Some nucleophilic substitution reactions in fluorocarbon chemistry

John Arthur Jackson

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SOME NUCLEOPHILIC SUBSTITUTION REACTIONS IN FLUOROCARBON CHEMISTRY

submitted by

JOHN ARTHUR JACKSON, Grad. R.I.C.

(Graduate Society)

A candidate for the degree of Doctor of Philosophy

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Thanks are also due to many technical and laboratory staff for their help, and to the Science Research Council for a maintenance grant.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1965 and June 1968.

This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

Part of this work has been reported by Dr. R.D. Chambers at the joint annual meeting of the Chemical Society and the Royal Institute of Chemistry at Dublin, April 1968 and has been the subject of one publication:-

R.D. Chambers, J.A. Jackson, R.A. Storey and W.K.R. Musgrave, J. Chem. Soc. (C), 2221 (1968).

Summary

Carbanions, produced by the action of fluoride ion on polyfluoro-olefins, have been found to react with aromatic substrates which are suitably activated to nucleophilic attack in a reaction which can be thought of as the nucleophilic equivalent of the Friedel-Craft reaction.

The scope of the reaction has been investigated using perfluoro-ethylene, -propene, -butene, and pentene and the reactivity of these olefins is in the inverse order of the resulting carbanion stabilities, i.e. primary $<$ secondary $<$ tertiary. The reaction between pentafluoropyridine and hexafluoropropene was investigated in detail and it was observed that mono- and di-substitution followed the normal pattern of orientation. However the third heptafluoroisopropyl carbanion is thought to enter at position 5, this can be attributed to activation of that position by the heptafluoroisopropyl groups in positions 2 and 4. Examination of the ^{19}F N.M.R. spectra of the perfluoro-(tri-isopropylpyridines) indicates that an "in situ" rearrangement occurs in the presence of fluoride ion of the 2,4,5 isomer to the thermodynamically more stable 2,4,6 isomer.

Side reactions which consume the olefin are a limitation of the reaction and, in the case of hexafluoropropene, it was possible to minimise this by introducing the olefin at an elevated temperature; thereby allowing the higher activation energy polyfluoroalkylation

process to compete effectively with the dimerisation of the olefin.

Some polyfluorohaloethylenes were also investigated as suitable olefins for this reaction. Due to unexpected side reactions it was difficult to compare their reactivities, however a general trend in susceptibility towards attack by fluoride ion was observed as being chlorotrifluoroethylene > 1,1-dichlorodifluoroethylene > bromotrifluoroethylene > 1,2-difluoro-1,2-dichloroethylene. Reactions in which phenyl acetylene and hexafluorobut-2-yne were used as the source of nucleophile were unsuccessful due to polymerisation of these acetylenes. However it was possible to achieve reaction between diethyl acetylene dicarboxylate and pentafluoropyridine to give $4\text{-}[F(CCOOEt)_2]C_5F_4N$.

A variety of polyfluoroaromatic compounds were examined as potential substrates and the general order of reactivity towards carbanions was established as being the same as that towards other nucleophiles. 2:4-Dinitrofluorobenzene was investigated as a reactive, but not highly fluorinated substrate; displacement of the nitro group occurred, this was similarly observed in a reaction between pentafluoronitrobenzene and a perfluoro-secondary butyl carbanion.

Variable temperature N.M.R. studies on some perfluoroalkylaromatic compounds indicate that there is a considerable energy barrier towards rotation of the alkyl group in these compounds. This is particularly noticeable in the secondary butyl and 2-pentyl derivatives; at room temperature it appears that they exist solely in the most stable conformational isomer.

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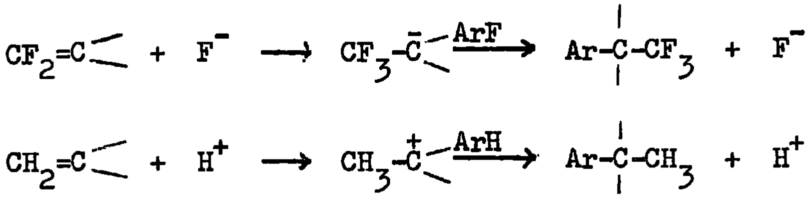
General Introduction

The replacement of hydrogen by fluorine in hydrocarbon systems, has led to a class of compounds whose chemistry complements that of the parent hydrocarbons. This replacement is usually accomplished without gross distortion of the geometry of the system, hence steric considerations are of lesser importance in fluorocarbon chemistry than in, for example, chlorocarbon chemistry.

Differences between fluorocarbons and hydrocarbons do arise due to the greater carbon-fluorine bond strength compared with the strength of the carbon-hydrogen bond. Also the relatively larger fluorine atom tends to shield the carbon chain from attack by reagents. These two effects enhance the stability of fluorocarbons over hydrocarbons, and this has led to useful applications in areas where thermal and chemical stability are of importance. Commercial applications, which have been in plastics, lubricants, aerosol propellants and polymers have provided the stimulus for research in this rapidly developing field.

Although interest in fluorine chemistry has been centered on synthetic methods, in recent years theoretical implications of highly fluorinated systems have become of interest. Unsaturated fluorocarbon compounds exhibit a chemistry that is complementary to that of similar hydrocarbon systems. Whereas the chemistry of the latter involves electrophilic attack giving carbonium-ion intermediates, unsaturated fluorocarbons undergo nucleophilic attack leading to carbanion intermediates.

The work described in this thesis is a study of reactions which can be regarded as the nucleophilic equivalent of Friedel-Craft reactions, i.e.



$$\mathrm{CF_2{=}C}< \; + \; \mathrm{F^-} \longrightarrow \mathrm{CF_3{-}\overset{-}{C}}< \xrightarrow{\mathrm{ArF}} \mathrm{Ar{-}C{-}CF_3} \; + \; \mathrm{F^-}$$

$$\mathrm{CH_2{=}C}< \; + \; \mathrm{H^+} \longrightarrow \mathrm{CH_3{-}\overset{+}{C}}< \xrightarrow{\mathrm{ArH}} \mathrm{Ar{-}C{-}CH_3} \; + \; \mathrm{H^+}$$

Carbanions derived from unsaturated fluorocarbon systems react with polyfluoroaromatic compounds to give polyfluoroalkylated products. The role of the fluoride ion in this reaction can be considered to be analogous to the role of the proton in the Friedel-Craft reactions.

Chapter 1

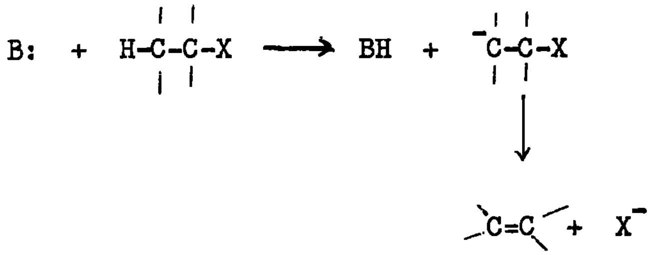
Fluoro-Olefins

1.1. Methods of Preparation of Fluoro-Olefins.

The classical methods of preparing organic fluorine compounds, direct fluorination and halogen exchange, are not the best routes to polyfluoro-olefins. Addition across carbon-carbon double bonds usually results in a low yield of the required olefin. There are however, many other methods of synthesis, of which the following three can be considered to be of practical and commercial importance.

[a] Dehydrohalogenation.

Dehydrohalogenation is a widely used laboratory method of preparing fluoro-olefins. The elimination is base-catalysed possibly an ElcB mechanism



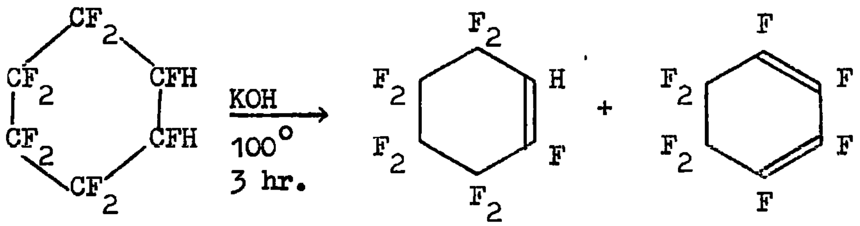
The ease of elimination of X (I > Br > Cl > F) is in decreasing order of bond strength. This is illustrated[1] by the removal of HI not HF from the compound $CF_2ICHFCFClCF_2Cl$ to give as product, the olefin $CF_2{=}CF{-}CFCl{-}CF_2Cl$. Of the numerous examples of hydrogen iodide removed, typical is the dehydroiodination of 2H,2H-1-iodononafluoro-

(3-methyl butane)[2]

$$(CF_3)_2CFCH_2CF_2I \xrightarrow[\text{2 hr.}]{\text{KOH } 90^{\circ}} (CF_3)_2CFCH=CF_2 \quad (85\%)$$

The base used for dehydrohalogenations is usually an alkali metal hydroxide, although alkoxides or tertiary amines can be used depending on the product and substrate. Tertiary amines[3] are effective dehydrohalogenating reagents for the preparation of dienes when alkali gives only the mono-olefin. The solvent used is usually an alcohol, although ether formation may reduce the yield of olefin.

Dehydrofluorinations are best accomplished using anhydrous, or very strong aqueous solutions of potassium hydroxide, e.g.



[4]

However hydrogen fluoride has been eliminated under relatively mild conditions using potassium hydroxide in di-n-butyl ether[5]

$$CF_3CHFCHF_2 \xrightarrow[\text{KOH; } 0^{\circ}]{\text{n-Bu}_2\text{O}} CF_3CF=CHF$$

Finally, lithium chloride in dimethylformamide[6] is selective for the removal of hydrogen iodide in systems where another hydrogen halide could be eliminated, i.e.

$$C_3F_7CH_2CF_2CH_2CF_2I \xrightarrow[\text{D.M.F. } 155^\circ]{\text{LiCl}} \begin{array}{l} \not\rightarrow C_3F_7CH_2CF{=}CHCF_2I \\ \rightarrow C_3F_7CH_2CF_2CH{=}CF_2 \ (90\%) \end{array}$$

[b] <u>Dehalogenation of 1,2-Dihalides.</u>

Dehalogenations of 1,2-dihalides are usually effected by zinc in ethanol.

$$\text{-CFX-CFY-} + \text{Zn} \xrightarrow{\text{EtOH}} \text{-CF=CF-} + \text{ZnXY}$$

X, Y usually Cl, Br, I

Other metals, magnesium in particular, can be used. The particular solvent chosen will depend on the boiling point and reactivity of the olefin. The solvent is thought to act as a Lewis base which ties up the ZnX_2 formed, removing it from the surface of the catalyst. Addition of zinc chloride will usually start the reaction which then proceeds sometimes violently to quantitative conversion. In some cases reduction of halogen can occur, e.g.[7]

$$CF_3CCl{=}CClCF_3 \longrightarrow CF_3CCl{=}CHCF_3$$

Good examples of this method are the important fluoro-olefins chlorotrifluoroethylene and trifluoroethylene.

8

$$[CCl_3CCl_3 \xrightarrow[\substack{SbCl_5 \\ 180^\circ}]{HF}]\ CF_2ClCFCl_2 \xrightarrow[\text{EtOH}]{\text{Zn}} CF_2CFCl \quad (90\%)$$

9

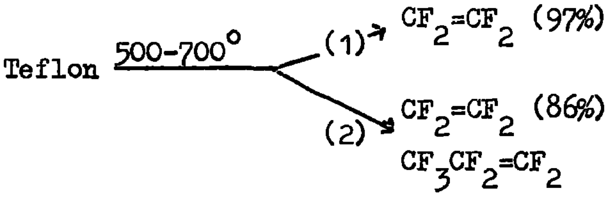
$$[HBr + CF_2CFCl \xrightarrow{\text{u.v.}}]\ CF_2Br\text{-}CFHCl \xrightarrow[\text{EtOH}]{\text{Zn}} CF_2CFH$$

Removal of chlorine-fluorine and iodine-fluorine, although not unknown, is less frequently encountered.

$$CF_3CH_2I \xrightarrow[\text{acetic anhydride}]{Mg} CF_2{=}CH_2 \quad (90\%) \quad ^{10}$$

[c] Pyrolytic Methods.

The pyrolysis of polytetrafluoroethylene is an important route to many fluoro-olefins,[11] the products formed depending on temperature, contact time and pressure.



(1) 5 mm. pressure

(2) 41 mm. "

At low pressures the chance that a difluorocarbene diradical will combine with another tetrafluoroethylene molecule is less than at a relatively higher pressure. Hence longer carbon-chain olefins result from higher pressures. Hexafluoropropene and isomeric octafluorobutenes are obtained by the pyrolysis of tetrafluoroethylene at 600° to 700° at one atmosphere pressure. Commercially tetrafluoroethylene is prepared by the pyrolytic dechlorination of chlorodifluoromethane.[12]

$$2CHCl_3 \xrightarrow[SbCl_5]{HF} 2CHF_2Cl \xrightarrow[\text{Pt tube}]{\sim 700^{\circ}} CF_2{=}CF_2 + 2HCl$$

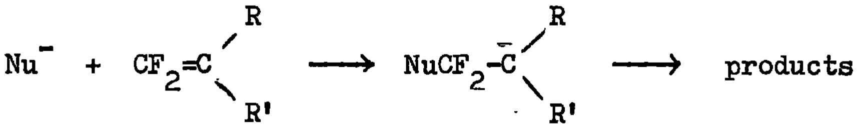
The pyrolysis of anhydrous sodium salts of perfluoroalkane carboxylic acids is a good method of preparing terminal olefins. The acids can be obtained by the electrochemical fluorination of the corresponding hydrocarbon acid fluoride.

$$R_fCF_2CF_2CO_2^- \xrightarrow{-CO_2} R_fCF_2\overset{-}{C}F_2 \longrightarrow R_fCF{=}CF_2$$

The pyrolysis of sodium perfluoro-n-butyrate is a useful method of preparing hexafluoropropene in the laboratory.

1.2. Nucleophilic Reactions of Fluoro-Olefins.

The replacement of hydrogen by fluorine in olefinic systems results in a removal of electron density from the π system. Hence polyfluoro-olefins are more susceptible to nucleophilic attack than their hydrocarbon analogues:



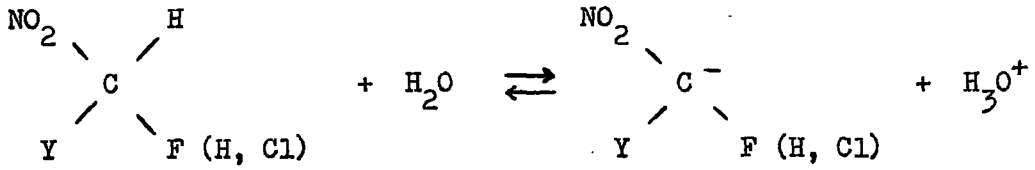
$$Nu^- + CF_2{=}C\begin{matrix}R\\R'\end{matrix} \longrightarrow NuCF_2\text{-}\overset{-}{C}\begin{matrix}R\\R'\end{matrix} \longrightarrow \text{products}$$

(A)

If the carbanion (A) can be approximated to the transition state, then a consideration of the stability of the carbanion will indicate the direction of initial nucleophilic attack. It is therefore relevant to consider the structural factors that influence the stability of a carbanion.

(a) α-Substituents.

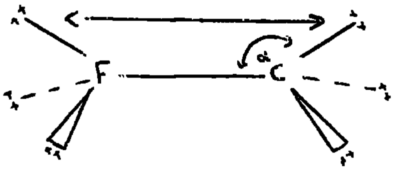
On the basis of base-catalysed hydrogen/deuterium exchange experiments on the haloforms CHF_3, $CHCl_3$, $CHBr_3$ and CHI_3, Hine[13] concluded that α (i.e. adjacent) halogen substituents lower the free energy of a carbanionic transition state, $\equiv C^{\delta-} - - - - H^{\delta+} - - -$ Base, and hence the corresponding carbanions. Therefore the ease of formation of trihalomethyl anions is in the order $CF_3^- < CCl_3^- < CBr_3^- < CI_3^-$. Adolph and Kamlet[16] measured the ionisation constants for a series of fluoronitromethanes:



Y = Cl, COOEt, $COONH_2$

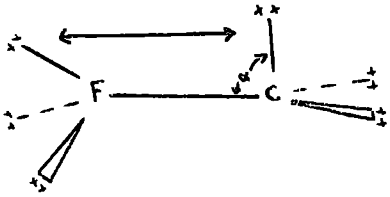
They found that the pKa values were in the order F > H > Cl for a given Y group.

This difference has been explained in terms of the conformation of the carbanion. If an α-substituent can exert a strong mesomeric effect (e.g. NO_2) then the carbanion will tend towards a planar geometry (i.e. sp^2 hybridised). The degree of planarity depends on the strength of the mesomeric effect. When the carbanion is planar it is possible to get repulsion between the electron pair in a p orbital on the carbon atom, and the electron pair in a filled p orbital on the fluorine. As indicated below, this effect (I_π interaction) will be at a maximum for an sp^2 carbanion:



sp^3 carbanion

$\alpha = 109^{o}$



sp^2 carbanion

$\alpha = 90^{o}$

Hydrogen has no p electrons, hence cannot exert an I_π effect. The order of I_π repulsion effects for the halogens has been shown[17] to be F > Cl > Br > I.

(b) **β-Substituents.**

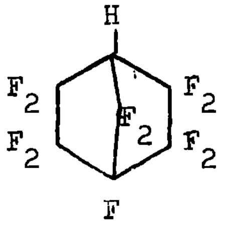
Andreades[18] measured the rate of hydrogen/deuterium exchange of the series of monohydrofluorocarbons indicated below, and showed that the formation of carbanions is made easier by β fluorine atoms and β fluoroalkyl groups.

	CF_3H	$CF_3(CF_2)_3CF_2H$	$(CF_3)_2CFH$	$(CF_3)_3CH$
$k_{(relative)}$	1	6	2×10^5	10^9

Andreades attributed this to the ability of a β fluorine atom to stabilize a carbanion by a "negative hyperconjugation" effect.

$$CF_3\text{-}\underset{-}{C}RR' \longleftrightarrow F^-CF_2{=}CRR'$$

However if this effect is of importance then the carbanion derived from bicyclic compound below would be incapable of extensive stabilization by this means, since it would require a bridgehead olefin structure.

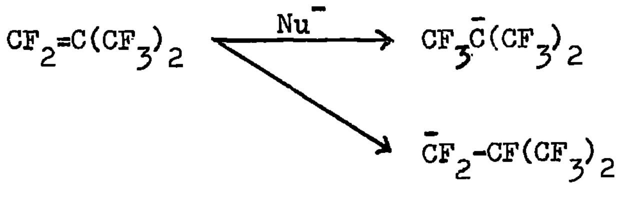


Streitweiser[19] measured the rate of hydrogen/deuterium exchange in this compound and found it to be $\sim 5 \times 10^5$ that of trifluoromethane. This suggests that the stabilization is more likely to be inductive in origin.

From a consideration of these effects it is seen that a fluoro-olefin would be favoured for attack by nucleophiles at a position that would give rise to a tertiary carbanion, and that for the series:

$CF_2{=}CF_2$ $\qquad$ $CF_2{=}CFCF_3$ $\qquad$ $CF_2{=}C(CF_3)_2$

the overall reactivity to nucleophilic attack should increase from left to right. These generalisations are found to be so in practice. A terminal difluoromethylene group is the most reactive position in a terminal olefin, for example perfluoroisobutene invariably undergoes nucleophilic addition at the $=CF_2$:

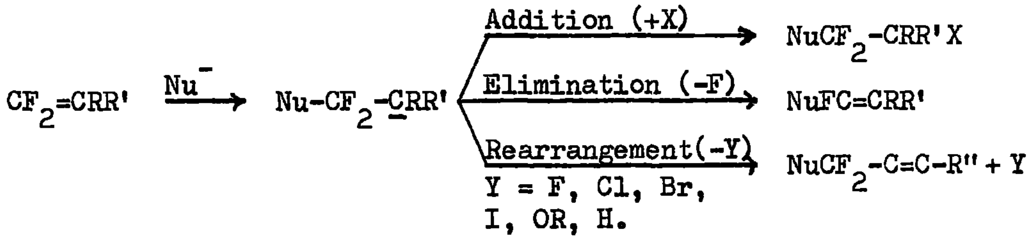


nine β fluorine atoms
no α fluorine atom

one β fluorine atom
two α fluorine atoms

Also tetrafluoroethylene and hexafluoropropene both require base for the addition of ethanol, whereas octafluoroisobutene[20] reacts in neutral media. It is however difficult to compare accurately the reactivity of a series of olefins towards a nucleophile because of solubility differences of the olefins in the medium employed.

Reagents used for nucleophilic attack on fluoro-olefins[21] include alcohols, phenols, thiols, thiophenols, fluoride ion, amines, Grignard reagents, and organo-lithium compounds. A general reaction scheme following nucleophilic attack can be summarized:

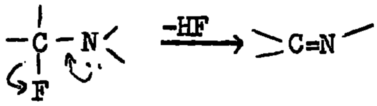


(a) Addition.

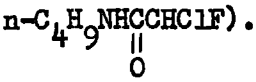
The carbanion stabilizes itself by abstraction of a proton from the solvent. This is the most common method for fluoroethylenes, for example, the reactions of chlorotrifluoroethylene given below:

CF_2CFCl +	Product	Yield
CH_3OH/Na	CH_3OCF_2CFClH	85%[22]
C_2H_5SH/NaOH	$C_2H_5SCF_2CClFH$	80%[23]
F^-/D.M.F.	CF_3CFHCl	46%[24]
$C_4H_9NH_2$	[n-$C_4H_9NHCF_2CHClF$] n-C_4H_9N=CFCHClF	33%[25]

The reaction of primary and secondary amines with fluoro-olefins is usually followed by dehydrofluorination. This is due to mesomeric electron release by nitrogen as indicated below



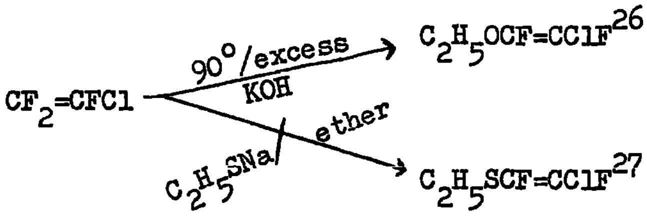
Under hydrolytic conditions the imine is hydrolysed to the amide (e.g.



$n\text{-}C_4H_9NHC(=O)CHClF$).

(b) Elimination.

Once formed the saturated compound may undergo elimination via proton abstraction by the base. Hence an increase in the strength of the base will favour products arising from elimination. However in a solvent chosen to minimise proton abstraction, or by the use of absolute alkali-metal salts, appreciable amounts of the elimination products can be formed.

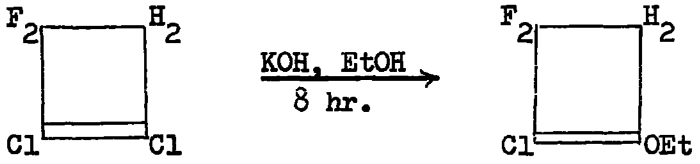


The structure of the olefin also has an important role in deciding whether saturated or unsaturated products are formed. Dimethylamine reacts quantitatively with octafluoroisobutene to give the enamine $(CF_3)_2C{=}CFN(CH_3)_2$ whereas reaction with tetrafluoroethylene gives the primary addition product $CF_2HCF_2NMe_2$.[28] If the carbanion is not sufficiently basic to abstract a proton from the reaction medium then elimination will occur without the saturated product being an intermediate in the overall elimination process, e.g.

$$(CF_3)_2C{=}CF_2 \xrightarrow[20^{\circ}]{(CH_3)_2CHOH} (CF_3)_2CHCF_2OCH(CH_3)_2 \ (35\%) \ + \ (CF_3)_2C{=}CFOCH(CH_3)_2 \ (26\%) \quad {}^{20,29}$$

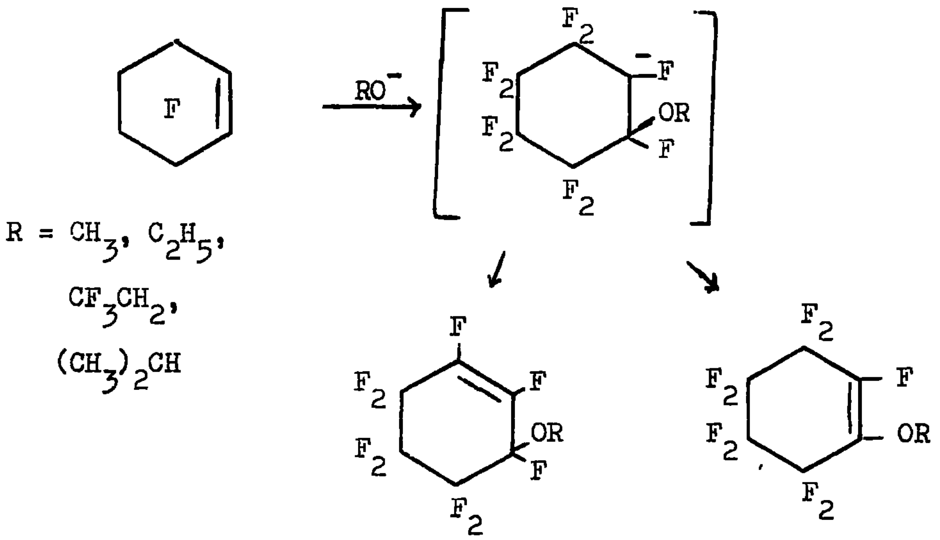
When the saturated ether was boiled with excess isopropyl alcohol it was not dehydrofluorinated to the unsaturated ether.

Cyclic olefins form unsaturated products exclusively, and an addition-elimination process has been proposed. The major directive influence is thought to be stabilization by the α-substituents. When the α-substituents are the same then nucleophilic attack will occur at that end of the double bond that will give the carbanion best stabilized by β substituents, e.g.



[30] quantitatively

Tatlow[31] noted that the isomer distribution ratio a:b for the reaction below was dependent on the electron-attracting power of R.

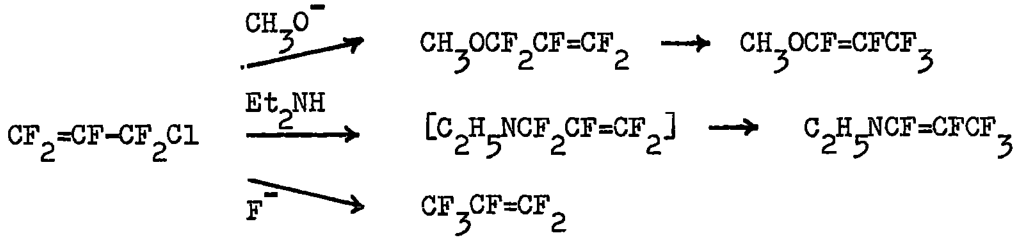


(a) (b)

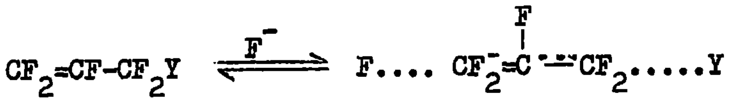
Product (a) is favoured by strongly electron attracting groups.

(c) Allylic Rearrangement.

Allylic displacement of halogens in 3-substituted pentafluoropropenes has been observed using a variety of nucleophiles.[32]



The important fluoride ion catalysed rearrangements are dealt with in chapter 2. Miller[32] established that the order of leaving groups is I > Br > Cl > F, and proposed a low energy Sn_2' transition state, with or without the intermediacy of a discrete carbanion.



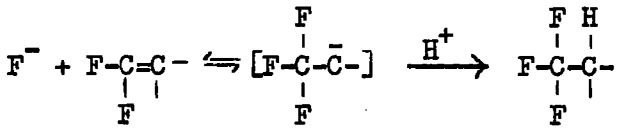
$$CF_2{=}CF{-}CF_2Y \xrightleftharpoons{F^-} F\ldots\ CF_2^-{\overset{\displaystyle F}{=}}C\cdots CF_2\ldots\ldots Y$$

The evidence lies in favour of a concerted mechanism, as attempts[33,34] to trap any transient fluorocarbanions by addition of water have failed.

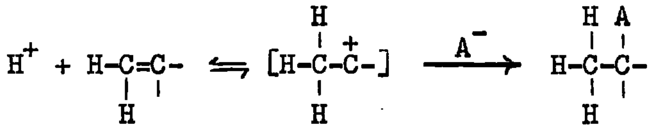
Chapter 2

Reactions Involving Fluoride Ion

The reactions of fluorine and other halide ions with fluoro-olefins were studied initially by Miller, who underlined the analogous role of fluoride ion in organic fluorine chemistry to that of the proton in hydrocarbon chemistry.



$$F^- + \underset{F}{F-C}{=}C- \rightleftharpoons \left[F-\overset{F}{\underset{F}{C}}-\overset{-}{C}-\right] \xrightarrow{H^+} F-\overset{F}{\underset{F}{C}}-\overset{H}{C}-$$



$$H^+ + \underset{H}{H-C}{=}C- \rightleftharpoons \left[H-\overset{H}{\underset{H}{C}}-\overset{+}{C}-\right] \xrightarrow{A^-} H-\overset{H}{\underset{H}{C}}-\overset{A}{C}-$$

Fluorocarbanions derived from the nucleophilic addition of fluoride ion to unsaturated systems are becoming of interest as synthetic intermediates. The choice of solvent and source of fluoride ion for such reactions merits attention, and problems associated with these will be discussed first. This will be followed by the more important reactions in which fluoride ion is involved.

2.1. Solvents and Sources of Fluoride Ion.

A solution of fluoride ion and a polyfluoro-olefin exist in equilibrium with a carbanion, and in order to push the equilibrium to the right (to favour the carbanion) it is desirable to have an excess of fluoride. This is difficult to achieve because most sources of fluoride ion are insoluble in the solvents used. In order to maintain the equilibrium the solvent must minimise side reactions, such as proton abstraction by the carbanion. It must also be capable of dissolving large amounts of the source of fluoride ion.

(a) Dipolar aprotic solvents.

Dipolar aprotic solvents have been found to be especially useful in fitting the first of these requirements. These are solvents classed[35] as those with dielectric constants greater than 15, which, although they contain hydrogen cannot donate suitably labile hydrogen atoms to form strong bonds with an appropriate species. Typical reaction media of this type are dimethylformamide, dimethylsulphoxide, tetramethylene sulphone, and the dialkyl ethers of ethylene glycol or polyethylene glycols ("glymes"), all of which have been found useful for reactions involving fluoride ion. Electrolytes are soluble in dipolar aprotic solvents because of the ability of these solvents to solvate cations. A high degree of cation solvation is due to these solvents having a region of high electron density, localised usually on a bare oxygen atom, which allows strong interaction with the cation. The type of dipole present is also important. Cations may be poorly solvated if the negative end of the solvent dipole is dispersed (e.g. nitrobenzene). In dipolar aprotic solvents solvation of the anion increases with the size of the anion,[36] i.e.

$$I^- > SCN^- > Br^- > N_3^- > Cl^- \gg F^-$$

Fluoride ion, being the smallest is the least solvated and hence the strongest nucleophile. Reaction rates involving fluoride ion are proportionally faster in dipolar aprotic solvents than in protic solvents. In protic solvents such as formamide, methanol, and water, anions are solvated by a small unshielded proton and steric resistance is negligible. Hence small anions can be highly solvated in protic solvents, leading to a reduction in nucleophilic strength and rates of reactions.

Other factors of importance are boiling point and decomposition temperature of the solvent. Tetraglyme although of high boiling point tends to decompose when heated to high temperatures ($\sim 200^{\circ}$)[37] for long periods.

However for temperatures below 100° the glymes appear to be useful solvents for reactions involving fluoride ion, the order of effectiveness being mono- < di- < tri- < tetraglyme.[38] Graham noted a substantial increase in the rate of self-condensation of tetrafluoroethylene on substituting monoglyme for diglyme. Increasing the amount of catalyst (CsF) also increased the rate of this reaction.[38] This suggests that the surface of the catalyst is involved in the initiation of the polymerisation, possibly by polarizing the olefin prior to the addition of fluoride ion.

(b) Sources of fluoride ion.

The most widely-used sources of fluoride ion are alkali metal fluorides and their efficiency in respect to halogen exchange reactions has been established as:

$$\mathrm{LiF} < \mathrm{NaF} < \mathrm{KF} < \mathrm{RbF} < \mathrm{CsF}$$ [39]

which closely resembles their order of crystal lattice energies. Tetraethylammonium fluoride has been used as a source of fluoride ion[40] and is conveniently soluble in halogenated solvents such as chloroform. However, it is difficult to prepare pure, and is hygroscopic, and thermally unstable. Potassium fluorosulphite 'KSO_2F', prepared by shaking potassium fluoride in sulphur dioxide, is soluble in sulphone solvents and has been used in halogen exchange reactions with cyanuric chloride.[41] This reagent is also thermally unstable. Alkali metal bifluorides have been used in fluoride ion catalysed additions of fluoroacyl fluoride to hexafluoropropene.[42] These compounds are of limited applicability because of low solubility in aprotic solvents.

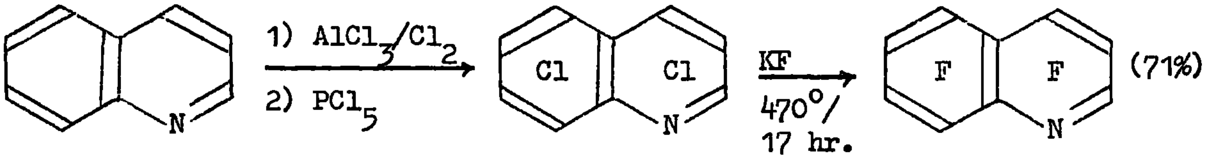
Reactions in absence of solvent.

By-products which are the result of reaction of the carbanion with the solvent can be eliminated by removal of the solvent. However reactions in absence of solvent sometimes produce products which are not formed in the presence of a solvent. The dimerisation of hexafluoropropene at 350° in absence of solvent gives perfluoro-(1,4-dimethyl butane) in reasonable yield.[43] This suggests a breakdown of the molecule to give fluorine radicals.

$$(CF_3)_2CF^- + F^\bullet \longrightarrow (CF_3)_2CF^\bullet + F^-$$

$$2[(CF_3)_2CF^\bullet] \longrightarrow (CF_3)_2CFCF(CF_3)_2$$

Halogen exchange reactions of perchloroaromatic compounds, in presence of a solvent, are only successful in a few cases.[44] A now well-established route to polyfluoroaromatic compounds involves heating the perchloroaromatic compound with potassium fluoride. Temperatures ranging from 300° to 500° are necessary to replace all the chlorine atoms, hence precluding the use of a solvent. An example of this procedure is the synthesis of heptafluoroquinoline[45]



This method has been used for the preparation of pentafluoropyridine,[46,47] heptafluoroisoquinoline,[45] tetrafluoropyrimidine,[48] -pyridazine,[49] and hexafluoroquinoxaline.[50]

2.2. Rearrangements Catalysed by Fluoride Ion.

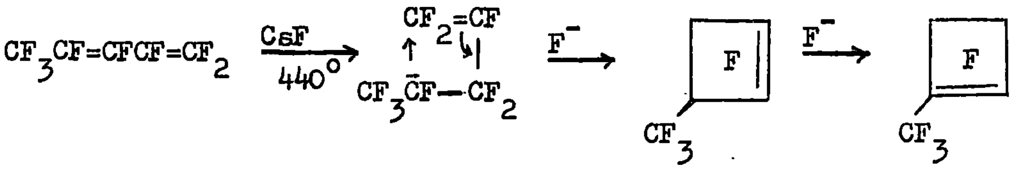
A terminal olefin is more susceptible to nucleophilic attack than an internal olefin and will rearrange by an S_N2' mechanism to an internal olefin. If the conditions are sufficiently vigorous the internal olefin will rearrange until the most highly-substituted olefin results. e.g. the rearrangement of perfluoro-1-heptene in chloroform using tetraethylammonium fluoride as catalyst:

$$n\text{-}C_5F_{11}CF{=}CF_2 \xrightleftharpoons{F^-} n\text{-}C_4F_9CF{=}CF\text{-}CF_3 \rightleftharpoons n\text{-}C_3F_7CF{=}CFC_2F_5$$ [24]

Such rearrangements can also be effected in absence of a solvent, perfluoro dienes are rearranged to acetylenes in the vapour phase using caesium fluoride as catalyst

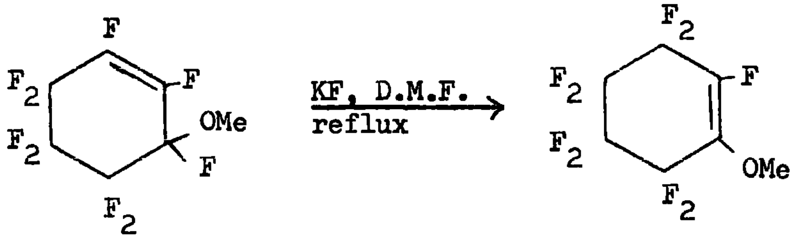
$$CF_3CF{=}CFCF{=}CF_2 \xrightarrow{F^-} CF_3CF{=}C{=}CFCF_3 \xrightarrow{F^-} CF_3CF_2C{\equiv}CCF_3$$

The acetylene is produced in 68% yield after heating at 80°C for half an hour.[51] However at higher temperatures a cyclobutene is formed



(30% conversion)

Workers at Birmingham have used fluoride ion catalysed rearrangements to confirm structural relationship between substituted cyclic olefins, which differ only in the position of the double bond. As expected the thermodynamically most stable olefin is produced.



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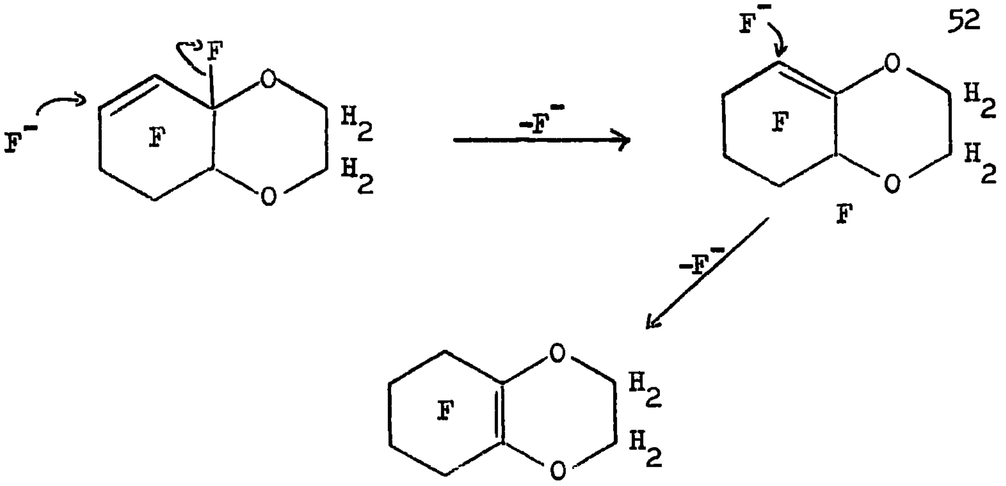

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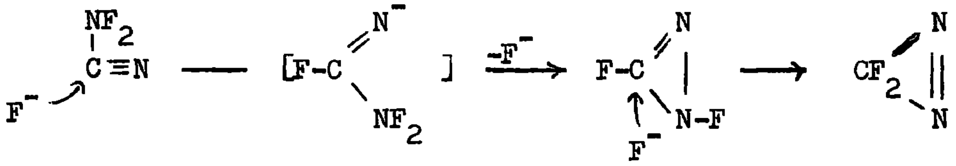
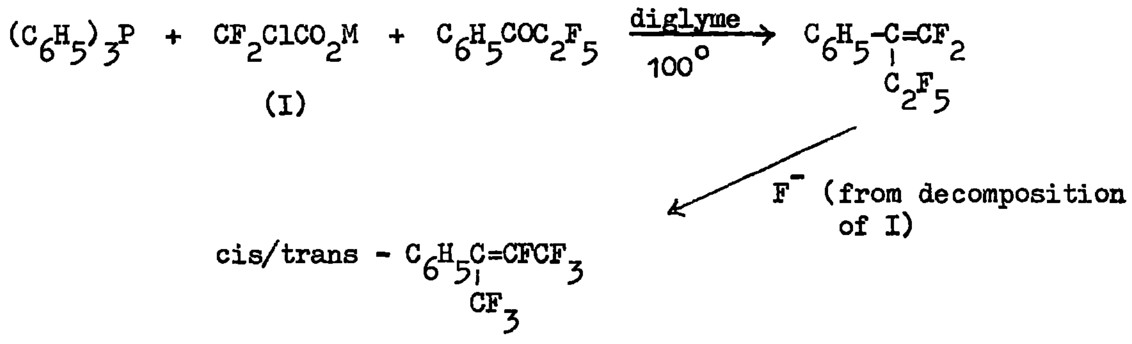
Fluoro epoxides have been rearranged, the product depends on the structure of the epoxide. Terminal epoxides give acid fluorides whereas epoxides of cyclic olefins give ketones.[53]

Meyer and Frank[54] reported that difluorocyanamide is converted at room temperature to diazirine by caesium fluoride and recently Mitsch[55] proposed a fluoride-ion initiated rearrangement.



In a Wittig synthesis of 2-phenyl heptafluoro-1-butene, Burton and Herkes[56] found the product rearranged "in situ" to the internal olefin



$$(C_6H_5)_3P + \underset{(I)}{CF_2ClCO_2M} + C_6H_5COC_2F_5 \xrightarrow[100^\circ]{\text{diglyme}} C_6H_5-\underset{\underset{C_2F_5}{|}}{C}=CF_2$$

$$C_6H_5-\underset{\underset{C_2F_5}{|}}{C}=CF_2 \xrightarrow{F^-\ \text{(from decomposition of I)}} \text{cis/trans} - C_6H_5\underset{\underset{CF_3}{|}}{C}=CFCF_3$$

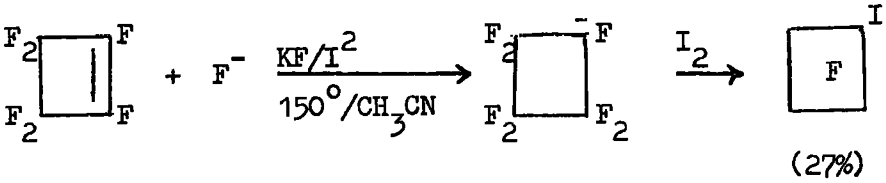
(M = K, Na)

The ratio of internal to external olefin, and the initial cis/trans ratio of the internal olefin was dependent on the choice of the alkali metal (M) and the reaction time.

2.3. Some other Nucleophilic Reactions Involving Carbanions.

Fluorocarbanions, formed from the addition of fluoride ion to fluoro-olefins, are becoming of increasing importance as synthetic intermediates in organic fluorine chemistry. The nature of the products resulting from fluoride-catalysed addition of fluoro-olefins present adequate proof of the intermediacy of fluorocarbanions. Some reactions which illustrate this are given below.

Fluorocarbon Iodides:- Krespan's[57] synthesis of fluoroalkyl iodides is a good example of the utilization of perfluorocarbanions as nucleophiles. A carbanion formed from the addition of fluoride ion to a fluoro-olefin reacts with iodide ion in the solution



Yield of iodide is poor when a carbanion is formed with difficulty or is susceptible to rearrangement; tetrafluoroethylene gives only 7% of the iodide CF_3CF_2I and perfluorobutene only 17% of the iodide $CF_3CFICF_2CF_3$.

Addition to Amines:- Hexafluoropropene adds to perfluoropiperidine in absence of solvent. It is of interest to note that in absence of alkali metal fluoride no reaction occurred below 300°.

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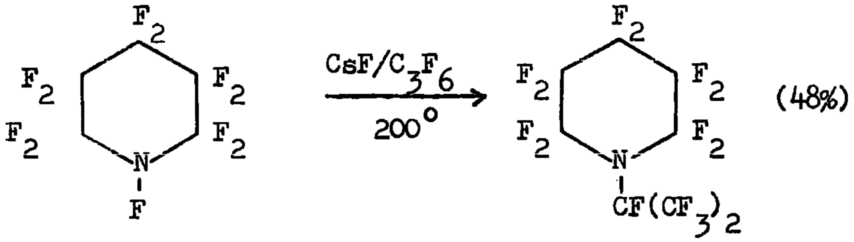
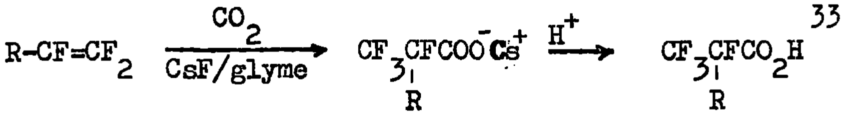


Reaction with Nitrosyl Fluoride:- Knunyants[58] recently explained the addition of nitrosyl fluoride to fluoro-olefins other than fluoroethylenes, in terms of nucleophilic attack by a carbanion.

$$CF_3\text{-}CF{=}CF_2 \xrightarrow[35^{\circ}]{KF/sulpholan} (CF_3)_2\bar{C}F \xrightarrow{FNO} (CF_3)_2CF\text{-}NO \quad (90\%)$$

Synthesis of Carboxylic Acids:- A useful synthesis of perfluoro carboxylic acids involves the addition of a carbanion to carbon dioxide. The mixture is acidified and the acid removed by distillation:



$$R\text{-}CF{=}CF_2 \xrightarrow[\text{CsF/glyme}]{CO_2} CF_3\underset{R}{CF}COO^-Cs^+ \xrightarrow{H^+} CF_3\underset{R}{CF}CO_2H$$ [33]

$R = Cl, F, CF_3$

Reaction with SF_4:- Fluorine has been displaced from sulphur tetrafluoride by a perfluoroisopropyl carbanion.[59]

$$2SF_4 + 3C_3F_6 \xrightarrow[150^\circ]{CsF} \underset{[1]}{(CF_3)_2CFSF_2CF(CF_3)_2} + \underset{[2]}{(CF_3)_2CFSF_3}$$

Formation of either 1 or 2 is controlled by the reactant ratios.

Additions to Carbonyl Compounds:- Possibly the most useful reactions synthetically have been the displacement of fluorine from carbonyl compounds.[42,60] The additions of carbonyl fluoride to the olefins $CF_3CF{=}CF_2$ (80% conversion), $CF_3CF{=}CFCF_3$ (62%), $CH_3OCF{=}CF_2$ (62%), $CF_2{=}CF_2$ (13%) and $CF_2CF{=}CFCF_2$ (54%) occurred smoothly to give acid fluorides. Acetonitrile was used as the solvent and caesium fluoride, potassium bifluoride, or tetraethylammonium fluoride were suitable catalysts.

$$CF_3{\cdot}CF{=}CF_2 + COF_2 \xrightarrow[50/100^\circ]{CH_3CN/KF} (CF_3)_2CFCOF$$

$$CF_3{\cdot}CF{=}CF_2 + COF_2 \xrightarrow[75^\circ - 100^\circ]{CsF/CH_3CN} [(CF_3)_2CF]_2CO$$

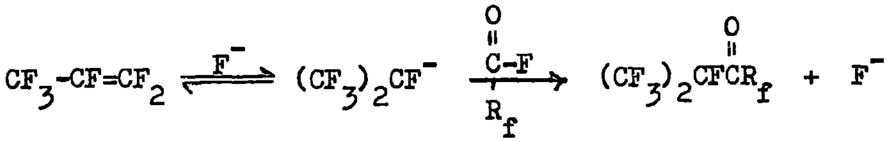
(38% conversion)

Ketones are produced by the action of olefins on fluoroacyl fluorides, as shown above symmetrical ketones can be made by reaction of excess olefin with carbonyl fluoride. Reactions of hexafluoropropene with a variety of fluoroacyl fluorides are given in Table 1.

Table 1

Acyl Fluoride	Ketone	% Conversion
CF_3COF	$CF_3COCF(CF_3)_2$	75
n-C_3F_7COF	n-$C_3F_7COCF(CF_3)_2$	60
iso-C_3F_7COF	$(CF_3)_2CFCOCF(CF_3)_2$	38
$CF_2(CF_2COF)_2$	$CF_2[CF_2COCF(CF_3)_2]$	75

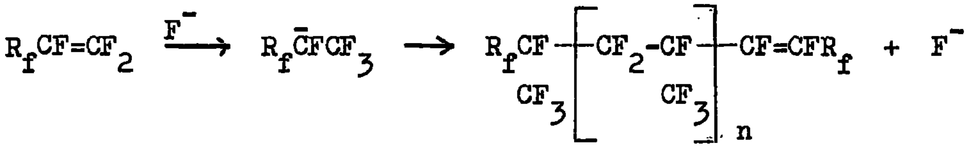
It is assumed that these additions proceed by the initial generation of carbanions which then react with the acid fluoride



$$CF_3\text{-}CF{=}CF_2 \xrightleftharpoons{F^-} (CF_3)_2CF^- \xrightarrow[R_f]{\overset{O}{\overset{\|}{C}}\text{-}F} (CF_3)_2CF\overset{O}{\overset{\|}{C}}R_f + F^-$$

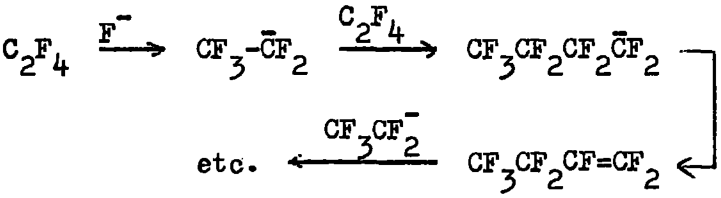
2.4. Polymerization of Fluoro-Olefins.

The elimination of fluoride ion by an internal olefin prevents the extensive anionic polymerization of fluoro-olefins by the following mechanism:



$$R_fCF{=}CF_2 \xrightarrow{F^-} R_f\bar{C}FCF_3 \longrightarrow R_f\underset{CF_3}{CF}-\left[CF_2-\underset{CF_3}{CF}\right]_n-CF{=}CFR_f + F^-$$

Graham[38] observed minor amounts of C_{14} olefins by the stepwise addition of tetrafluoroethylene, i.e.



$$C_2F_4 \xrightarrow{F^-} CF_3\text{-}\bar{C}F_2 \xrightarrow{C_2F_4} CF_3CF_2CF_2\bar{C}F_2 \longrightarrow CF_3CF_2CF{=}CF_2 \xrightarrow{CF_3\bar{C}F_2} \text{etc.}$$

although approximately half of the tetrafluoroethylene was used in reaction with the solvent (diglyme).

Hexafluoropropene has been condensed under a variety of conditions, the nature of the products and their ratio depends on the reaction conditions.

$$\begin{aligned} CF_3CF{=}CF_2 \xrightarrow{F^-}\; & CF_3CF{=}CFCF(CF_3)_2 && \text{(a)} \\ & + CF_3CF_2{=}C(CF_3)_2 && \text{(b)} \\ & + (CF_3)_2CFC(CF_3){=}CFCF(CF_3)_2 && \text{(c)} \\ & + (CF_3)_2C{=}C(CF_3)CF_2CF(CF_3)_2 && \text{(d)} \end{aligned}$$

In solvents, long reaction times and high temperatures favour the more substituted olefins (b) and (d); and low temperatures and pressures favour the dimers.[61] Passing hexafluoropropene through a mixture of dimethylformamide and potassium bifluoride is reported[62] to give a product distribution ratio of a:b:c:d = 19·7: 0·4: 35·1: 44·8%. In contrast to this result, when caesium fluoride is heated at 215° in an autoclave without solvent, a ratio of a:b:c + d = 1: 46: 23%[43] was found after 87 hours reaction time. The latter result was highly dependent on temperature, for after 11 days at 100° the percentage conversion of hexafluoropropene to products was only 26·7, of which 82% was (a).

The complete absence of a terminal olefin (e) which could be formed from initial attack by a perfluoroisopropyl carbanion:

$$(CF_3)_2CF^- \searrow CF_2{=}CF{-}CF_3 \longrightarrow (CF_3)_2CF{-}CF_2{-}\bar{C}F{-}CF_3$$

$$(CF_3)_2CFCF_2CF{=}CF_2 \quad (e) \longleftarrow$$

illustrates the preference of a fluoro-carbanion to form an internal over terminal olefin. However if the olefin (e) is formed, it is doubtful that it would exist for long before being attacked by fluoride ion at the terminal difluoromethylene group.

Higher olefins are less prone to self-addition, in the few reported experiments on the action of fluoride ion on C_3 and above acyclic olefins only dimers have been formed.

$$CF_3CF{=}CFCF_3 \xrightarrow[\text{CsF/D.M.F.}]{\text{Room temp.}} CF_3(C_2F_5)C{=}C(C_2F_5)CF_3 \quad {}^{63}$$

$$+ \; CF_3(C_2F_5)CF(CF_3)C{=}CFCF_3$$

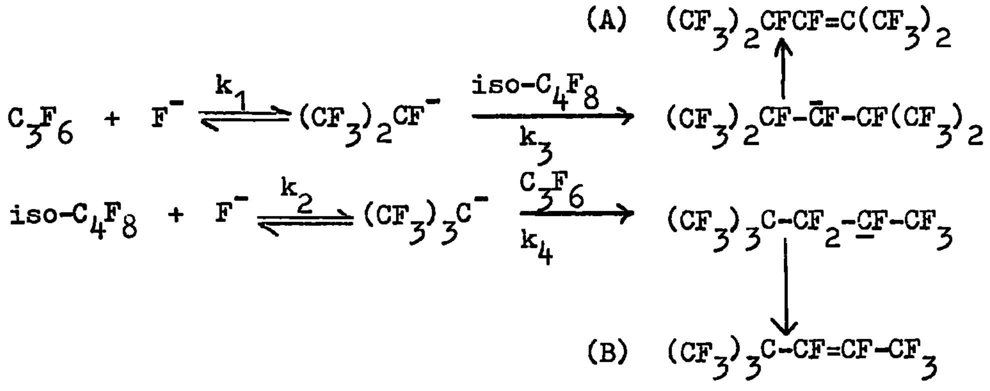
Some cyclic olefins have been dimerised, hexafluorocyclobutene[63] gives a mixture of dimers and trimers, and decafluorocyclohexene[64] dimerised.

2.5. Co-dimerisation Reactions.

When a mixture of two fluoro-olefins is heated with an alkali metal fluoride, alternative modes of reaction are possible. One or both of the olefins may dimerise or the carbanion from one olefin may attack the other olefin. The products from such a mixture depend on the reactivity of each olefin to fluoride ion and the relative tendency of the carbanions formed to eliminate, dimerise or abstract a proton from the solvent (if present). Hexafluoropropene has been reported to form co-dimers with the following olefins:

Octafluoroisobutene.

This olefin reacted with hexafluoropropene to form product A in the scheme below.[65]



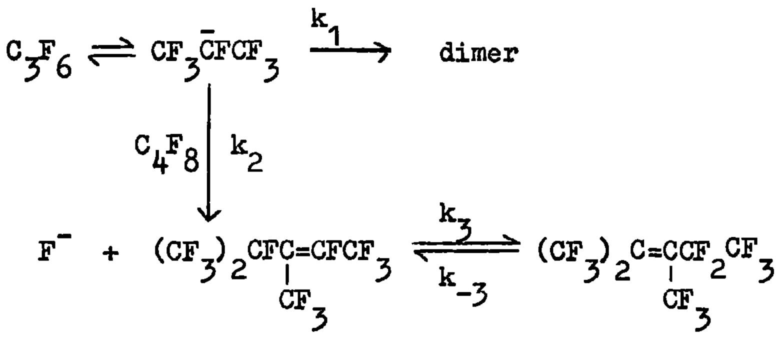
Although the reaction was not reported in detail, it was assumed that olefin (B) was absent in the product mixture. This result implies that the overall rate of the reaction leading to product (A) is much faster than the reaction which produces olefin (B) (i.e. $k_1 + k_3 \gg k_2 + k_4$).

Octafluoroisobutene is known to be more reactive than hexafluoropropene towards nucleophiles (i.e. $k_2 > k_1$ [see section 1.2]). The fact that product (A) is formed in preference to product (B) clearly illustrates the higher reactivity of a perfluoroisopropyl carbanion over a perfluoro-t-butyl carbanion. Although the latter anion is in a higher concentration, its high stability inhibits reaction with hexafluoropropene.

It is worth noting that although the formation of A can be explained in terms of the stability of the perfluoro-t-butyl carbanion, steric requirements of such a group may also affect the rate of the reaction.

Octafluorobut-2-ene.

Fraticelli co-dimerised this olefin with hexafluoropropene at room temperature in dimethylformamide, using caesium fluoride as the catalyst. The initial co-dimer was not isolated, it rearranged to a thermodynamically more stable olefin.[63]

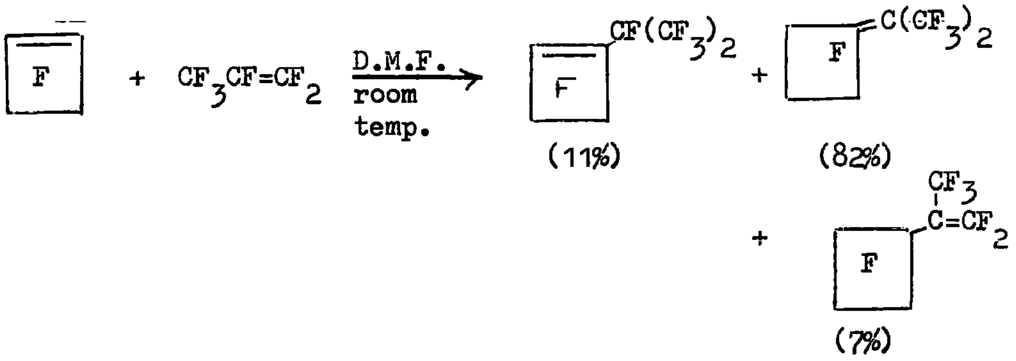


$$\begin{tikzcd} C_3F_6 \arrow[r, shift left] & CF_3\bar{C}FCF_3 \arrow[l, shift left] \arrow[r, "k_1"] \arrow[d, "C_4F_8"', "k_2"] & \text{dimer} \\ F^- + & (CF_3)_2CFC(CF_3){=}CFCF_3 \arrow[r, shift left, "k_3"] & (CF_3)_2C{=}C(CF_3)CF_2CF_3 \arrow[l, shift left, "k_{-3}"] \end{tikzcd}$$

$$k_1 < k_2 < k_3 << k_{-3}$$

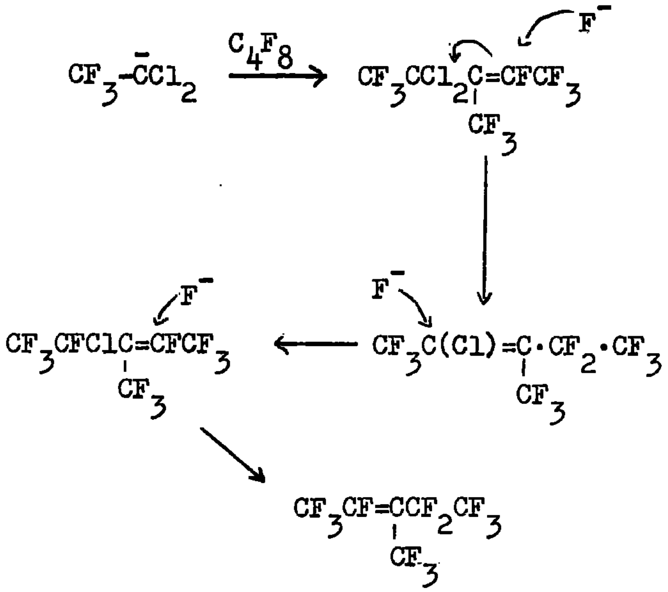
Cyclic Fluoro-Olefins.

Perfluorocyclobutene and hexafluoropropene gave, among other products, a mixture of three co-dimers[63] in the ratio shown below.



Attempts by the author to add hexafluoropropene to perfluorocyclohexene, were unsuccessful using caesium fluoride in sulpholan, at temperatures up to 200°.

Finally, 1,1-dichlorodifluoroethylene and octafluorobut-2-ene gave the olefin $CF_3CF{=}C(CF_3)CF_2CF_3$ by shaking in dimethylformamide with caesium fluoride.[63]



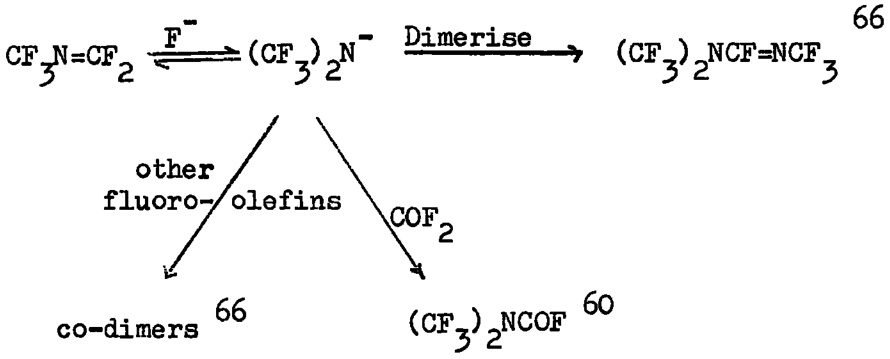
2.6. Nitrogen Anions.

The structural relationship of perfluoro-azomethines, $R_fN{=}CF_2$, to terminal fluoro-olefins suggests that addition of fluoride ion would produce the carbanion $R_f\bar{N}CF_3$, which may be synthetically useful.

Perfluoro-2-azapropene has been prepared by heating bis-(trifluoromethyl)-carbamyl fluoride:

$$\left[ClCON(CH_3)_2 \xrightarrow[\text{fluorination}]{\text{electrochemical}} \right] FCON(CF_3)_2 \xrightarrow[\text{18 hrs.}]{400^\circ} CF_3N{=}CF_2 \ (70\%)$$ [65]

From the information available, perfluoro-2-azapropene does undergo fluoride-ion catalysed reactions and produces products analogous to those from reactions using hexafluoropropene.



Fluoride ion also has been added to trifluoroacetonitrile[42] and hydrogen cyanide,[42] anions derived from these additions were reacted with carbonyl difluoride, e.g.

$$CF_3C\;N \xrightarrow[\substack{200-\\300^{\circ}\\CsF}]{COF_2} [CF_3CFN\,C\,OF] \longrightarrow CF_3CF_2N{=}C{=}O$$

(18%)

2.7. Oxygen Anions.

Primary and secondary alcohols are generally assumed to be incapable of existence because of the ease with which they would lose hydrogen fluoride. The one exception to this is perfluorocyclobutanol which has been isolated from the addition of hydrogen fluoride to cyclobutanone. However the alkali metal salts of some perfluoroalcohols do exist and are reasonably stable. The preparation of the trifluoromethoxides of potassium, rubidium and caesium by the addition of carbonyl fluoride to the metal fluoride in diglyme was first reported by Willis in 1964.[67] More recently,[68] the reaction was extended to perfluoro-ethoxides, -n-propoxides, -isopropoxides, -n-butoxides and -cyclic alkoxides by the reaction of alkali metal fluorides with the appropriate carbonyl compound.

$$\mathrm{MF} + \mathrm{R_fCOF} \rightleftharpoons \mathrm{MOCFR_f}$$

$$\mathrm{MF} + \mathrm{(CF_3)_2CO} \rightleftharpoons \mathrm{MOCF(CF_3)_2}$$

Hexafluoroacetone forms adducts with CsF, KF, AgF, and quaternary ammonium fluorides; it does not form adducts with NaF, LiF, ZnF_2, MgF_2, CaF_2, or BeF_2. This can be explained in terms of the lattice energy of the adduct, high lattice energies prohibiting salt formation. Measurements of the vapour pressures of Cs-, K-, and Rb-trifluoromethoxides indicated that the caesium salt was the most stable.[69] (10% dissociated after 1 hr. at 80°).

The effect of solvent on the formation of potassium and caesium heptafluoroisopropoxides was examined[68] by measuring temperature changes on formation. Dipolar aprotic solvents were found to be better than non-polar solvents (e.g. no adduct formed between $(CF_3)_2CO$ and CsF in benzene).

The nature of the alkyl group also affects stability. Substitution of chlorine for fluorine near the carbonyl group decreases the stability of the adduct and cyclic perfluoroalkyl groups were destabilizing relative to acyclic alkyl groups.

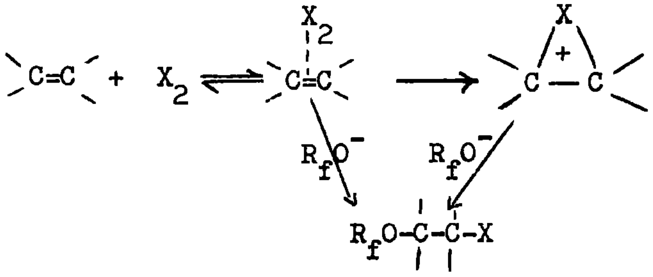
Perfluoroalkoxide ions have been used successfully in nucleophilic displacement reactions. The heptafluoroisopropoxide ion is a relatively weak nucleophile and this was illustrated by the isolation of an alcohol, not the ether $(CF_3)_2CFOCF_2CFH$, from a mixture of tetrafluoroethylene, hexafluoroacetone, and caesium fluoride in diglyme.[70]

$$\begin{tikzcd} CF_2{=}CF_2 + F^- \arrow[r, shift left] & CF_3\text{-}\bar{C}F_2 \arrow[l, shift left] \arrow[r, "(CF_3)_2CO"] & CF_3CF_2C(CF_3)_2O^- \arrow[d, "H^+"] \\ & & {} \end{tikzcd}$$

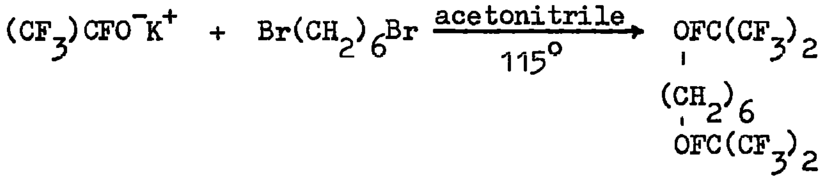
A recent paper[71] has shown that if a halogen is present in the above mixture then an ether is produced.

$$CF_2{=}CF_2 + I_2 + (CF_3)_2CO \xrightarrow[CH_3CN]{KF} (CF_3)_2CFO\text{-}CF_2\text{-}CF_2\text{-}I \quad (17\%)$$

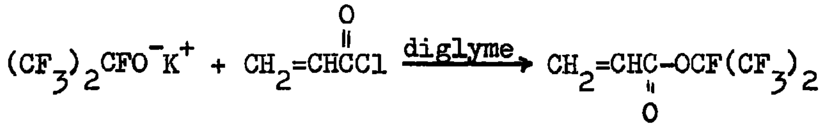
The conversion of olefin to ether varied with the reactants and solvent (17 - 60%). This result is explained by the authors as involving addition of the perfluoroisopropoxide ion to an iodine-olefin complex.



Halogens have been displaced from acid halides and alkyl halides, using heptafluoroisopropoxide ion.[73]

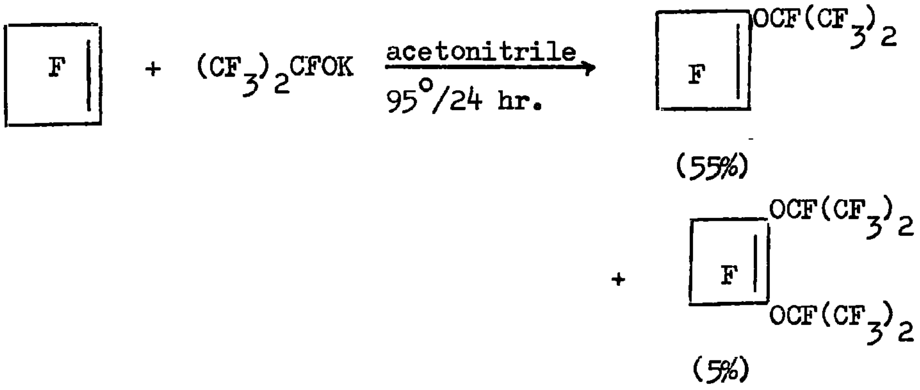


$$(CF_3)CFO^-K^+ + Br(CH_2)_6Br \xrightarrow[115^\circ]{\text{acetonitrile}} \begin{array}{l} OFC(CF_3)_2 \\ | \\ (CH_2)_6 \\ | \\ OFC(CF_3)_2 \end{array}$$



$$(CF_3)_2CFO^-K^+ + CH_2{=}CH\overset{O}{\overset{\|}{C}}Cl \xrightarrow{\text{diglyme}} CH_2{=}CH\underset{O}{\underset{\|}{C}}{-}OCF(CF_3)_2$$

The same ion has also been added to perfluorocyclobutene:[73]



The epoxides of tetrafluoroethylene and hexafluoropropene have been used as sources of alkoxide ion, recent patents[73,74] describe the reactions of acid fluorides and carbonyl compounds with these epoxides.

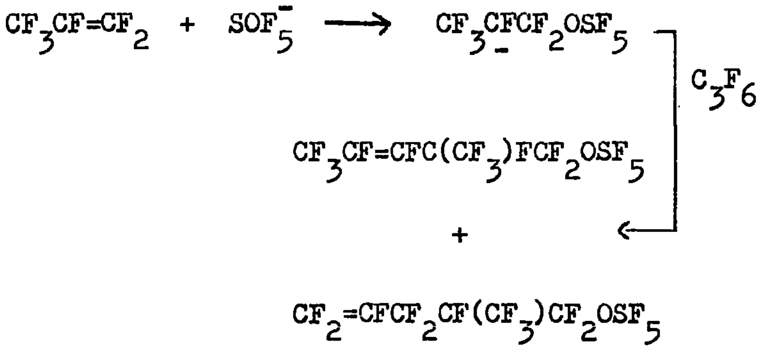
The preparation of fluoroxyperfluoroalkyl compounds by the fluorination of the carbonyl compound proceeds smoothly and almost quantitatively in the presence of KF

$$(CF_3)_2CO \xrightarrow[MF]{-78^\circ} (CF_3)_2CFOF \qquad (97\%)$$

$$M = K,\ Rb,\ Cs$$

Fluorination of hexafluoroacetone does not proceed at -78° in absence of an alkali metal fluoride,[75] this indicates the possible intermediacy of a perfluoroalkoxide anion.

Finally, the action of fluoride ion on thionyl tetrafluoride gives the oxy-anion SOF_5^-.[72] This is thought to react with hexafluoropropene in the following manner:



$$CF_3CF{=}CF_2 + SOF_5^- \longrightarrow CF_3\underset{-}{C}FCF_2OSF_5 \xrightarrow{C_3F_6} CF_3CF{=}CFC(CF_3)FCF_2OSF_5 + CF_2{=}CFCF_2CF(CF_3)CF_2OSF_5$$

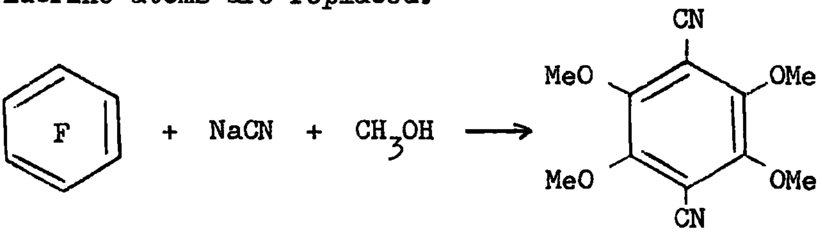
Chapter 3

Nucleophilic Substitution in Polyfluoroaromatic Compounds

The characteristic reaction of polyfluoroaromatic compounds is replacement of a fluoride ion by a nucleophile. This parallels the electrophilic replacement of a proton in the parent hydrocarbon. Reactions of highly fluorinated homocyclic compounds have been extensively studied at the University of Birmingham. Similar reactions of polyfluoroheterocyclic compounds, which have only relatively recently been synthesised, have been of interest at the Universities of Durham and Manchester.

(a) Nucleophilic Substitution in Polyfluoro Carbocyclic Compounds.

The reaction of hexafluorobenzene with an equimolar amount of nucleophilic reagent occurs in high yield to give a mono-substituted product. Of the wide variety of nucleophilic reagents that have been used, the following are typical: OCH_3^-,[76] OH^-,[77] SH^-,[78] NH_3,[79] CH_3NH_2,[79] $NH_2NH_2 \cdot H_2O$,[79] CH_3^-,[80] $C_6H_5^-$,[81] H^-,[82] $NH_2(CH_2)_2NH_2$[83] and $CH_3CH{=}CH^-$.[82] An interesting exception to the replacement of one fluorine atom with an equimolar amount of nucleophilic reagent is the reaction of cyanide ion with hexafluorobenzene in methanol, in which all fluorine atoms are replaced.[85]

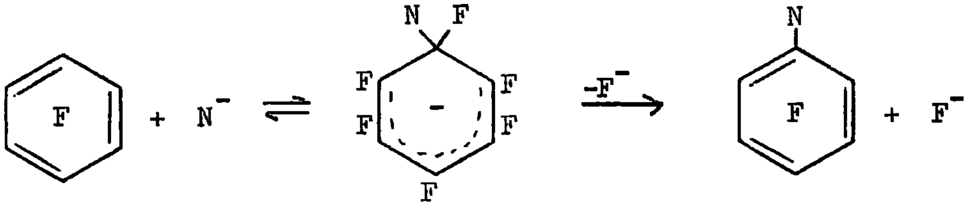


Pentafluorobenzenes: Nucleophilic substitution in pentafluorobenzenes is of considerable interest because of the possibility of positional isomerism. The orientation of nucleophilic replacement reactions in C_6F_5X compounds has been studied with many nucleophilic reagents and in most cases the fluorine para to the substituent was displaced.[86] For instance when X = H, CH_3, CF_3, SCH_3, SO_2CH_3, $N(CH_3)_2$, C_6F_5 and OCF_3, then para substitution predominates. However when X = O^- [87] or NH_2,[88] meta replacement predominates, and if X = OCH_3[87] or $NHCH_3$[88] then both meta and para substitution occurs to approximately the same degree. Para substitution predominates over ortho substitution in the pentafluorohalogeno benzenes and increases in the order X = Cl > Br > I.[89] In certain cases (X = NO_2,[90] NO,[91] COOH[92]) the ortho/para ratio is dependent on the nucleophile, this can be ascribed to hydrogen bonding between the nucleophile (e.g. amine) and substituent. Solvents can also influence isomer ratios, 3·8% methanol in ether gave 50% ortho replacement as compared with 8% ortho replacement in methanol alone in pentafluoronitrobenzene.[93]

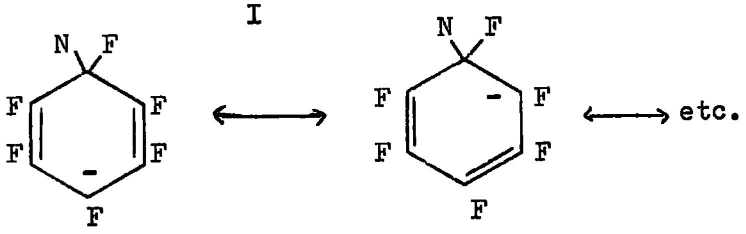
Highly Fluorinated Polycyclics: These compounds have been synthesised at Birmingham and their reactions with nucleophiles studied. Octafluoronaphthalene[94] and 1,2,3,4-tetrafluoroanthraquinone[95] reacted with nucleophiles at the 2 position. Replacement of fluorine from octafluoroacenaphthylene[96] occurred initially at the 3 position then at the 8, 5 and 6 positions (in that order).

Rationalization of Orientation: The first attempt at accounting for the orientation of nucleophilic substitution reactions in polyfluoroaromatic compounds was a suggestion[86,97] that all five fluorines in C_6F_5X compounds direct replacement para to X, and that X may oppose or enhance this effect. However there are many anomalies to this explanation. For example chloropentafluorobenzene reacts with methoxide ion faster than pentafluorobenzene,[98] implying that chlorine activates the para position more than hydrogen. But pentachlorobenzene reacts with nucleophiles at the para position,[99] which implies that hydrogen activates the para position more than chlorine.

To date, the best explanation of the orientation of nucleophilic substitution in polyfluoroaromatic systems has been put forward in a paper by Burdon.[100] In this he considers the relative stabilities of the possible transition states concerned for the mechanism shown below.



I



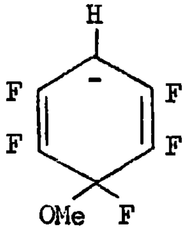
II

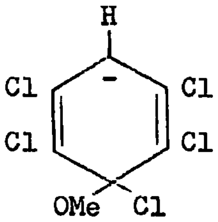
III

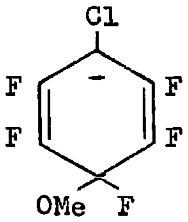
The Wheland intermediate I was taken as representative of the transition state, and resonance hybrid II is assumed to be the main contributor to the Wheland intermediate; according to molecular orbital calculations this assumption is valid. A consideration of the stability of the hybrid of type II is now seen to be highly relevant. In C_6F_5X compounds the problem is essentially a consideration of the effect of the substituent attached to the carbon bearing the negative charge. If a substituent X stabilizes the negative charge more than fluorine, then nucleophilic attack will take place para to that substituent; if it destabilizes the charge more than fluorine, then meta attack will occur. A statistical ratio (O:M:P: = 2:2:1) will result from a substituent which stabilizes the negative charge to the same extent as fluorine. These generalizations were forwarded with the proviso that solvent, steric, and nucleophile-substituent interactions can be neglected.

The effects of α substituents on a carbanion have been discussed in section 1.2, in which it was noted that I_π effects are at a maximum in planar carbanions. Carbanions which are part of an aromatic system have an enforced planar geometry, hence the order of I_π repulsion will be $F > Cl > Br > I > H$,[17] when these atoms are attached to an aromatic system. Unlike the halogens, the magnitudes of the I_π repulsive effects of oxygen and nitrogen cannot be derived from spectroscopic measurements, but are taken to be $N > O > F$.[100]

An explanation can now be offered on the observation that chloropentafluorobenzene reacts with methoxide ion faster than pentafluorobenzene, although pentachlorobenzene substitutes in the para position. Considering the intermediates of type II:

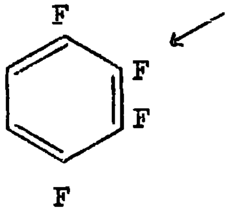




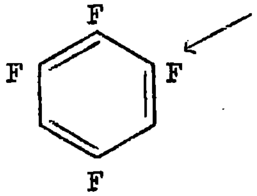


the orientation is explained, because the relative stabilities of negative charge on a carbon bearing hydrogen, chlorine, or fluorine is in the order H > Cl > F.

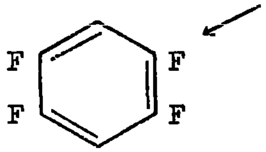
The three tetrafluorobenzenes have been synthesised, and react at the positions indicated with an arrow[101]



(IV)



(V)

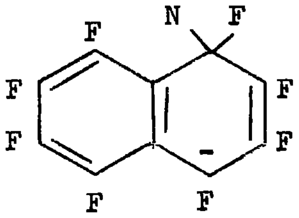


(VI)

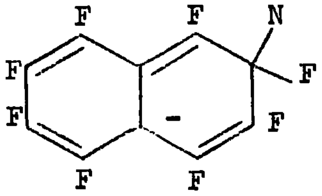
Reaction with methoxide ion is $\sim 10^3$ times slower with VI than IV or V. The hybrid of type II for substitution in VI requires a negative charge to be localized on a carbon atom attached to a fluorine atom.

Nucleophilic substitution in the 1,2,3,4-tetrafluoro-5-halobenzenes (Hal. = Br, Cl, I) occurred mainly at the 3 position.[102] Substitution at this position involves localizing a negative charge on a carbon bearing a hydrogen atom. Any other position would involve destabilization by an α halogen. The increase in the proportion of replacement para to the halogen along the series Cl < Br < I follows the decreasing π-electron repulsions in the same order.

The highly fluorinated naphthalene compounds mentioned earlier substitute in the β position, α substitution would involve localizing a negative charge on a carbon atom bearing a fluorine, e.g. perfluoronaphthalene:



is less stable than



Steric effects also need to be considered. The nucleophilic replacement reaction of the series of compounds C_6F_5X where X = NH_2, NHMe, and NMe_2 resulted in mainly meta and para substitution.[88] The mesomeric effect of the $-NH_2$ group would be expected to deactivate the ortho and para positions to nucleophilic attack. However replacement of hydrogen in the $-NH_2$ group by methyl leads to considerable steric inhibition of resonance, because of interaction of the methyl groups with the ortho ring fluorines. This results in mainly para substitution being observed.

(b) Nucleophilic Substitution in Perfluorinated Heterocyclic Systems.

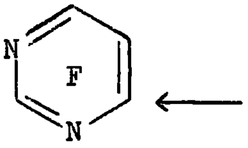
Perfluorinated heterocyclic systems have been synthesised only relatively recently, consequently less is known about their nucleophilic replacement reactions than polyfluorocarbocyclic systems. The heterocycles will be grouped according to the heteroatom.

Systems containing Nitrogen.

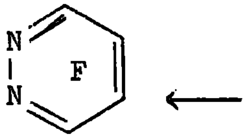
Pentafluoropyridine undergoes nucleophilic substitution in the 4-position,[103,104] and is noticeably more reactive than hexafluorobenzene. If this position is blocked, then 2-substitution occurs. It was found that the nitro group in 4-nitrotetrafluoropyridine was displaced by attack of methoxide ion in methanol, giving mainly 4-methoxytetrafluoropyridine.[105] These facts can be explained by assuming that the ring nitrogen is the greatest single factor determining the orientation of nucleophilic substitution, with I_π effects of secondary importance.

On the basis of I_π effects alone, the orientation of substitution in 4-nitrotetrafluoropyridine should be comparable to that in 2,3,5,6-tetrafluoronitrobenzene. In both systems the negative charge can be localized on to a ring atom which does not carry a fluorine atom. However 2,3,5,6-tetrafluoronitrobenzene undergoes substitution ortho to the nitro group, while the nitro group is displaced from 4-nitrotetrafluoropyridine; illustrating the considerable ability of a ring nitrogen to influence the orientation of substitution. An anomaly such as this suggests that caution must be exercised when applying arguments based on I_π effects to polyfluorinated heterocyclic systems.

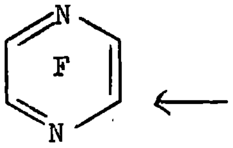
Tetrafluoropyrimidine (VII),[106] tetrafluoropyridazine (VIII)[49] and tetrafluoropyrazine (IX)[48] have been synthesised, and the order of reactivity appears to be VII and VIII > IX > pentafluoropyridine



(VII)

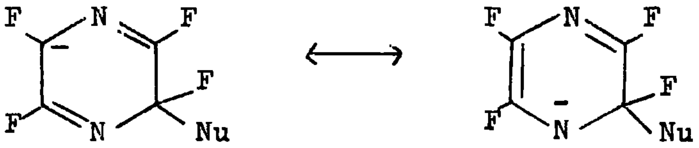


(VIII)



(IX)

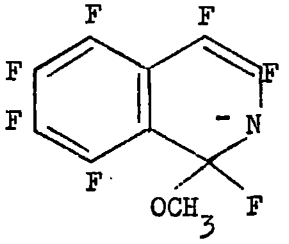
The position of substitution is indicated with an arrow. It is seen that transition states of type II for tetrafluoropyrimidine and tetrafluoropyridazine result in the negative charge being localized on a nitrogen atom. The relative decrease in reactivity of tetrafluoropyrazine can be explained in terms of a type III hybrid being necessary to allow an electron to be localized on a nitrogen atom.



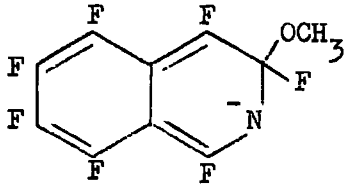
(least stable)

Further evidence of the importance of a ring nitrogen in the transition state is provided by nucleophilic substitution in perfluoroquinoline and -isoquinoline.

The observed 1-substitution in heptafluoroisoquinoline[107] apparently disregards the I_π effect, however this has been explained in terms of charge localization on nitrogen via a type III hybrid. A consideration of the transition states for 1-substitution (X) and 3-substitution (XI):



(X)



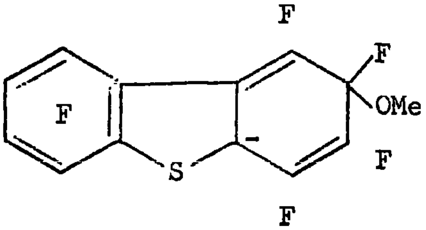
(XI)

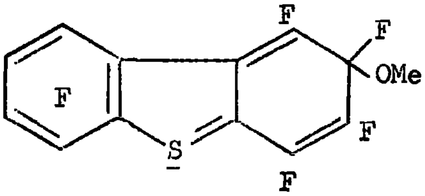
reveals that only for 1-substitution is the aromaticity of the adjacent ring preserved.

Heptafluoroquinoline[107] undergoes 2- and 4-substitution in the ratio 3·4:1 with methoxide in methanol. This illustrates that the ring nitrogen is allowing a considerable contribution from the type III hybrid in the transition state.

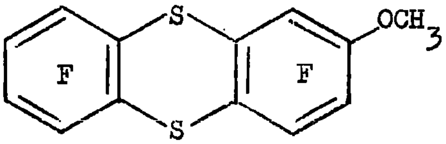
<u>Systems containing Sulphur</u>.

A sulphur atom can stabilize an adjacent negative charge and this can be explained by delocalization of the charge into the vacant sulphur 3d orbitals. This explanation has been offered for the observed[108] substitution para to sulphur in octafluorodibenzothiophen, i.e.

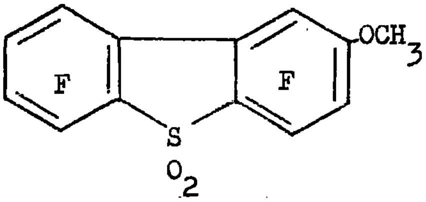




Recently it has been shown that methoxide ion reacts with octafluorothianthren[109] and octafluorodibenzothiophen-5,5-dioxide[110] to give the methoxy compounds XII and XIII respectively.



(XII)

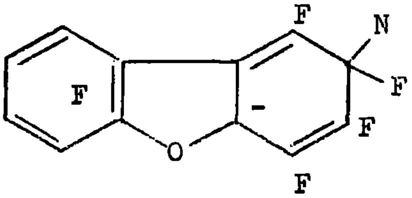


(XIII)

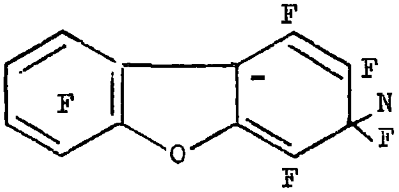
These results were explained in terms of d-orbital stabilization of the hybrid of type II in the transition state.

Systems containing Oxygen.

The heterocycles octafluorodibenzofuran[110] and 1,2,3,4-tetrafluorodibenzofuran[111] both undergo 3-substitution. This orientation can be attributed to the I_π effect of oxygen being greater than that of a ring carbon atom, i.e. XIV is less stable than XV.



(XIV)

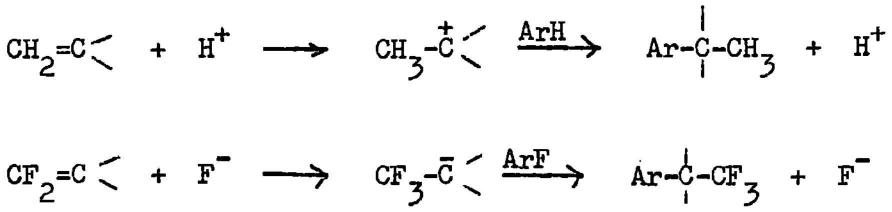


(XV)

DISCUSSION

Chapter 4

It was demonstrated in Chapter 2 that polyfluorocarbanions, generated by the action of fluoride ion on fluoro-olefins, are useful intermediates in synthetic fluorine chemistry. It was on this basis that it was thought to be possible to utilise such carbanions in polyfluoroalkylation reactions, in what can be regarded as the nucleophilic equivalent of a Friedel-Crafts reaction.



$$CH_2{=}C\lt \; + \; H^+ \longrightarrow CH_3{-}\overset{+}{C}\lt \xrightarrow{ArH} Ar{-}C{-}CH_3 \; + \; H^+$$

$$CF_2{=}C\lt \; + \; F^- \longrightarrow CF_3{-}\overset{-}{C}\lt \xrightarrow{ArF} Ar{-}C{-}CF_3 \; + \; F^-$$

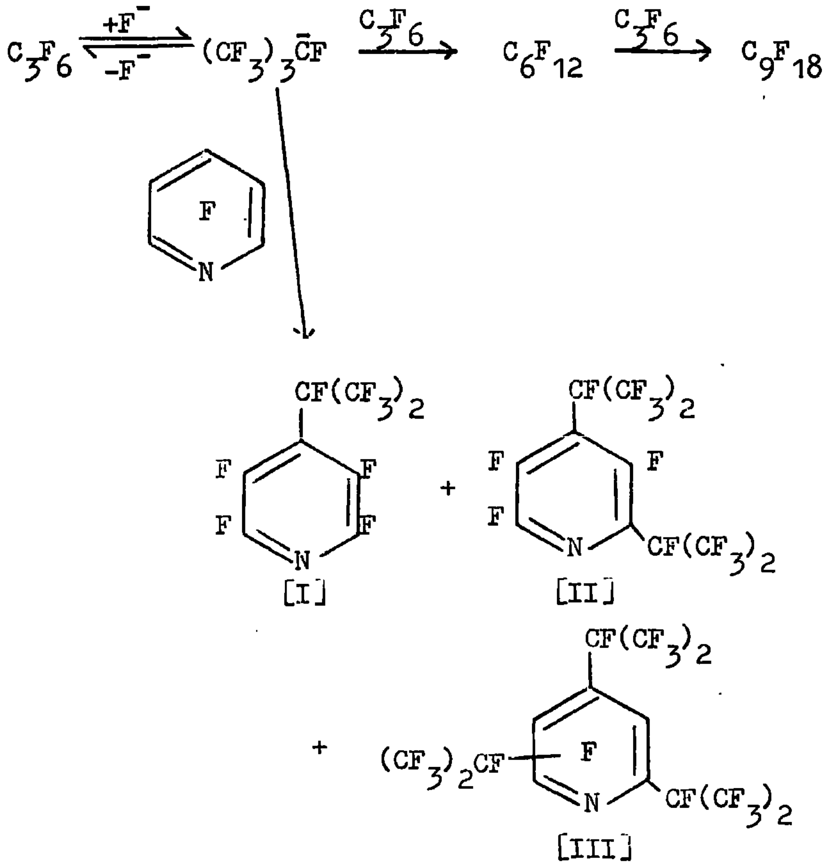
This reaction was first investigated at Durham by Chambers, Musgrave, and Storey who, in a communication[112] outlined the reaction of heptafluoroisopropyl carbanions with pentafluoropyridine and pentafluoronitrobenzene. The work presented in this thesis is a study of the scope of polyfluoroalkylation reactions in organic fluorine chemistry. A variety of fluoro-olefins have been found to react with selected aromatic substrates, and the discussion of the experimental work involved will be presented in sections concerned with the fluoro-olefins used in these reactions.

Section I. The Reaction of Hexafluoropropene with Polyfluoroaromatic Compounds

A. Pentafluoropyridine.

Pentafluoropyridine was chosen as a suitable substrate since it has been shown to be considerably activated to attack by nucleophiles. Hexafluoropropene has been found to add to this substrate in the presence of a solvent to give mono-, di- and tri-alkylated products. Conversion of the olefin to higher molecular weight products, which competes with the polyfluoroalkylation reaction, diminishes the effective concentration of the olefin, will be dealt with later.

Diagram 1



[I] [II] [III]

(a) Reactions in Carius Tubes.

When pentafluoropyridine and caesium fluoride are heated to 120° with a two molar excess of hexafluoropropene in a Carius tube, perfluoro-(4-isopropylpyridine) (I) was obtained in 94%[113] yield based on the C_5F_5N that had reacted. Only a trace of the di-isopropyl compound (II) was formed. This was due to the concentration of the olefin being reduced by the polymerisation reaction shown in diagram 1. However the initial concentration of the olefin in solution could be increased by introducing the Carius tube into a heated furnace, or by increasing the ratio of C_3F_6 to C_5F_5N.

(b) Reactions in Autoclaves.

When the reaction was carried out using an autoclave, which was inserted into a furnace heated to 150°, the pressure rose to 500 p.s.i., then fell to 50 p.s.i. after ½ hr. and it was possible to prepare a mixture of 4-, 2,4-di-, and tris-(heptafluoroisopropyl) derivatives. The same result was obtained using either sulpholan or tetraglyme under these conditions; with a slight variation in the ratio of alkylated products. Mass spectrometry of the mixture indicated a trace of a tetra-substituted compound, and the reaction was repeated under more vigorous conditions in order to establish if this derivative could also be isolated. In one experiment sufficient C_3F_6 was introduced to enable an initial pressure of 1000 p.s.i. to be reached and in another the autoclave was pressurised with nitrogen to give an initial pressure of 1,500 p.s.i. In both instances only a trace of a tetra-substituted derivative was found. An experiment utilising the tri-isopropyl derivative as 80% of the substrate was similarly negative. However these results are not surprising since Courtauld models of even the di-isopropyl pyridine were impossible to construct due to gross steric interference between the trifluoromethyl groups and the adjacent ring fluorines.

(c) The addition of hexafluoropropene at an elevated temperature.

An autoclave containing hexafluoropropene was coupled to a similar autoclave containing sulpholan, caesium fluoride, and pentafluoropyridine. Both autoclaves were heated to 190°, and the olefin added by opening a tap which was integral with the coupling. The result of this experiment (Reaction 1) is given below in a comparison with a similar experiment (Reaction 2) in which the olefin was allowed to warm up to the same temperature with the reactants.

Reaction	Products containing perfluoro-isopropyl group(s)		
	mono-	di-	tri-
1	32%	19%	29%
2	25%	14%	13%

It is obvious from these results that the yields of higher alkylated products can be increased by this method. Presumably at lower temperatures the rate of the olefin polymerisation is greater than that of the alkylation process. At higher temperatures the energy difference between the two competing processes becomes less important, and the higher activation energy polyfluoroalkylation process competes more effectively. It is also worth noting that the pressure fell to a constant minimum value only 30 mins. after the addition of hexafluoropropene, indicating that the reaction could then be stopped. A major problem in polyfluoroalkylation reactions is decomposition of the solvent, and this can be minimised by stopping the reaction as soon as it is thought to be complete.

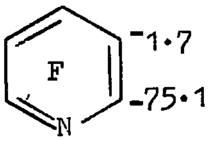
(d) Orientation of substitution.

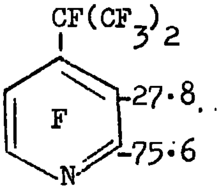
The orientation of the substituents in pentafluoropyridine was determined by the use of ^{19}F nuclear magnetic resonance (N.M.R.) spectroscopy. All chemical shifts quoted are from C_6F_6 as internal reference.

Monosubstitution.

The first position of substitution in pentafluoropyridine, using a range of nucleophilic reagents has been shown to be the 4-position. Storey confirmed that this was the orientation in perfluoro-(monoisopropylpyridine) which showed only two absorptions at -75·6 and -27·8 p.p.m. arising from ring fluorine.[113] It is known that the chemical shifts in 4-substituted polyfluoropyridines fall in the range -70 ± 20 p.p.m. for α fluorine and -5 ± 20 p.p.m. for β; hence the shifts

-75·6 and -27·8 p.p.m. were assigned to the 2,6 and 3,5-fluorines respectively. Comparing these with the shifts for 2,5 and 3,6-fluorines in pentafluoropyridine:





it is seen that the effect of introducing a perfluoroisopropyl group in the 4-position on the neighbouring fluorines is, meta: -0·5 p.p.m., ortho: -26·1 p.p.m.

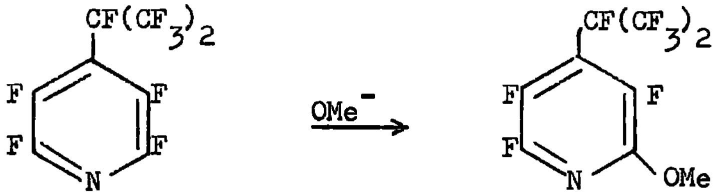
Disubstitution.

Disubstitution in pentafluoropyridine usually occurs at the 2-position, but the ortho-activating influence of a perfluoroisopropyl group could be significant. The ring fluorines in perfluoro-(diisopropyl pyridine) gave rise to three absorptions at -80·0, -40·2 and -50·6 p.p.m. As the 6-fluorine in the monosubstituted compound absorbed at -75·6 it is likely that the peak at -80·0 arises from a 6-fluorine. However because a perfluoroisopropyl group has such a large ortho-effect, the other two peaks cannot be assigned. Also if disubstitution occurred in the 3-position, the effect on neighbouring fluorine absorptions is unknown.

The effect of introducing a methoxyl group at C-2 on the 3- and 5-fluorine chemical shifts has been determined[114] for tetrafluoro-2-

methoxypyridine as being 0 and +11 respectively. As the position of entry of the second $C_3F_7^-$ could not be determined by referring to the N.M.R. spectrum, a methoxy derivative of the mono-substituted compound was prepared.

(I)



(IV)

The shifts arising from ring fluorine in IV were compared with the calculated values for the introduction of a methoxy group at C-2 in I, using the previously quoted ortho- and para-effects for a C-2 methoxyl group. The results are given below:

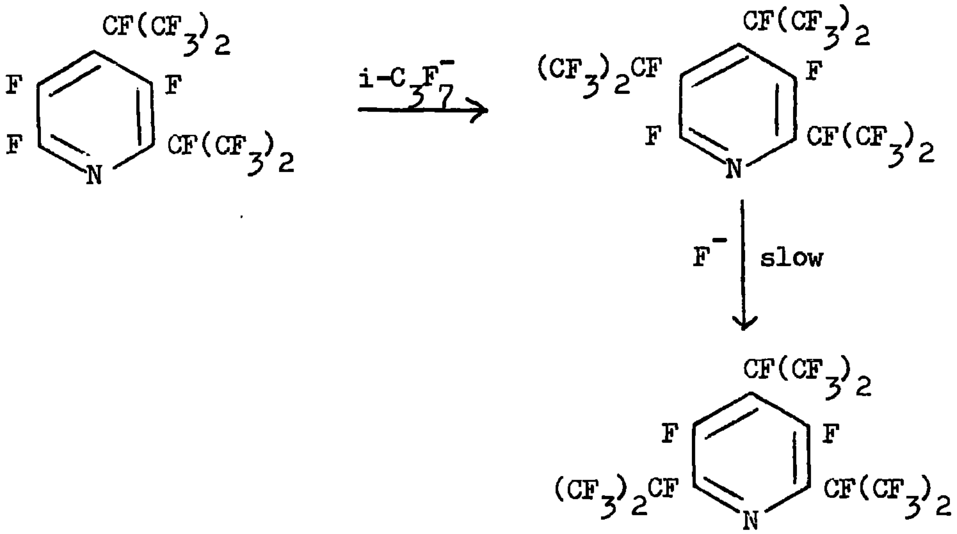
Chemical shifts for ring fluorine in IV

	3-	5-	6-
Observed	-28·0	-15·8	-71·4
Calculated	-27·8	-16·8	-71·6

The observed and calculated shifts are in reasonable agreement, indicating that methoxide ion substitutes in compound I at C-2. It is unlikely that a heptafluoroisopropyl carbanion enters at a different position, hence the second C_3F_7 group can be assigned to C-2.

Tri-substitution

The orientation of tri-substitution was expected to follow the previous pattern and occur at the 6-position. However on the basis of ^{19}F N.M.R. and v.p.c. evidence, the following mechanism is proposed.



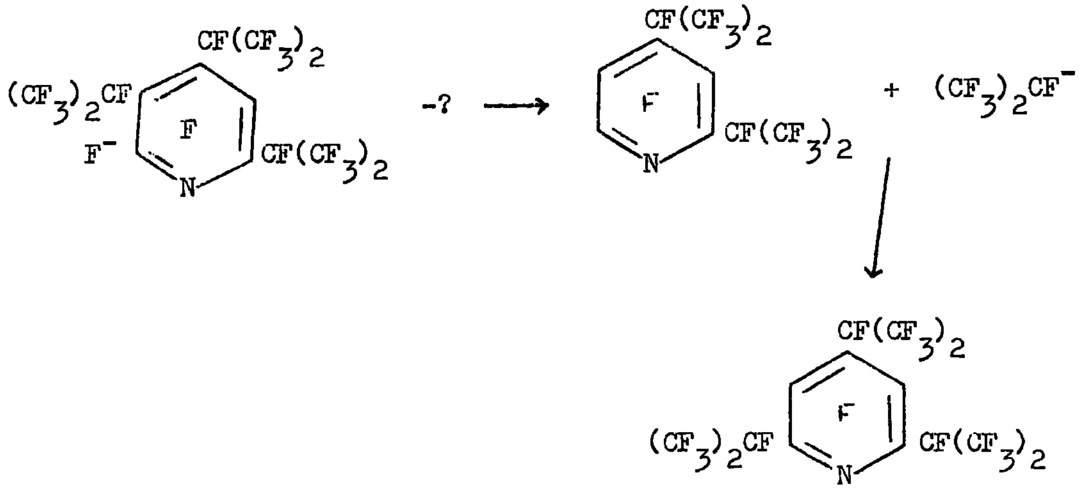
Some tri-isopropyl pyridine was separated by preparative-scale v.p.c. from a mixture derived from several experiments. Detailed examination of the high resolution ^{19}F N.M.R. spectrum of this material suggested that it was a mixture. This was endorsed by careful v.p.c. work on a 20 ft. column, which showed it to be an inseparable two-component mixture. It was also noted that the ratio of the isomers varied with the reaction time of the experiment. As the analysis of these mixtures corresponded to a tri-isopropyl pyridine, these observations suggested that a fluoride ion catalysed isomerisation was involved. A mixture of isomers was then shaken for 14 hr. with caesium fluoride in sulpholan at 180°;

v.p.c. indicated that one isomer had been converted almost quantitatively to the other. The experiment involving the addition of C_3F_6 at a high temperature also produced isomers, although in this experiment which had a shorter reaction time, the relative proportions of the isomers were reversed.

Approximate Composition of the Mixtures of Isomers

	Origin of mixture	Compound		
		A	B	C
(i)	Before shaking with fluoride ion	0	30	70
(ii)	After " " " "	5	90	5
(iii)	Addition of C_3F_6 at a high temp.	0	15	85

These results are best interpreted by assuming that isomer C is formed initially, then it rearranges to B. Compound A is thought to be a perfluoro-(tetrakis-isopropylpyridine) as the mass spectrum of mixture (ii) exhibited a peak at 7$\overset{6}{7}$9 in approximately the correct height for a 5% concentration. This suggests that the rearrangement may occur inter-molecularly, i.e.



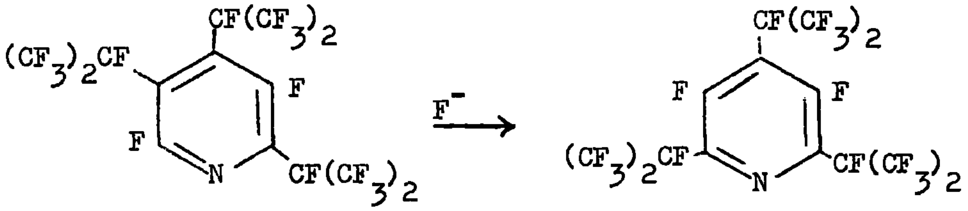
^{19}F Spectral Data of the Mixtures i and ii.

The ^{19}F N.M.R. data of mixtures i and ii, which is presented below, is difficult to interpret due to the ring fluorines being very broad, overlap of the trifluoromethyl absorptions, and large coupling constants between tertiary fluorine and ring fluorine leading to possible ambiguities in assignment.

Mixture	$(CF_3)C_2F$		ring* fluorine	$(CF_3)_2CF$	
	Shift	Fine Structure		Shift	Fine Structure
ii	-90·6	A complex mixture of peaks, ostensibly a triplet J = 6 c.p.s.	-60·3	+14	Broad
				+20·2	doublet of heptuplets J = 66 and 6 c.p.s.
i	-92·8	A mixture of two unlike peaks of equal area, separated by 36 c.p.s. (Two different CF_3 groups?)	-60·3	+1·5	broad
	-90·6	A mixture of two unlike triplets, separation = 19 c.p.s. (Two different CF_3 groups?). One of these triplets is identical with the CF_3 absorption in mixture ii. A broad peak lies to high field of the pair of triplets (?)		+14	broad
			-54·6	+20·2	A mixture of two overlapping doublets of heptuplets. J = 66 and 6 for both.

* Ring fluorine in both spectra was so broad that the spectrum had to be accumulated by a computer and read out after 30 sweeps.

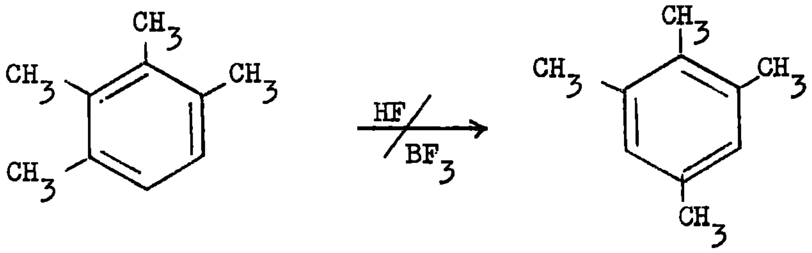
Due to the complexity of these spectra, heteronuclear decoupling experiments are necessary and this work is currently in progress at Liverpool University under the direction of Dr. L. Sutcliffe. The most obvious effect of shaking with fluoride ion is seen in a simplification of the trifluoromethyl absorption. It appears that an isomer is removed which has three magnetically different $(CF_3)C$ groups; this could be explained by the 2,4,5- rearranging to the 2,4,6-isomer, i.e.



[IIIa] [IIIb]

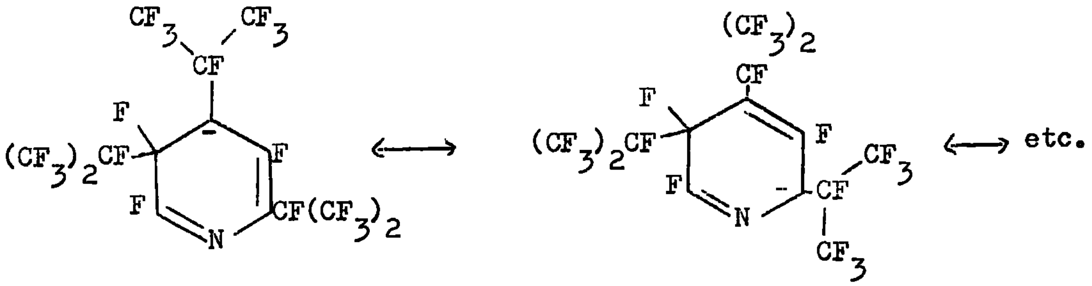
Assuming mixture (i) consists of these two isomers, then a 6-ring fluorine absorption (from IIIa) is conspicuously absent. It is possible that the broad peak which lies 6 c.p.s. to high field of the pair of triplets centered at -90·6 is due to the 6-fluorine, as this is the expected region for such an absorption (the 6-F in the di-substituted compound appears at -80 p.p.m.; assuming the presence of an ortho-i-C_3F_7 group then a -ve shift could be expected).

Such rearrangements of alkylated aromatic hydrocarbon compounds are well known. For example, prehnitrene (V) undergoes acid-catalysed rearrangement to isodurene (VI).



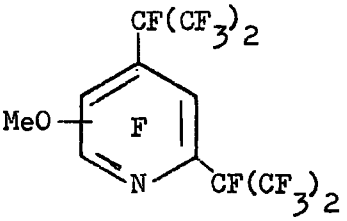
(V) (VI)

On the evidence presented so far, it appears that nucleophilic attack in perfluoro-(2,4-di-isopropyl pyridine) occurs predominantly at the 5-position. This is not unreasonable, as both perfluoroisopropyl groups are in a position to stabilise a negative charge in the transition state, and are capable of doing so:



however it is possible that substitution in the 6 position occurs also.

In order to investigate the initial position of attack, the di-substituted compound was reacted with one equivalent of methoxide ion in methanol. Two inseparable mono-methoxy derivatives were formed in an approximate ratio of 2:3. When this experiment was repeated using sulpholan instead of methanol as solvent, the same ratio of mono-methoxy derivatives was produced, together with di- and tri-methoxy compounds (thus illustrating the increased nucleophilic strength of methoxide ion in sulpholan). As both the ^{1}H and ^{19}F N.M.R. spectra of these mixtures could not be interpreted, it was hoped that a similar fluoride ion catalysed rearrangement of the mixture of monomethoxides would help in the spectrum analysis. After shaking the mixture of monomethoxides with caesium fluoride in sulpholan, v.p.c. indicated that the product ratio differed from the initial ratio, and a third component was produced. The final mixture analysed correctly for a mono-methoxy perfluoro-(di-isopropyl pyridine), i.e.



isomers x and y in ratio 2:3 $\xrightarrow{F^-}$ 3 isomers in ratio x:y:z = 1:2:1

The ^{19}F spectrum could not be interpreted, either before or after treatment with fluoride ion. The ^{1}H spectrum of the initial mixture was a broad complex of peaks centered at 4.3 (from $(CH_3)_4Si$), and extending over a region of 19 c.p.s. However on shaking with fluoride ion the shape of this peak changed in a manner which suggested that it is a doublet of doublets superimposed on a doublet of lesser intensity. (i.e. the doublet of doublets diminished in intensity and this was accompanied by the appearance of another doublet. It is not unreasonable to assign the doublet of doublets to a 5-methoxyl group, as this may couple with both the 6-fluorine and the tertiary fluorine of the heptafluoroisopropyl group. On this somewhat uncertain assumption, the isomer which predominates in attack by methoxide ion on perfluoro-(2,4-di-isopropyl pyridine) would be the 5-methoxy derivative. However, further work will be necessary to establish this point.

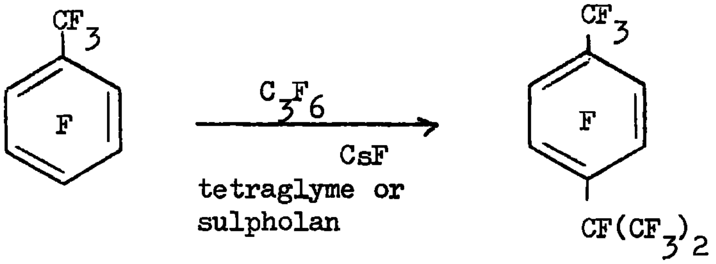
(e) 4-Methoxy- and 4-Chlorotetrafluoropyridine.

These compounds were also used as substrates for reaction with hexafluoropropene. Although vigorous reaction conditions were used for both compounds, only dimers and trimers of the olefin were recovered. These results can be rationalised in terms of the rate of 2-substitution being much slower than that of the olefin polymerisation (unless of course, the 2-position is activated by a 4-$(CF_3)_2CF$ group).

(f) Solvents.

As mentioned previously, a major problem in reactions involving carbanion intermediates is removal of the carbanion by proton abstraction from the solvent. The solvent must also be capable of dissolving the metal fluoride, and for these reasons dipolar aprotic solvents were chosen as suitable media for polyfluoroalkylation reactions.

Storey[113] varied the conditions for the reaction between pentafluoropyridine and hexafluoropropene in order to establish the relative effectiveness of sulpholan, diglyme, triglyme and dimethylformamide as solvent for this reaction. His results (see Table 1) indicate that sulpholan was the most useful solvent. A comparison by the author of the effectiveness of tetraglyme and sulpholan for the reaction between hexafluoropropene and octafluorotoluene:



indicated that tetraglyme is a better solvent than sulpholan (Table 2). In the light of this result, one of Storey's reactions (No. 9, Table 1) was repeated under identical conditions using tetraglyme instead of sulpholan. The products consisted of 11% of higher alkylated pyridines; this contrasts with their complete absence when sulpholan was used as the solvent. However it was found in subsequent experiments that tetraglyme tends to decompose if heated to temperatures greater than 150°, even for relatively short periods. Also the products from this decomposition are difficult to remove from the alkylated products. Decomposition products of sulpholan however were involatile and did not interfere with work-up procedures; this fact, coupled with thermal stability led to the use of sulpholan for reactions requiring temperatures of 100-200°.

Table 1

Reaction Between C_5F_5N (3·0 g., 17·75 m.moles) and C_3F_6 (5·0 g., 33·3 m.moles)

	Initiator/ Solvent	Temp.	Total yield (g)	$C_3F_7.C_5F_4N$ (g)	C_5F_5N recovered (g)	% Conversion of C_5F_5N	% yield (on C_5F_5N converted)	Olefin dimers etc. (g)
1)	KF/diglyme	130°	5·0	1·3	2·0	33	69	1·7
2)	KF/triglyme	130°	6·3	2·7	1·5	50	95	2·1
3)	KF/D.M.F.	130°	6·0	2·4	1·38	54	79	2·18
4)	KF/Sulpholan	130°	8·0	4·8	0·32	89	95	2·88
5)	KF/diglyme	20°	4·5	0·23	2·73	9	45	1·5
6)	KF/Sulpholan	20°	6·5	3·38	1·1	63	94	2·52
7)	CsF/diglyme	20°	6·0	1·9	1·8	40	84	2·3
8)	(8·0 g)CsF/diglyme	20°	6·5	2·0	1·74	42	84	2·26
9)	CsF/sulpholan	20°	7·3	4·7	0·37	88	95	2·9
10)	(8·0 g)CsF/Sulpholan	20°	8·5	5·61	0·07	98	100	2·82

All reactions in 100 ml. Carius tubes using 15 ml. of solvent.

All reactions at 20° were shaken.

Except where stated, 3·0 g. of fluoride were used.

Table 2

A Comparison between Sulpholan and Tetraglyme as Solvents for Polyfluoroalkylation of Octafluorotoluene

Initiator Solvent	Total product (g)	C_3F_6 polymers (g)	C_7F_8 recovered (g)	C_7F_8 reacted (%)	Wt. of product (g)	yield (based on C_7F_8 consumed) (%)
KF/sulpholan	11·6	7·3	2·5	45·6	1·8	49·9
KF/tetraglyme	11·8	6·9	1·6	63·1	3·3	64·0
CsF/sulpholan	9·9	4·8	2·5	45·7	2·6	71·9
CsF/tetraglyme	9·8	4·6	1·5	66·3	3·7	69·4

C_7F_8 (4·6 g.), C_3F_6 (8·0 g.), solvent (20 ml.), and Carius tubes (100 ml.) were used in all expts.

(g) Initiators.

Of the alkali metal fluorides, only CsF and KF were found to be effective in initiating a polyfluoroalkylation. Tables 1 and 2 illustrate that CsF is better than KF, this is to be expected as CsF is probably more soluble than KF in dipolar aprotic solvents. Although this reasoning assumes that the reaction occurs in solution, it was noted during the course of this work that the surface of the catalyst may be involved in the reaction, as larger amounts of catalyst gave slightly better conversions. This effect was mentioned by Graham in olefin co-dimerisation reactions involving tetrafluoroethylene, in which the catalyst was thought to be involved in the initial polarisation of the tetrafluoroethylene.

In absence of solvent, pentafluoropyridine and hexafluoropropene will react in the presence of CsF, but not KF. This result is in line with the findings on fluorination reactions with alkali metal fluorides, where the effectiveness of the metal fluorides decreases with increase in lattice energy.

Potassium fluoride in sulphur dioxide was investigated as a suitable medium for polyfluoroalkylation.

$$KF + SO_2 \rightleftharpoons KSO_2F$$

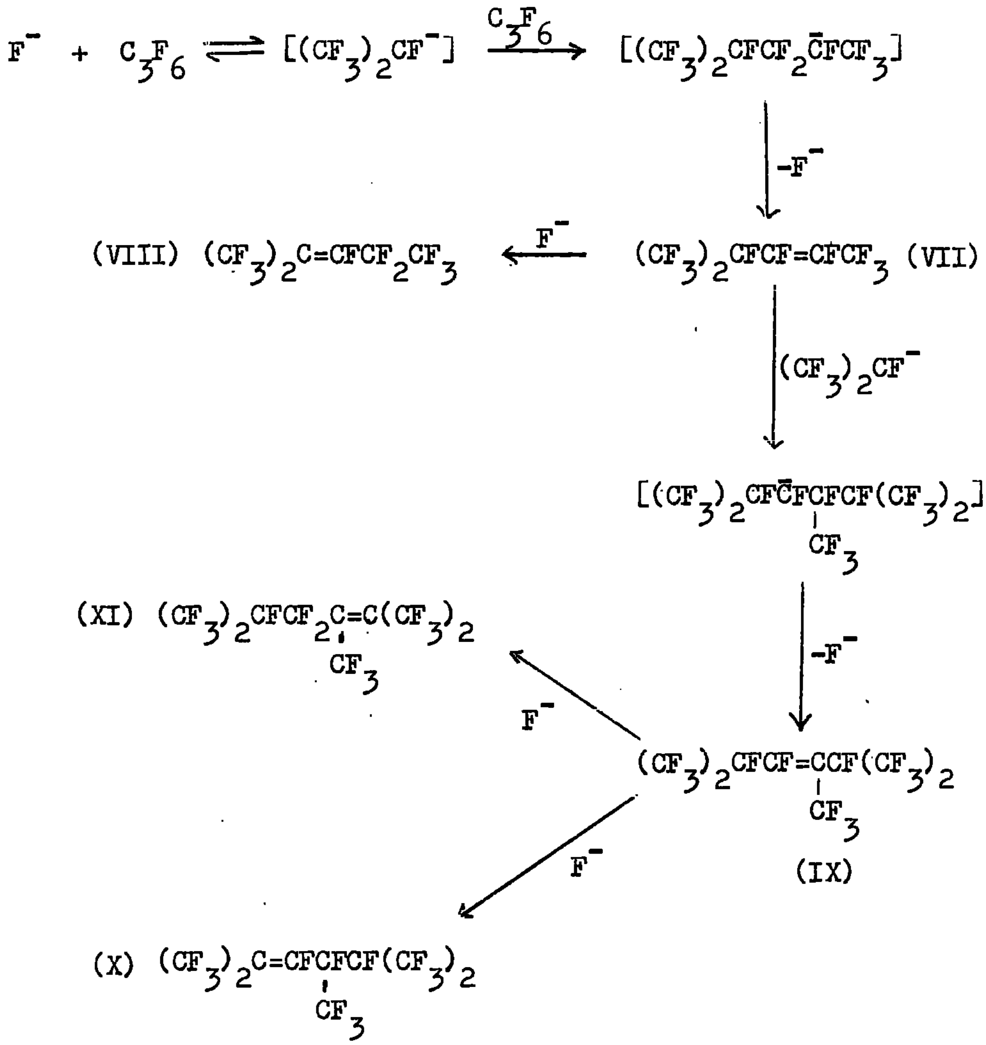
At room temperature, when the position of equilibrium lies to the right, no polyfluoroalkylation was observed. The result was similarly negative at 150°, at which temperature the potassium fluorosulphinate can be considered to be completely dissociated. The same results were obtained when caesium fluoride was used in place of potassium fluoride.

(h) Investigation of the Oligomers of Hexafluoropropene.

It has been mentioned that the rate of the polymerisation of the olefin has a considerable effect on determining the overall product distribution. The ease with which hexafluoropropene polymerises was demonstrated by shaking it with caesium fluoride in sulpholan for 30 mins., during which time heating was applied such that the temperature rose to 80°; 90% of the C_3F_6 was converted to dimers and trimers.

Although it was not recorded accurately, variation in the conditions used for polyfluoroalkylation reactions altered the proportion of dimers to trimers formed, low temperature and pressure favouring the dimers. Dimers could not be separated from trimers by distillation, but separation was achieved by vapour phase chromatography (v.p.c.). Infra-red and ^{19}F N.M.R. spectroscopy indicated that the principal component was perfluoro-(2-methyl pent-3-ene) (VII), together with a small amount of perfluoro-(2-methyl pent-2-ene) (VIII). The trimer was a mixture of three components which could be only partially resolved by v.p.c. As the boiling range of the mixture of trimers was 105-115°, it is quite likely that it is a mixture of the olefins IX (b.p. 110°),[62] X (b.p. 105·5)[62] and XI (b.p. 114°)[62] shown in the diagram below.

Diagram (ii)



B. Heptafluoroquinoline.

Heptafluoroquinoline, which has recently been synthesised[107] at Durham, is known to be more reactive towards nucleophilic attack than pentafluoropyridine. It was hoped that the rate of addition of hexafluoropropene to heptafluoroquinoline would be fast enough to compete effectively with the di- and trimerisation of the olefin.

On shaking heptafluoroquinoline with a 1·5M excess of hexafluoropropene in tetraglyme, a mixture was isolated which contained four components, one of which was heptafluoroquinoline (estimated recovery, 8% of initial weight). A mass spectrum of the mixture indicated that it also contained perfluorinated mono-, di-, and tri-isopropyl quinolines. Of the initial weight of hexafluoropropene, 28% was recovered in the form of dimers and trimers; illustrating that side reaction is appreciable, even with a very active substrate. Separation of the components of the mixture proved to be extremely difficult, however two compounds were isolated by v.p.c., and they were identified by analysis and mass spectrometry as perfluoro- (di- and tri-isopropyl quinolines). Yields were 49% [di] and 26% [tri], based on the amount of substrate that had reacted.

Orientation of Substitution.

Perfluoro-(di-isopropylquinoline).

The orientation of a variety of di-substituted heptafluoroquinolines has been examined by Hole,[116] and found to be 2,4. On the basis of this observation, the ^{19}F N.M.R. spectrum of the di-isopropyl derivative was examined for evidence of 2,4-disubstitution. The data obtained is given below in Table 3.

Table 3

Chemical shift (p.p.m.)	Relative Intensity	Peak shape (d = doublet) (t = triplet)
-90·8	3	d.d.d.; J = 30, 14 and 4 c.p.s.
-89·0	3	t; J = 7 c.p.s.
-54·4	1	d (broad); J = 72 c.p.s. showing further complex multiplet splitting
-34·4	1	d (v.broad); J = 200-205 c.p.s.
-20·4	1	complex multiplet
-18·4	1	" "
-12·2	1	" "
+14	1	d; J = 200-205 c.p.s.
+19	1	d; J = 72 c.p.s. v.broad

With reference to previously synthesised compounds, the chemical shifts of $(C\underline{F}_3)CF$ and $(CF_3)_2C\underline{F}$ occur at -[89(±3)] p.p.m. and [16(±5)] p.p.m. respectively. By comparison, the peaks at -90·8, -89·0,

+14 and +19 p.p.m. are assigned to the perfluoroisopropyl groups in the substituted quinoline. The relative intensities agree with this assignment.

The spectrum of heptafluoroquinoline exhibits some very large coupling constants (50 - 60 c.p.s.) on the 4- and 5-fluorine peaks due to peri F-F coupling;[107] indeed absence of a coupling of this order indicates a 4-substituted derivative. Referring to Table 3, it is seen that the tertiary fluorine at +14 p.p.m. exhibits an unusually large coupling constant of 200 - 205 c.p.s., which also occurs on the peak at -34·4 p.p.m. The magnetude of this coupling is such that it can only be ascribed to peri-coupling between the 5-fluorine and a tertiary fluorine at the 4-position. The other tertiary fluorine centered at +19 p.p.m., thought to be in the 2-position, exhibits the same coupling as the peak at -54·4 p.p.m. This ring fluorine absorption, which can now be assigned to the 3-fluorine, will couple also with the tertiary fluorine in the 4 position, and under the resolution available this interaction is observed as a broadening of both peaks.

The shape of the peak at -90·8 p.p.m. appears to be consistent with a $(C\underline{F}_3)_2CF$ group in the 4-position. By comparison with perfluoro-(4-isopropylpyridine), in which the $(C\underline{F}_3)_2CF$ fluorine couples with both the 3,5 fluorines (J = 13 c.p.s.) and the tertiary fluorine (J = 6 c.p.s.), the coupling constants of 14, 6, and 30 c.p.s. can be attributed to interaction with the 3-fluorine, adjacent tertiary fluorine, and the 5-fluorine respectively. The other $(C\underline{F}_3)_2CF$ absorption at -89·0 p.p.m. can be credited to the C_3F_7 group in the 2-position. Presumably the trifluoromethyl fluorines couple to the same degree with the 3-fluorine and the adjacent tertiary fluorine, to produce the observed triplet.

Perfluoro-(tri-isopropylquinoline).

In a rationalization[116] of the ^{19}F and ^{1}H N.M.R. spectra of trimethoxytetrafluoroquinoline, it was suggested that the third position of substitution was either the 6- or 7-position.

Due to extensive coupling with the perfluoroisopropyl groups, ring fluorine could only be observed under relatively high field values. The obtained spectrum was of poor quality, and only large coupling constants could be distinguished in the fine structure. The data is given below:-

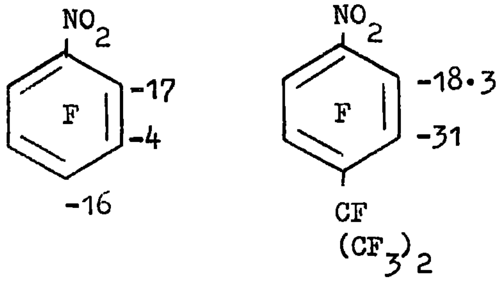
Table 4

Origin	Chemical Shift (p.p.m.)
$(C\underline{F}_3)_2CF$	-91·6 -90·0 -91·2
$(CF_3)_2C\underline{F}$	+4·0 (d; J = 200 - 205 c.p.s.) +12·4 (d; J = 105 - 110 c.p.s.) +19·2 (d; J = 72 c.p.s.)
ring fluorine	-74·6 (d; J = 200 - 205 c.p.s., with further complex splitting) -56·7 (broad) -32·6 (d; J = 110 c.p.s., with further complex splitting) -20·5

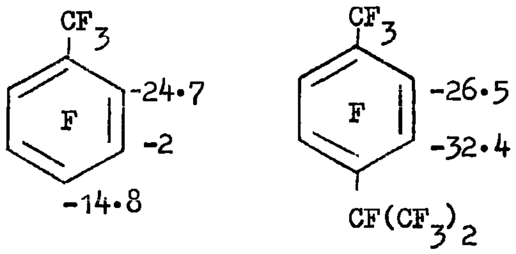
(d = doublet)

The large coupling constant exhibited by the ring fluorine absorption at -74·6 p.p.m. is readily ascribed to peri-coupling with the $(CF_3)_2C\underline{F}$ in position 4, allowing this peak to be assigned to the 5-fluorine. Comparing this value with the chemical shift obtained for the 5-fluorine in the di-substituted compound, it is seen that a downfield shift of 40·2 p.p.m. results from the introduction of a heptafluoroisopropyl group into the carbocyclic ring.

The effect of a heptafluoroisopropyl group on the chemical shifts of neighbouring fluorine (i.e. its substituent chemical shift) is obtained by comparison of the ^{19}F chemical shift of the substituted compound and the compound obtained by replacement of the substituent by fluorine, i.e.



ortho effect = -27
meta " = -1·3



ortho effect = -30·4
meta " = -1·6

The substituent chemical shifts of a $(CF_3)_2CF$ group are therefore ortho ~ -29 p.p.m. and meta ~ -1·5 p.p.m.

From the values calculated above, the orientation of the third substituent is more likely to be ortho and not meta to the 5-fluorine. However, there is a considerable difference between the calculated and observed substituent chemical shifts (29 v.s. 40) affecting the 5-fluorine. It may be that the carbocyclic ring of heptafluoroquinoline and the above ring systems are not strictly comparable.

C. Heptafluoroisoquinoline.

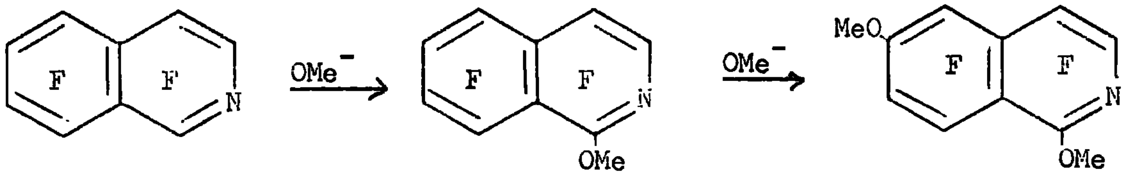
As in the previous example, heptafluoroisoquinoline was highly susceptible to polyfluoroalkylation, and the introduction of one or more heptafluoroisopropyl groups activated the system considerably.

When heptafluoroisoquinoline was shaken at 150° with caesium fluoride, sulpholan, and a 2·5 molar excess of hexafluoropropene, 60% of the substrate reacted giving an inseparable two-component mixture. As these products were perfluoroalkylated isoquinolines, an attempt was made to simplify the mixture by further reaction with olefin. However a three-component mixture resulted, the mass spectrum of which had significant mass peaks at 705, 855 and 1,005; corresponding to isoquinolines containing 3, 4 and 5 perfluoroisopropyl groups.

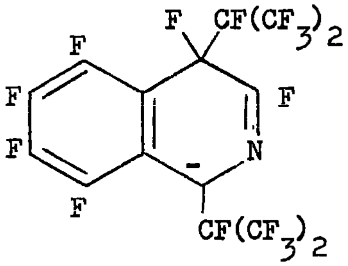
In order to provide a comparison with perfluoroquinoline, the experiment was repeated at room temperature using tetraglyme as solvent. This produced a mixture with five-components, one of which was identified by v.p.c. as unreacted substrate (33% recovery). A mass spectrum of the mixture revealed the presence of products containing up to four perfluoroisopropyl groups. Of these products, only two could be separated; one was a solid (m.p. 105 - 106°), identified by analysis and mass spectrometry as a perfluoro-[tetra-(isopropyl)-isoquinoline]. The other was a high-boiling straw-coloured oil, identified similarly as a perfluoro-[tri-(isopropyl)-isoquinoline]. This was produced in 28% yield, based on the initial weight of substrate. The formation of a tetra-substituted isoquinoline (4% yield) is significant, as it indicates that the introduction of heptafluoroisopropyl groups activates the isoquinoline more than the quinoline system.

Orientation.

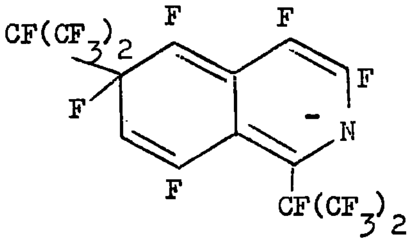
Using methoxide ion as the nucleophile, heptafluoroisoquinoline undergoes monosubstitution at position 1 and disubstitution at position 6, i.e.



When the nucleophile is $(CF_3)_2CF^-$, mono-substitution can be assigned unambiguously to position 1. However it has been mentioned that the directing influence of a heptafluoroisopropyl group can be significant, in which case the transition state for disubstitution will be weighted in favour of XIVa as opposed to XIVb



XIVa



XIVb

With this possibility in mind, the ^{19}F N.M.R. spectrum of the tri-substituted compound was examined for the presence of two heptafluoroisopropyl groups at positions 1 and 4. There was insufficient tetra-substituted compound for an N.M.R. spectrum. The spectral data for the tri-substituted compound is given below:-

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

Due to extensive coupling, ring fluorine peaks were very broad and an integration of the total spectrum was impossible.

$(\underline{CF_3})_2CF$

-92·2 and -88·8 p.p.m. in approx. ratio 2:1
Complex fine structure for both peaks.

ring fluorine

-106·6 p.p.m.; complex fine structure.
-76·0 p.p.m.; broad doublet (J = 190 - 200 c.p.s.)
-35·6 p.p.m.; area and shape suggested a mixture of two peaks, one being a doublet (J = 190 - 200 c.p.s.).

$\underline{(CF_3)_2C\underline{F}}$

+5·0 p.p.m.; doublet (J = 190 - 200 c.p.s.)

+9·6 p.p.m.; " (J = 190 - 200 c.p.s.)

+13·2 p.p.m.; thought to be a mixture of two doublets (J = 90 c.p.s. for both) of unequal height.

Storey noted unusually large coupling constants (60 - 65 c.p.s.) in the spectrum of heptafluoroisoquinoline, and they were assigned to peri-coupling between the 4,5 and 1,8 fluorine atoms. The ^{19}F data above also shows unusually large coupling constants ($\sim$195 c.p.s.), similar in magnitude to the peri-coupling between a 5-fluorine and a tertiary fluorine at position 4 in perfluoro alkylated quinolines. This large coupling is shown on both two tertiary fluorine and two ring fluorine absorptions, inferring that one of the two unassigned heptafluoroisopropyl groups is in either the 4- or 5-position. The latter position is unlikely, since the 4-position is activated towards nucleophilic attack by a heptafluoroisopropyl group in position 1. This reasoning is endorsed by the appearance of a ring fluorine absorption at -106·6 p.p.m.; in 1-substituted hexafluoroisoquinolines the peak appearing at highest field (-66 p.p.m.) is known to be the 3-fluorine. A chemical shift value of -106·6 p.p.m. for a 3-fluorine can only be explained in terms of an ortho-effect of a heptafluoroisopropyl group in the 4-position.

Although two of the $(CF_3)_2CF$ groups can be assigned to positions 1 and 4 with reasonable certainty, due to the quality of the spectrum it is impossible to assign (position 6 or 7?) the third group.

D. Octafluoronaphthalene and Decafluorobiphenyl.

Octafluoronaphthalene and decafluorobiphenyl were investigated as possible substrates for the addition of hexafluoropropene. Under almost identical conditions, only decafluorobiphenyl reacted with this olefin.

Decafluorobiphenyl was shaken at 160° for 19 hrs. with caesium fluoride, sulpholan, and a three molar excess of hexafluoropropene. A product separated from the substrate by v.p.c., was identified by mass spectrometry and analysis as a perfluoro-(isopropyl biphenyl). This was produced in 29% yield, based on the initial weight of decafluorobiphenyl.

Orientation.

The ^{19}F spectrum of the perfluoro-(isopropyl biphenyl) exhibited peaks at: -87·6 p.p.m. (relative area = 6), -28·6 p.p.m. (2), -27·5 p.p.m. (2), -25·9 p.p.m. (2), -13·6 p.p.m. (1), -2·4 p.p.m. (2), +14·6 p.p.m. (1).

On the basis of previous spectra, the peaks at -87·8 and +14·6 p.p.m. can be assigned to $(C\underline{F}_3)_2CF$ and $(CF_3)_2C\underline{F}$ respectively.

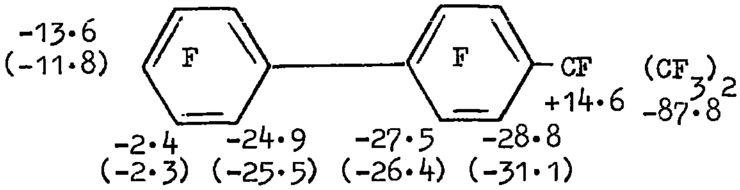
As decafluorobiphenyl is known to substitute in the 4-position, the ring fluorine chemical shifts can be calculated using the known substituent chemical shift values for a heptafluoroisopropyl substituent in a carbocyclic ring. These have been calculated for a former compound, the values were: ortho $\sim$ -29, meta $\sim$ -1·5 p.p.m. It is reasonable to assume that the introduction of a heptafluoroisopropyl group in the 4-position will not appreciably alter the chemical shift values for the unsubstituted ring fluorine.

The values[117] of the chemical shifts in decafluorobiphenyl are -24·9, -2·3, and -11·8 p.p.m. for the 2-, 3- and 4-positions respectively. Therefore the expected chemical shifts for the substituted ring fluorine are:

-31·3 p.p.m. for the 3-fluorine (-2·3 + [-29])
-26·4 " " " 2-fluorine (-24·9 + [-1·5])

It is now seen to be possible to assign the peaks in the recorded spectrum, and this is shown below.

^{19}F chemical shifts in p.p.m. for perfluoro-(4-isopropyl biphenyl)*



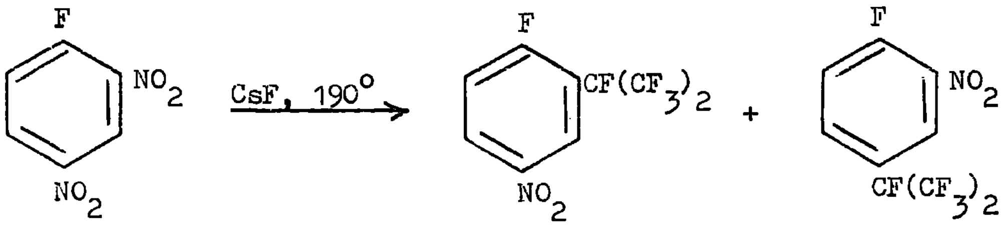
*Expected values are given in brackets.

The expected and observed chemical shifts are in reasonable agreement, and, coupled with observed intensities, there is little doubt that the orientation is as shown.

E. 2:4-Dinitrofluorobenzene.

This compound was investigated as a reactive, but not highly fluorinated substrate. As the reaction with hexafluoropropene was complicated by the formation of tars, several work-up procedures were attempted in order to achieve optimum conditions.

Using sulpholan as the solvent, 2:4-dinitrofluorobenzene was shaken at 190° with caesium fluoride and a 1·5 molar excess of hexafluoropropene. Benzene extraction of the resultant tar produced an inseparable mixture of the products XV and XVI, both in 15% yield.



(XV) (XVI)

The ^{19}F N.M.R. spectrum of the mixture showed absorptions at +20·4 and +13·4 p.p.m. $[C\underline{F}(CF_3)_2]$; -60·4 p.p.m. (the two ring fluorines presumably coincide); -87·6 and -88·0 p.p.m. $[CF(C\underline{F}_3)_2]$.

Displacement of a nitro group by a carbanion is not without precedent; Storey[113] observed displacement of the nitro group in pentafluoronitrobenzene with $(CF_3)_2CF^-$. However this will be discussed later with an analogous reaction using octafluorobut-2-ene as the source of carbanion, and pentafluoronitrobenzene as the substrate.

Most high temperature polyfluoroalkylations in the present study were accompanied by tar formation. However the extent of decomposition when 2,4-dinitrofluorobenzene was used as substrate was unique. This could be explained by abstraction of ring hydrogen by fluoride ion, which would be strongly basic in a dipolar aprotic solvent such as sulpholan.

2,4-Dinitrochlorobenzene: A repeat of the above experiment using 2,4-dinitrochlorobenzene resulted mainly in tar formation. Examination of the tar by column chromatography on alumina allowed the separation of a small quantity of what was thought to be 2,4-dinitrofluorobenzene, and the reaction was not further investigated. This was to be expected, as the reaction no doubt would proceed via 2,4-dinitrofluorobenzene by displacement of chlorine by fluoride ion.

F. Other Substrates.

$C_6F_5SO_3Me$: Storey attempted to add hexafluoropropene to the methyl ester of pentafluorophenylsulphonic acid; it was recorded that no reaction occurred, although no details were given. A re-investigation of this reaction by the author affirmed the absence of polyfluoroalkylated products, and it was found that the reaction proceeded according to the equation below.

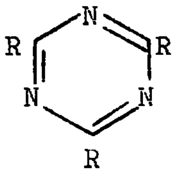
$$C_6F_5SO_3Me + CsF \longrightarrow C_6F_5SO_3Cs + MeF$$

The caesium salt of the sulphonic acid was characterised by conversion to the s-benzyl-iso-thiuronium salt.

Therefore it appears that S_N2 attack by fluoride ion occurs in preference to polyfluoroalkylation of the aromatic ring.

Cyanuric fluoride: Since the inception of the work described in this thesis, Young has reported the reaction of hexafluoropropene and the analogous olefin perfluoro-2-azapropene with cyanuric fluoride. His results are given below in Table 5.

Table 5[118]

Reactant	R	% conversion to:		
				
$CF_3CF{=}CF_2$	$(CF_3)_2CF^-$	39	51	5
$CF_3N{=}CF_2$	$(CF_3)_2N^-$	19	29	16

The conversions given are for a 2:1 olefin $(CNF)_3$ ratio; as expected, product ratio was found to be dependent on this initial ratio.

G. A Comparison of the Reactivity of Heptafluoroquinoline, Heptafluoroisoquinoline and pentafluoropyridine.

In a comparison[107] of the reactivity of the above compounds towards attack by methoxide ion, it was found that heptafluoroisoquinoline and heptafluoroquinoline are of comparable reactivity, and both are more reactive than pentafluoropyridine by a factor of approximately 2·5.

Initially it was hoped to compare their reactivities towards carbanionic attack in an experiment involving all three substrates, however due to the complexity of the final mixture it was impossible to determine their final concentrations. For this reason it was necessary to compare (1) pentafluoropyridine with heptafluoroisoquinoline and (2) pentafluoropyridine with heptafluoroquinoline under identical conditions (e.g. vol. of solvent, wt. of initiator, temp., etc.). It was not possible to separate the resultant mixtures by v.p.c. but integration of the ^{19}F N.M.R. spectrum of these mixtures allowed an approximate determination of the relative concentration of the substrates. By this method, heptafluoroisoquinoline and heptafluoroquinoline were found to be more reactive than pentafluoropyridine by factors of approximately 2·5 and 1·6 respectively. It therefore appears that the general order of reactivity towards a carbanion is the same as that towards methoxide, (i.e. pentafluoropyridine < heptafluoroquinoline and heptafluoroisoquinoline).

Section II

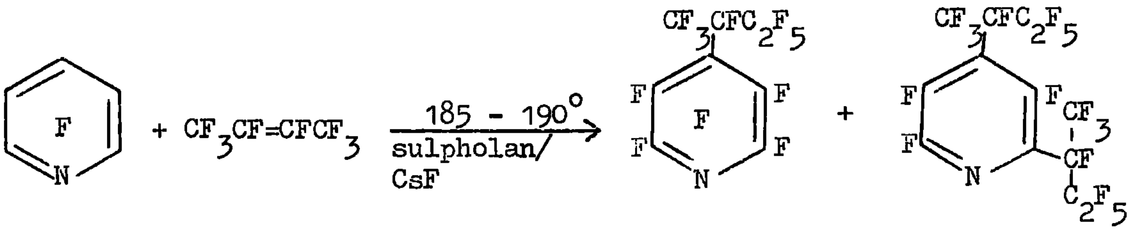
The Reaction of Octafluorobutene with Polyfluoroaromatic Compounds

It has been shown in Section I that the rate of self-condensation of hexafluoropropene is fast enough to reduce, and in some cases inhibit, the formation of polyfluoroalkylated products. However octafluorobut-2-ene [C_4F_8] is known to dimerize only under forcing conditions and for this reason it was chosen as a more suitable olefin for polyfluoroalkylation.

Anomalies in the ^{19}F N.M.R. spectra of the perfluoro-(sec.-butyl) derivatives so formed, have been interpreted in terms of restricted rotation between the C-C bond joining the substituent and the aromatic ring; this observation also led to a re-examination of some perfluoro-isopropyl derivatives. For this reason, the spectral evidence for orientation and restricted rotation in these compounds will be discussed separately, at the end of this section.

[A] Polyfluoropyridines.

Pentafluoropyridine: On shaking pentafluoropyridine with a 3·7 molar excess of C_4F_8, a mixture of mono-, di-, and a trace of tri-substituted pyridines was produced.



(XVII) (XVIII)

67% and 23% conversion

Dimerization of the olefin was not as extensive as would be expected in an analogous experiment, using hexafluoropropene. In this particular reaction, as in most subsequent reactions, the dimer of C_4F_8 was not isolated but characterization of this compound will be reported later in this section.

4-methoxytetrafluoropyridine: Under conditions which were identical with the above reaction, this compound failed to add C_4F_8. As with the heptafluoroisopropyl anion, the perfluoro-sec.-butyl anion is not sufficiently reactive to add to the 2-position.

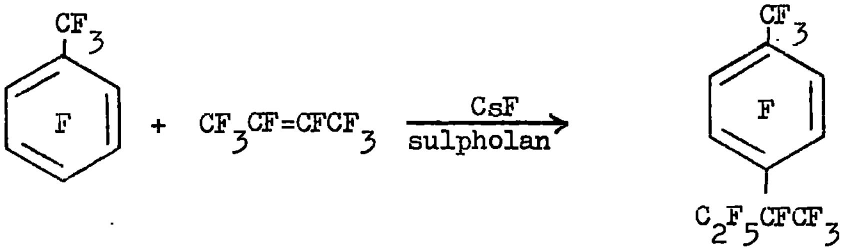
4-Chlorotetrafluoropyridine: Although hexafluoropropene did not react with this compound, it was hoped that C_4F_8 would do so; the expected product being the 2-substituted derivative.

The reaction was carried out at 160° and two products were isolated. These were separated by v.p.c. and characterized as 4-, and 2,4-derivatives, produced in 46 and 42% yield (based on substrate consumed) respectively. It therefore appears that 4-substitution by fluoride ion with subsequent loss of chlorine is preferred to 2-substitution by a heptafluoroisopropyl carbanion.

[B] Pentafluorophenyl Compounds [C_6F_5X]

X = F, Br: As with hexafluoropropene, C_4F_8 would not react with either hexafluorobenzene or bromopentafluorobenzene, even at 200°. The only observable reaction was displacement of the bromine atom by fluoride ion, as after 12 hours some 15% of the bromopentafluorobenzene was converted to hexafluorobenzene.

<u>$X = CF_3$:</u> On shaking octafluorotoluene for 16 hr. at 150° with an excess of C_4F_8, monosubstitution occurred according to the equation below:

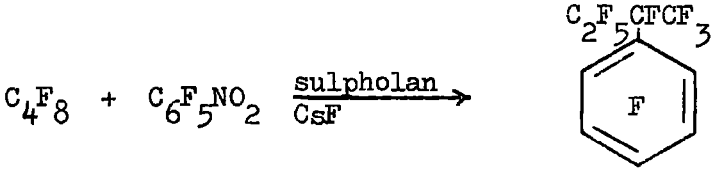


(90% conversion)

This result contrasts with a 52% conversion using hexafluoropropene under similar conditions.

<u>$X = C_6F_5$:</u> Only 10% of the initial weight of decafluorobiphenyl reacted when shaken with a two molar excess of C_4F_8 at 160°. As it was impossible to separate the product from the substrate, the reaction was repeated on the mixture at 190°. A mixture was extracted from this second reaction which contained decafluorobiphenyl (36%), the product formed initially (53%), and another product. These components were separated by preparative scale v.p.c. (it was necessary to take middle cuts of the peaks to isolate pure materials), and identified as perfluoro-(4-sec.butyl biphenyl) and perfluoro-(4,4'-di[sec.butyl]biphenyl). As with most of the perfluoro sec.-butyl derivatives, they were high boiling, gummy liquids.

X = NO_2: No reaction occurred between pentafluoronitrobenzene and C_4F_8 in an autoclave at 90°, however on raising the temperature to 150°, perfluoro-(sec.-butylbenzene) was produced in 68% yield.



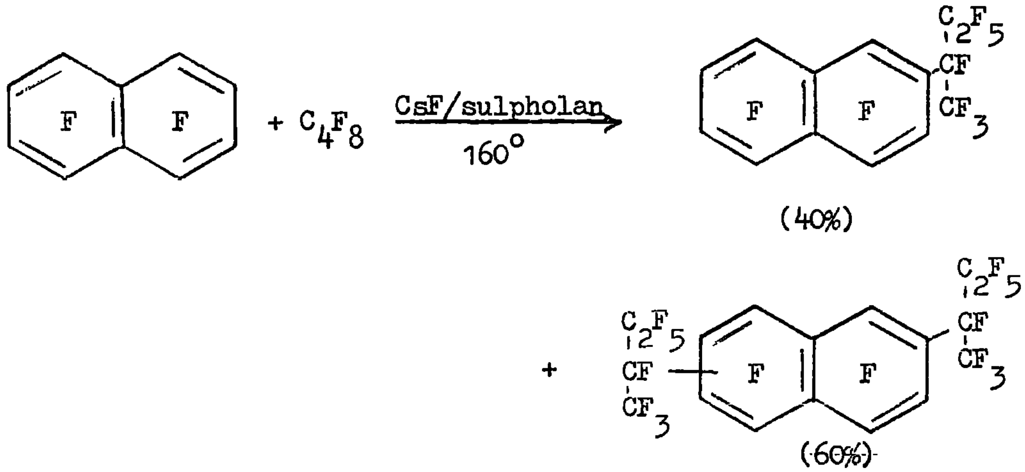
2 : 1 Ratio

Storey observed displacement of the nitro group at 150° by a heptafluoroisopropyl carbanion, and similarly found a critical dependence on reaction conditions; in a Carius tube at 120° a mixture of mono- and di-substituted nitrobenzenes and products arising from displacement of the nitro group was formed.

These results are unexpected since nucleophilic displacement of the nitro group has not been observed in pentafluoronitrobenzene. (Although in other systems it has been demonstrated[119] that nucleophilic displacement of the nitro group occurs with similar facility to that of fluoride). In order to investigate the possibility that this anomalous displacement was dependent on solvent, pentafluoronitrobenzene was stirred in sulpholan with an equivalent amount of sodium methoxide. This reaction produced a mixture containing methoxides of polyfluoronitrobenzenes, but no pentafluoroanisole. It is therefore difficult to provide an adequate explanation of these results.

[C] Other Substrates.

Octafluoronaphthalene: When shaken with a 3:1 ratio of C_4F_8 to octafluoronaphthalene, 20% of the substrate was consumed under the conditions given below:



It is of interest to note that under identical conditions hexafluoropropene failed to react with this substrate.

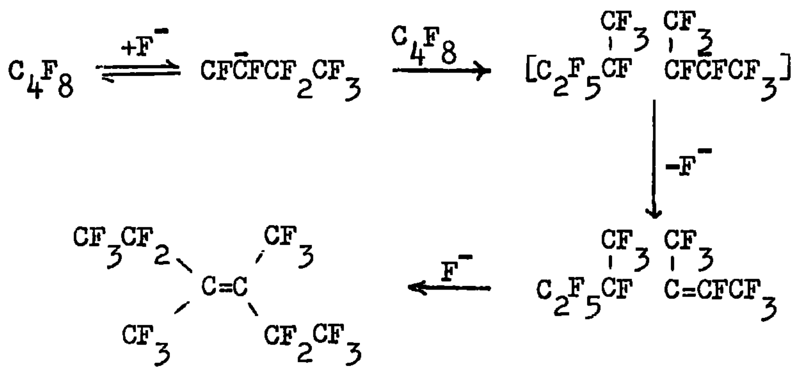
Heptafluoroquinoline: Heptafluoroquinoline was shaken at 100° with a deficiency of C_4F_8; 35% of the substrate reacted to give a mixture, the mass spectrum of which, indicated the presence of di-, tri-, and tetra-substituted quinolines. Separation of this mixture proved to be difficult but it was possible to isolate the major component, which was identified as perfluoro-(2,4-di-[sec.-butyl]quinoline) produced in an estimated 20% yield, based on the substrate consumed.

When the reaction was repeated either using the same solvent (sulpholan) at 50°, or using tetraglyme at room temperature, a similar mixture was produced, with only slight variations in product distribution.

Heptafluoroisoquinoline: Only 30% of this substrate reacted on shaking with a two molar excess of C_4F_8 at 100°. As the highly alkylated products were not present in sufficient quantity to enable separation, the mixture was shaken with more olefin. The major component (75%) of the mixture extracted from this reaction was separated by v.p.c. and subsequently characterized as perfluoro-(1,4,X-tri-[sec.-butyl]isoquinoline), where X = 6 or 7.

[D] Investigation of the Dimer of Octafluorobut-2-ene.

An illustration of the difficulty with which octafluorobut-2-ene dimerizes was provided when some 58% of the olefin was recovered after shaking for 16 hr. at 190° with caesium fluoride in sulpholan. Removal of the olefin from the volatiles distilled from the sulpholan left an essentially pure compound, the mass spectrum of which showed that it was a dimer of C_4F_8. The ^{19}F N.M.R. spectrum of this material had absorptions at -64·2, -88·8, and -106·2 p.p.m., in ratio 2:3:3. The most likely structure for the dimer is XIX which would be formed as shown in the scheme below:



(XIX)

As the I.R. spectrum did not exhibit a C=C absorption it is likely that the dimer XIX is produced mainly in the trans configuration. The peaks in the N.M.R. spectrum were too broad to allow their fine structure to corroborate this.

[E] The ^{19}F N.M.R. spectra of Perfluoro-(sec.-butyl) Compounds.

On examination of the spectra of perfluoro-(sec.-butyl) compounds, it was noticed that there were more ring fluorine absorptions than expected. Also some of the peaks did not have the expected symmetry under high resolution. The results could be explained in terms of restricted rotation about the bond joining the group to the aromatic ring, and in order to investigate this, the spectra of some perfluoro-(sec.-butyl) compounds were measured at different temperatures.

(i) Variable Temperature Experiments.

Perfluoro-(sec.-butylbenzene).

The low resolution spectra of this compound at the temperatures

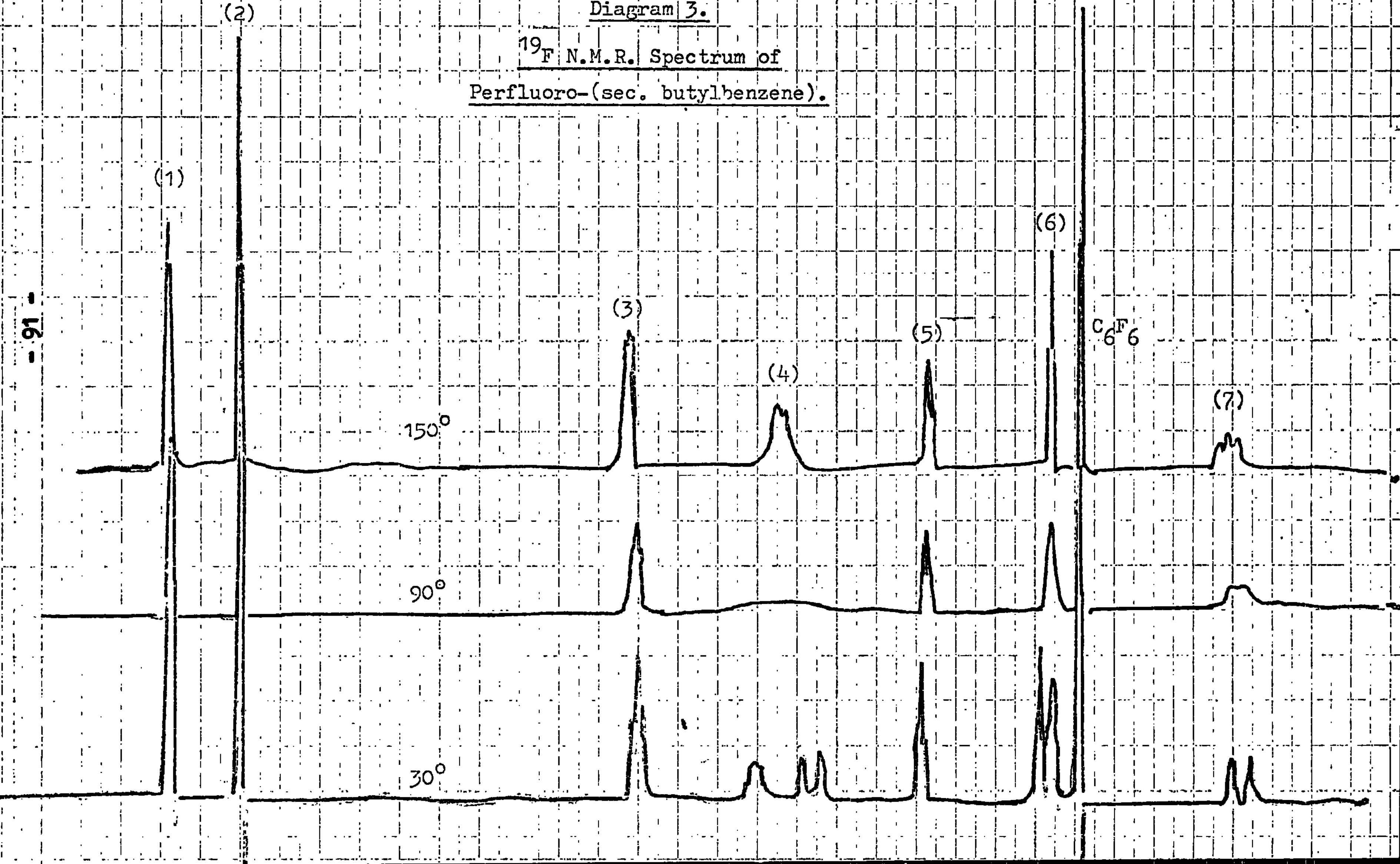
30°, 90°, and 150° are shown in Diagram 3. A fourth spectrum, measured at -15° is not included as it is identical with that at 30°. Considering the spectrum obtained at 150°, the peaks can be assigned by comparing their chemical shifts with the expected values(obtained from other sec.-butyl compounds). Hence: Peak 1, chemical shift -91·6 p.p.m. [assigned to $\mathrm{C\underline{F}_3CF_2}$]; 2, -84·1 [$\mathrm{C\underline{F}_3CF}$]; 3, -44·4 [$\mathrm{CF_3C\underline{F}_2}$]; 4, -30·4 [ortho-fluorine]; 5, -15·4 [para-fluorine]; 6, -3·2 [meta-fluorine] 7, +14·8 [$\mathrm{CF_3C\underline{F}}$].

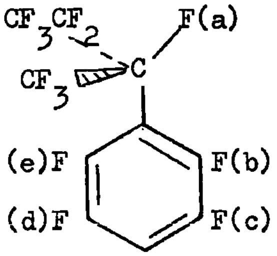
It is seen that on cooling the sample to 30°, the appearance of the spectrum changes. The ortho-fluorine absorption (originally peak 4) now appears as two peaks at -32·2 and -26·7 p.p.m., the latter absorption exhibits a coupling (J = 110 c.p.s.) which is identical with that on the tertiary-fluorine absorption. The tertiary-fluorine absorption (originally peak 7) which changed from a triplet to a doublet also moves to a higher field position [+16·0 p.p.m.]; the positions of the other peaks do not alter to any measurable extent. At 90°, the ortho-fluorine is observed as a broad peak, and the tertiary-fluorine absorption appears to be at a stage intermediate between the doublet at 30° and the triplet at 150°. The meta-fluorine absorption is a single peak at 150° (also 90°), whilst at 30° there are two chemically different meta-fluorines.

The most likely explanation of these observations is that, at 30° the spectrum is essentially that of the conformational isomer (XX) and at 150° the group rotates freely.

Diagram 3.

^{19}F N.M.R. Spectrum of Perfluoro-(sec. butylbenzene).





J_{ab} = 110 c.p.s.

c $\neq$ d

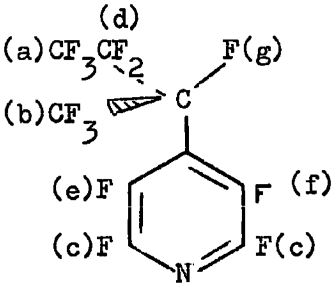
b $\neq$ e

(XX)

On the basis of the spectral data, it is apparent that there is a significant energy barrier towards rotation, even at room temperature.

Perfluoro-(4-sec.- butylpyridine).

The results for the low resolution spectrum of this compound at 33° and 130° are presented below. Again, it appears that the conformational isomer XXI predominates at 33°.



(XXI)

Peak	Chemical shift (p.p.m.) at: 33°	130°
a	-92	-92
b	-84	-84
c	ca. -75 (mixture of two unlike peaks; separation = 100 c.p.s.)	-75 (single absorption ∴ meta fluorines equivalent)
d	-44	-45
e	-31	-28 (broad)
f	-26(d[broad], J = 110 c.p.s.)	
g	+19 (d, J = 110 c.p.s.)	+17 (t, [unsym.]; J = 60 c.p.s.)

Perfluoro-(4-sec.-butyltoluene).

The low resolution spectrum of this compound was measured at 30° and 150°. The chemical shifts of the peaks at -106 (ring CF_3), -92 ($C\underline{F}_3CF_2$), and -89 p.p.m. ($C\underline{F}_3CF$) did not change. A broad peak centered at 44 p.p.m. ($CF_3C\underline{F}_2$) at 30° moved upfield to 46 p.p.m. at 150°. As with the above compounds, the tertiary fluorine absorption is a doublet (δ = +16 p.p.m.; J = 110 c.p.s.) at 30°, and a broad triplet (δ = +14 p.p.m.; J = 60 c.p.s.) at 150°.

At 30°, the ring fluorine absorptions appear as an overlapping complex of broad peaks extending from -36 to -24 p.p.m., which are impossible to assign. However at 150° only two peaks are seen, one at -32 p.p.m. (3,5F [v. broad due to interaction with sec.-butyl fluorines]) and the other at -26 p.p.m. (2,6F).

Perfluoro-(4-isopropyl pyridine).

In the light of the results obtained from the variable temperature N.M.R. studies on perfluoro-(sec.-butyl) compounds, it was thought that the spectra of heptafluoroisopropyl compounds (which have been unaccountably complex) may be complicated by the presence of rotational isomers. In order to investigate this possibility, the spectrum of perfluoro-(4-isopropyl pyridine) was recorded at -20°, 30°, and 160°.

Spectrum recorded at -20°

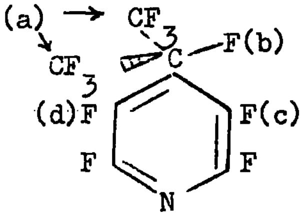
$(C\underline{F}_3)_2CF$: Two overlapping doublets, centered at -89 p.p.m. J = 25 c.p.s. for both.

2,6F: Two unlike peaks, centered at -77 p.p.m. complex fine structure for both.

3,5F: Two incompletely resolved, unlike peaks at -29.8 p.p.m. One of these is a doublet (J = 94 c.p.s.) with further complex splitting; the other is a complex multiplet which, under the resolution available, exhibits five lines of separation 25 c.p.s.

$(CF_3)_2C\underline{F}$: doublet of heptuplets (J = 94 and 7 c.p.s.) at +16 p.p.m.

It is probable that this spectrum corresponds to that of the conformational isomer XXII:



(XXII)

This is supported by the appearance of identical coupling constants on the trifluoromethyl absorption and only one of the absorptions due to adjacent ring fluorine atoms. (J_{ad}; similarly J_{bc}).

Spectrum recorded at 160°

$(C\underline{F}_3)_2C$: -84 p.p.m. (t.d.; J = 13.5 and 7.0 c.p.s.)

2,6F: -76 p.p.m. (v.broad)

3,5F: -28 p.p.m. (complex)

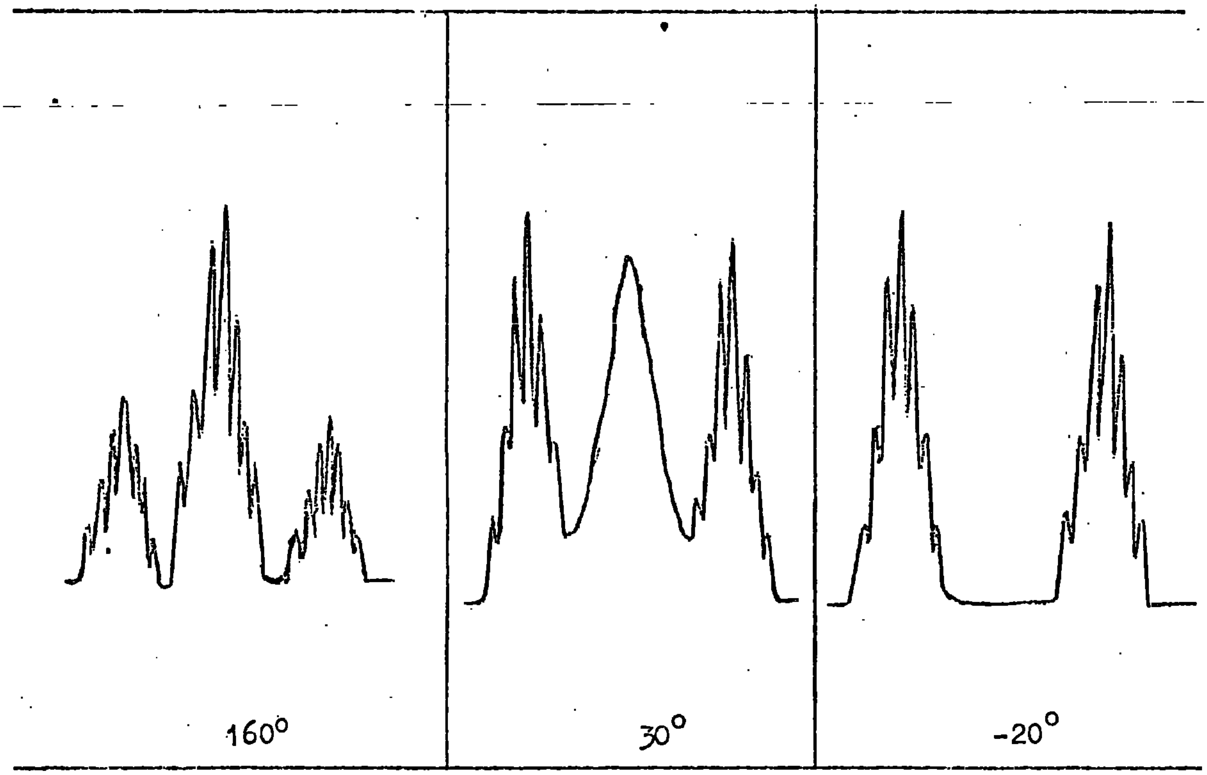
$(CF_3)_2C\underline{F}$: +14 p.p.m. (t.heptuplets; J = 48 and 7 c.p.s.)

The above data implies that rotation of the i-C_3F_7 is now unrestricted. As the spectrometer records an averaged spectrum, this is true only for the time scale of the instrument.

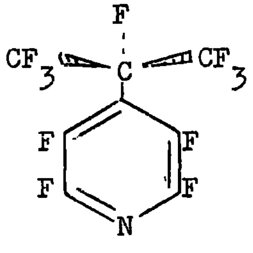
Spectrum recorded at 30°

As expected, all peaks were complicated by the presence of conformational isomers. The tertiary fluorine absorption was the least complex, and most interesting. This absorption is shown below, in a comparison with the fine structure observed at -20° and 160°.

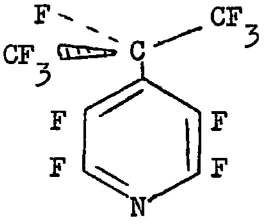
$CF_3C\underline{F}$ absorption



It appears that a broad absorption arises between the two extreme temperatures. This could be explained by the significant existence of either conformational isomer XXIII or XXIV (or a mixture of both)



(XXIII)

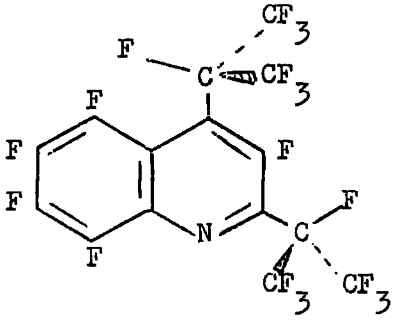


(XXIV)

Perfluoro-(2,4-di-isopropyl quinoline).

As the spectrum of this compound was difficult to interpret, its spectrum was re-recorded at 170° in an attempt to eliminate complications which could be due to conformational isomerism. However the spectrum did not simplify; the chemical shifts of the 6, 7 and 8 fluorines remained at the same value, all others moved downfield by approx. 3 p.p.m. The coupling constants attributed to peri-interaction and tertiary fluorine (in position 2) - 3-fluorine interaction remained at the same value.

On this evidence it appears that rotation of the heptafluoroisopropyl groups in XXV is restricted, even at 170°.

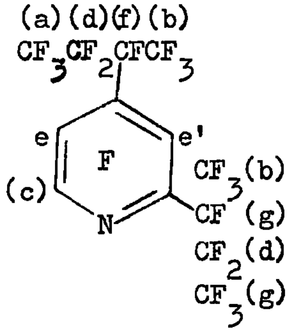


(XXV)

(ii) Spectra Measured at 33°.

The reason for the complexity of the spectra of perfluoro-sec.-butyl compounds was impossible to investigate until late in the present study, as a variable temperature probe was not available. Hence, the data for the compounds presented below was determined at the standard probe temperature of 33°.

Perfluoro-(2,4-di[sec.-butyl]pyridine).



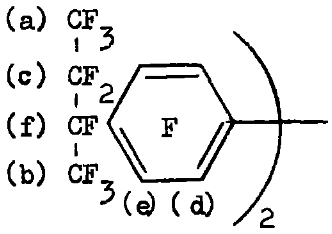
Shift(p.p.m.)	Ratio	Assignment
-91·6	6	a
-83·6	6	b
-82·0	1	c
-44·2	4	d
-38·6	1	e or e' *
+16·4	1	f
+20·4	1	g

* Due to extensive coupling, only one of the 3,5-fluorine absorptions could be seen.

Perfluoro-(4-sec.-butyl biphenyl).

Absorptions at -91·4 (relative intensity 3: $C\underline{F}_3CF_2$), -84·4 (3: $C\underline{F}_3CF$), -44·4 (2: $CF_3C\underline{F}_2$), mixture of peaks centered at -29·0 (6: 3,2,2'F), -14·0 (1: 4'F), -2·4 (2:3'F) and +17·0 p.p.m.[(1: $CF_3C\underline{F}$)-d; J = 108 c.p.s.].

Perfluoro-(4,4'-di[sec.-butyl]biphenyl).



Shift (p.p.m.)	Ratio	Assignment
-91·2	3	a
-84·4	3	b
-44·0	2	c
-32·2 (i)	2	d
-28·0 (ii)	2	e
+17·4 (iii)	1	f

(i) v. broad

(ii) complex mixture of peaks

(iii) d.; J = 108 c.p.s.

Perfluoro-(2-sec.-butylnaphthalene)

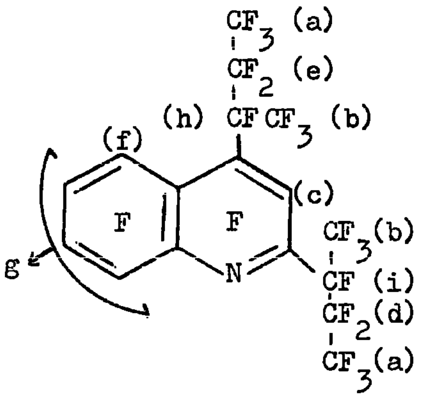
Absorptions at -90·9 (relative intensity 3), -83·1 (3), -44·0 (2), -31·7 (1), -26·8 [d. J = 105 c.p.s. (3)], -21·5 (1), -18·0 (1), -16·7 (1), -14·0 (1), -9·8 (1), and +15·2 p.p.m. [d. J = 105 c.p.s. (1)].

The peaks at -90·9, -83·1, -44·0,and +15·2 p.p.m. can readily be assigned to $\underline{CF_3}CF_2$, $\underline{CF_3}CF$, $CF_3\underline{CF_2}$, and $CF_3\underline{CF}$ respectively. The orientation in this compound is based on the known 2-substitution in octafluoronaphthalene; and it is worth noting that if 1-substitution had occurred, then a coupling constant of the order of 200 c.p.s. could be expected to arise through peri-interaction (as opposed to the observed 90 - 120 c.p.s. "normal" value).

Perfluoro-(2,X-di[sec.-butyl]naphthalene).

A 25 scan accumulated spectrum had absorptions at -91·0 (relative intensity 6), -83·4 (6), -56·0 (1), -50·4 (d. J = 105 c.p.s. (1)], -44·6 (4), -33·2 (1), -28·4 [d. J = 105 c.p.s. (1)], -21·0 (2), and +17·8 p.p.m. [d. J = 105 c.p.s. (2)]. Absence of a coupling constant of the order of 200 c.p.s. suggests that the second group is in either position 6 or 7.

Perfluoro-(2,4-di[sec.-butyl]quinoline)



Shifts p.p.m.	Ratio	Assignment
-91·0	6	a
-83·6	6	b
-56·0	1	c
-48·3	2	d
-44·6(iii)	2	e
-35·6(i)	1	f
-20·6	1	g
-18·6	1	
-12·4	1	
+6·4(i)	1	h
+19·8(ii)	1	i

(i) d. J = 210 c.p.s.

(ii) d. J = 72 c.p.s.

(iii) v.broad.

Perfluoro-(1,4,X-tri[sec. butyl)isoquinoline).

The spectrum of this compound was of very poor quality (even after accumulating 47 scans in a C.A.T.); ring fluorine absorption was extremely broad, consequently integration of the spectrum was impracticable. The spectrum exhibited peaks at -108·6, -94·0, -91·2, -78·0 (d. J ~ 210 c.p.s.), -48·2, -45·0, -38·0 (d. J ~ 210 c.p.s.) -33·6 (broad), +8·0 (d. J ~ 110 c.p.s.), +11·4 (d. J ~ 210 c.p.s.), and +15·6 p.p.m. (d. J ~ 210 c.p.s.).

As expected, a peri coupling constant was shown on two tertiary fluorines and two ring fluorines, indicating that two of the perfluoro-sec. butyl groups are in positions 1 and 4 (by analogy with the tris-heptafluoroisopropyl compound).

Section III

The Reactions of Polyfluoroethylenes with Aromatic Substrates.

[A] Tetrafluoroethylene.

When pentafluoropyridine and tetrafluoroethylene, in molar ratio 1:10, were heated in a pressure vessel containing caesium fluoride and sulpholan, a mixture of mono- to pentakis-pentafluoroethyl derivatives was produced. Of these, only the tetra and penta substituted pyridines could be separated, and the yields of these compounds, estimated from the chromatogram, were 11 and 6% respectively. Both of these compounds gave a correct molecular ion in the mass spectrum but there was insufficient of the former to allow an N.M.R. spectrum to be recorded. The N.M.R. spectrum of the perfluoro-(pentaethyl pyridine) exhibited two complex peaks centred at -93·6 ($C\underline{F}_3CF_2$) and -57·6 p.p.m. ($CF_3C\underline{F}_2$) in ratio 3:2; there was also a small spurious peak at 85 p.p.m. which remained in the spectrum even after repeated recrystallization of the compound from hexane.

It is relevant that 63% of the initial weight of tetrafluoroethylene was recovered, as this illustrates the difficulty with which a symmetrical olefin undergoes addition of fluoride ion. However, once formed, the pentafluoroethyl anion reacts rapidly with the substrate producing a mixture of highly alkylated products. This is in line with the known instability of primary fluorocarbanions.[18] Steric requirements will also be of importance in determining the extent of alkylation.

Tetrafluoroethylene has also been added to hexafluorobenzene and benzene. A patent[120] by Imperial Chemical Industries describes the preparation of a mixture of perfluoro-(mono-to hexa-ethyl benzenes) from hexafluorobenzene, tetrafluoroethylene, and potassium fluoride at 135° for 6 hrs. at about 34 ats. Tlumac and Harriman[121] in a U.S. patent outline the polyfluoroalkylation of benzene in a flow process using tetrafluoroethylene over caesium fluoride. The yields of fluoroalkylated benzenes were low, for example at 350° only 5% of the benzene was converted to fluorinated products. Possibly at this temperature the mechanism is free radical, as breakdown of the olefin had occurred and CF_3, C_2F_5, as well as $CF(CF_3)_2$ groups were introduced into benzene.

[B] Trifluoroethylene.

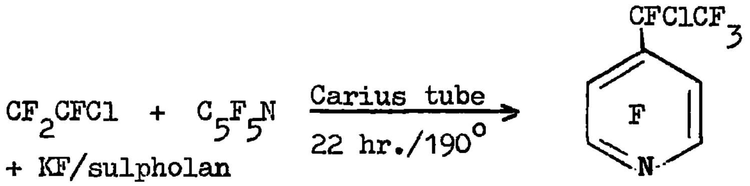
Pentafluoropyridine and trifluoroethylene, when shaken together at 200° in the presence of fluoride ion, failed to react and both the olefin and substrate were recovered almost quantitatively. The same result was obtained using heptafluoroisoquinoline as a more reactive substrate, and a reaction temperature of 180°.

Although a small amount of unidentified material (containing only C and F) was isolated from the reaction at 200°, the absence of alkylated products cannot be attributed to side reactions of the olefin as 86% of the initial weight was recovered. Hence, this somewhat surprising result infers that the anion $CF_3\bar{C}FH$ is formed with difficulty, or is not sufficiently reactive to attack the substrates.

[C] Chlorotrifluoroethylene.

(i) Pentafluoropyridine.

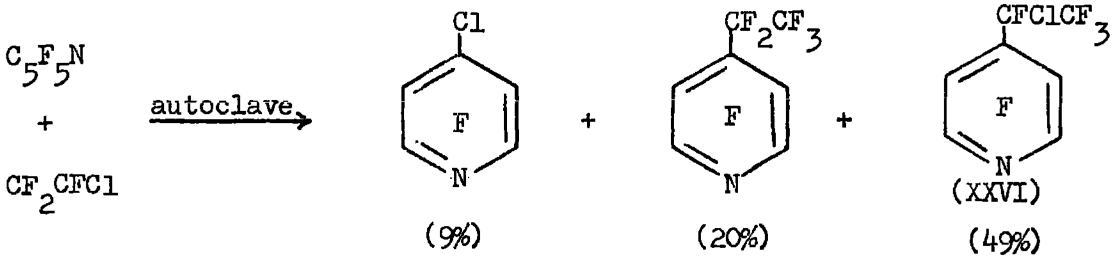
Storey[113] noted that severe conditions were needed to obtain reaction between chlorotrifluoroethylene and pentafluoropyridine. He obtained a 60% yield of 1-chloro-1-tetrafluoropyridyl tetrafluoroethane (XXVI) as well as 40% unreacted starting material under the conditions given in the scheme below:



(XXVI)

However other products which did not contain chlorine were thought to be present, and the overall mechanism was unclear. For this reason the reaction was repeated, using the same ratio of olefin to substrate on a larger scale in order to investigate the nature of these other products.

Pentafluoropyridine and chlorotrifluoroethylene were heated in an autoclave at 190° for 20 hr., in ratio 1:1·5. After cooling the autoclave, 10% of the initial weight of olefin was collected, and a 6-component mixture was extracted. One of the components was identified by v.p.c. retention time as pentafluoropyridine, an estimate from the chromatogram of the mixture indicated that 24% of the substrate had not reacted. It was possible to identify 3 major products in the mixture, the yields of these based on the substrate that had reacted are given below:

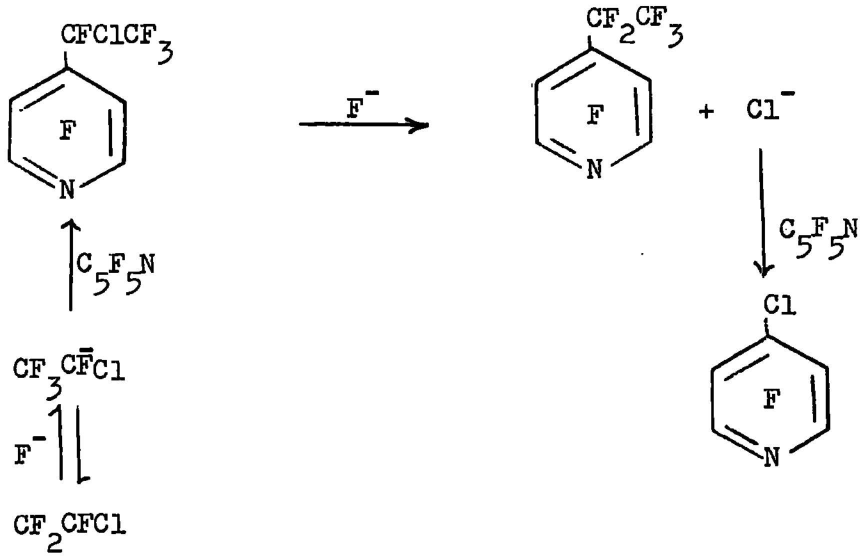


There are two possible routes that could explain the presence of perfluoro-(4-ethylpyridine), one involving benzylic displacement of chlorine from XXVI and the other involving addition of a pentafluoroethyl anion to the substrate. The latter is unlikely as a fluoride ion would have to attack the olefin at the wrong carbon atom, i.e.

$$CF_2CFCl + F^- \longrightarrow \bar{C}F_2CF_2Cl \xrightarrow{-Cl^-} CF_2{=}CF_2 \xrightarrow{F^-}$$

To prove this point, chlorotrifluoroethylene was shaken at the same temperature with caesium fluoride in sulpholan. A complex mixture of low boiling products was isolated, and tetrafluoroethylene was shown by I.R. spectroscopy to be absent.

To investigate the benzylic displacement mechanism, the chloro-compound XXVI was shaken with caesium fluoride in sulpholan at 190°; perfluoro-(4-ethylpyridine) was produced, albeit in low (16%) yield. On the basis of these results, the mechanism appears to be as follows:



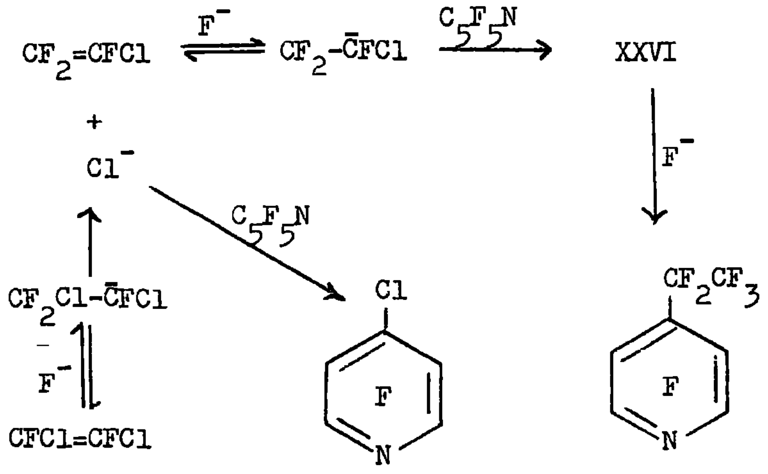
(ii) Heptafluoroquinoline.

Chlorotrifluoroethylene reacted with this compound (1:1 molar ratio) to form a complex mixture, 30% of which was unreacted substrate. Although it was impossible to isolate the individual components, a mixture of two products was separated by v.p.c. and a mass spectrum of this had significant mass peaks at 371 and 471. These correspond to products containing (1) CF_3CFCl- and (2) CF_3CFCl- + CF_3CF_2- groups. In the light of the previous experiment, this result is not unexpected.

[D] 1,2-Difluoro-1,2-dichloroethylene.

Storey[113] observed that pentafluoropyridine and the title olefin, when heated at 190° for 18 hr. with potassium fluoride in sulpholan, produced perfluoro-(4-ethylpyridine) in low yield. However, a repeat of this reaction by the author, using caesium fluoride under identical conditions, gave a significant amount of tarry material and a 46% yield of 4-chlorotetrafluoropyridine. Due to this somewhat unexpected result, the reaction was repeated using potassium fluoride, and indeed, perfluoro-(4-ethylpyridine) was formed in 36% yield.

It therefore appears that there are two possible reaction pathways:



The unexpectedly high yield of 4-chlorotetrafluoropyridine is thought to be due to the "in situ" formation of caesium chloride. In support of this, it was found that when caesium chloride is shaken at the same temperature with pentafluoropyridine, the yield is reduced to 7% (as opposed to 46%). It was noted that tarry material is formed when caesium fluoride is used as the initiator; although this accounts for the absence of products derived from chlorotrifluoroethylene, it is difficult to determine why side reactions predominate only when caesium fluoride is used.

The vigorous conditions necessary for reaction to occur reflect the difficulty with which symmetrical olefins undergo addition of a fluoride ion.

[E] 1,1-Dichlorodifluoroethylene.

This olefin was shaken with pentafluoropyridine, caesium fluoride and sulpholan at 150° for 22 hr. The volatile material was removed and v.p.c. indicated that it was essentially a three component mixture containing olefin, substrate, and an unknown product. The product, which was isolated by preparative-scale v.p.c., analysed correctly for the empirical formula $C_2F_3Cl_3$. As the N.M.R. spectrum of this material was a single unsplit peak (-81·4 p.p.m.) it could only be 1,1,1-trichlorotrifluoroethane (XXVII). Although the mass spectrum did not exhibit a molecular ion, peaks were observed corresponding to $C_2F_3Cl_2$, CCl_3, CF_3.

The formation of XXVII (in 26% yield based on the initial weight of olefin), although unexpected, can be explained by abstraction of chlorine from the olefin by fluoride ion, and subsequent addition of "ClF" to the olefin.

$$CF_2{=}CCl_2 \xrightarrow{F^-} CF_2\bar{C}Cl + ClF$$

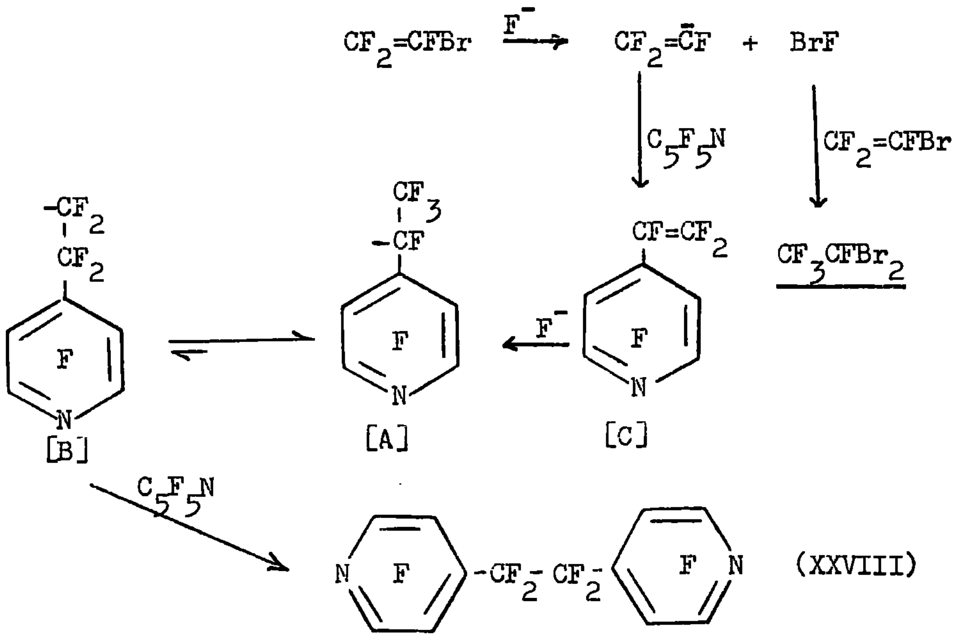
$$ClF + CF_2{=}CCl_2 \longrightarrow CF_3CCl_3 \quad \text{(XXVII)}$$

[F] Bromotrifluoroethylene.

Pentafluoropyridine and bromotrifluoroethylene were shaken at 170° for 16 hr. in the presence of fluoride ion. The volatile material which distilled from the mixture was characterised as a mixture of starting materials and 1,1-dibromotetrafluoroethane (Yield: 35%, based on initial weight of olefin). This product had the correct empirical formula of $C_2Br_2F_4$, as determined by analysis and mass spectrometry, and N.M.R. spectrum, which exhibited absorptions at -80·6 (d. J = 8 c.p.s.) and 84·9 (q. J = 8 c.p.s.) in ratio 3:1 respectively.

The remaining involatile material was very tarry, however it was possible to isolate bis-(1,2,5,6-tetrafluoropyridyl)tetrafluoroethane (XXVIII), which was produced in an estimated 27% yield based on the substrate consumed. The ^{19}F N.M.R. spectrum of this material showed absorptions of equal area at, -25·2 (3,5F), -75·8 (2,6F), and 85·4 p.p.m. (CF_2).

The formation of these products can be accounted for by the reaction scheme outlined below.



As shown, the equilibrium between intermediates A and B would favour A. However A would be expected to be much more stable than B because of the adjacent electron-withdrawing trifluoromethyl group and delocalization of the negative charge into the pyridine ring. As the order of stability is A $>$ B, the rate of the reaction of these intermediates with pentafluoropyridine will be in the order A $<$ B. Another product, which was formed in low yield and could not be isolated, may well have been the result of reaction between A and pentafluoropyridine.

In order to establish that the substrate was not involved in the formation of 1,1-dibromotetrafluoroethane, the olefin was shaken with caesium fluoride and sulpholan under the same conditions as the above experiment. A complex mixture of products was formed, one of which was the alkane (10% yield). Extensive tar formation indicated that side reactions involving the solvent had also occurred.

It would be of obvious interest to synthesise and observe the effect of fluoride ion on the proposed intermediate C.

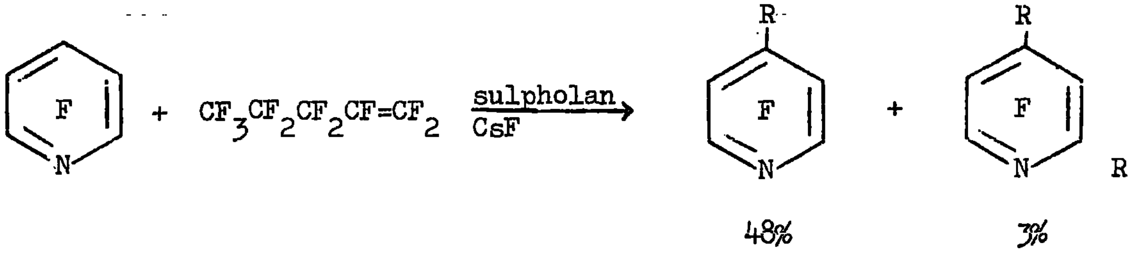
Section IV

The Addition of C 5 olefins to Pentafluoropyridine.

It was shown in chapter III that under the action of fluoride ion, long chain fluoro-olefins tend to rearrange to the most stable structure. However, since octafluorobutene is a suitable olefin for polyfluoroalkylation reactions, there was no apparent reason why a carbanion derived from a fluoro-pentene could not be trapped similarly.

(i) Straight-chain Olefins.

Decafluoropent-1-ene was shaken for 60 hr. with pentafluoropyridine at 185°. Two products were formed, they were isolated by v.p.c. and characterised as mono- and di-substituted pyridines.



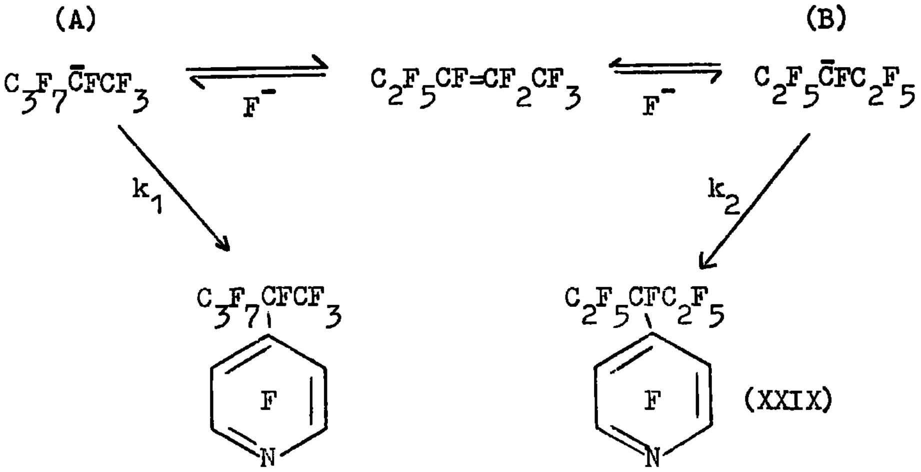
R = $C_3F_7CFCF_3$

It is unlikely that the terminal olefin is present in the above reaction mixture, as it was found to rearrange under milder conditions to the internal olefin.

$$CF_3CF_2CF_2CF{=}CF_2 \xrightarrow[45\text{ hr.}]{F^-/120^\circ} CF_3CF_2CF{=}CFCF_3 \quad (95\%)$$

Indeed, a repeat of the polyfluoroalkylation reaction using the internal olefin gave the same mixture of products.

Considering the reaction scheme below:



It is of interest that there was no evidence for the formation of compound XXIX; this can be rationalized in terms of the relative stability of the carbanions. (<u>i.e.</u> assuming $k_1 \sim k_2$, then the stability of A >> B).

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

As this data was obtained at 33°, it will correspond to that of the most stable conformational isomer.

The spectrum of the mono-substituted pyridine exhibited peaks at: -91·2 [(relative intensity 3) $\underline{CF_3}CF_2$], -82·6 [(3) $\underline{CF_3}CF$], -75·4 v.broad [(2) 2,6F], -47·6 [(2) $CF_3\underline{CF_2}$], -39·1 [(2) $CF_3CF_2\underline{CF_2}$], -30·4 [(1) either 3 or 5F], -25·6 [(1) either 3 or 5F], and +16·8 p.p.m. [(1) $CF_2\underline{CF}CF_3$].

The spectrum of the di-substituted compound was of poor quality, and, due to extensive coupling, absorptions due to ring fluorine and tertiary fluorine could not be observed. The spectrum exhibited broad peaks at chemical shifts of: -91·6 $[C\underline{F}_3CF_2]$, -83·2 $[C\underline{F}_3CF]$, -48·2 $[CF_3C\underline{F}_2]$ and -39·6 p.p.m. $[CF_2C\underline{F}_2CF]$.

(ii) Branched Olefins.

Decafluoro-(2-methylbut-2-ene) (XXX), which was prepared by the action of fluoride ion on the terminal olefin, failed to react with pentafluoropyridine, even after 4 days at 200°.

$$(CF_3)_2C{=}CFCF_3 \xrightarrow[\text{sulpholan}]{\text{CsF}} (CF_3)_2\bar{C}CF_2CF_3$$

(XXX) (XXXI)

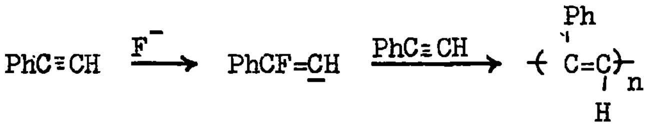
This can be attributed to the steric requirements of intermediate XXXI, and the inherent stability of a tertiary carbanion.

Section V

The Addition of Acetylenes to Pentafluoropyridine

(i) Phenylacetylene.

After shaking phenylacetylene with pentafluoropyridine at 160° for 23 hr. in the presence of fluoride ion, no product arising from the reaction of these two compounds could be isolated. Gummy material which was distilled from the reaction mixture had a molecular weight (determined by mass spectrometry) in excess of 1,400; column chromatography on alumina revealed that it was a mixture of polyphenylacetylenes, i.e.



$$PhC\equiv CH \xrightarrow{F^-} PhCF{=}\underset{-}{C}H \xrightarrow{PhC\equiv CH} \left(\overset{Ph}{C}{=}\underset{H}{C} \right)_n$$

(ii) Hexafluorobut-2-yne.

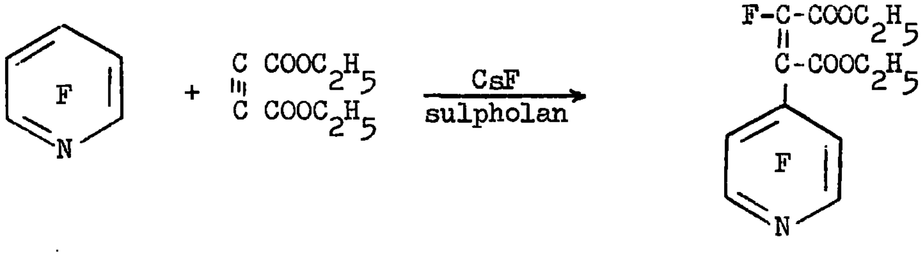
No reaction occurred between pentafluoropyridine and hexafluorobut-2-yne after 33 hr. at 130° in the presence of fluoride ion. Polymerisation of the acetylene took place, producing a light-grey material, of very high molecular weight. The molecular weight was recorded by mass spectrometry and varied with the probe temperature (e.g. 1156 at 250°; 1500 at 270°). Sublimation of this polymer at 110°, produced a small amount (3% of total weight) of white solid, the analysis of which gave the same empirical formula (C_4F_6) as the polymer.

Although the white solid was insoluble in the usual organic solvents, it was found to be slightly soluble in hexafluorobenzene and the N.M.R.

spectrum of this solution exhibited a mixture of broad peaks at 102-105 p.p.m. (i.e. CF_3). The mass spectrum of this material had significant mass peaks at ~1,450 (recorded at a probe temperature of 250°) and the I.R. spectrum, which was essentially the same as that of the parent material, resembled the spectrum of a polyperfluorobutyne which has been prepared[122] by irradiating (^{60}Co source) hexafluorobut-2-yne. The I.R. spectrum did not show a strong double bond absorption and, coupled with the absence of colour, it is likely that the polymer is of a cross-linked structure.

(iii) Diethyl Acetylene Dicarboxylate.

Several attempts at inducing reaction between this compound and pentafluoropyridine resulted in the formation of tars. However, at the optimum temperature of 135° after a 6 hr. reaction time, it was possible to isolate a small amount of the compound XXXII by v.p.c.



(XXXII)

The product was formed in 21% yield, based on the initial weight of pentafluoropyridine.

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

The spectrum of the product XXXII exhibited absorptions at (1) -71·5 p.p.m. (relative intensity 2), a complex unsymmetrical peak in the correct region for 2,6 ring fluorine, (2) -66·4 p.p.m. (relative intensity 1), an ill-defined triplet (J = 4 c.p.s.), which can be assigned to the olefinic fluorine, (3) two unlike absorptions of overall intensity 1, centred at -24·0 p.p.m. and -21·9 p.p.m., in the correct region for 3,5 ring fluorine. The appearance of two unlike peaks in this region could be credited to conformational isomerism but, as their relative intensities are not in the ratio 1:1, it is more likely that this is due to geometrical isomerism. Variable temperature N.M.R. studies will be necessary to establish this point.

^{1}H N.M.R. Data.

The proton spectrum of XXXII was that of two complex peaks centred at 4·3 and 1·3 p.p.m. from $(CH_3)_4Si$, in ratio 2:3 respectively. The methyl absorption was an unsymmetrical nine-peak multiplet; the methylene absorption was similarly complex.

EXPERIMENTAL WORK

Purification of Reagents.

The potassium and caesium fluorides used were reagent grade, dried by heating over a bunsen burner for several hours, and then stored in an oven at 150° until required. The sulpholan was dried and purified by repeated distillation under vacuum, collecting the middle fraction in each case, until the distillate solidified. It was then stored at 40° over a molecular sieve until required. Tetraglyme was dried by distillation from sodium under high vacuum.

The fluoro-olefins and acetylenes used were as supplied commercially except for

(1) chlorotrifluoroethylene, which was prepared by the dehalogenation of Isceon 113, using zinc dust and ethanol,

(2) C_5 olefins, the preparations of which will be referenced in the appropriate section.

Instruments.

Infrared (i.r.) spectra were recorded using Grubb-Parsons, type G.S.2A or "spectromaster" spectrometers, and a Perkin-Elmer "Infracord 137E" spectrophotometer. Samples were in the form of a thin liquid film between potassium bromide discs, or, in the case of gasses and volatile liquids, in a cylindrical cell with potassium bromide end windows. The cell could be attached to a vacuum-line by means of a ball joint. Solid samples were pressed into thin discs with potassium bromide.

Proton and fluorine nuclear magnetic resonance (N.M.R.) spectra were recorded on a Perkin-Elmer N10 spectrometer operating at 60 Mc/s. Samples which gave rise to weak signals were recorded with the help of a computer, which accumulated the spectrum. A variable temperature probe enabled spectra to be recorded at sample temperatures other than the standard 33°. However this device, and the computer only became available in the last few months of the work outlined in this thesis.

Mass spectra (M.S.) were recorded using an A.E.I. M.S.9. spectrometer, and all molecular weights were determined using this machine.

Analytical scale vapour phase chromatography (v.p.c.) was carried out using a Perkin-Elmer "Fractometer" model 451, the column packings which were most useful were (i) di-n-decylphthalate on celite (column "A") and (ii) silicone elastomer on celite (column "O"). A Griffin and George, D6 Gas Density Balance (G.D.B.) was also used for analytical work, and although resolution using this machine was not as good as the Perkin-Elmer, it had the advantage of needing no prior calibration. The number of moles of any compound present in the mixture is directly proportional to its peak area.

Typical Experimental Procedure.

Most polyfluoroalkylation reactions were carried out using a stainless-steel, 35 ml. autoclave which was shaken in a heater. The temperature was controlled by altering the applied voltage across the heater by means of a precalibrated variable transformer. The general technique employed when this autoclave was used is outlined below.

The required amount of metal fluoride was rapidly weighed out then placed in the autoclave. Immediately after this the solvent was added, followed by the substrate, and the autoclave sealed. After cooling in liquid air, an end screw was removed and replaced by a 2" threaded copper tube. The tube was connected to a vacuum-line, and a weighed amount of olefin added by vacuum-transfer. The end screw was then replaced, and the autoclave placed in the hot furnace, shaken at the required temperature, removed, and cooled to room temperature. After further cooling in liquid air, the autoclave was connected by means of rubber tubing and the copper tube to a two necked flask containing glass wool. This flask was coupled to a cold (liq.air) trap which was connected to a vacuum line. With the autoclave in liquid air, the system was evacuated; the autoclave was then warmed up after being inverted over the flask containing glass wool, by this means volatile material was transferred to the cold trap. On warming the flask it was possible to effect a vacuum distillation of the contents of the autoclave with no handling losses. This method was especially useful when, in high temperature reactions, tars were produced.

Products which would not easily distil under vacuum were isolated by solvent extraction of the material remaining in the flask. It was necessary to repeatedly wash the extracts with water in order to remove any solvent (or material derived from the solvent) that had been extracted.

Although this was the procedure for most experiments, some reactions were performed in Carius tubes and autoclaves equipped with pressure gauges; when this is the case it will be mentioned in the experimental.

(A) Reactions Involving Hexafluoropropene

(1) Using Polyfluoropyridines as Substrates.

(a) High Pressure Reactions

(i) In Sulpholan, using Pentafluoropyridine.

Pentafluoropyridine (5·0 g., 29·6 m.moles), anhydrous potassium fluoride (9·4 g.) and sulpholan (75 ml.) were placed into a 150 ml. rocking autoclave and hexafluoropropene (30 g., 200 m.moles) was condensed into it. The autoclave was evacuated, closed, and heated to 190° for 12 hr. The pressure rose to about 1,000 p.s.i., and then fell to about 600 p.s.i. after 30 min. The autoclave was cooled to room temperature, vented, and the contents poured into a round-bottomed flask and all of the reaction products were distilled out of the solvent by heating under vacuum. This distillate (32 g.) was fractionated at atmospheric pressure to give hexafluoropropene derivatives (24·2 g.) b.p. 20° - 115° and perfluoro-(alkylated pyridines) (7·8 g.) b.p. 115 - 195°. The latter was shown by v.p.c. (column "A", 100°) to consist of (a) perfluoro-(4-isopropylpyridine) (4·0 g., 42%) identified by comparison of I.R. spectrum with authentic material, (b) perfluoro-(2,4-di-isopropylpyridine) (2·9 g., 21%) b.p. 158-160° (Found: C, 27·9; F, 70·1%; M, 469. $C_{11}NF_{17}$ requires C, 28·1; F, 68·9%, M, 469) and (c) perfluoro-(tri-isopropylpyridines) (0·9 g., 5%) (Found: C, 27·3%; M, 619. $C_{14}NF_{24}$ requires C, 27·2%; M, 619).

(ii) In Tetraglyme, using Pentafluoropyridine.

Reaction (i) was repeated using hexafluoropropene (37 g., 250 m.moles), caesium fluoride (4·6 g.), pentafluoropyridine (5·0 g., 29·6 m.moles) and, as solvent, tetraglyme (90 ml.). The autoclave was heated to 150° for 12 hr., the maximum and minimum pressures being approximately the same as in (i). The products (40 g.) were worked up as before to give hexafluoropropene derivatives (34·4 g.) and perfluoro (alkylated pyridines) (5·6 g.). The latter consisted of perfluoro-(4-isopropylpyridine) (2·2 g., 23%), perfluoro-(2,4-di-isopropylpyridine) (2·5 g., 18%), and perfluoro-(tri-isopropylpyridine) (0·9 g., 5%).

(iii) In Sulpholan, using perfluoro-(di- and tri-isopropylpyridines).

Reaction (ii) was repeated using hexafluoropropene (50 g., 333 m.moles), caesium fluoride (3·0 g.), a mixture of perfluoro-(di- and tri-isopropylpyridines) in ratio 1:4 respectively, (5·1 g.), and sulpholan (20 ml.) in a 50 ml. rocking autoclave. The mixture was heated to 200° for 24 hr., the maximum and minimum pressures being approximately the same as in (i). The products were worked up as before to give hexafluoropropene derivatives (48 g.) and perfluoro-(alkylated pyridines) (4·0 g.). The latter consisted of perfluoro-(di-isopropylpyridine) (0·2 g.) and perfluoro-(tri-isopropylpyridines) (3·8 g.). Mass spectrometry indicated a trace of perfluoro-(tetra-isopropylpyridine) (M, 769) in the last fraction.

(iv) In Sulpholan, using Perfluoro-(tri-isopropylpyridines).

Reaction (iii) was repeated using hexafluoropropene (45 g.), caesium fluoride (3·0 g.), perfluoro-(tri-isopropylpyridine) (4·0 g.) and sulpholan (20 ml.) but in this case nitrogen was introduced into the autoclave so that the initial pressure while still at liquid air temperature, was 500 p.s.i. The maximum and final pressures were about 1500 and 1000 p.s.i. respectively. The products (40 g.) consisted of hexafluoropropene polymers (37 g.) and perfluoro-(tri-isopropylpyridine) (3·0 g.). Mass spectrometry indicated only a trace of perfluoro-(tetra-isopropylpyridine) in the latter.

(b) The Addition of Hexafluoropropene at an Elevated Temperature

Hexafluoropropene (45 g.; 0·3 moles) was loaded into a Baskerville autoclave (50 ml.) equipped with a pressure gauge and tap. This was coupled to a similar autoclave (100 ml.) containing pentafluoropyridine (17·3 g., 0·102 moles), sulpholan (60 ml.) and caesium fluoride (10·0 g., 0·65 moles). Both autoclaves were inserted into a heater, and warmed to 190° over 3 hr. The temperature inside the autoclave containing the reactants had been checked by pre-calibration using a thermometer. The initial pressure of the hexafluoropropene (i.e. at 190°) was 75 ats.; on opening the tap joining the autoclaves the pressure fell to 50 ats., after 30 min. it fell to 15 ats., and remained at this value. The heater was then switched off and the system allowed to cool. When cold, the 100 ml. autoclave was cooled in liquid air, and the junction broken.

After warming to room temperature, the contents were poured into water (500 ml.), and the bottom layer (60 g.) removed. No decomposition of the sulpholan had occurred, and the recovery of products was unusually high (94%). The organic layer was shown by v.p.c. (column "A", 100°C) to be a mixture of (a) products derived from hexafluoropropene (20%), (b) perfluoro-(4-isopropylpyridine) (32%), (c) perfluoro-(2,4-di-isopropylpyridine) (19%) and (d) perfluoro-(tri-isopropylpyridine) (29%).

(c) The Reaction of Perfluoro-(4-isopropylpyridine) with Sodium Methoxide.

To a stirred solution of perfluoro-(4-isopropylpyridine), (2·51 g., 7·87 m.moles) dissolved in methanol (20 ml.), was added a solution of sodium (0·167 g.) in methanol (20 ml.) over a period of 15 minutes at room temperature. The reaction mixture was stirred for a further 30 minutes, heated under reflux for 1 hr., then poured into water and the aqueous mixture extracted with methylene dichloride. The combined extracts were dried ($MgSO_4$), and the solvent distilled, leaving a pale yellow coloured oil. Distillation of this oil gave 4-heptafluoro-isopropyl-2-methoxy-3,5,6-trifluoropyridine, (2·3 g., 88%) b.p. 170°/760 mm. (Found: C, 32·8; H, 0·97. $C_9NF_{10}H_3O$ requires C, 32·6; H, 0·90%).

(d) The Action of Fluoride Ion on a Mixture of Perfluoro-(tri-isopropylpyridines).

A mixture of perfluoro-(tri-isopropylpyridines)(5·13 g.) was shaken in an autoclave (35 ml.) with caesium fluoride (4·5 g.) and sulpholan (24 ml.) at 180° for 14 hr. The contents were poured into water (200 ml.) and the products extracted with ether (3 x 15 ml.). Removal of solvent from the dried ($MgSO_4$) extracts left an almost pure (95%) compound (4·32 g., 84% recovery) which was identified by v.p.c. as one of the isomers present in the initial mixture of perfluoro-(tri-isopropylpyridines), b.p. 192 - 194°/760 mm. (Found: C, 27·2; F, 70·7; M, 619. $C_{14}NF_{23}$ requires C, 27·1; F, 70·6%; M, 619). The ratio of the isomers present in the initial and final mixtures as determined by v.p.c., is given on page 56, together with the implication of this result.

(e) The Reaction of Perfluoro-(2,4-di-isopropylpyridine) with Sodium Methoxide.

(i) In Methanol. To a stirred solution of perfluoro-(2,4-di-isopropylpyridine) (3·52 g., 7·52 m.moles) dissolved in methanol (30 ml.) was added a solution of sodium (0·171 g.) in methanol (20 ml.) over a period of 15 min. at room temperature. The solution was stirred under nitrogen overnight, then refluxed for 10 min. after which time it was poured into water (500 ml.) and the aqueous mixture extracted with methylene dichloride. The combined extracts were dried ($MgSO_4$) and removal of solvent left an oil (3·0 g.), b.p. 190 - 198°. V.p.c. (Aerograph, column "A", 145°) indicated that this was a mixture of two components, in ratio 2:3. Mass spectrometry, N.M.R., and analysis showed that the oil was a mixture of 5- and 6-methoxy perfluoro-(di-isopropylpyridines)

(81% yield) (Found: C, 30·0; H, 0·61%; M, 481. $C_{12}F_{16}NOH_3$ requires C, 29·9; H, 0·62%; M, 481).

(ii) In Sulpholan. Sodium wire (0·100 g.) was dissolved in methanol and the excess methanol removed by distillation. After drying the sodium methoxide for 12 hr. at 120° under vacuum, perfluoro-(2,4-di-isopropylpyridine) (2·00 g., 4·26 m.moles) in sulpholan (50 ml.) was added under nitrogen. The mixture was stirred at 40° for 90 min. then poured into water (500 ml.) and the aqueous mixture extracted with methylene dichloride. Removal of solvent from the extracts left an oil (1·3 g.), the chromatogram (Aerograph, column "A", 145°) of which indicated that it was a mixture of mono-methoxy isomers (approx. ratio 2:3) and higher boiling material thought to be di- and tri-methoxy derivatives in ratio 9:1 respectively.

(f) The Action of Fluoride Ion on a Mixture of 5- and 6-Methoxy perfluoro-(2,4-di-isopropylpyridines).

The mixture of methoxides obtained in experiment e(i) (2·2 g.) was shaken with caesium fluoride (2·7 g.) and sulpholan (20 ml.) in an autoclave (35 ml.) at 50° for 12 hr. The contents were then poured into water (250 ml.), ether extraction of which gave the rearranged mixture (2·0 g.). The chromatogram (Aerograph, column "A" 140°) of this indicated that the ratio of isomers had changed, and a third compound of similar retention time had been produced. The initial and final ratios of methoxides, as estimated by v.p.c., are given on page 60.

Analysis and mass spectrometry showed that all three components were monomethoxy di-isopropyl derivatives. (Found: C, 29·7%; M, 481. $C_{12}F_{16}NOH_3$ requires: C, 29·9%; M, 481).

(g) The Attempted Addition of Hexafluoropropene to 4-Substituted Tetrafluoropyridines.

(i) 4-Chlorotetrafluoropyridine: A mixture of hexafluoropropene (9·5 g., 63·3 m.moles), caesium fluoride (2·7 g., 17·8 m.moles), 4-chlorotetrafluoropyridine (3·0 g., 16·2 m.moles) and sulpholan (20 ml.) was shaken in an autoclave (35 ml.) at 180° for 12 hr. The autoclave was opened, the contents poured into water (100 ml.) and the aqueous solution ether extracted (3 x 30 ml.). Removal of ether from the dried ($MgSO_4$) extracts left a liquid (5 g.), which was shown by v.p.c. (column "O" 100°) to be a mixture of the trimers of hexafluoropropene and 4-chlorotetrafluoropyridine only.

(ii) 4-Methoxytetrafluoropyridine: The above experiment was repeated on the same scale using 4-methoxytetrafluoropyridine in place of 4-chlorotetrafluoropyridine. After shaking at 160° for 14 hr. the contents were examined in an identical manner, and it was concluded that only material derived from hexafluoropropene, and the substrate, was present.

(h) A Comparison of the Effectiveness of Sulpholan and Tetraglyme for the Polyfluoroalkylation of Octafluorotoluene.

Octafluorotoluene (4·6 g., 19·4 m.moles), caesium fluoride (6·8 g., 42·7 m.moles) and sulpholan (20 ml.) were introduced into a Carius tube (100 ml.) into which hexafluoropropene (8·0 g., 53·3 m.moles) was then condensed. The tube was sealed under vacuum and shaken for 20 hr. at 175°, then cooled in liquid air, opened, and the volatile contents (9·9 g.) removed by distillation under high vacuum. The distillate was shown by comparison of v.p.c. retention times (column "A", 130°) with authentic materials to be a mixture of (i) polymers of hexafluoropropene (4·8 g.), (ii) octafluorotoluene (2·5 g.) and (iii) perfluoro-(4-isopropyltoluene) (2·6 g.).

The experiment was repeated using tetraglyme (20 ml.) instead of sulpholan, and potassium fluoride (5·0 g., 86·7 m.moles) instead of caesium fluoride in both tetraglyme and sulpholan. The composition of the distillates as determined from the v.p. chromatograms are given in Table 2, (page 64).

(i) A Comparison of the Effectiveness of Sulpholan and Tetraglyme for the Polyfluoroalkylation of Pentafluoropyridine.

Pentafluoropyridine (3·0 g., 17·7 m.moles), caesium fluoride (3·0 g., 19·2 m.moles) and tetraglyme (15 ml.) were placed into a Carius tube and hexafluoropropene (5·0 g., 33·3 m.moles) was condensed into the tube. The tube was evacuated, sealed, and shaken on a vibroshaker for 18 hr. at room temperature. After this time the tube was cooled in liquid air, opened, and all volatiles (7·8 g.) removed by vacuum distillation up to 60°. Chromatography (G.D.B., column "A", 100°) indicated that the volatiles were a mixture of material derived from hexafluoropropene and perfluoro-(mono-, di-, and tri-isopropyl-pyridines) in ratio 5:84:8:4% respectively.

This experiment was a repeat of one by Storey, in which sulpholan was used as the solvent (p.63, Table 1, reaction 9). It was reported that no di- and tri-alkylated products were formed.

(j) The Attempted Addition of Hexafluoropropene to Pentafluoropyridine in Sulphur Dioxide.

(i) Pentafluoropyridine (6·0 g., 35·5 m.moles), potassium fluoride (2·0 g., 34·5 m.moles), hexafluoropropene (9·0 g., 60 m.moles), and sulphur dioxide (20 ml.) were loaded into a Carius tube which was then sealed and shaken at ambient temperature for 40 hrs. After cooling in liquid air the tube was opened and all volatile material transferred to a flask. The volatiles were fractionated up a 2' vigreux column at room temperature, and the residual liquid (5·8 g.) examined for the presence of perfluoro-alkylated pyridines. V.p.c. and N.M.R. spectroscopy indicated that it was essentially pure pentafluoropyridine.

The above experiment was repeated on the same scale, using caesium fluoride as the initiator. Only unchanged pentafluoropyridine was recovered.

(ii) The above experiments were repeated in a stainless-steel autoclave residue (0·1 g.) which remained after distillation of the pentafluoropyridine, there was no evidence that reaction had occurred.

(k) Composition of Mixture of Derivatives of Hexafluoropropene.

The polymeric products (20 g.) obtained from several experiments were combined and separated by preparative scale v.p.c. (column "A", 80°) to give (i) a dimer, b.p. 50·5, (9·2 g., 46%) and (ii) a mixture of three trimers (10·8 g., 54%). The dimer still showed as a single compound on the same v.p.c. column at 25° (Found: C, 23·9; F, 76·3; M, 300. Calc. for C_6F_{12}: C, 24·0; F, 76·0%; M, 300). The mass spectrum showed fragments with masses 281 (C_6F_{11}), 231 (C_5F_9), 212 (C_5F_8), 181 (C_4F_7), 143 (C_4F_5), 131 (C_3F_5), 93 (C_2F_3) and 69 (CF_3); and the double bond absorbed in the infrared at 5·92μ. Comparison of the infrared and N.M.R. spectra of the dimer with the corresponding data for the compound $(CF_3)_2C{=}CFCF_2CF_3$ indicates that the dimer consists principally of this compound. The reference compound had been prepared previously at Durham by Vince[123] from a reaction between hexafluoropropene and trimethylamine. The ^{19}F chemical shifts obtained from the N.M.R. spectrum of the dimer are given below in a comparison with those obtained by Vince.

Assignment	Chemical shifts from CF_3COOH as reference	
	Values recorded by Vince	Recorded values
$(CF_3)_2C=C$	-23·5	-23·9
$(CF_3)_2C=C$	-21·0	-21·1
CF_3-C-	+2·1	+2·3
$-CF=$	+16·4	+16·5
$-CF_2-$	+35·5	+35·5

However there were additional minor peaks in the spectrum indicating the presence of a small amount of another compound, probably $(CF_3)_2CFCF=CFCF_3$. The N.M.R. data given above is partly at variance with the corresponding data given by Dresdner[43] and co-workers for $(CF_3)_2C=CFCF_2CF_3$; it is possible that this difference could be accounted for by different referencing conditions.

The mixture of trimers could not be separated on the columns available, but analyses of two fractions obtained by partial separation both gave a molecular ion in the mass spectrum at 450 and the same elemental analyses (Found: C, 23·9; F, 76·1; and C, 23·9; F, 75·4 respectively. Calc. for C_9F_{18}: C, 24·0; F, 76·0%).

(2) The Reaction Between Heptafluoroquinoline[124] and Hexafluoropropene.

A mixture of heptafluoroquinoline (8·0 g., 31·4 m.moles), hexafluoropropene (13·5 g., 89·9 m.moles), caesium fluoride (5·0 g., 32·9 m.moles) and dry tetraglyme (50 ml.) was shaken in a Carius tube at room temperature for 14 hr. After cooling in liquid air the tube was opened and residual olefin (0·1 g.) collected in a cold (liq. air) trap. The contents of the tube were poured into water (200 ml.) and the bottom layer, which was an orange gummy liquid (18·0 g.), removed, washed with water, and distilled to 180°. The distillate (2·2 g.) was identified by v.p.c. as olefin dimers and trimers. The chromatogram (G.D.B., column "A", 150°) of the residual gum showed that it was a five-component mixture, one of which (5%) had a retention time identical with that of heptafluoroquinoline. Separation of this mixture by fractional sublimation proved to be impossible, but separation of the two major components was achieved by the use of preparative-scale v.p.c. (Aerograph, column "A", 150°). These compounds were subsequently identified as (i) <u>perfluoro-(2,4-di-isopropylquinoline)</u>, a straw liquid, b.p. 256° (yield, estimated from chromatogram, 49% based on heptafluoroquinoline consumed) (Found: C, 32·3; F, 64·0%; M, 555. $C_{15}F_{19}N$ requires C, 32·4; F, 65·4%; M, 555) and (ii) <u>perfluoro-(2,4,X-tri-isopropylquinoline</u>) (where X = 6 or 7; see page 71) a liquid, b.p. $\geqslant 268$ (estimated yield 26% based on amount (7·4 g.) of heptafluoroquinoline consumed) (Found: C, 30·9; F, 67·2%; M, 705. $C_{18}F_{25}N$ requires C, 30·7; F, 67·4%; M, 705).

(3) <u>The Reaction Between Heptafluoroisoquinoline[124] and Hexafluoropropene</u>.

(i) A mixture of heptafluoroisoquinoline (1·8 g., 7·5 m.moles), caesium fluoride (4·2 g., 27·6 m.moles), hexafluoropropene (4·0 g., 26·7 m.moles) and sulpholan (21 ml.) was shaken in an autoclave (35 ml.) at 150° for 20 hr. The autoclave was cooled, opened and the contents poured into water (175 ml.). After extraction with methylene chloride (3 x 20 ml.) the combined extracts were washed with water (3 x 10 ml.), dried ($MgSO_4$) and removal of solvent left an orange gum (3·0 g.). Analytical scale v.p.c. (column "O", 170°) indicated this to be a mixture containing heptafluoroisoquinoline (30%), trimers of hexafluoropropene and two products which appeared to be inseparable.

Further Polyfluoroalkylation: The mixture obtained from the above experiment was shaken in an autoclave (35 ml.) with caesium fluoride (2·0 g., 13·1 m.moles), sulpholan (20 ml.) and hexafluoropropene (9·0 g., 60m.m.) at 100° for 20 hr. After opening the autoclave, the contents were worked up in the same manner to produce a gum (3·4 g.), the chromatogram of which indicated that the proportion of substrate had fallen to 10% and the number of products had increased to three. A mass spectrum of the mixture had significant mass peaks at 705, 855 and 1,005 which would correspond to derivatives containing 3, 4 and 5 heptafluoroisopropyl groups.

(ii) A mixture of heptafluoroisoquinoline (2·4 g., 9·4 m.moles), caesium fluoride (3·0 g., 19·7 m.moles), hexafluoropropene (7·3 g., 48·7 m.moles) and tetraglyme (25 ml.) was shaken in a Carius tube at room temperature for 12 hr. The tube was opened and the contents worked up as in the previous experiments to give a five-component mixture

(4·2 g.), one of which was identified by v.p.c. retention time as heptafluoroisoquinoline (33% recovery estimated from chromatogram). Two products were separated in small amounts by preparative scale v.p.c. (Aerograph, column "A", 140°) and identified as (i) a perfluoro-(tetra-isopropylisoquinoline), a white solid, m.p. 105-106° (from ethanol/water) (Found: C, 29·4; M, 855. $C_{21}F_{31}N$ requires C, 29·5%; M, 855) and (ii) perfluoro-(1,4,X-tri-isopropylisoquinoline (where X = 6 or 7; see page 74) a straw oil b.p. ~ 240° (Found: C, 30·5%; M, 705. $C_{18}F_{25}N$ requires: C, 30·6%; M, 705). The yields of these compounds, as estimated from the chromatogram, were 4% (tetra) and 28% (tri).

(4) The Attempted Addition of Hexafluoropropene to Octafluoronaphthalene.[125]

A mixture of octafluoronaphthalene (2·9 g., 10·7 m.moles), caesium fluoride (2·4 g., 15·8 m.moles), hexafluoropropene (7·0 g., 46·6 m.moles) and sulpholan (20 ml.) was shaken in an autoclave (35 ml.) at 160° for 16 hr. After opening the autoclave, the contents were extracted in the usual manner, to give unchanged octafluoronaphthalene (2·6 g.; 90% recovery) and material derived from hexafluoropropene.

(5) The Reaction of Hexafluoropropene with Decafluorobiphenyl.[126]

A mixture of decafluorobiphenyl (5·0 g., 15·0 m.moles), hexafluoropropene (6·5 g., 43·3 m.moles), caesium fluoride (2·0 g., 13·2 m.moles) and sulpholan (20 ml.) was shaken in an autoclave (35 ml.) at 160° for 19 hr. The contents were ether extracted in the usual manner to give a mixture (6·8 g.) of decafluorobiphenyl and a product, both of which were isolated by preparative scale v.p.c. (Aerograph, column "O", 170°) and characterized by ^{19}F N.M.R. spectroscopy. The product was identified as perfluoro-(4-isopropylbiphenyl), 2·1 g. (29% yield), a solid m.p. 68-69° (from hexane) (Found: C, 37·4; F, 62·4%; M, 484. $C_{15}F_{16}$ requires C, 37·2; F, 62·8%; M, 484).

(6) The Reaction of 2,4-Dinitrofluorobenzene with Hexafluoropropene.

An autoclave (35 ml.) containing 2,4-dinitrofluorobenzene (2·0 g.; 10·7 m.moles), caesium fluoride (2·0 g., 13·3 m.moles), and sulpholan (20 ml.) was shaken at 190° for 16 hr.; after cooling and venting the contents were poured into water. A considerable amount of tarry material was precipitated and this was continuously extracted with benzene for 24 hr. After washing with water, the benzene layer yielded a deep red liquid (2·0 g.) which was distilled under high vacuum; the distillate contained mainly two components of very similar retention time. These components were isolated by preparative scale v.p.c. (Aerograph, column "O", 180°) and shown to be a mixture of 2-heptafluoroisopropyl-4-nitro and 4-heptafluoroisopropyl-2-nitro-fluorobenzene. (Found: C, 34·7; F, 48·7%; M, 309. $C_9H_3F_8NO_2$ requires C, 34·9; F, 49·2%; M, 309).

(7) A Comparison of the Reactivity of Heptafluoroquinoline (C_9F_7N), Heptafluoroisoquinoline (i-C_9F_7N) and Pentafluoropyridine (C_5F_5N).

Hexafluoropropane, C_5F_5N and either i-C_9F_7N or C_9F_7N, in approximately equimolar quantities, were sealed into an autoclave (35 ml.) with sulpholan (20 ml.) and caesium fluoride (3·0 g.). After shaking at 40° for 12 hr. the autoclave was opened and the contents poured into water which was extracted with methylene dichloride (2 x 10 ml.).

After adding a known weight of C_6F_6 to the extracts, several integrations of the ^{19}F N.M.R. spectrum of the mixture were determined using different field strengths (in order to detect saturation). Due to overlap, the areas of only three of the best defined peaks for each substrate were summed for each integration. The six best integrations were chosen, and the total summation for each substrate was used to determine relative concentrations.

Theory: The rate constant k_i/k_j for substrates i and j, is given by the expression:

$$\frac{k_i}{k_j} = \frac{\log_{10} \frac{n_i}{h_i^o}}{\log_{10} \frac{n_j}{n_j^o}} \qquad (128)$$

where n_i^o refers to the initial number of moles of i, similarly n_j^o. The number of moles of i in the mixture (n_i) is given by

$$n_i = \frac{A_i n_s}{A_s}, \text{ similarly } n_j = \frac{A_j n_s}{A_s},$$

where s refers to the number of moles of standard added, and A to the integration step height (i.e. area of peak).

Results:

(A) $i\text{-}C_9F_7N$ vs. C_5F_5N

	n_o	A
C_5F_5N (p)	0·02714 m	74·6 units
$i\text{-}C_9F_7N$ (i-q)	0·02767 m	64·2 "
C_6F_6 (s)	0·01124 m	34·6 "

$$n_p = \frac{A_p n_s}{A_s} = 0{\cdot}02423; \qquad \frac{n_p}{n_p^o} = 0{\cdot}8928$$

$$n_{i-q} = \frac{A_{i-q} n_s}{A_s} = 0{\cdot}02085; \qquad \frac{n_{i-q}}{n_{i-q}^o} = 0{\cdot}7535$$

$$\therefore \quad \frac{k_{i-q}}{k_p} = \frac{\log_{10} 0{\cdot}7535}{\log_{10} 0{\cdot}8928} = 2{\cdot}49$$

$$\therefore \quad \underline{k_{i-q} \sim 2{\cdot}5\, k_p}$$

(B) C_9F_7N vs. C_5F_5N

	n_o	A
C_5F_5N (p)	0·03089 m	55·6 units
C_9F_7N (q)	0·02659 m	36·6 "
C_6F_6 (s)	0·01785 m	49·6 "

$$n_p = \frac{A_p n_s}{A_s} = 0{\cdot}02000; \quad \frac{n_p}{n_p^o} = 0{\cdot}6475$$

$$n_q = \frac{A_q n_s}{A_s} = 0{\cdot}01317; \quad \frac{n_q}{n_q^o} = 0{\cdot}4953$$

$$\therefore \quad \frac{k_q}{k_p} = \frac{\log_{10} 0{\cdot}4953}{\log_{10} 0{\cdot}6475} = 1{\cdot}61$$

$$\therefore \quad \underline{k_q \sim 1{\cdot}6\ k_p}$$

(B) Reactions Involving Octafluorobut-2-ene

(1) Using Polyfluoropyridines as Substrates.

(a) Pentafluoropyridine.

Pentafluoropyridine (4·7 g., 36·0 m.moles), caesium fluoride (1·0 g., 6·6 m.moles), and sulpholan (15 ml.) were loaded into an autoclave (35 ml.) and octafluorobut-2-ene (11·1 g., 170 m.moles) introduced from a vacuum system. After sealing, the autoclave was shaken at 185° for 91 hr., cooled and a gas vented which was identified by I.R. spectroscopy as unchanged octafluorobut-2-ene (2·6 g., 23% recovery). The contents of the autoclave were ether extracted (3 x 20 ml.) after which the extracts were washed with water, dried ($MgSO_4$), and distilled to 120°. The distillate was examined by analytical scale V.P.C. and seen to be a mixture of solvent, pentafluoropyridine and the dimer of octafluorobut-2-ene. The residue was similarly examined (column "O", 125°) and found to be essentially a two component mixture which was separated by preparative-scale v.p.c. into (i) perfluoro-(4-sec.-butylpyridine) (6·4 g.; yield, estimated from the amount of substrate reacted, 67%) (Found: C, 29·4; F, 67·2%; M, 369. $C_9F_{13}N$ requires C, 29·3; F, 66·9%; M, 369), b.p. 147-148°.
(ii) Perfluoro-(2,4-di-[sec.-butyl]pyridine) b.p. 194° (3·3 g.; 23% yield, based on 94% of substrate consumed) (Found: C, 27·4; F, 71·6%; M, 569. $C_{13}F_{21}N$ requires C, 27·4; F, 70·3%; M, 569). A trace amount of a third compound was also collected, of molecular weight 769, corresponding

to the tri-substituted pyridine.

(b) 4-Chlorotetrafluoropyridine.

Octafluorobut-2-ene (9·0 g., 45·0 m.mole) was condensed into an autoclave containing 4-chlorotetrafluoropyridine (2·4 g., 12·9 m.moles), caesium fluoride (3·7 g., 24·4 m.moles) and sulpholan (20 ml.). After shaking at 170° for 14 hr. the autoclave was cooled, vented, and the contents poured into water (300 ml.). The aqueous mixture was ether-extracted, and removal of solvent gave an essentially three component mixture. This was separated by preparative-scale v.p.c. (Aerograph column "O", 160°) into (i) unchanged substrate, (ii) perfluoro-(4-sec.-butylpyridine), (iii) perfluoro-(2,4-di-sec.-butylpyridine), all of which were identified by I.R. and ^{19}F N.M.R. spectroscopy. The conversion of 4-chlorotetrafluoropyridine to compounds (ii) and (iii) was 46 and 42% respectively, (estimated from chromatogram).

(c) 4-Methoxytetrafluoropyridine.

Experiment (b), above, was repeated using 4-methoxytetrafluoropyridine (5·0 g., 27·6 m.moles), caesium fluoride (4·0 g., 25·3 m.moles), octafluorobut-2-ene (13·0 g., 65 m.moles), and sulpholan (17 ml.). Ether extraction in the usual manner gave unchanged 4-methoxytetrafluoropyridine (3·4 g., 68% recovery) only.

(2) Using Pentafluorophenyl Compounds as Substrates.

(a) Pentafluorobromobenzene.

A mixture of pentafluorobromobenzene[125] (7·2 g., 29·1 m.moles), octafluorobut-2-ene (7·2 g., 36·0 m.moles), caesium fluoride (3·0 g., 20 m.moles) and sulpholan (20 ml.) was shaken in an autoclave (35 ml.) at 180° for 12 hr. after which time it was cooled, vented, and the contents ether extracted in the usual manner. The material extracted (6·8 g.) was shown by v.p.c. (Autoprep, column "O", 80°) to consist of pentafluorobromobenzene and hexafluorobenzene in ratio 15:85; small amounts of both compounds were isolated and identified by I.R. spectroscopy.

(b) Hexafluorobenzene.

The experiment above was repeated, on approximately the same scale, using hexafluorobenzene. The autoclave was shaken at 200° for 48 hr. and, apart from material derived from octafluorobut-2-ene, only hexafluorobenzene was recovered.

(c) Octafluorotoluene.

Octafluorotoluene[125] (6·6 g., 27·9 m.moles), caesium fluoride (3·0 g., 19·7 m.moles) and sulpholan (17 ml.) were loaded into an autoclave (35 ml.) into which octafluorobut-2-ene (11·7 g., 58·5 m.moles) was condensed under vacuum. After sealing the autoclave it was shaken at 150° for 16 hr., cooled and all volatile material removed by vacuum transfer. This was distilled at atmospheric pressure into two fractions: (i) b.p. 105-107°, (10·1 g.) a mixture of the dimer of octafluorobut-2-ene and octafluorotoluene, (ii) b.p. 167-170° (3·6 g.), essentially a single compound (~95%) which was obtained pure by preparative scale v.p.c. (Aerograph, column "O", 150°) and identified as perfluoro-(4-sec. butyltoluene) (3·5 g.; ~90% yield, based on 32% substrate consumed), (Found: C, 30·2; F, 69·7%; M, 436. $C_{11}F_{16}$ requires C, 30·3; F, 69·7%; M, 436) b.p. 171°.

(d) Decafluorobiphenyl.

(i) A mixture of decafluorobiphenyl[126] (5·0 g., 15·0 m.moles), octafluorobut-2-ene (8·7 g., 43·5 m.moles), caesium fluoride (3·2 g., 21·1 m.moles) and sulpholan was shaken at 160° for 14 hr. in an autoclave (35 ml.). After cooling, the volatile material (2·0 g.) was vented, the contents of the autoclave poured into water, and the aqueous mixture ether extracted (2 x 20 ml.). The extracts were washed, dried ($MgSO_4$), and removal of solvent left a brown solid (6·1 g.), the chromatogram of which (G.D.B., column "O", 160°) indicated that it was a mixture of decafluorobiphenyl and a product in ratio 9:1 respectively. Due to similar retention times on the columns available it was not possible to isolate the product.

(ii) Further polyfluoroalkylation: The mixture isolated from experiment (i) was loaded into an autoclave (35 ml.) containing caesium fluoride (3·0 g., 19·7 m.moles) and sulpholan (20 ml.). After octafluorobut-2-ene (8·0 g., 40 m.moles) was condensed into the autoclave, it was sealed and shaken at 190° for 14 hr. The autoclave was opened and, in a similar procedure to the above experiment, a gummy solid (6·4 g.) extracted. This solid was seen (G.D.B., column "O", 180°) to be a three component mixture, the separation of which was achieved using preparative scale v.p.c. (Aerograph, column "O", 180°) into (i) decafluorobiphenyl (36% of mixture), (ii) perfluoro-(4-sec.-butylbiphenyl) (2·9 g.; 70% yield, based on 46% substrate consumed) (Found: C, 36·1; F, 64·3%; M, 534. $C_{16}F_{18}$ requires C, 36·0; F, 64·0%; M, 534). A liquid, b.p. > 220°, (iii) perfluoro-(4,4'-di-sec.-butylbiphenyl) (0·6 g., 10%) (Found: C, 32·8; F, 67·5%; M, 734. $C_{20}F_{26}$ requires C, 32·7; F, 67·3%; M, 734) a high boiling gum.

(e) Pentafluoronitrobenzene.

Pentafluoronitrobenzene[127] (4·2 g., 19·7 m.moles), caesium fluoride (5·0 g., 32·9 m.moles) and sulpholan (19 ml.) were loaded into an autoclave into which octafluorobut-2-ene (7·0 g., 35·0 m.moles) was condensed. After shaking at 150° for 15 hr. the autoclave was cooled, opened, and all volatile material (9·1 g.) distilled from the sulpholan. Fractionation to 120° of this material gave (i) octafluorobut-2-ene and its dimer (3·9 g.) and (ii) an almost pure compound (5·2 g.), a small amount of which was obtained pure by preparative scale v.p.c. (Aerograph, column "O", 120°) and subsequently characterized as perfluoro-(sec.-butylbenzene) b.p. 148·5° (4·9 g., 68%) (Found: C, 31·0; F, 68·6%; M, 386. $C_{10}F_{14}$ requires C, 31·1; F, 68·9%; M, 386).

(f) The Reaction of Pentafluoronitrobenzene with Sodium Methoxide in Sulpholan.

Sodium wire (0·55 g., 23·9 m.moles) was dissolved in methanol, the excess methanol removed by distillation, and the sodium methoxide dried under vacuum at 140° for 16 hr. After addition of sulpholan (75 ml.), pentafluoronitrobenzene (5·1 g., 23·9 m.moles) was added rapidly at 32°, and the temperature of the mixture rose ~ 10°. The solution was stirred for 30 mins. and poured into water, ether extraction of which gave a red liquid (4·8 g.). Analytical scale v.p.c. (column "O", 120°) indicated that this was mainly unchanged pentafluoronitrobenzene, but examination of the ^{19}F and ^{1}H N.M.R. spectra, both of which were complex, revealed that it was more likely to be a mixture of mono- and di-methoxy polyfluoronitrobenzenes and pentafluoronitrobenzene. The spectra were examined for the presence of pentafluoroanisole and it was concluded that it was absent. The above mixture was injected, with pentafluoroanisole, onto columns "O" and "A"; no material which had the same retention time as pentafluoroanisole was present.

(3) Using Octafluoronaphthalene as Substrate.

A mixture of octafluoronaphthalene[123] (2·7 g., 9·9 m.moles), caesium fluoride (5·2 g., 34·2 m.moles), octafluorobut-2-ene (6·1 g., 30·5 m.moles) and sulpholan (20 ml.) was shaken in an autoclave (35 ml.) for 16 hr. at 160°. After cooling, venting and opening, the contents were worked up in the usual manner to give a gum (3·6 g.) the chromatogram (G.D.B., column "O", 170°) of which indicated that it was a mixture of three components; these were separated by preparative-scale v.p.c. and characterized as (i) octafluoronaphthalene, (ii) perfluoro-(2-sec.-butylnaphthalene) (Found: C, 35·5; F, 64·2%; M, 472. $C_{14}F_{16}$ requires C, 35·6; F, 64·4%; M, 472) a solid, m.p. 69° (from hexane), (iii) a perfluoro-[di-(sec.-butyl)naphthalene] (Found: C, 32·2; F, 68·0%; M, 672. $C_{18}F_{24}$ requires C, 32·1; F, 67·8%; M, 672) a gum, b.p. > 240°, in approximately 40 and 60% yield respectively (based on 20% of initial weight of octafluoronaphthalene consumed).

(4) Using Heptafluoroquinoline as Substrate.

An autoclave (35 ml.) containing heptafluoroquinoline (8·0 g., 31·4 m.moles), octafluorobut-2-ene (5·4 g., 27·0 m.moles), caesium fluoride (5·0 g., 32·9 m.moles) and sulpholan (20 ml.) was shaken for 12 hr. at 100°. After cooling, the autoclave was vented and the contents poured into water (200 ml.); ether extraction in the usual manner gave a yellow paste (12·8 g.) which was shown by v.p.c. (G.D.B., column "A", 150°) to be a five-component mixture, in ratio (1) 30(2), 16(3), 11(4) 43% (fifth component was a shoulder on peak (2)). The two major components were separated by v.p.c. (Aerograph, column "A", 150°) and identified as heptafluoroquinoline (peak 4, 5·5 g., estimated recovery 70%) and perfluoro-[2,4-di(sec.-butyl)quinoline] (3·9 g. 28%, based on initial weight of substrate) (Found: C, 31·3; F, 66·6%; M, 655. $C_{17}F_{23}N$ requires C, 31·1; F, 66·7%; M, 655) a straw gum, b.p. > 240°. A mass spectrum of the mixture had significant mass peaks at 455, 655, 855 and 1055 mass units, corresponding to mono-, di-, tri- and tetra-substituted quinolines.

(5) Using Heptafluoroisoquinoline as Substrate.

A mixture of heptafluoroisoquinoline (6·1 g., 23·9 m.moles), octafluorobut-2-ene (13·5 g., 67·5 m.moles), caesium fluoride (5·0 g., 32·9 m.moles) and sulpholan (20 ml.) was shaken in an autoclave at 100° for 12 hr. After cooling and venting the autoclave, the contents were poured into water (100 ml.) and ether extracted (3 x 20 ml.). The extracts were washed with water, dried, and removal of solvent by distillation to 190° left a viscous liquid (11·5 g.), the chromatogram of which (G.D.B., 150°, column "O") indicated that is contained two major components. One of these was identified by v.p.c. retention time as heptafluoroisoquinoline (recovery, estimated from the chromatogram, 1·8 g., 30%). The other major component (which could be separated by neither distillation nor fractional sublimation) was isolated by preparative-scale v.p.c. (column "A", 150°) and identified as perfluoro-[1,4,X-tri-(sec.-butyl)isoquinoline] (where X = 6 or 7; see page 100) (yield, estimated from chromatogram, 42%) (Found: C, 29·6; F, 68·5%; M, 855. $C_{21}F_{31}N$ requires C, 29·5; F, 68·9; M, 855) a high boiling (~240°) gum.

(6) Investigation of the Dimer of Octafluorobut-2-ene.

Octafluorobut-2-ene (7·5 g., 37·5 m.moles) was condensed into an autoclave (35 ml.) containing caesium fluoride (6·0 g., 39·5 m.moles) and sulpholan (17 ml.). After sealing, the autoclave was shaken at 190° for 16 hr., cooled in liquid air, opened, and all volatile material distilled from the sulpholan. This was distilled into two pure fractions (1) b.p. ~ room temperature, identified by I.R. spectroscopy as octafluorobut-2-ene (4·3 g., 57% recovery), (2) perfluoro-(3,4-dimethylhexene-3) (3·0 g., 20%) a liquid, b.p. 108° (Found: C, 23·8; F, 76·5%; M, 400. C_8F_{16} requires C, 24·0; F, 76·0%; M, 400), identified by ^{19}F N.M.R. spectroscopy (p.88).

(C) Reactions of Fluoroethylenes with Aromatic Substrates.

(1) The Reaction Between Tetrafluoroethylene and Pentafluoropyridine.

Pentafluoropyridine (10·0 g., 59·3 m.moles), caesium fluoride (3·0 g., 19·5 m.moles) and sulpholan (80 ml.) were introduced into a 150 ml. rocking autoclave which was then cooled in liquid air, evacuated, and tetrafluoroethylene (60·8 g., 0·6 mole) added. The autoclave was heated to 170°; after 30 min. the pressure rose to 2,600 p.s.i. and then fell to 600 p.s.i. after two hours. After a total of 24 hours the autoclave was cooled to room temperature and vented through a liquid air trap where tetrafluoroethylene (38 g., identified by I.R. spectroscopy) collected. The residue in the autoclave was poured into water (400 ml.) and the whole extracted with ether (4 x 30 ml.). After drying the extracts ($MgSO_4$) and removal of ether, a residue (30 g.) remained which was fractionated to give (i) a liquid, b.p. up to 140° at atmospheric pressure (5 g.), (ii) a liquid b.p. 70° - 100° under high vacuum (10 g.), (iii) a liquid b.p. 100° - 200° under high vacuum (10 g.) and a tarry residue (~5 g.). All three fractions were shown by v.p.c. (column "A", 100°) to be a six-component mixture, the proportions of the constituents varying with the boiling range of the fraction. The first component was shown from its retention time to be pentafluoropyridine and, although retention times of the products were similar, it was possible to isolate small quantities of the last two components by repeated injection. They were shown to be perfluoro-(pentaethylpyridine) (Found: F, 71·6%; M, 669. $C_{15}F_{25}N$ requires F, 71·0%; M, 669) m.p. 77-78° (from ethanol/

water) and perfluoro-(tetraethylpyridine) (Found: M, 569. $C_{13}F_{21}N$ requires M, 569). Assuming the other compounds to be the mono-, di-, and tri-substituted fluoropyridines, the chromatogram indicates yields of 30% (mono-), 21% (di-), 21% (tri-), 11% (tetra-), and 6% perfluoro-(pentaethylpyridine).

(2) Reactions Attempted Using Trifluoroethylene.

(a) Pentafluoropyridine.

A mixture of pentafluoropyridine (7·0 g., 41·4 m.moles), caesium fluoride (2·5 g., 16·4 m.moles), trifluoroethylene (8·6 g., 10·5 m.moles) and sulpholan was shaken at 200° for 46 hr. After cooling in liquid air the autoclave was opened, and all the volatile material (13·0 g.) distilled from the solvent; this was fractionated at room temperature into trifluoroethylene (7·4 g., 86% recovery) and pentafluoropyridine (5·0 g., 71·4% recovery), both of which were chromatographically pure and identified by I.R. spectroscopy. The remaining tarry material was ether extracted in the usual manner but only products of the decomposition of sulpholan and a small amount of unidentified white solid were removed.

(b) Heptafluoroisoquinoline.

The above experiment was repeated using heptafluoroisoquinoline as substrate; after shaking the autoclave for 15 hr. at 180°, both the substrate (97% recovery) and trifluoroethylene (80%) were recovered.

(3) Reactions Involving Chlorotrifluoroethylene.

(a) With Pentafluoropyridine.

Pentafluoropyridine (10·0 g., 59·2 m.moles), potassium fluoride (4·5 g., 77 m.moles) and sulpholan (75 ml.) were introduced into a 150 ml. Baskerville rocking autoclave which was then cooled in liquid air, evacuated, and chlorotrifluoroethylene (11·0 g., 94·4 m.moles) added. The autoclave was heated to 190° for 22 hr. then cooled to room temperature and vented through a liquid air trap where mainly chlorotrifluoroethylene (1·1 g., identified by I.R. spectroscopy) collected. The residue in the autoclave was distilled under vacuum to 100°, all volatile material (12·7 g.) was collected in a cold trap; analytical scale v.p.c. indicated this to be a six-component mixture. Four components of this mixture were separated by preparative-scale v.p.c. (Aerograph, column "O", 130°) and found to be (i) pentafluoropyridine (estimated recovery, 2·4 g., 24%), identified by retention time and I.R. spectroscopy; (ii) 4-chlorotetrafluoropyridine (yield, estimated from the chromatogram and based on the weight of pentafluoropyridine consumed, 9%); (iii) perfluoro-(4-ethylpyridine) (20%) (IV) 1-chloro-1-tetrafluoropyridyltetrafluoroethane (49%). Products (II), (III), and (IV) were identified by comparison of I.R. and N.M.R. spectra with those of the authentic materials.

(b) With Fluoride Ion.

Chlorotrifluoroethylene (3·7 g., 31·7 m.moles) was condensed into a Carius tube (100 ml.) containing caesium fluoride (4·3 g., 48·3 m.moles) and sulpholan. The tube was sealed and heated at 200° for 18 hr. after which time it was cooled in liquid air, opened, and all volatile material (2·3 g.) removed by vacuum distillation up to 90° was collected in a cold trap. Decomposition of the solvent had occurred as the residue was very tarry. The volatile material was a four-component mixture, one of which had a retention time (column "A", room temperature) identical with that of chlorotrifluoroethylene (approx. 20% of mixture). A comparison of the I.R. spectrum of a gaseous sample of the mixture with that of tetrafluoroethylene indicated complete absence of the latter.

(c) The Action of Fluoride Ion on 1-Chloro-1-tetrafluoropyridyltetrafluoroethane.

The title compound (2·7 g., 9·1 m.moles), caesium fluoride (3·0 g., 19·7 m.moles) and sulpholan 30 ml. were sealed into a Carius tube (70 ml.) which was then heated for 23 hr. at 190°. After cooling the tube, the volatile material (1·2 g.) was distilled from the solvent under high vacuum at 100°, the v.p. chromatogram of this indicated that it was a four-component mixture (column "O", 100°), two of which were identified by coincident retention time as unchanged chloro-compound (estimated recovery, 6%) and perfluoro-(4-ethylpyridine) (16%). Injection of mixtures composed of the authentic compounds and the volatile material indicated that the former were present.

(d) With Heptafluoroquinoline.

A mixture of caesium fluoride (2·4 g., 15·8 m.moles), heptafluoroquinoline (8·0 g., 31·4 m.moles), chlorotrifluoroethylene (3·6 g., 30·9 m.moles) and sulpholan was shaken in an autoclave at 160° for 16 hr. After cooling and venting the autoclave, the contents were poured into water (200 ml.); the aqueous mixture was ether extracted (3 x 30 ml.), the extracts washed with water (2 x 50 ml.), dried ($MgSO_4$) and removal of solvent left a gum (10·7 g.). This was shown by v.p.c. (column "A", 150°) to be a five-component mixture, inseparable on the columns available. A mass spectrum of the gum had significant mass peaks at 371 and 471, corresponding to products containing (1) CF_3CFCl and (2) CF_3CFCl + CF_3CF_2 groups.

(4) Reaction Between 1,2-Difluoro-1,2-dichloroethylene and Pentafluoropyridine.

(a) Using Caesium Fluoride.

Pentafluoropyridine (4·8 g., 28·7 m.moles) caesium fluoride (3·6 g., 23·7 m.moles) and sulpholan (20 ml.) were placed into a Carius tube (100 ml.) and 1,2-dichloro-1,2-difluoroethylene (9·0 g., 68·2 m.moles) was condensed into the tube, which was then evacuated, sealed, and heated for 19 hr. at 200°. The tube was cooled, opened into a vacuum system, warmed and the transferred material (10·5 g.) was examined by analytical scale v.p.c. (column "O", 60°) and seen to be a two component mixture. This was separated by distillation into (i) a gas (8·1 g.), which, from its I.R. spectrum and low temperature (0^o) chromatogram was shown to be 70-80% of 1,2-dichloro-1,2-difluoroethylene (~63% recovery) and (ii) a liquid (b.p. 129^o) which had identical I.R. and N.M.R. spectra with that of 4-chlorotetrafluoropyridine (2·4 g., 46%). The reaction was accompanied by extensive tar formation, which was deposited on the wall of the Carius tube.

(b) Using Potassium Fluoride.

Experiment (a), above, was repeated under the same conditions and using the same quantities, except that potassium fluoride (5·0 g., 86·2 m.moles) was used instead of caesium fluoride. The volatile material (10·5 g.) was a three-component mixture consisting of (i) a gas (5·5 g.), mainly 1,1-difluoro-1,2-dichloroethylene; (ii) pentafluoropyridine (approx. 2·5 g., 52% recovery); (iii) perfluoro-(4-ethylpyridine) (3·5 g., 46% yield). Components (ii) and (iii) were isolated in small amounts by preparative-scale v.p.c. (Aerograph, column "A", 80^o) and characterized by comparison of their ^{19}F N.M.R. and I.R. spectra with the corresponding spectra of authentic compounds.

(5) The Action of Chloride Ion on Pentafluoropyridine.

Pentafluoropyridine (4·6 g., 27·2 m.moles), caesium chloride (6·6 g., 39·2 m.moles) and sulpholan (18 ml.) were loaded into an autoclave (35 ml.) which was sealed and shaken at 200^o for 18 hr. After cooling, the autoclave was opened and the volatile material (4·2 g.)

removed by heating to 100° under high vacuum. Analytical-scale v.p.c. (G.D.B., column "O", 80°) indicated this to be a mixture of pentafluoropyridine and a second component in ratio 92:8%. The latter was isolated by preparative-scale v.p.c. and identified as 4-chlorotetrafluoropyridine (approx. 7% yield).

(6) The Attempted Addition of 1,1-Dichlorodifluoroethylene to Pentafluoropyridine.

A mixture of pentafluoropyridine (4·0 g., 23·6 m.moles), potassium fluoride (1·0 g., 17·2 m.moles), 1,1-dichlorodifluoroethylene (6·3 g., 47·7 m.moles) and sulpholan (25 ml.) were shaken in an autoclave (35 ml.) at 150° for 22 hr. After cooling the autoclave was opened to a vacuum system and the volatile material (4·1 g.) removed by warming to 70°; v.p.c. indicated this to be a four-component mixture which was separated into (i) 1,1-dichlorodifluoroethylene (0·26 g., 4% recovery); (ii) pentafluoropyridine (1·55 g., 39% recovery); (iii) 1,1,1-trichlorotrifluoroethane (2·3 g., 26% yield) b.p. 45° (Found: C, 12·6; F, 30·1; Cl, 57·1. $C_2Cl_3F_3$ requires C, 12·8; F, 30·4; Cl, 56·8. The mass spectrum did not exhibit a molecular ion but prominent peaks corresponding to $P^+ - Cl$, $P^+ - CF_3$, and $P^+ - CCl_3$ were observed. The fourth component (*ca.* 7% of mixture) could not be isolated, however as the mass spectrum of the mixture indicated the presence of a trace amount of material with a molecular weight of 301, it is likely to be the mono-substituted pyridine. It is relevant that, due to reaction with the solvent, the material remaining in the autoclave was tarry.

(7) The Reaction of Bromotrifluoroethylene with Pentafluoropyridine.

Pentafluoropyridine (5·0 g., 29·6 m.moles) caesium fluoride (2·0 g., 13·2 m.moles) and sulpholan (19 ml.) were loaded into an autoclave (35 ml.) into which bromotrifluoroethylene (8·0 g., 49·7 m.moles) was condensed. The autoclave was sealed and shaken at 170° for 16 hr. after which time it was cooled, opened and all volatile material removed (7·5 g.) by transfer under vacuum. This was distilled up a 9" fractionating column to give (i) a liquid, b.p. 46° which was characterized by ^{19}F N.M.R. spectroscopy (p.108) as 1,1-dibromotetrafluoroethane (4·5 g., 35%) (Found: C, 9·3%; M, 260. $C_2F_4Br_2$ requires C, 9·2%; M, 260), the mass spectrum exhibited peaks corresponding to P^+, P^+-CF_3, and P^+-CFBr_2, the ions containing bromine were multiplets showing the correct intensity relationships for the requisite number of bromine atoms (i.e. parent peak multiplet was a three line pattern with intensities 1:2:1 approx., thereby establishing the presence of two bromine atoms in the molecular ion). Also (ii) pentafluoropyridine (2·5 g.); (iii) residue (~0·5 g., a four component mixture).

The material remaining in the autoclave was poured into water (100 ml.) which was ether extracted (3 x 15 ml.); the extracts were washed with water, dried ($MgSO_4$) and removal of solvent left a black liquid (5·3 g.) distillation of which under high vacuum enabled the collection of an orange gum (b.range, 80-160°/0·001 mm.) (2·3 g.).

Analytical scale v.p.c. showed (column "O", 240°) that this was a two-component mixture (ratio 3:7) which could not be separated on the columns available. A small amount of the major component was isolated by dissolving the gum in hot methanol, allowing to cool and filtering off a white solid which precipitated on cooling; this was characterized by ^{19}F N.M.R. spectroscopy as 1,2-bis-(1,2,5,6-tetrafluoropyridyl)tetrafluoroethane (1·6 g., 14%) (Found: C, 35·9; F, 56·7%; M, 400. $C_{12}F_{12}N_2$ requires C, 36·0; F, 57·0%; M, 400) m.p. 93-94° (from hexane).

(8) The Action of Fluoride Ion on Bromotrifluoroethylene.

Bromotrifluoroethylene (10·0 g., 62·1 m.moles) was condensed into an autoclave (35 ml.) containing caesium fluoride (4·9 g., 32·2 m.moles) and sulpholan (30 ml.); after sealing the autoclave it is shaken at 170° for 16 hr. after which time it was cooled, opened and all volatile material (5·7 g.) removed by distillation up to 90° under high vacuum. This material was fractionated into (i) volatiles b.p. $<$ room temperature (2·7 g.), a four-component mixture, inseparable by chromatographic methods; the major component (33%) being unchanged olefin and (ii) volatiles b.p. ~ room temperature (2·9 g.) a three-component mixture; 36% of which was 1,2-dibromotetrafluoroethane.

Ether extraction of the contents remaining in the autoclave produced a black tar which decomposed on distillation under reduced pressure.

(D) Reactions Involving C_5 Fluoro-olefins.

(1) The Action of Fluoride ion on Decafluoropent-1-ene.

A mixture of decafluoropent-1-ene[129] (9·4 g., 37·6 m.moles), caesium fluoride (1·2 g., 7·9 m.moles) and sulpholan (17 ml.) was shaken for 45 hr. at 120° in an autoclave (35 ml.), which was then cooled to room temperature. After opening the autoclave, the volatile material (9·0 g.) was removed and examination of this by analytical-scale v.p.c. (column "A", room temperature) indicated a minor (~3%) impurity which was removed by distillation to give a pure sample of decafluoropent-2-ene (8·7 g., 93%) b.p. 26° (Found: C, 24·0; F, 76·2%; M, 250. C_5F_{10} requires C, 24·0; F, 76·0%; M, 250). The compound isolated is likely to be in the trans configuration as the I.R. spectrum did not exhibit a strong C=C absorption; the ^{19}F N.M.R. spectrum had complex absorptions at -94·3 [relative intensity 3, assigned to $C\underline{F}_3CF_2$], -78·8 [3, $C\underline{F}_3CF=$], -42·2 [2, $CF_3C\underline{F}_2$] and -6·3 p.p.m. [2, $C\underline{F}=C\underline{F}$].

(2) The Action of Fluoride Ion on Decafluoro-(2-methylbut-1-ene.

An autoclave (35 ml.) containing caesium fluoride (2·0 g., 13·2 m.moles), sulpholan (20 ml.) and decafluoro-(2-methylbut-1-ene)[130] (3·2 g., 12·8 m.moles) was shaken at 50° for 12 hr. after which time it was cooled, and all volatile material (3·0 g.) removed by opening to a vacuum system. Analytical scale v.p.c. (column "A" room temp.) indicated this to be a pure compound which was characterized by comparison of the

I.R. spectrum with that of authentic[123] decafluoro-(2-methylbut-2-ene) (93·7% yield).

(3) The Addition of Decafluoropentenes to Pentafluoropyridine.

(a) Decafluoropent-1-ene.

Pentafluoropyridine (4·6 g., 27·2 m.moles), caesium fluoride (1·6 g., 10·5 m.moles) and sulpholan (20 ml.) were loaded into an autoclave (35 ml.) into which decafluoropent-1-ene (7·4 g., 29·6 m.moles) was condensed. The autoclave was sealed, shaken at 185° for 60 hr., cooled and vented at 50° into a cold trap where decafluoropent-2-ene (2·0 g., identified by comparison of I.R. spectrum with the material isolated in experiment 1, above) condensed. The contents of the autoclave were poured into water (100 ml.) which was then extracted with ether (2 x 20 ml.), the extracts were dried ($MgSO_4$) and the solvent removed to leave a mixture which was separated by preparative-scale v.p.c. (Aerograph, column "O", 150°) into (i) pentafluoropyridine (estimated recovery 0·6 g., 13%); (ii) perfluoro-[2-(2,3,5,6-tetrafluoropyridyl)-pentane] (5·3 g., 48%) b.p. 160° (Found: C, 28·8; F, 67·5%; M, 419. $C_{10}F_{15}N$ requires C, 28·6; F, 68·0%; M, 419); (iii) perfluoro[2,4-di-(2-pentyl)pyridine] (0·7 g., 4%) (Found: C, 26·8; F, 70·5%; M, 669. $C_{15}F_{25}N$ requires C, 26·9; F, 71·0%; M, 669) b.p. 194-196°. Product structures were determined from ^{19}F N.M.R. spectral data.

(b) Decafluoropent-2-ene.

The experiment above was repeated on the same scale, using decafluoropent-2-ene instead of the terminal olefin. Small amounts of the products (which were formed in approximately the same ratio) were separated and found to have identical spectral properties with those of the products from the experiment above.

(c) Decafluoro-(2-methylbut-2-ene).

A mixture of pentafluoropyridine (5·7 g., 33·7 m.moles) anhydrous caesium fluoride (3·0 g., 19·7 m.moles), decafluoro-(2-methylbut-2-ene) (8·0 g., 32·0 m.moles) and sulpholan (17 ml.) was shaken in an autoclave at 180° for 14 hr. After cooling the autoclave, the volatiles (13·0 g.) were removed in the usual manner and found to consist only of pentafluoropyridine and unchanged olefin.

The reaction was repeated at a temperature of 200° with a reaction time of 98 hr.; the result was similarly negative.

(E) Reactions Involving Acetylenes.

(1) The Attempted Addition of Phenyl Acetylene to Pentafluoropyridine.

Phenyl acetylene (6·5 g., 61·3 m.moles), pentafluoropyridine (7·3 g., 43·2 m.moles), potassium fluoride (4·0 g., 68·9 m.moles) and sulpholan (15 ml.) were placed into an autoclave (35 ml.) which was then sealed and shaken at 160° for 23 hr. The autoclave was cooled to room temperature, opened and the contents poured into water which, on ether extraction, yielded a brown gummy liquid (6·3 g., b.p. $>$ 130°). Examination of this liquid was attempted on an alumina column, the most satisfactory eluent being ether. The fractions eluted, (which varied in colour - (initially dark green then light brown through to dark brown), were submitted for mass spectrometric analysis and all were found to be polymers derived from phenyl acetylene (molecular weight varied from ~700 to ~ 1400).

(2) The Attempted Addition of Hexafluorobut-2-yne to Pentafluoropyridine.

A mixture of pentafluoropyridine (4·0 g., 23·7 m.moles), caesium fluoride (1·0 g., 6·6 m.moles), hexafluorobut-2-yne (4·1 g., 25·3 m.moles) and sulpholan (23 ml.) was shaken at 130° for 33 hr. On venting the autoclave at room temperature, no acetylene was recovered. The contents of the autoclave were poured into water and a white solid precipitated which was filtered off, washed and dried. Sublimation of this material (4·0 g.) was attempted at 110° for 24 hr. but only a small amount (0·15 g.) of a white solid was collected. Both the sublimate and the parent material were insoluble in the usual organic solvents however the sublimate was sufficiently soluble in hexafluorobenzene to enable an N.M.R. spectrum to be recorded (p.114). The molecular weight of both compounds, as recorded by mass spectrometry varied with the probe temperature (~1200 at 250; ~1500 at 270) and their analyses were similar (sublimate: C, 29•2; F, 70•1% residue: C, 29•4; F, 70•6%. C_4F_6 requires C, 29•6; F, 70•4%).

(3) The Addition of Diethyl Acetylene Dicarboxylate to Pentafluoropyridine.

This reaction was investigated initially at the conditions of (1) 170°, 35 hr., (2) 170°, 6 hr., (3) 130°, 16 hr. Although in each experiment tar formation was extensive, it was thought of interest to repeat the reaction under mild conditions and with a short reaction time because trace quantities of fluorine-containing products could be isolated from the tars by using an alumina column.

Pentafluoropyridine (4•0 g., 23•7 m.moles), diethyl acetylene dicarboxylate (1•5 g., 8•8 m.moles), caesium fluoride (1•0 g., 6•6 m.moles) and sulpholan (25 ml.) were loaded into an autoclave (35 ml.) which was then shaken at 135° for 5 hr. After cooling the autoclave, the contents were poured into water (120 ml.) which was then ether extracted (3 x 20 ml.); the extracts were washed, dried and distilled to 130° to remove the solvent and substrate. The residual liquid (tarry) distilled under high vacuum at 70-100° to give an oil (2•2 g.), the chromatogram of which indicated it to be a three-component mixture.

Preparative-scale v.p.c. (Aerograph, column "O", 180°) enabled the separation of a small quantity of the major component which was characterized by ^{19}F N.M.R. spectroscopy as 1-fluoro-1,2-bis(carbethoxy)-2-(2,3,5,6-tetrafluoropyridyl)ethylene (estimated yield 1·7 g., 21%) an oil, which decomposes at 200°. (Found: C, 45·8; F, 28·3; H, 3·0%; M, 339. $C_{13}F_5NO_4H_{10}$ requires C, 46·0; F, 28·0; H, 2·9%; M, 339).

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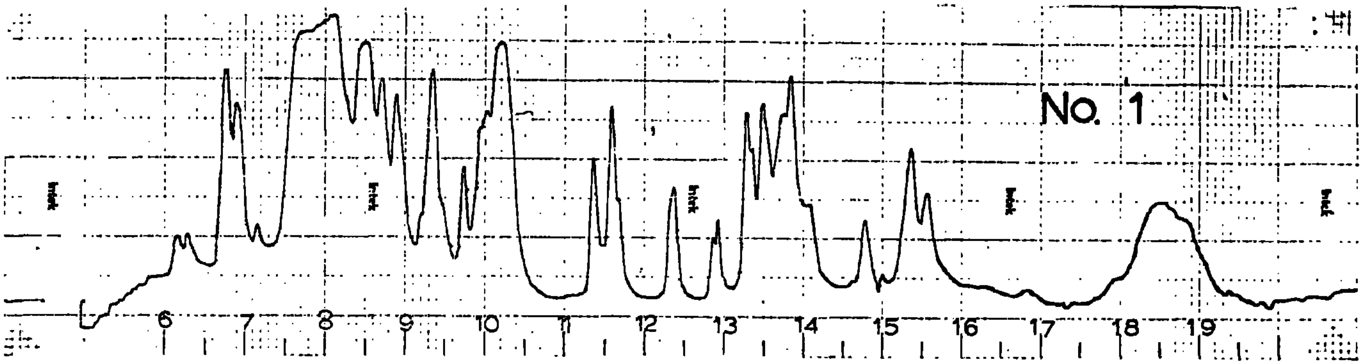
23. Perfluoro-[2-(2,3,5,6-tetrafluoropyridyl)-pentane]

24. Perfluoro-[2,4-di-(2-pentyl)pyridine]

25. Polymer of Hexafluorobut-2-yne

26. 1-Fluoro-1,2-bis(carbethoxy)-2-(2,3,5,6-tetrafluoropyridyl)ethylene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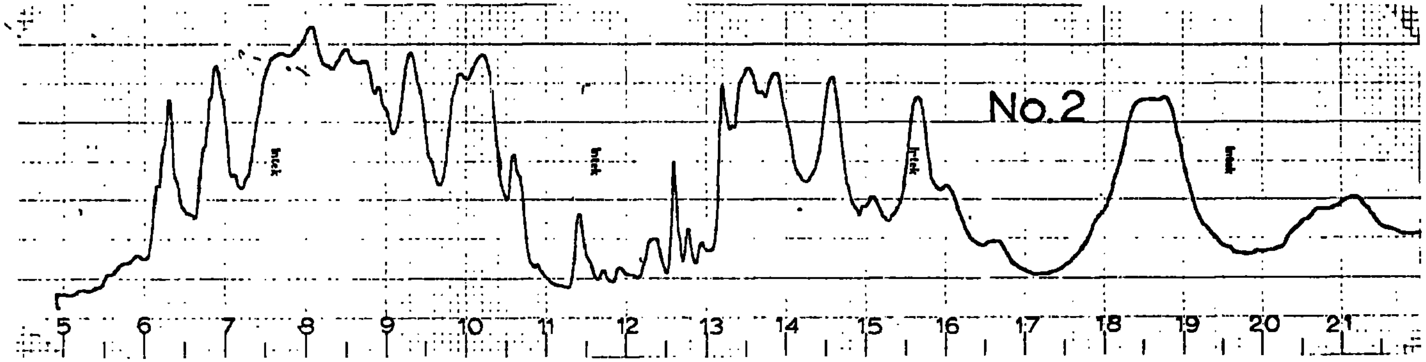
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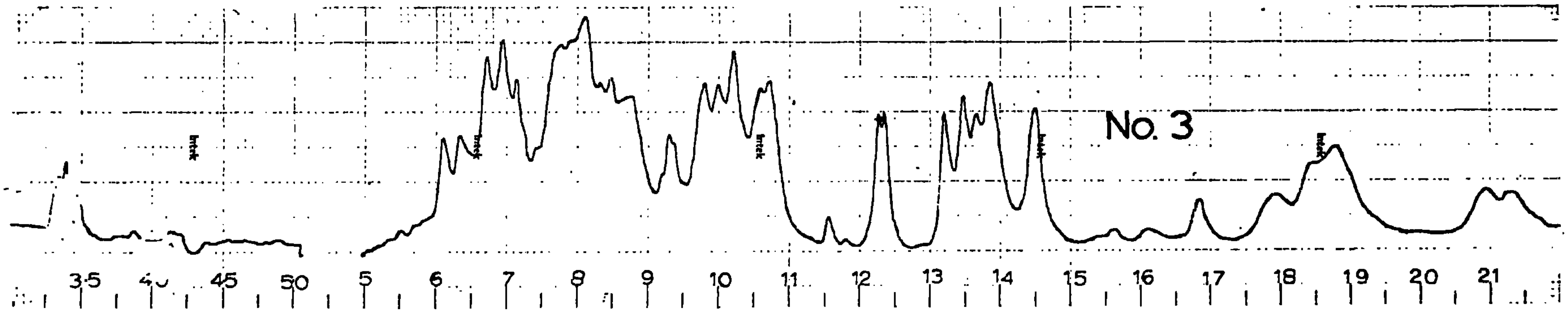
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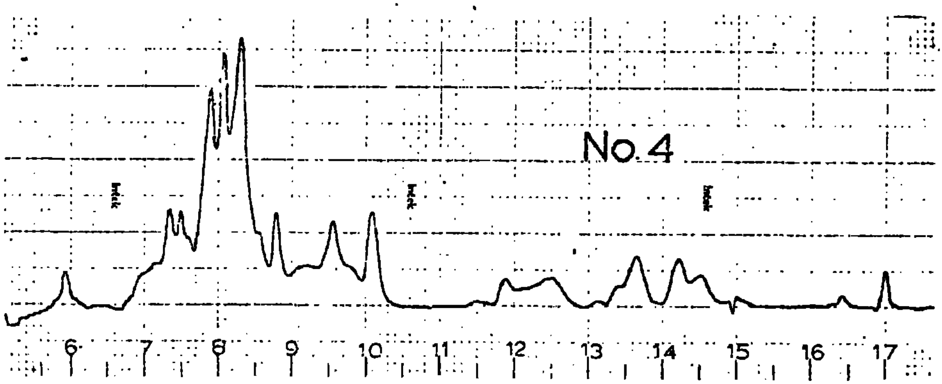
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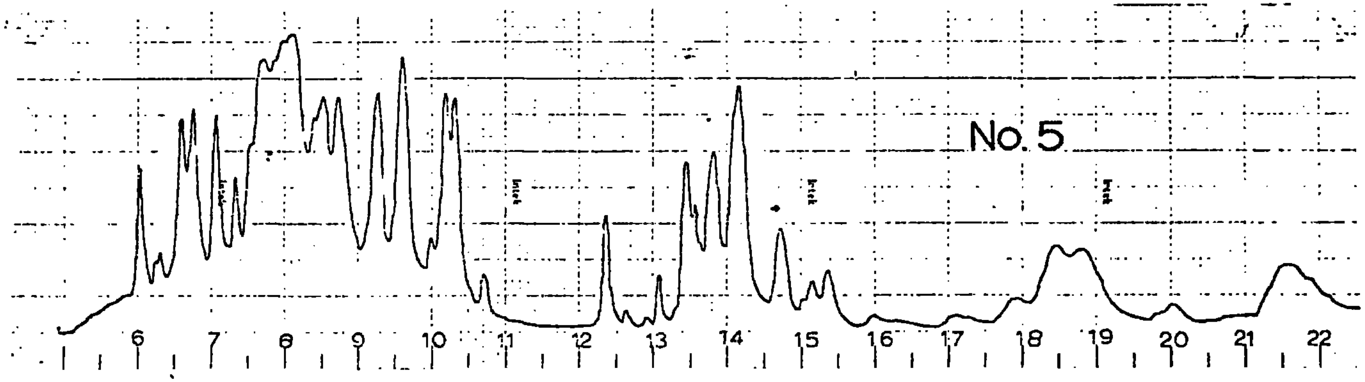
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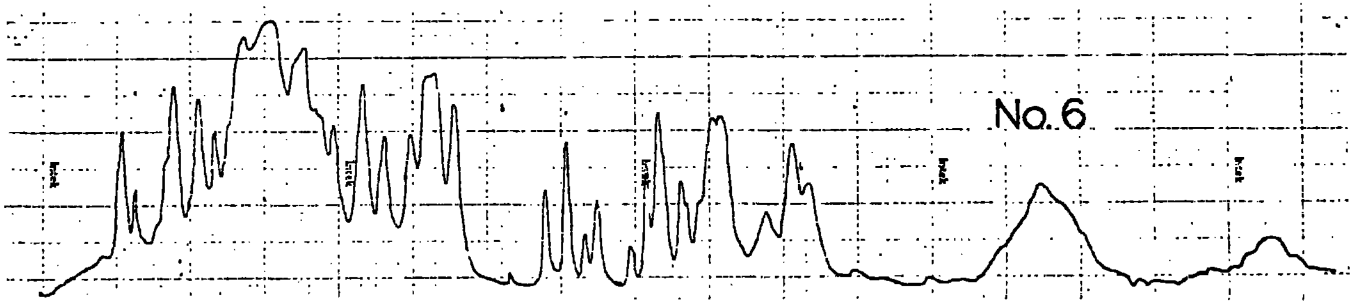
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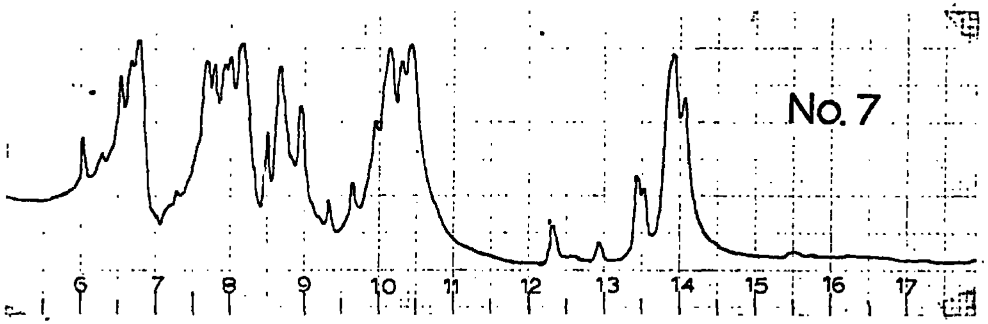

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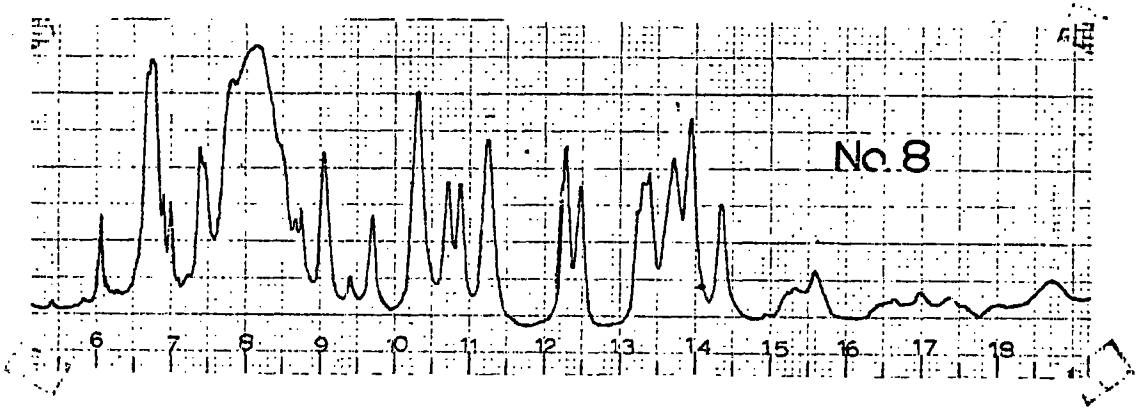

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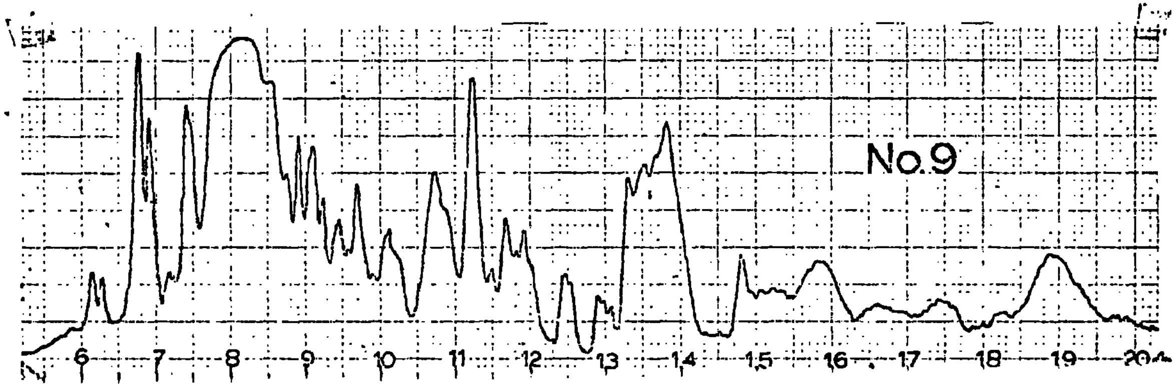

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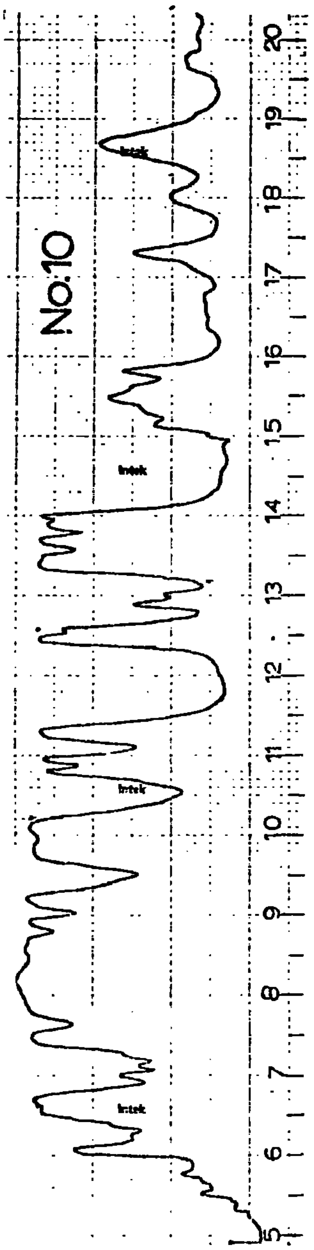
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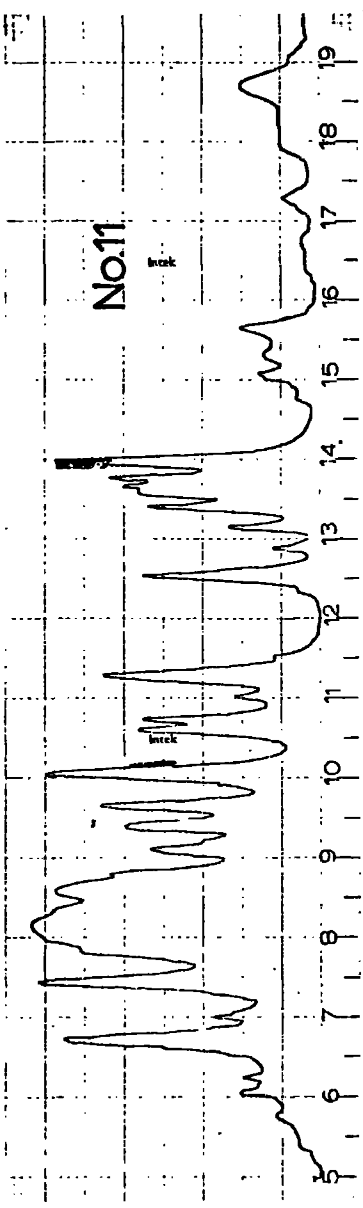
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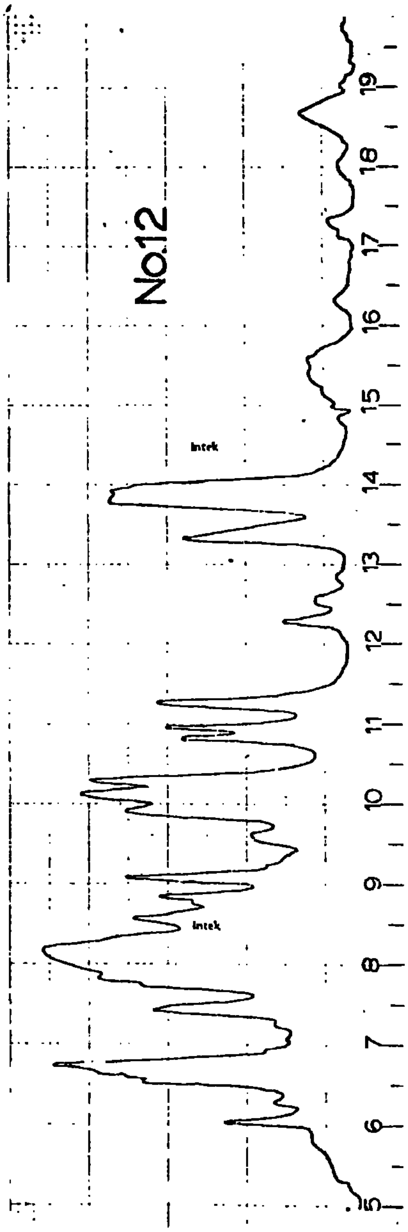
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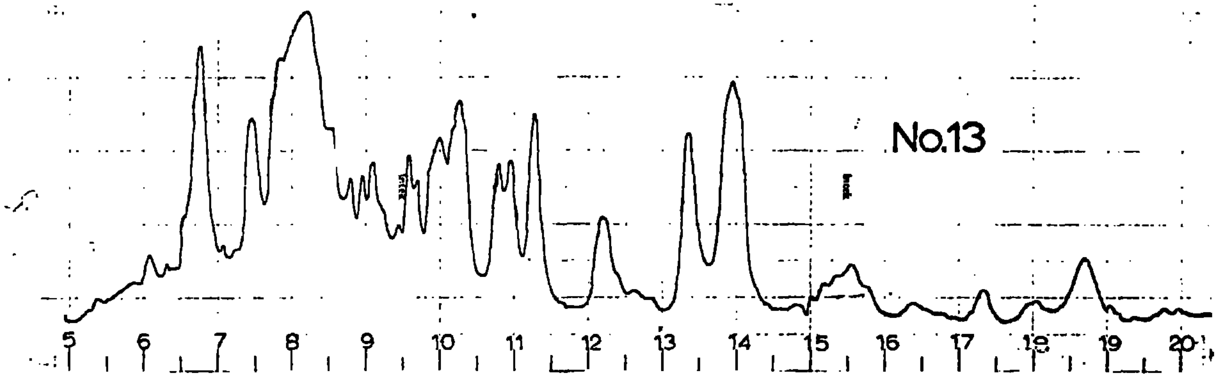
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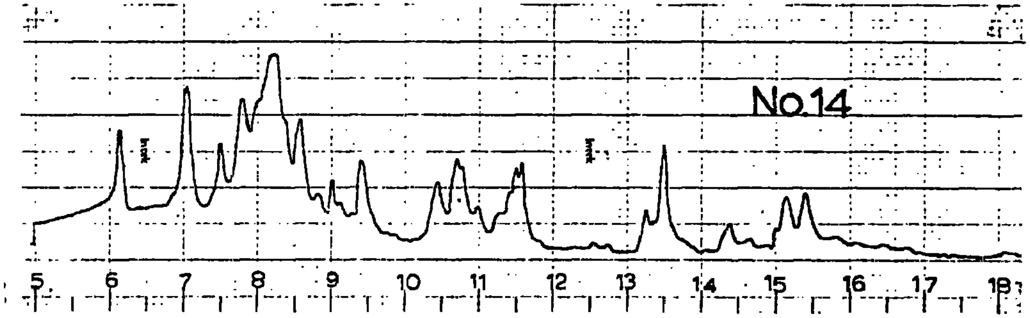
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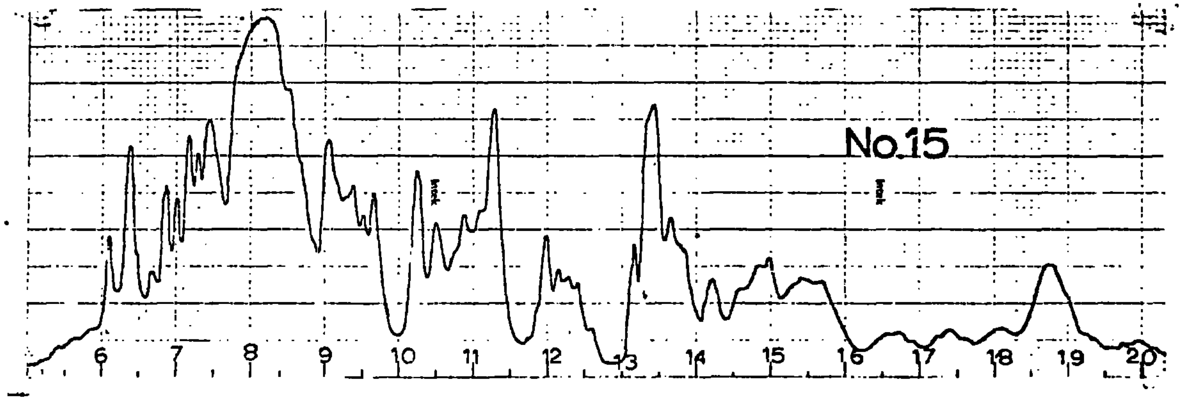
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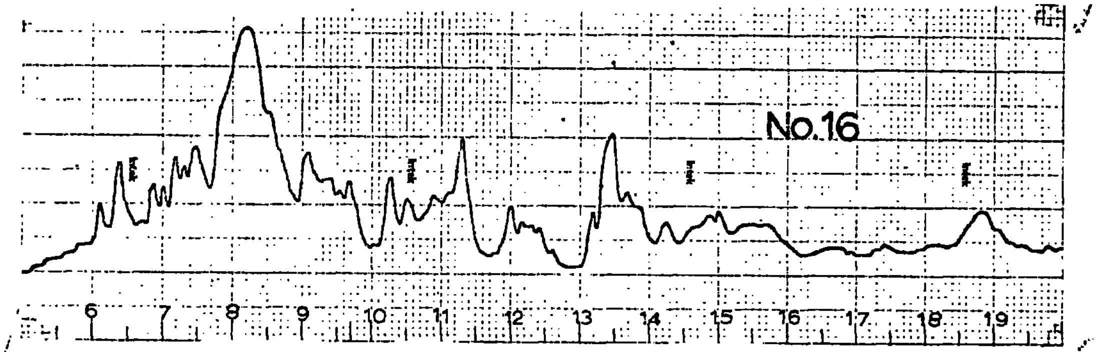
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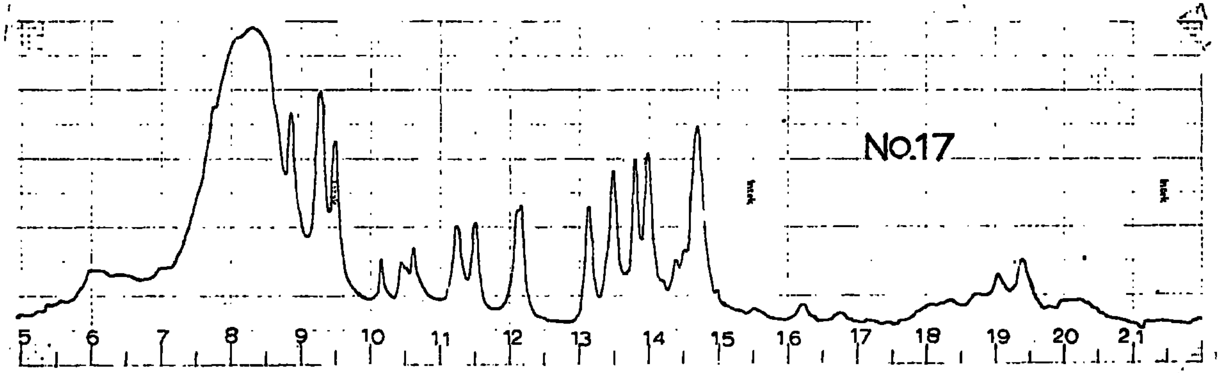
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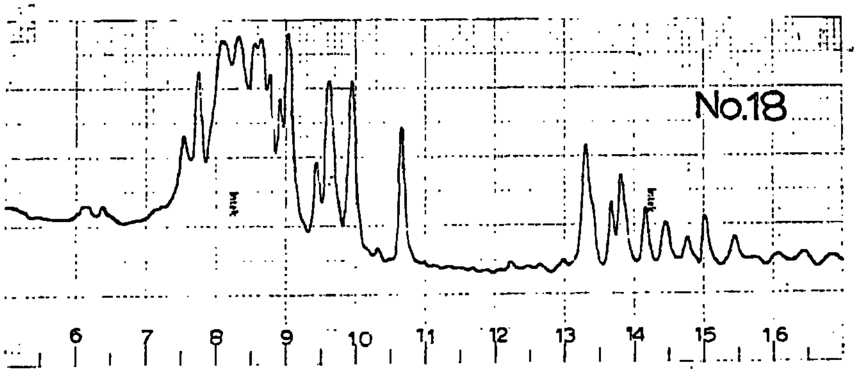
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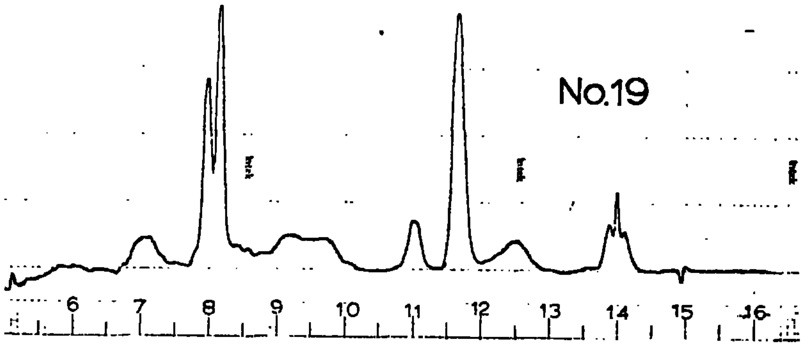

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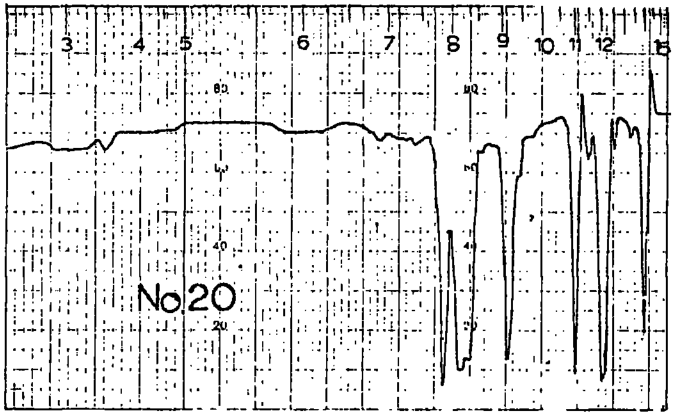

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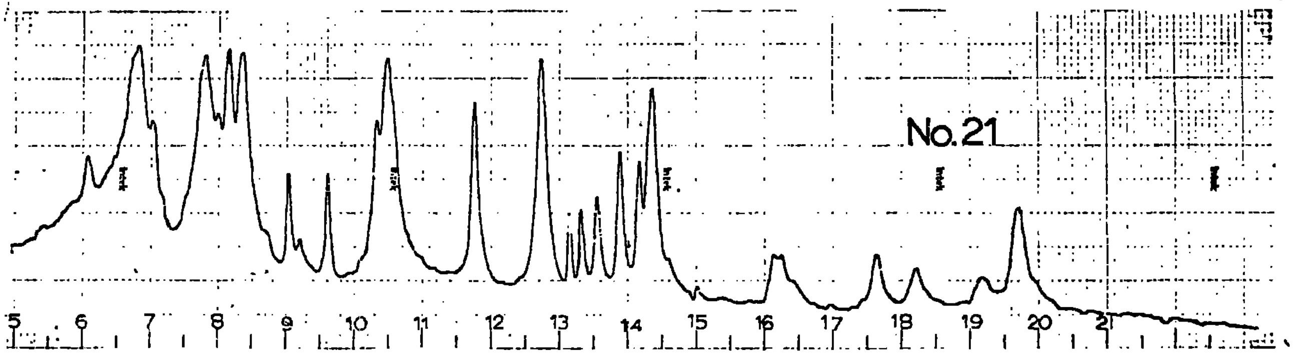

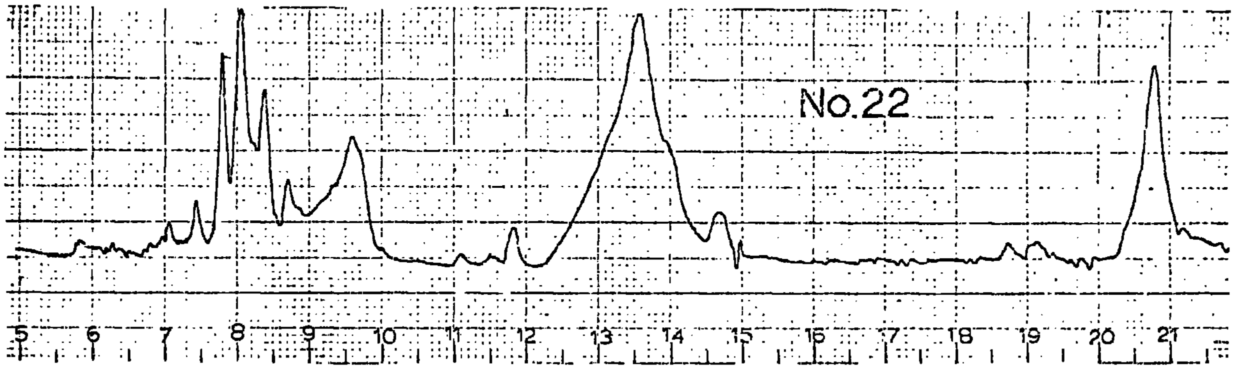
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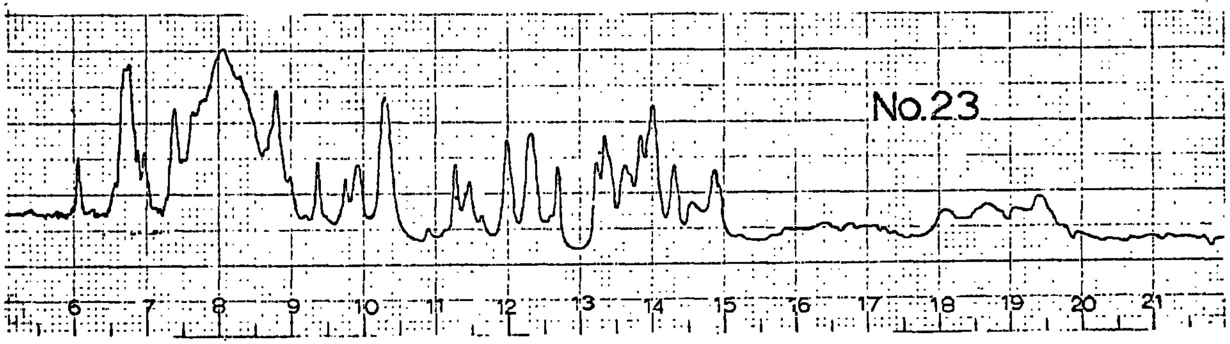
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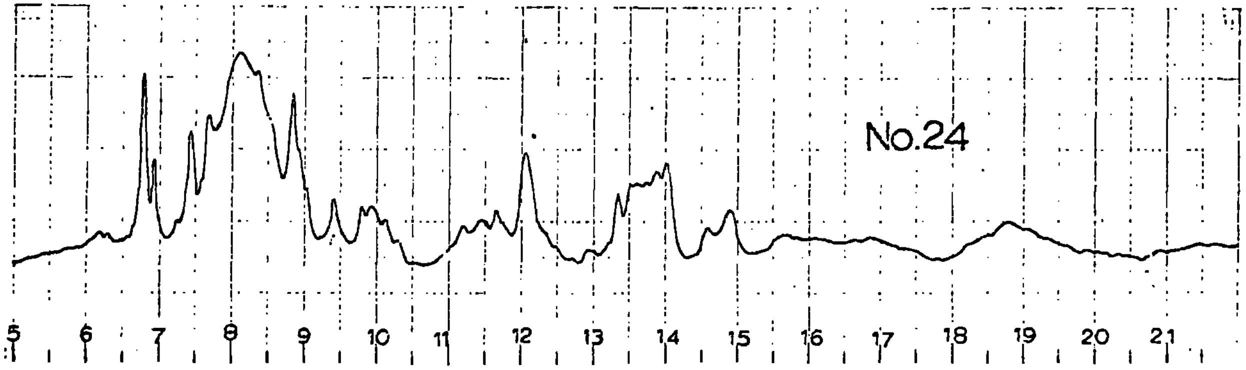
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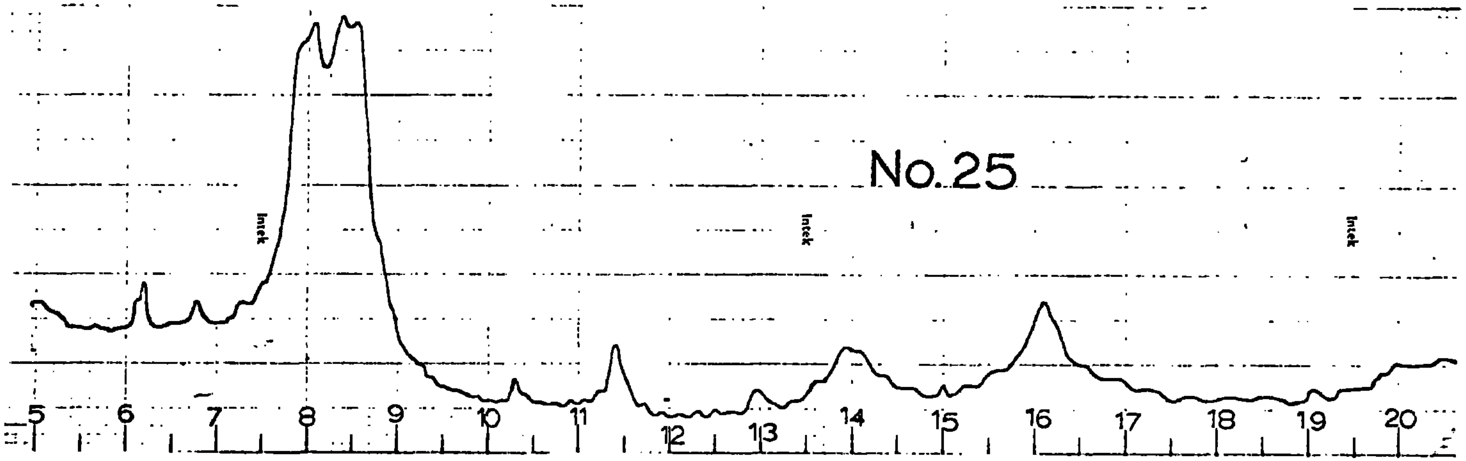
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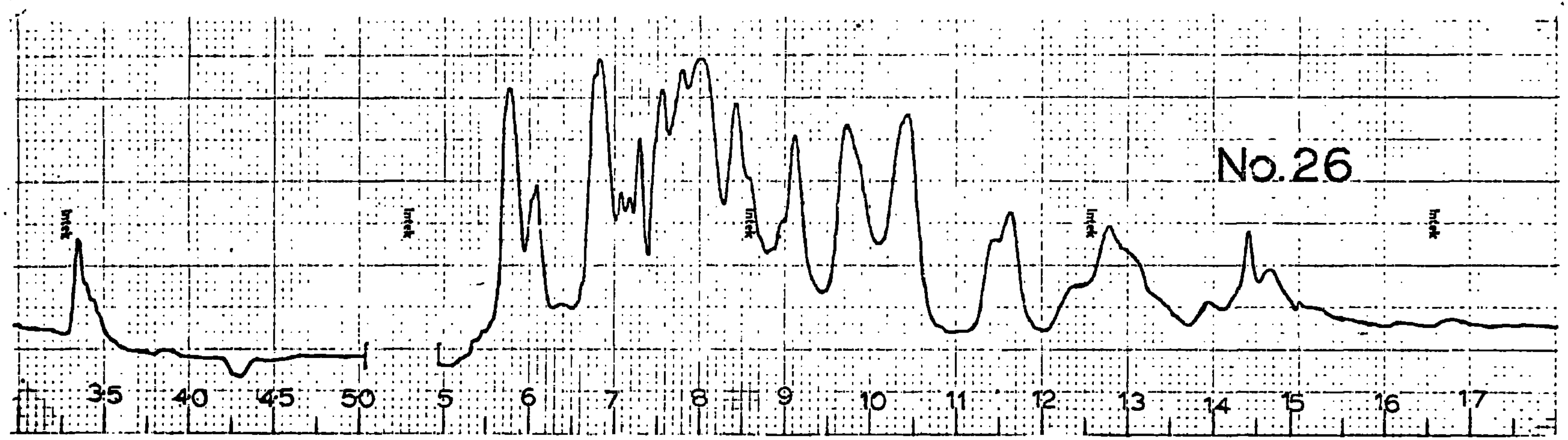
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