The synthesis and reactions of some polyfluoroalkenes

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Philpot, Paul David (1975) The synthesis and reactions of some polyfluoroalkenes. Doctoral thesis, Durham University.

UNIVERSITY OF DURHAM

A THESIS

entitled

THE SYNTHESIS AND REACTIONS OF SOME POLYFLUOROALKENES

Submitted by

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(Graduate Society)

A candidate for the degree of Doctor of Philosophy

1975

ACKNOWLEDGEMENTS

The author is indebted to Dr. R. D. Chambers for his continual help, encouragement and stimulating discussions during his supervision of the work described in this thesis, and to Dr. J. Hutchinson from I.C.I. (Mond) Ltd. for his interest and helpful discussions.

The author would also like to express his gratitude to the people concerned with fluorocarbon chemistry at I.C.I. (Mond) Ltd. for the resources and hospitality provided during visits to Runcorn.

Thanks are also due to Dr. R. S. Matthews for assistance in the interpretation of some nuclear magnetic resonance spectra, to Dr. M. Jones for assistance in the interpretation of some mass spectra, to the many technical and laboratory staff for their help, and to the author's wife, Diana, for typing this thesis.

Finally, thanks are due to the Science Research Council for a maintenance grant.

To my wife, Diana

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1972 and September 1975. 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 the subject of a paper presented at the 5th European Fluorine Symposium at Aviemore, Scotland, September 1974, and also the following publication:

R. D. Chambers, J. A. Jackson, S. Partington, P. D. Philpot and A. C. Young, J. Fluor. Chem., 1975, 6, 5.

SUMMARY

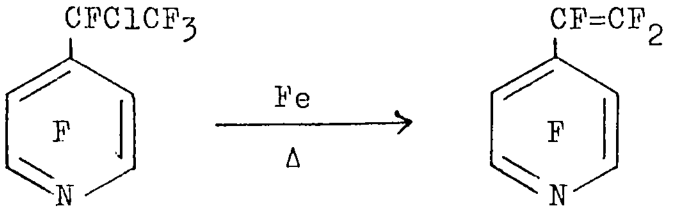
The work described in this thesis is concerned with the synthesis and reactions of two types of fluoro olefin, firstly vinylaromatic systems, and secondly a highly branched acyclic olefin.

The synthesis of chlorotetrafluoroethyl derivatives of activated aromatic systems was investigated, with a view to using these derivatives as precursors to vinylaromatic systems.

$$\mathrm{CF_2{=}CFCl} + \overset{-}{\mathrm{F}} \longrightarrow \mathrm{CF_3\overset{-}{C}FCl} \xrightarrow{\text{Ar-F}} \mathrm{CF_3CFCl{-}Ar} + \overset{-}{\mathrm{F}} \xrightarrow[\text{Fe}]{\Delta} \mathrm{CF_2{=}CF{-}Ar}$$

Under mild conditions pentafluoropyridine gave a single mono-chlorotetrafluoroethyl derivative, while tetrafluoropyrimidine and cyanuric fluoride both gave mono- and disubstituted products.

The chlorotetrafluoroethyl derivative of pentafluoropyridine provided an attractive route to perfluoro-4-vinylpyridine, formed after dehalogenation over hot iron.



Some nucleophilic and cycloaddition reactions of perfluoro-4-vinylpyridine have been investigated, for example, fluoride ion-initiated reactions gave a dimer, and with tetrafluoropyridazine a 4,5-disubstituted product.

Reaction with phenoxide indicated that the vinylic position was the most susceptible to nucleophilic attack, while methoxide gave an addition product.

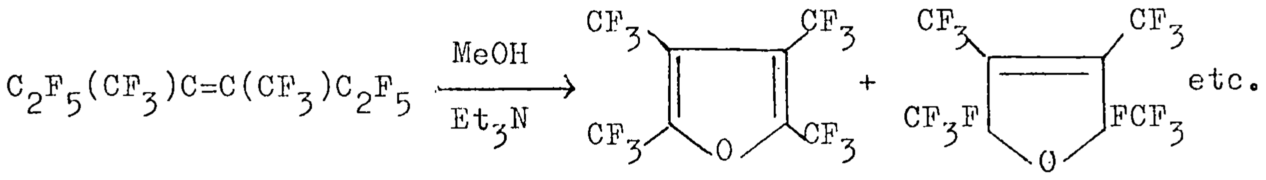
Heating perfluoro-4-vinylpyridine in a sealed tube yielded a cyclic dimer; mixed cycloadditions gave cyclobutanes all formed by a head-to-head addition. Photolysis with hexafluoroacetone gave a fluorinated oxetane.

Cyanuric fluoride in sulpholane gave the first reported case of a σ-complex formed by addition of fluoride ion, while heating with dry CsF yielded a glassy solid, which the data obtained suggests is a ring opened compound. Attempts to use E.S.C.A., however, as a means of observing highly fluorinated stable anions met with limited success.

The fluoride ion-initiated dimerisation of octafluorobut-2-ene gave perfluoro-3,4-dimethylhex-3-ene, an interesting olefin which, as well as being sterically crowded, possesses no readily displaceable vinylic fluorines, although the double bond is highly activated to nucleophilic attack.

$$CF_3CF{=}CFCF_3 \xrightarrow[\text{Solvent}]{\overset{-}{F}} C_2F_5(CF_3)C{=}C(CF_3)C_2F_5$$

A preliminary survey of some reactions of perfluoro-3,4-dimethylhex-3-ene has been carried out. Nucleophilic substitution reactions with diethylamine, plus methanol or phenol in the presence of an amine, gave products from substitution with rearrangement. In particular methanol gave cyclic derivatives, including a furan formed after an unusual defluorination reaction involving triethylamine.



Defluorination of perfluoro-3,4-dimethylhex-3-ene over hot iron gave a mixture of dienes.

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INTRODUCTION

General Introduction

In the last thirty years fluorocarbon chemistry has been the subject of a great deal of research, both in the academic and industrial sphere. The ability to replace hydrogen in an organic molecule, either partially or completely, without seriously affecting the geometry of the molecule makes these systems very interesting.

The main difference in properties between fluorocarbons and hydrocarbons arises from the difference in electronegativity between hydrogen and fluorine, consequently in fluorocarbon molecules the functional groups are relatively electron deficient when compared to their hydrocarbon analogues. Thus the chemistry of unsaturated fluorocarbons is complementary to that of unsaturated hydrocarbons, since the former undergo predominantly nucleophilic attack, whereas the latter undergo predominantly electrophilic attack.

A characteristic of many fluorocarbons is a high degree of thermal and chemical stability, a property which has been exploited extensively by industry, and a great variety of fluorocarbon products are now commercially available. Polymerisation of fluoro olefins, either as homopolymers or copolymers, have provided a wide range of useful polymers. For example, polytetrafluoroethylene as well as possessing a high degree of chemical and thermal stability, has a remarkably low coefficient of friction, making this compound very useful; the many areas in which this has been exploited include the manufacture of artificial joints, dry bearings, and as a non-stick coating for saucepans.

Some fluorochloroalkanes are now produced in large quantities, being used as refrigerants, inert aerosol propellants, and as coolants in sealed electrical systems, such as large transformers.

In the pharmaceutical industry certain organic compounds containing fluorine have become important, for example, the most widely used anaesthetic at present is a fluorocarbon, $CF_3CHClBr$, while 5-fluorouracil has been used in the treatment of certain cancers. The introduction of a single fluorine into certain steroids produces compounds with greatly enhanced anti-inflammatory properties, and in more recent times an exciting possibility of using compounds related to perfluorodecalin as blood substitutes has been investigated, although this is still at a very early stage of development.

In the area of surfactant chemistry fluoro olefins have become important, giving products which have the property of being both water and oil repellant. For example, the pentamer of tetrafluoroethylene provides the fluorocarbon skeleton for a whole series of surface active compounds, which have many uses including, protecting clothes from oil and water, mould release agents, and in fire extinguishers.

CHAPTER I

Synthesis and Stability of Fluoro Olefins

Introduction

In hydrocarbon chemistry olefins provide important starting materials for a wide range of complex organic molecules. Similarly fluoro olefins have become important as readily available starting materials in the syntheses of more complex fluorocarbon derivatives. The reactions of both systems are similar but differ in two areas. In hydrocarbon olefins ionic reactions are chiefly electrophilic, whereas in fluoro olefins nucleophilic reactions predominate. Also fluoro olefins readily partake in 1,2-cycloaddition reactions, the converse being true in the hydrocarbon case.

It is proposed in the introductory chapters of this thesis to provide a general discussion of the different types of syntheses and reactions important in fluoro olefin chemistry, and where a topic has special relevance to the work of the author a more comprehensive review will be undertaken. Several reviews have appeared covering different areas of fluoro olefin chemistry.[1,2,3]

I.A Synthesis of Fluoro Olefins

There are several different routes available to fluoro olefins, generally involving more than one stage, and the different routes will be discussed under their respective headings.

I.A.1 Synthesis Involving Dehydrohalogenation or Dehalogenation

Many of the more common fluoro olefins are prepared from precursors formed by fluorination of CCl_4, $CHCl_3$, or C_2Cl_6 using anhydrous hydrogen fluoride and $SbCl_5$. An important example of this reaction is the synthesis of tetrafluoroethylene.[4]

$$CHCl_3 \xrightarrow{HF/SbCl_5} CF_2HCl$$

$$2\ CF_2HCl \xrightarrow[\text{Ag or Pt tube}]{700^\circ} CF_2{=}CF_2 + 2HCl\quad 90\text{-}95\%$$

Similarly with chlorotrifluoroethylene,[5]

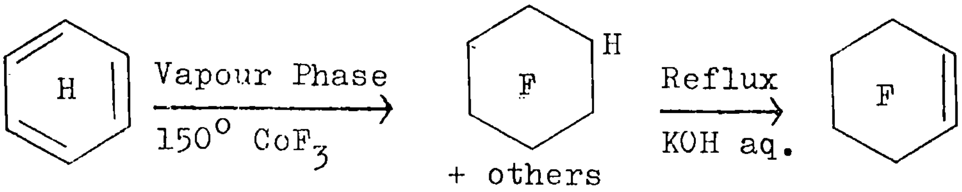
$$CCl_3CCl_3 \xrightarrow{HF/SbCl_5} CF_2ClCFCl_2$$

$$CF_2ClCFCl_2 \xrightarrow{Zn/EtOH} CF_2{=}CFCl$$

There are numerous other examples of fluoro olefins formed by dehalogentation and dehydrohalogenation of precursors and some of these are summarised in Table 1.

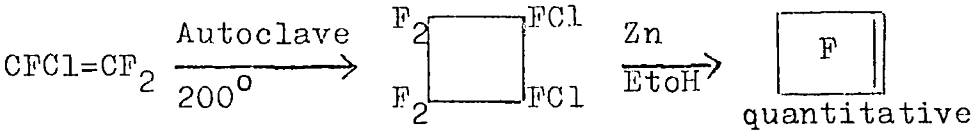
Table 1

Syntheses of Fluoro Olefins Involving Dehydrohalogenation or Dehalogenation

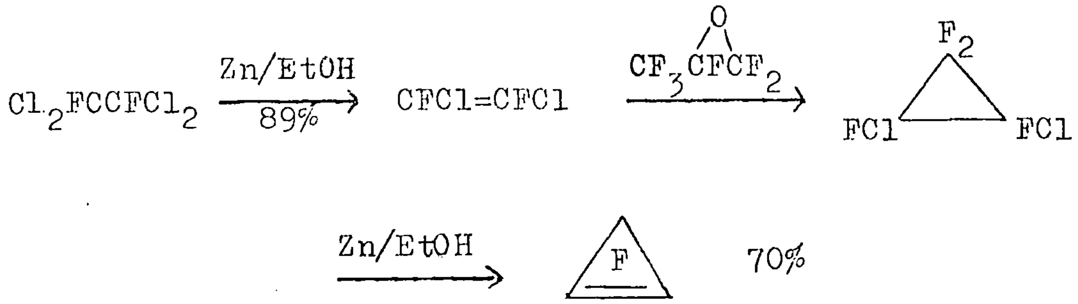


(6)

$$CF_2{=}CFCl + HBr \xrightarrow[\text{Vapour Phase}]{100^\circ} CF_2BrCFClH \xrightarrow{Zn} CF_2{=}CFH\ 85\% \qquad (7)$$


(8)

$$F_2ClCCClH_2 \xrightarrow[CH_3CONH_2,(C_6H_9)(C_2H_5)CHCH_2OH]{Zn, NaI} CF_2{=}CH_2 \quad 97\%$$ (9)


(10)

I.A.2 Synthesis of Higher Fluoro Olefins

Several of the higher fluoro olefins can be prepared from tetrafluoroethylene or more conveniently in the laboratory from polytetrafluoroethylene.[11]

$$(-CF_2-CF_2-)_n \xrightarrow{450^\circ} CF_2{=}CF_2 \xrightarrow{700^\circ} CF_2{=}CFCF_3 \ (32\%)$$
$$+\ CF_3CF{=}CFCF_3 \ (9\%)$$
$$+\ CF_2{=}C(CF_3)_2 \ (53\%)$$

Similarly perfluoro-isobutene can be prepared from hexafluoropropene.[12]

$$CF_3CF{=}CF_2 \xrightarrow{750^\circ} CF_2{=}C(CF_3)_2 \quad 95\% \text{ yield, } 50\% \text{ conversion}$$

Salts of straight chained fluoroacids decarboxylate on heating to yield the corresponding terminal olefin.[13] The yields by this method are good and allow formation of olefins with chain lengths of up to nine carbons.

$$C_5F_{11}CF_2CF_2CO_2Na \xrightarrow[-CO_2]{\Delta} C_5F_{11}CF{=}CF_2 + NaF \quad 86\%$$

I.A.3 β-substituted Fluoro Olefins

Burton and co-workers have developed a general route to a series of β-substituted fluoro olefins.[14,15] The synthesis involves reacting a Wittig reagent $(C_6H_5)_3P{=}CF_2$, generated in situ from sodium chlorodifluoroacetate and triphenyl phosphate, with a polyfluorinated ketone. In general the yields were high with the exception of p-dimethylaminotrifluoroacetophenone which gave only a 16% yield of olefin.

$$C_6H_5COCF_3 \xrightarrow[2CF_2ClCO_2Na]{(C_6H_5)_3P} C_6H_5C(CF_3){=}CF_2 \quad 84\%$$

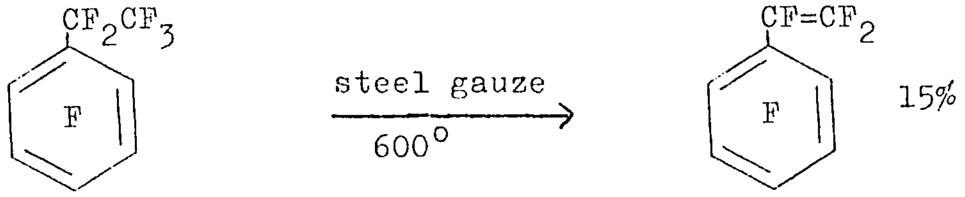
Similarly 1,1-difluoro olefins can be prepared by treating aldehydes or ketones with a solution of CF_2Cl_2 (or CF_2Br_2) and $P(NMe_2)_3$ in triglyme.[16,17] The lasting reactivity of the solution was demonstrated by reacting (1), with solution 300 hrs. old, to give (2) in 68% yield.

$$\underset{(1)}{PhCOCH_3} \xrightarrow[\text{Triglyme}]{CF_2Cl/P(NMe_2)_3} \underset{(2)}{PhCMe{=}CF_2} \quad 68\%$$

A solution of CF_2Br_2 and Ph_3P in triglyme reacted only with aldehydes or activated ketones.

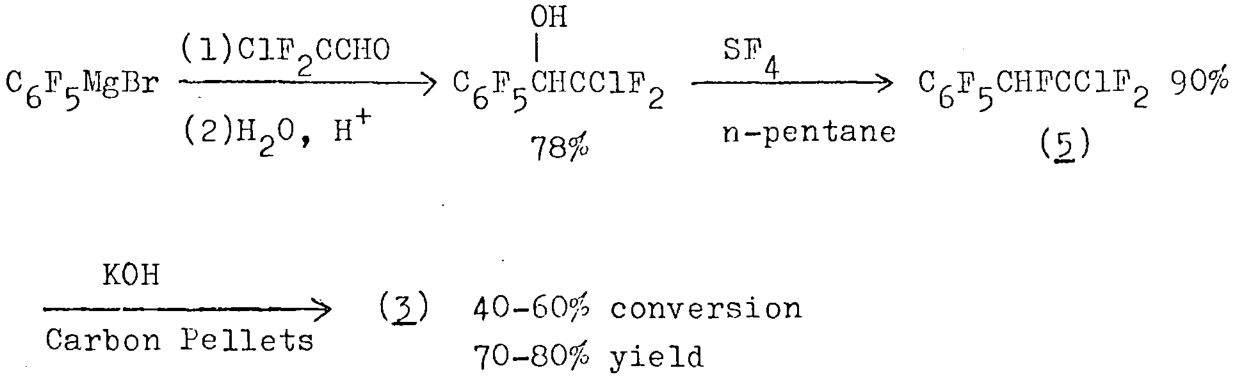
I.A.4 Synthesis of Trifluorovinylhaloaryl Compounds

Several routes have been developed leading to perfluorostyrene (3). Tatlow and co-workers produced (3) in low yields by defluorinating (4) over steel gauze.[18]



(4) (3)

Higher yields of (3) were obtained by passing (5), under reduced pressure, through a heated iron tube packed with carbon pellets impregnated with KOH, (Scheme 1).[19]



$$C_6F_5MgBr \xrightarrow[(2)H_2O,\ H^+]{(1)ClF_2CCHO} \underset{78\%}{C_6F_5\overset{OH}{\overset{|}{C}}HCClF_2} \xrightarrow[n\text{-pentane}]{SF_4} \underset{(5)}{C_6F_5CHFCClF_2}\ 90\%$$

$$\xrightarrow[\text{Carbon Pellets}]{KOH} (3)\quad \begin{array}{l}40\text{-}60\%\ \text{conversion}\\ 70\text{-}80\%\ \text{yield}\end{array}$$

Scheme 1

A general synthesis for compounds of the type $Ar_xCF=CF_2$ via reaction of $CF_2=CFI$ with polyhaloarylcopper has been reported.[20]

$$Ar_xCu + CF_2=CFI \longrightarrow Ar_xCF=CF_2$$

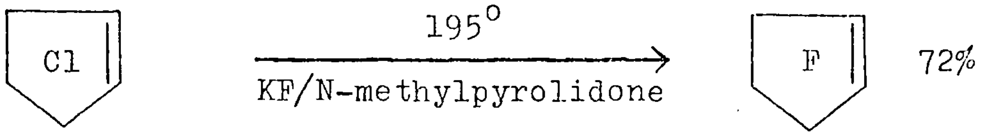
where $Ar_x = C_6F_5$, C_5F_4N, C_6F_4H, C_6F_4Br, C_6Cl_5, C_5Cl_4N.

In particular pentafluorophenylcopper dioxanate with CF_2=CFI gave (3) in high yield.

$$C_6F_5\text{-Cu dioxanate} + CF_2\text{=CFI} \xrightarrow[(2)H^+,H_2O]{(1)\ T.H.F.,0^o} (3)\ 88\%$$

I.A.5 One Step Synthesis

The only Perfluoro Olefin synthesised in a one stage synthesis from non-fluorinated starting material is the conversion of perchloropentene to its perfluoro analogue, using potassium fluoride and N-methylpyrrolidone[21] (in this laboratory sulpholane has been used with success).



I.B Reactivity of Fluoro Olefins

Substitution of hydrogen by fluorine in olefins increases their reactivity towards certain processes e.g. the heats of addition of halogens and halogen acids to tetrafluoroethylene are larger by 4 K cals/mole per C-F bond than in ethylene.[22] Similarly the formation of octafluorocyclobutane from tetrafluoroethylene is exothermic, whereas the analogous dimerisation of ethylene is unobserved.[22]

Two differing explanations have been used to account for this increased reactivity.

(i) An increase in C-F bond strength in going from an olefin to a saturated system.

(ii) Destabilisation of the π-system on fluorine substitution.

Explanation (i) was favoured by Peters[22] who suggested there was little difference in the strength of the c=c bond in tetrafluoroethylene and ethylene, and argued the increased reactivity was due to the increased C-F bond strength in changing the carbon atom hybridisation from $sp^2 \rightarrow sp^3$ i.e. the greater stability of the saturated compound rather than destabilisation of the π-system is the driving force of the reaction.

More recent data obtained from the heat of formation of the diradical $\dot{C}F_2-\dot{C}F_2$ suggests the π-bond in tetrafluoroethylene is 20 k cal/mole weaker than the corresponding bond in ethylene[23]. However from this result it is not possible to decide a reason for the increased reactivity as both explanations (i) and (ii) could be used to fit the case.

Cheswick used the ideas in explanation (ii) to account for the difference in ΔH values obtained for the ring opening reactions shown in Table 2[24].

Table 2

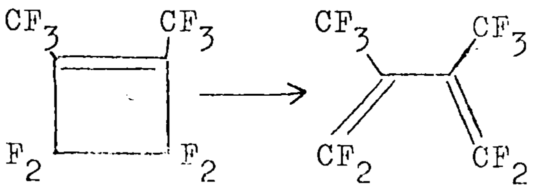
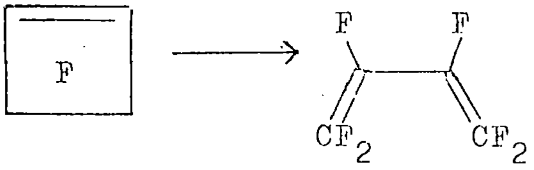
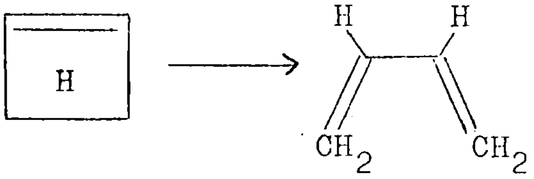
	Reaction	ΔH K cal/mole
A		0.4

Table 2 (cont'd)

Reaction		ΔH K cal/mole
B		11.7
C		-8

In reactions A and B the number of C-F bonds undergoing a change in hybridisation from $sp^2 \rightarrow sp^3$ is the same, consequently if changes in the C-F bond energies on changing hybridisation were responsible for the increased reactivity of fluoro olefins, A and B should have similar ΔH values. However, there is an observed difference of 11.3 K cal/mole and it was argued this was caused by destabilisation of the π-system by fluorine. In the systems used the change in the number of vinylic fluorines was the same, suggesting the destabilisation on substituting fluorine for hydrogen in ethylene is not additive, i.e. the destabilisation on substituting the first fluorine in ethylene is less than the increased destabilisation on substituting the second.

I.B.1 Nature of the Double Bond

The nature of the bonding and hybridisation of carbon in fluoroethylenes has received some attention.

The simplest picture suggests the carbon is sp^2 hybridised, as in ethylene, and there is strong electron-pair repulsion between the filled p orbitals of fluorine and the π-bond, leading to increased reactivity (Fig. 1)[25].

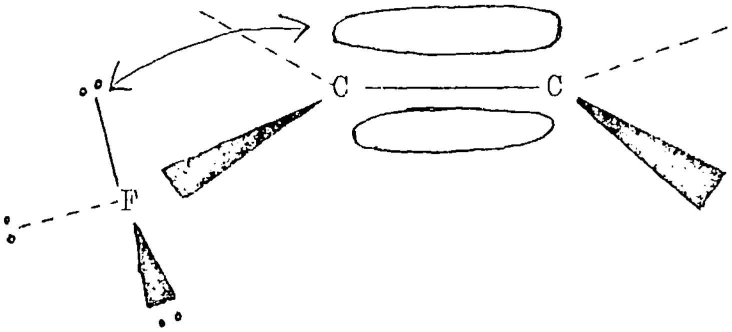


Fig. 1

A different approach was provided by Bernett[26], who from bond angle and hybridisation data suggested a change in hybridisation occurs on replacing hydrogen by fluorine in ethylene (Table 3).

Table 3

Bond Angles and Hybridisation in Difluoromethylene Groups

Compound	FCF	C-Fsp^x	C-FA^o
CF_2H_2	$108^o17'\pm6'$	3.18	1.358 ± 0.001
$CF_2=CH_2$	$109^o18'\pm24'$	3.03	1.321 ± 0.005
$CF_2=CF_2$	$110^o\pm2^o$	2.92	1.33 ± 0.02

Bernett concludes from the data that when an olefin contains a difluoromethylene group the high electronegativity of fluorine causes the hybridisation of the carbon to become essentially sp^3. Thus the carbon has either, two sp^3 hybrid atomic orbitals (H.A.O) (used in forming the C-F bonds) and an sp HAO along with an unhybridised p orbital (the former used in forming the σ-bond, the latter the π-bond), or four equivalent sp^3 orbitals at each carbon in the bent-bond configuration (Fig. 2).

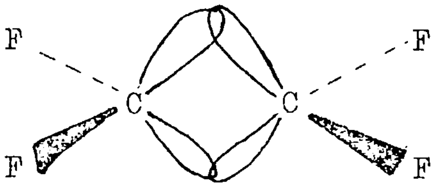


Fig. 2

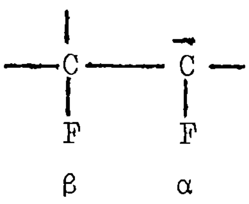
In the case of the bent-bond model repulsion between the fluorine and π-bond would be less pronounced, but the resultant strained system would account for the increased reactivity. Recent calculations by Dewar[27] has supported the ideas proposed by Bernett.

Photoelectron spectroscopy has also provided a picture of the fluoro-ethylene system[28]. Results show the σ-molecular orbitals are strongly stabilised by extensive mixing of the ethylene group orbitals with the σ-atomic orbitals of the highly electronegative fluorine. However, in the π-molecular orbitals this effect is much smaller and is counteracted by a strong C-F antibonding overlap.

CHAPTER II

Stability of Polyfluoroalkyl Anions

Since many reactions of fluoro olefins with nucleophiles are thought to proceed via an intermediate carbanion, including some work of the author to be discussed later, it is felt a detailed discussion of the factors affecting the stability of polyfluoroalkyl anions is required. The most commonly used nomenclature for the position of substituents is as shown.



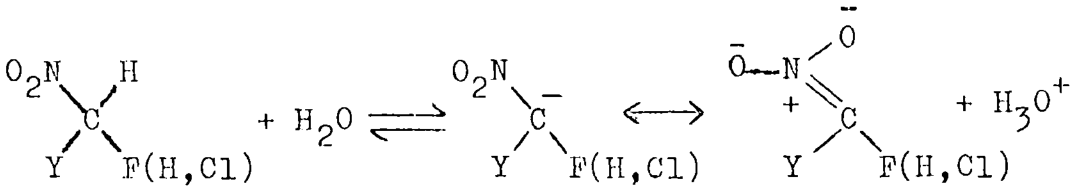
$$-\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{-}{\underset{\mathrm{F}}{\mathrm{C}}}-$$

The results show that, for α-substituents inductive (Iσ and Iπ), hybridisation (sp^2- sp^3), mesomeric and 2p-3d orbital overlap effects are important, while for β-substituents only inductive effects are important.

II.A.1 α-substituents

Hine[29] and co-workers, using kinetic measurements of the base-catalysed deuterium exchange for a series of haloforms, have shown that α-substituents facilitate carbanion formation in the order I>Br>Cl>F>OEt.

After measuring the ionisation constants for a series of substituted nitromethanes (6), Adolph and Kamlet[30] found that carbanions with structure (7) were stabilised by α-substituents in the order Cl>H>F for a given Y group, (except for Y=NO_2 where Cl≈H).

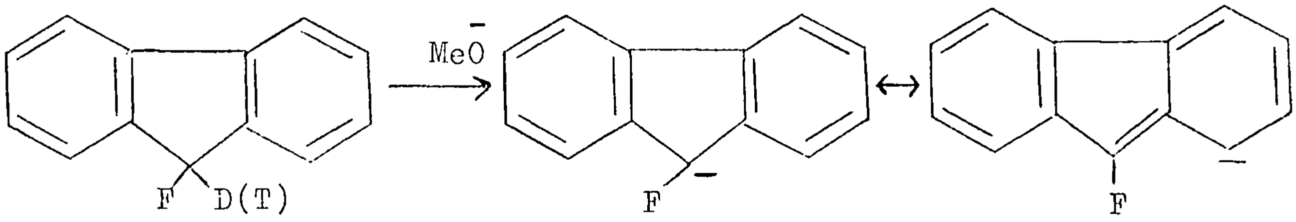


(6) (7)

Y = Cl, COOEt, $CONH_2$, NO_2.

Hine[31], after reviewing the available data, has concluded that the presence of an α-fluorine decreases the rate of formation of sp^2 hybridised polyfluoroalkyl anions, or at least increases to a lesser extent than expected from inductive effects, while with sp^3 hybridised anions an α-fluorine increases the reactivity.

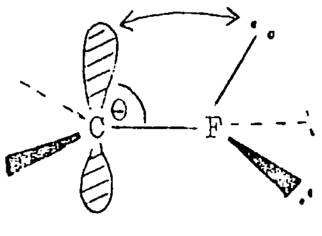
The dependence of carbanion stability on stereochemistry was demonstrated by Streitwieser[32], who compared the kinetic acidity of 9-fluorofluorene (8) and α,α-difluorotoluene with fluorene and toluene respectively. The results showed that with (8) substitution by fluorine at the 9-position decreased the rate of exchange by a factor of eight compared to fluorene, but with the 9-chloro and 9-bromo compounds an increase of 4×10^2 and 7×10^2 respectively was observed. In the case of toluene, substitution of α-hydrogens by two fluorines increased the rate of exchange by a factor $>10^4$.



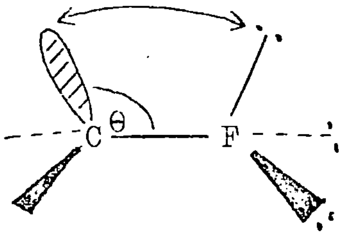
(8) (9)

Streitwieser suggested that the 9-fluorofluorenyl anion (9) was planar but the α,α-difluorobenzyl anion was pyramidal, and concluded that an α-fluorine atom will stabilise a pyramidal or non-conjugated anion, but destabilisation can occur with a conjugated anion.

The results discussed in this section show that the stability of a polyfluoroalkyl anion depends on the nature of the α-substituents as well as on the structure of the carbanion. It has been suggested that the Iπ effect[33,30] is the cause of destabilisation by an α-fluorine at a planar (sp^2) carbanion, in contrast to the stabilising effect, relative to hydrogen, of an α-fluorine at a pyramidal (sp^3) carbanion. For a planar (sp^2) carbanion (10) the electron pair is localised within a 2p orbital, consequently coulombic repulsion between the electron pair and the non-bonding electrons of fluorine (Iπ effect) is maximised, while at a pyramidal (sp^3) carbanion (11) the effect is minimised. The order of Iπ repulsion has been shown to be F>Cl>Br>I.



$\theta = 90^{o}$ (10)



$\theta = 109$ (11)

An alternative suggestion from Hine[31] proposes that bond weakening occurs, in cases where formation of a carbanion involves rehybridisation from $sp^3 \rightarrow sp^2$, due to a change in electronegativity of the carbon atom. It is argued that an sp^2 carbon is more electronegative than an sp^3 carbon, and, since the strength of a covalent bond is proportional to the square of the electronegativity differences of the atoms, an sp^3 carbon halogen bond will be stronger than the corresponding sp^2 carbon halogen bond. This effect will be greatest when the halogen is fluorine.

Other explanations for the observed effects of α-substituents include the electrostatic polarisation of the halogen, which increases $F < Cl < Br < I$[29], and carbon sp-substituent 3d orbital overlap[34]. In reality the effects of α-substituents, on polyfluoroalkyl anion stability, probably arises from a combination of these factors.

II.A.2 β-substituents

A systematic study of the effect of β-substituents on carbanion stability has only been reported for fluorine. Andreades[35] measured the kinetic acidity of a series of monohydrofluorocarbons and, from the results (Table 4) concluded that the order of decreasing stability in the fluorocarbon series is tertiary>secondary>primary.

Table 4[35]

Compound	Relative Reactivity	pKa value
CF_3H	1	25.5
$CF_3(CF_2)_5CF_2H$	6	-
$(CF_3)_2CFH$	$2x10^5$	22.5
$(CF_3)_3CH$	10^9	7

The acidities (pKa values) for a series of fluoroalkanes were also estimated from polarographic data, derived from the electrochemical reduction of the corresponding mercurial, $(R_F)_2Hg$, and these were found to be in reasonable agreement with those previously reported[36].

Further evidence of carbanion stabilisation by β-fluorine was provided by Knunyants[37] and Hine[38], the former finding the Ka value of $CF_3CH_2NO_2$ and $CH_3CH_2NO_2$ were 4.0×10^{-8} and 2.5×10^{-9} respectively, while the latter showed the acidity of CF_3CCl_2H was forty times that of $CFCl_2H$.

Andreades has rationalised the stabilising effect of β-fluorine in terms of negative hyperconjugation (analogous to stabilisation of carbonium ions by positive hyperconjugation) Fig. 3.

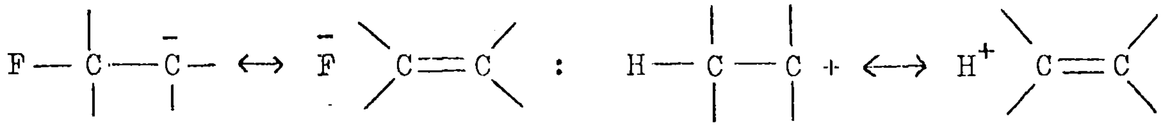
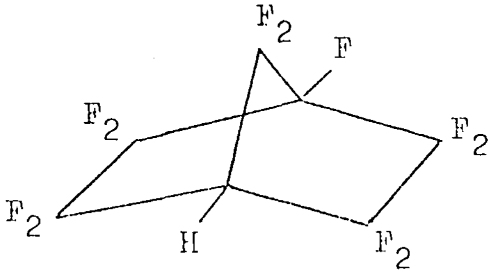
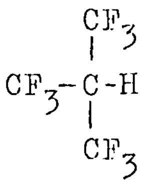


Fig. 3

To establish the significance of negative hyperconjugation Streitwieser[39] compared the kinetic acidities of 1H-undecafluorobicyclo [2.2.1] heptane (12) and (tristrifluoromethyl) methane (13).



(12)



$$(CF_3)_3C{-}H$$

(13)

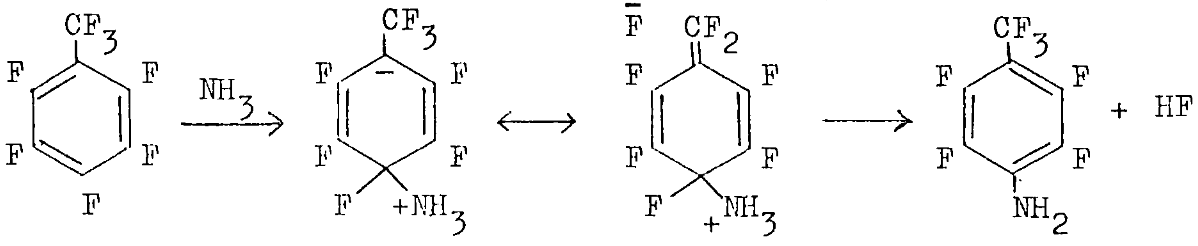
The carbanion intermediate derived from (12) will be forced to remain pyramidal and negative hyperconjugation will be greatly reduced, consequently if this type of hyperconjugation is important in polyfluoroalkyl anion stabilisation the kinetic acidity of (13) should be greater than (12). However the reverse was observed, with that of (12) being five times that of (13), and Streitwieser rationalised the greater stability of the internal carbanion from (12) as being due to enhanced inductive effects.

Further data concerning the role of negative hyperconjugation has been obtained at these laboratories^{40}. The rate constants for the reaction of ammonia with a series of perfluoroalkylbenzenes were measured and are summarised in Table 5.

Table 5

Compound	C_6F_6	$C_6F_5CF_3$	$C_6F_5CF_2CF_3$	$C_6F_5CF(CF_3)_2$	$C_6F_5C(CF_3)_3$
$10^3K(1\ mole^{-1}s^{-1})$	Too slow to measure	0.670 ($\pm$0.003)	1.44 ($\pm$0.01)	1.00 ($\pm$0.01)	1.73 ($\pm$0.01)

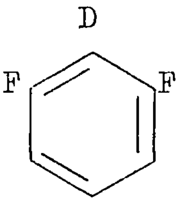
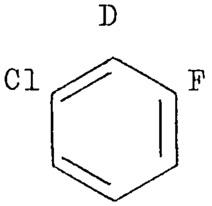
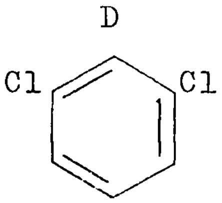
If negative hyperconjugation is important the fastest rate of substitution would be expected with perfluorotoluene, where the largest number of fluorine atoms able to participate in negative hyperconjugation are present (Scheme 2).



Scheme 2

However the observed rates indicate that perfluorotoluene is the least reactive, a result which Chambers and co-workers suggest raises doubts about the necessity of invoking the concept of negative hyperconjugation at all. The results are interpreted in terms of I_π stabilisation of adjacent charge by perfluoroalkyl groups in the transition state.

There is only a very limited amount of data available on the ability of other β-halogens to stabilise a carbanion, but deuterium exchange reactions of m-dihalobenzenes have shown replacement of a β-chlorine by a fluorine increases the kinetic acidity by a factor of about 7, a fact attributed to an inductive effect[41].

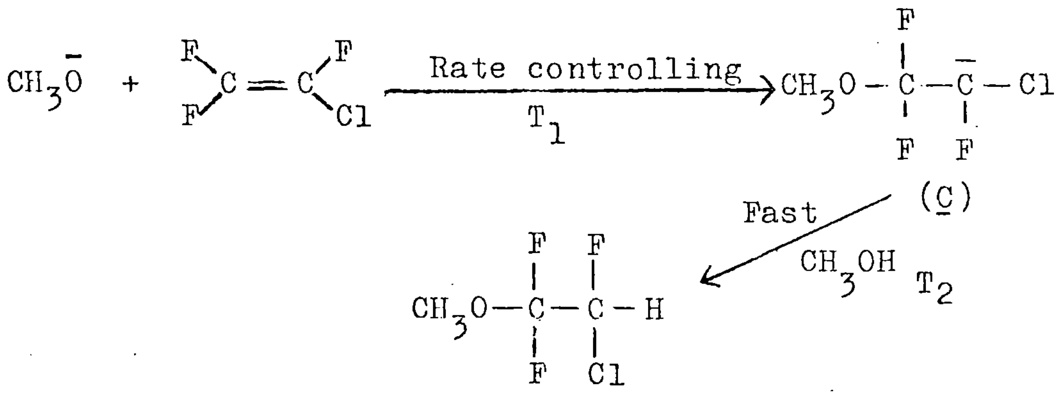
			
$10^6K(100^o)$	978	151	20.2

CHAPTER III

Ionic Reactions of Fluoro Olefins

III.A Nucleophilic Reactions

When hydrogen is replaced by fluorine in ethylene, strong electron withdrawal by fluorine renders the olefin susceptible to nucleophilic attack, contrasting with the mainly electrophilic nature of ionic reactions in hydrocarbon olefins. This was first demonstrated by Miller and co-workers[42] who studied the base catalysed addition of methanol to a series of fluoro olefins, proposing a mechanism for the reaction (Scheme 3), involving formation of an intermediate carbanion as the rate determining step.



Scheme 3

A possible energy profile for the reaction is represented in Fig. 4

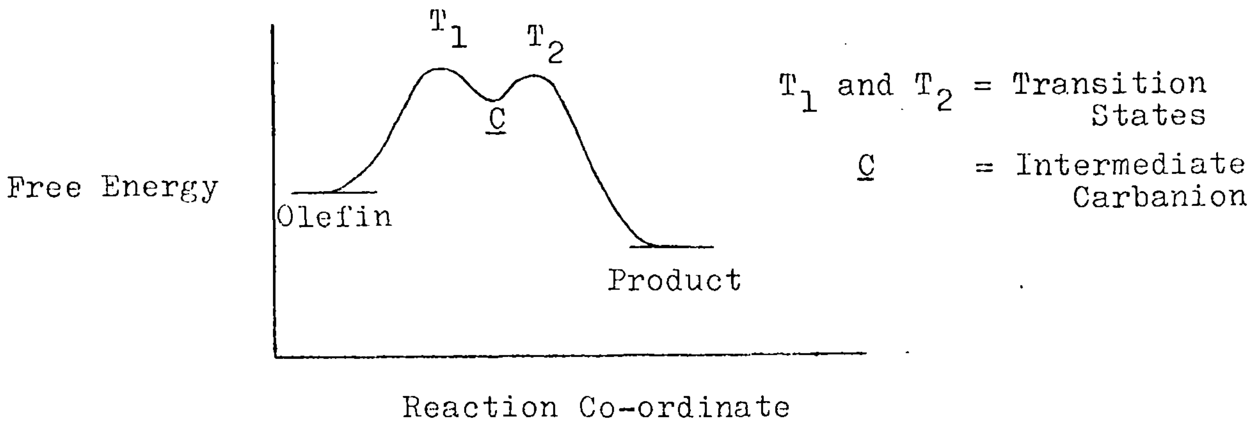
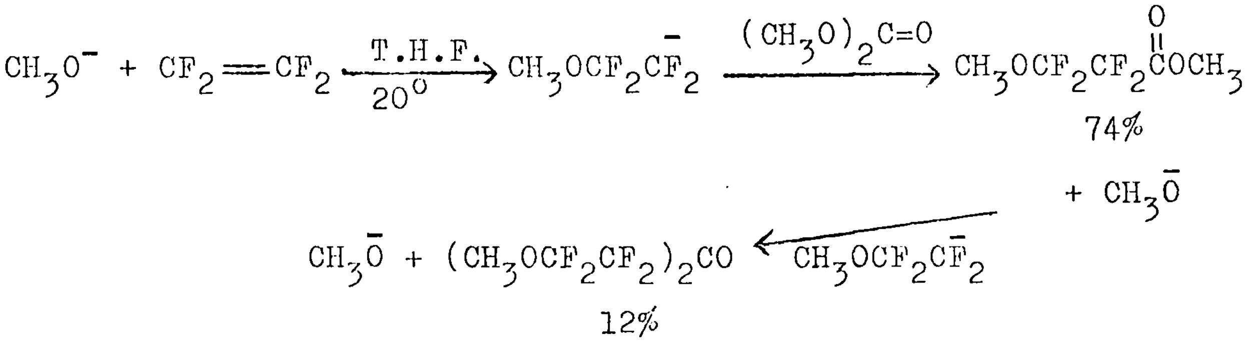


Fig. 4

The presence of carbanion intermediates, at least in the reaction of sodium methoxide with tetrafluoroethylene, was demonstrated by Wiley[43] who succeeded in trapping the intermediate carbanion with dimethoxycarbonate.



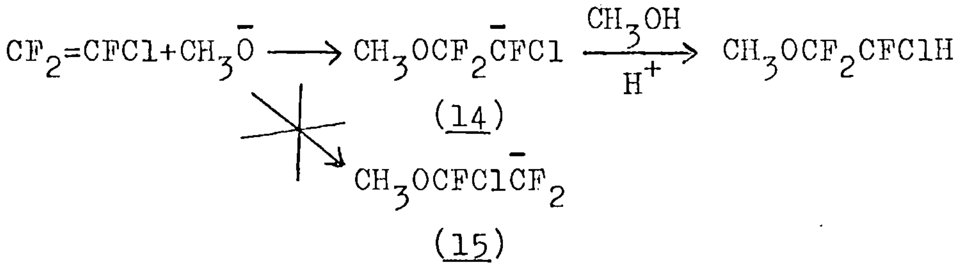
$$CH_3O^- + CF_2{=}CF_2 \xrightarrow[20^\circ]{T.H.F.} CH_3OCF_2\bar{C}F_2 \xrightarrow{(CH_3O)_2C=O} CH_3OCF_2CF_2\overset{\overset{O}{\|}}{C}OCH_3 \;\; 74\%$$

$$CH_3OCF_2CF_2\overset{\overset{O}{\|}}{C}OCH_3 + CH_3\bar{O}$$

$$CH_3\bar{O} + (CH_3OCF_2CF_2)_2CO \;\; 12\% \longleftarrow CH_3OCF_2\bar{C}F_2$$

III.A.1 Orientation of Addition

Nucleophilic attack on fluoro olefins preferentially occurs at a terminal difluoromethylene group[1], and this is illustrated by the examples shown below, where all the products isolated are consistent with nucleophilic attack at the difluoromethylene group.



$$CF_2{=}CFCl + CH_3\bar{O} \longrightarrow CH_3OCF_2\bar{C}FCl \xrightarrow[H^+]{CH_3OH} CH_3OCF_2CFClH$$

(14)

$$CF_2{=}CFCl + CH_3\bar{O} \not\longrightarrow CH_3OCFCl\bar{C}F_2$$

(15)

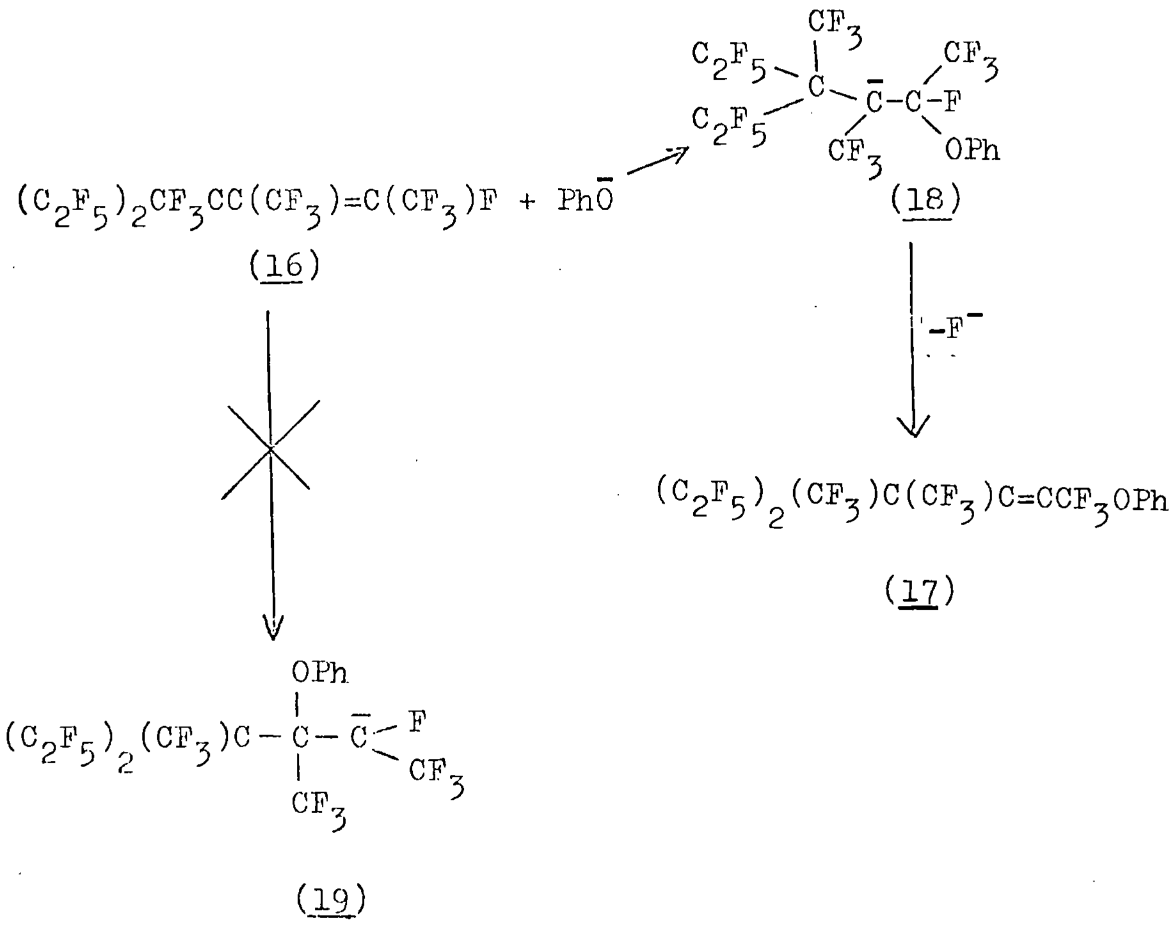
(44)

$$CF_3CF{=}CF_2 + \bar{O}Et \longrightarrow CF_3\bar{C}FCF_2OEt \longrightarrow CF_3CHFCF_2OEt \qquad (45)$$

$$CF_2{=}CFBr + Et_2NH \longrightarrow Et_2NCF_2CFBrH \qquad (46)$$

An explanation, which can account for the direction of attack, is obtained if the possible intermediate carbanions are examined. In the case of chlorotrifluoroethylene, carbanion (14) is stabilised by two β-fluorines and one α-chlorine, with possible destabilisation by an α-fluorine, but with carbanion (15) the roles are reversed with only one stabilising β-fluorine and two possibly destabilising α-fluorines. Therefore carbanion (14) would be expected to be more stable than (15).

In the case of internally unsaturated olefins the products formed are consistent with the reaction proceeding via the most stable intermediate carbanion i.e. the relative stabilities of the intermediate carbanions determines the direction of attack[47]. Thus reaction of the internally unsaturated olefin (16) with phenoxide gives the product (17) derived from the more stable carbanion (18), rather than from (19) which is possibly less stable because of the anion having an α-fluorine.



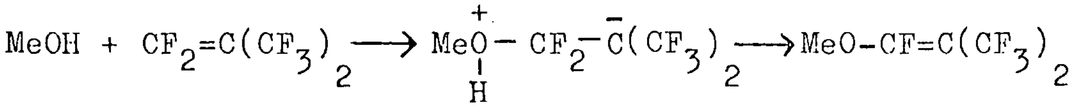
(48)

III.A.2 Relative Reactivities

Fluoro olefins containing a terminal difluoromethylene group are the most reactive towards nucleophiles[1], with relative reactivities indicating that the rate determining step is formation of the intermediate carbanion. For example, the order of reactivity increases along the series,

$$CF_2{=}CF_2 < CF_2{=}CFCF_3 << CF_2{=}C(CF_3)_2$$

a result that is consistent with the order of increasing carbanion stability. In fact, perfluoroisobutene is so reactive towards nucleophiles that reaction with alcohols can occur in neutral media, a property thought to be derived from the large stabilising influence of the trifluoromethyl groups upon the intermediate carbanion[49].



$$MeOH + CF_2{=}C(CF_3)_2 \longrightarrow Me\underset{\substack{|\\H}}{\overset{+}{O}}-CF_2-\overset{-}{C}(CF_3)_2 \longrightarrow MeO{-}CF{=}C(CF_3)_2$$

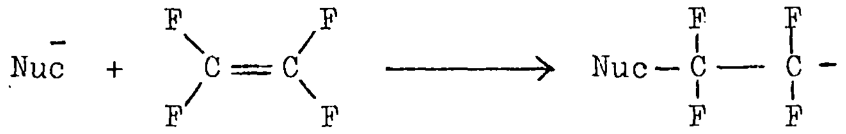
Similarly, the rates of addition of Et_2NH have been found to increase in the series,

$$CF_2{=}CF_2 < CF_2{=}CFCl < CF_2{=}CFBr$$

Again the order is the same as that proposed for the increasing stability of the intermediate carbanion[46].

Not all reactivity can be explained on the basis of the relative stabilities of intermediate carbanions, as is demonstrated by tetrachloroethylene being less susceptible to nucleophilic attack than tetrafluoroethylene. Examination of the intermediates (20) and (21) indicate that from substituent effects the reverse order could be expected. This result has been rationalised in terms of a greater degree of polarisation of the carbon-fluorine bond, $\overset{\delta+}{C} — \overset{\delta-}{F}$, compared to carbon-chlorine, which lowers the activation-energy of nucleophilic attack[49].

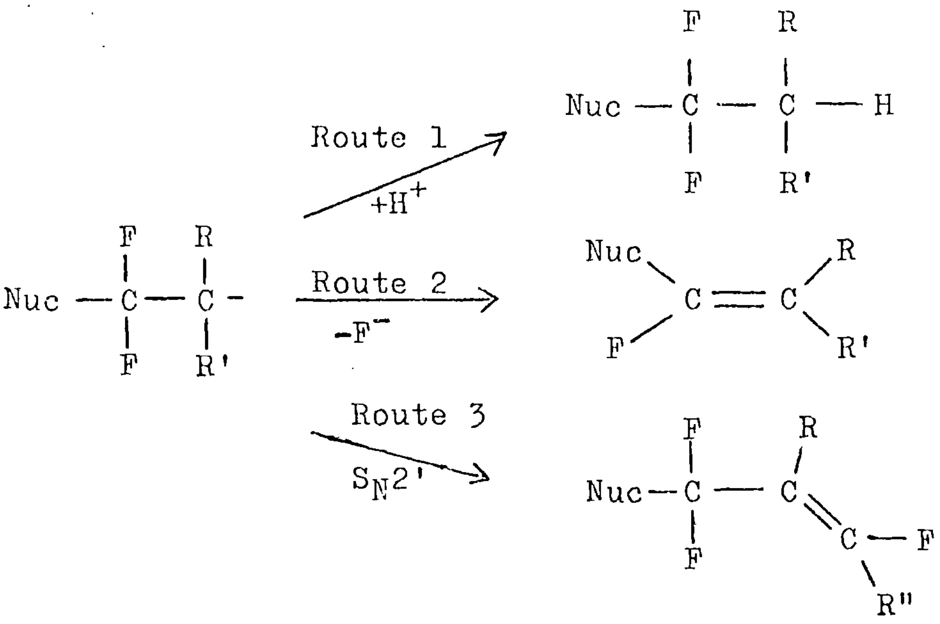
(20)



(21)

III.A.3 Product Formation

The nature of the products formed by nucleophilic attack on a fluoro olefin can be regarded as being dependent on the fate of the intermediate carbanion. There are three possible fates for an intermediate: (i) Addition of a proton (route 1), (ii) Elimination of fluoride ion (route 2), or (iii) Substitution with rearrangement via an S_N2' process (route 3), and these are shown in Scheme 4.



Scheme 4

III.A.3.a Addition versus Elimination

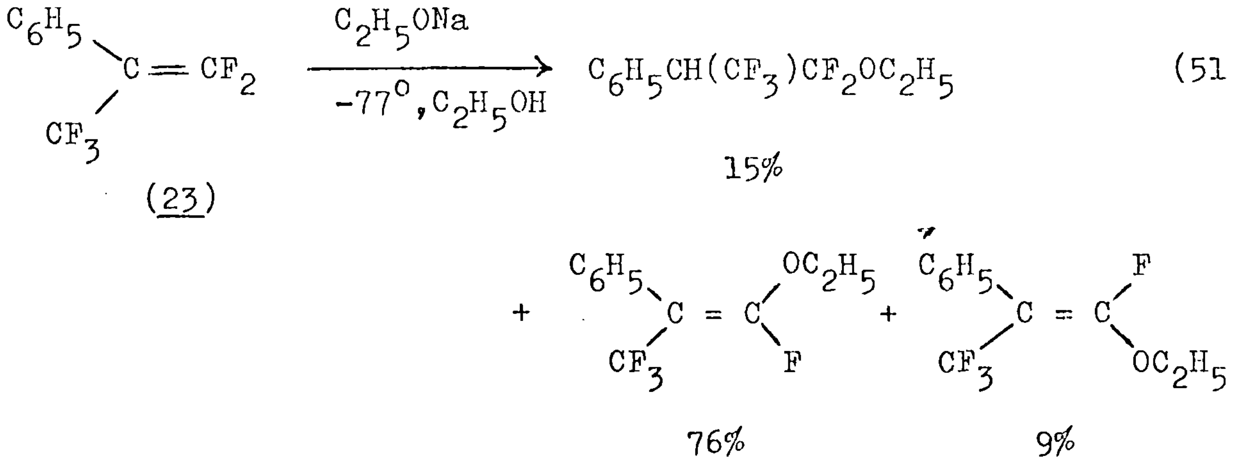
Addition across the double bond (route 1) is the common reaction of fluoroethylenes, but with higher fluoro olefins products derived from elimination of fluoride ion (route 2) are also formed.

$$C_2H_5OH + CF_2{=}CF_2 \xrightarrow{Na} C_2H_5OCF_2CHF_2 \qquad (1)$$

$$CH_3OH + CF_2{=}C(CF_3)_2 \longrightarrow \underset{65\%}{CH_3OCF_2CH(CF_3)_2} + \underset{8\%}{CH_3OCF{=}C(CF_3)_2}$$

The ratio of elimination to addition products increases with the reactivity of the olefin, this being due to the increasing stabilisation of the intermediate carbanion, subsequently reducing the base strength of the carbanion[50]. The effect of carbanion stabilisation on the ratio of elimination to addition products is demonstrated by the reaction of hexafluoropropene (22) with methanol and 2-phenylpentafluoropropene (23) with ethoxide. In the former only a small amount of elimination occurs but in the latter, where delocalisation of the charge into the ring can occur, elimination accounts for the major product.

$$CH_3OH + CF_2{=}CF.CF_3 \xrightarrow[\text{Autoclave}]{KOH/60^{o}} \underset{83\%}{CH_3OCF_2CHFCF_3} + CH_3OCF{=}CFCF_3 \qquad (1)$$



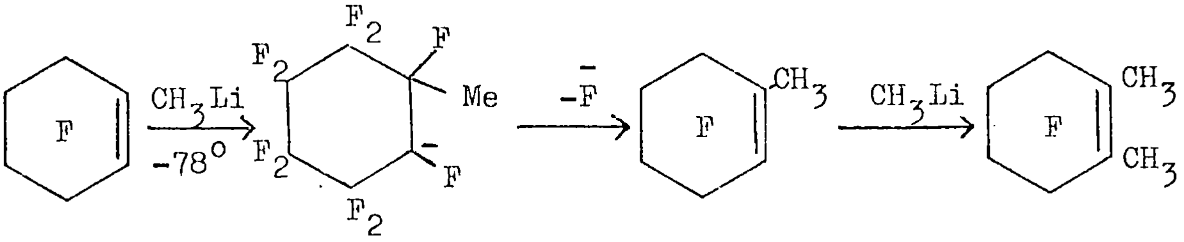
(51)

Steric interactions could also effect the ratio of elimination to addition, for example with perfluoroisobutene an addition product is probably less stable, due to greater steric crowding, than the corresponding elimination product.

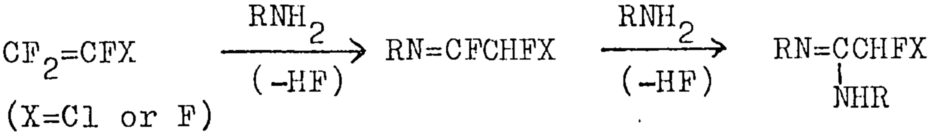
Allylic displacement (S_N2') shown in route 3 will be discussed fully in section III.A.4.

Nucleophilic reactions of fluoro olefins have been extensively investigated and a few typical reactions are shown in Table 6. A review which includes nucleophilic reactions of fluoro olefins has been published[1].

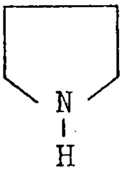
Table 6



(52)



$$\underset{(X=Cl\ or\ F)}{CF_2=CFX} \xrightarrow[(-HF)]{RNH_2} RN=CFCHFX \xrightarrow[(-HF)]{RNH_2} RN=\underset{NHR}{\underset{|}{C}}CHFX \qquad (1)$$



$$+ CF_2=CF_2 \xrightarrow[60^{\circ}]{\text{Temp. kept below}} \underset{60\%}{C_4H_8N.CF_2CF_2H} \qquad (53)$$

$$RSH + CF_2=CX_2 \xrightarrow{base} RSCF_2CX_2H \xrightarrow[D.M.S.O]{KOH} RSCF=CX_2 \qquad (54)$$

$$CF_3\ CCl=CCl\ CF_3(\underline{cis}) \xrightarrow[0^{\circ}\ diglyme]{NaBH_4} CF_3CH=CClCF_3\quad (100\%\ \underline{cis}) \qquad (55)$$

79% conversion

III.A.4 Substitution with Rearrangement

As this topic has direct relevance to some of the work carried out by the author (to be described in the discussion of the experimental), a more detailed review will be undertaken.

One of the features of fluoro olefin chemistry has been the common occurrence of substitutions with rearrangement (S_N2')

a topic investigated by various workers with many examples now being known, but in most cases uncertainty still exists as to whether a concerted S_N2' mechanism is involved, or a two stage addition-elimination type of process.

