The fluorination of perhalopyridines

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How to cite:

Holmes, Thomas Frederick (1971) *The fluorination of perhalopyridines*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/10032/

UNIVERSITY OF DURHAM

A THESIS

entitled

THE FLUORINATION OF PERHALOPYRIDINES

submitted by

THOMAS FREDERICK HOLMES, B.Sc.

A candidate for the degree of Master of Science

1971

Acknowledgements

The author is grateful to Professor W.K.R. Musgrave for his continual help and encouragement during his supervision of this work and to Dr. D.T. Clark for many helpful discussions.

Memorandum

The work described in this thesis was carried out in the University of Durham. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

SUMMARY

The Cobaltic Fluoride Fluorination of Perfluoro- and Polyfluoro-halopyridines

This work is concerned with the fluorination of pentafluoropyridine, monohalo- and dihalo-fluoropyridines. In certain cases, this reaction provides a route to polyfluoro-1-azacyclohexadienes.

The fluorination of pentafluoropyridine gives excellent yields of perfluoro-1-azacyclohex-1-ene and perfluoro-2-azahex-2-ene. The presence of a bromine or a chlorine atom on the 4-carbon atom of the tetrafluoropyridine affords, depending on the temperature of the fluorination, 4-bromo-, or 4-chloro-hexafluoro-1-azacyclohexa-1,3-diene or the corresponding octafluorocyclohex-1-enes. Halogen exchange, using potassium fluoride, gives the corresponding perfluoro derivatives. Dehalogenation, over iron filings at 350°, of the 4-bromo or 4-chloro-octafluoro-1-azacyclohex-1-ene also yields perfluoro-1-azacyclohexa-1,3-diene.

This perfluoro diene has been shown to be extremely reactive towards nucleophilic reagents.

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CHAPTER I

INTRODUCTION

INTRODUCTION

This introduction will take the form of a review of the several different methods of introducing fluorine into an organic molecule to form the perfluoro derivative.

1. The Fluorination of Organic Molecules using Elemental Fluorine.

Fluorination reactions are very exothermic since the heats of formation of C-F and H-F bonds are high (ca. 105 and 135 Kcal/mole respectively) and the bond dissociation energy of fluorine is only 37 Kcal/mole. In adopting a suitable technique for carrying out the reaction of fluorine with organic molecules, the main problem is to disperse the heat energy formed in the reaction. This is achieved as follows in each of the three different methods.

(a) Liquid Phase Fluorination.

This technique involves bubbling fluorine gas, diluted with an inert gas, through a cold solution of the organic compound in an inert solvent.[1] The reaction takes place in the gas phase of the bubbles and hence is relatively uncontrolled. Little use has been made of this technique.

(b) Catalytic Gas-Phase Fluorination.

This method has attracted by far the most attention. It was studied extensively during the 1940's and early 1950's at Columbia University[2] and at Birmingham University.[3]

The reaction between fluorine, diluted with nitrogen, and the organic vapour diluted with nitrogen, takes place in a heated reaction tube packed with finely divided catalyst which can be copper, silver coated copper or gold coated copper. The main function of the catalyst being to dissipate the heat of the reaction; doubtless, the surface coatings of gold and silver play some part in the fluorinations. The main facts which emerge from the study of this process are:-

i) as the chain length increases it becomes progressively more difficult to obtain good yields of the fully fluorinated material;

ii) alicyclic compounds give higher yields of perfluoroalkanes than aromatic compounds;

iii) partially fluorinated compounds give much better yields than the parent hydrocarbons;

iv) polymeric material is always formed.

(c) Gas-Phase Fluorination without a Catalyst.

A high dilution of the reactants with nitrogen is used in this reaction. Bigelow[4] and his co-workers have recently developed unpacked fluorinators with special inlet jets for the reactants, which promote mild fluorinations. By this method, they have prepared the fluorocarbons C_2F_6, C_3F_8, nC_4F_{10} and $(CF_3)_3CF$ in high yields from the corresponding hydrocarbons.

Mechanism.

It is generally accepted that the reaction of hydrocarbons with elemental fluorine proceeds via a free radical mechanism of the type associated with photochlorination.

$$CH_4 \xrightarrow{F^\bullet} HF + CH_3^\bullet \xrightarrow{F_2} CH_3F + F^\bullet \text{ etc.} \longrightarrow CF_4$$

Reactions between hydrocarbons and elemental fluorine are highly exothermic since the heats of formation of C-F and H-F bonds are high (ca. 105 and 135 Kcal/mole, respectively) and the bond dissociation energy of fluorine is only 37 Kcal/mole. For this reason, it is necessary to disperse rapidly, the heat liberated, in order to avoid carbon skeleton fragmentation and combustion. At elevated temperatures, fluorine atoms necessary for the initiation of chain reactions, can arise by the thermal dissociation of molecular fluorine.

$$F_2 \rightleftharpoons 2F^\bullet \quad [D(F\text{-}F) = 37 \text{ Kcal/mole}]$$

It has been shown that fluorine atoms are produced at low temperatures, for fluorine will sensitize the chlorination of tetrachloroethylene at -7°.[5]

2. Electrochemical Fluorination.

Many organic compounds, particularly those containing polar groups, dissolve in anhydrous hydrogen fluoride to give conducting solutions. Passage of a low voltage (4-6V) d.c. current through the solution causes hydrogen to be liberated at the cathode and the organic material to be fluorinated at the anode by some unknown process. Insoluble material must be suspended in anhydrous hydrogen fluoride and an electrolyte added to improve the conductivity, before the fluorination can be effected.

This method of fluorination was discovered by Simons[6] and his associates in 1941 and resembles fluorinations with elemental fluorine or cobaltic fluoride since all hydrogen in organic molecules is replaced by fluorine and unsaturated links are saturated. Fragmentation of carbon skeletons occurs but in general, functional groups, e.g. COF[7] and SO_2F[8] are retained.

Hydrocarbons and halogenocarbons are difficult to fluorinate electrochemically since they are only sparingly soluble in anhydrous hydrogen fluoride to give non-conducting solutions. This is not necessarily a disadvantage since many hydrocarbon derivatives, e.g. $R.OH$; $R.COOH$; $R.NH_2$ etc. are quite soluble in anhydrous hydrogen fluoride and the fluorination products usually contain a relatively large proportion of the fluorocarbon having the same carbon skeleton.

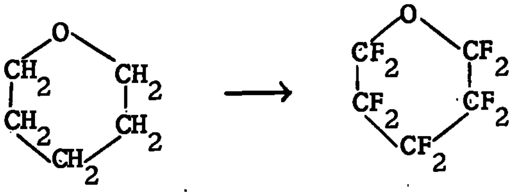
The compounds which can best be fluorinated in this way are:

(a) Ethers.

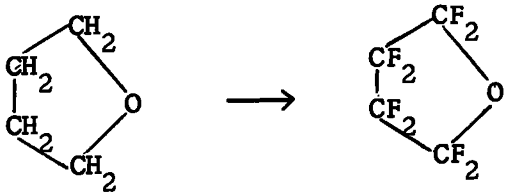
Ethers are extremely soluble in anhydrous hydrogen fluoride to give conducting solutions and can be fluorinated by the electrochemical process to give high yields of the corresponding perfluoroethers. Almost all of the published work on the electrochemical fluorination of ethers appears in the patent literature but no yields are quoted for the simple ethers.

Cyclic ethers have been reacted to give yields as high as 35% and 42%.[9]

e.g.



35%

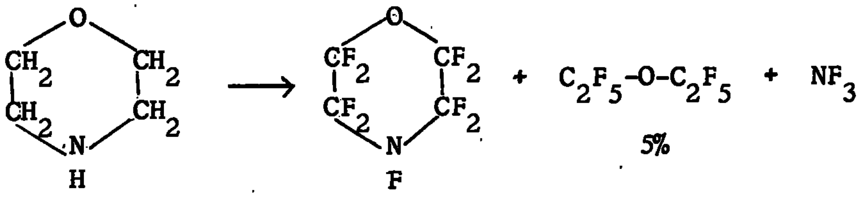


42%

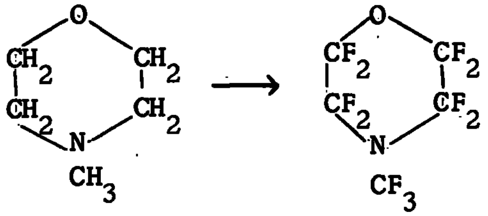
(b) Amines.

Primary, secondary and tertiary amines as well as heterocyclic bases have been electrochemically fluorinated but the yields of the perfluoro derivatives have usually been low. By-products from these reactions are fluorocarbons having the same number of carbon atoms as the substrate and nitrogen trifluoride. Simons[10] claimed the preparation of an homologous series of cyclic perfluoro-nitrides by the electrochemical fluorination of the corresponding piperidines.

Morpholine[11] and its 1-methyl derivative have been fluorinated electrochemically to give 13% and 14% respectively of the perfluoro compound:

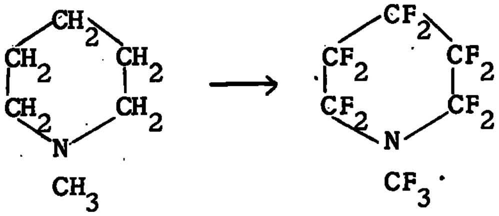


13%



14%

N-methyl piperidine[12] has been fluorinated to give 39% of perfluoro-N-methyl piperidine.



39%

Pyridine[11] has been fluorinated in a similar manner and the reaction products found to be perfluoropiperidine (10%), perfluoro(dipiperidyl) (1%), perfluoropentane (25%) and nitrogen trifluoride (30%). Even though the yields are not usually good and though aliphatic compounds give better results than do aromatic ones, the electrochemical process is the method of choice for the preparation of perfluorinated nitrides. A large number of products are usually formed when amines are fluorinated with elemental fluorine[13] or high valency metal fluorides.[14]

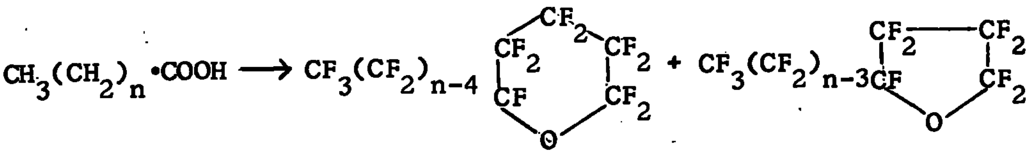
(c) Carboxylic acids.

The electrochemical fluorination of carboxylic acids is not a good method of preparing perfluorocarboxylic acids. However, acid fluorides can be efficiently fluorinated by this process,

$$CH_3COF \longrightarrow \underset{85\%}{CF_3COF} \quad {}^{7}$$

From carboxylic acids with six or more carbon atoms, cyclic ethers are important by-products,

15



The cyclic ethers have been found to have the same number of carbon atoms as the parent acid and are believed to be mixtures of five and six membered ring compounds; with the former predominating.

(d) Derivatives of carboxylic acids.

Anhydrides, primary acid amides, acid chlorides, bromides and iodides all give acid fluorides.

The apparatus required for electrochemical fluorinations is generally quite simple. It consists of an iron or nickel cell which contains the electrolyte and a pack of alternate nickel anodes and cathodes surmounted by a reflux condenser to prevent excessive loss of hydrogen fluoride. Normally the cell temperature is maintained at 0^o, although temperatures as high as 20 - 40^o have been used. The perfluorinated products are either swept from the cell by cathodic hydrogen or, being insoluble and dense, they settle to the bottom of the cell from where they are tapped off.

Mechanism.

It is very difficult to postulate a mechanism because the electrochemical process frequently gives rise to numerous products, many of which escape unidentified. Frequently the perfluoro analogue is produced in poor yields. It can however, be deduced that the process is very complex. Fluorinated and partially fluorinated material is produced by fragmentation, cyclisation and polymerisation as well as simple fluorination. An important example of a product being formed by cyclisation is that encountered when perfluorocyclic ethers are formed from carboxylic acids (p. 7). An example of polymerisation and fragmentation is afforded when pyridine is fluorinated (p. 6).

The fluorination definitely takes place at the anode and is almost certainly of a free radical nature for polymeric material is found adhering to the anode. Reactions involving either a high valency nickel fluoride or free elemental fluorine could take place by a free radical anodic process. The precise nature of the process is not fully understood but several suggestions have been made.[16] One suggestion is that the reaction is effected by a high valency nickel fluoride but this has been regarded as unacceptable for two main reasons:-

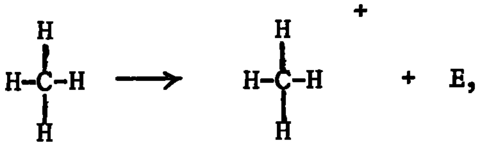
(i) no single nickel fluoride of higher valency than the difluoride has been prepared with certainty, and

(ii) the electrode potential for the reaction $Ni^{2+} \longrightarrow Ni^{3+} + e$ must be higher than that required to liberate fluorine because the reaction of fluorine with nickel produces the difluoride.

It has also been suggested that a complex high valency nickel fluoride, e.g. K_2NiF_6, is involved in the fluorination. This is a double salt that could conceivably be formed with potassium fluoride if the latter was used as a conductivity additive. A double salt believed to be $KCoF_4$ has recently[17] been investigated and found to be an effective fluorinating agent.

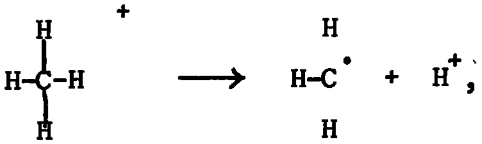
Alternatively the fluorinating agent could be a loose complex of nickel difluoride and atomic or molecular fluorine; the fluorination would then take place between the substrate and the complex.

Another possible suggestion that has been made, is that the substrate is directly oxidised by electron abstraction in the electrolysis,



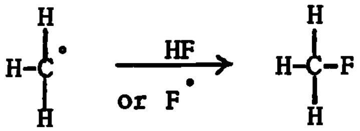
$$\mathrm{CH_4} \longrightarrow \mathrm{CH_4}^{+} + E,$$

breakdown of the resulting cation into a free radical,



$$\mathrm{CH_4}^{+} \longrightarrow \mathrm{CH_3}^{\bullet} + H^{+},$$

followed by fluorine abstraction from hydrogen fluoride or reaction with a fluorine atom,



$$\mathrm{CH_3}^{\bullet} \xrightarrow[\text{or } F^{\bullet}]{HF} \mathrm{CH_3F}$$

Whichever mechanism or mechanisms is involved, it is certainly complex!

3. Fluorination Effected by Metal Fluorides.

(a) Alkali Metal Fluorides.

Alkali metal fluorides have a limited yet useful application in introducing fluorine into an organic molecule. When heated with an alkali metal fluoride, some organic halogen compounds undergo a halogen exchange reaction to give the organic fluorine derivative. In this type of reaction, hydrogen and unsaturation remain unchanged, e.g. Hoffmann[18] has prepared a series of ω,ω'-difluoroalkanes of general formula $F(CH_2)_nF$, $n > 2$, using anhydrous potassium fluoride as the fluorinating agent and glycol as a solvent.

$$BrCH_2CH_2Br \xrightarrow{150^{o}} BrCH_2CH_2F$$

(23·7%)

$$Br(CH_2)_3Br \xrightarrow{150^{o}} F(CH_2)_3F + Br(CH_2)_3F + FCH_2CH{=}CH_2$$

(23·3%) (6·2%) (19·4%)

$$ClCH_2(CH_2)_2CH_2Cl \xrightarrow{170^{o}} F(CH_2)_4F + Cl(CH_2)_4F + F(CH_2)_2CH{=}CH_2$$

(44·2%) (6·6%) (2·2%)

$$ClCH_2(CH_2)_3CH_2Cl \xrightarrow{180^{o}} F(CH_2)_5F + Cl(CH_2)_5F + F(CH_2)_3CH{=}CH_2$$

(36·6%) (9·4%) (2·8%)

$$ClCH_2(CH_2)_4CH_2Cl \xrightarrow{185^{o}} F(CH_2)_6F + [Cl(CH_2)_6F] + F(CH_2)_4CH{=}CH_2$$

(30%) (0%) (2·5%)

With certain exceptions, namely 1-bromo-2-fluoroethane, 1-chloro-2-fluoroethane and 1-chloro-3-fluoropropane, the 1-halogeno-ω-fluoroalkane was prepared in a greater yield by carrying out the reaction at a lower temperature,[19] e.g.

$$Br(CH_2)_2Br \xrightarrow{90^{o}} Br(CH_2)_2F + F(CH_2)_2F$$

(24%) (0%)

$$\mathrm{Br(CH_2)_3Br} \xrightarrow{80\text{-}100^{\circ}} \mathrm{Br(CH_2)_3F} + \mathrm{F(CH_2)_3F}$$

(31%) (10·2%)

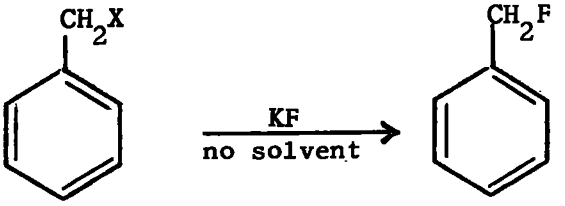
$$\mathrm{Cl(CH_2)_4Cl} \xrightarrow{101^{\circ}} \mathrm{Cl(CH_2)_4F} + \mathrm{F(CH_2)_4F}$$

(36·6%) (15·9%)

$$\mathrm{Cl(CH_2)_5Cl} \xrightarrow{130^{\circ}} \mathrm{Cl(CH_2)_5F} + \mathrm{F(CH_2)_5F}$$

(38·5%) (14·1%)

Kitano and Fukui[20] reacted C_5-C_8 alkyl halides with anhydrous potassium fluoride, in the absence of a solvent, at the boiling point of the mixtures and obtained yields of alkyl fluorides less than 20% and 2-7% of olefins produced simultaneously. By using a solvent (ethylene glycol) at 180° they were able to report that the yields of alkyl fluorides had been increased to 30 - 70%, e.g.



(20 - 28%)

Sulpholan has been used as a solvent by Fuller[21] who prepared polyfluoroaromatic compounds by the reaction of perhalogenoaromatic compounds with potassium fluoride in the aforementioned "aprotic" medium.

$$C_6Cl_6 \xrightarrow[230/240^\circ,\ 18\ \text{hrs.}]{\text{KF/sulpholan}} \underset{(0{\cdot}4\%)}{C_6F_6} + \underset{(25\%)}{C_6ClF_5} + \underset{(24\%)}{C_6Cl_2F_4} + \underset{(30\%)}{1,3,5\text{-}C_6Cl_3F_3}$$

Neither C_6Cl_6 nor C_6ClF_5 when reacted in this way gave any significant yield of hexafluorobenzene but the latter was obtained in 40% yield, when C_6ClF_5 was reacted with CsF in sulpholan at 160-190° for 18 hrs. Caesium fluoride has been shown to be a more powerful fluorinating agent than potassium fluoride.

(b) High Valency Metal Fluorides.

Exhaustive fluorinations to give fluorocarbon type products are effected by certain high valence metal fluorides. In this type of reaction, the high valence metal fluoride is reduced to the lower valence metal fluoride as the reaction proceeds.

$$-C-H + 2MF_n \longrightarrow -C-F + HF + 2MF_{n-1}$$

$$C=C + 2MF_n \longrightarrow CF-CF + 2MF_{n-1}$$

Replacement of hydrogen and saturation of unsaturated links normally takes place in this reaction.

Cobalt trifluoride is the most important high valency metal fluoride used to effect fluorinations of this type. The fluorinating agent is made by the reaction of elemental fluorine or halogen fluoride (e.g. ClF_3) with the lower valency fluoride or chloride of the metal. The reactions can be carried out in the liquid or vapour phase but the latter technique has proved the most useful.

Vapour Phase Fluorinations with Cobalt Trifluoride

The use of cobalt trifluoride as a fluorinating agent was suggested by Ruff and Ascher[22] in 1929. Two years later, Ruff and Keim[23] fluorinated carbon tetrachloride in the presence of cobalt trifluoride. The requirements of the U.S. Atomic Energy Project led to its further investigation by Fowler[24] and his associates, who in their pioneering experiments discovered that it gave up fluorine to organic compounds with the formation of cobaltous fluoride and hydrogen fluoride. By the reaction with cobaltic fluoride at high temperatures (up to 400°) all the hydrogen of an organic compound is replaced by fluorine and the addition of fluorine to unsaturated linkages takes place.

$$4CoF_3 + -CH_2- \longrightarrow 4CoF_2 + -CF_2- + 2HF$$

$$2CoF_3 + C{=}C \longrightarrow 2CoF_2 + CF{-}CF$$

It has been calculated[24] that the approximate heat of reaction is -104 Kcal for,

$$\tfrac{1}{2}(-CH_2-) + F_2 \longrightarrow \tfrac{1}{2}(-CF_2-) + HF$$

Since fluorinations with cobalt trifluoride achieve the same result in two steps,

$$\text{(i)}\quad 2CoF_2 + F_2 \longrightarrow CoF_3;\ \Delta H\ (250^{\circ}) \simeq -52\ \text{Kcal.}$$

$$\text{(ii)}\quad \tfrac{1}{2}(-CH_2-) + 2CoF_3 \longrightarrow \tfrac{1}{2}(-CF_2-) + HF + 2CoF_2;\ \Delta H \simeq -58\ \text{Kcal.}$$

it is evident that considerably less heat is liberated during the fluorination of a hydrocarbon with cobalt trifluoride than with elemental fluorine. Hence, provided the reaction conditions are carefully controlled, fluorinations with cobalt trifluoride can be effected without extensive C-C bond fission. Under such conditions, perfluorocyclohexane can be obtained from cyclohexane, cyclohexene, cyclohexadiene or even benzene. The main by-products from cobaltic fluoride fluorinations are incompletely fluorinated material, i.e. some hydrogen left in the molecule and sometimes unsaturation remaining. It is also possible for short chain fragments to arise from C-C bond fission. The extent to which the reaction goes is largely dependent upon the reaction temperature; under mild conditions (relatively low temperatures) incompletely fluorinated material can, indeed, be the main product. The reagent rarely causes polymerisation which is in contrast with what happens when elemental fluorine is used to effect the fluorination.

Apparatus.

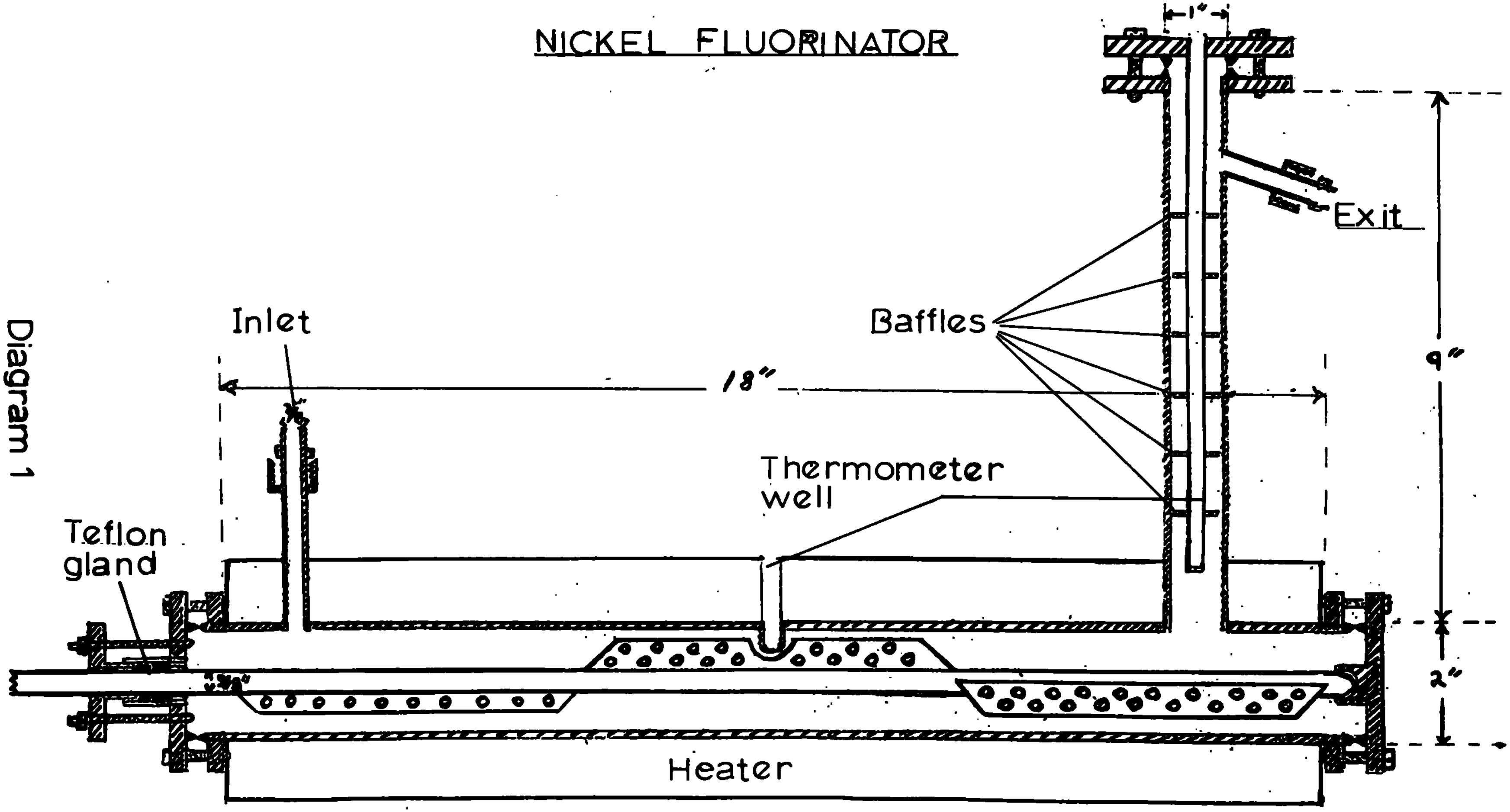
In the original version of this process[24] the organic substrate was passed as a vapour, in a steady stream of nitrogen gas, over a thinly spread bed of cobaltic fluoride in a copper tube. This type of reactor is referred to as a "Static Reactor". The reaction temperatures were usually in the region 150 - 400° and the products were trapped at liquid air temperature. Several static reactors of basically similar design have been described by other workers.[25] It has been found advantageous to agitate the bed of cobaltic fluoride during the reaction, and several suitable laboratory scale reactors have been described by different groups of workers.[26]

A typical laboratory unit is illustrated in diagram 1.

General Method and Reaction Conditions.

