1½" in diameter. The ends of these towers and the ends of the reactor were closed using aluminium

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* Assuming an average constitution of $C_6Cl_6F_6$ for the starting material.

knife edge seals.

The stirring mechanism had a metal-teflon bearing, which was sealed using compressed asbestos wool, which had been treated with teflon. The stirrer consisted of an axial shaft fixed with 6" paddles, driven by a $\frac{1}{4}$ h.p. motor at 6 revs/min. The reactor was heated by three rod like 1 k.w. heating elements which were wound round the reactor and the two towers. A glass wool jacket was used to insulate the apparatus. The temperature was recorded by a movable thermocouple in a glass sheath inside the stirrer shaft, this gave the temperature at any desired point along the axis of the reactor.

The samples were introduced and collected as before. No regeneration was necessary as spent iron filings were discarded and replaced with new iron filings.

<u>Perchlorofluorocyclohexanes.</u> (Av. constitution $C_6Cl_6F_6$).

The reactor was charged with 3000 gms. of course iron filings, and 574 gms. of perchlorofluorocyclohexanes, obtained from the reaction of fluorine and hexachlorobenzene, were dehalogenated to give 211.8 gms. of product.

The first two runs, (5 gms. and 10 gms. respectively), gave anomolous results, and although some aromatic material was formed, a large amount of impurities were present. After the initial 15 gms. all runs gave predominantly aromatic product.

i) 5 gms. were dehalogenated in 20 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 1.3 gms. of product were shown by

A.S.V.P.C. to contain $C_6F_6$ 14%*, $C_6ClF_5$ 18%, $C_6Cl_2F_4$ 9.5%, $C_6Cl_3F_3$ 2%, impurities were 15% of the product, total aromatic yield 43.5%.

ii) 10 gms. were dehalogenated in 40 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 2.9 gms. of product were shown by A.S.V.P.C. to contain $C_6F_6$ 15%, $C_6ClF_5$ 20%, $C_6Cl_2F_4$ 10%, $C_6Cl_3F_3$ 2%, impurities were 15% of the product, total aromatic yield 47%.

iii) 20 gms. were dehalogenated in 80 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 6.0 gms. of product were shown by A.S.V.P.C. to contain $C_6F_6$ 16%, $C_6ClF_5$ 21%, $C_6Cl_2F_4$ 11%, $C_6Cl_3F_3$ 2.5%, impurities were 15% of the product, total aromatic yield 50.5%.

iv) 20 gms. were dehalogenated in 40 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 6.2 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 13%, $C_6ClF_5$ 21%, $C_6Cl_2F_4$ 11%, $C_6Cl_3F_3$ 5%, impurities were 15% of the product, total aromatic yield 50%.

v) 20 gms. were dehalogenated in 20 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 7.0 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 15%, $C_6ClF_5$ 21%, $C_6Cl_2F_4$ 13%, $C_6Cl_3F_3$ 6%, impurities were 20% of the product, total aromatic yield 55%.

### Perchlorofluorocyclohexanes. (Av. constitution $C_6Cl_5F_7$)

The product from the reaction between fluorine and hexachlorobenzene was further fluorinated at room temperature, at 100°C and at 200°C to give an average constitution of $C_6Cl_5F_7$. 80 gms. of this

---

* Assuming an average constitution of $C_6Cl_6F_6$ for the starting material.

were dehalogenated to give 28.6 gms. of product.

i) 20 gms. were dehalogenated in 80 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 6.85 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 28%*, $C_6ClF_5$ 22%, $C_6Cl_2F_4$ 4%, impurities were 18% of the product, total aromatic yield 54%.

ii) 20 gms. were dehalogenated in 40 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 7.0 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 29%, $C_6ClF_5$ 23%, $C_6Cl_2F_4$ 4%, impurities were 18% of the product, total aromatic yield 56%.

## Perchlorofluorocyclohexenes and Perchlorofluorocyclohexanes.

The product from the reaction between hexachlorobenzene and chlorine trifluoride (molar ratio 1:3), gave a mixture of cyclohexenes and cyclohexanes. 60 gms. of this was dehalogenated to give 24.8 gms. of product.

20 gms. were dehalogenated in 40 minutes. Reactor temperature 330°C; nitrogen 60 ccs/min. 7.7 gms. of product were shown by A.S.V.P.C. to contain $C_6F_6$ 10%‡, $C_6ClF_5$ 30%, $C_6Cl_2F_4$ 30%, $C_6Cl_3F_3$ 15%, $C_6Cl_4F_2$ 5%, impurities 10%.

## Replacement of Iron Filings.

It was found that after about 700 gms. of material had been dehalogenated, it was necessary to change the iron filings, as the amount of nonaromatic material present was increasing.

---

* Assuming an average constitution of $C_6Cl_5F_7$ for the starting material.

‡ % of product.

Fine iron filings (5000 gms.) were introduced, and 993 gms. of perchlorofluorocyclohexanes were dehalogenated to give 339 gms. of aromatic product.

Typical Dehalogenations. (Av. constitution $C_6Cl_6F_6$)

i) 20 gms. were dehalogenated in 40 minutes. Reactor temperature 340°C; nitrogen 60 ccs/min. 6.8 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 22%, $C_6ClF_5$ 27%, $C_6Cl_2F_4$ 12.5%, $C_6Cl_3F_3$ 3%, impurities were 5% of the product, total aromatic yield 64.5%.

ii) 80 gms. were dehalogenated in 160 minutes. Reactor temperature 345°C; nitrogen 60 ccs/min. 27.5 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 22.5%, $C_6ClF_5$ 27.5%, $C_6Cl_2F_4$ 13%, $C_6Cl_3F_3$ 3%, impurities were 5% of the product, total aromatic yield 66%. A typical chromatogram is shown in fig. xv.

After 900 gms. of this material were dehalogenated, the yield of the more highly chlorinated compounds rose.

100 gms. were dehalogenated in 200 minutes. Reactor temperature 340°C; nitrogen 60 ccs/min. 33.7 gms. of product were shown by A.S.V.P.C. to be $C_6F_6$ 18%, $C_6ClF_5$ 26.5%, $C_6Cl_2F_4$15%, $C_6Cl_3F_3$ 3%, $C_6Cl_4F_2$ (trace), impurities were 5% of product, total aromatic yield 62.5%.

Distillation of Dehalogenation Material.

A concentric tube distillation column with a heating jacket was set up, using a mixture of n-heptane and methylcyclohexane to obtain the platage (see page 87 ). A platage of 22 was found.

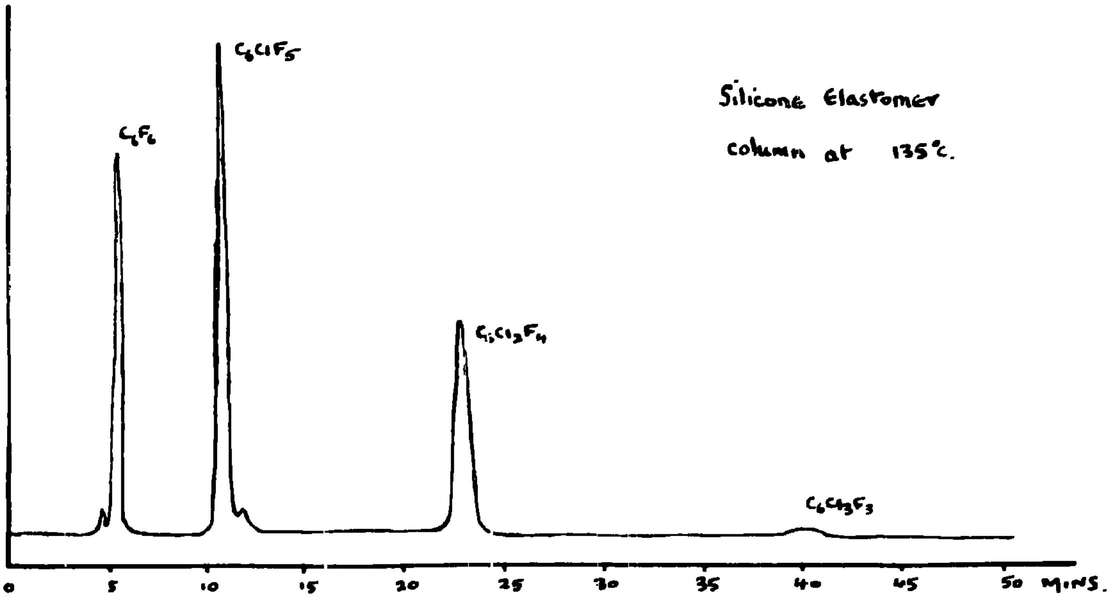

Fig xv. Dehalogenation of $C_6Cl_6F_6$. Fine Iron filings dehalogenation.

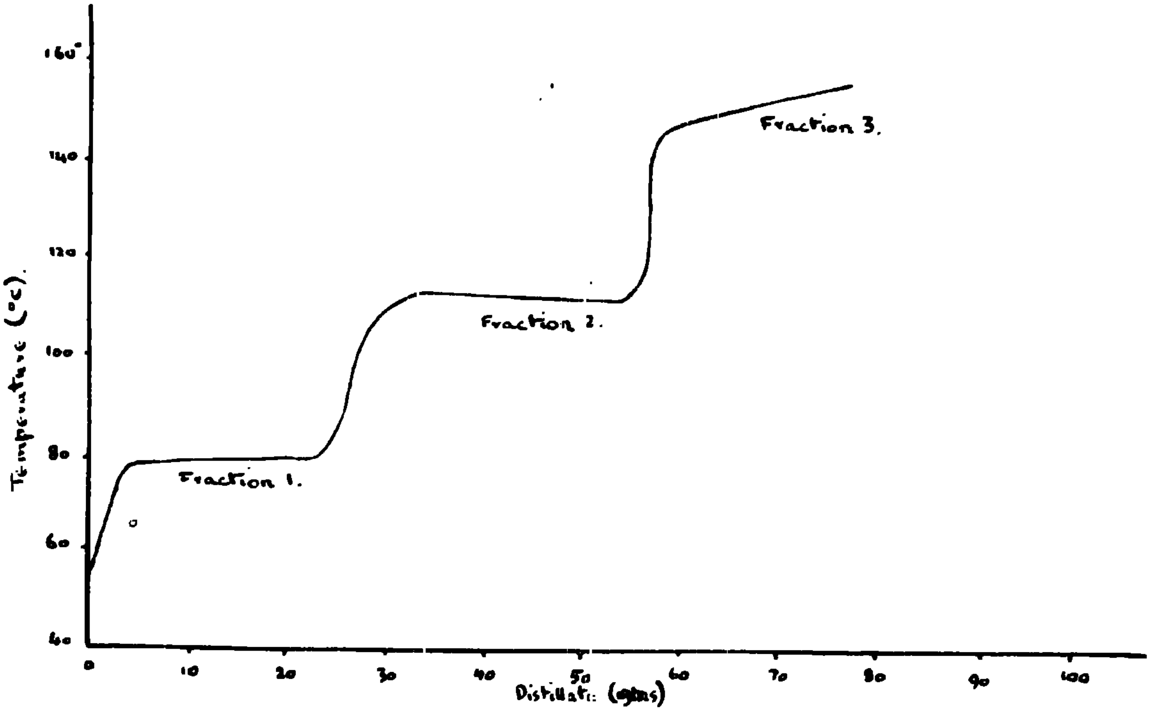

Fig xvi. Distillation curve for 100 gms reaction product from dehalogenation of $C_6Cl_6F_6$.

The products from the dehalogenation of perchlorofluorocyclohexanes, prepared from the reaction of fluorine and hexachlorobenzene, were combined, washed with sodium hydroxide (N) and water, and dried (Anh. $MgSO_4$). The boiling range and weight of each fraction is given in table 17.

Table 17. Distillation 6. (see fig. xvi)

| Fraction No. | Boiling Range ° C. | Size of Fraction gms. | Component. |
|---|---|---|---|
| 1 | 77.5 | 18.9 | $C_6F_6$ |
| 2 | 112.5 | 25.9 | $C_6ClF_5$ |
| 3 | 150-153 | 12.5 | $C_6Cl_2F_4$ |
| Residue | - | 15.7 | $C_6Cl_3F_3$ |

Intermediate fractions 19.9 gms. Recovery 93%.

Each fraction was shown by A.S.V.P.C. to be pure. A pure sample of $C_6Cl_3F_3$ was separated (P.S.V.P.C. Si.El. column at 170°C; P.D. 45 cms. Hg; nitrogen 175 ccs/min.). Infra red spectra confirmed their identity.

## Calculation of Yields.

In all the reactions carried out to give perchlorofluorocyclohexanes, -cyclohexenes and -benzenes, the yields quoted assume equimolar response on the analytical scale vapour phase chromatography.

This assumption was verified by making standard solutions containing weighed samples of each compound in a series. These were chromatographed, and the area of each "peak" found by cutting it out and weighing it. There was a slight trend for the more highly fluorinated compounds to give smaller peak areas for equimolar amounts; this trend, however, was small and within experimental error ( ± 10%).

Correction factors for:-

i) Perchlorofluorobenzenes.

| $C_6F_6$ | $C_6ClF_5$ | $C_6Cl_2F_4$ | $C_6Cl_3F_3$ | $C_6Cl_5F$ | $C_6Cl_6$ |
|---|---|---|---|---|---|
| 1.08 | 1.08 | 1.05 | 1.00 | 0.96 | 0.98 |

ii) Perchlorofluorocyclohexenes.

| $C_6Cl_3F_7$ | $C_6Cl_4F_6$ | $C_6Cl_5F_5$ | $C_6Cl_6F_4$ |
|---|---|---|---|
| 1.08 | 1.10 | 1.00 | 1.04 |

iii) Perchlorofluorocyclohexanes.

| $C_6Cl_4F_8$ | $C_6Cl_5F_7$ | $C_6Cl_6F_6$ | $C_6Cl_7F_5$ |
|---|---|---|---|
| 1.00 | 0.94 | 0.97 | 0.89 |

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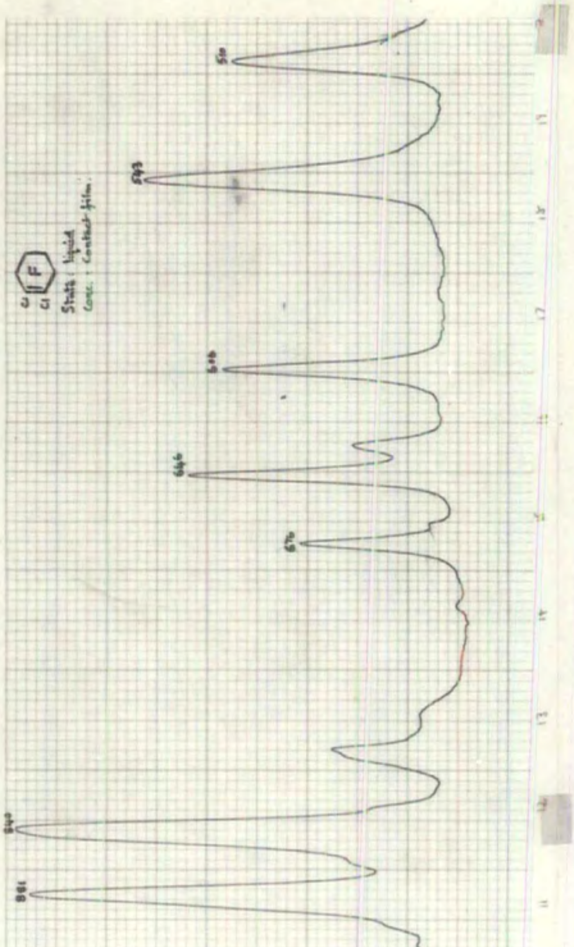
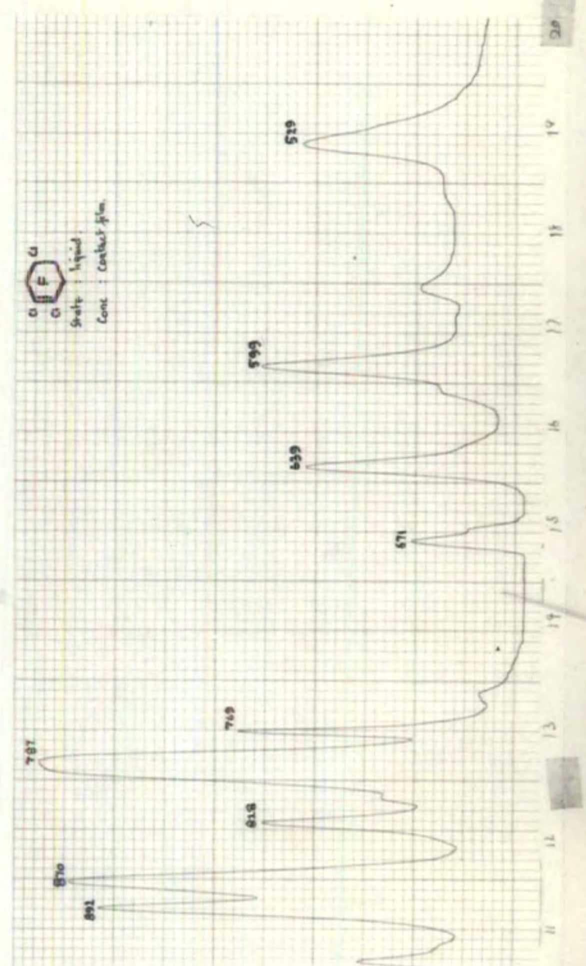
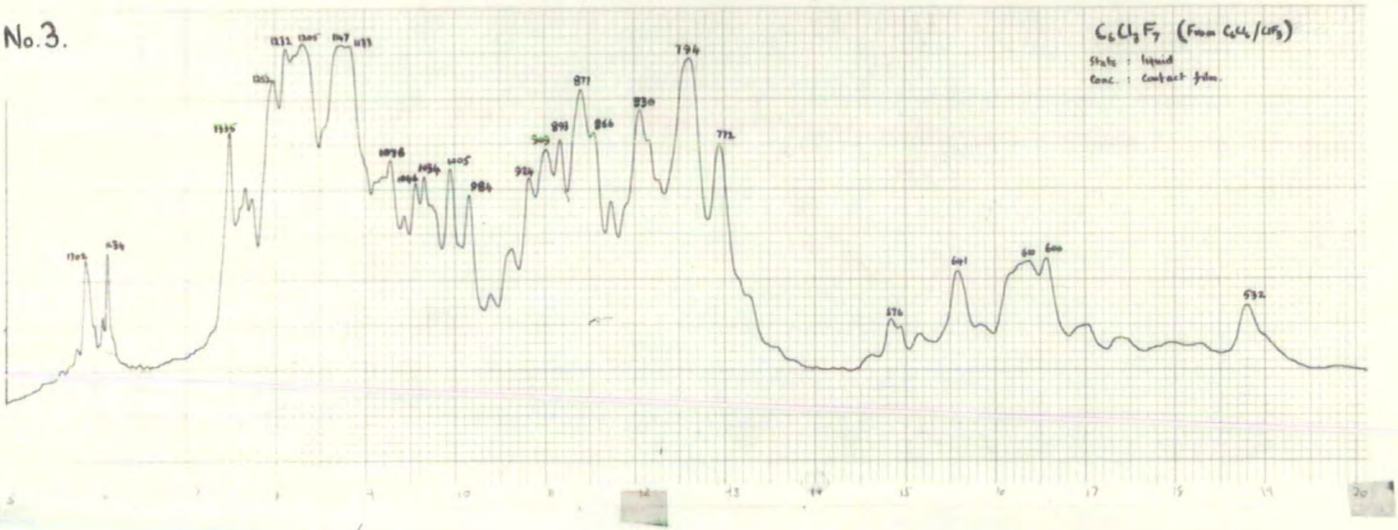
No. 1.