In the fifties Miller and co-workers[56] investigating the reaction of iodide ion on a series of fluoro olefins observed with (24) allylic displacement occurring to give (25), while with (26) there was no reaction.

$$CF_2{=}CFCF_2Cl + I^- \rightleftharpoons CF_2ICF{=}CF_2 + Cl^-$$

(24) (25)

$$CFCl{=}CFCF_2Cl + I^- \nrightarrow$$

(26)

The fact that (24) gives products derived from allylic displacement while (26) remains unreacted, was accounted for by the suggestion that, with (24) a concerted S_N2' mechanism operates, (Scheme 5), while the lower susceptibility of the CFCl=group to nucleophilic attack, compared to $CF_2{=}$, renders (26) unreactive towards such a process. Although the possibility of a mechanism involving a carbanion intermediate was acknowledged it was felt unlikely in this case as no saturated products, derived by proton abstraction by a carbanion, were observed.

$$CF_2{=}CFCF_2Cl + I^- \rightleftharpoons \left[I\cdots CF_2\overset{\cdots}{=}CF\overset{\cdots}{=}CF_2\cdots Cl\right] \rightleftharpoons CF_2ICF{=}CF_2 + Cl^-$$

Scheme 5

Although evidence indicated that (25) was formed via an S_N2' mechanism, S_N2 and S_N1 mechanisms could also account for the products. More unambiguous evidence of an S_N2' type of mechanism operating was provided by the reaction of (27) with various halide ions[57]. The results, (Table 7), indicate that only rearranged products were formed, confirming that the reaction proceeded via a substitution with rearrangement.

Table 7

$$\underset{(27)}{CF_2{=}CHCCl_2F} + F^- \longrightarrow CF_3CH{=}CFCl + Cl^-$$

$$CF_2{=}CHCCl_2F + Cl^- \longrightarrow CF_2ClCH{=}CFCl + Cl^-$$

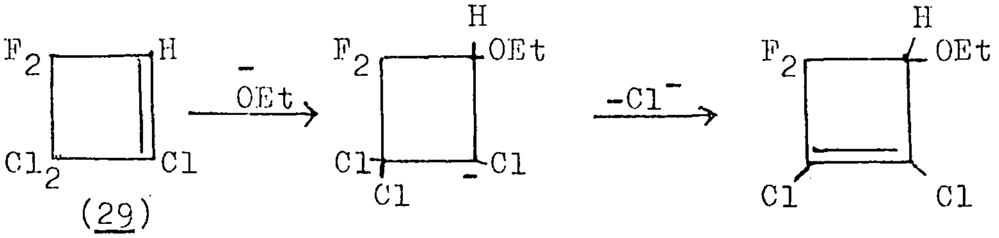
$$CF_2{=}CHCCl_2F + I^- \longrightarrow CF_2ICH{=}CFCl + Cl^-$$

$$CF_2{=}CFCCl_2F + F^- \longrightarrow CF_3CF{=}CFCl + Cl^-$$

The rates of reaction using different halide ions showed that the relative reactivities of the halide ions were $F^- > Cl^- > I^-$, i.e. the opposite of that found in S_N2 reactions. A further unambiguous example of an S_N2' mechanism operating was claimed by Goldwhite and Valdez in the reaction of (28) with chloride ion.

$$\underset{(28)}{CF_2{=}CClCCl_2F} \xrightarrow[25^o]{Et_4N^+Cl^-} CClF{=}CClCClF_2 + Cl^-$$

From inspection of the products formed in the reaction of ethoxide ion with the cyclobutene (<u>29</u>) involving substitution with rearrangement, and evidence collected from other cyclobutene substitution reactions, Park[59] suggested that a mechanism involving a discrete carbanion intermediate, rather than S_N2 or S_N2' processes, was consistent with the available data.



The lack of saturated products in Millers reactions[56], used as evidence of a concerted mechanism, was explained on the basis of a stable carbanion being less likely to abstract a proton from the solvent, and also if a proton was abstracted it would be just as easily lost. Park suggested that the argument presented could also be applied to a transition state with a large amount of carbanion character.

Evidence, derived from comparing the rates of reaction of olefins (<u>23</u>), (<u>30</u>) and (<u>31</u>) with ethoxide in ethanol under pseudo first-order conditions (Table 8), suggests that the reaction proceeds via a carbanion intermediate[51]. In olefins (<u>23</u>) and (<u>31</u>) the leaving group is a fluoride ion, but with (<u>30</u>) elimination of a chloride ion occurs.

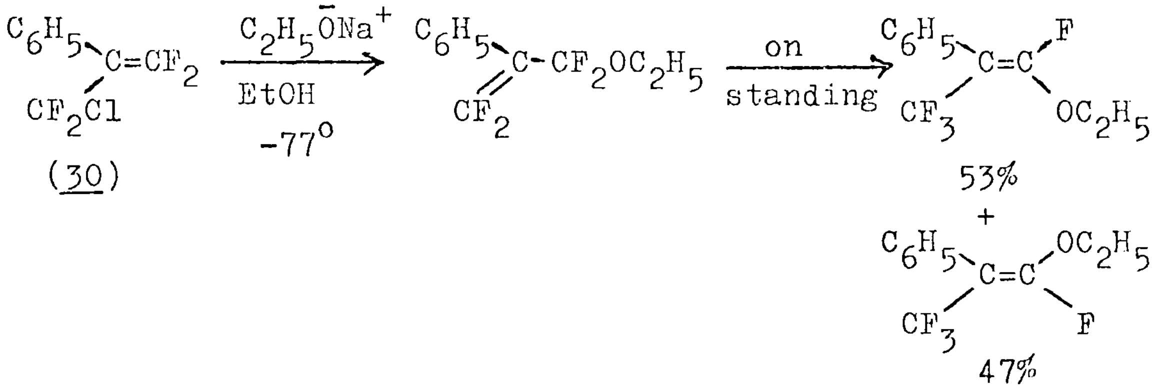
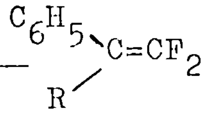


Table 8

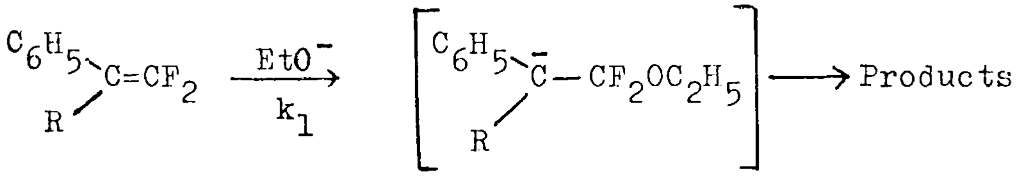
Rates of Reaction of EtO^-Na^+ with



$C_6H_5(R)C=CF_2$

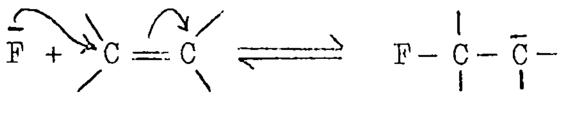
R	$k_1 x 10^3$ sec^{-1}
(23) CF_3	1.9
(30) CF_2Cl	1.8
(31) CF_2CF_3	0.67

If the mechanism involved a concerted process, changing the leaving group from chlorine to fluorine would have an effect on the rates of reaction, but the results show for olefins (23), (30) and (31) that they are comparable, indicating the rate determining step (k_1) involves addition, leading to an intermediate carbanion.

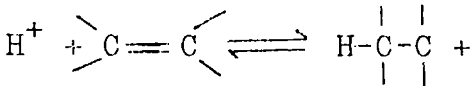


III.A.5 Fluoride Ion Reactions

In fluoro olefin chemistry fluoride ion occupies a position which is analogous to that of the proton in hydrocarbon olefin chemistry.



Cf.



The topic has received considerable attention and in this section a description of various fluoride ion reactions involving fluoro olefins will be given. A review of fluoride ion reactions has been published[60].

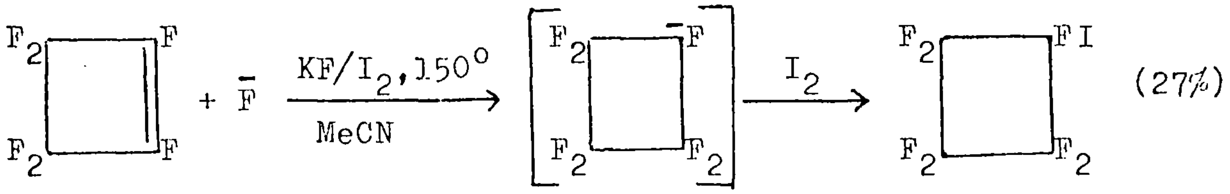
III.A.5.a Addition Reactions

Addition reactions of fluoro olefins usually involve the use of an alkali metal fluoride, in an aprotic solvent, with the resulting carbanion being trapped in various ways[60].

When a fluoro olefin is reacted with fluoride ion in a protogenic solvent proton abstraction can occur giving HF addition[1].

$$F^- + CF_2{=}CClF \xrightarrow[65^o]{KF/formamide} \left[CF_3\bar{C}ClF\right] \xrightarrow[solvent]{H^+} CF_3CHClF \quad 72\%$$

The reaction of fluoride ion with various fluoro olefins in the presence of iodine gives fluoroalkyl iodides in yields varying from 7% for pentafluoroethyl iodide to 60-70% for heptafluoroisopropyl iodide.



The addition of carbonyl fluoride to fluoro olefins in the presence of fluoride ion gives perfluoroacyl fluorides, and the reaction is thought to proceed by reaction of a polyfluorocarbanion with carbonyl fluoride. The conversions varied from 80% for hexafluoropropene to only 13% for tetrafluoroethylene.[62]

$$CF_3CF{=}CF_2 + \bar{F} \rightleftharpoons (CF_3)_2\bar{C}F \xrightarrow{COF_2} (CF_3)_2CF.COF \quad (80\%\ conversion)$$

Perfluorocarboxylic acids have been prepared by the addition of perfluoroalkyl anions to carbon dioxide, thus tetrafluoroethylene yields perfluoro-propionic acid (32)[63].

$$F^- + CF_2{=}CF_2 \underset{}{\overset{100^\circ}{\rightleftharpoons}} CF_3\bar{C}F_2 \xrightarrow[100^\circ]{CO_2} CF_3CF_2CO\bar{O} \xrightarrow{H^+} CF_3CF_2CO_2H \quad (75\%)$$

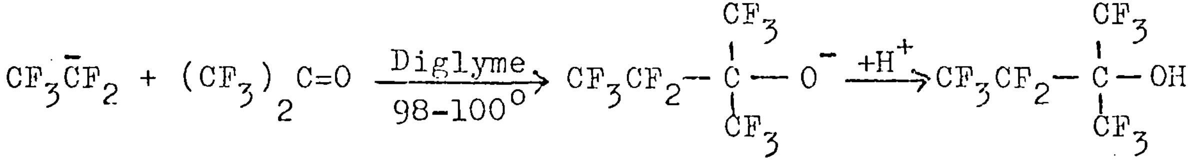
(32)

The results showed that the more complex the olefin the more unstable the resulting acid, and this was demonstrated by no perfluoropivalic acid (33) being isolated from the reaction of perfluoroisobutene with carbon dioxide

$$(CF_3)_3\bar{C} + CO_2 \xrightarrow{+H^+} (CF_3)_3CCOOH$$

(33) Not isolated

Similarly pentafluoroethyl anion reacts with hexafluoroacetone to give perfluoro-t-pentyl alcohol (34).[64]



$$CF_3\bar{C}F_2 + (CF_3)_2C{=}O \xrightarrow[98-100^\circ]{\text{Diglyme}} CF_3CF_2-C(CF_3)_2-O^- \xrightarrow{+H^+} CF_3CF_2-C(CF_3)_2-OH$$

(34)

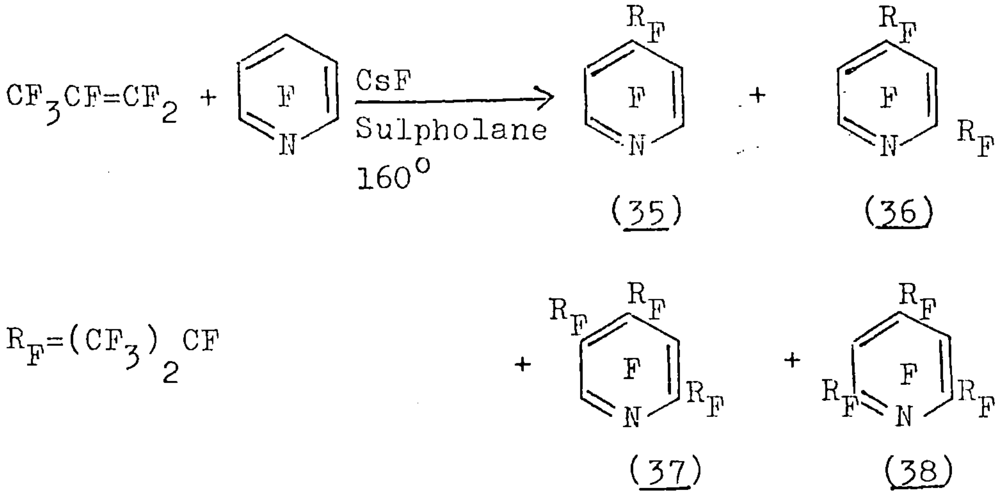
III.A.5.b Polyfluoroalkylations

Polyfluoroalkyl anions, generated by the addition of fluoride ion to fluoro olefins, will react with activated aromatic systems in what can be described as the nucleophilic counterpart of the Friedel-Crafts reaction[65].

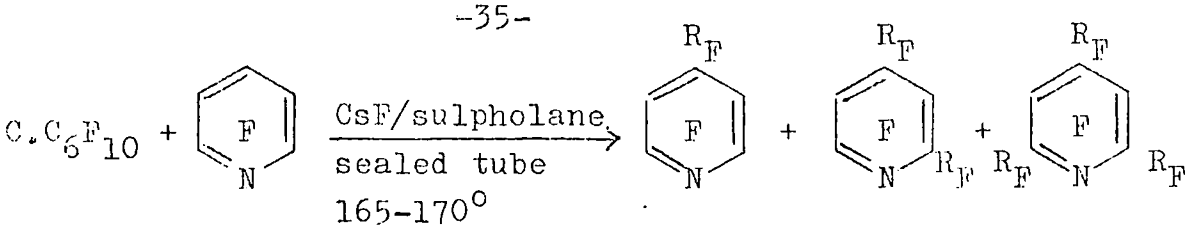
$$F^- + CF_2{=}C\langle \rightleftharpoons CF_3-\bar{C}- \xrightarrow{Ar_F-F} CF_3-C-Ar_F + \bar{F}$$

$$\text{Cf.}\ -C^+ + Ar-H \longrightarrow -C-Ar + H^+$$

This area has been well investigated, particularly in these laboratories, with results demonstrating the operation of aromatic rearrangements, as well as kinetic and thermodynamic control on products[66]. The reaction of hexafluoropropene with pentafluoropyridine, in the presence of fluoride ion, gives four products (35)-(38), including the product of kinetic control (37) and thermodynamic control (38)[67]. Heating (37) in the presence of fluoride ion causes rearrangement of the isopropyl groups around the ring to give as the major product (38), i.e. the thermodynamically controlled product.



Similarly perfluorocyclohexene and pentafluoropyridine, in the presence of sulpholane and caesium fluoride at 80°, gave perfluoro-4-cyclohexylpyridine, and under more forcing conditions in a sealed tube at 170°, significant yields of di- and tri-substituted derivatives were formed. However, with perfluorocyclobutene and-pentene oligomerisation becomes an important competitive reaction and only mono substituted pyridines are obtained[68].



$R_F = C.C_6F_{11}$

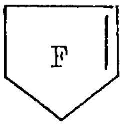
III.A.5.c Fluoride Ion Catalysed Rearrangement of Olefins

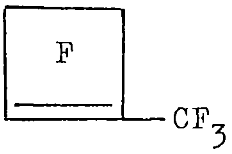
Fluoro olefins containing a terminal difluoromethylene group normally rearrange, in the presence of fluoride ion, to more stable internal olefins, the reactions usually proceeding by a series of S_N2' substitutions.

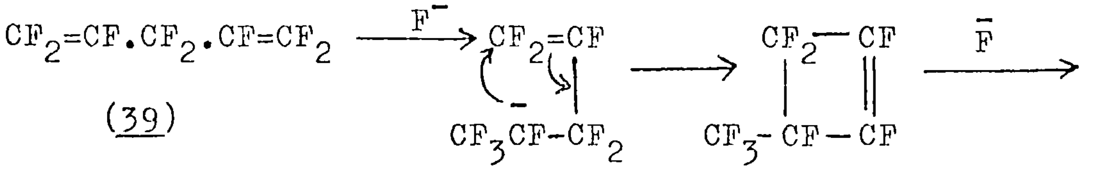
Miller and co-workers[69] have observed the fluoride ion-initiated isomerisation of some perfluorodienes to perfluoroalkylacetylenes, and have suggested the reaction proceeds through a series of S_N2' rearrangements. Thus perfluoro-1, 4-pentadiene (39) rearranged, in the presence of caesium fluoride and the absence of a solvent, to perfluoro-2-pentyne (40), with the intermediates (41) and (42) being isolated from reaction at 80°.

$$\begin{tikzcd}
\underset{(\underline{39})}{CF_2{=}CFCF_2CF{=}CF_2} \arrow[r, "80^{o}", "CsF"'] \arrow[d, "F^-"] & \underset{(\underline{40})}{CF_3CF_2C{\equiv}CCF_3} \\
\underset{(\underline{41})}{CF_3CF{=}CF{-}CF{=}CF_2} \arrow[r, "F^-"] & \underset{(\underline{42})}{CF_3CF{=}C{=}CFCF_3} \arrow[u, "F^-"']
\end{tikzcd}$$

Similar isomerisations of (39) at 400°,led to the formation of cyclic olefins (43) and (44). The formation of (43) occurred in the absence of a catalyst, suggesting an internal cycloaddition reaction, but with (44) the presence of a fluoride ion source was required indicating that the mechanism involved an internal attack of a carbanion (45) on the other terminal double bond.[70] This cyclisation provides evidence for rearrangements of fluoro olefins proceeding via a carbanion intermediate rather than a concerted S_N2' process.


(43)


(44)


(39)

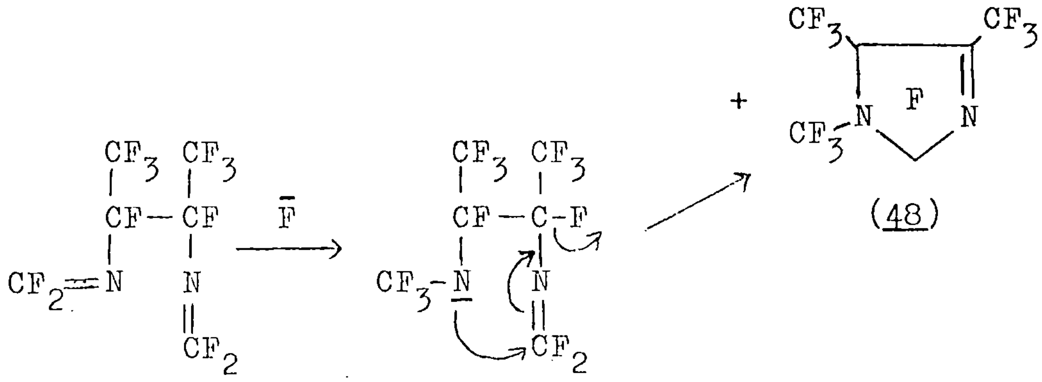
(45)

(44)

Further evidence of a carbanionic intermediate was obtained by the isomerisation of perfluoro-2,4-diazapenta-1,4-diene (46), in the presence of fluoride ion, to (47) and the cyclic isomer (48)[71]. Formation of (48) is again thought to proceed via an intramolecular carbanion attack.

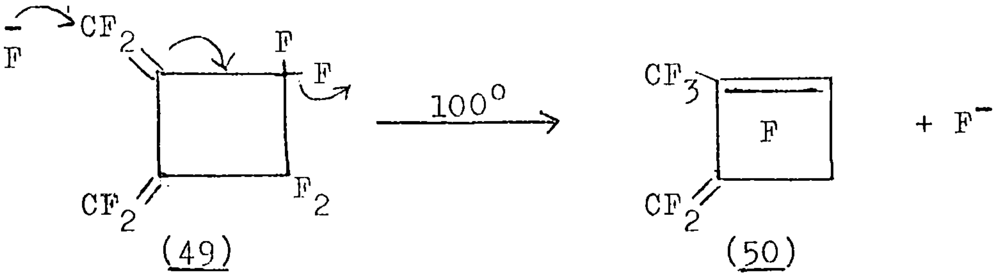
$$CF_2{=}NCF(CF_3)CF(CF_3)N{=}CF_2 \xrightarrow[R.T.]{F^-} CF_3N{=}C(CF_3)C(CF_3){=}NCF_3$$

(46) (47)


(48)

(46)

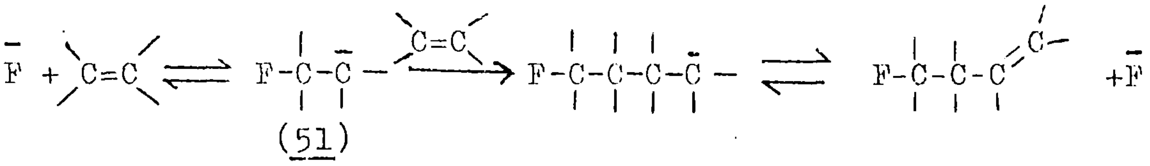
Quantitative isomerisation of perfluoro-(1,2-dimethylenecyclobutane) (49) to perfluoro-(2-methyl-3-methylenecyclobutene) (50) occurs in the presence of dry caesium fluoride and autogeneous pressure[72].

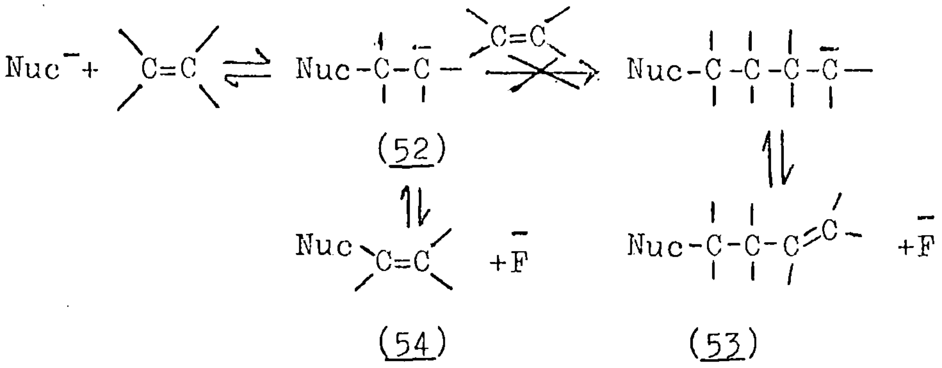


III.A.5.d Oligomerisation

Again this topic has particular relevance to the work of the author and consequently will be discussed fully. In theory anionic polymerisation of fluoro olefins would appear to be a viable process, but in practice, due to the availability of several chain termination processes, which compete favourably with chain propagation, only oligomers are formed. Double bond migration, rather than self-condensation, will occur in olefins containing more than three linear carbon atoms, and in olefins where β-elimination of fluorine is not possible, or self-condensation does not readily occur, highly branched internally unsaturated oligomers are formed.

Oligomerisation reactions of fluoro olefins are confined to those initiated by fluoride ion, with products such as (53) not being formed in reactions of fluoro olefins with other nucleophiles. Examination of the equilibria, involving intermediates (51) and (52) provides a possible explanation, which can account for products of the type (53) not being formed.





In the case involving fluoride ion an equilibrium exists between olefin, fluoride ion and the anion (51), and from this point the reaction can only proceed in one direction, that is addition to another olefin molecule. Examination of the anion (52) shows that two equilibria can exist, the first involving loss of nucleophile to give starting materials again, analogous to the fluoride ion equilibrium, the second elimination of fluoride ion which produces a new olefin (54) (in fact the product normally obtained). Therefore it is possible that comparison of the activation energies for the two processes would show elimination of fluoride ion is a more favourable reaction than addition to a further molecule of olefin.

(i) Acyclic

Oligomerisation reactions of tetrafluoroethylene have been reported by both Graham[73] and Fielding[74], and in each case the products formed consisted of a complex mixture of highly branched internally unsaturated compounds, with a general formula $(C_2F_4)_n$ where n=4,5,6 and 7.

Fielding and co-workers at I.C.I. Ltd. carried out the oligomerisations using a variety of solvents and fluoride ion sources, the results being summarised in Table 9.

The best yields of oligomers were obtained using caesium fluoride as catalyst, coupled with dimethylformamide or hexamethylphosphoramide as solvent, and a typical product composition is shown in Table 10.

Table 9 [74]

Solvent	Fluoride ion source	Temperature	Reaction Time	Wt. of Oligomers
D.M.F.	CsF	80	6	265
D.M.F.	KF	125	6	140
D.M.F.	Et_4NF	110	6	100
D.M.F.	KF.HF	135	6	115
D.M.F.	KSO_2F	140	4	85
D.M.F.	$CsSO_2F$	110	4	70
D.M.F.	CsF	60	1	220
N.M.P.	CsF	100	4	135
D.M.S.O.	CsF	100	4	110
H.M.P.	CsF	100	4	230
D.G.	CsF	120	6	80
D.M.E.	CsF	120	6	60

Table 10

Product Distribution of T.F.E. Oligomers[48]

n	4	5	6
%	15	65	10

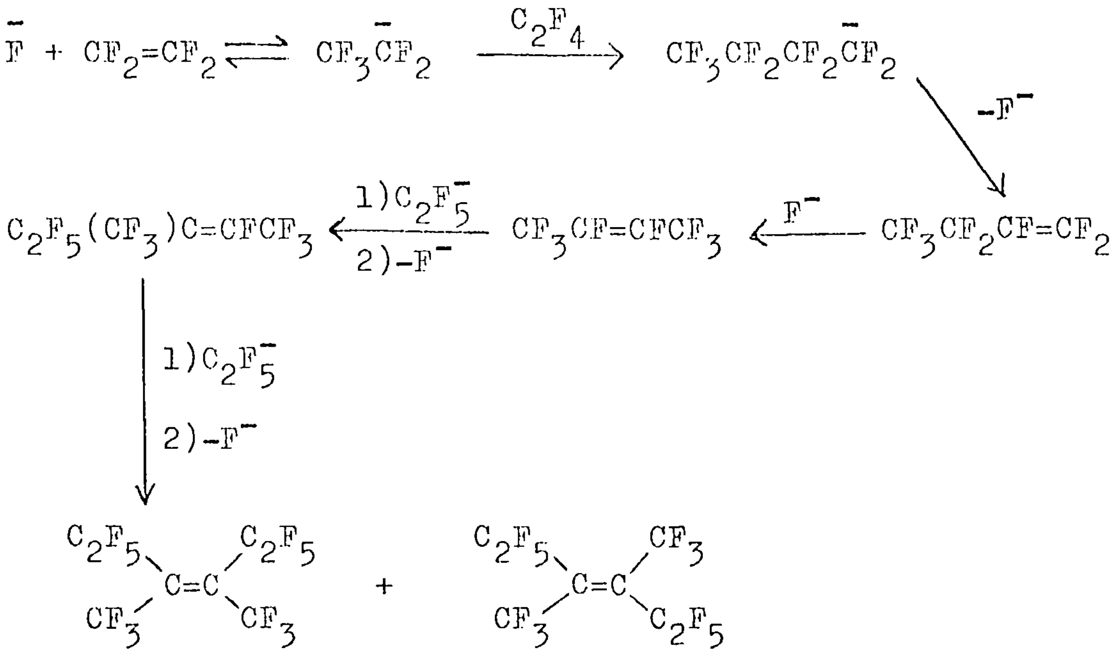
Graham[73] found the distribution of products was dependent on the pressure in the reaction vessel, with more heptamer being produced at higher pressures at the expense of the pentamer fraction (Table 11).

Table 11 [73]

Pressure psi	% Composition of products				
	n=4	n=5	n=6	n=7	Residue
10-20	3	65	21	2	9
150-200	6	21	25	42	6

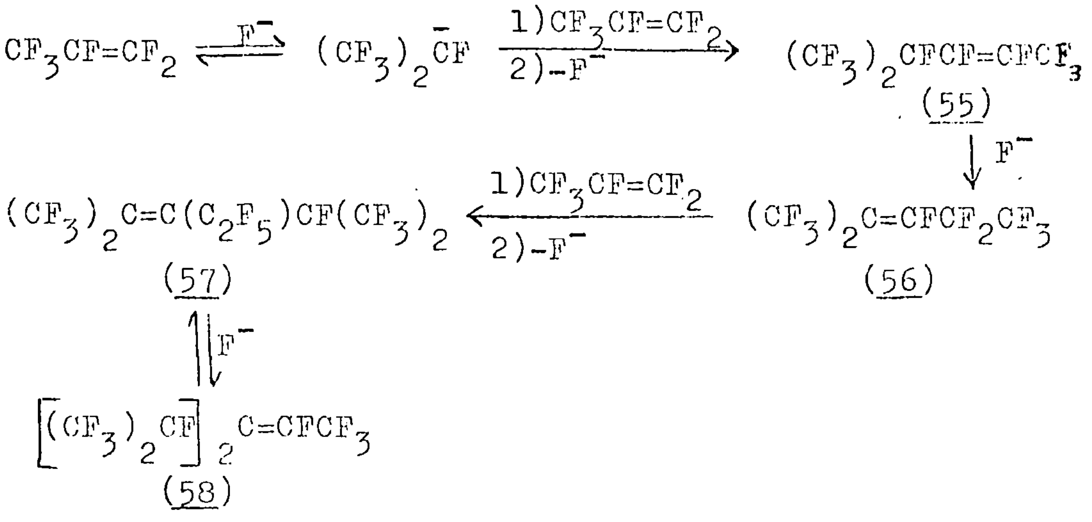
The rate of reaction, when using caesium fluoride, was found to be dependent on the amount of caesium fluoride added, and, as this has only limited solubility in the solvents employed, some interaction between tetrafluoroethylene and the surface of the solid caesium fluoride was thought to be occurring[73].

The mechanism proposed[73,74] involves addition of pentafluoroethyl anion to tetrafluoroethylene, elimination of fluoride ion followed by possible rearrangement of the olefin, which then reacts with a further pentafluoroethyl anion (Scheme 6).



Scheme 6

Oligomerisation of hexafluoropropene occurs under very mild conditions, with dimers and trimers being formed in the presence or absence of a solvent[70,75]. Haszeldine and co-workers[75] isolated two dimers, (55) and (56), plus two trimers, (57) and (58), from a solvent reaction at 25°, and found at higher temperatures (55) rearranged to give the dimer from thermodynamic control (56). A mechanism proposed (Scheme 7) involves a carbanion intermediate but the possible involvement of a concerted process was acknowledged.



Scheme 7

When the reaction was performed at temperatures above 100° a third trimer (<u>59</u>) was formed, and was thought to arise from attack of a heptafluoroisopropyl anion on the terminally unsaturated dimer (<u>60</u>), although a dimer not yet isolated.

$$(CF_3)_2\bar{C}F + CF_2{=}C(CF_3)CF_2CF_2CF_3 \xrightarrow{>100^{\circ}} (CF_3)_2CFCF_2\bar{C}(CF_3)CF_2CF_2CF_3$$

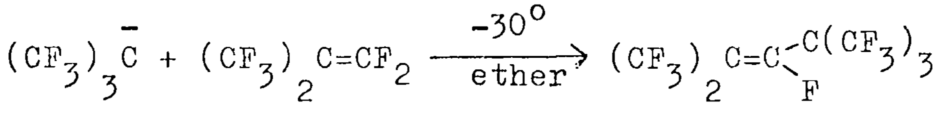
$$\Big\downarrow -F^-$$

$$(CF_3)_2CFCF{=}C(CF_3)CF_2CF_2CF_3$$

(<u>59</u>)

Recent oligomerisation reactions of hexafluoropropene, catalysed by different tertiary amines, have yielded exclusively dimers or trimers[76]. When acetonitrile containing $[CF_3CHFCF_2O(CH_2)_2]_3N$ (<u>61</u>) was used as solvent only the dimer (<u>55</u>) was produced, but using a mixture of acetonitrile containing (<u>61</u>) and Et_3N only trimers (<u>57</u>) and (<u>58</u>) were formed. A mixture of trimers containing (<u>57</u>), (<u>58</u>) and (<u>59</u>) (76%) was obtained when the reaction was performed using a solution of D.M.S.O. containing (<u>61</u>) and 1,4-Diazabicyclo [2.2.2.] octane.

Only dimers of perfluoro-isobutene (<u>62</u>) have been observed[73,77] with dimer (<u>63</u>) being formed on shaking (<u>62</u>) in ether and caesium fluoride at -30° [77].

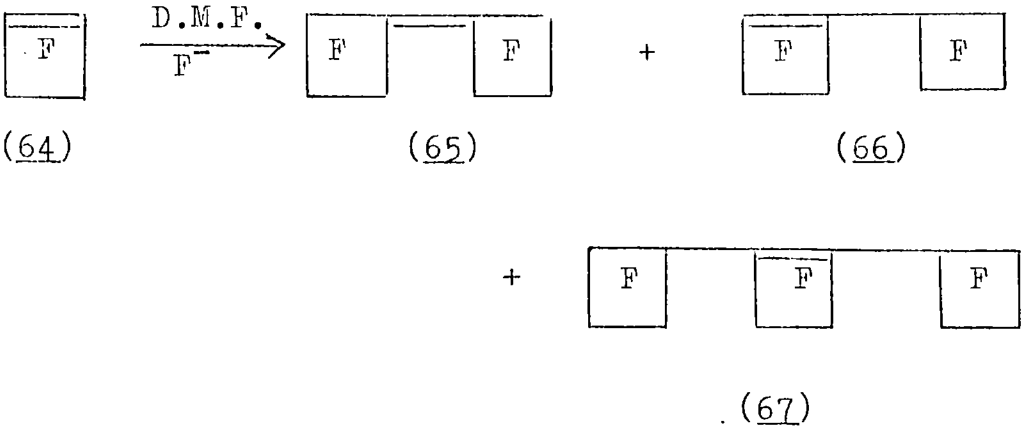


$$(CF_3)_3\bar{C} + (CF_3)_2C{=}CF_2 \xrightarrow[\text{ether}]{-30^{\circ}} (CF_3)_2C{=}C\begin{matrix}\nearrow C(CF_3)_3\\ \searrow F\end{matrix}$$

(<u>62</u>) (<u>63</u>)

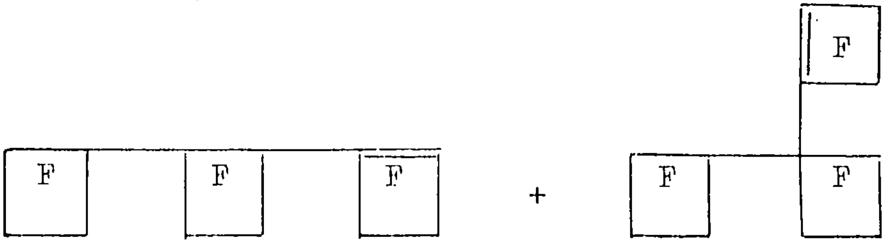
(ii) <u>Cyclic</u>

Several polyfluorocyclicolefins have been shown to oligomerise, but in general less readily than hexafluoropropene. The oligomerisation of perfluorocyclobutene (64) has been studied by various workers, using either pyridines[78] or fluoride ion to initiate the reactions[79,68], thus (64) in the presence of dimethylformamide and fluoride ion gives two dimers (65) and (66) plus a trimer (67)[79].



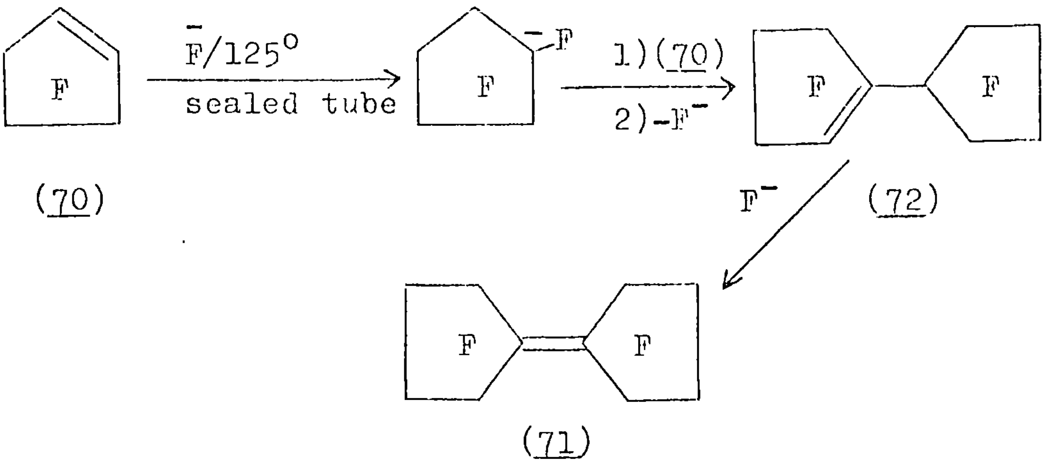
(64) (65) (66) (67)

There has been some contradiction, concerning the structure of the trimer, with (67)[79], (68)[78] and (69)[68] all being suggested. Chambers and co-workers[68] have provided ^{19}F n.m.r. data which can only be consistent with structure (69), and more recently Clark[80] has published E.S.C.A. data which supports the structures proposed by Chambers.

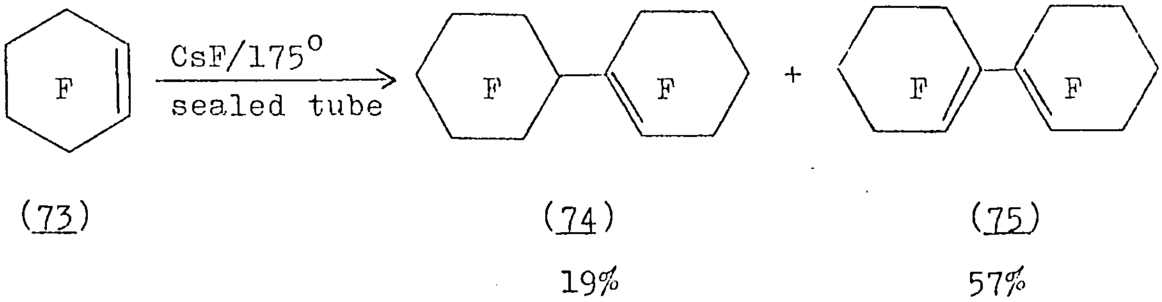


(68) (69)

Under forcing conditions, octafluorocyclopentene (70) will dimerise to give (71), a reaction sequence suggested involves rearrangement of the initially formed olefin (72) to (71)[68].



Similarly, only dimers were formed with perfluorocyclohexene (73), giving an unsymmetrical olefin (74) and a defluorinated product (75)[68].



III.B Electrophilic Reactions

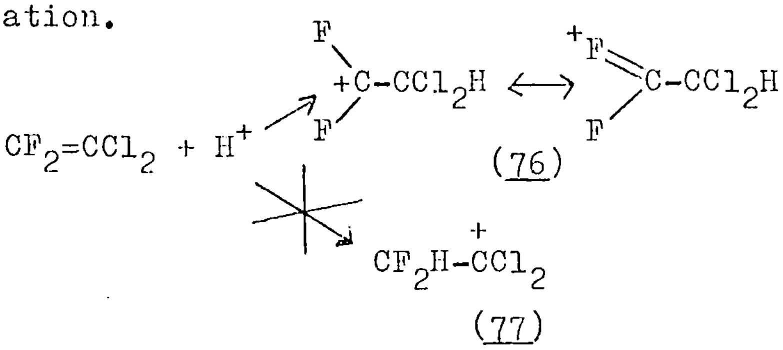
The reduction of electron density of the π-system in fluoro-olefins renders the system relatively resistant to electrophilic attack, but many reactions involving the addition of halogens, hydrogen halides and alkyl halides, in the presence of a Lewis acid are thought to involve electrophilic attack. A review dealing with electrophilic reactions of fluoro olefins is available[2].

The addition of hydrogen fluoride, in the presence of boron trifluoride, to fluoro olefins readily occurs[81], and the results indicate the reaction proceeds by formation of the most stable carbonium ion intermediate.

$$CF_2{=}CCl_2 + HF \xrightarrow{BF_3} CF_3CCl_2H + \text{Polymer}$$

$$CF_3CH{=}CClF + HF \xrightarrow{BF_3} CF_3CH_2CClF_2$$

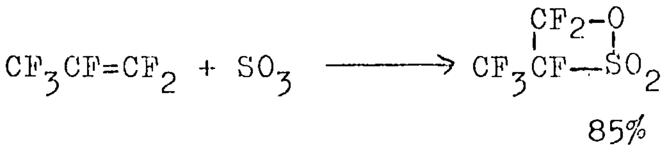
Although carbonium ion (76) is destabilised by the inductive effect of fluorine, the greater stability of (76) compared to (77) can be accounted for on the basis of mesomeric stabilisation.



A variety of addition reactions of fluoro olefins thought to involve electrophilic attack are summarised in Table 12.

Table 12

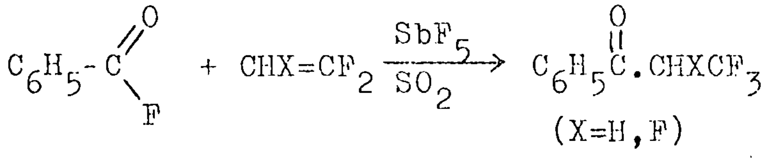
$$CF_2{=}CF_2 + CHCl_3 \xrightarrow{AlCl_3} CHCl_2CF_2CF_2Cl \quad 83\% \qquad (82)$$



$$CF_3CF{=}CF_2 + SO_3 \longrightarrow CF_3CF{-}SO_2 \text{ (ring with } CF_2{-}O) \quad 85\% \qquad (83)$$

$$ClOSO_2F + CF_3CF{=}CF_2 \longrightarrow CF_3CFClCF_2OSO_2F \quad 95\% \qquad (84)$$

$$CH_2{=}CF_2 + HF + HNO_3 \xrightarrow{-60^\circ} CF_3CH_2NO_2 \quad 57\% \qquad (85)$$



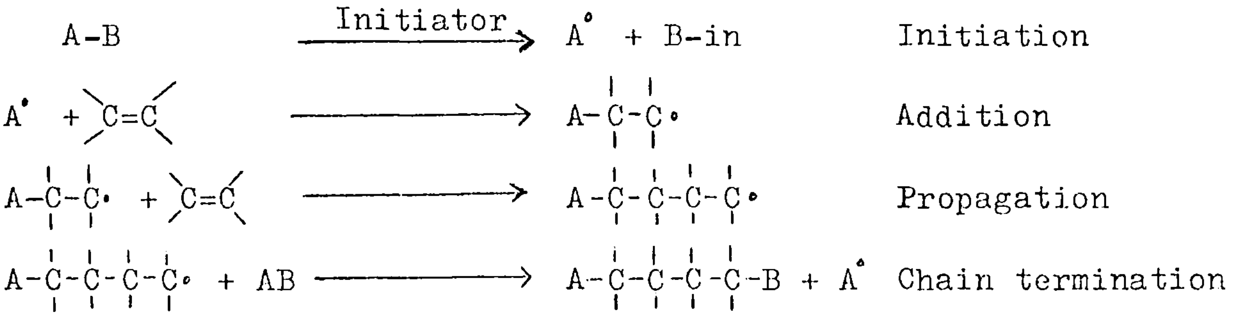
$$C_6H_5C(O)F + CHX{=}CF_2 \xrightarrow[SO_2]{SbF_5} C_6H_5\overset{O}{\overset{\|}{C}}.CHXCF_3 \quad (X{=}H,F) \qquad (86)$$

CHAPTER IV

Non-Ionic Reactions of Fluoro Olefins

IV.A Free-Radical Addition

A wide range of free-radical addition reactions with fluoro olefins are known and a probable reaction process is shown in Scheme 8.



Scheme 8

If the bond A-B is weak and the ratio of A-B to olefin high a 1:1 addition across the double bond can occur, competing successfully with chain propagation.

IV.A.1 Orientation of Addition

The orientation of radical addition to unsymmetrical fluoro olefins, unlike nucleophilic and electrophilic ionic reactions, is not completely stereospecific, a fact demonstrated by the reaction of trifluoroethylene with HBr[87] and methyl mercaptan[88].

$$CHF{=}CF_2 + HBr \xrightarrow{h\nu} \underset{58\%}{CHFBrCHF_2} + \underset{42\%}{CH_2FCF_2Br}$$

$$CFH{=}CF_2 + CH_3SH \xrightarrow{X\text{-rays}} \underset{75\%}{CH_3SCFHCF_2H} + \underset{25\%}{CH_3SCF_2CFH_2}$$

The ability of α-substituents to stabilise a radical have been shown to increase in the order $H<F<Cl$[89], and from available data Stacey and Harris[90] have concluded that the products of free radical addition to fluoro olefins are derived from the most stable intermediate radical, i.e. the relative stabilities of the intermediate radicals determines the orientation of addition.

More recent work by Tedder and co-workers[91] suggests that steric and polar factors, of the olefin and radical, are more important than the stability of the intermediate radical in deciding the orientation of addition. For example, with CF_2=CFH free radical addition at the CFH= group increases in the series $\dot{C}F_3 < \dot{C}Cl_3 < \dot{C}Br_3$, indicating that as the radical size increases more addition to the less crowded CFH= group occurs[91].

In Fig. 5 the difference in orientation due to polar effects is demonstrated, with a nucleophilic radical, $\dot{C}H_3$, preferentially adding to an electron deficient carbon, while a relatively electrophilic radical, $\dot{C}F_3$, adds to the more electron rich carbon[91].

1 : 0.5 Ratio of addition to each end 1 : 7.26

Fig. 5

In reality the orientation of addition is probably dependent on a combination of factors rather than a single factor.

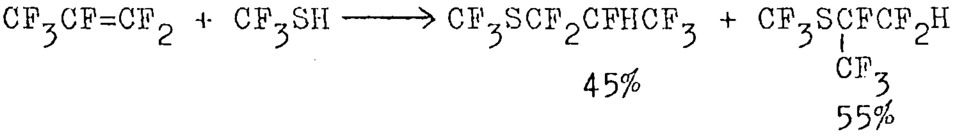
IV.A.2 Addition Reactions

The examples of free-radical addition across the double bond of a fluoro olefin are numerous, and some of these are shown in Table 13.

Table 13

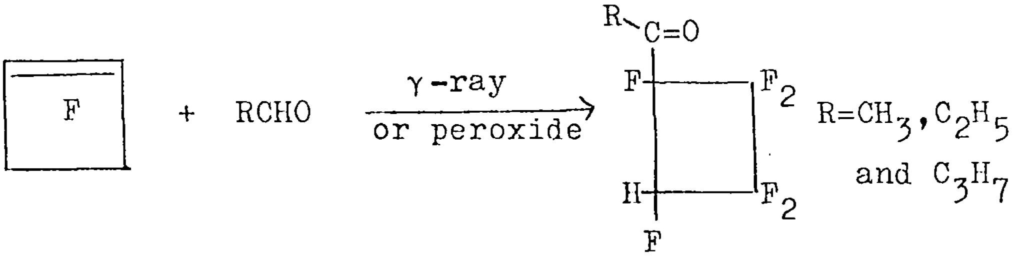
Free-Radical Additions to Fluoro Olefins

$$CF_3CF{=}CHF + Br_2 \xrightarrow{h\nu} \underset{93\%}{CF_3CFBrCHFBr} \qquad (92)$$



$$CF_3CF{=}CF_2 + CF_3SH \longrightarrow \underset{45\%}{CF_3SCF_2CFHCF_3} + \underset{55\%}{CF_3S\underset{CF_3}{\underset{|}{C}}FCF_2H} \qquad (88)$$

$$CF_2{=}CFH + i\text{-}C_3F_7I \longrightarrow \underset{85\%}{(CF_3)_2CFCHFCF_2I} + \underset{15\%}{(CF_3)_2CFCF_2CHFI} \qquad (93)$$



R=CH$_3$, C$_2$H$_5$ and C$_3$H$_7$ (94)

$$CF_3CF{=}CF_2 + CH_3OH \longrightarrow CF_3CFHCF_2CH_2OH \quad 90\% \qquad (95)$$

$$CF_2{=}CF_2 + PH_3 \xrightarrow{150^{\circ}} \underset{53\%}{HCF_2CF_2PH_2} + \underset{7\%}{(HCF_2CF_2)_2PH} + \underset{9\%}{H_2PCF_2CF_2PH_2} \qquad (96)$$

IV.A.3 Telomerisation

Free-radical addition reactions of fluoro olefins are often accompanied by the formation of telomers and with tetrafluoroethylene their production often occurs to the exclusion of simple addition. For example, reaction of bistrifluoromethyl disulphide (78) and tetrafluoroethylene produced only telomers (79) and (80)[97].

$$CF_2{=}CF_2 + CF_3S.SCF_3 \xrightarrow{h\nu} \underset{(79)}{CF_3S(CF_2CF_2)_2SCF_3}\ 3\% + \underset{(80)}{CF_3S(CF_2CF_2)_nSCF_3}\ 97\%$$

where n is large

Similarly, with hexafluoropropene the major product consisted of telomer (81) but some 1:1 addition product (82) was formed.

$$CF_3CF{=}CF_2 + CF_3S.SCF_3 \xrightarrow{h\nu} \underset{(82)}{CF_3S.CF(CF_3)CF_2SCF_3}\ 9.5\%$$

$$+\ \underset{(81)}{CF_3S\left[CF(CF_3)CF_2\right]_2 SCF_3}\ 90.5\%$$

Chambers and co-workers[98] investigating the reaction of various perfluoroalkyl iodides with 1,1-difluoroethylene found the length of the telomer chain was dependent on the ratio of telogen to olefin, and also on the strength of the R_F-I bond i.e. a short telomer chain occurs when the R_F-I bond is weak, due to the chain termination process being more competitive.

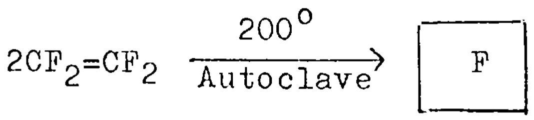
IV.A.4 Polymerisation

Free-radical polymerisation of $CF_2{=}CF_2$, $CF_2{=}CFCl$, and $CF_2{=}CH_2$ have produced polymers with high thermal stability and chemical inertness, factors which have made these homopolymers commercially important. Polymerisation of hexafluoropropene is difficult but copolymerisation with tetrafluoroethylene produced a copolymer, which, along with polychlorotrifluoroethylene has advantages over polytetrafluoroethylene by having a definite melting point, allowing the material to be used for moulding.

Copolymers, including $C_3F_6/CH_2=CF_2$ and $CFCl=CF_2/CH_2=CF_2$, are very good elastomers, and can be vulcanised, by peroxides and polyamines, to yield fluorinated rubbers, compounds which have been used to line pumps carrying corrosive chemicals, and as sealants in aircraft fuel tanks. A review dealing with fluorocarbon polymers has been published[99].

IV.B. Cycloaddition Reactions

One of the unusual features of fluorocarbon chemistry is the large number of four membered ring compounds formed by thermal cycloadditions of fluoro olefins. For example, tetrafluoroethylene gives octafluorocyclobutane when heated in an autoclave[100].



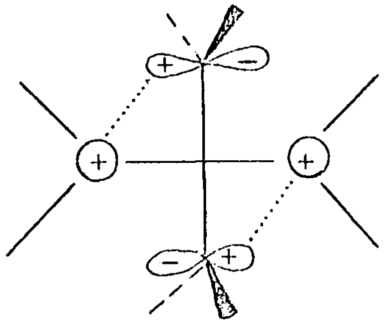
A feature of cycloaddition reactions of fluoro olefins is that the reaction takes precedence over Diels-Alder reactions, and, with a few exceptions, Diels-Alder products are not formed in the thermal reaction of fluoro olefins and dienes.

A requirement for cycloaddition to occur is the presence of a terminal difluoromethylene group, and from considerations of the factors effecting fluoro olefin stability (Chapter I, Section B) some insight into the driving force of the dimerisation can be obtained. In fluoro olefins possessing terminal difluoromethylene groups coulombic repulsion between the non-bonding electrons of fluorine and the π-bond, increases the energy of the double-bond, relative to that of hydrocarbon analogues. On formation of a cyclobutane ring these repulsive forces are removed and $-CF_2-$ groups formed, which have strong carbon-fluorine bonds.

IV.B.1 Mechanism of Cycloadditions

Cycloaddition reactions have particular relevance to part of the work of the author, and consequently a more detailed review of the mechanism involved is felt to be appropriate.

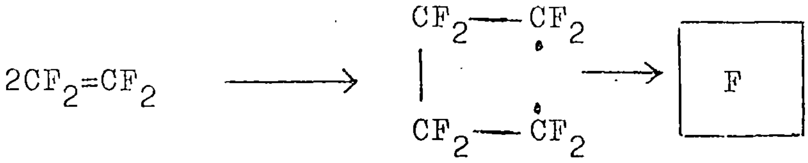
Thermal cycloaddition reactions of fluoro olefins involve 2π+2π addition and thermally induced (2πS+2πS) concerted processes are symmetry-forbidden by the Woodward-Hoffman rules[101], however the rules do allow a (2πS+2πa) concerted process, shown in Fig. 6, such a mechanism involving retention of configuration by the suprafacial molecule and inversion of the antarafacial molecule



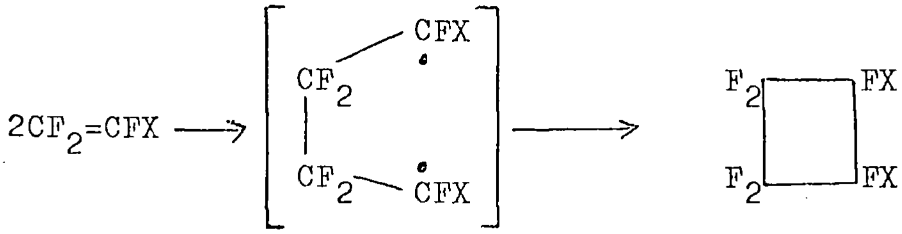
Suprafacial-Antarafacial

Fig. 6

However studies on the mechanism involved in cycloaddition of fluoro olefins, particularly by Bartlett and co-workers, have shown the reaction to proceed through a two-step diradical mechanism rather than a concerted process. A diradical intermediate was first suggested by Lewis and Naylor, who observed the formation of octafluorocyclobutane from tetrafluoroethylene.[102]

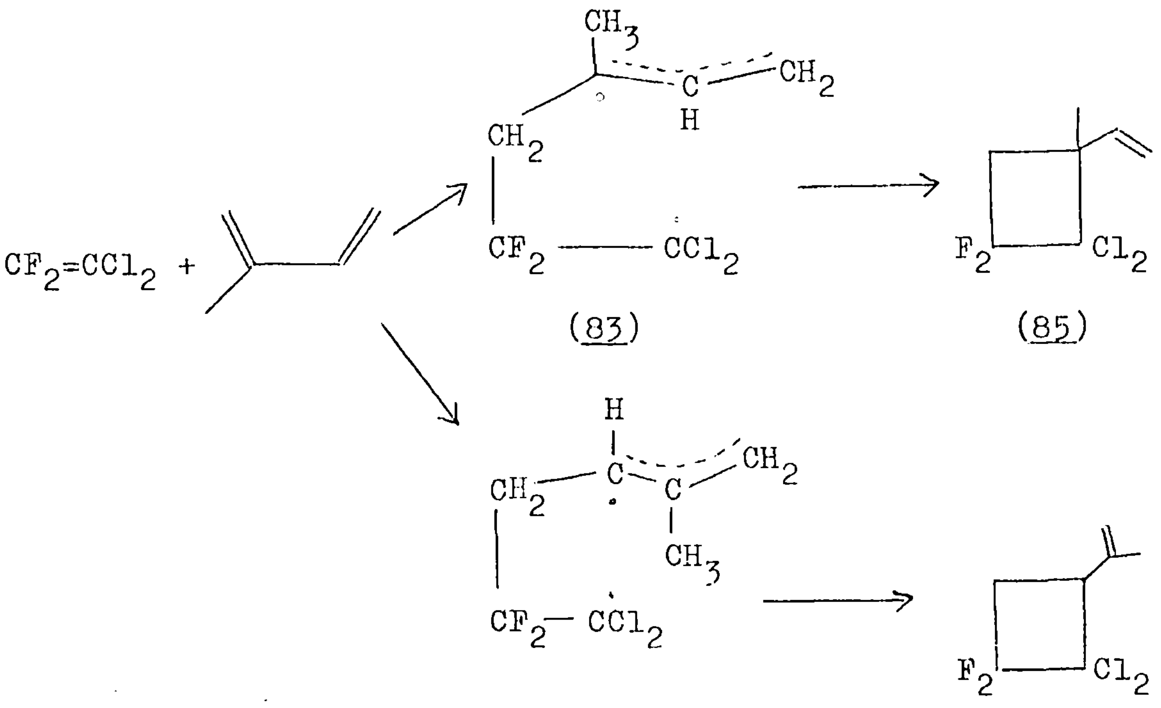


Park and co-workers[103] studying cyclobutanes produced by the cyclisation of $CF_2=CFX$ (where X = Cl, Br or I), concluded the more stable diradical is the precursor of the final product. The relative abilities of halogens to stabilise free radicals being I>Br>Cl>F[104].



The fact that the reaction proceeds via the more stable diradical provides an explanation as to why products mainly derived from head to head addition are formed in cycloadditions of fluoro olefins.

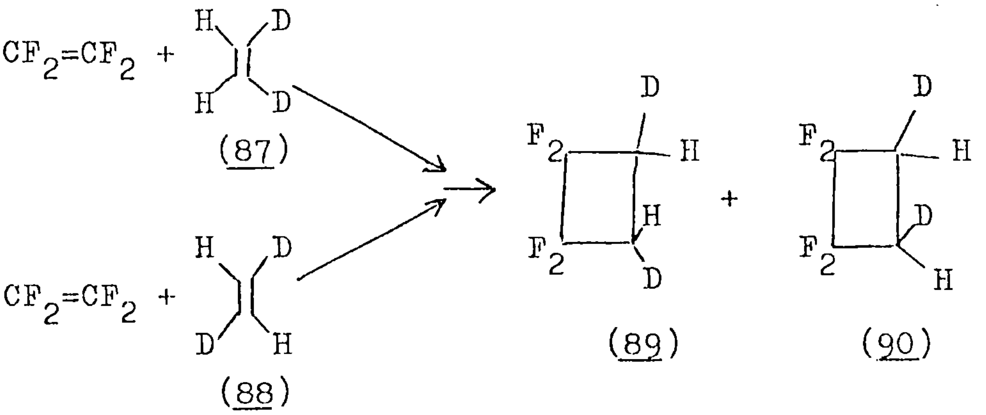
Further evidence of a two-stage mechanism going through the most stable diradical is seen with the cycloaddition of $CF_2=CCl_2$ with isoprene[105], where two possible radical intermediates are possible.



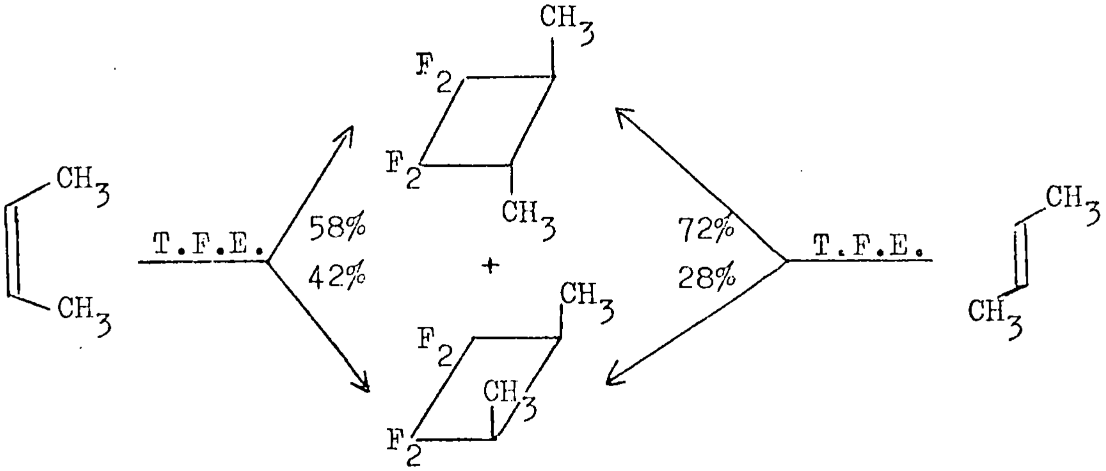
(<u>83</u>) (<u>85</u>) (<u>84</u>) (<u>86</u>)

In the intermediate (<u>83</u>) the CH_3 group is at one of the resonance positions of the radical and consequently contributes to its stabilisation, whereas with (<u>84</u>) the radical cannot be stabilised by the CH_3 group, a fact reflected in the product distribution where (<u>85</u>):(<u>86</u>) is 5.4:1.