When carrying out small scale fluorinations it is convenient to charge the substrate into a modified burette and to add it dropwise, by dropping it directly into the fluorinator or into a vaporiser, in a steady stream of nitrogen gas. Throughout the reaction, the fluorinator bed is agitated by a motor turning at about 4 r.p.m. so that a fresh surface of cobalt trifluoride is continually brought into contact with the substrate vapour. The reaction products are trapped at liquid air temperature. Regeneration of the spent fluorinating agent has been effected by ClF_3 and BrF_3.[27] The availability of fluorine makes it an attractive reagent for regeneration which is carried out by passing fluorine through the spent reactor at 250 - 300°. The degree of fluorination of a particular substrate is affected by the following operating parameters:

NICKEL FLUORINATOR



Paddle stirrer speed = 4 r.p.m.

Diagram 1

i) the temperature,

ii) the input rate of the substrate,

iii) the flow rate of the nitrogen gas used as a diluent,

iv) the degree of exhaustion of the cobaltic fluoride.

The effect of these operating parameters will be discussed in turn.

The Effect of Temperature.

The operating temperature is the most important variable in this process for, in general, complete fluorination occurs in the temperature range 300 - 350^o and higher temperatures cause extensive carbon chain breakdown. In the temperature range 150 - 200^o partial fluorination occurs to give hydrogen containing material.

The Effect of the Substrate Input Rate.

The slower the rate of addition, the lesser the concentration of substrate vapour in the diluent and this favours a greater degree of fluorination.

The Effect of the Flow Rate of the Diluent.

The slower the flow rate the longer the contact time and hence the more complete the fluorination. Conversely, high flow rates favour partial fluorinations.

The Effect of the Degree of Exhaustion of the Cobaltic Fluoride.

The degree of exhaustion is the percentage of available fluorine used in a reaction. The greater the degree of exhaustion of the cobaltic fluoride the lesser the degree of fluorination achieved in a particular reaction. For complete fluorination it may be necessary to limit the degree of exhaustion to 50%.

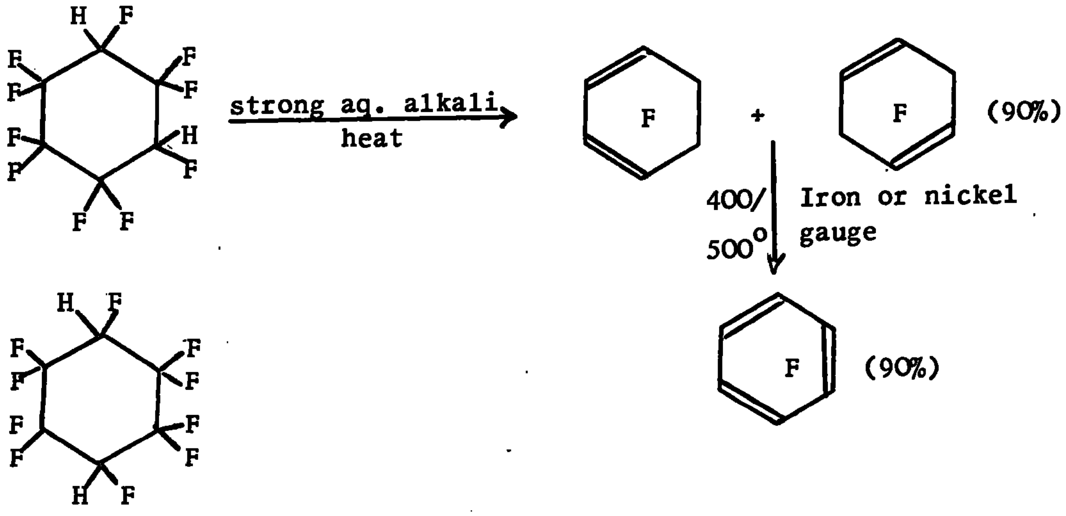
The Fluorination of Benzene.

The cobaltic fluoride fluorination of benzene can be controlled, by the suitable choice of reaction temperature, to give predominantly polyfluorocyclohexanes or perfluorocyclohexane.

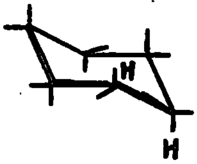
The Mild Fluorination of Benzene.

The fluorination of benzene in stirred reactors at 150 - 200° yields predominantly partially fluorinated material. Under these conditions, the major products are polyfluorocyclohexanes of general formula $C_6H_nF_{12-n}$, where n=1-4.[28]

Dehydrofluorination of the decafluorocyclohexanes, which are formed together with other polyfluorocyclohexanes, by reaction with strong alkaline reagents,[29] gives rise to a mixture of perfluorocyclohexa-1,3-diene and -1,4-diene. Pyrolytic defluorination[30] of the perfluorodienes affords an excellent yield of hexafluorobenzene.



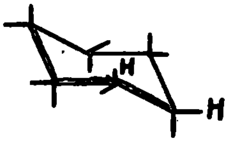
It has been demonstrated by Smith and Tatlow,[31] that the structural conformation of the 1H:2H-decafluorocyclohexanes has a very striking influence on the ease with which dehydrofluorination can be effected. Compounds in which trans-elimination of hydrogen fluoride can take place, i.e. those compounds in which the hydrogen atom and fluorine atom on adjacent carbon atoms both occupy axial positions, undergo the elimination of hydrogen fluoride more readily than when this does not apply.



I

trans 1H:2H-decafluorocyclohexane

(two axial H atoms)

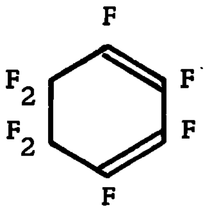


II

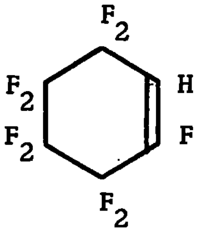
cis 1H:2H-decafluorocyclohexane

(one axial and one equatorial H atom)

The dehydrofluorination of the cis and trans isomers carried out under identical conditions, using aqueous potassium hydroxide, does not afford identical reaction mixtures. The isomer I affords the -1,3-diene (III), the 1H-mono-ene (IV) and a large amount of unchanged starting material whereas isomer II affords only the 1H-mono-ene (IV) with no unchanged starting material.



III

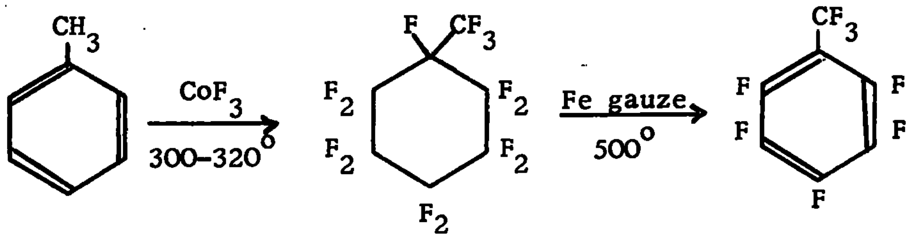


IV

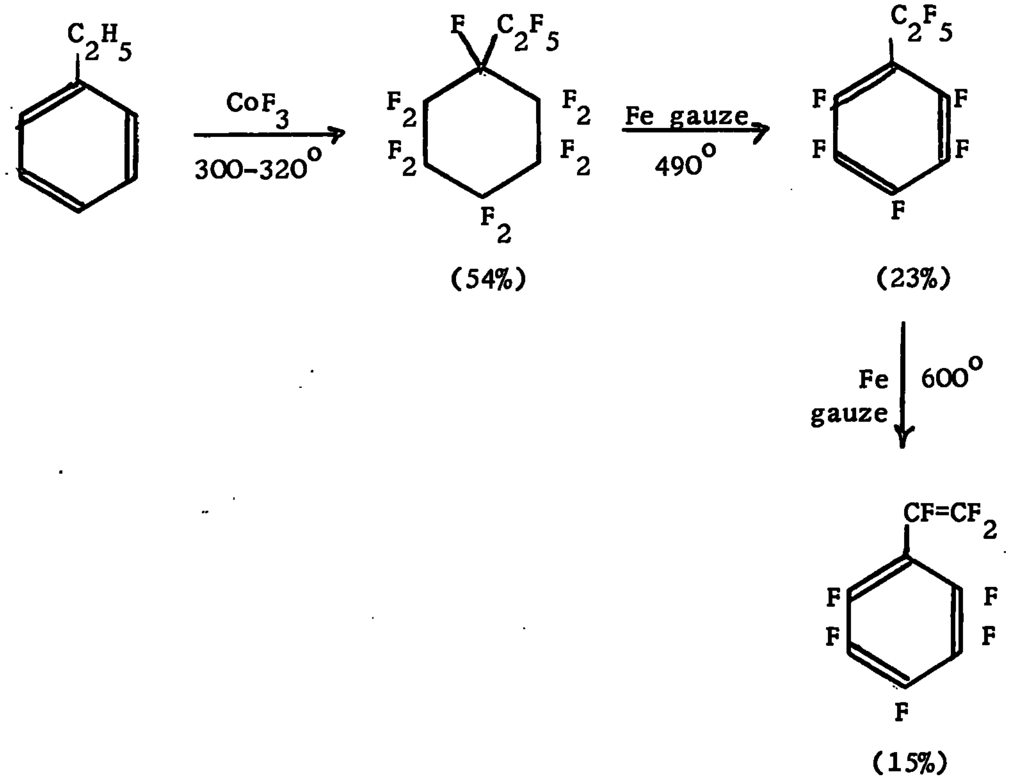
It is clear that the fluorination of benzene under mild conditions is of preparative value only for the polyfluorocyclohexanes, as any partly fluorinated aromatic and other unsaturated products are only present in minor quantities.

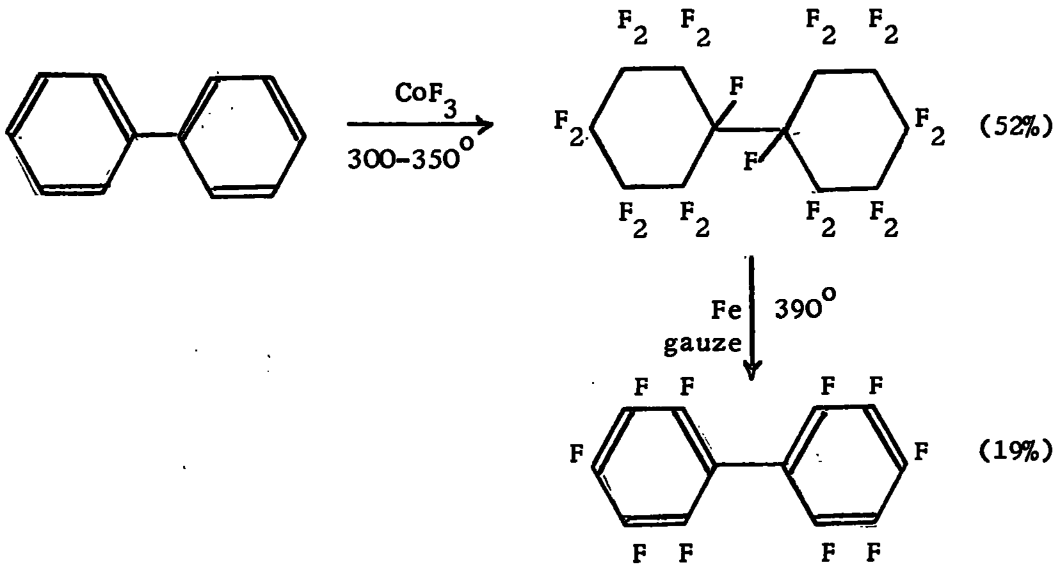
<u>The Exhaustive Fluorination of Benzene</u>.

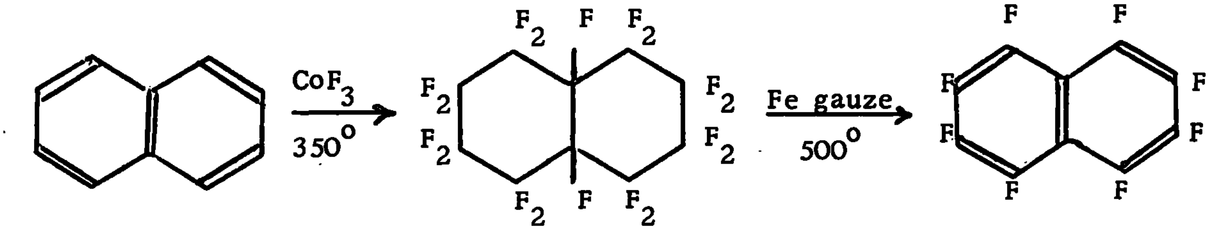
If the fluorination is carried out at temperatures of 300 - 350°, maximum yields of perfluorocyclohexane are obtained and defluorination of the latter, over hot finely divided nickel or iron, provides a route to hexafluorobenzene. The discovery of this defluorination reaction led to the development, in the late 1950's, of the only general preparative route to fluoro-aromatic compounds known, namely, exhaustive fluorination of an aromatic or alicyclic hydrocarbon to the corresponding saturated alicyclic fluorocarbon, followed by aromatisation through controlled defluorination over hot divided nickel or iron, e.g.



(70%) (25%)


C2H5
CoF3
300-320°
F C2F5
F2 F2 F2 F2 F2
(54%)
Fe gauze
490°
C2F5
F F F F F
(23%)
Fe gauze
600°
CF=CF2
F F F F F
(15%)


CoF3
300-350°
F2 F2 F2 F2
F2 F F F2
F2 F2 F2 F2
(52%)
Fe gauze
390°
F F F F
F F
F F F F
(19%)



Saturated solution
in tetralin.

Reaction Mechanism.

There appears to be a great deal of speculation as to the correct reaction mechanism. Without much experimental evidence, certain workers[32] have suggested that the process is of a free radical nature. Their conclusions have been based on the fluorination of isomeric pentanes from which the following observations were made:-

(i) unsaturated material was found amongst the products,

(ii) no polymeric material was formed,

(iii) it was found necessary to increase the reaction temperature as the reaction proceeded,

(iv) some polyfluorocyclopentane was formed during the fluorination of n-pentane,

(v) some rearrangement of neopentane to isopentane occurred during the fluorination.

To explain the above observed facts, the following reaction mechanism was proposed:-

(a) the formation of a free radical by a process such as

$$RH + CoF_3 = R^{\bullet} + HF + CoF_2,$$

(b) almost immediate destruction of the free radicals by reaction with cobalt trifluoride,

$$R^{\bullet} + CoF_3 = RF + CoF_2,$$

(c) thermal decomposition, particularly of monofluorides, with the elimination of hydrogen fluoride,

$$C_5H_{11}F \longrightarrow C_5H_{10} + HF,$$

(d) addition of fluorine, from cobalt trifluoride, to the double bond,

(e) the removal of a double bond by ring closure.

These workers[32] have suggested the combination of a free radical mechanism with an addition-elimination reaction.

If free radicals do play any part in the reaction it might have been expected that polymeric material would have been found amongst the products; this was clearly not so.

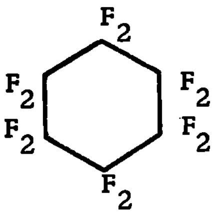
Qualitatively there are often differences between the products obtained from this process, and those from direct fluorinations with elemental fluorine and from electrochemical fluorinations.[33]

Comparison of the elemental fluorine and cobalt trifluoride fluorinations of ketones have been carried out, and it has been shown that the milder cobalt trifluoride reaction brings about total cleavage whereas the more vigorous reagent only causes partial fragmentation. At first sight, this appears to be contrary to expectation but it has been attributed to the formation of transition metal complex compounds between the ketones and the cobaltic fluoride which would be expected to promote cleavage.

With cobaltic fluoride, polymeric products are formed less readily than when using the other two methods of fluorination. Elemental fluorine is considered to react by a free radical mechanism and indeed, polymeric material is usually formed in such reactions. The only fluorinations with cobaltic fluoride that give rise to appreciable polymerisation are those with such compounds as 2-methyl indole, thiophen and thionaphthene. At least one of the compounds, 2-methyl indole, is readily resinified by acids and this is probably the explanation.

A great deal of effort has gone into the study of the cobaltic fluoride fluorination of benzene and the results obtained provide further evidence against a free radical mechanism.

The major products from the cobaltic fluoride fluorination of benzene at 150 - 200°[34] are polyfluorocyclohexanes of general formula $C_6H_nF_{12-n}$ where n = 1 - 4. Workers[35] at Birmingham University have isolated and characterized the components of the reaction mixture.



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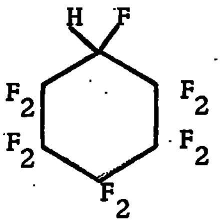

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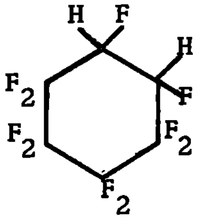
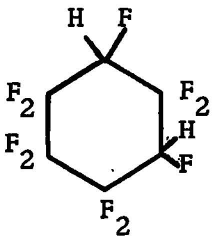


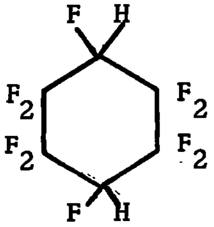
III 1H/2H-

IV 1H,2H-



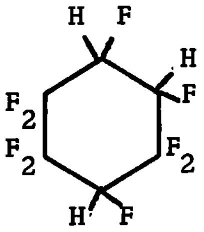
V 1H/3H-

VI 1H,3H-



VII 1H/4H-

VIII 1H,4H-

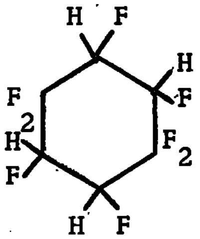


IX 1H,4H/2H-

X 1H/2H,4H-

XI 1H,2H/4H-

XII 1H,2H,4H/-

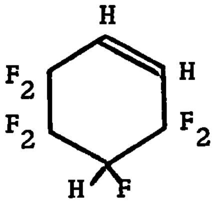


XIII 1H,4H/2H,5H-

XIV 1H,5H/2H,4H-

XV 1H,2H/4H,5H-

XVI 1H,2H,4H/5H-



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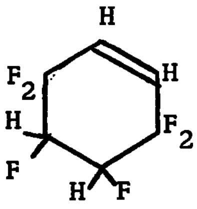

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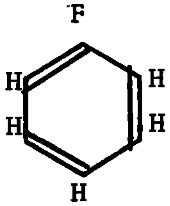
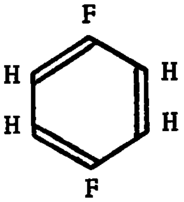
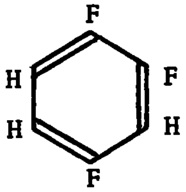


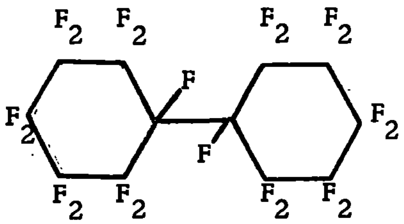
XIX



XX



XXI

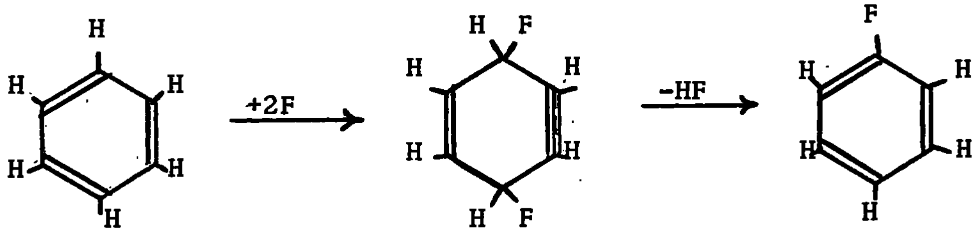


XXII

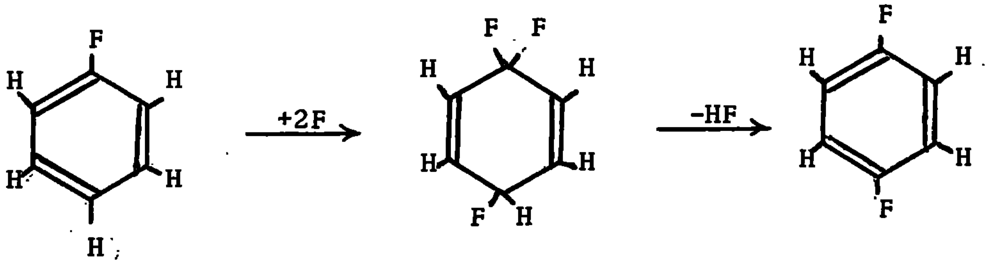
These workers point out that it is most unlikely that a free radical mechanism would give exclusively 1H,2H,4H,5H-octafluorocyclohexane and 1H,2H,4H-nonafluorocyclohexane. A similar range of products is obtained when fluorobenzene and p-difluorobenzene are fluorinated under comparable conditions but this is not the case when o and m-difluorobenzenes are fluorinated. Fluorobenzene and p-difluorobenzene have been found to be more readily fluorinated than benzene itself. It has also been observed that when fluorocyclohexenes and dienes are fluorinated,[35] hydrogen is replaced and unsaturation removed but, in general, the latter is removed first.

The observed results suggest that fluorobenzene and p-difluorobenzene are intermediates in the fluorination reaction and that it is most unlikely that o and m-difluorobenzenes are. This being so, then it is most unlikely that a free radical mechanism is involved for such a mechanism would surely not give exclusively the p-difluorobenzene. Evidence has been obtained to show that fluorobenzene, p-difluorobenzene and hexafluoro-p-xylene react more readily than benzene itself and the opposite is true of toluene and p-xylene. Consideration of the "Inductive" effect of the substituent groups does rather suggest a nucleophilic attack on the benzene nucleus. The evidence against it being a true nucleophilic substitution reaction is the absence of m-difluorobenzene. It has been suggested[36] that the first stage in the fluorination reaction is an addition-elimination. A reaction scheme which does account for the products formed, has been postulated on the assumption that the reagent reacts with an aromatic ring by addition of fluorine to the 1,4-position of a Kekule form in which fluorine occupies the 1-position, if present. 1-4 Elimination of hydrogen fluoride is then assumed to follow.

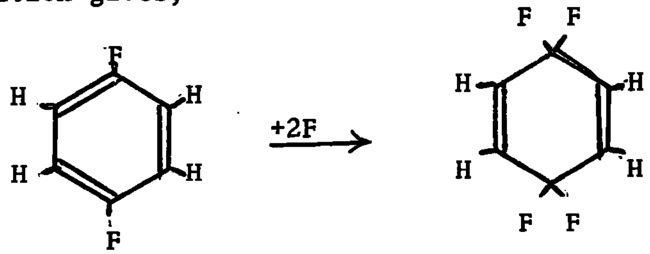
The 1,4-addition of fluorine to benzene, followed by 1,4-elimination of hydrogen fluoride, would give fluorobenzene.



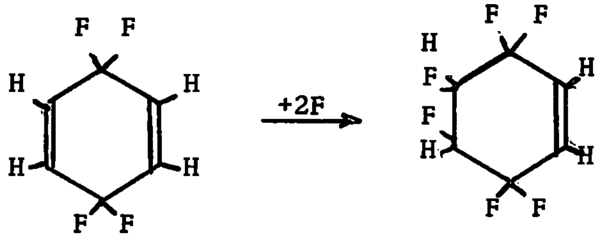
Further reaction would give p-difluorobenzene,



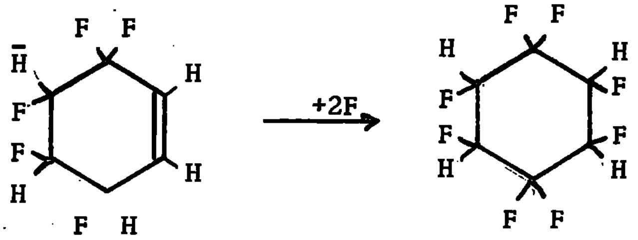
Further addition gives,



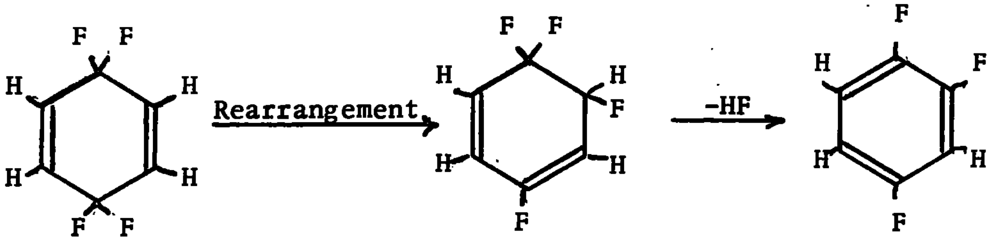
3,3,6,6-tetrafluorocyclohexa-1,4-diene which cannot readily undergo elimination of hydrogen fluoride and hence, is available to react further by 1,2-addition to give the 1H,2H,4H,5H-olefin.



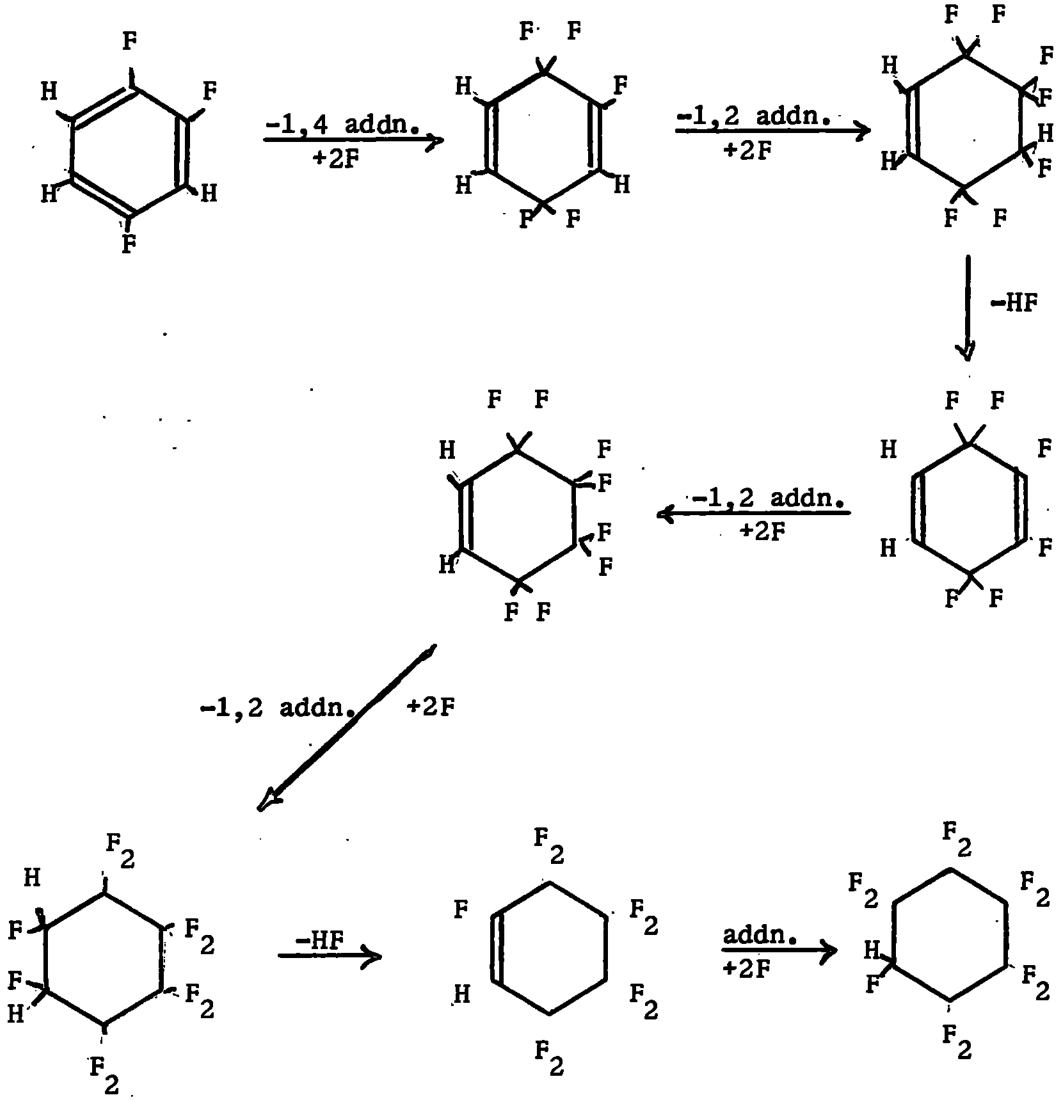
this undergoes further addition to give the octafluorocyclohexanes.



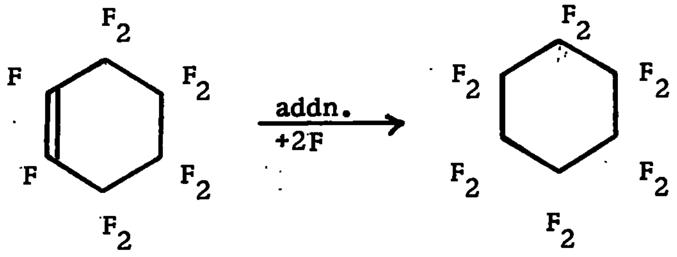
Rearrangement of 3,3,6,6-tetrafluorocyclohexa-1,4-diene by the hot metal fluoride - a type of reaction known to occur[37] with -1,4-dienes - to give a -1,3-diene, which would then readily undergo the elimination of hydrogen fluoride to give the observed 1,2,4-trifluorobenzene.



By the same mechanism, the 1,2,4-trifluorobenzene can give rise to 1,3,3,6,6-pentafluorocyclohexa-1,4-diene.



Undecafluorocyclohexane, by elimination of hydrogen fluoride and further 1,2-addition of fluorine, would give perfluorocyclohexane.



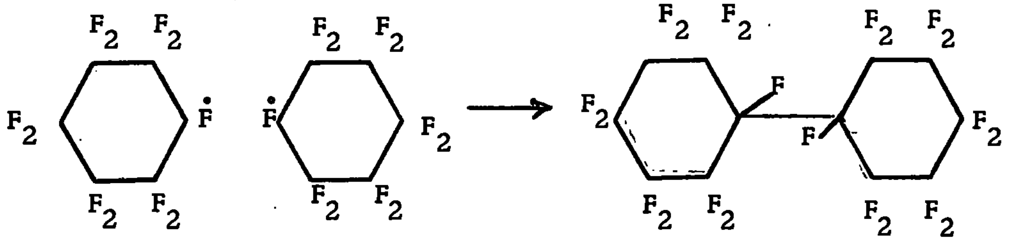
It is quite conceivable that undecafluorocyclohexane might form a free radical by a reaction such as,

$$R\text{-}H + CoF_3 \longrightarrow R^{\bullet} + HF + CoF_2 .$$

Destruction of the free radicals by reaction with CoF_3 would give perfluorocyclohexane,

$$R^{\bullet} + CoF_3 \longrightarrow RF + CoF_2$$

The free radicals might combine thus,



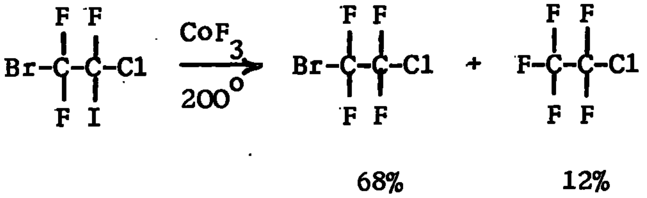
Such a reaction scheme does account for all of the products that have been isolated from the reaction mixture.

It is quite clear, from evidence in the literature, that all cobaltic fluoride fluorinations may not proceed via the same precise route. The fluorination of saturated compounds may well involve a free radical process although at present, there is no evidence to prove it.

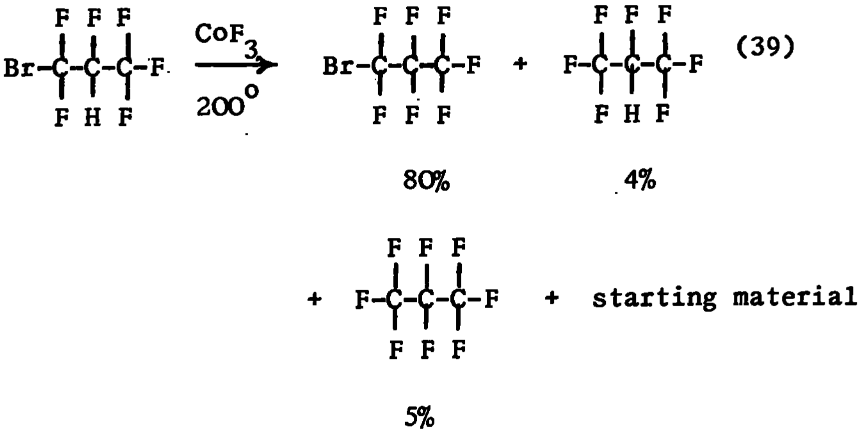
Cobaltic Fluoride Fluorinations of Chloro-, Bromo-, and Iodo- Compounds.

Early work on the vapour phase cobaltic fluoride fluorinations of various C_7 and C_8 chlorofluorohydrocarbons showed that hydrogen was readily replaced by fluorine, but chlorine was retained to a large extent. Tatlow and Worthington[38] fluorinated chlorobenzene and o-dichlorobenzene at 300 - 350°, and the main products from the former were perfluorocyclohexane and chloroundecafluorocyclohexane. The fluorination of o-dichlorobenzene gave, in addition to the same products, dichloro-decafluorocyclohexane and trichloro-nonafluorocyclohexane. The latter material had been formed by the chlorine which had been displaced, as elemental chlorine or chlorine fluorides being resubstituted into the carbon skeleton.

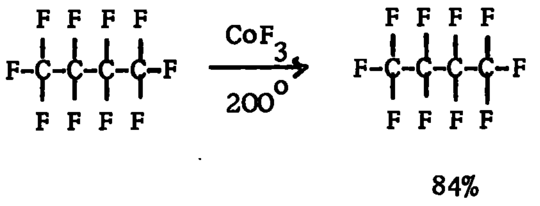
It appears that iodine is completely eliminated from perfluoroalkyl iodides under the usual fluorinating conditions. A number of perfluoroalkyl iodides[39,40] have been converted into the corresponding fluorocarbons in good yields. Two examples suggest that bromine falls into the usual intermediate position; it is more readily eliminated than chlorine and less readily than iodine.



$$\text{BrCF}_2\text{CFICl} \xrightarrow[200^{\circ}]{\text{CoF}_3} \underset{68\%}{\text{BrCF}_2\text{CF}_2\text{Cl}} + \underset{12\%}{\text{FCF}_2\text{CF}_2\text{Cl}} \qquad (39)$$



$$\text{BrCF}_2\text{CHFCF}_3 \xrightarrow[200^{\circ}]{\text{CoF}_3} \underset{80\%}{\text{BrCF}_2\text{CF}_2\text{CF}_3} + \underset{4\%}{\text{CF}_3\text{CHFCF}_3} + \underset{5\%}{\text{CF}_3\text{CF}_2\text{CF}_3} + \text{starting material} \qquad (39)$$



$$\mathrm{F{-}\overset{F}{\underset{F}{C}}{-}\overset{F}{\underset{F}{C}}{-}\overset{F}{\underset{F}{C}}{-}\overset{F}{\underset{F}{C}}{-}F} \xrightarrow[200^{o}]{\mathrm{CoF_3}} \mathrm{F{-}\overset{F}{\underset{F}{C}}{-}\overset{F}{\underset{F}{C}}{-}\overset{F}{\underset{F}{C}}{-}\overset{F}{\underset{F}{C}}{-}F} \qquad (39)$$

84%

Vapour Phase Fluorinations with Manganese Trifluoride.

Manganese trifluoride is said to be similar to cobaltic fluoride in its behaviour, but it is less reactive. Similar reactors to those described for use with cobaltic fluoride are suitable for this reagent. The use of manganese trifluoride as an alternative fluorinating agent, has been investigated by Fowler and his co-workers.[41] These workers concluded, after comparing the two fluorinating agents for the fluorination of n-heptane, in the temperature range 150 - 250°, that MnF_3 effected a lesser degree of fluorination. Their investigation was extended to the production of fluoro oils and they found that manganese trifluoride gave better yields, presumably because it caused less chain breakdown. Fear and Thrower[42] investigated the fluorination of benzene with manganese trifluoride and, in the temperature range 200 - 350°, they obtained a complex mixture which was found to contain polyfluorocyclohexenes, dimeric material, monofluorobenzene and unreacted benzene. Two of the major reaction products obtained, were described as an octa and a nonafluorocyclohexane. The same reaction has been repeated[43] and the products have been identified as 1H,4H-octafluorocyclohex-1-ene and 1H,2H,4H-heptafluorocyclohex-1-ene.

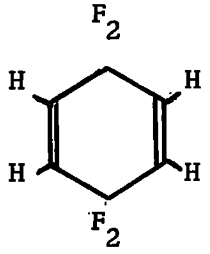
In reactions attempted below 200°, no reaction was found to have taken place at all; even at 350° only traces of perfluorocyclohexane were detected.

Evidence does show that manganese trifluoride is a much milder fluorinating agent than cobalt trifluoride and it does appear to be specifically less reactive towards unsaturation. In fact, the manganese trifluoride fluorination of benzene, at 200-350°, does provide the best route to 1H,4H-octafluorocyclohex-1-ene and 1H,2H,4H-heptafluorocyclohex-1-ene.

Vapour Phase Fluorinations with Potassium Tetrafluorocobaltinate.

Recently,[17] a complex cobalt trifluoride ($KCoF_4$) has been investigated as a possible fluorinating agent. Benzene, fluorobenzene and p-difluorobenzene have been fluorinated with this reagent and the results compared with those obtained by using cobalt trifluoride. The reactions were carried out using a stirred bed reactor similar to that used for cobalt trifluoride and manganese trifluoride fluorinations. Regeneration was effected in the usual manner, using elemental fluorine.

When benzene was fluorinated at 280°, the product mixture was found to be much simpler than that which resulted when cobalt trifluoride was used. Apart from a small amount of perfluorocyclohexane, the products were nearly all unsaturated. Perfluorocyclohexene was formed to a very small extent but 1H,2H,4H,5H-hexafluorocyclohexene constituted some 35 - 50% of the mixture. The following compounds were isolated and characterized:-



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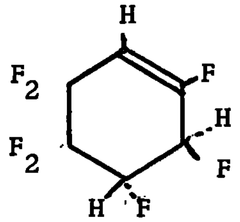

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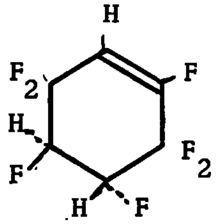

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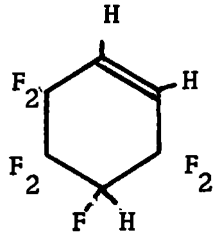

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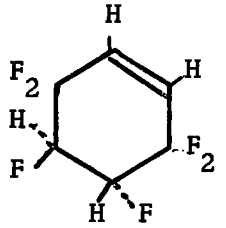

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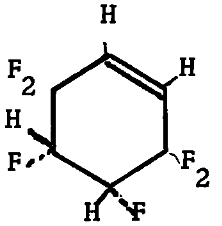

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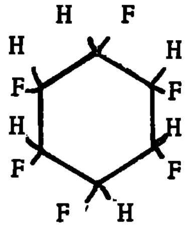


0·5%
(7)

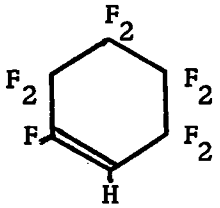
The addition-elimination reaction mechanism previously proposed for cobalt trifluoride fluorination of benzene, postulates compounds 1-4 as intermediates in this reaction. In the cobalt trifluoride fluorination of benzene, fluorobenzene and p-difluorobenzene were present in trace amounts in the reaction mixture. These two compounds have been fluorinated using the complex fluorinating reagent ($KCoF_4$) and the reaction mixtures found to be the same as that obtained when benzene is fluorinated using the same reagent.

In conclusion it has been stated that an addition-elimination mechanism in which fluorobenzene p-difluorobenzene and 3,3,6,6-

tetrafluorocyclohexa-1,4-diene are intermediates, is plausible.

Vapour Phase Fluorinations with Cerium Tetrafluoride.

Although cerium tetrafluoride had previously been used[44] to fluorinate hydrocarbon oils, hexachlorobutadiene and dichlorodecafluorocyclohexane, it has only recently[45] been investigated as a possible exhaustive fluorinating agent for hydrocarbons. Tatlow and his co-workers examined the fluorination of benzene and found that below 400°, little fluorination occurred. At 480°, the reaction product was found to contain unsaturated alicyclics (40%), fluoroaromatics (10%), benzene (30%), and unidentified residue (20%). No saturated fluorocarbons were isolated. The following compounds were isolated:-



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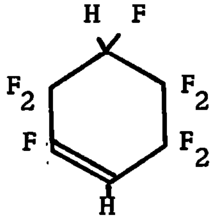

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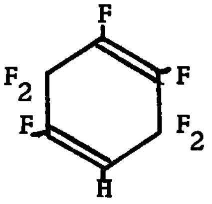

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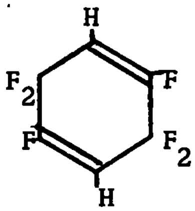

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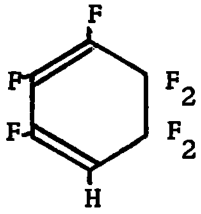
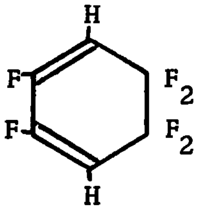


V



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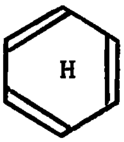

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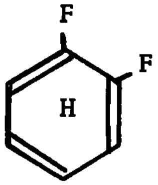

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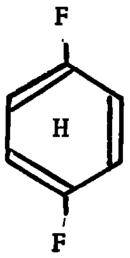

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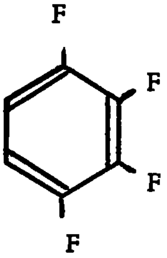
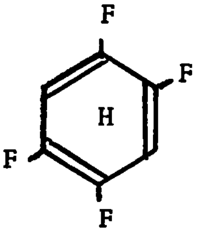


X



XI

I 1H-Nonafluorocyclohex-1-ene.

II 1H,4H-Octafluorocyclohex-1-ene.

III 1H-Heptafluorocyclohexa-1,4-diene.

IV 1H,4H-Hexafluorocyclohexa-1,4-diene.

V 1H-Heptafluorocyclohexa-1,3-diene.

VI 1H,4H-Hexafluorocyclohexa-1,3-diene.

VII Benzene.

VIII o-Difluorobenzene.

IX p-Difluorobenzene.

X 1,2,3,4-Tetrafluorobenzene.

XI 1,2,4,5-Tetrafluorobenzene.

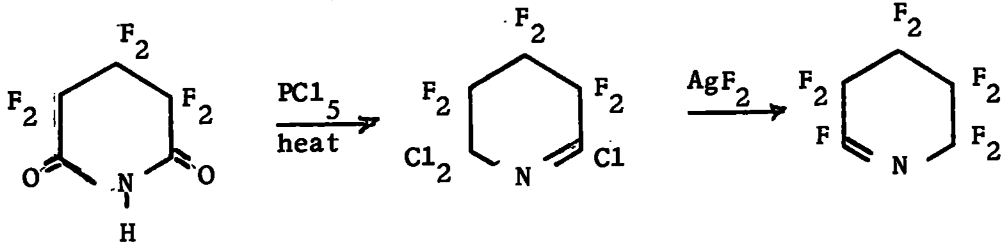
The Fluorination of Nitrogen Heterocyclic Compounds.

Simons[46] reported that the electrolysis of pyridine in anhydrous hydrogen fluoride, yields some perfluoropentane and nitrogen trifluoride but principally perfluoro-1-azacyclohexane. The same fluorination reaction was re-examined by Simmons et. al.[47], who isolated perfluoro-1-azacyclohexane in 7% yield along with perfluoropentane and other cleavage products. Both the catalytic and cobaltic fluoride methods of fluorinating pyridine have been investigated by Haszeldine,[48] who described his results as being successful although he recorded yields of perfluoro-1-azacyclohexane of 0•2% and 0•3% respectively for the two methods. It was suggested that the low yields were due to the formation of the involatile hydrofluoride which then underwent decomposition. During these fluorinations the elimination of nitrogen occurred, probably as nitrogen trifluoride and the straight chain fluorocarbon, C_5F_{12}, was reported along with compounds in which C-C bond fission had occurred instead of C-N bond fission. This led Banks and Williamson[49] to attempt the direct vapour phase fluorination of the less basic and more volatile 2-fluoropyridine; they obtained virtually none of the desired perfluoro-1-azacyclohexane but a highly complex reaction mixture due to the disruption of the pyridine ring and splitting out of the nitrogen. Pyridine has however been fluorinated in the liquid phase using nitrogen to dilute the fluorine, fluorotrichloromethane as solvent, and a temperature of -80^{o}, by Meinert[50] who succeeded in isolating a precipitate of 2-fluoropyridine fluoride (F_2py.) which decomposed violently when allowed to warm to above -2^{o}. The decomposition product was found to be 2-fluoropyridine.

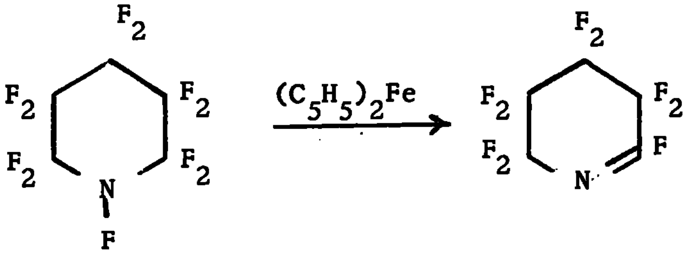
Pentafluoropyridine has been obtained by the defluorination of perfluoro-1-azacyclohexane, at atmospheric pressure, over nickel at 560° [51] but the yield was only about 12%. A similar reaction has been carried out using finely divided iron[52] for the defluorination and a pressure less than 1 mm. Hg to afford a similar low yield.

In looking for a suitable route to pentafluoropyridine from pentachloropyridine, Chambers et al.[53] developed Sell and Dootson's[54] method for the chlorination of pyridine with phosphorus pentachloride and were able to report excellent yields (68·5%) of pentafluoropyridine by reacting pentachloropyridine with anhydrous potassium fluoride in the absence of a solvent. The same route has also been reported by workers at Manchester University.[55]

Not unexpectedly, the direct fluorination of pyridine has not given rise to any unsaturated material. The only perfluoro-1-azacyclic olefin to be reported, perfluoro-1-azacyclohex-1-ene was first synthesised by Ulrich et al.[56] from hexafluoroglutarimide which was heated with phosphorus pentachloride to form 2,6,6-trichlorohexafluoro-1-azacyclohexene-1 which was subsequently treated with silver difluoride.



The same olefin has been obtained by Mitsch[57] in the reductive defluorination of perfluoro-1-azacyclohexane, using dicyclopentadienyl iron.

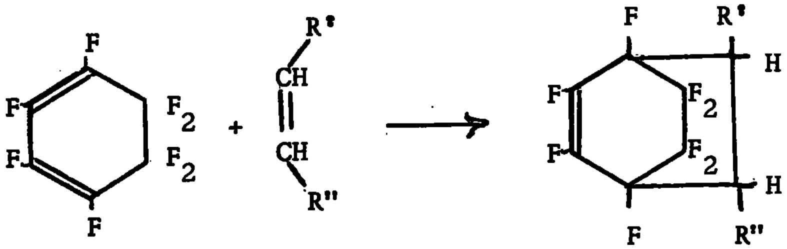


Banks et al.[58] also obtained the same compound during the pyrolytic defluorination of perfluoro-1-azacyclohexane to obtain pentafluoropyridine.

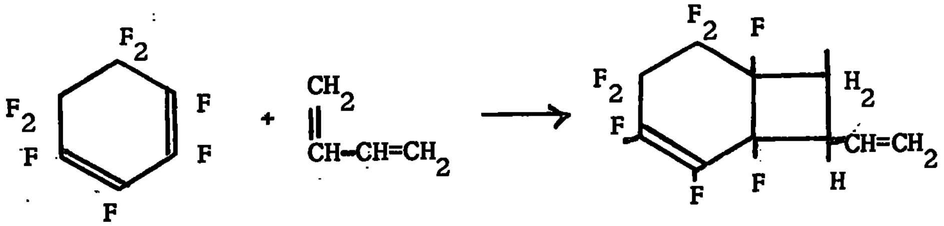
Although perfluorocyclohexadienes can be prepared[59] in excellent yields by the mild cobaltic fluoride fluorination of benzene to polyfluorohydrocyclohexanes, followed by exhaustive dehydrofluorination, there appears to be no parallel method for preparing perfluoro-1-azacyclohexadienes, for no polyfluorohydro-1-azacyclohexanes have been isolated during the fluorination of pyridine. All attempts at fluorinating pyridine have resulted in low yields of perfluoro-1-azacyclohexane and a great deal of fragmentary material formed by the fission of both C-C and C-N bonds.

In looking for a suitable route to perfluoro-1-azacyclohexadienes, pentafluoropyridine has been chosen as a suitable starting material. It was anticipated that the more stable molecule would undergo fluorination without any appreciable fragmentation. This has been achieved, but the difficulty has been in stopping the reaction at the diene stage. Nevertheless, perfluoro-1-azacyclohexa-1,3-diene has been successfully prepared and it is thought important to prepare it because it is anticipated that it will undergo Diels-Alder additions and lead to the preparation of polyfluorinated nitrogen bridge compounds.

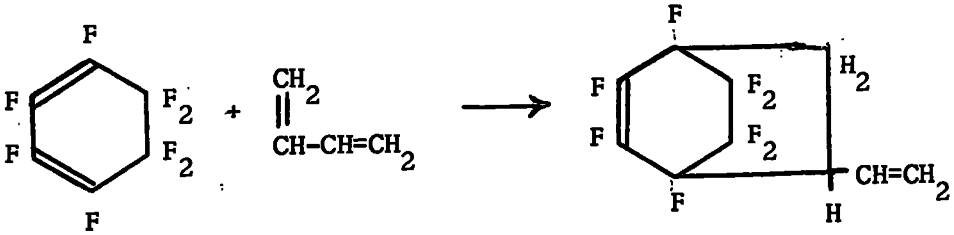
The first example of a polyfluorinated diene to undergo Diels-Alder additions was demonstrated by Chambers et al.[60] These workers prepared a number of Diels-Alder adducts between octafluorocyclohexa-1,3-diene and various substituted ethylenes and anthracene.



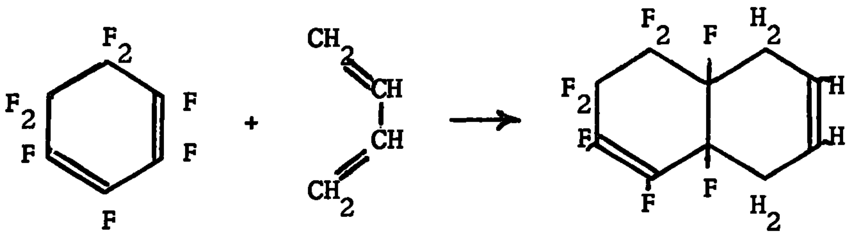
With butadiene, octafluorocyclohexa-1,3-diene was shown to react as both a diene and a dienophile.



(a)



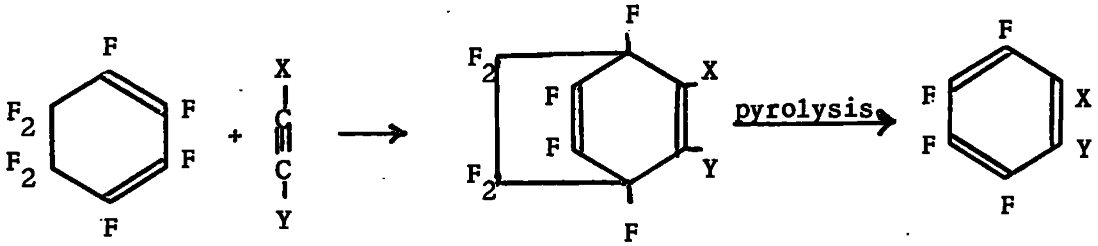
(b)



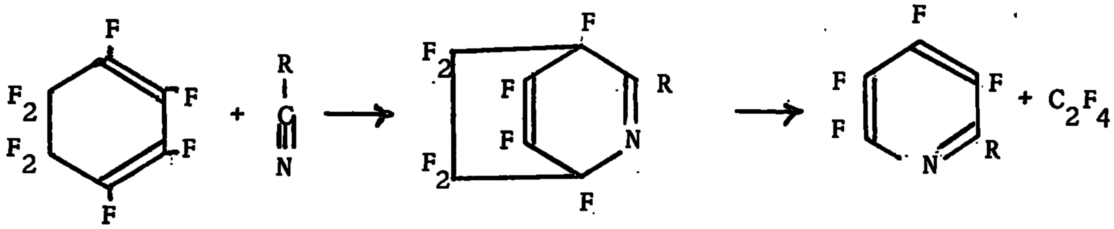
(c)

Passage of a mixture of these compounds over steel wool at 425°, caused isomerisation of structures a and b to c, which was simultaneously dehydrofluorinated and defluorinated to give a convenient synthesis of tetrafluoronaphthalene.

An extension of this work to cover the reaction of octafluorocyclohexa-1,3-diene with alkynes[61] has provided an excellent route to 1,2-disubstituted tetrafluorobenzenes.



It has recently been reported[62] that nitriles with strongly electronegative substituents and perfluorocyclohexa-1,3-diene undergo 1,4-addition reactions under forcing conditions and that the primary adducts eliminate tetrafluoroethylene to give 2-substituted tetrafluoropyridines as the major products.



R = $-CF_3$; $-Br$; $-C_6F_5$; $[CF_2]_3CN$; $[CF_2]_3C_5F_4N$

The object of this research has been to find a route to perfluoro-1-azacyclohexadienes.

CHAPTER II

DISCUSSION

DISCUSSION

Fluorination of Hexafluorobenzene

Elemental Fluorination of Hexafluorobenzene.

In a series of preliminary experiments, hexafluorobenzene has been reacted, in a suitable solvent, with elemental fluorine to ascertain whether or not the reaction could be controlled to leave unsaturation in the molecule. Several low temperature (-30 to -55^{o}) liquid phase fluorinations were carried out in which fluorine gas, diluted with nitrogen, was passed through a solution of hexafluorobenzene in a) perfluorokerosene and b) Isceon 113 (1,1,2-trichlorotrifluoroethane). Examination of the reaction mixtures showed small amounts of perfluorocyclohexane, -ene and -1,4-diene along with large amounts of high molecular weight material. It was found possible to vary the relative amounts of monomeric material formed by varying the temperature and the amount of fluorine used. However, it was not possible to reduce greatly, the amount of polymeric material. The results are not surprising since it has been well established that such reactions proceed via a free radical mechanism. This method was abandoned in favour of the vapour phase cobaltic fluoride fluorination process.

The Cobaltic Fluoride Fluorination of Hexafluorobenzene.

With 600 g. of cobaltic fluoride in the reactor, a number of exploratory reactions were carried out at various temperatures and nitrogen flow rates. The rate of addition of the substrate and the degree of exhaustion of the fluorinating agent being kept as constant as possible. From the results obtained (see Table 1) it would appear that the reaction can be readily controlled to give good yields of perfluorocyclohexane or perfluorocyclohexene but insignificant amounts of perfluorocyclohexa-1,4-diene and none of the corresponding -1,3-diene.

The Cobaltic Fluoride/Calcium Fluoride Fluorination of Hexafluorobenzene.

The reactor was packed with cobaltic fluoride (150 g.) and calcium fluoride (150 g.) in the hope that the reaction would be moderated to produce significantly more of the perfluorocyclohexa-1,4-diene. In this series of reactions, better yields were achieved and the results (see Table 2) do indicate that it is possible to produce significantly more of the -1,4-diene but do not point to it being a feasible preparative route to the latter.

The Manganese Trifluoride Fluorination of Hexafluorobenzene.

The reactor was packed with manganese trifluoride (600 g.) to see if its known lesser activity as a fluorinating agent would give rise to more unsaturated material. The results (see Table 3) show that manganese trifluoride gives rise to a better yield of the -1,4-diene than does cobalt trifluoride but a slightly poorer yield than is obtained when the fluorinating agent is a 50:50 mixture of cobalt trifluoride and calcium fluoride.

TABLE I. Products from the Cobaltic Fluoride Fluorination of Hexafluorobenzene.

Reaction No.	Substrate (gms.)	Yield (gms.)	Temp. (^{o}C)	N_2 flow (cc./min.)	 (%)	 (%)	 (%)	 (%)	 (%)
1	6•4	6•0	100/106	80	32	68	0	0	0
2	6•4	4•6	85/87	80	17	83	0	0	0
3	6•4	3•5	70/75	80	7	93	0	0	0
4	6•4	3•0	60/65	200	8	92	0	0	0
5	6•4	3•0	RT	200	trace	98	trace	0	0
6	6•4	3•2	RT	200	0	44	17	0	39

Remarks: Reactor packed with 600 gms. of cobaltic fluoride.

In reactions 1 — 5 the substrate was dropped directly into the reactor during a period of 45 mins.

In reaction 6, the substrate was carried into the reactor as a vapour.

TABLE 2. Products from the Cobaltic Fluoride/Calcium Fluoride Fluorination of Hexafluorobenzene.

Reaction No.	Substrate (gms.)	Yield (gms.)	Temp. (^oC)	N_2 flow (cc./min.)	 (%)	 (%)	 (%)	 (%)	 (%)
7	6•4	9•0	150	50	100	0	0	0	0
8	6•4	8•0	150	250	58	42	0	0	0
9	6•4	8•8	100	80	9	89	2	0	0
10	6•4	6•7	80/86	80	0	88	12	0	0
11	6•4	7•0	70/72	80	0	80	20	0	0
12	6•4	6•0	50	80	0	51	26	0	23
13	6•4	5•5	50	250	0	35	22	0	43

Remarks: Reactor packed with cobaltic fluoride (150 g.) and calcium fluoride (150 g.).

In reactions 7 — 12 the substrate was dropped directly into the reactor during a period of 40 mins.

In reaction 13 the substrate was dropped into a vaporizer at 100° during a period of 40 mins.

TABLE 3. Products from the Manganese Trifluoride Fluorination of Hexafluorobenzene.

Reaction No.	Substrate (gms.)	Yield (gms.)	Temp. (^{o}C)	N_2 flow (cc./min.)	 (%)	 (%)	 (%)	 (%)	 (%)
14	6•4	6•0	100/104	80	0•1	6•3	11•1	0	82•5
15	6•4	7•0	210	80	3•7	52•9	20•9	0	22•5

Remarks: Reactor packed with 600 gms. of manganese trifluoride.

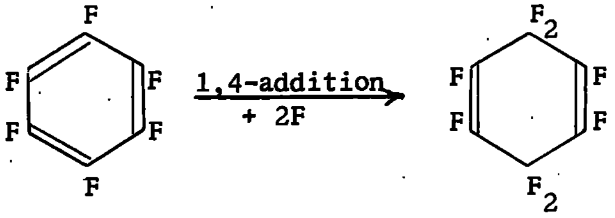
The substrate was dropped directly into the reactor.

As expected, the composition of the reaction mixture has been found to be dependent upon the reactor temperature and the nitrogen flow rate; the rate of addition of the substrate and the degree of exhaustion of the fluorinating agent have been kept as constant as possible. By a suitable choice of reactor temperature and nitrogen flow rate, it has been found possible to obtain excellent yields (90-100%) of perfluorocyclohexane and perfluorocyclohexene but only moderate yields (20%) of perfluorocyclohexa-1,4-diene.

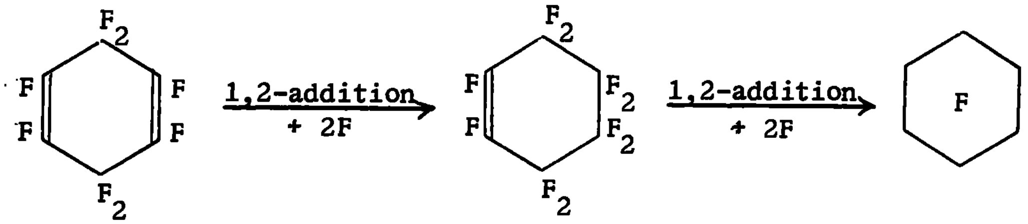
Mechanism.

Bearing in mind the reaction mechanism postulated for the cobaltic fluoride fluorination of benzene (36), namely, that the reaction proceeds via a series of 1,4- and 1,2-additions of fluorine, followed by 1,4-elimination of hydrogen fluoride, it is quite conceivable that the fluorination of hexafluorobenzene also proceeds via 1,4-addition followed by 1,2-addition of fluorine.

It is significant that at no time was any perfluorocyclohexa-1,3-diene formed and so it is likely that the initial step in the reaction is the 1,4-addition of fluorine,



and this is followed by 1,2-addition.

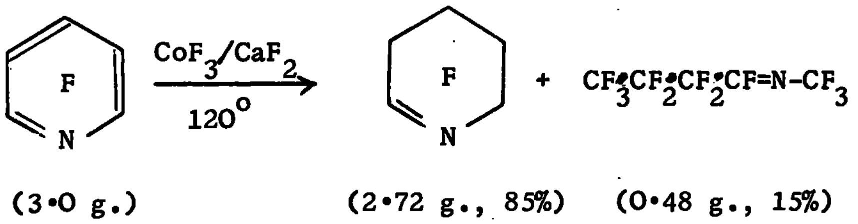


It can only be concluded that the addition of fluorine is a kinetically controlled reaction. The energy barrier for the addition of fluorine across the 1,4-position to form the non-conjugated diene must be lower than for 1,2-addition to form the conjugated diene which is in fact the more stable.

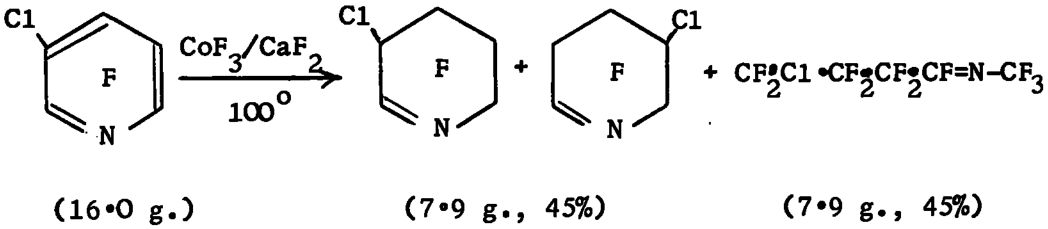
The Cobaltic Fluoride/Calcium Fluoride Fluorination of Tetrafluoro- and Polyfluorohalo-pyridines.

It has been reported in the literature[48] that cobaltic fluoride fluorinations of pyridine have resulted in C-C and C-N bond fission and very low yields of the desired perfluoro-1-azacyclohexane. The poor yields were accounted for by suggesting salt formation between the parent amine or lightly fluorinated intermediates, and hydrogen fluoride liberated during the reaction. The direct vapour phase fluorination of the less basic and more volatile 2-fluoropyridine[49] did not however, result in the formation of any perfluoro-1-azacyclohexane but did produce a highly complex reaction mixture due to the disruption of the pyridine ring and splitting out of the nitrogen.

If it is the basicity of the substrate that is the reason for the poor results, then this difficulty should not arise when pentafluoropyridine and other non basic substrates are fluorinated. Hence it should be possible to use the latter for preparing perfluoroazacyclohexadienes, which may undergo Diels-Alder addition and lead to the preparation of polyfluorinated nitrogen bridge compounds. To achieve this, the non basic and more stable pentafluoropyridine, -3-chloro-, -4-chloro-, -4-bromo-, -3,4-dichloro- and -3,5-dichloro-derivatives have been examined as possible starting materials. These compounds have been fluorinated using a mixture of cobaltic fluoride (150 g.) and calcium fluoride (150 g.) as described earlier for hexafluorobenzene because this appeared to be the most easily controlled method. In each case the substrate was dropped directly into the reactor. The reactions are summarised below:-



(A)



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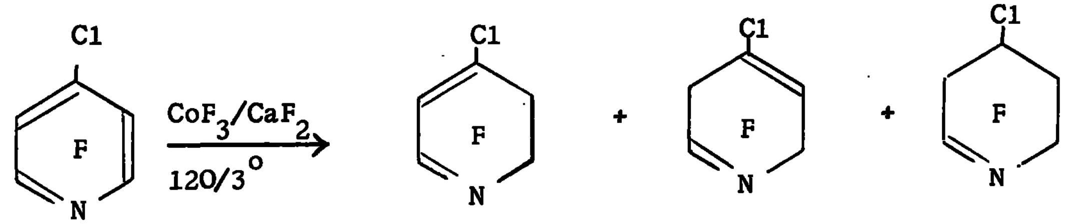
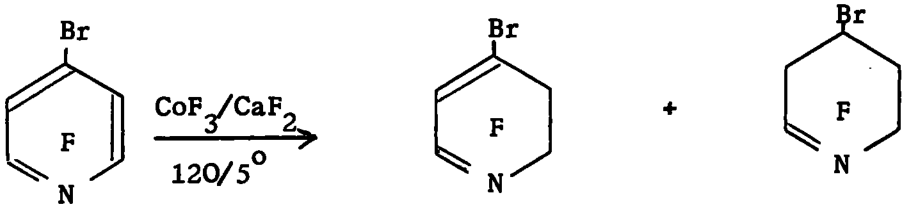
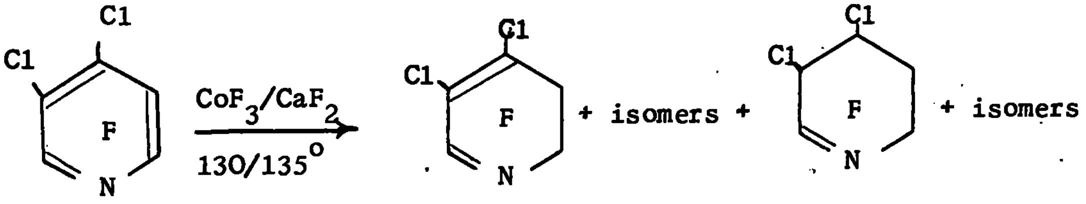


(14·75 g.) (8·0 g., 52·4%) (0·4 g., 2·6%) (2·5 g., 16·4%)



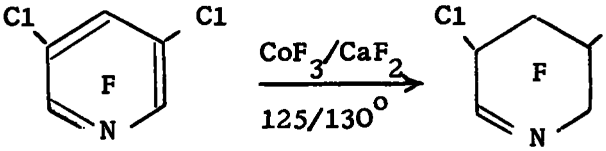
(5·0 g.) (0·46 g., 9%) (4·18 g., 82%)



(15·0 g.) (2·9 g., 21·8%) (6·0 g., 44·5%)

+ $CF_2Cl \cdot CFCl \cdot CF_2 \cdot CF{=}N{-}CF_3$ (C)

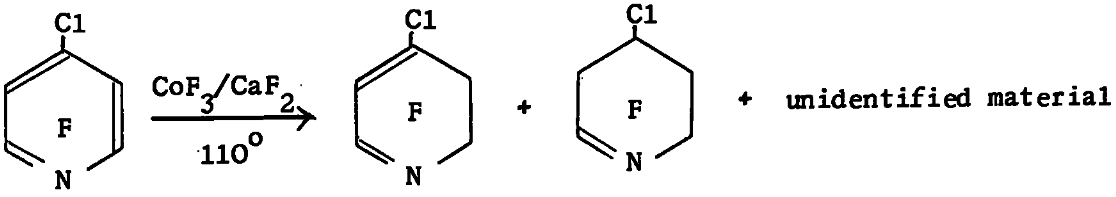
(1·65 g., 12·2%)



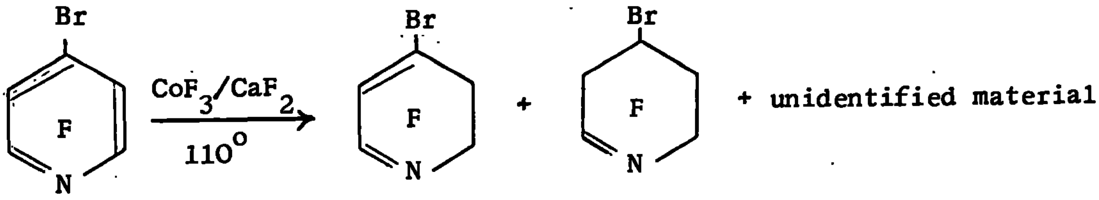
+ $CF_2Cl \cdot CF_2 \cdot CFCl \cdot CF{=}N{-}CF_3$ (D)

(16·0 g.) (8·0 g., 67·0%) (3·36 g., 28·0%)

It would appear from the above results that 4-bromotetrafluoropyridine fluorinates more readily than the 4-chloro-derivative. Since it could be argued that at the same fluorination temperature, the less volatile 4-bromo compound would have a longer contact time with the fluorinating agent and hence a greater degree of fluorination would be expected, both substrates were fluorinated under identical conditions, i.e. the same reactor temperature (110°) and the same contact time. This was achieved by heating the substrate at 30° below its boiling point and carrying it through the reactor by passing a steady stream of nitrogen gas (150 cc./min.) through it. These results are summarised below:-



(2·0 g.) (0·53 g., 31·4%) (0·88 g., 51·9%) (0·29 g., 16·7%)



(2·0 g.) (0·05 g., 3·6%) (1·07 g., 67·0%) (0·48 g., 29·4%)

A literature survey has revealed that no attempt has previously been made to react perfluoro heterocyclic aromatic compounds with cobaltic fluoride and hence, there is no evidence other than that now presented regarding the reaction mechanism. In regard to the fluorinations under consideration, the correct reaction mechanism must explain:-

1) the presence of unsaturated material in the products,
2) the absence of polymeric material,
3) the ring opening of perfluoro-1-azacyclohex-1-ene and its haloderivatives,
4) the retention of the halogen other than fluorine,
5) whereas hexafluorobenzene has been shown to give all 1,4-diene and no 1,3-diene, the 4-halo-derivatives of pentafluoropyridine give almost all 1,3-dienes and negligible amounts of 1,4-dienes,
6) hexafluorobenzene gives considerable amounts of perfluorocyclohexane but pentafluoropyridine gives no perfluoro-1-azacyclohexane.

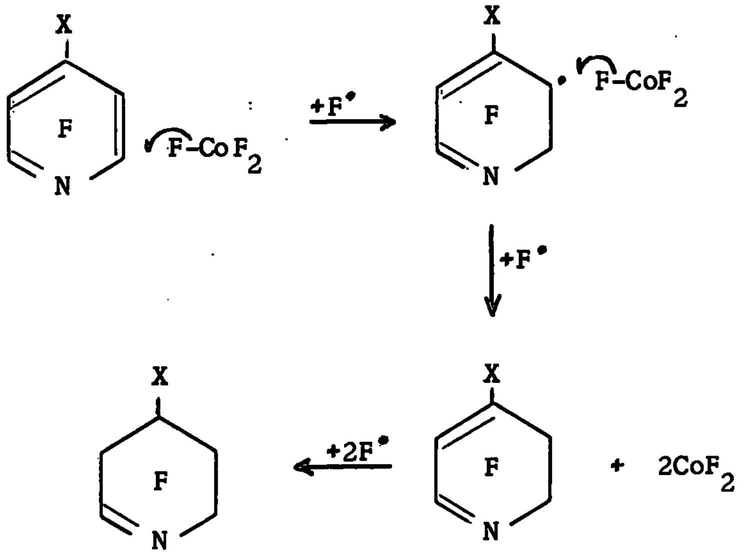
Possible Mechanisms for the Fluorination.

There being insufficient evidence on which to base a detailed mechanism for the fluorination, only some tentative suggestions as to the possible mechanisms will be discussed.

All the fluorination mixtures proved to be relatively simple; no saturated cyclic material but large amounts of unsaturated cyclic material along with perfluoro-2-azahex-2-ene or its halo-derivative (see compounds A, B, C and D, pp. 51 and 52) was obtained.

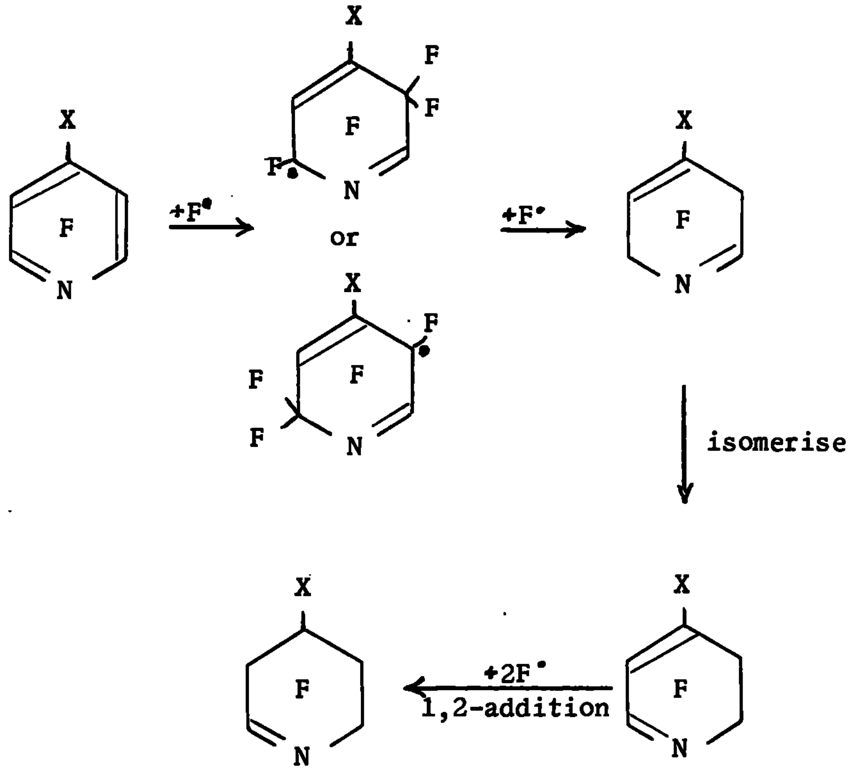
The initial steps in the reactions could well involve a simple addition of fluorine from the cobaltic fluoride to the double bonds by a radical reaction of the type indicated in the following two reaction paths.

(a) The reaction may proceed via a succession of 1,2-additions of fluorine



X = F, Cl, Br

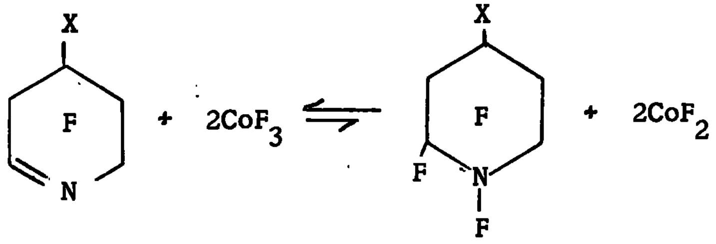
(b) The initial step may well be 1,4-addition to give the 1,4-diene and then rapid isomerisation to the conjugated 1,3-diene followed by 1,2-addition.



A molecule of cobalt trifluoride reacts with the substrate by addition of one fluorine atom and the resulting radical is immediately destroyed by reaction with a second molecule of cobalt trifluoride.

From a large scale fluorination of 4-chlorotetrafluoropyridine (16•0 g.), the unconjugated 1,4-diene has been isolated, the yield being 2•6%. This does present some evidence that the fluorination proceeds via the outlined path b.

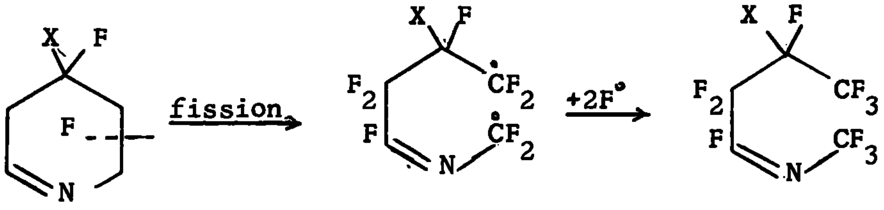
In none of the reactions carried out was any material found in which the -C=N- group had been saturated. For example, the following reaction does not take place under any of the conditions used.



X = F, Cl, Br

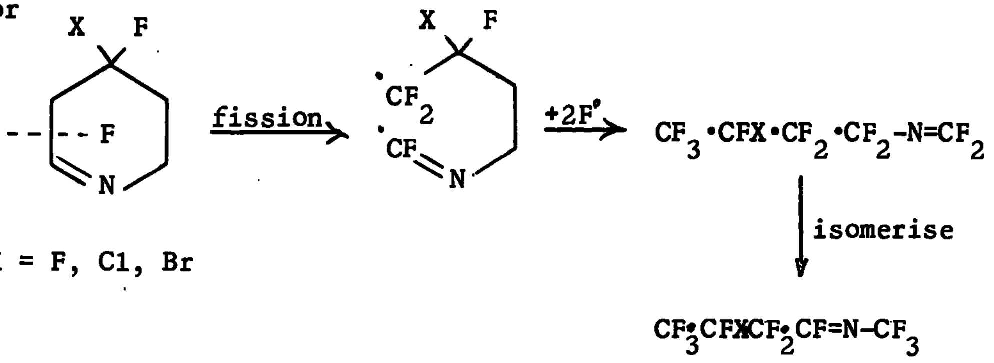
This is not surprising, for ΔH^o for this reaction, calculated from bond strengths (C=N $\simeq$ 75 Kcals/mole; Co-F $\simeq$ 50 Kcals/mole; C-F $\simeq$ 105 Kcals/mole and N-F $\simeq$ 60 Kcals/mole) is approximately + 10 Kcals/mole and ΔS^o would be expected to be $\simeq$ 0. The calculated value for the equilibrium constant, K at 100°, is approximately $1{\cdot}3 \times 10^{-6}$, indicating that the equilibrium would favour the reactants. It is the relatively low N-F bond strength that is unfavourable for the formation of the saturated compound.

The next step in the reaction involves carbon-carbon bond fission and hence it must be assumed that the precursor of the imine is the perfluoro-1-azacyclohex-1-ene.



X = F, Cl, Br

or

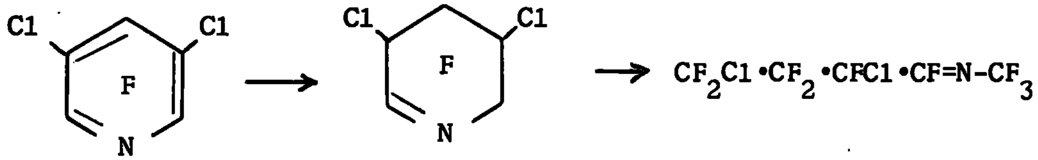


$CF_3\cdot CFX\cdot CF_2\cdot CF_2-N=CF_2$

$CF_3\cdot CFX\cdot CF_2\cdot CF=N-CF_3$

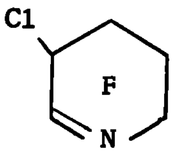
X = F, Cl, Br

Carbon-carbon bond fission produces a di-radical which immediately reacts with two molecules of cobalt trifluoride. In the latter reaction path, the resulting straight chain compound would be expected to isomerise to the thermodynamically more stable isomer, having a terminal-CF_3 group. The same reaction paths could be postulated for the reaction:-

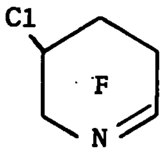


$CF_2Cl\cdot CF_2\cdot CFCl\cdot CF=N-CF_3$

However, the fluorination of the unsymmetrical molecule 3-chlorotetrafluoropyridine results in the formation of a pair of isomers (ratio 1:1), which analyse as cyclic monomers, and have defied separation by g.l.c. These isomers are assumed to have the following structures,



and

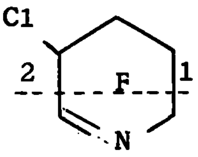


isomer (a)

isomer (b)

One would expect further fluorination to produce two straight chain compounds:-

isomer(a)



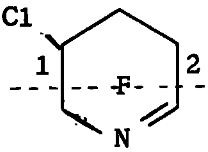
$\xrightarrow{\text{fission}}$

1. $CF_3\cdot CF_2\cdot CFCl\cdot CF{=}N{-}CF_3$
2. $CF_2Cl\cdot CF_2\cdot CF_2\cdot CF_2{-}N{=}CF_2$

$$\Big\downarrow \text{isomerise}$$

$$CF_2Cl\cdot CF_2\cdot CF_2\cdot CF{=}N{-}CF_3$$

isomer (b)



$\xrightarrow{\text{fission}}$

1. $CF_2Cl\cdot CF_2\cdot CF_2\cdot CF{=}N{-}CF_3$
2. $CF_3\cdot CF_2\cdot CFCl\cdot CF_2{-}N{=}CF_2$

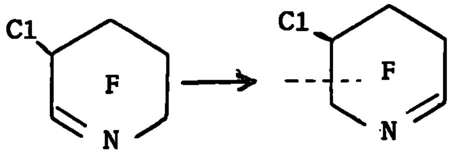
$$\Big\downarrow \text{isomerise}$$

$$CF_3\cdot CF_2\cdot CFCl\cdot CF{=}N{-}CF_3$$

Quite unexpectedly, only one isomer is formed:-

$$CF_2Cl\cdot CF_2\cdot CF_2\cdot CF{=}N{-}CF_3$$

Clearly, this could arise if isomer a rearranged to isomer b prior to carbon-carbon bond fission.

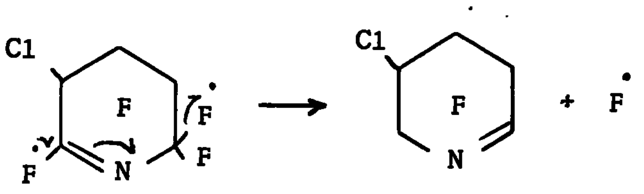


$\xrightarrow{\text{fission}}$ $\dot{C}FCl\cdot CF_2\cdot CF_2\cdot CF{=}N{-}\dot{C}F_2$

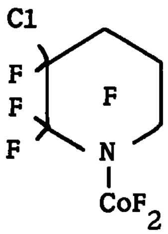
$$\Big\downarrow {+2F^{\bullet}}$$

$$CF_2Cl\cdot CF_2\cdot CF_2\cdot CF{=}N{-}CF_3$$

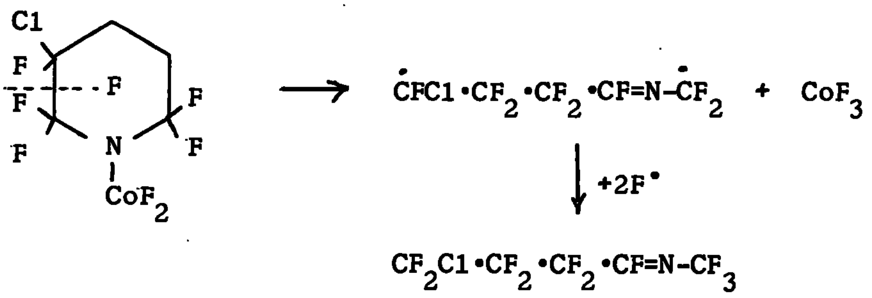
It is proposed that the isomerisation is induced by fluorine radicals,



Alternatively, it is tentatively suggested that the isomers form a symmetric complex with the cobalt trifluoride, e.g.



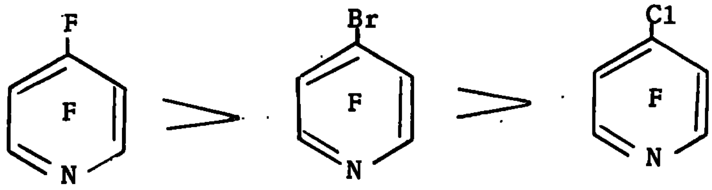
which might be formed by the addition of cobaltic fluoride across the double bond of the cyclic monoenes. It is proposed that subsequently, the carbon-carbon bond, $-CFCl-CF_2-$, undergoes fission and the complex breaks down to give the imine.



Although there is no evidence to support the suggestion that the reaction involves the addition of cobaltic fluoride to the double bond of the fluoro-olefin, it is well known that certain metal fluorides e.g. mercuric and silver, do react in this way. The latter reactions have been reviewed by Chambers and Mobbs.[64]

Under the mild conditions of the fluorinations, it is not surprising that the halogen other than fluorine has been retained. The cobaltic fluoride fluorination, at 300-350°, of chlorobenzene[38] has been shown to produce both perfluorocyclohexane and chloroundecafluorocyclohexane. It has also been demonstrated,[39] that bromine is more readily eliminated than chlorine but less readily than iodine. No replacement of chlorine or bromine was observed when chloro- and bromo-tetrafluoropyridines were reacted with cobaltic fluoride under the very mild conditions of the present experiments.

Fluorination of the series pentafluoropyridine, 4-chloro- and 4-bromo-tetrafluoropyridine indicates that the order of ease of reaction is:-

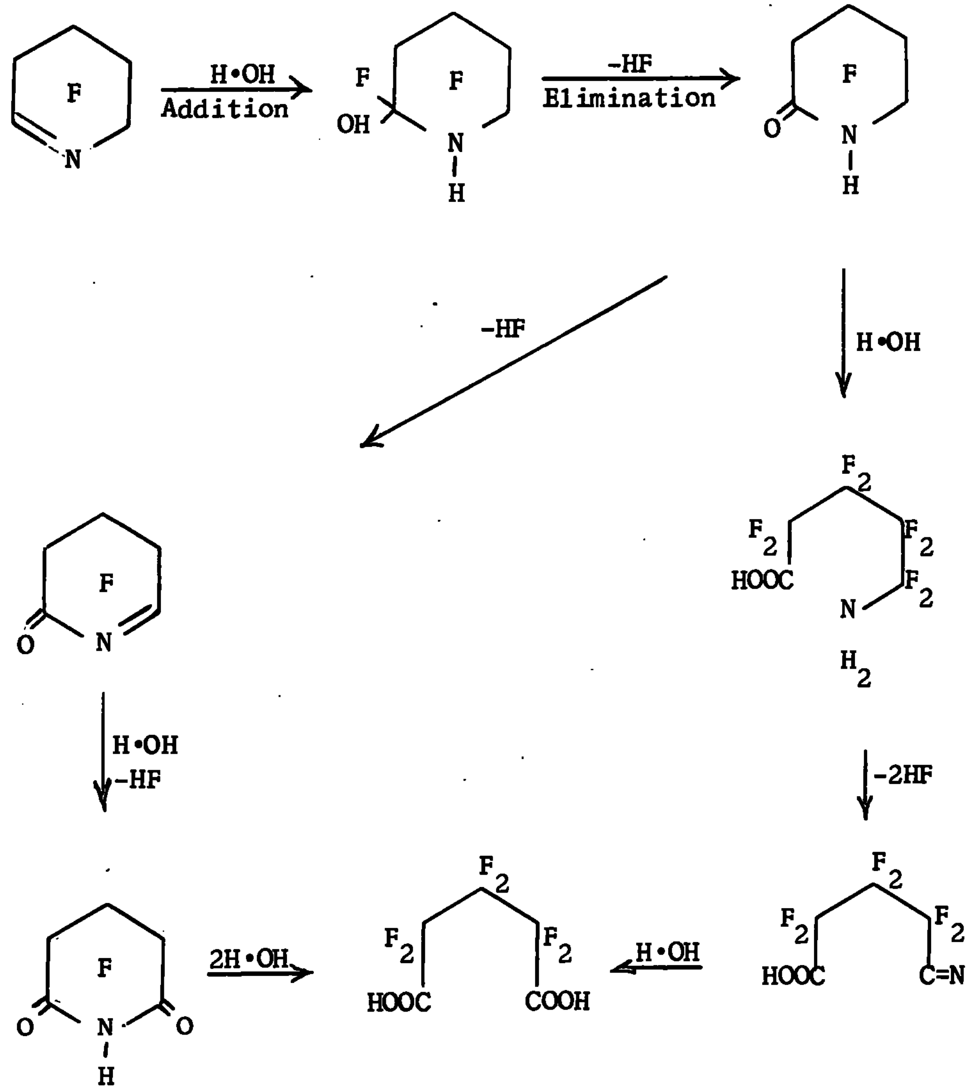


It was assumed that the unexpected order was due to the fact that at the temperature of the fluorination, the less volatile 4-bromotetrafluoropyridine would have a longer contact time, with the cobaltic fluoride and that this would explain the greater degree of fluorination. Consequently the fluorination of the 4-chloro- and 4-bromo-tetrafluoropyridine was repeated and the results of these reactions do confirm the peculiar order for which, so far, there is no evidence to suggest any explanation.

Nucleophilic Attack on Polyfluoro-1-azacyclohex-1-enes and -dienes.

The Hydrolysis of Perfluoro-1-azacyclohex-1-ene.

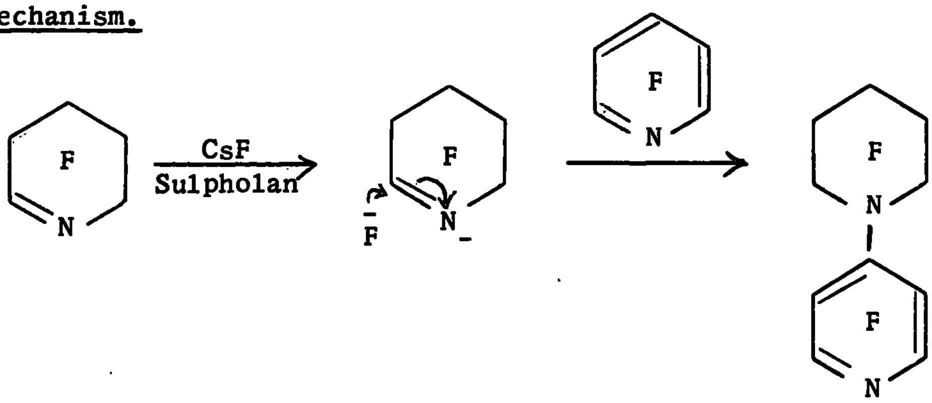
Perfluoro-1-azacyclohex-1-ene has been prepared in excellent yields by the cobaltic fluoride fluorination of pentafluoropyridine. The latter substrate was investigated with a view to preparing perfluoro-1-azacyclohexadienes. Similar attempted reactions with pyridine have been shown to result in C-N and C-C bond fission and for this reason, the more stable pentafluoropyridine was selected as a more likely starting material, in the hope that the afore mentioned fission would be avoided. Although none of the desired products were obtained, an excellent yield of perfluoro-1-azacyclohex-1-ene was obtained. This compound has been found to undergo rapid aqueous alkaline hydrolysis to hexafluoroglutaric acid, which has been conveniently isolated as the di-(S-benzylthiouranium) derivative. This is in agreement with the findings of Banks et al.[58] who proposed the following reaction scheme.



The Fluoride Ion Induced Reaction of Perfluoro-1-azacyclohex-1-ene with Pentafluoropyridine.

Perfluoro-1-azacyclohex-1-ene has been induced, by fluoride ion, to react with pentafluoropyridine to form 1-(4'-tetrafluoropyridyl)-decafluoro-1-azacyclohexane. The reaction was carried out in sulpholan and caesium fluoride was used as a source of fluoride ions.

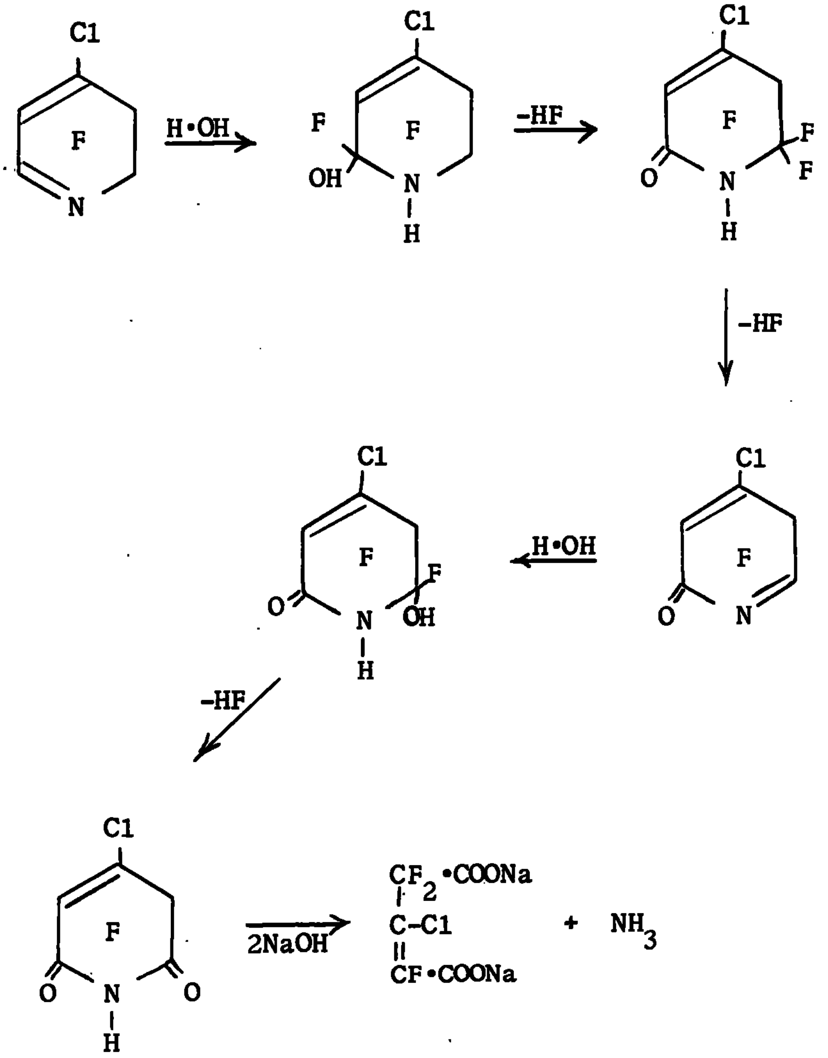
Mechanism.



The Hydrolysis of 4-Chlorohexafluoro-1-azacyclohexa-1,3-diene.

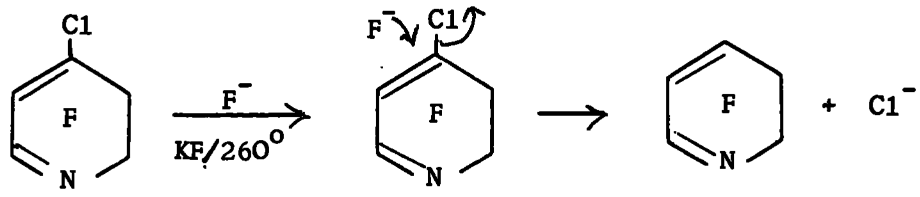
4-Chlorohexafluoro-1-azacyclohexa-1,3-diene has been prepared in good yield by the cobaltic fluoride fluorination of 4-chlorotetrafluoropyridine. The reason for examining this reaction was that it was believed that the chlorine would be retained during the fluorination, and bearing in mind the products obtained when pentafluoropyridine was similarly reacted, it was expected that the reaction could be arrested at the stage when two double bonds had been saturated, i.e. leaving the cyclic compound with a C=N grouping. The chlorine would then provide an active centre and facilitate the introduction of a second double bond into the molecule to give an azacyclohexadiene. This is a possible route to diene formation but it gives rise only to perfluoro-1-azacyclohexa-1,3-diene.

It was found that when 4-chlorotetrafluoropyridine was fluorinated, the conditions could be adjusted so that the major product was 4-chlorohexafluoro-1-azacyclohexa-1,3-diene. This compound has also been found to undergo rapid hydrolysis.



The Reaction of 4-Chlorohexafluoro-1-azacyclohexa-1,3-diene with Fluoride Ions.

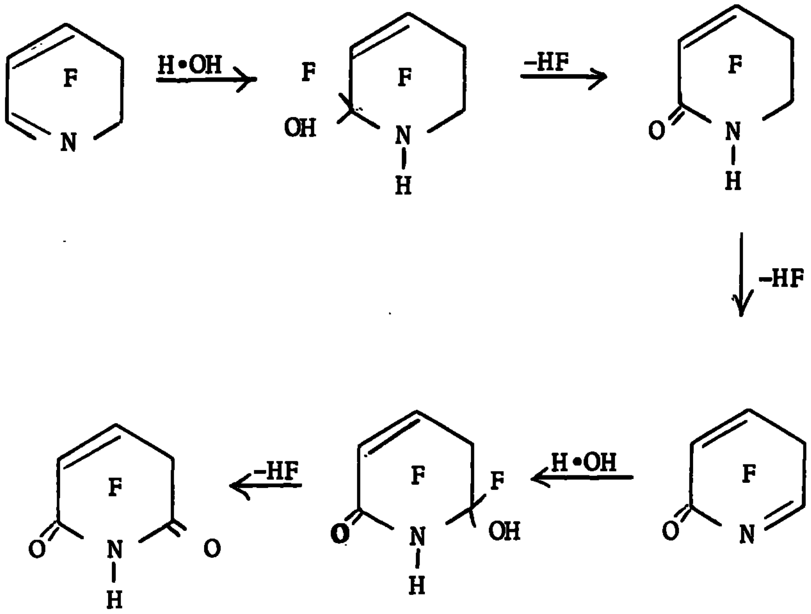
Perfluoro-1-azacyclohexa-1,3-diene has been prepared from the 4-chloro-derivative by the halogen exchange reaction, using anhydrous potassium fluoride, in the absence of a solvent, as the halogen exchange reagent.



Reactions of Perfluoro-1-azacyclohexa-1,3-diene.

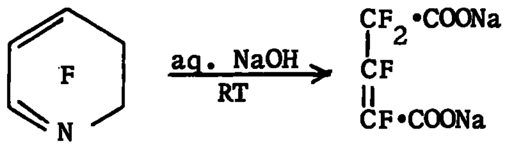
Aqueous Hydrolysis.

The perfluoro-diene is readily hydrolysed by water:-



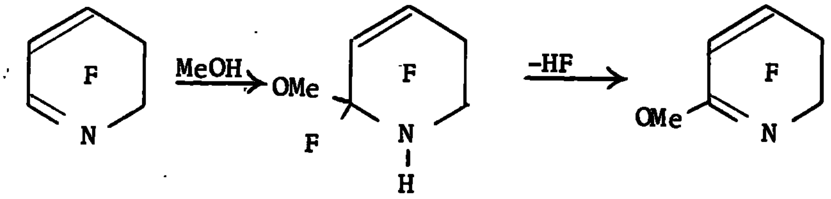
Aqueous Alkaline Hydrolysis.

With aqueous alkali, ammonia is liberated and the salt of the dicarboxylic acid is formed.

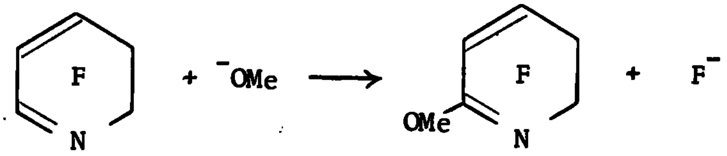


With Dry Methanol.

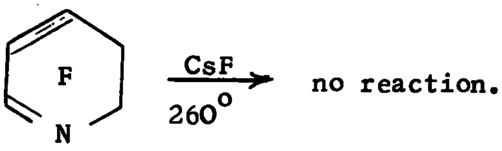
With dry methanol the diene reacts vigorously to form the 2-methoxy derivative, according to the following Addition-Elimination process,



or nucleophilic displacement of fluorine,



Reaction with Fluoride Ion.

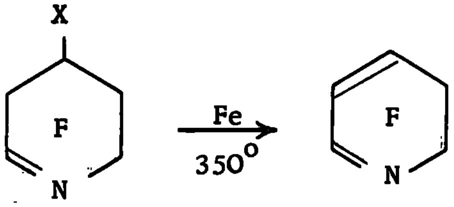


The object of this experiment was to try and isomerise the 1,3-diene to the 1,4-diene but this did not take place.

Dehalogenation Reactions

Dehalogenation of 4-Chloro- and 4-Bromo-octafluoro-1-azacyclohex-1-enes.

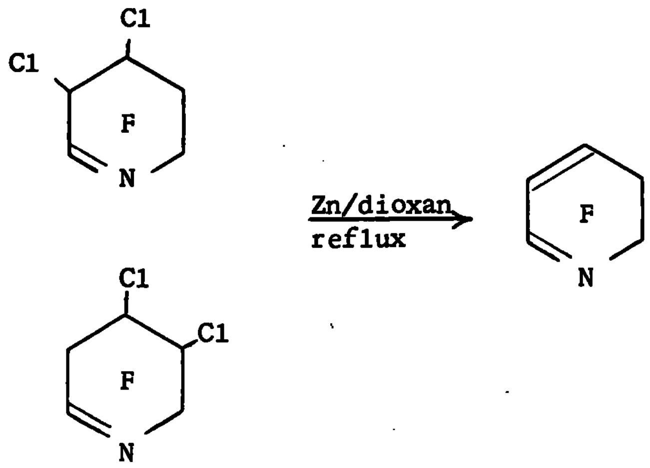
The dehalogenation reactions were carried out over iron filings at 350° and it was anticipated that a mixture of perfluoro-1-azacyclohexa-1,3- and 1,4-dienes would be produced. Unfortunately only the 1,3-diene was obtained.



X = Cl or Br

Considering the vigorous conditions under which this reaction had been carried out, it was thought possible that any 1,4-diene formed may have undergone a thermal rearrangement to the 1,3-diene.

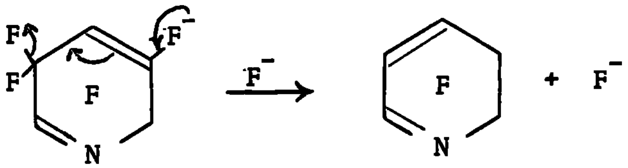
Dehalogenation of 3,4- and 4,5-Dichloroheptafluoro-1-azacyclohex-1-ene.



This was also considered as a feasible route to a mixture of the 1,3- and 1,4-perfluorodienes but again, only the perfluoro-1-azacyclohexa-1,3-diene was obtained. It was also observed that the isomer ratio of the starting material was the same as that of the recovered, unreacted material.

The evidence from these reactions clearly indicates that the energy of the conjugated 1,3-diene is less than the unconjugated 1,4-diene. The latter diene may be formed during the dechlorination of the dichloro isomer mixture and rapidly isomerises to the more stable conjugated diene. If this is the case, the rate of isomerisation must be greater than the rate of dehalogenation otherwise a change in the isomer ratio would have been observed. On the other hand, assuming that the isomer is an equilibrium mixture, it is possible that the isomer favouring the formation of the conjugated diene dehalogenates more rapidly than the other, which then equilibrates. At this stage, it is difficult to be more definite.

The suggested isomerisation of the 1,4-diene could well be explained by the presence of fluoride ions, in which case the mechanism would be:-



CHAPTER III

EXPERIMENTAL

EXPERIMENTAL

This is a summary of the instruments and apparatus used for obtaining the results throughout the Experimental Section.

Infrared Spectra.

Spectra were recorded on Perkin-Elmer 137 and Grubb-Parsons Spectromaster Spectrophotometers.

Ultraviolet Spectra.

Unicam SP 800 U.V. Spectrophotometer.

Mass Spectra.

A.E.I. MS9 Spectrometer.

N.M.R. Spectra.

Perkin-Elmer R10 and Varian A56/60 Spectrometers, operating at 56·4 Mc. for ^{19}F spectra. Samples were examined as neat liquids with hexafluorobenzene as an internal reference, unless otherwise stated. The chemical shifts have been quoted in p.p.m.; negative values denote downfield shifts with respect to the reference. Coupling constants have been quoted in c.p.s.

Analytical g.l.c.

Analytical gas chromatography was carried out using a 6 ft. x $\frac{1}{4}$ in. diameter column packed with di-iso decylphthalate on crushed firebrick (Column A) in a Perkin-Elmer model 452 and a Griffin and George Gas Density Balance Gas Chromatograph.

Preparative g.l.c.

All separations were carried out using a Perkin-Elmer model F21 automatic Gas Chromatograph fitted with a 4•5M x 9•5 m.m. diameter column packed with di-isodecylphthalate on Chromosorb P (1:4) (Column A).

Fluorinations.

Fluorinations were carried out in the vapour phase, using a 1:1 mixture of cobalt trifluoride and calcium fluoride which was contained in a nickel apparatus (44 cm. x 4•4 cm. diameter) and fitted with a stirrer (diagram 1, see p.17). At no time was more than 50% of the available fluorine used up and after 16 gm. of a substrate had been passed through the reactor, it was regenerated at about 300° using elemental fluorine from a 10 amp. I.C.I. generator.

Fluorine Generator.

The generator is a medium temperature cell operating at about 80°C. The electrolyte consists of a fused mixture having the approx. composition KF.2HF. Gaseous anhydrous hydrogen fluoride is added from time to time through a dip-pipe to replace that decomposed by electrolysis.

The 10 amp cell has a maximum fluorine output of approximately 6•5 g./hr. (4 l./hr.) at a pressure not exceeding 2 inches water gauge. It is most important that this pressure should not be exceeded for fluorine may be displaced from the cathode chamber to the anode chamber where it will combine explosively with hydrogen.

See Figures 1 and 2 for general appearance of the cell. The anode is a carbon rod and the wall of the mild steel container serves as the cathode.

The cell consists of a mild steel electrolyte container surrounded by a jacket containing thermostatically controlled heating units. Low voltage D.C. is supplied by a suitable variable source. The base is fitted with cooling fins. The anode is a carbon rod and the wall of the mild steel container serves as the cathode.

The top of the generator is insulated from the body and from the anode. Insulated flanged joints are fitted to the HF inlet and fluorine outlet, and an insulating polythene tube is provided for the hydrogen outlet. Beyond the insulated joint in the fluorine exit line is a safety lute containing sufficient 'fluorube' to allow a pressure equivalent to 2" water.

The hydrogen passes through a cross-piece fitted with a plug giving access for sampling and measuring the electrolyte level (by using a dip-stick). The positive lead of the low voltage D.C. supply is connected to the anode by means of an insulated plug and the negative lead is bolted to one of the cooling fins.

Hydrogen fluoride is added to the cell via a dip-pipe (HF inlet) which is connected through a valve (HF vent valve) to the hydrogen exit.

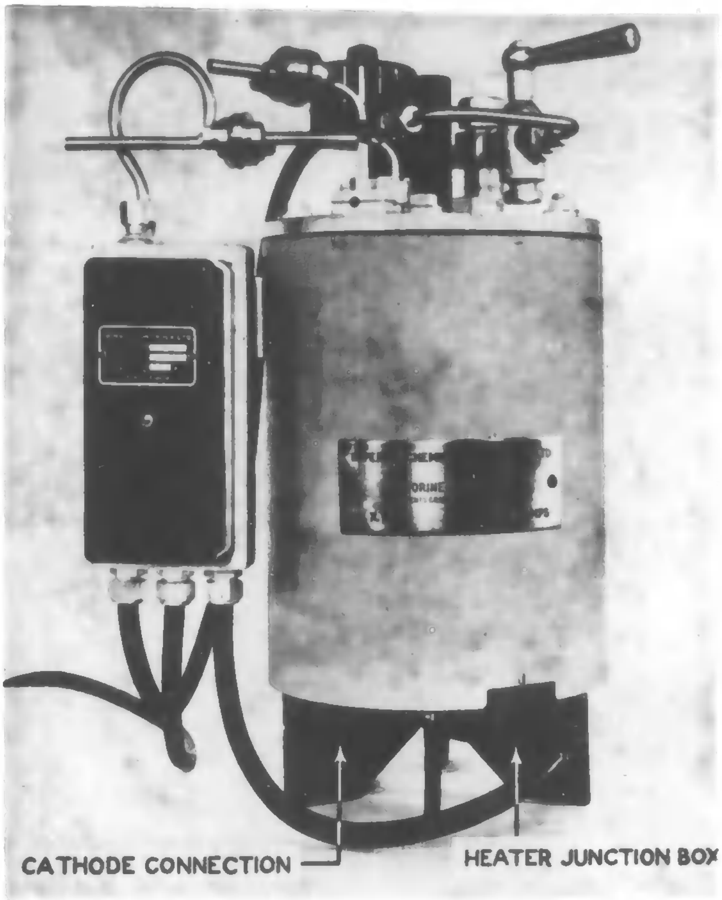

CATHODE CONNECTION
HEATER JUNCTION BOX

Fig 1

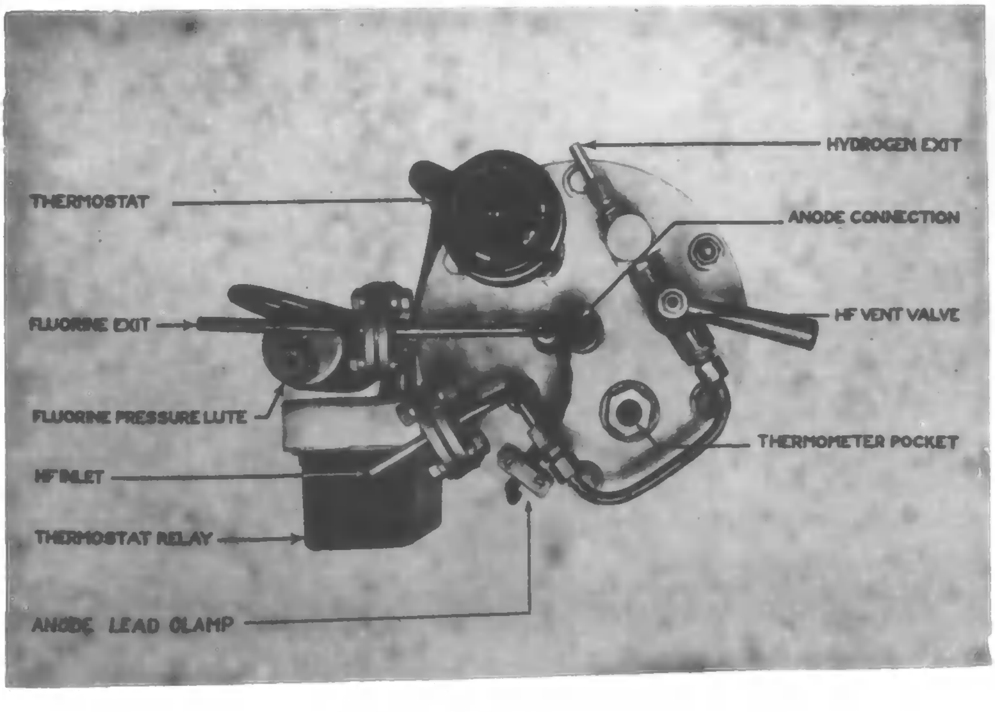

HYDROGEN EXIT
THERMOSTAT
ANODE CONNECTION
FLUORINE EXIT
HF VENT VALVE
FLUORINE PRESSURE LUTE
THERMOMETER POCKET
HF INLET
THERMOSTAT RELAY
ANODE LEAD CLAMP

Fig 2

Pockets are provided for a thermostat control and a thermometer, the pocket for the control being fitted with insulators to prevent earthing of the generator top by the control. The cell temperature is regulated by the thermostat control operating a relay between the electric power supply and the heater junction box.

Operation of Fluorine Generator.

The electrolyte was kept molten at all times as freezing, which begins at 72°C, would cause damage to the anode. The thermostatic control was adjusted to give a temperature of 82 ± 5°C. A power pack supplied a variable D.C. voltage of 4 - 10 volts, at 2 - 10 amps, for the anode. When starting, the generator was run at 2 - 3 amps for 2 minutes after which it was adjusted to any desired current value up to 10 amps.

As hydrogen and fluorine were produced the hydrogen fluoride content of the electrolyte was reduced and this was accompanied by a drop in electrolyte level. The HF content of the electrolyte was maintained in the region 40 - 42% by weight, and consequently it was necessary to add anhydrous hydrogen fluoride from time to time. The electrolyte level was thus a guide to the HF content and this was determined using a dip-stick. It was necessary to determine the electrolyte level when the cell was producing fluorine for when stopped, the porous anode absorbed electrolyte and thus gave a false level.

The level of the cell falls by 0•25 inches when the HF content falls from 42 - 40%. By removing about 1 g. of electrolyte, weighed in a nickel crucible, dissolving it in 100 mls. boiling water, in a polythene beaker, and titrating the solution against normal sodium hydroxide solution, the hydrogen fluoride concentration was determined. Thus by determining the concentration at a particular electrolyte level, it was possible to calculate the 42 and 40% levels.

After each 1,000 amp hrs. of current had been passed the HF content was determined and new 42 and 40% levels defined. These levels were used as an everyday guide to the hydrogen fluoride content of the electrolyte.

When anhydrous HF was added to the cell it was always producing fluorine and the HF cylinder, which was maintained at 25 - 35°C, was connected to the hydrogen fluoride inlet tube. Having measured the electrolyte level, the valve of the HF cylinder was opened gently until a steady stream of HF was observed to be issuing from the end of the hydrogen exit tube. The HF vent valve on the generator was then closed. This caused the HF to pass down a dip-pipe into the electrolyte. The course of the addition was followed by frequent measurement of the electrolyte level. When sufficient HF had been added, the HF vent valve was first opened and then the cylinder valve closed. The addition was usually completed in about 20 mins.; it was added at such a rate that the electrolyte temperature did not rise above 90°C.

A full and accurate record of all operations was kept in the log book provided.

In order to gain experience in carrying out cobalt trifluoride fluorinations in the vapour phase, a series of preliminary reactions was carried out using hexafluorobenzene as the substrate. The resulting reaction mixtures were examined quantitatively by g.l.c. (Column A - di-iso-decylphthalate on Chromosorb P, at room temperature) using a Griffin and George Gas Density Balance Chromatograph. The assignment of the individual peaks was done by the technique of enrichment chromatography. Having measured the area beneath each peak, the compositions of the reaction mixtures were determined quantitatively by making use of the fact that the response of the Gas Density Balance is directly proportional to the molar concentration of the constituents. Knowing the molecular weights, and hence having all the necessary information, it was a simple matter to calculate the molar ratios in the mixtures and hence the percentage composition, e.g.

C = concentration

A = area

$\mathrm{M.wt.}_n$ = molecular weight of nitrogen

$$C_a = \frac{\dfrac{A_a}{\mathrm{M.wt.}_a - \mathrm{M.wt.}_n}}{\dfrac{A_a}{\mathrm{M.wt.}_a - \mathrm{M.wt.}_n} + \dfrac{A_b}{\mathrm{M.wt.}_b - \mathrm{M.wt.}_n} + \dfrac{A_c}{\mathrm{M.wt.}_c - \mathrm{M.wt.}_n}} \quad \text{etc.}$$

Hence C_a; C_b; C_c and C_d can be calculated.

C_a x M.wt.$_a$ = mass in g. of a (m_a)

C_b x M.wt.$_b$ = mass in g. of b (m_b)

C_c x M.wt.$_c$ = mass in g. of c (m_c)

C_d x M.wt.$_d$ = mass in g. of d (m_d)

$$m_a + m_b + m_c + m_d = 100\%$$

$$\% a = \frac{m_a}{m_a + m_b + m_c + m_d} \times \frac{100}{1} \quad \text{etc.}$$

The Vapour Phase Fluorination of Hexafluorobenzene using Cobalt Trifluoride.

With the reactor filled with 600 g. of cobaltic fluoride, a number of fluorinations were carried out at different temperatures (room temperature -100°) and different nitrogen flowrates. Except where otherwise stated, the procedure was to drop the substrate, from a suitably modified burette, directly into the reactor.

Reaction 1.

Hexafluorobenzene (6·4 g., 0·034 mole) was dropped into the reactor, which was at 100 - 106°, over a period of 45 mins., in a steady stream of nitrogen gas (4·81/hr.) and the products (6·0 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hours. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed only two components, which were identified as (i) perfluorocyclohexane (32%) and (ii) perfluorocyclohexene (68%).

Reaction 2.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 85 - 87°, over a period of 45 min., in a steady stream of nitrogen gas (4•8 l./hr.) and the products (4•6 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed only two components, which were identified as (i) perfluorocyclohexane (17%) and (ii) perfluorocyclohexene (83%).

Reaction 3.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 70 - 75°, over a period of 45 min., in a steady stream of nitrogen gas (4•8 l./hr.) and the products (3•5 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed only two components which were identified as (i) perfluorocyclohexane (7%) and (ii) perfluorocyclohexene (93%).

Reaction 4.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 60 - 65°, over a period of 45 min., in a steady stream of nitrogen gas (12 l./hr.) and the products (3·0 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed only two components which were identified as (i) perfluorocyclohexane (8·0%) and perfluorocyclohexene (92%).

Reaction 5.

Hexafluorobenzene (6·4 g., 0·034 mole) was dropped into the reactor, which was maintained at room temperature, over a period of 45 min., in a steady stream of nitrogen gas (12 l./hr.) and the products (3·0 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed one major component along with trace amounts of two others. The components of the mixture were identified as (i) perfluorocyclohexane (trace), (ii) perfluorocyclohexene (ca. 98%) and (iii) perfluorocyclohexa-1,4-diene (trace).

Reaction 6.

Hexafluorobenzene (6·4 g., 0·034 mole) was carried into the reactor, which was maintained at room temperature, in a steady stream of nitrogen gas (12 l./hr.) and the products (3·2 g.) trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed three components which were identified as

(i) perfluorocyclohexene (44%), (ii) perfluorocyclohexa-1,4-diene (17%) and (iii) hexafluorobenzene (39%).

For the following reactions the reactor was repacked with cobaltic fluoride (150 g.) and calcium fluoride (150 g.).

Reaction 7.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 150°, over a period of 40 min., in a steady stream of nitrogen gas (3•0 l./hr.) and the products (9•0 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed one component which was identified as perfluorocyclohexane (100%).

Reaction 8.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 150°, over a period of 40 min., in a steady stream of nitrogen gas (15 l./hr.) and the products (8•0 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed two components which were identified as (i) perfluorocyclohexane (58%) and (ii) perfluorocyclohexene (42%).

Reaction 9.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 100°, over a period of 40 mins., in a steady stream of nitrogen gas (4•8 l./hr.) and the products (8•8 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed three components which were identified as (i) perfluorocyclohexane (9%), (ii) perfluorocyclohexene (89%) and (iii) perfluorocyclohexa-1,4-diene (2%).

Reaction 10.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 80/86°, over a period of 40 min., in a steady stream of nitrogen gas (4•8 l./hr.) and the products (6•7 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. (Column A at room temperature) examination of the reaction mixture revealed two components which were identified as (i) perfluorocyclohexene (88%) and (ii) perfluorocyclohexa-1,4-diene (12%).

Reaction 11.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 70/72°, over a period of 40 min., in a steady stream of nitrogen gas (4•8 l./hr.) and the products (7•0 g.) were trapped at liquid air temperature. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed two components which were identified as (i) perfluorocyclohexene (80%) and (ii) perfluorocyclohexa-1,4-diene (20%).

Reaction 12.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 50^o, over a period of 40 min., in a steady stream of nitrogen gas (4•8 l./hr.) and the products (6•0 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed three components which were identified as (i) perfluorocyclohexene (51%), (ii) perfluorocyclohexa-1,4-diene (26%) and (iii) unchanged hexafluorobenzene (23%).

Reaction 13.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into a vaporizer (heated at 100^o) over a period of 40 min., and carried into the reactor, which was at 50^o, in a steady stream of nitrogen gas (15 l./hr.) and the products (5•5 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed three components which were identified as (i) perfluorocyclohexene (35%), (ii) perfluorocyclohexa-1,4-diene (22%) and (iii) unchanged hexafluorobenzene (43%).

The reactor was again emptied and re-packed with manganese difluoride 600 g. which was subsequently oxidised to manganese trifluoride.

Reaction 14.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor which was at 100/4°, over a period of 40 min., in a steady stream of nitrogen gas (4•8 l./hr.) and the products (6•0 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen gas for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed four components which were identified as (i) perfluorocyclohexane (0•1%), (ii) perfluorocyclohexene (6•3%), (iii) perfluorocyclohexa-1,4-diene (11•1%) and (iv) unchanged hexafluorobenzene (82•5%).

Reaction 15.

Hexafluorobenzene (6•4 g., 0•034 mole) was dropped into the reactor, which was at 210°, over a period of 40 min., in a steady stream of nitrogen gas (4•8 l./hr.) and the products (7•0 g.) were trapped at liquid air temperature. The reactor was flushed with nitrogen for 2 hrs. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed four components which were identified as (i) perfluorocyclohexane (3•7%), (ii) perfluorocyclohexene (52•9%), (iii) perfluorocyclohexa-1,4-diene (20•9%) and (iv) unchanged hexafluorobenzene (22•5%).

The Fluorination of Perfluoro- and Polyfluorohalopyridines.

Starting materials.

Pentafluoropyridine, 3-chlorotetrafluoropyridine and 3,5-dichlorotrifluoropyridine were prepared by reacting pentachloropyridine with anhydrous potassium fluoride in a stainless steel autoclave at 460-480° for 16 hrs.[53] 4-Chlorotetrafluoropyridine was prepared from 4-aminotetrafluoropyridine by the Sandmeyer reaction in 80% aqueous hydrogen fluoride. 4-Bromotetrafluoropyridine was prepared from 4-hydrazinotetrafluoropyridine by reaction with 50% aqueous hydrogen bromide in the presence of cupric bromide.[63] 3,4-Dichlorotrifluoropyridine was prepared from 3-chloro-4-hydrazinotrifluoropyridine by an analogous reaction using concentrated hydrochloric acid and cupric chloride.

The following fluorination reactions were carried out over 300 g. of a 1:1 mixture of cobaltic fluoride and calcium fluoride in the nickel reactor previously described. The yields have been quoted as a percentage of the reaction product recovered from the reactor.

The Fluorination of Pentafluoropyridine.

Pentafluoropyridine (3•0 g., 0•01735 mole) was fluorinated in a steady stream of nitrogen gas (4•8 l./hr.) at 120°. The substrate was dropped directly into the reactor over a period of 10 mins. and the products (3•2 g.) were trapped at liquid air temp. On completion of the addition, the reactor was flushed for 30 mins. The flushing period was found to depend on the amount of substrate added and the reactor temperature. Quantitative g.l.c. examination (Column A at room temperature) of the product mixture revealed two components which were identified as (i) perfluoro-1-azacyclohex-1-ene (85%) and (ii) perfluoro-2-azahex-2-ene (15%).

The above compounds are known and have been well characterised by Haszeldine et al.[58] and Mitsch.[57]

The Reaction of Perfluoro-1-azacyclohex-1-ene with Pentafluoropyridine in the presence of Caesium Fluoride.

Perfluoro-1-azacyclohex-1-ene (5•0 g., 0•020 mole), and pentafluoropyridine (3•4 g., 0•020 mole) were sealed into a small stainless steel reaction vessel (85 cc.) with caesium fluoride (3•0 g., 0•020 mole) and sulpholan (15 ml.). The reaction vessel was heated, with shaking, at 180° for 24 hrs. after which, the contents were transferred with water (25 ml.) into a solvent extractor and continuously extracted with ether. The ether solution was dried over anhydrous magnesium sulphate and the solvent stripped off to give a dark red oil (6•0 g.) which was vacuum distilled and the distillate vacuum sublimed to give 1-(4'-tetrafluoropyridyl)-decafluoro-1-azacyclohexane (3•6 g.; 45•0%). M.pt. 52°. (Found: C, 28•8. $C_{10}F_{14}N_2$ requires C, 29•0%). M (mass spectrometry), 414. λ_{max} 275 mμ (in cyclohexane). I.R. No. 12. ν_{max} 1639, 1481, 1424, 1370, 1333, 1282, 1235, 1217, 1190, 1163, 1136, 1070, 1053, 1020, 995, 962, 862, 754, 733, 694 $cm.^{-1}$

The ^{19}F n.m.r. spectrum (in acetone) showed five groups of chemically shifted peaks in the intensity ratios 1:2:2:1:1. The chemical shifts were -77•0 p.p.m.; -71•7 p.p.m.; -31•4 p.p.m.; -30•5 p.p.m. and -21•0 p.p.m. The resonances at -77•0 and -21•0 p.p.m. were consistent with fluorine nuclei in a 4-substituted pentafluoropyridine and that at -71•7 p.p.m. was assigned to the 2-F and 6-F nuclei of the azacyclohexane ring. The resonance at -31•4 p.p.m. was assigned to the 3-F and 5-F nuclei and that at -30•5 p.p.m. to the 4-F nuclei.

The Fluorination of 3-Chlorotetrafluoropyridine.

3-Chlorotetrafluoropyridine (16•0 g., 0•086 mole) was fluorinated in the usual manner, at 100°, to give a reaction mixture (17•5 g.) which consisted of two major products (i) a mixture of isomers 3-chloro and 5-chloro-octafluoro-1-azacyclohex-1-ene (7•9 g.; 45%). (ii) 6-Chlorodecafluoro-2-azahex-2-ene (7•9 g.; 45%). B.pt. 62°. (Found: C, 20•05; Cl, 11•7. $C_5ClF_{10}N$ requires C, 20•0; Cl, 11•85%). I.R. No. 1. ν_{max} 1786, 1335, 1258, 1215, 1170, 1145, 1135, 1116, 1081, 1020, 1010, 971, 917, 887, 847, 816, 794, 769, 741, 722 cm.$^{-1}$

The ^{19}F n.m.r. spectrum showed five groups of chemically shifted peaks in the intensity ratios 1:3:2:2:2. The chemical shifts were:-

CF_2Cl ——	CF_2 ——	CF_2 ——	CF=N ——	CF_3
-95•8	-46•9	-43•0	-141•2	-105•8

^{19}F Chemical shift	Multiplet structure
-141•2 p.p.m.	A very broad single peak.
-105•8 "	A doublet (J = 14 c.p.s.)
-95•8 "	1:2:1 triplet (J - 10 c.p.s.)
-46•9 "	A quadruplet (J = 10 c.p.s.)
-43•0 "	A doublet (J = 7 c.p.s.)

The structure of this compound was confirmed by hydrolysis to 4-chlorohexafluorobutyric acid and formation of the S-benzylthiouronium derivative. M.pt. 198°. (Found: C, 36•2; H, 2•5. $C_{12}H_{11}ClF_6N_2O_2S$ requires C, 36•3; H, 2•8%).

The Fluorination of 4-Chlorotetrafluoropyridine.

4-Chlorotetrafluoropyridine (14•75 g., 0•0795 mole) was fluorinated at 120/123°, in the usual manner, to give a reaction mixture (15•25 g.) which consisted of two major products (i) 4-Chlorohexafluoro-1-aza-cyclohexa-1,3-diene (8•0 g.; 53•2%). B.pt. 96°. (Found: C, 26•7; F, 50•6; Cl, 15•4. C_5ClF_6N requires C, 26•9; F, 50•1; Cl, 15•8%). λ_{max} (in cyclohexane) 248 mμ (e = 9380). I.R. No. 6. ν_{max} 1705, 1660, 1380, 1280, 1250, 1175, 1150, 1080, 940, 890, 722, 688 $cm.^{-1}$ The ^{19}F n.m.r. spectrum showed four groups of chemically shifted peaks in the intensity ratios 1:2:2:1. The chemical shifts were -114•7 (2-F); -64•7 (6-F); -47•7 (5-F) and -38•7 (3-F) p.p.m.

^{19}F Chemical shift	Multiplet structure
-114•7 p.p.m.	A very broad doublet (J_{23} = 24 c.p.s.)
-64•7 "	A single peak.
-47•7 "	Triplets of doublet (J_{56} = 8 c.p.s.)
-38•7 "	Triplets of doublet (J_{35} = 15 c.p.s.)

(ii) 4-Chloro-octafluoro-1-azacyclohex-1-ene (2•5 g.; 13•5%). B.pt. 71•5°. (Found: C, 22•9; Cl, 13•8. C_5ClF_8N requires C, 22•95; Cl, 13•8%). I.R. No. 3. ν_{max} 1749, 1340, 1290, 1252, 1220, 1200, 1176, 1155, 1132, 1095, 1070, 1038, 990, 955, 910, 820, 740, 685 cm.$^{-1}$

(iii) 4-Chlorohexafluoro-1-azacyclohexa-1,4-diene (0•4 g.; 2•15%). B.pt. 81•5°. (Found: C, 26•5; Cl, 15•8. C_5ClF_6N requires C, 26•8; Cl, 15•9%). λ_{max} (in cyclohexane) 217mμ. I.R. No. 7. ν_{max} 1754 1715, 1366, 1340, 1330, 1285, 1215, 1172, 1099, 938, 879, 818, 725, 714, 692, 680 cm.$^{-1}$ The ^{19}F n.m.r. spectrum showed four groups of chemically shifted peaks in the intensity ratios 1:2:2:1. The chemical shifts were -110•0 (2-F); -79•8 (6-F); -58•1 (3-F); and -46•5 (5-F) p.p.m.

^{19}F Chemical shift	Multiplet structure
-110•8 p.p.m.	Very broad triplet (J_{23} = 30 c.p.s.)
-79•8 "	Broad doublet.
-57•6 "	Doublet of doublets (J_{35} = 10 c.p.s.)
-46•8 "	(J_{56} = 27 c.p.s.) Septet.

The Reaction of 4-Chlorohexafluoro-1-azacyclohexa-1,3-diene with Water.

To a solution of 4-chlorohexafluoro-1-azacyclohexa-1,3-diene (2•235 g., 0•01 mole) in tetrahydrofuran (5 mls.) was added water (0•18 ml., 0•01 mole) and the mixture refluxed for 30 mins. The solvent was removed under reduced pressure and the solid residue (2•0 g.; 90•5%)

was vacuum sublimed at room temperature, using an oil pump, to give 2-hydroxy-4-chloropentafluoro-1-azacyclohexa-1,3-diene. M (mass spectrometry) 221; (Found: C, 27·5; H, 0·6; Cl, 15·4; F, 42·3. C_5HClF_5NO requires C, 27·1; H, 0·44; Cl, 16·0; F, 42·9%). The ^{19}F fluorine n.m.r. spectrum showed three groups of chemically shifted peaks in the intensity ratios 2:2:1. The chemical shifts were -71·5 (6-F); -49·7 (5-F); and -45·3 (3-F) p.p.m.

^{19}F Chemical shift	Multiplet structure
-71·5 p.p.m.	Triplet (J_{56} = 7 c.p.s.)
-49·7 "	Triplets(J_{56} = 7 c.p.s.) of Doublet (J_{35} = 14 c.p.s.)
-45·5 "	Triplet (J = 14 c.p.s.)

The Hydrolysis of 2-Hydroxy-4-chloropentafluoro-1-azacyclohexa-1,3-diene.

On storage, 2-hydroxy-4-chloropentafluoro-1-azacyclohexa-1,3-diene was found to have further hydrolysed to give N-hydro-2,6-dioxo-4-chlorotrifluoro-1-azacyclohex-3-ene, which was purified by vacuum sublimation at 50°. M.pt. 94°. (Found: C, 29·74; H, 0·58; N, 7·07. $C_5HClF_3NO_2$ requires C, 30·07; H, 0·50; N, 7·01%). I.R. No. 11. ν_{max} 3257, 1770, 1724, 1681, 1408, 1325, 1277, 1239, 1136, 1087, 939, 909, 781, 733, 704, 588, 510 $cm.^{-1}$ The ^{19}F n.m.r. spectrum showed two groups of chemically shifted peaks in the intensity ratios 2:1. The chemical shifts were -64·1 (5-F) and -43·2 (3-F) p.p.m.

^{19}F Chemical shift	Multiplet structure
-64•1 p.p.m.	Doublet (J = 12•5 c.p.s.)
-43•2 "	Triplet (J = 12•5 c.p.s.)

The Alkaline Hydrolysis of 4-Chlorohexafluoro-1-azacyclohexa-1,3-diene.

4-Chlorohexafluoro-1-azacyclohexa-1,3-diene underwent alkaline hydrolysis to give a dicarboxylic acid which was readily isolated as the di-S-benzylthiouronium derivative.

4-Chlorohexafluoro-1-azacyclohexa-1,3-diene (1•5 g.) was shaken for 30 min. with aqueous sodium hydroxide (10 mls. of 2N) to effect the complete hydrolysis; the pH of the solution was adjusted to 4 and a solution of S-benzylthiouronium chloride (2 g., in 10 mls. of water) was added. A thick white precipitate was formed immediately; this was filtered off and recrystallised from hot water. This was the di-(S-benzylthiouronium) derivative of 3-chlorotrifluoro-2-pentenedioic acid. M.pt. 178°. (Found: C, 46•2; H, 4•12; N, 10•2. $C_{21}H_{22}ClF_3N_4O_4S_2$ requires C, 45•8; H, 3•99; N, 10•2%).

The Alkaline Hydrolysis of 4-Chlorohexafluoro-1-azacyclohexa-1,4-diene.

4-Chlorohexafluoro-1-azacyclohexa-1,4-diene (0•25 g.) was shaken for 30 mins. with aqueous sodium hydroxide (2 mls. of 2N) and the S-benzylthiouronium derivative formed in the usual manner. This compound was the di-(S-benzylthiouronium) derivative of 3-chlorotrifluoro-2-pentenedioic acid. M.pt. 178°d. (Found: C, 46•1; H, 3•99; N, 9•70.

$C_{21}H_{22}ClF_3N_4O_4S_2$ requires C, 45•8; H, 3•99; N, 10•2%).

The Replacement of Chlorine by Fluorine in 4-Chlorohexafluoro-1-azacyclohexa-1,3-diene.

A mixture of 4-chlorohexafluoro-1-azacyclohexa-1,3-diene (10 g., 0•0447 mole) and anhydrous potassium fluoride (5 g., 0•1285 mole) was sealed, on a vacuum line, in a Carius tube (100 cc.) and heated in a furnace for 16 hrs. at 260° after which the product (8•0 g.) was vacuum transferred. The material was shown, by analytical g.l.c., to consist essentially of one compound along with a small amount of unchanged starting material and a number of unidentified, minor impurities. The main component was isolated by preparative scale g.l.c. (Column A at 70°) and characterised as perfluoro-1-azacyclohexa-1,3-diene (5•6 g.; 70%). B.pt. 54°. (Found: C, 29•2; F, 63•8. C_5NF_7 requires C, 29•0; F, 64•2%). λ_{max} (in cyclohexane) 233 mμ (e 3,400). I.R. No. 5. ν_{max} 1750, 1700, 1395, 1290, 1190, 1170, 1115, 1040, 965, 723 $cm.^{-1}$ The ^{19}F n.m.r. spectrum showed five groups of chemically shifted peaks in the intensity ratios 1:2:2:1:1. The chemical shifts were -118•4 (2-F); -64•4 (6-F); -42•4 (5-F); -23•3 (3-F) and -13•6 (4-F).

^{19}F chemical shift	Multiplet structure
-118•4 p.p.m.	A very broad triplet which is probably a doublet of doublets. (J_{23} = 33 c.p.s.; J_{24} = 24 c.p.s.; J_{25} = 0•5 c.p.s.).

^{19}F chemical shift	Multiplet structure
-64·8 p.p.m.	A single broad peak.
-42·6 "	A triplet of doublets of a doublet (J_{56} = 6 c.p.s.).
-23·3 "	Triplets of a doublet. (J_{34} = 3 c.p.s.; J_{35} = 18 c.p.s.; J_{36} = 6 c.p.s.).
-13·6 "	Triplets of a doublet. (J_{45} = 18 c.p.s.; J_{46} = 3 c.p.s.).

The Reaction of Perfluoro-1-azacyclohexa-1,3-diene with Water.

Water (0·5 g., 0·0278 mole) was added to perfluoro-1-azacyclohexa-1,3-diene (1·0 g., 0·00447 mole) in tetrahydrofuran (2 mls.) and the mixture refluxed for 30 mins. The solvent was removed under reduced pressure and the solid residue vacuum sublimed (oil pump press.) at room temperature to yield N-hydro-2,6-dioxotetrafluoro-1-azacyclohex-3-ene (0·7 g.; 79%). M.pt. 103°. M 183 (mass spectrometry). (Found: C, 32·6; H, 0·65, F, 41·2. $C_5HF_4NO_2$ requires C, 32·8; H, 0·54; F, 41·5%). λ_{max} (in ethanol) 240mμ. I.R. No. 10. ν_{max} 3205, 3125, 2841, 1724, 1399, 1370, 1316, 1250, 1149, 1099, 1087, 964, 810, 746, 716 $cm.^{-1}$ The ^{19}F n.m.r. spectrum showed three groups of chemically shifted peaks in the intensity ratios 2:1:1. The chemical shifts were -57·8 (5-F); -16·3 (3-F) and -13·5 (4-F) p.p.m.

^{19}F Chemical Shift	Multiplet structure
-57•8 p.p.m.	Doublets of doublet.
-16•3 "	Doublets of triplet. (J_{34} = 7 c.p.s.; J_{35} = 13•5 c.p.s.).
-13•5 "	Doublets of triplet. (J_{45} = 23•5 c.p.s.).

The Reaction of Perfluoro-1-azacyclohexa-1,3-diene with Methanol.

A mixture of perfluoro-1-azacyclohexa-1,3-diene (0•65 g., 0•0029 mole) and tetrahydrofuran (2 mls.) was stirred at room temperature and dry methanol (1:1 g., 0•0031 mole) was added dropwise from a micro-syringe. Sodium carbonate (0•2 g.) was added, and the mixture heated under reflux for 30 mins. After filtration, the mixture was analysed and separated by preparative scale g.l.c. (column 'A' at 100^{o}). Apart from the solvent, only one other peak appeared on the chromatogram and was identified as 2-methoxy-1-azacyclohexa-1,3-diene (0•3 g.; 47•2%). M 219 (mass spectrometry). (Found: C, 32•9; H, 1•5; F, 51•8. $C_6H_3F_6NO$ requires C, 32•9; H, 1•37; F, 52•0%). λ_{max} (in cyclohexane) 208mμ. I.R. No. 9. ν_{max} 2941, 1730, 1634, 1449, 1383, 1355, 1299, 1266, 1206, 1168, 1139, 1104, 1040, 973, 931, 749, 735 cm.$^{-1}$ The ^{19}F n.m.r. spectrum showed four groups of chemically shifted peaks in the intensity ratios 2:2:1:1. The chemical shifts were -69•1 (6-F); -41•6 (5-F); -15•0 (3-F) and -11•9 (4-F) p.p.m.

^{19}F Chemical shift	Multiplet structure
-69·1 p.p.m.	A broad single peak.
-41·6 "	A triplet of a doublet of a doublet. (J_{56} = 7 c.p.s.).
-15·0 "	Triplets of a doublet. (J_{34} = 1·5 c.p.s.; J_{35} = 16·5 c.p.s.).
-11·9 "	A complex band of nine peaks.

The Dechlorofluorination of 4-Chloro-octafluoro-1-azacyclohex-1-ene.

4-Chloro-octafluoro-1-azacyclohex-1-ene (3·0 g., 0·0115 mole) was passed, in a steady stream of nitrogen (31/hr.), through a pyrex reaction tube (12" long x 1" o.d.) packed with iron filings and heated at 350°. The products (2·2 g.) were trapped out at liquid air temperature. Examination of the product mixture, by analytical g.l.c. (Column A at 50°) showed that it consisted of (i) perfluoro-1-azacyclohexa-1,3-diene (0·46 g.; 21%). (ii) Pentafluoropyridine (0·17 g.; 7·7%), unchanged starting material (1·43 g.; 65%) and a mixture of unknown materials (0·02 g.; 6%). Both the n.m.r. and I.R. spectra of the perfluoro-1-azacyclohexa-1,3-diene were identical with those of previously prepared material. Perfluoro-1-azacyclohexa-1,4-diene was not isolated from the reaction mixture.

The Fluorination of 4-Chloro-octafluoro-1-azacyclohex-1-ene.

4-Chloro-octafluoro-1-azacyclohex-1-ene (6•6 g., 0•02525 mole) was fluorinated, in the usual manner, at 140° to give a reaction mixture (4•0 g.) which consisted of one major product (1•56 g.; 39%) along with unchanged starting material (1•91 g.; 47•8%) and a number of compounds which were not identified. The major product was 5-chlorodecafluoro-2-azahex-2-ene. B.pt. 65°. (Found: C, 19•8; N, 4•6; Cl, 11•4; F, 66•1. $C_5ClF_{10}N$ requires C, 20•0; N, 4•73; Cl, 11•8; F, 63•4%). I.R. No. 13. ν_{max} 1764, 1299, 1250, 1209, 1129, 1087, 968, 939, 926, 858, 813, 794, 741, 709 cm.$^{-1}$ The ^{19}F n.m.r. spectrum showed five groups of chemically shifted peaks in the intensity ratios 1:3:3:2:1. The chemical shifts were:-

CF_3 —	CFCl —	CF_2 —	CF=N —	CF_3
-85•3	-24•6	-49•3	-140•4	-105•0

The Fluorination of 4-Bromotetrafluoropyridine.

4-Bromotetrafluoropyridine (5•0 g., 0•0216 mole) was fluorinated, at 120-125°, in the usual manner to give a reaction mixture (5•1 g.) which consisted of two major components (i) 4-bromohexafluoro-1-azacyclohexa-1,3-diene (0•46 g.; 9•0%). B.pt. 96°. (Found: C, 22•5; F, 43•4; Br, 29•7. C_5BrF_6N requires C, 22•4; F, 42•5; Br, 29•9%). λ_{max} (in cyclohexane) 260mμ. I.R. No. 8. ν_{max} 1724, 1667, 1379, 1285, 1276, 1242, 1176, 1156, 1080, 932, 838, 758, 723, 690 cm.$^{-1}$ The ^{19}F n.m.r. spectrum showed four groups of chemically shifted peaks in the intensity ratios 1:2:2:1. The chemical shifts were -114 (2-F); -64•8 (6-F); -51•0 (5-F) and -47•0 (3-F) p.p.m.

^{19}F Chemical shift	Multiplet structure
-114•0 p.p.m.	A broad doublet (J_{23} = 24 c.p.s.)
-64•8 "	A broad peak showing no fine structure.
-51•0 "	Triplet of a doublet (J_{56} = 8 c.p.s.)
-47•0 "	Triplet of a doublet (J_{35} = 15 c.p.s.)

(ii) 4-Bromo-octafluoro-1-azacyclohex-1-ene (4•18 g.; 82%). B.pt. 88-89°. (Found: C, 19•2; Br, 26•4. C_5BrF_8N requires C, 19•6; Br, 26•2%). I.R. No. 4. ν_{max} 1786, 1359, 1305, 1263, 1235, 1212, 1190, 1168, 1147, 1101, 1080, 1040, 926, 905, 826, 725, 685 cm.$^{-1}$

The De-bromofluorination of 4-Bromo-octafluoro-1-azacyclohex-1-ene.

4-Bromo-octafluoro-1-azacyclohex-1-ene (3•6 g., 0•0118 mole) was dehalogenated over iron filings at 350° to give a reaction mixture (1•6 g.) which was analysed by g.l.c. (Column A at 50°) and found to consist of perfluoro-1-azacyclohexa-1,3-diene (54%); pentafluoropyridine (17•4%); unchanged starting material (6•8%) and a mixture of unidentified compounds (21•8%).

The Fluorination of 3,5-Dichlorotrifluoropyridine.

3,5-Dichlorotrifluoropyridine (16•0 g., 0•079 mole) was fluorinated, at 120-130°, in the usual manner to give a reaction mixture (12•0 g.) which consisted of (i) a mixture of geometrical isomers of 3,5-dichloroheptafluoro-1-azacyclohex-1-ene (67•1%). (Found: C, 21•3; N, 4•95; F, 47•9; Cl, 25•1. $C_5Cl_2F_7N$ requires C, 21•6; N, 5•04; F, 47•9; Cl, 25•9%). The ^{19}F n.m.r. spectrum was extremely complex and indicated a mixture of isomers. (ii) 4,6-Dichlorononafluoro-2-azahex-2-ene (28•0%), B.pt. 92°. (Found: C, 19•3; N, 4•1; F, 54•3; Cl, 21•8. $C_5Cl_2F_9N$ requires C, 19•0; N, 4•4; F, 54•1; Cl, 22•5%). I.R. No. 15. ν_{max} 1764, 1361, 1294, 1256, 1205, 1143, 1111, 1015, 978, 840, 805, 774, 702, 685 cm.$^{-1}$ The ^{19}F n.m.r. spectrum showed five groups of chemically shifted peaks in the intensity ratios 1:3:2:2:1. The chemical shifts were:-

CF_2Cl —	CF_2 —	$CFCl$ —	$CF{=}N$ —	CF_3
-97•3	-48•2	-36•6	-140•0	-105•8

The Fluorination of 3,4-Dichlorotrifluoropyridine.

3,4-Dichlorotrifluoropyridine (15•0 g., 0•074 mole) was fluorinated, at 130-135°, in the usual manner to give a complex reaction mixture (13•5 g.) which consisted of dichloropentafluoro-1-azacyclohexadiene isomers (2•94 g., 21•8%) from which the major component was isolated and identified as (i) 3,4-dichloropentafluoro-1-azacyclohexa-1,3-diene (1•9 g., 65•3%) of the isomer mixture). B.pt. 127°.

(Found: C, 24·7; F, 40·8; Cl, 29·7. $C_5Cl_2F_5N$ requires C, 25·0; F, 39·6; Cl, 29·6%). λ_{max} (in cyclohexane) 260mμ (, 6140). I.R. No. 16, ν_{max} 1718, 1618, 1346, 1297, 1255, 1233, 1163, 1114, 1053, 895, 864, 722 $cm.^{-1}$ The ^{19}F n.m.r. spectrum showed three groups of chemically shifted peaks in the intensity ratios 1:2:2. The chemical shifts were -126·3 (2-F); -63·8 (6-F); and -46·3 (5-F). (ii) Dichloroheptafluoro-1-azacyclohex-1-ene isomer mixture (6·0 g.; 44·5%) which it was not possible to resolve. (Found: C, 21·8; N, 4·8; F, 49·1; Cl, 25·3. $C_5Cl_2F_7N$ requires C, 21·6; N, 5·0; F, 47·8; Cl, 25·5%) and (iii) 5,6-Dichlorononafluoro-2-azahex-2-ene (1·65 g.; 12·2%). B.pt. 86°. (Found: C, 19·29; N, 4·27; F, 54·6; Cl, 22·6. $C_5Cl_2F_9N$ requires C, 19·00; N, 4·40; F, 54·1; Cl, 22·5%). I.R. No. 14. ν_{max} 1770, 1316, 1258, 1215, 1163, 1130, 1099, 951, 930, 862, 845, 806, 791, 775 $cm.^{-1}$ The ^{19}F n.m.r. spectrum showed five groups of chemically shifted peaks in the intensity ratios 1:3:2:2:1. The chemical shifts were:-

$$\begin{array}{ccccccccc} CF_2Cl & — & CFCl & — & CF_2 & — & CF{=}N & — & CF_3 \\ -100{\cdot}1 & & -32{\cdot}8 & & -52{\cdot}3 & & -141{\cdot}8 & & -105{\cdot}8 \end{array}$$

<u>The Dechlorination of Dichloroheptafluoro-1-azacyclohex-1-ene Isomer mixture</u>

The isomer mixture (3·0 g., 0·0108 mole) in 1 ml. of dry dioxan, was added to a stirred suspension of activated zinc dust (4·3 g., 0·066 mole) in refluxing dioxan (6·0 ml.) and the mixture refluxed for 4 hrs. after which, it was vacuum transferred. Quantitative g.l.c. examination (Column A at 50^{o}) revealed one major reaction product and unchanged starting material. Disregarding the solvent, the composition of the reaction mixture was shown to be (i) perfluoro-1-azacyclohexa-1,3-diene (66%) and unchanged starting material (34%). The mixture was separated by preparative scale g.l.c. It was also shown that the ratio of isomers in the unchanged starting material recovered from the reaction mixture was the same as in the original starting material.

APPENDIX 1

^{19}F N.M.R. DATA

^{19}F Nuclear Magnetic Resonance Spectra

^{19}F Nuclear magnetic resonance spectra of chloro-derivatives of perfluoro-2-azahex-2-ene are reported herein (see Table 4). Both the parent (I) and its derivatives, 6-chloro- (II), 5-chloro- (III),

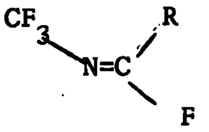
$CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}CF{=}N{-}CF_3$

(6) (5) (4) (3) (1)

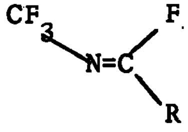
4,6-dichloro- (IV) and 5,6-dichloro- (V), were prepared by the cobaltic fluoride/calcium fluoride fluorination of polyfluorochloropyridines, and the primary objective of this study was the determination of the isomerism in the products and the consequent elucidation of stereospecificity in the preparation.

The chemical shifts, referenced to internal C_6F_6, are reported in the experimental section of this thesis. The n.m.r. spectra of these compounds were re-examined; the spectra of neat liquids were obtained at 56•4 Mc (Varian A56/60 spectrometer) and 40°C, and referenced to external $CFCl_3$ (uncorrected for volume susceptibility differences). In the case of compound II, a microcell (50 µl) was used and this resulted in a reduction in resolution.

Stereoisomerism about the C=N bond is well known,



anti



syn

TABLE 4

(Chemical Shifts of Compounds I - V (see text)*

Compound	C(1)	-N=C(3)	C(4)	C(5)	C(6)
I	60·80	26·31	121·19	129·50	83·91
II	59·52	24·69	119·41	123·58	69·91
III***	59·87	23·37	114·70	139·82	79·59
IV	59·11	24·06	128·70	115·30 ** 117·15	67·96
V	59·43	22·78	112·30	132·27	65·25

* In p.p.m. upfield of external $CFCl_3$ and uncorrected for bulk susceptibility differences.

** Two distinct chemical shifts, presumably from inhibited rotation.

*** Impurities detected in ^{19}F spectrum.

and Cavelli and Piccardi[65] noted the temperature dependence of the ^{19}F spectrum of the analogous 4-chlorohexafluoro-2-azabut-1-ene; they concluded that only the syn-isomer existed from the coupling constant of the CF_3-N=CF- and found no evidence for even a trace of the other isomer. This was in agreement with n.m.r. data for $CF_3\cdot N{=}CF\cdot CF_2\cdot CF_3$,[66,67] $CF_3\cdot N{=}CF\cdot CF_2\cdot CF_2\cdot CF_3$,[66-68] $CF_3\cdot N{=}CF\cdot CFCl\cdot CF_3$[67] and $CF_2Cl\cdot CF_2\cdot N{=}CF\cdot CF_2Cl$[69] which was consistent with the presence of an isomerically pure product. In other cases[70] such as $CF_3\cdot N{=}CF\cdot CF(CF_3)\cdot N{=}CF_2$ and $CF_3\cdot N{=}CF\cdot C(CF_3){=}N\cdot CF_3$ different geometrical isomeric forms were clearly distinguished in the n.m.r. spectra and permitted the conclusion that $J_{CF_3(1),\ CF(3)}$ was 14·2 c.p.s. in the syn-isomer and 6 c.p.s. in the anti-isomer by comparison with fluorinated olefins.

Assignment of the shifts in all five compounds was based on integrations, signal multiplicity and shift consistency for at least the $CF_3\cdot N{=}CF$- resonances; the three fluorine $CF_3(1)$ signal was found in the 60 ± 1 p.p.m. region whereas the single fluorine was observed at 24 p.p.m. The N-CF_3 resonance invariably appeared as a doublet ($J = 14 \pm 0{\cdot}4$ c.p.s.) and the CF signal was an unresolved multiplet.

The spectrum of the parent (I) also gave a triplet for the terminal $CF_3(6)$ and a doublet and quintet, each equivalent to two fluorines. Assignment to $CF_2(5)$ and $CF_2(4)$ followed from previous observations that $^3J_{F,F}$ is usually much smaller than $^4J_{F,F}$ in perfluoroaliphatic molecules.

Coupling constants extracted on a first order basis led to $J_{1,3}$ = 14•0 c.p.s., $J_{3,4}$ = 9•0 c.p.s., $J_{3,5}$ = 7•0 c.p.s. and $J_{4,6}$ = 9•0 c.p.s.

Assignment of the spectrum of II followed from that of I. The $CF_2Cl(6)$ signal was still a triplet and the $CF_2(5)$ resonance remained as a doublet but the $CF_2(4)$ resonance became a quartet and $J_{1,3}$ = 14•0 c.p.s., $J_{3,4}$ = 11•0 c.p.s., $J_{3,5}$ = 7•0 c.p.s. and $J_{4,6}$ = 11•0 c.p.s. Rotational averaging of the coupling constants appeared to be similar to that in the parent compound.

In the spectrum of III, the signal for the terminal $CF_3(6)$ became a pair of similar overlapping doublet-of quartets, constituting sixteen individual absorptions, of which ten were visible. A $CF_2(4)$ sextet split into a pair of sextets at a lower temperature (-40°C), inferring two different environments and hindered rotation in the butylidene moiety; the CFCl(5) octet, did not alter at the lower temperature and neither did the $CF_3(6)$ multiplet.

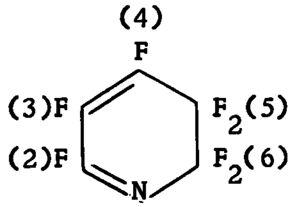
For compound IV, the $CF_2Cl(6)$ resonance was a very close pair of doublets, one of which was further split by 1•3 c.p.s.; CFCl(4) was observed as a similar pair of overlapping doublet of quartets, and these signals were temperature independent. The distinct quartets, separated by 105 c.p.s., were found for $CF_2(5)$ where the upfield quartet was an apparent triplet. In the lower field quartet, the coupling constants were 14•8 c.p.s. and 4•0 c.p.s. at room temperature, and in the higher field quartet 9•0 c.p.s. and 9•0 c.p.s.; at low temperature (-20°C) these became 17·8, 3·2, 6·3 and 12·2 c.p.s. respectively with the shift difference being 167 c.p.s.

The spectrum of compound V was also complex with CF_2(4), CFCl(5) and CF_2Cl(6) signals being complex multiplets. It was assumed that hindered rotation was occurring.

Low temperature studies gave rise to the sharpening of the broad CF(3) multiplet, in accordance with similar observations by Cavalli and Piccardi[65] who ascribed it to the natural decoupling of ^{14}N - ^{19}F coupling, from a more effective quadrupolar relaxation at lower temperatures. In particular, the CF(3) signal was a complex multiplet at 0°C.

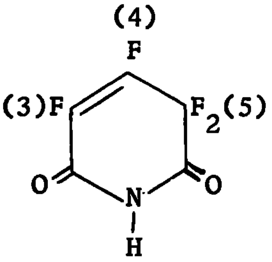
Thus the evidence so far noted, indicates that the isomers were <u>syn</u>-isomers.

Perfluoro-1-azacyclohexa-1,3-diene



^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment	Coupling constants (c.p.s.)
118•4	1	2	$J_{2,3}$ = 33 $J_{2,4}$ = 24 $J_{2,5}$ = 0•5
64•8	2	6	Half height = 19
42•6	2	5	$J_{5,6}$ = 6
23•3	1	3	$J_{3,4}$ = 3 $J_{3,5}$ = 18 $J_{3,6}$ = 6
13•6	1	4	$J_{4,5}$ = 18 $J_{4,6}$ = 3

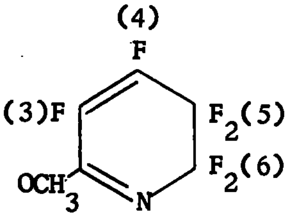
N-Hydro-2,6-dioxotetrafluoro-1-azacyclohex-3-ene



Solvent: Acetone

^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment	Coupling constants (c.p.s.)
57•8	2	5	
23•5	1	3	$J_{3,5}$ = 13•5
			$J_{3,4}$ = 7•0
16•3	1	4	$J_{4,5}$ = 23•5

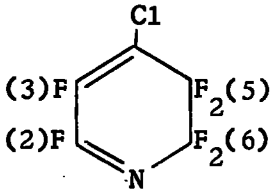
2-Methoxy-hexafluoro-1-azacyclohexa-1,3-diene



Neat liquid

^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment	Coupling constants (c.p.s.)
69•0	2	6	Half height = 21
42•0	2	5	$J_{5,6}$ = 7•0
15•0	1	3	$J_{3,4}$ = 1•5 $J_{3,5}$ = 16•5
12•0	1	4	

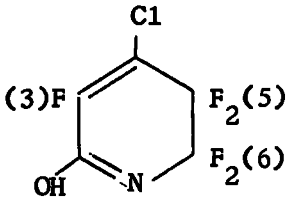
4-Chloro-hexafluoro-1-azacyclohexa-1,3-diene



Neat liquid

^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment	Coupling constants (c.p.s.)
114•7	1	2	$J_{2,3}$ = 24
64•7	2	6	Half height = 21
47•7	2	5	$J_{5,6}$ = 8
38•7	1	3	$J_{3,5}$ = 15

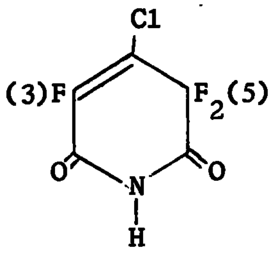
2-Hydroxy-4-chloropentafluoro-1-azacyclohexa-1,3-diene



Solvent: Acetone

^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment	Coupling constants (c.p.s.)
71•3	2	6	$J_{3,5} = 14$
48•5	2	5	$J_{5,6} = 7$
44•5	1	3	

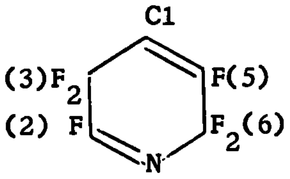
N-Hydro-2,6-dioxo-4-chlorotrifluoro-1-azacyclohex-3-ene



Solvent: Acetone

^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment	Coupling constants (c.p.s.)
64•1	2	5	
43•2	1	3	$J_{3,5}$ = 12•5

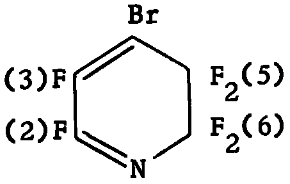
4-Chloro-hexafluoro-1-azacyclohexa-1,4-diene



Neat liquid

^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment	Coupling constants (c.p.s.)
110•8	1	2	$J_{2,3}$ = 30
79•8	2	6	
57•6	2	3	$J_{3,5}$ = 10
46•8	1	5	$J_{5,6}$ = 27

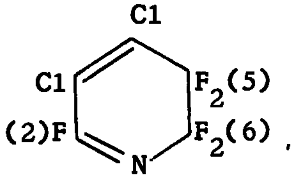
4-Bromo-hexafluoro-1-azacyclohexa-1,3-diene



Neat liquid

^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment	Coupling constants (c.p.s.)
114•0	1	2	$J_{2,3} = 24$
64•8	2	6	Half height = 21
51•0	2	5	$J_{5,6} = 8$
47•0	1	3	$J_{3,5} = 15$

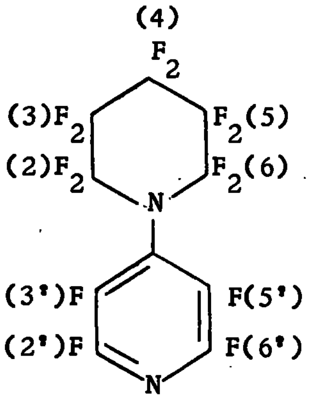
3,4-Dichloropentafluoro-1-azacyclohexa-1,3-diene



Neat liquid

^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment	Coupling constants (c.p.s.)
126·3	1	2	
63·8	2	6	
46·3	2	5	$J_{5,6} = 7·5$

1-(4'-Tetrafluoropyridyl)-decafluoro-1-azacyclohexane



Solvent: Acetone

^{19}F shift relative to int. C_6F_6 (p.p.m.)	Relative intensity	Assignment
77•0	1	2',6'
71•7	2	2,6
31•4	2	3,5
30•5	1	4
21•1	1	3',5'

APPENDIX 2

INFRA-RED SPECTRA

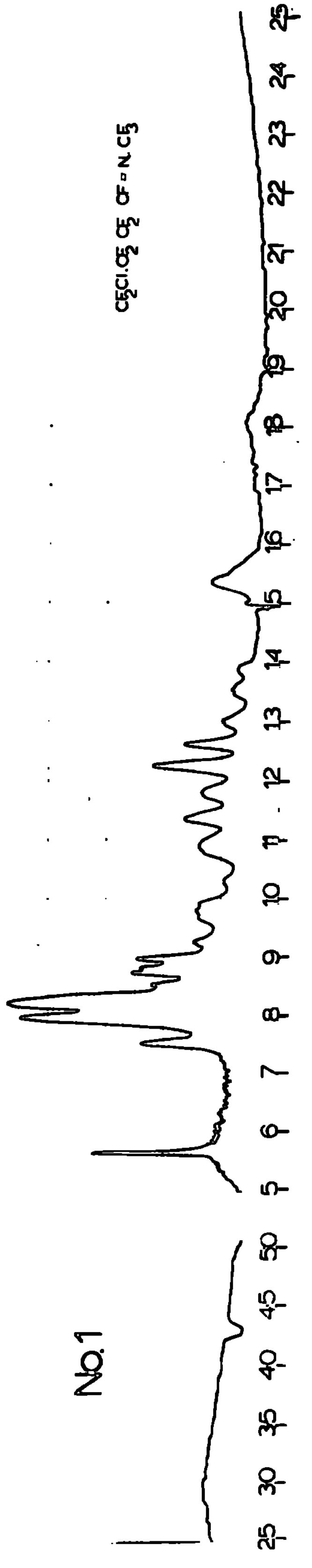
Index to Infra-Red Spectra

The infra-red spectra reported in this thesis were recorded with the sample in the form of a thin layer (L), or as a vapour in a gas cell (G) or KBr disc (D).

All compounds are new except perfluoro-1-azacyclohex-1-ene.

Spectrum No.	Phase or Solvent	Name
1	G	6-Chlorodecafluoro-2-azahex-2-ene
2	G	Perfluoro-1-azacyclohex-1-ene
3	L	4-Chloro-octafluoro-1-azacyclohex-1-ene
4	L	4-Bromo-octafluoro-1-azacyclohex-1-ene
5	G	Perfluoro-1-azacyclohexa-1,3-diene
6	L	4-Chlorohexafluoro-1-azacyclohexa-1,3-diene
7	L	4-Chlorohexafluoro-1-azacyclohexa-1,4-diene
8	L	4-Bromohexafluoro-1-azacyclohexa-1,3-diene
9	L	2-Methoxyhexafluoro-1-azacyclohexa-1,3-diene
10	D	N-Hydro-2,6-dioxotetrafluoro-1-azacyclohex-3-ene
11	D	N-Hydro-2,6-dioxo-4-chlorotrifluoro-1-azacyclohex-3-ene
12	L	1-(4'-Tetrafluoropyridyl)-decafluoro-1-azacyclohexane
13	G	5-Chlorodecafluoro-2-azahex-2-ene

Spectrum No.	Phase or Solvent	Name
14	G	5,6-Dichlorononafluoro-2-azahex-2-ene
15	G	4,6-Dichlorononafluoro-2-azahex-2-ene
16	L	3,4-Dichloropentafluoro-1-azacyclohexa-1,3-diene



No.1

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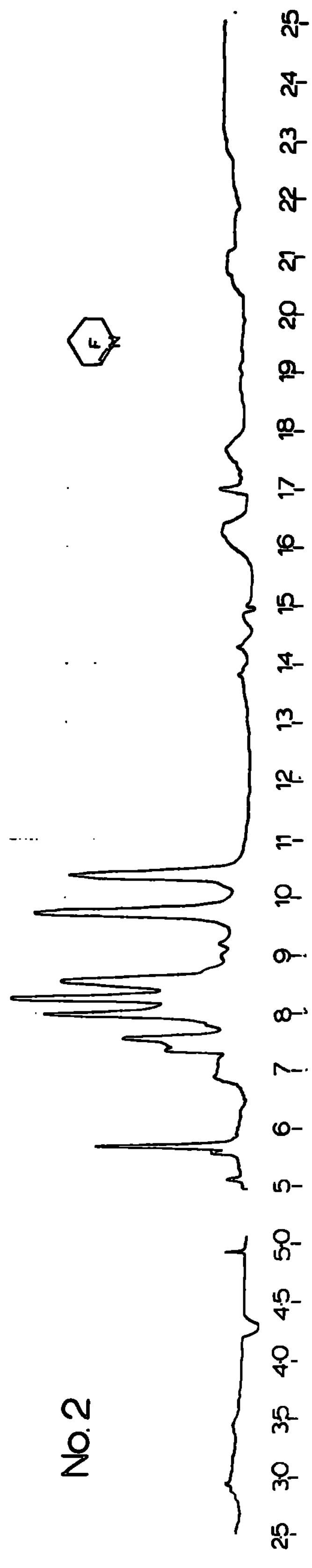

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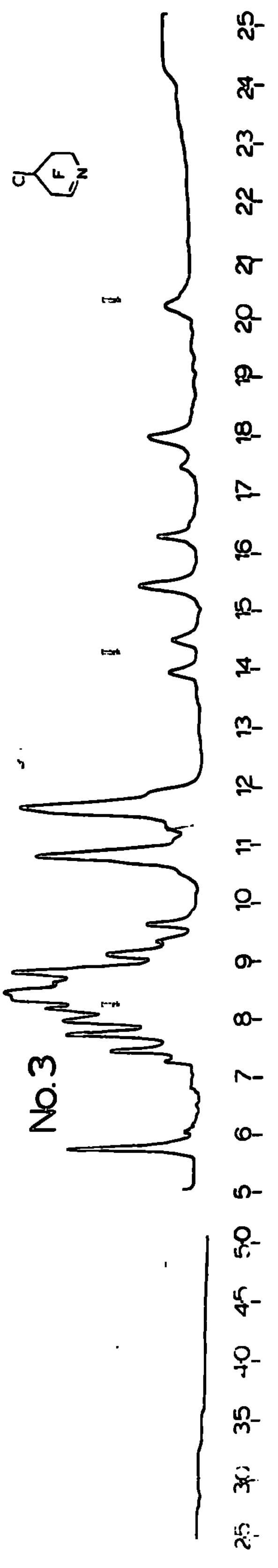

No.3

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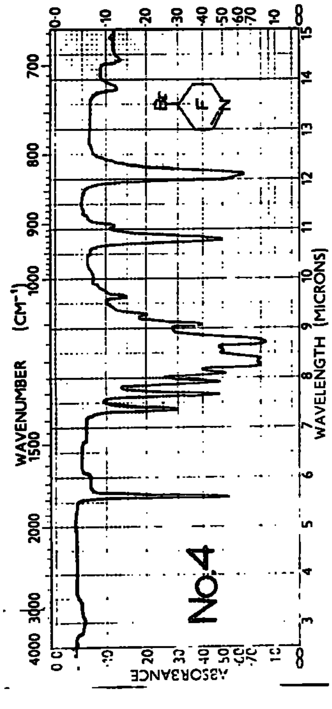
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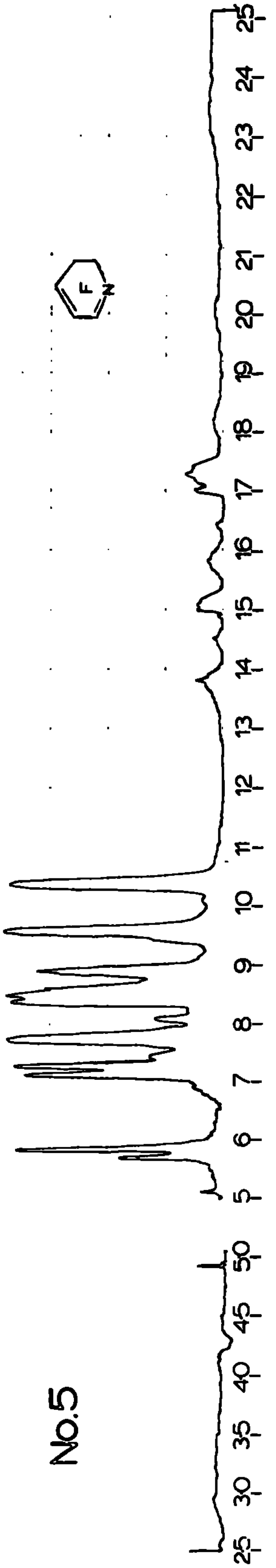
Br
F
N

No.4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25 30 35 40 45 50
F
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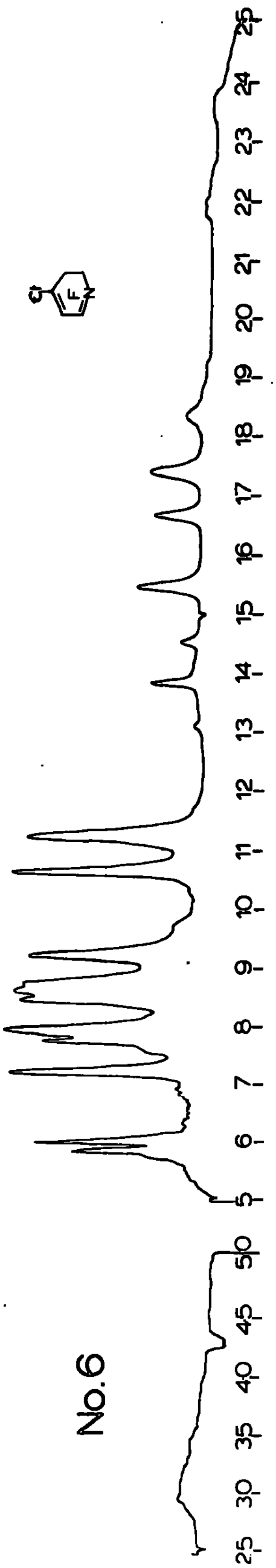
No.5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Cl
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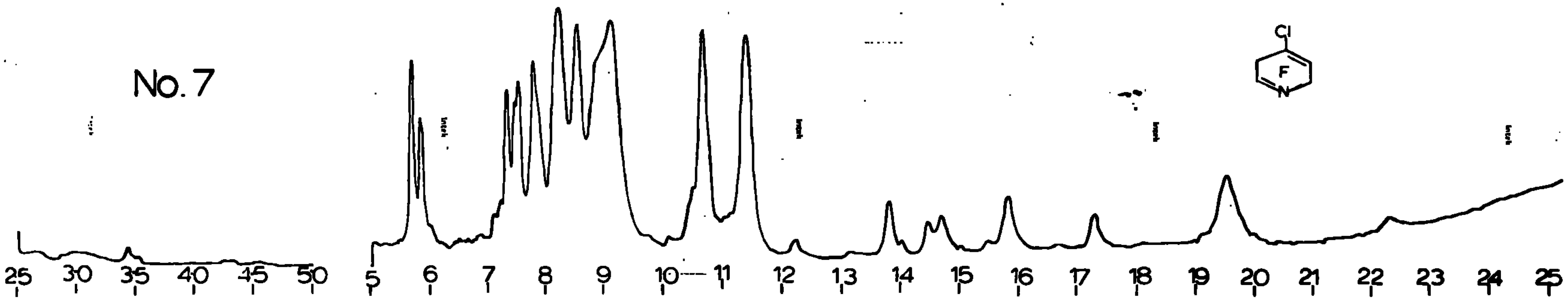
No.6

No. 7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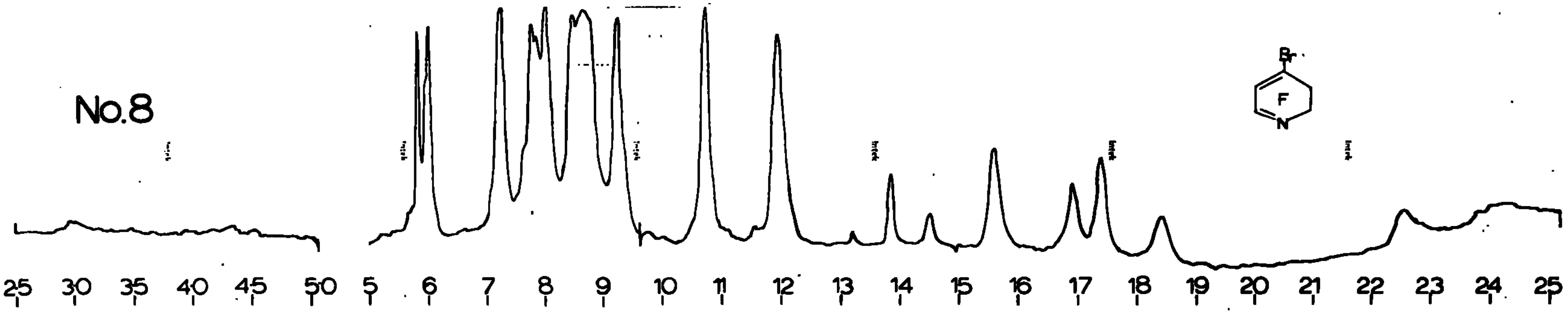
No.8


Br
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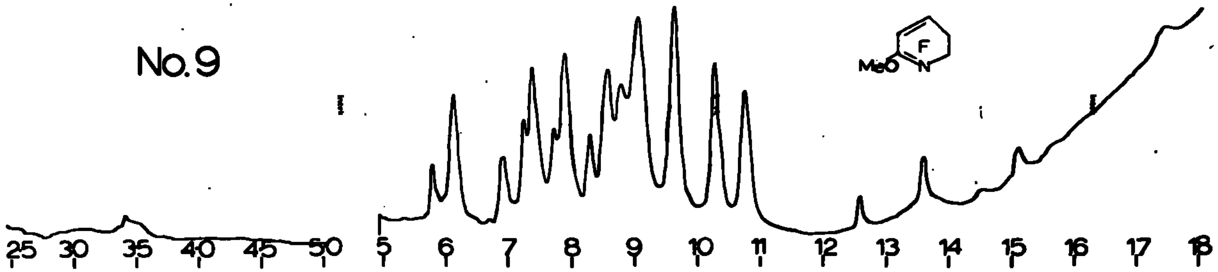
No.9


MeO
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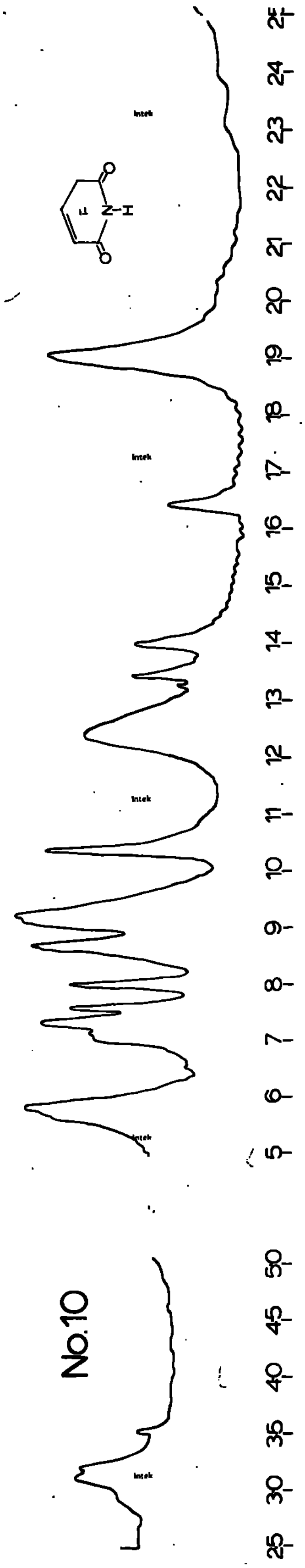
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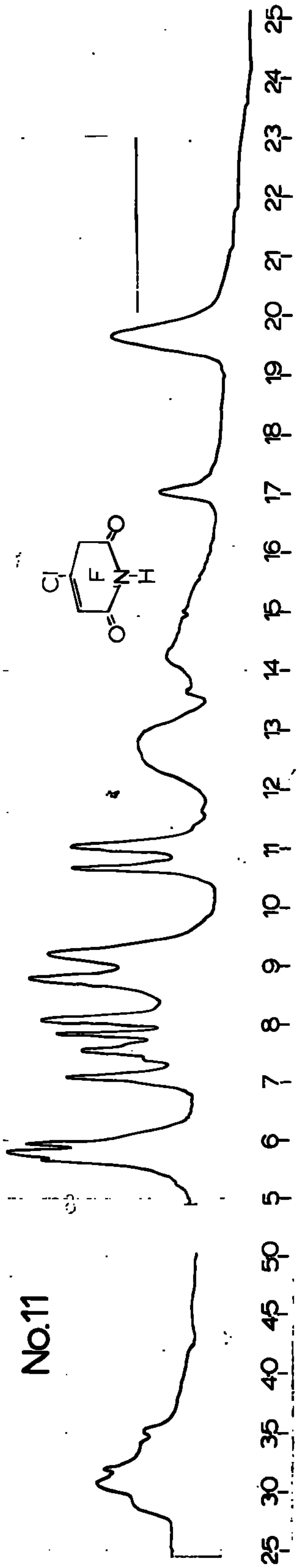
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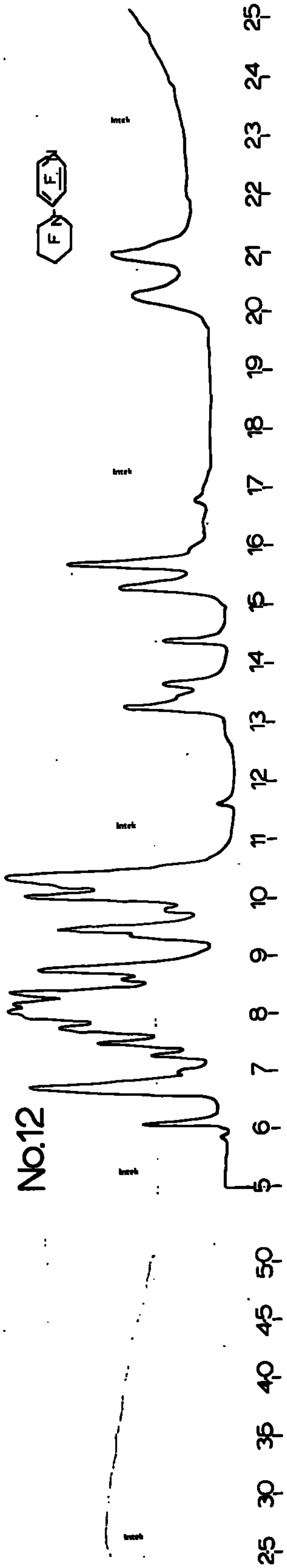
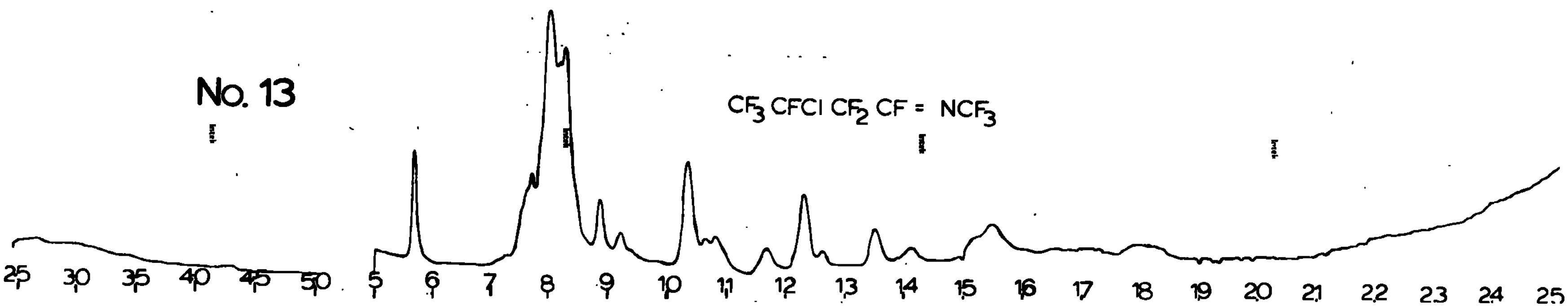
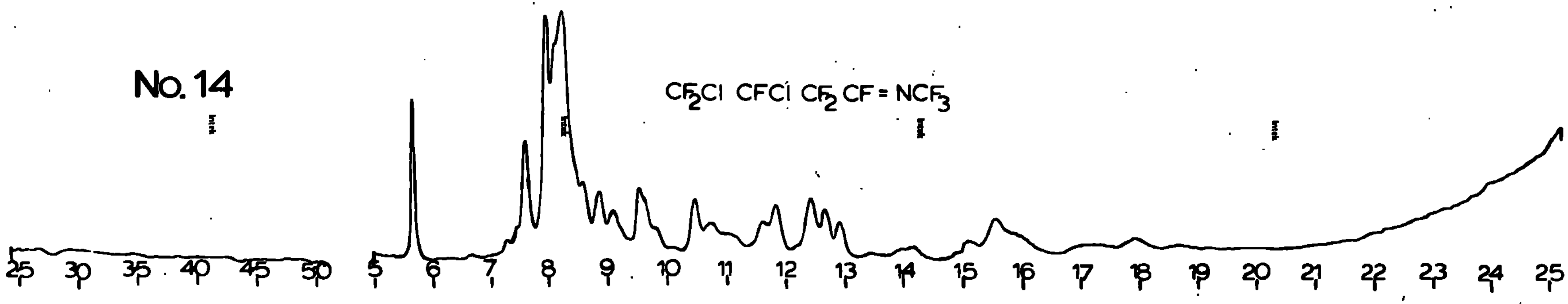

No.12

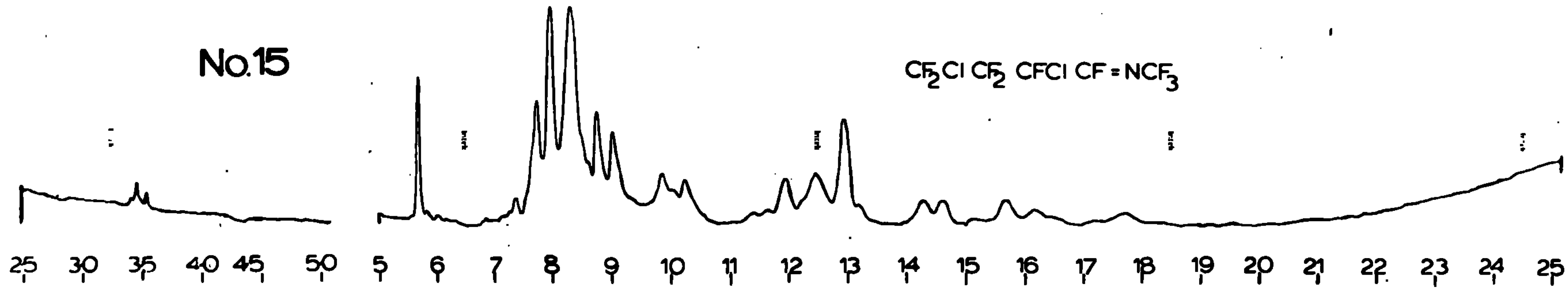
No. 13

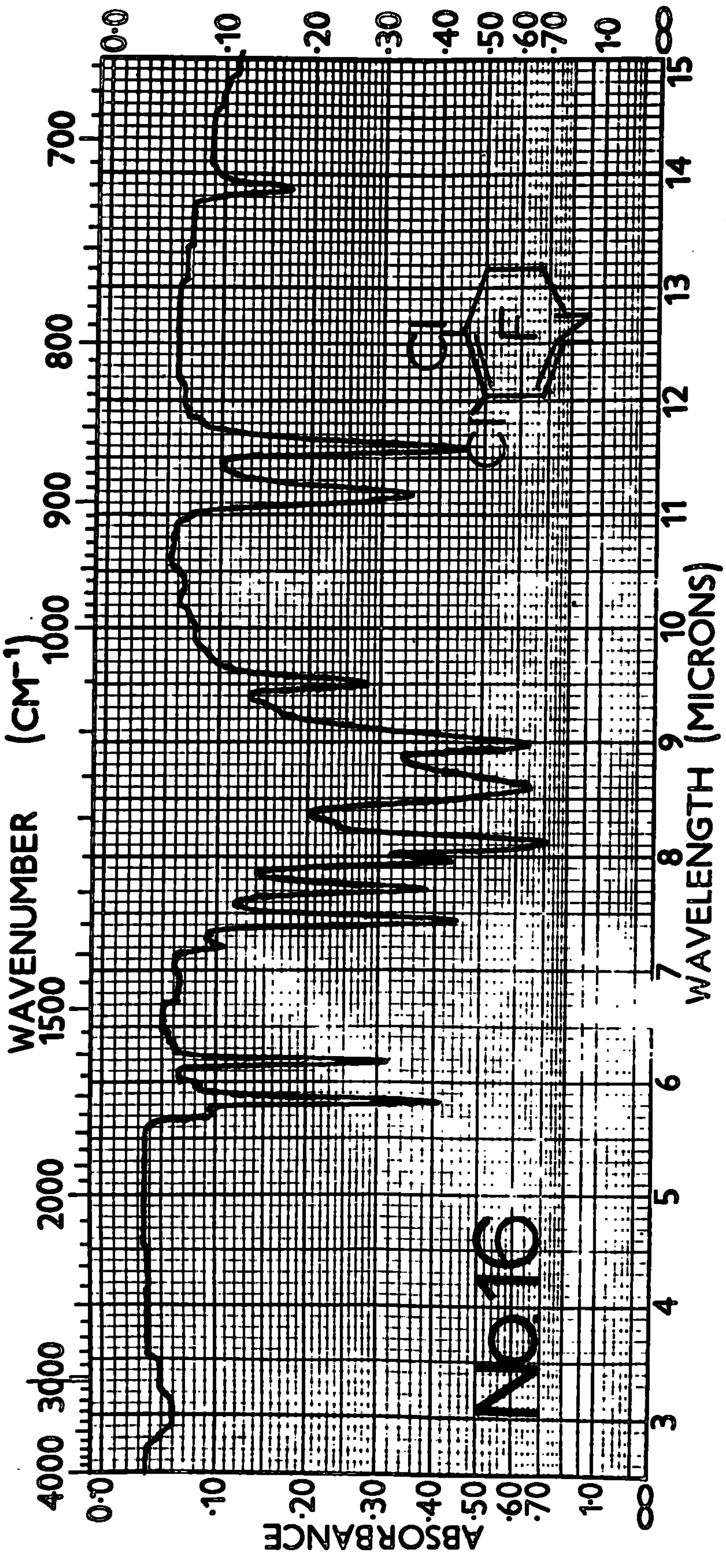

$CF_3\,CFCl\,CF_2\,CF = NCF_3$

No. 14


$CF_2Cl\ CFCl\ CF_2\,CF = NCF_3$

No.15


$CF_2Cl\,CF_2\ CFCl\ CF = NCF_3$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800
700
WAVELENGTH (MICRONS)
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6
7
8
9
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11
12
13
14
15
ABSORBANCE
0·0
·10
·20
·30
·40
·50
·60
·70
1·0
∞
No 16
Cl
Cl
F

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