Cl
Cl
F
State : liquid
Conc : Contact film.
1613
1337
1258
1205
1166
1153
1046
990
881
840
670
646
618
543
510
5
10
11
12
13
14
15
16
17
18
19
20

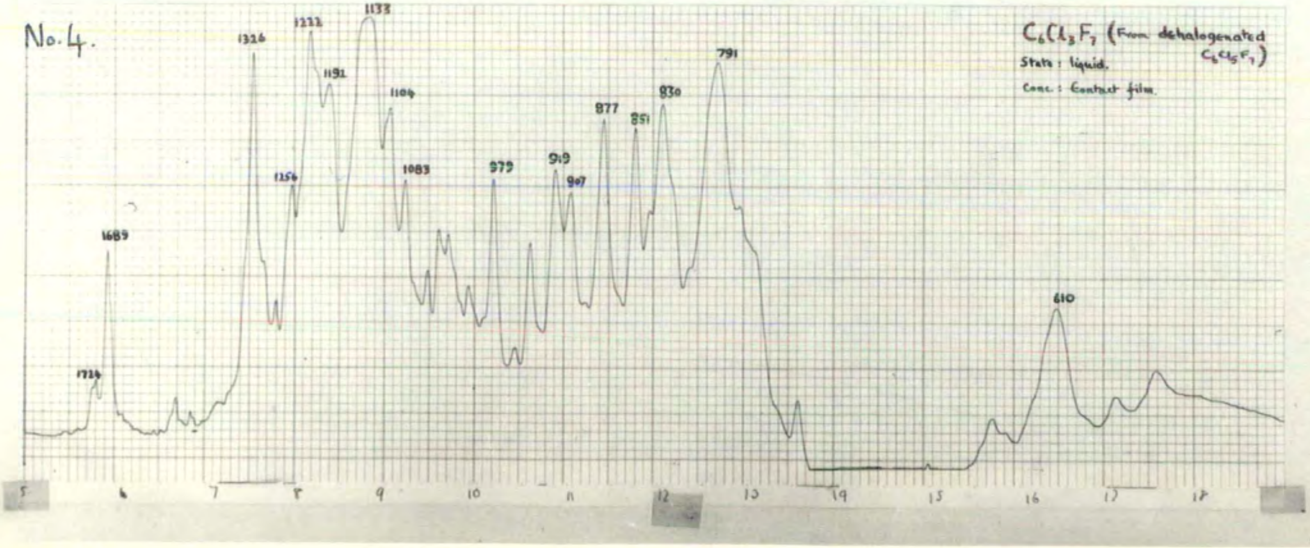
No. 2


Cl
Cl
F
Cl
State : liquid.
Conc : Contact film.
1621
1299
1247
1227
1198
1165
1125
1096
1001
891
870
818
787
769
671
639
599
529
5
8
9
10
11
12
13
14
15
16
17
18
19
20

No. 3.


$C_6Cl_3F_7$ (From $C_6Cl_6$/$ClF_3$)
State : liquid
Conc. : Contact film.
1702
1634
1335
1263
1232
1205
1147
1133
1078
1044
1034
1005
984
924
909
898
877
866
830
794
772
576
641
610
600
532
5
7
8
9
10
11
12
13
14
15
16
17
18
19
20

No. 4.


$C_6Cl_3F_7$ (From dehalogenated $C_6Cl_5F_7$)
State : liquid.
Conc. : Contact film.
1724
1689
1326
1256
1232
1192
1133
1104
1083
979
919
907
877
851
830
791
610
5
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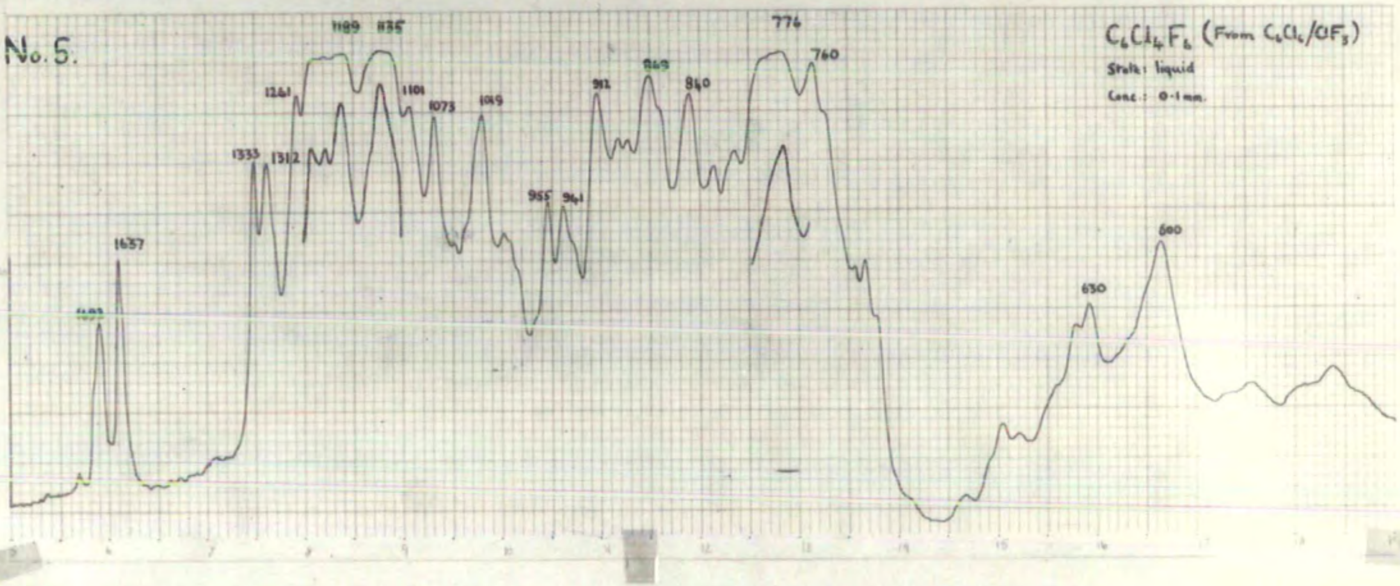
15
16
17
18

No. 5.

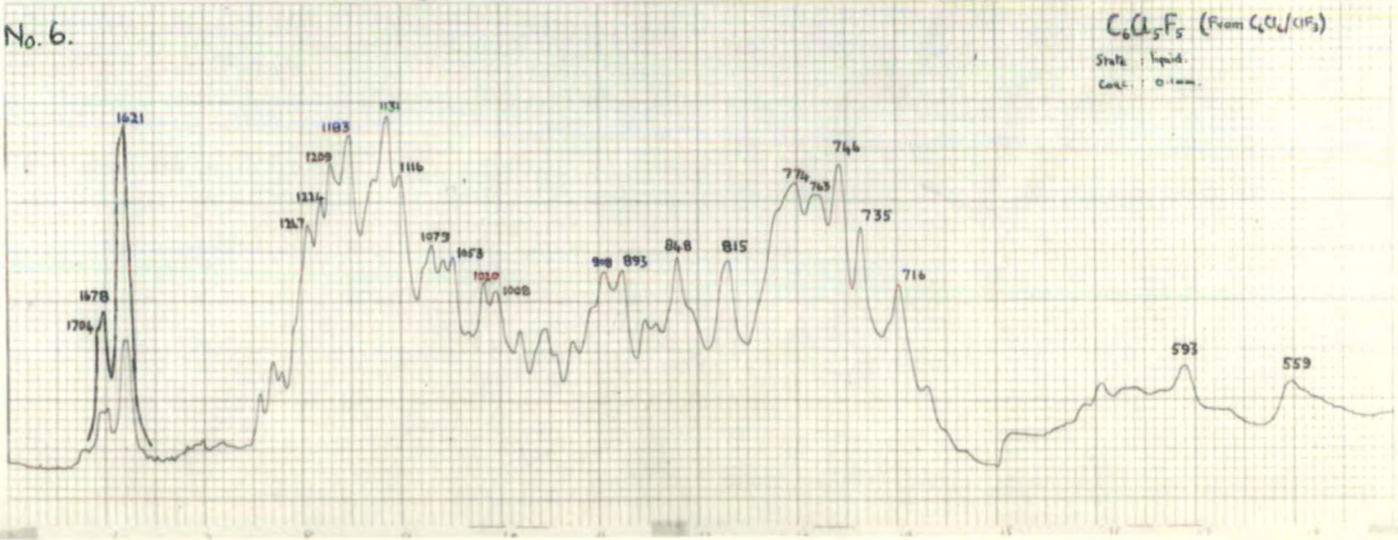


$C_6Cl_4F_6$ (From $C_6Cl_6/ClF_3$)

State: liquid

Conc.: 0·1 mm.

No. 6.

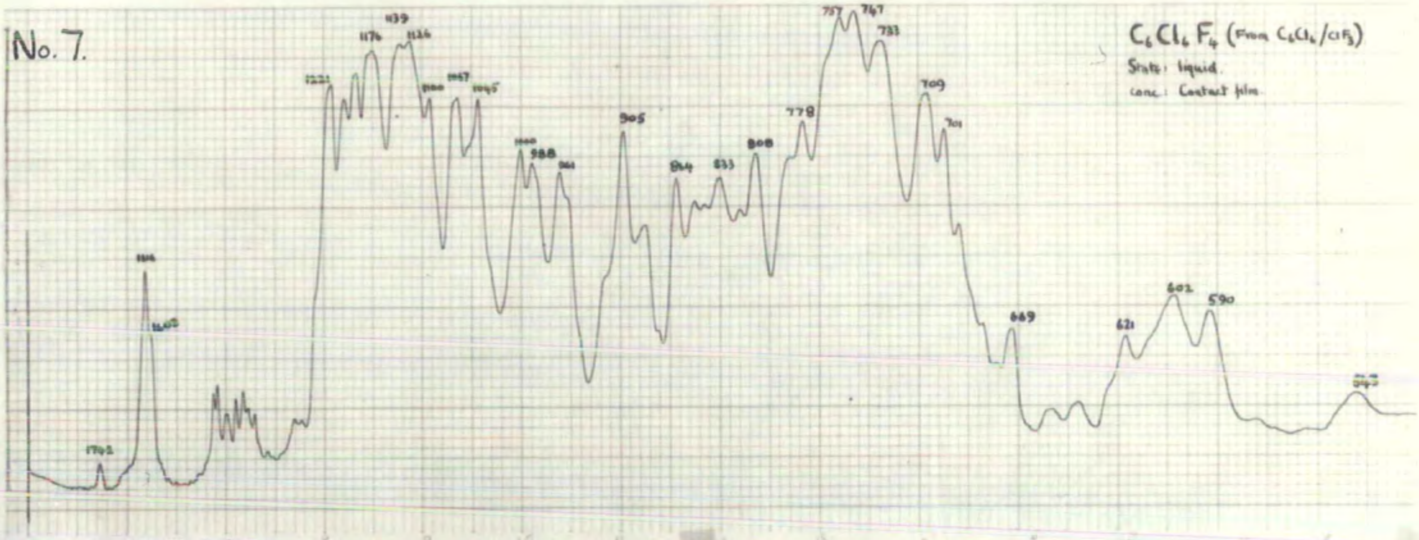


$C_6Cl_5F_5$ (From $C_6Cl_6/ClF_3$)

State: liquid.

Conc.: 0·1 mm.

No. 7.

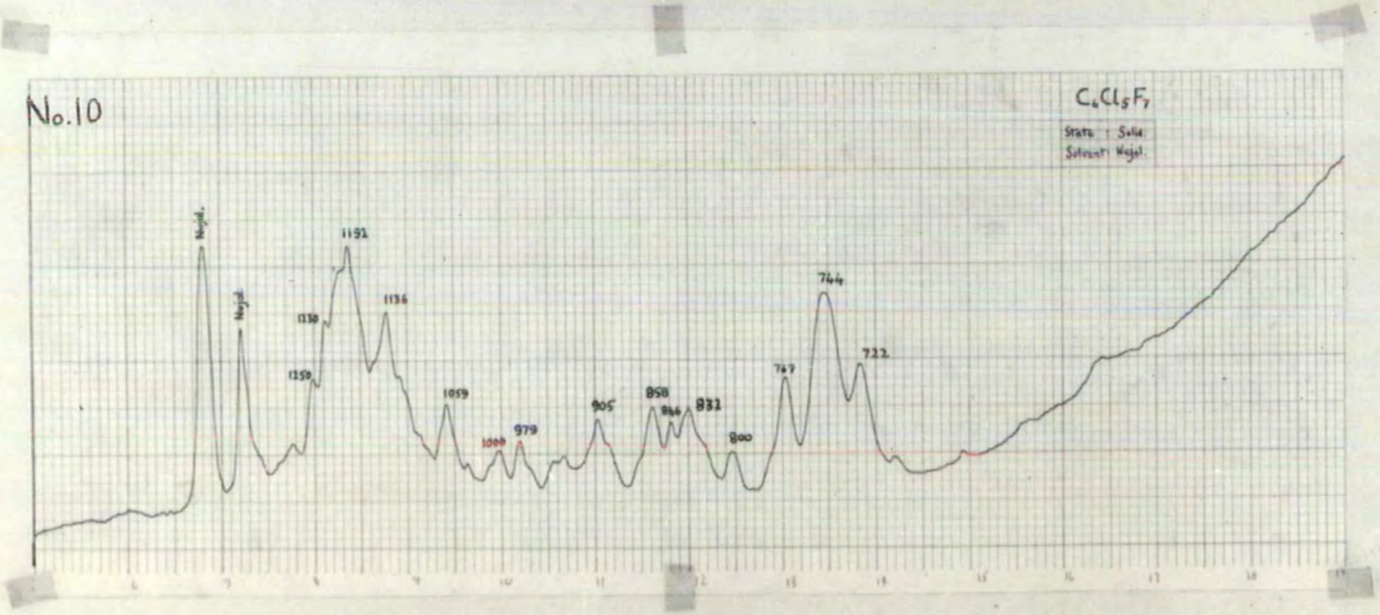


$C_6Cl_6F_4$ (From $C_6Cl_6/ClF_3$)
State: liquid.
conc.: Contact film.

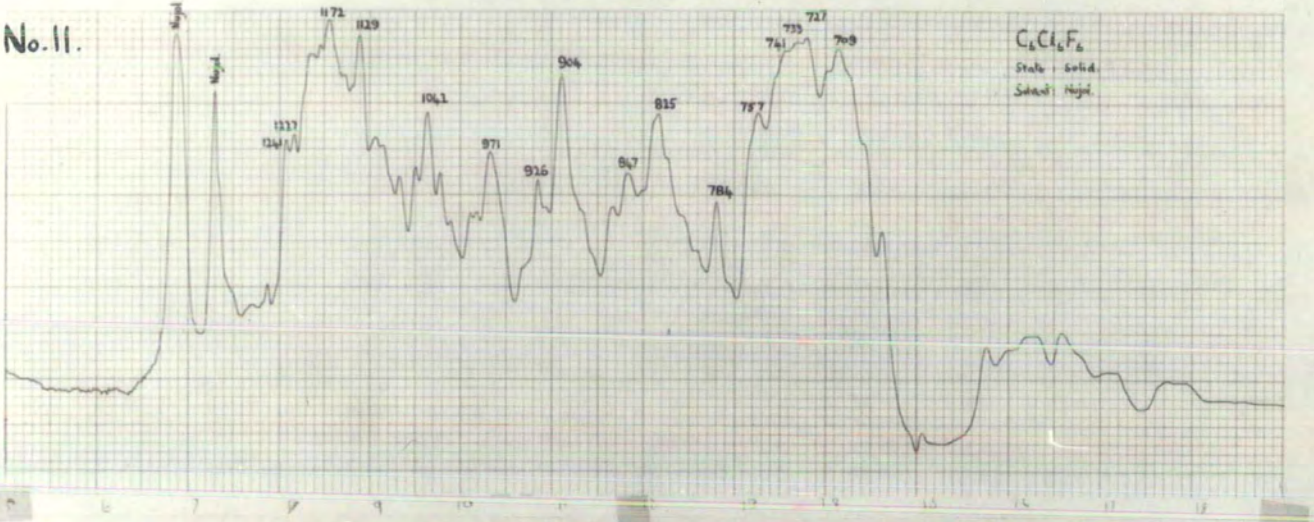
No. 8

State: liquid
conc.: Contact film.

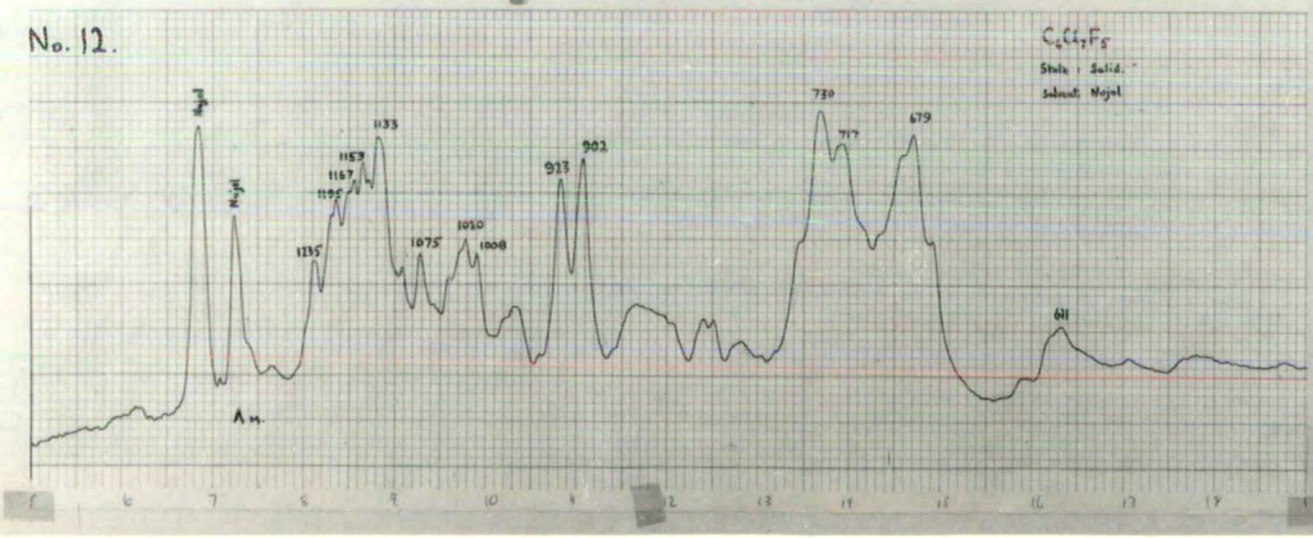

No. 9
$C_6Cl_4F_8$
State : Semi-solid.
Solvent: Nujol
Nujol
Nujol
1292
1238
1206
1143
1115
1070
1031
974
909
869
843
813
804
785
763
744
613
6
7
8
9
10
11
12
13
14
15
16
17
18


No. 10
$C_6Cl_5F_7$
State : Solid.
Solvent: Nujol.
Nujol.
Nujol.
1250
1230
1192
1136
1059
1009
979
905
858
846
832
800
767
744
722
6
7
8
9
10
11
12
13
14
15
16
17
18

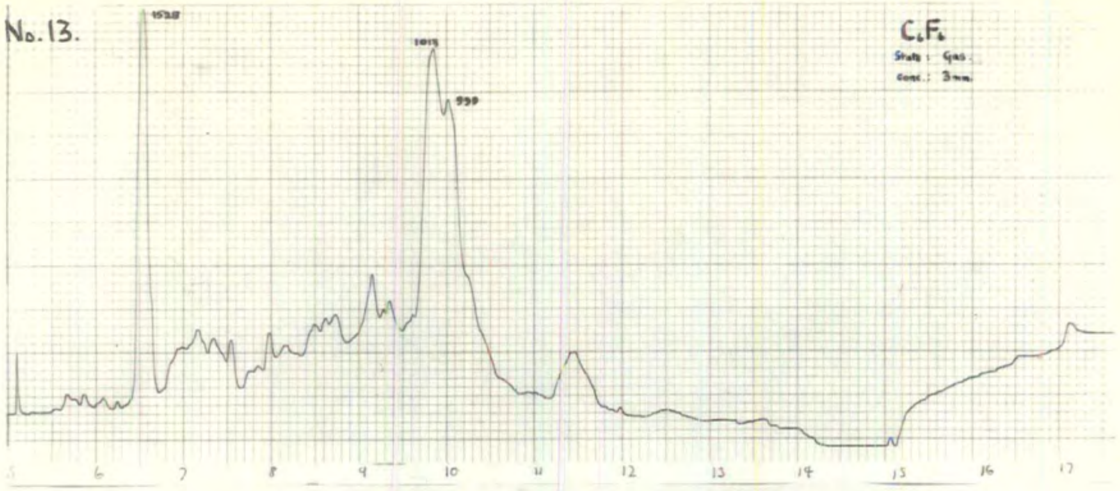
No. 11.


$C_6Cl_6F_6$
State : Solid.
Solvent: Nujol.
Nujol
Nujol
1241
1227
1172
1129
1041
971
926
904
847
815
784
757
741
733
727
709
6
7
8
9
10
11
12
13
14
15
16
17
18

No. 12.


$C_6Cl_7F_5$
State : Solid.
Solvent: Nujol
Nujol
Nujol
Am.
1235
1195
1167
1153
1133
1075
1020
1008
923
902
730
717
679
611
6
7
8
9
10
11
12
13
14
15
16
17
18

No. 13.



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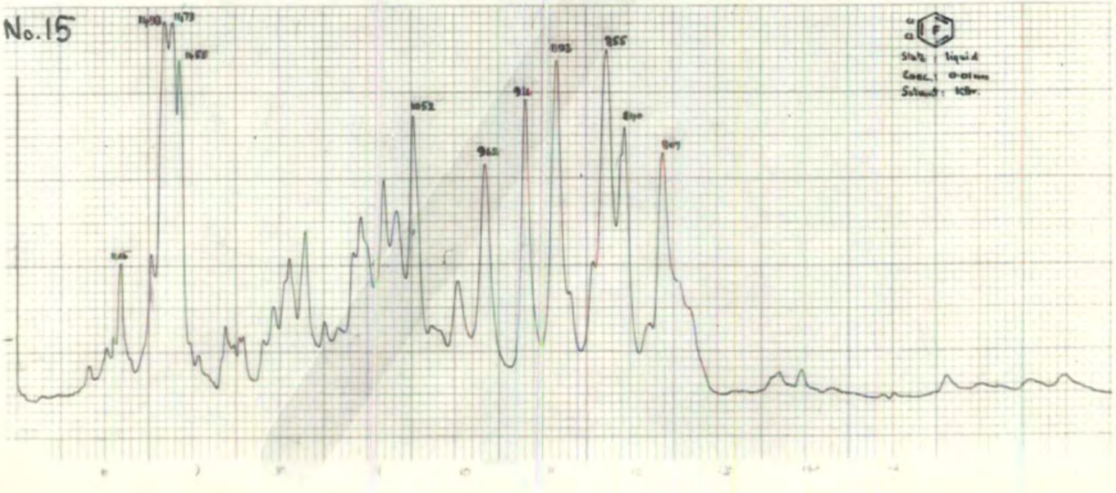
No. 15



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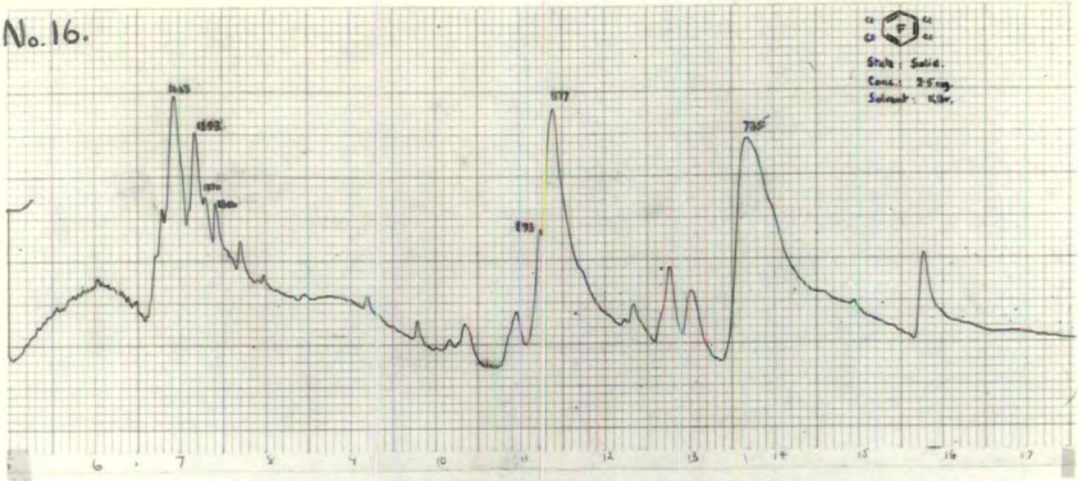

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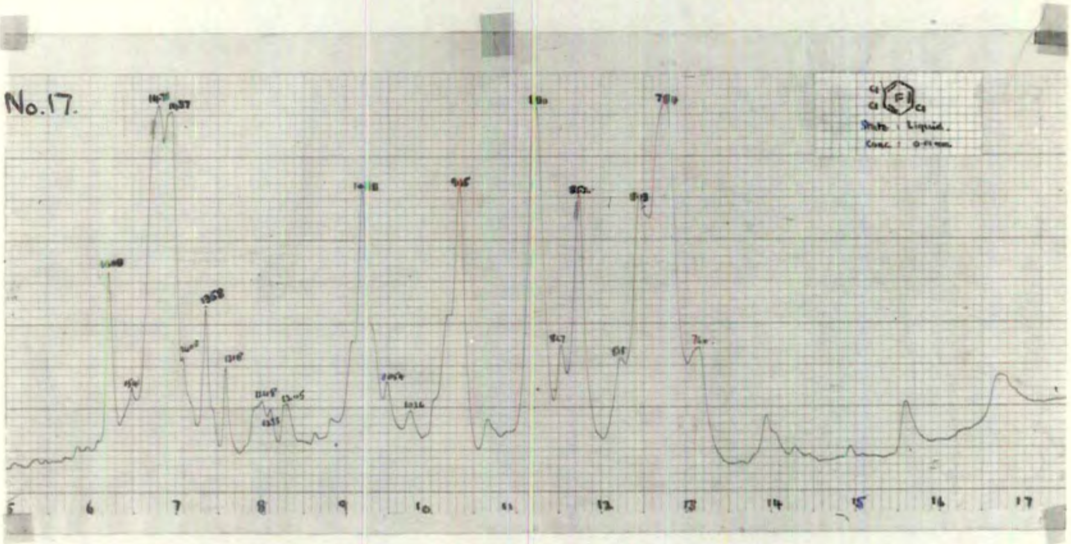

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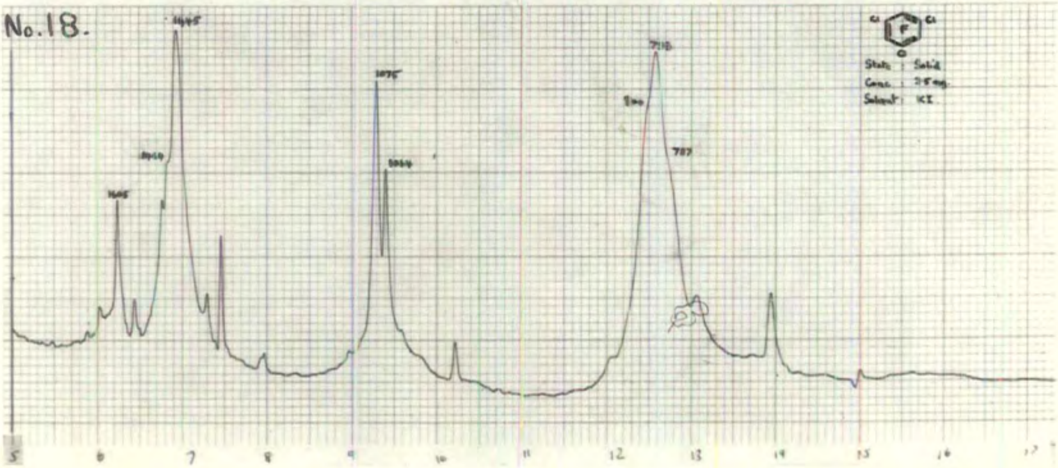
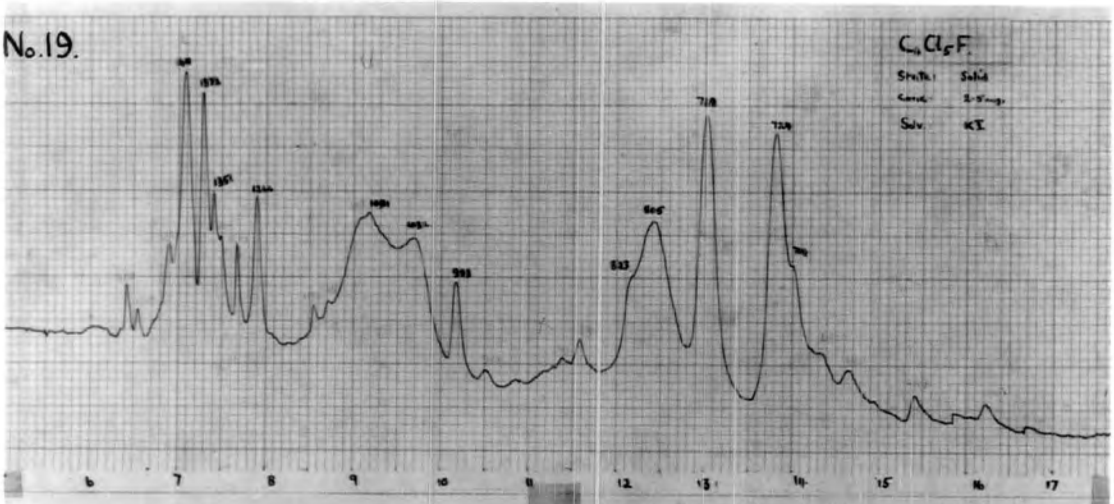
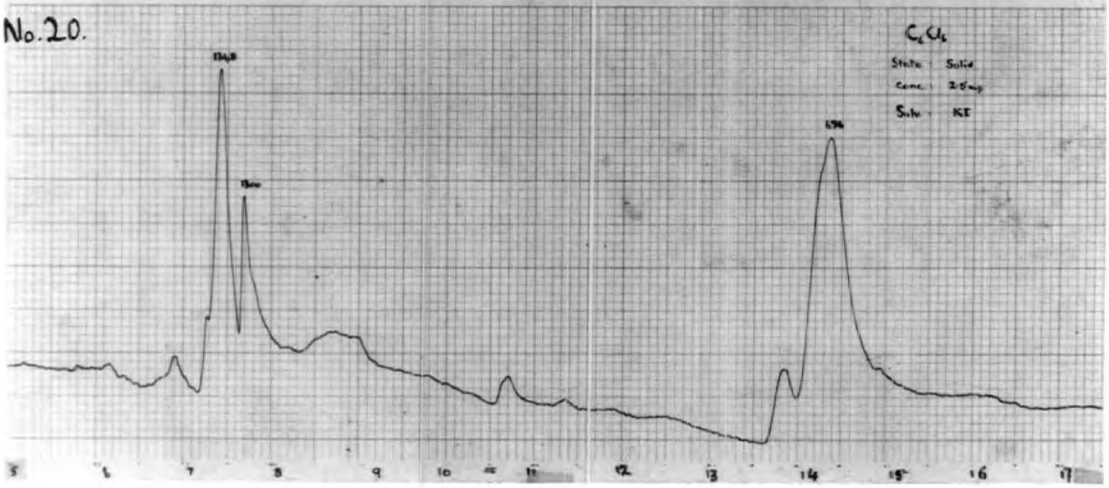



No.19.
$C_6Cl_5F$.
State: Solid
Conc.: 2·5mg.
Solv. KI
1351
993
833
805
724
6
7
8
9
10
11
12
13
14
15
16
17


No.20.
$C_6Cl_6$
State: Solid
Conc.: 2·5mg
Solv.: KI
1348
1300
694
5
6
7
8
9
10
11
12
13
14
15
16
17

# PART II

# SOME REACTIONS OF CHLOROPENTAFLUOROBENZENE.

## Chapter 4

## INTRODUCTION

## Nucleophilic Reactions of Highly Fluorinated Benzenes.

Two main routes are available for the synthesis of highly fluorinated aromatic compounds containing a reactive grouping. The first route is via electrophilic attack on hydrofluorobenzenes, and then using the reactivity of this group in further reactions. The most widely investigated example of this is the electrophilic attack on pentafluorobenzene by iodine or bromine, to form iodo- or bromopentafluorobenzenes.[1,2] These are readily formed into the Grignard reagents, and from this a wide variety of mono-substituted pentafluorophenyl compounds can be formed.[1,3-6] An extension of this method involves the preparation of pentafluorophenyl lithium by the reaction between n-butyl-lithium and a halopentafluorobenzene.[7]

The second route to substituted polyfluoro aromatic compounds is by the nucleophilic replacement of fluorine, and it is these reactions which are summarized below. Many mono-substituted pentafluorobenzenes have been formed in this manner by nucleophilic attack on hexafluorobenzene. The further attack by nucleophiles on these compounds is extremely interesting, as various positional isomers may be formed.

### Hexafluorobenzene.

The nucleophilic attack on hexafluorobenzene has been thoroughly investigated, and a summary of these reactions is given below. Almost all the reactions occur under moderate reaction conditions, to give good yields of the mono-substituted product.

| Nucleophile | Reaction Conditions | Product | Reference |
|---|---|---|---|
| $OCH_3^-$ | a) $CH_3OH$, $CH_3ONa$ Reflux | $C_6F_5OCH_3$ 60%<br>p-$C_6F_4(OCH_3)_2$ 3% | 8 |
| | b) With pyridine | $C_6F_5OCH_3$ | 9 |
| $OC_2H_5^-$ | $C_2H_5OH$, $C_2H_5ONa$ | $C_6F_5OC_2H_5$ | 10 |
| $OH^-$ | a) KOH, Pyridine. Reflux | $C_6F_5OH$ 20% | 9 |
| | b) KOH, t-butyl alcohol, reflux. | $C_6F_5OH$ 71% | 10 |
| $SH^-$ | $H_2S$, NaOH, Ethylene glycol, Pyridine. | $C_6F_5SH$ 70% | 11 |
| $NH_2^-$ | a) $NaNH_2$. liq.$NH_3$ | $C_6F_5NH_2$<br>$(C_6F_5)_2NH$ 3% | 12, 13 |
| | b) $NH_3$, Ethanol, 167°C. | $C_6F_5NH_2$ 70% | 13 |
| $NHNH_2^-$ | $NH_2NH_2.H_2O$. Ethanol, reflux. | $C_6F_5NHNH_2$ 73% | 13, 14 |
| $NHCH_3^-$ | a) $CH_3NH_2$, Ethanol 115°C | $C_6F_5NHCH_3$ 69% | 13 |
| | b) $CH_3NH_2$, Ethanol, 170°C | p-$C_6F_4(NHCH_3)_2$ 60% | 13 |
| $CH_3^-$ | a) $CH_3Li$, Ether. Reflux. | $C_6F_5CH_3$ 69%<br>p-$C_6F_4(CH_3)_2$ 10% | 3, 15 |
| | b) $CH_3MgBr$ | $C_6F_5CH_3$ 3% | 9 |

| | | | |
|---|---|---|---|
| $R^-$ | a) n-$C_4H_9Li$ | $C_6F_5C_4H_9$ 56% | 15 |
| | | $C_6F_4(C_4H_9)_2$ 20% | |
| | b) PhLi | $C_6F_5 \cdot C_6H_5$ | 16 |
| | c) $CH_3CH=CHLi$ | $C_6F_5CH=CHCH_3$ 70% | 17 |
| | $2CH_3CH=CHLi$ | p-$C_6F_4(CH=CHCH_3)_2$ 82% | 17 |
| [H] | Pt.$H_2$,300°C. | $C_6F_5H$ 40% | 18 |
| | | $C_5F_4H_2$ 10% | |

The pentafluorophenyl compounds summarized above have the normal chemistry associated with these functional groupings, and in many cases derivatives have been formed to aid identification. Further reactions, on the functional groups of these compounds, which are of more synthetic importance are mentioned below.

| Reactant | Conditions | Product | | References |
|---|---|---|---|---|
| $C_6F_5OCH_3$ | $AlCl_3$, 120°C | $C_6F_5OH$ | 58% | 9, 19 |
| $C_6F_5SH$ | Diazomethane | $C_6F_5SCH_3$ | 45% | 11 |
| $C_6F_5NH_2$ | $CF_3CO_3H$ | $C_6F_5NO_2$ | 85% | 20 |
| $C_6F_5NH_2$ | $HCO_3H$ | $C_6F_5NO$ | | 21 |
| $C_6F_5NH_2$ | Diazotised in HF. $Cu_2X_2$. | $C_6F_5X$ (X = Cl,Br,I) | | 16 |
| $C_6F_5NHNH_2$ | Heat 180°C | $C_6F_5H$ | 39% | 14 |
| | | $C_6F_5NH_2$ | 44% | |
| $C_6F_5NHNH_2$ | Reduction | $C_6F_5NH_2$ | | 14 |
| $C_6F_5NHNH_2$ | Oxidation in Benzene | $C_6F_5^{\cdot}$ | | 14 |

| | | | |
|---|---|---|---|
| $C_6F_5CH = CHMe$ | $KMnO_4$ | $C_6F_5COOH$ | 17 |
| $C_6F_5CF_3$ | Fuming $H_2SO_4$ | $C_6F_5COOH$ | 22, 23 |

Pentafluorophenyl derivatives.

Nucleophilic attack on mono-substituted pentafluorobenzenes has recently been investigated by Birmingham workers. The attack by a nucleophile is of considerable interest, as different positional isomers can be formed. Although nuclear magnetic resonance spectra can determine the orientation of these disubstituted derivatives, it is necessary to compare them with tetrafluorobenzene derivatives of a known structure.

The compounds available for this work were the dihydrotetrafluorobenzenes, which were synthesised by the defluorination and dehydrofluorination of polyfluorocyclohexanes.[24-26] Their structures were confirmed by comparison with the compounds prepared by Finger[27,28] and Wall.[29] Another compound which was available, was tetrafluoro-p-benzoquinone, prepared by the hydrolysis of octafluorocyclohexa-1,4-diene with sulphuric acid.[30] The nucleophilic attack on pentafluorophenyl derivatives is summarized in the table below.

| Reactant | Nucleophilic Reagent | Product | References |
|---|---|---|---|
| $HC_6F_5$ | $LiAlH_4$ | p-$HC_6F_4H$ 83%<br>o-6% m-1% | 31 |

| Reactant | Nucleophilic Reagent | Product | | References |
|---|---|---|---|---|
| $HC_6F_5$ | $NH_2NH_2$ | p-$HC_6F_4NHNH_2$ | 63% | 31, 13 |
| | | o-2% m-0.3% | | |
| | $NH_3$ | p-$HC_6F_4NH_2$ | 62% | 31, 13 |
| | $NaOCH_3$ | $HC_6F_4OMe$ | 47% | 32, 33 |
| | | (92% p-) | | |
| | NaSH | p-$HC_6F_4SH$ | 85% | 11 |
| | KSPh | p-$HC_6F_4SPh$ | 46% | 11 |
| | p-$HC_6F_4SK$ | (p-$HC_6F_4)_2S$ | | 16 |
| $CH_3OC_6F_5$ | $NH_2NH_2$ | $C_6F_5ON_2H_5$ | 60% | 19, 33 |
| | | p-$CH_3OC_6F_4NHNH_2$ | 24% | |
| $CH_3SC_6F_5$ | $NH_3$ | p-$CH_3SC_6F_4NH_2$ | | 16 |
| $CH_3SO_2C_6F_5$ | $NH_3$ | p-$CH_3SO_2C_6F_4NH_2$ | | 16 |
| $NH_2C_6F_5$ | $NH_3$ | m-$NH_2C_6F_4NH_2$ | 34% | 13 |
| | $NH_2NH_2$ | m-$NH_2C_6F_4NHNH_2$ | 24% | 33 |
| $NH_2NHC_6F_5$ | $NH_2NH_2$ | m-$NH_2NHC_6F_4NHNH_2$ | 0.5% | 33 |
| $CH_3NHC_6F_5$ | $CH_3NH_2$ | p-$CH_3NHC_6F_4NHCH_3$ | 24% | 33 |
| $CH_3CONHC_6F_5$ | NaSH | p-$CH_3CONHC_6F_4SH$ | | 16 |
| $\frac{1}{2}SO_4^{--}\cdot\overset{+}{N}_2C_6F_5$ | NaOH | p-$NH_2C_6F_4OH$ | | 16 |
| $NO_2C_6F_5$ | $NH_3$ | o-$NO_2C_6F_4NH_2$ | 67% | 20, 33 |
| | | p-29% | | |
| $CH_3C_6F_5$ | $CH_3Li$ | p-$CH_3C_6F_4CH_3$ | 83% | 3 |
| $CF_3C_6F_5$ | $LiAlH_4$ | p-$CF_3C_6F_4H$ | 50% | 34 |

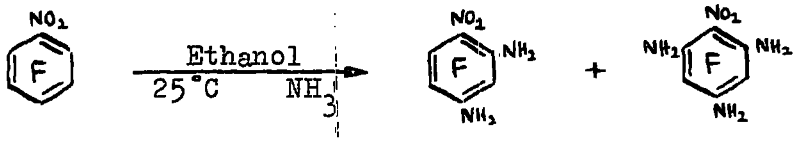
| Reactant | Nucleophilic Reagent | Product | References |
|---|---|---|---|
| $CF_3C_6F_5$ | $CH_3Li$ | p-$CF_3C_6F_4CH_3$ 40% | 34 |
| | $NH_2NH_2$ | p-$CF_3C_6F_4NHNH_2$ 36% | 34 |
| | $NH_3$ | p-$CF_3C_6F_4NH_2$ 82% | 34 |
| | NaSH | p-$CF_3C_6F_4SH$ 52% | 34 |
| | $NaOC_2H_5$ | p-$CF_3C_6F_4OC_2H_5$ 90% | 34 |
| $ClC_6F_5$ | [H] | $C_6F_4H_2$, $C_6F_3H_3$ | 18 |
| | $NaOCH_3$ | p-$ClC_6F_4OCH_3$ 50%<br>o-17% | 35 |
| | $NH_3$ | p-$ClC_6F_4NH_2$ 41%<br>o-15% | 35 |
| | $NH_2NH_2$ | p-$ClC_6F_4NHNH_2$ 45%<br>o-16% | 35 |
| | $LiAlH_4$ | $C_6F_5H$, p-$ClC_6F_4H$<br>o-$ClC_6F_4H$ | 35 |

Further reactions on these functional groups, as described before, provide an even wider variety of disubstituted tetrafluorobenzenes with known structures. Some general observations have been made about the orientation of the product, from the nucleophilic attack on pentafluorobenzenes,[16,20,34] however no mechanisms are given.

The orientation of the products appears to depend little on the reagent used; and if the substituent has no powerful electronic effects, the five fluorine atoms direct the attack to the para position. Powerful electron donating substituents direct attack into the meta position, and deactivate the nucleus. Powerful electron accepting substituents render the ortho position more susceptible to nucleophilic attack, and activate the nucleus.

## Multiple Nucleophilic Attack.

The previous examples of nucleophilic attack have been concerned with a single replacement of fluorine. However if the substituent in a pentafluorophenyl derivative can activate the system to nucleophilic attack by the withdrawal of electrons, multiple nucleophilic attack is more likely. This is illustrated by the reaction of ammonia on pentafluoronitrobenzene,[20] where at room temperature in ethanol solution both a di- and triamine were produced.



Similarly the pentafluorophenyl diazonium ion[12] is unstable in neutral or alkaline conditions, and one or more fluorine atoms are displaced by the hydroxyl group.

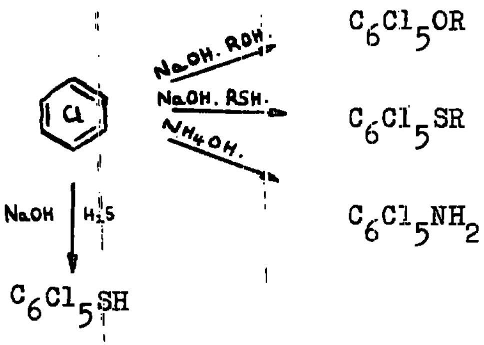
Although an activating group does help the multiple nucleophilic attack, if the reactant is submitted to nucleophilic attack either under drastic conditions, or for prolonged periods, this activation is not necessary.

Thus potassium thiophenoxide on hexafluorobenzene,[11,16] under normal conditions, gave a disulphide ($p\text{-}C_6F_4(SC_6H_5)_2$), under forcing conditions 1,4-difluorotetrakisthiophenylbenzene was formed. Similarly if an excess of potassium hydroxide in methanol is reacted with trifluoromethyldichlorotrifluorobenzene, three fluorine atoms are displaced.[36]

$$CF_3C_6Cl_2F_3 + KOH \xrightarrow[CH_3OH]{Reflux} CF_3C_6Cl_2(OMe)_3$$

The nucleophilic attack on octafluoronaphthalene has been investigated,[37] and fluorine displacement occurs in the $\beta$ position to give good yields of the heptafluoronaphthalene derivatives. (Reagents used were $NH_2NH_2$, $CH_3Li$, $LiAlH_4$, KOH and $NaOCH_3$).

Hexachlorobenzene will also undergo nucleophilic attack,[38] if pyridine is used as the solvent. This substitution does not occur so readily, compared with hexafluorobenzene, although good yields of the ether, thioether, thiophenol and amine are obtained.



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# Chapter 5.

# DISCUSSION

## Orientation in Substituted Pentafluorobenzenes.

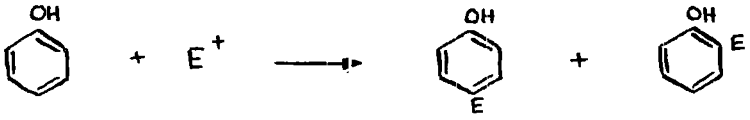
### Mono-Substituted Benzenes.

Substitution reactions involving benzene normally occur by the attack of electrophilic reagents, and it is only if a position can be suitably activated that nucleophilic attack will occur.

$$C_6H_6 + E^+ \longrightarrow C_6H_5E + H^+$$

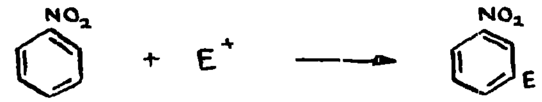
It is generally accepted that in electrophilic attack on $C_6H_5X$, the position of attack is controlled by the substituent, and not by the entering electrophile. The orientation powers of this substituent can be broadly divided into two. Firstly where X has electron donating powers, which will activate the ring towards electrophilic attack, and the positions of substitution will be ortho and para to the first substituent.

i.e.

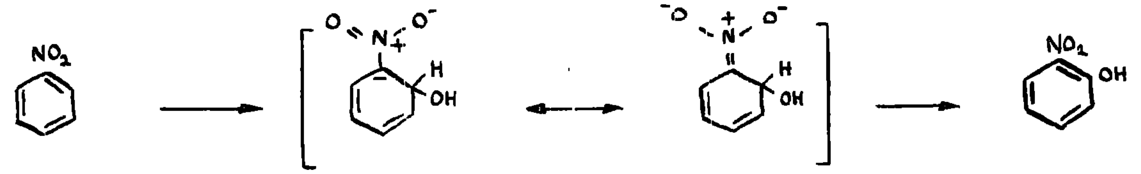


Secondly where X has electron withdrawing powers, which will deactivate the ring towards electrophilic attack, and the position of substitution will be meta to the first substituent.

i.e.



The nucleophilic attack on mono-substituted benzenes resulting in the displacement of hydrogen is not well known. However the presence of a strongly electron-withdrawing substituent might be expected to help attack by a nucleophile, if the withdrawal from the nucleus is sufficiently great. In fact, the fusion of potash with nitrobenzene, in the presence of air, will give o-nitrophenol.

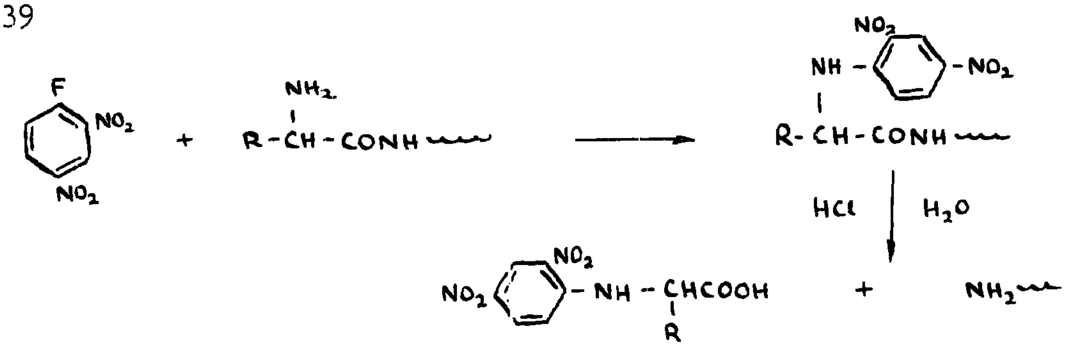


The nitro group is able to stabilize the transition state, if the hydroxyl ion enters the ortho or para positions.

Nucleophilic attack on substituted benzenes normally involves the replacement of some group other than hydrogen. This substituent is usually activated in a similar manner to that described above. The industrial preparation of phenol, is an exception to this, although very vigorous conditions have to be used.

$$C_6H_5Cl \xrightarrow[330^\circ C]{\text{Steam}} C_6H_5OH$$

The nitro substituent is the most common activating group, and nucleophilic replacements of halogens in halobenzenes containing one, two and even three nitro groups, in the ortho and para positions, are well known. One of the most interesting applications of this type of reaction is the degradation of polypeptides with 2,4-dinitrofluorobenzene.[39]

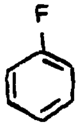


The replacement of the fluorine atom by the nitrogen atom of a free amine group occuring under very mild conditions.

Thus the nucleophilic attack on substituted benzenes will not only rely on the activation effects of the various substituents in the ring, but also on the group which is replaced. For the reaction to occur under mild conditions, the group which is displaced by the nucleophile must be a good leaving group, i.e. it must have a reasonably high electron affinity. The most easily replaceable group is the fluorine atom, followed by the nitro group and then the other halogen atoms. The position of orientation in these reactions is unambiguous, as there is normally only one replaceable group.

## Pentafluorobenzenes.

In the past discussion it has been shown that fluorine is a very effective leaving group. Also, because of its high electronegativity, it has a very strong electron withdrawing effect on the benzene nucleus. Thus it can activate the ring system towards nucleophilic attack.

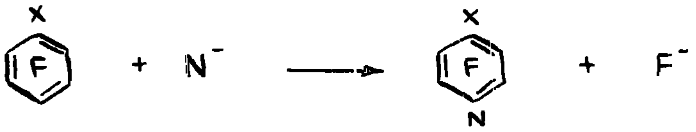


Dipole Moment ↑ 1.5D.[41]

Therefore an aromatic ring system containing a number of fluorine atoms, must be very susceptible to nucleophilic attack; and the question of the position of such an attack must enter the discussion.

Perhaps the most interesting compounds to study are the mono-substituted pentafluorobenzenes ($C_6F_5X$). It is of great interest to find if the position of attack is controlled by the five fluorine atoms, by the substituent (X), or in fact by both.

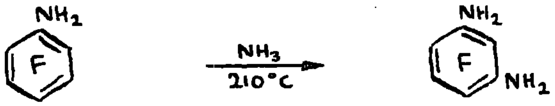
It has been found that nucleophilic attack on mono-substituted pentafluorobenzenes, normally occurs in the para position (see page 150).



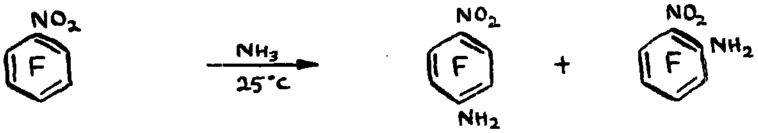
In a few cases a very small percentage of the ortho and meta isomers have also been isolated. However, if the substituent (X) is either very strongly electron withdrawing or very strongly electron donating, the orientation of nucleophilic attack is affected.

i.e.

1)



2)



In the reaction giving meta substitution (1) the ring is deactivated by the powerful electron donating power of the amine grouping, and a high temperature has to be used for attack to occur. However in the substitution of pentafluoronitrobenzene, the nitro group is able to withdraw electrons from the ring. This activation towards nucleophilic substitution allows the reaction to occur at room temperature.

Nucleophilic reactions on pentafluorobenzene, pentafluoro-N-methylaniline, pentafluorotoluene, octafluorotoluene and pentafluorophenyl diazonium sulphate give only the para substituted derivatives. Thus it seem that the five fluorine atoms control the reaction, and substitution occurs in the para position, unless the substituent has sufficiently strong electron donating, or withdrawing powers to overcome this effect.

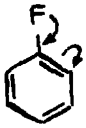
Pentafluorobenzene.

The first case which will be considered is pentafluorobenzene ($C_6F_5H$). This should be the simplest case as hydrogen should have no electronic effect on the ring system. The electron distribution in pentafluorobenzene can be found by considering the distribution in hexafluorobenzene, and then considering the effect of removing one fluorine atom, and replacing it with a hydrogen atom. The electronic effects of a fluorine atom on an aromatic ring system must therefore be considered[41].

It is well known that fluorine has a large electronegativity and can withdraw electrons from an aromatic ring (-ve inductive effect). However fluorine can also donate electrons from its full p orbitals, into the empty antibonding orbitals of the aromatic ring system. This effect (+ve mesomeric effect) is quite strong, as both orbitals are of the same energy level and symmetry.

(-I)

and

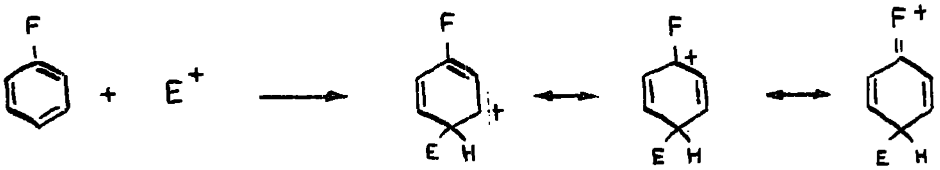


(+M)

The dipole moment of fluorobenzene is 1.5D, this is 0.3D less than methyl fluoride (1.8D), where the mesomeric effect cannot operate.

Thus the mesomeric effect is considerably less than the inductive effect, in the ground state of the fluorobenzene molecule. However electrophilic attack on fluorobenzene occurs mainly in the para position, at a rate slightly greater than the electrophilic attack on benzene. This is explained by the fact that the fluorine atom has a very much more powerful mesomeric effect, at the demand of the reagent; this is called the electromeric effect.

i.e.

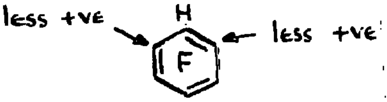


Therefore the overall effect of the fluorine atom, in the electrophilic attack on fluorobenzene, must be the donation of electrons into the ring system, mainly in the para position. This electromeric effect can only occur with electrophilic attack, and the overall effect of the fluorine atom in nucleophilic attack is, therefore, the strong withdrawal of the electrons from the ring system.

If one fluorine is removed from hexafluorobenzene and replaced by hydrogen, both the inductive and mesomeric effects on the rest of the molecule must be considered.

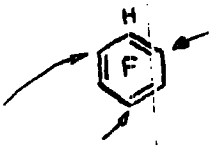
<u>Inductive effect</u>. Fluorine removes electrons mainly from the ortho positions. Thus on replacement by hydrogen, we have:-

(I)



Mesomeric effect. This is not such a strong effect as the inductive, but it is felt by donation of electrons to the ortho and para positions equally. Therefore on replacement by hydrogen, we have:-

(M)

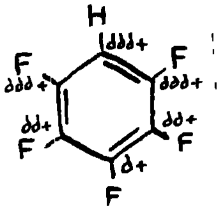


Slightly more + ve

Slightly more + ve

The electronic effect of the five fluorine atoms on the carbon-hydrogen bond must also be considered. It is probable that as the ring is depleated of electrons by the fluorine atoms, that the hydrogen atom will be electron-donating. However this donation of electrons to the ring system will probably be taken up by the fluorine atoms in positions 2 and 6 (i.e. the ortho positions).

Thus the overall electronic picture of the ring system can be shown thus:-*



Therefore considering the electronic distribution in pentafluorobenzene, nucleophilic attack should occur in the para position. However the nucleophile should also attack in a position where the extra electron can be shared most profitably in the transition state. From the

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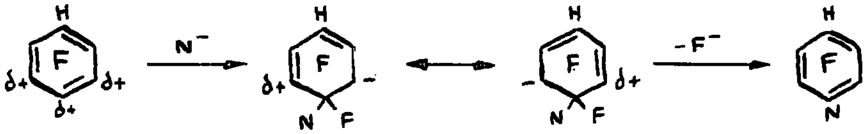
( * Successive δs indicate smaller quantities).

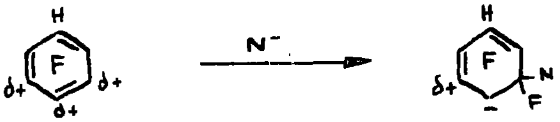
electronic picture of the ring system, it can be seen that carbon atoms 1, 2 and 6 are almost neutral, whereas carbon atoms 3, 4 and 5 are positive. Thus attack should occur in position 4, where the -ve charge, in the transition state, can be shared equally by carbon atoms 3 and 5.

i.e.



If nucleophilic attack occurred in the meta position, only one carbon atom can share this electron.

i.e.



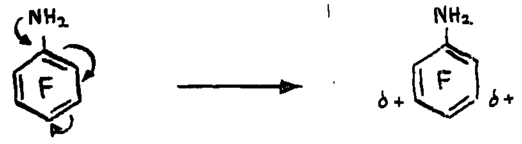
The nucleophilic attack on pentafluorobenzene is summarized on page 150, and it can be seen that attack occurs almost exclusively in the para position.

The effect of other substituents can be found, although it is necessary to consider each in turn. The examples given below are the most interesting and cover the widest range possible.

Pentafluoroaniline.

The inductive effect of the nitrogen in the amine group is fairly small, and is counteracted by the nitrogen atoms pronounced ability to release electrons, mesomerically, into the aromatic system. It will do this, equally, in the ortho and para positions.

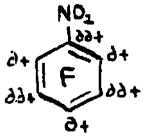
i.e.



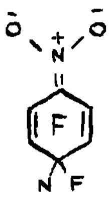
Therefore pentafluoroaniline should be very much less susceptible to nucleophilic attack than pentafluorobenzene. The position of such an attack should be in the meta position, with relation to the amine group. These observations are borne out in practice (page 151).

Pentafluoronitrobenzene.

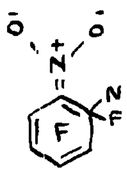
The nitro group, due to the mesomeric effect, is very powerfully electron attracting. Thus the overall charge on the carbon atoms can be shown thus:-



The ring system is, therefore, greatly activated towards nucleophilic attack, and attack should occur in the ortho and para positions. The electromeric effect (the supply or withdrawal of electrons at the demand of the reagent), is probably operating, and the transition state is stabilized by such resonance structures as:-



and



(a)

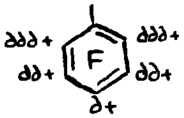
(b)

However it can be seen from these structures that the carbon atom containing the nitro group must be in the same plane as the ring. The para quinoid structure (a) cannot very easily attain this planarity, due to steric hinderence from the two planar ortho fluorine atoms. The ortho quinoid structure (b) should be more stable as one ortho fluorine atom is no longer planar. The reaction between pentafluoronitrobenzene and ammonia (page 151) occurs very readily at room temperature to give mainly ortho aminotetrafluoronitrobenzene.

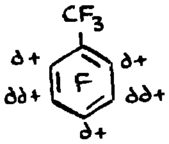
Both pentafluoroaniline and pentafluoronitrobenzene have extremely powerful electronic effects on the aromatic ring system. It is naturally of interest to study pentafluorophenyl compounds where the substituent is not quite so powerful; but where these effects are substantially different from the hydrogen atom present in pentafluorobenzene.

Octafluorotoluene.

It has been shown that the electronic distribution of the pentafluorophenyl ring system can be represented as (1) below.

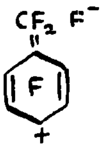


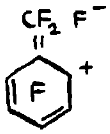
(1)



(2)

The trifluoromethyl group, which has a strong inductive effect but no mesomeric effect, can withdraw electrons from the ortho positions, giving the electron distribution as shown in (2). It has been suggested[41] that the trifluoromethyl group has a hyperconjugative effect on the aromatic ring system.

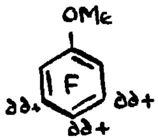
i.e. 

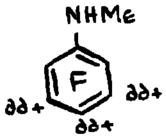
and 

Although there is no definite proof of this, the ortho and para positions would become more positive, accentuating the above electronic distribution (2). The nucleophile should therefore attack in both the ortho and para positions. However it has been observed (see page 151 ) that attack occurs almost exclusively in the para position. This is probably due to steric hindrance, in the ortho positions, by the large trifluoromethyl group.

Pentafluoroanisole and Pentafluoro-N-methylaniline.

Both these substituents can back donate electrons into the system, which should be deactivated towards nucleophilic attack. This donation should not be as great as the amine group.[40] The electronic distribution in the ring system is given below.



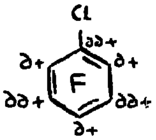


The nucleophilic reactions of these compounds have not been thoroughly investigated; however the reaction of the anisole with further methoxide ion, and the methylaniline with methylamine, gave mainly the para orientated substituent (see page 151), although it is possible that some meta substitution occurred.

The main position of attack (as explained before), occurs in such a position that the negative charge, in the transition state, can be removed most easily. This is the para position as the negative charge can be shared equally by the two meta fluorine atoms.

Chloropentafluorobenzene.

The electonic effects of the chlorine atom are very similar to those of the fluorine atom. Thus the nucleophilic attack should be more of a random nature than in for example, pentafluorobenzene. The inductive effect of chlorine and fluorine are almost identical; however, the mesomeric back donation of the chlorine electrons is slightly less than in fluorine. This will make both the ortho and para positions more positive. The electronic distribution in the ring system should be as shown below:-



Therefore, attack should occur in both the ortho and para positions. It will be seen from the following discussion that nucleophilic attack on chloropentafluorobenzene gives both the ortho and para orientated substituents. The nature of the nucleophile seems to have little affect on the distribution of the isomeric derivatives.

# Discussion of Experimental Work

## Chloropentafluorobenzene and Sodium Methoxide.

The reaction between chloropentafluorobenzene and a slight excess of sodium methoxide gave a good yield (70%) of the chlorotetrafluoroanisoles. The analytical scale vapour phase chromatogram of the product is shown in Fig. XVII page 180a, and has three peaks. The two major components were isolated by preparative scale V.P.C., and shown by N.M.R. to be o-$C_6ClF_4OMe$ and p-$C_6ClF_4OMe$.

The separation in any quantity of the pure isomers, by this method, was extremely laborious, as the retention times were almost identical. The pure compounds, uncontaminated by other isomers, could only be obtained if the material was recycled three times. The chromatogram, as well as showing the two major components, contained a small peak in between the two major ones. This could be the meta isomer, however it was present in very small quantity and could not be isolated for identification.

The possibility of this unidentified material being pentafluoroanisole, or tetrafluorodimethoxybenzene (i.e. by removal of chlorine), was eliminated by preparing these compounds by the reaction of hexafluorobenzene with sodium methoxide.[8,9]

$$C_6F_6 + CH_3ONa \longrightarrow C_6F_5OMe + C_6F_4(OMe)_2$$

These had retention times, using analytical scale V.P.C., very different from the chlorotetrafluoroanisoles. The possibility of substitution of the chlorine atom, was also checked by treating the acidified water effluent (produced in the working up procedure), with silver nitrate solution. No precipitate was formed indicating that no chloride ion was present.

Thus if we assume the minor component to be m-$C_6ClF_4OMe$, the isomer distribution can be given. It must be borne in mind that this distribution differs slightly due to the amount and ratio of the reactants.

| Average distribution:- | o-$C_6ClF_4OMe$ | 25% |
|---|---|---|
| | m-$C_6ClF_4OMe$ | 5% |
| | p-$C_6ClF_4OMe$ | 70% |

This is in agreement with the postulate that nucleophilic attack on chloropentafluorobenzene will give the ortho and para isomers, rather than just the para isomer found in most nucleophilic reactions of pentafluorobenzenes. (see page 150). Similar nucleophilic attacks on chloropentafluorobenzene described in the following pages, show that this isomer distribution is not altered.

The chlorine atom present in chloropentafluorobenzene appears to be considerably more stable to nucleophilic attack than the fluorine atoms. However work in these laboratories[42] has shown that a considerable amount of chlorine can be removed in the reaction of chloropentafluorobenzene and lithium aluminium hydride. This is a relatively powerful nucleophilic reagent,[31] and will replace the halogens with hydrogen. The product has been shown to contain pentafluorobenzene and para dihydrotetrafluorobenzene, as well as the ortho and para isomers of chlorotetrafluorobenzene. The amount of chlorine removed was found by titration to be 44%.

$$C_6ClF_5 + LiAlH_4 \longrightarrow C_6HF_5 + p\text{-}C_6H_2F_4 + o\text{-}C_6HClF_4 + p\text{-}C_6HClF_4$$

Two other reactions have been found where the chlorine can be eliminated; firstly the Ullmann reaction, which is described on page 179; and secondly by the formation of the Grignard reagent and consequent hydrolysis.[42] Thus chloropentafluorobenzene, gives pentafluorophenyl magnesium chloride. Hydrolysis of this gives a 65% yield of pentafluorobenzoic acid.

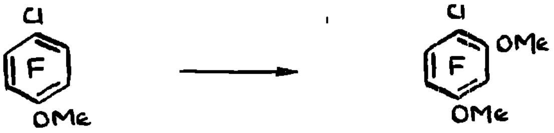
$$C_6ClF_5 + Mg \xrightarrow{Et_2O} C_6F_5MgCl \xrightarrow[CO_2]{T.H.F.} C_6F_5COOH.$$

Para Chlorotetrafluoroanisole.

This was isolated by preparative scale V.P.C. more easily than the ortho isomer, as it was present in larger proportions (70%).

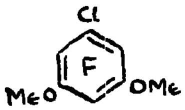
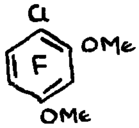
i) The position of the substituants was verified by a chemical method. The p-$C_6ClF_4OMe$ was reacted with magnesium to form the Grignard reagent, consequent hydrolysis gave the p-tetrafluoroanisole, which was identified by its infra red spectrum.[32]

ii) Further reaction with sodium methoxide gave the chlorotrifluorodimethoxybenzene (59%). From the previous discussion (see page 169), it was shown that chloropentafluorobenzene will direct nucleophilic attack mainly to the ortho and para positions, and pentafluoroanisole to the meta and para positions. However both the para positions are filled in p-chlorotetrafluoroanisole, so the next substitution would be expected to occupy the ortho position to the chlorine.



The analytical scale vapour phase chromatogram showed the presence of mainly one isomer (95%). This was isolated and shown by N.M.R. to be 1-chlorotrifluoro-2,4-dimethoxybenzene.

N.M.R. shows that a fluorine atom ortho to a methoxy group can couple with the three hydrogen atoms. In the chlorotrifluorodimethoxybenzene prepared above, the N.M.R. spectrum shows that one fluorine present couples with six hydrogens, i.e. it must have two ortho methoxy groups. There are only two structures where the fluorine can have two methoxy groups in the ortho position.

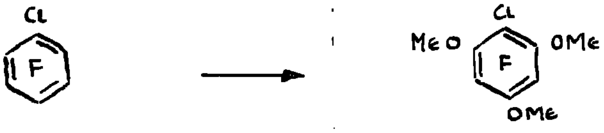
i.e.  (1)  (2)

The spectrum also shows that one fluorine present does not couple with any hydrogens. This shows that 1-chlorotrifluoro-2,4-dimethoxybenzene is the compound prepared above.

## Further reaction of Chloropentafluorobenzene with Sodium Methoxide.

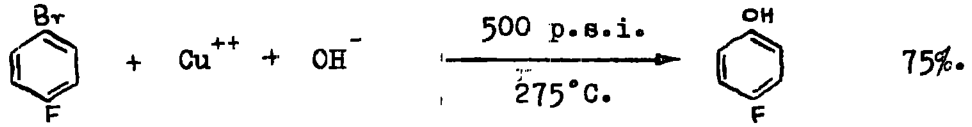
Pyridine has been used as a solvent to facilitate nucleophilic substitution reactions in highly halogenated benzenes.[9,11,38] It was thought that the reaction between chloropentafluorobenzene and sodium methoxide in pyridine solution, might aid the removal of chlorine and produce pentafluoroanisole. However analytical scale V.P.C. showed that this reaction product contained only the chlorotetrafluoroanisole and unreacted starting material.

The reaction of chloropentafluorobenzene with excess sodium methoxide (see Fig. XVIII page 180a), gave the 1-chlorotrifluoro-2,4-dimethoxybenzene (46%), and a further substituted chlorodifluorotrimethoxybenzene (37%). The latter compound was shown by analytical scale V.P.C. to contain mainly one isomer. This is probably the 1-chlorodifluoro-2,4,6-trimethoxybenzene.

i.e. 

## Chloropentafluorobenzene and Calcium Hydroxide.

It was noticed in the hydrolysis of p-bromofluorobenzene with aqueous calcium hydroxide, at elevated temperatures and pressures, and in the presence of a copper catalyst, that p-fluorophenol was produced.[43] The bromine was preferentially eliminated and no p-bromophenol was produced.



Chloropentafluorobenzene was reacted under similar conditions, to eliminate chlorine in preference to fluorine, and produce pentafluorophenol. However analytical scale V.P.C. indicated the absence of this compound in the reaction product. An authentic sample was prepared by the action of potassium hydroxide and tertiary butyl alcohol on hexafluorobenzene.[10]

## Chloropentafluorobenzene and Sodium Iodide.

The reaction of chloropentafluorobenzene and sodium iodide in acetone solution was investigated.

i.e. $$C_6ClF_5 + NaI \xrightarrow{\text{Acetone}} C_6IF_5 + NaCl$$

The insolubility of sodium chloride should facilitate this reaction. Analytical scale V.P.C. indicated only the presence of unreacted starting material.

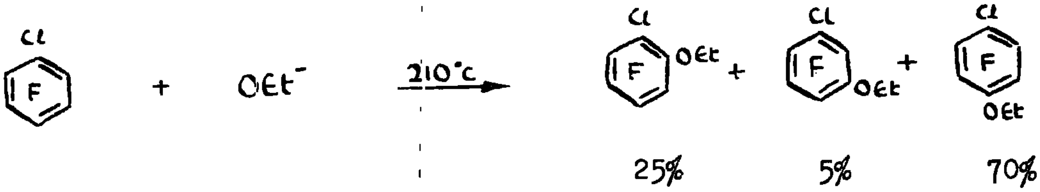
## Chloropentafluorobenzene and Ammonia.

Chloropentafluorobenzene was reacted with a large excess of ammonia at 175 ° C, to produce chlorotetrafluoroaniline (58%). The amine group will deactivate the molecule to further nucleophilic attack, and thus the disubstituted amine would only be formed at higher temperatures.

The chlorotetrafluoroaniline was shown by analytical scale V.P.C. to contain two main and one minor component. The two major components (see fig. XIX page 167a) were isolated by preparative scale V.P.C., and shown by N.M.R. to be the ortho and para isomers. The minor component could not be separated, however assuming this to be the meta isomer, the product distribution was:-

| | |
|---|---|
| o-$C_6ClF_4NH_2$ | 25% |
| m-$C_6ClF_4NH_2$ | 5% |
| p-$C_6ClF_4NH_2$ | 70% |

The presence of a small amount of impurity (5%), found in the reaction where a temperature of 210 ° C was reached, is rather interesting. Analytical scale V.P.C. (see Fig. XIX) showed that it was composed of three compounds present in the same ratio as the ortho, meta and para chlorotetrafluoroanilines. Impurities present in the amination of other highly fluorinated compounds[20,34] have been shown to be due to the nucleophilic attack, by the solvent ethanol. The amination of chloropentafluorobenzene does not form the pentafluoroaniline, as no chloride ion can be detected. Thus the impurities present are probably due to nucleophilic attack by the solvent



Chloropentafluorobenzene and Hydrazine.

The reaction between chloropentafluorobenzene and hydrazine hydrate gave a white crystalline solid, chlorotetrafluorophenylhydrazine (65%), which was found to be water soluble. The compound decomposed on heating to its melting point, and thus the isomers could not be separated by preparative scale V.P.C. However pentafluorophenylhydrazine had been reduced by aqueous hydriodic acid to pentafluoroaniline.[14] Thus the chlorotetrafluorophenylhydrazine was reduced by this method, to give the chlorotetrafluoroanilines. The isomer ratio of this was determined by analytical scale V.P.C., and thus the original isomer distribution of the chlorotetrafluorophenylhydrazines found.

| | |
|---|---|
| o-$C_6ClF_4NHNH_2$ | 22% |
| m-$C_6ClF_4NHNH_2$ | 6.5% |
| p-$C_6ClF_4NHNH_2$ | 71.5% |

## Chloropentafluorobenzene and Copper Powder.

The reaction between chloropentafluorobenzene and copper powder gives good yields of decafluorodiphenyl. However the reaction time was substantially longer than that required for the condensation of bromopentafluorobenzene[1].

# Chapter 6.

# EXPERIMENTAL WORK

## Chloropentafluorobenzene and Sodium Methoxide.

1) Chloropentafluorobenzene (20gms, 0.1M) was refluxed with sodium methoxide (8.1 gms, 0.15M) in dry methanol (120 mls) for two hours. The reaction product was poured into water (250 mls) and ether extracted (three times with 75 mls of diethyl ether). The etherial extract was dried (anhydrous $MgSO_4$), and the ether and methanol distilled. The residue (16.4 gms) was shown by A.S.V.P.C. (see fig. XVII) to contain unreacted $C_6ClF_5$ 7%; $C_6ClF_4OMe$ 90%, (mainly the ortho and para isomers, although a small peak with a retention time inbetween these isomers, could be the meta isomer); $C_6ClF_3(OMe)_2$ 3%.

The mixture of isomers was separated, (P.S.V.P.C. T.C.P. column at 150°C; P.D. 15 cms. Hg; nitrogen 200 ccs/min.).
Analysis gave: Cl, 16.3, F, 35.3%; calc. for $C_6ClF_4OMe$: Cl, 16.5, F, 35.4%.

The two main isomers were separated, (P.S.V.P.C. T.C.P. column at 150°C; P.D. 15 cms Hg; nitrogen 200 ccs/min; recycled twice). They were shown by N.M.R. measurements to be the ortho and para chlorotetrafluoroanisoles.

Ortho chlorotetrafluoroanisole. $n_D^{20}$ 1.44805. B.p. 176°C. Infra red spectrum no. 21, page 192.
Analysis gave: Cl, 15.7, F, 35.7%; calc. for $C_6ClF_4OMe$: Cl, 16.5, F, 35.4%.

Para chlorotetrafluoroanisole. $n_D^{20}$ 1.45534. B.p. 177.5°C. Infra

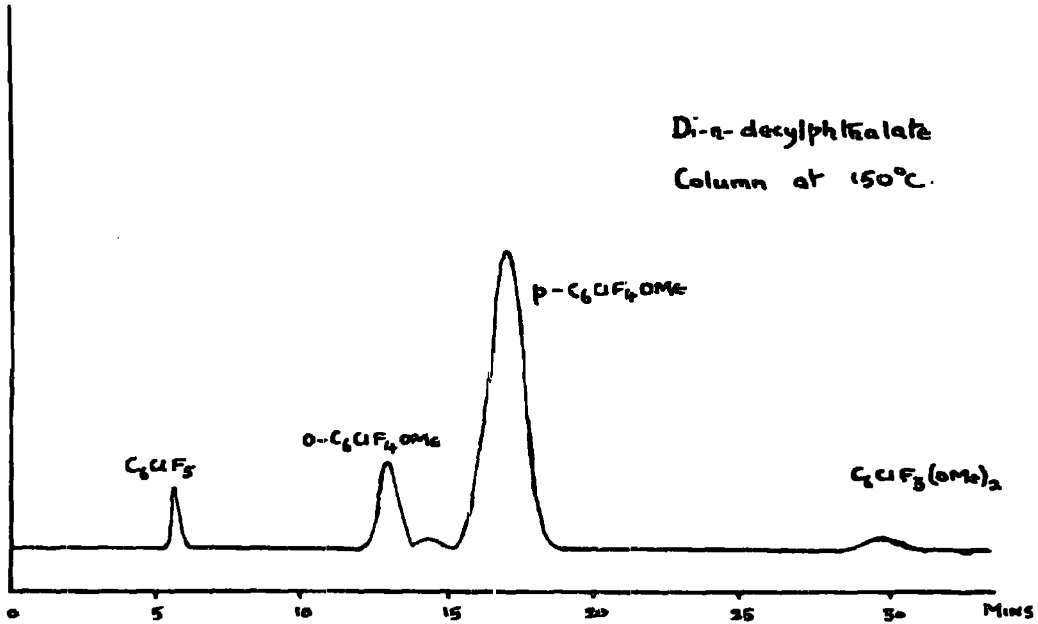


Fig XVII Reaction product from $CH_3ONa$ and $C_6ClF_5$

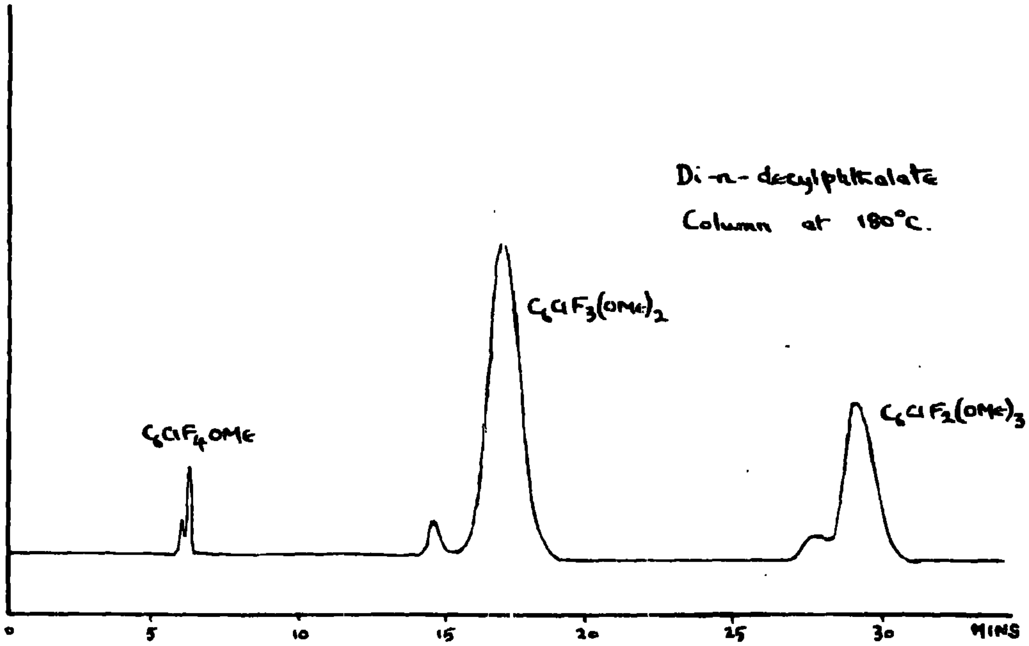


Fig. XVIII Reaction product from excess $CH_3ONa$ and $C_6ClF_5$

red spectrum no. 22.

Analysis gave: Cl, 16.1, F, 35.2%; Calc. for $C_6ClF_4OMe$: Cl, 16.5, F, 35.4%.

The overall yield of the mixed isomers was 70%. The relative response of each isomer on the A.S.V.P.C. was found by injecting weighed samples. The isomer distribution in the product, assuming the middle peak to be the meta isomer, was:-

| | |
|---|---|
| o-$C_6ClF_4OMe$ | 20% |
| m-$C_6ClF_4OMe$ | 4% |
| p-$C_6ClF_4OMe$ | 76% |

2) The above reaction was repeated using chloropentafluorobenzene (5 gms, 0.025M) and sodium methoxide (2.7 gms, 0.05M) in dry methanol (30 mls). This was refluxed for three and a half hours to give 3.6 gms. of product, which was shown by A.S.V.P.C. to contain $C_6ClF_4OMe$ 91% and $C_6ClF_3(OMe)_2$ 9%.

Addition of silver nitrate to the acidified water effluant showed only a very slight cloudyness. This indicated that no chlorine had been removed. The isomer distribution showed:-

| | |
|---|---|
| o-$C_6ClF_4OMe$ | 31% |
| m-$C_6ClF_4OMe$ | 7% |
| p-$C_6ClF_4OMe$ | 66% |

## Para Chlorotetrafluoroanisole and Magnesium.

Magnesium (1.5 gms., 0.065 M), in diethyl ether (15 mls.), was refluxed with ethylene bromide (1.0 mls.) for twenty minutes. p-Chlorotetrafluoroanisole (1.0 gms., 0.005 M) was then added to the refluxing mixture. The addition of ethylene bromide (0.5 mls.) was repeated after twenty minutes and one hour. The reaction mixture was cooled after refluxing for a further one and a half hours. The liquid, which formed two layers, was decanted and acidified with sulphuric acid (10 mls., 2 N). The etherial layer was separated, dried (anhydrous $MgSO_4$), and the ether distilled.

The product (0.7 gms.) was shown by A.S.V.P.C. to contain starting material 7%, and $C_6HF_4OMe$ 85% (yield 50%). The anisole was separated, using the Griffin and George V.P.C. M.K.2a. (Si. El. column at 130°C), and shown to be 2,3,5,6-tetrafluoroanisole by comparison of the infra red spectrum (No. 25) with the spectrum of 2,3,5,6-tetrafluoroanisole prepared by the reaction of sodium methoxide on pentafluorobenzene[32,42].

## Para Chlorotetrafluoroanisole and Sodium Methoxide.

p-Chlorotetrafluoroanisole (1.5 gms., 0.007 M) was refluxed with sodium methoxide (2.0 gms., 0.035 M) in dry methanol (10 mls.) for seven hours. The reaction product was poured into water (50 mls.), and ether extracted. The extract was dried, (anhydrous $MgSO_4$) and the ether and methanol distilled. The residue (1.1 gms) was shown by A.S.V.P.C. to contain p-$C_6ClF_4OMe$ 10%, $C_6ClF_3(OMe)_2$ 80% (yield 56%, this consisted of two peaks present in 20:1 ratio, they were probably two isomers), $C_6ClF_2(OMe)_3$ 10%.

The major isomer was separated ( P.S.V.P.C. Si. El. Column at 210°C; P.D. 10 cms Hg; nitrogen 250 ccs/min. ) , and shown by N.M.R. to be 1-chlorotrifluoro-2,4-dimethoxybenzene. This was twice recrystallized from petroleum ether (40-60°C).

$C_6ClF_3(OMe)_2$. M.p. 25°C. Infra red spectrum no. 23.
Analysis gave:- Cl, 16.0, F, 24.4%; calc. for $C_6ClF_3(OMe)_2$: Cl, 15.7, F, 25.2%.

Other Reactions with Sodium Methoxide.

i) Chloropentafluorobenzene (2.0 gms, 0.01M) in pyridine (10 mls) was added slowly to sodium methoxide (0.54 gms, 0.01M) in dry methanol (2.5 mls), and refluxed for one hour. The reaction product was made slightly acidic, (dil. $H_2SO_4$) and ether extracted. The etherial extract was dried, and the ether distilled to give 0.8 gms of product. This was shown by A.S.V.P.C. to contain $C_6ClF_5$ 15%, and $C_6ClF_4OMe$ 85% (as a mixture of isomers).

ii) Chloropentafluorobenzene (5 gms, 0.025M) was refluxed with excess sodium methoxide (10.8 gms, 0.2M) in dry methanol (30 mls), for seven hours. The reaction product was poured into water (100 mls), and ether extracted. The extract was dried, and the ether and methanol distilled. The residue (4.3 gms.) was shown by A.S.V.P.C. (see fig. XVIII) to contain $C_6ClF_4OMe$ 3%, $C_6ClF_3(OMe)_2$ 60%, (yield 46%, this consisted of 93% of the major isomer), $C_6ClF_2(OMe)_3$ 37%, (yield 28%, this consisted of two peaks in 1:5 ratio, they were probably two isomers).

$C_6ClF_3(OMe)_2$ was separated, (P.S.V.P.C. Si. El. column at 210°C; P.D. 40 cms. Hg; nitrogen 170 ccs/min.) and shown by N.M.R. measurements to be 1-chlorotrifluoro-2,4-dimethoxybenzene.

$C_6ClF_2(OMe)_3$ was separated by distillation as a mixture of isomers (at 0.1 mm. of mercury). Infra red spectrum no. 24.

Analysis gave: C, 45.1, Cl, 14.6, F, 16.5%; calc. for $C_6ClF_2(OMe)_3$: C, 45.3, Cl, 14.9, F, 15.9%.

iii) Hexafluorobenzene (1.86 gms., 0.01 M) was refluxed with sodium methoxide (0.54 gms., 0.01 M) in dry methanol (12 mls.) for one hour[8]. The reaction mixture was worked up as before to give 1.90 gms. of product, which was shown by A.S.V.P.C. to contain methanol 13%, $C_6F_6$ 7% and $C_6F_5OMe$ 80%.

A similar reaction with hexafluorobenzene (0.93 gms., 0.005 M), sodium methoxide (0.54 gms., 0.01 M) and methanol (8 mls.) was refluxed for one and a half hours to give 0.4 gms. of product. This was shown by A.S.V.P.C. to contain $C_6F_5OMe$ 80% and $C_6F_4(OMe)_2$ 20%.[8]

The retention times (using A.S.V.P.C.) of pentafluoroanisole and tetrafluorodimethoxybenzene, were used to determine if these compounds were formed in the reactions between chloropentafluorobenzene and sodium methoxide. However in no reaction could the slightest trace of either compound be detected.

## Chloropentafluorobenzene and Aqueous Calcium Hydroxide.

Chloropentafluorobenzene (2.63 gms, 0.013M), calcium hydroxide (0.96 gms, 0.013M), water (9mls) and cuprous oxide (0.026 gms) were placed in a revolving autoclave (50 ml capacity). The autoclave was heated at 250°C for two and a half hours.

The product was washed out with ether (10 mls) and water (10 mls), filtered and acidified. The organic product was extracted with ether, dried (anhydrous $MgSO_4$) and the ether distilled. The product (0.65 gms) was shown by A.S.V.P.C. and an infra red spectrum to contain only starting material.

## Hexafluorobenzene and Potassium Hydroxide.

Hexafluorobenzene (1.86 gms, 0.01M) and potassium hydroxide (1.4 gms, 0.03M) were refluxed for one hour in tertiary butyl alcohol (15 mls).[10] Water (30 mls) was added to the product and the alcohol distilled. The cooled suspension was filtered and the filtrate acidified with sulphuric acid (20 mls, 2.0N). The organic product was extracted with ether, dried (anhydrous $MgSO_4$) and the ether distilled. The product (1.35 gms) was shown by A.S.V.P.C. to contain tertiary butyl alcohol 30% and pentafluorophenol 70%.

The retention time (using A.S.V.P.C.) of pentafluorophenol was used to determine if it was formed in the reaction between chloropentafluorobenzene and aqueous calcium hydroxide.

## Chloropentafluorobenzene and Sodium Iodide.

Chloropentafluorobenzene (1.2 gms, 0.006 M) was placed in a Carius tube with sodium iodide (0.87 gms, 0.006M) and dry acetone (10 mls). The tube was sealed and shaken for twelve hours at 70°C. The product was poured into water (50 mls) and ether extracted. The extract was dried and the ether distilled to give 0.9 gms of product. This was shown by A.S.V.P.C. and an infra red spectrum to be only unchanged starting material.

## Chloropentafluorobenzene and Ammonia.

Two Carius tubes were separately charged with chloropentafluorobenzene (5.0 gms, 0.025 M), '880' ammonia (10 mls, 0.25 M) and ethanol (20 mls). They were heated for sixteen hours, one at 165°C, the temperature of the other inadvertently rose to 210°C. It was not thought necessary to work up the reaction product separately. The contents of both tubes were poured into ether (250 mls) and dried (anhydrous $MgSO_4$). The ether and ethanol were removed by distillation to give 7.45 gms. of a liquid, shown by A.S.V.P.C. (see fig. XIX) to contain ethanol 20%, $C_6ClF_4NH_2$ 75% (mainly the ortho and para isomers, although a small peak, with a retention time in between these isomers, could be the meta isomer), and 5% of an unidentified material.

The two main isomers were separated (P.S.V.P.C. Si. El. column at 160°C; P.D. 10 cms. Hg; nitrogen 250 ccs/min.; recycled twice), and shown by N.M.R. to be the ortho and para isomers of $C_6ClF_4NH_2$

o-$C_6ClF_4NH_2$. Further purified using the Griffin and George V.P.C. Mk. 2a. (Si. El. column at 150°C). M.p. 22-23°C. Infra red spectrum no. 26.

Analysis gave: Cl, 17.6, F, 37.6%; calc. for $C_6ClF_4NH_2$: Cl, 17.8, F, 38.1%.

p-$C_6ClF_4NH_2$. Twice recrystallized from carbon tetrachloride. M.p. 55-56°C. Infra red spectrum no. 27.

Analysis gave: Cl, 17.6, F, 38.2%; calc. for $C_6ClF_4NH_2$: Cl, 17.8, F, 38.1%.

The overall yield of $C_6ClF_4NH_2$ was 58%. The isomer distribution in the product, if the small middle peak was the meta isomer, was

| | |
|---|---|
| o-$C_6ClF_4NH_2$ | 25%. |
| m-$C_6ClF_4NH_2$ | 5%. |
| p-$C_6ClF_4NH_2$ | 75%. |

A similar experiment was carried out using chloropentafluorobenzene

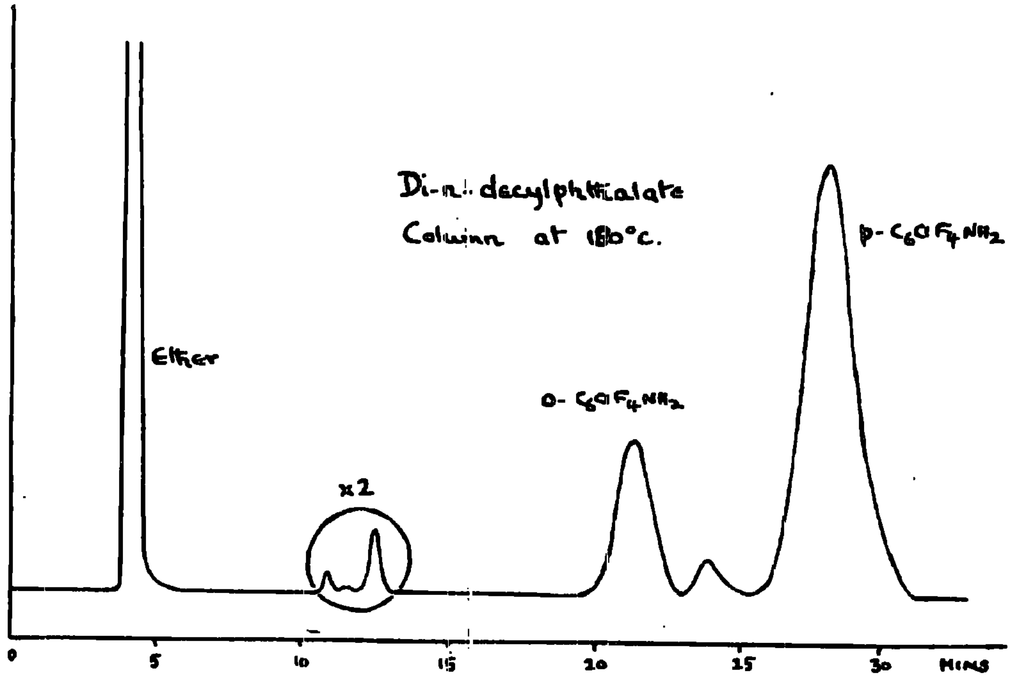


Fig XIX Reaction product from $NH_3$ and $C_6ClF_5$

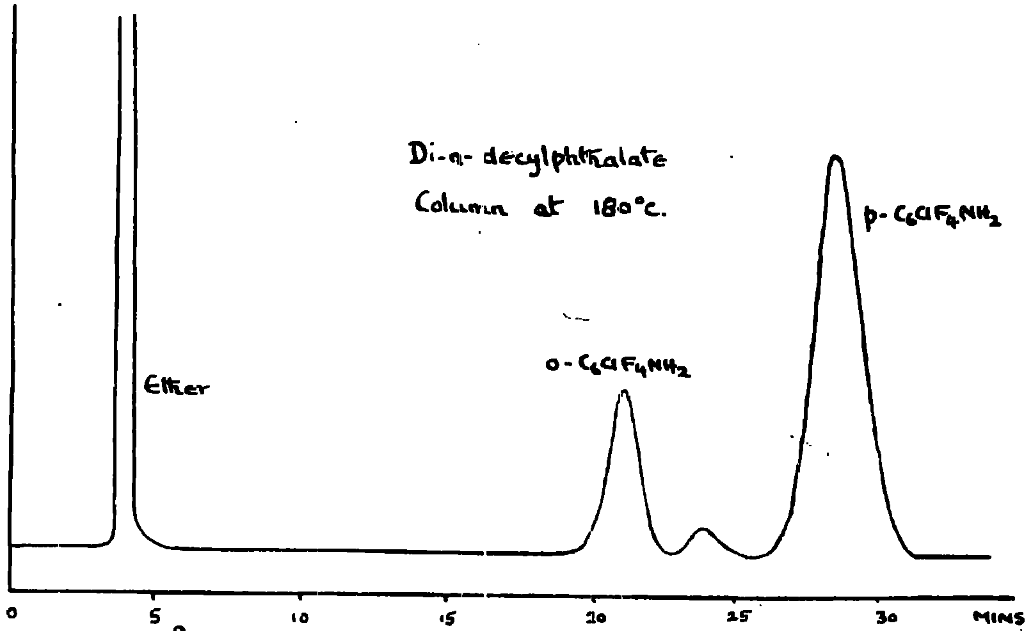


Fig XX Reaction product from HI and $C_6ClF_4NHNH_2$

(2.0 gms., 0.01 M), "880" ammonia (4 mls., 0.1 M) and ethanol (8 mls.). The tube was heated at 175°C. for seventeen hours. The contents of the tube were poured into ether (150 mls.), and the small water layer tested for chloride ion, (a sample was acidified with dilute sulphuric acid, and silver nitrate was added). No precipitate of silver chloride was formed.

The two layers were treated with anhydrous $MgSO_4$, and the ether distilled from the filtrate. The product was then distilled at 100-130°C., at 0.1 mm. of mercury, to give 0.8 gms. of a white solid, which slowly turned black in air. This was sublimed to give $C_6ClF_4NH_2$ (mixture of isomers). Melting range 50-70°C.

Chloropentafluorobenzene and Hydrazine Hydrate.

i) Chloropentafluorobenzene (5.0 gms., 0.025 M) and hydrazine hydrate (15 gms., 0.3 M) were refluxed together in water (10 mls.) and ethanol (30 mls.) for twelve hours. The product was poured into ice water (100 mls.), and the precipitate formed was filtered to give 1.6 gms. of $C_6ClF_4NHNH_2$ in a 35% yield. When twice recrystallized from absolute alcohol a white crystalline solid was formed. M.p. 173°C. (decomposes).

ii) Chloropentafluorobenzene (20.0 gms., 0.1 M) and hydrazine hydrate (60 gms., 1.2 M) were refluxed together in water (40 mls.) and ethanol (120 mls.) for fifty hours. The product was poured into ice water (400 mls.), and the precipitate formed was filtered off to give $C_6ClF_4NHNH_2$ (1.1 gms.).

The water was removed from the aqueous extract by distillation to give 11.0 gms. of crude $C_6ClF_4NHNH_2$. M.p. 159°C. The total yield of $C_6ClF_4NHNH_2$ was 65%. This was recrystallized from absolute alcohol to give a white crystalline solid.

$C_6ClF_4NHNH_2$. Twice recrystallized from absolute alcohol. M.p. 173°C (decomposes). Infra red spectrum No. 28.
Analysis gave: C, 33.7 , Cl, 16.1, F, 36.2%; calc. for $C_6ClF_4NHNH_2$: C, 33.6, Cl, 16.5, F, 35.4%.

<u>Chlorotetrafluorophenylhydrazine and Aqueous Hydiodic Acid.</u>

Chlorotetrafluorophenylhydrazine (2.0 gms., 0.01 M) and aqueous hydriodic acid (55%, 12 mls., 0.16 M) were refluxed for three hours. The solution was treated with sodium metabisulphite (10 gms.) and steam distilled. The distillate was ether extracted, dried (anhydrous $MgSO_4$) and the ether distilled to give 0.24 gms. of a black residue. This was sublimed to give a white solid (0.2 gms.) which was shown by A.S.V.P.C. (see fig. xx), and an infra red spectrum, to be a mixture of isomers of $C_6ClF_4NH_2$. If the middle peak in the chromatogram is the meta isomer, the isomer distribution of the amine, and thus of the chlorotetrafluorophenylhydrazine, was:-

| | |
|---|---|
| o-$C_6ClF_4NHNH_2$ | 22%. |
| m-$C_6ClF_4NHNH_2$ | 6.5%. |
| p-$C_6ClF_4NHNH_2$ | 71.5%. |

## Chloropentafluorobenzene and Copper Powder.

i) Chloropentafluorobenzene (2.0 gms., 0.01 M) and copper powder (2.0 gms., 0.03 M) were reacted in a sealed tube for sixty hours at 210°C. The product was extracted with ether, filtered to remove the copper, dried (anhydrous $MgSO_4$) and the ether distilled. The product (1.7 gms.) was shown by A.S.V.P.C. to contain starting material 90%, together with 10% of a compound with the same retention time as decafluorodiphenyl obtained by the reaction of bromopentafluorobenzene and copper powder[1].

ii) Chloropentafluorobenzene (5.0 gms., 0.025 M) and copper powder (5 gms., 0.075 M) were reacted in a sealed tube for 280 hours at 230°C. The product was extracted as above to give 2.85 gms. of a solid, crude M.p. 60-62°C. This was shown by an infra red spectrum to be decafluorodiphenyl. Twice recrystallized from benzene. M.p. 69°C.

## Bromopentafluorobenzene and Copper Powder.

Bromopentafluorobenzene (1.0 gms., 0.004 M) and copper powder (1.0 gms., 0.015 M) were reacted in a sealed tube for sixty hours at 200°C.[1] Decafluorodiphenyl (0.4 gms.) was isolated as above. Recrystallized from benzene. M.p. 67°C. Tatlow et. al.[1] gave 68-69°C.

## REFERENCES

| | | |
|---|---|---|
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| 40. | idem, | ibid, 447. |
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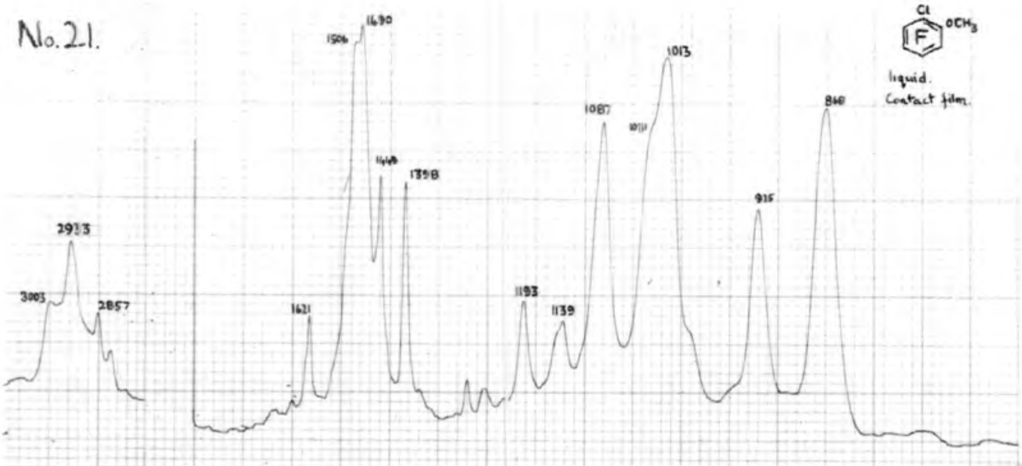
| 42. | Brooke, | Unpublished work. |

No. 21.



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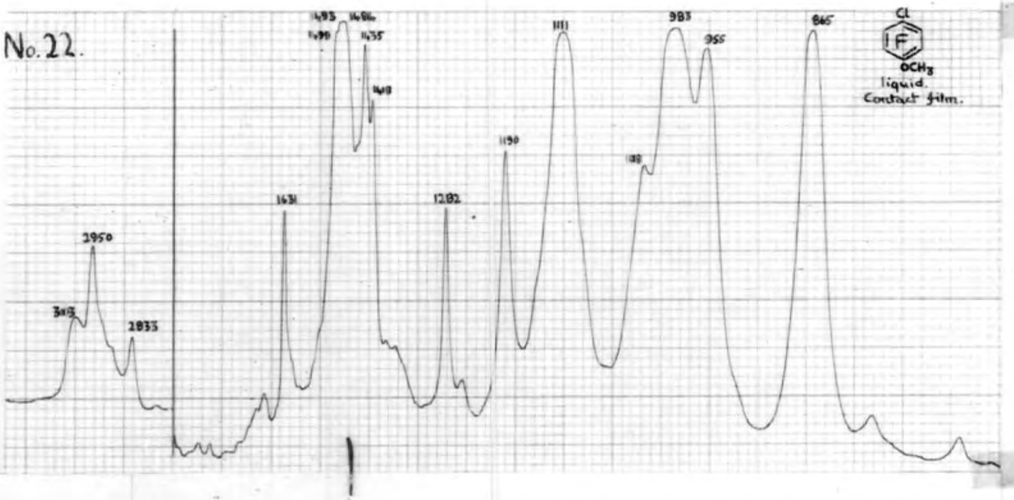

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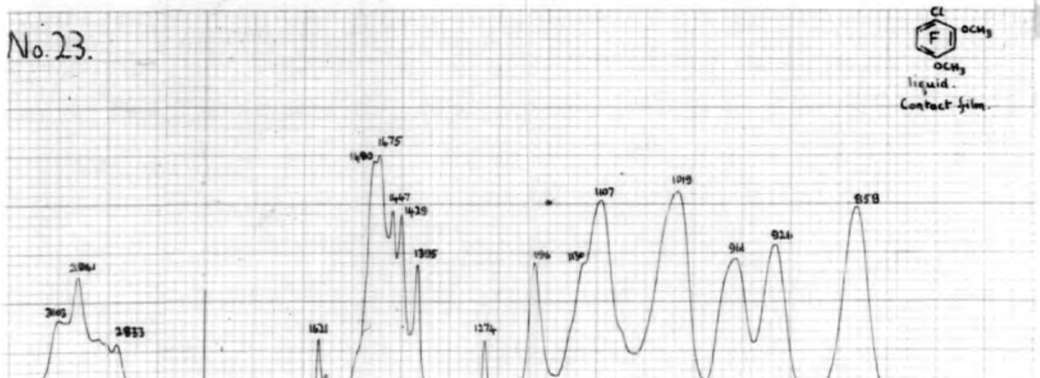

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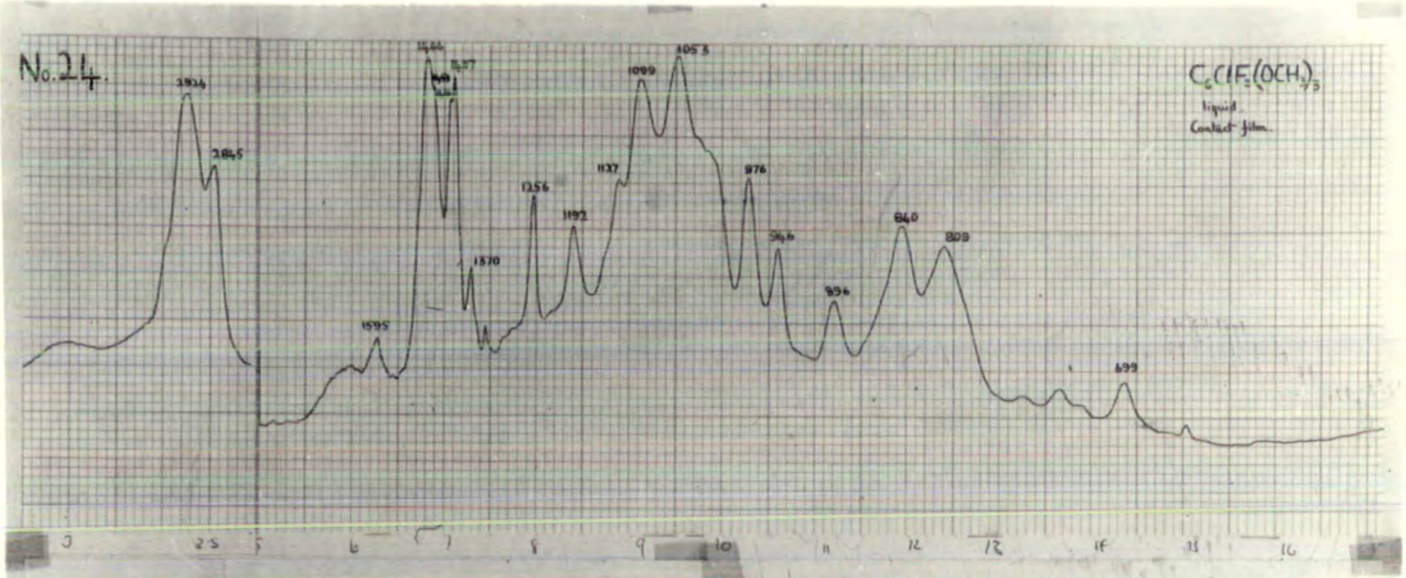
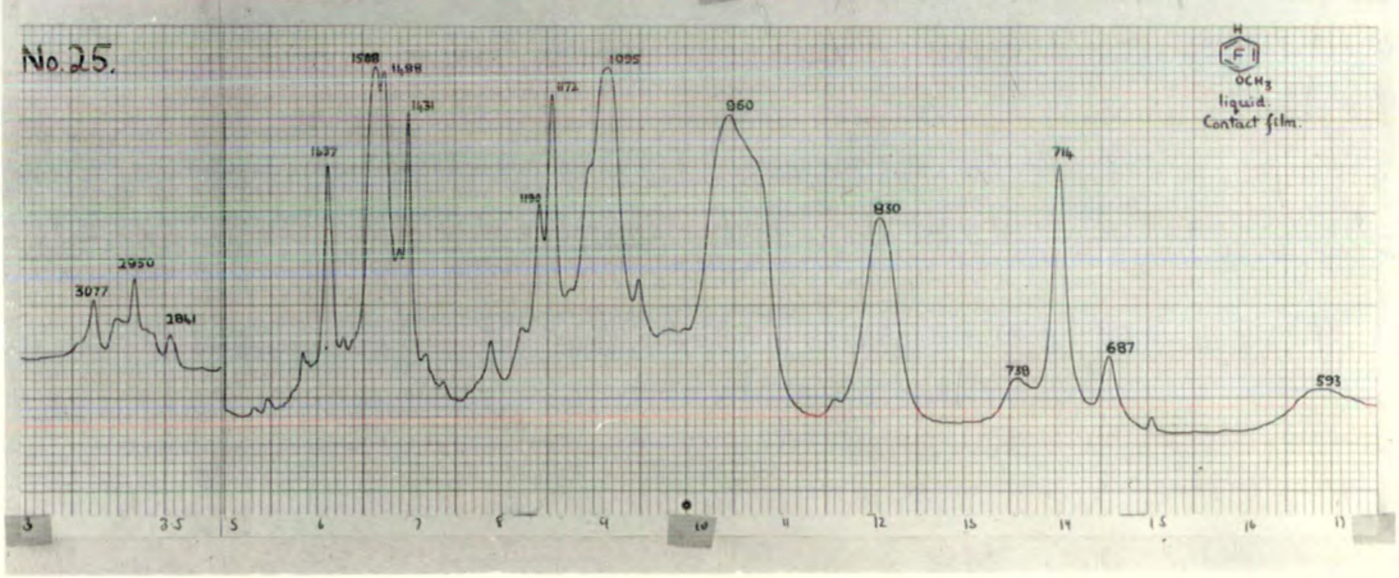

$C_6ClF_2(OCH_3)_3$
liquid.
Contact film.
2924
2845
1595
1466
1437
1370
1256
1192
1137
1099
1053
976
946
896
840
809
699
3
2.5
5
6
7
8
9
10
11
12
13
14
15
16

No. 25.


H
F
OCH₃
liquid.
Contact film.
3077
2950
2841
1637
1588
1498
1431
1190
1172
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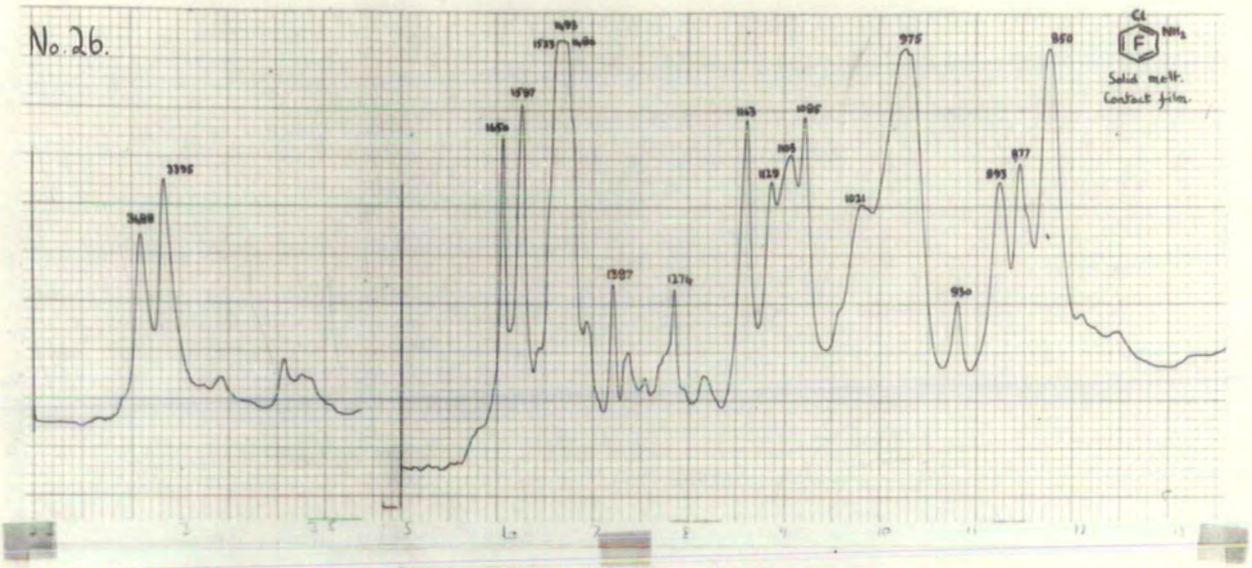
960
830
738
714
687
593
3
3.5
5
6
7
8
9
10
11
12
13
14
15
16
17

No. 26.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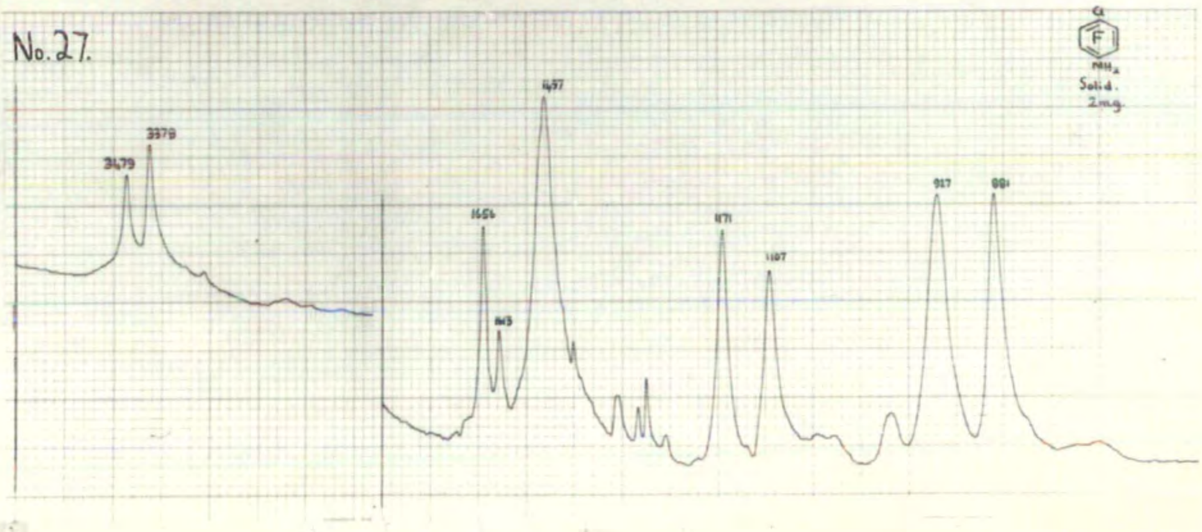
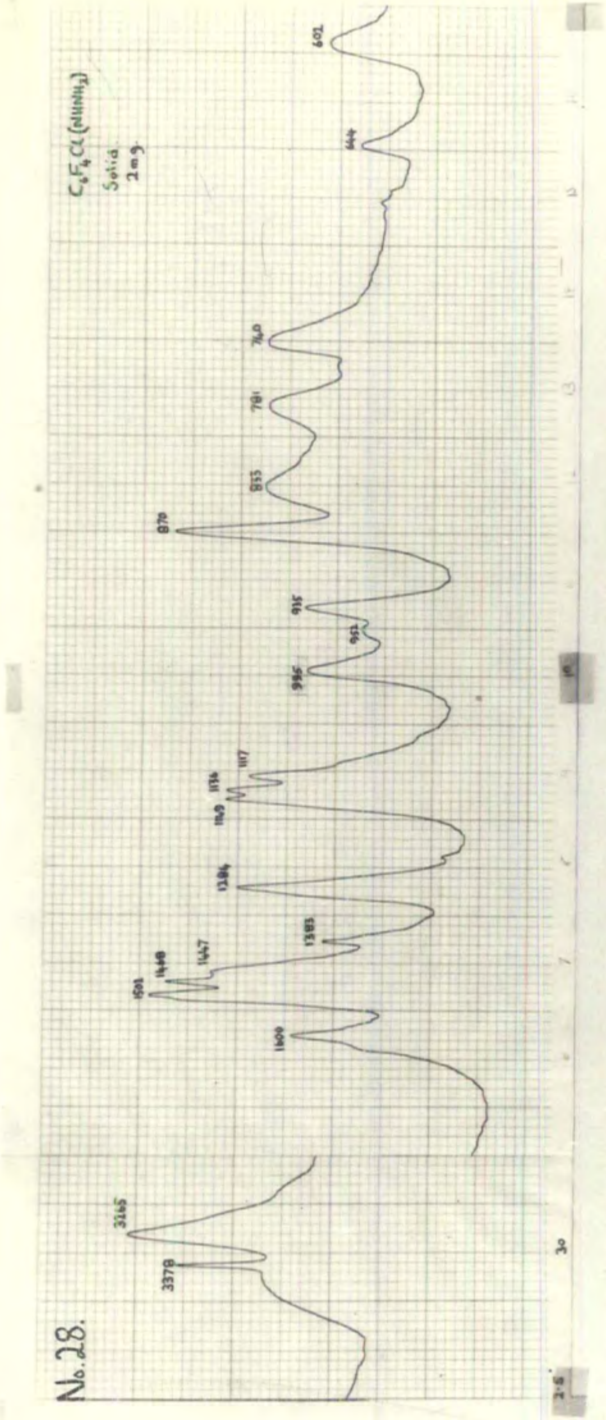
3395
1650
1597
1535
1495
1486
1387
1274
1163
1129
1105
1085
1031
975
930
893
877
850
Cl
F
NH₂
Solid melt.
Contact film.
3
5
6
7
8
9
10
11
12
13

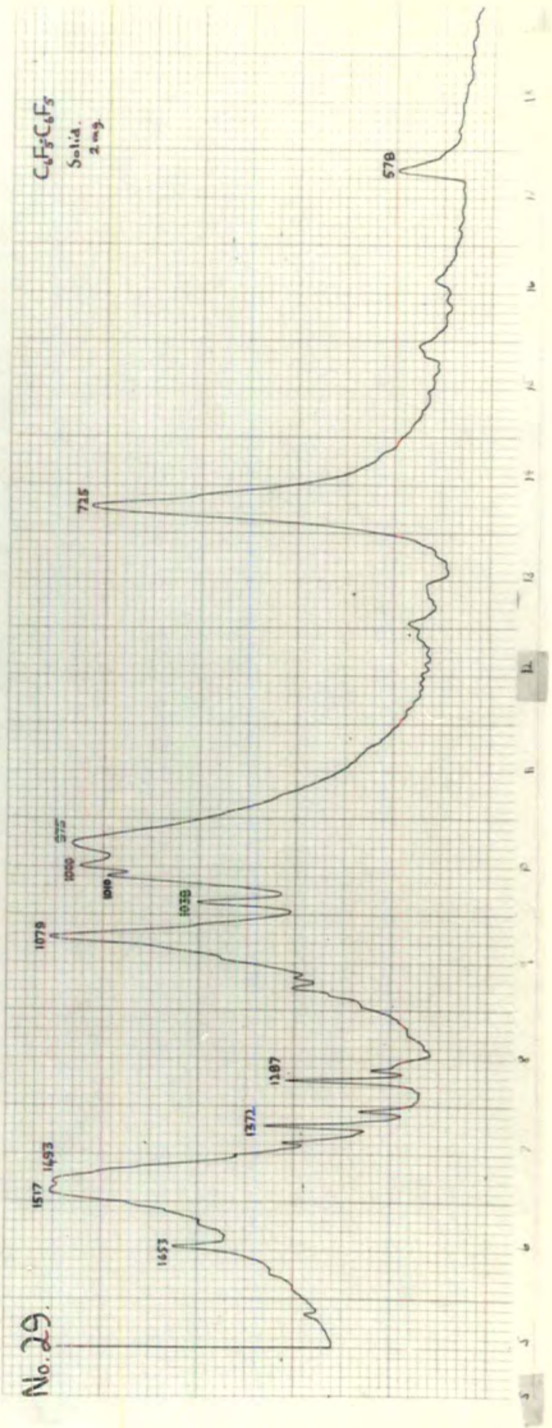
No. 27.


3479
3379
1656
1613
1497
1171
1107
917
881
Cl
F
NH₂
Solid.
2mg.

No. 28.


C6F4Cl(NHNH2)
Solid
2mg.
3378
3165
1600
1502
1488
1447
1383
1286
1149
1136
1117
986
952
915
870
815
781
740
644
601
2.5
30

No. 29.


C6F5·C6F5
Solid.
2mg.
1653
1517
1493
1372
1187
1079
1038
1010
1000
975
725
578