In concerted ($2\pi s+2\pi a$) reactions observed, the antarafacial components normally contains one carbon atom with no bulky groups attached, e.g. allenes and ketenes, so reducing the amount of hinderance on the close approach for reaction[106]. To see if a concerted process was operating in cycloadditions, Bartlett and co-workers[106] studied the reaction of tetrafluoroethylene with <u>cis</u>- and <u>trans</u>-1,2-deuteroethylene, the deuterated ethylenes containing no bulky groups, so leading the case in favour of the concerted process, and also allowing any stereoselectivity during the reaction to be observed. For a concerted reaction, the *cis* isomer (90) is expected to be formed from (88), and the *trans* isomer (89) from (87). However, examination of the infra-red spectra of the two product mixtures show them to be the same, but were found to differ from an authentic infra-red spectrum of (90). From these results the authors conclude a mixture of (90) and (89) are formed, regardless of whether the starting olefin is (87) or (88), and suggest the results are inconsistent with a stereospecific mechanism, i.e. concerted, but are those expected from a stepwise cycloaddition.



It is now obvious that a criterion of a two-step diradical cycloaddition is partial loss of configuration in the products, but a second criterion is partial loss of configuration in the reactants during, and only during, cycloaddition. Bartlett and co-workers[107] investigating the reaction of tetrafluoroethylene with *cis* and *trans* but-2-ene, (Scheme 9), found considerable loss of configuration in the products, and also some loss of configuration in the recovered unreacted but-2-ene. For example, after reaction of *cis*-but-2-ene the *trans* isomer had increased from 0.3% to 5.9%, while with the trans isomer the amount of cis-but-2-ene increased from 0.1% to 3.1%. As a check, samples of cis and trans-but-2-ene were heated under the conditions used in the reactions, but found no loss of configuration. The authors concluded the reaction proceeded in a step-wise fashion, fulfilling both criteria mentioned above.



Scheme 9

Similar evidence that cycloaddition reactions proceed via a diradical is shown in the reaction of cyclooctene and $CFCl=CFCl$[108]. The results again showing loss of configuration in the products (Table 14). In the cyclooctene part of the molecule only slight loss of configuration occured, a fact explained on the basis of unfavourable trans-annular interactions preventing isomerisation of the ring.

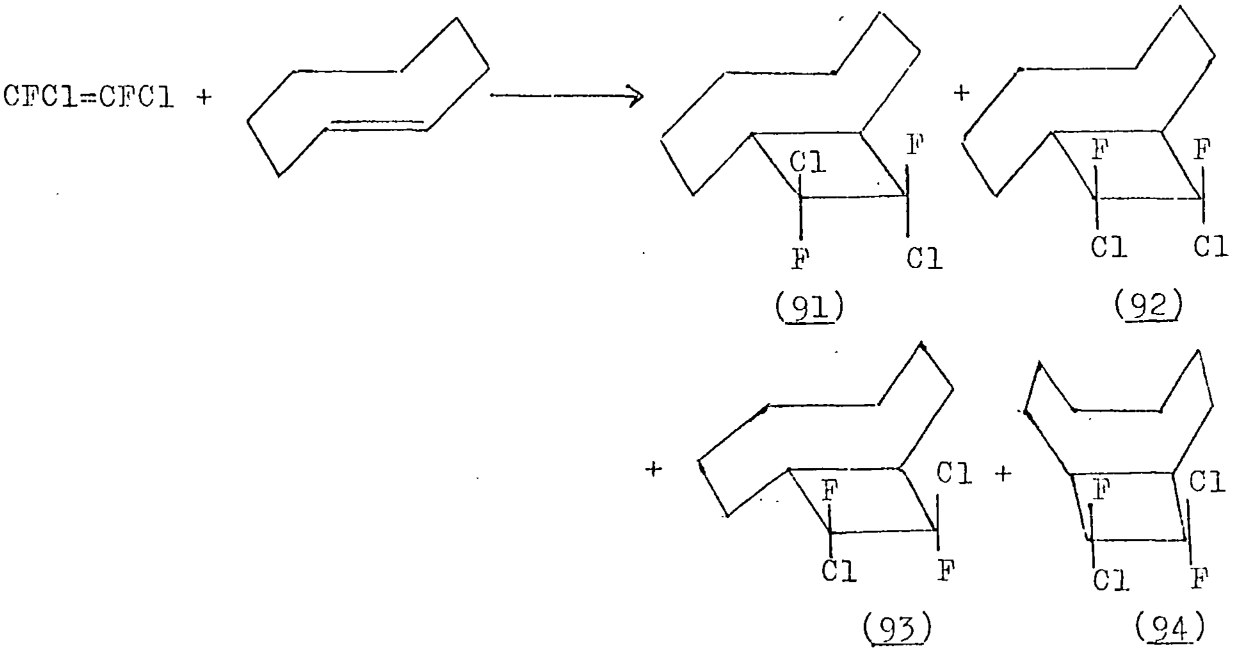


Table 14

Cycloaddition of trans-cyclooctene to ClFC=CFCl

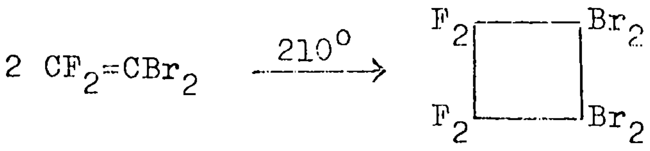
Configuration of CFCl=CFCl	Relative area in g.l.c. trace of products			
	(91)	(92)	(93)	(94)
99.3% trans	27.2	20.2	49.2	3.4
95.4% cis	10.2	67.0	21.4	1.4
51.3% cis	17.8	46.9	33.8	1.5

IV.B.2 Cycloadditions

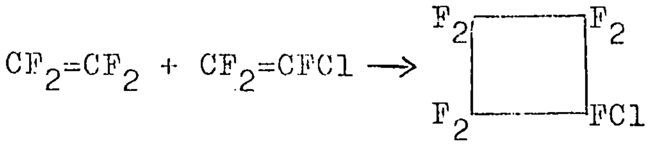
The examples of cycloaddition reactions are numerous, and have been well reviewed[3]. A few typical reactions are shown in Table 15.

Table 15

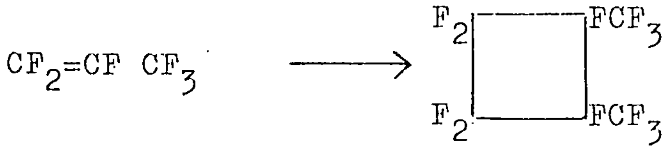
Cycloaddition Reactions



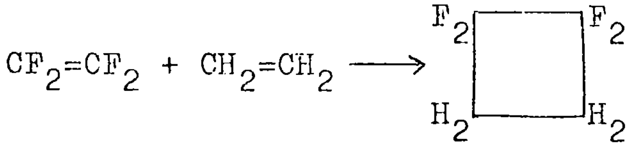
(103)



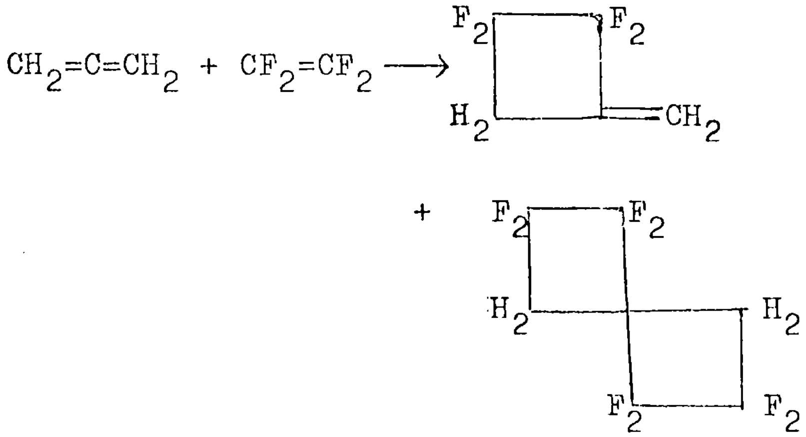
(110)



(111)



(112)



(112)

DISCUSSION

CHAPTER V

Fluoride Ion-Initiated Reactions of Chlorotrifluoroethylene

Introduction

The initial objective of this work was to synthesise vinyl aromatic compounds, with a view to using these systems as precursors in the study of highly fluorinated, long-lived, conjugated anions. Earlier work carried out in these laboratories[113] led to the synthesis of perfluoro-4-vinylpyridine, and the object of this work was to develop this synthesis, and also attempt to extend the method to other systems, with a possibility of the preparation of di- or tri-vinyl compounds. The route used involves fluoride ion-initiated reactions between chlorotrifluoroethylene and an activated aromatic species, to give the corresponding chlorotetrafluoroethyl derivative, which on passing over hot iron-filings dechlorofluorinates to give a vinyl aromatic compound (Scheme 10)

$$CF_3\overset{-}{C}FCl + Ar_F{-}F \longrightarrow Ar_F{-}CFClCF_3 + \overset{-}{F} \xrightarrow[\Delta]{Fe} Ar_F{-}CF{=}CF_2$$

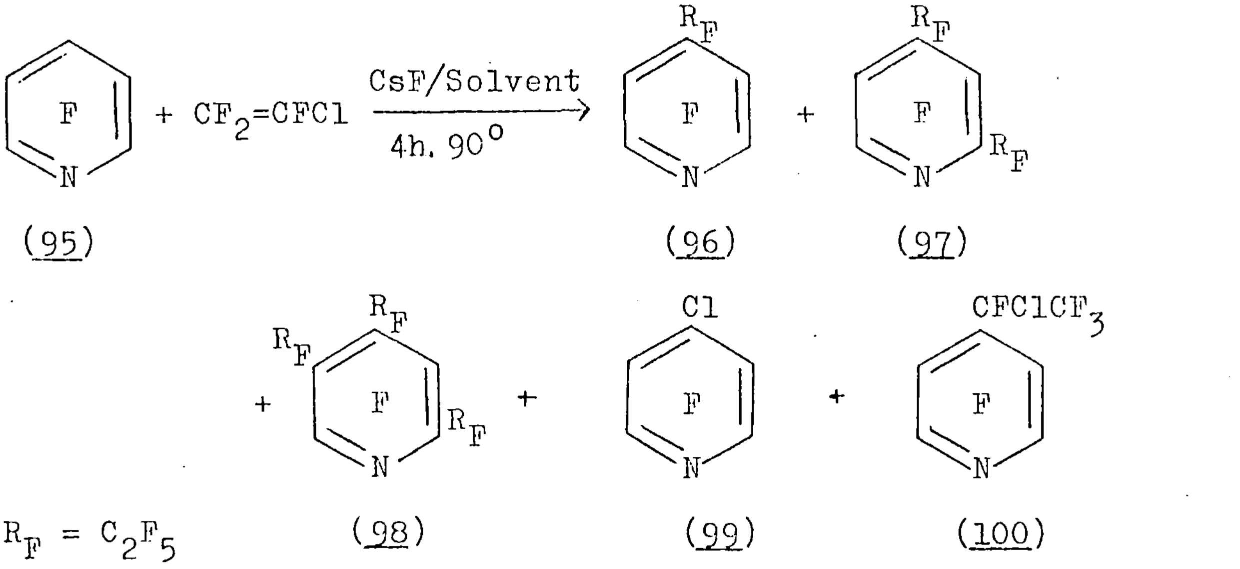
Scheme 10

The main part of this chapter will deal with fluoride ion-initiated reactions between chlorotrifluoroethylene and various aromatic substrates, including pentafluoropyridine, tetrafluoropyrimidine and cyanuric fluoride. A section at the end of the chapter will discuss the attempts to produce oligomers of chlorotrifluoroethylene.

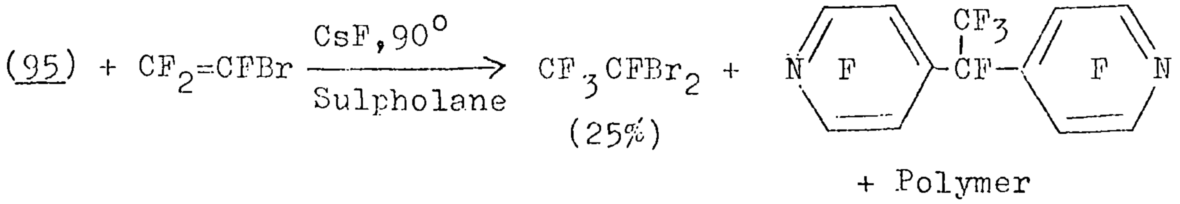
V.A. Polyfluoroalkylations with chlorotrifluoroethylene

Polyfluoroalkylations of activated carbocyclic and heterocyclic aromatic systems, using acyclic and alicyclic fluoro olefins in fluoride ion-initiated reactions, are well documented and were discussed in Chapter III, Section A.5.d.

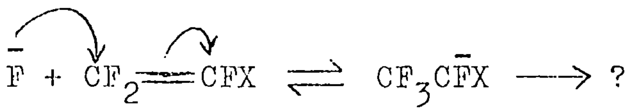
Fluoride ion-initiated reactions between activated N-heteroaromatic species and various polyfluoroethylenes have been studied in these laboratories, and in general give complex product mixtures. For example, a fluoride ion-initiated reaction between chlorotrifluoroethylene and pentafluoropyridine (95) gives a complex mixture of products (96)-(100).[114]



A similar reaction between bromotrifluoroethylene and pentafluoro-pyridine (95) gave different types of products.



The reason for the complex nature of the products is due to the ability of the intermediate carbanion, formed by addition of fluoride ion to the fluoro olefin, to react further in a variety of ways[114] (Scheme 11).



$$\bar{F} + CF_2{=}CFX \rightleftharpoons CF_3\bar{C}FX \longrightarrow ?$$

X = F, Cl, or Br

1) Polyfluoroalkylation

$$CF_3\bar{C}FX + Ar_F{-}F \longrightarrow Ar_FCFXCF_3 + \bar{F}$$

2) Carbene Formation

$$CF_3\bar{C}FX \longrightarrow X^- + CF_3CF{:} \underset{}{\overset{\bar{F}}{\rightleftharpoons}} CF_3\bar{C}F_2$$

3) Halogen Exchange

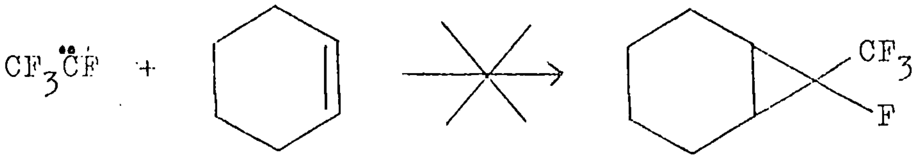
$$CF_3\bar{C}FX + CF_2{=}CFX \longrightarrow CF_3CFX_2 + CF_2{=}\bar{C}F$$

4) Charge Transfer

$$CF_3\bar{C}FX + Ar_F \longrightarrow \left[Ar_F\right]^{\dot{-}} + CF_3\dot{C}FX$$

Scheme 11

Products derived from polyfluoroalkylation and halogen exchange have been isolated from reactions involving chlorotrifluoroethylene and bromotrifluoroethylene respectively, with charge transfer processes suggested as possible routes to polymeric materials recovered.[114] However, attempts to trap any carbenes formed in the reaction between chlorotrifluoroethylene and fluoride ion, in the presence of excess cyclohexene, failed to give a norcarane derivative (101).



(101)

V.A.1 Reaction Conditions

The results of fluoride ion-initiated reactions carried out in these laboratories have shown that in general the most effective combination of solvent and fluoride ion source is caesium fluoride in sulpholane,[115] although exceptions to this combination are known.[116]

In theory only catalytic amounts of fluoride ion are required, but due to the insolubility of alkali metal fluorides in the solvents used, a large excess has to be used in the reaction. The amount of alkali metal fluoride added has been found to affect the rate of reaction, for example, Graham[73] noticed that the rate of tetrafluoroethylene oligomerisation increased as the amount of caesium fluoride added was increased, and concluded that some reaction was occurring at the surface of the solid caesium fluoride.

Originally fluoride ion-initiated reactions were carried out in autoclaves at high temperatures (>120°) and pressures,[117] but these conditions produced unwanted side-reactions, including oligomerisation of the olefin, rearrangements, and decomposition of the solvent.[116,73,68]

In recent years techniques which allow these reactions to be carried out at atmospheric pressure have been developed in these laboratories.[118] The apparatus consists of a variable volume reservoir (football bladder) attached to a round-bottomed flask into which the solvent and fluoride ion source are introduced. After evacuating and degassing, the apparatus is returned to atmospheric pressure with the required fluoro olefin, and the aromatic substrate introduced via a syringe through the septum (Fig. 7).

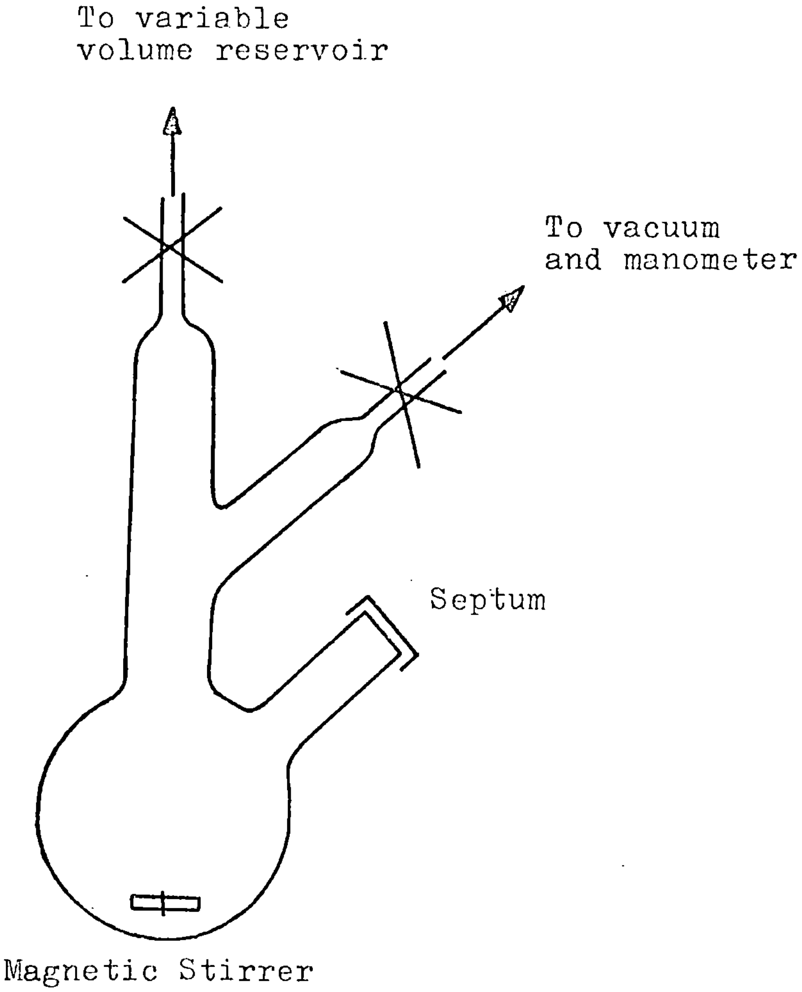


Fig. 7

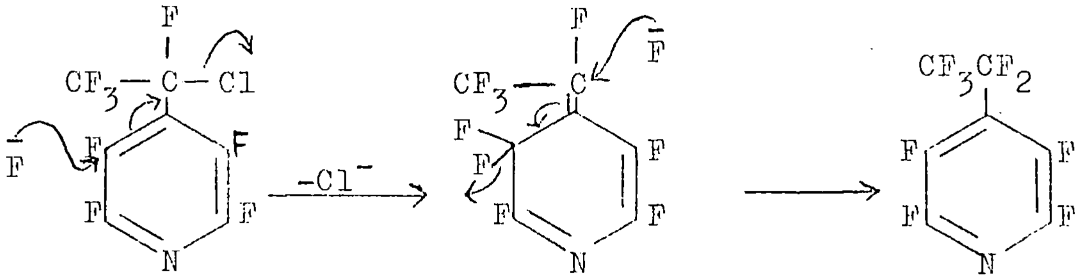
V.A.2 Reactions of Chlorotrifluoroethylene with Pentafluoropyridine

The object of the work described in this section was to improve on the yields of 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl) tetrafluoroethane (100) formed in the fluoride ion-initiated reaction between pentafluoropyridine and chlorotrifluoroethylene.

The first fluoride ion-initiated reactions of chlorotrifluoroethylene with pentafluoropyridine (95) were carried out in autoclaves at high temperatures (190°). This yielded a product consisting of unreacted starting material and five products, three of which have been isolated and identified as perfluoro-(4-ethyl)pyridine (96), 4-chlorotetrafluoropyridine (99), and 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl) tetrafluoroethane (100).[115,116,119]

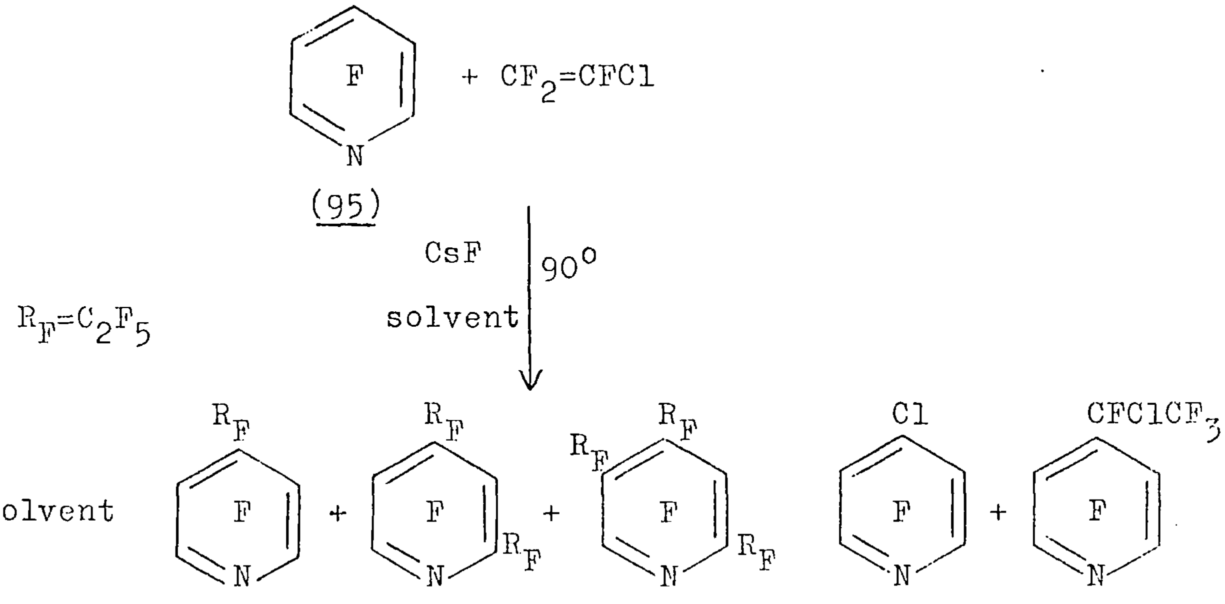
More recent work,[114] using a combination of caesium fluoride and sulpholane or tetraglyme, at atmospheric pressure gave a complex mixture, with the product distribution being dependent on the solvent used. (Table 16).

The results in Table 16 show that chlorine displacement occurs, especially when sulpholane is used as the solvent, and this displacement has been rationalised in terms of a pseudo-S_N2' mechanism (Scheme 12).[114]



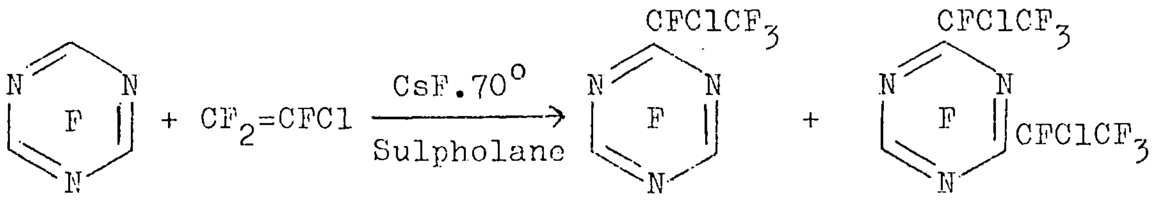
Scheme 12

Table 16[114]



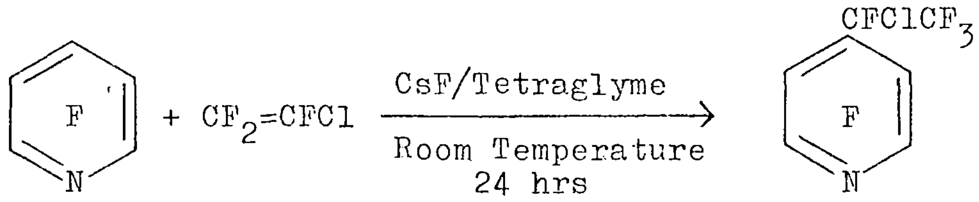
Solvent	(96)	(97)	(98)	(99)	(100)
Sulpholane	15	4	3	4	15
Tetraglyme	0	6	4	8	46

Confirmation of this mechanism is provided by the reaction of chlorotrifluoroethylene with cyanuric fluoride (104) where the chlorotetrafluoroethyl compounds (102) and (103) are the the only products isolated. In compounds (102) and (103) there are no carbon atoms ortho or para to chlorotetrafluoroethyl groups, a requirement for the pseudo-S_N2' mechanism, and consequently no chlorine displacement occurs.



(104) (102) (103)

Atmospheric pressure reaction between pentafluoropyridine (95) and chlorotrifluoroethylene, carried out at room temperature using a combination of caesium fluoride and tetraglyme, gave a colourless liquid. Chromatographic analysis showed this to consist of unreacted pentafluoropyridine, dissolved olefin and one product, identified as 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl) tetrafluoroethane (100) by comparison of infra-red and n.m.r. spectra with those of an authentic sample.



(95) (100)

Comparison of the yields obtained from reactions at room temperature and 90° (Table 17) show that reducing the reaction temperature has inhibited chlorine displacement, but reduced the conversion of pentafluoropyridine to products.

From the involatile residues of the reaction a viscous brown oil was recovered, a polymer probably formed by an electron transfer process, similar to that previously suggested by Chambers and co-workers to account for polymer formation in the reaction of tetrafluoroethylene with tetrapyridazine.[114]

Table 17

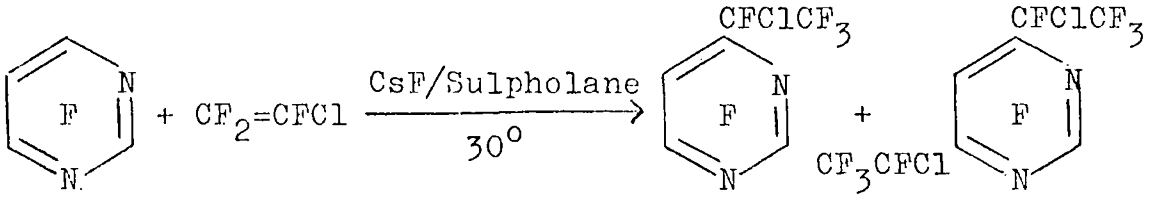
Yields of products from the reaction of Pentafluoropyridine with Chlorotrifluoroethylene

Reaction Time hrs	Reaction Temp °C	*Percentage Yields					% Conversion
		(96)	(97)	(98)	(99)	(100)	
24	25°	-	-	-	-	83	45
24	90°	-	5	8	9	40	76 114

*Based on (95) consumed

V.A.3 Reaction of Chlorotrifluoroethylene with Tetrafluoropyrimidine

Atmospheric pressure reaction between chlorotrifluoroethylene and tetrafluoropyrimidine (105), using a combination of caesium fluoride and sulpholane at 30°, gave a colourless liquid, which on chromatographic analysis was shown to consist of unreacted (105) and two products, identified as 4-chlorotetrafluoroethyl-2,5,6-trifluoropyrimidine (106) and 4,6-bischlorotetrafluoroethyl-2,5-difluoropyrimidine (107).



(105) (106) (107)

20% 19%

As in the case of pentafluoropyridine a viscous oil was recovered from the involatile residues suggesting once again the formation of a polymer via an electron transfer process.

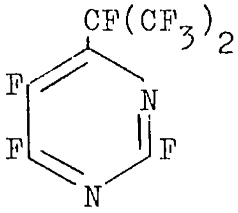
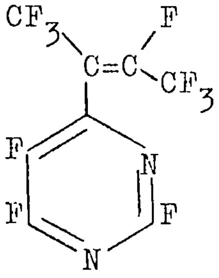
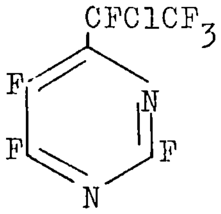
Repetition of the reaction using tetraglyme as solvent yielded a large amount of intractable tar, plus a small amount of volatile material, which chromatographic analysis indicated consisted of unreacted tetrafluoropyrimidine, (106)(9%), (107) (3%), and two other unidentified components. These results indicated that in the case of tetrafluoropyrimidine, changing solvents from sulpholane to tetraglyme produced more unwanted side-reactions, and reduced the yields of (106) and (107) obtained.

V.A.3.a Structure of the Products

The two compounds (106) and (107) were characterised as single components after separation, using preparative scale chromatography. Both (106) and (107) gave satisfactory elemental analysis and strong parent peaks in the mass spectrum, with n.m.r. spectroscopy confirming the positions of substitution as 4-, and 4,6 in (106) and (107) respectively. The observed chemical shift values for the ring fluorines are in good agreement with those for similar compounds (Tables 18 and 19).

Table 18

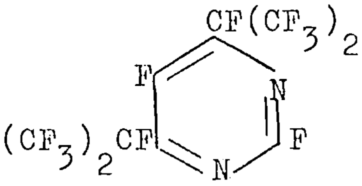
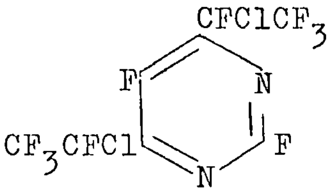
Chemical Shifts* in 4-substituted Trifluoropyrimidines

Compound	Chemical Shift, Ring Fluorines			Ref.
	2	5	6	
	46.7	152.5	70.5	(120)
	48.2	154.4	74.0	(121)
 (106)	45.0	149.8	69.4	

*p.p.m. Relative to external $CFCl_3$

Table 19

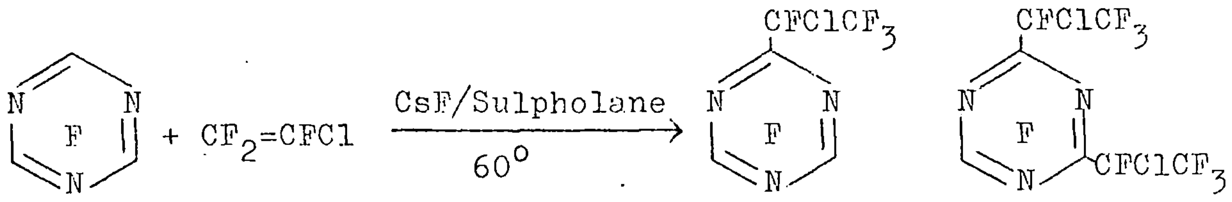
Chemical Shifts*, in 4,6-substituted-difluoropyrimidines

Compound	Chemical Shifts, Ring Fluorines		
	2	5	
	46.7	130	(120)
 (107)	47.6	131.4	

*p.p.m. Relative to external $CFCl_3$

V.A.4 Reaction of Chlorotrifluoroethylene with Cyanuric Fluoride

Atmospheric pressure reaction between cyanuric fluoride (104) and chlorotrifluoroethylene, using a combination of caesium fluoride and sulpholane gave a colourless liquid, which chromatographic analysis showed to consist of unreacted cyanuric fluoride and two products, identified as 2-chlorotetrafluoroethyl-4,6-difluoro-s-triazine (102) and 2,4-bis chlorotetrafluoroethyl-6-fluoro-s-triazine (103).



(104) (102) (103)

The results in (Table 20) show that the reaction is temperature dependent, with only the mono-substituted compound, (102), being produced in low yields from reactions carried out at room temperature. The results also show that as the yields of (102) and (103) increased with temperature, the conversion of cyanuric fluoride to products decreased.

Table 20

Variation in Yields of (102) and (103) with Temperature

Solvent	Reaction Temperature	Reaction Time hrs.	*% Yields of Products		Conversion %
			(102)	(103)	
Sulpholane	25°	22	30.4	-	69
Sulpholane	60°	48	61.5	10.8	51
Sulpholane Tetraglyme	80°	69	68.5	7.0	44

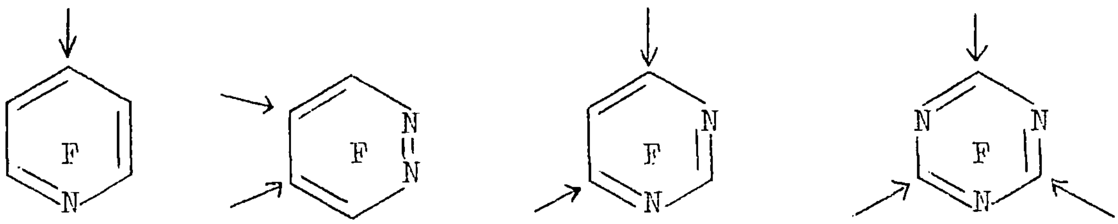
*Based on cyanuric fluoride consumed

V.A.4.a Determination of Structure

The two compounds (102) and (103) were characterised as single components, after separation using preparative scale chromatography. Both compounds gave satisfactory elemental analysis and strong parent peaks in the mass spectra. The n.m.r. were simple and consistent with the proposed structures.

V.A.4.b Discussion

The elevated temperatures required in the reaction of cyanuric fluoride with chlorotrifluoroethylene were unexpected, as kinetic studies carried out in these laboratories have shown that the susceptibility towards nucleophilic attack of a series of perfluoroheterocyclic compounds increases in the order:[122]

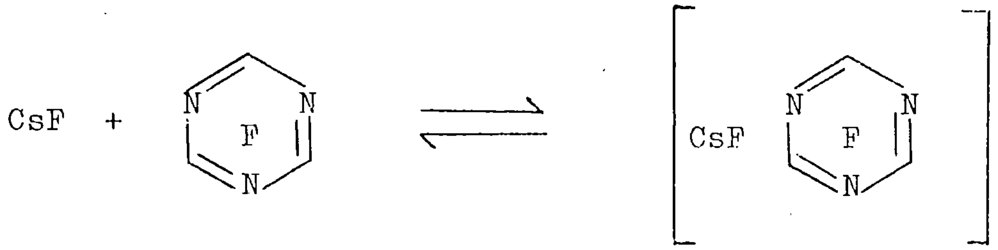


$1 \quad : \quad 37 \quad : \quad 1980 \quad : \quad > 10^5$

An explanation that accounts for these observations, is that fluoride ion reacts with cyanuric fluoride in preference to chlorotrifluoroethylene, due to the greater susceptibility of the former to nucleophilic attack, and it is only at elevated temperatures when the reaction becomes less selective that polyfluoroalkylation occurs to any great extent.

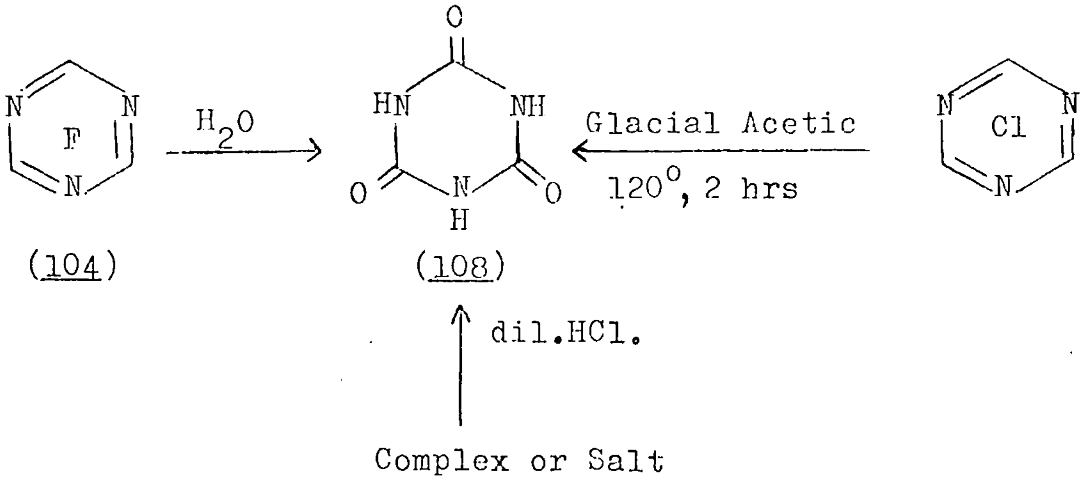
When caesium fluoride is heated with an excess of cyanuric fluoride in sulpholane, after one hour only a small amount of finely divided solid remained, indicating that almost all the caesium fluoride had gone into solution. On removing as much cyanuric fluoride as possible from the reaction mixture, under high vacuum, the amount of finely divided solid increased considerably, and addition of dilute hydrochloric acid to the remaining involatile sulpholane yielded a cream solid, identified from its infra-red spectrum as cyanuric acid.

These observations and results are all consistent with formation of a soluble salt or complex between cyanuric fluoride and caesium fluoride, and the increased precipitation of finely divided caesium fluoride on removal of cyanuric fluoride from the reaction mixture indicated a reversible reaction. The formation of cyanuric acid on addition of dilute hydrochloric acid to the sulpholane residues, again indicated that an involatile salt or complex of cyanuric fluoride was formed in solution.



Complex or salt

The hydrolysis products were identified from comparison of the infra-red spectrum with that of an authentic sample of cyanuric acid (<u>108</u>) prepared by hydrolysis of cyanuric chloride with glacial acetic acid.[123] Hydrolysis of a sample of cyanuric fluoride also gave cyanuric acid.

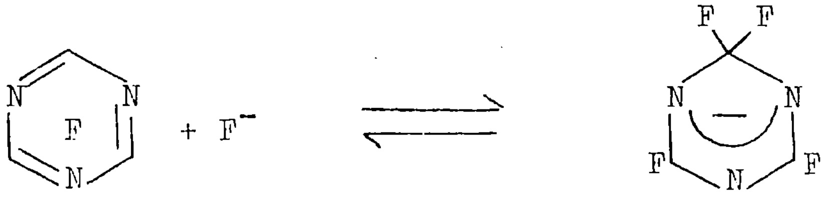


(104) (108)

Further evidence of a soluble complex or salt being formed was obtained from a simple experiment, using n.m.r. techniques. On adding dry caesium fluoride to a mixture of cyanuric fluoride and sulpholane, the n.m.r. spectrum of the supernatent liquor showed no absorption at the position expected for cyanuric fluoride (34.4 p.p.m. relative to $CFCl_3$), but a very broad absorption downfield at 32.3 p.p.m. which sharpened considerably on heating in the probe.

Also, on gradual addition of cyanuric fluoride to a sample of supernatent liquor, the peak gradually sharpened and moved upfield (Fig. 8).

An explanation that is consistent with most of the available data is that some form of exchange was occuring and the most obvious type is a rapid exchange between fluoride ion and cyanuric fluoride, to give an averaged signal, δobs..



$\delta 1$ $\delta 2$

$$\delta obs = \frac{(\delta 1 + \delta 2)}{2}$$

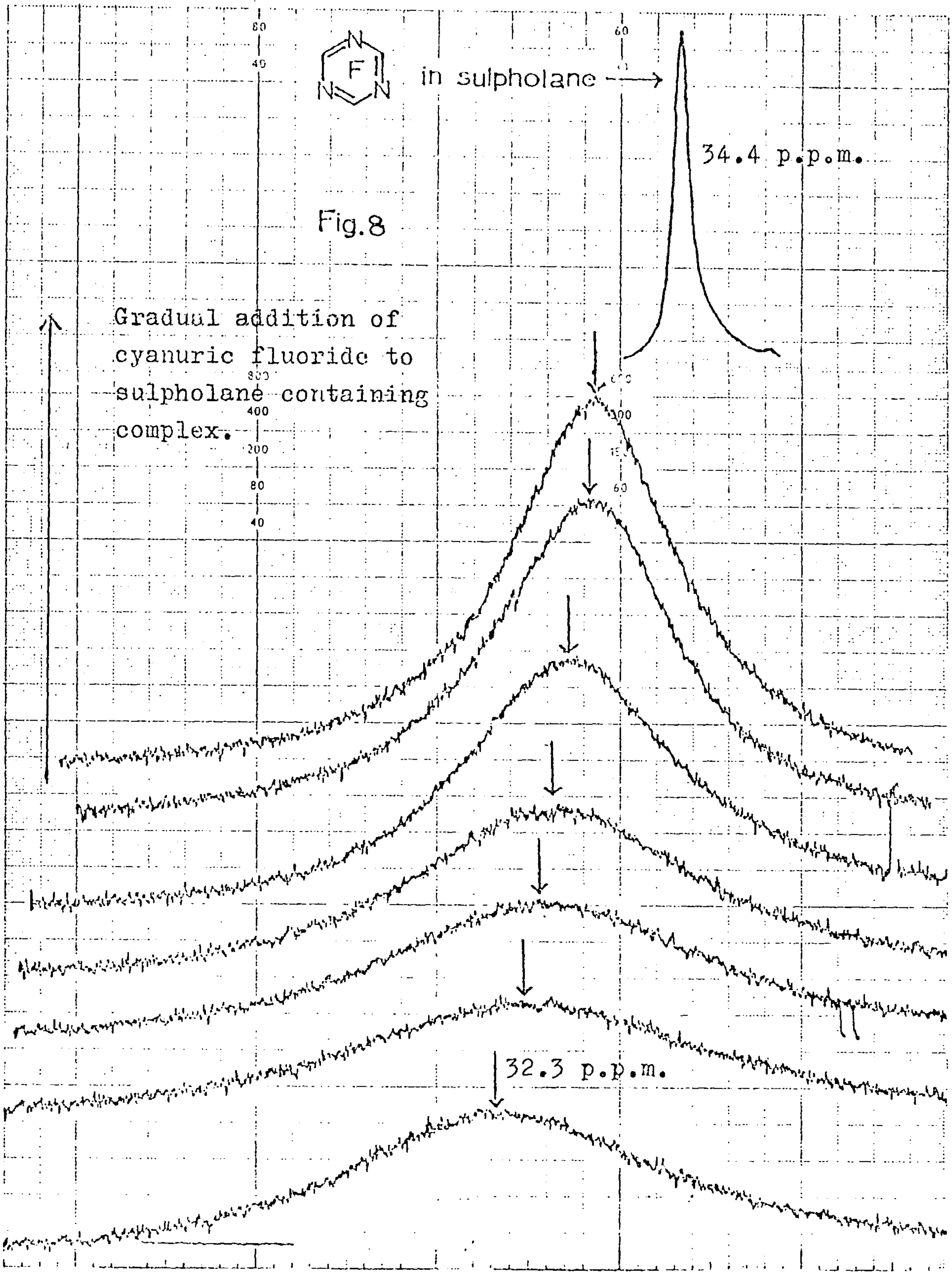
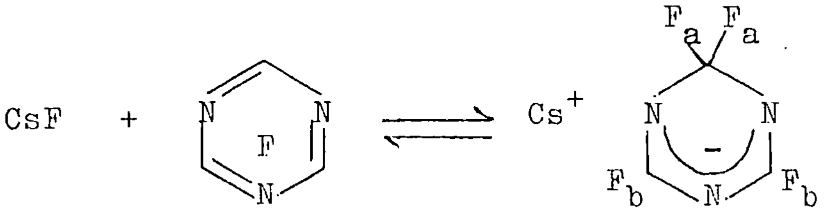


Fig.8

in sulpholane
34.4 p.p.m.
Gradual addition of cyanuric fluoride to sulpholane containing complex.
32.3 p.p.m.
80
40
60
800
400
200
80
40
600
300
150
60

However, as δ1 and δ2 have values of 34.4 p.p.m. and ca. 120 p.p.m.[155] respectively, a δobs. of ca. 76 p.p.m. would be expected, considerably upfield of that observed.

Therefore, the observed spectrum must be an averaged signal involving some other species in solution, and since cyanuric fluoride can be recovered, indicating that no ring opening occurs, this must involve a σ-complex (<u>109</u>).



(<u>109</u>)

δ2 δ1

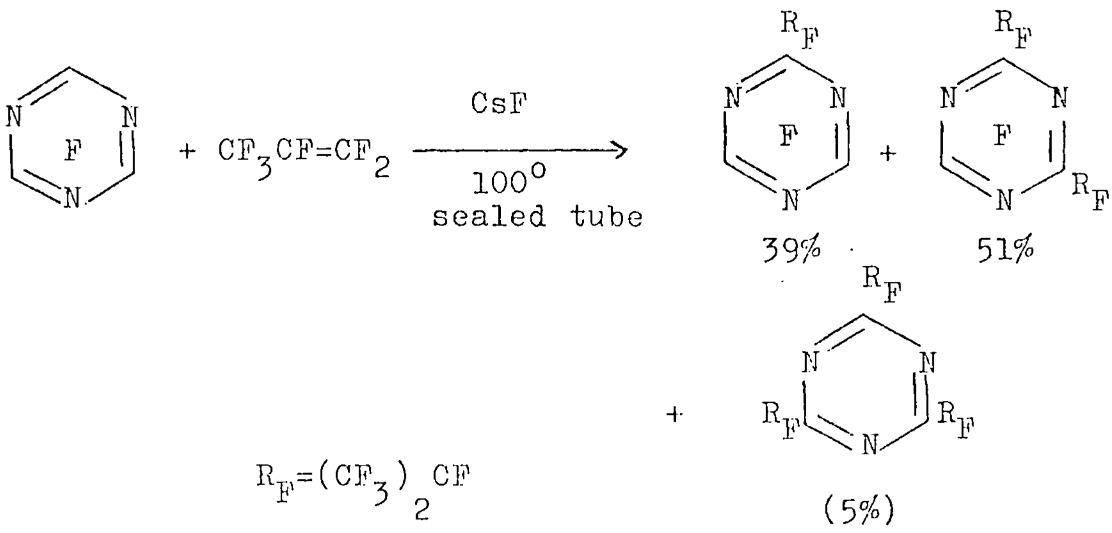
$$\delta 3 = \frac{(\delta a + \delta b)}{2}$$

The observed chemical shift for such a system would be an averaged signal of δ1, δ2 and δ3 with the exact value being dependent on the concentration of each component. Therefore, as δ1 and δ2 are known to have values of 34.4 p.p.m. and ca. 120 p.p.m. respectively, and δobs was 32.3 p.p.m., δ3 must be to low field. Neutral, model compounds indicate values of 74.0 p.p.m.[126] and 62.3 p.p.m.[100] for δa and δb respectively, which would give a value for δ3 upfield of that observed, and in a negatively charged species this chemical shift could be expected to move even further upfield. The observed shift downfield must be due to the presence of the caesium cation, which is having a large effect on the electronic environment of (<u>109</u>).

The formation of a σ-complex is consistent with the observations discussed earlier, thus addition of cyanuric fluoride to the supernatent liquor, increases the contribution of δ1 to the observed chemical shift, δobs., and causes an upfield shift. Raising the temperature of the solution would increase the rate of exchange and this was observed by the peak becoming sharper, in the n.m.r. spectrum, on warming. Theoretically, cooling the system should reduce the rate of exchange, so allowing observation of δ1, δ2 and δ3 as discrete peaks, but on cooling (-5°) caesium fluoride precipitated and no separation was observed.

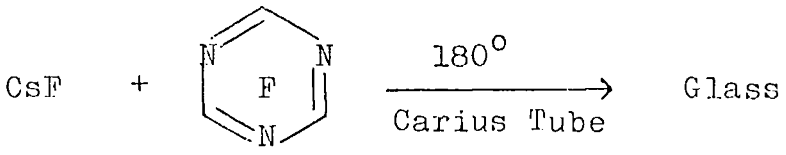
V.A.4.c Formation of a Solid Cyanuric Fluoride/Caesium Fluoride Complex

Young and co-workers[124] have reported the polyfluoroalkylation of cyanuric fluoride with hexafluoropropene, in the presence of caesium fluoride and the absence of a solvent, with good yields of mono- and di-alkylated products being formed.



A similar reaction between octafluorobut-2-ene and cyanuric fluoride, carried out in these laboratories, gave a solid product of unknown composition, with no cyanuric fluoride being recovered after the reaction.[125]

When caesium fluoride and cyanuric fluoride (104) were heated (180°) under autogeneous pressure in a Carius tube, a transparent yellow syrup was formed, which on cooling yielded a brittle, pale yellow, glassy solid.



(104)

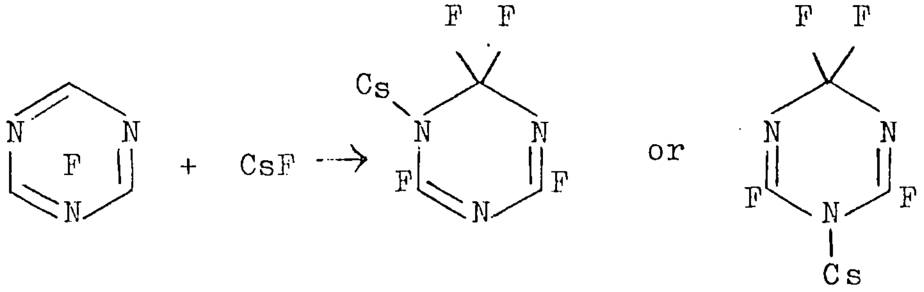
Examination of the contents of the tube showed unreacted cyanuric fluoride present, but no caesium fluoride, and a combination of a mass balance with elemental analysis indicated that the glass contained a 1:1 molar ratio of caesium fluoride: cyanuric fluoride.

Attempts to deduce a definite structure for this glass have met with little success, but with the n.m.r. data obtained and examination of the hydrolysis products it has proved possible to infer a type of structure, which is consistent with the available data. The author would like to emphasise that the reactions proposed are those which at the time of writing provide products which are consistent with most of the available data, but it is possible that in the future more data will be obtained which will confirm, or provide evidence for, a different type of reaction and products.

The n.m.r. spectrum of the complex, formed by heating caesium fluoride and cyanuric fluoride in a sealed n.m.r. tube showed four absorptions, at 26.0, 43.0, 47.6 and 49.0 p.p.m. (relative to external $CFCl_3$), with intensities 9; 30; 46; 15 respectively. The spectrum of a weak solution of the complex in dimethylformamide (D.M.F.) was also obtained and gave peaks at 32.7, 33.2, 50.6 and 51.4 p.p.m. with approximate relative intensities, 1; 1; 4; 1 respectively.

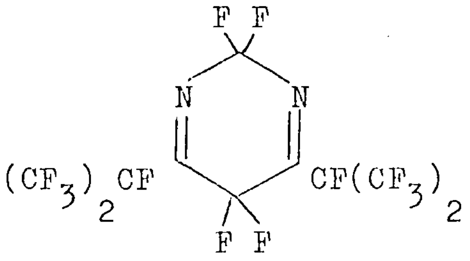
As the stoichiometry of the reaction indicated a 1:1 complex between cyanuric fluoride and caesium fluoride it is possible to predict two types of product: (i) where the ring remains intact, (ii) where the ring is cleaved.

If the ring remained intact the most obvious structure for the product would be a σ-complex, formed by either 1,2-(110) or 1,4-(111) addition of caesium fluoride to cyanuric fluoride.



(110) (111)

Structures (110) and (111) both contain a N-CF_2-N group, which by comparison with the same grouping in the fluorinated pyrimidine (112) is expected to have a chemical shift of about 74 p.p.m.[126] However, the n.m.r. data on the complex showed no absorptions above 51.4 p.p.m., suggesting that the structure is neither (110) or (111).



(112)

Chemical Shifts*, Ring Fluorines

2	5	
73.9	114	(126)

*Relative to $CFCl_3$

In contrast an alternative reaction in which the ring has opened gives products that are more consistent with the n.m.r. data, ring cleavage producing compounds containing CF_3-N= and FC=N- groups, which in known compounds are shown to absorb in the region 20 - 60 p.p.m., the same area of absorption as the complex (Table 21).

Table 21

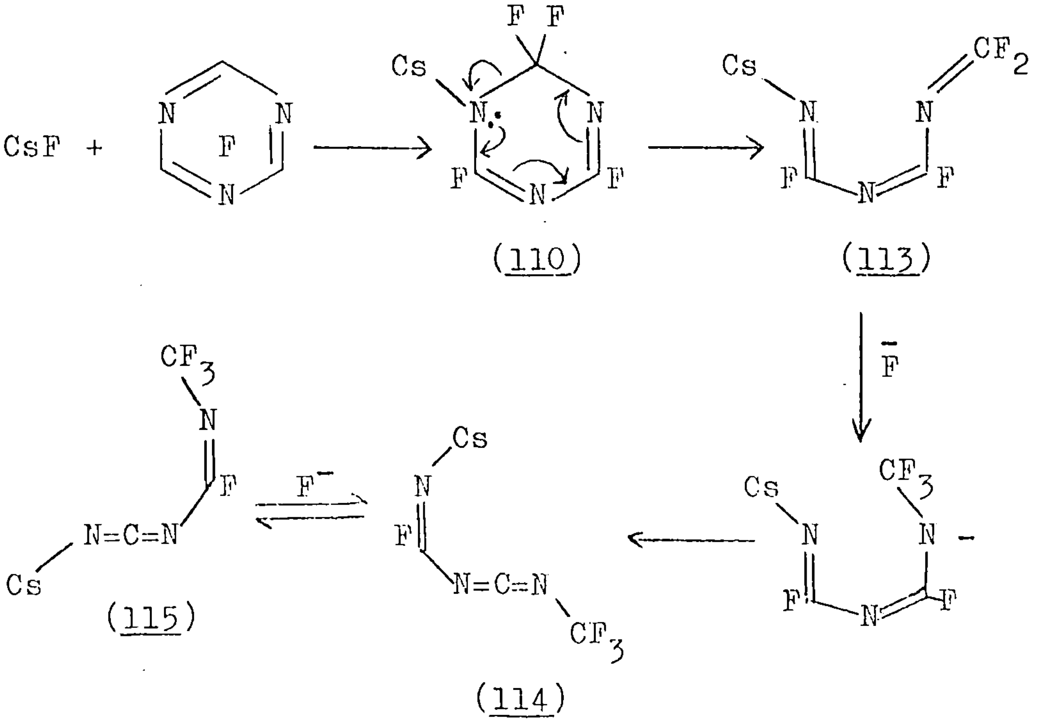
Compound	Group	Chemical Shift*	
CF_2=N-CF_3	CF_3	57.7	(127)
	CF	31.9	
	CF	51.3	
C_3F_7CF=NCF_3	CF	23.8	(127)
	CF_3	40.3	

*p.p.m. relative to external $CFCl_3$

If, as the n.m.r. suggests, ring opening has occured it is possible to predict reaction sequences that lead to products consistent with the n.m.r. spectra. The initial step of the reaction probably involves formation of a σ-complex, (110) or (111), from addition of caesium fluoride, and depending on which intermediate is formed ring opening could produce different products.

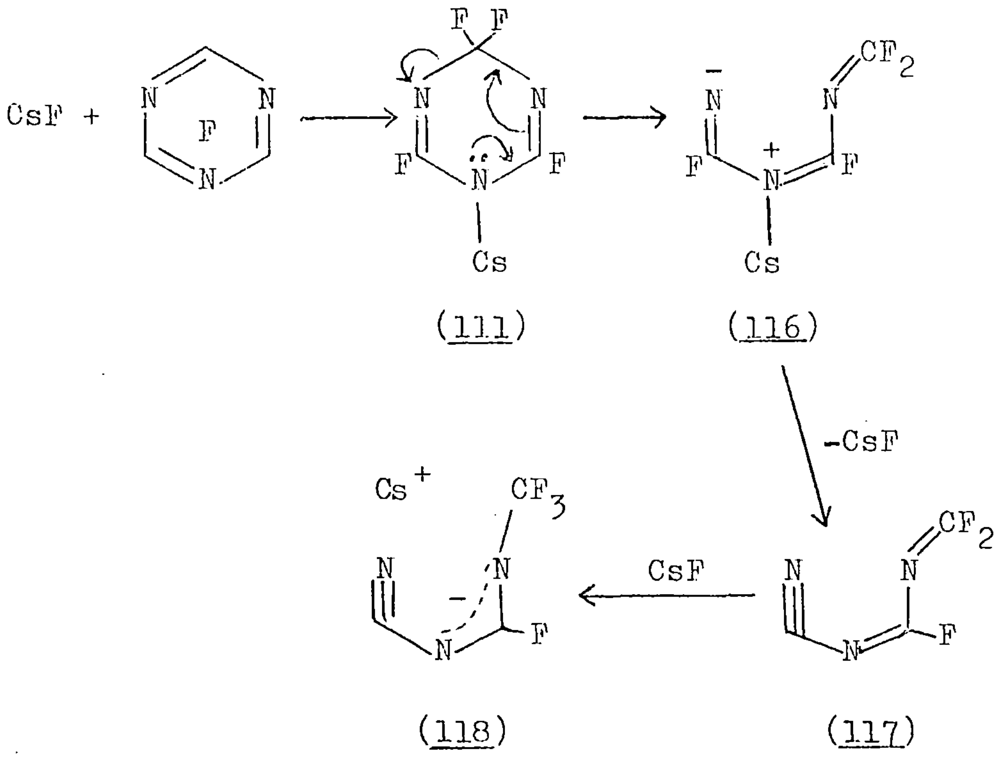
(i) Ring opening via a σ-complex

The structure (110) contains a tertiary nitrogen which could donate its lone pair into the ring system, so promoting a movement of electrons around the ring leading to cleavage, and formation of a further σ-complex (113). Structure (113) contains a terminal CF_2=N- group which would be very reactive, and in the presence of fluoride ion would rearrange to give (114) or (115). (Scheme 13).



Scheme 13

A different reaction pathway could occur if a 1,4-σ-complex (111) is formed, ring cleavage producing (116), which on losing caesium fluoride could produce a nitrile (117). This structure (117) also contains a terminal CF_2=N- group and in the presence of fluoride ion could form an allylic anion (118) (Scheme 14).



Scheme 14

The n.m.r. spectrum of the complex formed in the spectrometer is consistent with a mixture of two components containing CF_3-N= and a vinylic fluorine N=C-F, with the peaks at 26.0 and 43.0 p.p.m. integrating to Ca 1:3 and also those at 49.0 and 47.6 p.p.m. to 1:3.

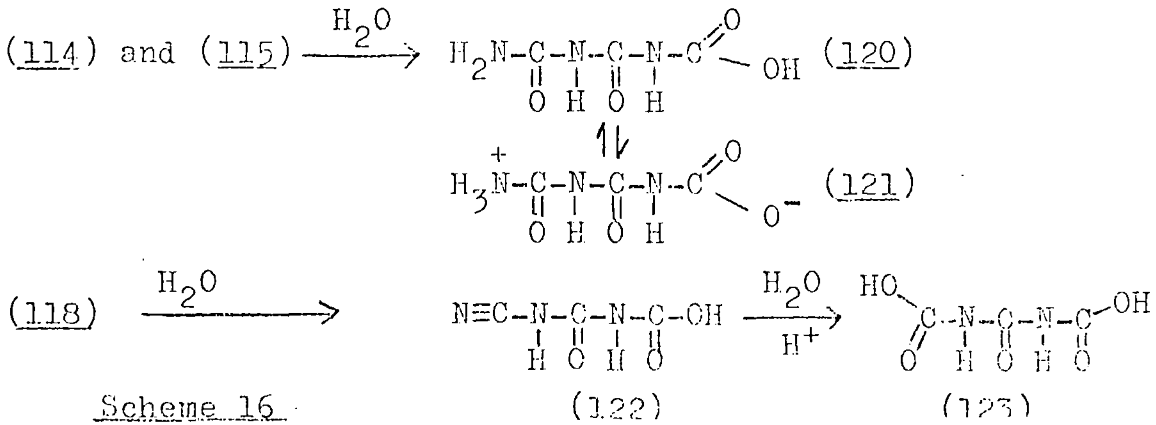
All three products, (114), (115) and (118) contain a CF_3-N= and F-C=N- group, and consequently, either a mixture of two of these compounds or a single compound, but a mixture of cis and trans isomers, would fit the n.m.r. data.

However the n.m.r. spectrum of the product in D.M.F. is less easy to understand, as although the peaks are consistent with CF_3-N= and F-C=N groups present, the integrations do not fit in with the compounds described, and at present it is not possible to explain this spectrum.

(ii) Hydrolysis Product

Addition of the solid to water produced a vigorous reaction from which a white solid was recovered. The product was found to be soluble in hot base; slightly soluble in hot water, producing a solution with pH 3.5; but insoluble in organic solvents. The infra-red spectrum showed broad, unresolved peaks at 3500-2760 cm^{-1}, 1740-1580 cm^{-1}, and 1485-1450 cm^{-1}, facts consistent with a carboxylic acid, possibly containing amide groups as well. Comparison of the spectrum with that of cyanuric acid, the expected product from a cyclic structure, showed them to differ, so providing possible further evidence against a cyclic complex.

However, carboxylic acids containing amide groups, are the products expected from the hydrolysis of compound (114), (115) and (118), providing possible further evidence of a ring opening reaction (Scheme 16).



Scheme 16

In all three compounds the CF_3 groups have been shown to hydrolyse, a fact consistent with carbon-fluorine bonds adjacent to nitrogen, which are activated towards nucleophilic attack.[128] Complete hydrolysis of (<u>114</u>) and (<u>115</u>) initially forms an α,ω-amido-acid type of compound (<u>120</u>) but this could exist as the zwitterion (<u>121</u>).

Although no definite proof exists that the reactions proposed in the previous three reactions occur, the evidence provided is consistent with such reactions. It must also be remembered that the very reactive intermediates (<u>117</u>) and (<u>113</u>) could in the presence of fluoride ion oligomerise or even polymerise, so possibly producing glassy solids.

Attempts to produce similar complexes with KF/cyanuric fluoride, CsF/tetrafluoropyridazine, and CsF/Tetrafluoropyrimidine all failed.

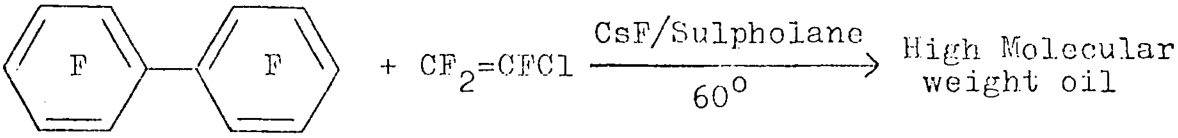
V.A.5 <u>Exploratory Fluoride-Ion-Initiated reactions between Chlorotrifluoroethylene and Various Perfluoroaromatic Substrates</u>

Several exploratory fluoride ion-initiated reactions between chlorotrifluoroethylene and various highly fluorinated aromatic species were briefly investigated in an attempt to extend the range of chlorotetrafluoroethyl substituted aromatic compounds. The systems investigated included: (a) Perfluorobiphenyl, (b) Pentafluoronitrobenzene, (c) Pentafluorobenzonitrile, (d) Octafluorotoluene, and each system will be discussed briefly under its respective heading.

Only in the case of pentafluorobenzonitrile was a chlorotetrafluoroethyl derivative produced, and then in low yield, most of the reactions producing high molecular weight oils or pentafluoroethyl derivatives.

(a) Perfluorobiphenyl

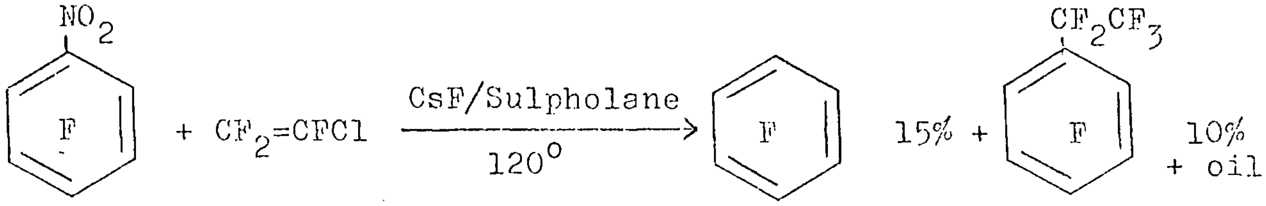
Reaction of perfluorobiphenyl (124) and chlorotrifluoroethylene, in a combination of sulpholane and caesium fluoride gave a mixture containing unreacted starting material and a high molecular weight oil. A possible mechanism for the formation of the oil involves a charge transfer process.[114]



(124)

(b) Pentafluoronitrobenzene

Atmospheric pressure reaction between pentafluoronitrobenzene (125) and chlorotrifluoroethylene gave a volatile liquid consisting of unreacted (125) and two products. A g.l.c./mass spectrum gave m/e values for these products consistent with hexafluorobenzene (126) and perfluoroethylbenzene (127). Again a high molecular weight oil was isolated from the involatile reaction mixture.

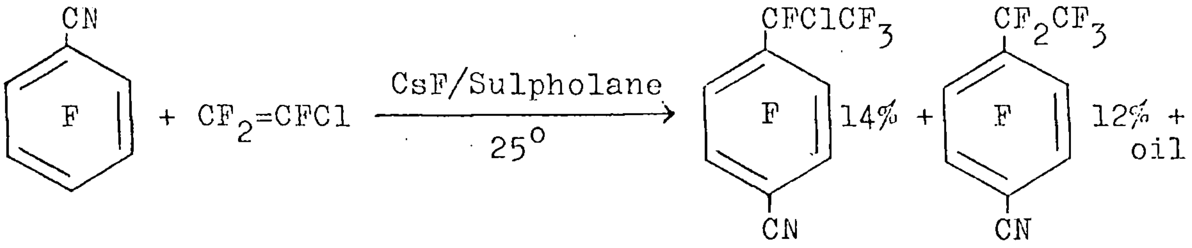


(125) (126) (127)

Repetition of the experiment at a lower temperature (70°) gave no reaction and only pentafluoronitrobenzene (125) was recovered.

(c) Pentafluorobenzonitrile

Reaction at atmospheric pressure between pentafluorobenzonitrile (128) and chlorotrifluoroethylene, in a combination of sulpholane and caesium fluoride, gave a volatile liquid containing mainly unreacted (128) and two products. A g.l.c./mass spectrum showed these two products to have m/e values consistent with (129) and (130). Again a large amount of high molecular weight oil was recovered from the involatile residues.

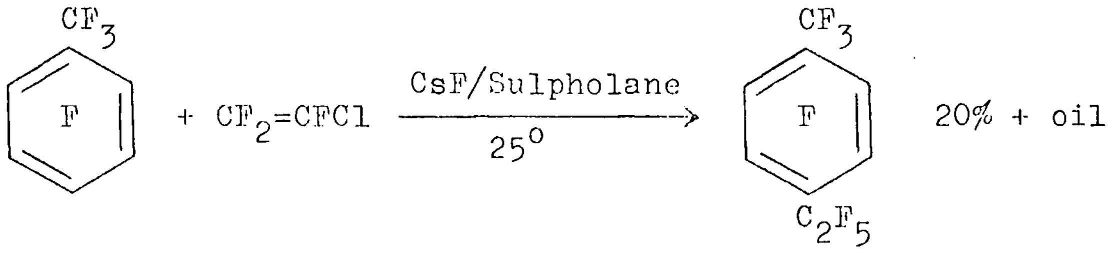


(128) (129) (130)

On repetition of the experiment using tetraglyme as solvent lower yields of (129) and (130) were recovered, 2% and 3% respectively, (Yields based on (128) consumed).

(d) Octafluorotoluene

Reaction at atmospheric pressure between octafluorotoluene (131) and chlorotrifluoroethylene, in the presence of fluoride ion, gave a colourless liquid containing unreacted (131) and one product. A g.l.c./mass spectrum showed the product to have a m/e consistent with the perfluoroethyl derivative (132). A high molecular weight, pale yellow oil was recovered from the involatile residues.

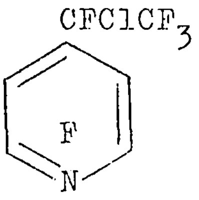


(131) (132)

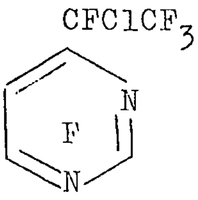
V.A.6 General Conclusions on Polyfluoroalkylations with Chlorotrifluoroethylene

The results discussed in this chapter show that the formation of a series of vinylic aromatic systems, via a scheme involving fluoride ion-initiated reactions of chlorotrifluoroethylene with activated aromatics has a very limited scope. The main factors limiting the reactions appear to be: (i) the ease with which chlorine displacement occurs, and (ii) formation of high molecular weight materials.

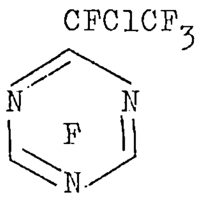
The amount of chlorine displacement occuring in the N-heteroaromatic series, (100), (106) and (102) can be explained on the basis of a pseudo-S_N2' mechanism proposed by Chambers and co-workers.[114]



(100)



(106)



(102)

The fact that chlorine displacement occurs in (100) and not in (102) has been explained in section V.A.2 of this chapter, but the results obtained with tetrafluoropyrimidine provide further evidence which suggests that a pseudo-S_N2' mechanism is operating. In (106) the only position ortho or para to the chlorotetrafluoroethyl group at which fluoride ion attack can occur, is the 5-position, the least activated towards nucleophilic attack, and consequently no chlorine displacement occurs at low temperatures.

In most of the reactions described the products include varying amounts of high molecular weight oils, and if, as is suggested by Chambers,[114] these are formed by an electron transfer process, the chlorotetrafluoroethyl anion appears to be very susceptible to this type of reaction, so much so that in some cases considerable amounts of reactants are consumed in such reactions.

V.B. Fluoride Ion-Initiated Oligomerisation of Chlorotrifluoroethylene

In the introduction of this thesis (Chapter III.A.V) fluoride ion-initiated oligomerisations of certain fluoro olefins, including tetrafluoroethylene and hexafluoropropene, were discussed. However, no oligomers of chlorotrifluoroethylene have been reported, although on the surface the reaction appears to be highly probable.

When chlorotrifluoroethylene, caesium fluoride, and tetraglyme were heated in a nickel tube, a small amount of volatile liquid was recovered, which chromatographic analysis showed to consist of two major and several minor components. The main product was identified as perfluoro-3,4-dimethylhex-3-ene (<u>176</u>) after comparison of the g.l.c. retention time and the mass spectrum, with those of an authentic sample. A g.l.c./mass spectrum of the product mixture indicated that the other major component had an empirical formula, $C_{10}F_{18}$, and that the minor components had molecular weights varying from 524 to over 800. It would appear from the mass spectra that some defluorination has occured and this probably happened on the nickel walls of the bomb. In no cases did the products contain chlorine, demonstrating the ease with which allylic chlorine is displaced by fluoride ion.

$$CF_2{=}CFCl + CsF \xrightarrow[140^{o}]{\text{Tetraglyme}} \underset{\underline{(176)}}{C_2F_5(CF_3)C{=}C(CF_3)C_2F_5}\ 17.5\% + C_{10}F_{18}\ 11\%$$

$$+ \text{ others}$$

Lowering the reaction temperature changed the product distribution (Table 22) but still gave low yields of products, and due to the complex nature of these and the low yields obtained this reaction has not been pursued further.

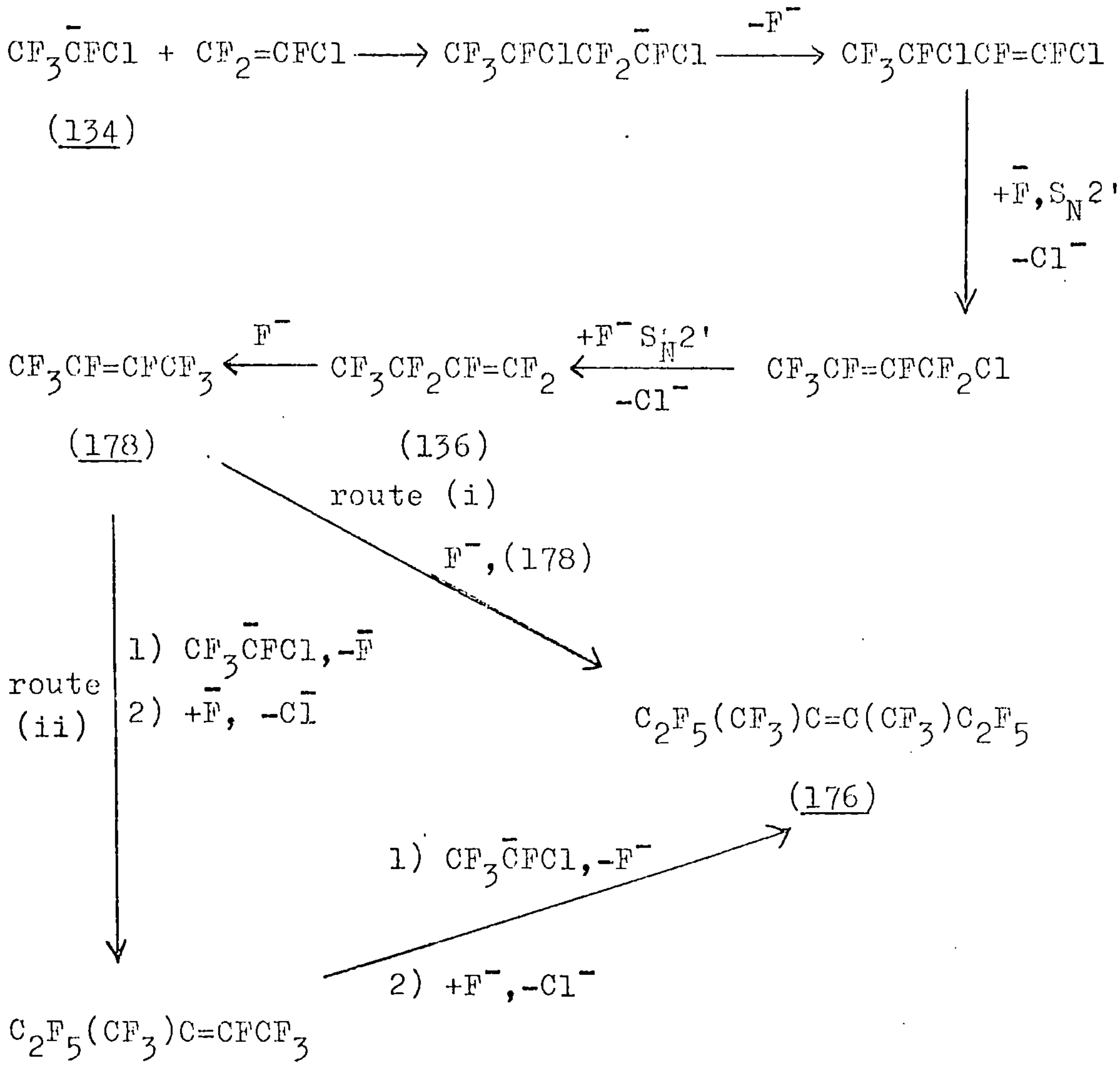
The low conversion to products was probably due to the relative insolubility of caesium fluoride in the solvents used, and as fluoride ion was displacing chlorine during the reaction caesium fluoride was no longer just a catalyst but one of the reactants, i.e. one molecule of caesium fluoride was required for every molecule of chlorotrifluoroethylene.

Table 22

Percentage Yields of Products from Oligomerisation of Chlorotrifluoroethylene

Solvent	Temp ^{o}C	Percentage Yields					
		C_8F_{16}	$C_{10}F_{18}$	$C_{12}F_{20}$	$C_{12}F_{22}$	$C_{14}F_{24}$	$C_{14}F_{24}$
Tetraglyme	56	10	16	2	4	5	10
Sulpholane	68	6	1	-	5	6	3
Tetraglyme	140	18	11	2	3	2	3

A possible reaction sequence, accounting for formation of (176) is shown in Scheme 17. This mechanism involves addition of chlorotetrafluoroethyl anion (134) to chlorotrifluoroethylene, followed by loss of fluoride ion to give (135). A series of S_N2' type processes then displace the two chlorine atoms producing (136), which after a fluoride ion induced rearrangement yields octafluorobut-2-ene (178). The mechanism can now follow two routes: (i) straightforward fluoride ion dimerisation of (178) to give (176), or (ii) addition of two further anions (134) followed by chlorine displacement and fluoride ion rearrangement to give (176).


CF3C̄FCl + CF2=CFCl → CF3CFClCF2C̄FCl
(134)
-F⁻
CF3CFClCF=CFCl
+F̄, SN2'
-Cl⁻
CF3CF=CFCF2Cl
+F⁻ SN2'
-Cl⁻
CF3CF2CF=CF2
(136)
F⁻
CF3CF=CFCF3
(178)
route (i)
F⁻, (178)
C2F5(CF3)C=C(CF3)C2F5
(176)
route (ii)
1) CF3C̄FCl, -F̄
2) +F̄, -Cl̄
C2F5(CF3)C=CFCF3
1) CF3C̄FCl, -F⁻
2) +F⁻, -Cl⁻

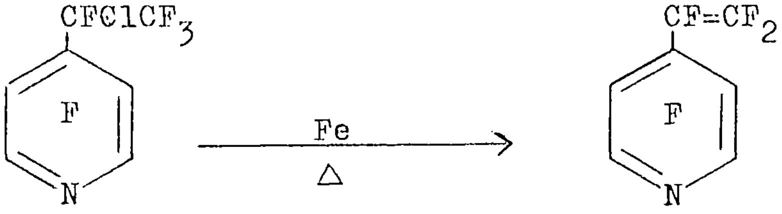
Scheme 17

CHAPTER VI

Synthesis and Reactions of Perfluoro-4-vinylpyridine

Introduction

The work described in this chapter will deal with the synthesis, and some reactions, of perfluoro-4-vinylpyridine (138) obtained by dehalogenation of 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl)-tetrafluoroethane (100).

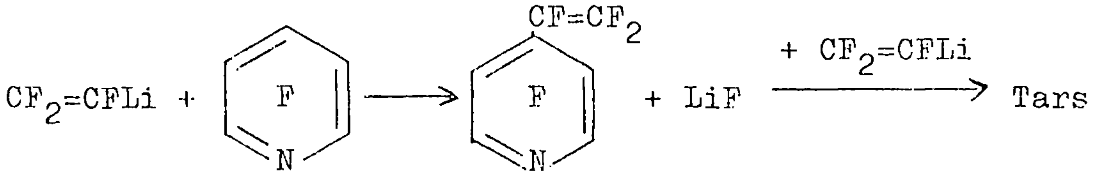


(100) (138)

The reactions described in Chapter V Section A, between chlorotrifluoroethylene and various activated aromatic species in the presence of fluoride ion, showed that formation of chlorotetrafluoroethyl derivatives, as precursors to trifluorovinylaryl compounds, had only limited possibilities. In general the yields or conversions were low, and therefore only the preparation and chemistry of perfluoro-4-vinylpyridine has been pursued.

This route has the advantage of using chlorotrifluoroethylene as starting material, which is readily available, rather than iodotrifluoroethylene, which is difficult to obtain, and is used as starting material for trifluorovinyl copper described by Tamborski et al (Chapter 1, Section A.4.)

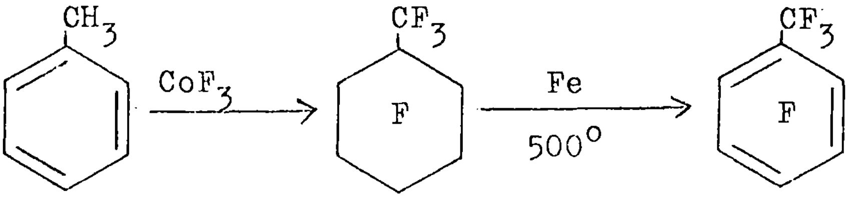
Efforts in these laboratories to synthesise (138), by the reaction of trifluorovinyl lithium with pentafluoropyridine, gave tarry products,[129] thought to be formed by further reaction of (138) with trifluorovinyl lithium so giving high molecular weight tars.



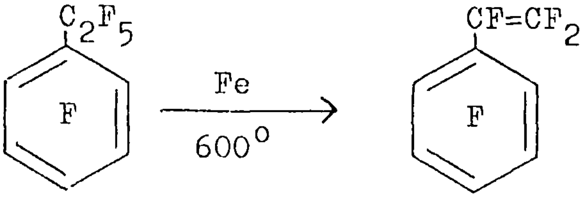
(138)

VI.A Dehalogenation of 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl)-tetrafluoroethane

Dehalogenation of perfluoroalicyclic compounds, by passing over hot iron or nickel, has now become an established method of rearomatising materials derived from CoF_3 fluorinations of aromatic hydrocarbons.[130] For example, the synthesis of octafluorotoluene from toluene, involves a final defluorinating step.

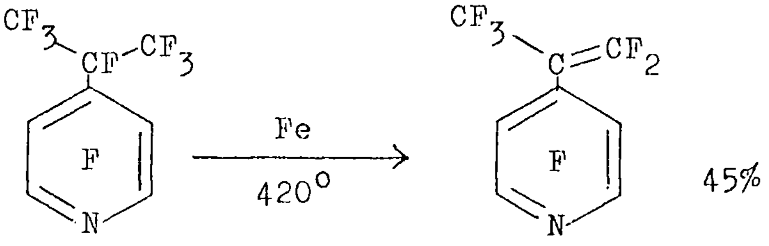


Similar attempts to defluorinate perfluoroethylbenzene with hot iron gave low yields of perfluorostyrene.[18]



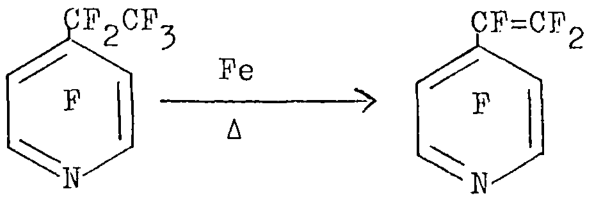
15%

Defluorination reactions using heated iron-filings have been carried out in these laboratories with varying success. For example, perfluoro-4- isopropylpyridine gives moderate yields of (139).[113]



(139)

However, defluorination of perfluoro-4- ethylpyridine (140) gives (138) in low yields and conversions[113] (Table 23).



(140) (138)

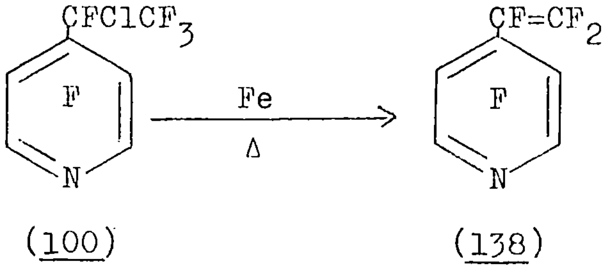
Table 23

Yields of (138) from Defluorination of (140) at varying Temperatures[113]

Temp. °C	* Percentage Yield of (138)	Conversion %
410	50	35
420	40	60
450	25	95

* Based on (140) consumed.

Passage of (100), in a stream of nitrogen, over heated iron-filings, gave a colourless liquid, which on chromatographic analysis was shown to be a single product, identified as perfluoro-4-vinylpyridine (138), from comparison of n.m.r. and infra-red spectra with those of an authentic sample.



The results (Table 24) show that much lower temperatures are required for dechlorofluorination of (100), compared to those for defluorination of (140) (Table 23).

Table 24

Yields of (138) from Defluorination of (100)

Temp. °C	Percentage Yield of (138)	% Conversion
310	68	100
500	46	100

VI.B. Reactions of Perfluoro-4- vinylpyridine

In the introduction to Chapter V the initial aims of this work were stated, these included the study of highly fluorinated, stable, conjugated anions, and it was hoped addition of fluoride ion to (138) would provide a suitable system for this study. Two different methods were employed in attempts to study long-lived anions (a) Chemical trapping, and (b) E.S.C.A.; each will be discussed under their respective heading.

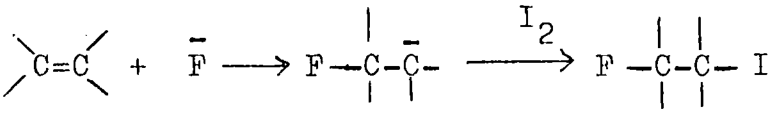
VI.B.1 Fluoride Ion Reactions

VI.B.1.a) Chemical Trapping

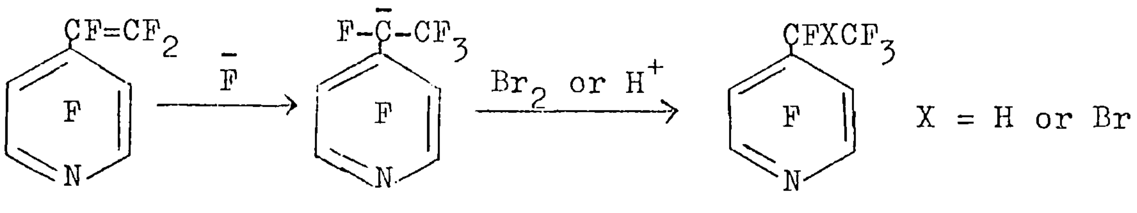
In Chapter III Section A.5.a, addition reactions of fluoro olefins in the presence of fluoride ion were described, including the addition of HF to chlorotrifluoroethylene. The reaction scheme suggested for this reaction involves formation of a carbanion, followed by abstraction of a proton from the solvent.[1]

$$F^- + CF_2{=}CFCl \xrightarrow[65^\circ]{\text{KF/Formamide}} \left[CF_3\bar{C}FCl\right] \xrightarrow{H^+} \underset{72\%}{CF_3CHClF} \qquad (1)$$

Similarly reaction of some fluoro olefins with fluoride ion, in the presence of iodine leads to addition of IF at the double bond.

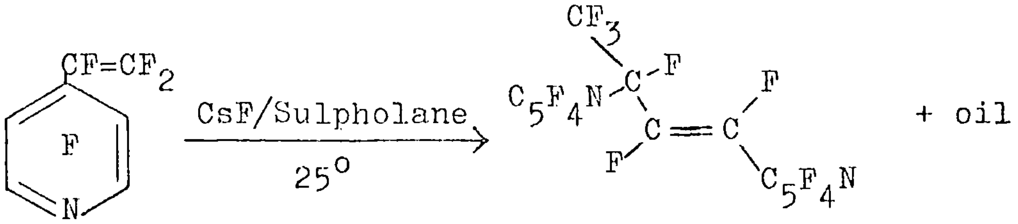


Therefore, it was anticipated that reaction of (138) with fluoride ion would give a stable carbanion (141), which in the presence of bromine or a proton source could give addition of FBr or HF across the double bond.



(141)

Addition of bromine to a vigorously stirred mixture of (138) and caesium fluoride in sulpholane, yielded after extraction with ether, a white crystalline solid, identified as trans-1,3-bis(2',3',5',6'-tetrafluoropyridyl)-hexafluorobut-1-ene (142), and a high molecular weight oil, but no products containing bromine.



(138)

(142)

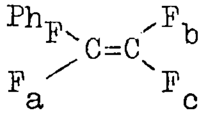
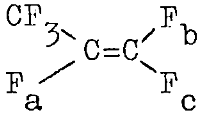
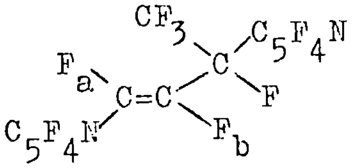
A similar reaction in which dil.HCl was used to quench the reaction also gave dimer (142) and an oil. In neither case were products from simple addition across the double bond isolated.

(i) Determination of Structure

The dimer (142) was characterised as a crystalline solid, which gave a satisfactory elemental analysis, and showed a parent peak in the mass spectrum. The structure was determined using n.m.r. spectroscopy, the spectrum containing absorptions which indicated the presence of: $\geq$C-CF$_3$; -C-F; and two vinylic fluorines, of which one was obscured by the peak for the 3,5-ring fluorines. These absorptions were all consistent with structure (142), and the trans isomer was shown to be the correct assignment, and the only isomer observable, from the large coupling constant of the vinylic fluorines. The coupling constants are in good agreement with those of other olefins containing trans vinylic fluorines (Table 25).

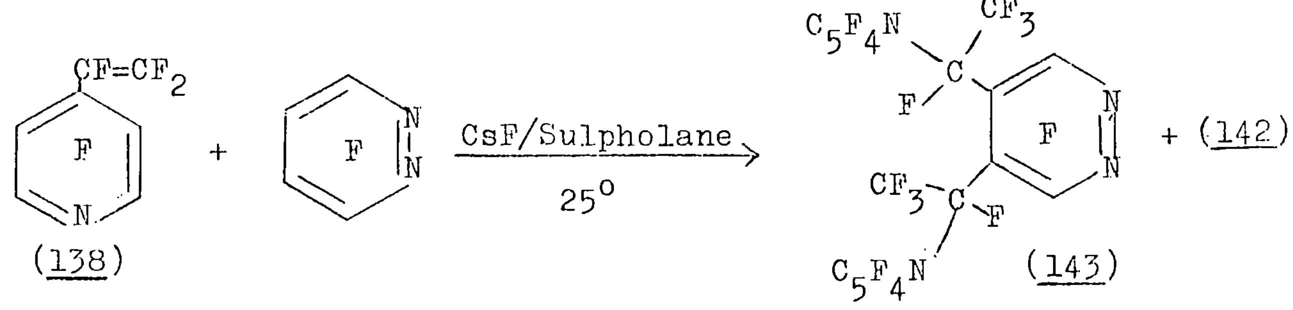
Table 25

Coupling Constants for Cis and Trans Vinylic Fluorines

Compound	Coupling Constants (Hz)		
	Jab	Jac	
	117	36	(131)
	120	40	(132)
 (142)	138		

VI.B.1.b Reaction with Tetrafluoropyridazine

Slow addition of (138) to a vigorously stirred mixture of tetrafluoropyridazine, sulpholane and caesium fluoride, yielded after extraction with ether a white crystalline solid, identified as 4,5,-di[1'-(2",3",5",6"-tetrafluoropyridyl)-tetrafluoroethyl]-3,6-difluoropyridazine (143) plus a small amount of the dimer (142).



(138) (143)

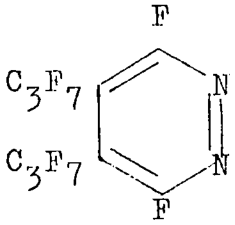
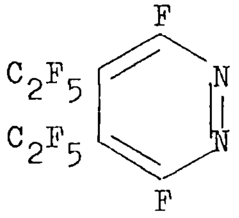
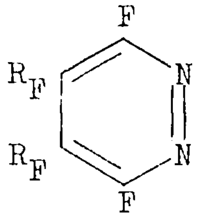
(i) Determination of Structure

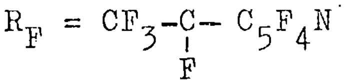
The derivative (143) was characterised by a parent peak in the mass spectrum and a satisfactory fluorine analysis.

The substitution pattern in the pyridazine ring was shown by n.m.r. spectroscopy to be at the 4,5-positions. The observed chemical shift values of the 3,6-ring fluorines were in close agreement with those of similar substituted pyridazines (Table 26).

Table 26

Chemical Shifts* in 4,5-disubstituted-difluoropyridazines

Compound	Chemical shift, Ring fluorines		
	3	6	
	68.5	68.5	(134)
	77.7	77.7	(135)
 (143)	73.7	73.7	



$R_F = CF_3-\underset{F}{\underset{|}{C}}-C_5F_4N$

*p.p.m. Relative to external $CFCl_3$

The n.m.r. spectrum was generally broad, but showed absorptions corresponding to CF_3-C- and $-C-F$ groups, which are consistent with structure (143).

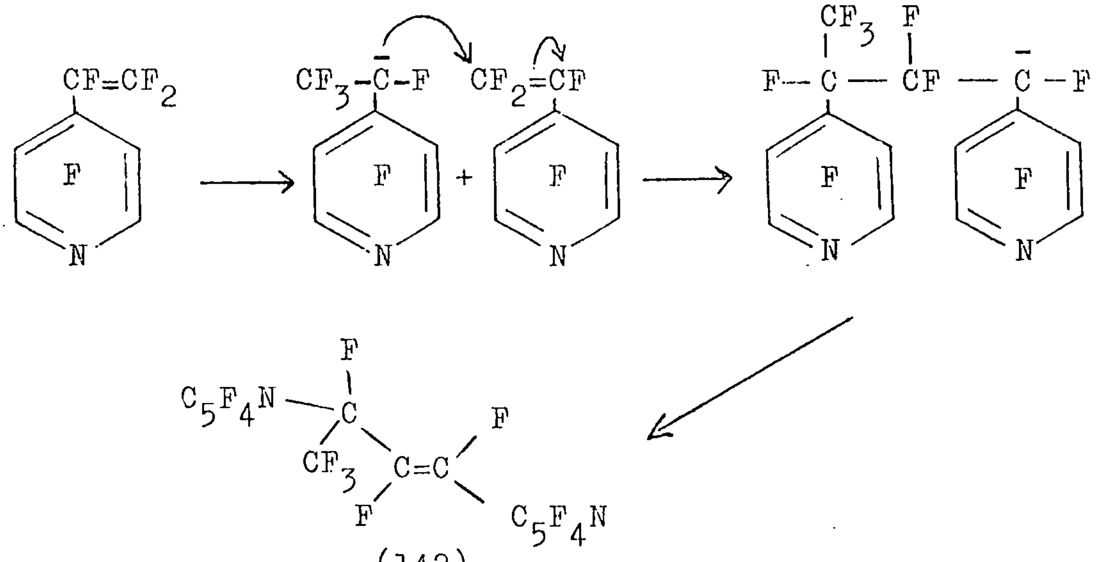
VI.B.1.c Reaction with Hexafluoropropene

An attempt to react hexafluoropropene with (138), in the presence of fluoride ion in sulpholane, gave mainly oligomers of hexafluoropropene, and a small amount of oil, which chromatographic analysis showed to be a complex mixture.

$$CF_3CF=CF_2 + (\underline{138}) \xrightarrow[25^o]{CsF/Sulpholane} \text{Oligomers of } CF_3CF=CF_2 + \text{oils}$$

VI.B.1.d Discussion of Fluoride Ion Reactions

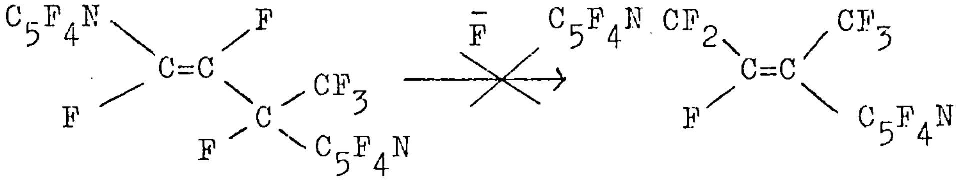
The results of the trapping experiments with bromine and acid, in the presence of fluoride ion, indicated that the secondary carbanion (141) was relatively unstable, and reacted readily with a further molecule of (138) to give the dimer (142) (Scheme 18).



Scheme 18

The product (142) was shown by n.m.r. spectroscopy to be entirely the *trans* isomer, the *cis* product probably being less stable due to steric interaction of the tetrafluoropyridyl groups.

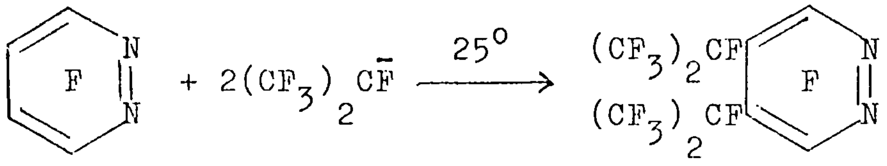
It was possible that, during the reaction, fluoride ion induced rearrangement of (142) had occured to give (144), however, the n.m.r. spectrum clearly indicated that (144) is not the structure of the recovered product



(142) (144)

Structure (142) contains -C-F and -C-CF_3, groups which are observed in the n.m.r. spectrum, and are easily distinguishable from -CF_2- and $\overset{CF_3\searrow}{\nearrow}C=$ groups, which would be observed for (144).

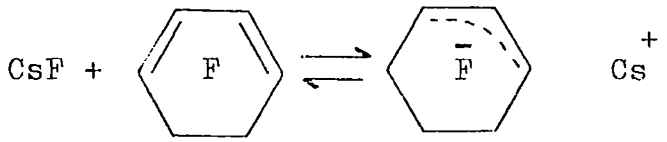
The reaction with tetrafluoropyridazine gave similar results to those observed with hexafluoropropene under mild conditions[134]



It was noticed that during fluoride ion reactions with (138) high molecular weight oils were recovered, and formation of these oils appears to occur in many fluoride ion-initiated reactions, but as yet no conclusive proof is available concerning their mode of formation.

VI.B.1.e An approach to studying stable anions using E.S.C.A.

Previous work carried out in these laboratories has shown that polyfluoroalkylation reactions are possible using 'doped' caesium fluoride, i.e. caesium fluoride with a thin layer of solvent on the surface, and during these reactions it was observed that the surface turned dark red.[136] Similarly, condensing octafluorocyclohexa-1,3-diene onto 'doped' caesium fluoride also produced colouration of the surface, and it is thought that these colours could indicate the presence of stable conjugated anions, for example, with octafluorocyclohexa-1,3-diene (146) an allylic anion (147) is formed.[135]



(146) (147)

However, these colours are not formed when normal caesium fluoride is used, indicating that some solvent is required.

If stable carbanions are formed on the surface of 'doped' caesium fluoride this could provide a method for observing stable carbanions using E.S.C.A., where only molecules at the surface are observed.

Electron spectroscopy for Chemical Analysis (E.S.C.A.) is a very sensitive spectroscopic technique used for measuring binding energies of core, and valence energy level electrons, of molecules at a surface; these are calculated from measurements made of the kinetic energies of electrons emitted after interaction of the molecule and a monoenergetic beam of X-rays. If the binding energies of the different carbon atoms in a carbanion could be measured, information concerning the electron distribution of that carbanion could be obtained.

Attempts to use E.S.C.A. for this purpose met with limited success, and the methods used, problems encountered, plus results obtained will be discussed under their respective headings.

(i) Method

The method devised to study long-lived conjugated carbanions, using E.S.C.A., involved the following procedure. A sample of dry caesium fluoride was mixed with sulpholane, in a Schlenk tube, and filtered to give a sample of caesium fluoride with a layer of solvent on the surface. This 'doped' caesium fluoride was pressed into a disc, similar to those used in infra-red spectroscopy, and this placed in a tube attached to a vacuum line. The sample under study was then condensed onto the surface of the disc, where it was anticipated that a stable carbanion would be formed on the thin layer of solvent around the caesium fluoride, and this would remain on the surface after the excess sample had been pumped off. The prepared disc was then placed into the analyser of the spectrometer and a spectrum obtained.

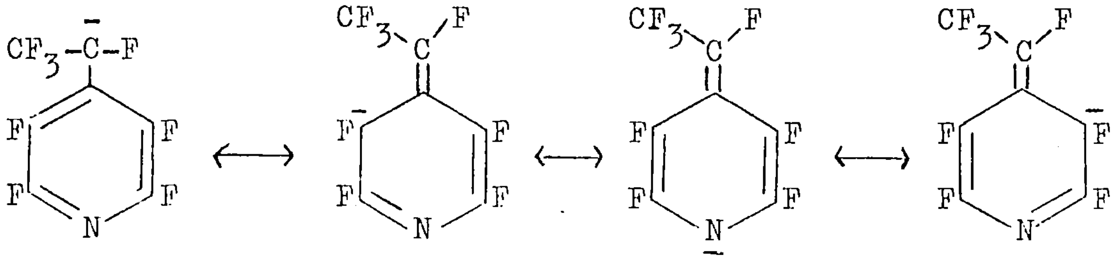
(ii) Problems of using E.S.C.A.

The method described in the previous section proved to have several problems, and the first difficulty was obtaining a disc of caesium fluoride in which the surface was not completely coated with chloride ion. Although analar caesium fluoride was used in these experiments it was difficult to prevent contamination of the surface with chloride ion, but this was kept to a minimum by using apparatus in which chlorocarbons or any other source of chlorine had not been used.

At the time this work was carried out samples, and discs, had to be prepared in the authors laboratory, then transported a considerable distance to the spectrometer, all the time providing possible sources of contamination, and as E.S.C.A. only measures binding energies of molecules at the surface any contamination will affect the quality of the spectra recorded. However, more recent modifications to the spectrometer, including attachment of a greaseless vacuum line and sample chamber, should enable preparation of 'cleaner' sample discs, consequently giving better spectra.

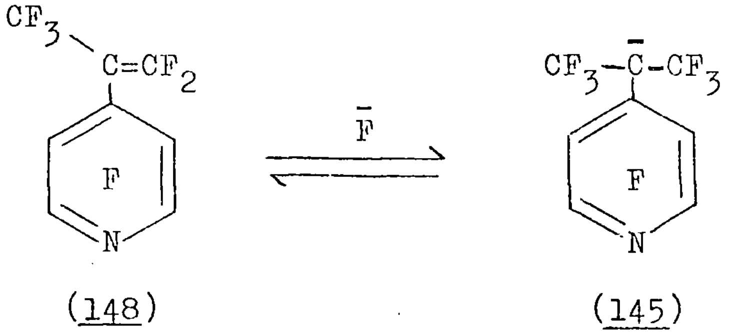
(iii) Results

Two models were used for this study, perfluoro-4-vinyl pyridine (138) and octafluoro-cyclohexa-1,3-diene. It was anticipated that addition of fluoride ion to (138) would produce a carbanion stabilised by delocalisation of the negative charge over the pyridyl ring (141).



(141)

However, attempts to observe the anion (141), by condensing (138) onto a 'doped' caesium fluoride disc produced no colouration, and a spectrum of the carbon 1s level showed only hydrocarbon present, probably due to the solvent. Attempts to trap (141) using bromine, described earlier, indicated that the secondary carbanion was not very stable, and on reflection a better system for studying stable carbanions could be perfluoro-4-isopropenlpyridine (148) which on addition of fluoride ion would form a tertiary anion (145)



Condensing octafluoro-cyclohexa-1,3-diene onto a disc did produce colouration, and a carbon 1s level spectrum (Fig. 9) showed a shoulder on the hydrocarbon peak, which could be consistent with carbons attached to fluorines, but, as can be seen in Fig. 9 any conclusions drawn from such a spectrum would be very speculative. However, Fig. 9 does indicate that to obtain good spectra of the fluorocarbon species, a layer is required over the complete surface, otherwise interference from the hydrocarbon solvent affects the spectrum.

At the time of writing modifications to the spectrometer, described earlier, are almost complete, and further work to improve techniques, and a better choice of substrate, could produce good spectra of stable carbanions.

Carbon 1s level spectrum of octafluorocyclohexa-1,3-diene on 'doped' CsF.

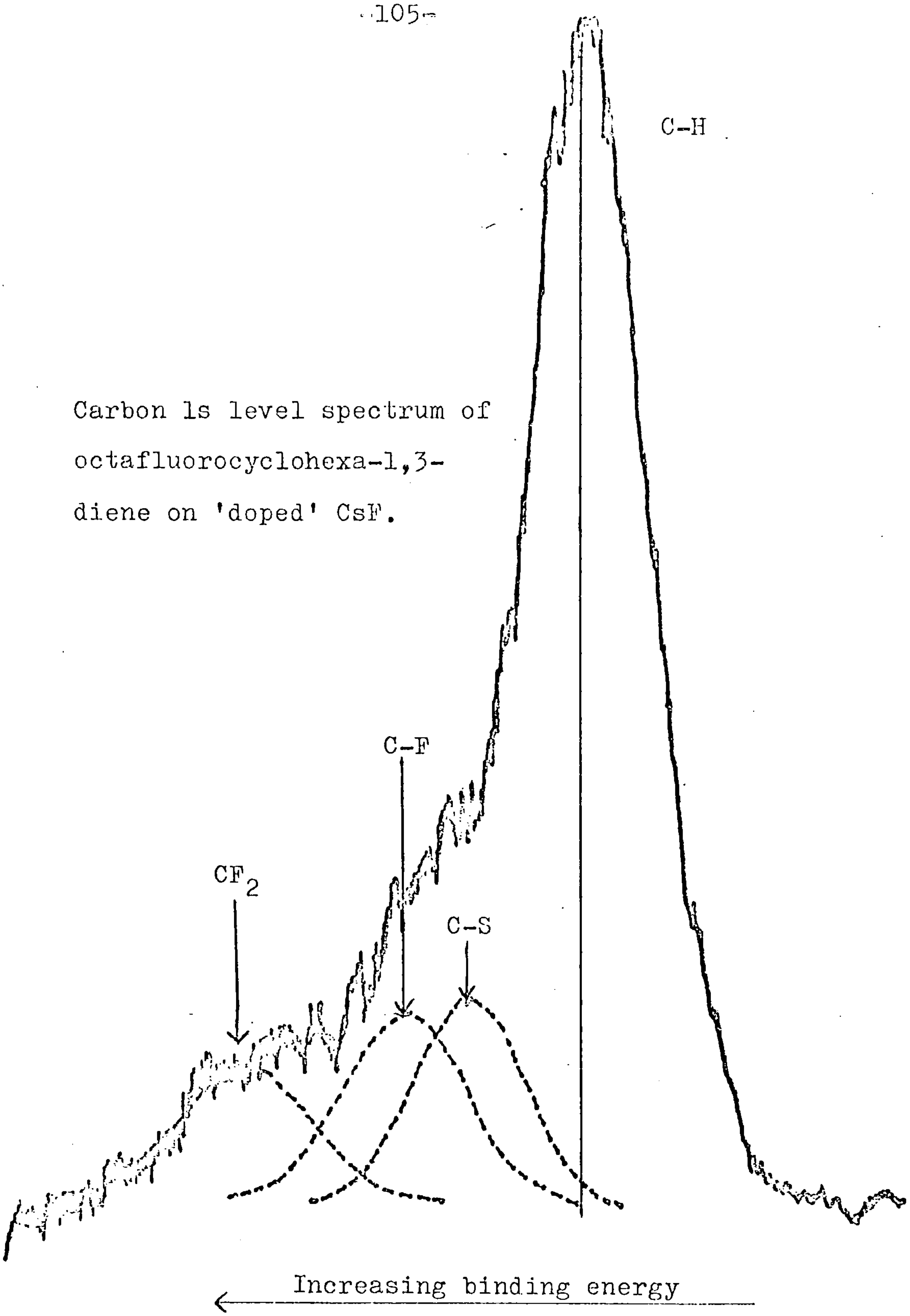
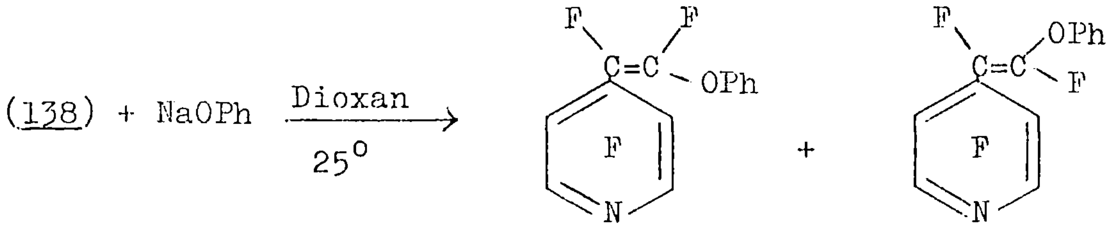


Fig. 9

VI.B.2 Reaction with other nucleophiles

VI.B.2.a Phenoxide

Addition of (138) to a vigorously stirred mixture of sodium phenoxide in dioxan, using a 1:1 molar ratio of (138): phenoxide, gave a high boiling liquid, which on chromatographic analysis was shown to be a mixture of two components, identified as <u>cis</u> and <u>trans</u> 1-phenoxy-2-(2',3',5',6'-tetrafluoropyridyl)-difluoroethylene, (149) and (150) respectively.



(149) 50%

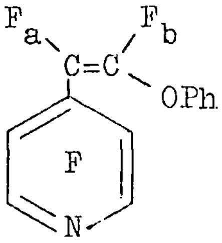
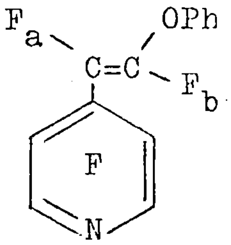
(150) 50%

(i) Determination of Structure

The two phenoxy derivatives, (149) and (150), were characterised as a mixture, giving a satisfactory elemental analysis, and a parent peak in the mass spectrum. The n.m.r. spectrum clearly showed, by integration of the vinylic fluorines, that a 50:50 mixture existed and the structures were assigned from the coupling constants of the vinylic fluorines. (Table 27) (See Table 25).

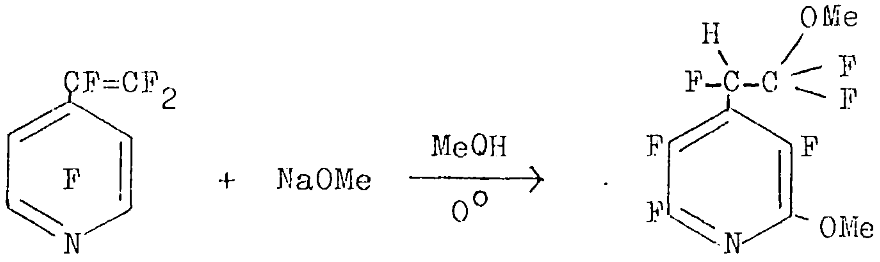
Table 27

Coupling Constants between Vinylic Fluorines in (149) and (150)

Compound	Coupling Constants, Jab Hz
 (149)	16
 (150)	121

VI.B.2.b Methoxide

Into a vigorously stirred mixture of (138) and dry methanol, was slowly added a solution of sodium methoxide in dry methanol, using a 1:1 molar ratio of (138) to methoxide, which yielded a high boiling liquid. Chromatographic analysis showed this to be a single component, identified as 2-oxa-4-(2'-methoxy-3',5',6'-trifluoropyridyl)-3,3,4-trifluorobutane (151)



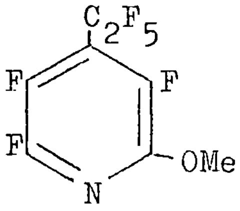
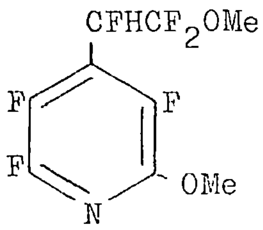
(138) (151)

(i) Determination of Structure

The ether (151) was characterised as a pure liquid, giving a good elemental analysis and a parent peak in the mass spectrum. The position of ring substitution was confirmed by n.m.r. spectroscopy, the chemical shifts being in good agreement with those of similarly substituted pyridine (Table 28).

Table 28

Chemical Shifts* in 2,4-substituted Trifluoropyridines

Compound	Chemical Shifts, Ring Fluorines 3	 5	 6	
	134.4	146.4	90.8	(65)
 (151)	143.4	154.1	98.1	

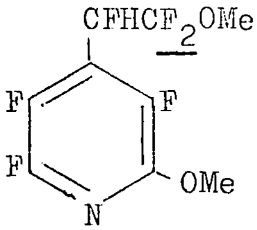
---

* p.p.m. Relative to external $CFCl_3$

Similarly the chemical shift of the CF_2OMe was in good agreement with similar compounds. (Table 29).

Table 29

Chemical Shifts* of $-CF_2OMe$ Groups

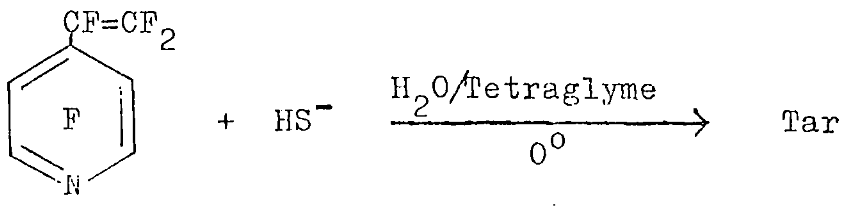
Compound	Chemical Shift, difluoromethylene groups	
$CH_3O-C\underline{F_2}CHFCl$	91.0	(136)
 (151)	89.5	

* p.p.m. relative to external $CFCl_3$

The ^1H n.m.r. spectrum showed two distinct CH_3 absorptions and a doublet of triplets, integrating to one hydrogen, a spectrum consistent with structure (151).

VI.B.2.c Bisulphide

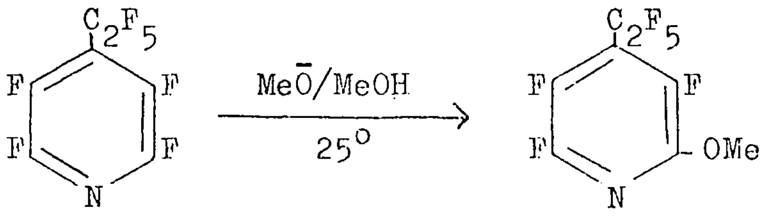
Addition of (138) to a freshly prepared solution of sodium bisulphide gave after extraction with ether an intractable tar.



(138)

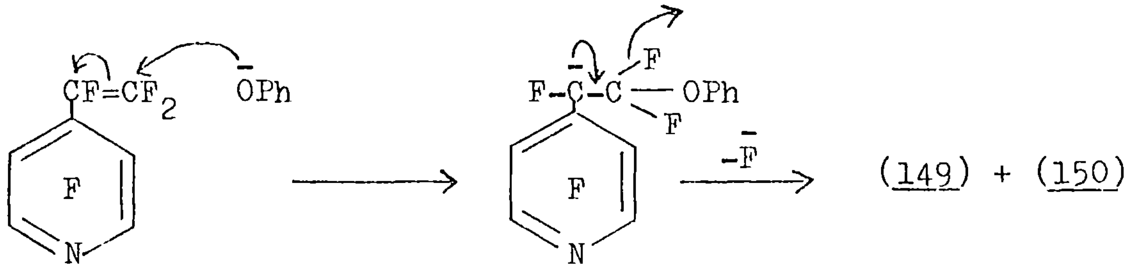
VI.B.2.d Discussion of Nucleophilic Reactions

Previous work from these laboratories has shown that methoxide will displace fluorine from the ring in perfluoro-4- ethylpyridine (152) to give the 2-methoxy-derivative (153).[65]

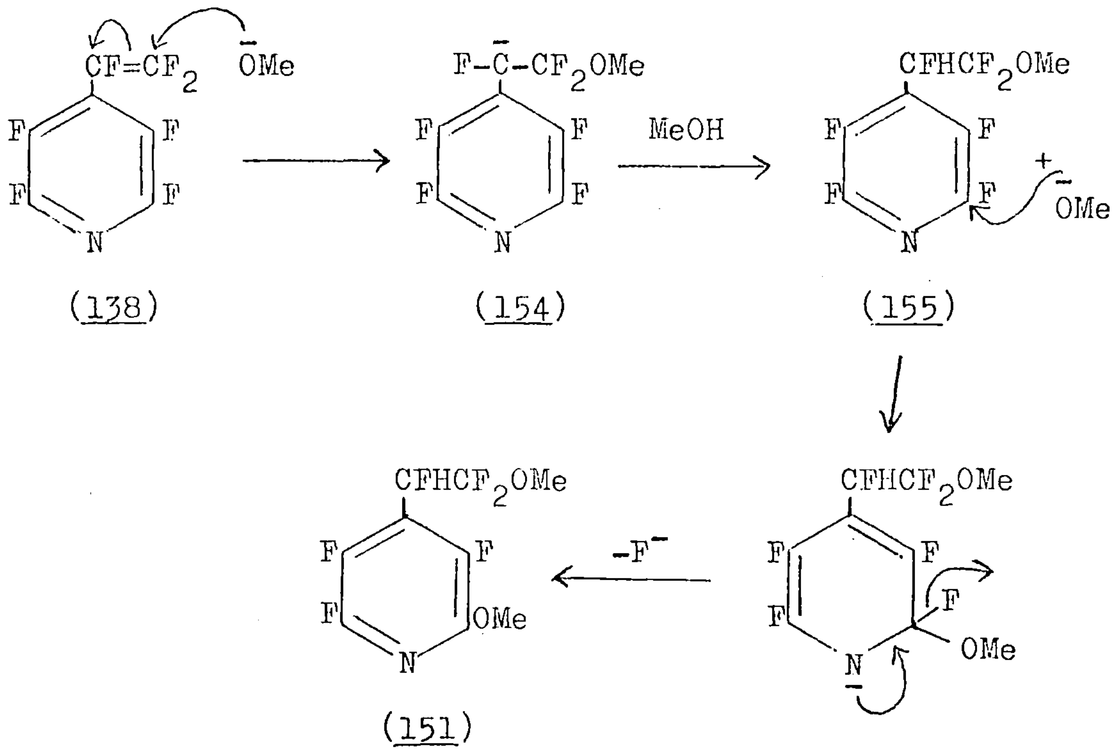


(152) (153)

Therefore, in (138) there exists two positions at which nucleophilic attack can occur, either at the ring, or at the unsaturated side-chain, and the reaction with phenoxide, clearly showed that the vinylic position was the more susceptible towards nucleophilic attack.

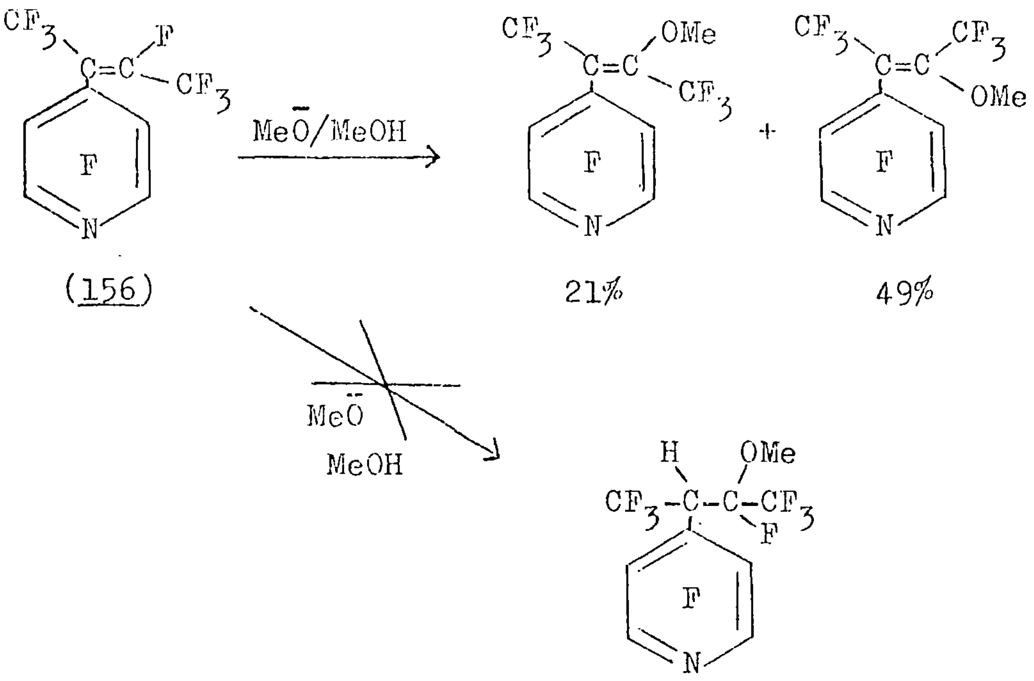


Reaction of (138) with methoxide gave both addition of methanol across the double bond, and substitution at the ring. The reaction with phenoxide has clearly established that the vinylic fluorines are more susceptible to nucleophilic displacement than the ring fluorines, indicating that the initial step of the reaction involved attack of methoxide at the terminal difluoromethylene group to give a carbanion (154), followed by abstraction of a proton from methanol to give (155), plus another methoxide ion which substituted in the ring to give (151). (Scheme 19).

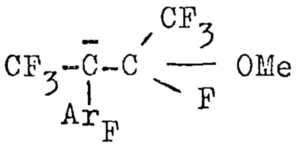


Scheme 19

The fact that addition occurs across the double bond is a possible further indication of the low stability of the carbanion formed by addition of a nucleophile to (138). In similar reactions of perfluoro-4-butenylpyridine (156) with methoxide, substitution occurred, with no addition products being formed.[121]



The lack of addition has been rationalised in terms of the stability of the intermediate tertiary anion, being relatively stable due to the stabilising influence of trifluoromethyl and perfluoroheterocyclic groups[121] i.e.



$$CF_3-\underset{Ar_F}{\overset{-}{C}}-C\begin{smallmatrix}CF_3\\ F\end{smallmatrix}-OMe$$

It was suggested that a tertiary carbanion was less likely to abstract a proton from the solvent than a secondary or primary, and, if protonation did occur the proton would be readily lost under the basic conditions used, followed by elimination of fluoride ion.[121]

This explanation could account for the formation of addition products with (<u>138</u>), where a relatively unstable secondary anion was formed, which readily abstracted a proton from the solvent.

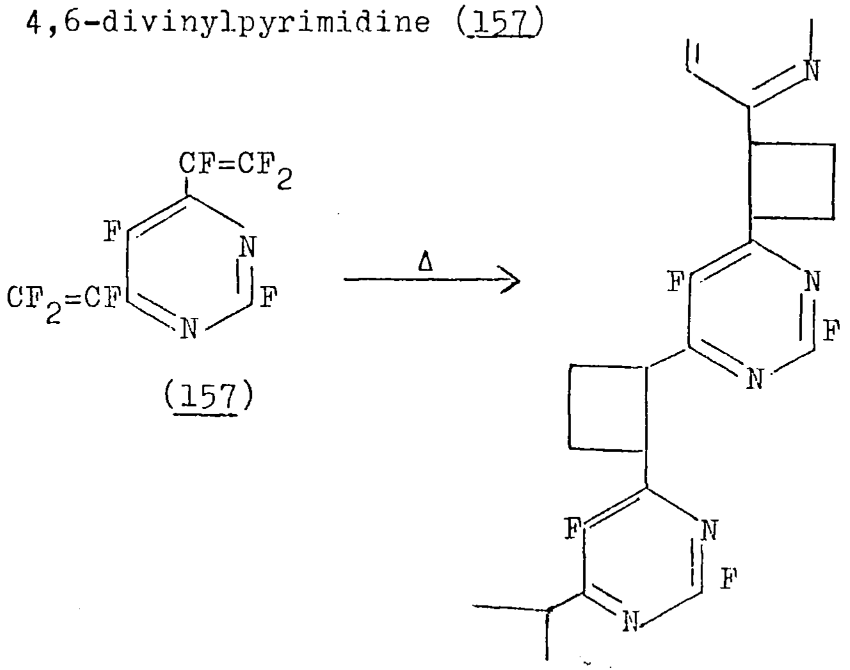
However, an alternative explanation for no addition products being formed with (156) involves steric crowding, with addition across the double bond producing a crowded molecule, which is less stable than the product from substitution, where steric crowding is less pronounced.

VI.C Cycloaddition Reactions

Introduction

One of the unusual properties of fluoro olefins containing a terminal difluoromethylene group, is formation of products derived from a 1,2-cycloaddition reaction. In Chapter IV, Section B the mechanism of cycloadditions in fluoro olefins was discussed, and the evidence presented clearly showed that the reactions proceed via a diradical intermediate, normally in a head-to-head fashion so producing the more stable diradical intermediate.

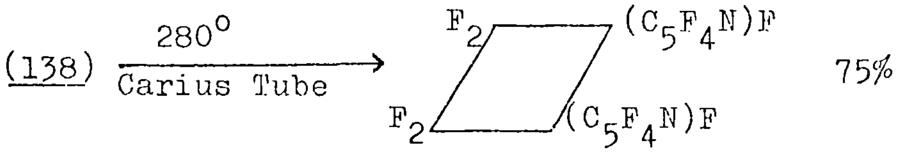
The possibility of cycloaddition reactions involving divinylaromatic species could provide a useful route to highly fluorinated, cross-linked polymers, for example with perfluoro-4,6-divinylpyrimidine (157)



The reactions discussed in this section describe a series of thermal cycloaddition reactions and some photochemical reactions of perfluoro-4-vinylpyridine (<u>138</u>).

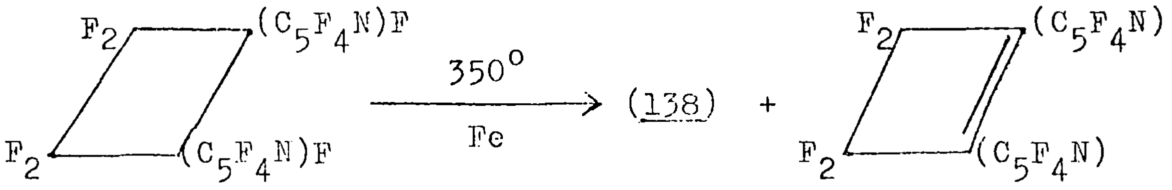
VI.C.1 <u>Dimerisation of Perfluoro- 4-vinylpyridine</u>

When (<u>138</u>) was heated (280°), under autogeneous pressure, in a small Carius tube, a low melting point solid was formed, which was identified as 1,2-(2',3',5',6'-tetrafluoropyridyl) hexafluorocyclobutane (<u>158</u>). At temperatures below 280° the rate of the reaction was slow with only small yields of products recovered.



(<u>158</u>)

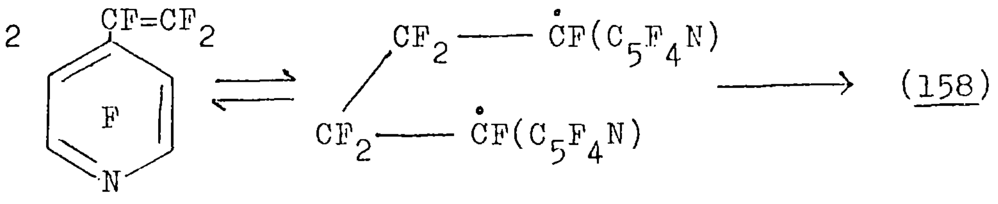
Passage of (<u>158</u>) over heated iron filings gave a mixture of products identified as starting material (<u>158</u>), (<u>138</u>) produced by a retro-cycloaddition reaction, and some defluorinated material (<u>159</u>). At the time of writing a pure sample of (<u>159</u>) had not been isolated, but the n.m.r. spectrum indicated the loss of tertiary fluorines and an equivalence of the $-CF_2-$ fluorines, facts consistent with structure (<u>159</u>).



(<u>158</u>)

(<u>159</u>)

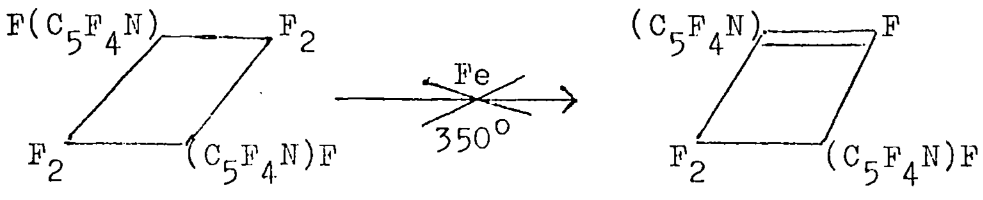
The formation of (159) on defluorination of (158) indicated that the initial cycloaddition reaction of (138) proceeded in a head-to-head manner, via the more stable diradical intermediate (160).



(138) (160)

(a) Determination of Structure

The cyclobutane (158) was characterised as a crystalline solid, giving a satisfactory elemental analysis and a parent peak in the mass spectrum. The n.m.r. spectrum of the defluorinated material showed the presence of a single $-CF_2-$ absorption, plus those for ring fluorines, a spectrum consistent with structure (159) and indicated that dimer (158) was formed by a head-to-head cycloaddition. Defluorination of the head-to-tail dimer (161) would give a product (162), and the n.m.r. spectrum of (162) would show the presence of vinylic and tertiary fluorines, which were not observed.



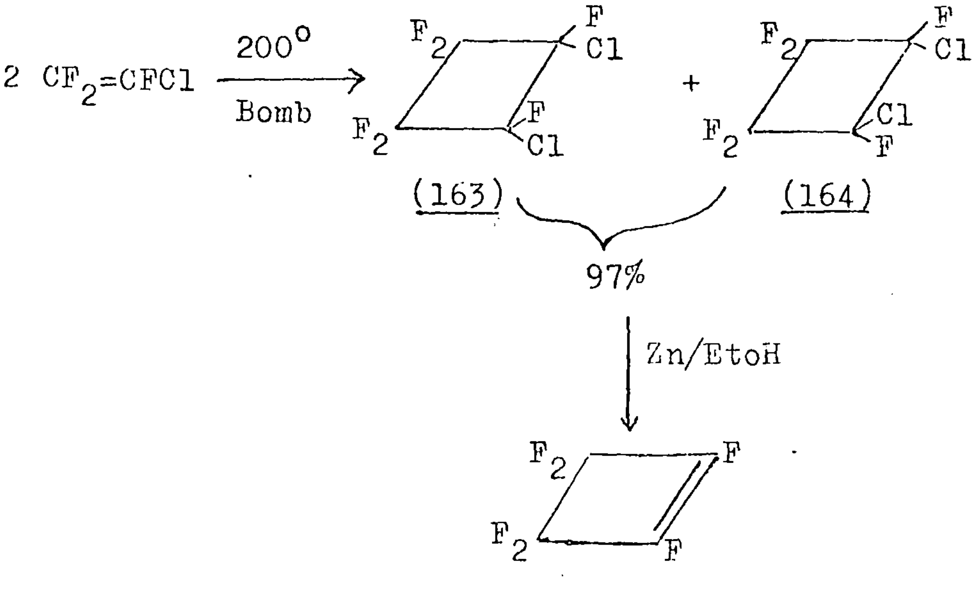
(161) (162)

The n.m.r. spectrum of (158) shows a single tertiary fluorine and an AB quartet, data consistent with a single isomer. However, from the evidence available it is not possible to tell whether the *cis* or *trans* isomer is present.

VI.C.2 Cycloaddition of Chlorotrifluoroethylene

Examples of cycloaddition reactions involving chlorotrifluoroethylene are numerous and some of these have been summarised in a review[3]. Henne and co-workers dimerised chlorotrifluoroethylene in a stainless steel bomb at 200° and obtained a mixture of *cis* and *trans*-1,2-dichloro-hexafluorocyclobutane, (163) and (164) respectively.[137]

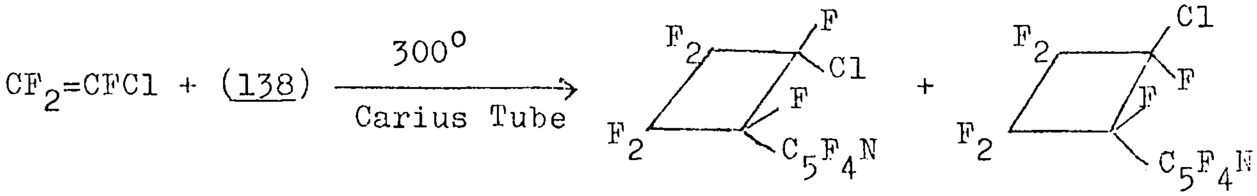
A similar reaction, carried out in these laboratories, gives high yields of (163) and (164), which on dechlorination give hexafluorocyclobutene (165).[138]



(163) (164)

(165)

Heating (138) with chlorotrifluoroethylene, under autogeneous pressure in a small Carius tube, gave a mixture consisting of starting material (138), and five products, identified as dimers (163), (164) and (158) plus *cis* and *trans* 1-chloro-2-(2',3',5',6'-tetrafluoropyridyl)-hexafluorocyclobutane (166) and (167) respectively.



(166) (167)

+ (163)+(164)+(158)

The reaction at 300° gave a combined yield of (166) and (167) of 73% with a 57% conversion (based on (138) consumed), but at lower temperatures, Ca 230°, the product consisted mainly of dimers (163) and (164) plus recovered (138), indicating that higher energy was needed in cycloaddition reactions of (138), compared to chlorotrifluoroethylene. It was only at higher temperatures, 300°, when the reaction became less specific that reaction between (138) and chlorotrifluoroethylene occured.

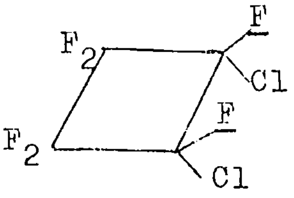
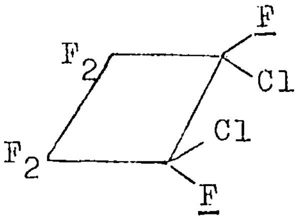
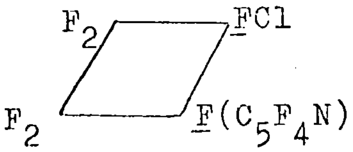
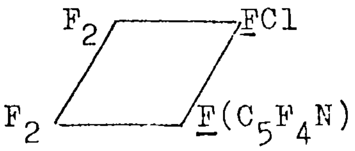
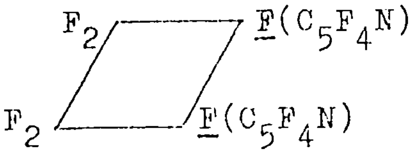
(a) Determination of Structure

The *cis*- and *trans*-cyclobutanes (166) and (167) were characterised as a mixture, giving a parent peak in the mass spectrum and a satisfactory halogen analysis.

The n.m.r. spectrum indicated that a mixture of isomers was present, and integration of the tertiary fluorines showed a 53:47 ratio. The two sets of tertiary fluorines were assigned by comparison with other cyclobutanes (Table 30).

Table 30

Chemical Shifts* of Tertiary Fluorines in Substituted Fluorinated Cyclobutanes

Compound	Chemical Shift, tertiary fluorines	
	140.8	(139)
	131.2	(139)
 (166) + (167)	141.0 and 144.0	
 (166) + (167)	154.5 and 160.5	
	164.3	

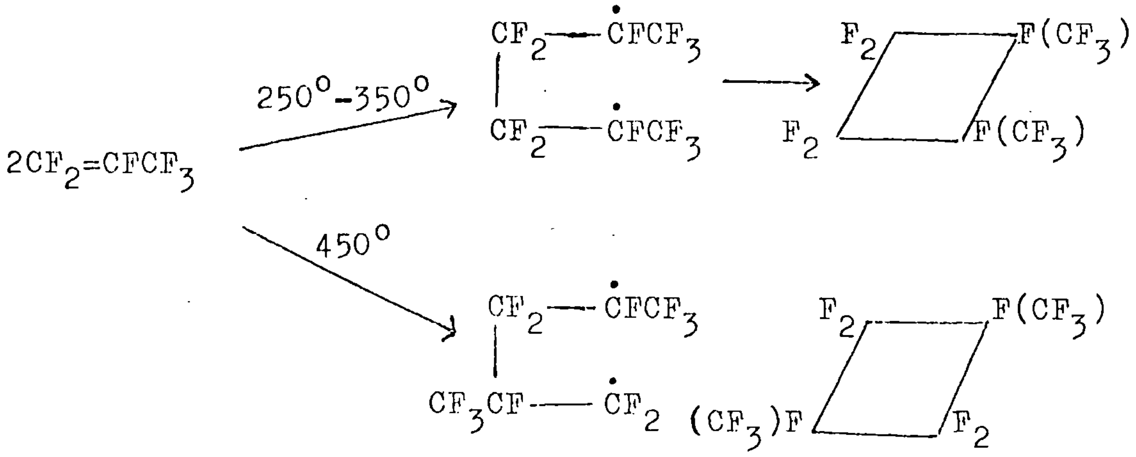
*p.p.m. relative to $CFCl_3$

The head-to-head nature of the cycloaddition was confirmed by examination of the absorptions due to $-CF_2-$ groups, a spectrum run at 84.67 MHz clearly showed four AB quartets, indicating that (166) and (167) were the correct structures. A product derived by a head-to-tail addition would have equivalent $-CF_2-$ groups, and so show a single AB quartet, a mixture of *cis* and *trans* isomers therefore showing only two AB quartets.

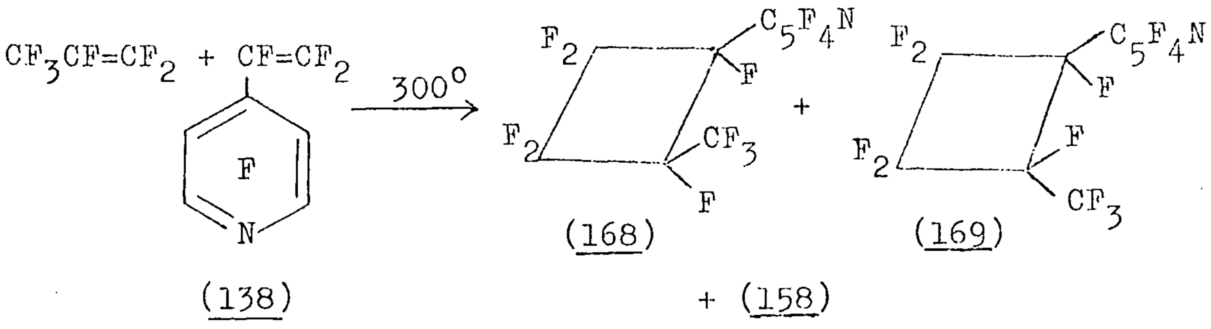
However, at the time of writing it has proved impossible to assign peaks to either the *cis* or *trans* isomers.

VI.C.3 Cycloaddition with Hexafluoropropene

Cycloaddition reactions involving hexafluoropropene occur less readily than those involving fluorinated ethylenes; dimerisation requires temperatures above 250° before reasonable yields are obtained. At temperatures between 250-350° head-to-head dimerisation occurs, but at higher temperatures more head-to-tail dimer is formed, until at 450° it becomes the main product.[111] These results have been interpreted as an indication that there is little difference between CF_2 and $CFCF_3$ in their ability to stabilise a radical, and at higher temperatures the less sterically hindered product is formed.[141]



Heating (138) with hexafluoropropene, under autogeneous pressure in a small Carius tube, gave a solid, identified as the perfluoro-4-vinylpyridine dimer (158), plus a liquid, which chromatographic analysis showed to be starting material (138) and two products identified as cis and trans-1-(2',3',5',6'-tetrafluoropyridyl)-2-trifluoromethyl-hexafluorocyclobutane, (168) and (169) respectively.



(138) (168) (169)

+ (158)

The two isomers were labelled A and B, their order of emergence from a chromatography column, silicone elastomer, and showed a 40:60 distribution. It was not possible from the n.m.r. data to show which isomer was cis or trans, but from consideration of the steric requirements, the trans isomer would be expected to be the major product, i.e. isomer B. However, in general the more symmetrical trans isomer could be expected to have a lower boiling point than the cis and this would suggest that A was the trans isomer, but as both isomers are relatively unsymmetrical this argument may not apply.

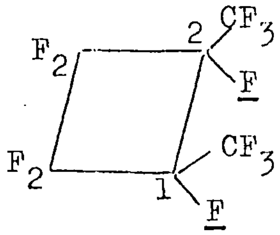
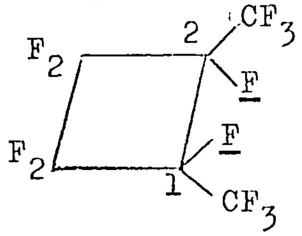
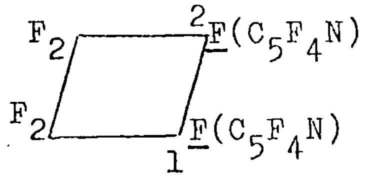
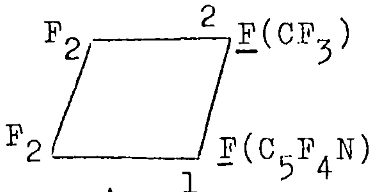
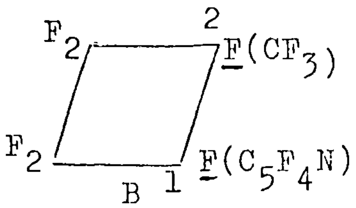
(a) Determination of Structure

The two isomers (168) and (169) were characterised as single components, after separation using preparative scale chromatography. Both isomers had identical mass spectra showing a parent peak, and gave satisfactory fluorine analysis.

The tertiary fluorines were assigned by comparison with those of the hexafluoropropene dimers, which have been fully analysed[142], and (158), the former being considerably upfield of the latter (Table 31).

Table 31

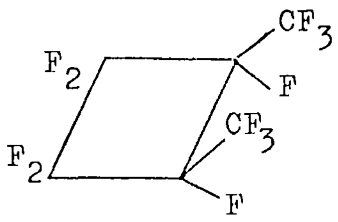
Chemical Shifts* of Tertiary Fluorines of Fluorinated Cyclobutanes

Compound	Chemical Shift		
	1	2	
	193.0	193.0	(142)
	191.5	191.5	(142)
	164.3	164.3	
 A	168.4	193.8	
 B	170.8	188.4	

* p.p.m. relative to external $CFCl_3$

The results in Table 31 show that the tertiary fluorines of the cis-hexafluoropropene dimer, are upfield to those of the trans, consequently if a similar trend existed with (168) and (169) components A and B would be the cis and trans isomers respectively, assignments consistent with those previously made after steric considerations.

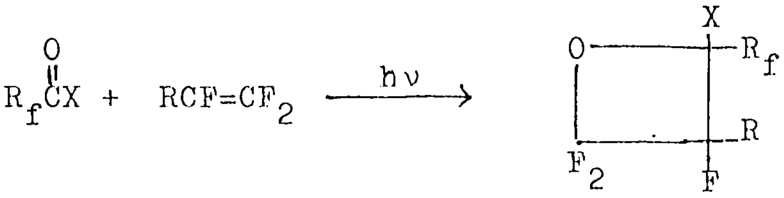
The $-CF_2-$ absorptions in the n.m.r. spectra showed that the products had been formed by a head-to-head cycloaddition, both isomers having similar spectra, comprising of a broad peak and an AB quartet, indicating that the $-CF_2-$ groups in each isomer were not equivalent (see Chapter VI.C.2.a). The fact that one of the $-CF_2-$ groups gave a broad peak, rather than an AB quartet, suggested that this absorption was due to the $-CF_2-$ group derived from hexafluoropropene. Atkinson and Stockwell[142] found that the $-CF_2-$ absorptions in hexafluoropropene dimers all gave single peaks, except in the cis isomer (170) where an AB quartet was observed.



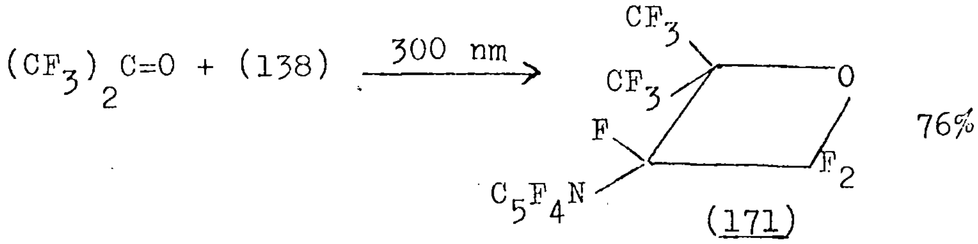
(170)

VI.C.4 Cycloaddition with Hexafluoroacetone

Photolysis of fluoroaldehydes, fluoroketones or fluoroacyl fluorides with fluoro olefins can result in the formation of polyfluorooxetanes, for example,[157]



When (138) and hexafluoroacetone were sealed in a silica tube and irradiated with ultra-violet light (300 nm), a white volatile solid was formed, identified as 2,2-bistrifluoromethyl-2-(2',3',5',6'-tetrafluoropyridyl)-trifluoro-oxetane (171), and a brown involatile solid.



(171)

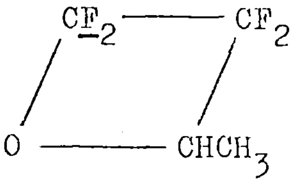
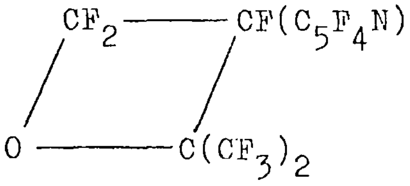
a) Determination of Structure

The oxetane (171) was characterised as a crystalline solid, giving a parent peak in the mass spectrum and a satisfactory fluorine analysis.

The structure of (171) was confirmed by the n.m.r. spectrum which showed the $-CF_2-$ group peaks had a chemical shift downfield to those in fluorinated cyclobutanes, indicating that it was adjacent to an oxygen atom (Table 32).

Table 32

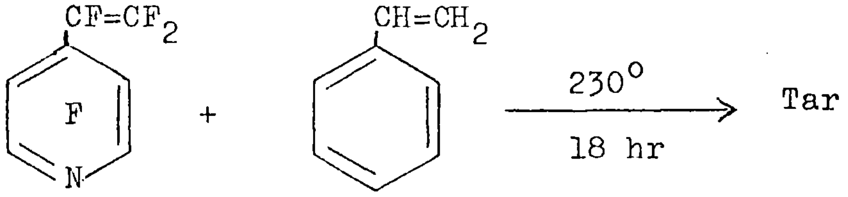
Chemical Shifts* of $-CF_2-$ groups in Fluorinated Oxetanes

Compound	Chemical Shift, CF_2 group	
	80.0 AB 85.5	(143)
 (171)	76.2 AB 75.0	

*p.p.m. relative to external $CFCl_3$

VI.C.5 Cycloaddition with Styrene

Heating (138) and styrene, under autogeneous pressure in a small Carius tube, yielded an intractable tar, which suggested that at the temperatures required for (138) to cycloadd, decomposition or polymerisation of styrene occured.



VI.C.6 Photolysis of Perfluoro-4- vinylpyridine

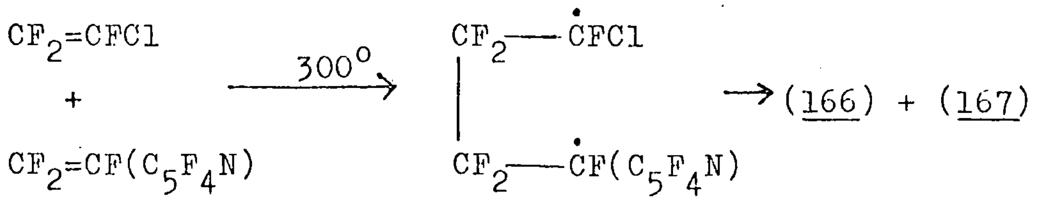
Irradiation of (138) with ultra-violet light (257.3 nm), in a silica Carius tube, yielded a pale brown, involatile solid. Attempts to purify by recrystallisation or sublimation failed, and it appears the product was probably a polymer.

$$(\underline{138}) \xrightarrow{h\nu\ 257.3\ \mathrm{nm}} \text{Polymer}$$

If a polymer has been formed this is unexpected, as perfluorostyrene polymerises only under high pressure.[156]

VI.C.7 Discussion of Cycloaddition Reactions

All the cycloaddition reactions have given products consistent with reactions proceeding via the most stable diradical intermediate. For example, the intermediate diradical (172) formed by reaction between (138) and chlorotrifluoroethylene, is stabilised by an α-tetrafluoropyridyl group and an α-chlorine, the ability of α-substituents to stabilise a radical having been shown to increase in the order H< F< Cl.[89]

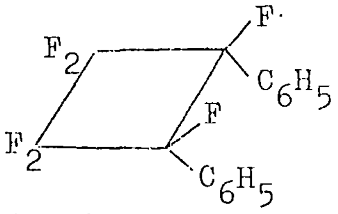


(138) (172)

The dimerisation of (138) proved to be very interesting, as only one isomer was formed. Bartlett and co-workers[144] investigating the thermal dimerisation of α, β, β-trifluorostyrene, (173) showed that the two products formed were the isomers (174) and (175), in almost equal amounts.

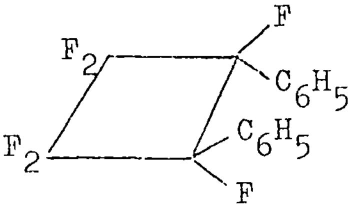
2 $C_6H_5CF{=}CF_2$

(173)



(174)

47%



(175)

53%

Why the dimer (158) should exist as a single isomer, when dimerisation of (173) gives both cis and trans isomers, (174) and (175) respectively, is not clear but there are two possible reasons. Firstly, the difference in steric requirements between a phenyl and a tetrafluoropyridyl group could be great enough to cause stereospecificity in the case of (158). For example, interaction of the orthofluorines in the two pyridyl groups could make formation of the cis isomer unfavourable. An alternative explanation is that a tetrafluoropyridyl group is able to stabilise a radical better than a phenyl group, consequently the diradical formed on dimerisation of (138) is relatively long-lived, allowing the more stable isomer to be formed. It is possible that a combination of these two factors is operating, and from steric considerations the trans isomer would be the expected product.

CHAPTER VII

The Synthesis and Some Reactions of Perfluoro-3,4-dimethylhex-3-ene

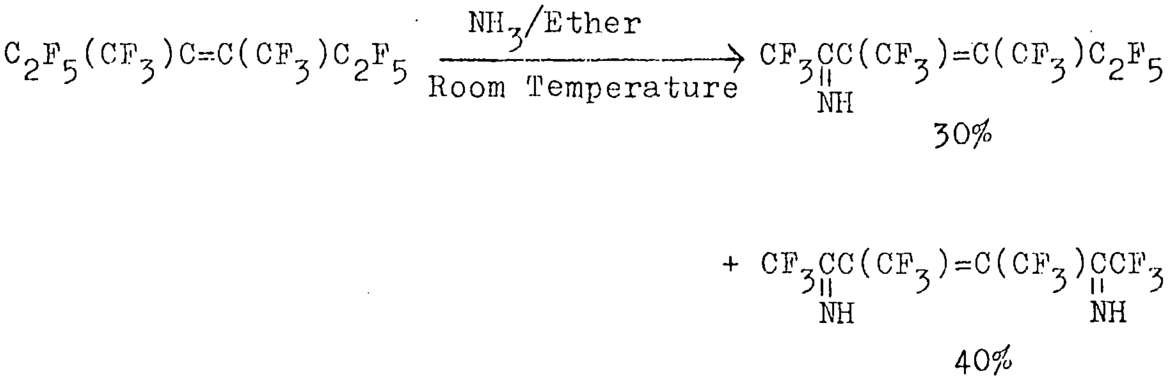
Introduction

The interest in the work discussed in this chapter initially arose after preliminary investigations into the fluoride ion-initiated dimerisation of octafluorobut-2-ene (178) had shown the major product formed was perfluoro-3,4-dimethylhex-3-ene (176)

$$\underset{(\underline{178})}{CF_3CF{=}CFCF_3} \xrightarrow[\text{Sulpholane}]{F^-} \underset{(\underline{176})}{C_2F_5(CF_3)C{=}C(CF_3)C_2F_5}$$

The dimer (176) is a particularly interesting olefin as the double bond is surrounded by electron withdrawing groups, which make it potentially very susceptible to nucleophilic attack, but as it possesses no readily displaceable groups simple vinylic substitution cannot occur. Straightforward addition across the double bond is possible, but due to steric crowding this reaction would probably be unfavourable. These properties make some investigation into the chemistry of such a system desirable, and fortunately as this olefin (176) is of interest to I.C.I. Ltd., with whom the author is connected by a C.A.S.E. award, it was felt appropriate that such an investigation should be undertaken. Unfortunately this work was carried out during the latter part of the author's research programme and only a preliminary investigation into some of the chemistry has been possible.

Some reactions of (176) have already been reported by workers at I.C.I. Ltd., for example, a mixture of two products are formed on reaction with ammonia.[145]



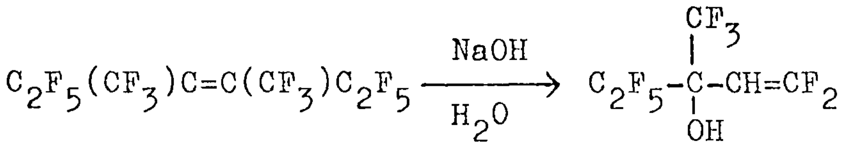
$$C_2F_5(CF_3)C{=}C(CF_3)C_2F_5 \xrightarrow[\text{Room Temperature}]{NH_3/\text{Ether}} CF_3\underset{\underset{NH}{\|}}{C}C(CF_3){=}C(CF_3)C_2F_5$$

30%

$$+\ CF_3\underset{\underset{NH}{\|}}{C}C(CF_3){=}C(CF_3)\underset{\underset{NH}{\|}}{C}CF_3$$

40%

Also reaction of (176) with sodium hydroxide in water gives a product, the spectroscopic data of which is consistent with structure (177).[146]



$$C_2F_5(CF_3)C{=}C(CF_3)C_2F_5 \xrightarrow[H_2O]{NaOH} C_2F_5-\overset{\overset{CF_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH{=}CF_2$$

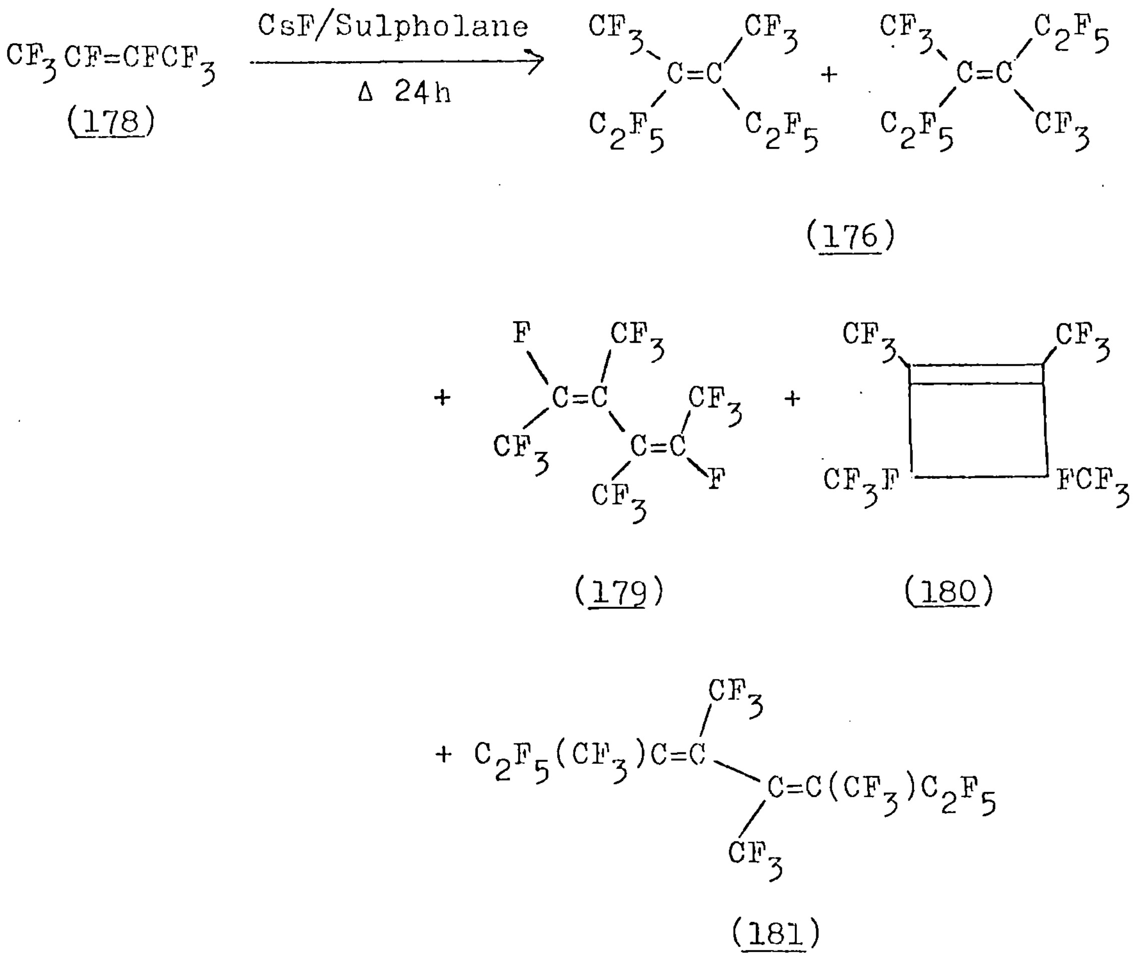
(176) (177)

Base catalysed reactions of phenol with (176) have given a phenyl ether but no structures were reported.[15~~0~~4]

$$C_2F_5(CF_2)C{=}C(CF_3)C_2F_5 \xrightarrow[\text{D.M.F.}]{Na_2CO_3/\text{Phenol}} C_8F_{15}OC_6H_5$$

VII.A Synthesis of Perfluoro-3,4-dimethylhex-3-ene

When octafluorobut-2-ene (178) was heated with caesium fluoride in sulpholane, contained in a nickel tube, unreacted olefin (178) and colourless volatile liquid were recovered.[147] Chromatographic analysis of the volatile products showed that it consisted mainly of *cis* and *trans* isomers of (176) plus two minor components, one having a higher and one a lower boiling point than (176). The n.m.r. spectrum of the lowest boiling component showed that it consisted of two products, identified but not isolated (see later Section VII.B.1), as perfluoro-3,4-dimethylhexa-2,4-diene (179), and perfluoro-1,2,3,4-tetramethylcyclobutene (180). The highest boiling component was isolated and identified as perfluoro-3,4,5,6-tetramethylocta-3,5-diene (181).



Dimerisation of (178) proved to be temperature dependent (Table 33), with the best yield of (176) being formed at 100°, although better conversions were obtained at higher temperatures.

Table 33

Yields of Products from Fluoride Ion Dimerisation

Octafluorobut-2-ene (178)

Temp °C	*Percentage Yields			Percentage Conversion
	(179)+(180)	(176)	(181)	
58	19.5	75.0	8.0	8
100	3.0	85.0	11.5	38
130	11.5	69.0	15.5	44

*Based on (178) consumed

Dimerisation of (178) has also been reported by another worker, although no temperature was given.[79] Fluoride ion-initiated oligomerisation of tetrafluoroethylene, discussed in detail in Chapter III.A.5.d.i, also gives (176) as a minor product,[73,74] and a typical product mixture obtained by workers at I.C.I. Ltd. contained 15% (176).[48]

Attempts to oligomerise chlorotrifluoroethylene, reported in Chapter I, also gave (176) as one of the major products, although in very low yields.

VII.A.1 Determination of Structure

The dimer (176) was identified by comparison of the n.m.r. and infra-red spectra with those of an authentic sample. The n.m.r. spectrum showed a mixture of *cis* and *trans* isomers present, in a ratio of 56:44, although it was not known which was the predominant isomer.

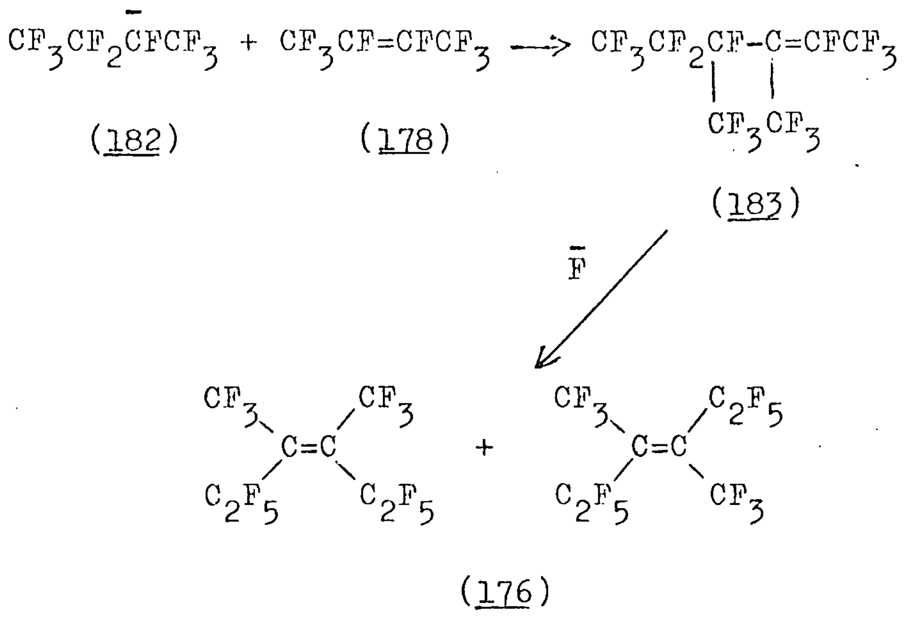
The diene (181) was identified after separation using preparative scale chromatography, and gave a P-19 peak in the mass spectrum. The n.m.r. spectrum showed the presence of $CF_3-C\leqslant$ x1; $\overset{CF_3}{>}C=$ x2; and $-CF_2-$x1; a spectrum consistent with structure (181). The n.m.r. spectrum indicated that a mixture of isomers were present in a ratio of 34:66, although which isomer predominated was not known.

VII.A.2 Discussion

The conditions required showed that dimerisation of octafluorobut-2-ene (178) occured less readily than the corresponding reaction with hexafluoropropene, which readily dimerises at room temperature and atmospheric pressure.[148] The presence of a terminal difluoromethylene group in a fluoro-olefin generally renders it more reactive to nucleophilic attack than an internal olefin, and this probably accounts for the difference in reactivity between the internal olefin octafluorobut-2-ene (178) and hexafluoropropene. However, the conversions of octafluoro-but-2-ene (178) to (176) were low, and this was possibly due to steric effects, which make approach of a bulky perfluorobutenyl anion to a molecule of octafluorobut-2-ene (178) relatively unfavourable, although it has also been suggested that the perfluorobutenyl anion is possibly more stable than perfluoroisopropyl, so affecting the ease of dimerisation.[147]

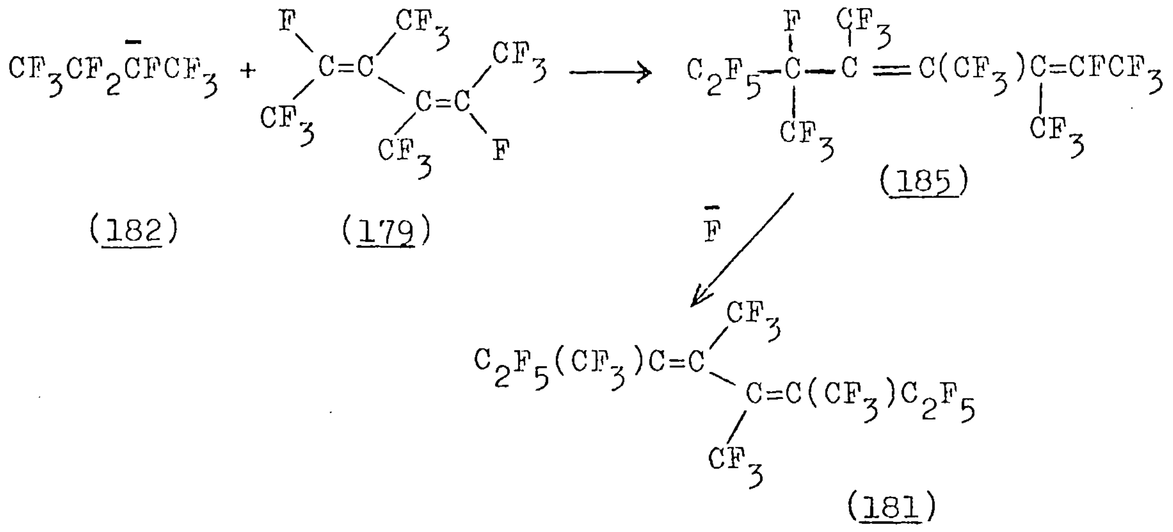
a) Mechanism

A mechanism which accounts for the formation of (176), by a fluoride ion-initiated dimerisation of octafluorobut-2-ene (178), involves addition of a perfluorobutenyl anion (182) to octafluorobut-2-ene (178), followed by elimination of fluoride ion to give an olefin (183), which in the presence of fluoride ion re-arranges to give the more stable isomers, *cis* and *trans* (176) (Scheme 20).



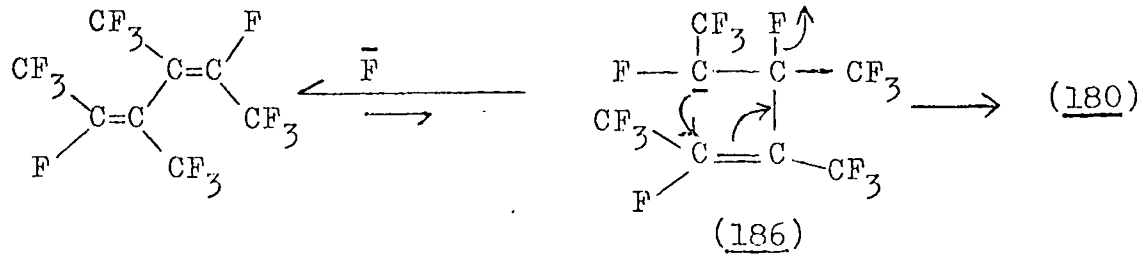
Scheme 20

Formation of the diene (181) can occur by two routes, either by addition of a perfluorobutenyl anion (182) to the diene (179) to give (185), which in the presence of fluoride ion rearranges to the more symmetrical diene (181) (Scheme 21), or by defluorination of a trimer of octafluorobut-2-ene (178), but, as no trimers of (178) were observed in the reaction products, the former mechanism is favoured.



Scheme 21

Formation of the diene (179) involved a defluorination step and this probably occured by reaction of the dimer (176) with the nickel walls of the bomb. The most likely mechanism which could account for formation of the cyclobutene (180), involves addition of fluoride ion to the diene (179) to give an intermediate carbanion (186), which then undergoes an intramolecular nucleophilic substitution to give (180).

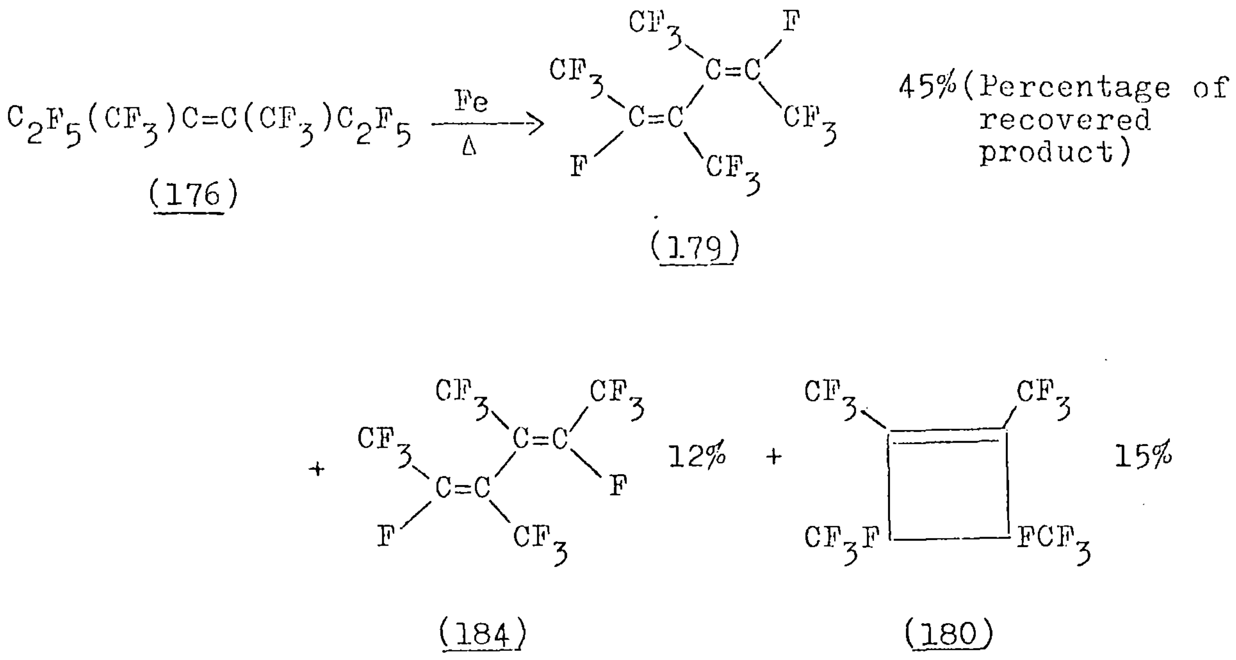


An alternative mechanism is an intramolecular 1,2-cycloaddition of the diene (179), but as all reported cases of cycloadditions involve olefins with terminal difluoromethylene groups this mechanism appears to be unlikely (see later VII.B.1).

VII.B Reactions of Perfluoro-3,4-dimethylhex-3-ene

VII.B.1 Defluorination

Passage of (176) over heated iron-filings gave a volatile colourless liquid, which n.m.r. spectroscopy showed consisted of a complex mixture of dienes, and a cyclobutene (180). Attempts to achieve separation of the components using chromatographic techniques failed, with no separation being obtained even at room temperature, and although some enrichment of different fractions with various dienes was achieved by distillation, it proved impossible to obtain pure samples for characterisation. However, since this work was carried out new apparatus has been obtained in these laboratories which should enable a better separation by distillation. From the n.m.r. spectra of enriched samples the three major components have been identified as perfluoro-*trans*,*trans*,-3,4-dimethylhexa-2,4-diene (179), perfluoro-*cis*,*trans*-3,4-dimethylhexa-2,4-diene (184), and perfluoro-1,2,3,4-tetramethylcyclobutene (180).



The conversion of (176) to dienes was found to increase with higher temperatures, but the yields decreased (Table 34), suggesting that possible decomposition was occuring at high temperatures, although no evidence of breakdown products was obtained.

Table 34

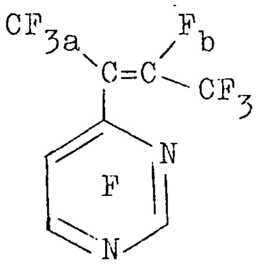
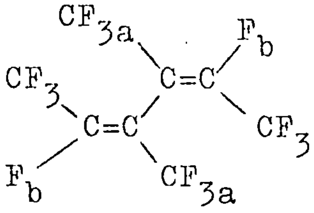
Yields of Dienes After Defluorinating (176)

Temp. °C	Percentage Yield of Dienes	Percentage Conversion
430	74	69
500	61	91

When a mixture of dienes and (180) were heated with caesium fluoride in sulpholane, the product distribution altered, with the ratio of component (179) to (184) increasing, suggesting that (179) is the more stable

Table 35

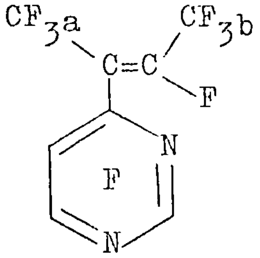
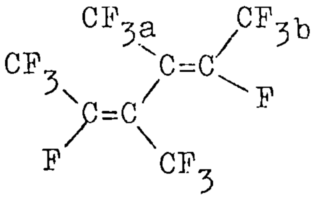
Coupling Constants between Vinylic Fluorines and Vicinal Trifluoromethyl Groups

Compound	Coupling Constant, Hz. Jab.	
	22	(150)
 (179)	18	

The n.m.r. spectrum of the diene (184) showed the presence of four different $CF_3\diagdown C=$ groups and two different vinylic fluorines. One of the $CF_3\diagdown C=$ peaks consisted of a doublet, with a coupling constant consistent with $CF_3\diagdown C=C\diagup F$, and two others showed quartets with coupling constants expected for $CF_3\diagdown C=C\diagup CF_3$ (Table 36), a spectrum consistent with structure (184).

Table 36

Coupling Constants between Cis Trifluoromethyl Groups

Compound	Coupling Constants, Hz Jab	
	11	(150)
 (184)	10	

The n.m.r. spectrum of the cyclobutene (180) showed the presence of $CF_3-C\leq$ x1; $CF_3-C=$ x1; and $F-C\leq$; a spectrum consistent with structure (180).

VII.B.2 Reaction with Diethylamine

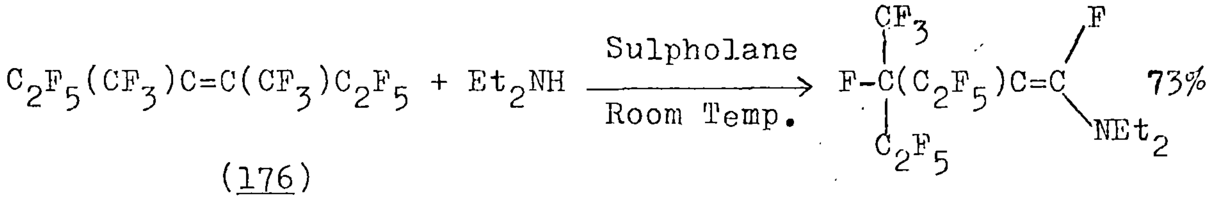
In general fluoro olefins can react with diethylamine in two ways, either by substitution or by addition, for example, hexafluoropropene with diethylamine gives either the saturated tertiary amine or a mixture of saturated and unsaturated products, depending on the conditions used.[1]

$$CF_3CF{=}CF_2 + Et_2NH \xrightarrow[(C_2H_5)_2O]{\text{Room Temp.}} CF_3CHFCF_2NEt_2 + CF_3CF{=}CFNEt_2$$

However perfluoroisobutene gives only substitution, even when the reaction is carried out at low temperatures.[1]

$$(CF_3)_2C{=}CF_2 + Et_2NH \xrightarrow[(C_2H_5)_2O]{0^{\circ}} (CF_3)_2C{=}CFNEt_2$$

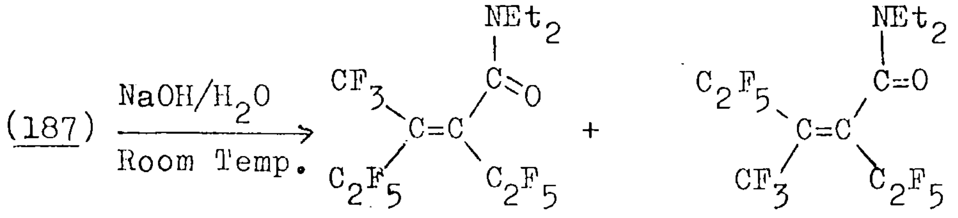
Addition of diethylamine to a vigorously stirred mixture of (<u>176</u>) in sulpholane gave, after pouring into water, an immiscible lower layer, which chromatographic analysis showed consisted of unreacted (<u>176</u>) and one product, identified as 3-trifluoromethyl-4-diethylaminofluoromethene-undecafluorohexane (<u>187</u>).



$$\underset{(176)}{C_2F_5(CF_3)C{=}C(CF_3)C_2F_5} + Et_2NH \xrightarrow[\text{Room Temp.}]{\text{Sulpholane}} F{-}C(CF_3)(C_2F_5)(C_2F_5)C{=}C(F)NEt_2 \quad 73\%$$

(<u>187</u>)

On stirring (<u>187</u>) with a sodium hydroxide solution hydrolysis occured, giving a mixture of <u>cis</u> and <u>trans</u> 3-trifluoromethyl-4-(N,N-diethylamido)-decafluorohex-3-ene, (<u>188</u>) and (<u>189</u>) respectively. The n.m.r. spectrum showed an isomer ratio of 41.5:58.5, the predominant product showing a broad splitting for the $CF_3{>}C{=}$ group, a possible indication that this was the trans isomer (189), where due to the configuration, more coupling would be expected.



(188) (189)

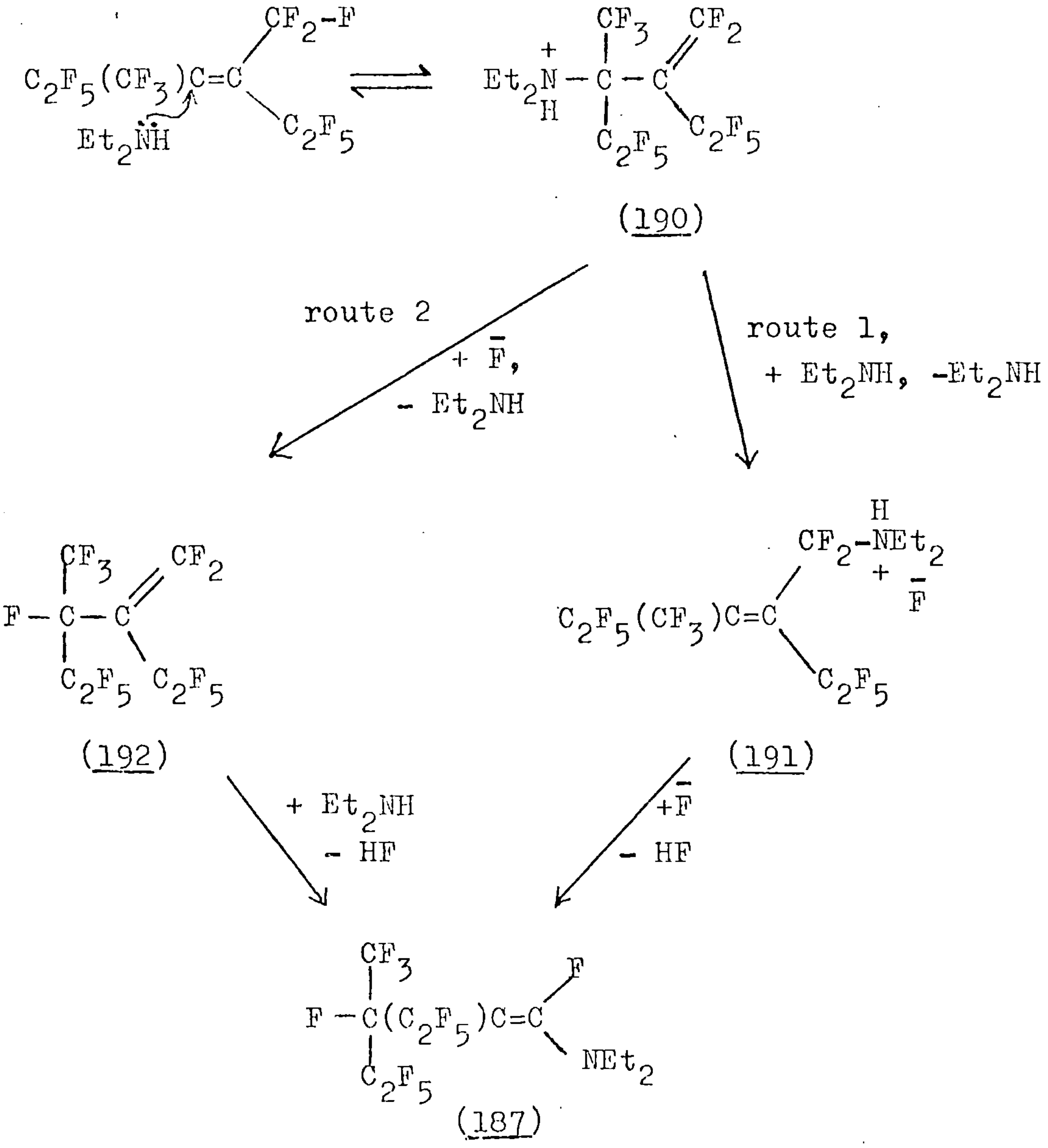
VII.B.2.a Determination of Structure

The enamine (187) was characterised, after vacuum distillation, by elemental analysis and a very small parent peak in the mass spectrum. The n.m.r. spectrum showed the presence of $CF_3\text{-}C\leqslant(x3)$; $-CF_2-(x2)$; tertiary fluorine (x1); and a single fluorine downfield at 42 p.p.m., consistent with a $=\overset{F}{C}-N-$. These data are all consistent with the structure (187).

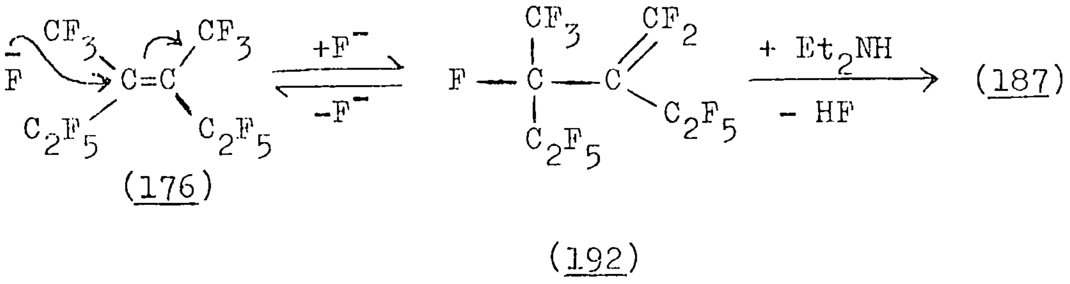
The amides (188) and (189) were characterised as a mixture by elemental analysis and a parent peak in the mass spectrum. The n.m.r. spectrum showed that two isomers were present each containing $CF_3\text{-}C=(x1)$; $CF_3\text{-}C\leqslant(x2)$; $-CF_2-(x1)$; and the infra-red spectrum showed a carbonyl absorption at 1670 cm^{-1}. These data are consistent with structures (188) and (189).

VII.B.2.b Mechanism

The structure of the enamine (187) shows that diethylamine has substituted at a vinylic trifluoromethyl group, indicating that an allylic displacement of fluorine had occured prior to final substitution by diethylamine. A possible mechanism involves S_N2' displacement of fluoride ion from a trifluoromethyl group by diethylamine to give an intermediate (190). The reaction can then proceed via two slightly different routes, either by addition and elimination of diethylamine to give (191), which after rearrangement in the presence of fluoride ion and loss of HF gives (187) (route 1), or by displacement of diethylamine from (190) by fluoride ion to give a terminal olefin (192), which after addition of diethylamine and loss of HF gives (187) (route 2).

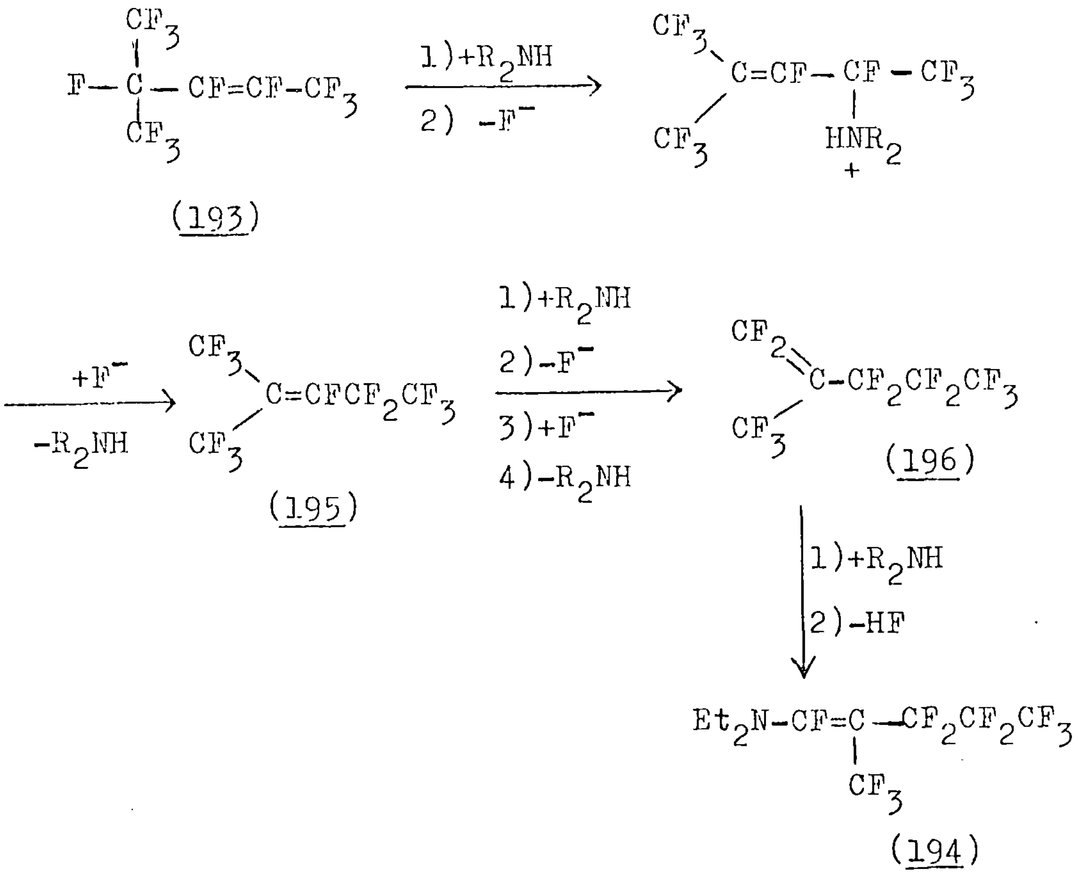


Although the initial rearrangement of (176) to a terminal olefin (192) was promoted by attack of diethylamine it is possible that this became a fluoride ion-initiated reaction after displacement of fluoride ion by diethylamine had occured. (Scheme 22).



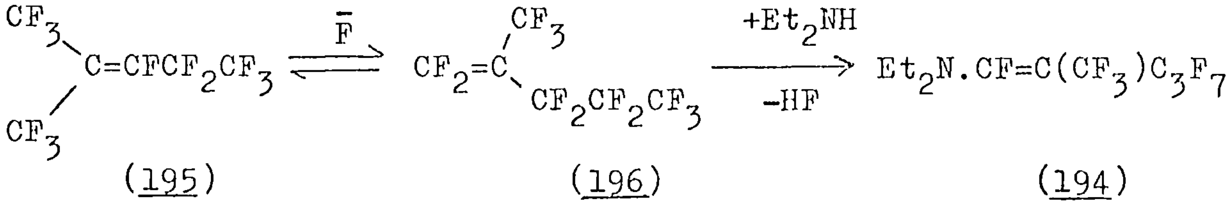
Scheme 22

Similar rearrangement products have been produced by reaction of hexafluoropropene dimers with diethylamine. Tsukamoto and co-workers[151] observed that reaction between perfluoro-4-methylpent-2-ene (193) and diethylamine gives a terminal enamine (194), and the mechanism proposed involves a double allylic displacement of fluoride ion, before (194) is formed (Scheme 23).

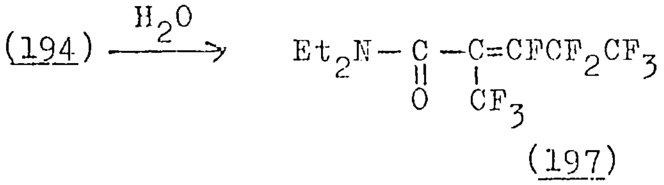


Scheme 23

Haszeldine and co-workers[152] also observed the formation of enamine (194) by addition of diethylamine to perfluoro-2-methylpent-2-ene (195), and suggested the initial isomerisation from (195) to (196) is a fluoride ion-initiated reaction.



Both groups of workers[151,152] observed that (194) hydrolysed to give an amide (197)

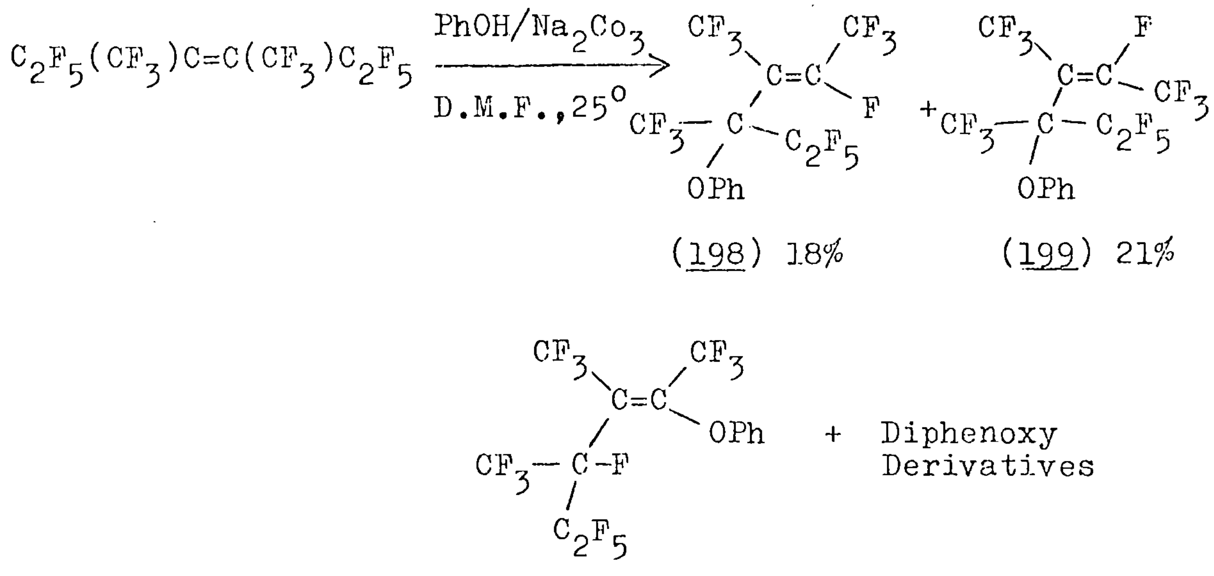


VII.B.3 Reaction with Phenol

Workers at I.C.I. Ltd. have studied reactions of various phenols with oligomers of tetrafluoroethylene, including (176) with phenol, but although they report formation of a phenyl ether no structures have been reported.[154] The objective of this work was to investigate this reaction and obtain structures for the ethers.

VII.B.3.a Using Sodium Carbonate as a Base

Addition of a solution of phenol in D.M.F. to a vigorously stirred mixture of (176) and sodium carbonate in D.M.F. yielded a volatile and an involatile liquid. Chromatographic analysis of the volatile components showed a mixture of two major and one minor product, identified as cis and trans-4-phenoxy-3,4-bistrifluoromethyl-nonafluorohex-2-ene, (198) and (199) respectively, plus cis-2-phenoxy-3,4-bistrifluoromethyl-nonafluorohex-2-ene (200). The involatile products were not identified, but gave a parent peak in the mass spectrum corresponding to disubstituted derivatives.



(198) 18%

(199) 21%

(200) 2.5%

28%

VII.B.3.b Using Triethylamine as a base

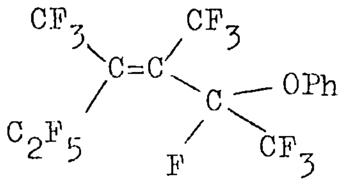
This experiment was exactly the same as that described in section VII.B.3.a except that sodium carbonate was replaced by triethylamine. After pouring the reaction mixture into water and washing with dil.HCl an immiscible lower layer was recovered, which proved to be a mixture of monophenoxy derivatives (198)-(200), in almost quantitative yields. Chromatographic analysis of the products showed that the distribution of products had altered considerably on changing from sodium carbonate to triethylamine, the proportion of (200) formed having much increased.

$$CF_5(CF_3)C{=}C(CF_3)C_2F_5 \xrightarrow[Et_3N,25^{o}]{PhOH/D.M.F.} \underset{37\%}{(198)} + \underset{28\%}{(199)} + \underset{25\%}{(200)}$$

VII.B.3.c Determination of Structure

All three products, (198)-(200) were characterised as single components, after separation using preparative scale chromatography, all giving satisfactory elemental analysis and parent peaks in the mass spectra.

The structure of (200) was confirmed from the n.m.r. spectrum, which showed the presence of $\overset{CF_3}{\,}\!\!>\!C{=}$ (x2); $CF_3{-}C\!\leqslant$ (x2); $-CF_2-$(x1); and a tertiary fluorine. A compound containing these groups could have two structures, either (200) or (201), however, the chemical shift of the tertiary fluorine (181 p.p.m.) indicated that the structure was (200), as the tertiary fluorine for (201) would be expected to absorb approximately 20 ppm downfield from 181, due to the presence of an α-oxygen.

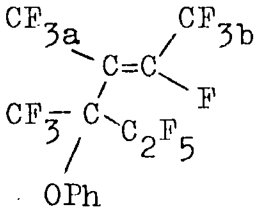
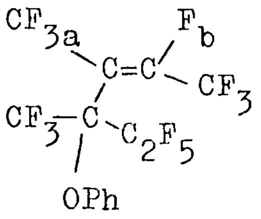
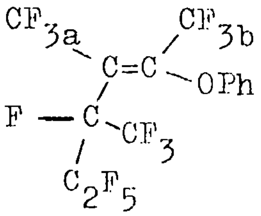


(201)

The structures of (198) and (199) were also confirmed from their n.m.r. spectra, which showed the presence of 4 CF_3 groups, a single $-CF_2-$ group and a vinylic fluorine. The configuration of all three compounds were determined from the coupling constants of the groups adjacent to the double bond (Table 37).

Table 37

Coupling Constants Between Vinylic Groups in (198)-(200)

Compounds	Coupling Constants, Hz Jab
 (198)	11
 (199)	26
 (200)	15

VII.B.3.d Equilibration of Phenyl Ethers (198)-(200)

(i) A reaction using triethylamine was carried out, and a sample withdrawn from the flask to determine the initial composition of the products (Table 38). The reaction mixture was then divided between two separate flasks, and one enriched with (200) (Sample 1), the other with (199) (Sample 2). After stirring the two samples for 60 h at room temperature the product distributions were again measured (Table 38), and the results showed that although the composition of the products had not returned to the same as the initial mixture, a certain amount of equilibration had occured.

Table 38

Distribution of Products in Equilibration Experiment

Sample	*Percentage Composition of Products		
	(198)	(199)	(200)
Initial Reaction Product	48	30	22
Sample 1 (initial)	40	17	42
Sample 2 (initial)	35	50	15
Sample 1 (final)	46	27	27
Sample 2 (final)	39	32	29

*Determined using Gas Density Balance

(ii) A sample of phenyl ethers enriched in component (200) was divided into two; one half was stirred with triethylamine in tetraglyme for 36 h at room temperature, the other with caesium fluoride in tetraglyme. The product distributions were then measured and the results (Table 39) showed that some rearrangement had occured with triethylamine but more in the case of caesium fluoride.

Table 39

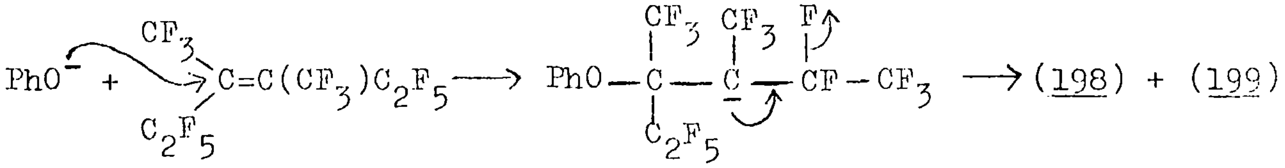
Distribution of Products in Equilibration Experiment Using CsF or $(C_2H_5)_3N$

Sample	*Percentage Composition of Products		
	198	199	200
Initial Composition	29	13	58
After stirring with CsF	37.5	25	37.5
After stirring with Et_3N	32	19	49

*Determined using Gas Density Balance

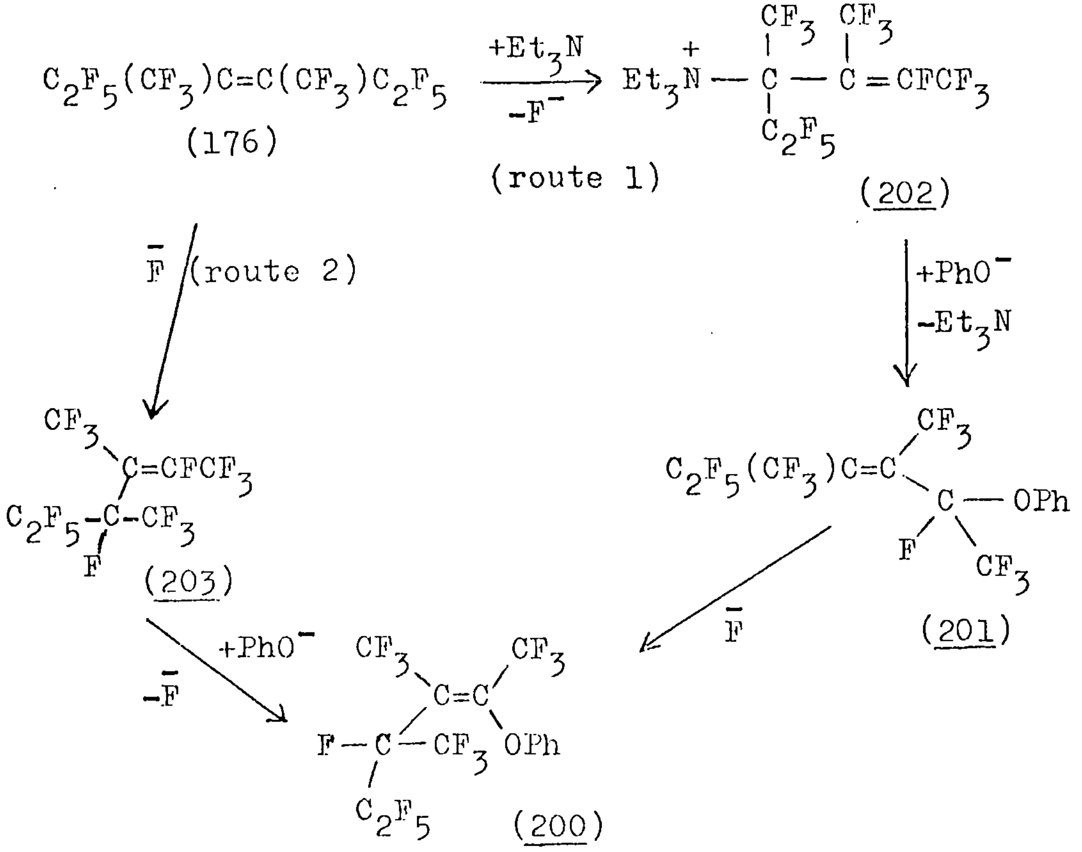
VII.B.3.e Discussion of Mechanism

The reaction of phenol with (176) gave differing isomer distributions, depending on the base employed, for example, when sodium carbonate was used the monosubstituted products were almost entirely derived from attack of phenoxide at the double bond followed by allylic displacement of fluoride ion, to give (198) and (199).



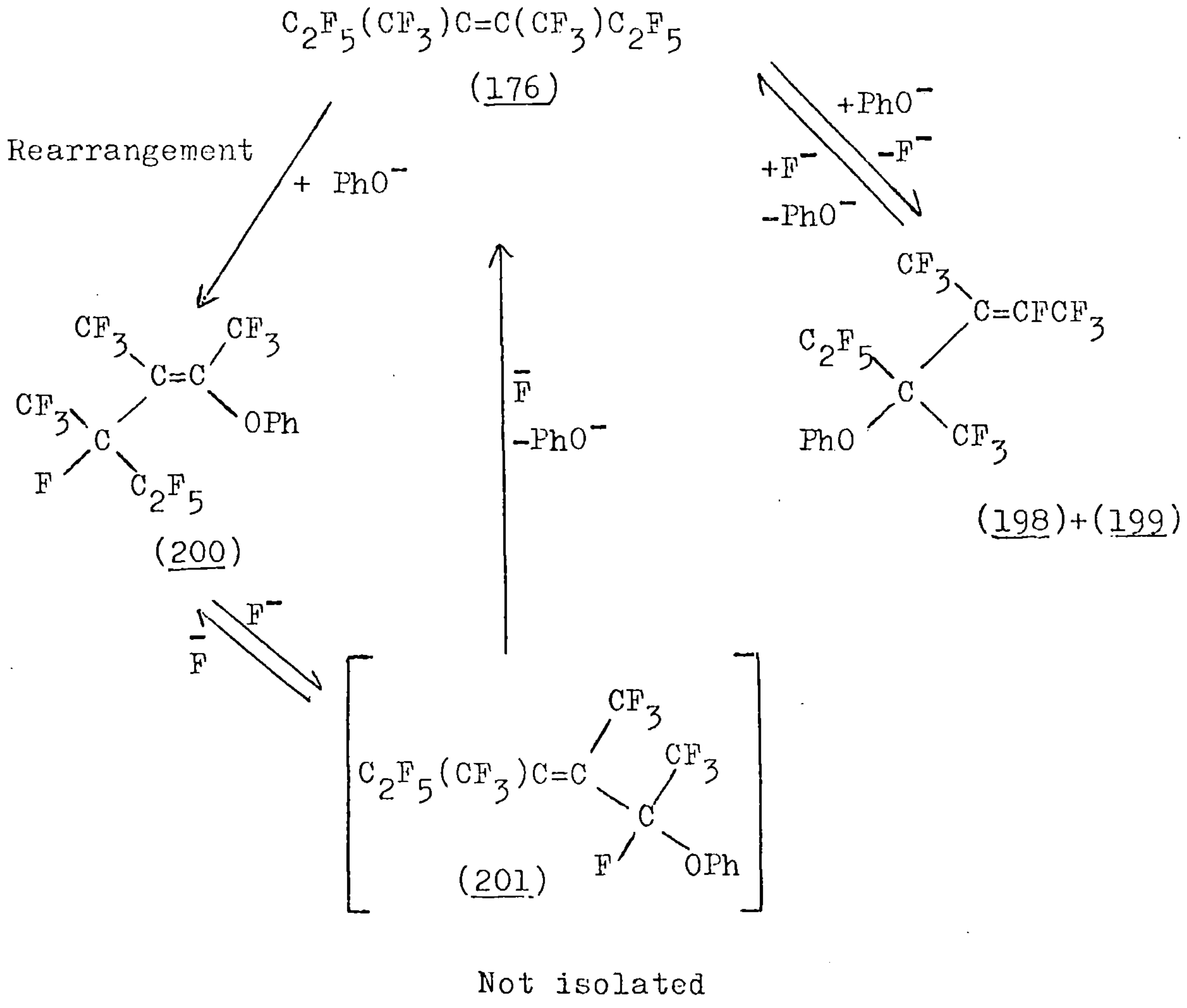
However, when triethylamine was used the amount of product obtained by rearrangement prior to substitution, (200), was greatly increased, and two possible mechanisms which could account for the observed product (200) are shown in Scheme 24. Firstly, elimination of fluoride ion from (176) by triethylamine leads to (202), which after addition of phenoxide followed by elimination of amine gives the internal olefin (201); a fluoride ion-initiated rearrangement then yields the product (200) (route 1).

An alternative mechanism involves a fluoride ion-initiated rearrangement of (176) to (203), which then reacts with phenoxide to give (200) (route 2).



Scheme 24

The equilibration experiments showed that the three isomers, (198)-(200) were interconvertible, and some possible mechanisms leading to rearrangement are shown in Scheme 25. The results showed that more rearrangement occured in the presence of caesium fluoride, than with triethylamine, suggesting that these are mainly initiated by fluoride ion, as indicated in Scheme 25.



Scheme 25

As can be seen elimination of phenoxide from (198) and (199) could lead to formation of the initial olefin (176), which can then either react with phenoxide, to give (198) or (199), or rearrange, then react with phenoxide to give (200). A fluoride ion-initiated rearrangement of (200) to (204), followed by elimination of phenoxide and further rearrangement yields the starting olefin (176), which can then react as described previously to give (198)-(200).

The results of the reactions with phenol suggest that the main difference between using sodium carbonate and triethylamine could be the solubility of the resulting fluoride ion. In the case of sodium carbonate relatively insoluble sodium fluoride would be formed, but with triethylamine a soluble amine hydrogen fluoride, $Et_3\overset{+}{N}H\overset{-}{F}$, would provide an active form of fluoride ion, and hence more rearranged products.

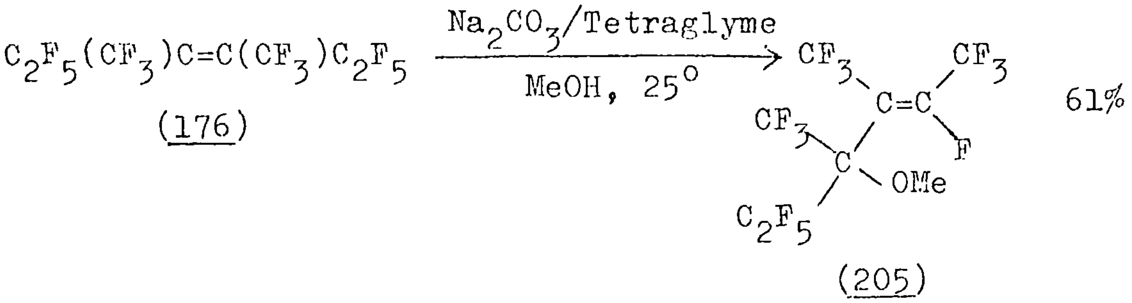
VII.B.4 Reaction with Methanol

In general reaction of fluoro olefins with methanol give either addition or substitution products (III.A.3.1), for example, hexafluoropropene with methoxide gives a mixture of addition and substitution.[1]

$$CH_3OH + CF_2{=}CFCF_3 \xrightarrow[\text{Autoclave}]{\text{KOH}/60^{\circ}} \underset{83\%}{CH_3OCF_2CHFCF_3} + CH_3OCF{=}CFCF_3$$

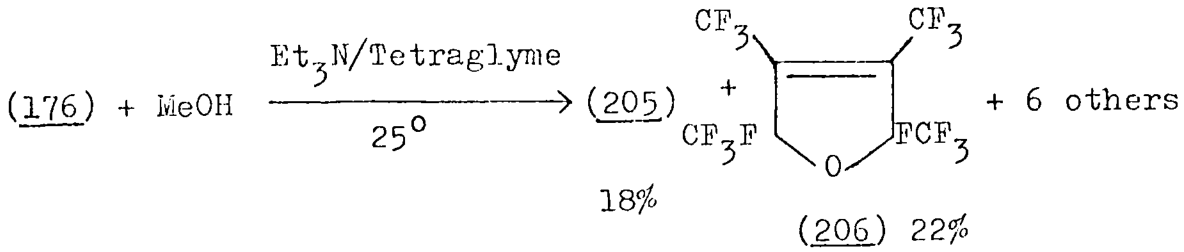
VII.B.4.a Using Sodium Carbonate as base

Addition of methanol to a vigorously stirred mixture of (176) and sodium carbonate in tetraglyme gave, after filtration and pouring into water, a lower organic layer, which chromatographic analysis indicated consisted of unreacted (176) plus one major product, identified as 4-methoxy-3,4-trifluoromethyl-nonafluorohex-2-ene (205), and two minor unidentified products.



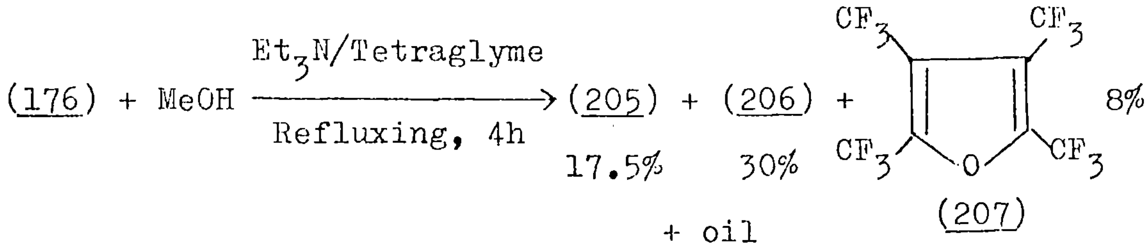
VII.B.4.b Using Triethylamine

Addition of methanol to a vigorously stirred mixture of (176) and triethylamine in tetraglyme gave, after pouring into water, a lower organic layer which chromatographic analysis showed to consist of unreacted (176) and at least eight products, two of which have been identified as (205) plus *cis* and *trans* perfluoro-2,5-dihydro-tetramethylfuran (206).



VII.B.4.c Rapid addition of Methanol to a Refluxing Mixture of Triethylamine and Perfluoro-3,4-dimethylhex-3-ene in Tetraglyme

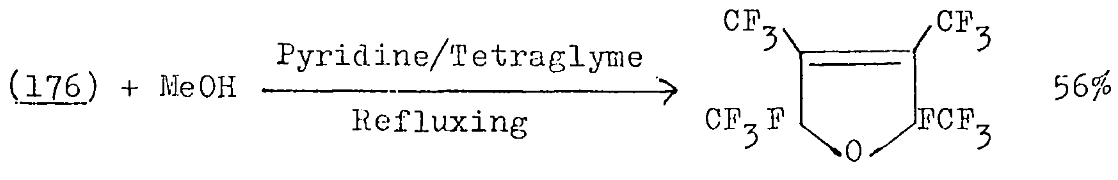
Methanol was added to a refluxing mixture of (176) plus triethylamine in tetraglyme, which was then refluxed for a further 4 hours. After pouring the reaction mixture into water a dark brown organic layer separated, composed of an involatile oil plus a volatile colourless liquid which chromatographic analysis showed consisted of three products identified as (205), (206) and perfluoro-tetramethylfuran (207).



(207)

VII.B.4.d Addition of Methanol to a Refluxing Mixture of Perfluoro-3,4-dimethylhex-3-ene plus Pyridine in Tetraglyme

This was a repeat of the previous experiment (VII.B.4.c) except that triethylamine was replaced by pyridine. After pouring the reaction mixture into water an almost colourless lower layer separated which proved to consist of unreacted (176) plus (206).



(206)

VII.B.4.e Refluxing a mixture consisting mainly of Perfluoro-2,5-dihydrotetramethylfuran with Triethylamine in Tetraglyme

A mixture containing mainly (206) was refluxed with triethylamine in tetraglyme for 16 hours and gave, after pouring into water, a lower organic layer consisting of a black involatile oil plus a volatile colourless liquid which chromatographic analysis indicated to be almost entirely (207).

$$\underset{32\%}{\underline{(205)}} + \underset{55\%}{\underline{(206)}} + \underset{13\%}{\underline{(207)}} \xrightarrow[\text{Reflux, 16h}]{\text{Et}_3\text{N/Tetraglyme}} \underset{56\%}{\underline{(207)}} + \underline{(205)} + \text{oil}$$

VII.B.4.f Refluxing a mixture consisting mainly of Perfluoro-2,5-dihydrotetramethylfuran with Pyridine in Tetraglyme

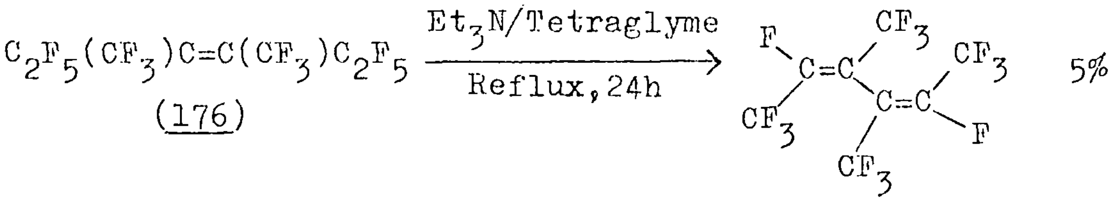
This was a repeat of the previous experiment (VII.B.4.e) except that the base was changed from triethylamine to pyridine, but gave only unreacted starting material.

VII.B.4.g Refluxing Methanol with Perfluoro-3,4-dimethylhex-3-ene in Tetraglyme

Refluxing a mixture of methanol and (176) in tetraglyme gave only unreacted starting material, confirming that a base is required for reaction to occur.

VII.B.4.h Refluxing a mixture of Perfluoro-3,4-dimethylhex-3-ene and Triethylamine in Tetraglyme

Refluxing a mixture of (176) and triethylamine in tetraglyme gave mainly unreacted starting material but also a very small amount of defluorinated material (179).

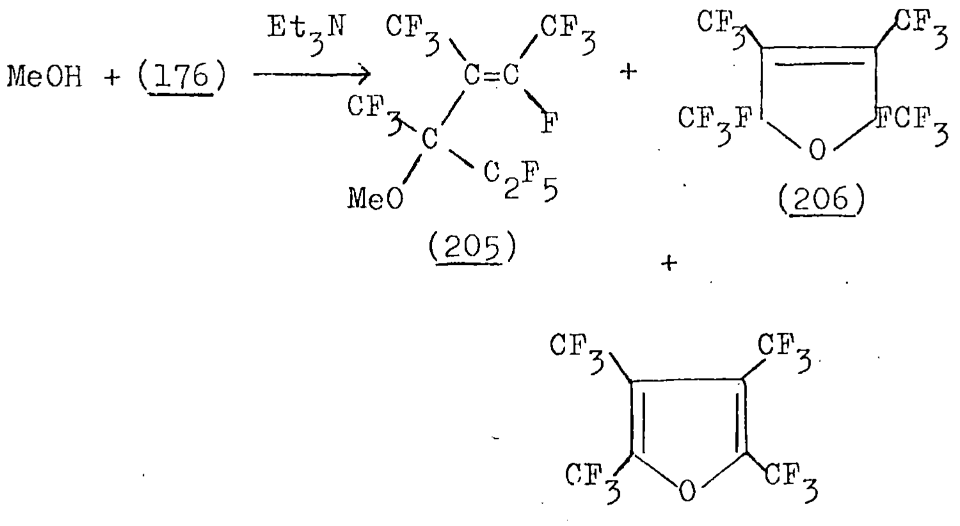


(176) (179)

VII.B.4.i Refluxing Perfluoro-3,4-dimethylhex-3-ene, water and Triethylamine in Tetraglyme

Addition of water to a refluxing mixture of (176) and triethylamine in tetraglyme, gave an involatile oil plus a volatile colourless liquid, which n.m.r. showed consisted of unreacted (176) and unidentified products.

VII.B.4.j Determination of Structures



(205) (206) (207)

The furan (207) was characterised, after separating using both distillation plus preparative scale chromatography, giving a parent peak in the mass spectrum, and satisfactory fluorine analysis. The infra-red plus ^{1}H n.m.r. spectra indicated that no hydrogen was present, and the ^{19}F n.m.r. spectrum showed only two peaks at 60.4 and 65.8 p.p.m.

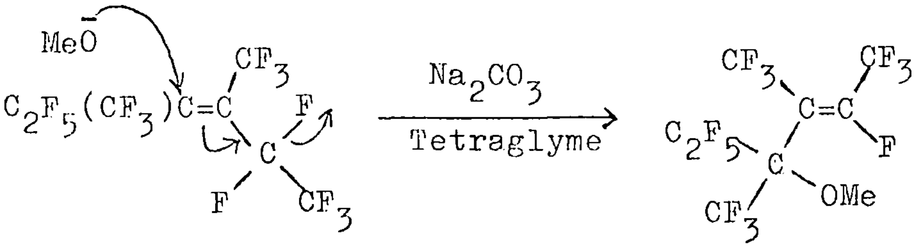
The partially saturated furan (<u>206</u>) was also separated using distillation plus preparative scale chromatography, and a mass spectrum gave a P-19 peak, common in fluorocarbons with a large degree of saturation. The infra-red plus ^{1}H n.m.r. spectra again indicated that no hydrogen was present, and the ^{19}F spectrum clearly showed two geometric isomers present in a ratio of 1:2, although which isomer predominated is not known. The tertiary fluorines were downfield at 122.6 and 112.2 p.p.m. a result expected for a structure with an α-oxygen.

The acyclic ether (<u>205</u>) was characterised after separation using preparative scale chromatography, giving satisfactory fluorine analysis and a P-19 peak in the mass spectrum. The n.m.r. spectrum showed that the peaks for the $\overset{CF_3}{\diagup}\!\!C=$ groups were split into quartets, with a coupling constant of 13 Hz, a coupling consistent with a <u>cis</u> conformation.

VII.B.4.k <u>Discussion of Mechanism</u>

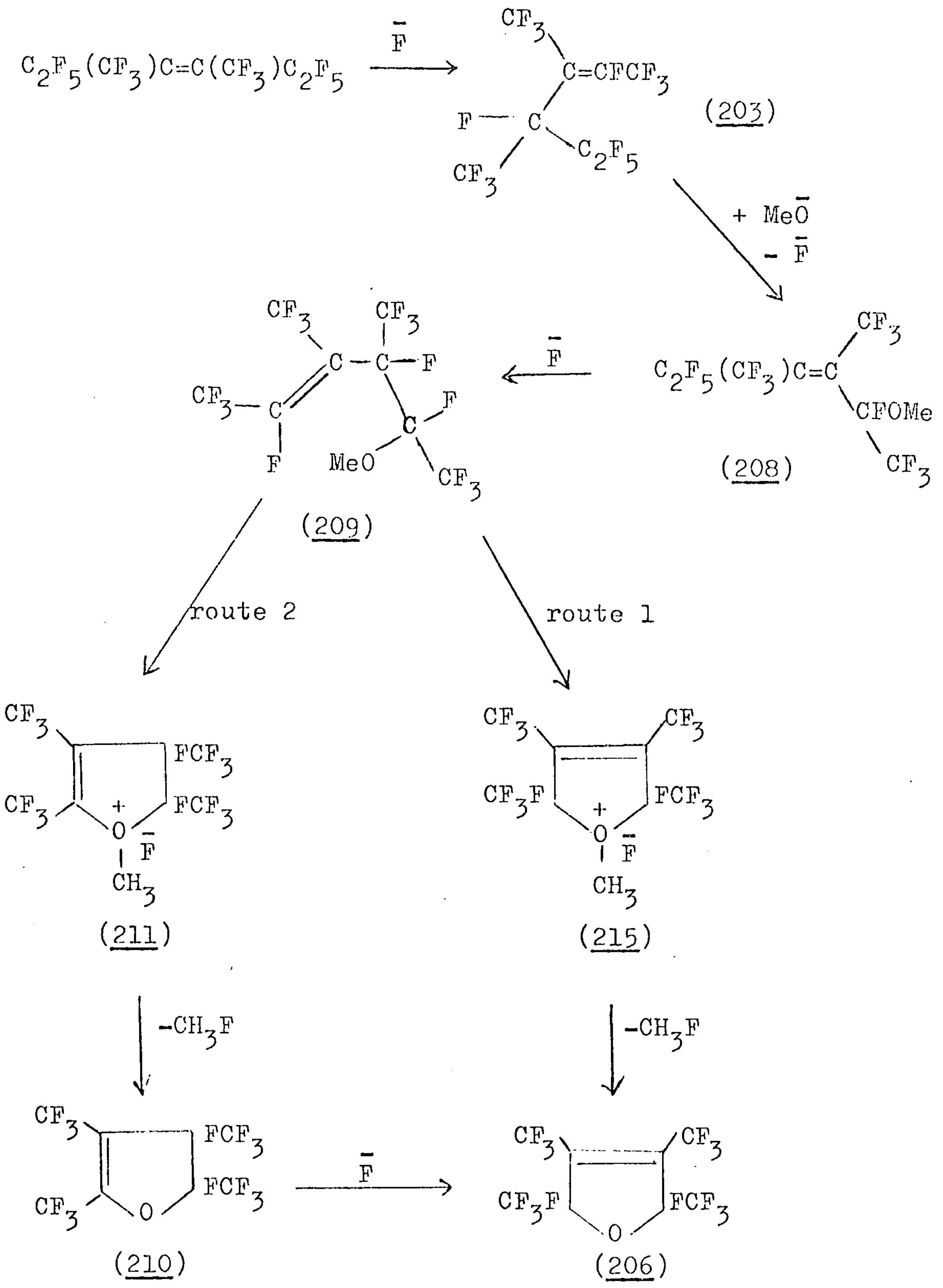
Perfluoro-isobutene and methanol react in the absence of a base[1] but experiment showed that reaction between (<u>176</u>) and methanol occured only in the presence of a base, suggesting that (<u>176</u>) is not as susceptible to nucleophilic attack as perfluoro-isobutene. Haszeldine and co-workers[153] found perfluoro-2,3-dimethylbut-2-ene also reacted with methanol only in the presence of a base, and they suggested that although the intermediate carbanion was stabilised by trifluoromethyl groups, steric hindrance made approach of a nucleophile less favourable. In a similar manner steric crowding could reduce the susceptibility of (<u>176</u>) to nucleophilic attack.

In a similar fashion to phenol, the products obtained from the reaction of methanol with (<u>176</u>) are dependent on the base employed, for example, with sodium carbonate a single major product was obtained derived from substitution followed by allylic displacement of fluoride ion. Unlike phenol, where both <u>cis</u> and <u>trans</u> isomers were formed methanol gave predominantly the <u>cis</u> isomer (<u>205</u>), but the reason for this selectivity is not known at present.



(<u>176</u>) (<u>205</u>)

Formation of a cyclic ether, (<u>206</u>), when using amines suggests that rearrangement occured prior to substitution, and a possible reaction sequence is shown in Scheme 26.


$C_2F_5(CF_3)C{=}C(CF_3)C_2F_5$
$\bar{F}$
(203)
+ $Me\bar{O}$
− $\bar{F}$
(208)
$\bar{F}$
(209)
route 2
route 1
(211)
(215)
$-CH_3F$
$-CH_3F$
(210)
$\bar{F}$
(206)

Scheme 26

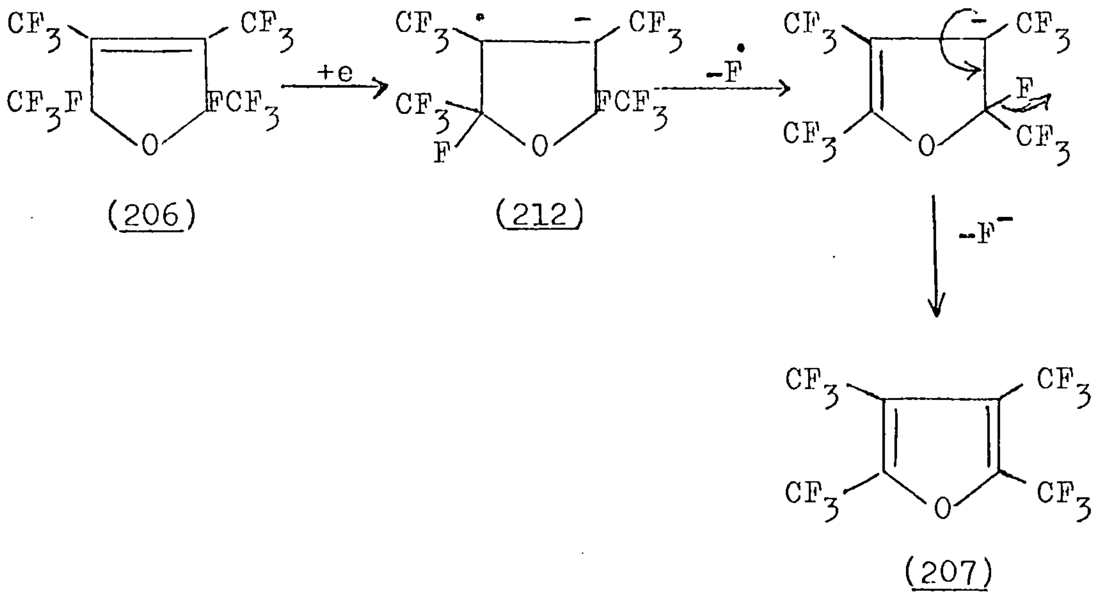
As can be seen from Scheme 26 the mechanism proposed involves several double bond migrations, and all are shown to be fluoride ion-initiated, although in reality these could equally involve some amine-initiated rearrangements.

An initial double bond migration could lead to the olefin (203), which reacts with methanol to give an unsaturated ether (208); a fluoride ion-initiated rearrangement of (208) then yields (209). Intramolecular nucleophilic substitution, involving (209), can now occur to give two different oxonium salts, (211) and (215). Substitution involving an allylic displacement of fluoride ion would give (215) (route 1), which after cleavage yields (206). An alternative reaction (route 2) involves vinylic substitution, leading to the oxonium salt (211) which, after cleavage in the presence of fluoride ion, yields (210); rearrangement of (210) in the presence of fluoride ion then gives (206).

Although the intermediate (210) was not isolated, evidence was obtained which suggests that it was one of the unidentified reaction products. A sample enriched by distillation, in (205) and an unidentified component, was heated with caesium fluoride in tetraglyme, and gave a product consisting of unchanged (205) and (206). This suggested that the unidentified component was (210) which had rearranged in the presence of fluoride ion to the more stable isomer (206).

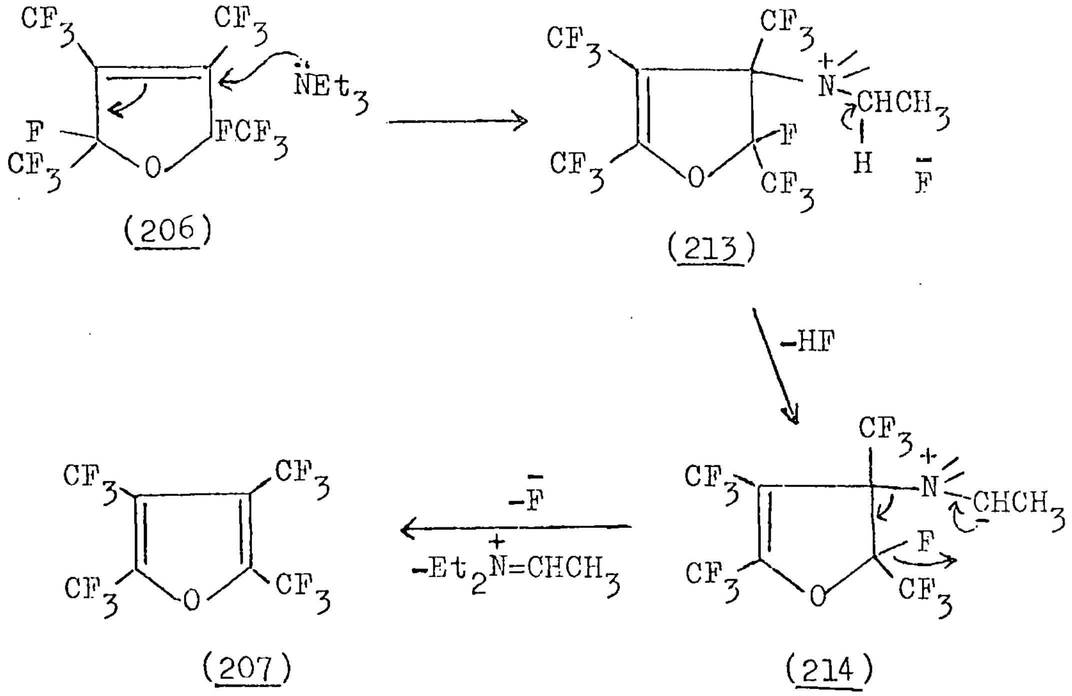
(i) Defluorination

Formation of a symmetrical furan (207), after refluxing a mixture consisting mainly of the partially saturated furan (206), with triethylamine, indicated that defluorination had occured. There are two possible mechanisms by which defluorination could occur, the first involves an electron transfer from an amine to (206), producing a radical anion (212), which, after loss of fluoride ion and a fluorine atom, gives (207) (Scheme 27). However, defluorination, by an electron transfer process, could be expected using either triethylamine or pyridine, but experiments showed that no reaction occured when pyridine was used, suggesting that a different mechanism was operating.



Scheme 27

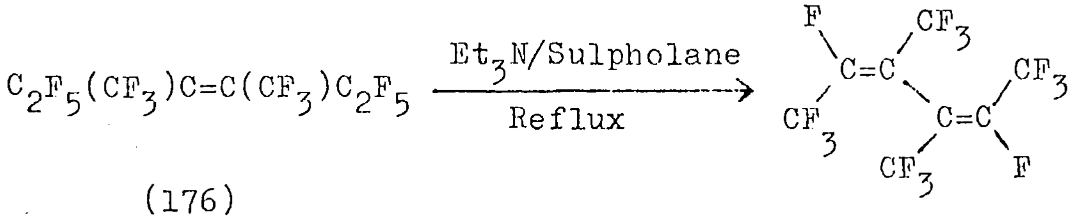
A more likely mechanism involves an initial double bond migration to give (213), which in the presence of fluoride ion loses a proton to form an ylid type intermediate (214). Loss of the amino group, as an iminium ion, followed by elimination of fluoride ion then gives the defluorinated product (207) (Scheme 28).



Scheme 28

Support for this mechanism was provided by no defluorination occuring with pyridine, which has no labile α-hydrogen, a requirement if defluorination is to occur via the route shown in Scheme 28.

Another noticeable effect when using pyridine, in place of triethylamine, was formation of a single product (206) instead of a complex mixture, indicating that more side reactions probably occured with triethylamine. This is possibly due to defluorination occuring at other stages of the reaction, for example, a small amount of defluorinated material (179) was observed after refluxing (176) with triethylamine in sulpholane.



(176)

(179)

More work needs to be done to try and identify some of the other products formed, which might possibly provide further evidence to help confirm the various mechanisms proposed or indeed suggest new mechanisms.

EXPERIMENTAL

Chemicals

Chlorotrifluoroethylene was prepared by dechlorination of Arcton 113, $CF_2ClCFCl_2$, with zinc dust suspended in ethanol. Perfluoro-3,4-dimethylhex-3-ene was provided by I.C.I. (Mond) Ltd.

Pentafluoropyridine, tetrafluoropyrimidine, tetrafluoropyridazine, and pentafluoronitrobenzene were prepared as described in the literature.[159,160,161,163] Octafluorotoluene, pentafluorobenzonitrile and perfluorobiphenyl were commercially available samples purchased from Imperial Smelting Corporation.

The caesium fluoride was reagent grade, and was dried by heating (160°) under high vacuum for 24h, ground to a fine powder in a glove bag, then heated under vacuum for a further 24h.

Solvents

Sulpholane was purified by fractional vacuum distillation, and the middle fraction collected over dried molecular sieve (Type IVA), then stored at room temperature under dry nitrogen. Tetraglyme was purified by fractional vacuum distillation over sodium, and the middle fraction collected over dry molecular sieve (Type IVA), then stored under dry nitrogen.

Dimethylformamide (D.M.F.) was purified by stirring with barium hydroxide for 24h, followed by fractional vacuum distillation, when the middle fraction was collected over dried molecular sieve (Type IVA) then stored under dry nitrogen, in a dark cupboard.

Instrumentation

Infra-red spectra were recorded on a Grubb-Parsons "Spectromaster" spectrometer and a Perkin-Elmer 457 spectrophotometer. Volatile liquid or gaseous samples were vapourised into an evacuated cylindrical cell with potassium bromide end windows: liquid and low melting point solid samples were recorded as thin contact films between potassium bromide plates: solid samples were pressed into homogeneous thin discs with potassium bromide.

Mass spectra were recorded on an A.E.1. M.S9 spectrometer, or on a V.G. Micromass 12B, fitted with a Pye 104 gas chromatograph, and all molecular weights were determined using these instruments.

Proton (^{1}H) and fluorine (^{19}F) nuclear magnetic resonance spectra were recorded on a Varian A56/60D spectrometer operating at 60 and 56 MHz respectively, and chemical shifts are quoted relative to external T.M.S. and $CFCl_3$. Variable temperature facilities permitted spectra to be recorded at temperatures different from the standard probe temperature of 40^{o}. Fluorine-fluorine decoupling spectra were recorded on a Brücker HX90E spectrometer operating at 84.67 MHz.

E.S.C.A. spectra were recorded on an A.E.1. Model 200A spectrometer.

Quantitative vapour phase chromatographic analysis was carried out on a Griffin and George D6 Gas Density Balance, using columns packed with 30% silicone gum rubber SE-30 on Chromosorb P (Column 'O'), 20% Di-isodecyl phthalate on chromosorb P (Column 'A'), or 30% Trixylenyl phosphate on chromosorb P (Column 'TXP'). Preparative scale vapour phase chromatography was performed on a Varian Aerograph instrument using column 'O' or 'A'.

Carbon, nitrogen and hydrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analysis for halogens were carried out as described in the literature.[162]

Boiling points were determined by Siwoloboff's Method, unless otherwise stated, and are not corrected for changes in atmospheric pressure.

CHAPTER VIII

Experimental to Chapter V

VIII.A Reaction of Chlorotrifluoroethylene with various activated aromatic species

A static atmospheric pressure system, developed by previous workers in these laboratories and described earlier (Chapter V.A.1), was used for many of the reactions described, but in some cases the variable volume reservoir (football-bladder) was replaced by a glass storage sphere (21). This modification was employed after it was discovered that chlorotrifluoroethylene was either reacting with, or diffusing through the walls of the rubber bladder.

The required quantities of dry caesium fluoride and dry aprotic solvent were rapidly introduced into the baked, purged reaction apparatus, against a flow of dry nitrogen. After evacuation of the apparatus and degassing of the solvent, chlorotrifluoroethylene was introduced into the system to equilibrate it to atmospheric pressure. The activated aromatic species was then introduced into the apparatus by a syringe, through a self-sealing rubber cap.

Collapse of the variable volume reservoir, or reduction in pressure in the case of the glass storage sphere, indicated that reaction was occuring.

On completion of the reaction, the volatile products were vacuum transferred to a cold trap (liquid air), at temperatures up to 100^{o}C, and chromatographic analysis (Gas Density Balance, G.D.B.) of the products allowed estimation of their yields.

1. Preparation of 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl) tetrafluoroethane (100)

Preparation of 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl) tetrafluoroethane (100) was carried out on many occasions and a typical experiment is described below.

A mixture of caesium fluoride (10 g, 66.0 m.moles), tetraglyme (120 cm^3), pentafluoropyridine (16 g, 94.7 m.moles), and chlorotrifluoroethylene (23.5 g, 202.5 m.moles) was vigorously stirred at room temperature for 24h, during which time a partial vacuum had formed in the apparatus. Chromatographic analysis (G.D.B. column 'O', 78°) of the volatile material (19 g) indicated that it consisted of unreacted pentafluoropyridine and one product, identified as 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl)-tetrafluoroethane (100)[113] (83% yield, 45% conversion, based on pentafluoropyridine consumed), by comparison of its infra-red and ^{19}F n.m.r. spectra with those of an authentic sample.[113]

The product was purified by distillation, using a spinning band distillation apparatus.

2. Reaction of Tetrafluoropyrimidine with Chlorotrifluoroethylene in Sulpholane

A mixture of caesium fluoride (6.0 g, 40.0 m.moles), sulpholane (60 cm^3), tetrafluoropyrimidine (5.6 g, 36.7 m.moles), and chlorotrifluoroethylene (10.5 g, 90.5 m.moles) was vigorously stirred at room temperature for 5h, during which time the variable volume reservoir completely collapsed. Chromatographic analysis (G.D.B. column 'TXP', 125°) of the volatile material (5.1 g) indicated that it consisted of unreacted tetrafluoropyrimidine and two products identified as: 4-chlorotetrafluoroethyl-2,5,6-trifluoropyrimidine (106), b.p. 142° (Found: C, 26.7; F, 49.8; Cl, 13.4; N, 10.2; $M^{+\cdot}$ 268. $C_6F_7ClN_2$ requires C, 26.8; F, 49.5; Cl, 13.2; N, 10.4; M 268), infra-red spectrum No. 1, ^{19}F n.m.r. spectrum No. 1; and 4,6-Bis-chlorotetrafluoroethyl-2,5-difluoropyrimidine (107), b.p. 176° (Found: C, 24.9; F, 49.0; Cl, 18.6; N, 7.3; $M^{+\cdot}$ 385. $C_8F_{10}Cl_2N_2$ requires C, 24.9; F, 49.4; Cl, 18.4; N, 7.3; M 385), infra-red spectrum No. 2, ^{19}F n.m.r. spectrum No. 2.

Both (106) and (107) were purified using preparative scale chromatography (Aerograph, column 'A', 125°).

3. Reaction of Tetrafluoropyrimidine with Chlorotrifluoroethylene in Tetraglyme

A mixture of caesium fluoride (3.0 g, 20.0 m.moles), tetraglyme (25 cm^3), tetrafluoropyrimidine (3 g, 19.7 m.moles), and chlorotrifluoroethylene (7.5 g, 64.5 m.moles) was vigorously stirred at room temperature for 3h, during which time the variable volume reservoir completely collapsed. Chromatographic analysis (G.D.B. column 'TXP', 125°) of the volatile material (1.7 g) indicated that it consisted of unreacted tetrafluoropyrimidine, 4-chlorotetrafluoroethyl-2,5,6-trifluoropyrimidine (106), 4,6-Bis-chlorotetrafluoroethyl-2,5-difluoropyrimidine (107) and two other unidentified products. Products (106) and (107) were formed in Ca. 9% and 3% yields, 80% conversion based on tetrafluoropyrimidine used.

Addition of water to the involatile residues yielded an intractable tar (4 g).

4. Reaction of Cyanuric Fluoride with Chlorotrifluoroethylene at 60°

A mixture of caesium fluoride (2.0 g, 13.2 m.moles), sulpholane (20 cm^3), cyanuric fluoride (8.6 g, 63.6 m.moles), and chlorotrifluoroethylene (17 g, 146.5 m.moles) was vigorously stirred at 60° for 48h, during which time a partial vacuum formed in the apparatus. Chromatographic analysis (G.D.B. column '0', 78°) of the volatile material indicated that it consisted of unreacted cyanuric fluoride and two products identified as: 2-Chlorotetrafluoroethyl-4,6-difluoro-S-triazine (102), (61.5% yield, 51% conversion based on cyanuric fluoride consumed), b.p. 120°, (Found: C, 23.6; F, 45.3; Cl, 14.3; N, 17.1; M^+, 251. $C_5F_6ClN_3$ requires C, 23.9; F, 45.3; Cl, 14.1; N, 16.7; M , 268), infra-red spectrum No. 3, ^{19}F n.m.r. spectrum No.3; and 2,4-Bis-chlorotetrafluoroethyl-6-fluoro-S-triazine (103), (10.8% yield, 51% conversion based on cyanuric fluoride consumed) b.p. 163°, (Found: C, 22.7; F, 46.2; Cl, 19.1; N, 11.8; M^+, 367. $C_7F_9Cl_2N_3$ requires C, 22.8; F, 46.5; Cl, 19.3; N, 11.4; M , 367), infra-red spectrum No 4, ^{19}F n.m.r. spectrum No. 4.

Product (102) was purified by distillation, using a Fischer Spaltrohr one-piece distillation apparatus, and (103) by preparative scale chromatography (Aerograph, column '0', 145°).

5. Reaction of Cyanuric Fluoride with Chlorotrifluoroethylene at Room Temperature

A mixture of caesium fluoride (6.0 g, 40.0 m.moles), sulpholane (60 cm^3), cyanuric fluoride (5.8 g, 43.0 m.moles), and chlorotrifluoroethylene (10.5 g, 90.5 m.moles) was vigorously stirred at room temperature for 22h, during which time the variable volume reservoir collapsed completely. Chromatographic analysis (G.D.B. column '0', 78^o) of the volatile material (4.0 g) indicated that it consisted of two components, unreacted cyanuric fluoride and 2-chlorotetrafluoroethyl-4,6-difluoro-S-triazine (<u>102</u>) (30.4% yield, 69% conversion).

6. <u>Reaction of Cyanuric Fluoride with Chlorotrifluoroethylene at 80^o</u>

A mixture of caesium fluoride (3.0 g, 20 m.moles), sulpholane/tetraglyme (17/4 cm^3), cyanuric fluoride (14 g, 103.7 m.moles), and chlorotrifluoroethylene (18 g, 156.2 m.moles) was vigorously stirred at 80^o for 69h, during which time a partial vacuum formed in the apparatus. Chromatographic analysis (G.D.B. column '0', 78^o) of the volatile material (16.1 g) indicated a mixture of three components, unreacted cyanuric fluoride, 2-Chlorotetrafluoroethyl-difluoro-S-triazine (<u>102</u>) (68.5%, 44% conversion) and 2,4-Bis-chlorotetrafluoroethyl-6-fluoro-S-triazine (<u>103</u>) (7.0%).

7. <u>Reaction of Perfluorobiphenyl with Chlorotrifluoroethylene</u>

A mixture of caesium fluoride (3 g, 20.0 m.moles), sulpholane (50 cm^3), perfluorobiphenyl (6 g, 18.0 m.moles), and chlorotrifluoroethylene (17 g, 146.5 m.moles) were vigorously stirred at 60^o for 24h, during which time very little olefin appeared to react. The products were extracted with ether (3 x 40 cm^3), washed with water (3 x 20 cm^3), dried ($MgSO_4$) and the ether removed by vacuum transference. The residues on sublimation yielded unreacted perfluorobiphenyl (2.7 g) and a high molecular weight tar (1.3 g).

8. Reaction of Pentafluoronitrobenzene with Chlorotrifluoroethylene at 120°

A mixture of caesium fluoride (3 g, 20.0 m.moles), sulpholane (20 cm^3), pentafluoronitrobenzene (4 g, 18.8 m.moles), and chlorotrifluoroethylene (16.5 g, 142.2 m.moles) were vigorously stirred at 120° for 24h, during which time a positive pressure built up in the apparatus. Chromatographic analysis (G.D.B. column 'O', 78°) of the volatile material (1.1 g) indicated that two components were present, and a g.l.c./mass spectrum showed that these had parent peaks at 286 and 186, consistent with perfluoroethylbenzene (10%) and hexafluorobenzene (15%) respectively.

The same experiment repeated at 70° gave no reaction, and only pentafluoronitrobenzene was recovered.

9. Reaction of Pentafluorobenzonitrile with Chlorotrifluoroethylene in Sulpholane

A mixture of caesium fluoride (3 g, 20.0 m.moles), sulpholane (20 cm^3), pentafluorobenzonitrile (4.5 g, 23.3 m.moles), and chlorotrifluoroethylene (16.5 g, 142.2 m.moles) was vigorously stirred at room temperature for 48h, during which time a partial vacuum formed in the apparatus. Chromatographic analysis (G.D.B. column 'O', 125°) of the volatile material (2.9 g) indicated that three components were present, unreacted pentafluorobenzonitrile and two products, which a g.l.c./mass spectrum showed had parent peaks at 293 and 309, consistent with perfluoro-4-ethylbenzonitrile (130) (12%), and 4-chlorotetrafluoroethyl-tetrafluorobenzonitrile (129) (14%), respectively.

On addition to water the involatile residues yielded an intractable tar (2.7 g).

Repetition of this experiment, changing the solvent to tetraglyme, gave similar products, but in lower yields, (130) (3%) and (129) (2%).

10. Reaction of Octafluorotoluene with Chlorotrifluoroethylene

A mixture of caesium fluoride (3 g, 20.0 m.moles), sulpholane (20 cm^3), octafluorotoluene (6.4 g, 27.1 m.moles), and chlorotrifluoroethylene (17 g, 146.5 m.moles), were stirred at room temperature for 20h, during which time a partial vacuum formed in the apparatus. Chromatographic analysis (G.D.B. column 'O', 78^0) of the volatile material (5.2 g) indicated that two components were present, unreacted octafluorotoluene and a product which a g.l.c./mass spectrum showed to have a parent peak consistent with perfluoro-4-ethyltoluene (20%).

Addition of water to the involatile residues yielded a pale yellow oil (1.2 g) which a mass spectrum showed to have a molecular weight in excess of 600.

VIII.B Oligomerisation of Chlorotrifluoroethylene

1. Oligomerisation of Chlorotrifluoroethylene at 140^0

A mixture of caesium fluoride (11.2 g , 73.7 m.moles) and tetraglyme (30 cm^3) was rapidly introduced into a baked nickel tube (80 cm^3), against a flow of dry nitrogen. After evacuation, accompanied by degassing of the solvent, the tube was cooled (liquid air) and chlorotrifluoroethylene (17.5 g, 150.8 m.moles) was condensed inside.

Following sealing, under dry nitrogen, the tube was heated in an oil bath, with constant agitation, at 140° for 24h, when it was again cooled (liquid air), opened, and the volatile material (13.5 g) vacuum transferred to a cold trap (liquid air), at Ca 100°.

On warming, to room temperature, the volatile material was found to consist of a gas (8 g) plus a colourless liquid (5.5 g) which chromatographic analysis (G.D.B. column 'O', 78°) showed to be a complex mixture, with two major and many minor components. A g.l.c./mass spectrum (micro-mass 12) indicated that the most abundant component had a similar mass spectrum to perfluoro-3,4-dimethylhex-3-ene (176), and also a mixed injection, with a sample of (176) showed that they had the same retention times. The mass spectra of the other components indicated that these had molecular weights ranging from 462 to over 800, and the approximate percentage yields of the products, calculated from g.l.c. traces (G.D.B. column 'O', 78°) are shown in Table 40.

A mass spectrum of the recovered gas indicated a mixture of unreacted chlorotrifluoroethylene and HF addition product CF_3CFClH.

2. Oligomerisation of Chlorotrifluoroethylene at 56° in Tetraglyme

Caesium fluoride (4 g, 26.6 m.moles), tetraglyme (15 cm^3), and chlorotrifluoroethylene (5 g, 43.1 m.moles) were heated together in a nickel tube (80 cm^3), with constant agitation, at 56° for 20h. (See VIII.B.1). The volatile material recovered consisted of a gas (1.5 g) and a colourless liquid (1.9 g), which chromatographic analysis (G.D.B. column '0', 78°) showed to be a complex mixture. The approximate yields of the products are shown in Table 40.

3. Oligomerisation of Chlorotrifluoroethylene at 68° in Sulpholane

Caesium fluoride (5.3 g, 34.9 m.moles), sulpholane (25 cm^3), and chlorotrifluoroethylene (17 g, 146.5 m.moles) were heated in a nickel tube (80 cm^3), with constant agitation, at 68° for 60h. (See VIII.B.1). The volatile material recovered consisted of a gas (5 g) and a colourless liquid (3.25 g), which chromatographic analysis indicated was a complex mixture. The approximate yields of products are shown in Table 40. The lack of recovered gas suggests that the tube leaked.

Table 40

Percentage Yields of Products on Oligomerisation of CF_2=CFCl

Solvent	Temp. °C	Percentage Yields					
		C_8F_{16}	$C_{10}F_{18}$	$C_{12}F_{20}$	$C_{12}F_{22}$	$C_{14}F_{24}$	$>C_{14}F_{24}$
Tetraglyme	56	10	16	2	4	5	10
Sulpholane	68	6	<1	-	5	6	3
Tetraglyme	140	18	11	2	3	2	3

VIII.C Reaction of Caesium Fluoride with various aromatic species in the absence of a solvent

A series of reactions was carried out in which caesium fluoride and various perfluoroheteroaromatic species were heated together, under autogeneous pressure, in a Carius tube. A standard method was adopted for all these reactions and this is described in VIII.C.1.

1. Reaction of Cyanuric Fluoride with Caesium Fluoride at 180°

Caesium fluoride (16 g, 105.3 m.moles) was rapidly introduced into a dry Carius tube (80 cm^3), which was then evacuated, cooled (liquid air), and cyanuric fluoride (15 g, 111.1 m.moles) condensed inside, under vacuum. The tube was then sealed and heated in an oil bath, with constant agitation, at 180° for 20 h, during which time a clear yellow syrup was produced, which yielded a transparent yellow glass when cooled to room temperature. After opening the tube, under nitrogen, the products proved to consist of unreacted cyanuric fluoride (<0.1 g) and a transparent yellow glass (27 g) (stored under nitrogen to prevent hydrolysis). (Found: C, 12.9; F, 26.5; N, 17.0; $C_3F_4N_3Cs$ requires C, 12.5; F, 26.5; N, 14.6).

An infra-red spectrum of the product, proved to be very broad with no apparent resolution.

A similar experiment using potassium fluoride instead of caesium fluoride gave no reaction.

a) Hydrolysis

Addition of the product (2 g) from experiment VIII.C.1 to water gave a vigorous reaction, producing a white precipitate

(1 g), a small amount of which was recrystallised (H_2O). An infra-red spectrum of the recrystallised material showed broad, unresolved peaks at 3500-2760 cm^{-1}, 1740-1580 cm^{-1}, and 1485-1450 cm^{-1}, which differed from the spectrum of cyanuric acid obtained by hydrolysis of cyanuric chloride.

Attempts to purify by sublimation (300°, 0.05 mmHg) failed, the material being recovered unchanged.

The product was soluble in hot NaOH solution (2 M), and a dilute solution in water had a pH 3.5 (Universal Indicator).

2. Heating Caesium Fluoride with Tetrafluoropyridazine

Caesium fluoride (1.8 g, 11.8 m.moles) and tetrafluoropyridazine (5.5 g, 36.2 m.moles) were heated together, with constant agitation, in a Carius tube (80 cm^3) at 120° for 22h. No reaction occured and tetrafluoropyridazine (5.2 g) was recovered unchanged.

A similar reaction, but at 180°, gave a carbonaceous solid plus unreacted tetrafluoropyridazine.

3. Heating Caesium Fluoride with Tetrafluoropyrimidine at 180°

Caesium fluoride (2.6 g, 17.1 m.moles) and tetrafluoropyrimidine (3.2 g, 21.0 m.moles) were heated together, with constant agitation, in a Carius tube (80 cm^3), at 180° for 20h. No reaction occured and tetrafluoropyrimidine (3.0 g) was recovered unchanged.

4. Heating Caesium Fluoride with Cyanuric Fluoride in a n.m.r. tube

Caesium fluoride (0.5 g, 3.3 m.moles) and cyanuric fluoride (0.6 g, 4.4 m.moles) were sealed, under vacuum, in a pyrex n.m.r. tube, and after heating in an oil bath at 170° for 15 minutes the reactants had formed a yellow syrup. The n.m.r. spectrum, obtained at a probe temperature of 183.5°, of the syrup showed four absorption, at 26.0, 43.0, 47.6 and 49.0 p.p.m., with relative intensities 9:30:46:15 respectively.

VIII.D.1 Heating Caesium fluoride and Cyanuric Fluoride together in Sulpholane

Caesium fluoride (3.6 g, 23.7 m.moles), cyanuric fluoride (4.9 g, 36.3 m.moles), and sulpholane (20 cm^3) were vigorously stirred together at 110°, during which time it was observed that the caesium fluoride appeared to dissolve, but, on cooling to room temperature, finely divided caesium fluoride precipitated. The volatile material (2.3 g) was vacuum transfered to a cold trap (liquid air), at Ca 90°, and chromatographic analysis (G.D.B. column '0', 78°) indicated that this consisted of unreacted cyanuric fluoride.

Addition of dil.HCl (50 cm^3) to the involatile residues yielded a white precipitate (1.5 g), which after recrystallisation (H_2O) was identified as cyanuric acid, by comparison of the infra-red spectrum with that of an authentic sample, produced by hydrolysis of cyanuric chloride with glacial acetic acid.

VIII.D.2 N.m.r. spectrum of Cyanuric Fluoride and Caesium Fluoride in Sulpholane

Cyanuric fluoride (5 g, 37.0 m.moles), caesium fluoride (6.0 g, 39.5 m.moles), and sulpholane (15 cm^3) were stirred together at room temperature, during which time most of the caesium fluoride dissolved. After allowing to settle a sample of yellow supernatent liquor was withdrawn and a n.m.r. spectrum obtained which showed a broad absorption centred at 32.3 p.p.m. On gradual addition of small quantities of cyanuric fluoride the peak slowly sharpened and moved upfield, towards the absorption expected for cyanuric fluoride (34.4 p.p.m.) in sulpholane Fig. 8.

CHAPTER IX

Experimental to Chapter VI

Reactions of Perfluoro-4-vinylpyridine

Elemental Analysis

During characterisation of many of the compounds described in this, and the following chapter it was not possible to obtain satisfactory carbon and nitrogen figures from elemental analysis. However, discrepancies in the analysis of fluorocarbons are not unusual, and in general where these discrepancies occur the results show low carbon and high nitrogen values.

An explanation that could account for these discrepancies has been suggested,[134] but before this can be understood it is first necessary to understand the theory behind the method employed in C, H and N analysis, and consequently a brief description is given below.

A known weight of the compound to be analysed is first heated to 600° in an atmosphere of oxygen, when all C, H and N present are converted to CO_2, H_2O and N_2 respectively. The products of combustion are then passed through a series of filters to remove the oxidation products of other elements, leaving a gaseous mixture of CO_2, H_2O and N_2, the thermal conductivity of which is measured and recorded. After passing the gases through soda-lime, to remove the CO_2, the thermal conductivity of the remaining H_2O and N_2 is measured, thus allowing calculation of the percentage of C present in the compound. A final conductivity measurement, made after removal of the water with magnesium perchlorate, enables the percentage of H and N in the original compound to be determined. The final thermal conductivity should be that of N_2 only.

However, if, as is thought to occur with some fluorocarbons, incomplete combustion occurs, not all the C will be converted to CO_2, and consequently a thermal conductivity measurement, made after removal of the CO_2, gives a low C figure. The incompletely combusted fluorocarbon fragments then pass through the magnesium perchlorate and are included, with the N_2, in the final conductivity measurements, consequently giving a high nitrogen value.

In general, however, the halogen analysis figures, obtained by fusion with potassium, were found to be satisfactory.

IX.A Defluorination

All the defluorination reactions carried out by the author, used a method previously employed in these laboratories. The procedure used involved passing the material to be defluorinated through a silica tube (ca. 50 cm in length), packed with coarse iron-filings and heated by a cylindrical heater. The material was passed through the tube in a steady stream of dry nitrogen and the products collected in a cold trap (Drikold).

1. Defluorination of 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl)tetrafluoroethane (100)

The defluorination of (100) was investigated at two temperatures, 310° and 500°, and in both cases chromatographic analysis (G.D.B. column 'O', 78°) of the recovered material indicated that a single component was present, identified as perfluoro-4-vinylpyridine (138), by comparison of infrared and n.m.r. spectra with those of an authentic sample.[113] The yields obtained are shown in Table 41.

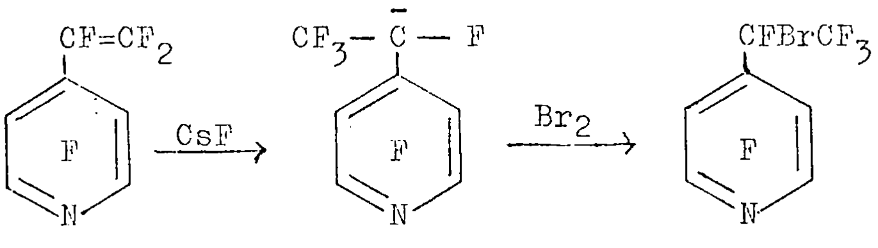
Table 41

Temp. °C	(100)	Weight Recovered	Product Yield (138)	Conversion
310	3.2 g, 11.2 m.moles	2.0 g	68	100
500	27.6 g, 96.7 m.moles	10.2 g	46	100

IX.B Fluoride Ion Reactions

1. Chemical Trapping of Anions

The following two reactions were carried out in an attempt to trap stable fluorinated carbanions with bromine or acid. The substrate (138) was stirred with caesium fluoride, in a solvent, when it was anticipated a stable anion would be formed, which after 'quenching' with bromine or acid would yield the products of FBr or HF addition respectively. For example,



(138)

a) 'Quenching' with Bromine

A mixture of caesium fluoride (1 g, 6.6 m.moles), perfluoro-4-vinylpyridine (138) (0.9 g, 3.9 m.moles), and sulpholane (5 cm^3) was stirred together in a dry flask (50 cm^3), under an atmosphere of dry nitrogen. On first mixing the reactants the reaction mixture turned red. After 1h the reaction was 'quenched' with bromine (2 g, 11.2 m.moles), heated to 40^o, and the excess bromine reacted with sodium bicarbonate solution. The product, a yellow oil, was extracted with ether (3x20 cm^3), washed (H_2O, 3x20 cm^3), dried ($MgSO_4$), and the ether removed by vacuum transference. The recovered product, on sublimation (70^o, 0.005 mm. Hg), yielded a white wolid (0.3 g) identified as Trans-1,3-bis (2',3',5',6'-tetrafluoropyridyl)-hexafluorobut-1-ene (142), (33%) m.p. 60.5^o (Found: C, 36.2; F, 57.9; N, 6.4; M^+ 462. $C_{14}F_{14}N_2$ requires C, 36.4; F, 57.6; N, 6.1; M 462), infrared spectrum No. 5, ^{19}F n.m.r. spectrum No. 5.

A small amount of involatile material (0.2g) was also recovered.

b) 'Quenching' with dil.HCl.

A mixture of caesium fluoride (6 g, 39.5 m.moles), perfluoro-4-vinylpyridine (138) (1.9 g, 8.2 m.moles), and sulpholane (5 cm^3) was stirred in a flask (50 cm^3), under an atmosphere of dry nitrogen. After 'quenching' the reaction with dil.HCl (20 cm^3, 2 M) a red oil separated, which was extracted with ether (3x20 cm^3), washed (H_2O, 3x20 cm^3), dried ($MgSO_4$) and the ether removed. The product, a yellow oil, yielded a white solid on sublimation (70^o, 0.005 mm. Hg), which after recrystallisation (cyclohexane) was identified as Trans-1,3-bis(2',3',5',6'-tetrafluoropyridyl)-pentafluorobut-1-ene (142)(0.5g)

2. Reaction with Tetrafluoropyridazine

A mixture of caesium fluoride (2 g, 13.1 m.moles), sulpholane (8 cm^3), and tetrafluoro-pyridazine (0.5 g, 3.3 m.moles) were stirred together in a flask (50 cm^3), under an atmosphere of dry nitrogen, and perfluoro-4-vinyl-pyridine (138) (1.5 g, 6.5 m.moles) was slowly added, over a 15 minute period, via a syringe through a self-sealing cap. On addition of (138) the reaction turned red, but the colour faded after 5 mins. The product was extracted with ether (3x20 cm^3), but on addition of water a white solid (1.3 g) formed at the interface. After filtration and recrystallisation ($CHCl_3$) this yielded a white crystalline solid (0.6 g), identified as 4,5-Bis-(1'-(2",3",5",6"-tetrafluoropyridyl)-tetrafluoroethyl)-3,6-difluoropyridazine (143) (30%) m.p. 168° (Found: F, 55.7; M^+ 614. $C_{18}F_{18}N_4$ requires F, 55.7; M 614), infra-red spectrum No. 6, ^{19}F n.m.r. spectrum No. 6.

During recrystallisation some involatile and insoluble material was recovered (0.3 g). The ether layer on drying ($MgSO_4$), and removal of the ether yielded Trans-1,3-bis (2',3',5',6'-tetrafluoropyridyl)-pentafluorobut-1-ene (0.2 g).

3. Reaction with Hexafluoropropene

A static atmospheric pressure system, as described in Chapter VIII.A, was used for this reaction.

A mixture of caesium fluoride (3 g, 20.0 m.moles), sulpholane (50 cm^3), and hexafluoropropene (30 g, 200 m.moles) were vigorously stirred together and perfluoro-4-vinylpyridine (1.8 g, 7.8 m.moles) slowly added via a syringe, through a self-sealing cap. Chromatographic analysis (G.D.B. column 'O', 78^o) of the volatile material (25 g) indicated that this was mainly oligomers of hexafluoropropene, and on fractionation this yielded an oil (2.2 g) which chromatographic analysis (G.D.B. column 'O', 78^o) showed to consist of 5 components.

IX.C Other Nucleophilic Reactions

1. Phenoxide, 1:1 Molar Ratio

Perfluoro-4-vinylpyridine (138) (1.5 g, 6.5 m.moles) was added to a solution of sodium phenoxide in dioxan (6.5 cm^3, 1M, 6.5 m.moles) at room temperature. On pouring the reaction mixture into water (50 cm^3) the products separated as a lower organic layer, which after drying ($MgSO_4$) yielded a colourless liquid (1.2 g). Chromatographic analysis (G.D.B. column 'O', 200^o) indicated that the products consisted of two components, in equal amounts, identified as Cis and Trans-1-phenoxy-2-(2',3',5',6'-tetrafluoropyridyl)-difluoroethylene (149) and (150), (60%) and these were characterised as a mixture, b.p. 247^o. (Found: C, 50.9; F, 37.2; N, 4.9; H, 2.0; M^+ 305. $C_{13}H_5F_6NO$ requires C, 51.1; F, 37.4; N, 4.6; H, 1.6; M 305), infra-red spectrum No. 7, ^1H and ^{19}F spectra No. 7 and 8.

2. Methoxide, 1:1 Molar Ratio

A solution of sodium methoxide in methanol (6.5 cm^3, 1M.6.5 m.moles) was added slowly to a stirred mixture of perfluoro-4-vinylpyridine (138) (1.5 g, 6.5 m.moles) in dry methanol (2 cm^3), maintained at 0^oC by immersion in an ice/water bath. After pouring the reaction mixture into water (30 cm^3) the products separated as a lower organic layer, which after drying ($MgSO_4$) yielded a colourless liquid (1.4 g). Chromatographic analysis (G.D.B. column '0', 100^o) of the product indicated that it consisted of a single component identified as 2-oxa-4(2'-methoxy-3',5',6'-trifluoropyridyl)-3,3,4-trifluorobutane (151) (79%), b.p. 219^oC, (Found: C, 39.5; F, 41.0; N, 5.2; H, 2.4; M^+ 275. $C_9F_6NO_2H$, requires C, 39.3; F, 41.5; N, 5.1; H 2.5; M 275), infra-red spectrum No. 8, ^1H and ^{19}F spectra No. 9.

3. Bisulphide, 1:1 Molar Ratio

a) Preparation of Sodium Bisulphide Solution

Hydrogen sulphide was bubbled through a solution of sodium hydroxide in water (50 cm^3, 1M) until a sample just turned phenol phthalien red on mixing. The solution was then ready for using.

b) A solution of sodium bisulphide (4.5 cm^3, 1M 4.5 m.moles) was added to perfluoro-4-vinylpyridine (1 g, 4.3 m.moles) in tetraglyme (40 cm^3) at 0^oC, upon which the solution turned red. On pouring the reaction mixture into water a brown oil separated, which after extraction with ether (3x20 cm^3), washing (H_2O, 3x20 cm^3), drying ($MgSO_4$), and removal of the ether yielded a brown tarry solid (0.7 g). Attempts to purify the product by recrystallisation, and sublimation (0.001 mm. Hg. 120^o) failed.

IX.D Thermal Cycloadditions

The thermal cycloaddition reactions of perfluoro-4-vinylpyridine were carried out using a standard procedure. This involved introducing the required amounts of reactants into a small Carius tube (15 cm^3) which was then cooled (liquid air), evacuated and sealed. After heating in a stainless steel vessel, fitted with a jacket heater, for the required time, the Carius tube was recovered, cooled (liquid air), opened and the products extracted.

1. Dimerisation

Perfluoro-4-vinylpyridine (2.7 g, 11.7 m.moles) was heated in a small Carius tube, at 280° for 16h. The recovered material (2.3 g), after sublimation (100°, 0.005 mm Hg), yielded a white solid (2.0 g) identified as 1,2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane (158) (75%) m.p. 124°, (Found: C, 36.4; F, 57.4; N, 5.7; M^+ 462. $C_{14}F_{14}N_2$ requires C, 36.4; F, 57.6; N, 6.1; M 462), infra-red spectrum No. 9, ^{19}F n.m.r. spectrum No. 10.

a) Defluorination of Dimer (158)

Dimer (158) (2 g) was passed through a silica tube, at 350°, packed with coarse iron-filings (See IX.A). The nitrogen carrier gas was preheated by passing through a copper coil, immersed in hot oil. The flask containing (158) was also heated to 170° in an oil bath.

The products recovered consisted of a colourless liquid (0.2 g), which chromatographic analysis (G.D.B. column 'O', 78°) showed consisted of a single component identified as perfluoro-4-vinylpyridine, by comparison of the infra-red spectrum with that of an authentic sample, and a white solid (0.9 g).

A g.l.c. mass spectrum of the solid in ether, showed two components present with parent peaks at 434 and 462, corresponding to (158)-F_2, and (158) respectively. The n.m.r. spectrum of a solution in acetone indicated that the products consisted of unreacted (158) (55%) and 1,2-di (2',3',5',6'-tetrafluoropyridyl)tetrafluorocyclobut-1-ene (159) (45%). The n.m.r. spectrum of (159) showed the presence of ring fluorines at 91.1 and 138.6 p.p.m. and a single $-CF_2-$ absorption at 113.0 p.p.m.

Attempts to obtain a pure sample of (159) by preparative scale chromatography (Aerograph, column '0', 250°) led to loss of most of the material.

2. a) Chlorotrifluoroethylene at 300°

Perfluoro-4-vinylpyridine (138) (1 g, 4.3 m.moles) and chlorotrifluoroethylene (1 g, 8.6 m.moles) were heated in a small Carius tube (15 cm^3) at 300° for 38h. The recovered material consisted of a solid (0.2 g), identified as 1,2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane, and a volatile liquid (1.65 g). Chromatographic analysis (G.D.B. column '0', 100°) of the volatile material indicated that it consisted of three components, identified as, unreacted (138); dimers of chlorotrifluoroethylene, by comparison of infra-red and ^{19}F n.m.r. spectra with those of an authentic sample; and a mixture of Cis- and trans-1-chloro-2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane (166) and (167) respectively. (73% yield, 57% conversion). The products (166) and (167) were characterised as a mixture, b.p. 173° (Found: F, 54.1; Cl, 10.3; M^+ 347. $C_9NF_{10}Cl$ requires F, 54.7; Cl, 10.2; M 347) infra-red spectrum No. 10, ^{19}F n.m.r. spectrum No. 11.

The n.m.r. spectrum indicated that a 53:47 isomer ratio was present, but it was not possible to say which isomer predominated.

b) at 230°

Perfluoro-4-vinylpyridine (1 g, 4.3 m.moles) and chlorotrifluoroethylene (1 g, 8.6 m.moles) were heated in a Carius tube (15 cm^3) at 230° for 21h. The products consisted of a volatile liquid (1.6 g) which chromatographic analysis indicated consisted of unreacted (138), dimers of chlorotrifluoroethylene, and a mixture of cis and trans-1-chloro-2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane (<10%).

3. Hexafluoropropene

Perfluoro-4-vinylpyridine (138) (1 g, 4.3 m.moles) and hexafluoropropene (1.3 g, 8.6 m.moles) were heated in a Carius tube (15 cm^3) at 300° for 61h. The products recovered consisted of a solid (0.2 g), identified as the dimer of (138), and a volatile liquid (1.25 g). Chromatographic analysis of the volatile material (G.D.B. column '0', 78° indicated that it consisted of three components, identified as unreacted (138) plus cis and trans 1-(2',3',5',6'-tetrafluoropyridyl)-2-trifluoromethyl-hexafluorocyclobutane (168) and (167) respectively. (80%, 67% conversion).

The two isomers (168) and (167) were separated using preparative scale chromatography (Aerograph, column 'O' 150°), but it has not proved possible to determine which component was *cis* or *trans*, and so they were identified as **A** and **B**, there order of emergence from column 'O'. Isomer **A**, b.p. 161° (Found, C, 31.0; F, 65.4; M^+ 381. $C_{10}F_{13}N$ requires C, 31.5; F, 64.8; M 381), infra-red spectrum No. 11, ^{19}F n.m.r. spectrum No. 12.

Isomer **B**, b.p. 165° (Found, F, 65.2; M^+ 381. $C_{10}F_{13}N$ requires F, 64.8; M 381), infra-red spectrum No. 12, ^{19}F n.m.r. spectrum No. 13.

The v.p.c. traces (G.D.B. column 'O', 78°) indicated an initial mixture of **A** and **B** in a 40:60 ratio.

4. Styrene

Perfluoro-4-vinylpyridine (1 g, 4.3 m.moles) and styrene (0.5 g, 4.8 m.moles) were heated in a Carius tube (15 cm^3) at 230° for 18h, after which time only an intractable tar was recovered.

IX.E Photochemical Reactions

1. Photolysis

Perfluoro-4-vinylpyridine (1 g, 4.3 m.moles) was sealed in a silica tube (200 cm^3) and irradiated with ultra-violet light (253.7 n.m.) for 569h, after which time a brown involatile solid (0.9 g) was recovered. Attempts to purify by recrystallisation, or sublimation (180°, 0.01 mm. Hg) failed, and the infra-red spectrum showed a strong peak at 1475 cm^{-1}, plus broad, unresolved peaks at 1200-1300 cm^{-1} and 1725 cm^{-1}.

2. Photolysis with Hexafluoroacetone

Perfluoro-4-vinylpyridine (1 g, 4.3 m.moles) and hexafluoroacetone (0.5 g, 3.0 m.moles) were sealed in a silica tube (200 cm^3) and irradiated with ultra-violet light (300 n.m.) for 590h. The products recovered consisted of a brown involatile solid (0.1 g) and a volatile white solid (0.9 g), identified as 2,2-Bis-trifluoromethyl-3-(2',3',5',6'-tetrafluoropyridyl)-trifluorooxetane (171), (76%) m.p. 35° (Found: F, 61.6; M^+ 397. $C_{10}F_{13}NO$ requires F, 62.2; M 397), infra-red spectrum No. 13, ^{19}F n.m.r. spectrum No. 14.

The product (171) was purified by sublimation (40°, 0.005 mm.Hg).

IX.F E.S.C.A.

The use of E.S.C.A. as a method of studying stable carbanions was discussed in Chapter VI.B.1.e, and the general method used, and the precautions taken during this work, are described below.

a) Preparation of 'doped' Caesium Fluoride

All the glass apparatus used in this work was rigorously cleaned with chromic acid, rinsed well with distilled water, and dried in an oven, prior to being used.

Dry, powdered caesium fluoride (20 g) and sulpholane (20 cm^3) were rapidly introduced, against a stream of dry nitrogen, into a limb of a Schlenk tube, and stirred with a magnetic follower. After five minutes the mixture was filtered, and the 'doped' caesium fluoride sucked under vacuum for 1h to remove as much solvent as possible. The 'doped' caesium fluoride was then removed from the Schlenk tube, in a glove bag, and stored in a flask under dry nitrogen.

b) Preparation of a Disc

The method used in the preparation of 'doped' caesium fluoride discs was the same as that used in the preparation of discs for infra-red spectroscopy. All the preparation was carried out in a glove bag except for pressing in a hydraulic press. After making the discs the top surface was scraped with a new scalpel blade to present a new uncontaminated surface onto which the substrate was to be condensed.

c) Formation of Carbanions

A disc of 'doped' caesium fluoride was carefully placed inside a flask (50 cm^3) with the prepared surface uppermost. The flask was attached to a vacuum line, evacuated, cooled (liquid air) and the required substrate condensed inside. After warming to room temperature, and possibly heating, the excess substrate was removed under vacuum. The disc was then removed from the flask, in a glove bag, and stuck to a probe, using double-sided Scotch tape. The probe was placed inside a large polythene bag, flushed with dry nitrogen, and transported to the spectrometer, where it was inserted into the analyser as rapidly as possible.

d) Using Octafluorocyclohexa-1,3-diene

Condensing octafluorocyclohexa-1,3-diene onto a disc of 'doped' caesium fluoride turned the surface red, even after the excess diene had been pumped off. A Cls spectrum of this disc showed a large hydrocarbon peak with a shoulder at higher binding energy (Fig. 9). Deconvolution of the shoulder, using a curve resolver, could give two peaks of equal intensities with binding energies 3 eV and 6 eV higher than the hydrocarbon peak, values consistent with CF and CF_2 respectively. However, these results are by no means conclusive, but do indicate that with more refined techniques spectra of carbanions could possibly be obtained.

e) Using Perfluoro-4-vinylpyridine

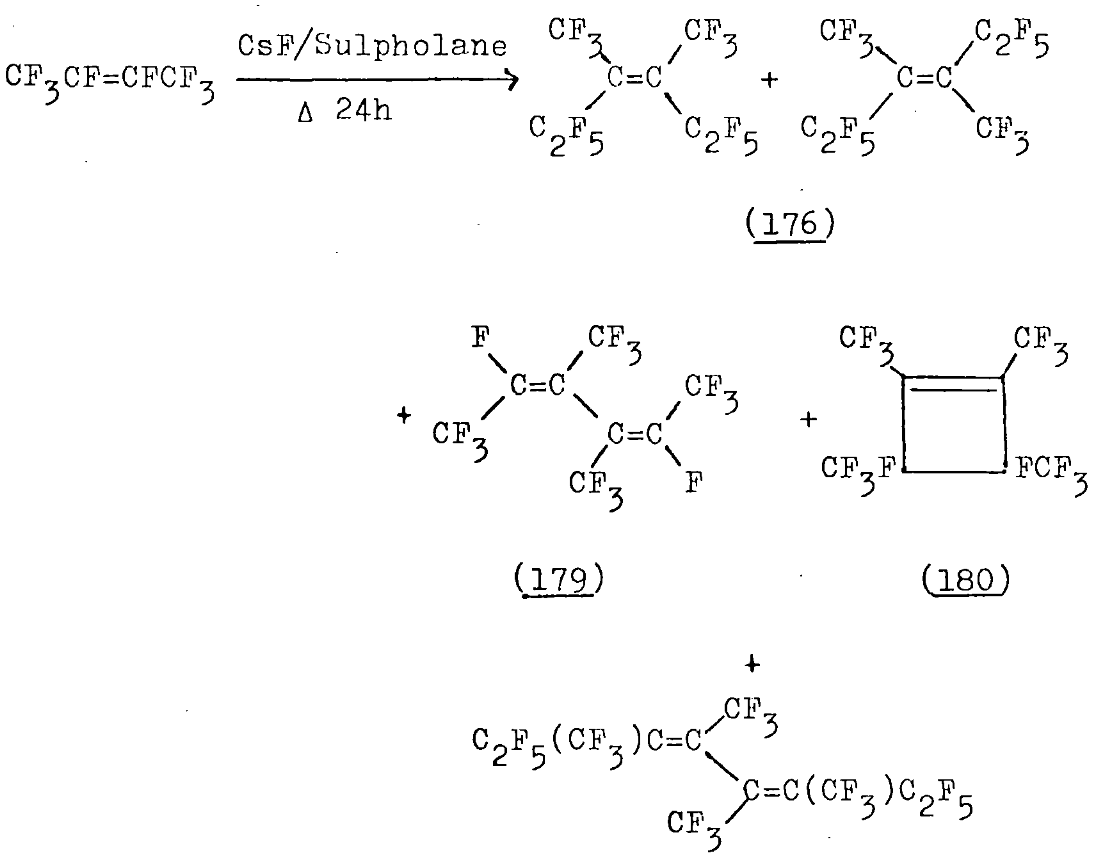
Condensing perfluoro-4-vinylpyridine onto a 'doped' caesium fluoride disc produced no colouration of the surface, and a Cls level spectrum showed only a hydrocarbon peak.

CHAPTER X

Experimental to Chapter VII

X.A. Synthesis of Perfluoro-3,4-dimethylhex-3-ene

Perfluoro-3,4-dimethylhex-3-ene (176) was synthesised by the fluoride ion-initiated dimerisation of octafluorobut-2-ene (178), carried out in a similar manner to the oligomerisation of chlorotrifluoroethylene discussed earlier (Chapter VIII.B).



(176)

(179)

(180)

(181)

1. Dimerisation of Octafluorobut-2-ene

A mixture of caesium fluoride (4 g, 26.3 m.moles), octafluorobut-2-ene (19.5 g, 97.5 m.moles), and sulpholane (20 cm^3) were heated in a nickel tube (80 cm^3), with constant agitation, at 100° for 24h. The volatile material recovered consisted of unreacted olefin (12.1 g) and a colourless, volatile liquid (7 g), which chromatographic analysis (G.D.B., column 'O', 78°) indicated consisted of three products, two minor and one major, the yields of which are shown in Table 42. The major product was identified as perfluoro-3,4-dimethylhex-3-ene (176) by comparison of the infra-red and ^{19}F n.m.r. spectra with those of an authentic sample. The n.m.r. spectrum indicated that a 56:44 isomer distribution was present, but which isomer predominated is not known.

The most volatile component was in fact shown by n.m.r. spectroscopy to consist of a mixture of two compounds, identified as perfluoro-3,4-dimethylhexa-2,4-diene (179) and perfluoro-1,2,3,4-tetramethylcyclobutene (180). The least volatile component was identified as perfluoro-3,4,5,6-tetramethylocta-3,5-diene (181) b.p. 147.5; infra-red spectrum No. 14; ^{19}F n.m.r. spectrum No. 15. The n.m.r. spectrum indicates a 34:66 isomer distribution.

The products were separated using distillation and preparative scale chromatography (Aerograph, column 'O', 90°).

The reaction was repeated at 58° and 130°, the results of which are shown in Table 42.

Table 42

Temp. °C	Solvent	CsF g	Weight of (178)	Weight of Products	*Percentage Yields			Percentage Conversions
					(179) + (180)	(176)	(181)	
58	Sulpholane	10 g 65.8 m.moles	21 g 105 m.moles	2 g	19.5	75.0	8.0	8
100	Sulpholane	4 g 26.3 m.moles	19.5 g 97.5 m.moles	7 g	3.0	85.0	11.5	38
130	Sulpholane	3 g 20 m.moles	20 g 100 m.moles	8.8 g	11.5	69.0	15.5	44

*Based on (178) consumed

X.B Defluorination of Perfluoro-3,4-dimethylhex-3-ene

The method of defluorination was the same as that used in the synthesis of perfluoro-4-vinylpyridine and described in Chapter IX.A.

Perfluoro-3,4-dimethylhex-3-ene (176) was passed over hot iron-filings at two temperatures, 430° and 500°, and the yields and conversions obtained are shown in Table 43. Chromatographic analysis (G.D.B., column 'O', 30°) indicated that the recovered material consisted of starting material and a single product. However, n.m.r. spectroscopy showed that a complex mixture of products was present, three of which have been identified as perfluoro-_trans_,_trans_-3,4-dimethylhexa-2,4-diene (179) (45% of product mixture), perfluoro-_cis_,_trans_-3,4-dimethylhexa-2,4-diene (184) (12%) and perfluoro-1,2,3,4-tetramethylcyclobutene (180), (15%). ^{19}F n.m.r. spectra Nos. 16, 17 and 18 respectively.

Table 43

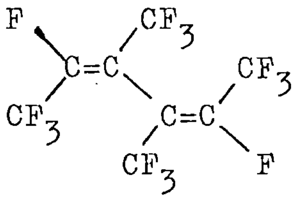
Yields from Defluorination of Perfluoro-3,4-dimethylhex-3-ene

Temp. °C	(176)	Weight of Recovered Material	*Percentage Yield of Dienes	Percentage Conversion
430	10 g, 25 m.moles	7.7 g	74	69
500	10 g, 25 m.moles	5.0 g	61	91

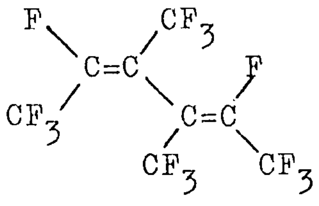
*Based on (176) consumed

Attempts to obtain pure samples of products by distillation, using a Fischer Spaltrohr one-piece distillation apparatus, gave fractions enriched in single components, but nowhere near pure enough for characterisation.

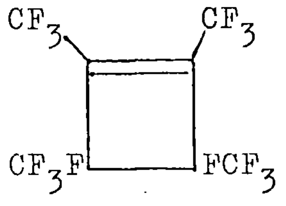
1. Reflux Dienes with Fluoride Ion



(179)



(184)



(180)

A mixture of caesium fluoride (3 g, 20.0 m.moles), sulpholane (20 cm^3), and dienes (2 g), the composition of which is shown in Table 44, was refluxed with vigorous agitation for 4 days, after which the volatile material (1.5 g) was collected, under vacuum in a cold trap (liquid air). The composition of the initial and final material was determined using ^{19}F n.m.r. spectroscopy (Table 44).

Table 44

Sample	Percentage Composition		
	(179)	(184)	(180)
Initial	45	12	15
After refluxing with fluoride ion	65	13	22

2. Dienes Heated in a Carius Tube

A mixture of dienes (2 g), of known composition, were sealed in a Carius tube (15 cm^3) and heated at 300^o for 20h., the n.m.r. spectrum of the recovered material (1.8 g) indicated that no change in composition had occured.

X.C Reaction of Perfluoro-3,4-dimethylhex-3-ene with Nucleophiles

1. Reaction with Diethylamine

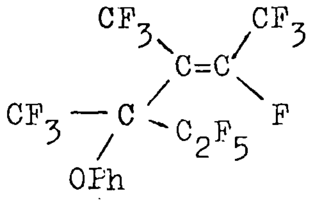
A mixture of perfluoro-3,4-dimethylhex-3-ene (176) (10 g, 25.0 m.moles), sulpholane (20 cm^3), and diethylamine (3.6 g, 49.3 m.moles) was vigorously stirred at room temperature for 16h. The reaction mixture was then poured into water (50 cm^3), when the products separated as a lower organic layer (10 g). After washing with water (3x20 cm^3), and removal of unreacted (176) under vacuum, a high boiling point liquid (8.25 g) remained, which chromatographic analysis (G.D.B. column '0', 125^o) showed to consist of a single product, identified as 3-Trifluoromethyl-4-diethylaminofluoromethene-undecafluorohexane (187), (73%). b.p. 93^o at 18 mm. Hg. (Found: C, 32.0; F, 62.5; H, 2.4; N, 3.5; M^+ 453. $C_{12}F_{15}NH_{10}$ requires C, 31.8; F, 62.9; H, 2.2; N, 3.1; M 453), infra-red spectrum No. 15, ^{19}F and ^1H n.m.r. spectra No. 19.

a) Hydrolysis of Diethylamine Derivative

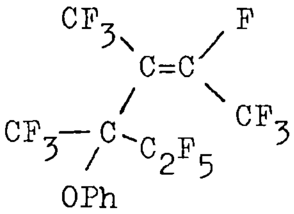
The enamine (187) (6 g, 13.2 m.moles) was vigorously stirred with sodium hydroxide solution (20 cm^3, 2M) for 2 days, after which the lower organic layer (4 g) was withdrawn and dried ($MgSO_4$). Chromatographic analysis (G.D.B., column '0',

125°) indicated that the products consisted of a single component, identified as cis and trans-3-trifluoromethyl-4-(N,N-diethylamido)decafluorohex-3-ene (188) and (189) respectively (70%). The amides were characterised as a mixture, b.p. 201° (Found: C, 33.2; F, 57.3; N, 3.6; H, 2.7; M^+ 431. $C_{12}F_{13}NH_{10}O$ requires C, 33.4; F, 57.3; N, 3.3; H, 2.3; M 431), infra-red spectrum No. 16, ^{19}F and ^{1}H n.m.r. spectra No. 20 and No. 21.

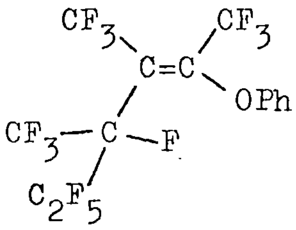
2. Reaction with Phenol



(198)



(199)



(200)

a) Using Triethylamine

A mixture of perfluoro-3,4-dimethylhex-3-ene (10 g, 25.0 m.moles), triethylamine (5 g, 50.0 m.moles), phenol 2.4 g, 25.5 m.moles), and tetraglyme (20 cm^3) was vigorously stirred at room temperature for 16h, and after pouring the reaction mixture into water (20 cm^3), the products separated as a lower organic layer (10.9 g). Chromatographic analysis (G.D.B., column 'A', 125°) indicated that this consisted of three products, identified as Trans-4-phenoxy-3,4-bis-trifluoromethyl-nonafluorohex-2-ene (199) (28%). b.p. 194°. (Found: C, 35.4; F, 60.4; H, 1.2; M^+ 474. $C_{14}F_{15}H_5O$ requires C, 35.4; F, 60.2; H, 1.0; M 474), infra-red spectrum No. 17,

^{19}F and ^{1}H spectra No. 22; Cis-4-phenoxy-3,4-bis-trifluoromethyl-nonafluorohex-2-ene (198), (37%), b.p. 193°. (Found: C, 35.6; F, 60.4; H, 1.3; M^+ 474. $C_{14}F_{15}H_5O$ requires C, 35.4; F, 60.2; H, 1.0; M 474), infra-red spectrum No. 18, ^{19}F and ^{1}H spectra No. 23; and Cis-2-phenoxy-3,4-bis-trifluoromethyl-nonafluorohex-2-ene (200), (35%), b.p. 191°. (Found: C, 35.7; F, 60.4; H, 1.3; M^+ 474. $C_{14}F_{15}H_5O$ requires C, 35.4; F, 60.2; H, 1.0; M 474), infra-red spectrum No. 19, ^{19}F and ^{1}H spectra No. 24.

b) Using Sodium Carbonate

A mixture of perfluoro-3,4-dimethylhex-3-ene (8 g, 20.0 m.moles), anhydrous sodium carbonate (2.1 g, 20.0 m.moles), phenol (1.9 g, 20.2 m.moles), and dimethylformamide (30 cm^3) was vigorously stirred at room temperature for 48h. After filtering and then pouring into water (50 cm^3) the products separated as a lower organic layer, which yielded a volatile fraction (3.75 g) identified as a mixture of (198), (199) and (200) in yields of 18%, 21% and 2.5% respectively. The involatile residues (3.1 g) were not identified, but a mass spectrum showed a parent peak at 548, consistent with dephenoxy derivatives.

c) Equilibration Experiments

i) A reaction mixture was prepared in a similar manner to that described in X.C.2.a, and a sample withdrawn to determine the product composition (Table 45) by chromatographic analysis (G.D.B., column 'A', 125°). This reaction mixture was then divided into two, one half enriched with (200) (Sample 1), the other with (199) (Sample 2), and the composition of the new samples determined (Table 45). After vigorously stirring each for 17h the composition of the final products was determined. The results (Table 45) indicate that some equilibration had occured.

Table 45

Distribution of Phenyl Ethers in Equilibration Experiment

Sample	Percentage Composition		
	(198)	(199)	(200)
Initial Reaction Product	48	30	22
Sample 1, Initial	40	17	42
Sample 2, Initial	35	50	15
Sample 1, Final	46	27	27
Sample 2, Final	39	32	29

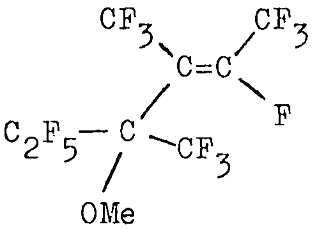
ii) A mixture of phenyl ethers of known composition (Table 46) was divided into two, one half added to a mixture of caesium fluoride (3 g, 20.0 m.moles) in tetraglyme (15 cm^3), the other to triethylamine (1 g, 10.0 m.moles) in tetraglyme (15 cm^3). After vigorously stirring at room temperature for 36h, both samples were poured into water and the product compositions determinedby chromatographic analysis (G.D.B., column 'A', 125^o). The results (Table 46) indicate that more equilibration occured with caesium fluoride

Table 46

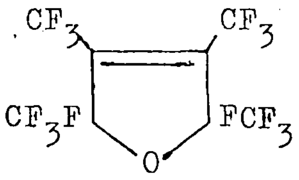
Results of Equilibration using Triethylamine and Caesium Fluoride

Sample	Percentage Composition of Products		
	(198)	(199)	(200)
Initial Composition	29.0	13.0	58.0
After stirring with CsF	37.5	25.0	37.5
After stirring with Et_3N	32.0	19.0	49.0

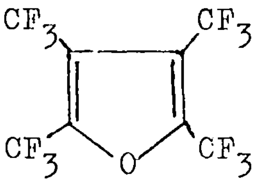
3. Reaction with Methanol



(205)



(206)



(207)

a) Using Sodium Carbonate

A mixture of perfluoro-3,4-dimethylhex-3-ene (176) (10 g, 25.0 m.moles), methanol (0.75 g, 23.4 m.moles), anhydrous sodium carbonate (2.5 g, 24.8 m.moles), and tetraglyme (20 cm^3) was vigorously stirred at room temperature for 24h. After filtering and pouring the reaction mixture into water the products separated as a lower organic layer, which chromatographic analysis (G.D.B. column 'A', 78^o)

indicated consisted of unreacted (176), two minor, unidentified components, plus Cis-4-methoxy-3,4-trifluoromethyl-nonafluorohex-2-ene (205), (61%, 67% conversion), b.p. 122°. (Found: H, 0.6; F, 69.7; M^+ 393. $C_9F_{15}OH_3$ requires H, 0.73; F, 69.2; M 412), infra-red spectrum No. 20, ^{19}F and ^1H n.m.r. spectra No. 25. The product (205) was purified using preparative scale chromatography.

b) Using Triethylamine

Methanol (0.75 g, 23.4 m.moles) was slowly added to a vigorously stirred mixture of perfluoro-3,4-dimethylhex-3-ene (10 g, 25.0 m.moles), triethylamine (5g, 49.5 m.moles) in tetraglyme (20 cm^3). After pouring the reaction mixture into water the products (9.5 g) separated as a lower organic layer, which was washed with dil.HCl (2x20 cm^3) and dried ($MgSO_4$). Chromatographic analysis (G.D.B. column 'A', 78°) indicated a mixture of eight products, two of which were identified as (205) (18%), and cis and trans-perfluoro-2,5-dihydro-tetramethylfuran (206), (22%). b.p. 83°, infra-red spectrum No. 21, ^{19}F n.m.r. spectrum No. 26 and 27. The mass spectrum showed a P-19 peak at 359.

At the time of writing a satisfactory elemental analysis has not been obtained, the fluorine figures being low, but a possible explanation for this result is that evaporation of the volatile compound (206) was occuring before fusion with the alkali metal, so giving low fluorine analysis.

The product (206) was purified by distillation and preparative scale chromatography (Aerograph, column 'A', 65°).

c) Rapid addition of Methanol to a refluxing mixture of Perfluoro-3,4-dimethylhex-3-ene in Tetraglyme

i) Using Triethylamine

Methanol (0.75 g, 23.4 m.moles) was rapidly added to a vigorously stirred, refluxing mixture of perfluoro-3,4-dimethylhex-3-ene (10 g, 25.0 m.moles), triethylamine (5 g, 49.5 m.moles) and tetraglyme (20 cm^3). After refluxing for 4h the reaction mixture was poured into water when the products separated as a lower organic layer, which on vacuum transference gave an involatile black oil, and a colourless volatile liquid (5.1 g). Chromatographic analysis (G.D.B., column 'A', 78°) of the volatile products indicated that they consisted of three components, identified as (205) (17.5%),(206) (30%), and perfluoro-tetramethylfuran (207) (8%), b.p. 103°. (Found: F, 67.6; M^+ 340. $C_8F_{12}O$ requires F, 67.0; M 340), infra;red spectrum No. 22, ^{19}F n.m.r. spectrum No. 28.

The furan (207) was purified by distillation and preparative scale chromatography (Aerograph, column 'A', 65°.)

ii) Using Pyridine

The previous experiment was repeated except that pyridine (4 g, 50.5 m.moles) was substituted for triethylamine. Chromatographic analysis (G.D.B., column 'A', 78°) indicated that the products (6.5 g) consisted of unreacted olefin (176) and perfluoro-2,5-dihydrotetramethylfuran (206) (56%).

d) Refluxing a mixture consisting mainly of Perfluoro-2,5-dihydrotetramethylfuran with base

i) With Triethylamine

A mixture (5 g) consisting of (205) (32%), (206) (55%), and (207) (13%), was refluxed with triethylamine (3 g, 30 m.moles) in tetraglyme (10 cm^3) for 16 h. After pouring the reaction mixture into water the products separated as a lower layer, which on vacuum transference yielded an involatile black oil (1.6 g), and a volatile, colourless liquid (2 g). Chromatographic analysis (G.D.B., column 'A', 78^0) indicated that the volatile material consisted of a mixture of (205) (16%) and (207) (84%).

ii) With Pyridine

In a repeat of the previous experiment, using pyridine instead of triethylamine, no change in the composition between starting material and final product was observed.

e) Refluxing Perfluoro-3,4-dimethylhex-3-ene with Methanol

A mixture of methanol (0.75 g, 23.4 m.moles), perfluoro-3,4-dimethylhex-3-ene (176) (10 g, 25.0 m.moles), and tetraglyme (25 cm^3) was refluxed for 24h. Chromatographic analysis (G.D.B. column 'A', 78^0) of the recovered material (9.5 g) indicated that only starting material (176) was present.

f) Refluxing Perfluoro-3,4-dimethylhex-3-ene with Triethylamine

A mixture of perfluoro-3,4-dimethylhex-3-ene (176) (10 g, 25.0 m.moles), triethylamine (7.5 g, 75.0 m.moles), and sulpholane (20 cm^3) were refluxed for 24h, when a sample of the lower product layer was withdrawn. The n.m.r. spectrum indicated that this consisted mainly of starting material (176) and perfluoro-3,4-dimethylhexa-2,4-diene (179) ($<5\%$).

g) Refluxing Perfluoro-3,4-dimethylhex-3-ene with water and Triethylamine

A mixture of perfluoro-3,4-dimethylhex-3-ene (10 g, 25.0 m.moles), water (1 g, 56.0 m.moles), triethylamine (5 g, 50.5 m.moles), and tetraglyme (25 cm^3) was refluxed for 4h. On pouring into water the products separated as a lower layer, which after vacuum transference yielded an involatile black oil (4.5 g) and a volatile liquid (3 g). The ^{19}F n.m.r. spectrum of the volatile material indicated that neither (206) nor (207) had been formed, and the reaction was not investigated further.

APPENDIX 1

^{19}F and ^{1}H n.m.r. Spectra

APPENDIX 1

^{19}F and ^{1}H n.m.r. Spectra

Index to n.m.r. spectra

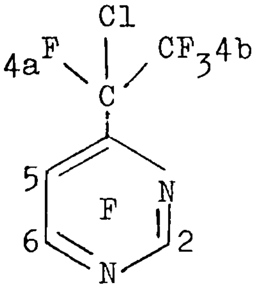
1. 4-Chlorotetrafluoroethyl-2,5,6-trifluoropyrimidine (106)
2. 4,6-Bis-chlorotetrafluoroethyl-2,5-difluoropyrimidine (107)
3. 2-Chlorotetrafluoroethyl-6,5-difluoro-S-triazine (102)
4. 2,4-Bis-chlorotetrafluoroethyl-6-fluoro-S-triazine (103)
5. Trans-1,3-bis-(2',3',5',6'-tetrafluoropyridyl)-hexafluorobut-1-ene (142)
6. 4,5-Bis-(1'-(2",3",5",6"-tetrafluoropyridyl)-tetrafluoroethyl)-3,6-difluoropyridazine (143)
7. Cis-1-phenoxy-2-(2',3',5',6'-tetrafluoropyridyl)-difluoroethylene (149)
8. Trans-1-phenoxy-2-(2',3',5',6'-tetrafluoropyridyl)-difluoroethylene (150)
9. 2-Oxa-4(2'-methoxy-3',5',6'-trifluoropyridyl)-3,3,4-trifluorobutane (151)
10. 1,2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane (158)
11. Cis and Trans-1-chloro-2-(2',3',5',6'-tetrafluoropyridyl) hexafluorocyclobutane (166) and (167)
12. 1-(2',3',5',6'-tetrafluoropyridyl)-2-trifluoromethylhexafluorocyclobutane, Isomer A
13. 1-(2',3',5',6'-tetrafluoropyridyl)-2-trifluoromethylhexafluorocyclobutane, Isomer B
14. 2,2-Bis-trifluoromethyl-3-(2',3',5',6'-tetrafluoropyridyl)-trifluorooxetane (171)

15. Perfluoro-3,4,5,6-tetramethylocta-3,5-diene (181)
16. Perfluoro-*trans*,*trans*-3,4-dimethylhexa-2,4-diene (179)
17. Perfluoro-*cis*,*trans*-3,4-dimethylhexa-2,4-diene (184)
18. Perfluoro-1,2,3,4-tetramethylcyclobutene (180)
19. 3-Trifluoromethyl-4-diethylaminofluoromethene-undecafluorohexane (187)
20. 3-Trifluoromethyl-4-(N,N-diethylamido)decafluorohex-3-ene Isomer A
21. 3-Trifluoromethyl-4-(N,N-diethylamido)decafluorohex-3-ene Isomer B
22. Trans-4-phenoxy-3,4-bis-trifluoromethylnonafluorohex-2-ene (199)
23. Cis-4-phenoxy-3,4-bis-trifluoromethylnonafluorohex-2-ene (198)
24. Cis-2-phenoxy-3,4-bis-trifluoromethylnonafluorohex-2-ene (200)
25. Cis-4-Methoxy-3,4-trifluoromethylnonafluorohex-2-ene (205)
26. Perfluoro-2,5-dihydro-tetramethylfuran (206), Isomer A
27. Perfluoro-2,5-dihydro-tetramethylfuran (206), Isomer B
28. Perfluoro-tetramethylfuran (207)

The following abbreviations have been used in describing spectra:- M-multiplet; S-singlet; Q-quartet; D-doublet.

1. 4-Chlorotetrafluoroethyl-2,5,6-trifluoropyrimidine (106)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
45.0	D($J_{5,2}$=29)	1	2
69.4	D($J_{5,6}$=20)	1	6
79.8	D($J_{4a,4b}$=6) of D($J_{4b,5}$=5)	3	4b
130.6	Q($J_{4a,4b}$=6) of D($J_{4a,5}$=38)	1	4a
149.8	M	1	5

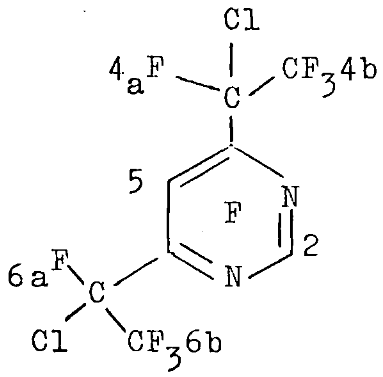


(106)

Recorded neat with external $CFCl_3$ reference

2. 4,6-Bis-chlorotetrafluoroethyl-2,5-difluoropyrimidine (107)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
47.6	D($J_{5,2}$=30)	1	2
80.8	D($J_{5,4a}$=5) of D($J_{4a,4b}$=5)	3	4b
80.8	D($J_{5,6a}$=5) of D($J_{6a,6b}$=5)	3	6b
131.4	Complex overlapping M	3	5, 4a, 4b.

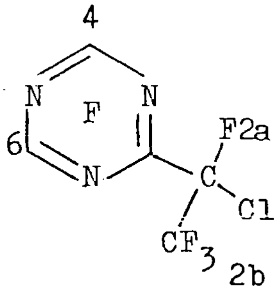


(107)

Recorded neat with external $CFCl_3$ reference

3. 2-Chlorotetrafluoroethyl-4,6-difluoro-S-triazine (102)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
32.9	Broad S	2	4,6
81.0	D($J_{2a,2b}$=6)	3	2b
134.3	Q($J_{2a,2b}$=6)	1	2a

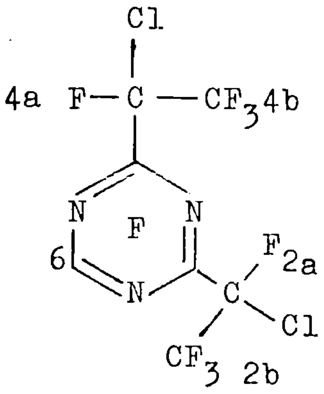


(102)

Recorded neat with external $CFCl_3$ reference

4. 2,4-Bis-chlorotetrafluoroethyl-6-fluoro-S-triazine (103)

Shift p.p.m.	Fine Structure Coupling constants in Hz	Relative Intensity	Assignment
33.7	S	1	6
81.0	$D(J_{2a,2b}=6)$	3	2b
81.0	$D(J_{4a,4b}=6)$	3	4b
131.1	$Q(J_{2a,2b}=6)$	1	2a
131.1	$Q(J_{4a,4b}=6)$	1	4a

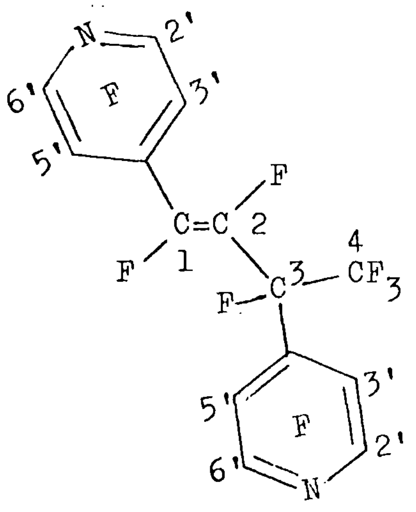


(103)

Recorded neat with external $CFCl_3$ reference

5. Trans-1,3-bis-(2',3',5',6'-tetrafluoropyridyl)-pentafluorobut-1-ene (142)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
78.2	M	3	4
88.0	Broad M	4	2',6'
138.4 139.5 141.8	Broad overlapping resonances	5	3',5' and 2 or 1
148.6	D($J_{1,2}$=138)	1	2 or 1
167.0	Broad, unresolved	1	3

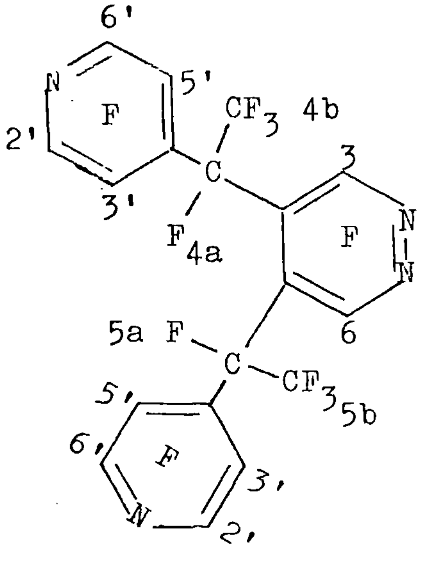


Recorded in acetone solution with external $CFCl_3$ reference

(142)

6. 4,5-Bis-1'-(2",3",5",6"-tetrafluoropyridyl)-tetrafluoroethyl)-3,6-difluoropyridazine (143)

Shift p.p.m.	Fine structure Coupling contants in Hz	Relative Intensity	Assignment
73.7	Broad M	2	3,6
75.8	Complex M	6	4b, 5b
91.3	Complex M	4	2', 6'
140.9	Complex M	4	3', 5'
158.8	Complex M	2	4a, 5a.

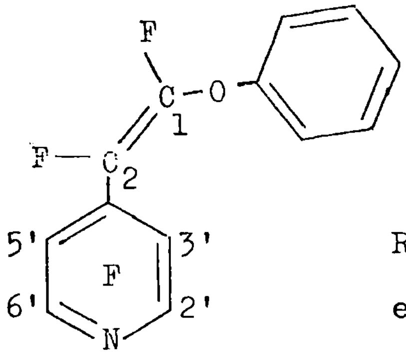


Recorded in acetone solution with external $CFCl_3$ reference

(143)

7. Cis-1-phenoxy-2-(2',3',5',6'-tetrafluoropyridyl)-difluoroethylene (149)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
90.9	Complex M	2	2', 6'
94.65	D($J_{1,2}$=16)	1	1
137.3	Complex M	2	3', 5'
161.4	T($J_{2-3',5'}$=10) of D($J_{1,2}$=16)	1	2



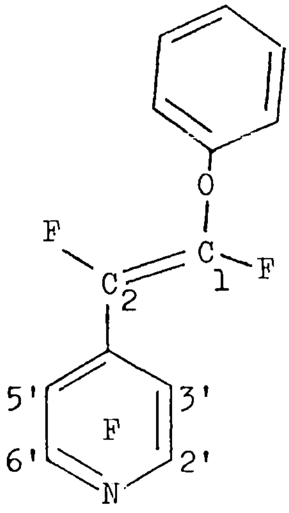
Recorded neat with an external $CFCl_3$ reference

(149)

The ^1H n.m.r. spectrum showed a single complex multiplet 6.8 p.p.m. downfield from external T.M.S.

8. Trans-1-phenoxy-2-(2',3',5',6'-tetrafluoropyridyl)-difluoroethylene (150)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
90.9	Complex M	2	2', 6'
114.4	$T(J_{1-3',5'}=18)$ of $D(J_{1,2}=121)$	1	1
137.3	Complex M	2	3', 5'
166.4	$T(J_{2-3',5'}=10)$ of $D(J_{1,2}=121)$	1	2



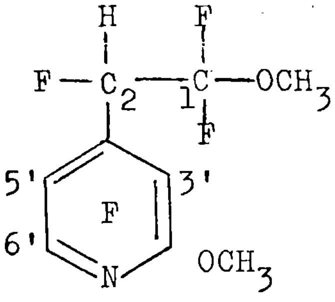
(150)

Recorded neat with an external $CFCl_3$ reference

The ^1H n.m.r. spectrum showed a single complex multiplet 6.8 p.p.m. downfield from external T.M.S.

9. 2-Oxa-4(2'-methoxy-3',5',6'-trifluoropyridyl)-3,3,4-trifluorobutane (151)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
89.5	M	2	1
98.1	D($J_{5',6'}$=21) of D($J_{3',6'}$=31)	1	6'
143.4	M of D($J_{3',6'}$=31)	1	3'
154.1	M	1	5'
206.8	M	1	2



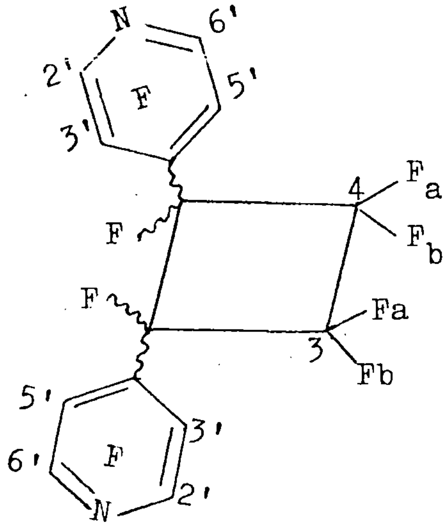
Recorded neat with an external $CFCl_3$ reference

(151)

^1H n.m.r. spectrum showed three resonances, 3.4, 3.7 and 5.6 p.p.m. downfield from external T.M.S. which integrated in the ratio 3:3:1. These have been assigned to the two methyl groups and 2H.

10. 1,2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane (158)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensities	Assignment
97.5	Broad M	2	2',6'
121.1	AB D($J_{a,b}$=220)	1	3,4-a or b
131.8	AB D($J_{a,b}$=220)	1	3,4-a or b
138.5	Broad M	2	3',5'
164.3	M	1	1,2

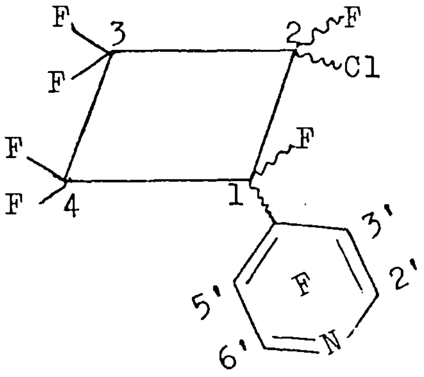


Recorded in acetone solution with external $CFCl_3$ reference

(158)

11. Cis and Trans-1-chloro-2-(2',3',5',6'-tetrafluoropyridyl) hexafluorocyclobutane (166) and (167)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
89.8	Complex M	4	2',6'
117→135.6	4 overlapping AB quartets	8	3,4
137.6	Complex M	4	3',5'
141.0	Broad M	1	2
144.0	Broad M	1	2
154.5	M	1	1
160.6	M	1	1



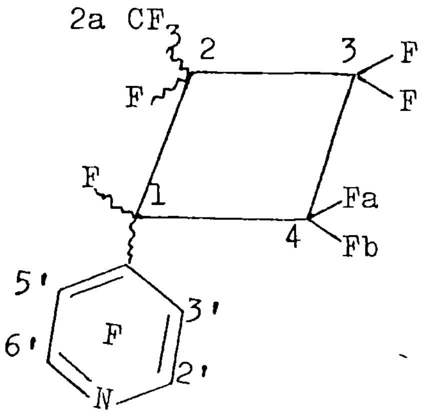
Recorded neat with external $CFCl_3$ reference

(166) and (167)

12. 1-(2',3',5',6'-tetrafluoropyridyl)-2-trifluoromethylhexafluorocyclobutane

Isomer A

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
76.6	Broad S	3	2a
92.6	M	2	2', 6'
123.9	AB D($J_{4a,4b}$=224)	1	4a or b
131.6	AB D($J_{4a,4b}$=224)	1	4a or b
131.6	Broad S	2	3
135.6	Broad M	2	3',5'
168.4	Broad M	1	1
193.8	M	1	2

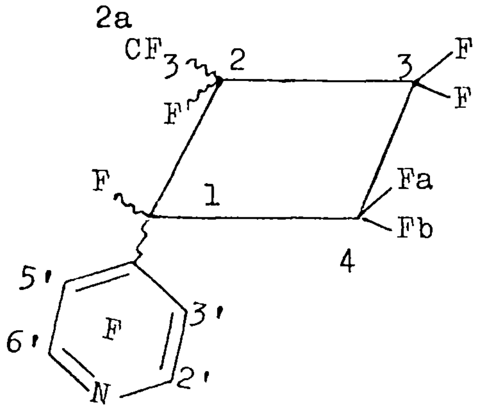


Recorded neat with an external $CFCl_3$ reference

13. 1-(2',3',5',6'-tetrafluoropyridyl)-2-trifluoromethylhexafluorocyclobutane

Isomer B

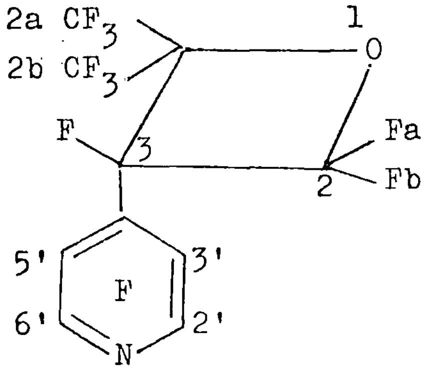
Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
73.1	M	3	2a
90.6	M	2	2', 6'
126.2	AB D($J_{4a,4b}$=229)	1	4a or b
126.5	Complex M	2	3
133.0	Q($J_{2a-4a \text{ or } 4b}$=14) of AB D($J_{4a,4b}$=229)	1	4a or b
138.8	M	2	3', 5'
170.8	M	1	1
188.4	M	1	2



Recorded neat with an external $CFCl_3$ reference

14. 2,2-Bis-trifluoromethyl-3-(2',3',5',6'-tetrafluoropyridyl)-trifluorooxetane (171)

Shift p.p.m.	Fine Structure Coupling constants in Hz	Relative Intensity	Assignment
74.0	M	6	2a, 2b
75.0	AB D($J_{4a,4b}$=94) partially obscured	1	4a or b
76.2	AB D($J_{4a,4b}$=94)	1	4a or b
89.7	M	2	2', 6'
139.7	M	2	3', 5'
153.9	M	1	3

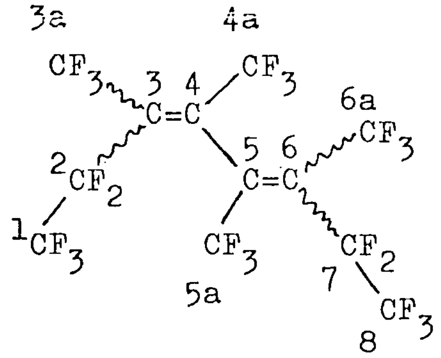


(171)

Recorded in acetone solution with external $CFCl_3$ reference

15. Perfluoro-3,4,5,6-tetramethylocta-3,5-diene (181)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
58.5 59.4 58.8	Broad overlapping resonances	12	3a,4a,5a,6a.
85.4 85.9	Broad overlapping resonances	6	1,8
116.0	Broad M	4	2,7
118.2	Broad M		



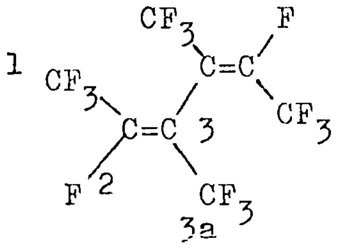
(181)

Recorded neat with external $CFCl_3$ reference

Mixture of isomers

16. Perfluoro-trans,trans-3,4-dimethylhexa-2,4-diene (179)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
64.5	D($J_{2,3a}$=18)	3	3a
73.5	D($J_{1,2}$=4)	3	1
106.4	Broad Q($J_{2,3a}$=18)	1	2

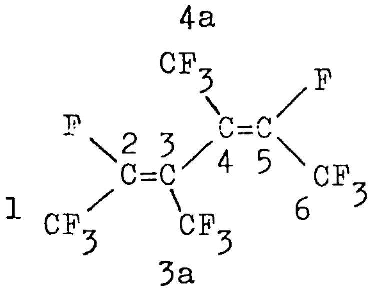


Recorded neat with external $CFCl_3$ reference

(179)

17. Perfluoro-cis,trans-3,4-dimethylhexa-2,4-diene (184)

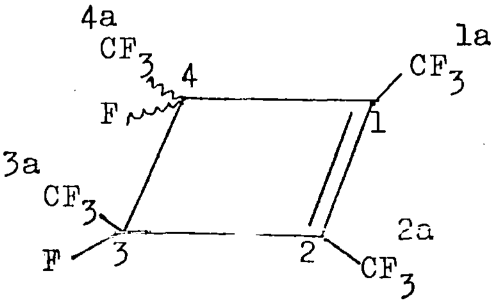
Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
60.9	M	3	3a
64.6	D($J_{5,4a}$=18)	3	4a
72.4	D($J_{1,2}$=6) of Q($J_{1,3a}$=10)	3	1
73.3	Broad S	3	6
103.3	Broad M	1	2
106.5	M	1	5



Recorded neat with external $CFCl_3$ reference

18. Perfluoro-1,2,3,4-tetramethylcyclobutene (180)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
67.2	M	6	1a,2a
78.8	D($J_{4a,3a}$=7)	6	4a,3a
172.2	M	2	3,4

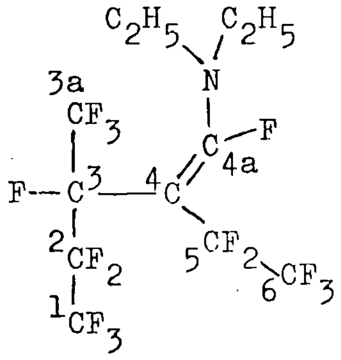


Recorded neat with external $CFCl_3$ reference

(180)

19. 3-Trifluoromethyl-4-diethylaminofluoromethene-undecafluorohexane (187)

Shift p.p.m.	Fine Structure Coupling constants in Hz	Relative Intensity	Assignment
42.0	Broad unresolved	1	4a
77.2	Broad S	3	3a
82.5	Broad D(J=18)	3	1 or 6
84.1	D(J=28)	3	1 or 6
103.5	Broad, unresolved	2	5
117.0	M of AB D(J=228)	1	2
122.4	M of AB D(J=228)	1	2
181.5	Broad, unresolved	1	3



(187)

Recorded neat with external $CFCl_3$ reference

The ^1H spectrum shows two resonances at 1.0 and 3.1 p.p.m. downfield from external T.M.S. which integrated in the ratio 3:2. These have been assigned to the CH_3 and CH_2 groups.

20. 3-Trifluoromethyl-4-(N,N-diethylamido)decafluorohex-3-ene

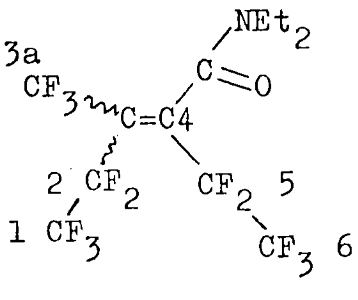
Isomer A

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
58.0	M	3	3a
81.1	M	3	1 or 6
82.2	M	3	1 or 6
106.3 110.5	Complex Overlapping AB Q(J=280)	4	2,5

21.

Isomer B

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
60.2	M	3	3a
81.1	M	3	1 or 6
82.2	M	3	1 or 6
106.3 110.5	Complex Overlapping AB Q(J=280)	4	2,5

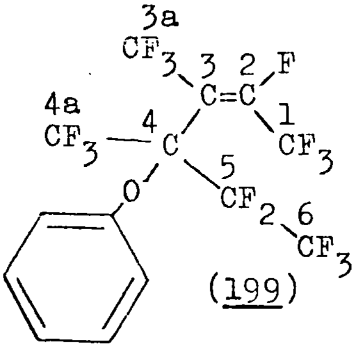


Recorded neat with external CFCl$_3$ reference

The ^1H spectrum shows two resonances at 1.1 and 3.3 p.p.m. downfield from external T.M.S. which integrated in the ratio 3:2. These have been assigned to the CH_3 and CH_2 groups.

22. Trans-4-phenoxy-3,4-bis-trifluoromethylnonafluorohex-2-ene (199)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
61.9	Broad unresolved	6	4a, 3a
71.6	M	3	1
76.1	M	3	6
100.4	Broad M	2	5
105.6	Q($J_{1,2}$=10) of Q($J_{2,3a}$=26)	1	2



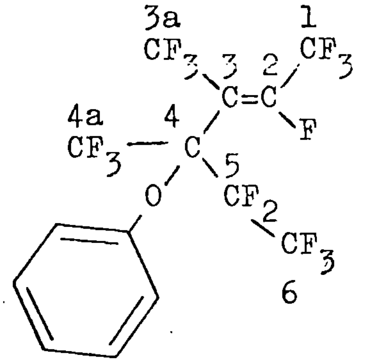
(199)

Recorded neat with external $CFCl_3$ reference

The ^1H n.m.r. spectrum showed a single complex multiplet 7.8 p.p.m. downfield from external T.M.S.

23. Cis-4-phenoxy-3,4-bis-trifluoromethylnonafluorohex-2-ene (198)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
58.8 59.4	Overlapping M	6	3a, 4a
72.2	D($J_{1,2}$=6) of Q($J_{3a,1}$=11)	3	1
81.0	Q($J_{3a,6}$=5) of D($J_{2,6}$=21)	3	6
99.5	Broad, unresolved	2	5
106.2	Broad, unresolved	1	2



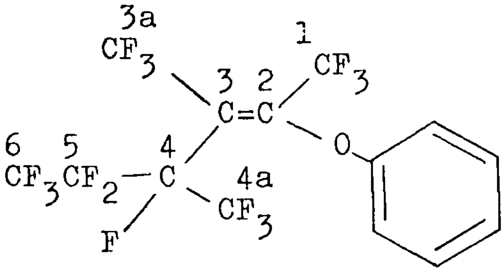
(198)

Recorded neat with external $CFCl_3$ reference

The ^1H n.m.r. spectrum showed a single complex multiplet 7.8 p.p.m. downfield from external T.M.S.

24. Cis-2-phenoxy-3,4-bis-trifluoromethyl-nonafluorohex-2-ene (200)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
58.6	M	3	3a
60.4	$Q(J_{1,3a}=15)$	3	1
73.5	Broad S	3	4a
82.6	Broad $D(J_{4,6}=18)$	3	6
120.8	Complex AB Q	2	5
181.0	M	1	4



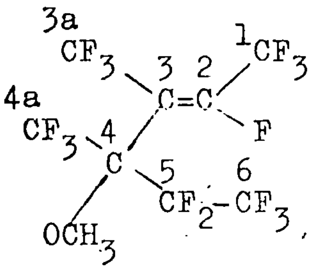
(200)

Recorded neat with external $CFCl_3$ reference

The ^1H n.m.r. spectrum showed a single complex multiplet 7.8 p.p.m. downfield from external T.M.S.

25. Cis-4-Methoxy-3,4-trifluoromethylnonafluorohex-2-ene (205)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
55.8	M	3	3a
67.0	Broad S	3	4a
70.1	D($J_{1,2}$=3) of Q($J_{1,3a}$=13)	3	1
82.7	M	3	6
93.6	Broad unresolved	1	2
120.3	M	2	5



(205)

Recorded neat with external $CFCl_3$ reference

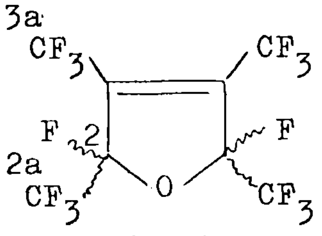
The ^1H n.m.r. spectrum showed a single resonance 3.7 p.p.m. downfield from external T.M.S.

26. Perfluoro-2,5-dihydro-tetramethylfuran (206), Isomer A

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
63.3	M	3	3a
85.0	M	3	2a
122.6	Broad M	1	2

27. Perfluoro-2,5-dihydro-tetramethylfuran (206), Isomer B

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
62.9	M	3	3a
83.4	M	3	2a
112.2	Broad M	1	2

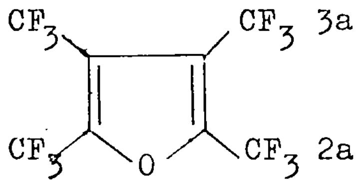


(206)

Recorded neat with external $CFCl_3$ reference

28. Perfluoro-tetramethylfuran (207)

Shift p.p.m.	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
60.4	M	1	2a
65.8	M	1	3a



(207)

Recorded neat with external $CFCl_3$ reference.

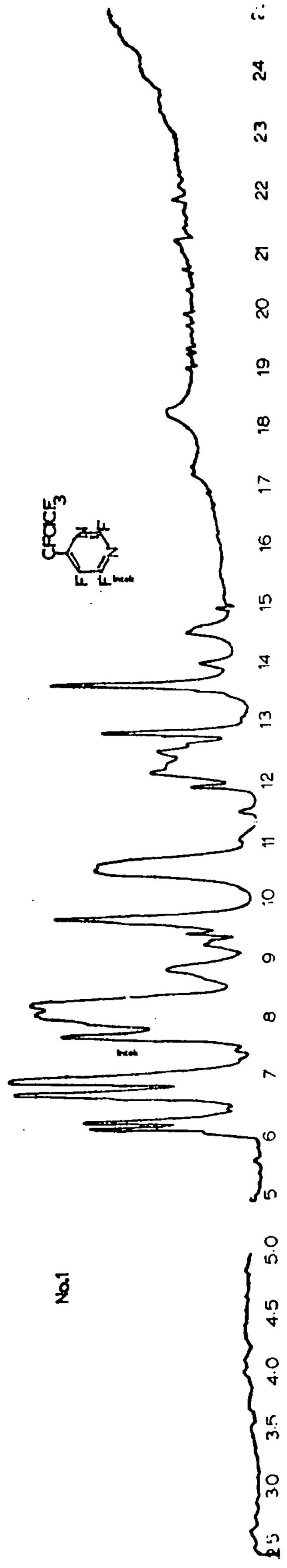
APPENDIX 2

Infra-red Spectra

Solid samples were recorded as KBr discs and liquid or low melting samples as contact films between KBr plates.

Spectrum No.	Compound
1	4-Chlorotetrafluoroethyl-2,5,6-trifluoropyrimidine (106)
2	4,6-Bis-chlorotetrafluoroethyl-2,5-difluoropyrimidine (107)
3	2-Chlorotetrafluoroethyl-4,6-difluoro-S-triazine (102)
4	2,4-Bis-chlorotetrafluoroethyl-6-fluoro-S-triazine (103)
5	*Trans*-1,3-Bis-(2',3',5',6'-tetrafluoropyridyl)—hexafluorobut-1-ene (142)
6	4,5-Bis-(1'-(2",3",5",6"-tetrafluoropyridyl)-tetrafluoroethyl)-3,6-difluoropyridazine (143)
7	*Cis* and *Trans*-1-phenoxy-2-(2',3',5',6'-tetrafluoropyridyl)-difluoroethylene (149) and (150)
8	2-oxa-4-(2'-methoxy-3',5',6'-trifluoropyridyl)-3,3,4-trifluorobutane (151)
9	1,2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane (158)
10	*Cis* and *Trans*-1-chloro-2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane (166) and (167)
11	1-(2',3',5',6'-tetrafluoropyridyl)-2-trifluoromethyl-hexafluorocyclobutane, Isomer A.

Spectrum No.	Compound
12	1-(2',3',5',6'-tetrafluoropyridyl)-2-trifluoromethyl-hexafluorocyclobutane Isomer B.
13	2,2-Bis-trifluoromethyl-3-(2',3',5',6'-tetrafluoropyridyl)-trifluorooxetane (171)
14	Perfluoro-3,4,5,6-tetramethylocta-3,5-diene (181)
15	3-Trifluoromethyl-4-diethylaminofluoromethene-undecafluorohexane (187)
16	Cis and Trans-3-trifluoromethyl-4-(N,N-diethylamido)decafluorohex-3-ene (188) and (189)
17	Trans-4-phenoxy-3,4-bis-trifluoromethyl-nonafluorohex-2-ene (199)
18	Cis-4-phenoxy-3,4-bis-trifluoromethyl-nonafluorohex-2-ene (198)
19	Cis-2-phenoxy-3,4-bis-trifluoromethyl-nonafluorohex-2-ene (200)
20	Cis-4-Methoxy-3,4-trifluoromethylnonafluorohex-2-ene (205)
21	Cis and Trans-perfluoro-2,5-dihydro-tetramethylfuran (206)
22	Perfluoro-tetramethylfuran (207)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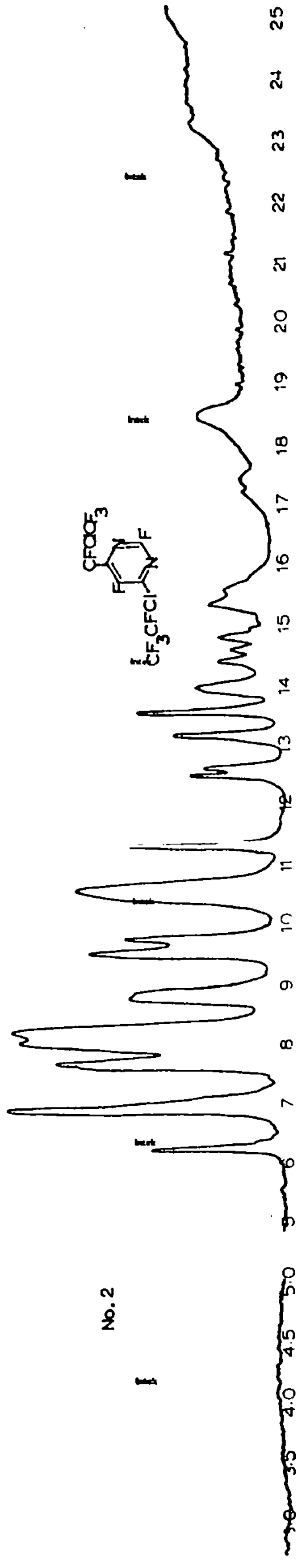
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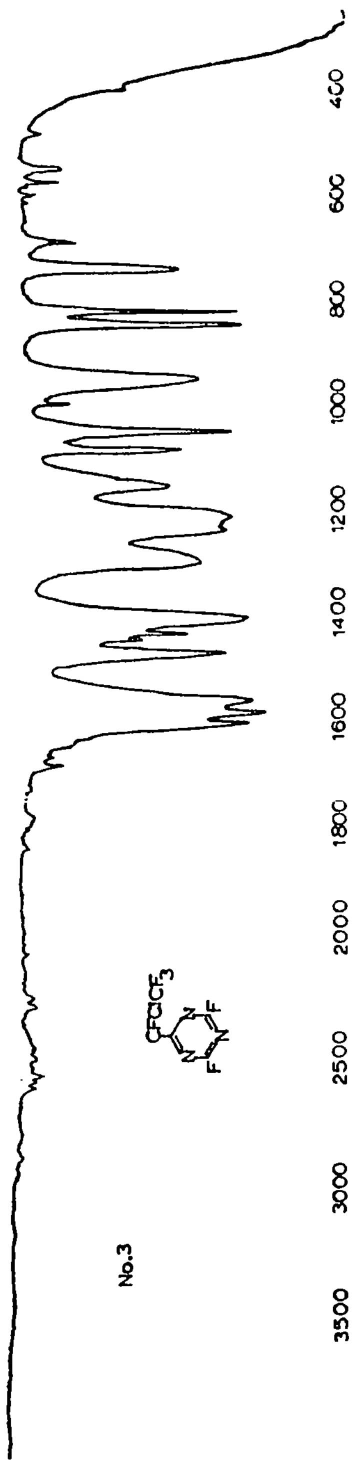
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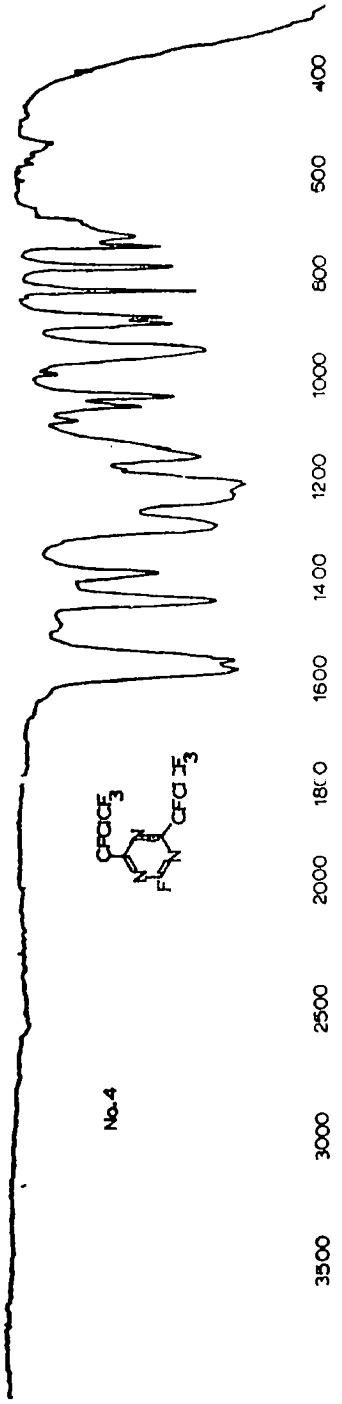
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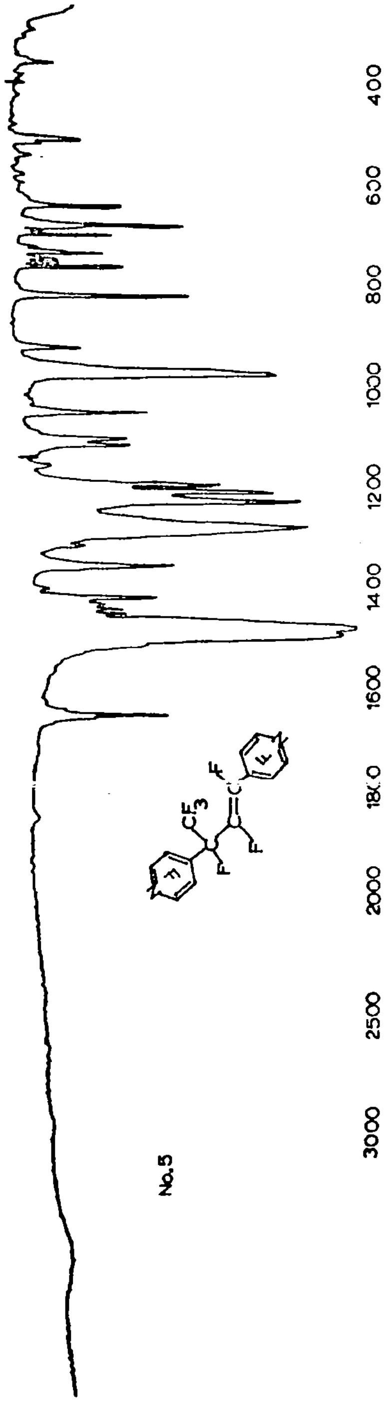
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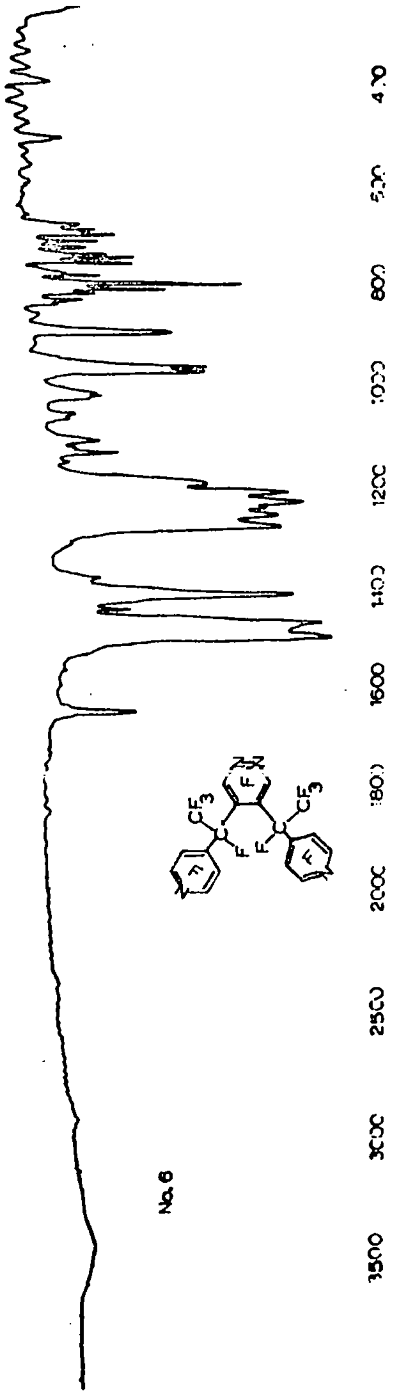
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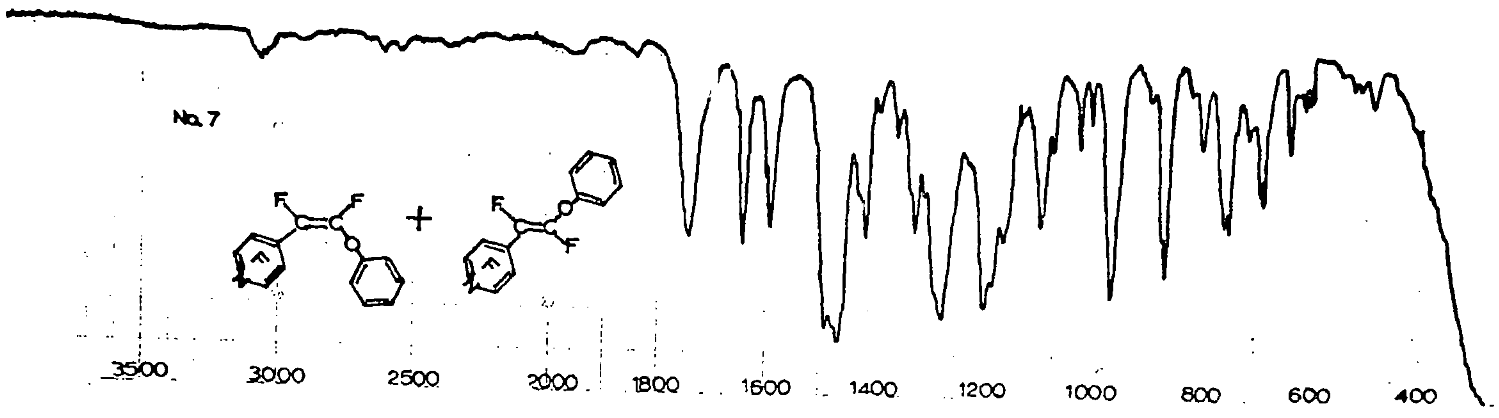
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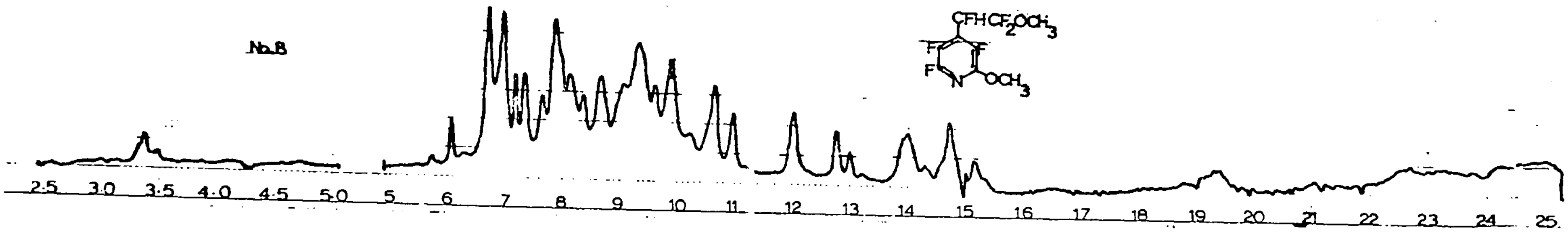
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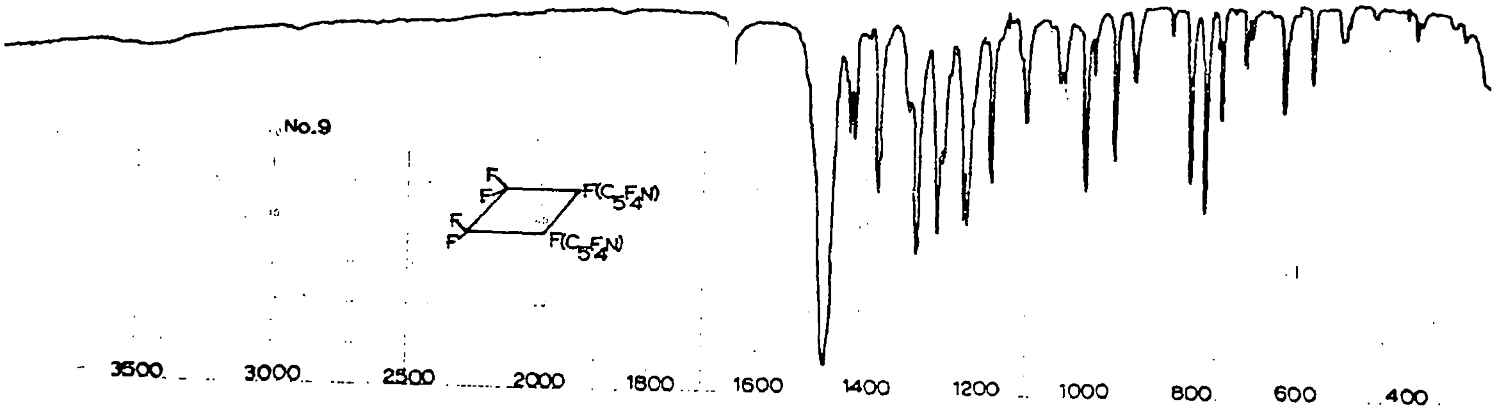
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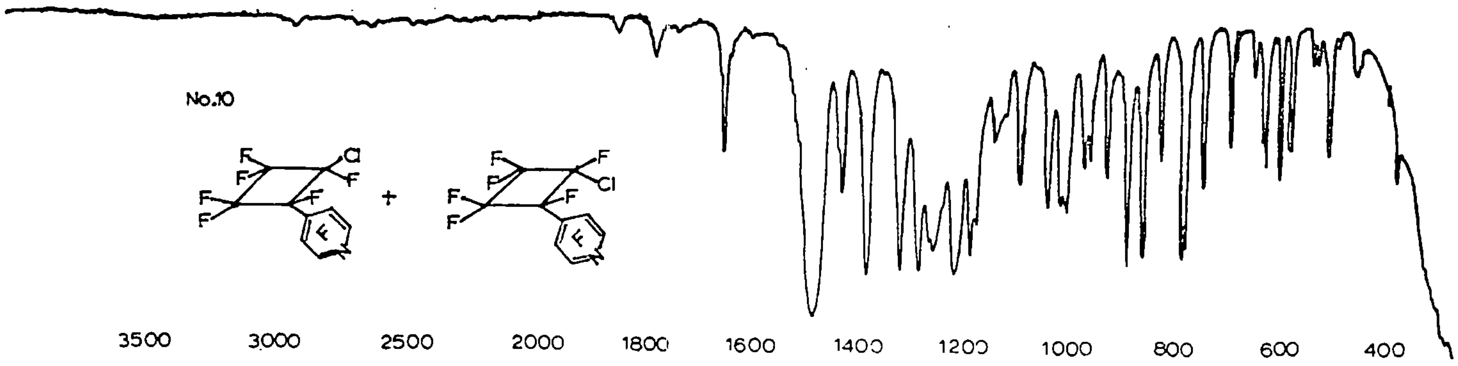

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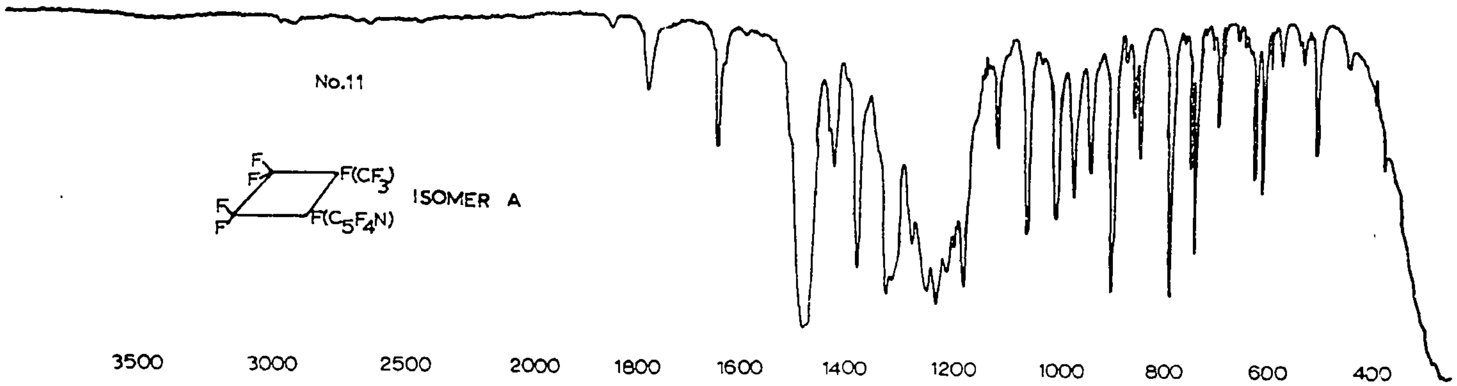

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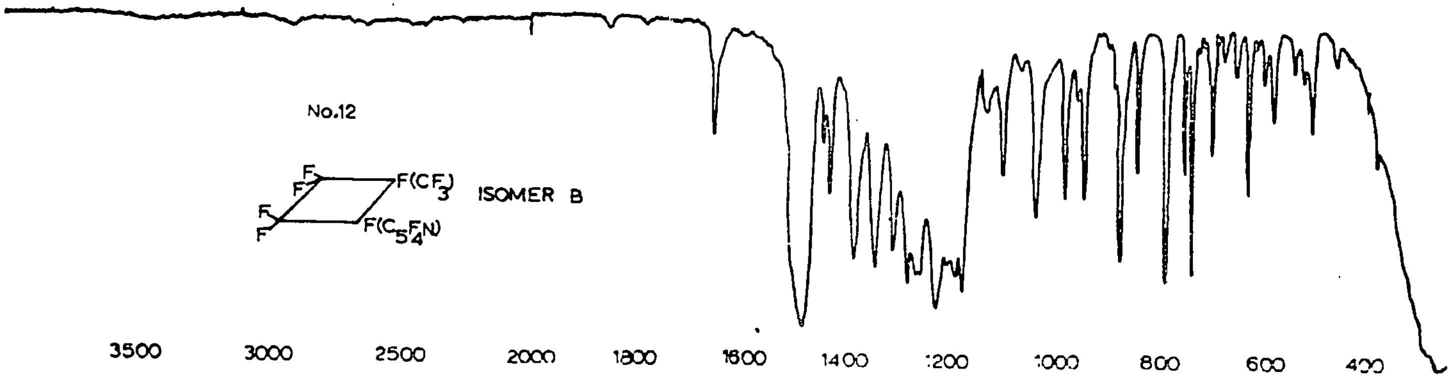

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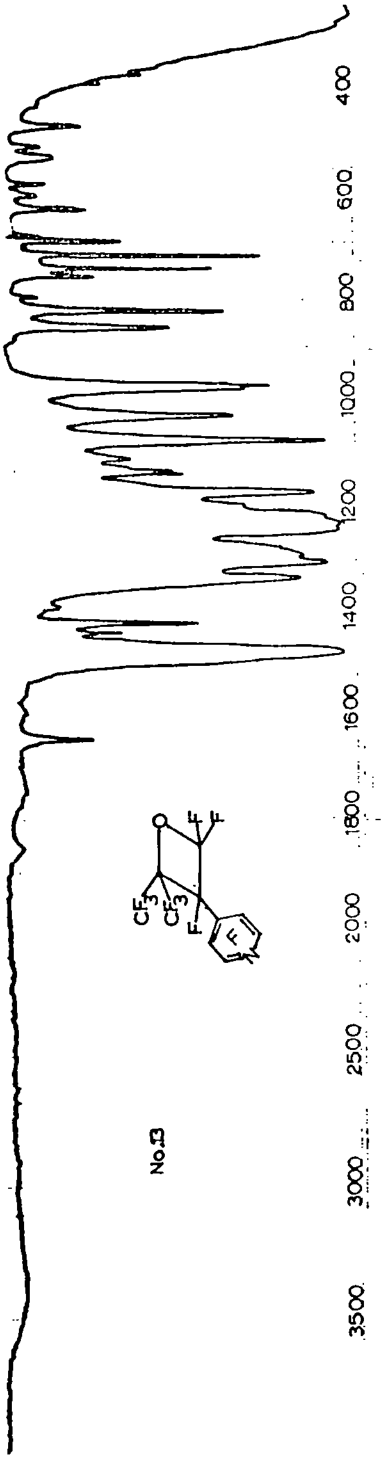

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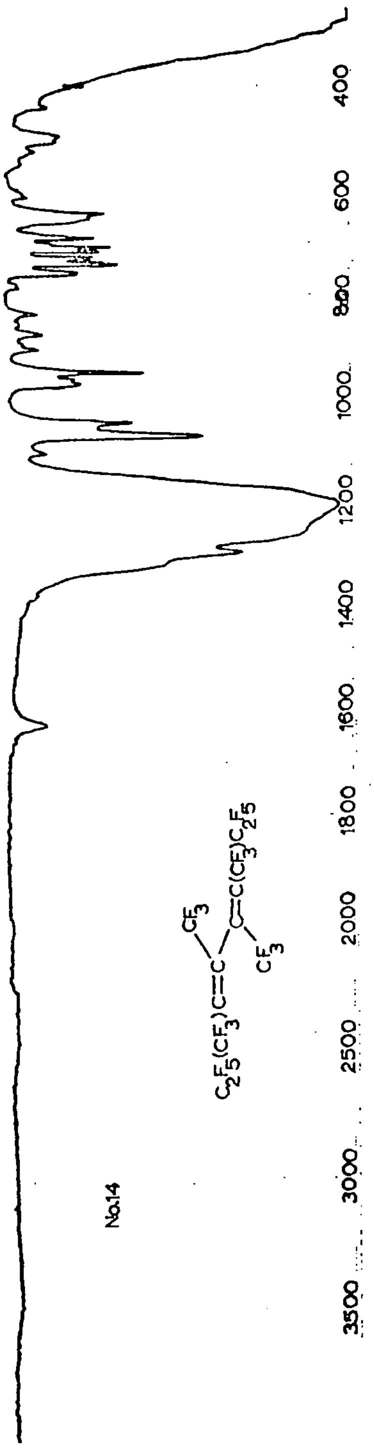

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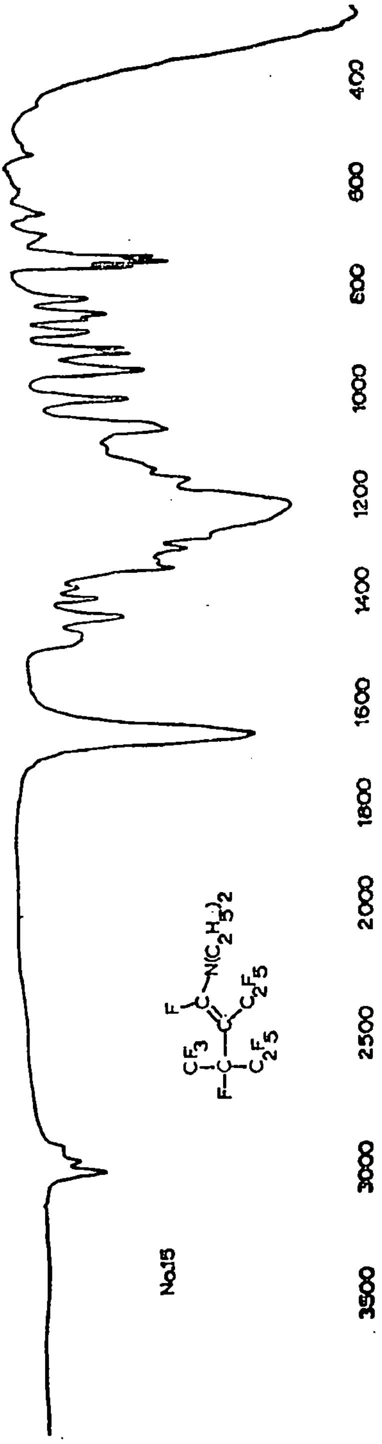

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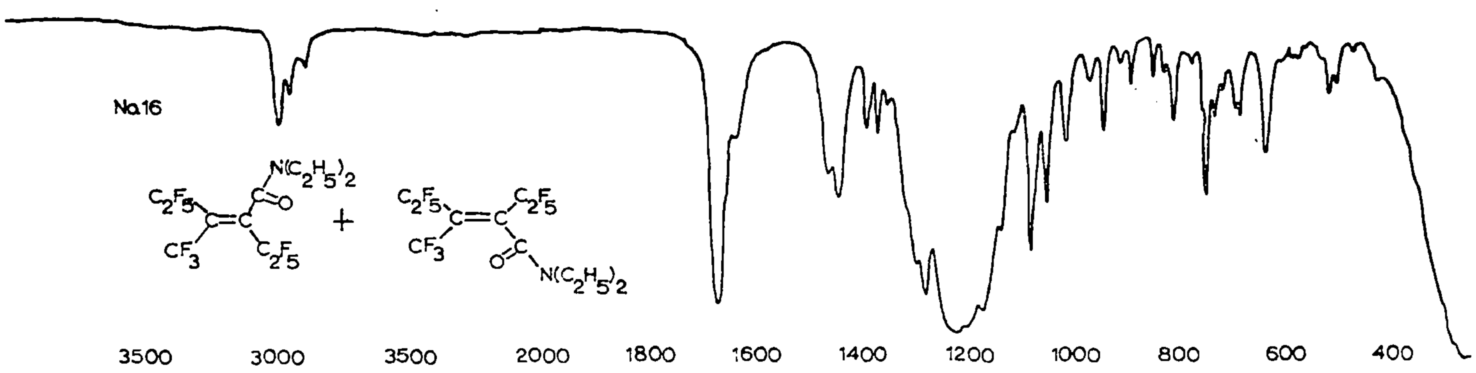

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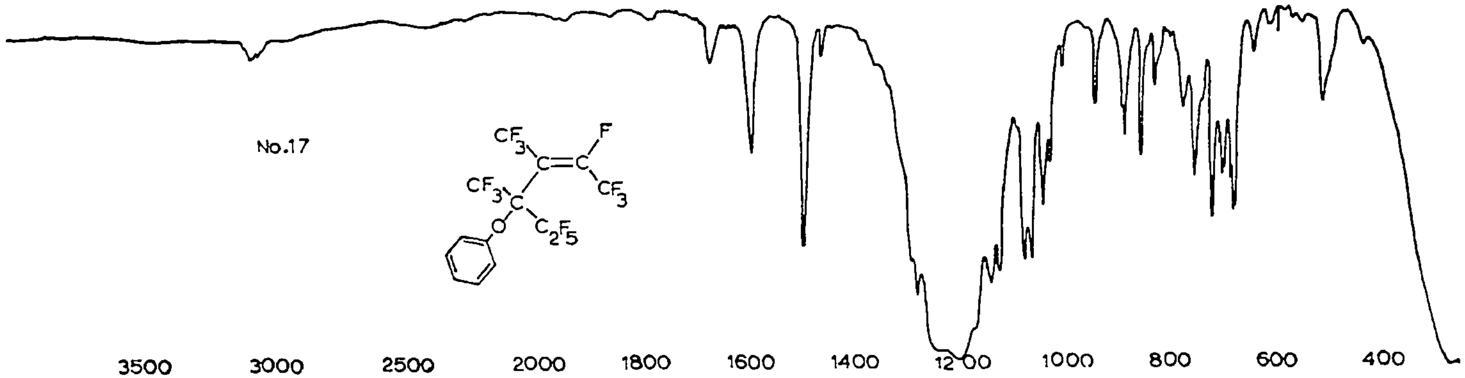

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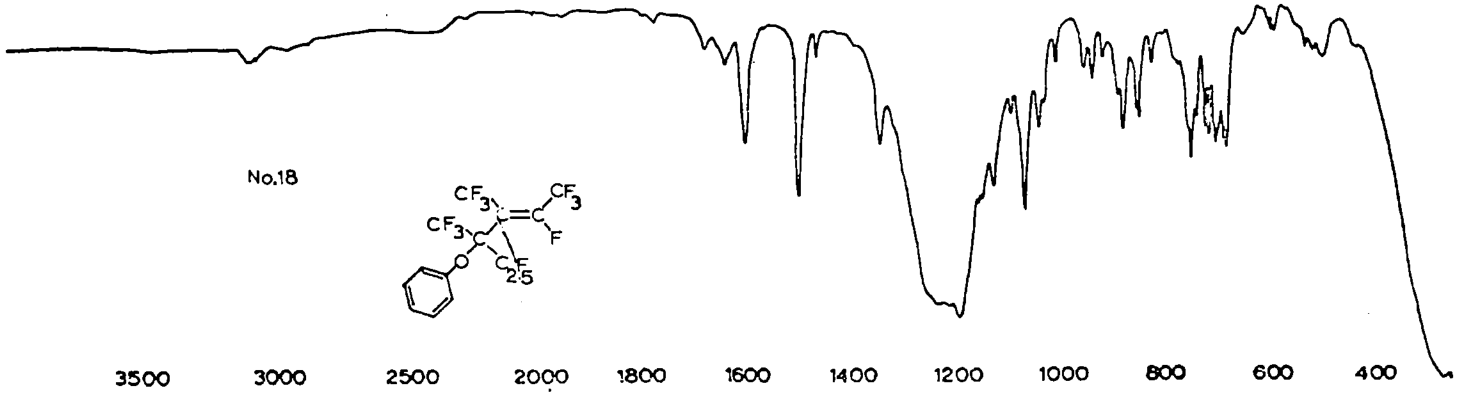

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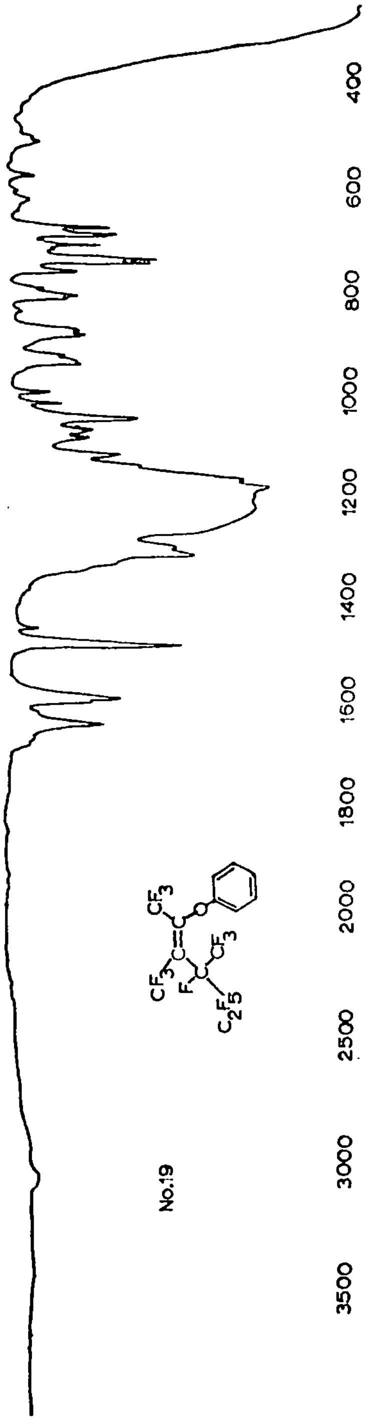

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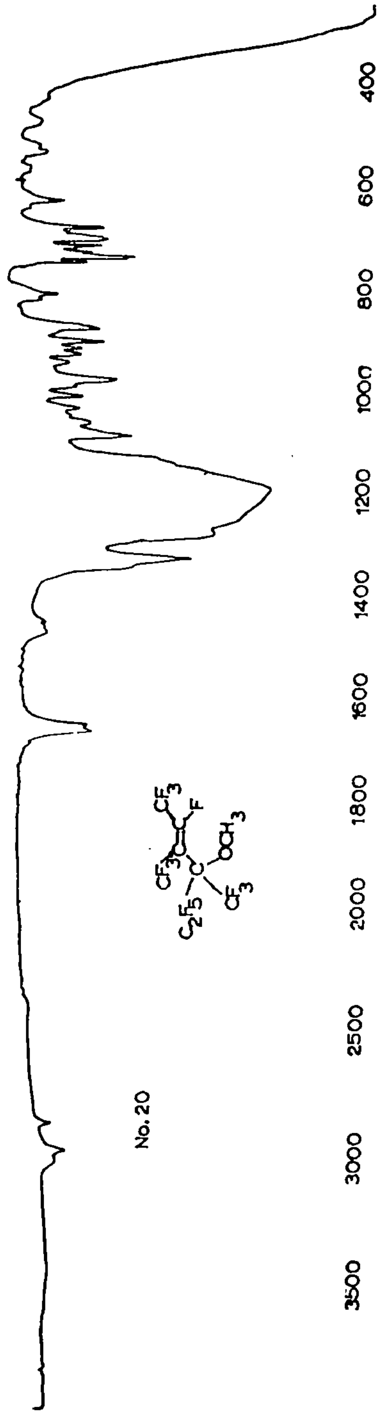

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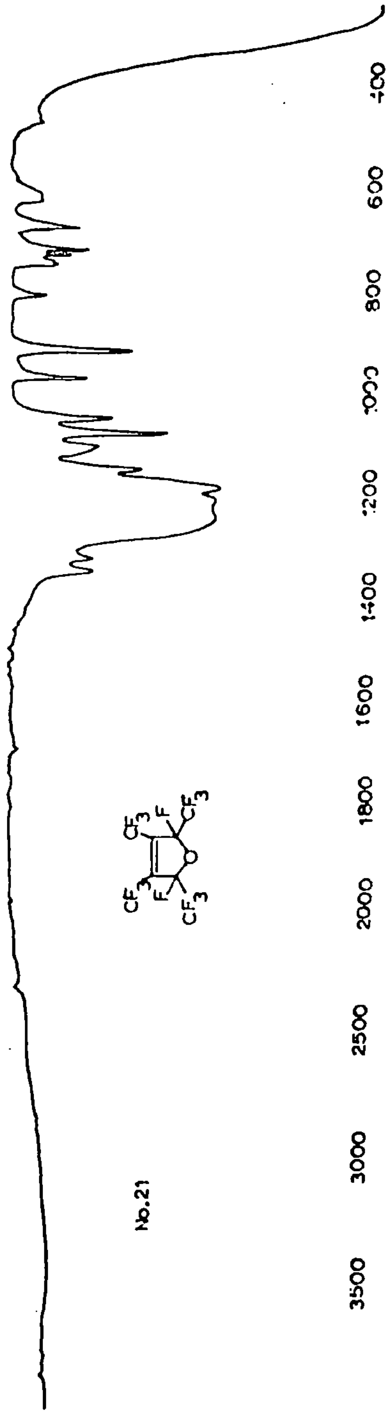

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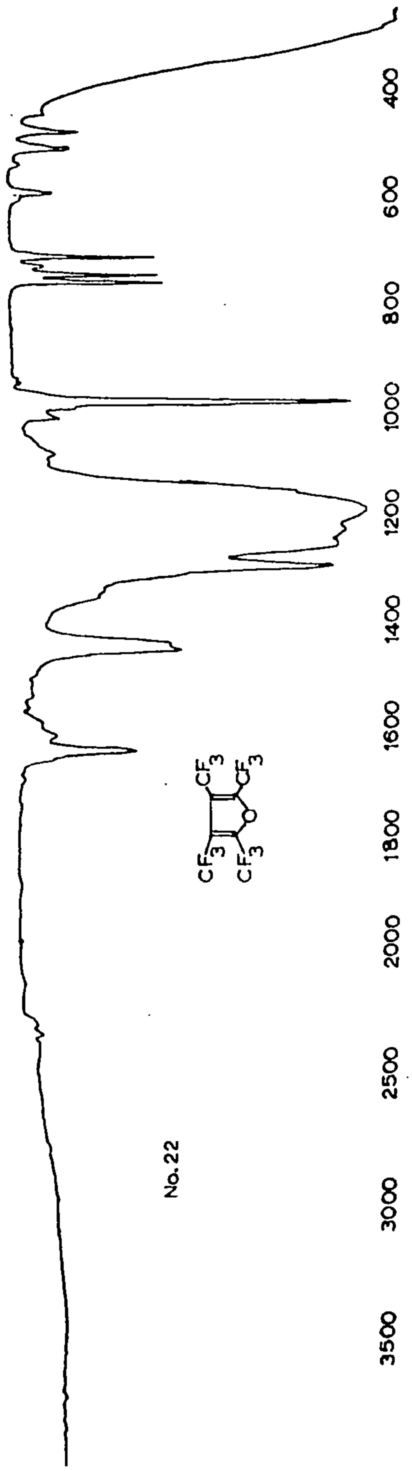
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REFERENCES

REFERENCES

1. R. D. Chambers and R. H. Mobbs, Adv. Fluor. Chem., 1965, 4, 50.
2. B. L. Dyatkin, E. P. Mochalina and I. L. Knunyants, Fluor. Chem. Rev., 1969, 3, 45.
3. W. H. Sharkey, Fluor. Chem. Rev., 1968, 2, 1.
4. J. D. Park, A. F. Benning, F. B. Downing, J. F. Laucius and R. C. McHarness, Ind. Eng. Chem., 1947, 39, 354
5. E. A. Belmore, W. M. Ewalt and B. H. Wajcik, Ind. Eng. Chem., 1947, 39, 338.
6. A. K. Barbour, H. D. Mackenzie, M. Stacey and J. C. Tatlow, J. Appl. Chem.,1954, 4, 347.
7. J. D. Park, W. R. Lycan and J. R. Lacher, J. Amer. Chem. Soc., 1951, 73, 711.
8. A. L. Henne and R. P. Ruh, J. Amer. Chem. Soc., 1947, 69, 279.
9. E. T. McBee, H. M. Hill and G. B. Bachman, Ind. Eng. Chem., 1949, 41, 70.
10. P. B. Sargeant and C. G. Krespan, J. Amer. Chem. Soc., 1969, 91, 415.
11. A. T. Morse, P. B. Ayscough and L. C. Leitch, Canad. J. Chem., 1955, 33, 453.
12. J. A. Young and T. M. Reed, J. Org. Chem., 1967, 32, 1682.
13. J. D. LaZerte, L. J. Hals, T. S. Reid and G. H. Smith, J. Amer. Chem. Soc., 1953, 75, 4525.
14. F. E. Herkes and D. J. Burton, J. Org. Chem., 1967, 32, 1311.

15. D. J. Burton and F. E. Herkes, J. Org. Chem., 1968, 33, 1854.

16. D. G. Naae and D. J. Burton, Syn. Commun., 1973, 3, 197.

17. D. G. Naae, Diss. Abstr. Int., 1973, 5741.

18. B. R. Letchford, C. R. Patrick, M. Stacey and J. C. Tatlow, Chem. and Ind., 1962, 32, 1472.

19. L. A. Wall and J. M. Antonucci, U.S.P. 3,513,206/1970.

20. E. J. Soloski, W. E. Ward and C. Tamborski, J. Fluor. Chem., 1972, 21, 361.

21. J. T. Maynard, J. Org. Chem., 1963, 28, 112.

22. D. Peters, J. Chem. Phys., 1963, 38, 561.

23. H. E. O'Neal and S. W. Benson, J. Phys. Chem., 1968, 72, 1866.

24. J. P. Cheswick, J. Amer. Chem. Soc., 1966, 88, 4800 and references therein.

25. R. D. Chambers, 'Fluorine in Organic Chemistry', Wiley Interscience, 1973, page 143.

26. W. A. Bernett, J. Org. Chem., 1969, 34, 1772 and references therein.

27. M. J. S. Dewar and D. H. Lo, J. Amer. Chem. Soc., 1972, 94, 5296.

28. C. R. Brundle, M. B. Robin, N. A. Keubler and H. Basch, J. Amer. Chem. Soc., 1972, 94, 1451.

29. J. Hine, N. W. Burske, M. Hine and P. B. Langford, J. Amer. Chem. Soc., 1957, 79, 1406.

30. H. G. Adolph and M. J. Maklet, J. Amer. Chem. Soc., 1966, 88, 4761.

31. J. Hine, L. G. Mahone and C. L. Liotta, J. Amer. Chem. Soc., 1967, 89, 5911.

32. A. Streitwieser and F. Mares, J. Amer. Chem. