Part I: some fluorinated ethers and esters. Part II; mass spectrometric studies on halogenated aromatic compounds

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UNIVERSITY OF DURHAM

A THESIS

entitled

PART I: Some Fluorinated Ethers and Esters.

PART II: Mass Spectrometric Studies on Halogenated Aromatic Compounds.

Submitted by

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A candidate for the degree of Doctor of Philosophy 1969.

ACKNOWLEDGEMENTS

The work described in this thesis was carried out under the supervision of Professor W.K.R. Musgrave and I take pleasure in thanking him for his help and encouragement throughout. I should also like to thank Mr. J. Cook and Mr. L. Chadwick formerly in the Chemistry Department at the University of Durham for their help, Mr. J.D. Dyson for n.m.r. measurements, Mr. P. Nutter for some mass spectrometric measurements and Mrs. E. Duddy for typing this thesis. I am indebted to Dr. C.G. Allison, Dr. L.P. Anderson, Mr. M. Clark, Dr. D.J. Spring and Dr. J.G. Thorpe for the provision of compounds for mass spectrometric examination.

Finally thanks are due to Monsanto Chemicals Ltd. for the award of a Research Studentship.

T O J E A N

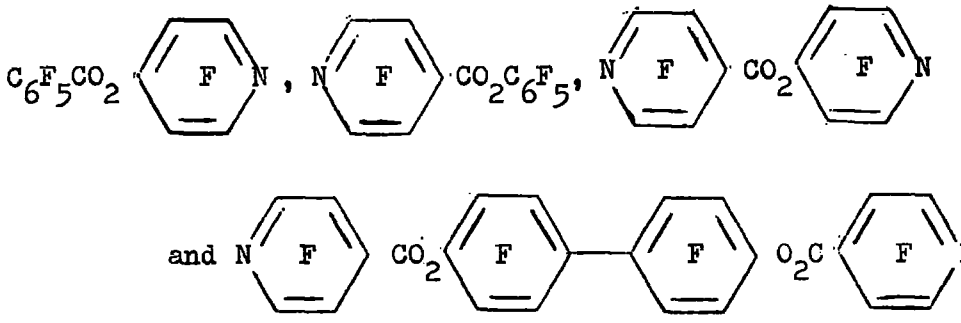
MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1965 and September 1968 and is the original work of the author except where acknowledged by reference.

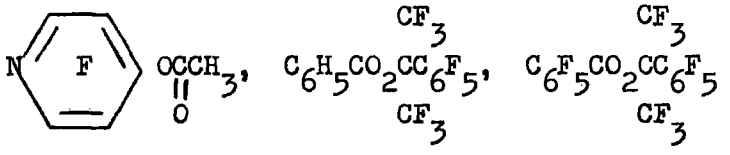
SUMMARY

Part I: Some Fluorinated Ethers and Esters.

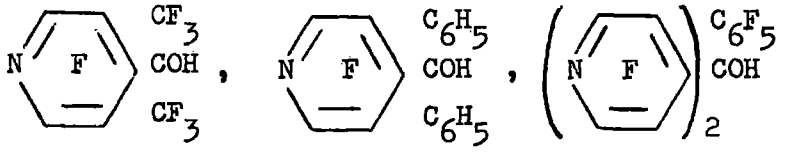
The perfluorinated aromatic esters



have been prepared by reaction of aromatic acid chlorides and phenols in the presence of N,N-diethylaniline in refluxing benzene. The aromatic esters

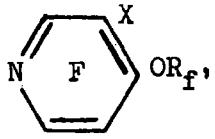


have also been prepared from tetrafluoro-4-hydroxypyridine and acetyl chloride and perfluoro-α,α-dimethylbenzyl alcohol and pentafluorobenzoyl chloride or benzoyl chloride by refluxing them alone without solvent. The carbonyl frequencies of these esters have been compared with the values obtained for other aromatic fluorinated esters. The fluorinated tertiary alcohols

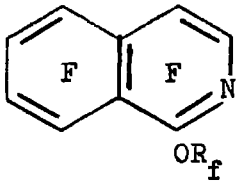


have also been prepared.

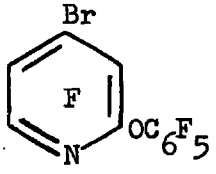
Pentafluorophenoxy and 2',3',5',6'-tetrafluorophenoxy ethers of general formula



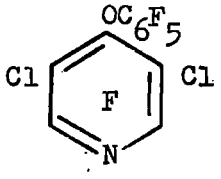
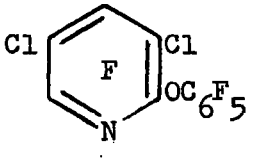
where X = F, R_f = C_6F_5 or C_6F_4H; X = Cl, R_f = C_6F_5 or C_6F_4H, or



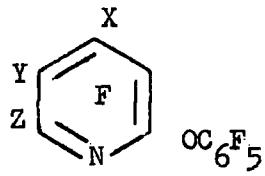
where R_f = C_6F_5 or C_6F_4H have been prepared by the reaction of pentafluoropyridine, 3-chlorotetrafluoropyridine or heptafluoroisoquinoline with a metal pentafluorophenate or 2,3,5,6-tetrafluorophenate in tetrahydrofuran at 90°. Similar reactions of 4-bromotetrafluoropyridine and 3,5-dichlorotrifluoropyridine with a metal pentafluorophenate gave 2-pentafluorophenoxy-4-bromotrifluoropyridine,



and an isomeric mixture of 2- and 4-pentafluorophenoxy-3,5-dichlorodifluoropyridine,

 and 

By using an excess of metal pentafluorophenate bis- and tris-pentafluorophenoxy ethers of general formula



,

where X = C_6F_5O, Y and Z = F or Y = F and Z = C_6F_5O or Z = F and Y = Cl; X = Br, Y = F and Z = C_6F_5O, were prepared. Nucleophilic substitution reactions on three of the pentafluorophenoxy ethers have shown that in certain circumstances the pentafluorophenoxy substituent is a good leaving group.

Caesium fluoride and octafluoroacetophenone in acetonitrile gave the alkoxide $C_6F_5(CF_3)CFOCs$ which reacted with excess octafluoroacetophenone or with pentafluoropyridine, tetrafluoropyridazine, or benzyl bromide to give ethers of general formula $C_6F_5(CF_3)CFOX$, where e.g. X = $C_6H_5CH_2$, in fair yield. Caesium fluoride and decafluorobenzophenone in diglyme gave the alkoxide $(C_6F_5)_2CFOCs$ which reacted with excess decafluorobenzophenone or pentafluoropyridine. Hexafluoroacetone, caesium fluoride, and pentafluoropyridine in diglyme at 90° gave a mixture provisionally thought to be heptafluoroisopropoxy-tetrafluoropyridine and bis(heptafluoroisopropoxy)-trifluoropyridine. Octafluoroacetophenone and n-perfluorobutyrophenone have been prepared by reactions of pentafluorophenyl-lithium with ethyl trifluoroacetate and ethyl n-perfluorobutyrate. 1,3-Bispentafluorobenzoylhexafluoro-n-propane,

prepared impure by reaction of pentafluorophenyl-lithium with perfluoroglutaryl chloride, reacted further with pentafluorophenyl-lithium as shown by the following equation:-

$$C_6F_5CO(CF_2)_3COC_6F_5 \xrightarrow{C_6F_5Li} C_6F_5CO(CF_2)_3COC_6F_4C_6F_5 + (C_6F_5)_2C_{OH}(CF_2)_3COC_6F_5$$

Part II: Mass Spectrometric Studies on Halogenated Aromatic Compounds.

In the mass spectra of fluorinated aromatic and heterocyclic ketones the main fragmentation paths of the molecular ion are usually determined by the carbonyl group itself and substantial differences in the spectra of fluorinated and hydrogenated ketones are observed only for fragmentation processes associated with cleavage of the aromatic rings. Fluorinated tertiary alcohols exhibit peaks usually associated with aromatic carbonyl compounds.

The molecular ion forms the base peak in the spectra of polyhalopyridines and diazines. Polyfluoropyridines exhibit an abundant $C_4F_2N^+$ ion and in $X\text{-}C_5F_4N$ compounds (X = halogen) the most important primary fragmentation process of the molecular ion is loss of a halogen radical. In polybromo- and polychloro-pyridines fragmentation of the molecular ion by successive loss of halogen radicals is favoured. The primary fragmentation processes of the molecular ions of polyhalogenated

pyrazines and quinoxalines are losses of F·, Cl·, and Br· and successive loss of FCN and ClCN. The molecular ions of polyhalopyridazines suffer losses of nitrogen.

Methyl or methoxy substituents have an appreciable effect on the primary fragmentation of the molecular ions of fluorinated pyrazines derivatives. Substitution of fluorine for hydrogen in an aromatic ether manifestly changes the initial fragmentation processes of the molecular ion.

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PART I

CHAPTER I

Some Fluorinated Esters

SECTION 1.

Preparation of Fluorinated Esters

Introduction.

It has been found in the past that esters derived from both fluorinated acids and fluorinated alcohols have possible application as lubricants and hydraulic fluids. Acrylic esters have provided polymeric solvent resistant elastomers. Polyesters, prepared from fluorinated glycols, have shown good thermal stability and elastomeric properties. It has proven more difficult to synthesise esters derived from fluorinated alcohols, because of their acidic nature, but this has been achieved by several methods outlined in the introduction.

1. Reaction of Acyl Halides with Alcohols.

Acyl halides have been much used in the synthesis of fluoroesters, because early attempts at direct esterification by the reaction of carboxylic acids with fluorinated alcohols resulted in low yields of esters.

1,1-Dihydroperfluorobutanol was found to react slowly with the low boiling n-perfluorobutyryl chloride at reflux temperature[1]:-

$$C_3F_7COCl + HOCH_2C_3F_7 \xrightarrow[2\ \text{days}]{\text{reflux}} C_3F_7CO_2CH_2C_3F_7 \qquad (40\%)$$

In a similar manner, the higher boiling perfluoro-octanoyl chloride reacted more rapidly:-

$$C_7F_{15}COCl + HOCH_2C_3F_7 \xrightarrow[10\ hrs.]{reflux} C_7F_{15}CO_2CH_2C_3F_7 \qquad (60\%)$$

1,1-Dihydroperfluoroethanol reacted similarly:-

$$C_3F_7COCl + HOCH_2CF_3 \xrightarrow[2\text{-}5\ days]{reflux} C_3F_7CO_2CH_2CF_3 \qquad (25\%)$$

This method was extended to the synthesis of $\alpha,\alpha,\omega,\omega$-tetrahydroperfluoroglycol esters of perfluoro acids, $C_3F_7CO_2CH_2(CF_2)_nCH_2O_2CC_3F_7$, where n = 3 or 4. The reaction was carried out for 2 days, the mixture finally being heated to 150°. A number of diesters of general formula $CnF_{2n+1}CO_2(CH_2)_xO_2CCnF_{2n+1}$ have been prepared by the same method.[2] The preparation of a series of esters and diesters derived from hydrogenated carboxylic acid chlorides and 1,1-dihydroperfluoro alcohols, a fluorinated secondary alcohol, and an $\alpha,\alpha,\omega,\omega$-tetrahydroperfluorodiol has also been described,[3] e.g.

$$[(CH_2)_4COCl]_2 + C_3F_7CH_2OH \xrightarrow[2\ days]{180^\circ} [(CH_2)_4CO_2CH_2C_3F_7]_2 \qquad (75\%)$$

Phenyl trifluoroacetate[4] has been prepared in low yield by the reaction of sodium phenoxide and trifluoroacetyl chloride:-

$$C_6H_5ONa + CF_3COCl \longrightarrow CF_3CO_2C_6H_5 + NaCl \qquad (20\%)$$

On refluxing equivalent amounts of phenyl chloroformate, trifluoroacetic acid and triethylamine in dry tetrahydrofuran for 1 hour, phenyl trifluoroacetate could be isolated in 75-80% yield.[5]

$$C_6H_5O\overset{\overset{O}{\|}}{C}Cl + CF_3CO_2H \longrightarrow C_6H_5O\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}CF_3 \longrightarrow C_6H_5O\overset{\overset{O}{\|}}{C}CF_3 + CO_2$$

Phenyl esters of perfluorocarboxylic acids have been prepared in 45-65% yield by heating the acid, phenol and phosphoryl chloride together. By this method the phenyl esters of perfluoropropionic, perfluorobutyric acids and the diphenyl esters of perfluorosuccinic, perfluoroglutaric and perfluoroadipic acids have been synthesised.[6] The carboxylic acid chloride is an intermediate in the reaction. The diphenyl esters of perfluorosuccinic and perfluoroglutaric acids were also prepared directly from the acid chlorides and phenol by heating them together for 3 hours at 160-180°. The perfluorosuccinyl and perfluoroglutaryl chlorides were prepared in yields of 67 and 53·5% respectively, by heating the acids with thionyl chloride in the presence of catalytic amounts of potassium chloride.

Treatment of a phenol and an equimolar amount of pyridine in ether with a perfluoroacid chloride results in the formation of a fluoroester,[7] e.g.

$$p\text{-}NO_2C_6H_4OH + CF_3CF_2CF_2COCl \xrightarrow{C_5H_5N} p\text{-}NO_2C_6H_4O\overset{\overset{O}{\|}}{C}C_3F_7 + C_5H_5N.HCl \quad (76\%)$$

2. Reaction of Acids or Acid Salts with Alcohols.

The direct esterification of an acid or its salt is generally applicable for the preparation of fluoroesters. The preparation of fluoroesters from fluorinated acids and alcohols is similar to the method used for non-fluorinated esters. Some of the fluorinated acids, e.g. trifluoroacetic acid, possess such acidic strength that a catalyst is not required. Even so, strong acids, especially sulphuric acid,

are generally used. The numerous catalysts that have been used include hydrogen chloride, concentrated sulphuric acid, fluorosulphonic acid and p-toluenesulphonic acid. The direct esterification of α,α-dihydroperfluoroalcohols with hydrocarbon carboxylic acids was not thought to be easy, but concentrated sulphuric acid has been shown to be an excellent catalyst for the preparation of such esters.[8] Concentrated sulphuric acid was found to be a better catalyst than p-toluenesulphonic acid, because of the higher rate of esterification and the simple purification of the product ester. p-Toluenesulphonic acid formed sulphonate esters as a side product that made purification of the fluoroester difficult.

The reaction of an acid salt with an alcohol has been used for the preparation of fluoroesters. Ethyl trifluoroacetate has been prepared by reacting sodium or silver trifluoroacetate with ethanol in sulphuric acid.[9,10,11]

Trifluoroacetic anhydride is a most useful catalyst for the promotion of esterification and will promote reaction between 1,1-dihydroheptafluorobutanol and acrylic acid:[12]

$$CH_2{=}CHCO_2H + C_3F_7CH_2OH \xrightarrow{(CF_3CO)_2O} CH_2{=}CHCO_2CH_2C_3F_7 \quad (85\text{-}90\%)$$

If trifluoroacetic anhydride is not used as catalyst, acrylic anhydride or acrylyl chloride are required to prepare the ester. No trifluoroacetyl esters are isolated as by-products.

3. The Reaction of Anhydrides with Alcohols.

Trifluoroacetic anhydride may also be used to esterify alcohols directly,[13] e.g.:

$$(CF_3CO)_2O + HOCH_2CHClCO_2C_2H_5 \xrightarrow{0^\circ} CF_3CO_2CH_2CHClCO_2C_2H_5$$

Acetic anhydride acetylates fluoroalcohols in good yields:[14]

$$(CH_3CO)_2O + C_2F_5CHOHCH_3 \longrightarrow CH_3CO_2CH(CH_3)C_2F_5 \qquad (61\%)$$

Fluorodibasic acid cyclic anhydrides have been used to prepare diesters:[15]

$$OC(CF_2)_3COO + C_3F_7CH_2OH \longrightarrow C_3F_7CH_2O_2C(CF_3)_3CO_2H + C_3F_7CH_2O_2C(CF_2)_3CO_2CH_2C_3F_7 \qquad (59\%)$$

4. The Hydrolysis of α,α-Difluoroethers.

A difluoromethylene group in the α-position in a difluoroether can be easily hydrolysed to a carbonyl group, e.g.

$$CH_2ClCF_2OC_2H_5 \xrightarrow{H_2O} CH_2Cl\cdot CO_2C_2H_5$$

However, the substitution of fluorine or perfluoroalkyl groups on the β-carbon atoms greatly reduces the ease of hydrolysis.[16] Concentrated sulphuric acid at 15° is then required. The addition of powdered glass to the reaction mixture, to react with the hydrogen fluoride formed, helps. Examples of this reaction are:

$$CHClFCF_2OC_3H_7 + H_2SO_4 \longrightarrow CHClFCO_2C_3H_7 \qquad (60\%)$$

$$CHF_2CF_2OC_2H_5 + H_2SO_4 \longrightarrow CHF_2CO_2C_2H_5 \qquad (60\%)$$

β-Trifluoromethyl substituted α,α-difluoroethers undergo this hydrolysis at higher temperatures,[17] e.g.

$$CF_3CHFCF_2OCH_3 + H_2SO_4 \xrightarrow{60\text{-}65^\circ} CF_3CHFCO_2CH_3 \qquad (66\%)$$

Aliphatic perfluoroethers have great hydrolytic stability similar to that of perfluoroalkanes.

5. Reaction of Haloalkanes with Carboxylic Acid Salts.

The reaction of a silver perfluorocarboxylate with an alkyl halide has been used to prepare fluoroesters. Silver perfluorobutyrate has been reacted with a number of α,ω-polymethylene di-iodides in 1,1,2-trichlorotrifluoroethane to provide the diesters[2], in good yields, e.g.

$$2CF_3CF_2CF_2CO_2Ag + I(CH_2)_{10}I \xrightarrow[2\text{ hrs.}]{\text{reflux}} C_3F_7CO_2(CH_2)_{10}O_2CC_3F_7 \qquad (83\%)$$

This method has been used to prepare t-butyl heptafluorobutyrate[18] from silver heptafluorobutyrate and t-butyl chloride.

An attempt to prepare a perfluorinated ester by heating silver perfluorobutyrate and n-perfluoropropyl iodide at 275 to 335° yielded only n-perfluorohexane.[19]

SECTION 2.

Discussion of the Experimental.

From the foregoing introduction to the preparation of fluorinated esters, it can be seen that at the start of this work there was no reference to the preparation of perfluorinated esters. It was thought that perfluorinated esters might have good thermal stability, and that

any polymer based on them would have good elastomeric properties too.

The preparation of a perfluorinated ester by the reaction between the acid and the phenol in the presence of trifluoroacetic anhydride unfortunately was not successful. Tetrafluoroisonicotinic acid and pentafluorophenol in equimolar amounts were heated with an excess of trifluoroacetic anhydride at 60° for 2 hours. The work-up of the reaction mixture yield a 90% recovery of starting materials and 0·1 g. of an oil. Gas-liquid chromatography showed that the oil was a mixture of four components. Purification of any one of these was not attempted.

Consequently, attempts to synthesise esters were based on the reactions of acid chlorides with phenols. Pentafluorobenzoyl chloride[20] and tetrafluoroisonicotinyl chloride[21] were prepared by heating the acids with phosphorus pentachloride.

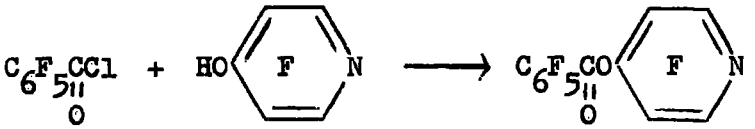
4-Hydroxytetrafluoropyridine was prepared by refluxing pentafluoropyridine with aqueous sodium hydroxide solution.[22] 4,4'-Dihydroxyoctafluorobiphenyl was prepared by reacting decafluorobiphenyl with potassium hydroxide in t-butanol.[23]

It was found that perfluorinated esters could be prepared by slowly adding an equimolar amount of N,N-diethylaniline, in dry benzene, to an equimolar solution of acid chloride and phenol, in dry benzene, boiling under reflux. N,N-Diethylaniline hydrochloride was precipitated and the reaction was completed by refluxing the mixture for a few hours. The mixture was washed with dilute hydrochloric acid and with

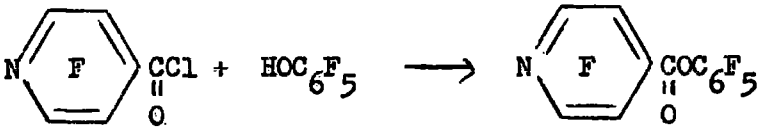
water to remove the diethylaniline hydrochloride and the dried benzene solution was distilled and the remaining ester purified by distillation or recrystallisation. The function of the diethylaniline was to remove the hydrogen chloride as it was formed.

Using this method the following esters were prepared:-

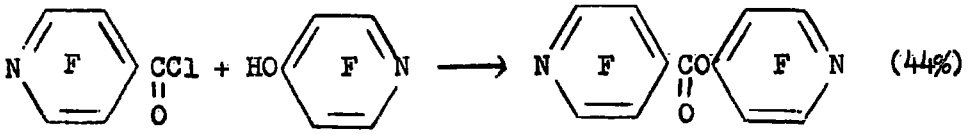
(a) 4-Pentafluorobenzoyloxy-tetrafluoropyridine from tetrafluoro-4-hydroxypyridine and pentafluorobenzoyl chloride.



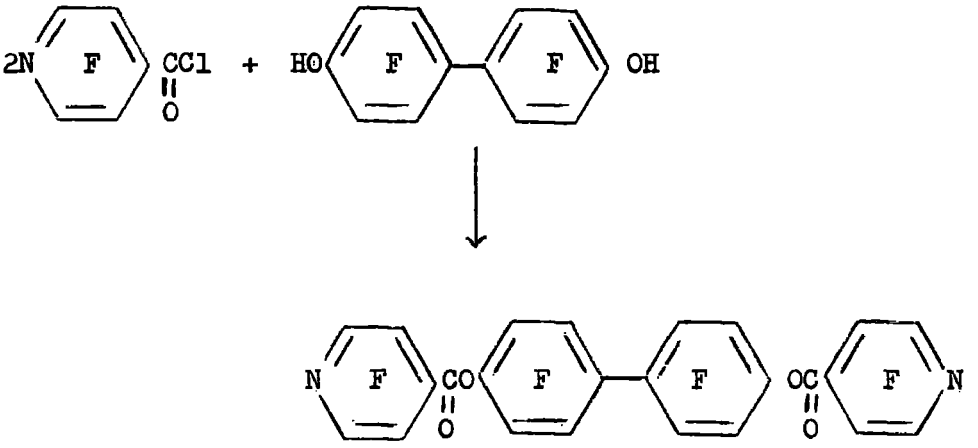
(b) Tetrafluoroisonicotinyloxy-pentafluorobenzene from pentafluorophenol and tetrafluoroisonicotinyl chloride.



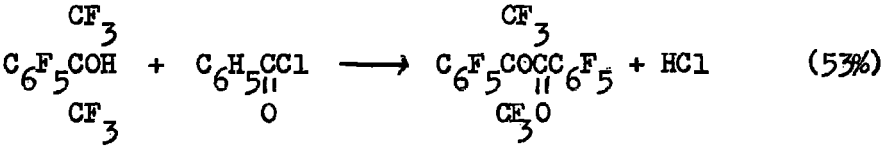
(c) 4-Tetrafluoroisonicotinyloxy-tetrafluoropyridine from tetrafluoro-4-hydroxypyridine and tetrafluoroisonicotinyl chloride.



(d) 4,4'-Bistetrafluoroisonicotinyloxy-octafluorobiphenyl from 4,4'-dihydroxyoctafluorobiphenyl and tetrafluoroisonicotinyl chloride.



An ester was prepared by the reaction of benzoyl chloride with perfluoro-α,α-dimethylbenzyl alcohol.



An attempt to prepare undecafluoro-α,α-dimethylbenzyl benzoate, by refluxing equimolar amounts of undecafluoro-α,α-dimethylbenzyl alcohol, benzoyl chloride and N,N-diethylaniline in dry benzene for 48 hours, was unsuccessful. Unchanged starting materials were recovered, as was the case when a similar reaction was attempted using pentafluorobenzoyl chloride instead. This illustrates the difficulty of esterifying perfluorinated tertiary alcohols, as compared with the

phenols, pentafluorophenol and tetrafluoro-4-hydroxypyridine, which can be esterified using the above conditions. Undecafluoro-α,α-dimethylbenzyl benzoate was finally prepared by refluxing benzoyl chloride and undecafluoro-α,α-dimethylbenzyl alcohol together without solvent for 5 days. The course of reaction was followed by taking an infrared spectrum of the mixture from time to time. The hydroxyl stretch of the alcohol and the carbonyl stretch of the acid chloride was slowly replaced by the carbonyl stretch of the ester. The low-melting ester was isolated in fair yield by distillation under reduced pressure.

Undecafluoro-α,α-dimethylbenzyl pentafluorobenzoate was prepared by refluxing pentafluorobenzoyl chloride and undecafluoro-α,α-dimethylbenzyl alcohol together for 15 days. The low-melting ester was isolated in fair yield by distillation under reduced pressure.

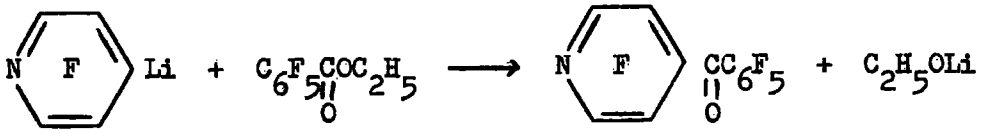
$$C_6F_5\overset{\overset{O}{\|}}{C}Cl + HO\overset{\overset{CF_3}{|}}{C}C_6F_5 \longrightarrow C_6F_5\overset{\overset{O}{\|}}{C}O\overset{\overset{CF_3}{|}}{C}C_6F_5 + HCl \qquad (51\%)$$

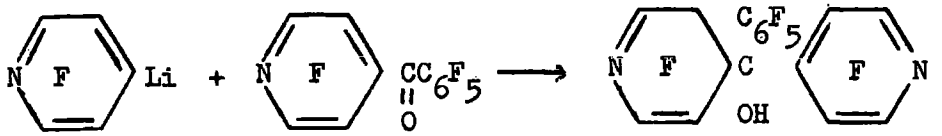
The perfluoro-(α,α-dimethylbenzyl)alcohol was prepared in good yield by reaction of hexafluoroacetone with pentafluorophenyl-lithium at -55°.[24]

Ethyl pentafluorobenzoate was prepared in good yield by refluxing pentafluorobenzoic acid with absolute ethanol, using concentrated sulphuric acid as catalyst. This ester was prepared to investigate

$$C_6F_5\overset{\overset{O}{\|}}{C}OH + C_2H_5OH \longrightarrow C_6F_5\overset{\overset{O}{\|}}{C}OC_2H_5 + H_2O \qquad (66\%)$$

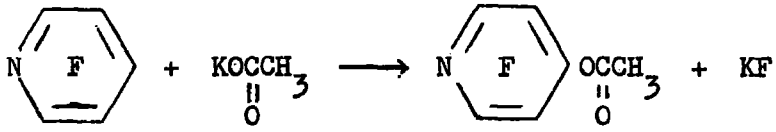
the feasibility of using ethyl esters of fluorinated acids to prepare perfluorinated tertiary alcohols. To this end, it was reacted with two molar proportions of tetrafluoropyridyl-4-lithium, prepared by halogen exchange of 4-bromo-tetrafluoropyridine with butyl-lithium, at -70°. Work-up of the reaction product resulted in the isolation of ethyl pentafluorobenzoate, 2,3,5,6-tetrafluoropyridine and a solid containing predominantly bis(2,3,5,6-tetrafluoropyridyl)-pentafluorophenyl carbinol, together with 4-tetrafluoropyridyl pentafluorophenyl ketone. Fractional sublimation and recrystallisation of this mixture afforded the pure alcohol.



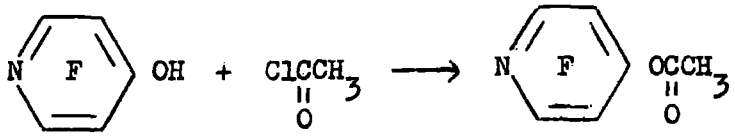


The yield of this tertiary alcohol would probably have been improved with a longer reaction time.

The possibility of preparing esters by an aromatic nucleophilic substitution reaction was investigated. Direct reaction of pentafluoropyridine with anhydrous potassium acetate, dissolved in a mixture of diglyme and acetic acid, was attempted:-



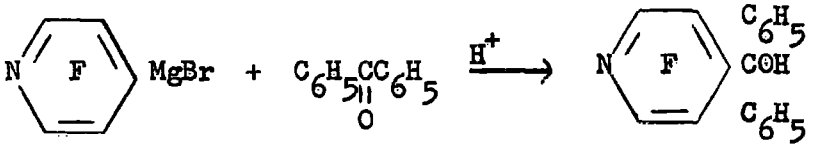
The reactants were sealed in a tube and heated to 150° for 2 days. Work-up of the reaction product yielded a mixture of five compounds. To help in the characterisation of the reaction mixture, a sample of 4-acetyloxy-tetrafluoropyridine was prepared by heating acetyl chloride and tetrafluoro-4-hydroxy-pyridine under reflux.



Comparing the mass and infra-red spectra of authentic samples of known materials with that of the mixture of five compounds showed that 4-acetyloxy-tetrafluoropyridine had been formed in low yield, together with 4-hydroxy-tetrafluoropyridine, diglyme, a small amount of acetic acid and a compound of unknown structure. It was not found to be possible to isolate pure 4-acetyloxy-tetrafluoropyridine from the mixture and the reaction was abandoned as a synthetic attempt to prepare fluorinated esters directly from a polyfluoroheterocyclic compound.

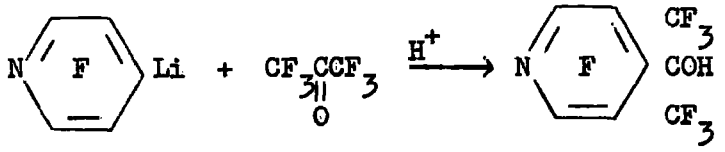
Two other fluorinated tertiary alcohols were prepared with a view to preparing esters from them. Unfortunately time was not available. 2,3,5,6-Tetrafluoropyridyl magnesium bromide, prepared by the reaction of magnesium and 4-bromo-tetrafluoropyridine at -10° in tetrahydrofuran,

was mixed with benzophenone in dry ether at -10° and stirred for an hour. Acidification of the mixture allowed the isolation of 2,3,5,6-tetrafluoropyridyl-diphenyl carbinol. After this compound was prepared,



a method for its synthesis involving reaction of benzophenone and 2,3,5,6-tetrafluoropyridyl magnesium iodide was published.[25]

Reaction of tetrafluoropyridyl-4-lithium in ether/hexane solution with an excess of hexafluoroacetone at -75° allowed the isolation of 2,3,5,6-tetrafluoropyridyl-bis-trifluoromethyl carbinol on acidification. The tetrafluoropyridyl-4-lithium was prepared by adding the required amount of n-butyl-lithium in ether/hexane to a stirred solution of 4-bromotetrafluoropyridine in ether under nitrogen at -75°.



Since the completion of this work, a publication concerning the preparation and carbonyl stretching frequencies of polyfluorinated aromatic esters appeared.[26]

Pentafluorophenyl trifluoroacetate was prepared by the reaction of pentafluorophenol with trifluoroacetyl chloride:-

$$CF_3COCl + HOC_6F_5 \xrightarrow[2{\cdot}5\ hr.]{-28^\circ} CF_3CO_2C_6F_5 + HCl$$

Phenyl pentafluorobenzoate, pentafluorophenyl benzoate and pentafluorophenyl pentafluorobenzoate were prepared by refluxing the acid chloride and the phenol together:-

$$C_6F_5COCl + HOC_6H_5 \xrightarrow{1\cdot5\ hr.} C_6F_5CO_2C_6H_5 \qquad (24\%)$$

$$C_6H_5COCl + HOC_6F_5 \xrightarrow{1\cdot5\ hr.} C_6H_5CO_2C_6F_5 \qquad (17\%)$$

$$C_6F_5COCl + C_6F_5OH \xrightarrow{3\ days} C_6F_5CO_2C_6F_5 \qquad (99\%)$$

Trifluoroethyl pentafluorobenzoate was prepared by refluxing pentafluorobenzoyl chloride and trifluoroethanol together, using anhydrous aluminium chloride as catalyst.

$$C_6F_5COCl + HOCH_2CF_3 \xrightarrow{AlCl_3} C_6F_5CO_2CH_2CF_3 \qquad (78\%)$$

Ethyl pentafluorobenzoate was prepared by adding pentafluorobenzoyl chloride slowly to a slight excess of absolute ethanol and the mixture was heated to 70-80° for 3 hours.

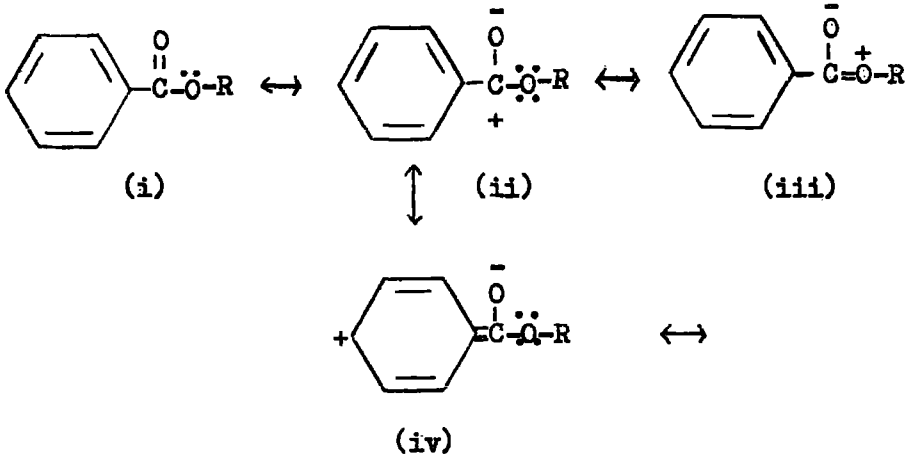
$$C_6F_5COCl + HOC_2H_5 \longrightarrow C_6F_5CO_2C_2H_5 \qquad (54\%)$$

The infra-red spectra of these esters were studied with reference to the influence of pentafluorophenyl substitution on the carbonyl frequency.

Carbonyl Frequencies of Aromatic Esters

Compound	$\nu_{C=O}(cm.^{-1})$
$C_6H_5CO_2C_6H_5$	1740
$C_6F_5CO_2C_6H_5$	1770
$C_6H_5CO_2C_6F_5$	1765
$C_6F_5CO_2C_6F_5$	1780
$C_6F_5CO_2C_2H_5$	1741
$C_6F_5CO_2CH_2CF_3$	1760, 1765
$CF_3CO_2C_6F_5$	1787

The data was rationalised by means of both the inductive and mesomeric effects.



(i) (ii) (iii)

(iv)

In the resonance structures written above, when R is an alkyl group, electron release causes the relative contribution of structure (iv) to be greater than when R is a phenyl group, thus giving greater

single bond character to the carbonyl group, which results in a lower frequency of the group. The carbonyl absorption of 1724 cm.$^{-1}$ in the spectrum of methyl benzoate[27] is shifted to 1740 cm.$^{-1}$ for phenyl benzoate. The same behaviour occurs with ethyl pentafluorobenzoate and phenyl pentafluorobenzoate.

The authors also suggested that when the phenyl group is replaced by a pentafluorophenyl group, in the acid part of the ester, the strong electron-attracting inductive effect of the pentafluorophenyl group diminishes the contributions of structures (ii), (iii) and (iv), thus increasing double bond character of the carbonyl group relative to that of the phenyl substituted ester. However, the mesomeric effect is exerted in the other direction increasing contributions of type (iv). The inductive effect was shown to be much stronger than the mesomeric effect in the pentafluorophenyl group in other experiments by the authors. The observed increase in the carbonyl frequency is, thus, explained. Where R is a pentafluorophenyl group in the structures written above, structure (iii) is greatly destabilised by the inductive effect. This is illustrated by the shift to higher frequency of pentafluorophenyl pentafluorobenzoate (1780 cm.$^{-1}$), compared to pentafluorophenyl benzoate (1765 cm.$^{-1}$), compared to phenyl benzoate (1740 cm.$^{-1}$). Pentafluorophenyl pentafluorobenzoate shows the influence of a pentafluorophenyl group at both sides of the molecule (1780 cm.$^{-1}$), but it is found that the effect is less than additive.

Naturally, it was of interest to compare the carbonyl stretching

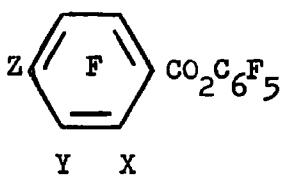
frequencies of the esters with the values obtained for the fluorinated esters prepared by Filler and his colleagues. Carbonyl bands are intense and absorb in a region of the spectrum generally free from interference from other functional groups. However, the olefinic C=C stretching vibration of fluoro-olefins gives bands of similar intensity in the same region of the spectrum. As already described, the changes in position of the ester carbonyl bands can be explained in terms of changes of the electrical interactions of substituents with the carbonyl group. Unfortunately, the polarity of the carbonyl group, and hence its stretching frequency, can be changed by outside interaction with other polar compounds. To avoid such difficulties, group frequencies are usually quoted for carbon tetrachloride solutions.[27] Other solvents generally give different frequencies. The frequencies quoted below are for the esters dissolved in a 5% solution of carbon tetrachloride, the same concentration as was used by Filler and his colleagues.

The values of some of Filler's compounds are placed in the same table by way of comparison.

Literature values[26,28] ν(C=O) cm.$^{-1}$		Author's values ν(C=O) cm.$^{-1}$	
$C_6F_5CO_2C_2H_5$	1741, 1750	$C_6F_5CO_2C_2H_5$	1747
$C_6F_5CO_2C_6F_5$	1780	4-$C_6F_5CO_2C_5F_4N$	1785
		4-$NC_5F_4CO_2C_6F_4C_6F_4O_2CC_5F_4N$-4'	1795
$CF_3CO_2C_6F_3$	1787	4-$NC_5F_4CO_2C_5F_4N$-4'	1799
$C_6H_5CO_2C_6F_5$	1765	$C_6H_5CO_2C(CF_3)_2C_6F_5$	1764
		$C_6F_5CO_2C(CF_3)_2C_6F_5$	1779

The observed increase in carbonyl frequency, when a 4-tetrafluoropyridyl group is substituted instead of a pentafluorophenyl group, in either the acid or alcohol part of the ester, seems to indicate that the inductive effect is much stronger than the mesomeric effect in a 4-tetrafluoropyridyl group, and that the inductive effect of this group is greater than that found for a pentafluorophenyl group. The 4-tetrafluoropyridyl group seems to give a greater increase in carbonyl frequency, when substituted in the acid portion of the ester, as was found for the pentafluorophenyl group. It is interesting to note the similarity in the carbonyl stretching frequencies of undecafluoro-α,α-dimethylbenzyl benzoate and pentafluorophenyl benzoate, and that substitution of the phenyl group by a pentafluorophenyl group gives the same increase in carbonyl frequency. This suggests that the pentafluorophenyl group and the undecafluoro-α,α-dimethylbenzyl group have a similar inductive effect.

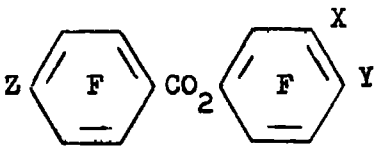
Recently, the perfluorinated aromatic esters[29] shown below were synthesised by the reaction of the phenol and acid chloride in equimolar proportions in hot benzene using slightly more than an equimolar amount of N,N-diethylaniline to remove the hydrogen chloride, as it was formed. The method was similar to that used by the author.



(i) X = $CO_2C_6F_5$, Y and Z = F

(ii) Z = $C_6F_5O_2C$, X and Y = F

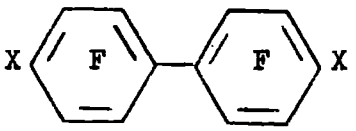
(iii) X and Z = F, Y = $C_6F_5O_2C$



Z = Y = F, X = $C_6F_5CO_2$

Z = X = F, Y = $C_6F_5CO_2$

Z = H, Y = F, X = 2,3,5,6-tetrafluorobenzoyloxy.



X = $C_6F_5CO_2$

X = $C_6F_5OC(O)O$

The reaction of equimolar amounts of pentafluorophenol and carbonyl chloride, provided the acid chloride for the preparation of the 4,4'-diphenyl derivative, where X = $C_6F_5OC(O)O$.

From the foregoing discussion, it is apparent that there now exists a number of instances of the synthesis of partially fluorinated and perfluorinated esters from both phenols and tertiary alcohols. The most important method is the reaction of an acid chloride with a phenol either alone or with benzene and a base to neutralise the liberated hydrogen chloride. A recent method for the preparation of esters, involving the reaction of the metal salt of a perfluorinated primary or secondary aliphatic alcohol with an acid chloride in a dipolar aprotic solvent, is discussed, more appropriately, in the section concerning fluoride ion initiated reactions. It has not been found possible, as yet, to prepare a perfluorinated ester using this method. The difficulty involved in the first method is the preparation of a pure sample of the perfluorinated acid chloride, free from phosphorus oxychloride, which makes the synthesis of the esters time consuming. A further investigation

of the preparation of perfluorinated esters directly from the acid and phenol or tertiary alcohol would merit attention. Even more satisfactory would be the discovery of a method of preparing esters directly from a reactive aromatic or heterocyclic perfluorinated compound and the metal salt of the acid, thus improving the overall yield of the ester. Now that a method of preparation of certain types of fluorinated esters exists, a study of their chemistry would be appropriate, especially their behaviour towards bases, acids and oxidising agents, and an estimation of their thermal stability, to assess their potential use as fluids.

EXPERIMENTAL WORK.

Fluorinated Esters

Preparation of Starting Materials

A. Hydroxy Compounds.

Tetrafluoro-4-hydroxypyridine.[22]

Pentafluoropyridine (14·5 g.), sodium hydroxide (7·2 g.) and water (120 ml.) were heated under reflux for 16½ hr. The homogeneous product was acidified with concentrated hydrochloric acid (30 ml.) and extracted with ether (3 x 250 ml.). The ethereal extract was dried ($MgSO_4$) and then evaporated to give a white solid that was sublimed at 60°/1 mm. to yield tetrafluoro-4-hydroxypyridine (11·0 g., 81% yield; m.p. 95-97°).

4,4'-Dihydroxyoctafluorobiphenyl.[23]

Decafluorobiphenyl (41·5 g.) in t-butanol (200 ml.) was stirred

while powdered 85% KOH (43 g.) was added. The mixture was refluxed for 50 minutes. 300 Ml. of water was then added and the t-butanol distilled off. The aqueous solution was acidified with hydrochloric acid and extracted with ether. The extracts were dried ($MgSO_4$) and evaporated to leave a semi-solid, which crystallised on being triturated with water (100 ml.). The solid was dried in vacuo to give 4,4'-dihydroxy-octafluorobiphenyl (36·1 g.), m.p. 190-199°. After purification by sublimation at 120-130°/0·01 mm. Hg, it had m.p. 212°.

Preparation of Perfluoro-(α,α-dimethylbenzyl)alcohol.[24]

A solution (16 ml., 2·4 molar) of n-butyl-lithium in hexane was cooled -55° under dry nitrogen. Pentafluorobenzene (6·5 g.) in dry ether (20 ml.) was added over 15 minutes. The reaction mixture was stirred for 2 hours. An excess of hexafluoroacetone was added above the surface of the stirred mixture, whose temperature was maintained between -50 and -60° during the addition. The product was warmed to 10° and hydrolysed with dilute sulphuric acid. The organic layer and two ether extracts of (10 ml.) of the aqueous layer were combined and dried ($MgSO_4$). Fractional distillation gave perfluoro-α,α-dimethyl-benzyl alcohol, boiling at 158-165°. Yield 7·6 g., (75%).

B. Acid Chlorides.[20,21]

Pentafluorobenzoic acid (4·2 g.) and phosphorus pentachloride (4·7 g.) were stirred together. On warming slightly, a vigorous

reaction occurred, with rapid evolution of hydrogen chloride. When the reaction had moderated, the solution was heated at 100° for 1 hr. On cooling and standing at room temperature for 1 hr., the excess phosphorus pentachloride crystallised out. The liquid product was decanted off and distilled under reduced pressure (18 mm.) yielding two fractions.

(1) Phosphorus oxychloride, b.p. 23-40°.

(2) Pentafluorobenzoyl chloride, b.p. 60-61°.

The yield of acid chloride (based on weight of fraction (2)) was 83·9%.

Tetrafluoroisonicotinyl Chloride.

Tetrafluoroisonicotinic acid (10 g.) and phosphorus pentachloride (12·2 g., 10% excess) were stirred together. On slight warming, a vigorous reaction occurred, with rapid evolution of hydrogen chloride. When the reaction had moderated, the solution was heated under reflux for 1 hr. On cooling and standing at room temperature for 1 hr., the excess phosphorus pentachloride crystallised out. The liquid product (19·65 g.) was decanted off and distilled under reduced pressure (13 mm.) through a Vigreux column to yield two fractions.

(1) b.p. 16-42°.

(2) b.p. 42-43°, 6·70 g.

The yield of acid chloride (based on the weight of fraction (2)) was 61%. However, the infra-red spectrum of fraction (1) showed the presence in it of acid chloride.

Preparation of Fluorinated Esters and Alcohols

Preparation of 4-Pentafluorobenzoyloxy-tetrafluoropyridine.

N,N-Diethylaniline (1·56 g., 10·47 m.mole) in dry benzene (5 ml.) was slowly added to a solution of tetrafluoro-4-hydroxypyridine (1·47 g., 8·80 m.mole) and pentafluorobenzoyl chloride (2·30 g., 8·80 m.mole) in benzene (15 ml.) boiling under reflux. The mixture was refluxed for 6 hr., cooled, diluted with benzene (20 ml.), washed with N-hydrochloric acid (4 x 25 ml.) and then with water (50 ml.). The benzene solution was dried ($MgSO_4$) and the solvent was removed by distillation. Distillation of the residual liquid under reduced pressure afforded 4-pentafluorobenzoyloxy-tetrafluoropyridine (1·92 g., 53%) (Found: C, 40·1; F, 47·5; M, 361. $C_{12}F_9O_2N$ requires C, 39·9; F, 47·4%; M, 361), b.p. 152-153° at 18 mm. (i.r. spectrum No. 1), indicated pure by v.p.c. (silicone elastomer on Celite at 200°).

Preparation of Tetrafluoroisonicotinyloxy-pentafluorobenzene.

N,N-Diethylaniline (1·56 g., 10·47 m.mole) was added slowly to a solution of pentafluorophenol (1·84 g., 10 m.mole) and tetrafluoroisonicotinyl chloride (2·14 g., 10 m.mole) in dry benzene (10 ml.) boiling under reflux. The mixture was refluxed for 4 hr., cooled, diluted with benzene (20 ml.), washed with 1N hydrochloric acid (4 x 25 ml.) and then with water (50 ml.). The benzene solution was dried ($MgSO_4$) and the solvent was removed by distillation. Distillation of the residual liquid under reduced pressure afforded a product (1·75 g.), shown by v.p.c. (silicone elastomer on Celite at 200°) to be contaminated by a small amount of pentafluorophenol. Redistillation

of this liquid gave pure tetrafluoroisonicotinyloxy-pentafluorobenzene (1·2 g.). (Found: C, 39·6; F, 47·3; M, 361. $C_{12}F_9O_2N$ requires C, 39·9; F, 47·4%; M, 361), b.p. 140-142° at 18 mm. (i.r. spectrum No. 2).

4-Tetrafluoroisonicotinyloxy-tetrafluoropyridine.

N,N-Diethylaniline (1·56 g., 10·47 m.mole) was added slowly to a solution of tetrafluoro-4-hydroxypyridine (1·67 g., 10 m.mole) and tetrafluoroisonicotinyl chloride (2·14 g., 10 m.mole) in dry benzene boiling under reflux. The mixture was refluxed for 4 hr., cooled, diluted with benzene (20 ml.), washed with 1N hydrochloric acid (4 x 25 ml.) and then with water (50 ml.). The benzene solution was dried ($MgSO_4$) and the solvent was removed by distillation. Distillation of the residual liquid under reduced pressure afforded 4-tetrafluoroisonicotinyloxy-tetrafluoropyridine (1·52 g., 44%). (Found: C, 38·3; F, 44·0; M, 344. $C_{11}F_8N_2O_2$ requires C, 38·4; F, 44·2%; M, 344), b.p. 152-153° at 14 mm. (i.r. spectrum No. 3), indicated pure by v.p.c. (silicone elastomer on Celite at 200°).

Preparation of 4,4'-Di(tetrafluoroisonicotinyloxy)octafluorobiphenyl.

N,N-Diethylaniline (1·67 g., 11·2 m.mole) was added to tetrafluoroisonicotinyl chloride (2·135 g., 10 m.mole) and 4,4'-dihydroxyoctafluorobiphenyl (1·65 g., 5 m.mole) in benzene (20 ml.) and the mixture was boiled under reflux with stirring for 5 hr. When cold, benzene (100 ml.) was added to the mixture and the solution was washed with 2N-hydrochloric acid (15 ml.) and with water (2 x 50 ml.).

Evaporation of the dried ($MgSO_4$) benzene solution gave a solid (4·3 g.), which was recrystallised from light petroleum (b.p. 70-90°) to give 4,4'-di(tetrafluoroisonicotinyloxy)octafluorobiphenyl, m.p. 135-136°. (Found: C, 41·9; F, 44·2; M, 684. $C_{24}F_{16}N_2O_4$ requires C, 42·1; F, 44·4%; M, 684) (i.r. spectrum No. 4).

Preparation of Undecafluoro-α,α-dimethylbenzyl benzoate.

Perfluoro-α,α-dimethylbenzyl alcohol (1·8 g., 5·4 m.mole) and benzoyl chloride (0·84 g., 5·4 m.mole) were heated under reflux for 5 days. The infra-red spectrum of the crude product contained a strong carbonyl absorption and no hydroxyl absorption, indicating completion of the reaction. The brown liquid was distilled under reduced pressure to yield undecafluoro-α,α-dimethylbenzyl benzoate (1·26 g., 53%) (Found: C, 43·5; F, 47·4; H, 1·0; M, 438. $C_{16}F_{11}H_5O_2$ requires C, 43·8; F, 47·7; H, 1·1%; M, 438), b.p. 136-140° at 11 mm. (i.r. spectrum No. 5).

Preparation of Undecafluoro-α,α-dimethylbenzyl pentafluorobenzoate.

Perfluoro-α,α-dimethylbenzyl alcohol (1·67 g., 5 m.mole) and pentafluorobenzoyl chloride (1·15 g., 5 m.moles) were heated under reflux for 15 days. The reaction was followed by taking the infra-red spectrum of the mixture at intervals. Distillation of the brown liquid under reduced pressure afforded undecafluoro-α,α-dimethylbenzyl pentafluorobenzoate (1·35 g., 51%). (Found: C, 36·1; F, 57·3;

M, 528. $C_{16}F_{16}O_2$ requires C, 36·4; F, 57·6%; M, 528), b.p. 138-142° at 10 mm. (i.r. spectrum No. 6).

Preparation of Ethyl Pentafluorobenzoate.

Pentafluorobenzoic acid (10·4 g.), absolute ethanol (35 ml.) and concentrated sulphuric acid (1·0 ml.) were heated under reflux for 17 hr. The excess of alcohol was distilled off. The residue was poured into water (50 ml.), the ester layer separated and the aqueous layer extracted with ether (20 ml.). The ester and ether extract were combined, washed with sodium bicarbonate solution, water, dried ($MgSO_4$) and the ether distilled off. The residual liquid on distillation under reduced pressure yielded ethyl pentafluorobenzoate (7·49 g., 66%) (Found: C, 45·0; F, 39·6; H, 2·0; M, 240. $C_9F_5H_5O_2$ requires C, 45·0; F, 39·6; H, 2·1%; M, 240), b.p. 165-166° at 450 mm. (i.r. spectrum No. 7).

Preparation of Bis(2,3,5,6-tetrafluoropyridyl)-pentafluorophenyl Carbinol.

4-Bromotetrafluoropyridine (4·6 g., 20 m.mole) in dry ether (12 ml.) was stirred under dry nitrogen at -75°. N-Butyl-lithium (7·15 ml., 2·75 molar solution in hexane, 20 m.mole) in ether (3 ml.) was added dropwise and the solution was stirred for 1 hr. Ethyl pentafluorobenzoate (2·40 g., 10 m.mole) in dry ether (3 ml.) was added dropwise over 20 minutes. The temperature was maintained between -65 and -75° with stirring for 1 hr. and slowly allowed to

rise to room temperature. The mixture was hydrolysed with dilute sulphuric acid (10 ml.). The ether layer was separated and the aqueous layer extracted twice with ether (10 ml.). The combined ethereal solutions were dried ($MgSO_4$) and the ether removed by distillation. A residual liquid and a solid ramained. The liquid was separated from the solid by vacuum transfer and shown to be a mixture of ethyl pentafluorobenzoate and 2,3,5,6-tetrafluoropyridine by the mass and infra-red spectra. Fractional sublimation of the solid yielded 4-tetra-fluoropyridyl-pentafluorophenyl ketone (0·1 g., m.p. 66°) and the residual solid on recrystallisation from ethanol yielded bis(2,3,5,6-tetra-fluoropyridyl)-pentafluorophenyl carbinol (1·1 g., 22%). (Found: C, 41·0; F, 49·8; M, 496. $C_{17}F_{13}N_2OH$ requires C, 41·1; F, 49·8%; M, 496), m.p. 135° (i.r. spectrum No. 8).

Preparation of 4-Acetyloxy-tetrafluoropyridine.

Acetyl chloride (1·57 g., 20 m.mole) and tetrafluoro-4-hydroxy-pyridine (3·34 g., 20 m.mole) were heated under reflux with stirring for 17 hr. When cool the mixture was dissolved in ether, washed successively with water, 5% sodium carbonate solution, and water, dried ($MgSO_4$) and the ether removed. Distillation of the residual oil under reduced pressure yielded 4-acetyloxy-tetrafluoropyridine (2·15 g., 51%). (Found: C, 40·5; F, 36·0; H, 1·3; M, 209. $C_7F_4H_3O_2N$ requires C, 40·2; F, 36·4; H, 1·5%; M, 209), b.p. 61-63° at 9 mm. (i.r. spectrum No. 9).

Preparation of 2,3,5,6-Tetrafluoropyridyl-diphenylcarbinol.

A four-necked flask fitted with stirrer and dropping funnel, and containing magnesium (0·4 g., 16·6 m.mole) and dry tetrahydrofuran (9 ml.) was purged with dry nitrogen and cooled to -20°. A solution of 4-bromotetrafluoropyridine (2·0 g., 8·7 m.mole) in dry tetrahydrofuran (1 ml.) was added and, after a few minutes, reaction commenced. The mixture was allowed to warm to -10 to 0° and maintained at this temperature for 1 hr. before further reactant was added. Benzophenone (1·58 g., 8·7 m.mole) in dry ether (9 ml.) was then added to the Grignard reagent at -10°. The mixture was stirred at this temperature for 30 min., then at room temperature for 30 min., before being hydrolysed with dilute sulphuric acid and then extracted with ether. The extracts were dried ($MgSO_4$) and the solvent was removed by distillation to yield a yellow solid (0·85 g.). Recrystallisation of the solid from aqueous methanol afforded white crystals of 2,3,5,6-tetrafluoropyridyl-diphenylcarbinol. (Found: C, 65·0; F, 22·9; H, 3·0; M, 333. $C_{18}H_{11}F_4NO$ requires C, 64·9; F, 22·8; H, 3·3%; M, 333), m.p. 107-108° (i.r. spectrum No. 10).

Preparation of 2,3,5,6-Tetrafluoropyridyl-bis-trifluoromethylcarbinol.

4-Bromotetrafluoropyridine (4·6 g., 20 m.mole) in dry ether (12 ml.) was stirred under dry nitrogen at -75°. n-Butyl-lithium (8·2 ml., 2·4 molar, 20 m.mole) in hexane and ether (3 ml.) were added dropwise and the solution was stirred for 1 hr. An excess of hexafluoroacetone

was introduced above the surface of the stirred mixture. The temperature was maintained at -75° during the addition and for 90 minutes after. The product was warmed to 10° and hydrolysed with dilute sulphuric acid. The organic layer and two ether extracts (10 ml.) of the aqueous layer were combined and dried ($MgSO_4$). The ether and hexane were removed by distillation. The residue was distilled under reduced pressure (450 mm.) to give 3 fractions of boiling points 20-120°, 120-140° and 140-146°. Examination of the 3 fractions by gas liquid chromatography (silicone grease at 180°) showed that the two highest boiling fractions were identical and consisted of a single product peak, which was shown to be 2,3,5,6-tetrafluoropyridyl-bis-trifluoromethylcarbinol. (Found: C, 30·1; F, 59·8; M, 317. $C_8F_{10}NOH$ requires C, 30·3; F, 59·9%; M, 317). The yield, based on the total weight of the highest boiling fractions was 2·5 g. (37%) (i.r. spectrum No. 11). The lowest boiling fraction contained some product alcohol together with two other compounds.

CHAPTER II

Some Pentafluorophenoxy and 2,3,5,6-Tetrafluorophenoxy Aromatic Ethers

SECTION 1.

Discussion of Experimental

The synthesis of fluorinated ethers has been an object of research by investigators for some years. For example, from perfluorophenyl ether thermal stability data could be obtained which may be applicable to polyfluorophenylene ethers. Interest in perfluorodiphenyl ether followed the synthesis of poly-perfluorobiphenyl,[30] which had undesirable properties, such as insolubility and brittleness, but good thermal stability. It was thought that these elastic properties could be bettered by the introduction of some atom or organic group between the phenyl rings to form bond angles other than 180°. Aryl ethers are among the most stable organic compounds,[31,32] so it was hoped that poly-perfluorophenylene ethers and related compounds would have good thermal stability, and improved physical properties.

Partially fluorinated diphenyl ethers had been prepared by Ullmann reactions, involving phenolic salts and a halobenzene with copper catalysts at high temperatures in sealed tubes. By this method 3(trifluoromethyl)phenyl ether[33] and pentafluorophenyl phenyl ether[34] were prepared, e.g.

$$C_6F_5OK + C_6H_5Br \xrightarrow[210^\circ,\ 6\ hr.]{Cu} C_6F_5OC_6H_5 \qquad (15\%)$$

Pentafluorophenyl phenyl ether[34] was also prepared by the reaction of hexafluorobenzene with potassium phenoxide in dimethylformamide. Some 1,4-diphenoxy-tetrafluorobenzene was also obtained, which indicated that a phenoxy group activated the pentafluorobenzene ring to further reaction in the 4-position.

$$C_6H_5OK + C_6F_6 \xrightarrow[120^\circ,\ \frac{1}{2}\ hr.]{D.M.F.} C_6F_5OC_6H_5 + 1,4\text{-}C_6H_5OC_6F_4OC_6H_5$$

(31%) (7%)

Some fluoroaromatic polyethers have also been prepared. Poly(perfluorophenylene ether)[35] and polyfluorophenylene thio ether[36] were synthesised by thermal decomposition of sodium pentafluorophenate and potassium pentafluorothiophenate. A polyfluoroether was prepared from pentafluorobenzyl alcohol.[37]

Although it was found that potassium phenate reacted with hexafluorobenzene in dimethylformamide,[34] potassium pentafluorophenate failed to react under these conditions, but by refluxing for 14 hours a 16% yield of perfluorophenyl ether was obtained. These reactions indicated that the phenate ion is a stronger nucleophile than pentafluorophenate, because even at room temperature some 1,4-diphenoxy-tetrafluorobenzene was obtained. In these reactions hydrated phenoxide salts were used. Attempts to react potassium pentafluoro-phenate with hexafluorobenzene in dimethylformamide using anhydrous materials under reflux resulted in the formation of pentafluoro-N,N-dimethylaniline, because of the thermal decomposition of the solvent to yield dimethylamine.[38] Attempting the reaction of potassium pentafluorophenate with hexafluorobenzene in a bomb at 120° for 18 hours using tetrahydrofuran as solvent gave no improvement in the yield of perfluorodiphenyl ether. Use of methanol as solvent yielded

only exchange products such as pentafluoroanisole. No polymers were formed in the reactions in these solvents.

The reactivity of the pentafluorophenate salts was increased greatly using water as solvent, and reaction occurred readily with or without hexafluorobenzene. The reactions in these aqueous systems were complex giving rise to a variety of products. From these reactions perfluorodiphenyl ether, bis(pentafluorophenoxy)tetrafluorobenzene, 2,3,5,6-tetrafluororesorcinol, pentafluorophenoxytetrafluorophenol and several polyfluorophenylene ethers of varying chain length were isolated. The thermal decomposition of sodium pentafluorophenate yielded poly(perfluorophenylene)ethers with a hydroxyl end group.[38]

$$XC_6F_5ONa \xrightarrow{345^\circ} C_6F_5(OC_6F_4)_{x-1}ONa \longrightarrow C_6F_5(OC_6F_4)_{x-1}OH$$

An experiment was attempted to prepare polyethers without the hydroxyl end group by heating slightly more than a molar proportion of

$$XC_6F_5OK + C_6F_6 \longrightarrow C_6F_5O(C_6F_4O)_{x-1}C_6F_5 + XKF$$

hexafluorobenzene with a bimolar proportion of potassium hydroxide at 175° for 5 hours and then at 225° for 15 hours, but, in fact, the mixture stated above was obtained.

Sodium pentafluorophenate on heating to 345° at 1 mm. gave octafluorodiphenylene dioxide and polymeric material. Potassium pentafluorophenate on refluxing with excess pentafluorophenol gave polymeric material, which analysis indicated had the composition C_6F_4O.

Poly(perfluorophenylene ethers) were prepared having molecular weights of 1700, 4300, 6500 and 12,500.

These results indicated that the pentafluorophenate ion is a relatively weak nucleophile and under the conditions used gave poly-perfluoroethers in low yields. For synthesis of a polymer it is desirable that the reaction should proceed in good yield, using mild conditions, so that side reactions, caused for example by thermal decomposition of the solvent, do not interfere with the polymer formation. It was decided to study the reaction of pentafluorophenate ion with a substrate more reactive than hexafluorobenzene. Pentafluoropyridine was considered to be a prime candidate, because of its ready reaction with nucleophiles to form di- and tri-substituted derivatives, even when the 4-substituent deactivates the ring towards further substitution. For example, 4-methoxytetrafluoropyridine readily reacts with sodium methoxide in refluxing methanol to form 2,4-dimethoxy-trifluoropyridine[39] or 2,4,6-trifluoromethoxy-difluoropyridine,[40] whilst 1-methoxy-pentafluorobenzene reacts only slowly with methoxide ion to form a mixture of para-, meta-, and ortho-dimethoxytetrafluorobenzenes in the ratios 52:32:16 respectively.[41] This is because of the activating effect of the nitrogen atom in pentafluoropyridine on the 2 and 6-positions.

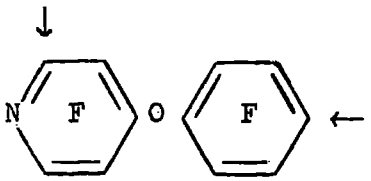
Potassium pentafluorophenate was prepared as the dihydrate by adding a concentrated solution of potassium hydroxide in water to a

solution of pentafluorophenol in aqueous potassium hydroxide cooled in ice. The precipitated salt was filtered off and recrystallised from a small amount of water to give the dihydrate, from which the anhydrous salt was prepared by azeotropic distillation with benzene. The pentafluorophenol was either bought or prepared by refluxing hexafluorobenzene with potassium hydroxide in t-butanol. The pentafluorophenol was not isolated but water was added to the reaction mixture, the t-butanol distilled off and the aqueous solution of potassium pentafluorophenate used directly. The dihydrate of the potassium salt of 2,3,5,6-tetrafluorophenol was prepared similarly from 2,3,5,6-tetrafluorophenol.

4-Pentafluorophenoxy-tetrafluoropyridine was prepared by reacting equimolar amounts of anhydrous potassium pentafluorophenate and pentafluoropyridine in tetrahydrofuran as solvent at 90° for 4 hours. The solution darkened somewhat and a brown precipitate of potassium fluoride was formed. The high boiling liquid reaction product was purified by preparative scale gas-liquid chromatography. The yield of crude product was good (65%) and, as expected, pentafluoropyridine reacted far more readily than hexafluorobenzene with potassium pentafluorophenate.

Reaction of a two-fold molar amount of anhydrous potassium pentafluorophenate with pentafluoropyridine in tetrahydrofuran at 90° for 8 hours yielded a mixture of 4-pentafluorophenoxy-tetrafluoro-

pyridine and 2,4-bis(pentafluorophenoxy)-trifluoropyridine in a ratio of approximately 2 to 1. The 2,4-bis(pentafluorophenoxy)-trifluoropyridine was isolated by distillation under reduced pressure. This experiment illustrates that the fluorine ortho to the ring nitrogen is more susceptible to nucleophilic displacement than the 4-fluorine in the pentafluorophenyl ring, and, hence, that the activating effect of a

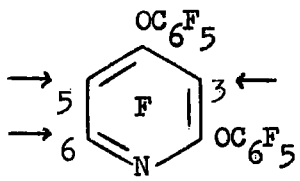


Expected possible positions of nucleophilic attack.

4-tetrafluoropyridyloxy group towards the pentafluorophenyl ring is not as great as the activating effect of the ring nitrogen on the 2-position of the tetrafluoropyridyl ring. The 2-position in the tetrafluoropyridyl ring of 4-pentafluorophenoxy-tetrafluoropyridine seems to be less reactive than the 4-position in pentafluoropyridine suggesting no significant activating effect by a pentafluorophenoxy-group in the meta position, but repetition of the reaction between equimolar amounts of potassium pentafluorophenate and pentafluoropyridine in tetrahydrofuran at 90° for a longer period of time (17 hours), using larger quantities of reagent to facilitate isolation of the products, yielded a mixture containing predominantly 4-pentafluorophenoxy-tetrafluoropyridine together with small amounts of 2,4-bis(pentafluorophenoxy)-tetrafluoropyridine and 2,4,6-tris(pentafluorophenoxy)-difluoropyridine.

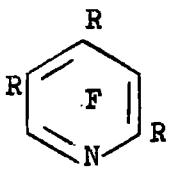
This would suggest some meta-activating effect or a neutral effect by a pentafluorophenoxy group in the 2-position of a tetrafluoropyridine ring, but no significant ortho activating effect of a pentafluorophenoxy group on the 3-position of a tetrafluoropyridine ring towards further attack by pentafluorophenoxide ion.

Reaction of pentafluoropyridine with a threefold molar amount of anhydrous potassium pentafluorophenate in tetrahydrofuran at 90° for 7 days yielded 2,4,6-tris(pentafluorophenoxy)-difluoropyridine in good yield. This result indicates that the activating effect of the

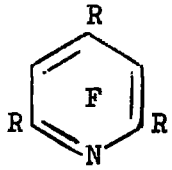


Possible positions of nucleophilic attack in 2,4-bis(pentafluorophenoxy)-trifluoropyridine.

ring nitrogen on the 6-position of 2,4-bis(pentafluorophenoxy)-difluoropyridine outweighs the para-activating effect of a pentafluorophenoxy group on the 5-position, or the ortho activating effect of such a group on the 3-position, towards further attack by pentafluorophenoxide ion. This result is of interest, because it was found later that 2,4-bis(heptafluoroisopropyl)-trifluoropyridine reacted with perfluoropropene and potassium fluoride at 130° in sulpholan to give a mixture of isomeric trisubstituted compounds, whose structures are (I) and (II) with a predominance of (I).[42]



(I)

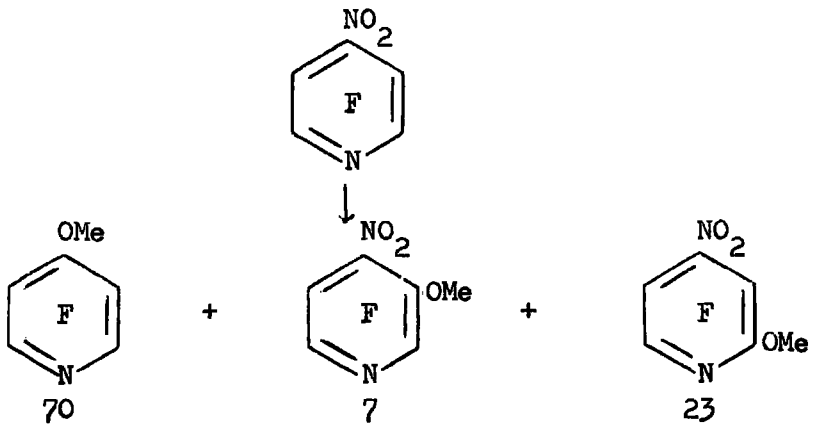


(II)

$R = -CF(CF_3)_2$

It has been shown that the heptafluoroisopropyl group has an unusually large steric effect by variable temperature n.m.r. studies.[43] Thus, the activating effect of a heptafluoroisopropyl group in the para-position must outweigh the activating effect of the ring nitrogen atom in the 2-position, despite the steric requirement of the nucleophile. Thus, possibly the attack of pentafluorophenoxide ion on 2,4-bis(pentafluorophenoxy)-trifluoropyridine is determined by the relative activating effects of a para-pentafluorophenoxy group or an ortho ring nitrogen, and not by the larger steric requirement of substitution in the 5-position.

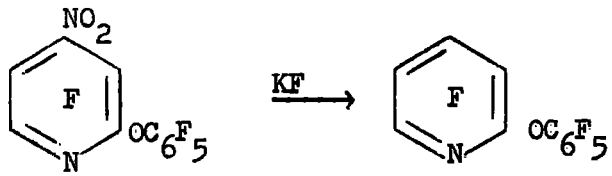
Attempts were made to synthesise 2-pentafluorophenoxy-tetrafluoropyridine, in order to compare its reactivity towards pentafluorophenoxide ion with pentafluoropyridine and 4-pentafluorophenoxy-tetrafluoropyridine. Tetrafluoro-4-nitropyridine reacted with sodium methoxide in methanol to give a mixture of products:-[44]



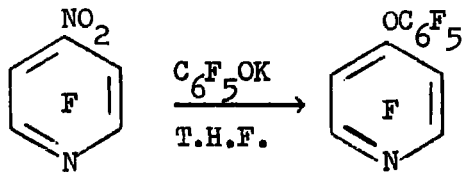
composition of product (mole %)

70 7 23

It was hoped that the reaction of tetrafluoro-4-nitropyridine with potassium pentafluorophenate in refluxing tetrahydrofuran would give a similar mixture of pentafluorophenoxy-substituted products, from which it would be possible to isolate 2-pentafluorophenoxy-4-nitrotrifluoropyridine. The nitro-group and fluorine are comparable in their efficiency as leaving groups in nucleophilic aromatic substitution, and are much more efficient than the halogens. Thus, it should have been possible to replace the nitro-group by fluorine in 2-pentafluorophenoxy-4-nitropyridine by the use of potassium fluoride and a dipolar aprotic solvent.



Unfortunately, reaction of tetrafluoro-4-nitropyridine with potassium pentafluorophenate at 90° in tetrahydrofuran yielded only 4-pentafluorophenoxy-tetrafluoropyridine by replacement of the nitro-group.

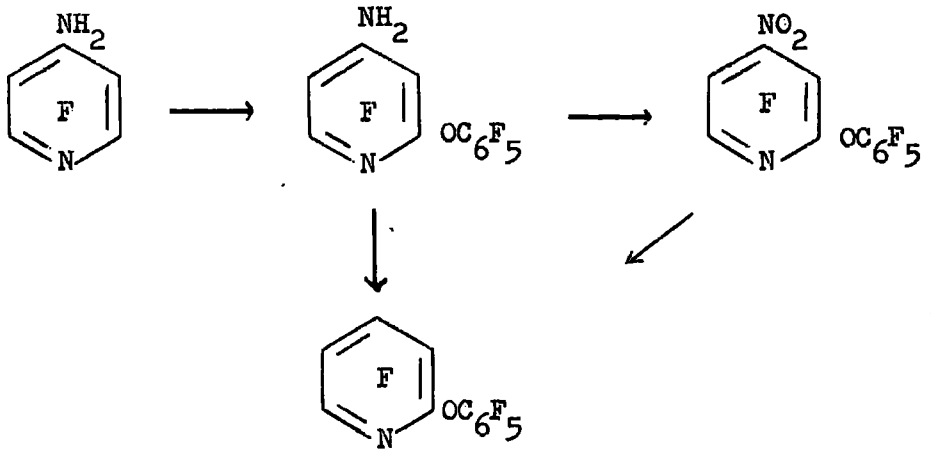


This possibly occurs, because the pentafluorophenoxy ion being less reactive than methoxide is more selective in its position of attack, and only substitutes at the most reactive position in tetrafluoro-4-nitropyridine.

4-Aminotetrafluoropyridine was reacted with potassium pentafluorophenoxide dissolved in tetrahydrofuran in a sealed tube at 150° for

48 hours. From this reaction it was possible to isolate a mixture of unreacted 4-aminotetrafluoropyridine and 2-pentafluorophenoxy-4-amino-trifluoropyridine. Unreacted 4-amino-tetrafluoropyridine predominated in the mixture. The reaction was repeated, heating the mixture at 200° for 4 days, and it was possible to isolate a crude sample of 2-pentafluoro-phenoxy-4-amino-trifluoropyridine.

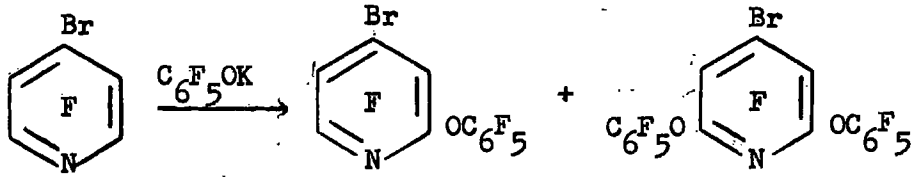
From this reaction it was hoped to isolate 2-pentafluorophenoxy-4-amino-trifluoropyridine in good yield and to convert this to 2-penta-fluorophenoxy-4-nitrotrifluoropyridine, by oxidation of the amino-group with peroxy-trifluoroacetic acid, or directly to 2-pentafluorophenoxy-tetrafluoropyridine by diazotisation in hydrofluoric acid.



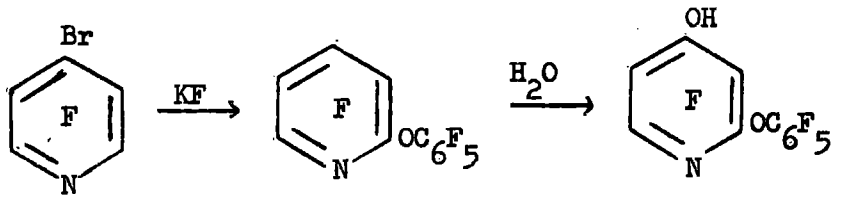
However, the yield of 4-amino-2-pentafluorophenoxy-trifluoropyridine was too low to make this a good synthetic route.

Reaction of equimolar amounts of potassium pentafluorophenoxide dihydrate, 4-bromotetrafluoropyridine and tetrahydrofuran at 90° for 8½ hr. yielded a small amount of unreacted 4-bromotetrafluoropyridine and

2-pentafluorophenoxy-4-bromotrifluoropyridine. Repetitition of the same reaction using larger quantities, and a longer period of heating (17 hr.), allowed the isolation of 2-pentafluorophenoxy-4-bromotrifluoropyridine and 2,4-bis(pentafluorophenoxy)-4-bromotrifluoropyridine.



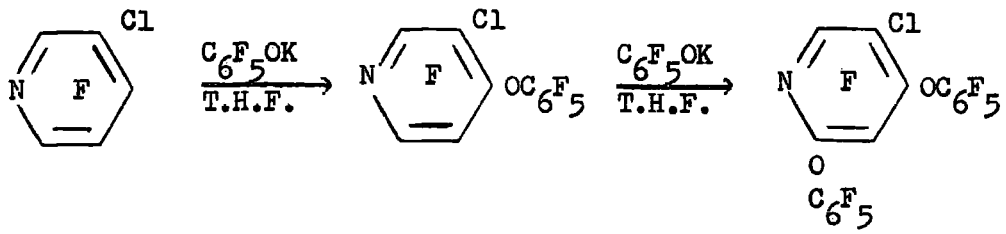
It was hoped to convert 2-pentafluorophenoxy-4-bromotrifluoropyridine to 2-pentafluorophenoxy-tetrafluoropyridine by heating it with potassium fluoride in sulpholan at 150° for 2 days.



The reaction product isolated was 2-pentafluorophenoxy-4-hydroxy-trifluoropyridine instead of the expected 2-pentafluorophenoxy-tetrafluoropyridine. The only explanation for this surprising result seems to be the presence of water, either in the reaction medium or in the work-up procedure, that converted the expected product to its hydroxy derivative. Unfortunately, there was insufficient time to pursue this further.

4-Pentafluorophenoxy-3-chlorotrifluoropyridine was prepared by reacting equimolar proportions of 3-chlorotetrafluoropyridine and potassium

pentafluorophenate dihydrate together in refluxing tetrahydrofuran for 17 hours. The ether was isolated by distillation under reduced pressure. A higher boiling fraction was collected which was shown by g.l.c. to contain about equal amounts of 4-pentafluorophenoxy-3-chlorotrifluoropyridine, and a higher boiling product, which mass spectroscopy showed to be a diether formed by the reaction of 3-chlorotetrafluoropyridine with 2 moles of potassium pentafluorophenate. Reaction of a twofold molar proportion of potassium pentafluorophenate with 3-chlorotetrafluoropyridine gave 2,4-bis(pentafluorophenoxy)-5-chlorodifluoropyridine in good yield using the same conditions. Thus, the chlorine

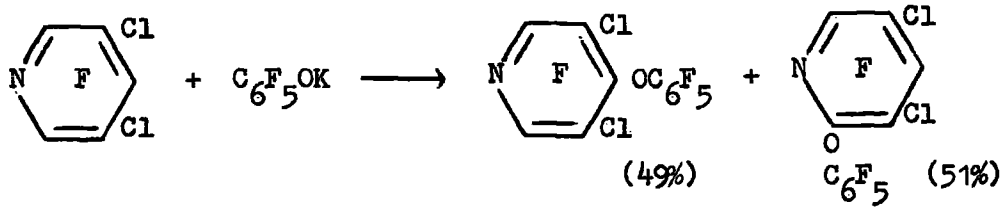


atom in the 5-position was found to be entirely para-activating, this being the first instance of disubstitution by the same nucleophile in 3-chloro-tetrafluoropyridine.

Pentafluorochlorobenzene was found to react with nucleophiles in high yield to give fluorine replacement ortho:meta:para to the chlorine atom in the approximate ratio 25:5:70.[45] Thus, the chlorine substituent gave rise to a significant amount of ortho substitution. Perhaps no substitution occurred ortho to the chlorine atom in 2,4-bis(pentafluorophenoxy)-5-chlorodifluoropyridine, because of a steric effect caused by the

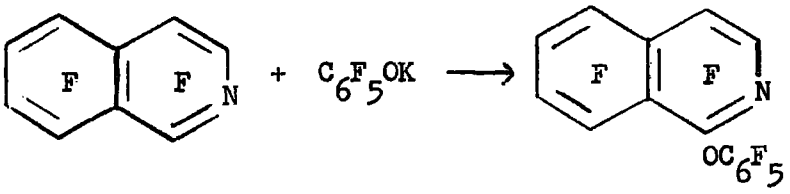
chlorine atom and the bulky pentafluorophenoxide ion. The nucleophiles ($LiAlH_4$, NH_3, NaOMe and N_2H_4) that gave ortho replacement with pentafluorochlorobenzene were, in fact, smaller than pentafluorophenoxide ion.

Reaction of equimolar proportions of 3,5-dichlorotrifluoropyridine and potassium pentafluorophenate under the usual conditions gave a high boiling reaction product, which was shown by ^{19}F n.m.r. to consist of a



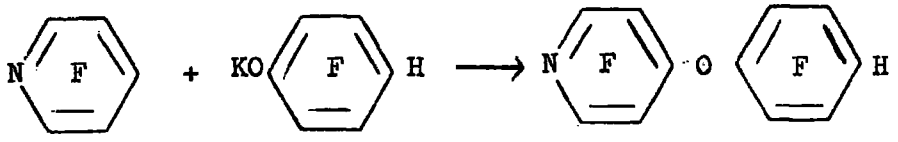
mixture of 4-pentafluorophenoxy-3,5-dichlorodifluoropyridine and 2-pentafluorophenoxy-3,5-dichloro-difluoropyridine. 3,5-Dichlorotrifluoropyridine reacted with ammonia exclusively in the 4-position and perhaps the size of the pentafluorophenoxy substituent allows the 2-position to compete in the nucleophilic substitution. Unfortunately it was not found to be possible to resolve the mixture of isomers by g.l.c. to enable an estimate of the isomeric proportions to be ascertained, and consequently it was not possible to isolate pure samples of these isomers.

Reaction of equimolar amounts of anhydrous potassium pentafluorophenate and heptafluoroisoquinoline in refluxing tetrahydrofuran for $1\frac{1}{2}$ hrs. provided 1-pentafluorophenoxy-hexafluoroisoquinoline in good yield.

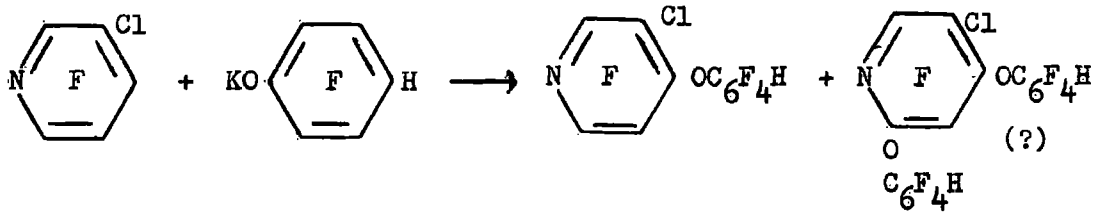


It was of interest to compare the reactivity of potassium 2,3,5,6-tetrafluorophenate dihydrate with that of potassium pentafluorophenate dihydrate. In addition, the presence of the hydrogen atom in place of the fluorine atom in the 4-position would prevent nucleophilic substitution in the benzene ring of any heterocyclic ether that was formed, thus hoping to simplify the orientation of nucleophilic substitution.

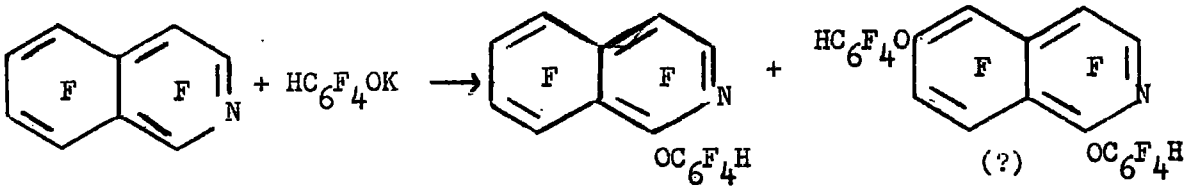
Reaction of equimolar amounts of pentafluoropyridine and potassium 2,3,5,6-tetrafluorophenate dihydrate in refluxing tetrahydrofuran gave 4-(2',3',5',6'-tetrafluorophenoxy)-tetrafluoropyridine in good yield. It was not possible to isolate any disubstituted product as was the case with the reaction of potassium pentafluorophenate dihydrate with pentafluoropyridine.



Reaction of equimolar amounts of 3-chlorotetrafluoropyridine and potassium 2,3,5,6-tetrafluorophenate dihydrate in refluxing tetrahydrofuran gave a mixture of 4-(2',3',5',6'-tetrafluorophenoxy)-3-chlorotrifluoropyridine and bis(2',3',5',6'-tetrafluorophenoxy)-3-chlorodifluoropyridine. The monosubstituted ether was separated from the mixture by distillation.



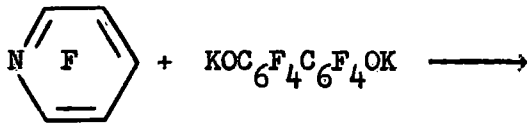
Reaction of potassium 2,3,5,6-tetrafluorophenate dihydrate with an equimolar amount of heptafluoroisoquinoline in refluxing tetrahydrofuran yielded 1-(2',3',5',6'-tetrafluorophenoxy)-hexafluoroisoquinoline. Repetition of the reaction on a larger scale yielded a mixture of this ether and bis-(2',3',5',6'-tetrafluorophenoxy)-pentafluoroisoquinoline. The disubstituted isoquinolyl ether is possibly 1,6-bis-(2',3',5',6'-tetrafluorophenoxy)-pentafluoroisoquinoline, because dimethoxy-pentafluoroisoquinoline is 1,6-substituted, but the n.m.r. data is not conclusive. These reactions show in a qualitative sense that the



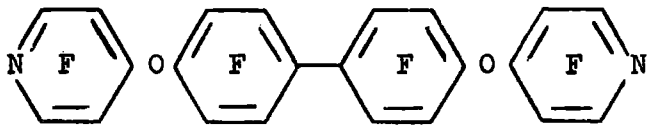
potassium pentafluorophenate dihydrate and potassium 2,3,5,6-tetrafluorophenate dihydrate show similar reactivity towards polyfluoro-heterocyclic compounds.

4-(γ-Tetrafluoropyridyloxy)-4'-hydroxy-octafluorobiphenyl was prepared by the reaction of equimolar amounts of pentafluoropyridine and the dipotassium salt of 4,4'-dihydroxyoctafluorobiphenyl in refluxing tetrahydrofuran. The product was isolated by pouring the reaction mixture

into dilute acid and extracting the mixture with ether. Distillation of the ether solvent and sublimation and recrystallisation of the residual solid yielded pure hydroxy-ether.

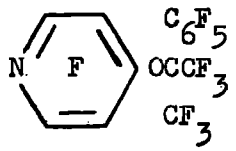


An attempt to prepare 4,4'-bis(tetrafluoropyridyloxy)-octafluorobiphenyl



by the reaction of a two-fold molar amount of pentafluoropyridine with the dipotassium salt of 4,4'-dihydroxyoctafluorobiphenyl was not successful. 4-(γ-Tetrafluoropyridyloxy)-4'-hydroxyoctafluorobiphenyl was isolated from the reaction product after acidification. The reaction time would have to be increased and an excess of pentafluoropyridine used to prepare the diether.

Potassium perfluoro-α.α-dimethylbenzoxide was prepared by adding perfluoro-α,α-dimethylbenzyl alcohol to a saturated solution of potassium hydroxide in water. The precipitated salt was filtered off and dried. Impure 4-undecafluoro-α,α-dimethylbenzoxy-tetrafluoropyridine

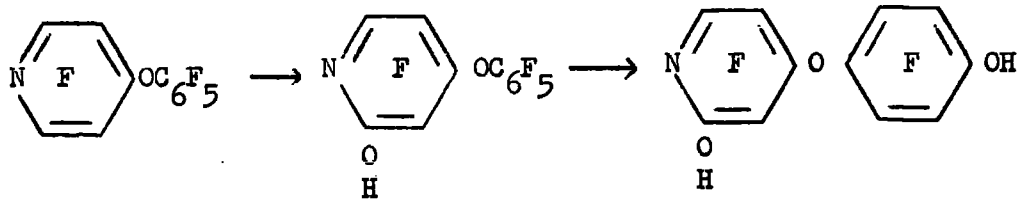


was prepared in low yield by reacting equimolar proportions of pentafluoropyridine and potassium undecafluoro-α,α-dimethylbenzoxide together in refluxing tetrahydrofuran for 16 hrs. The ether was isolated by distillation under reduced pressure and examination of the product collected using g.l.c. showed that it mainly contained a new compound, undecafluoro-α,α-dimethylbenzoxy-tetrafluoropyridine, together with small amounts of perfluoro-α,α-dimethylbenzyl alcohol and a trace of product of highest boiling point. This was confirmed by the mass spectrum of the product. The trace amount of highest boiling product was probably a diether formed by reaction of two moles of potassium undecafluoro-α,α-dimethylbenzoxide with one mole of pentafluoropyridine. A similar reaction of 3,5-dichlorotrifluoropyridine with an equimolar proportion of potassium undecafluoro-α,α-dimethylbenzoxide yielded a mixture containing perfluoro-α,α-dimethylbenzyl alcohol, 3,5-dichlorotrifluoropyridine and undecafluoro-α,α-dimethylbenzoxy-3,5-dichlorodifluoropyridine.

Some nucleophilic displacement reactions of fluorinated heterocyclic ethers were carried out, to see what the directive effect of a pentafluorophenoxy group on a fluorinated heterocyclic ring would be.

Reaction of 4-pentafluorophenoxy-tetrafluoropyridine with a twofold molar proportion of potassium hydroxide in t-butanol at reflux temperature

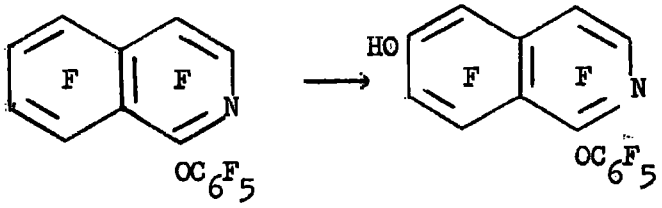
for 5 hrs. afforded 2-hydroxy-4-pentafluorophenoxy-trifluoropyridine in 75% yield, after acidification of the reaction mixture. A similar reaction of 4-pentafluorophenoxy-tetrafluoropyridine with a fourfold molar proportion of potassium hydroxide gave a solid, whose structure is thought to be 2-hydroxy-4-(4'-hydroxytetrafluorophenoxy)-trifluoropyridine. The n.m.r. spectrum of this compound was difficult to obtain, because of its sparing solubility in all solvents tried at room temperature, but a computer of average transients spectrum over a large number of accumulations indicated that the second hydroxyl group had substituted in the pentafluorophenoxy group, and that the most likely position of substitution was para to the ether linkage.



Substitution of the first hydroxyl group in the 2-position of the pyridine ring would be expected. However, the hydroxyl group deactivates the 6-position in the pyridine ring to such an extent that further substitution by hydroxyl group occurs in the other ring. This behaviour contrasts with that of 2,4-(bispentafluorophenoxy)-trifluoropyridine on further reaction with potassium pentafluorophenate.

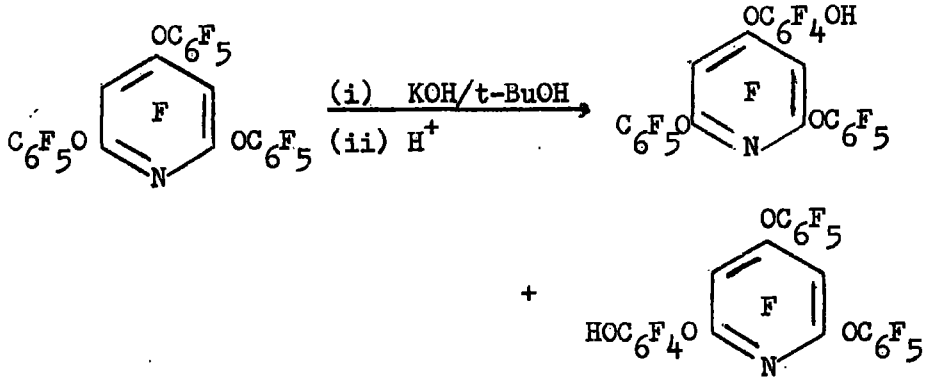
Reaction of 1-pentafluorophenoxy-hexafluoroisoquinoline with a twofold molar proportion of potassium hydroxide in t-butanol at reflux

temperature for 5 hours gave a solid, whose structure could be 1-pentafluorophenoxy-6-hydroxypentafluoroisoquinoline, although a suitable n.m.r. spectrum was once again found to be difficult to obtain because of the sparing solubility of this compound in all solvents.

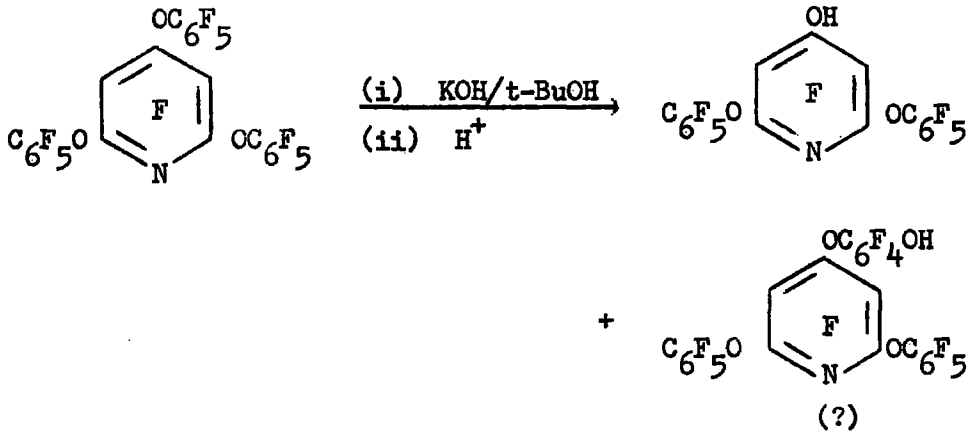


Although the pentafluorophenoxy group would probably activate the positions of further substitution in comparison with many other 1-substituted hexafluoroisoquinolines, it seems to have no effect on orientation of further substitution.

The reaction of 2,4,6-tris(pentafluorophenoxy)-difluoropyridine with a twofold molar proportion of potassium hydroxide in t-butanol at reflux temperature for five hours was expected to give the result shown below:-

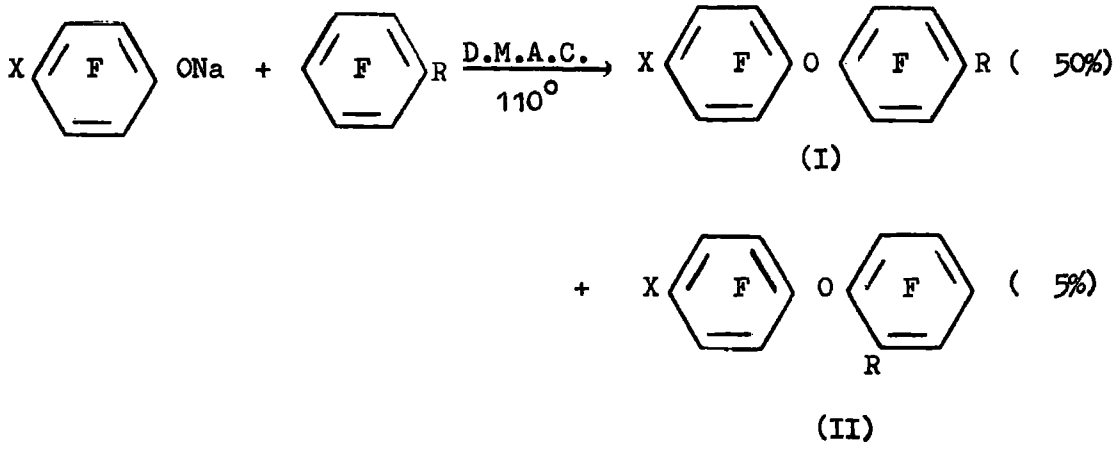


Acidification of the reaction mixture yielded a solid, which on fractional sublimation afforded 2,6-bis(pentafluorophenoxy)-4-hydroxydifluoropyridine at the lower temperature, and at the higher temperature a mixture of this compound, and a product formed by the replacement of a fluorine atom in 2,4,6-tris(pentafluorophenoxy)-difluoropyridine by a hydroxyl group. An unsublimable residue was left behind. The product obtained by



replacement of the pentafluorophenoxy group predominated in the reaction products. This interesting result will be discussed in connection with reactions of pentafluorophenoxy ethers later in the text.

After the foregoing work was completed, a number of publications appeared describing the use of metal salts of fluorinated phenols in the preparation of fluorinated aromatic ethers. Anhydrous sodium pentafluorophenate and sodium 2,3,5,6-tetrafluorophenate were treated with an excess of substituted pentafluorobenzenes in dimethylacetamide at 110° to give mainly product (I) with small amounts of product (II) and isomeric triphenyl ethers.[46]



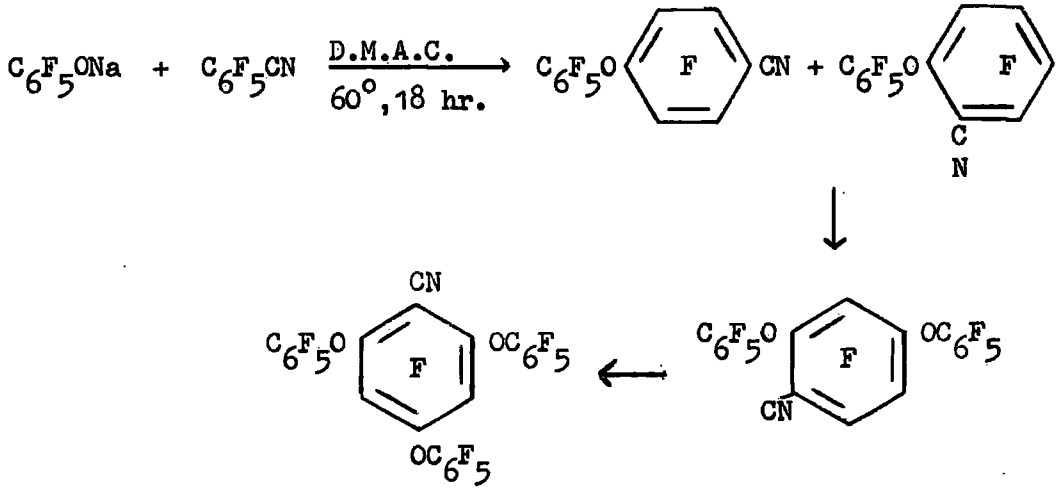
(I)

(II)

X = F, R = Br, Cl, F, H, CF_3, CO_2Et, C_6F_5

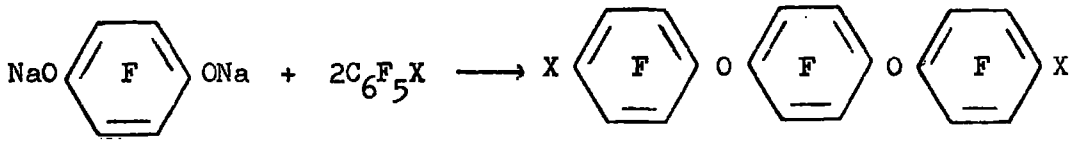
X = H, R = F, C_6F_5

When X = F and R = CN, product (I) was obtained in 85% yield in acetone at 25° after 3 days.[47] Reaction of a 2·24-fold molar amount of sodium pentafluorophenate with pentafluorobenzonitrile proceeded as illustrated:-

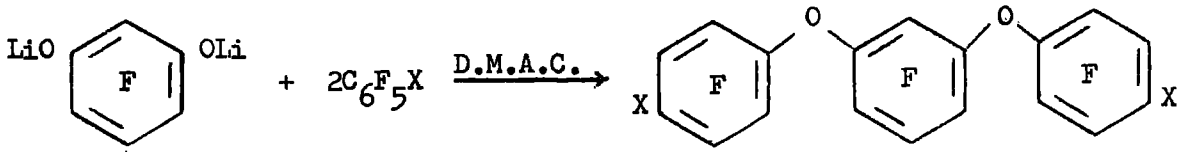


Heating together equimolar amounts of potassium pentafluorophenate and

pentafluoronitrobenzene at 150° for 5 hrs. yielded a mixture of 2-nitrononafluorodiphenyl ether (52%) (III), 4-nitrononafluorodiphenyl ether (48%) (IV).[48] Interestingly, the same reaction of pentafluorophenol or its alkali metal salts occurred almost exclusively para to the nitro group in solvents of high dielectric constant, e.g. acetonitrile gave 98% IV and 2% III, whereas significant amounts of substitution ortho to the nitro group occurred in solvents of low dielectric constant, e.g. dioxane gave 89% III and 11% IV. When a metal pentafluorophenate was reacted with pentafluoronitrobenzene, it was found that the lithium and sodium salts produced more ortho substitution to the nitro group than did the potassium salt, whilst the caesium salt increased the amount of para substitution. The reactions illustrated below were successful with bifunctional sodium salts:-



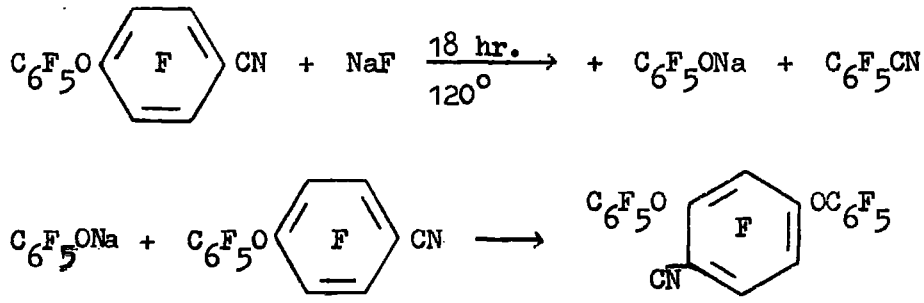
The reaction was carried out in acetone for 12 days at 20°, when X = CN, and in dimethylacetamide for 5 hrs. at 100°, when X = CF_3.[49]



(V)

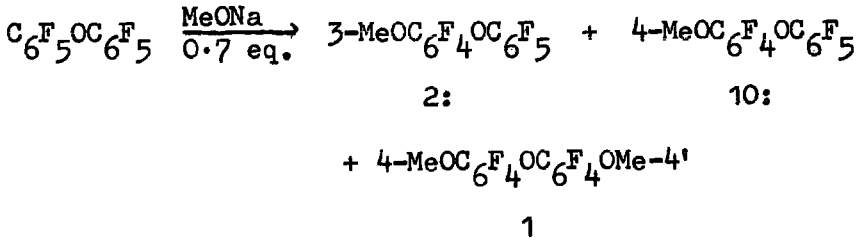
An isomeric mixture containing predominantly V was obtained, when X = CN or F.

Interestingly, it was found that when 4-cyanononafluorodiphenyl ether was reacted with anhydrous sodium fluoride under forcing conditions in dimethylacetamide both pentafluorobenzonitrile and 2,4-bis(pentafluorophenoxy)-trifluorobenzonitrile were formed in small amount:-

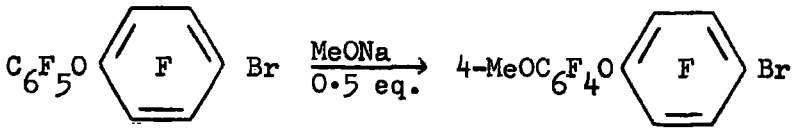


The nitrile group seems to be able to stabilise the rate determining transition state to the extent that reversibility can occur.

Nucleophilic displacement reactions of fluorinated diphenyl ethers were studied to estimate the directive effect of a p-OC_6F_4R group.[50] The displacement reactions with methanolic sodium methoxide indicating the number of equivalents of reagent used and the ratio of products formed are shown below:-



1



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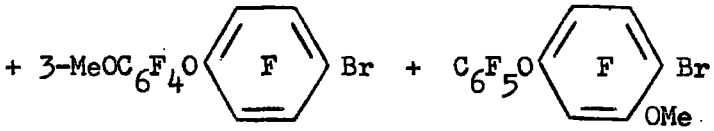

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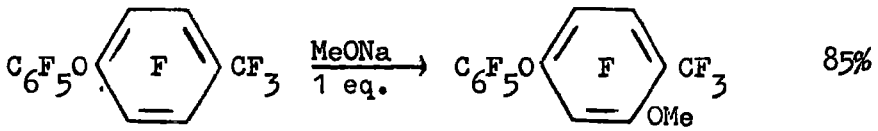
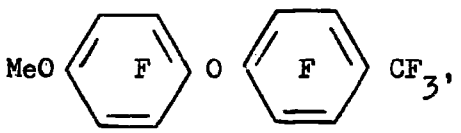


Higher boiling products, which were probably disubstituted isomers, 4-methoxyheptafluorotoluene and unreacted starting material accounted for the remainder of the material from the reaction of 4-trifluoromethyl-nonafluorodiphenyl ether. It was thought that 4'-replacement would occur leading to



but this was found not to be so.

It has been shown that the pentafluorophenoxide ion will not only react with compounds considerably more activated towards nucleophilic substitution than hexafluorobenzene, but also will react with less activated compounds, e.g. pentafluorobromobenzene, if dimethyl-

acetamide is used as solvent, instead of the solvents originally used in the attempted preparation of perfluorodiphenyl ether in good yield. Although with the less reactive C_6F_5X compounds dimethylacetamide is required as a solvent, and is far more efficient for promotion of reaction than acetone or tetrahydrofuran, the use of these latter two solvents would be recommended for reactive compounds, such as pentafluorobenzonitrile and pentafluoropyridine, in that these solvents would inhibit polysubstitution.

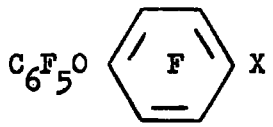
It is noteworthy that no substitution of a single C_6F_5O group in the 2-position of pentafluoropyridine was detected, although this occurred with pentafluorobenzonitrile. Although pentafluorobenzonitrile seems to be less reactive than pentafluoropyridine in the 4-position it may be more reactive in the 2-position, and hence pentafluorobenzonitrile seems more likely to give polysubstitution than pentafluoropyridine. A way of resolving this problem would be to react 4-cyano-tetrafluoropyridine with pentafluorophenoxide ion.

Pentafluoronitrobenzene is very much more reactive in the 2-position than either pentafluoropyridine or pentafluorobenzonitrile, although this is dependent on the polarity of the solvent. Unfortunately polysubstitution was not studied with an activating group such as C_6F_5O.

The reversibility of the reaction of 4-cyano-nonafluorodiphenyl ether with sodium fluoride is of great interest. Although

the potential reversibility of the reaction of 4-pentafluorophenoxy-tetrafluoropyridine was not studied, it seems likely that this would occur.

The nucleophilic substitution reactions of fluorinated diphenyl ethers are of interest. As expected, the pentafluorophenoxy group is para-directing although some meta-activating effect is apparent. No ortho activating effect was found. With an ether

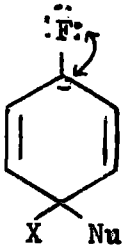


when X has a slight ortho-activating effect, e.g. when X = Br, a small amount of substitution takes place ortho to this group. With a stronger ortho activating group, e.g. X = CF_3, predominantly ortho substitution occurred, although some cleavage of the pentafluorophenoxy group was detected. With the powerful pyridine ring nitrogen activating group only displacement of the fluorine ortho to the ring nitrogen was found.

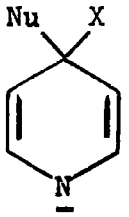
The detection of 4-methoxyheptafluorotoluene in the products of nucleophilic substitution of 4-trifluoromethyl-nonafluorodiphenyl ether is of great interest in view of the formation of 2,6-bis-(pentafluorophenoxy)-4-hydroxydifluoropyridine from 2,4,6-tris-(pentafluorophenoxy)-difluoropyridine on reaction with hydroxide ion.

The 'Iπ effect' of fluorine[51,52] has been successfully used to explain the orientation of nucleophilic substitution in polyfluoro-

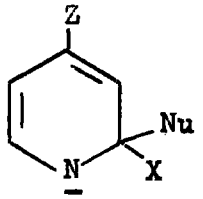
benzene compounds. This effect depends on repulsion between non-bonding electron pairs on fluorine and the adjacent carbanionic carbon atom (VI). The electron density is assumed to be greatest at the position para to the entry of the nucleophile. The transition state is considered to be similar to intermediate (VI).



(VI)



(VII)

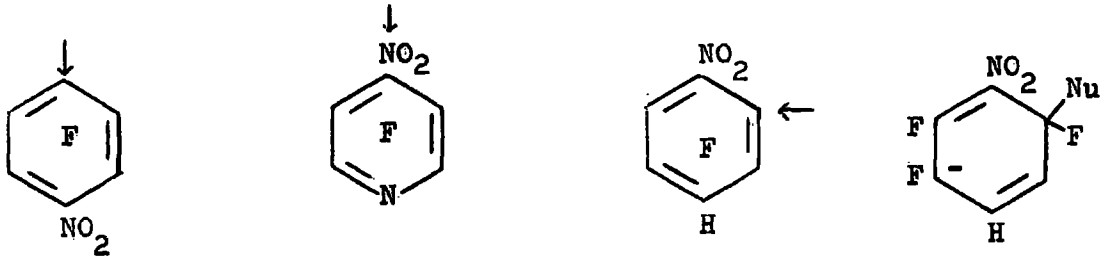


(VIII)

It seems that in the nucleophilic substitution of polyfluoro-aromatic nitrogen heterocyclic compounds the localisation energies of the transition states are much more influenced by the stabilising effect of ring nitrogen. This is indicated by forms such as (VII) and (VIII). It nevertheless remains true that this Iπ effect should be considered in the nucleophilic substitution of polyfluoro-nitrogen heterocyclic compounds. However, a high electron density on nitrogen in the transition state requires a relatively lower electron density on the carbon atoms as compared with nucleophilic substitution in a polyfluorobenzene. This implies a diminished importance of Iπ destabilisation by fluorine in the nitrogen heterocyclic system.

A result,[44] which shows that factors governing nucleophilic substitution in polyfluorobenzenes cannot be applied directly to

perfluoroaromatic nitrogen heterocyclic compounds, is found when the nitro compounds (IX to XI) are reacted with sodium methoxide. Pentafluoronitrobenzene (IX) is substituted at the 4-position (as indicated by the arrow) while 4-nitrotetrafluoropyridine (X) suffers, predominantly, replacement of the nitro-group. It would be expected that the nitro-group of 1,2,4,5-tetrafluoro-3-nitrobenzene (XI) would also be replaced, if both of these reactions were controlled by the 'Iπ effect'.

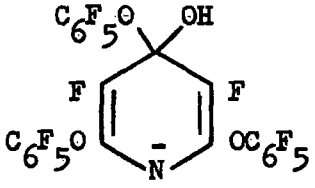


(IX) (X) (XI) (XII)

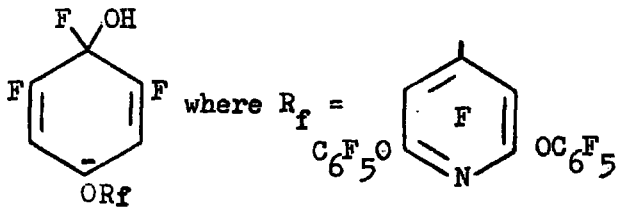
It is found, however, that only substitution of fluorine ortho to the nitro-group is observed. The contrasting behaviour of 4-nitrotetrafluoropyridine (X) and 1,2,4,5-tetrafluoro-3-nitrobenzene (XI) illustrates that the position of substitution is governed by the stabilisation of a transition state in which the electron density can be placed on a ring-nitrogen, or a nitro-group. This occurs instead of the avoidance of transition states destabilised by the 'Iπ effect' of fluorine as shown in (XII).

As discussed previously, the reaction of 2,4,6-tris(pentafluorophenoxy)-difluoropyridine with a twofold molar proportion of potassium

hydroxide yields a mixture containing predominantly 2,6-bis(pentafluorophenoxy)-4-hydroxydifluoropyridine, together with a product formed by the replacement of a fluorine atom in 2,4,6-tris(pentafluorophenoxy)-difluoropyridine by a hydroxyl group. This predominant replacement of the pentafluorophenoxy group by hydroxyl provides a further illustration that a nucleophilic substitution reaction of a perfluoroaromatic nitrogen heterocyclic compound is controlled by the stabilisation of a transition state, such as (XIII), in which the electron density is placed on the nitrogen atom. However, the Iπ effect of fluorine seems to compete to some extent in this particular



(XIII)



(XIV)

system, as illustrated by a transition state such as (XIV) and showing the replacement of a single fluorine in the compound by a hydroxyl group.

This competition may occur, because although the displacement of the pentafluorophenoxy group is stabilised by the placement of the negative charge on the nitrogen atom, this is to some extent offset by the fact that fluorine is a better leaving group than pentafluorophenoxy in aromatic nucleophilic substitution reactions.

SECTION 2.

Experimental Work

Preparation of the Potassium Salts of the Phenols.[53]

These were prepared by dissolving the phenols in a large excess of hot 6N potassium hydroxide and cooling the solution in ice. The precipitated salts were filtered off and recrystallised from a small volume of water. The anhydrous salts were prepared by azeotropically distilling the hydrated salts with benzene for 6 hr.

General Procedure for the Preparation of Pentafluorophenoxy and 2,3,5,6-Tetrafluorophenoxy Aromatic Ethers.

The polyfluoroheterocyclic compound and the required molar proportion of the metal salt of the fluorinated phenol were added to tetrahydrofuran and heated under reflux with stirring at 90° for a number of hours. When the reactants were sufficiently soluble, enough tetrahydrofuran was used to dissolve them completely. As the reaction proceeded a brown precipitate of potassium fluoride was formed. At the end of the reflux period the reaction mixture was cooled and poured into three times its volume of water. The precipitated oil was separated and the aqueous layer extracted thrice with a volume of ether approximately three times that of the volume of tetrahydrofuran used. The precipitated oil and the ethereal extracts were combined and the resulting solution was dried with magnesium sulphate, filtered, and most of the ether and tetrahydrofuran was removed by distillation. If the reaction product(s) were liquid(s),

they were purified by distillation under reduced pressure and the purity of the product assessed by gas liquid chromatography (silicone grease at 200°). If the reaction product(s) were solid(s), they were purified by fractional vacuum sublimation and recrystallisation from a suitable solvent.

The Reaction of Pentafluoropyridine with an Equimolar Proportion of Potassium Pentafluorophenate.

Anhydrous potassium pentafluorophenate (1·38 g., 6·2 m.mole), pentafluoropyridine (1·0 g., 5·9 m.mole) and tetrahydrofuran (10 ml.) were heated at 90° for 4 hr. The usual work-up afforded 4-pentafluorophenoxy-tetrafluoropyridine (1·28 g., 65%). (Found: C, 39·4; F, 51·1; M, 333. $C_{11}F_9NO$ requires C, 39·6; F, 51·3%; M, 333), b.p. 112° at 15 mm. (i.r. spectrum No. 12).

The Reaction of Pentafluoropyridine with an Equimolar Proportion of Potassium Pentafluorophenate on a Larger Scale.

Potassium pentafluorophenate dihydrate (11·1 g., 40·5 m.mole), pentafluoropyridine (7·0 g., 41·4 m.mole) and tetrahydrofuran (84 ml.) were heated at 90° for 20 hr. The usual work-up afforded 4-pentafluorophenoxy-tetrafluoropyridine (7·1 g., 53%), b.p. 112-117° at 13 mm., and a higher boiling fraction, b.p. 117-186° at 13 mm. (2·5 g.) shown by v.p.c. and mass spectrometry to be a mixture of 4-pentafluorophenoxy-tetrafluoropyridine, bis(pentafluorophenoxy)-trifluoropyridine and tris(pentafluorophenoxy)-difluoropyridine.

The Reaction of Pentafluoropyridine with a Twofold Molar Proportion of Potassium Pentafluorophenate.

Anhydrous potassium pentafluorophenate (2·76 g., 12·4 m.mole), pentafluoropyridine (1·0 g., 5·9 m.mole) and tetrahydrofuran (10 ml.) were heated at 90° for 8 hr. The usual work-up afforded 4-pentafluorophenoxy-tetrafluoropyridine (0·64 g.), b.p. 102° at 15 mm. and 2,4-bis(pentafluorophenoxy)-trifluoropyridine (0·30 g.). (Found: C, 41·0; F, 49·7; M, 497. $C_{17}F_{13}NO_2$ requires C, 40·6; F, 49·7%; M, 497), b.p. 165-167° at 15 mm. (i.r. spectrum No. 13).

The Reaction of Pentafluoropyridine with a Threefold Molar Proportion of Potassium Pentafluorophenate.

Pentafluoropyridine (3·12 g., 18·5 m.mole), anhydrous potassium pentafluorophenate (14·25 g., 64·7 m.mole) and tetrahydrofuran (110 ml.) were heated at 90° for 7 days. The mixture was poured into water and an oil was precipitated that solidified on trituration. The solid was filtered off and dried over phosphorus pentoxide. The crude product (14·51 g.) was distilled under reduced pressure (0·01 mm.) and four fractions were collected: 22-124°, 0·4 g.; 124-134°, 4·5 g.; 134-148°, 3·0 g.; 148-150°, 4·8 g. The highest boiling fraction, that readily solidified, was recrystallised from mixed ethanol (5 ml.)/methanol (18 ml.) to afford 2,4,6-tris-(pentafluorophenoxy)-difluoropyridine. (Found: C, 41·5; F, 48·8; M, 661. $C_{23}F_{17}O_3N$ requires C, 41·7; F, 48·9%; M, 661), m.p. 104° (i.r. spectrum No. 14).

Mass spectrometry showed the other fractions to contain this tris ether together with small amounts of the 2,4-bis ether.

The Reaction of 4-Nitrotetrafluoropyridine with Potassium Pentafluorophenate.

4-Nitrotetrafluoropyridine (1·96 g., 10 m.mole), potassium pentafluorophenate dihydrate (2·58 g., 10 m.mole) and tetrahydrofuran (20 ml.) were heated at 90° for 17 hr. The usual work-up afforded 4-pentafluorophenoxy-tetrafluoropyridine (2·15 g., 64%). (Found: C, 39·5; F, 51·1; M, 333. $C_{11}F_9NO$ requires C, 39·6; F, 51·3%; M, 333), b.p. 113-115° at 20 mm. Examination of the crude reaction product by v.p.c. (silicone grease at 200°) showed it to be a mixture of 4-pentafluorophenoxy-tetrafluoropyridine and a small proportion of unreacted 4-nitrotetrafluoropyridine.

The Reaction of 4-Bromotetrafluoropyridine with an Equimolar Proportion of Potassium Pentafluorophenate.

Potassium pentafluorophenate dihydrate (2·58 g., 10 m.mole), 4-bromotetrafluoropyridine (2·30 g., 10 m.mole) and tetrahydrofuran (20 ml.) were heated at 90° for 8½ hr. The usual work-up afforded unreacted 4-bromotetrafluoropyridine (0·30 g.), b.p. 40° at 16 mm. and 2-pentafluorophenoxy-4-bromotrifluoropyridine (1·04 g., 27%). (Found: C, 33·5; F, 39·3; Br, 19·9; M, 393. $C_{11}F_8BrNO$ requires C, 33·5; F, 38·6; Br, 20·3%; M, 393), b.p. 144° at 16 mm. (i.r. spectrum No. 15).

The Reaction of 4-Bromotetrafluoropyridine with a Twofold Molar Proportion of Potassium Pentafluorophenate.

Potassium pentafluorophenate dihydrate (5·16 g., 20 m.mole), 4-bromotetrafluoropyridine (2·30 g., 10 m.mole) and tetrahydrofuran (50 ml.) were heated at 90° for 17 hr. The usual work-up afforded 4-bromo-2-pentafluorophenoxy-trifluoropyridine (2·90 g.), b.p. 75-80 at 0·01 mm. and 2,6-bis(pentafluorophenoxy)-4-bromodifluoropyridine (0·55 g.). (Found: C, 36·6; F, 40·4; Br, 14·1; M, 558. $C_{17}F_{12}BrO_2N$ requires C, 36·6; F, 40·9; Br, 14·3%; M, 558), b.p. 145-150 at 0·01 mm. (i.r. spectrum No. 16).

The Reaction of 2-Pentafluorophenoxy-4-bromotrifluoropyridine with Potassium Fluoride in Sulpholan.

2-Pentafluorophenoxy-4-bromotrifluoropyridine (1·0 g., 3·9 m.mole), potassium fluoride (1·0 g., 17·2 m.mole) and sulpholan (7 ml.) were heated with stirring at 200° for 4 hr. The cooled reaction mixture was poured into water (120 ml.) and the aqueous solution extracted with ether (3 x 50 ml.). The combined ether extracts were washed with water (2 x 100 ml.), dried ($MgSO_4$) and the ether removed by distillation. Distillation of the residual oil under reduced pressure afforded 2-pentafluorophenoxy-4-hydroxytrifluoropyridine (0·31 g.) (Found: C, 39·7; F, 45·6; M, 331. $C_{11}F_8NO_2H$ requires C, 39·9; F, 45·9; M, 331), b.p. 148-152° at 13 mm. (i.r. spectrum No. 17). The mass spectrum of the product showed the peaks characteristic of a pentafluorophenoxy group showing that the hydroxyl group was substituted in the pyridine ring.

The Reaction of 3-Chlorotetrafluoropyridine with an Equimolar Proportion of Potassium Pentafluorophenate.

Potassium pentafluorophenate dihydrate (8·38 g., 32·48 m.mole), 3-chlorotetrafluoropyridine (6·0 g., 32·43 m.mole) and tetrahydrofuran (60 ml.) were heated at 90° for 17 hr. The usual work-up afforded 4-pentafluorophenoxy-3-chlorotrifluoropyridine (4·25 g., 36%). (Found: C, 37·7; F, 43·0; Cl, 10·0; M, 349. $C_{11}F_8ClNO$ requires C, 37·8; F, 43·5; Cl, 10·2%; M, 349), b.p. 140-144° at 15 mm. (i.r. spectrum No. 18), together with a fraction, b.p. 144-182° at 15 mm. (4·10 g.), shown by v.p.c. and mass spectrometry to contain approximately equal amounts of 4-pentafluorophenoxy-3-chlorotetrafluoropyridine and bis(pentafluorophenoxy)-3-chlorodifluoropyridine.

The Preparation of 2,4-Bis(pentafluorophenoxy)-5-chlorodifluoropyridine.

A mixture of approximately equal amounts of 4-pentafluorophenoxy-3-chlorotrifluoropyridine and bis(pentafluorophenoxy)-5-chlorodifluoropyridine (4 g.), potassium pentafluorophenate dihydrate (1·47 g.) and tetrahydrofuran (20 ml.) were heated at 90° for 24 hr. The usual work-up afforded a semi-solid that was distilled under reduced pressure and two fractions were collected. Fraction (1), b.p. 114-120° at 0·05 mm., 1·43 g., was shown to be 2,4-bis(pentafluorophenoxy)-5-chlorodifluoropyridine. (Found: C, 39·8; F, 44·2; Cl, 6·6; M, 513. $C_{17}F_{12}O_2NCl$ requires C, 39·8; F, 44·4; Cl, 6·9%; M, 513) (i.r. spectrum No. 19). Fraction (2), b.p. 120-140° at

0·05 mm., 1·69 g., was shown by mass spectrometry to contain mainly 2,4-bis(pentafluorophenoxy)-5-chlorodifluoropyridine together with a small amount of tris(pentafluorophenoxy)-5-chlorofluoropyridine.

The Reaction of 3,5-Dichlorotrifluoropyridine with an Equimolar Proportion of Potassium Pentafluorophenate.

Potassium pentafluorophenate dihydrate (3·87 g., 15 m.mole), 3,5-dichlorotrifluoropyridine (3·03 g., 15 m.mole) and tetrahydrofuran (40 ml.) were heated at 90° for 17 hr. The usual work-up afforded an isomeric mixture of 2- and 4-pentafluorophenoxy-3,5-dichlorodifluoropyridine (3·23 g., 59%) (Found: C, 35·9; F, 36·0; Cl, 19·0; M, 365. $C_{11}F_7Cl_2NO$ requires C, 36·1; F, 36·3; Cl, 19·4; M, 365), b.p. 167° at 15 mm. (i.r. spectrum No. 20).

The Reaction of Heptafluoroisoquinoline with Potassium Pentafluorophenate.

Anhydrous potassium pentafluorophenate (0·666 g., 3 m.mole), heptafluoroisoquinoline (0·765 g., 3 m.mole) and tetrahydrofuran (10 ml.) were heated at 90° for 1½ hr. The usual work-up afforded a yellow solid, that was purified by vacuum sublimation (80° at 0·001 mm.) and recrystallisation from methanol to give 1-pentafluorophenoxy-hexafluoroisoquinoline (0·756 g., 62%). (Found: C, 42·6; F, 49·6; M, 419. $C_{15}F_{11}NO$ requires, C, 42·9; 49·9%; M, 419), m.p. 124-125° (i.r. spectrum No. 21).

The Reaction of Pentafluoropyridine with an Equimolar Proportion of Potassium 2,3,5,6-Tetrafluorophenate.

Potassium 2,3,5,6-tetrafluorophenate dihydrate (2·40 g., 10 m.mole), pentafluoropyridine (1·69 g., 10 m.mole) and tetrahydrofuran (30 ml.) were heated at 90° for 17 hr. The usual work-up afforded 4-(2',3',5',6'-tetrafluorophenoxy)-tetrafluoropyridine (1·76 g., 56%). (Found: C, 42·1; F, 48·7; M, 315. $C_{11}F_8HNO$ requires C, 41·9; F, 48·3%; M, 315), b.p. 120° at 15 mm., m.p. 66°. (i.r. spectrum No. 22).

The Reaction of 3-Chlorotetrafluoropyridine with an Equimolar Proportion of Potassium 2,3,5,6-Tetrafluorophenate.

Potassium 2,3,5,6-tetrafluorophenate dihydrate (2·40 g., 10 m.mole), 3-chlorotetrafluoropyridine (1·85 g., 10 m.mole) and tetrahydrofuran (30 ml.) were heated at 90° for 17 hr. The usual work-up afforded 4-(2',3',5',6'-tetrafluorophenoxy)3-chlorotrifluoropyridine (1·65 g., 50%). (Found: C, 39·6; F, 39·8; Cl, 10·3; M, 331. $C_{11}F_7ClHNO$ requires C, 39·8; F, 40·1; Cl, 10·7%; M, 331), b.p. 76 at 0·01 mm. (i.r. spectrum No. 23) and a fraction (0·3 g.), b.p. 145-150° at 0·01 mm. shown by mass spectrometry to be a mixture of 4-(2',3',5',6'-tetrafluorophenoxy)-3-chlorotrifluoropyridine and bis(2',3',5',6'-tetrafluorophenoxy)-5-chlorodifluoropyridine.

The Reaction of Heptafluoroisoquinoline with an Equimolar Proportion of Potassium 2,3,5,6-Tetrafluorophenate.

Potassium 2,3,5,6-tetrafluorophenate dihydrate (0·48 g., 2 m.mole),

heptafluoroisoquinoline (0·51 g., 2 m.mole) and tetrahydrofuran (10 ml.) were heated at 90° for 1½ hr. The usual work-up afforded a yellow solid (0·93 g., m.p. 101-105°), that was purified by vacuum sublimation (80° at 0·001 mm.) and recrystallisation from methanol to give 1-(2',3',5',6'-tetrafluorophenoxy)-hexafluoroisoquinoline. (Found: C, 44·8; F, 47·6; M, 401. $C_{15}F_{10}NOH$ requires C, 44·9; F, 47·4%; M, 401), m.p. 110·5°. (i.r. spectrum No. 24).

Potassium 2,3,5,6-tetrafluorophenate dihydrate (0·96 g., 4 m.mole), heptafluoroisoquinoline (1·02 g., 4 m.mole) and tetrahydrofuran (30 ml.) were heated at 90° for 17 hr. The usual work-up afforded a yellow solid (1·96 g.) that was purified by vacuum sublimation, first at 80° at 0·001 mm. to give 1-(2',3',5',6'-tetrafluorophenoxy)-hexafluoroisoquinoline, m.p. 110·5°, and then at 130° at 0·001 mm. to give a white solid which after recrystallisation from ethanol afforded pure bis(2',3',5',6'-tetrafluorophenoxy)pentafluoroisoquinoline. (Found: C, 46·1; F, 45·0; M, 547. $C_{21}F_{13}H_2NO_2$ requires C, 46·1; F, 45·1%; M, 547), m.p. 155°. (i.r. spectrum No. 25).

Reaction of a Twofold Molar Proportion of Pentafluoropyridine with the Dipotassium Salt of 4,4'-Dihydroxyoctafluorobiphenyl.

Pentafluoropyridine (3·38 g., 20 m.mole), the dipotassium salt of 4,4'-dihydroxyoctafluorobiphenyl (4·06 g., 10 m.mole) and tetrahydrofuran (45 ml.) were heated at 90° for 42 hr. The reaction mixture was poured into dilute hydrochloric acid and the oil that was

precipitated was extracted into ether. The ethereal extract was dried ($MgSO_4$) and the ether removed by distillation. Purification of the solid product by sublimation and recrystallisation from water yielded 4-(γ-tetrafluoropyridyloxy)-4'-hydroxyoctafluorobiphenyl (1·63 g.). (Found: C, 42·3; F, 47·5; M, 479. $C_{17}F_{12}NO_2H$ requires C, 42·6; F, 47·6%; M, 479), m.p. 179°. (i.r. spectrum No. 26).

The Reaction of 4-Pentafluorophenoxytetrafluoropyridine with a Twofold Molar Proportion of Potassium Hydroxide.

4-Pentafluorophenoxy-tetrafluoropyridine (1·16 g., 3·5 m.mole), potassium hydroxide (0·46 g., 7 m.mole) and t-butanol (11 ml.) were heated under reflux for 5 hr., water (10 ml.) added, the t-butanol distilled off and the solution allowed to cool. Acidification of the solution with concentrated hydrochloric acid (5 ml.) precipitated a white solid which on recrystallisation from ethanol afforded pure 2-hydroxy-4-pentafluorophenoxy-trifluoropyridine (0·87 g., 75%). (Found: C, 39·8; F, 45·5; M, 331. $C_{11}F_8NO_2H$ requires C, 39·9; F, 45·9%; M, 331), m.p. 169°. (i.r. spectrum No. 27).

The Reaction of 4-Pentafluorophenoxytetrafluoropyridine with a Fourfold Molar Proportion of Potassium Hydroxide.

4-Pentafluorophenoxy-tetrafluoropyridine (1·16 g., 3·5 m.mole), potassium hydroxide (0·95 g., 14 m.mole) and t-butanol (11 ml.) were heated under reflux for 5 hr., water (10 ml.) added, the t-butanol distilled off and the solution allowed to cool. Acidification of the

solution with concentrated hydrochloric acid (9 ml.) precipitated a white solid which on recrystallisation from water afforded a pure solid provisionally assigned the structure 2-hydroxy-4-(4'-hydroxy-tetrafluorophenoxy)-trifluoropyridine (1·128 g., 87%). (Found: C, 39·8; F, 40·1; M, 229. $C_{11}F_7NO_3H_2$ requires C, 40·1; F, 40·4%; M, 229), m.p. 161°. (i.r. spectrum No. 28).

The Reaction of 1-Pentafluorophenoxy-hexafluoroisoquinoline with a Twofold Molar Proportion of Potassium Hydroxide.

1-Pentafluorophenoxy-hexafluoroisoquinoline (0·42 g., 1 m.mole), potassium hydroxide (0·13 g., 2 m.mole) and t-butanol (10 ml.) were heated under reflux for 5 hr., water (10 ml.) added, the t-butanol distilled off and the solution allowed to cool. Acidification of the solution with concentrated hydrochloric acid (5 ml.) precipitated a yellow solid (0·35 g.) which on recrystallisation from ethanol yielded a solid provisionally assigned the structure 1-pentafluorophenoxy-6-hydroxy-pentafluoroisoquinoline. (Found: C, 43·2; F, 45·4; M, 417. $C_{15}F_{10}NO_2H$ requires C, 43·2; F, 45·6%; M, 417), m.p. 195°. (i.r. spectrum No. 29).

The Reaction of 2,4,6-Tris(pentafluorophenoxy)-difluoropyridine with a Twofold Molar Proportion of Potassium Hydroxide.

2,4,6-Tris(pentafluorophenoxy)-difluoropyridine (0·66 g., 1 m.mole), potassium hydroxide (0·13 g., 2 m.mole) and t-butanol (10 ml.) were heated under reflux for 5 hr., water (10 ml.) added, the t-butanol

distilled off and the solution allowed to cool. Acidification of the solution with concentrated hydrochloric acid (5 ml.) precipitated a white solid, which was filtered off and dried. The residual solution had a phenolic smell. This solution was extracted with ether (10 ml.) and the ethereal solution was dried ($MgSO_4$) and the ether removed by distillation to give a small amount of an oil, which was shown by mass spectroscopy to be pentafluorophenol. The dry solid (0·47 g.) was sublimed under vacuum (0·01 mm.), and at 80° a solid sublimate (0·24 g.) was obtained which was shown to be pure 2,6-bis(pentafluorophenoxy)-4-hydroxydifluoropyridine. (Found: C, 41·0; F, 46·1; M, 495. $C_{17}F_{12}NO_3H$ requires C, 41·2; F, 46·1%; M, 495), m.p. 116°. (i.r. spectrum No. 30). Sublimation of the residual solid at 150° at 0·01 mm. gave a solid which was shown by mass spectroscopy to be a mixture of 2,6-bis(pentafluorophenoxy)-4-hydroxydifluoropyridine and a product obtained by the replacement of a single fluorine in 2,4,6-tris(pentafluorophenoxy)-difluoropyridine by a hydroxyl group.

CHAPTER III

Fluoride Ion Initiated Reactions of Perfluoroketones

Introduction.

In the reactions discussed in the following section, a negatively charged species such as, but not always, a carbanion is formed by the addition of fluoride ion to the positive centre of a polarised multiple bond. This negatively charged species then either undergoes β-elimination of fluoride ion, resulting in migration of the double bond, or participates in nucleophilic attack causing elimination of another anion. The second of the alternatives often proceeds by an SN_2 mechanism, and it is the synthetic importance of these displacement reactions that constitute much of the present interest in fluoride ion reactions. Consequently, these displacement reactions are discussed in greater detail than the synthetically less important rearrangement reactions which are mentioned only briefly.

Miller and his colleagues[54] established two different paths for the reaction of halide ions with fluoro-olefins.

(1) Substitution with rearrangement (SN_2'), e.g.

$$F^- + CF_2{=}CF{-}CClF \rightleftharpoons CF_3CF{=}CClF + Cl^-$$

(2) Addition,

$$F^- + CF_2{=}CF{-}CF_3 \rightleftharpoons CF_3{-}\overset{-}{C}F{-}CF_3 \xrightarrow[\text{solvent}]{H^+} CF_3CFHCF_3$$

Substitution with Rearrangement.

The SN_2' process governs the reactions of fluoroallyl halides and attack on the terminal difluoromethylene group by fluoride ion occurs

in the reactions of $CF_2=CFCF_2Cl$ or $CF_2=CCl-CF_2Cl$.[54,55-57] The relative order of reactivity of halide ions in the SN_2' process is $F^- > Cl^- \gg I^-$.

Substitution of allylic or vinylic halogen by fluorine occurs in preference to the addition of hydrogen fluoride by a carbanion intermediate, and a terminal difluoromethylene is more susceptible to attack by fluoride ion than a terminal chlorofluoromethylene, as is illustrated by the reaction of $CClF=CF\cdot CClF_2$ with potassium fluoride in formamide, which has been interpreted as proceeding via two SN_2' replacements of chlorine by fluoride ion, and then addition of hydrogen fluoride.[54]

$$F^- + CClF=CF\cdot CF_2\text{-}Cl \xrightarrow[CHCl_3,\ 60^\circ,\ 3\ days]{(C_2H_5)_4NF/} CClF_2\cdot CF=CF_2 + Cl^-$$

$$F^- + CF_2=CF\cdot CF_2\text{-}Cl \longrightarrow CF_3\cdot CF=CF_2 + Cl^-$$

$$F^- + CF_2=CF\cdot CF_3 \longrightarrow [CF_3\bar{C}FCF_3] \xrightarrow{H^+} CF_3CHFCF_3 \quad (52\%)$$

Rearrangements Catalysed by Fluoride Ion.

This type of reaction involves SN_2' displacement of fluorine by fluoride ion. Fluoride ion attacks a terminal double bond much more easily than an internal one. Rearrangement of a terminal to an internal olefin proceeds easily, but with vigorous enough conditions attack at internal unsaturation occurs, and the subsequent double bond migration leads to the most thermodynamically stable product, i.e. the most highly substituted olefin. Perfluoro-1-heptene,[54] on treatment

with tetraethylammonium fluoride in chloroform for five minutes at room temperature, gave a mixture of olefins containing only 12% of the original olefin, and with a higher concentration of fluoride ion and a longer contact time only 2% of the original olefin remained. This was interpreted, as follows.

$$CF_3CF_2CF_2CF_2CF_2CF{=}CF_2 \overset{F^-}{\rightleftharpoons} CF_3CF_2CF_2CF_2CF{=}CFCF_3$$

$$\overset{F^-}{\rightleftharpoons} CF_3CF_2CF_2CF{=}CFCF_2CF_3$$

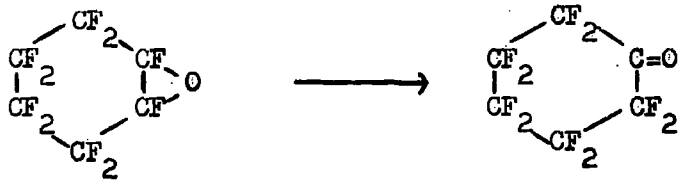
A number of other fluoride ion catalysed rearrangements of olefins have been described in the literature.

The addition of fluoride ion to perfluorodimethylketene yields an intermediate that can give either the ketene or isomeric perfluoromethacrylyl fluoride. The higher energy ketene is favoured over the more stabilised conjugated acrylyl fluoride in a 60:40 ratio, showing the strong preference for internal saturation in fluoride ion catalyst rearrangements.[58]

$$F^- + (CF_3)_2C{=}C{=}O \rightleftharpoons (CF_3)_2\overset{-}{C}\text{-}\overset{F}{C}{=}O \rightleftharpoons CF_2{=}\overset{F}{\underset{CF_3}{C}}\text{-}C{=}O + F^-$$

The heavier metal fluorides catalyse the rearrangement of perfluoroepoxides, terminal epoxides producing acid fluorides and symmetrically substituted epoxides yielding ketones,[59] e.g.

$$CF_3\underset{O}{CF\text{-}CF_2} \longrightarrow CF_3CF_2COF$$



The following rearrangements of unsaturated fluorine containing nitrogen compounds to more thermodynamically favoured isomers have been observed.[60]

$$NF_2CN \xrightarrow{CsF} CF_2\begin{matrix}N\\ \|\\ N\end{matrix}$$

$$CF_3\overline{CFN{=}CF} \xrightarrow{F^-} CF_3C{=}NCF_2 \quad [61]$$

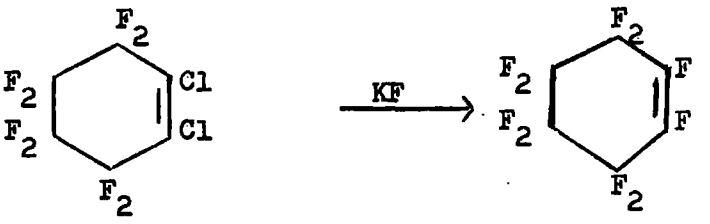
Direct Vinyl Substitution.

Vinyl substitution of chlorine by fluoride ion in $CClF{=}CF{\cdot}CClF_2$ is considered to occur via two SN_2' reactions. Direct vinyl substitution by fluoride ion has not been established, but has been proposed as the first step in the reaction of $CClF{=}CClCF_3$ with potassium fluoride-formamide at 60°.[54]

$$CClF{=}CClCF_3 + F^- \longrightarrow CF_2{=}CClCF_3$$

$$CF_2{=}CClCF_3 + F^- \longrightarrow [CF_3\bar{C}ClCF_3] \xrightarrow{H^+} CF_3CHClCF_3 \quad (55\%)$$

Reactions of potassium fluoride in N-methyl-2-pyrrolidone with polychlorofluoro-olefins at 190°, and above, probably involve direct substitution of vinylic chlorine by fluoride ion,[62] e.g.



(71%)

Addition Reactions.

Hydrogen Fluoride. In the olefin-fluoride ion reactions described previously, where substitution of allylic or vinylic halogen by fluorine or addition of fluoride ion to form a carbanion could result from attack on a given unsaturated carbon, substitution was found to take place first. The resulting more highly fluorinated olefins containing a terminal difluoromethylene group were then rapidly converted into their hydrogen fluoride addition products, whilst fluoro-olefins with an internal -CF=CF- grouping reacted more slowly. When olefins not containing replaceable allylic or vinylic halogen other than fluorine, and which could not undergo SN_2' rearrangement, were reacted with potassium fluoride in formamide, the results shown in Table 1 were obtained. Reactions with the solvent caused dark coloured mixtures. Olefins with a terminal difluoromethylene group readily added hydrogen fluoride whilst hexafluoro-2-butene with its internal -CF=CF- grouping reacted more slowly.[54] As these reactions took place in mildly basic media with a high concentration of fluoride ion, the only consistent mechanism involves the initial addition of fluoride ion.

$$F^- + F_2C{=}\overset{\curvearrowleft}{\underset{|}{C}}- \rightleftharpoons [F_3C-\bar{\underset{|}{C}}-] \xrightarrow{H^+} CF_3-\overset{H}{\underset{|}{C}}-$$

Table 1

Olefin	Temp. °C	Reaction time hr.[a]	Product	Yield %
$CF_2=CFCl$	55	30	CF_3CHClF	72
$CF_2=CFCF_3$	25	5	CF_3CHFCF_3	60
$CF_2=CFCF_3$	65	b	CF_3CHFCF_3	21[c]
$CF_2=CClCF_3$	25	6	$CF_3CHClCF_3$	61
$CF_3CF=CFCF_3$	81	24	$CF_3CHFCF_2CF_3$	ca.35

[a] In a rocker shaker.

[b] Bubbled very slowly through the KF-formamide solution.

[c] Recovered 50% of $CF_2=CFCF_3$.

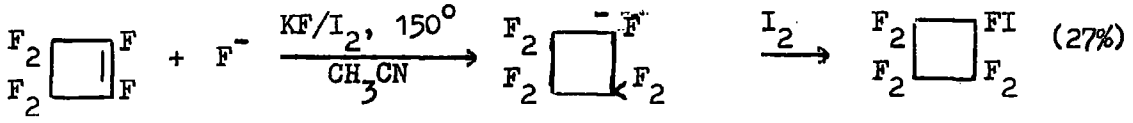
The solvent anion, formed along with the addition product, reacts with the fluoro-olefin in competition with fluoride ion, thus limiting the yield of hydrogen fluoride addition product.

Isolation of CF_3CHCF_3 from the reaction of hexafluoropropene with an aqueous dioxan solution of potassium fluoride further substantiated the mechanism.

$$CF_3CF=CF_2 \xrightarrow{F^-} CF_3\overset{-}{C}FCF_3 \xrightarrow{H_2O} CF_3CFHCF_3 + OH^-$$

Fluorocarbanion formation by hydrogen abstraction was also shown when fluoro-olefins were allowed to react with tetraethylammonium fluoride in homogeneous aqueous chloroform solution.

The carbanion, formed by the addition of fluoride ion to a fluoro-olefin, has been reacted with iodine in acetonitrile solution to yield fluoroalkyl iodides,[63] e.g.



A good yield was obtained with hexafluoropropene (61%), but tetrafluoro-ethylene, $CF_3CF=CFCF_3$ and 8H-perfluoro-1-octene provided CF_3CF_2I (7%) and CF_2ICF_2I, $CF_3CFICF_2CF_3$ (17%) and $H(CF_2)_6CFICF_3$ (13%) in low yields.

The additions of carbonyl fluoride to olefins of different types have been achieved using excess carbonyl fluoride in acetonitrile in the presence of catalytic amounts of caesium fluoride, potassium bifluoride, or tetraethylammonium fluoride.

Table 2.

Addition of Carbonyl Fluoride to Fluoro-olefins.[64]

Olefin	Product	Reaction temp.	Conversion
$CF_3CF=CF_2$	$(CF_3)_2CFCOF$	50-100	80
$CF_3CF=CFCF_3$	$CF_3CF_2CF(CF_3)COF$	150	62
$CH_3OCF=CF_2$	$CH_3OCF_2CF_2COF$	50-125	62
$\overline{CF_2CF_2CF=CF}$	$\overline{CF_2CF_2CF_2CFCOF}$	125-150	54
$CF_2=CF_2$	CF_3CF_2COF	100-150	13
$CF_3N=CF_2$	$(CF_3)_2NCOF$	50-150	56

The displaceable fluorine in these fluoroacyl fluorides enables them to react further with olefins under similar conditions to produce

symmetric or asymmetric ketones. Symmetric ketones can be made in lower yield by reaction of excess olefin with carbonyl fluoride, e.g.

$$2CF_3CF{=}CF_2 + COF_2 \xrightarrow[75 - 100^\circ]{CH_3CN/CsF} [(CF_3)_2CF]_2CO \quad (39\% \text{ conversion})$$

Reactions of hexafluoropropene with a number of acyl fluorides show that the reaction can be extended to α- and γ-diketones.

Table 3

Addition of Acyl Fluorides to Fluoro-olefins.[65]

Acyl Fluoride	Product	Conversion
COF_2	$(CF_3)_2CFCOCF(CF_3)_2$	39
$(CF_3)_2CFCOF$	$(CF_3)_2CFCOCF(CF_3)_2$	38
CF_3COF	$CF_3COCF(CF_3)_2$	75
$CF_2CF_2CF_2CFCOF$	$CF_2CF_2CF_2CFCOCF(CF_3)_2$	28
$CF_2(CF_2COF)_2$	$CF_2[CF_2COCF(CF_3)_2]_2$	75

It is assumed that these reactions proceed by the initial formation of a carbanion, which subsequently reacts with the acid fluorides, e.g.

$$F^- + CF_2{=}CFCF_3 \longrightarrow (CF_3)_2CF^-$$

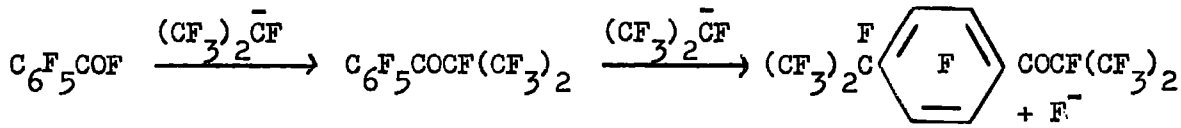
$$(CF_3)_2CF^- + O{=}CFR \longrightarrow (CF_3)_2CFCOR + F^-$$

R = F or fluorocarbon group

Pentafluorobenzoyl fluoride and tetrafluoroisonicotinyl fluoride both react with the heptafluoroisopropyl anion, prepared from hexafluoropropene and catalytic amounts of potassium fluoride in acetonitrile

solution at 135°, to give perfluoro(isopropylphenyl ketone) and perfluoro-(isopropyl-4-pyridyl ketone) respectively, thus behaving analogously to perfluoroacyl fluorides.[66]

With pentafluorobenzoyl fluoride, another compound obtained was perfluoro(isopropyl-4-isopropylphenyl ketone) which resulted from attack of the perfluoroisopropyl anion on the perfluoro(isopropylphenyl ketone) that was first formed.



The order in which the reactions occur is supported by the facts that no perfluoro-(4-isopropylbenzoyl fluoride) is isolated and, under the same conditions, pentafluorobenzoyl chloride does not react with perfluoroisopropyl anion. It illustrates that the $COCF(CF_3)_2$ group is more powerfully electron attracting than the COCl and COF groups, since it makes the para-fluorine atom more susceptible to nucleophilic attack.

Tetrafluoroethylene with perfluoroketones in the presence of caesium fluoride formed the caesium salts of the perfluorotertiary alcohols, from which the free alcohols can be obtained on acidification.[67] $CF_3CF_2C(CF_3)_2OH$, $(CF_3CF_2)_2C(CF_3)OH$, and $(C_2F_5)_3COH$ were obtained in conversions of 86, 80 and 60%, respectively. The latter two compounds were made in low yields by the reaction of excess tetrafluoroethylene with trifluoroacetyl fluoride and carbonyl fluoride, respectively.

In the actual experiments, the olefin was added to a diglyme solution of caesium heptafluoroisopropoxide, but no products were detected which could be formed by the addition of heptafluoroiso-

$$CF_3COCF_3 + CsF \rightleftharpoons FCOCs(CF_3)_2$$

$$CsF + CF_2{=}CF_2 \rightleftharpoons CF_3CF_2Cs \xrightarrow{CF_3COCF_3} CF_3CF_2COCs(CF_3)_2$$

propoxide to tetrafluoroethylene, thus suggesting that the reaction producing the alcohol involved attack by pentafluoroethyl anion, derived from the tetrafluoroethylene and caesium fluoride, upon the equilibrium concentration of hexafluoroacetone. When excess caesium fluoride was used, the rate of formation of the alcohol was much increased but some by-product liquid perfluoro-olefin polymer was produced by polymerisation of the tetrafluoroethylene.

Direct addition of a metal fluoride complex of a perfluoro-olefin, in a suitable solvent, to carbon dioxide followed by separation of the product by acidification and distillation yielded perfluorocarboxylic acids.[68] The condensation was found to be reversible, the stability of the metal carboxylate decreasing with increasing complexity of the olefin. Because of this thermal reversal of direction in the reaction $R_f^- + CO_2 \rightleftharpoons R_fCOO^-$, it was necessary to reverse the reaction temperature from 100° for $CF_2{=}CF_2$ to 70° for $CF_3CF{=}CF_2$ and to 25° for $(CF_3)_2C{=}CF_2$.

Dimerisation and Polymerisation of Olefins.

Tetrafluoroethylene with caesium fluoride in diglyme self-condensed to the extent of about 50% after 80 hrs. at 100°, the remainder of the olefin reacting with the solvent. About 60% of the product contained 10 carbon atoms with C_8, C_{12} and C_{14} fractions each accounting for 10-15%. The C_8 fraction was cis- and trans-$C_2F_5C(CF_3)=C(CF_3)C_2F_5$ and the other fractions were considered to be similarly substituted internal olefins. The extensive branching in these structures arises from the formation and reaction of internal olefins, perhaps formed as follows.

$$CF_2=CF_2 \xrightarrow{F^-} CF_3CF_2^- \xrightarrow{CF_2=CF_2} CF_3CF=CFCF_3 + F^-$$

$$CF_3CF_2^- + CF_3CF=CFCF_3 \longrightarrow CF_3CF_2\underset{CF_3}{C}=CFCF_3$$

$$CF_3CF_2^- + CF_3CF_2\underset{CF_3}{C}=CFCF_3 \longrightarrow CF_3CF_2\underset{CF_3CF_3}{C}=CCF_2CF_3$$

The rate of self condensation of tetrafluoroethylene in diglyme increased with increasing amounts of caesium fluoride, indicating that carbanion formation is perhaps the rate determining step in this reaction.

Perfluorovinyl ethers merely dimerise rather than polymerise on reaction with fluoride ion.[70]

$$F^- + R_fOCF=CF_2 \longrightarrow R_fO\bar{C}FCF_3 \longrightarrow R_fO\underset{CF_3}{C}F-CF=CFOR_f + F^-$$

Hexafluoropropene has been converted to unsaturated dimers and trimers using potassium hydrogen fluoride in dimethylformamide.[71]

$$CF_3CF{=}CF_2 + KHF_2 \xrightarrow[25\text{-}30^\circ]{HCON(CH_3)_2} \begin{cases} CF_3CF{=}CFCF(CF_3)_2 & (98\%) \\ CF_3CF_2CF{=}C(CF_3)_2 & (2\%) \end{cases} \quad \begin{cases} (CF_3)_2CFC(CF_3){=}CFCF(CF_3)_2 & (44\%) \\ (CF_3)_2C{=}C(CF_3)CF_2CF(CF_3)_2 & (51\%) \end{cases}$$

Displacement Reactions on Sulphur and Nitrogen.

Displacement reactions on sulphur, and nitrogen have been observed. When a mixture of hexafluoropropene and nitrogen trifluoride was passed over caesium fluoride at 320°, approximately equal amounts of $(CF_3)_2CFNF_2$, $(CF_3)_2C{=}NF$, and $(CF_3)_2CFCF(CF_3)_2$ were obtained.[72] The reaction was assumed to proceed by a free radical mechanism and the formation of $(CF_3)_2CFCF(CF_3)_2$ indicates that such a mechanism was responsible in part. However, use of sodium fluoride instead raised the temperature required for reaction to 520°, and gave a completely different set of products, mainly iso-C_3 to C_6-fluorocarbons and fluorocarbon imines. Such an effect, involving a change in the nature of the surface, corresponds better to an ionic mechanism.

Perfluoropiperidine reacted with hexafluoropropene in the presence of caesium fluoride at 200° to give a 48% yield of adduct.[73]

$$\overbrace{CF_2(CF_2)_4NF} \xrightarrow[CsF]{C_3F_6} \overbrace{CF_2(CF_2)_4NCF(CF_3)_2}$$

Hexafluoropropene reacted easily with sulphur tetrafluoride in the presence of caesium fluoride.[74]

$$CF_3CF=CF_2 + SF_4 \longrightarrow (CF_3)_2CFSF_3 + (CF_3)_2CFSF_2CF(CF_3)_2$$

Perfluoroalkylation of Aromatic Compounds.

As discussed previously, perfluoro-olefins react with acid fluorides in the presence of fluoride ion to give perfluoroketones. Compounds containing fluorine atoms with similar reactivity to that of an acid fluoride should undergo similar reactions. Halotriazines are in some respects similar to acid fluorides and fluorotriazines readily undergo reaction with fluoro-compounds containing carbon-carbon or carbon-nitrogen unsaturation in the presence of fluoride ion.

Cyanuric fluoride, heated under autogeneous pressure with caesium fluoride and hexafluoropropene, without solvent, for 12 hours at 100°, was converted (> 95%) to a mixture of mono-, bis-, and tris-(heptafluoroisopropyl)-triazines. Using a $C_3F_6:(CNF)_3$ ratio of approximately 2:1 the ratio of mono-, di-, and tri-substituted compounds was 8:10:1, whilst a reactant ratio of 1:1·25 yielded a product ratio of 28:6:1.[75]

Functionally active perfluoroalkyl substituents could be introduced into the triazine ring if these substituents were unreactive towards fluoride ion. Perfluoroallyl cyanide reacted under the same conditions with a slight excess of 2,4-bis(perfluoroisopropyl)-6-fluoro-S-triazine to yield perfluoro-[2-(β-cyanoisopropyl)-4,6-di-isopropyl]-triazine.

Perfluoro-2-azapropene reacted similarly with caesium fluoride and cyanuric fluoride in a 2:1 $CF_3N{=}CF_2$:$(CFN)_3$ ratio giving a mixture of mono-, bis-, and tris(perfluorodimethylamino)-substituted triazines in the ratio 1:2:1.

It was found that neither hexafluorobenzene nor pentafluorobromobenzene reacted with either hexafluoropropene or perfluoro-2-azapropene, when heated with caesium fluoride, either alone or in acetonitrile solution at temperatures up to 175°.[75] Even benzene itself can be reactive towards perfluoroalkyl anions using vigorous enough conditions. Benzene and halogenated benzenes have been polyfluoroalkylated by reaction with tetrafluoroethylene and an alkali metal fluoride at 280-370°.[76] Both mono- and poly-substitution occur and $C_2F_4H^-$ and CF_3^- groups as well as $C_2F_5^-$, are introduced.

Pentafluoropyridine, on heating with hexafluoropropene and caesium fluoride in sulpholan contained in a Carius tube at 120°, gave perfluoro-(4-isopropylpyridine) in high yield together with a trace of disubstituted product.[77]

$$C_5F_5N + CF_3CF{:}CF_2 \xrightarrow[130^\circ,\ 12\ hr.]{KF,\ sulpholan} 4\text{-}[(CF_3)_2CF]C_5F_4N + 2,4\text{-}[(CF_3)_2CF]_2C_5F_3N \qquad (94\%)$$

The conditions were varied so as to ascertain the relative effectiveness of sulpholan, diglyme, triglyme and dimethylformamide as solvents and of potassium and caesium fluoride as initiators. The results for two series of reactions, one with potassium fluoride in different solvents at 130°, and the other with caesium, or potassium fluoride at 20° are shown in Table 4.

Table 4

Reaction between Pentafluoropyridine (17·75 m.moles) and Hexafluoropropene (33·3 m.moles)

Initiator/solvent	Temp.	Conversion of C_5F_5N	Yield (% based on consumed C_5F_5N)
KF/diglyme	130°	33	69
KF/triglyme	130	50	95
KF/DMF	130	54	79
KF/sulpholan	130	89	95
KF/diglyme	20	9	45
KF/sulpholan	20	63	94
CsF/diglyme	20	40	84
CsF (8·0 g.) diglyme	20	42	84
CsF/sulpholan	20	88	95
CsF (8·0 g.) sulpholan	20	98	100

All reactions in Carius tubes (100 ml.) with solvent (15 ml.). All reactions at 20° were shaken. Except where stated quantity of fluoride was 3·0 g.

Sulpholan is shown to be the best solvent for this reaction, but this need not be so for others, especially if a different fluoro-olefin is used. For example, tetraglyme seemed more effective in reactions with octafluorotoluene. Caesium fluoride is the more effective initiator, as expected, as it has been shown in fluorination reactions with alkali metal fluorides that the effectiveness of the fluoride decreases with

increase in lattice energy. However, these polyfluoroalkylation reactions occur partly in solution making the effect of the gegenion on the nucleophilic strength of the fluoride ion of importance. The smaller gegenions seem to have a greater influence because of solvation. Reactions in which potassium fluoride was used were unsuccessful in the absence of a solvent, whereas those in which caesium fluoride was used reacted as expected, although less efficiently than in the presence of a solvent.

Pentafluoronitrobenzene was reacted with hexafluoropropene under similar conditions yielding mono- and di-substituted products by displacement of fluorine, but other products also arose by displacement of the nitro-group by fluoride ion. When this reaction was

$$C_6F_5NO_2 + CF_3CF{:}CF_2 \xrightarrow[12\ hr.,\ 120^\circ]{KF,\ sulpholan} \begin{array}{l} p\text{-}[(CF_3)_2CF]C_6F_4NO_2 \quad (25\%) \\ + Op\text{-}[(CF_3)_2CF]_2C_6F_3NO_2 \quad (20\%) \\ + m\text{- and } p\text{-}[(CF_3)_2CF]_2C_6F_4 \end{array}$$

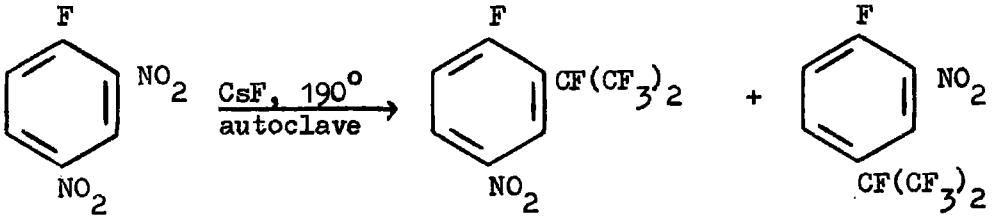
repeated using an autoclave on a larger scale at a higher temperature, replacement of the nitro-group was found to be much more extensive, and the major product was perfluoro(isopropylbenzene).

Under the mild reaction conditions used for pentafluoropyridine in a Carius tube, hexafluorobenzene, bromopentafluorobenzene or 1,3,5-trichlorotrifluorobenzene would not react with hexafluoropropene. More reactive compounds such as octafluorotoluene and methyl pentafluorobenzoate gave the expected perfluoro-(4-isopropyltoluene)

and methyl perfluoro-(4-isopropylbenzoate). The efficiency of sulpholan and tetraglyme was compared using the reaction between octafluorotoluene and hexafluoropropene. With caesium fluoride they were found to be equally effective, but with potassium fluoride tetraglyme gave a considerably greater yield of perfluoro(4-isopropyltoluene). This suggests that solvation of the caesium cation does not greatly affect the reactivity of the caesium cation, but solvation of the potassium cation is important and is more efficient in tetraglyme.

Reaction with pentafluorobenzonitrile occurred much more easily than with other benzene derivatives, and was only controllable at 20°, when 4-heptafluoroisopropylbenzonitrile was obtained.

With 2,4-dinitrofluorobenzene replacement of the nitro-group occurred to give a low yield of the corresponding heptafluoroisopropyl derivatives and tar.



In the Carius tube reactions described, no more than traces of disubstitution occurred, because the molar excess of olefin used was consumed in side reactions, which produced dimers and trimers of hexafluoropropene. Thus, the main reason for monosubstitution was the low concentration of olefin at the reaction site. The concentration of hexafluoropropene was increased by reacting it with pentafluoropyridine

in an autoclave using caesium or potassium fluoride in sulpholan. Pressures of 30 to 100 atmospheres and temperatures of 150° to 190° enabled mixtures of 4-, 2,4-bis-, and a mixture of 2,4,5- and 2,4,6-tris(heptafluoroisopropyl) derivatives to be prepared, but no more than a trace of tetrakis(heptafluoroisopropyl)monofluoropyridine was obtained. When tetrafluoroethylene was used instead of hexafluoropropene, a mixture of mono- to pentakis-pentafluoroethyl derivatives was obtained. The reaction of the pentafluoroethyl anion at the 3- to 5-positions of pentafluoropyridine, where no reaction occurred with the heptafluoroisopropyl anion suggests greater reactivity of the primary anion, although the greater steric requirements of the heptafluoroisopropyl anion would inhibit polysubstitution.

A mixture of perfluoro-(mono-, di-, tri-, tetra-, penta-, and hexa-ethylbenzenes) is obtained from hexafluorobenzene, tetrafluoroethylene at 135° in 6 hr. at ca. 34 atm.

The dimer of hexafluoropropene obtained in these reactions were shown to be principally perfluoro-(2-methylpent-2-ene), with a little perfluoro-(4-methylpent-2-ene) formed by self-condensation of the olefin followed by fluoride-ion initiated rearrangements. The trimer was a mixture of three components only partially resolvable by g.l.c.

$$F^- + CF_2{:}CFCF_3 \longrightarrow (CF_3)_2\bar{C}F + CF_2{:}CF\cdot CF_3$$

$$(CF_3)_2C{:}CFCF_2CF_3 \xleftarrow{F^-} CF_3CF\cdot CF{=}CFCF_3$$

Nitrogen Anions.

Perfluoro-2-azapropene is extremely reactive towards fluoride ion and dimerises at room temperature in contact with caesium fluoride. The intermediate perfluorodimethylamino anion $(CF_3)_2N^-$ is analogous to the perfluoroisopropyl ion. Perfluoro-2-azapropene reacts with itself,[78] with cyanuric fluoride,[79] with carbonyl fluoride,[64] and with nitrosyl fluoride[80] resulting in dimerisation, alkylation, acid fluoride formation, and nitrosamine formation.

$SF_5N=CF_2$ and $(CF_3)_2NN=CF_2$ have been found to undergo many reactions analogous to those of $CF_3N=CF_2$,[81,82] e.g.

$$SF_5N=CF_2 \longrightarrow SF_5N(CF_3)CF=NSF_5$$

$$(CF_3)_2NN=CF_2 \longrightarrow (CF_3)_2NN(CF_3)CF=NN(CF_3)$$

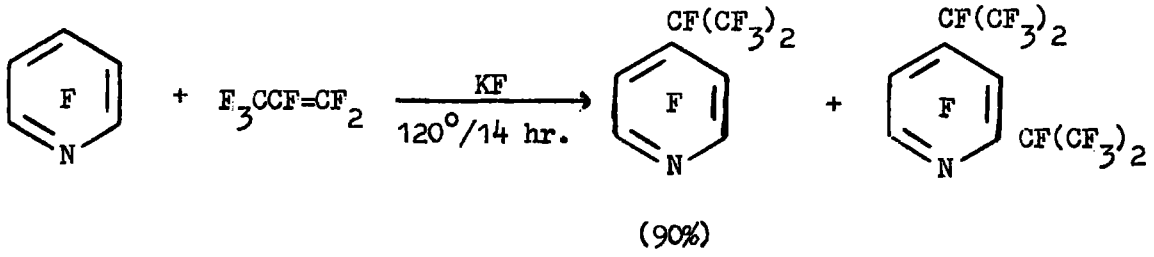
The following reaction has been reported.

$$R_fN=SF_2 + (CF_3)_2CF \longrightarrow R_fN=SFCF(CF_3)_2 + F^-$$

SECTION 2.

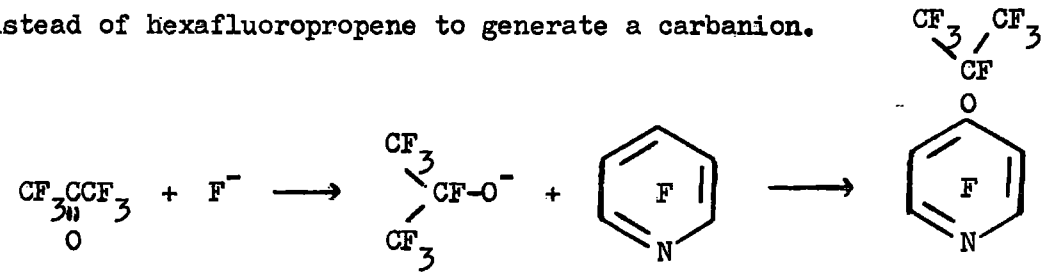
Discussion of the Experimental.

An interesting modification of the method discovered for the preparation of polyfluoroalkylpyridines,[77] i.e.



(90%)

would be the preparation of 4-heptafluoroisopropoxy-tetrafluoropyridine, by an analogous method, using hexafluoroacetone to generate an oxyanion, instead of hexafluoropropene to generate a carbanion.



However, unreacted starting materials were recovered after pentafluoropyridine, a slight excess of hexafluoroacetone, potassium fluoride and dry sulpholan were heated together in a Carius tube, for up to 6 days at temperatures ranging from 150° to 250°. Similarly, no reaction occurred when caesium fluoride, which is a more effective initiator of the polyfluoroalkylation reaction, was used. A publication that appeared shortly after these preliminary experiments explained the first unsuccessful attempt to prepare fluorinated ethers by this method.

The publication[83] described how ionic, fully fluorinated ethoxides, n-propoxides, iso-propoxides and n-butoxides were prepared by the reaction

of alkali metal fluorides with the corresponding acid fluoride or hexafluoroacetone.

$$MF + R_fCOF \longrightarrow MOCF_2R_f$$

$$MF + (CF_3)_2CO \longrightarrow MOCF(CF_3)_2$$

where M = K, Rb, Cs and R_f = CF_3, C_2F_5 or C_3F_7.

However, all of these solid salts decomposed in vacuo to give the metal fluoride and carbonyl compound. The caesium salts were more thermally stable than the rubidium or potassium salts, but decomposition became quite rapid at 80°. These salts were soluble in polar solvents. With the acid fluorides or ketone, the solid metal fluoride dissolved in the acetonitrile to give a small amount of suspension or a clear solution. The solid salt could be isolated by removing the acetonitrile at 20°. The use of fluorinated alkoxides as synthetic intermediates was limited by the ease with which they eliminated a fluoride ion. However, the perfluoroisopropoxides, $(CF_3)_2CFO^-$, reacted with the more reactive alkyl halides, e.g. with allyl bromide to yield allyl heptafluoroisopropyl ether.

$$CH_2{:}CHCH_2Br + K^+[(CF_3)_2CFO^-] \xrightarrow[\text{diglyme}]{55^\circ} CH_2{:}CHCH_2OCF(CF_3)_2HBr$$

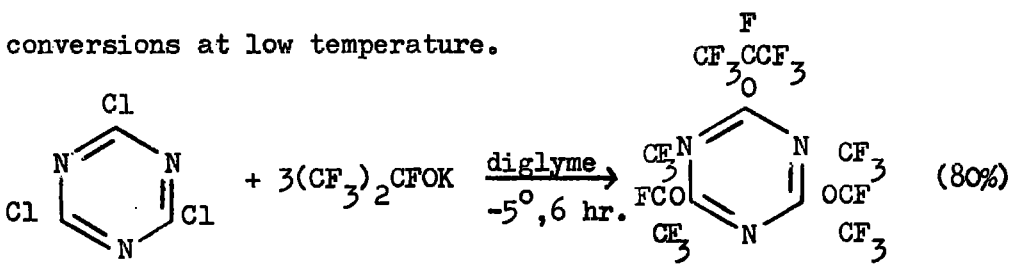
Great care was taken to exclude moisture from the reaction mixture, and the reaction was carried out at a low enough temperature to prevent appreciable decomposition of fluorinated alkoxide.

In the first reactions of caesium or potassium fluoride with hexafluoroacetone and pentafluoropyridine, the lowest reaction temperature was 150°, which would have caused complete thermal decomposition of any caesium heptafluoroisopropoxide formed into hexafluoroacetone and caesium fluoride. Also, although reasonable precautions were taken to exclude moisture from the reaction mixture, the measures taken were by no means as stringent as those used by Redwood and Willis. It was later found that heptafluoroisopropyl glycidyl ether had been prepared by the reaction of potassium heptafluoroisopropoxide with epibromohydrin in diglyme for 10 hours at 80-90°.[84] This experiment showed that potassium heptafluoroisopropoxide is stable at 90°.

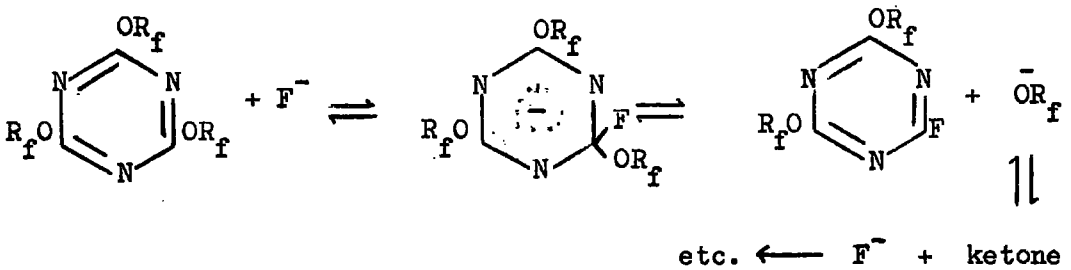
$$(CF_3)_2C{=}O + KF \longrightarrow (CF_3)_2CFO^-K^+$$

$$(CF_3)_2CFO^-K^+ + CH_2\text{-}CHCH_2Br \longrightarrow (CF_3)_2CFOCH\text{-}CH_2 + KBr$$

A later communication[85] claimed that potassium heptafluoroisopropoxide reacted with cyanuric chloride to form a triether in high conversions at low temperature.



When this reaction was attempted at higher temperatures (25 - 100°), cyanuric fluoride was formed in good yield. This was explained by fluoride ion displacement of any perfluoroalkoxy-substituted triazine formed. When a mixture of perfluoroisopropoxy-substituted triazine, a catalytic amount of potassium fluoride and diglyme was allowed to stand at room temperature for 2 days, hexafluoroacetone and cyanuric fluoride were produced almost quantitatively. A good yield of perfluoroisopropoxy substituted triazine could be obtained at -5°, because of the significant enough difference in rate of displacement between R_fO^- and fluoride ion decomposition. The authors illustrated the path of fluoride ion displacement of alkoxide in diglyme thus:



etc. ⟵ F^- + ketone

This path was consistent with the observation that cyanuric fluoride will not yield the perfluoroisopropoxy-triazine.

The authors found that attempts to displace fluoride ion from octafluorotoluene and pentafluorobenzonitrile, by heating them with potassium fluoride in diglyme at 90°, resulted in nearly quantitative recovery of starting materials. They suggested that these failures may be due to unfavourable selection of reaction path, once an

intermediate complex was formed.

These experiments suggested that, for promoting the reaction of heptafluoroisopropoxide ion with pentafluoropyridine, the use of caesium fluoride at approximately 90° with diglyme or acetonitrile as solvent under strictly anhydrous conditions would be best. An excess of caesium fluoride in the earlier reactions could well have been detrimental to the reaction and prevent it from proceeding to completion. It would probably have been best to use at least a two-fold molar amount of hexafluoroacetone compared with that of caesium fluoride, so that the excess hexafluoroacetone would react with the caesium fluoride produced as the reaction proceeded to minimise the amount of free caesium fluoride present.

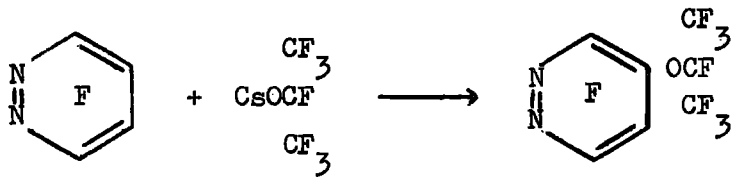
Caesium fluoride, an excess of hexafluoroacetone, anhydrous diglyme and pentafluoropyridine were sealed in a Carius tube under anhydrous conditions. The caesium heptafluoroisopropoxide dissolved on shaking at room temperature to form a solution of caesium heptafluoroisopropoxide. The contents of the tube were heated to 100° for 7 days and they gradually became darker in appearance. The reaction product was isolated by washing the mixture with water to remove diglyme and distilling the dried residual liquid under reduced pressure. A mixture of heptafluoroisopropoxy-tetrafluoropyridine and bis(heptafluoroisopropoxy)-trifluoropyridine (minor product) seem to have been formed in about 50% yield. The mixture was contaminated with

a small amount of diglyme. The diglyme could not be removed by further water washing, and it was not possible to purify the compounds by further distillation, as the mixture of compounds seemed to co-distil. Attempted separation of the compounds by preparative scale gas liquid chromatography was unsuccessful due to the inadequacy of the trapping system.

An attempt to prepare further quantities of 4-heptafluoroisopropoxy-tetrafluoropyridine resulted in the formation of a spurious reaction product. Approximately equimolar quantities of pentafluoropyridine and caesium fluoride were heated with an excess of hexafluoroacetone in diglyme at 95° for 7 days. Work-up of the reaction mixture yielded a reaction product, which so far has resisted identification. The pure product contained carbon (29·3%), hydrogen (1·7%) and fluorine (63·3%). 4-Heptafluoroisopropoxy-tetrafluoropyridine would have a 28·7% carbon content and a 62·4% fluorine. The infra-red spectrum of the product contained a C-H, stretch, an absorption of medium to weak intensity at 6·9 microns of similar intensity to the absorption found in diglyme, instead of the strong absorptions expected at 6·1 and 6·65 - 6·75 microns for the tetrafluoropyridyl group, a broad absorption between 7·3 and 9·7 microns, which could be explained by a mixing of aliphatic fluorine and ether absorptions, and a number of absorptions between 13 and 14·6 microns. The ^{19}F n.m.r. spectrum consists of an unsymmetrical triplet centred at

74·8 p.p.m. upfield from CF_3Cl_3. The mass spectrum contains peaks at 388, 370, 358, 350 and 320 mass units. The base peak of the spectrum is at 206 mass units. Accurate mass measurements on these peaks gave no conclusive results.

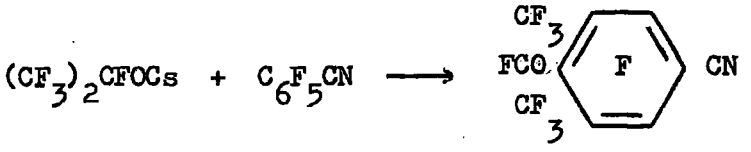
The attempted preparation of 4-heptafluoroisopropoxy-trifluoropyridazine by reacting equimolar amounts of tetrafluoropyridazine, hexafluoroacetone and caesium fluoride in acetonitrile in a sealed tube for 2 days at 60° yielded only an intractable black tar.



These results were probably caused by the use of impure caesium fluoride. A new batch of caesium fluoride was used for the first time in the reactions of perfluoropyridazine and pentafluoropyridine with hexafluoroacetone. Two separate fluorine analyses of this caesium fluoride gave the results 16·25 and 15·9%. This expected figure is 12·5%F. A separate analysis for hydrogen fluoride indicated that the caesium fluoride had a hydrogen fluoride content of 2%. The caesium fluoride was made usable by neutralising a solution of it and pumping off the water. The presence of hydrogen fluoride would certainly cause decomposition of the perfluoropyridazine and explain the isolation of the tar in its reaction with hexafluoroacetone. What the effect of the hydrogen fluoride on the preparation of 4-heptafluoroisopropoxy-tetrafluoropyridine would be was not clear, but it would

certainly be a plausible explanation for the failure of the reaction. The purity of the caesium fluoride is clearly of critical importance in these caesium fluoride initiated reactions.

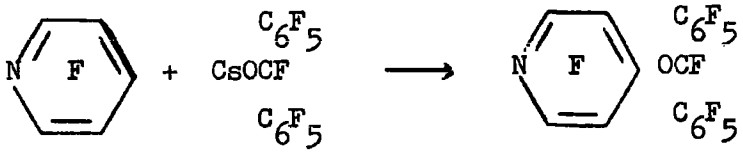
Reaction of equimolar amounts of pentafluorobenzonitrile, hexafluoroacetone and caesium fluoride dissolved in acetonitrile, contained in a sealed rotating nickel tube at 95° for 14 days, yielded mainly unreacted pentafluorobenzonitrile together with a small amount of material provisionally thought to be heptafluoroisopropoxy-tetrafluorobenzonitrile, as indicated by g.l.c. and mass spectroscopy. The pentafluorobenzonitrile would be expected to undergo substitution in the 4-position.



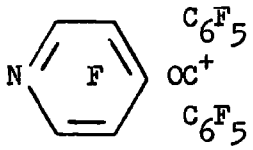
It was not possible to separate the reaction product from the pentafluorobenzonitrile by distillation.

Evidence for the preparation of perfluoro-(4-pyridyloxydiphenylmethane) in low yield was found. Equimolar amounts of decafluorobenzophenone and pentafluoropyridine in diglyme were heated with a molar excess of caesium fluoride in a sealed tube at 100° for 2 days. The reaction product was isolated by washing the contents of the tube with water before distilling the residue under reduced pressure to yield a high boiling liquid and a solid that sublimed along with the liquid. Vapour phase chromatographic analysis of the solid distillate (silicone grease at 200°) showed it to contain two peaks which were

just resolved, one of which was decafluorobenzophenone. The infrared spectrum of the product contained the absorptions expected for decafluorobenzophenone and, in addition, absorptions at 5·74 microns, suggesting a tetrafluoropyridyl group, 7·7 to 8·3 microns, suggesting aliphatic fluorine, and 8·6 to 9·4 microns, suggesting an ether linkage. The mass spectrum of the solid contained a peak at 512 mass units, which was the highest in the spectrum, and was shown by accurate mass measurement to have the composition $C_{18}F_{14}NO$, peaks at the values for found decafluorobenzophenone, and in addition peaks between 195 and 362 mass units, which were not present in the spectrum of pure decafluorobenzophenone. The evidence was consistent with the reaction product containing a mixture of unreacted decafluorobenzophenone and perfluoro-(4-pyridyloxydiphenylmethane) formed as shown:-



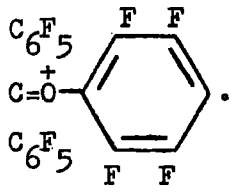
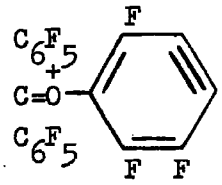
Although the orientation of the substitution reaction was not proven, it was, of course, expected to proceed in the 4-position of pentafluoropyridine. Attempts to obtain a pure sample of the product ether by column chromatography of the reaction product on alumina were unfortunately not successful. It is not surprising that the molecular ion is absent from the mass spectrum of perfluoro-(4-pyridyloxydiphenylmethane) because the loss of a fluorine radical to give tertiary carbonium ion $C_{18}F_{14}NO^+$



would be expected to be a very favourable process.

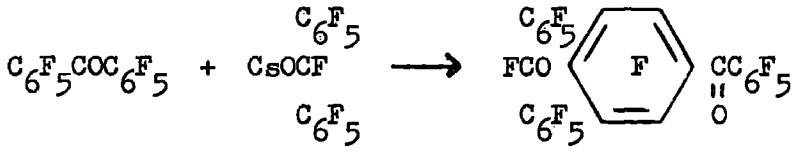
In a later experiment equimolar amounts of decafluorobenzophenone and caesium fluoride in diglyme were heated with a molar excess of pentafluoropyridine in a sealed tube at 150° for 3 days. It was hoped that the higher reaction temperature, longer reaction time, and the excess of pentafluoropyridine would promote the formation of perfluoro-(4-pyridyloxydiphenylmethane). It was also of interest to see what the effect of changing the relative amounts of caesium fluoride and decafluorobenzophenone would be. By triturating the reaction product with water a brown solid was obtained. Fractional sublimation of this solid at 0·01 mm. yielded decafluorobenzophenone at 70° and a white solid reaction product at 130°. After recrystallisation of the sublimate collected at 70°, its mass and infrared spectra were identical with an authentic sample of decafluorobenzophenone. After recrystallisation of the sublimate collected at 130° a white solid, m. range 186-214° was obtained, which after further recrystallisation had m.p. 216°, whose mass and infra-red spectra were different from the spectra of pure decafluorobenzophenone and the product obtained from the first attempted preparation of perfluoro-(4-pyridyloxy-diphenylmethane). The infrared spectrum bore some similarity to that of decafluorobenzophenone but contained additional absorptions at 8·7 - 9·5 microns, instead of a sharp absorption at 9·0

microns, suggesting an ether linkage and at 7·6 to 8·0 microns suggesting aliphatic fluorine. The mass spectrum of the solid contained the following peaks at the highest mass numbers, whose compositions were established by accurate mass measurement. The possible structures of these peaks are shown in the table below.

Mass Number	Composition	Possible structure
510	$C_{19}F_{14}O^+$	
491	$C_{19}F_{13}O^+$	
343	$C_{13}F_9O^+$	$^+C_6F_4CC_6F_5$ (O)
340	$C_{13}F_8O_2^{+\cdot}$	$\cdot OC_6F_4CC_6F_4^+$ (O)

The base peak of the spectrum occurred at 195 mass units and was shown by accurate mass measurement to have the composition $C_7F_5O^+$, the probable structure of this ion being $C_6F_5C{\equiv}O^+$. Although the first mass spectrum did not possess a molecular ion, determination of a second mass spectrum using the spectrometer under conditions of maximum sensitivity allowed the detection of a minute molecular peak at 724 mass units. There

were no peaks detected above this peak up to 1,000 mass units. The n.m.r. spectrum consisted of complex multiplets at 144·3, 148·6, 161·7 and 164·6 p.p.m. upfield from $CFCl_3$. The carbon and fluorine analyses and mass spectral measurements are consistent with a composition $C_{26}F_{20}O_2$ for the reaction product. The formation of this compound would arise by addition of caesium fluoride across the carbonyl group of decafluorobenzophenone to yield caesium perfluorodiphenylmethoxide which would then react with unchanged decafluorobenzophenone to yield 1-pentafluorobenzoyl-4-perfluoro-(diphenylmethoxy)-tetrafluorobenzene, assuming that decafluorobenzophenone suffered fluorine displacement in the 4-position:-



It has not been found possible to interpret the n.m.r. spectrum of the product ether, but its surprisingly small number of peaks together with their great complexity suggest the values of the chemical shifts of a number of fluorine atoms in different environments are equivalent. The melting point range of the compound at first suggested that it was a mixture of isomers or a mixture of mono and disubstituted compounds formed by the reaction of two molecules of caesium perfluorodiphenylmethoxide with decafluorobenzophenone, but further recrystallisation yielded a solid of sharp m.p. The simplicity of the n.m.r. spectrum, and the fact that no disubstituted ether or unreacted decafluorobenzophenone were detected in

the mass spectrum suggest that the product ether arises from the reaction of a molecule of caesium perfluorodiphenylmethoxide with decafluorobenzophenone, most probably in the 4-position, although this has not been proven conclusively.

The critical factor, that would explain the difference in the results of the two experiments, seems to be the relative amounts of caesium fluoride and decafluorobenzophenone. In the first experiment an excess of caesium fluoride could have ensured that all the decafluorobenzophenone was converted into caesium perfluorodiphenylmethoxide, which then reacted with the pentafluoropyridine. This assumes that the unreacted caesium perfluorodiphenylmethoxide on hydrolysis with water reverts to decafluorobenzophenone. In the second experiment the equimolar proportion of caesium fluoride could have caused part of the decafluorobenzophenone to be converted into caesium perfluorodiphenylmethoxide, which then reacted preferentially with unchanged decafluorobenzophenone rather than pentafluoropyridine. This may seem surprising in view of the known reactivity of pentafluoropyridine. However, decafluorobenzophenone seems to be highly activated towards nucleophilic substitution. This is illustrated in qualitative fashion in the preparation of decafluorobenzophenone by reaction of two molecules of pentafluorophenyl-lithium with one molecule of dimethyl carbonate. If the reaction product

$$2C_6F_5Li + CH_3OCOCH_3 \longrightarrow C_6F_5CC_6F_5 + 2CH_3OLi$$
(O)

is allowed to warm to room temperature before hydrolysis, an appreciable proportion of 2-methoxynonafluorobenzophenone is also obtained by reaction between the product and lithium methoxide.[86]

A stock of octafluoroacetophenone was prepared so as to study its reaction with pentafluoropyridine and caesium fluoride. Octafluoroacetophenone had been previously been prepared by reaction of pentafluorophenyl magnesium iodide in ether at room temperature with lithium trifluoroacetate or in poorer yield with trifluoroacetic anhydride.[87] It had also been prepared by reaction of trifluoroacetaldehyde with pentafluorophenyl magnesium bromide in ether at reflux temperature, the resulting secondary alcohol being oxidised by chromic oxide in acetic acid.

$$CF_3\underset{\underset{O}{\|}}{C}H + C_6F_5MgBr \longrightarrow C_6F_5\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}CF_3 \xrightarrow{CrO_3} C_6F_5COCF_3$$

In this work the octafluoroacetophenone was prepared by the reaction of pentafluorophenyl-lithium with ethyl trifluoroacetate in ether/hexane solution at -55°. The hydrolysis of the reaction mixture was carried out at a low temperature to prevent possible reaction of lithium ethoxide with the octafluoroacetophenone. The product was obtained in 50% yield,

$$C_6F_5Li + CF_3\underset{\underset{O}{\|}}{C}OC_2H_5 \longrightarrow C_6F_5\underset{\underset{O}{\|}}{C}CF_3 + C_2H_5OLi$$

but almost half the pentafluorobenzene was recovered unreacted. The yield would probably have been improved with a longer reaction time.

The previously unknown ketone, n-perfluorobutyrophenone was prepared in 50% yield by a similar method using ethyl n-perfluorobutyrate instead of ethyl trifluoroacetate. Once again, unreacted pentafluorobenzene

$$C_6F_5Li + CF_3CF_2CF_2\underset{\underset{O}{\|}}{C}OC_2H_5 \longrightarrow C_6F_5\underset{\underset{O}{\|}}{C}CF_2CF_2CF_3 + C_2H_5OLi$$

was recovered, so that the yield was not optimal. After the ketone was prepared, two different methods of preparation of this compound appeared in the literature.[89] One method was analogous to a method already used for octafluoroacetophenone:-

$$CF_3CF_2CF_2\underset{\underset{O}{\|}}{C}H + C_6F_5MgBr \longrightarrow C_6F_5\underset{OH}{\overset{H}{C}}CF_2CF_2CF_3$$

$$C_6F_5\underset{OH}{\overset{H}{C}}CF_2CF_2CF_3 \xrightarrow{CrO_3} C_6F_5\underset{\underset{O}{\|}}{C}CF_2CF_2CF_3$$

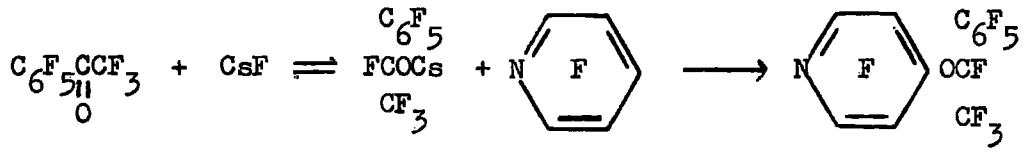
The most promising synthesis of this compound was the reaction of pentafluorophenyl magnesium bromide with n-perfluorobutyryl chloride in ether at room temperature followed by acid hydrolysis. Unfortunately

$$C_6F_5MgBr + CF_3CF_2CF_2\underset{\underset{O}{\|}}{C}Cl \longrightarrow C_6F_5\underset{\underset{O}{\|}}{C}CF_2CF_2CF_3 \qquad (66\%)$$

time was not available to study fluoride ion initiated reactions with n-perfluorobutyrophenone.

Evidence for the preparation of 4-nonafluoro-α-phenylethoxy-tetrafluoropyridine in low yield by the fluoride ion initiated reaction of octafluoroacetophenone with pentafluoropyridine was found, and the yield

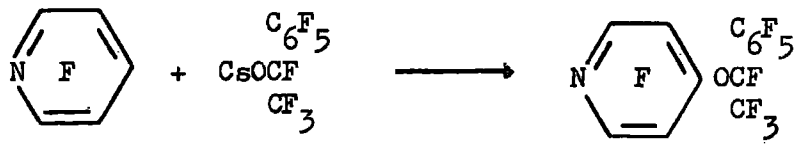
of reaction product was subsequently improved.



The earliest attempts to prepare 4-nonafluoro-α-phenylethoxy-tetrafluoropyridine by heating equimolar amounts of octafluoroacetophenone, caesium fluoride and pentafluoropyridine in diglyme in a sealed tube at 100° for 7 days, or by heating equimolar amounts of octafluoroacetophenone and caesium fluoride and a molar excess of pentafluoropyridine in diglyme in a flask with stirring at 100° for 1½ days, resulted in 3% and 6% yields respectively of the product ether. The difficulties found in the first experiment were lack of agitation of the heterogeneous mixture, which probably resulted in the formation of a surface coating of caesium nonafluoro-α-phenylethoxide on the caesium fluoride, which retarded complete formation of the caesium alkoxide, and insolubility of the caesium alkoxide once it was formed. Incomplete conversion of caesium fluoride and hexafluoroacetone to caesium heptafluoroisopropoxide in diglyme occurred unless the mixture was properly agitated. A disadvantage of using diglyme in the second experiment was that the pentafluoropyridine refluxed out of the reaction mixture. The product was isolated by washing the reaction mixture with water, drying the fluorocarbon layer and isolating the ether from this layer by distillation under reduced pressure. It was found difficult to rid the reaction product of diglyme by washing it with water because of the high mutual solubility of the

product ether and the solvent. Purification of the reaction mixture by distillation was complicated by the co-distillation of the diglyme with the reaction product, as well as its own high boiling point. Monoglyme and acetonitrile were found to be more satisfactory than diglyme. The solvents needed to be scrupulously dry. The monoglyme was dried by distillation from potassium and redistilled from lithium aluminium hydride shortly before use. The acetonitrile was dried by distillation from phosphorus pentoxide and the distillate was refluxed with stirring with calcium hydride for 2 days before being redistilled and stored over calcium hydride.

Equimolar amounts of octafluoroacetophenone and pentafluoropyridine and somewhat less than an equimolar quantity of caesium fluoride in dry monoglyme were heated with stirring at 100° for 6¾ days. 4-Nonafluoro-α-phenylethoxy-tetrafluoropyridine was isolated from the reaction mixture in 17% yield. No disubstituted product was isolated, as was found with the reaction of equimolar amounts of pentafluoropyridine and potassium pentafluorophenate.



The formation of 2,4-bis(nonafluoro-α-phenylethoxy)-trifluoropyridine in good yield, important for the synthesis of a polymer, either by reaction of pentafluoropyridine with twofold molar amounts of caesium fluoride and

octafluoroacetophenone, or by reaction of equimolar amounts of 4-nonafluoro-α-phenylethoxy-tetrafluoropyridine, octafluoroacetophenone and caesium fluoride, would be prevented if the caesium nonafluoro-α-phenylethoxide reacted preferentially with the equilibrium concentration of octafluoro- rather than at the 2-position of 4-nonafluoro-α-phenylethoxy-tetrafluoropyridine. Consequently, the self-condensation of octafluoroacetophenone and the attempted preparation of 2,4-bis(nonafluoro-α-phenylethoxy)-trifluoropyridine were studied. Caesium fluoride and a twofold molar amount of octafluoroacetophenone in dry acetonitrile on heating with stirring at 95° for 7½ days afforded 4-nonafluoro-α-phenylethoxy-heptafluoroacetophenone in 9% yield.

$$C_6F_5\overset{F}{\underset{CF_3}{C}}COCs + C_6F_5\overset{}{\underset{O}{C}}CF_3 \longrightarrow 4\text{-}C_6F_5\overset{F}{\underset{CF_3}{C}}OC_6F_4\overset{}{\underset{O}{C}}CF_3 + CsF$$

Caesium fluoride and a threefold molar quantity of octafluoroacetophenone in dry acetonitrile were also heated with stirring at 95° for 14 days. It was hoped that the following reaction would occur:-

$$3C_6F_5\overset{}{\underset{O}{C}}CF_3 + CsF \longrightarrow C_6F_5\overset{F}{\underset{CF_3}{C}}OC_6F_4\overset{F}{\underset{CF_3}{C}}OC_6F_4\overset{}{\underset{O}{C}}CF_3$$

However, work-up of the reaction mixture yielded only 4-nonafluoro-α-phenylethoxy-heptafluoroacetophenone and unreacted octafluoroacetophenone.

The preparation of 2,4-bis(nonafluoro-α-phenylethoxy)-trifluoropyridine was attempted by reacting pentafluoropyridine with twofold molar amounts of caesium fluoride and octafluoroacetophenone in dry

acetonitrile with stirring at 95° for 14 days. Work-up of the reaction product yielded a mixture of 4-nonafluoro-α-phenylethoxy-tetrafluoropyridine and 4-nonafluoro-α-phenylethoxy-heptafluoroacetophenone as indicated by the infra-red and mass spectra of the product. This shows that caesium nonafluoro-α-phenylethoxide reacts preferentially with the equilibrium concentration of octafluoroacetophenone rather than at the 2-position of 4-nonafluoro-α-phenylethoxy-tetrafluoropyridine.

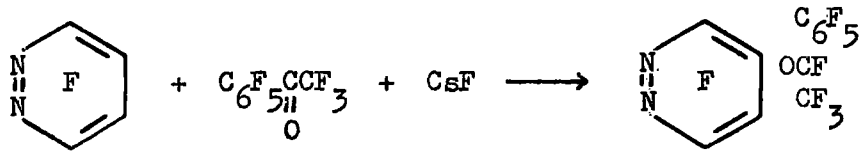
Benzyl heptafluoroisopropyl ether[85] has been prepared in approximately 60% yield by the reaction of potassium heptafluoroisopropoxide in diglyme with benzyl bromide at room temperature for 24 hours. By carrying out a similar reaction using caesium nonafluoro-α-phenyl ethoxide, it was possible to compare the reactivity of this salt with that of potassium heptafluoroisopropoxide. Consequently, equimolar amounts of caesium fluoride, octafluoroacetophenone and benzyl bromide in acetonitrile were heated under reflux for $1\frac{1}{2}$ days. A separate experiment using the same amounts of material was heated at 95° for $3\frac{3}{4}$ days. Benzyl nonafluoro-α-phenylethyl ether was obtained from both reactions in 30% yield.

$$C_6H_5CH_2Br + CsF + C_6F_5\overset{\overset{O}{\|}}{C}CF_3 \longrightarrow C_6H_5CH_2O\overset{C_6F_5}{\underset{CF_3}{C}}F$$

These experiments indicate that caesium nonafluoro-α-phenylethoxide is present in large enough concentrations at 95° to react in fair yield with a substrate more reactive than pentafluoropyridine. However, potassium heptafluoroisopropoxide seems to be a more reactive nucleophile than

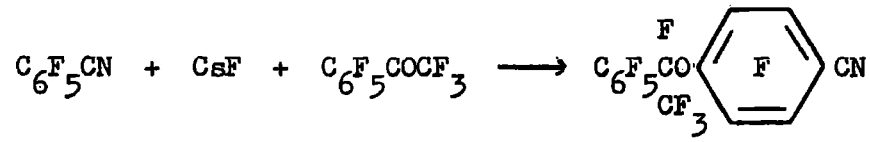
caesium nonafluoro-α-phenylethoxide, unless it is that the higher reaction temperature causes the caesium salt to dissociate thus reducing its concentration.

It was hoped that reaction of caesium nonafluoro-α-phenylethoxide with a fluorinated compound more reactive than pentafluoropyridine would proceed in reasonable yield. Tetrafluoropyridazine[90] is much more reactive than pentafluoropyridine and disubstitution should occur more easily.



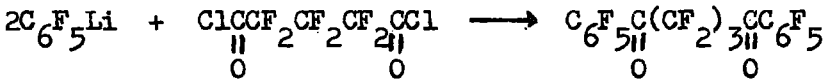
Equimolar amounts of caesium fluoride, octafluoroacetophenone and tetrafluoropyridazine in dry monoglyme were stirred at room temperature for 4 hours and then at 60° for 41 hours. Work-up of the reaction product without contact with water gave a 7·2% yield of the liquid, nonafluoro-α-phenylethoxy-trifluoropyridazine. The analysis, infrared and mass spectra were in agreement with the suggested structure. The yield of ether was low, considering the increased reactivity of tetrafluoropyridazine, but was probably not optimal.

The reaction of equimolar quantities of pentafluorobenzonitrile, caesium fluoride and octafluoroacetophenone in acetonitrile at 95° for 7 days gave a reaction product in 10% yield, whose identity has not been established. The reaction product is suspected to be.



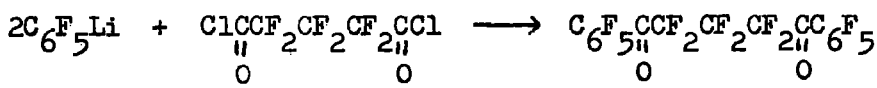
4-nonafluoro-α-phenylethoxy-tetrafluorobenzonitrile, although this has not been established beyond doubt.

It was of interest to react a perfluorinated diketone with caesium fluoride and a suitably activated substrate in order to form a diether. This would be an important step towards the synthesis of a polymer. The high boiling diketone, 1,3-bispentafluorobenzoyl-hexafluoropropane, was prepared by the reaction of a molar excess of pentafluorophenyl-lithium with perfluoroglutaryl chloride in mixed ether and hexane solvent at -65°. Although the material had a suitable mass spectrum and analysis, g.l.c. showed the presence of a small amount of unidentified impurity of



similar volatility. It was not found to be possible to purify the diketone by redistillation.

Attempted preparation of 1,3-bispentafluorobenzoyl-hexafluoropropane on a larger scale gave a strange and interesting result. A mixture of 1-hydroxy-1,1-bispentafluorophenyl-4-pentafluorobenzoylhexafluoro-n-butane and (γ-pentafluorobenzoyl-n-hexafluoropropyl)-nonafluorobiphenyl ketone was obtained instead of the expected 1,3-bispentafluorobenzoyl-n-hexafluoropropane.

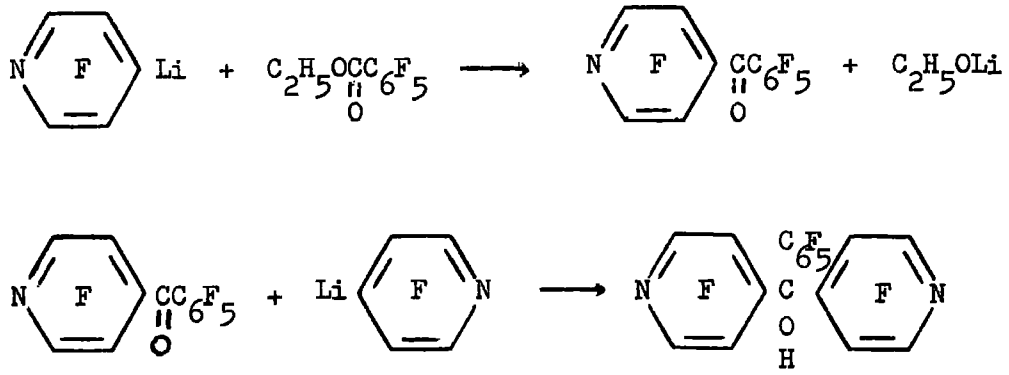


$$C_6F_5\overset{\overset{O}{\|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}C_6F_5 + C_6F_5Li \longrightarrow C_6F_5\overset{\overset{O}{\|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}C_6F_4C_6F_5$$

$$+ (C_6F_5)_2\overset{\overset{OH}{|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}C_6F_5$$

These products were formed by the reaction of an excess of pentafluorophenyl-lithium with 1,3-bispentafluorobenzoyl-hexafluoro-n-propane. The only explanation for the large excess of pentafluorophenyl-lithium being in the reaction mixture was the presence of impurity in the perfluoroglutaryl chloride, probably formed by its hydrolysis by traces of moisture. The reaction products were separated by trituration of the semi-solid reaction product mixture with acetonitrile in which the diketone reaction product was sparingly soluble. The diketone comprised about 30% of the reaction product.

Tris(pentafluorophenyl)carbinol has been prepared in 72% yield by the reaction of pentafluorophenyl-lithium with decafluorobenzophenone in n-hexane solution at -78°, or in 60% yield, by reaction of pentafluorophenyl-lithium with ethyl pentafluorobenzoate at -65°, or in better than 50% yield by the reaction of diethyl carbonate with 3 equivalents of pentafluorophenyl-lithium at -25°.[91] In these reactions no product was formed by nucleophilic attack by pentafluorophenyl-lithium on the aromatic ring of decafluorobenzophenone, but only reaction of the lithium reagent at the carbonyl group to give the tertiary alcohol. In the reaction investigated by the author, discussed earlier and illustrated below, attack on the pentafluorophenyl-4-tetrafluoropyridyl ketone, formed in situ,



by 4-tetrafluoropyridyl-lithium gave the carbinol. No nucleophilic displacement of fluorine in either aromatic ring was detected.

The difference of behaviour of 1,3-bispentafluorobenzoyl-hexafluoro-n-propane on reaction with pentafluorophenyl-lithium could be the result of a $C_6F_5CO(CF_2)_3CO$ group activating a pentafluorophenyl ring to such an extent that nucleophilic displacement of ring fluorine by pentafluorophenyl-lithium becomes competitive with reaction at the carbonyl group to give the tertiary alcohol.

(γ-Pentafluorobenzoyl-n-hexafluoropropyl)-nonafluorobiphenyl ketone was reacted with twofold molar proportions of pentafluoropyridine and caesium fluoride in acetonitrile at 95° for 14 days. Only unreacted starting materials were obtained. It was hoped that the reaction illustrated below would occur:-

$$2C_5F_5N + C_6F_5C(=O)(CF_2)_3C(=O)C_6F_4C_6F_5 \xrightarrow{2CsF} NC_5F_4OC(C_6F_5)(C_6F_4C_6F_5)(CF_2)_3COC_5F_4N$$

At the start of this work the only report of the formation of a metal perfluoroalkoxide was the preparation of caesium trifluoromethoxide

by the reaction of carbonyl fluoride with caesium fluoride in acetonitrile.[92] A number of publications concerned with the formation of metal perfluoroalkoxides and their synthetic uses have since appeared. A study of the reaction of hexafluoroacetone with different metal fluorides in acetonitrile has been studied.[93] Adducts were prepared

$$MF + CF_3CCF_3 \xrightarrow{CH_3CN} FCOM \qquad M = Cs, K, Ag \text{ and } (C_2H_5)_4N$$

from CsF, KF, AgF and $(C_2H_5)_4NF$ while none was formed from NaF, LiF, ZnF_2, MgF_2, CuF_2 and BeF_2. These results were interpreted in terms of the lattice energies of the salts. In the alkali metal fluoride series, LiF and NaF, that have large lattice energies, were found to be unable to form adducts, whereas the others did yield adducts. Also, the stability of the adduct decreased with increasing lattice energy, the CsF adduct being more stable than the KF adduct. Silver fluoride formed an adduct in acetonitrile, even though its lattice energy is greater than that of sodium fluoride. This was thought to be due to the complexing of silver ions with acetonitrile, which made the solvation energy in this solvent higher than the solvation energy of the alkali metal fluorides.

A solvent which had a high heat of formation for the adduct favoured formation of the adduct. Hexafluoroacetone formed an adduct with potassium fluoride in many aprotic solvents e.g. dimethyl formamide, sulpholane, diglyme, dimethoxyethane and butyrolactone. In nitrobenzene

and 3-methyl sulphone hexafluoroacetone formed an adduct only with caesium fluoride whilst in a non-polar solvent e.g. benzene, no adduct formation occurred.

The ketones CF_3COCF_2Cl, $(CF_2Cl)_2CO$ and $CF_2ClCOCFCl_2$ formed adducts as shown by the preparation of a derivative. The reactivity of the ketone was shown to decrease with increasing chlorine content as $CF_2ClCOCFCl_2$ formed an adduct only with CsF and not with KF. The adduct with $(CFCl_2)_2CO$ probably had some stability, but $CFCl_2COCCl_3$ to hexachloroacetone would not form adducts. Perfluoroalicyclic ketones formed adducts slowly. A more rapid method for forming cyclic alkoxides was to treat the fluorosulphonate esters with potassium fluoride in a suitable solvent e.g. diglyme at room temperature.[85]

$$\overbrace{(CF_2)_n}CFOSO_2F + KF \longrightarrow \overbrace{(CF_2)_n}CFOK + SO_2F_2$$

n = 3, 4 or 5

The acid fluorides COF_2,[85,92] CF_3COF,[83,85,94-96] C_2F_5COF,[83,95] $CF_3CF_2CF_2COF$,[83] $(CF_3)_2CFCOF$,[95] $ClCF_2COF$,[94] $BrCF_2COF$,[94] ICF_2COF[97] have been shown to give adducts by their isolation from the solvent in which they were prepared, or by their reaction with another compound to give a derivative. The diacid fluorides $(COF)_2$[95] and $CF_2(CF_2COF)_2$[98] were shown to give bifunctional alkoxides by the formation of a derivative.

Fluoro-oxyanions have been found to react readily with acyl halides to yield esters, but these reactions have been found to have a

characteristic side reaction in which the acyl halogen is replaced by fluorine. The general reaction is illustrated by the equation:

$$RCCl + R_fOK \longrightarrow RCOR_f + KCl$$

R = CH_2=CH-; R_f = $(CF_3)_2CF$,[99] $(CF_2Cl)_2CF$,[99] C-C_5F_7,[100] C-C_6F_{11}.

R = CH_2=C(CH_3)-,[99] CH_3,[85] C_2H_5,[99] C_6H_5;[85] R_f = $(CF_3)_2CF$.

R = CH_3,[85] C_6H_5;[85] R_f = C-C_4F_7.

Where R_f = $(CF_2Cl)_2CF$[99] caesium fluoride was used instead of potassium fluoride. The yield of ester was generally better than 50%. A number of the reactions were carried out successfully at room temperature, although in some instances acyl fluoride formation was so extensive that none of the ester was obtained. In such cases, the reaction was begun at low temperatures and allowed to warm only to 0°. Diglyme was usually used as solvent, although other solvents such as acetonitrile were employed successfully. Sulphonyl chlorides behaved in a similar fashion to acyl chlorides in their reactivity towards fluoroanions.[85] Low reaction temperatures were necessary for a good yield of ester.

$$RSO_2Cl + R_f\text{-}OK \xrightarrow{\text{diglyme}} RSO_2OR_f$$

R = C_6H_5, CH_3 $\qquad$ R_f = $(CF_3)_2CF$

R = C_6H_5 $\qquad$ R_f = C-C_4F_9

The origin of the acid fluoride side products in these reactions was thought to be due to the reaction of the product esters with potassium fluoride,[85,99] e.g.

$$R\text{-}\overset{O}{\overset{\|}{C}}OR_f + KF \rightleftharpoons R\text{-}\overset{OK}{\overset{|}{C}}\text{-}OR_f \rightleftharpoons \overset{O}{\overset{\|}{R\text{-}C}}F + R_fOK \rightleftharpoons \text{ketone} + KF$$

Fluoroalkoxides react in an analogous manner to hydrocarbon alkoxides to form ethers, but they are less reactive than hydrocarbon alkoxides. The general reaction is illustrated by the equation:

$$RBr + R_fOK \longrightarrow ROR_f + KBr$$

$R = C_6H_5CH_2$,[85] CH_3,[85] $n\text{-}C_3H_7$,[85] $i\text{-}C_3H_7$,[85] $BrCH_2CH_2$,[101] $ClCH_2CH_2$,[101] $CH_2CO_2CH_3$.[102] $R_f = (CF_3)_2CF$

$R = n\text{-}C_3H_7$,[85] $C_6H_5CH_2$[85] $R_f = C\text{-}C_4F_7$

$R = C_6H_5CH_2$[85] $R_f = C_2F_5$, $C\text{-}C_5F_9$

$R = CH_2{=}CHCH_2$[101] $R_f = (CF_3)_2CF$, $(CF_3)(CF_2Cl)CF$, $(CF_2Cl)_2CF$.

Where R = $(CF_3)(CF_2Cl)CF$ and $(CF_2Cl)_2CF$,[101] caesium fluoride was used instead of potassium fluoride. The yield of ether was usually better than 50%. Benzyl bromide reacted readily at room temperature,[85] but in general these displacement reactions require temperatures of 50 to 90° for 12 to 20 hours. This is in contrast to the relatively short reaction time required for hydrocarbon alkoxides. The following reaction was also carried out:-[85]

$$(CF_3)_2CFOCH_2CH_2Br + (CF_3)_2CFOK \xrightarrow[95^\circ]{CH_3CN} (CF_3)_2CFOCH_2CH_2OCF(CF_3)_2$$

80 hrs. (40%)

Either diglyme or acetonitrile were used as solvents in these reactions.

A difficulty found in the synthetic use of metal perfluoroalkoxides was that they could easily lose metal fluoride, which then underwent a halogen exchange reaction with regeneration of the carbonyl compound.[103]

$$(CF_3)_2CFO^- + (CH_3)_3SiCl \longrightarrow (CF_3)_2C{=}O + (CH_3)_3SiF + Cl^-$$

$$(CF_3)_2CFO^- + R_fCOCl \longrightarrow (CF_3)_2C{=}O + R_fCOF + Cl^-$$

This prevents the formation of perfluorinated esters, but is of some value for preparing fluorides from other halides.

Perfluoroepoxides have been used for alkoxide formation, e.g., perfluoropropylene oxide and caesium fluoride in a suitable solvent form caesium n-perfluoropropoxide.[104] Perfluoroepoxides have been found to react with perfluoroalkoxides in a solvent such as diglyme, e.g.

$$\underset{\diagdown O \diagup}{CF_2CF_2} + C_2F_5OCs \longrightarrow C_2F_5OC_2F_4OCs$$

$$\xrightarrow{\text{heat}} C_2F_5OCF_2\underset{O}{CF}$$

$$C_2F_5OC_2F_4OCs + \underset{\diagdown O \diagup}{CF_2CF_2} \longrightarrow C_2F_5OC_2F_4OC_2F_4OCs$$

$$\longrightarrow C_2F_5O(C_2F_4O)nCF_2COF \qquad n = 1 \text{ to } 4.$$

By using an excess of perfluoroepoxide polyetherperfluoroalkoxides have been formed, which on heating yield the corresponding acid fluoride.[94]

The equations and references given below illustrate the scope of the reaction.

$$XCF_2OCs + \underset{O}{CF_2CF_2} \longrightarrow XCF_2OCF_2COF$$

X = $ClCF_2$, $BrCF_2$.[94]

$$XCF_2OCs + \underset{O}{CF_3CFCF_2} \longrightarrow XCF_2OCF(CF_3)COF$$

X = CF_3,[95,96] ICF_2,[97] C_2F_5,[95] $(CF_3)_2CF$.[95]

$$CsOCF_2CF_2OCs + 2\underset{O}{CF_3CFCF_2} \longrightarrow \overset{CF_3}{\underset{O}{FCCOCF_2CF_2OCCF}}\overset{CF_3}{\underset{O}{\|}\quad\|}F \quad [95]$$

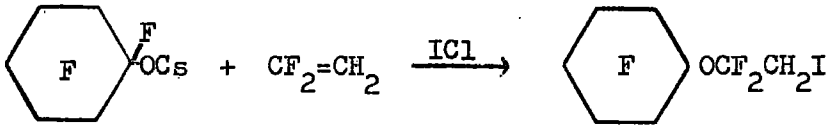
$$CsO(CF_2)_5OCs + 2\underset{O}{CF_3CFCF_2} \longrightarrow \overset{CF_3}{\underset{O}{FCCO(CF_2)_5OCCF}}\overset{CF_3}{\underset{O}{\|}\quad\|}F \quad [98]$$

Reaction of the adduct of a perhalogenated carbonyl compound and a metal fluoride with an olefin in the presence of a halogen in a suitable solvent was found to form a fluorinated ether as shown in the equation:-[105]

$$\rangle C{=}C\langle + X_2 + R_fO^- \longrightarrow R_fO\overset{|}{C}-\overset{|}{C}-X + X^-$$

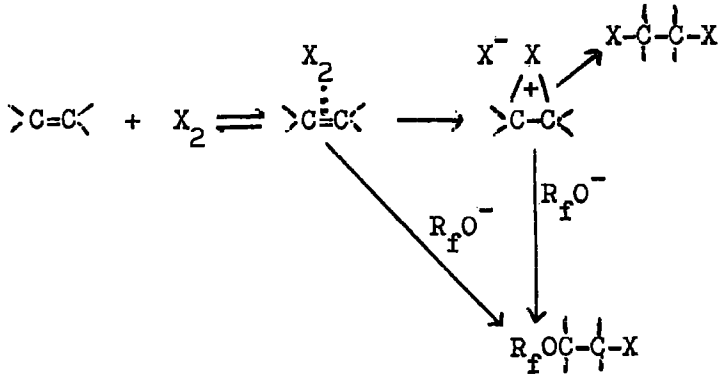
Non-fluorinated and fluorinated olefins, perfluorinated ketones and acid fluorides and chlorofluorosubstituted ketones, iodine, iodine monochloride, bromine and chlorine have all been used successfully as reactants in the preparation of various iodides, bromides and chlorides. Acetonitrile was found to be the best solvent. The equations below illustrate the scope of the reaction:-

$$\begin{matrix} CF_2Cl \\ FCOK \\ CF_3 \end{matrix} + CF_2{=}CF_2 \xrightarrow{I_2} \begin{matrix} CF_2Cl \\ FCOCF_2CF_2I \\ CF_3 \end{matrix}$$



$$\begin{matrix} CF_3 \\ FCOK \\ CF_3 \end{matrix} + CH_2{=}CH_2 \xrightarrow{I_2} \begin{matrix} CF_3 \\ FCOCH_2CH_2I \\ CF_3 \end{matrix}$$

It was suggested that the fluorinated alkoxide reacted in a modified halohydrin reaction with an "olefin-halogen complex" which, depending on the structure of the olefin could be a π complex, a halonium ion, or a carbonium ion. Alternatively, this ion pair could collapse to form the dihalogenated olefin or attack the solvent to give a variety of side reaction products. With fluoro-olefins iodine and iodine monochloride would probably only produce a π complex. This species apparently



reacted rapidly with anions but was too stable to attack the weak basic

acetonitrile. With non-fluorinated olefins, the initial π-complex broke down to an ion pair which involved a halonium ion. Attack of the highly reactive halonium ion on the perfluoroalkoxide ion, on the solvent, or on a halide ion then occurred to give the products found.

Perfluorinated aliphatic ketones and acid fluorides have thus formed a variety of adducts with potassium and caesium fluoride that have been successfully used in reactions with reactive acid halides and alkyl halides. This study extends the synthetic usefulness of these adducts to aryl, alkyl and diaryl ketones. It should be possible to obtain useful yields of monosubstituted heptafluoroisopropyl ethers from polyfluoroaromatic and heterocyclic compounds more reactive than pentafluoropyridine, if great care is taken to ensure purity of the caesium fluoride and dryness of the reagents. The reaction of hexafluoroacetone with caesium fluoride and pentafluoropyridine would merit further investigation. A great difficulty in the synthesis of these compounds would be the probable ease of displacement of a heptafluoroisopropyl group by fluoride ion, the reaction being probably more easily reversible than the displacement of pentafluorophenoxide ion from 4-cyanononafluorodiphenyl ether. A disadvantage of using these metal fluoride-hexafluoroacetone adducts compared with, e.g. potassium perfluoro-t-butoxide is the disproportionation of the metal perfluoroisopropoxide with increasing reaction temperature.

It is not certain that decafluorobenzophenone and octafluoro-

acetophenone form adducts that are insoluble in dipolar aprotic solvents, or that the alkoxides are just formed in low concentration, the caesium fluoride being mainly unchanged. There is, however, a change in the crystalline appearance of the caesium fluoride. The ease of formation and reactivity of these adducts seems to follow the order

$$CF_3\underset{\underset{O}{\|}}{C}CF_3 > CF_3\underset{\underset{O}{\|}}{C}F > C_6F_5\underset{\underset{O}{\|}}{C}CF_3 > C_6F_5\underset{\underset{O}{\|}}{C}C_6F_5$$

A disadvantage of using decafluorobenzophenone and octafluoroacetophenone in fluoride ion reactions is their possible self-condensation instead of reaction with another substrate. Compounds more reactive towards nucleophilic substitution than octafluoroacetophenone or decafluorobenzophenone could only be used successfully. An interesting ketone to study fluoride ion initiated reactions upon would be 4-tetrafluoropyridyl-trifluoromethyl ketone. Self condensation of the ketone could well be less favourable, as the 2-position in the pyridine ring would be less reactive than the 4-position in octafluoroacetone towards nucleophilic substitution. The ketone may well form a more stable and reactive adduct than octafluoroacetophenone. A study of the nucleophilic substitution reactions of fluorinated heterocyclic ethers derived from the metal salts of primary and secondary perfluorinated alcohols would probably yield some interesting results.

SECTION 3.

Experimental Work

The Reaction of Hexafluoroacetone, Caesium Fluoride and Pentafluoropyridine in Diglyme

Caesium fluoride (3·2 g., 21·1 m.mole), hexafluoroacetone (4·7 g., 28·3 m.mole) and pentafluoropyridine (4·5 g., 26·6 m.mole) were sealed in a tube. On shaking the tube at room temperature the caesium fluoride dissolved to give a clear solution of caesium heptafluoroisopropoxide. The tube was then heated to 100° for 7 days. The contents of the tube were poured into water (90 ml.). The lower fluorocarbon layer was removed and washed 3 times with 7 ml. portions of water, dried ($MgSO_4$) and distilled under reduced pressure (0·01 mm.) to give 2 fractions:- (1) 20 - 75°, 4·0 g., (2) 75 - 145°, 0·5 g. The mass spectrum of fraction (1) had a peak of small intensity at 335 mass units that corresponded to the molecular weight of 4-heptafluoroisopropoxy-tetrafluoropyridine. There was a fragmentation peak of large intensity at 316 mass units due to fluorine loss from the molecular ion.

The v.p.c. of fraction (1) showed that it contained two new reaction products together with a third component shown to be diglyme. The more volatile of the reaction products predominated. Infra-red spectrum ($cm.^{-1}$): 2900m, 1460s, 1250-1200s, 1150-1050s, 1000-950s, 730w. ^{19}F n.m.r. spectrum (peaks upfield from $CFCl_3$ with their relative areas in brackets):- 65·8(20), 70·4(44), 72·4(30), 80·4(27), 93·5(12), 157·5(15). The mass spectrum of fraction (1) contained a peak of

small intensity at 335 mass units that corresponded to the molecular weight of heptafluoroisopropoxy-tetrafluoropyridine. There was a fragmentation peak of large intensity at 316 mass units due to fluorine loss from the molecular ion.

The v.p.c. of fraction (2) contained the same component as fraction (1) but the less volatile reaction product predominated. The infra-red spectrum of fraction (2) was similar to that of fraction (1). ^{19}F n.m.r. spectrum (peaks upfield from $CFCl_3$ with their relative areas in brackets):- 71·7(1), 78·4(2·8), 80·9(12·3), 86·3(2·5), 92·0(2·5), 155·3(2). The mass spectrum of fraction (2) contained the peaks found in the spectrum of fraction (1) and in addition peaks at 342, 389, 412, 445, 463, 480 mass units. Fractions (1) and (2) are provisionally considered to be mixtures of heptafluoroisopropoxy-tetrafluoropyridine, bis(heptafluoroisopropoxy)-trifluoropyridine and diglyme.

Attempted Preparation of 4-Heptafluoroisopropoxy-tetrafluoropyridine.

Four tubes containing pentafluoropyridine, hexafluoroacetone, caesium fluoride and diglyme were heated to 95° for 7 days. The quantities of the reagents contained in the tubes are shown below.

	Tube 1	Tube 2	Tube 3	Tube 4
diglyme ml.	20	20	40	20
C_5F g.	2·3	3	3·2	2·6
C_5F_5N g.	2·5	3·4	4·5	2·6
CF_3COCF_3 g.	2·9	4·2	4·7	3·0

The contents of the tubes became dark red in appearance. The reaction mixture was poured into water (400 ml.). The lower fluorocarbon layer was removed with a teat pipette, placed in a tap funnel and washed seven times with 50 ml. portions of water, dried ($MgSO_4$) and distilled to remove unreacted pentafluoropyridine (0·7 g.).

The residue was distilled under reduced pressure (15 mm.) using a fractionating column 10 cm. long filled with glass helices to yield two fractions:-

(a) 2·28 g., b.pt. 50°, collected over a range 45-50°.

(b) 5·82 g., b.pt. 84°, collected over a range 55-84°.

Some residual liquid remained in the distillation flask. Vapour phase chromatography showed that fraction (a) contained a single compound which was not pure 4-heptafluoroisopropoxy-tetrafluoropyridine.

Fraction (b) contained approximately equal amounts of the compound found in fraction (a) and a compound whose retention time was similar to that of diglyme. The examination of fraction (a) is described in the discussion of the experimental.

Accurate mass measurements determined for fraction (a):-

387·9722; 370·0310; 357·9952; 349·9307; 320·0304; 206·0236.

<u>The Reaction of Hexafluoroacetone, Caesium Fluoride and Pentafluorobenzonitrile in Acetonitrile.</u>

Caesium fluoride (1·5 g., 10 m.mole), hexafluoroacetone (2·3 g., 14 m.mole) and pentafluorobenzonitrile (1·9 g., 10 m.mole) were heated

in a sealed rotating nickel tube at 95° for 14 days. The reaction product, isolated by washing the reaction mixture with water, was dried ($MgSO_4$). This material was shown by g.l.c. (silicone grease at 200°) to contain pentafluorobenzonitrile and a small amount of a new reaction product. The mass spectrum contained a peak corresponding to the molecular ion of pentafluorobenzonitrile but not to the molecular ion of heptafluoroisopropoxy-tetrafluorobenzonitrile. The spectrum contained a peak at M/e 314 which was probably formed by such a facile loss of FCN from the molecular ion that it was not present in the spectrum. Attempted separation of this mixture was not successful.

Attempted Preparation of Perfluoro-4-pyridyloxydiphenylmethane.

(i) Caesium fluoride (3·0 g., 19·7 m.mole), dry diglyme (40 ml.), decafluorobenzophenone (3·7 g., 10·2 m.mole) and pentafluoropyridine (1·7 g., 10·0 m.mole) were sealed in a tube and heated to 100° for 2 days. The contents of the tube became dark in appearance. The tube was then opened and the contents were poured into water (90 ml.). The lower fluorocarbon layer was removed with a teat pipette, placed in a tap-funnel and washed five times with 7 ml. portions of water, dried ($MgSO_4$) and distilled under reduced pressure (·01 mm.) to a liquid product (b.pt. 120-145°) and a solid that sublimed along with the liquid.

The weight of product was 0·91 g. The examination of this mixture is described in the discussion of the first attempted preparation of perfluoro-4-pyridyloxy-diphenylmethane.

Accurate mass measurement of the m/e 512 peak in the mass spectrum.

Observed Mass	Calculated Mass	Formula
511·9743	511·9755	$C_{18}F_{14}NO$

(ii) Caesium fluoride (1·5 g., 9·9 m.mole), dry diglyme (40 ml.), decafluorobenzophenone (3·7 g., 10·2 m.mole) and pentafluoropyridine (3·4 g., 20·12 m.mole) were sealed in a tube and heated to 150° for 3 days. The tube was then opened and poured into water (90 ml.). A semi-solid oil was precipitated which on trituration solidified. The solid was filtered off and dried. Fractional sublimation of this solid (3·75 g.) at 0·01 mm. yielded:-

(a) decafluorobenzophenone at 70°, 2·18 g., m.pt. 84-89°,

(b) a white solid, 0·34 g., m.pt. 133-189°.

Some dark brown solid remained which could not be sublimed. Recrystallisation of fraction (a) from 40/60° petrol ether yielded pure decafluorobenzophenone m.pt. 91-92°. Recrystallisation of fraction (b) from meths. yielded a solid that slowly softened between 186° to 214°.

Further recrystallisation of this solid from meths. yielded pentafluorobenzoyl-perfluoro-(diphenylmethoxy)-tetrafluorobenzene. (Found: C, 43·0; F, 52·2; M, 724. $C_{26}F_{20}O_2$ requires C, 43·1; F, 52·5%; M, 724), m.p. 216° (i.r. spectrum No. 31).

Accurate mass measurements of ions in the spectrum of pentafluorobenzoyl-perfluoro-(diphenylmethoxy)-tetrafluorobenzene.

Observed Mass	Calculated Mass	Formula
194·9863	194·9869	C_7F_5O
509·9217	509·9725	$C_{19}F_{14}O$
490·9735	490·9741	$C_{19}F_{13}O$
343·9799	342·9805	$C_{13}F_9O$
340·9763	339·9770	$C_{13}F_8O_2$

Preparation of Ethyl Trifluoroacetate.[106]

Trifluoroacetic acid (500 g.) and absolute alcohol (400 g.) were mixed in a flask and refluxed for 1½ hours under a very efficient condenser. The mixture was then distilled, the fraction of boiling point 53-56° being collected. This fraction, which was an azeotropic mixture of ethyl trifluoroacetate, ethanol and water, was washed three times with an excess of water, dried ($CaCl_2$), filtered and distilled to yield ethyl trifluoroacetate (512 g.), b.pt. 59-60°. Ethyl perfluoro-n-butyrate was prepared by a similar method.

Preparation of Octafluoroacetophenone.

Pentafluorobenzene (20 g., 120 mm.) in a mixture of ether (20 ml.) and hexane (20 ml.) was added dropwise to a stirred solution of n-butyl lithium in hexane (56 ml., 120 mm.) and ether (50 ml.) at -55 to -60°. The mixture was stirred for 3½ hrs. at -55 to -60°. This cold solution was then transferred to a dropping funnel cooled to -60 to -70° and added dropwise to a stirred solution of ethyl trifluoroacetate (17 g., 120 mm.) dissolved in ether (20 ml.) and hexane (20 ml.) at -55 to -60°. The mixture was stirred for 2 hrs. at -55° and then allowed to warm up to -20° before being hydrolysed by 2N sulphuric acid (105 ml.). The mixture was

extracted with ether, the extracts dried ($MgSO_4$), filtered and the ether removed by distillation. The residue was distilled yielding pentafluorobenzene (10 g.), b.p. 80-90°, and octafluoroacetophenone (16 g., 50%) (Found: C, 36·3; F, 57·5; M, 264. C_8F_8O requires C, 36·4; F, 57·6%; M, 264), b.p. 132°.

Preparation of n-Perfluorobutyrophenone.

A solution containing n-butyl-lithium in hexane (10 c.c., 2·14 molar) and hexane (6·8 c.c.) was cooled to -55° and treated with pentafluorobenzene (3·59 g., 21·4 m.mole) in diethyl ether (11 ml.). The reaction mixture was stirred for 4 hrs. Ethyl perfluoro-n-butyrate (5·17 g., 21·4 m.mole) in diethyl ether (6·8 c.c.) was added keeping the temperature at -55°. The reaction mixture was stirred for 1½ hours at -55°. Work-up similar to that employed in the preparation of octafluoroacetophenone afforded n-perfluorobutyrophenone (3·9 g., 51%). (Found: C, 33·1; F, 62·4; M, 364. $C_{10}F_{12}O$ requires C, 33·0; F, 62·6%; M, 364), b.p. 166°. (i.r. spectrum No. 32).

Preparation of 4-Nonafluoro-α-phenylethoxytetrafluoropyridine.

Caesium fluoride (1·25 g., 8·2 m.mole), dry monoglyme (20 ml.), octafluoroacetophenone (2·64 g., 10 m.mole) and pentafluoropyridine (1·69 g., 10 m.mole) were heated with stirring under reflux at 100° in a flask protected from moisture by a drying tube for 6¾ days. The contents of the flask became dark brown. The reaction mixture was poured into water (100 ml.). The lower fluorocarbon layer was removed with a teat pipette, dried ($MgSO_4$) and distilled under reduced pressure to give

4-nonafluoro-α-phenylethoxy-tetrafluoropyridine, (0·699 g., 17%). (Found: C, 36·4; F, 57·50; M, 433. $C_{13}F_{13}NO$ requires C, 36·0; F, 57·0%; M, 433), b.p. 68° at 0·4 mm. (i.r. spectrum No. 33)

Preparation of 4-Nonafluoro-α-phenylethoxyheptafluoroacetophenone.

The acetonitrile was dried by distilling it from phosphorus pentoxide and then refluxing it with calcium hydride for 2 days before redistilling it. It was stored over calcium hydride. Caesium fluoride (1·11 g., 7·3 m.mole), octafluoroacetophenone (3·84 g., 14·6 m.mole), and dry acetonitrile were heated with stirring under reflux at 95° in a flask protected from moisture by a drying tube for 7½ days. The mixture was poured into water (200 ml.). The lower fluorocarbon layer was removed with a teat pipette, dried ($MgSO_4$) and distilled to recover unreacted octafluoroacetophenone (1·5 g.). The residue was distilled under reduced pressure to yield 4-nonafluoro-α-phenylethoxyheptafluoroacetophenone, (0·35 g., 9%), b.p. 60° at 0·01 mm. (Found: C, 35·9; F, 57·1; M, 528. $C_{16}F_{16}O_2$ requires C, 36·3; F, 57·6; M, 528). (i.r. spectrum No. 34). The compound was shown to be pure by v.p.c.

Attempted Preparation of 2,4-Bis(nonafluoro-α-phenylethoxy)trifluoropyridine.

Caesium fluoride (2·03 g.), dry acetonitrile (40 ml.), octafluoroacetophenone (3·52 g.) and pentafluoropyridine (1·12 g.) were heated with stirring at 95° in a flask protected from moisture by a drying tube for 14 days. The contents of the flask became dark brown. The reaction

mixture was poured into water (200 ml.). The lower fluorocarbon layer was removed with a teat pipette, dried ($MgSO_4$) and distilled under reduced pressure to give a liquid, 0·413 g., b.pt. 58-63° at 0·02 mm. This was shown by v.p.c., infrared and mass spectrometry to be a mixture of 4-nonafluoro-α-phenylethoxy-tetrafluoropyridine and 4-nonafluoro-α-phenylethoxy-heptafluoroacetophenone.

Preparation of Benzyl-Nonafluoro-α-phenylethyl ether.

Caesium fluoride (1·52 g., 10 m.mole), octafluoroacetophenone (2·64 g., 10 m.mole), benzyl bromide (1·71 g., 10 m.mole), and dry acetonitrile (40 ml.) were heated with stirring at 100-105° in a flask protected from moisture by a drying tube for $3\frac{3}{4}$ days. A precipitate of caesium bromide was slowly formed on the sides of the flask. The contents of the flask became dark brown. The reaction mixture was poured into water (200 ml.). The aqueous layer gave a white precipitate with silver nitrate solution. The lower fluorocarbon layer was removed with a teat pipette, dried ($MgSO_4$) and the ether and a small amount of octafluoroacetophenone (0·15 g.) removed by distillation. The residue was distilled under reduced pressure to afford benzyl nonafluoro-α-phenylethyl ether, (1·184 g., 31%), b.p. 80-84° at 0·01 mm. (Found: C, 47·9; F, 45·2; M, 374. $C_{15}F_9H_7O$ requires C, 48·1; F, 45·7%; M, 374). (i.r. spectrum No. 35).

Preparation of Nonafluoro-α-phenylethoxytrifluoropyridazine.

Caesium fluoride (1·23 g., 8·1 m.mole), monoglyme (20 ml.),

octafluoroacetophenone (2·11 g., 8·0 m.mole), and tetrafluoropyridazine (1·23 g., 8·1 m.mole) were heated with stirring under reflux at 60° in a flask protected from moisture by a drying tube for 41 hrs. The dark brown reaction product was removed from the white solid with a syringe, filtered to remove any caesium fluoride and the monoglyme distilled off. The solid from which the reaction product had been decanted was completely soluble in water. The residual liquid was distilled under reduced pressure to yield nonafluoro-α-phenylethoxytrifluoropyridazine (0·241 g., 7·2%), b.p. 62° at 0·01 mm. (Found: C, 34·98; F, 55·1; M, 416. $C_{12}F_{12}N_2O$ requires C, 34·61; F, 54·8%; M, 416). (i.r. spectrum No. 36). There was insufficient material to obtain a satisfactory ^{19}F n.m.r. spectrum. The position of substitution, therefore, remains in doubt, although it is most likely to be in the 4-position.

Preparation of Impure 1,3-Bispentafluorobenzoylhexafluoro-n-propane.

Pentafluorobromobenzene (3 g., 12·1 m.mole) in ether (20 ml.) was stirred at -65°. n-Butyl-lithium in hexane (4·6 ml., 2·7M) and ether (10 ml.) were added and the mixture was stirred for 30 minutes at -65°. Perfluoroglutaryl chloride (1·65 g., 6·1 m.mole) in ether (10 ml.) was added all at once and the mixture was stirred for 3 hrs. During this time the temperature was allowed to rise to -10°. The mixture was acidified with dilute hydrochloric acid and extracted with ether. The combined ether extracts were washed with sodium carbonate solution and then with water, dried ($MgSO_4$), and the ether was removed by

distillation. Distillation of the residual liquid under reduced pressure (0·01 mm.) yielded 2·1 g. of a product (M, 540. $C_{17}F_4O_2$ requires M, 540) (b.p. 160-162° at 0·01 mm.) which was a semi-solid at room temperature.

Attempted Preparation of 1,3-Bispentafluorobenzoyl-hexafluoro-n-propane on a Larger Scale.

The above preparation of impure 1,3-bispentafluorobenzoyl-hexafluoro-n-propane was repeated under the same conditions using pentafluorobromobenzene (15 g., 60·5 m.mole) and corresponding quantities of the other reagents.

An identical work-up procedure yielded a distillate (12·5 g., b.p. 150-180° at 0·01 mm.) whose mass spectrum was unlike that of 1,3-bispentafluorobenzoyl-hexafluoro-n-propane, and, in fact, contained peaks at much higher mass. Trituration of a portion of the semi-solid reaction product (3·5 g.) with cold acetonitrile gave a yellow solution and a sparingly soluble white solid, which was filtered off and recrystallised from meths. to yield pure (γ-pentafluorobenzoyl-n-hexafluoropropyl)-nonafluorobiphenyl ketone (1·1 g.). (Found: C, 40·1; F, 55·2; M, 688. $C_{23}F_{20}O_2$ requires C, 40·1; F, 55·2; M, 688), m.p. 140° (i.r. spectrum No. 37). Distillation of the residue obtained by evaporation of the acetonitrile solution, under reduced pressure yielded 1-hydroxy-1,1-bispentafluorophenyl-4-pentafluorobenzoyl-hexafluoro-n-butane (0·5 g.). (Found: C, 39·9; F, 44·7; M, 708. $C_{23}F_{21}O_2H$ requires C, 40·0; F, 44·8; M, 708), b.p. 150-157 at 0·01 mm. (i.r. spectrum No. 38).

PART II

CHAPTER IV

Mass Spectrometric Studies on Halogenated Aromatic Compounds

Introduction.

The mass spectrum of an organic molecule is obtained by bombarding the compound under investigation with a beam of electrons of medium energy in a high vacuum. The ions produced are separated into a spectrum according to their mass to charge ratio and the relative abundance of each ion species is recorded by the mass spectrometer. A recent review[107] summarises the salient facts concerning the theory and design of these instruments. Single focussing instruments utilising a magnetic field to separate ions by their mass to charge ratio were used in the majority of early mass spectrometric studies. Such instruments at the best gave a resolution of one part in three thousand.

High resolution mass spectrometers have revolutionised the subject. By careful design, electric and magnetic fields have been combined to increase the resolution by elimination of the angular divergence of the ion beam and variations in the velocity of the ions. These aberrations are responsible for the limitation of the resolution of magnetic sector instruments. High resolution instruments are capable of measuring the mass of ions with a precision of a few parts per million and providing ion abundance values with a high degree of accuracy. These instruments can provide the exact elemental analysis of every ion in the spectrum. Such data can be of vital importance in structural analysis. For example, loss of 28 mass units from an ion in a low resolution spectrum could be identified as C_2H_4, NCH_2, CO or N_2 loss by measurements with a high resolution instrument.

Electron bombardment of gaseous organic molecules causes the following interaction

$$e + ABC \longrightarrow ABC^+ + 2e$$

$$ABC^+ \longrightarrow AB^+ + C; \text{ or } BC^+ + A; \text{ or } A^+ + BC \text{ etc.}$$

The electron beam energy (70 eV) normally employed is in excess of the minimum energy required to cause ionisation.

The mass spectrum produced under specified conditions is sometimes named the cracking or fragmentation pattern and is characteristic of the compound being studied. This pattern will contain all possible ions combinations as shown before, together with ions of the type AC^+, which arise by a rearrangement process, since in the original molecule the two parts of this ion were separately attached to B.

One of the difficulties encountered in the correlation of the mass spectrum of a compound with its structure is caused by the presence of these ions in the spectrum. This difficult aspect of mass spectrometry has been studied in detail for hydrogen containing organic molecules with the intention of finding generally applicable rules, but when the work described in this thesis was begun there were few publications concerned with the spectra of organic fluorine compounds in general. The early work concerned with the mass spectrometry of fluorine compounds has been described in an excellent review[108] by Majer.

Experimental.

Recording Mass Spectra.

Spectra were recorded on an A.E.I. M.S.9 double focussing instrument. Routine measurements, such as high resolution mass measurements, were carried out as described in the instruction manual and ions were produced under the following conditions:

Ionising electron beam voltage = 70 eV.

Trap current (i.e. electron beam voltage) = 100 μ amps.

Ion repeller voltage = -2 to +4 volts.

Source temperature = 190 to 210°C.

Obtaining Spectra for Abundance Measurements.

These were recorded using a resolution of 1 part in 1,000 and a source pressure not so high that sparking of the high voltage employed in the source occurred. It is also important that a constant monitor current (i.e. a quantity proportional to the total ion current issuing from the ionisation chamber found by intercepting part of the ion beam before it enters the magnetic sector) is maintained whilst the spectrum is recorded, if meaningful abundances are to be obtained. With the inlet systems which have a leak to regulate the flow of material into the source (i.e. the cold, heated and gallium systems) this is relatively easy, but when using the direct insertion probe some manipulation is necessary, especially with solids, m.pt. $> 100^{\circ}$, before constant evaporation into the source is obtained.

Detection of Metastable Peaks.

For the detection of such peaks an ion repeller voltage of +20 to +25 volts and a resolving power of one part in 500 to 1,000 were sometimes used, since it has been shown[109] that the height of these peaks increases relative to the others under these conditions.

Presentation of Data.

Mass spectral data is often presented in tabular form, listing the mass number of the peaks and their intensities relative to the most intense peak in the spectrum - the base peak - which is assigned a value of 100. If spectra are to be compared it is much better to relate the intensity of a certain peak to the total ion current, i.e. the sum of the intensities of all the peaks in the spectrum. The intensity of a peak expressed in percent of the total ionisation (Σ), then shows the extent to which the molecular ion decomposes to this particular fragment ion. For a comparison of the spectra of two compounds the mass range over which the peaks are summed has to be the same and the lowest mass of this range can be shown as a subscript, e.g. Σ_{31} signifies the sum of all the intensities of the peaks from m/e 31 to the molecular weight or the peak of highest mass in the spectrum.

Thus, for simplicity, peaks due to doubly charged ions and metastable ions are omitted. The metastable ions are listed in a separate table. The mass and intensity of the doubly charged ions relative to the base peak in the spectrum are also presented separately.

Calculation of Abundances.

For ions containing monoisotopic elements abundances are determined easily from the peak heights produced by the ions in the low resolution spectra. Thus, if A^+ is of peak height 4 arbitrary units (a.u.), B^+ 3 a.u., C^+ 2 a.u., and D^+ 1 a.u., the abundance of A^+ as a percentage of total ion current is 40%. In comparing the abundances of ions containing polyisotopic elements with other types contributions from each isotope combination must be summed, if the abundances are to be expressed in terms of the percentage of the total ion current. For example, a spectrum showing three peaks of relative height 2:1:1 due to $^{127}I^+$, $^{81}Br^+$, and $^{79}Br^+$ corresponds to a 1:1 ratio of I^+ to Br^+ (^{81}Br = 49%; ^{79}Br = 51%).

In calculating the abundances of ions in terms of the percentage of the total ion current allowance has been made for the presence of ^{13}C. The natural abundance of ^{13}C is 1% and for ions containing n carbon atoms n% of the ions will contain a ^{13}C atom. Thus, if the effects of the ^{13}C are neglected, the abundances of ions containing a large number of carbon atoms will be underestimated.

Ion currents are measured in arbitrary units (a.u.) which depend upon sample pressure in the source and upon instrument sensitivity of ion detection while the spectrum is being recorded. Abundances, however, are dimensionless quantities and are hence not dependent, at least to a first approximation, upon instrument sensitivity.

When a single peak in a low resolution spectrum was known to include currents of two or more ionic species, the current at this mass number

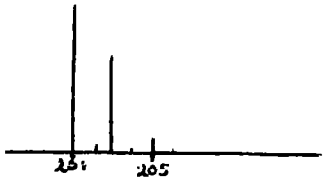
was divided amongst the ion species present in the ratio of the ion currents measured for the species, when separated under high resolution (1:20,000).

The abundances of the compounds have been presented in both different ways depending on the type of compound studied. Some compounds, for example, pentachloropyridine or perfluorodiphenyl ether, give spectra containing ions whose composition can be assigned without having to resort to accurate mass measurements. If the structure of such a compound is known, and its composition and purity assured, then the composition of every ion in the spectrum is known. In this case, a table of the composition of the ions in decreasing molecular weight and their abundances, as a percentage of the total ion current, is given. The carbon 13 isotope contribution to an ion is calculated using the formula:-

$$\%\ \text{length of } C^{13} \text{ isotope peak relative to } C^{12} \text{ peak}$$

$$= \frac{1{\cdot}1 \times \text{no. C atoms in ion } \%}{100} + \frac{0{\cdot}36 \times \text{no. N atoms in ion } \%}{100}$$

and the abundance compared with that observed. If the observed abundance is greater, then there is another ion present. The fraction of the ion current due to this ion is listed separately. With a compound containing polyisotopic elements, such as 3,5-dichlorotrifluoropyridine, contributions from each isotope combination are summed. Thus, the molecular peak of 3,5-dichlorotrifluoropyridine consists of six peaks. Because of the



molecular ion of 3,5-dichloro-trifluoropyridine

isotopic pattern of two chlorine atoms, the molecular ion peaks consist of three ions of composition $C_5Cl_2^{35}F_3N$, $C_5Cl^{35}Cl^{37}F_3N$, $C_5Cl_2^{37}F_3N$ at 201, 203 and 205 mass units in the relative ratios 100:65:10. The ions at 202, 204 and 206 mass units are the carbon 13 isotope peaks. All these peaks are summed and assigned the composition $C_5Cl_2F_3N$ and the abundance of this ion, as a percentage of the total ion current, is expressed as a single figure. All peaks less than 2% of the length of the base peak, determined by summing over all isotopes, if necessary, are omitted, if the molecular ion is of reasonable intensity. In the situation where the composition of all the ions in the spectrum cannot be determined uniquely without accurately mass measuring every ion in the spectrum, then the most intense single ion in the spectrum is chosen as the base peak and all abundances less than 2% of the base peak are omitted. Carbon and polyisotopic species are not summed and the mass over charge value of each ion is given and its abundance expressed as the percentage intensity relative to that of the base peak, which is considered to be 100%. The composition of the major ions in the spectrum determined by accurate mass measurements are presented in a separate table. This may appear conflicting, but the first method is the best way to present the data if the composition of all the

ions is known, but if not, then the most efficient way of using the mass spectrometer is to measure the abundances of the ions and to determine the composition of the major ions,so that the main features of the behaviour of the compound on electron impact can be elucidated.

Metastable Ions.

It is not always possible to determine the relationship between the ions derived from the molecular ion. The fragmentation pattern of the positive ions is elucidated by the help of metastable ions which are small diffuse ions,which usually appear at a non-integral mass number in the spectrum. The m/e value of a metastable ion is related to the parent and daughter ions of a fragmentation process by the expression:

$$m^* = m_2^2/m_1$$

where m* is the mass of the metastable ion and m_1 and m_2 are the masses of parent and daughter ions respectively. The difference between m_1 and m_2 determines the mass and composition of the neutral fragment lost in a decomposition process. Such metastable ions are associated with ion fragmentations which occur in the field free space of a sector instrument. The formula given above will not hold if dissociation occurs with a release of internal energy.[110]

The values m_1 and m_2 associated with a metastable peak m* are determined by simple but tedious arithmetic. Tables of m* values that occur for various values of m_1 and m_2 ($m_1 \leqslant 500$ and $500 \geqslant m^* \geqslant 1$)

are of help in the assignment of metastables.[111]

A useful rule is that the distances measured on the mass spectral chart between the parent ion and the daughter ion and the daughter ion and the metastable should be equal in length.

Doubly Charged Ions.

Doubly charged ions can be obtained, if in the initial ionisation process two electrons are ejected from the molecule and the doubly charged molecular ion formed then decomposes into doubly charged and neutral fragments:

$$AB + e^- \longrightarrow AB^{2+} + 3e^-$$

$$AB^{2+} \longrightarrow A^{2+} + B\cdot$$

The decomposition of a singly charged ion into a doubly charged fragment and a negative ion could conceivably occur, however.

$$AB^+ \longrightarrow A^{2+} + B^-$$

The doubly charged ion will be recorded at a m/e ratio which corresponds to half its weight. If the mass of a singly charged ion occurs at an odd m/e value then the corresponding doubly charged ion will occur at a half mass number and is easy to recognise.

Although a doubly charged ion of even mass occurs at an integral mass number, it will still be possible to recognise it by the presence of a small peak $\frac{1}{2}$ of a mass unit higher, which is the doubly charged

C^{13}-isotope peak of the fragment. From the intensity of the C^{13}-isotope peak the peak height at the integral mass can be calculated to see whether the peak is due entirely to a doubly charged species. The absence of a peak one mass unit above the peak, in question, will show that it is due solely to a doubly charged ion.

Discussion of the Experimental

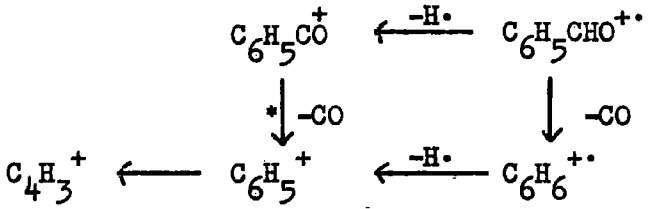
Aromatic and Heterocyclic Carbonyl Compounds.

The first group of compounds to be studied were aromatic and heterocyclic carbonyl compounds, because the molecular ions of such carbonyl compounds were expected to decompose by a few, easily understood paths. After the study of the spectra of these compounds was completed, a publication[112] describing the mass spectra of fluorinated aromatic ketones appeared. This publication is complementary to the material described here, so the two investigations are discussed together.

The replacement of hydrogen atoms by fluorine atoms in an aromatic hydrocarbon greatly changes the mode of breakdown of the ring.[108] The mass spectra of polyfluorinated compounds contain ions formed by the loss of CF, CF_2, and CF_3 fragments from the molecular and fragment ions. Aromatic hydrocarbons do not suffer loss of the corresponding hydrogen containing fragments but usually show quite prominent loss of a hydrogen radical from the molecular ion. Corresponding loss of a fluorine radical from aromatic fluorocarbons is often absent or of low abundance.

It has been found in the case of carbonyl compounds that the main fragmentation paths of the molecular ion are determined by the carbonyl group itself and substantial differences in the spectra of fluorinated and hydrogenated aromatic carbonyl compounds are observed only for fragmentation processes associated with cleavage of the ring.

The molecular ion of benzaldehyde,[109] which forms the base peak in the spectrum, suffers loss of the aldehydic hydrogen to give a fragment ion as intense as the abundant molecular ion. This M-H$^+$ ion loses CO to yield $C_6H_5^+$, which eliminates acetylene to give a $C_4H_3^+$ ion. The formation of HCO^+ occurs to a small extent as does loss of CO from the molecular ion.



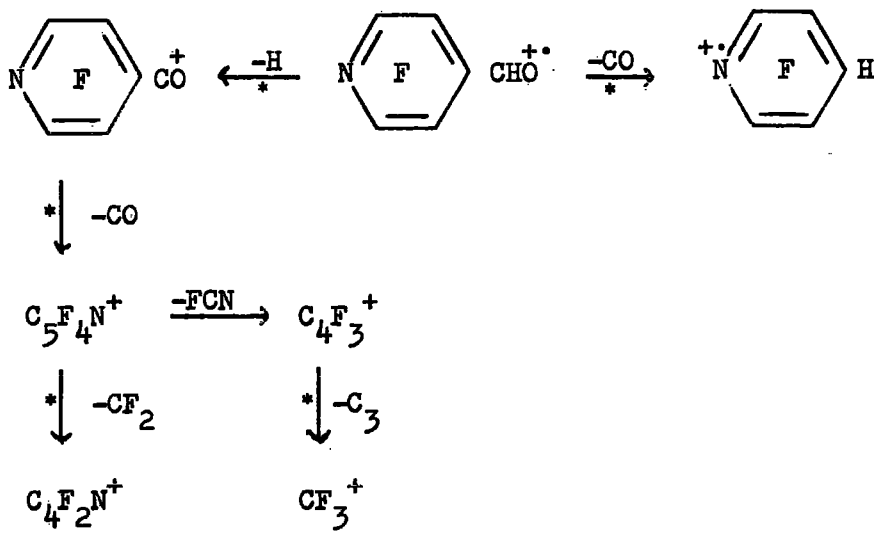
Fragmentation of the molecular ion of benzaldehyde.

Once again, the molecular ion of pentafluorobenzaldehyde[112] provides the base peak in the spectrum. The M-H peak has almost the same intensity and loses CO with the formation of $C_6F_5^+$. Loss of CO from the molecular ion gives $C_6F_5H^+$ and the probabilities of loss of CO from the M and M-H ions are about the same. Although the primary fragmentations of benzaldehyde and pentafluorobenzaldehyde are governed by the carbonyl group and hence are similar, the secondary fragmentations of the ions $C_6F_5^+$ and $C_6F_5H^+$ differ from those of $C_6H_5^+$ and $C_6H_6^+$, as shown:-

$$C_6F_5^+ \xrightarrow{*} C_5F_3^+ + CF_2$$

$$C_6F_5H^+ \xrightarrow{*} C_5F_2H^+ + CF_3$$

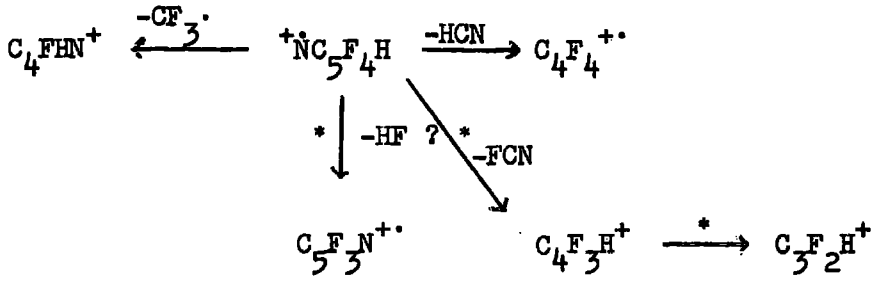
The molecular ion of tetrafluoropyridine-4-aldehyde, the base peak in the spectrum, suffers the expected primary fragmentation processes, although the $M-H^+$ ion is less abundant and the $M-CO^+$ ion more abundant than found in pentafluorobenzaldehyde. The HCO^+ and CF^+ ions are much more abundant in the spectrum of tetrafluoropyridine-4-aldehyde than in pentafluorobenzaldehyde.



Fragmenation of the molecular ion of tetrafluoropyridine-4-aldehyde.

The increased abundance of the $M-CO^+$ ion in tetrafluoropyridine-4-aldehyde could be explained by partial localisation of the charge of the molecular ion on the nitrogen atom. The breakdown of the fragment ions $C_5F_4N^+$ and $C_5F_4HN^+$ are governed by the ring nitrogen atom to a great extent. It would be of interest to compare the fragmentation of the molecular ion formed from 2,3,5,6-tetrafluoropyridine with that of the

ion $C_5F_4HN^+$, found in the spectrum of tetrafluoropyridine-4-aldehyde.



Fragmentation of the $NC_5F_4H^+$ ion formed in the spectrum of tetrafluoro-4-aldehyde.

$\cdot CF_3$ fragments from both the $\overset{+\cdot}{N}C_5F_4H$ ion and the $C_6F_5H^{+\cdot}$ ion in the spectrum of pentafluorobenzaldehyde. The rearrangement process involving loss of HCN from $\overset{+\cdot}{N}C_5F_4H$ is noteworthy. Thus, the primary fragmentation processes of tetrafluoropyridine-4-aldehyde are controlled by the carbonyl group and the secondary processes by the ring nitrogen atom, although the nitrogen atom may have an effect on the enhanced loss of CO from the molecular ion.

The spectra of pentafluoro- and octafluoro-acetophenone have been compared.[108] The acetyl radical ion is the base peak in the spectrum of pentafluoroacetophenone, but the trifluoroacetyl radical ion is absent from the spectrum of octafluoroacetophenone. As expected, the acetyl radical ion is a much stabler species, because the electron donating methyl group stabilises the positive charge.

The features of the spectrum of octafluoroacetophenone presented here by the author and in the article by Majer are similar. The molecular ion is of quite low abundance, the base peak in the spectrum

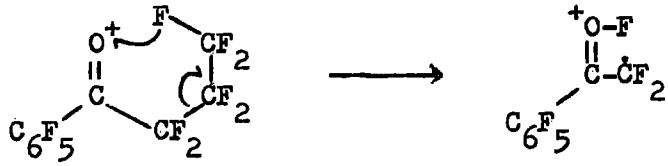
being $C_6F_5C\equiv\overset{+}{O}$. The author found two metastables in the spectrum corresponding to the fragmentations

$$C_6F_5\overset{+}{C}O \longrightarrow C_6F_5^+ + CO$$
$$C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2$$

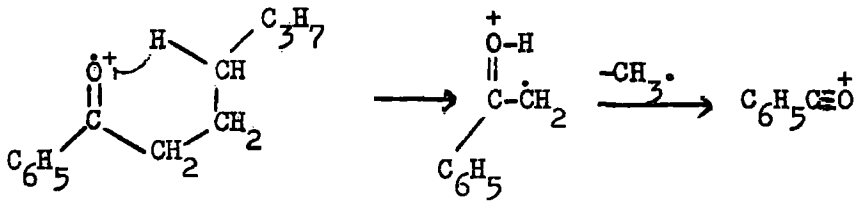
The $C_6F_5\overset{+}{C}O$ ion was formed directly from the molecular ion. A CF_3^+ ion of low abundance was present in the spectrum.

The spectra of the ketones $C_6F_5COR_f$, where $R_f = C_6F_5$, $CF_2CF_2CF_3$ and $CF(CF_3)_2$ are similar to that of octafluoroacetophenone. The abundance of the molecular ion decreases in intensity in the order $R_f = C_6F_5 > CF(CF_3)_2 > CF_3 > CF_2CF_2CF_3$. The base peak in the spectrum is $C_6F_5C\equiv\overset{+}{O}$ and the other prominent ions are $C_6F_5^+$ and $C_5F_3^+$ formed as in octafluoroacetophenone. None of the aryl alkyl ketones show peaks for the ions R_f^+ or R_fCO^+. Part of the $C_6F_5^+$ ion in decafluorobenzophenone could of course have been formed by the process $C_6F_5C\overset{+}{\cdot}OC_6F_5 \longrightarrow C_6F_5^+ + C_6F_5CO\cdot$ although there is no metastable transition to support this.

The molecular ion of perfluoro-n-butyrophenone suffers loss of a fluorine radical to a small extent, but more interestingly does not undergo a "McHafferty rearrangement", i.e.



This rearrangement occurs in the hexyl phenyl ketone spectrum and would



most certainly be expected in the spectrum of n-butyrophenone.

The study of these spectra show, that as a useful generalisation, the presence of $C_6F_5C{=}O$ group in a compound may be detected by the presence of ions at 195, 167 and 117 mass units with metastable peaks at 143·0 and 82·0 mass units. This is not always correct, as will be seen later, and the infra-red spectrum of the compound would offer useful confirmation. Another useful generalisation is that a C_6F_5 group is detected by the presence of ions at 167 and 117 mass units with a metastable peak at 82·0 mass units.

As would be predicted, the primary fragmentation of the molecular ion of 4-aminononafluorobenzophenone[112] takes two courses:

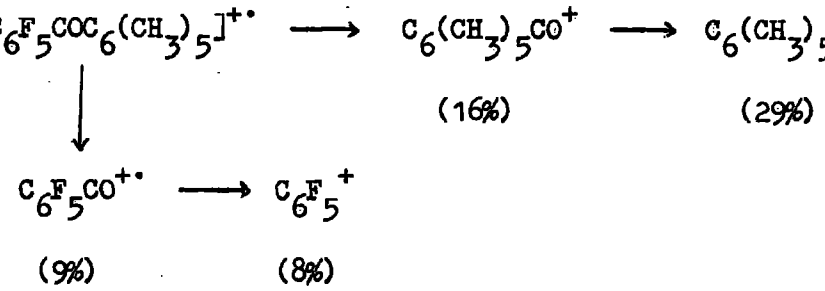
$$[C_6F_5COC_6F_4NH_2]^{+\cdot} \xrightarrow{*} H_2NC_6F_4CO^+$$

$$\downarrow * \qquad\qquad \downarrow *$$

$$C_6F_5CO^+ \ (41\%) \qquad\qquad H_2NC_6F_4^+ \ (19\%)$$

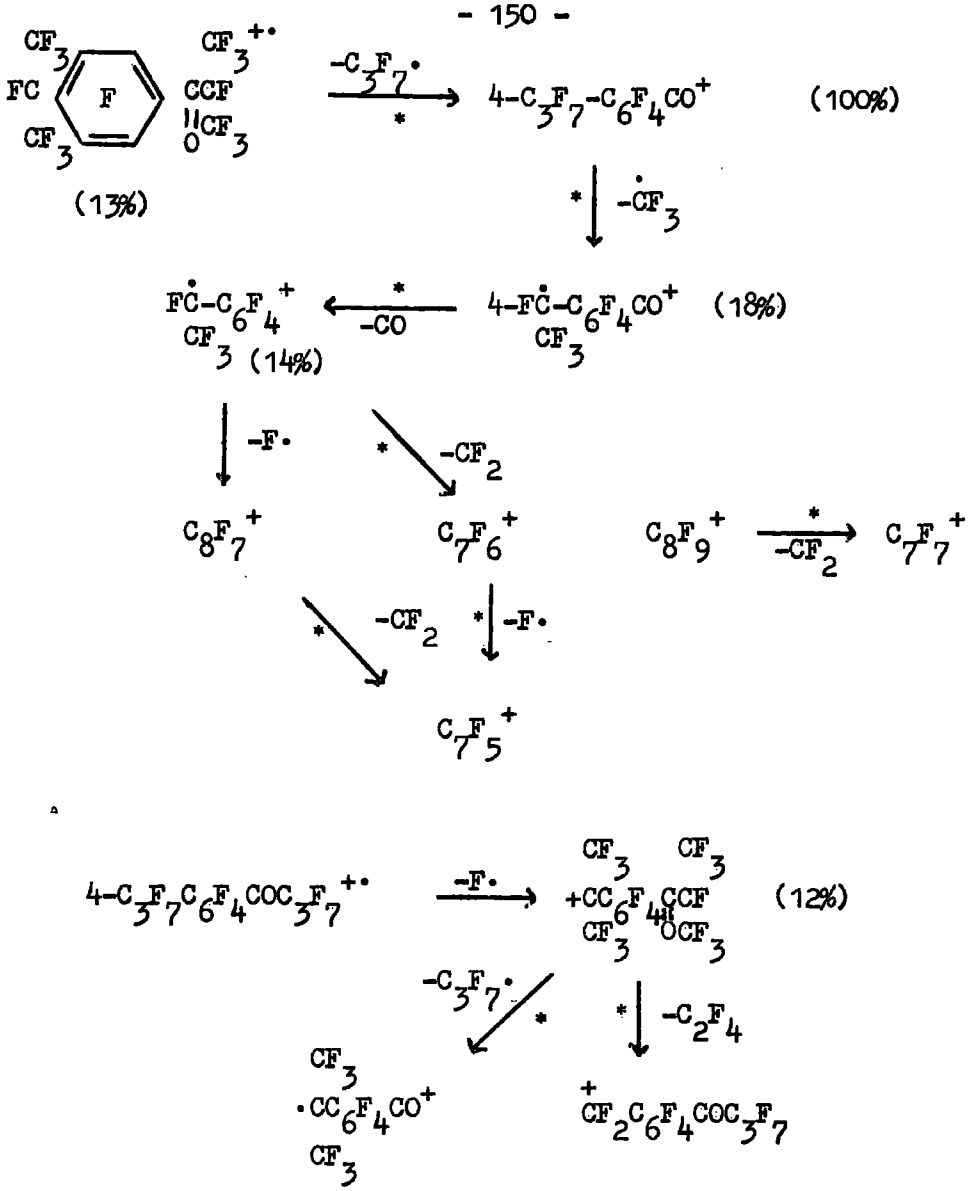
The $C_6F_5CO^+$ ion behaved as expected. The $H_2NC_6F_4^+$ suffered further loss of HCN (m^* = 114·5) or HF (n^* = 126·5).

Although the primary fragmentation processes expected for 2,3,4,5,6-pentafluoro-2',3',4',5',6'-pentamethylbenzophenone[112] were observed, i.e.



specific features in the spectrum were the formation of the 307^+ ion ($M-HF-CH_3$), which was the base peak in the spectrum, and loss of a fluorine radical, a methyl radical or a water molecule from the molecular ion. This illustrates that substituents in the aromatic ring can exert a profound effect upon the primary fragmentation processes of a fluorinated ketone.

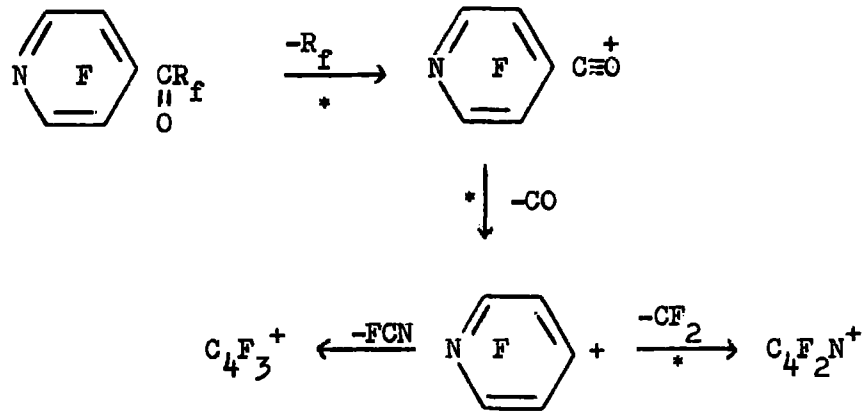
A further interesting illustration of this principle is found in the spectrum of 4-heptafluoroisopropyl-tetrafluorophenyl-heptafluoroisopropyl ketone. This ketone contains a peak due to fluorine radical loss almost as intense as the molecular ion. This loss is likely to originate from the 4-heptafluoroisopropyl substituent in the benzene ring, because of its very low abundance in the spectra of the ketones already discussed. The formation of the major ions in the spectrum, supported by appropriate metastable transitions, is illustrated below. The structures of the ions shown cannot be proved but are written so as to illustrate the structure of the compound.



Fragmentation of the molecular ion of 4-heptafluoroisopropyl-tetrafluorophenyl-heptafluoroisopropyl ketone.

Fragmentation of the molecular ion of this compound seems to be determined by the localisation of the charge both on the carbonyl group and on the 4-heptafluoroisopropyl group in the ring. The base peak in the spectrum is very probably formed by loss of the perfluoroisopropyl group adjacent to the carbonyl group. Direct loss of carbon monoxide from this ion surprisingly does not occur, loss of a trifluoromethyl radical being preferred, after which carbon monoxide is found to be eliminated from the resulting ion $C_9F_8O^+$. The CF_3^+ ion, as expected, forms an ion of moderate intensity in the spectrum.

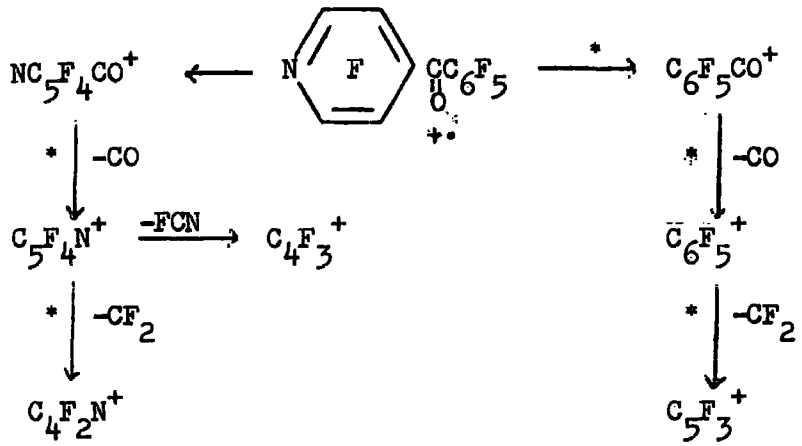
The molecular ions of 4-tetrafluoropyridyl heptafluoroisopropyl ketone and 4-tetrafluoroisonicotinyl-tetrafluoropyridine behave exactly as expected yielding the same ions that were formed following the loss of a hydrogen radical from tetrafluoropyridine-4-aldehyde, the ion $NC_5F_4C\equiv\overset{+}{O}$ forming the base peak in each spectrum:-



4-Tetrafluoropyridyl heptafluoroisopropyl ketone has quite an abundant

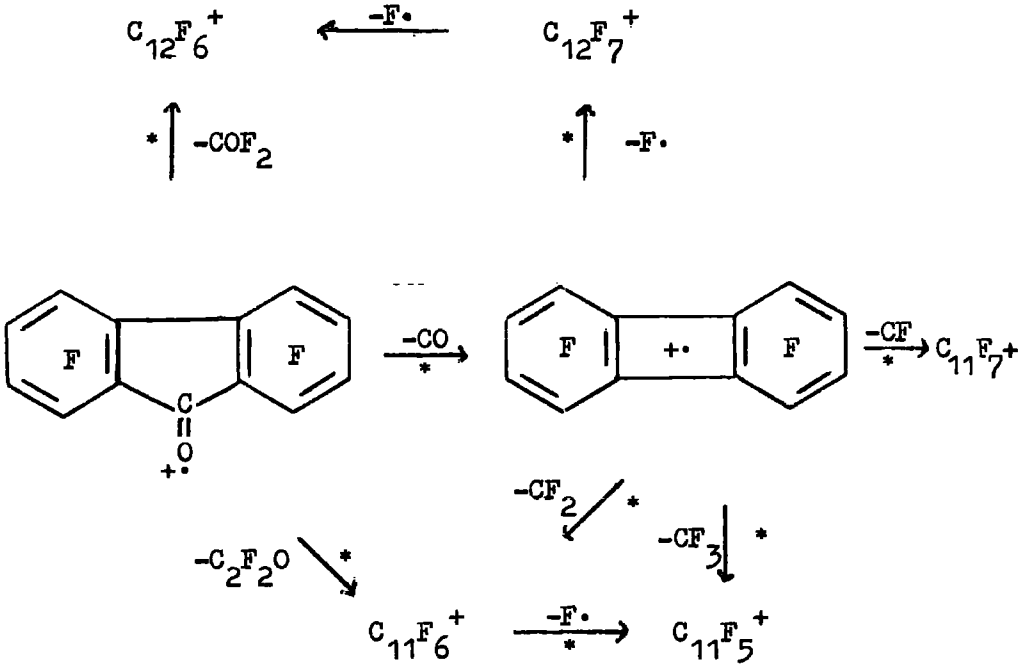
CF_3^+ ion, but no i-$C_3F_7CO^+$ or i-$C_3F_7^+$ ions were detected. As a useful generalisation, a tetrafluoroisonicotinyl group is detected as a structural feature by ions at 178, 150, 105 and 100 mass units with metastable peaks at 126·4 and 66·7 mass units. Likewise, a 4-tetrafluoropyridyl group is detected by the presence of ions at 150, 105 and 100 mass units with a metastable peak at 66·7 mass units.

The abundant molecular ion of 4-tetrafluoroisonicotinylpentafluorobenzene fragments in a readily predictable manner:-



The pentafluorobenzoyl ion is more abundant than the 4-tetrafluoroisonicotinyl ion, which possesses the electron-withdrawing ring nitrogen atom that destabilises the positive ion. It will be remembered that the base peak in the spectrum of 4-aminononafluorobenzophenone[112] was the $H_2NC_6F_4CO^+$ ion which was more abundant than the $C_6F_5CO^+$ ion, because of the electron donating amino group.

The base peak in the spectrum of octafluorofluorenone is the molecular ion. An intense ion is formed by the loss of carbon monoxide from the molecular ion. This behaviour is similar to that exhibited by the molecular ion of fluorenone, and contrasts with non-cyclic fluorinated ketones that never show carbon monoxide elimination from the molecular ion. The other ions in the spectrum of octafluorofluorenone are small in comparison.



Fragmentation of the molecular ion of octafluorofluorenone.

The elimination of difluoro-oxirene from the molecular ion by an obscure rearrangement process is of interest, because this same elimination from the molecular ion of decafluorodiphenyl ether is observed. More easily understandable is the elimination of carbonyl fluoride from the

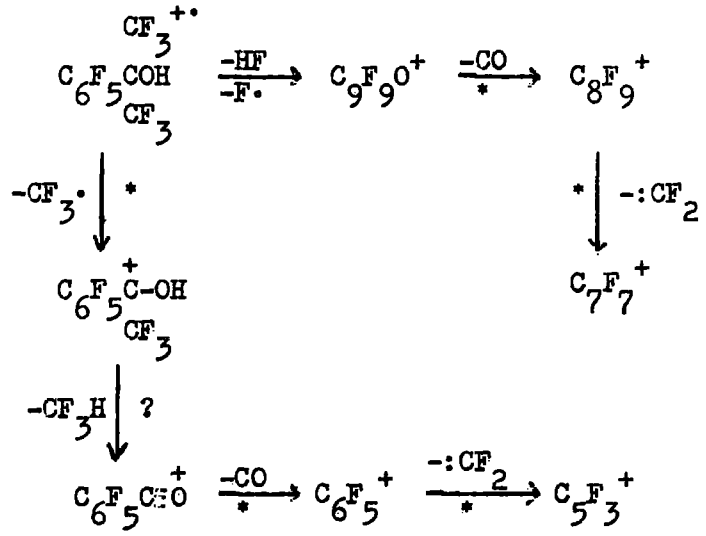
molecular ion of octafluorofluorenone.

The molecular ion of decafluorobenzil is very weak and loses carbon monoxide to give an even smaller fragment ion. The base peak in the spectrum is the pentafluorobenzoyl ion, formed by the cleavage of the bond between the carbonyl groups. This ion fragments in the usual way.

Fluorinated Tertiary Alcohols.

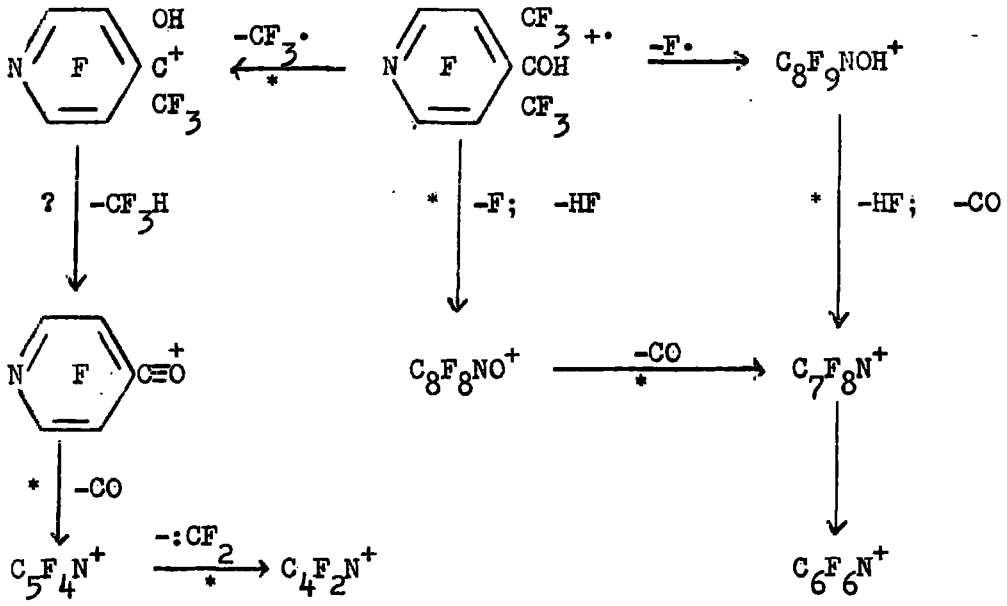
Very little information on the mass spectra of fluorinated tertiary alcohols exists in the literature.[113] It is of interest to find that the base peak in the spectra of both dimethyl trifluoromethyl carbinol and methyl bistrifluoromethyl carbinol occurs at m/e 43. In the latter alcohol, this fragment must be CH_3CO^+, and this probably also applies to dimethyl trifluoromethyl carbinol, although high resolution data would be required to settle the issue. Consequently, it was of interest to examine the spectra of available fluorinated tertiary alcohols to see if fluorinated aromatic or aliphatic analogues of this CH_3CO^+ ion were obtained as fragment ions.

The spectrum of perfluoro-α,α-dimethylbenzyl alcohol contains a molecular ion of reasonable intensity but the base peak in the spectrum is due to $C_6F_5C{\equiv}O^+$, which decomposes as described previously. CF_3^+ and C_2F^+ provide quite abundant ions. The origin of the $C_6F_5C{\equiv}O^+$ ion is obscure, but a suggestion for its formation is included in the diagram below.



Fragmentation of the molecular ion of perfluoro-α,α-dimethyl-benzyl alcohol.

The fragmentation of the reasonably abundant molecular ion of



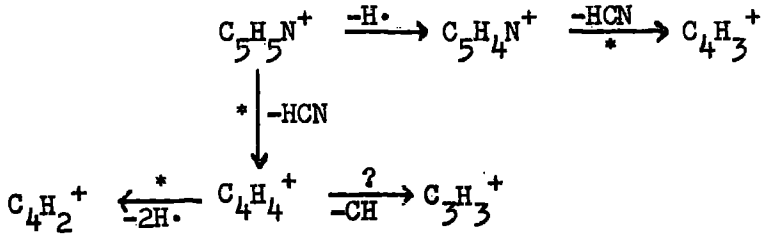
Fragmentation of the molecular ion of 2,3,5,6-tetrafluoro-pyridyl-bis-trifluoromethyl carbinol.

2,3,5,6-tetrafluoropyridyl-bis-trifluoromethyl carbinol is similar in many respects. The $NC_5F_4C{\equiv}O^+$ ion is the base peak in the spectrum, although it carries a somewhat smaller share of the total ion current than the $C_6F_5C{\equiv}O^+$ in the spectrum of perfluoro-α,α-dimethylbenzyl alcohol.

Thus, the presence in the spectrum of peaks associated with a pentafluorobenzoyl and tetrafluoroisonicotinyl group does not necessarily indicate their presence in the molecule, although the infra red spectrum of the compound in question would distinguish these possibilities.

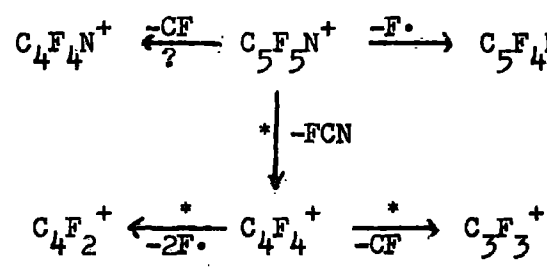
Perhalogenated Pyridine Derivatives.

The spectrum of pyridine has been compared with that of pentafluoropyridine by Majer,[108] although he did not identify any of the fragmentation processes by analysis of the metastable peaks in the spectra. The molecular ion forms the base peak in both spectra. The two spectra are quite similar, but pentafluoropyridine contains the ions CF^+, $C_4F_4N^+$, $C_4F_3N^+$ and $C_4F_2N^+$, the corresponding hydrogen containing ions of which are absent from the spectrum of pyridine.



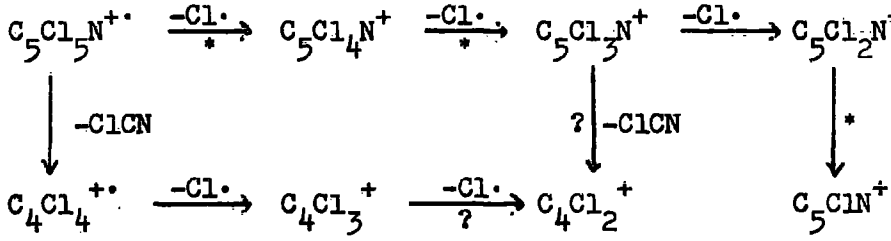
Fragmentation of the molecular ion of pyridine.

The major ions in the spectrum of pentafluoropyridine in order of decreasing abundance are $C_5F_5N^+$, CF^+, $C_4F_2N^+$, $C_4F_4^+$ and $C_3F_3^+$.



Fragmentation of the molecular ion of pentafluoropyridine.

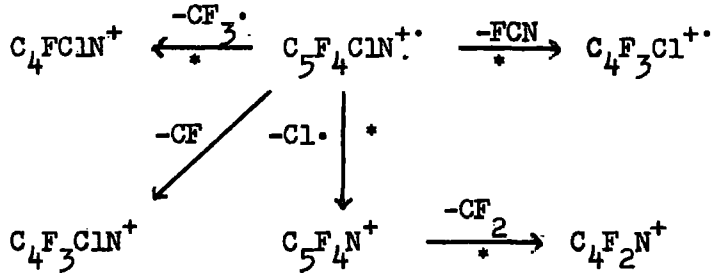
The major ions in the spectrum of pentachloropyridine in order of decreasing abundance are M^+, $M\text{-}Cl^+$, $C_4Cl_2^+$ and C_5ClN^+. Successive losses of chlorine radicals are favoured in pentachloropyridine, perhaps



Fragmentation of the molecular ion of pentachloropyridine.

because of the lower carbon-chlorine bond strength. The loss of Cl· from the molecular ion is far more favourable than the loss of ClCN.

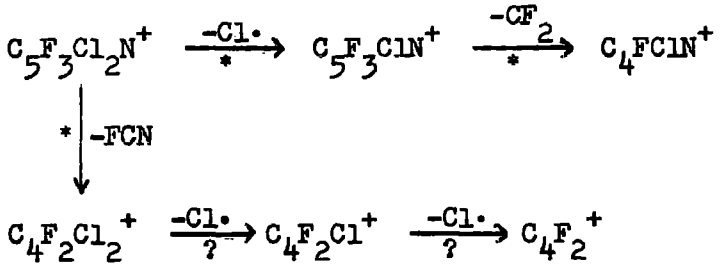
The most abundant ions in the spectrum of 3-chlorotetrafluoropyridine are M^+, $C_4F_2N^+$, CF^+, $C_4F_3ClN^+$, $C_5F_4N^+$ and C_4FClN^+ in decreasing order of intensity. Loss of a chlorine radical from the



Fragmentation of the molecular ion of 3-chlorotetrafluoropyridine.

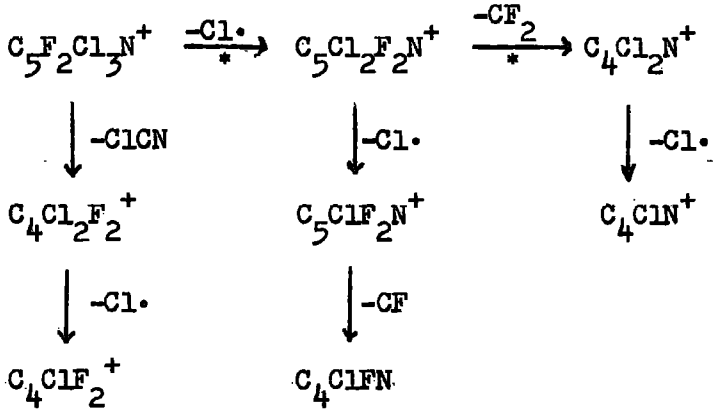
molecular ion is more favourable than loss of a fluorine radical and competes equally with loss of FCN from the molecular ion.

The most abundant ions in the spectrum of 3,5-dichlorotrifluoropyridine are M^+, C_4FClN^+, $C_5F_3ClN^+$ and CF^+ in decreasing order of intensity. Fragmentation of the molecular ion is reduced compared with 3-chlorotetrafluoropyridine and pentafluoropyridine. Fluorine radical loss from the molecular ion is now a very minor fragmentation process but chlorine radical loss from the molecular ion is now found to be more favourable than the loss of FCN.



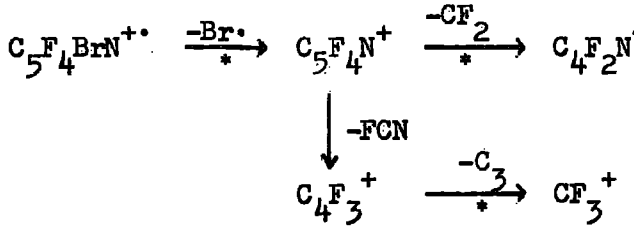
Fragmentation of the molecular ion of 3,5-dichlorotrifluoropyridine.

The three major ions in the spectrum of 2,4,6-trichlorodifluoropyridine are $\overset{+}{M}$, $C_5Cl_2F_2N^+$ and $C_4Cl_2N^+$, the molecular ion being the base peak.



Fragmentation of the molecular ion of 2,4,6-trichlorodifluoropyridine.

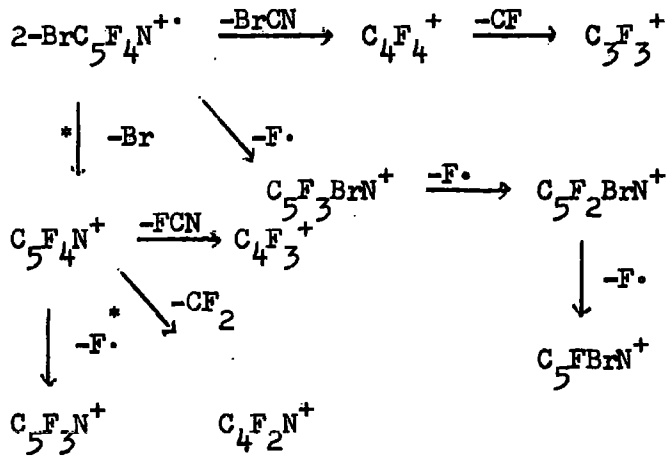
Just over half the ion current of 4-bromotetrafluoropyridine is carried by the molecular ion, other major ions being $C_4F_2N^+$ and $C_5F_4N^+$.



Fragmentation of the molecular ion of 4-bromotetrafluoropyridine.

The spectrum of 2-bromotetrafluoropyridine provides an interesting comparison. Although the molecular ion forms the base peak in the spectrum, it is appreciably less abundant. Presumably, the pyridyne ion formed by bromine radical loss from 2-bromotetrafluoropyridine

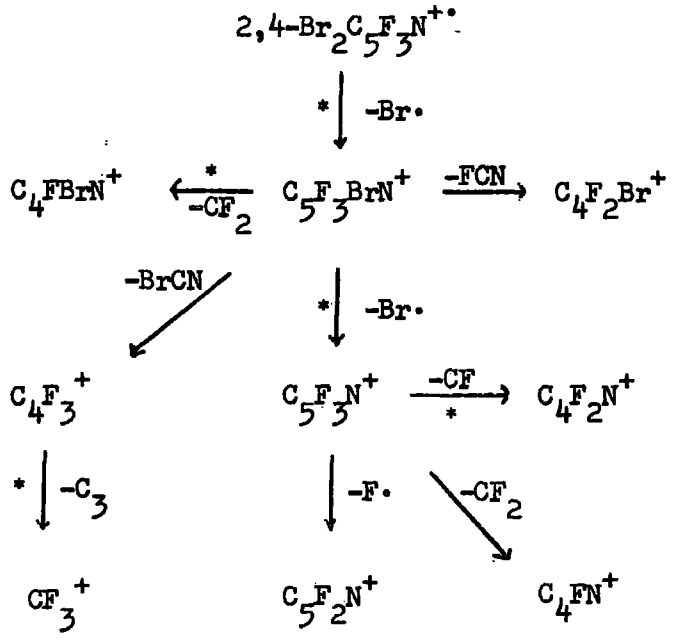
is stabler than the $C_5F_4N^+$ ion, formed by bromine radical loss from 4-bromotetrafluoropyridine, and so facilitates fragmentation of the molecular ion. Interestingly, the Br^+ ion formed in the spectrum of the 2-isomer is absent from the spectrum of the 4-isomer and, if it is formed from the molecular ion, this implies that the neutral species, that is simultaneously formed, is of greater stability in the 2-isomer. The $C_4F_4^+$ ion, probably formed by the elimination of BrCN from the



Fragmentation of the molecular ion of 2-bromotetrafluoropyridine.

molecular ion, serves to distinguish between the isomers.

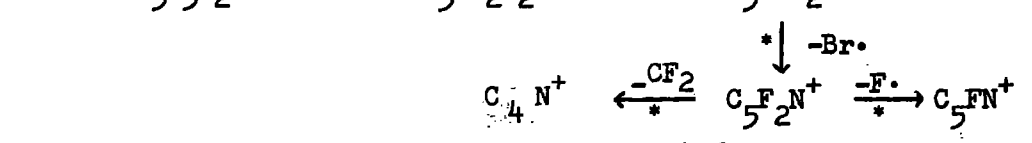
The major ions in the spectrum of 2,4-dibromotrifluoropyridine in decreasing order of abundance are M^+, $M\text{-}Br^+$, CF^+ and $C_5F_3N^+$. The molecular ion of 2,4-dibromotrifluoropyridine is more stable than that of 2-bromotetrafluoropyridine but less stable than that of 4-bromotetrafluoropyridine.



Fragmenation of the molecular ion of 2,4-dibromotrifluoro-pyridine.

The Br^+ ion is presumably derived from the 2-bromo-substituent.

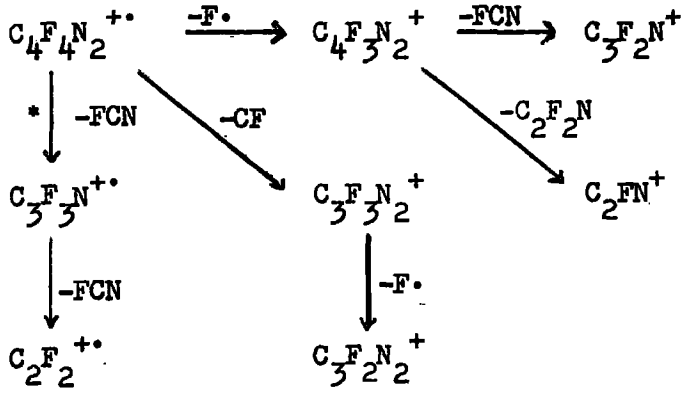
The most abundant ions in the spectrum of 2,4,6-tribromodifluoro-pyridine, in decreasing order of intensity, are M^+, $M\text{-}Br^+$, $M\text{-}2Br^+$, and CF^+. The spectrum is dominated by the consecutive loss of two bromine radicals from the molecular ion. The Br^+ ion is more abundant than in the spectrum of 2,4-dibromotrifluoropyridine and the CBr^+ ion is detected, although it is less abundant than the CF^+ ion.



Fragmentation of the molecular ion of 2,4,6-tribromodifluoro pyridine.

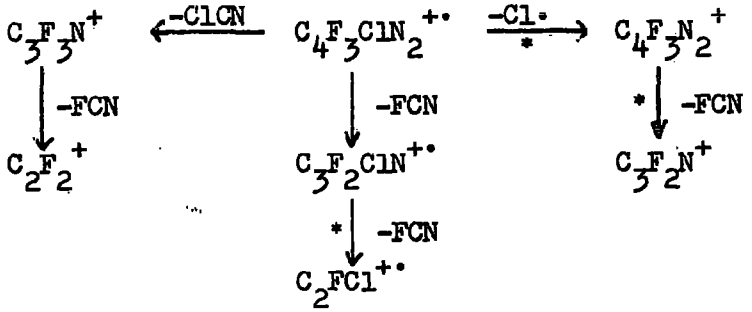
Polyhalogenated Monocyclic and Bicyclic Diazines.

The molecular ion of tetrafluoropyrazine provides the base peak in the spectrum but the CF^+ ion is almost as intense. The $C_2F_2^+$ ion is probably formed by the consecutive loss of two molecules of FCN from the molecular ion.



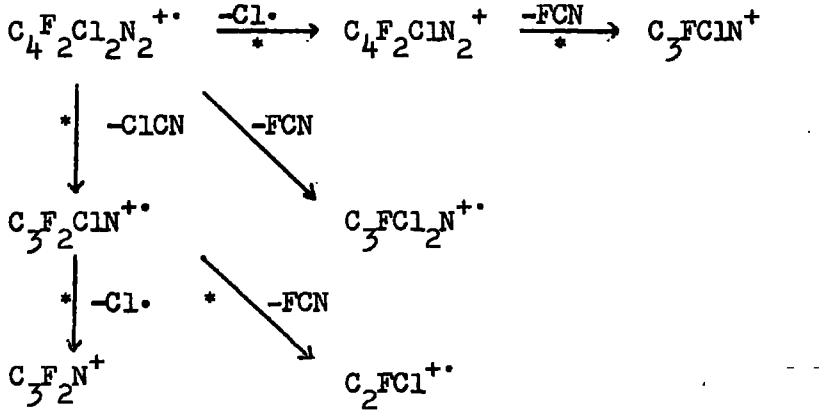
Fragmentation of the molecular ion of tetrafluoropyrazine.

The molecular ion of 2-chlorotrifluoropyrazine is more abundant than that of tetrafluoropyrazine, but the CF^+ and $M-F^+$ ions are less abundant. The $M-Cl^+$ ion is second most intense ion in the spectrum. Losses of FCN or ClCN from the molecular ion give ions of almost equal intensity.



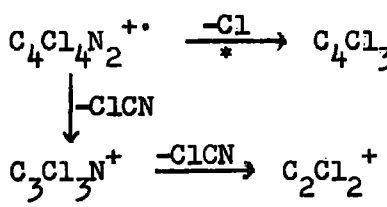
Fragmentation of the molecular ion of 2-chlorotrifluoropyrazine.

The molecular ion and the CCl^+ ion of 2,5-dichlorodifluoropyrazine are more abundant and the CF^+ ion less abundant than the corresponding ions in the spectrum of 2-chlorotrifluoropyrazine. Loss of a fluorine radical from the molecular ion of 2,5-dichloro-difluoropyrazine is not detected, whereas loss of a chlorine radical is a major process. Loss of ClCN from the molecular ion is now more favourable than loss of FCN.



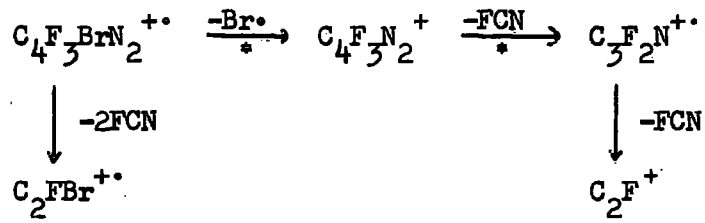
Fragmentation of the molecular ion of 2,5-dichlorodifluoropyrazine.

The molecular ion of tetrachloropyrazine is more abundant than any of the fluoropyrazines so far discussed. Chlorine loss from the molecular ion provides the second major ion in the spectrum. The mode of formation of the rearrangement ion $C_2Cl_3^+$ is obscure.



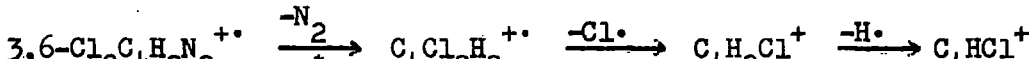
Fragmentation of the molecular ion of tetrachloropyrazine.

Once again, the base peak in the spectrum of 2-bromotrifluoropyrazine is the molecular ion, which seems to suffer simultaneous loss of two molecules of FCN.



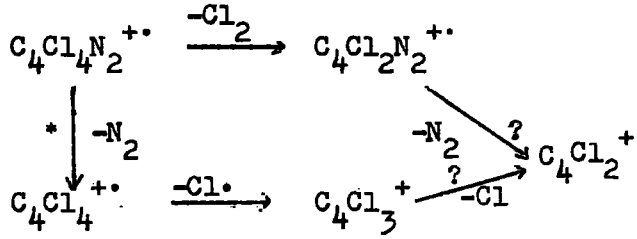
Fragmentation of the molecular ion of 2-bromotrifluoropyrazine.

The molecular ion of pyridazine suffers successive loss of nitrogen and hydrogen, and 3,6-dichloropyridazine[114] behaves similarly.



Fragmentation of the molecular ion of 3,6-dichloropyridazine.

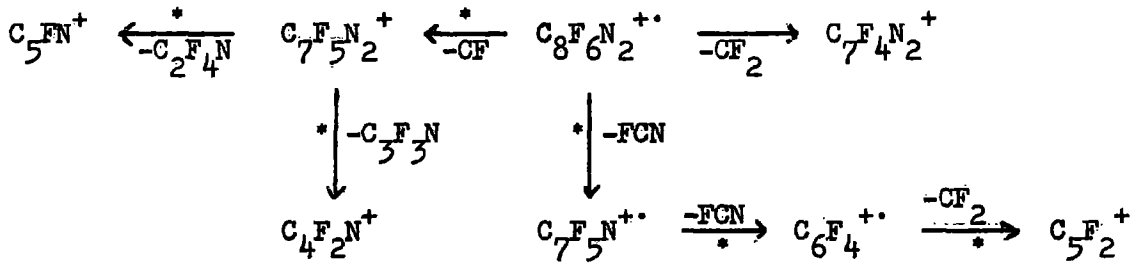
The molecular ion of tetrachloropyridazine similarly successively loses nitrogen and a chlorine radical to give $C_4Cl_3^+$, which probably loses Cl• to give $C_4Cl_2^+$. The molecular ion also seems to lose chlorine directly to give $C_4Cl_2N_2^+$, which could eliminate nitrogen to give $C_4Cl_2^+$.



Fragmentation of the molecular ion of tetrachloropyridazine.

The molecular ion of tetrafluoropyridazine, the base peak in the spectrum, loses nitrogen to give $C_4F_4^+$, which fragments by loss of F, CF and CF_2. Loss of FCN from the molecular ion is found to be a minor process. The CF^+ ion, less abundant than $C_3F_3^+$ ion, is, however, the third most abundant ion in the spectrum and is far more intense than the CCl^+ ion in tetrachloropyridazine.

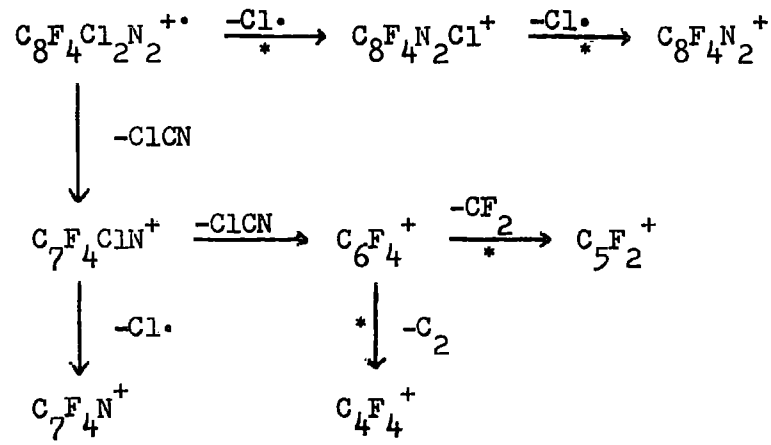
The CF^+ ion is the second most abundant ion in the spectrum of perfluoroquinoxaline, the molecular ion providing the base peak.



Fragmentation of the molecular ion of perfluoroquinoxaline.

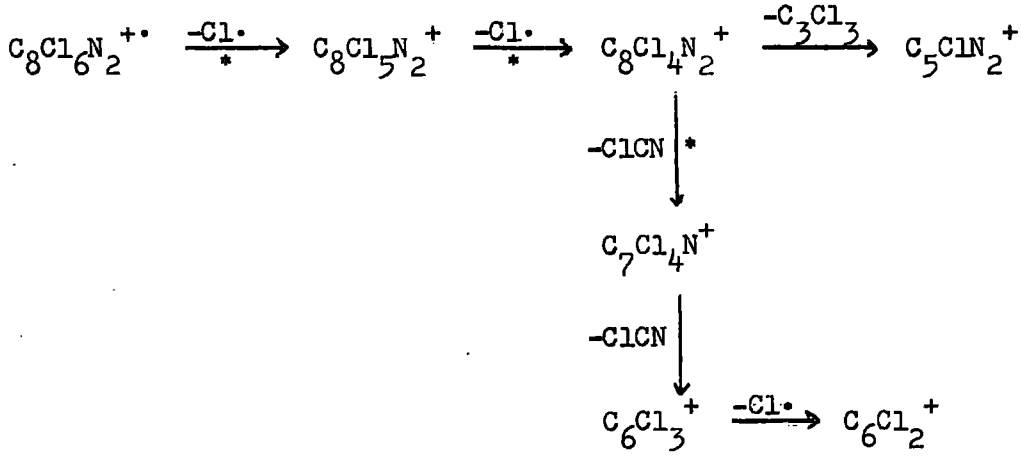
The simultaneous loss of two molecules of FCN is readily understandable, because of the known stability of the benzyne cation in mass spectrometry. However, the mode of formation of the ions C_5FN^+ and $C_4F_2N^+$ is obscure.

As expected, the molecular ion of 2,3-dichlorotetrafluoroquinoxaline seems to suffer consecutive losses of ClCN to give a presumed benzyne cation, that fragments further by losses of CF_2 and C_2. The molecular ion also shows consecutive loss of two chlorine radicals. The intensity of the CF^+ ion is much less than it is in perfluoroquinoxaline.



Fragmentation of the molecular ion of 2,3-dichlorotetrafluoroquinoxaline.

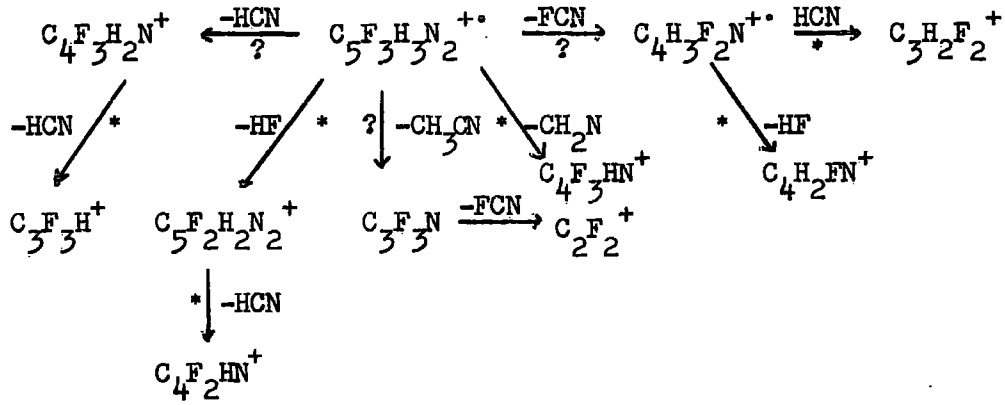
Most of the ion current of hexachloroquinazoline is carried by the M^+ and $M\text{-}Cl^+$ ions. The $M\text{-}Cl^+$ ion fragments as illustrated.



Fragmentation of the molecular ion of hexachloroquinazoline.

Fluorinated Pyrazine Derivatives.

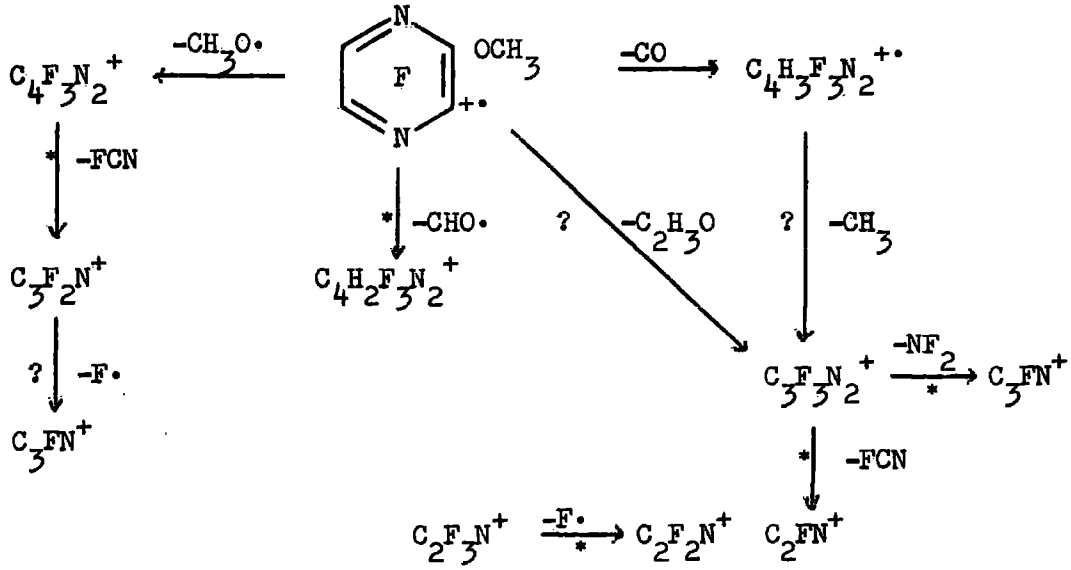
The mass spectra of derivatives of fluorinated pyrazines to be described are of interest, because little information concerning simple pyrazine derivatives is available. Interestingly, the spectrum of 2-methylpyrazine[115] shows the loss of both acetonitrile and hydrogen cyanide in a ratio suggesting random decomposition of the molecular ion. The behaviour of 2-methyltrifluoropyrazine is much more complicated. The molecular ion is of small intensity and it suffers losses of H·, CH_3·, F·, ·CH_2N, HF and probably FCN and HCN. The $C_2F_2^+$ ion is probably formed by consecutive loss of acetonitrile and FCN from the molecular ion. The base peak in the spectrum is the CF^+ ion. Other peaks of reasonable intensity whose composition were determined by mass measurement are $C_3H_2F^+$, $C_2N_2^+$, CHF_2^+, $CHFN^+$, C_2N^+, $C_2H_3^+$ and $C_2H_2^+$. Thus, the presence of the methyl group, is responsible for a number of



Fragmentation of the molecular ion of 2-methyltrifluoropyrazine.

rearrangement processes, in addition to the expected losses of CH_3CN and FCN from the molecular ion.

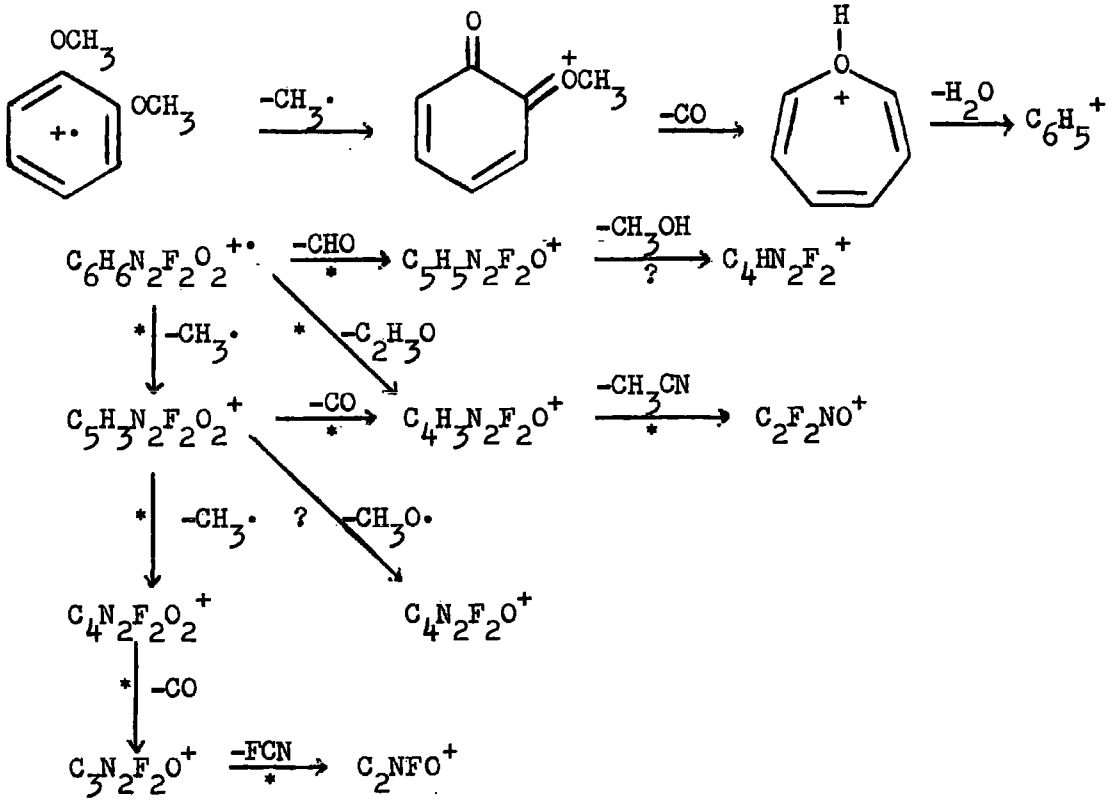
The molecular ion of 2-methoxytrifluoropyrazine, which is of small abundance, suffers loss of CO, CHO·, formaldehyde and possibly C_2H_3O·, although the $C_3F_2N_2^+$ ion could be formed by successive losses of CO and ·CH_3. Unlike anisole,[116,117,118] the molecular ion does not suffer loss of a methyl radical. Thus, the primary fragmentation paths are determined entirely by the ether linkage. The base peak in the spectrum occurs at m/e 31. It is uncertain that the ion is CF^+ or CH_3O^+ or that both ions are present.



Fragmentation of the molecular ion of 2-methoxytrifluoropyrazine.

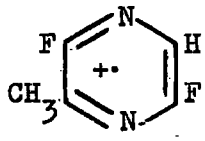
The primary fragmentation processes of 2,3-dimethoxy-difluoropyrazine are also controlled by the ether linkages. The molecular ion

of the dimethoxy-derivative is more abundant than that of 2-methoxy-trifluoropyrazine and suffers loss of H· to a small extent, as well as loss of F·, CO, HCO· and formaldehyde. The base peak in the spectrum is $C_4N_2F_2O_2^+$, formed by consecutive loss of the methyl groups. The consecutive loss of a methyl radical and CO is also found in the spectrum of o-dimethoxybenzene[115] and is, in fact, responsible for the major fragment ions in the spectrum of this compound, which are thought to arise as illustrated below:-

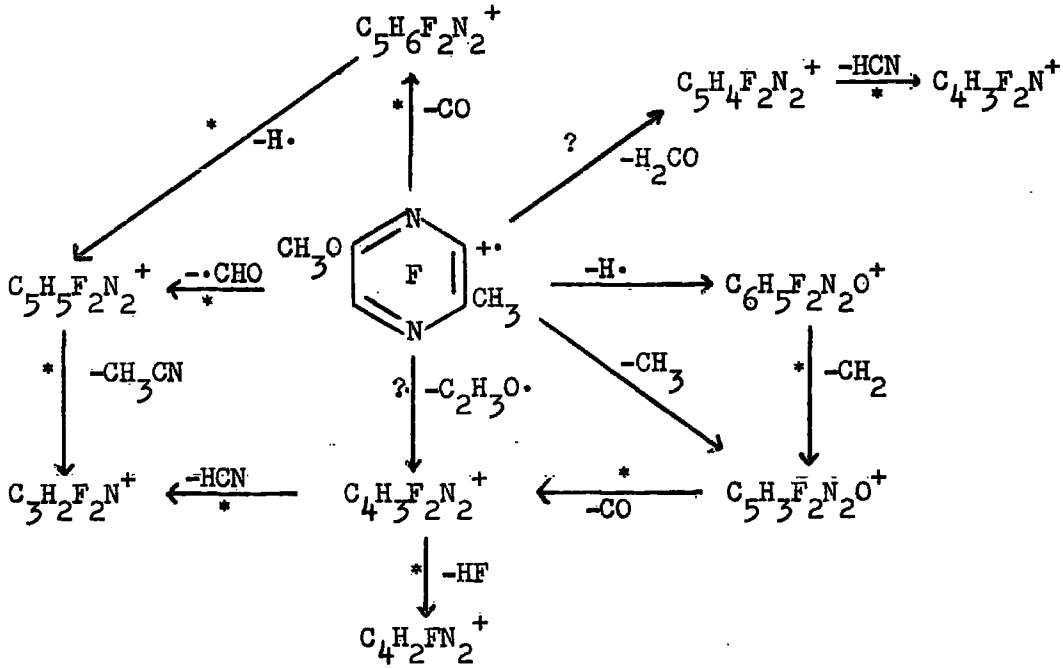


Fragmentation of the molecular ion of 2,3-dimethoxy-difluoropyrazine.

The spectra of 2-methyl-5-methoxydifluoropyrazine and 2-methyl-3-methoxydifluoropyrazine provide an interesting comparison. The base peak in the spectrum of 2-methyl-5-methoxydifluoropyrazine is the $C_5H_5F_2N_2^+$ ion, the molecular ion being the second most abundant peak. Once again, the primary fragmentation processes of the molecular ion seem to be controlled by the ether linkage. The ion $C_5H_4F_2N_2^+$, probably formed by the loss of formaldehyde from the molecular ion as is observed in the methyl-anisoles, most likely has the structure

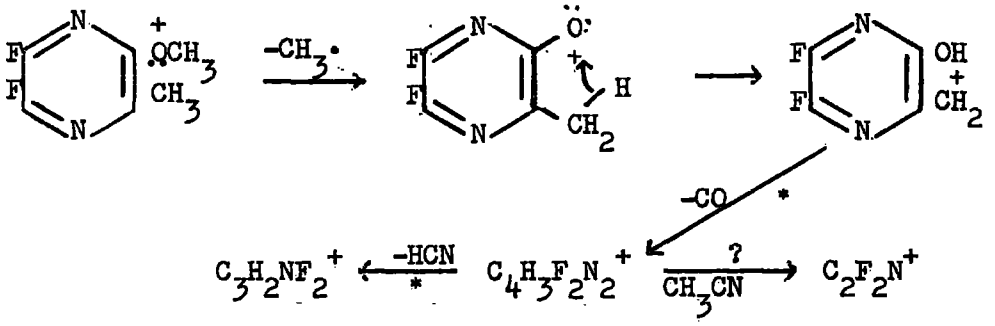


because of its fragmentation by loss of HCN.



Fragmentation of the molecular ion of 2-methyl-5-methoxy-difluoropyrazine.

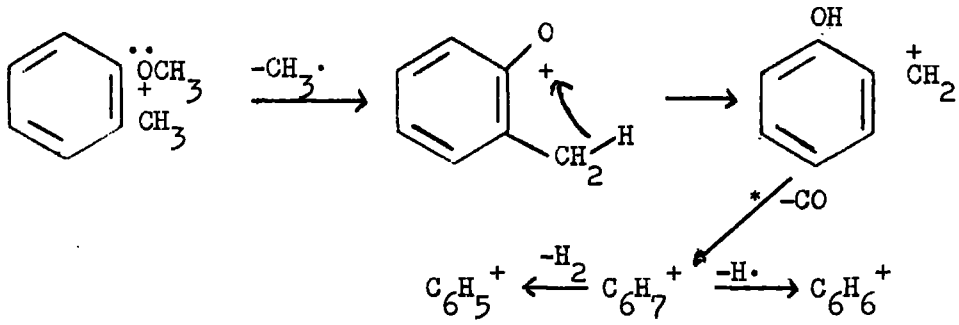
The molecular ion of 2-methyl-3-methoxydifluoropyrazine is about seven times less intense than that of 2-methyl-5-methoxydifluoropyrazine. The base peak of the ortho-isomer is at m/e 31 and could be CF, CH_3O or a combination of the two. Metastable transitions confirm the loss of CO and ·CHO from the molecular ion of the ortho isomer, as well as successive loss of CO and H·.



Fragmentation of the molecular ion of 2-methyl-3-methoxy-difluoropyrazine.

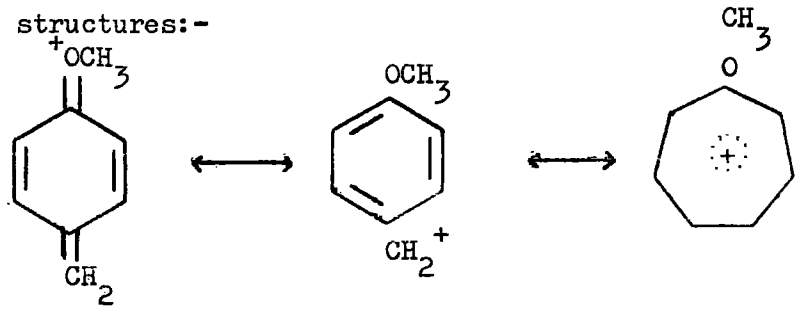
The ion $C_2NF_2^+$ is of much greater abundance in the ortho isomer because it can be formed easily by loss of CH_3CN from the ion $C_4H_3F_2N_2^+$, whereas in the para isomer this ion could be formed only by gross rearrangement.

It has been found that loss of a methyl radical from the molecular ion of o-methylanisole is more pronounced than the loss from p-methyl-anisole, possibly because of hydride ion transfer to give a benzyl or tropylium cation, which decomposes further as shown:-[117]

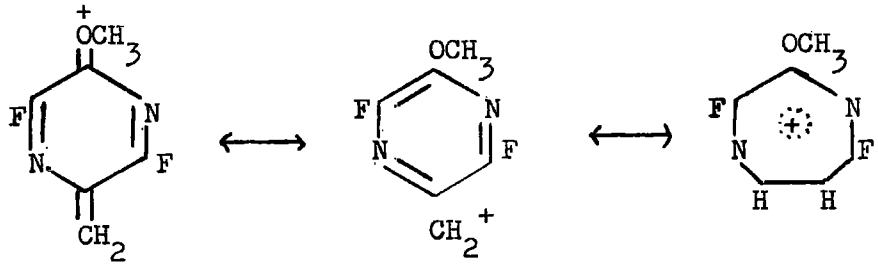


It is, therefore, of interest to find that the ion $C_4H_3F_2N_2^+$, formed by successive loss of a methyl radical and carbon monoxide from the molecular ion, in the ortho isomer is more intense than the ion found in the para isomer, possibly for a similar reason.

It has also been found[116] that all the methylanisoles lose a hydrogen radical from the molecular ion, but that the para isomer suffers the most pronounced loss, showing stabilisation of this ion by non-tropinoid structures:-



Similarly, the loss of a hydrogen radical from the molecular ion of 2-methyl-5-methoxy-difluoropyrazine is much more pronounced than in the spectrum of 2-methyl-3-methoxy-difluoropyrazine, presumably because of the non-tropinoid structures, i.e.



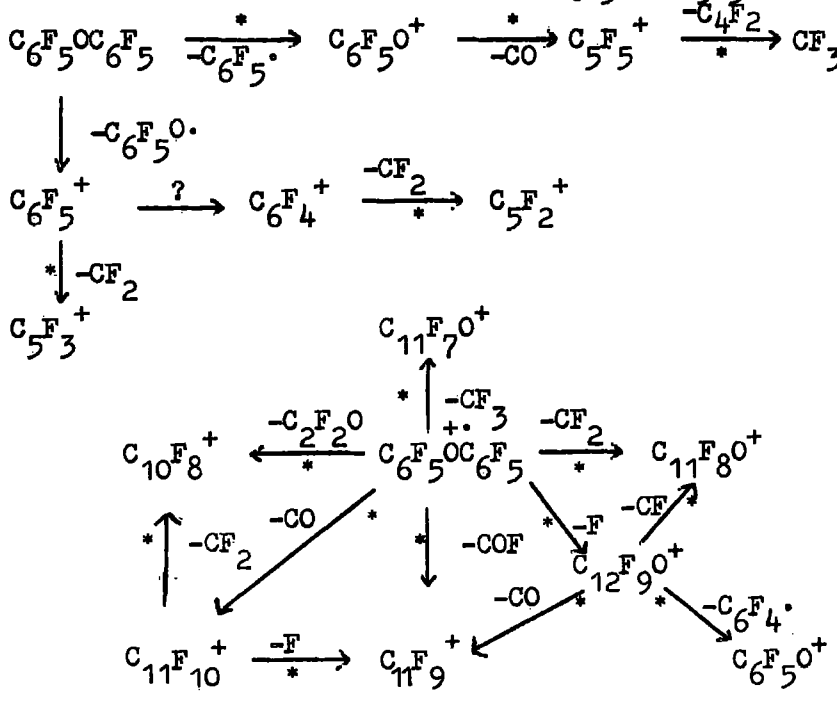
Polyfluorinated Aromatic Ethers.

The major ions in the spectrum of diphenyl ether[109, 119, 120] in order of decreasing abundance are M^+, $C_4H_3^+$, $C_6H_5^+$, $M-CHO^+$, $M-CO^+$ and $M-H^+$. Formation of the molecular ion with partial localisation of the positive charge on the oxygen atom causes cleavage of the ether linkage with charge retention on the phenyl or the phenoxy group.

$$C_6H_5O^+ + \cdot C_6H_5 \longleftarrow C_6H_5\overset{+\cdot}{O}C_6H_5 \longrightarrow C_6H_5^+ + \cdot OC_6H_5$$

Because of the greater electronegativity of oxygen, the $C_6H_5O^+$ ion is of low abundance and the positive charge prefers to remain on the C_6H_5 group, which loses acetylene to give the $C_4H_3^+$ ion. The elimination of carbon monoxide from the molecular ion proceeds by a complicated rearrangement process.

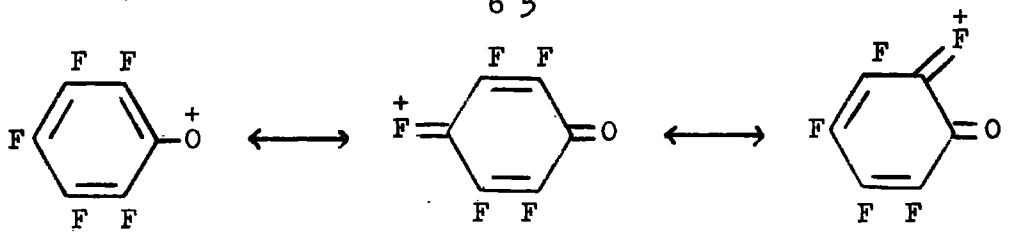
Surprisingly, the major ions in the spectrum of decafluorodiphenyl ether in order of decreasing abundance are M^+, $C_6F_5O^+$, $C_5F_5^+$ and $C_5F_3^+$.



Fragmentation of the molecular ion of decafluorodiphenyl ether.

The fragmentations of the molecular ion analogous to those of diphenyl ether are of much less importance, but, in addition, there are the expected minor losses of CF_3 and CF_2. The interesting loss of difluoro-oxirene from the molecular ion may give an ion whose structure is equivalent to the molecular ion of octafluoronaphthalene.

The fundamental difference in the spectra is the relative stability of the $C_6F_5O^+$ and the $C_6H_5^+$ ions, and, the low abundance of the $C_6H_5O^+$ and $C_6F_5^+$ ions. The effect of the substitution of fluorine for hydrogen in the phenoxy ion must cause an increase in the stability of the $C_6F_5O^+$ ion relative to that of the $C_6F_5^+$ ion. The ionisation constant of pentafluorophenol (K_a = 3·0 x 10^{-6} at 25°)[121] shows that back co-ordination with electron release from fluorine counteracts the inductive effect of the fluorine atoms in the C_6F_5 group, because pentachlorophenol is found to be a stronger acid (K_a = 5·5 x 10^{-6}).[122] This electron release from the fluorine atoms in the $C_6F_5O^+$ ion will serve to stabilise the positive charge by greater delocalisation than is possible in the $C_6H_5O^+$, and to an extent that makes the $C_6F_5O^+$ ion more stable than the

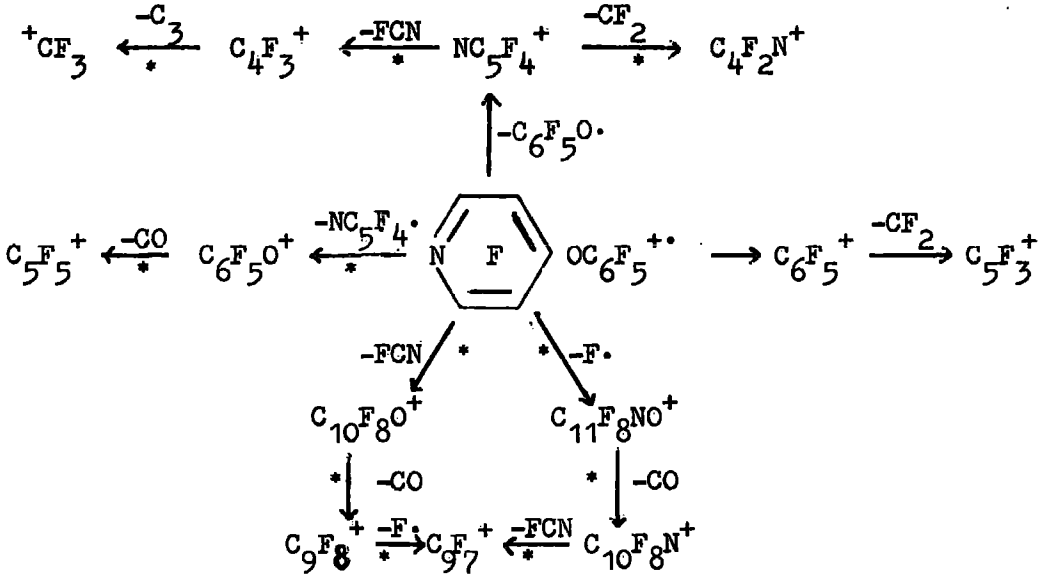


$C_6F_5^+$ ion.

The $C_6F_5O^+$ ion decomposes by loss of carbon monoxide to yield the $C_5F_5^+$ ion. The $C_5F_3^+$ ion is formed by the loss of CF_2 from the $C_6F_5^+$ ion, which contrasts with the abundant loss of acetylene from the $C_6H_5^+$ ion to yield the $C_4H_3^+$ ion.

This interesting difference in the behaviour of diphenyl and decafluorodiphenyl ether illustrates that substitution of fluorine for hydrogen in an aromatic ether manifestly changes the initial fragmentation processes, whereas that was not found to be the case for fluorinated carbonyl derivatives.

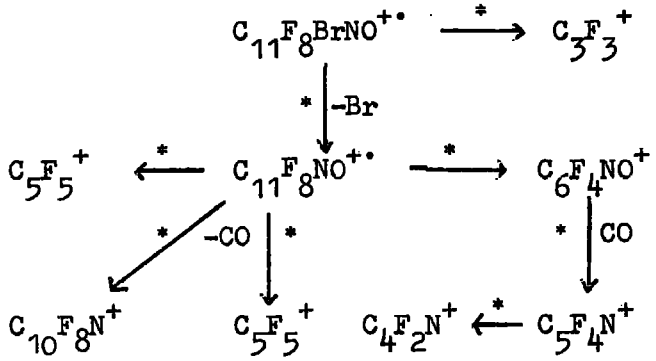
The major ions in the spectrum of 4-pentafluorophenoxy-tetrafluoropyridine in order of decreasing abundance are M^+, $C_5F_5^+$, $C_6F_5O^+$ and $C_5F_3^+$. Thus, the major ions are formed in the same manner as in decafluorodiphenyl ether. Rupture of the C-O of either substituent also gives $C_6F_5^+$ and $NC_5F_4^+$ ions of low abundance but no $NC_5F_4O^+$ ion.



Fragmentation of the molecular ion of 4-pentafluorophenoxy-tetrafluoropyridine.

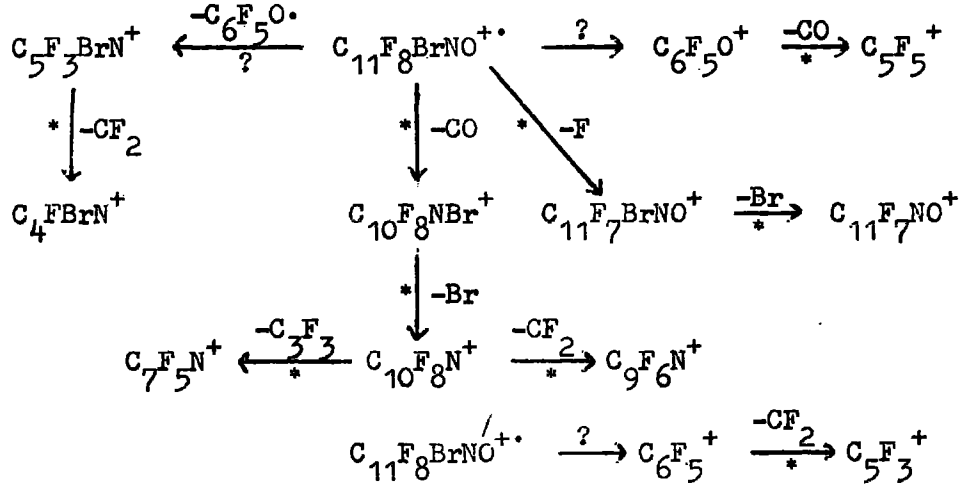
The molecular ion of 4-pentafluorophenoxy-tetrafluoropyridine is not as abundant as that of decafluorodiphenyl ether. The introduction of the ring nitrogen atom provides a site for minor fragmentation processes. Unlike decafluorodiphenyl ether, the molecular ion of 4-pentafluorophenoxy-tetrafluoropyridine does not suffer loss of $\cdot CF_3$, CO or difluoro-oxirene. Loss of FCN from the molecular ion occurs as would be expected from the behaviour of pentafluoropyridine.

The major ions in the spectrum of 2-pentafluorophenoxy-4-bromotrifluoropyridine are entirely different from those peaks expected if the spectrum showed an analogy to that of 4-pentafluorophenoxy-tetrafluoropyridine. The major ions in order of decreasing abundance are in fact, M^+, $C_3F_3^+$, $C_6F_4NO^+$, $M\text{-}Br^+$, $C_3F_3^+$ and $C_5F_3^+$.



The formation of the major ions in the spectrum of 2-pentafluorophenoxy-4-bromotrifluoropyridine and their subsequent fragmentation.

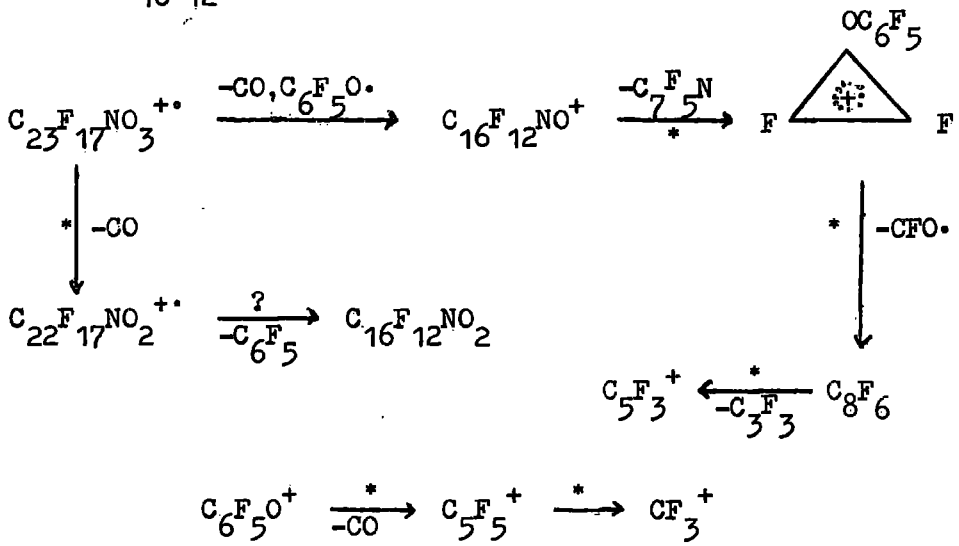
The molecular ion of 2-pentafluorophenoxy-4-bromotrifluoropyridine is less abundant than that of 4-pentafluorophenoxy-tetrafluoropyridine, as would be expected from the spectrum of 4-bromotetrafluoropyridine, which shows that the bromine substituent provides another site for fragmentation. The fragmentation of a bromine radical from the molecular ion is, in fact, responsible for the formation of a number of major ions in the spectrum. The $M-Br^+$ ion undergoes an interesting rearrangement process to give the $C_6F_4NO^+$ ion whose structure is uncertain. The direct formation of the abundant $C_3F_3^+$ ion from the molecular ion is a mode of fragmentation without parallel in the ethers so far examined.



The formation of minor ions in the spectrum of 2-pentafluorophenoxy-4-bromotrifluoropyridine.

The important fragmentation processes of 2-pentafluorophenoxy-4-bromotrifluoropyridine are, thus, influenced by the bromine substituent rather than the pentafluorophenoxy substituent.

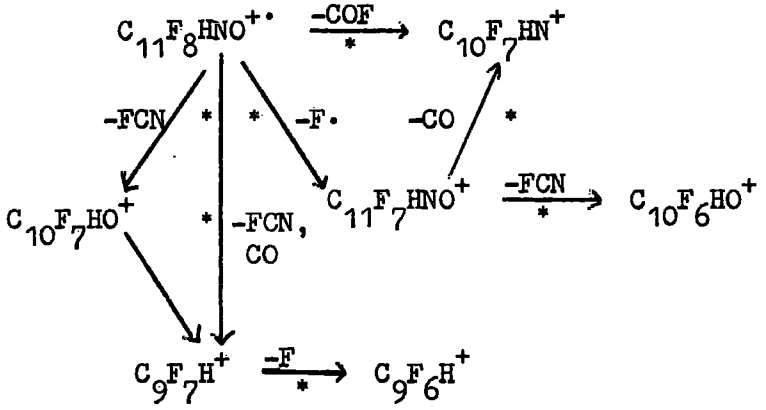
2,4,6-Tris(pentafluorophenoxy)-difluoropyridine, on electron impact, fragments in a different manner from the ethers so far discussed. The major ions in the spectrum in decreasing order of abundance are $C_9F_7O^+$, M^+ and $C_{16}F_{12}NO^+$.



Fragmentation processes in the spectrum of 2,4,6-tris-(pentafluorophenoxy)-difluoropyridine.

The base peak in the spectrum could have the structure illustrated. Of interest is a rearrangement ion $C_{20}F_{11}O_3^+$, of obscure origin, which could be formed by expulsion of C_3F_6N from the molecular ion. It is not certain that the ions $C_6F_5O^+$ and $C_6F_5^+$ are derived by direct cleavage of the molecular ion. The simultaneous loss of carbon monoxide and $C_6F_5O\cdot$ from the molecular ion should involve the 2 and 6-pentafluorophenoxy substituents, unless the $C_9F_7O^+$ ion has been formed by a rearrangement process.

The major ions in the spectrum of 4-(2',3',5',6'-tetrafluorophenoxy)-tetrafluoropyridine in decreasing order of abundance are M^+, $C_5F_4H^+$, $C_5F_2H^+$ and $C_6F_4H^+$. Unlike 4-pentafluorophenoxy-tetrafluoropyridine,

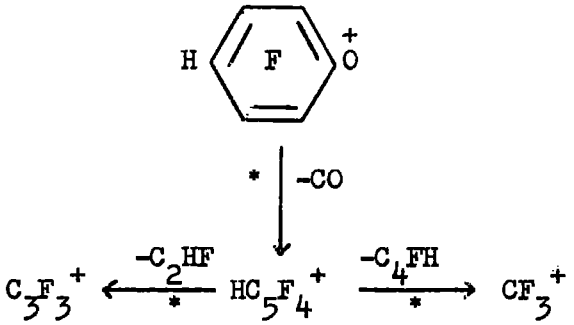


Fragmentation of the molecular ion of 4-(2',3',5',6'-tetrafluorophenoxy)-tetrafluoropyridine.

the molecular ion of this compound suffers loss of carbon monoxide and simultaneous loss of both carbon monoxide and FCN. The ions $HC_6F_4O^+$, $HC_6F_4^+$ and $C_5F_4N^+$ are presumably formed by cleavages around the ether linkages of the molecular ion. It is of interest to find that the $HC_6F_4^+$ ion is more abundant than the $HC_6F_4O^+$, whereas in the spectrum of 4-pentafluorophenoxy-tetrafluoropyridine the $C_6F_5O^+$ ion is more abundant than the $C_6F_5^+$ ion. This could be explained by the absence of a para fluorine atom in the $HC_6F_4O^+$ ion, which would considerably reduce stabilisation of this ion, because the delocalisation of the positive charge on the oxygen by back co-ordination with the para fluorine atom would be absent. The localisation of the positive charge

upon the more electronegative oxygen atom in the ion $HC_6F_4O^+$ would result in the ion $HC_6F_5^+$ having greater stability, because the positive charge would reside on the more electropositive carbon atom.

The fragmentation of the 4-(2',3',5',6'-tetrafluorophenoxy)-ion is illustrated:-



A metastable peak shows that the $4\text{-}HC_6F_4^+$ ion loses difluoromethylene to give the ion $C_5F_2H^+$.

Methods of Preparation of Compounds Examined Mass Spectrometrically.

Many of the compounds examined have been reported in other publications, as indicated: tetrafluoropyridine-4-aldehyde, 4-tetrafluoroisonicotinyl-pentafluorobenzene, and 4-tetrafluoroisonicotinyl-tetrafluoropyridine;[123] 4-tetrafluoropyridyl-heptafluoroisopropyl ketone, 4-heptafluoroisopropyl-tetrafluorophenyl-heptafluoroisopropyl ketone, and perfluoro-iso-butyrophenone;[21] decafluorobenzophenone;[20] octafluorofluorenone;[86] perfluoro-α,α-dimethylbenzyl alcohol;[24] pentafluoropyridine, 3-chlorotetrafluoropyridine, 3,5-dichlorotrifluoropyridine and pentachloropyridine;[124] 2,4,6-trichlorodifluoropyridine, 2,4-dibromotrifluoropyridine, and 2,4,6-tribromodifluoropyridine;[125] 4-bromotetrafluoropyridine;[126] 2-bromotetrafluoropyridine;[127] tetrafluoropyrazine, tetrachloropyrazine, and 2,5-dichlorodifluoropyrazine;[128] tetrachloropyridazine and tetrafluoropyridazine;[90] perfluoroquinoxaline and hexachloroquinoxaline;[129] and decafluorodiphenyl ether.[46]

The preparation of octafluoroacetophenone, perfluoro-n-butyrophenone, 2,3,5,6-tetrafluoropyridyl-bis-trifluoromethylcarbinol, 4-pentafluorophenoxy-tetrafluoropyridine, 2-pentafluorophenoxy-4-bromotrifluoropyridine and 4-(2',3',5',6'-tetrafluorophenoxy)-tetrafluoropyridine are described in this thesis.

Decafluorobenzil[130] was prepared by reaction of a twofold molar proportion of pentafluorophenyl lithium with diethyl oxalate in ether/hexane solution at -78° followed by hydrolysis of the reaction product at -78°.

2-Chlorotrifluoropyrazine[131] was prepared in 77% yield by adding trifluoro-2-hydrazino pyrazine to a solution of cupric chloride in 36% hydrochloric acid.

2-Bromotrifluoropyrazine[131] was prepared in 77% yield by adding trifluoro-2-hydrazino pyrazine to a solution of cupric bromide in 50% hydrobromic acid.

2,3-Dichlorotetrafluoroquinoxaline[131] was prepared in 82% yield by adding tetrafluoro-2,3-dihydrazino-quinoxaline to a solution of cupric bromide in 50% hydrobromic acid.

2-Methyltrifluoropyrazine[131] was prepared in 70% yield by reacting tetrafluoropyrazine with one molecular proporation of ethereal methyl-lithium at -70°.

2-Methoxytrifluoropyrazine[131] was prepared in 60% yield by reacting tetrafluoropyrazine with one molecular proportion of sodium methoxide in methanol at -20°.

2,3-Dimethoxydifluoropyrazine[131] was prepared in 90% yield by reacting tetrafluoropyrazine with two molecular proportions of sodium methoxide in methanol at 20°.

2-Methyl-5-methoxydifluoropyrazine[131] was prepared in 85% yield by reacting 2-methyltrifluoropyrazine with one molecular proportion of sodium methoxide in methanol at -40°.

2-Methyl-3-methoxydifluoropyrazine[131] was prepared in 90% yield by reacting 2-methoxytrifluoropyrazine with one molecular proportion of methyl-lithium in diethyl ether at -20°.

APPENDIX 1

Abundances, Metastable Ions, and Accurate Mass Measurements Determined in the Mass Spectrometric Studies on Halogenated Aromatic Compounds.

a. I(%) is the intensity of an ion relative to the base peak (100%). All peaks with intensity $>$ 2% of the base peak are recorded.

b. Intensities are expressed as percent total ionisation defined as Σ(Int)n where n refers to all ions with m/e $>$ 30 whose intensities are $>$ 2% of the base peak.

Tetrafluoropyridine-4-aldehyde[a]

M/e	180	179	178	152	151	150	132	131	124	120
I(%)	7	100	20	5	62	25	9	14	14	20
M/e	113	112	107	106	105	101	100	99	93	87
I(%)	2	3	3	30	18	8	50	3	8	8
M/e	86	83	82	81	76	75	74	71	69	68
I(%)	27	3	36	12	3	24	13	2	37	5
M/e	67	63	62	58	57	56	55	51	50	45
I(%)	2	5	9	3	2	16	20	5	3	2
M/e	44	43	42	41	39	38	37	36	31	29
I(%)	6	14	3	12	4	3	10	4	69	77

4-Heptafluoroisopropyl-tetrafluorophenyl-heptafluoroisopropyl ketone.

Ion, Intensity[b]

$C_{13}F_{18}O$, 6·1; $C_{13}F_{17}O$, 5·6; $C_{11}F_{13}O$, 1·0; $C_{10}F_{11}O$, 46·4; $C_{10}F_{10}O$, 2·3; C_9F_8O, 8·5; C_8F_9, 1·6; C_9F_7O, 1·0; C_8F_8, 6·7; C_8F_7, 1·0; C_7F_7, 1·3; C_7F_6, 7·8; C_7F_5, 2·2; C_6F_4, 1·0; CF_3, 7·5.

Octafluorofluorenone. Ion, Intensity

$C_{13}F_8O$, 66·6; $C_{12}F_8$, 18·0; $C_{12}F_7$, 2·1; $C_{11}F_7$, 2·5; $C_{12}F_6$, 1·7; $C_{11}F_6$, 3·6; $C_{11}F_5$, 5·6.

$C_{13}F_8O^{2+}$, I(%) 3·8; $C_6F_4^{2+}$, I(%) 7.

	Intensity [b]			
Ion	$C_6F_5COCF_3$	$C_6F_5COC_6F_5$	n-$C_6F_5COC_3F_7$	i-$C_6F_5COC_3F_7$
$C_{10}F_{12}O$			0·6	6·4
$C_{10}F_{11}O$			1·4	
$C_{13}F_{10}O$		18·8		
C_8F_8O	3·4			
C_7F_7			1·3	
C_7F_5O	37·4	54·6	51·5	49·5
C_7F_4O	1·7		1·7	1·2
C_6F_5	19·5	13·2	14·6	17·7
C_6F_4	2·4	1·3	2·1	1·8
C_6F_3	0·8			
C_5F_3	13·3	8·3	10·3	10·1
C_6F_2	0·8			
C_2F_4			1·3	
C_5F_2	3·6	1·5	2·1	2·0
C_3F_3	3·3	2·3	2·9	2·8
C_4F_2	0·9			
C_5F	2·7		1·4	1·2
C_3F_2	1·1			
CF_3	4·8		5·5	5·6
C_2FO			1·3	
C_2F	1·2			
C_3				0·1
CF	3·4		2·0	1·9

	Intensity [b]			
Ion	$4,4'-(NC_5F_4)_2CO$	$i-4-NC_5F_4COC_3F_7$	$4-NC_5F_4COC_6F_5$	$C_6F_5COCOC_6F_5$
$C_{14}F_{10}O_2$				0·8
$C_{13}F_{10}O$				0·7
$C_9F_{11}NO$		9·7		
$C_{11}F_8N_2O$	25·1			
$C_{12}F_8NO$			0·9	
C_7F_5O			39·9	68·4
C_6F_4NO	38·2	45·0	8·0	
C_6F_5			8·6	14·8
C_6F_4O	0·8			
C_5F_4N	13·4	14·7	4·1	
C_6F_4			0·9	
C_5F_3N		1·3		
C_5F_3			4·8	8·4
C_4F_3	3·0	3·1	1·2	
C_4F_2N	10·4	12·1	3·0	
C_5F_2			1·0	1·6
C_4F_2	1·7	1·2		
C_3F_3			1·6	2·7
CF_3	1·6	8·2	0·9	
C_3F	1·8	1·1		
CF	4·9	2·4	1·5	1·3

Perfluoro-(α,α-dimethylbenzyl)alcohol. Ion, Intensity[b]

$C_9F_{11}OH$, 4·1; C_9F_9O, 1·8; C_8F_9, 2·4; C_8F_8OH, 6·4; C_7F_7, 3·4; C_7F_5O, 37·0; C_7F_5, 1·8; C_6F_5, 4·1; C_6F_4, 1·9; C_5F_3, 4·1; C_5F_2H, 1·5; C_5F_2, 1·3; C_3F_3, 1·5; C_5F, 0·9; CF_3, 5·8; C_2FO, 4·9; C_2F, 14·9; HF_2, 0·9; CF, 1·2.

2,3,5,6-Tetrafluoropyridyl-bis-trifluoromethylcarbinol[a]

M/e	317	298	278	250	248	200	198	179	178
I(%)	5	1	1	7	7	10	2	8	100
M/e	162	151	150	132	131	124	117	112	105
I(%)	3	3	27	3	8	2	6	2	8
M/e	100	93	86	82	81	74	69	55	51
I(%)	22	5	9	3	3	4	43	4	2
M/e	50	41	31						
I(%)	4	2	18						

2,3-Dichlorotetrafluoroquinoxaline. Ion, Intensity[b]

$C_8F_4N_2Cl_2$, 40·6; $C_8F_4N_2Cl$, 20·3; C_7F_4NCl, 2·2; $C_8F_4N_2$, 6·8; C_7F_4N, 4·0; C_6F_4, 7·0; C_4F_4, 5·6; C_5F_3, 1·2; C_4F_3, 1·1; C_4F_2N, 1·4; C_5F_2, 1·6; C_3F_3, 2·0; C_5F, 1·0; C_5N, 1·0; CF, 3·9.

Hexachloroquinazoline. Ion, Intensity[b]

$C_8Cl_6N_2$, 42·1; $C_8Cl_5N_2$, 23·4; $C_8Cl_4N_2$, 5·7; C_7Cl_4N, 6·1; C_7Cl_3N, 5·3; C_6Cl_3, 1·6; C_6Cl_2, 1·7; C_5ClN_2, 3·4; C_4Cl_2, 2·1; C_3Cl_2, 1·8; C_6Cl, 1·9; C_5ClN, 1·1; C_7N, 1·2; C_3Cl, 1·2; C_3, 1·5.

Pentafluoropyridine. Ion, Intensity[b]

C_5F_5N, 24·6; C_5F_4N, 3·8; C_4F_4N, 2·6; C_4F_4, 8·3; C_4F_3N, 0·9; C_4F_3, 1·5; C_4F_2N, 12·2; C_3F_3, 7·8; C_4F_2, 1·4; C_4FN, 1·4; C_3F_2, 4·3; CF_3, 4·5; C_2F_2, 2·12; C_3F, 3·4; CF_2, 0·6; C_2N, 0·6; C_3, 0·83; CF, 19·3.

Pentachloropyridine. Ion, Intensity[b]

C_5Cl_5N, 32·3; C_5Cl_4N, 12·7; C_4Cl_4, 0·1; C_5Cl_3N, 5·7; C_4Cl_3, 4·7; C_5Cl_2N, 3·4; C_4Cl_2N, 0·9; C_4Cl_2, 7·4; C_5ClN, 7·1; C_3Cl_2, 1·7; C_5Cl, 1·47; C_2Cl_2, 4·3; C_4Cl, 2·8; C_5N, 2·1; C_3Cl, 2·1; C_4N, 1·0; C_4, 0·9; CCl, 4·1; C_2N, 1·2; C_3, 1·0; Cl, 1·5.

3-Chlorotetrafluoropyridine. Ion, Intensity[b]

C_5F_4ClN, 47·5; C_5F_3ClN, 1·8; C_4F_3ClN, 2·4; C_5F_4N, 5·9; C_4F_3Cl, 5·9; C_4FClN, 4·2; C_3F_2Cl, 2·7; C_4F_3, 1·9; C_4F_2N, 8·2; C_3F_3, 2·0; C_3FCl, 2·0; C_4F_2, 1·4; C_3F_2, 2·1; CF_3, 2·1; C_3F, 1·9; CF, 7·9.

3,5-Dichlorotrifluoropyridine. Ion, Intensity[b]

$C_5F_3Cl_2N$, 75·6; C_5F_3ClN, 5·4; $C_4F_2Cl_2$, 2·6; C_4F_2Cl, 2·4; C_4FClN, 8·0; C_4F_2, 1·6; CF, 4·5.

2,4,6-Trichlorodifluoropyridine. Ion, Intensity[b]

$C_5Cl_3F_2N$, 52·7; $C_5Cl_2F_2N$, 18·1; $C_4Cl_2F_2$, 1·1; C_5ClF_2N, 3·0; C_4Cl_2N, 12·2; C_4ClF_2, 3·4; C_4ClFN, 4·4; C_4ClF, 2·1; C_4ClN, 1·7; CF, 1·3.

4-Bromotetrafluoropyridine. Ion, Intensity[b]

C_5F_4BrN, 53·8; C_4F_3BrN, 1·3; C_4FBrN, 1·1; C_5F_4N, 10·1; C_4F_3, 4·8; C_4F_2N, 12·9; C_4F_2, 2·0; C_4FN, 1·1; C_3F_2, 1·9; CF_3, 1·9; C_3F, 2·6; CF, 6·6.

2-Bromotetrafluoropyridine. Ion, Intensity[b]

C_5F_4BrN, 29·3; C_5F_3BrN, 1·2; C_4F_2BrN, 2·2; C_4FBrN, 1·3; C_5F_4N, 13·9; C_5F_3N, 1·7; CF_2Br, 2·2; C_4F_4, 0·8; C_4F_3, 1·8; C_4F_2N, 17·2; C_3F_3, 3·5; C_4F_2, 1·3; C_4FN, 2·6; Br, 1·2; C_3F_2N, 0·7; C_3F_2, 2·5; CF_3, 3·1; C_2F_2, 1·4; C_3F, 1·9; CF, 10·1.

2,4-Dibromotrifluoropyridine. Ion, Intensity[b]

$C_5F_3Br_2N$, 38·1; C_5F_3BrN, 13·7; C_4F_2Br, 1·4; C_4FBrN, 7·2; C_5F_3N, 8·9; C_5F_2N, 1·1; C_4F_3, 1·5; C_4F_2N, 2·9; C_3F_3, 0·8; C_4F_2, 3·0; C_4FN, 3·8; Br, 1·4; C_3F_2, 2·2; CF_3, 1·0; C_2F_2, 1·5; C_3F, 2·0; CF, 9·8.

2,4,6-Tribromodifluoropyridine. Ion, Intensity[b]

$C_5Br_3F_2N$, 29·8; $C_5Br_2F_2N$, 10·4; C_5BrF_2N, 13·7; C_4BrF_2, 1·8; C_4BrFN, 1·7; C_4BrF, 0·8; C_4BrN, 0·9; C_2BrF, 1·7; C_3Br, 0·6; C_5F_2N, 7·3; C_5FN, 6·2; CBr, 1·1; C_8F_2, 4·2; C_4FN, 1·5; Br, 3·0; C_5FN, 1·2; C_3FN, 0·6; C_4F, 0·7; C_4N, 3·3; C_3F, 1·4; C_3, 0·7; CF, 7·7.

Tetrafluoropyrazine. Ion, Intensity[b]

$C_4F_4N_2$, 27·1; $C_4F_3N_2$, 3·0; $C_3F_3N_2$, 1·2; C_3F_3N, 8·3; $C_3F_2N_2$, 0·4; C_4FN_2, 0·2; C_3F_2N, 3·2; C_3FN_2, 2·0; C_4NF, 1·1; C_2F_2N, 3·0; C_3FN, 5·0; C_2F_2, 13·3; C_2FN, 2·1; CF_2, 0·9; CFN, 0·5; C_2F, 0·4; C_2N, 1·7; CF, 25·7.

2-Chlorotrifluoropyrazine. Ion. Intensity[b]

$C_4F_3ClN_2$, 45·5; $C_4F_2ClN_2$, 1·5; $C_4F_3N_2$, 12·9; C_3F_2ClN, 2·3; C_3F_3N, 2·3; C_3F_2N, 4·4; C_3ClN, 1·1; C_3FN_2, 2·3; C_4FN, 1·7; C_2FCl, 5·2; C_3FN, 1·6; C_2F_2, 4·6; C_2FN, 1·1; C_2N, 1·3; CF, 12·2.

2,5-Dichlorodifluoropyrazine. Ion, Intensity[b]

$C_4F_2Cl_2N_2$, 49·5; $C_4F_2ClN_2$, 11·7; C_3FCl_2N, 0·9; C_3F_2ClN, 2·3; C_3FClN, 5·3; C_3ClN_2, 0·5; C_4ClN, 2·6; C_3F_2N, 2·2; C_3ClN, 1·2; C_3FN_2, 0·4; C_2FCl, 7·8; C_2F_2N, 0·4; C_3FN, 3·7; CCl, 2·9; C_2N, 1·2; CF, 7·4.

Tetrachloropyrazine. Ion, Intensity[b]

$C_4Cl_4N_2$, 65·1; $C_4Cl_3N_2$, 10·1; C_3Cl_3N, 2·8; C_3Cl_2N, 4·9; C_2Cl_3, 4·9; C_2Cl_2, 8·0; $CClN$, 1·7; CCl, 2·3.

2-Bromotrifluoropyrazine. Ion, Intensity[b]

$C_4F_3BrN_2$, 37·6; $C_4F_3N_2$, 17·1; C_2FBr, 1·9; $C_2F_3N_2$, 0·9; CF_3N_2, 0·8; C_2F_3N, 1·3; C_3F_2N, 6·8; CF_3N, 4·1; C_2F_3, 3·5; C_2F_2N, 6·5; C_3NF, CF_3, 0·2; 0·2; C_4F, 0·1; C_2F_2, 0·3; C_2FN, 0·2; C_3F, 0·2; CF, 1·6.

Tetrachloropyridazine. Ion, Intensity[b]

$C_4Cl_4N_2$, 36·9; C_4Cl_4, 8·2; C_4Cl_3, 22·0; $C_4Cl_2N_2$, 2·1; C_4Cl_2, 9·3; C_2Cl_2, 3·1; C_3ClN, 3·2; C_4Cl, 2·1; C_4N_2, 1·7; C_2Cl, 1·3; CCl, 2·6; C_2N, 1·9; C_3, 5·6.

Tetrafluoropyridazine.

$C_4F_4N_2$, 32·2; $C_4F_3N_2$, 0·6; C_4F_4, 3·1; $C_4F_2N_2$, 1·3; C_3F_3N, 0·9; C_4F_3, 3·0; C_3F_3, 21·2; C_3F_2N, 1·4; C_2NF, 1·1; C_3F_2, 8·0; C_3FN, 4·1; C_2F_2, 4·1; C_3F, 2·5; C_2N, 0·9; CF, 15·7.

Hexafluoroquinoxaline. Ion, Intensity[b]

$C_8F_6N_2$, 31·5; $C_8F_5N_2$, 1·7; $C_7F_5N_2$, 2·0; C_7F_5N, 1·4; $C_7F_4N_2$, 0·9; $C_7F_3N_2$, 0·9; C_6F_4, 3·8; C_5F_3N, 0·7; C_4F_4, 4·7; C_5F_2N, 0·8; C_4F_3, 1·5; C_4F_2N, 2·7; C_5F_2, 3·1; C_5FN, 4·5; C_3F_2N, 1·0; C_4F_2, 1·7; C_4FN, 1·7; C_5F, 2·6; C_2F_2N, 2·4; C_3F_2, 3·4; CF_3, 3·6; C_2F_2, 3·0; C_2NF, 1·1; C_3F, 2·8; CF_2, 2·4; FCN, 2·2; C_2N, 1·4; CF, 10·6.

2-Methyltrifluoropyrazine[a]

M/e	149	148	147	133	129	128	121	120	107
I(%)	0·9	10	4	3	3	6	7	4	3
M/e	103	102	101	98	97	95	94	88	84
I(%)	19	8	6	2	2	3	3	10	4
M/e	83	82	81	77	76	75	72	71	70
I(%)	9	4	3	7	27	6	2	2	12
M/e	69	64	63	62	58	57	56	55	53
I(%)	8	3	3	22	16	49	21	3	2
M/e	52	51	50	46	45	44	42	41	40
I(%)	15	15	5	11	7	4	4	3	6
M/e	39	38	37	33	32	31	28	27	26
I(%)	5	10	6	5	3	100	4	16	15
M/e	25	15							
I(%)	2	7							

2-Methoxytrifluoropyrazine[a]

M/e	164	136	135	134	133	122	121	115	102
I(%)	5	13	6	4	4	3	65	3	6
M/e	99	95	92	91	89	88	83	81	76
I(%)	2	4	2	4	3	14	8	4	49
M/e	73	70	69	64	62	60	57	54	51
I(%)	4	3	14	3	6	3	24	8	2
M/e	50	47	46	45	43	41	38	31	30
I(%)	7	4	5	6	3	3	7	100	3
M/e	29	15	14	13	12				
I(%)	21	45	8	2	2				

	2-Methyl-5-methoxydifluoropyrazine[a]								
	2-Methyl-3-methoxydifluoropyrazine[a]								
M/e	161	160	159	146	145	144	143	142	133
I(%)	8	71	10	5	2	4	6	7	3
I(%)	1	8	1	1	3			2	1
M/e	132	131	130	129	118	117	113	112	111
I(%)	13	100	18	7	3	19	4	2	6
I(%)	6	18	5	2	4	41	3	1	2
M/e	110	104	103	102	100	99	98	97	92
I(%)	3	3	6	3	7	4	4	10	8
I(%)	1	1	3	4	2	1	3	7	9
M/e	91	90	89	88	86	85	84	83	77
I(%)	9	30	2	7	7	4	4	4	3
I(%)	8	24	3	4	2	2	2	3	3
M/e	76	74	73	72	71	70	69	67	66
I(%)	8	10	9	21	7	9	2		2
I(%)	45	1	4	5	11	12	2	4	
M/e	64	60	59	58	57	56	54	53	52
I(%)	4	9	3	7	12	6,4	5	4	15
I(%)	4	3,4	1	3	12	2,1	3,6	4	12
M/e	51	47	46	45	44	43	42	41	40
I(%)	8	18	14	8	4	2	16	5	4
I(%)	7	4	10	7	3	2	6	5	5
M/e	39	38	33	31	29	28	27	26	19
I(%)	3	3	7	34	5	11,9	16	12	3
I(%)	4	5	2,2	100	7	4	19	15	
M/e	15	14							
I(%)	25	3							
I(%)	26	4							

2,3-Dimethoxydifluoropyrazine.[a]

M/e	177	176	175	162	161	157	148	147	146
I(%)	4	65	2	2	24	2	3	24	100
M/e	134	133	130	119	118	117	116	115	103
I(%)	4	57	12	4	37	3	8	10	3
M/e	102	100	99	93	92	89	88	83	76
I(%)	8	2	9	3	84	4	6	3	14
M/e	74	73	71	70	62	60	58	57	54
I(%)	3	70	4	4	2	10	2	21	13
M/e	52	50	47	46	45	43	42	38	33
I(%)	3	9	13	4	10	11	4	4	3
M/e	32	31	30	29	28	27	26	15	14
I(%)	2	27	3	16	17	5	3	63	6

Decafluorodiphenyl ether. Ion, Intensity[b]

$C_{12}F_{10}O$, 36·8; $C_{12}F_9O$, 3·3; $C_{11}F_{10}$, 0·4; $C_{12}F_8O$, 0·4; $C_{11}F_9$, 2·9; $C_{11}F_8O$, 0·7; $C_{11}F_7O$, 1·0; $C_{10}F_8$, 3·9; C_6F_5O, 19·7; C_6F_5, 3·1; C_5F_5, 12·9; C_6F_4, 1·4; C_5F_3, 0·8; C_4F_3, 1·5; C_5F_2, 1·8; C_3F_3, 3·1; C_4F_2, 0·8; C_5F, 0·8; CF_3, 2·7; CF, 1·8.

4-Pentafluorophenoxy-tetrafluoropyridine. Ion, Intensity[b]

$C_{11}F_9NO$; 27·4; $C_{11}F_8NO$, 2·8; $C_{10}F_8O$, 1·9; $C_{10}F_8N$, 2·5; C_9F_8, 3·1; C_9F_7N, 2·1; C_9F_7, 2·1; C_6F_5O, 10·8; C_6F_5, 2·2; C_5F_5, 11·0; C_5F_4N, 1·1; C_6F_4, 0·6; C_5F_3, 5·0; C_4F_3, 2·3; C_4F_2N, 3·5; C_5F_2, 1·1; C_3F_3, 2·9; C_4FN, 1·9; C_4F_2, 1·1; C_2F_3N, 0·6; C_3F_2, 1·1; C_3FO, 0·7; CF_3, 3·4; C_2FN, 1·2; C_3F, 1·0; CFN, 1·38; C_2F, 2·3; CF, 3·3.

2-Pentafluorophenoxy-4-bromotrifluoropyridine. Ion, Intensity[b]

$C_{11}F_8BrNO$, 14·7; $C_{11}F_7BrNO$, 3·2; $C_{10}F_8BrN$, 2·6; $C_{10}F_7BrN$, 0·6; $C_{11}F_8NO$, 5·9; $C_{11}F_7NO$, 0·6; $C_{10}F_8N$, 3·8; $C_{10}F_6N$, 0·4; C_9F_6N, 0·5; C_7F_5N, 0·7; C_5F_3NBr, 3·9; C_4F_3NBr, 1·2; C_6F_5O, 2·2; C_6F_4NO, 7·6; C_6F_5, 1·6; C_4FBrN, 3·5; C_5F_5, 5·4; C_8F_3, 0·5; C_5F_4N, 2·6; C_6F_4, 0·6; C_5F_3NO, 0·8; C_5F_4, 0·7; C_5F_3N, 0·5; C_4F_4, 0·6; C_5F_2NO, 0·5; C_4F_3N, 0·5; C_5F_3, 5·4; C_4F_4, 0·6; C_4F_3, 2·3; C_4F_2N, 4·3; C_5F_2, 1·3; C_3F_3, 9·8; C_4F_2, 1·9; C_4FN, 2·3; C_5F, 0·7; C_3F_2, 3·9; CF_3, 3·2; C_2F_2, 0·6; C_3F, 1·4; CNO, 0·6; CF, 4·6.

2,4,6-Tris(pentafluorophenoxy)-difluoropyridine. Ion, Intensity[b]

$C_{23}F_{17}NO_3$, 15·2; $C_{23}F_{16}NO_3$, 2·0; $C_{22}F_{17}NO_2$, 0·4; $C_{20}F_{11}O_3$, 0·6; $C_{16}F_{12}NO_2$, 3·1; $C_{16}F_{12}NO$, 5·5; $C_{10}F_7O_2$, 1·0; $C_{10}F_7NO$, 1·0; $C_{10}F_7N$, 1·0; $C_{10}F_6NO$, 0·6; C_9F_7O, 22·9; C_9F_7N, 0·7; $C_{10}F_7$, 0·6; $C_{10}F_6N$, 1·4; C_9F_7, 1·1; C_9F_6N, 0·9; C_8F_7, 0·7; C_8F_6N, 0·9; C_7F_7, 1·0; C_8F_6, 0·9; C_7F_5O, 2·3; C_6F_6, 0·7; C_6F_5O, 2·6; C_7F_5, 1·1; C_6F_5, 4·4; C_5F_5, 4·2; C_6F_4, 1·0; C_5F_4, 0·7; C_5F_2NO, 0·8; C_4F_4, 0·7; C_5F_3, 4·1; C_5F_2N, 0·7; C_4F_3, 0·8; C_4F_2N, 4·8; C_5F_2, 0·7; C_3F_3, 2·9; C_3F_2, 1·8; CF_3, 1·7; CFO, 0·6; CF, 2·0.

4-(2',3',5',6'-tetrafluorophenoxy)-tetrafluoropyridine.

$C_{11}F_8NOH$, 26·3; $C_{11}F_7NOH$, 3·4; $C_{11}F_6NOH$, 0·7; $C_{10}F_7OH$, 1·6; $C_{10}F_7NH$, 3·4; $C_{10}F_6OH$, 0·8; $C_{10}F_5NOH$, 3·3; C_9F_7H, 1·4; C_9F_8NH, 3·0; C_9F_6H, 2·9; C_8F_7H, 0·9; C_4F_4OH, 2·5; C_5F_4N, 1·4; C_6F_4H, 5·3; C_4F_4N, 1·2; C_5F_4H, 10·8; C_6F_3H, 0·7; C_5F_3, 0·9; C_4F_3, 1·5; C_4F_2N, 1·8; C_5F_2H, 7·5; C_3F_3, 2·5; C_4F_2H, 0·8; C_4F_2, 1·0; C_5FH, 1·2; C_5F, 0·6; C_3F_2H, 1·9; C_3F_2, 1·3; CF_3, 3·0; C_4FH, 0·6; C_2F_2, 0·7; C_3F, 1·0; CF, 3·8.

Metastable Ions Observed in the Mass Spectra of Polyhalogeno-aromatic Compounds.

Tetrafluoropyridine-4-aldehyde

Obsd. m/e	Calcd. m/e	Transition
177·4	177·0	179 → 178
127·5	127·4	179 → 151
126·5	126·4	178 → 150
113·7	113·7	151 → 131
101·8	101·8	151 → 124
66·7	66·7	150 → 100
53·1	53·1	106 → 75
45·3	45·3	105 → 69
44·5	44·5	151 → 82
31·5	31·5	151 → 69

$C_6F_5COCF_3$, $C_6F_5COC_6F_5$, $C_6F_5COCF_2CF_2CF_3$, $C_6F_5COCF(CF_3)_2$ and $C_6F_5COCOC_6F_5$

Obsd. m/e	Calcd. m/e	Transition
143·0	143·0	195 → 167
82·0	82·0	167 → 117

$C_6F_5COCF(CF_3)_2$

Obsd. m/e	Calcd. m/e	Transition
104·5	104·5	364 → 195
64·9	64·9	148 → 98

4-Heptafluoroisopropyl-tetrafluorophenyl-heptafluoroisopropyl ketone

Obsd. m/e	Calcd. m/e	Transition
315.0	315.2	495 → 395
231.5	231.5	514 → 345
223.0	222.9	276 → 248
221.0	220.8	345 → 276
214.7	214.7	495 → 326
176.4	176.4	267 → 217
162.0	161.8	198 → 179
158.0	158.1	248 → 198
140.0	140.0	229 → 179

4,4'-Bis(tetrafluoropyridyl)ketone

Obsd. m/e	Calcd. m/e	Transition
126.3	126.4	178 → 150
96.8	96.6	328 → 178
66.7	66.7	150 → 100

4-Tetrafluoropyridyl-heptafluoroisopropyl ketone

Obsd. m/e	Calcd. m/e	Transition
126.4	126.4	178 → 150
91.3	91.3	347 → 178
66.6	66.7	150 → 100

4-Tetrafluoropyridyl pentafluorophenyl ketone

Obsd. m/e	Calcd. m/e	Transition
143·0	143·0	195 → 167
126·5	126·4	178 → 150
110·3	110·3	345 → 195
82·0	82·0	167 → 117
66·7	66·7	150 → 100

Perfluoro-(α,α-dimethylbenzyl)alcohol

Obsd. m/e	Calcd. m/e	Transition
242·0	241·6	295 → 267
210·2	210·2	234 → 265
176·3	176·4	267 → 217
143·0	143·0	195 → 167
105·6	105·7	267 → 168
93·0	93·0	176 → 129
82·0	82·0	167 → 117
64·8	64·9	148 → 98

2,3,5,6-Tetrafluoropyridyl-bis-trifluoromethylcarbinol

Obsd. m/e	Calcd. m/e	Transition
225·0	224·8	278 → 250
209·7	209·7	298 → 250
194·2	194·0	317 → 248
160·0	160·0	250 → 200
126·5	126·4	178 → 150
66·7	66·7	150 → 100
45·4	45·3	105 → 69

Compound	Obsd. m/e	Calcd. m/e	Transition
C_5F_5N	91·0	91·0	164 → 124
	69·8	69·8	124 → 93
	66·7	66·7	150 → 100
	59·5	59·7	124 → 86
$3\text{-}ClC_5F_4N$	121·6	121·6	185 → 150
	106·0	106·0	185 → 140
	72·8	72·8	185 → 116
	66·7	66·7	150 → 100
$3,5\text{-}Cl_2C_5F_3N$	137·1	137·1	201 → 166
	121·1	121·0	201 → 156
	81·0	81·1	166 → 116
C_5Cl_5N	184·0	184·0	249 → 214
	149·7	149·7	214 → 179
	82·5	82·5	144 → 109
$4\text{-}BrC_5F_4N$	98·3	98·3	229 → 150
	66·7	66·7	150 → 100
	45·4	45·3	105 → 69
$2\text{-}BrC_5F_4N$	83·5	83·5	212 → 133
	58·2	58·2	133 → 88

Compound	Obsd. m/e	Calcd. m/e	Transition
$2,4\text{-}Br_2C_5F_3N$	152·6	152·9	289 → 210
	121·9	122·0	210 → 160
	81·8	81·7	210 → 131
	76·3	76·3	131 → 100
	50·1	50·1	131 → 81
	45·4	45·3	105 → 69
$2,4,6\text{-}Br_3C_5F_2N$	207·8	207·5	351 → 270
	135·1	135·1	270 → 191
	77·2	77·2	112 → 93
	65·7	65·7	191 → 112
	34·3	34·3	112 → 62
$1,4\text{-}N_2C_4F_4$	75·4	75·3	152 → 107
	58·2	58·2	133 → 88
	31·4	31·5	133 → 57
$1,4\text{-}N_2C_4F_3Cl$	105·4	105·2	168 → 133
	58·2	58·2	133 → 88
	49·5	49·5	123 → 78
$2,5\text{-}Cl_2\text{-}1,4\text{-}N_2C_4F_2$	120·6	120·7	184 → 149
	82·2	82·2	184 → 123
	72·7	72·6	149 → 104
	64·7	64·7	99 → 80
	63·1	63·0	123 → 88
	49·5	49·5	123 → 78
	45·8	45·8	104 → 69
	39·2	39·1	83 → 57

Compound	Obsd. m/e	Calcd. m/e	Transition
$1,4\text{-}N_2C_4Cl_4$	151·8	151·7	216 → 181
$1,4\text{-}N_2C_4F_3Br$	83·5	83·5	212 → 133
	58·2	58·2	133 → 88
$1,2\text{-}N_2C_4Cl_4$	163·6	163·6	216 → 188
$1,2\text{-}N_2C_4F_4$	101·2	101·2	154 → 124
	69·7	69·8	124 → 93
	45·3	45·3	105 → 69
	44·2	44·2	124 → 74
	41·8	41·8	114 → 69
Hexachloroquinazoline	267·8	267·7	334 → 299
	235·1	235·1	299 → 264
Perfluoroquinoxaline	180·0	180·0	238 → 207
	148·5	148·5	238 → 188
	113·5	113·5	193 → 148
	64·9	64·9	148 → 98
	48·3	48·3	207 → 100
	45·3	45·3	105 → 69
	41·8	41·8	207 → 93
	34·4	34·4	88 → 55
2,3-Dichlorotetrafluoro-quinoxaline	204·6	204·6	270 → 235
	170·2	170·2	235 → 200
	104·0	103·9	148 → 124
	88·4	88·4	174 → 124
	64·9	64·9	148 → 98

2-Methyltrifluoropyrazine

Obsd. m/e	Calcd. m/e	Transition
110·6	110·7	148 → 128
97·2	97·3	140 → 120
80·7	80·4	117 → 97
79·7	79·7	128 → 101
73·0	73·0	121 → 94
67·0	66·9	103 → 83
56·1	56·1	103 → 76
37·2	37·2	70 → 51

2-Methoxytrifluoropyrazine

Obsd. m/e	Calcd. m/e	Transition
111·3	111·1	164 → 135
61·0	60·8	95 → 76
58·3	58·2	133 → 88
47·8	47·9	121 → 76
39·3	39·3	83 → 57

2-Methyl-3-methoxydifluoropyrazine

Obsd. m/e	Calcd. m/e	Transition
131·0	131·2	160 → 145
130·0	130·0	132 → 131
107·3	107·3	160 → 131
81·5	80·4	117 → 97
69·2	69·2	117 → 90

2,3-Dimethoxydifluoropyrazine

Obsd. m/e	Calcd. m/e	Transition
132·3	132·4	161 → 146
123·0	122·8	176 → 147
110·0	109·9	161 → 133
100·6	100·5	176 → 133
95·4	95·4	146 → 118
63·6	63·6	138 → 92
45·2	45·2	118 → 73
24·5	24·3	76 → 43

2-Methyl-5-methoxydifluoropyrazine

Obsd. m/e	Calcd. m/e	Transition
132·0	132·2	159 → 145
131·0	131·2	160 → 145
130·0	130·0	132 → 131
109·6	109·6	159 → 132
108·6	108·9	160 → 132
107·3	107·3	160 → 131
81·7	81·6	130 → 103
80·5	80·4	117 → 97
72·0	72·0	74 → 73
69·2	69·2	117 → 90
63·6	63·6	111 → 84
		133 → 92
61·9	61·8	131 → 90

Decafluorodiphenyl Ether

Obsd. m/e	Calcd. m/e	Transition
313·0	313·0	350 → 331
296·5	296·2	350 → 322
285·0	285·0	322 → 303
277·5	277·3	331 → 303
272·0	271·9	331 → 300
262·5	262·2	350 → 303
257·3	257·1	350 → 300
229·8	229·8	322 → 272
225·5	225·6	350 → 281
211·5	211·3	350 → 272
131·4	131·2	183 → 155
100·8	101·2	331 → 183
95·7	95·7	350 → 183
82·0	82·0	167 → 117
65·0	64·9	148 → 98
30·8	30·7	155 → 69

4-Pentafluorophenoxy-tetrafluoropyridine

Obsd. m/e	Calcd. m/e	Transition
296·0	296·1	333 → 314
260·2	260·5	314 → 286
249·1	249·1	333 → 288
235·0	234·7	288 → 260
223·5	223·4	260 → 241
203·1	203·1	286 → 241
		333 → 260
131·4	131·2	183 → 155
100·7	100·5	333 → 183
66·7	66·7	150 → 100
45·4	45·3	105 → 69
30·8	30·9	98 → 55

2,4,6-Tris(pentafluorophenoxy)-difluoropyridine

Obsd. m/e	Calcd. m/e	Transition
606·0	606·1	661 → 633
306·0	306·4	661 → 450
231·0	230·3	267 → 248
171·5	171·6	257 → 210
147·0	146·8	450 → 257
131·4	131·4	183 → 155
100·7	100·7	136 → 117
82·0	82·0	167 → 117
78·1	78·1	128 → 100
65·0	65·2	210 → 117
30·7	30·7	155 → 69

2-Pentafluorophenoxy-4-bromotrifluoropyridine

Obsd. m/e	Calcd. m/e	Transition
358.0	358.0	393 → 377
340.0	340.0	393 → 365
260.7	260.5	314 → 286
250.1	250.8	393 → 314
232.9	232.7	374 → 295
224.1	224.2	365 → 286
194.9	194.7	286 → 236
171.5	171.2	229 → 198
164.5	164.6	286 → 217
131.3	131.2	183 → 155
126.5	126.4	178 → 150
122.0	121.9	210 → 160
100.7	100.9	314 → 178
82.0	82.1	167 → 117
76.5	76.5	314 → 155
66.7	66.7	150 → 100
27.5	27.5	314 → 93

4-(2',3',5',6'-Tetrafluorophenoxy)-tetrafluoropyridine

Obsd. m/e	Calcd. m/e	Transition
278·3	278·2	315 → 296
243·6	243·6	315 → 277
242·6	242·6	296 → 268
231·5	231·5	315 → 270
228·0	228·0	315 → 268
217·0	216·9	270 → 242
212·7	212·8	296 → 251
205·5	205·5	242 → 223
192·0	192·1	315 → 246
186·0	185·9	315 → 242
114·0	113·7	165 → 137
66·7	66·7	150 → 100
65·8	65·8	149 → 99
63·2	63·1	137 → 93
34·8	34·7	137 → 69

Accurate Mass Measurements on Ions in the Spectra of Polyhalo-Heterocyclic Compounds

Compound	Measured Mass	Calculated Mass	Formula
NC_5F_4-4-CHO	106·0028	106·0030	C_4F_3H
	99·9997	99·9998	C_4F_2N
	82·0090	82·0092	C_4FHN
	Peak at 69 singlet with standard		CF_3
i-4-$NC_5F_4COC_3F_7$	149·9970	149·9967	C_5F_4N
	99·9995	99·9998	C_4F_2N
	Peak at 69 singlet with standard		CF_3
4,4'-$(NC_5F_4)_2CO$	149·9967	149·9967	C_5F_4N
	99·9994	99·9998	C_4F_2N
NC_5F_4-4-$C(OH)(CF_3)_2$	247·9941	247·9945	C_7F_7NOH
	149·9967	149·9967	C_5F_4N
	99·9995	99·9998	C_4F_2N
	Peak at 69 singlet with standard		CF_3
C_5F_5N	Peak at 69 singlet with standard		CF_3
3-ClC_5F_4N	115·9700	115·9702	C_4FClN
	99·9996	99·9998	C_4F_2N

Compound	Measured Mass	Calculated Mass	Formula
$3,5\text{-}Cl_2C_5F_3N$	115·9701	115·9702	C_4FClN
$4\text{-}BrC_5F_4N$	99·9998	99·9998	C_4F_2N
$2\text{-}BrC_5F_4N$	99·9997	99·9998	C_4F_2N
$1,4\text{-}N_2C_4F_4$	61·9967	61·9968	C_2F_2
$1,4\text{-}N_2C_4F_3Cl$	61·9968	61·9968	C_2F_2
$1,4\text{-}N_2C_4F_3Br$	61·9968	61·9968	C_2F_2
Perfluoroquinoxaline	99·9999	99·9999	C_4F_2N
	97·9969	97·9968	C_5F_2
	93·0015	93·0015	C_5FN
	78·9989	78·9984	C_5F
	76·0002	75·9999	C_2F_2N
	73·9968	73·9968	C_3F_2
	Peak at 69 singlet with standard		CF_3

2-Methyltrifluoropyrazine

Measured Mass	Calculated Mass	Formula	
148.0248	148.0248	$C_5H_3N_2F_3$	
76.01242	76.01245	$C_3H_2F_2$	
70.00937	70.00930	C_3HNF	
61.99695	61.99680	C_2F_2	
58.02184	58.02187	C_3H_3F	4
58.00961	58.00930	C_2HNF	1
57.01407	57.01405	C_3H_2F	
52.00622	52.00615	C_2N_2	10
52.01897	52.01872	C_3H_2N	1
52.03117	52.03130	C_4H_4	1
51.00479	51.00462	CHF_2	
46.02176	46.02187	C_2H_3F	1
46.00946	46.00929	CHNF	10
38.00291	38.00307	C_2N	
27.02349	27.02347	C_2H_3	
26.01562	26.01565	C_2H_2	

2-Methoxytrifluoropyrazine

Measured Mass	Calculated Mass	Formula
164.0197	164.0197	$C_5H_3F_3N_2O$
136.0241	136.0248	$C_4H_3N_2F_3$
121.0012	121.0013	$C_3N_2F_3$
87.99998	87.99987	C_3NF_2
75.99960	75.99987	C_2NF_2
69.00163	69.00147	C_3NF
57.00134	57.00147	C_2NF

2,3-Dimethoxydifluoropyrazine

Measured Mass	Calculated Mass	Formula	
176.0396	176.0396	$C_6H_6N_2F_2O_2$	
161.0167	161.0163	$C_5H_3N_2F_2O_2$	
147.0375	147.0370	$C_5H_5N_2F_2O$	1
146.9962	146.9962	$^{12}C_3{}^{13}CN_2F_2O$	1
145.9930	145.9928	$C_4N_2F_2O$	
133.0213	133.0213	$C_4H_3N_2OF_2$	
129.9977	129.9978	$C_4N_2F_2O$	
117.9979	117.9978	$C_3N_2F_2O$	
115.0107	115.0108	$C_4HN_2F_2$	
98.99946	98.99946	C_3N_2FO	
91.99440	91.99479	C_2NF_2O	
75.99988	95.99987	C_2NF_2	
72.99638	72.99640	$C_4N_2F_2O^{++}$	

2-Methyl-5-methoxydifluoropyrazine

Measured Mass	Calculated Mass	Formula	
132.0496	132.0499	$C_5H_6N_2F_2$	3
132.0457	132.0454	$^{12}C_4{}^{13}CH_5N_2F_2$	4
131.0423	131.0420	$C_5H_5N_2F_2$	
130.0339	130.0342	$C_5H_4N_2F_2$	
117.0261	117.0264	$C_4H_3F_2N_2$	
90.01552	90.01552	$C_3H_2NF_2$	

2-Methyl-3-methoxydifluoropyrazine

Measured Mass	Calculated Mass	Formula
131·0423	131·0420	$C_5H_5N_2F_2$
117·0260	117·0264	$C_4H_3N_2F_2$
90·01517	90·01552	$C_3H_2NF_2$
75·99988	75·99988	C_2NF_2
71·01725	71·01712	C_3H_2NF

4-Pentafluorophenoxy-tetrafluoropyridine

Measured Mass	Calculated Mass	Formula
182·9870	182·9869	C_6F_5O
166·9919	166·9920	C_6F_5
149·9959	149·9966	C_5F_4N
116·9948	116·9952	C_5F_3
104·9947	104·9952	C_4F_3
99·9996	99·9998	C_4F_2N
92·9948	92·9952	C_3F_3

2-Pentafluorophenoxy-4-bromo-tetrafluoropyridine

Measured Mass	Calculated Mass	Formula
209.9162	209.9166	C_5F_3NBr
154.9928	154.9920	C_5F_5
116.9953	116.9952	C_5F_3
104.9953	104.9952	C_4F_3
99.9998	99.9998	C_4F_2N
92.9946	92.9952	C_3F_3
73.9965	73.9968	C_3F_2
68.9952	68.9952	CF_3

2,4,6-Tris(pentafluorophenoxy)-difluoropyridine

Measured Mass	Calculated Mass	Formula
496.9681	496.9671	$C_{20}F_{11}O_3$
465.9735	465.9737	$C_{16}F_{12}NO_2$
449.9786	449.9788	$C_{12}F_{12}NO$
256.9835	256.9837	C_9F_7O
166.9919	166.9920	C_6F_5
154.9920	154.9920	C_5F_5
116.9953	116.9952	C_5F_3
99.9999	99.9999	C_4NF_2
92.9952	99.9952	CF_3

APPENDIX 2

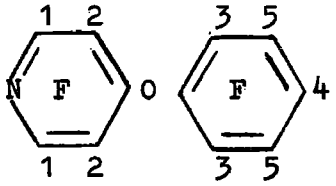
^{19}F N.M.R. Spectra

Key for the Peak Appearance of the ^{19}F N.M.R. Spectra

bd	broad doublet.
bdf	broad doublet with fine structure.
bm	broad multiplet.
btf	broad triplet with fine structure.
d	doublet.
dd	doublet of doublets.
ddf	doublet of doublets with fine structure.
df	doublet with fine structure.
dt	distorted triplet.
dtf	distorted triplet with fine structure.
m	multiplet.
q	quartet.
qd	quartet of doublets.
s	sextet.
sf	sextet with fine structure.
sg	singlet.
st	sextet of triplets.
t	triplet.
tf	triplet with fine structure.
tt	triplet of triplets.

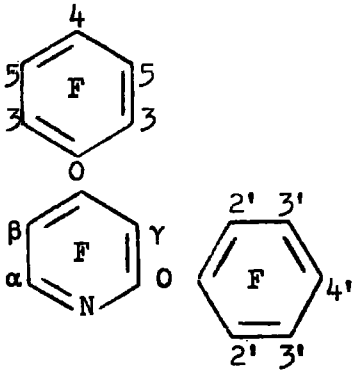
^{19}F Chemical Shifts in p.p.m. Relative to $CFCl_3$ (upfield).

4-Pentafluorophenoxy-tetrafluoropyridine



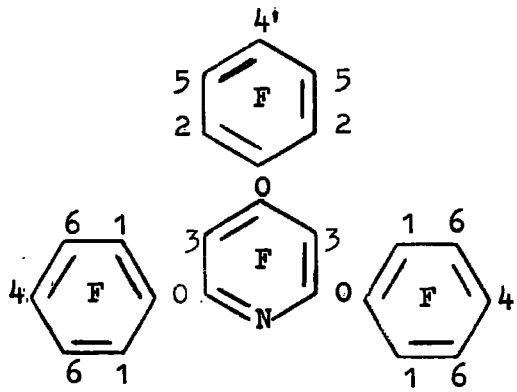
Peak centre	appearance	assignment
87·1	s	1
155·1	bdf	3
157·0	st	2
157·6	dt	4
161·4	ddf	5

2,4-Bis(pentafluorophenoxy)-trifluoropyridine



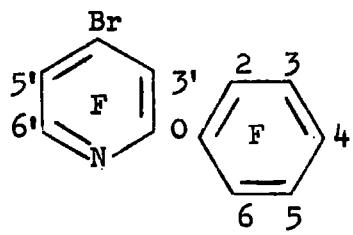
Peak centre	appearance	assignment
88·5	dd	α
152·7	bd	2'
155·0	bd	3
156·4	d	γ
157·5	m	4 and 4'
159·0	d	β
161·5	m	5 and 3'

2,4,6-Tris(pentafluorophenoxy)-difluoropyridine



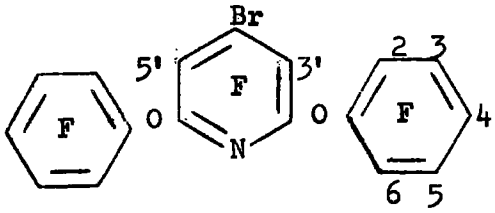
Peak centre	appearance	assignment
152·6	bd	1
155·5	bd	2
158·2	sf	3
158·5	dt	4
158·9	dt	4'
162·2	dtf	5
163·1	dtf	6

2-Pentafluorophenoxy-4-bromo-trifluoropyridine



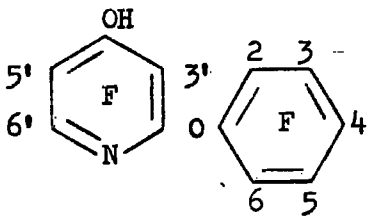
Peak centre	appearance	assignment
89·2	dd	6'
128·6	d	3'
135·5	d	5'
152·3	bd	2,6
157·6	dt	4
161·8	dtf	3,5

2,6-Bis(pentafluorophenoxy)-4-bromo-difluoropyridine



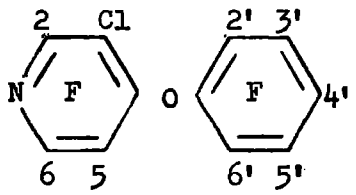
Peak centre	appearance	assignment
134·9	sg	3',5'
152·2	bd	2,6
157·7	dt	4
162·3	dtf	3,5

2-Pentafluorophenoxy-4-hydroxy-trifluoropyridine



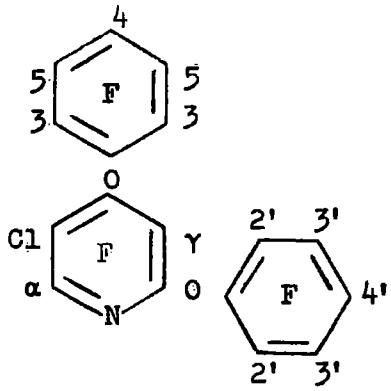
Peak centre	appearance	assignment
94·6	tf	6'
154·5	bd	2,6
160·1	t	4
161·8	dd	3'
164·1	dtf	3,5
165·4	dd	5'

3-Chloro-4-pentafluorophenoxy-trifluoropyridine



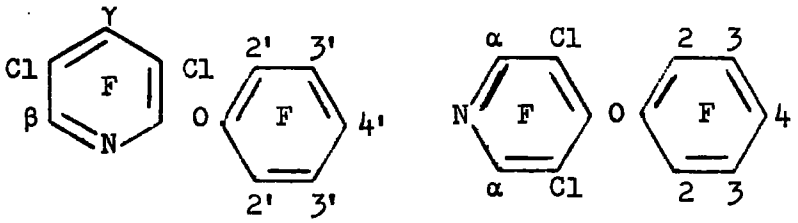
Peak centre	appearance	assignment
70·7	t	2
85·7	t	6
155·2	bd	2',6'
158·2	t	5 and 4'
159·2	t	
161·5	dt	3',5'

2,4-Bis(pentafluorophenoxy)-5-chloro-difluoropyridine



Peak centre	appearance	assignment
74·9	d	α
155·4	d	2'
157·7	d	3
159·5	d	γ
159·8	dt	4 and 4'
160·9	dt	
164·6	q	3' and 5

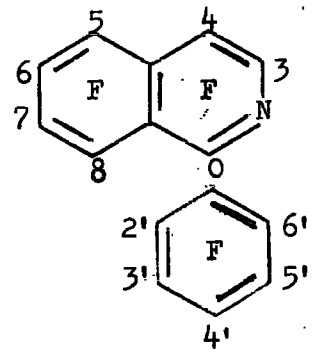
Isomeric Mixture of Pentafluorophenoxy-3,5-dichlorodifluoro-pyridine



Peak centre	Appearance	Assignment
71·1	sg	α
72·3	d	β
96·0	d	γ
155·1	dd	2'
158·0	d	2
160·0	t	4 and 4'
161·7	q	
164·6	m	3 and 3'

The relative areas of the peaks at 71·1 and 72·3 p.p.m. are 5·3: 2·7. The mixture therefore contains 49% of the 4-isomer and 51% of the 2-isomer.

1-Pentafluorophenoxy-hexafluoroisoquinoline



Peak centre	Appearance	Relative area
100·6	m	1
138·0	m	1
148·6	m	2
154·6	bdf	2
155·0	m	1
159·5	dt	1
160·8	qd	1
164·1	ddf	2

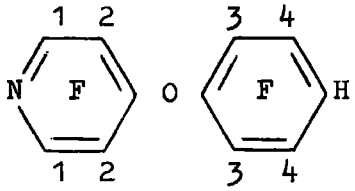
1-(2',3',5',6'-Tetrafluorophenoxy)-hexafluoroisoquinoline

Peak centre	Relative area
101·3	1
141·6	4
152·7	1
156·1	2
159·2	1
161·5	1

^{19}F n.m.r. and chemical methods have shown that sodium methoxide reacts with an equimolar proportion of heptafluoroisoquinoline to give 1-methoxy-hexafluoroisoquinoline.[132]

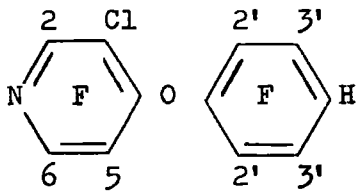
The two lowest-field peaks (61·0 and 96·5 p.p.m. relative to $CFCl_3$) in the spectrum of heptafluoroisoquinoline arise from the 1- and 3-fluorine atoms, being ortho to ring nitrogen, since this low field shift is seen in the pyridine series. The very low field peak found in the spectrum of heptafluoroisoquinoline does not appear in the spectrum of 1-methoxyhexafluoroisoquinoline and hence must arise from the 1-fluorine atom while the peak at 96·5 p.p.m. must be due to the 3-fluorine atom. The very low-field peak is also absent from the spectra of 1-pentafluorophenoxy-hexafluoroisoquinoline and 1-(2',3',5',6'-tetrafluorophenoxy)-hexafluoroisoquinoline and this indicates the positions of substitution of these derivatives. These spectra were recorded on a 60 Mc./sec. instrument and insufficient resolution was obtained to enable analyses to be carried out as first order spectra.

4-(2',3',5',6'-tetrafluorophenoxy)-tetrafluoropyridine



Peak centre	appearance	assignment
89·1	s	1
138·4	q	4
156·1	q	3
157·7	s	2

3-Chloro-4-(2',3',5',6'-tetrafluorophenoxy)-trifluoropyridine



Peak centre	appearance	assignment
72·7	dd	2
87·1	dd	6
138·3	m	3'
156·1	m	2'
160·0	ddt	5

Bis(2',3',5',6'-Tetrafluorophenoxy)-pentafluoroisoquinoline

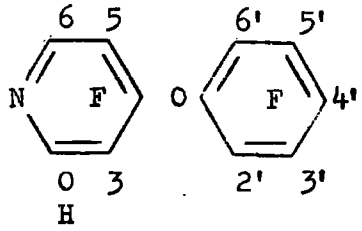
Peak centre	Relative area
100·6	1
140·9	5
152·0	1
155·7	4
158·6	1
161·1	1

This computer of average transients spectrum was recorded on a 60 Mc./sec. instrument and insufficient resolution was obtained to enable an analysis to be carried out as a first order spectrum.

4-(γ-Tetrafluoropyridyloxy)-4'-hydroxyoctafluorobiphenyl

Peak centres: 89·0, 138·6, 142·5, 156·5, 158·1, 162·2

2-Hydroxy-4-pentafluorophenoxy-trifluoropyridine



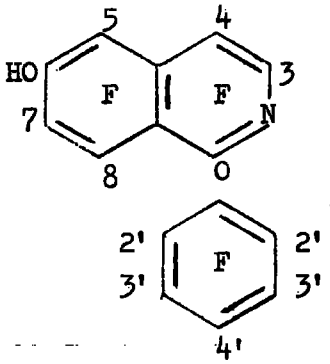
Peak centre	Appearance	Assignment
90·3	t	6
155·4	bdf	2',6'
158·0	t	3
158·9	dt	4'
161·9	dtf	3',5'
166·7	df	5

2-Hydroxy-4-(hydroxytetrafluorophenoxy)-trifluoropyridine

Peak centres: 92·8, 161·4, 164·8, 170·5

This computer of average transients spectrum was recorded on a 60 Mc./sec. instrument and insufficient resolution was obtained to enable an analysis to be carried out as a first order spectrum.

Suspected 1-Pentafluorophenoxy-6-hydroxy-pentafluoroisoquinoline

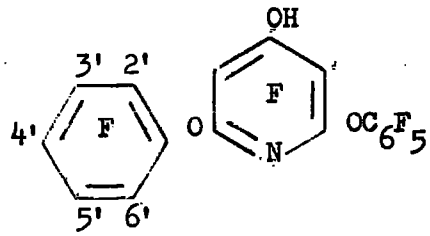


Peak centre	Appearance	Assignment	Relative area
103·4	m	3	1
142·9	tf	8?	1
149·7	df	5	1
154·3	df	7?	1
156·0	bd	2'	2
161·1	dt	4'	1
164·0	dd	4	1
165·7	dtf	3'	2

The peak at 164·0 p.p.m. was assigned to the 4-fluorine because the 4-fluorine is attached to the carbon atom which has the highest π-electron density in the isoquinoline ring. The 5-fluorine was

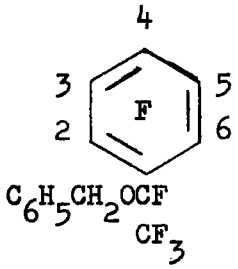
easily assigned because of the presence of a large coupling constant, due to peri fluorine-fluorine coupling, of the order of 50 c.p.s., which was also present on the 4-fluorine. The 3-fluorine was also easily recognised by the fact that it occurred at very low field. It was not found to be possible with the computer of average transients spectrum to determine the fine structure of the peaks at 142·9 and 154·3 p.p.m. and so evaluate coupling constants that would be useful in finding the position of substitution of the hydroxyl group. The hydroxyl group could have entered the 6-position by analogy with the formation of 1,6-dimethoxypentafluoroisoquinoline from 1-methoxy-hexafluoroisoquinoline.[132]

2,6-Bispentafluorophenoxy-4-hydroxydifluoropyridine



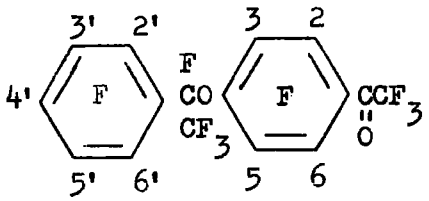
Peak centre	Appearance	Assignment
153·1	bdf	2,6
159·6	dt	4
163·2	sg	3'
164·0	dtf	3,5

Benzyl-nonafluoro-α-phenylethyl Ether



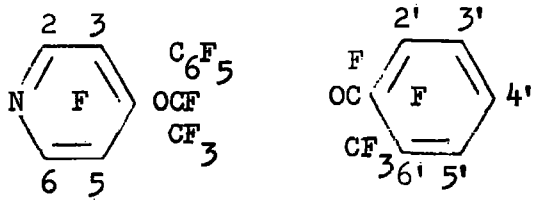
Peak centre	Area	Appearance	Assignment
86·3	3	m	$-CF_3$
121·6	1	tf	-CF
140·4	2	m	2,6
151·3	1	tf	4
162·9	2	tf	3,5

4-Nonafluoro-α-phenylethoxy-heptafluoroacetophenone



Peak centre	Area	Appearance	Assignment
77·7	3	t	CF_3
78·9	3	t	CF_3
86·6	1	m	OCF
138·7	2	m	2,6
142·1	2	m	2',6'
154·7	1	t	4'
163·0	2	m	3',5'
164·1	2	tf	3,5

4-Nonafluoro-α-phenylethoxytetrafluoropyridine



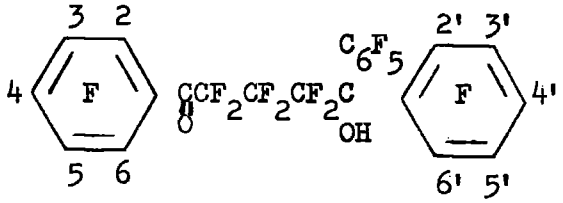
Peak centre	Area	Appearance	Assignment
77·7	2	s	2,6
78·3	3	m	CF_3
84·9	1	tf	OCF
137·7	2	m	2',6'
149·8	1	tf	4'
156·3	2	s	3,5
164·0	2	tf	3',5'

Pentafluorobenzoyl-perfluoro-(diphenylmethoxy)-tetrafluorobenzene

Peak centres: 144·3, 148·6, 161·7, 164·6.

This computer of average transients spectrum was recorded on a 60 Mc./sec. instrument and insufficient resolution was obtained to enable an analysis to be carried out as a first order spectrum.

1-Hydroxy-1,1-bispentafluorophenyl-4-pentafluorobenzoyl-hexafluoro-n-butane.



Peak centre	Area	Appearance	Assignment
113·1	2	m	
118·0	2	m	$-CF_2-$
120·0	2	btf	
136·8	4	btf	2',6'
141·1	2	bm	2,6
148·8	1	tt	4
155·4	2	tt	4'
162·6	2	m	3,5
164·8	4	tf	3',5'

(γ-Pentafluorobenzoyl-n-hexafluoropropyl)-nonafluorodiphenyl ketone.

Peak centres: 113·2, 118·3, 122·4, 125·0, 127·7, 131·4, 134·1, 135·5, 140·3, 149·0, 155·8, 158·1.

This spectrum was recorded on a 60 Mc./sec. instrument and insufficient resolution was obtained to enable an analysis to be carried out as a first order spectrum.

APPENDIX 3

Instrumental Techniques Used in the Experimental Work and Purification of Reagents

Instrumental Techniques Used in the Experimental Work.

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

These were recorded on a Perkin-Elmer R10 or an A.E.I. R.S.2. spectrometer at 60 Mc/sec. Samples were examined as neat liquids or as solids dissolved in acetone with $CFCl_3$ as internal reference.

Mass Spectra were recorded on an A.E.I. M.S.9 instrument.

Infra-red Spectra were recorded using Grubb-Parsons type G.S.2A or Spectromaster instruments.

The high resolution determinations of the carbonyl frequencies of the fluorinated esters were carried out on a Grubb-Parsons type G.S.2A instrument. The frequencies quoted are for the esters dissolved in a 5% solution of carbon tetrachloride.

Vapour Phase Chromatography. Analytical scale vapour phase chromatography (v.p.c.) was carried out using a Perkin-Elmer 'Fractometer' model 451 and preparative scale vapour phase chromatography (v.p.c.) was carried out using an Aerograph 'autoprep' instrument.

Drying of Solvents.

Benzene.

After preliminary drying over magnesium sulphate, the benzene was dried over sodium wire and then stored over fresh sodium wire until needed.

Hexane.

Hexane was dried in the same way as benzene.

Diethyl Ether (Ether).

After preliminary storage over potassium hydroxide, the diethyl ether was dried over sodium wire and then stored over fresh sodium wire until needed.

Tetrahydrofuran.

Tetrahydrofuran was twice heated under reflux with potassium, distilled under dry nitrogen and then stored under nitrogen over lithium aluminium hydride. It was freshly distilled off under nitrogen when needed.

Diglyme.

Diglyme was dried in the same way as tetrahydrofuran but was stored over calcium hydride instead of lithium aluminium hydride.

Monoglyme.

Monoglyme was dried in the same way as tetrahydrofuran.

Acetonitrile.

Acetonitrile was dried by distillation from phosphorus pentoxide and the distillate was refluxed with stirring with calcium hydride for 2 days before being redistilled and stored over calcium hydride.

Caesium Fluoride.

If a separate analysis for hydrogen fluoride in the caesium fluoride was positive, the caesium fluoride was made usable by neutralising a

solution of it and pumping off the water under high vacuum at 100°. Normally the caesium fluoride was dired directly in a high vacuum at 100°. 'Flaming' the caesium fluoride in the Carius tube is not to be recommended because it is suspected that this may cause the lattice structure of the compound to change. 'Flamed' caesium fluoride was sometimes found to be insoluble in a mixture of hexafluoroacetone and diglyme.

Temperatures.

All reaction temperatures were those of surrounding heating or cooling baths.

Melting Points.

All melting points are uncorrected.

APPENDIX 4

Infra-red Spectra

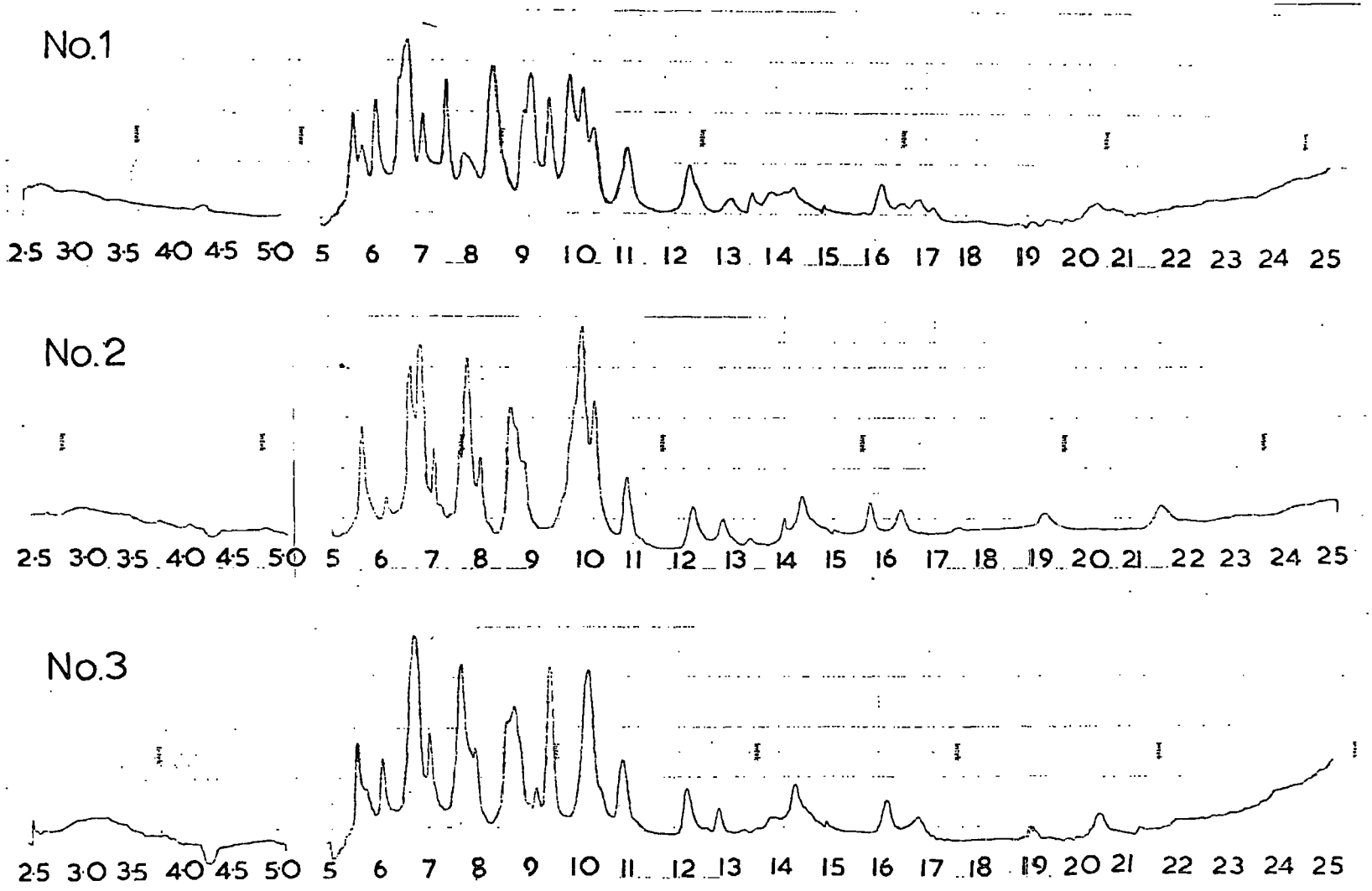
Infra-red Spectra

The spectra of liquid samples were recorded as contact films in potassium bromide cells. The spectra of solid samples were recorded as potassium bromide discs.

Spectrum No.	Compound
1	4-Pentafluorobenzoyloxy-tetrafluoropyridine.
2	Tetrafluoroisonicotinyloxy-pentafluorobenzene.
3	4-Tetrafluoroisonicotinyloxy-tetrafluoropyridine.
4	4,4'-di(tetrafluoroisonicotinyloxy)-octafluorobiphenyl.
5	Undecafluoro-α,α-dimethylbenzyl benzoate.
6	Undecafluoro-α,α-dimethylbenzyl pentafluorobenzoate.
7	Ethyl pentafluorobenzoate.
8	Bis(2,3,5,6-tetrafluoropyridyl)-pentafluorophenyl carbinol.
9	4-Acetyloxy-tetrafluoropyridine.
10	2,3,5,6-Tetrafluoropyridyl-diphenylcarbinol.
11	2,3,5,6-Tetrafluoropyridyl-bis-trifluoromethylcarbinol.
12	4-Pentafluorophenoxy-tetrafluoropyridine.
13	2,4-Bis(pentafluorophenoxy)-trifluoropyridine.
14	2,4,6-Tris(pentafluorophenoxy)-difluoropyridine.
15	2-Pentafluorophenoxy-4-bromotrifluoropyridine.
16	2,6-Bis(pentafluorophenoxy)-4-bromodifluoropyridine.
17	2-Pentafluorophenoxy-4-hydroxytrifluoropyridine.
18	4-Pentafluorophenoxy-3-chlorotrifluoropyridine.

Spectrum No.	Compound
19	2,4-Bis(pentafluorophenoxy)-5-chlorodifluoropyridine.
20	Isomeric mixture of 2- and 4-pentafluorophenoxy-3,5-dichlorodifluoropyridine.
21	1-Pentafluorophenoxy-hexafluoroisoquinoline.
22	4-(2',3',5',6'-Tetrafluorophenoxy)-tetrafluoropyridine.
23	4-(2',3',5',6'-Tetrafluorophenoxy)-3-chlorotrifluoropyridine.
24	1-(2',3',5',6'-Tetrafluorophenoxy)-hexafluoroisoquinoline.
25	Bis(2',3',5',6'-Tetrafluorophenoxy)-pentafluoroisoquinoline.
26	4-(γ-Tetrafluoropyridyloxy)-4'-hydroxyoctafluorobiphenyl.
27	2-Hydroxy-4-pentafluorophenoxy-trifluoropyridine.
28	2-Hydroxy-4-(hydroxytetrafluorophenoxy)-trifluoropyridine.
29	1-Pentafluorophenoxy-hydroxy-pentafluoroisoquinoline.
30	2,6-Bis(pentafluorophenoxy)-4-hydroxydifluoropyridine.
31	Pentafluorobenzoyl-perfluoro-(diphenylmethoxy)-tetrafluorobenzene.
32	n-Perfluorobutyrophenone.
33	4-Nonafluoro-α-phenylethoxytetrafluoropyridine.
34	4-Nonafluoro-α-phenylethoxy-heptafluoroacetophenone.
35	Benzyl-nonafluoro-α-phenylethyl ether.

Spectrum No.	Compound
36	Nonafluoro-α-phenylethoxy-trifluoropyridazine.
37	(γ-Pentafluorobenzoyl-n-hexafluoropropyl)-nonafluoro-biphenyl ketone.
38	1-Hydroxy-1,1-bispentafluorophenyl-4-pentafluorobenzoyl-hexafluoro-n-butane.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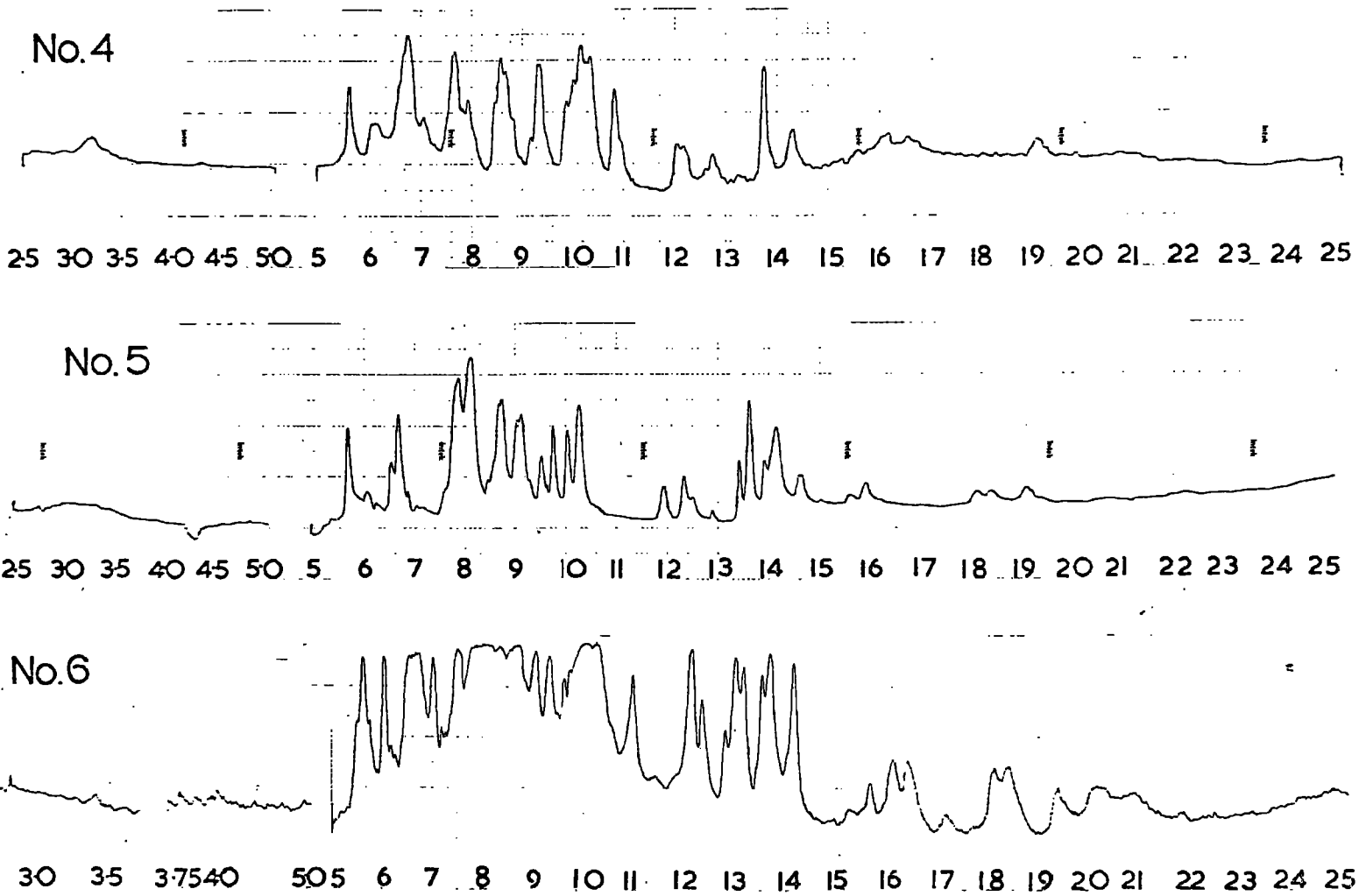
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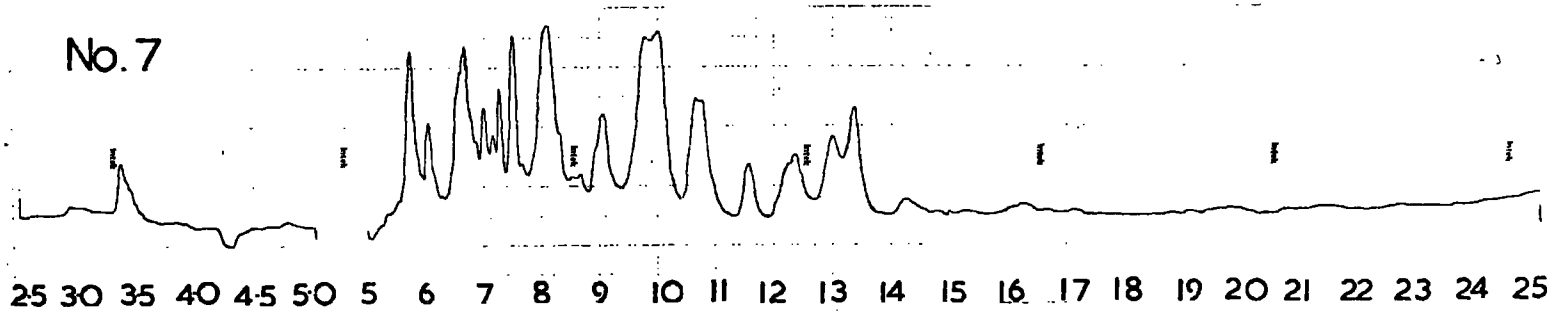
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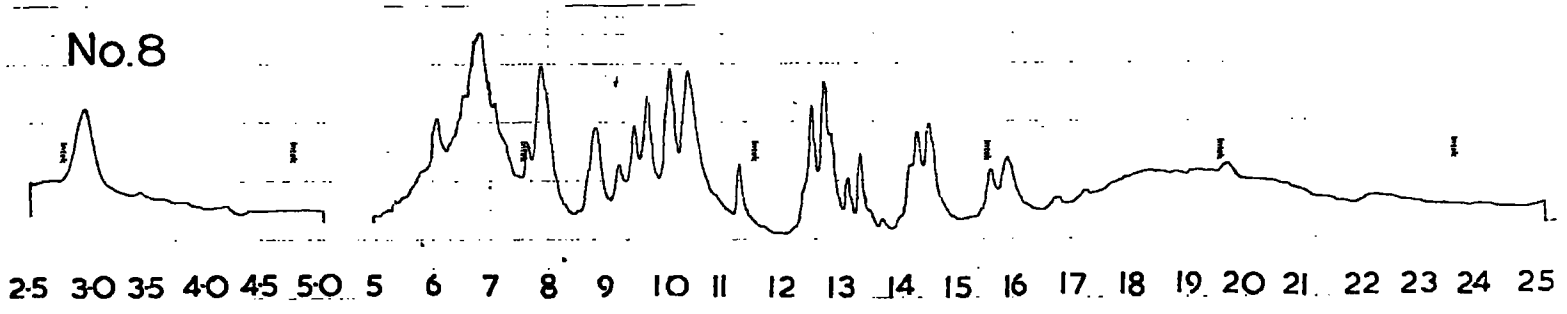
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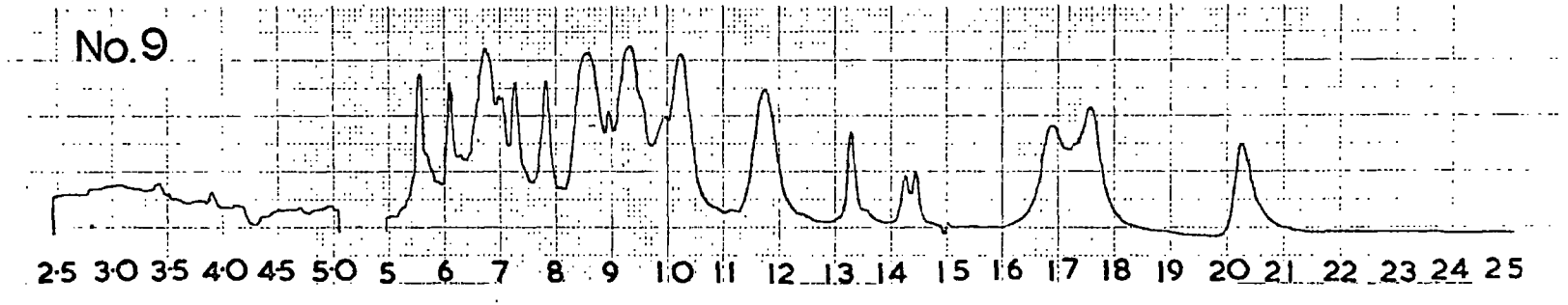
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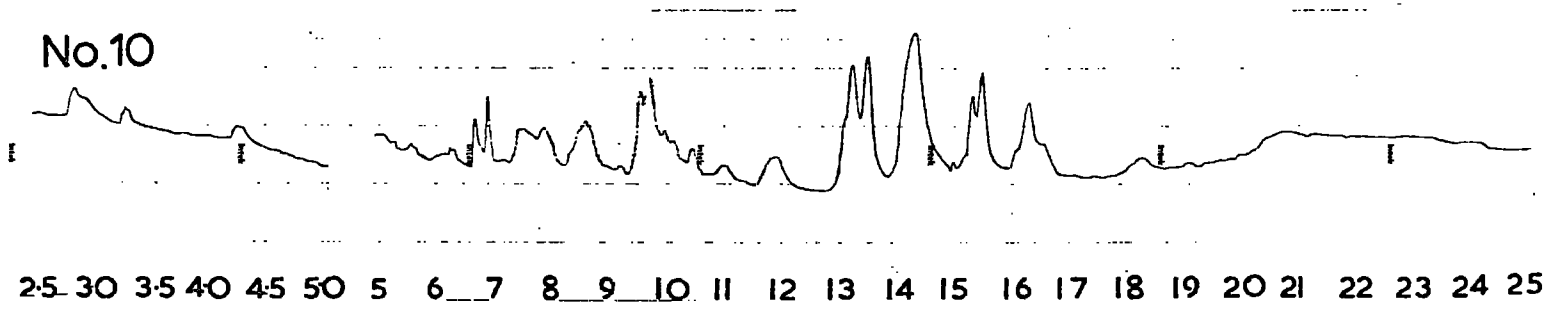
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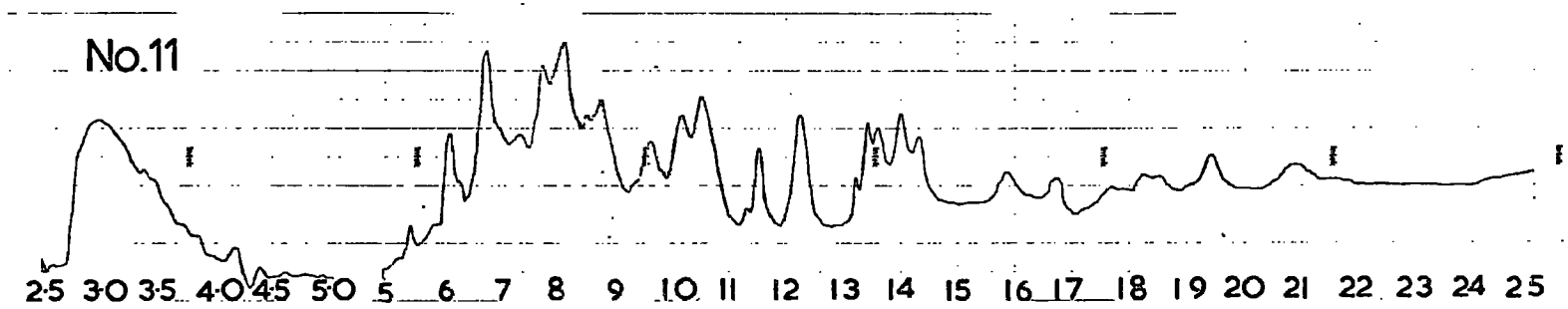
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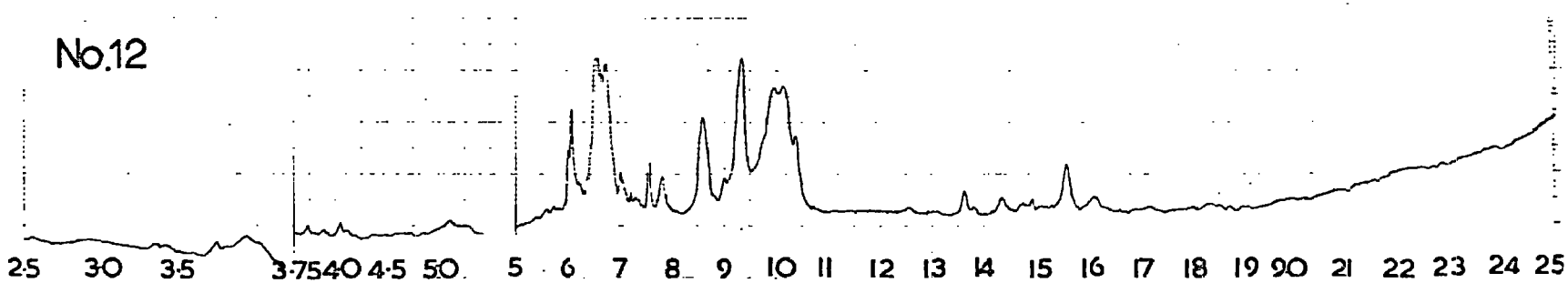
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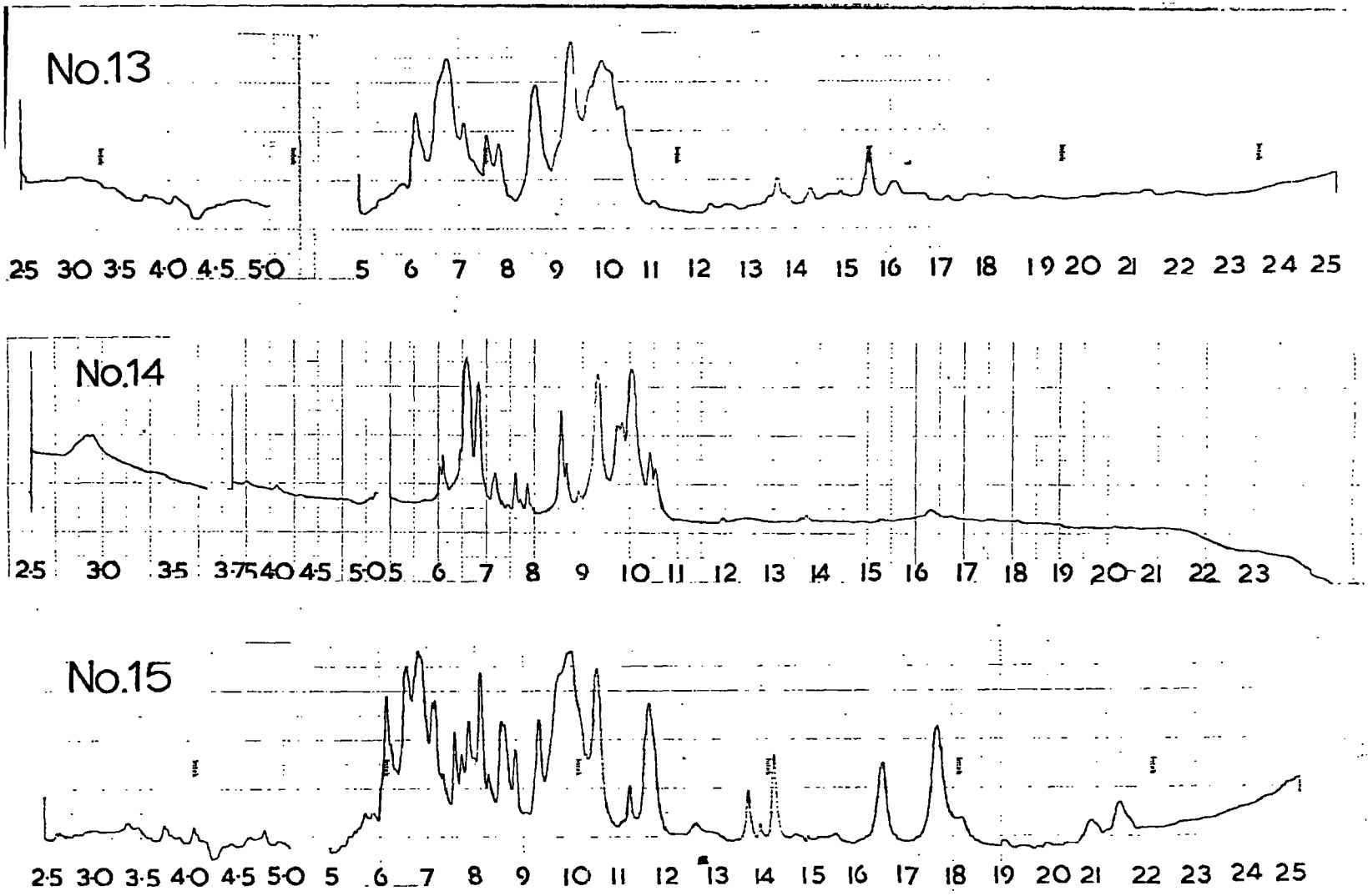
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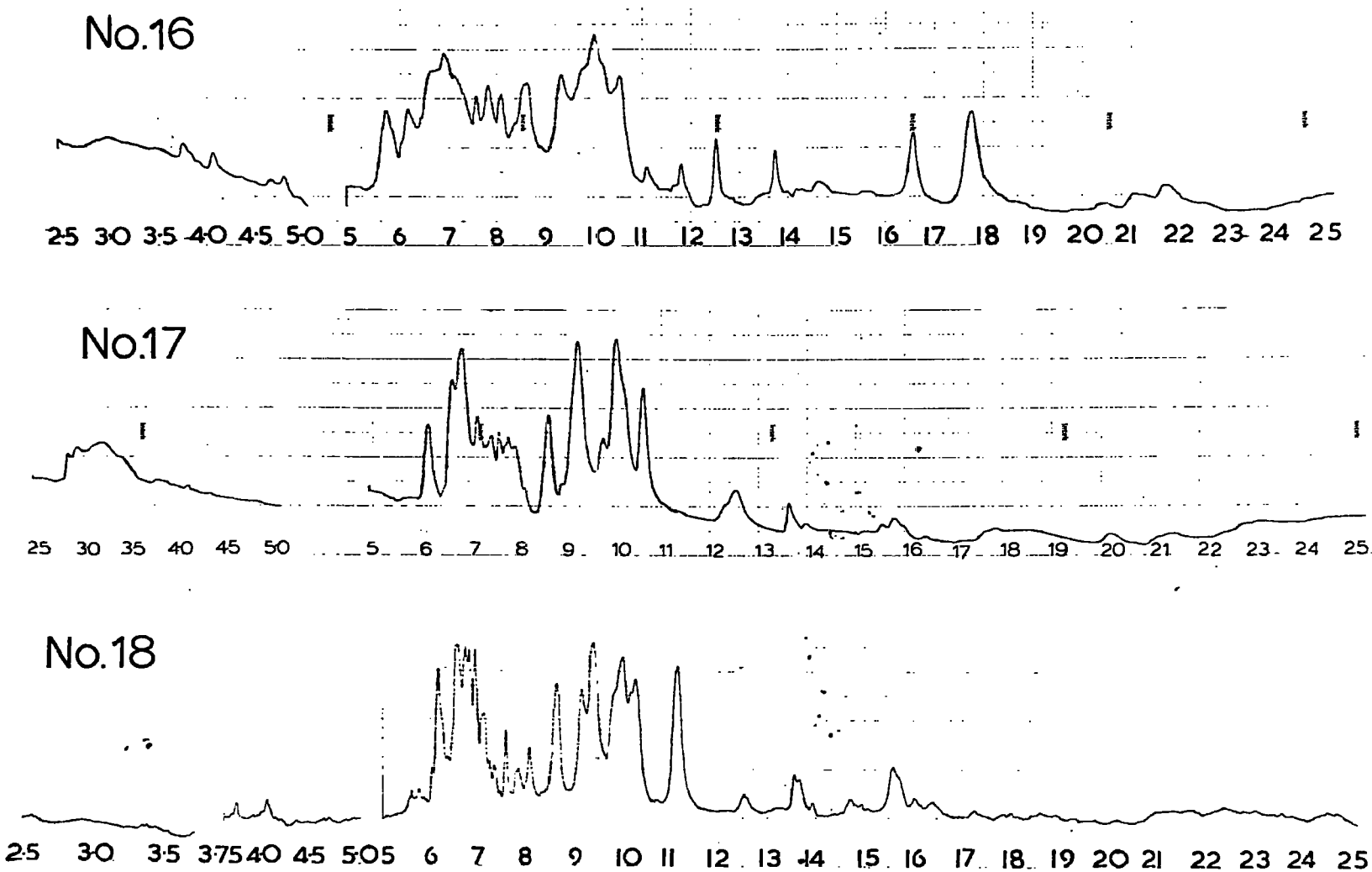
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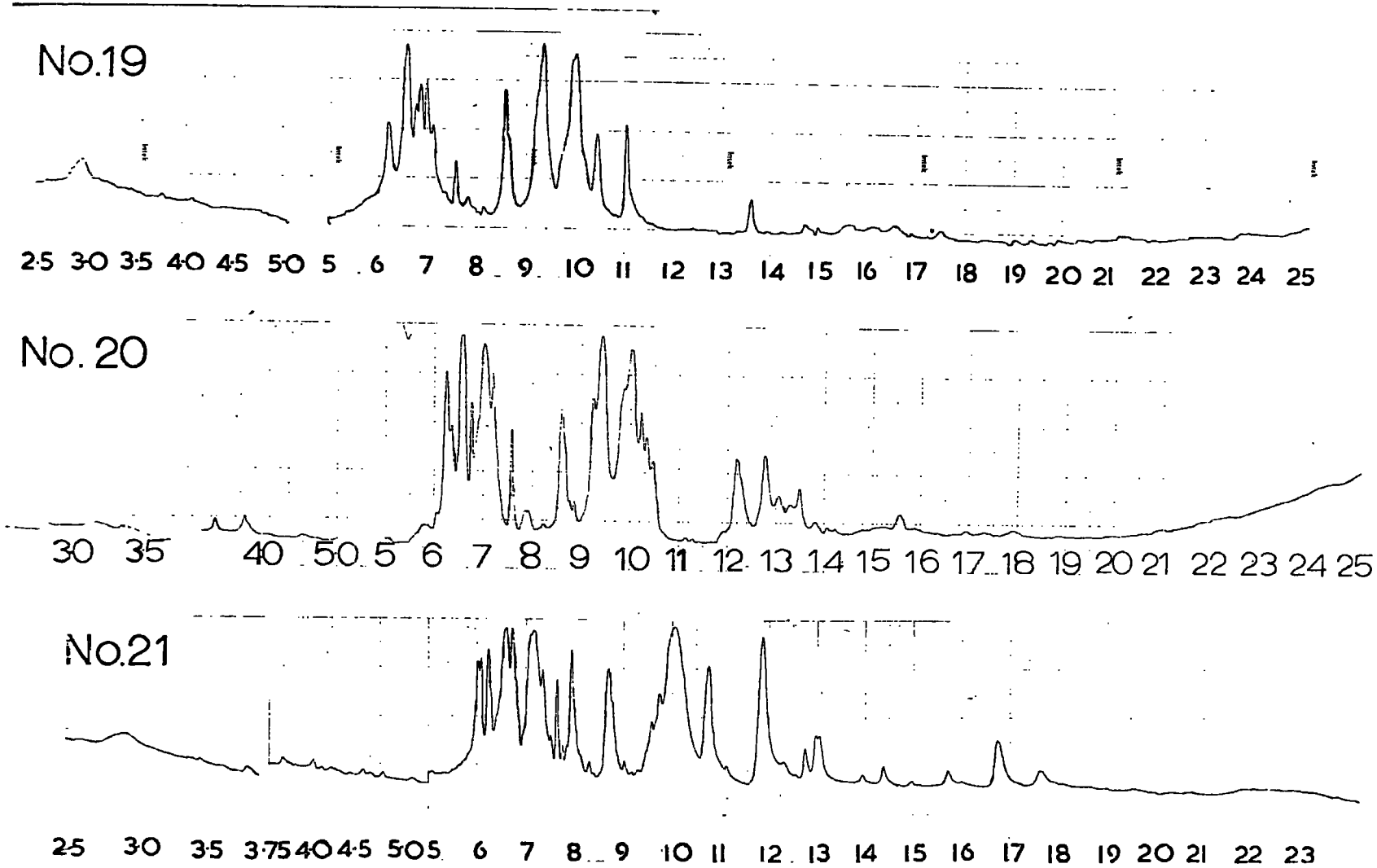
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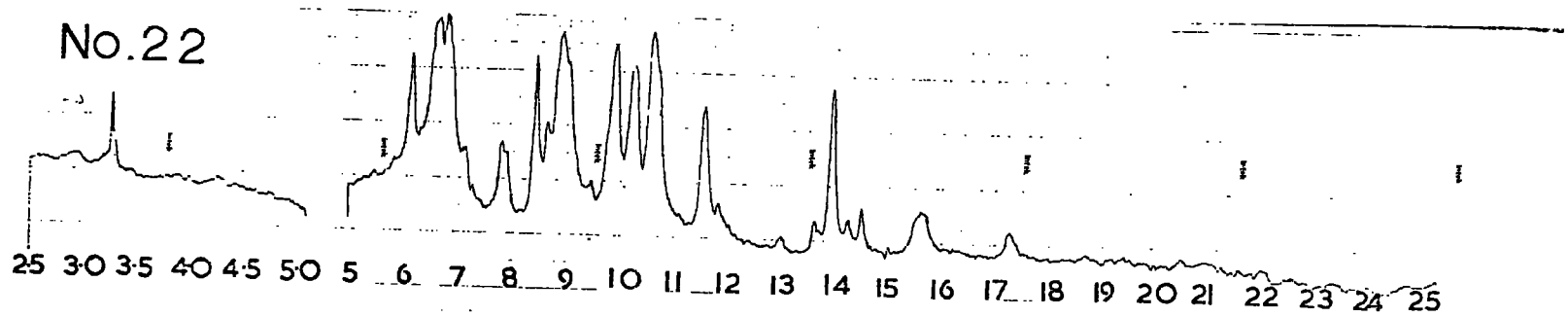
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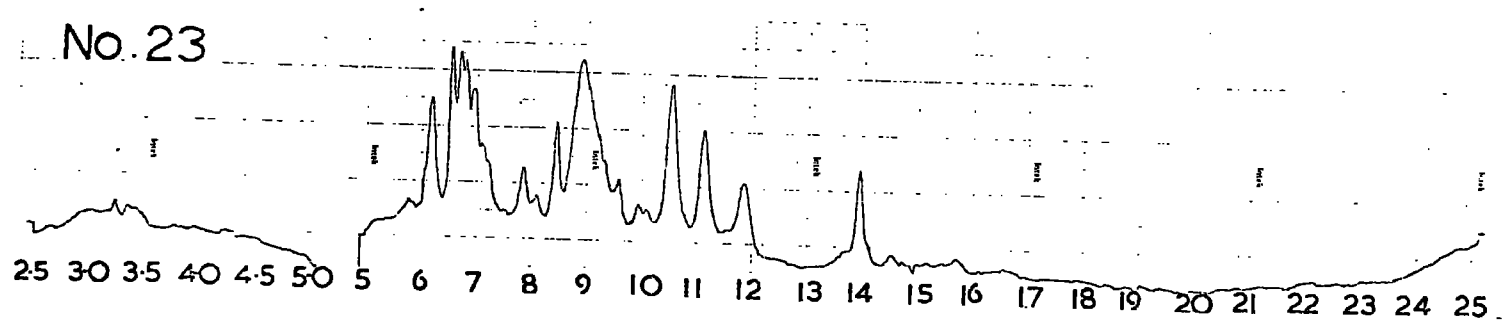
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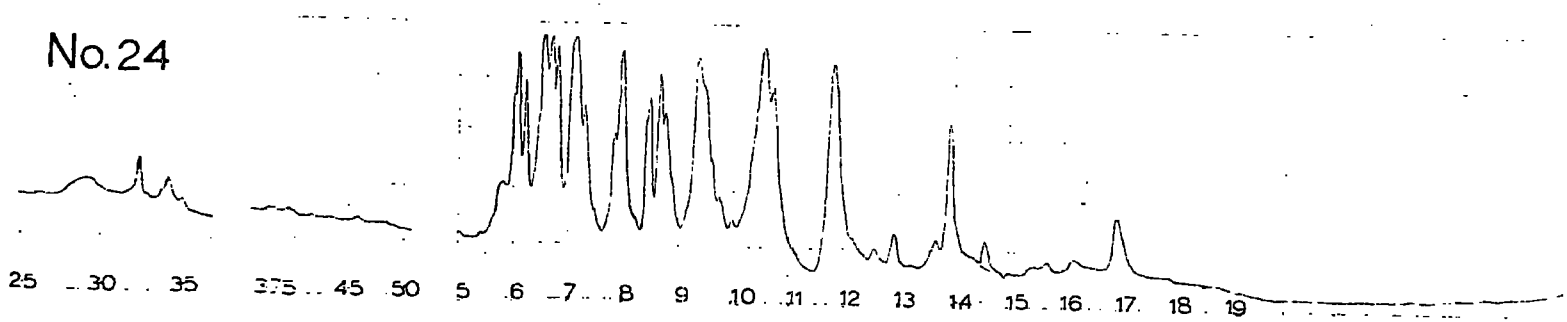
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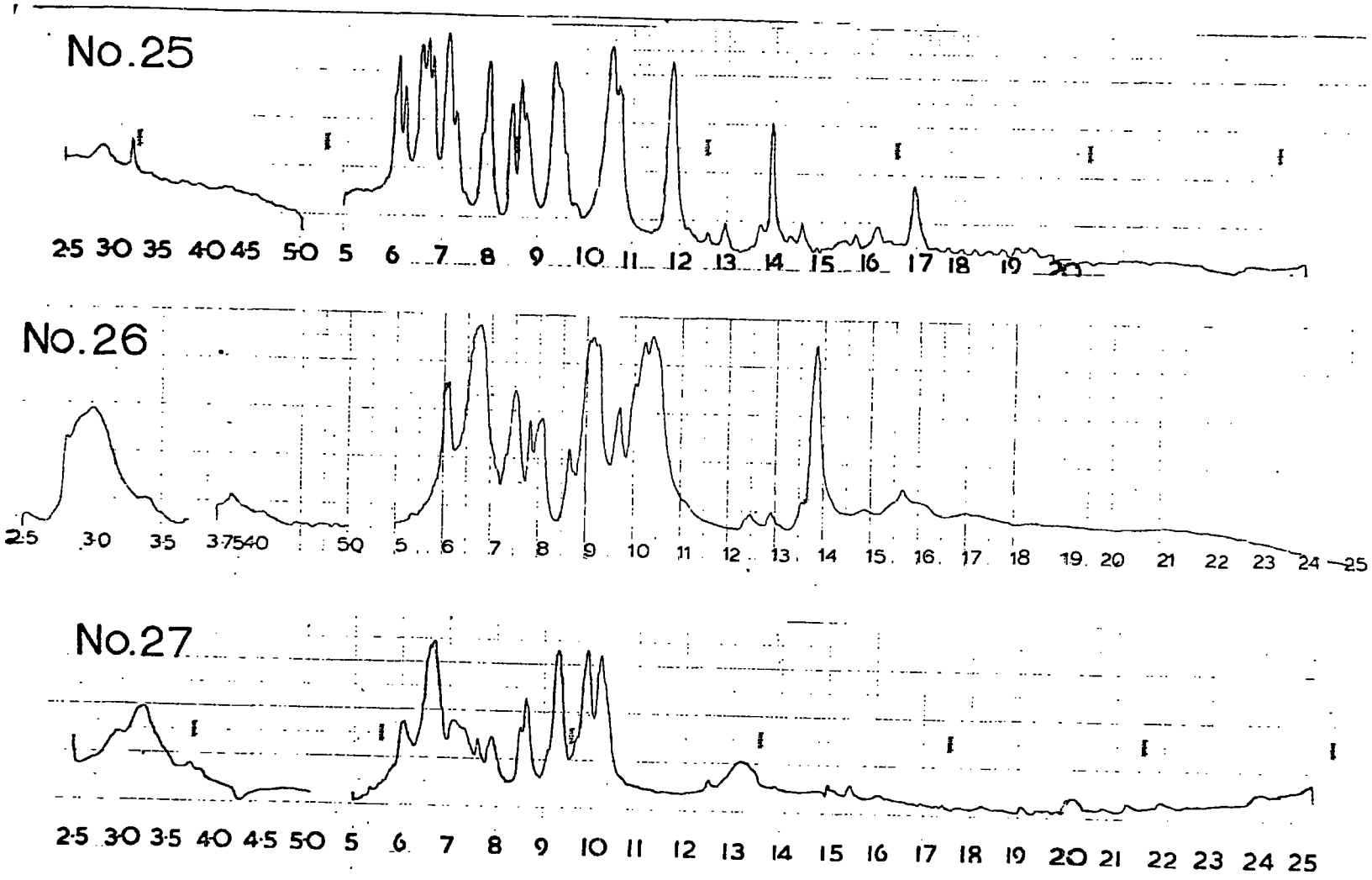
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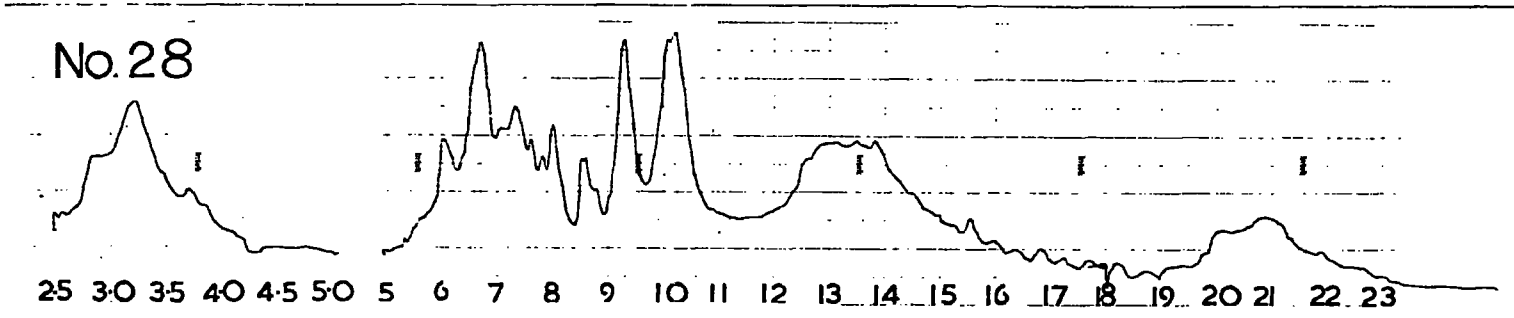
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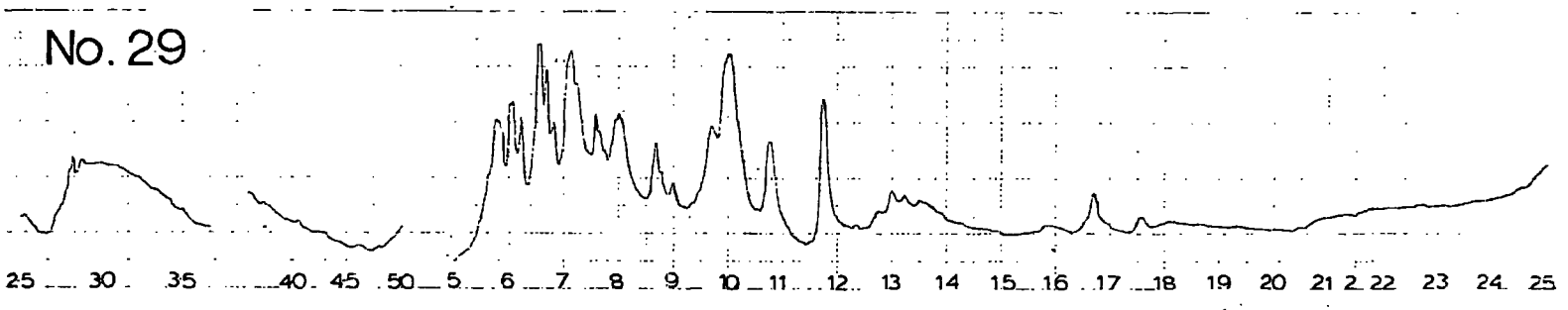
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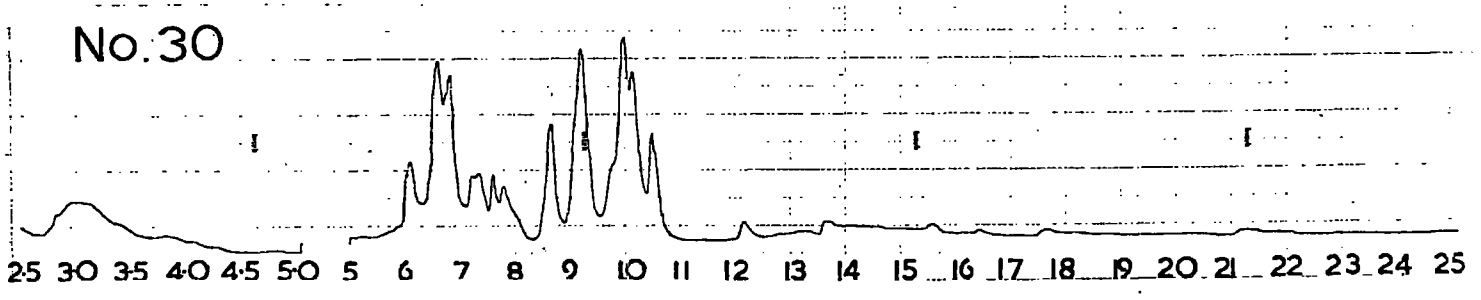
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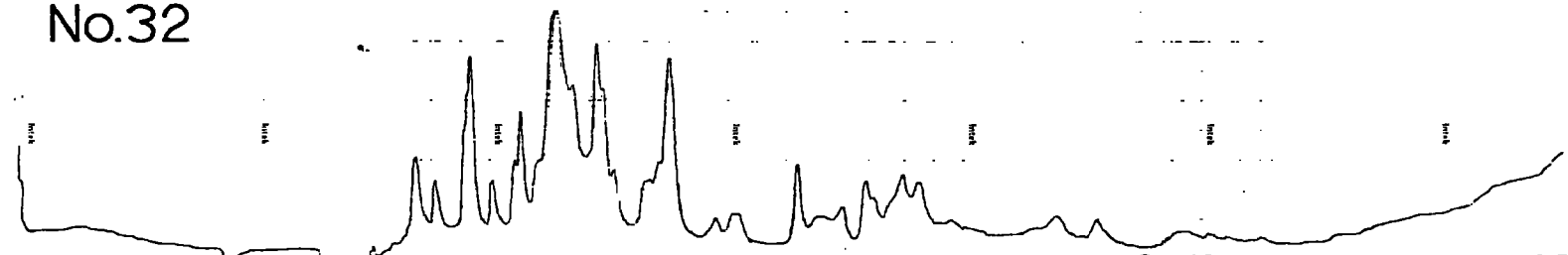

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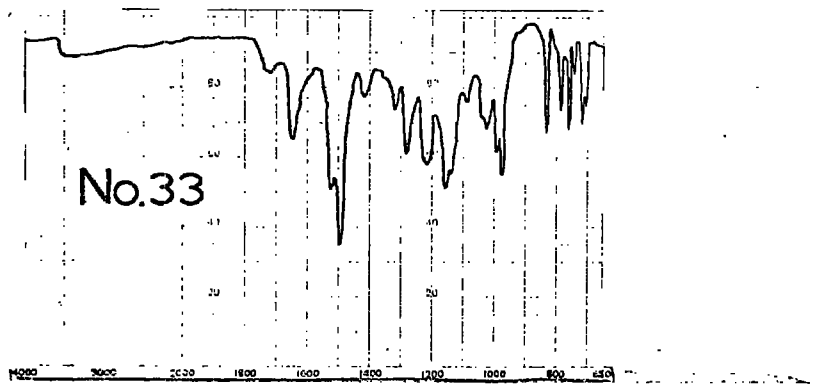

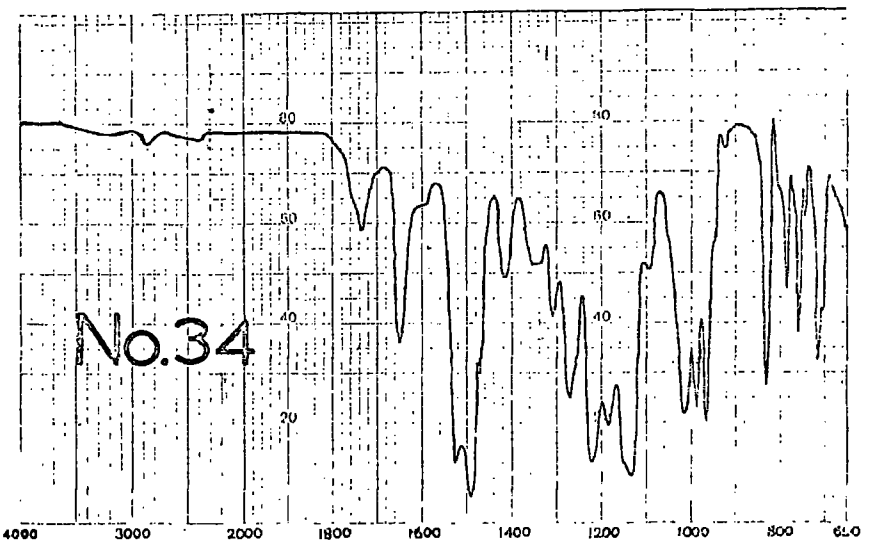
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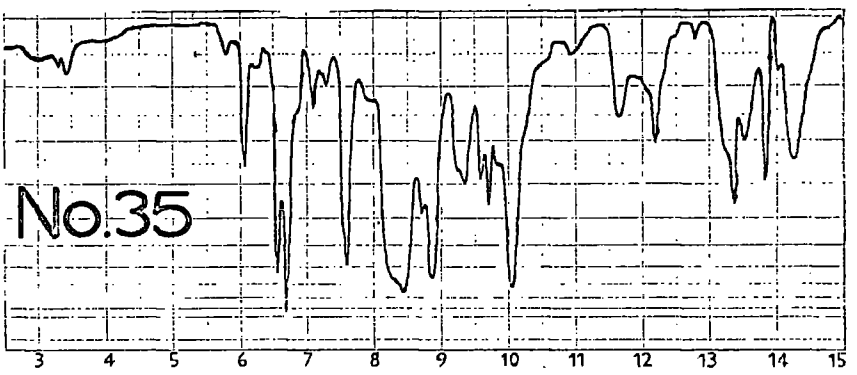
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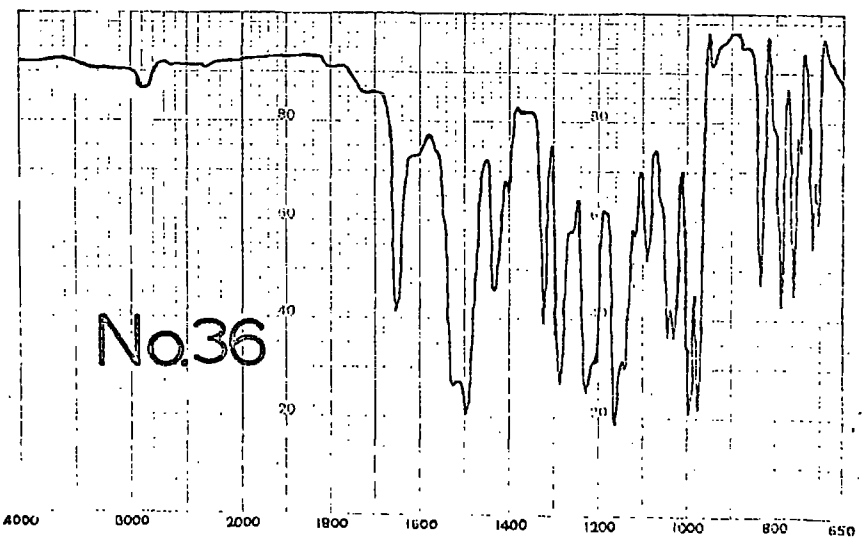
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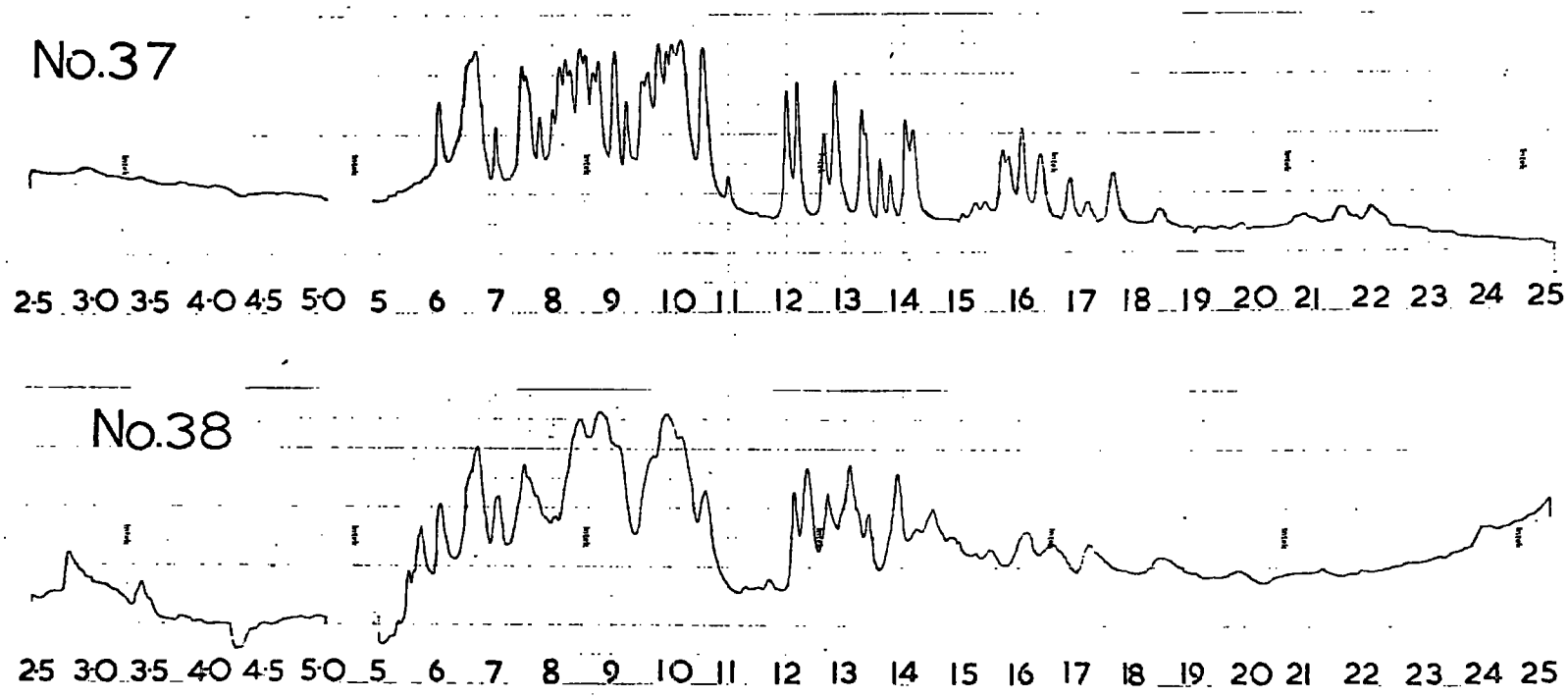
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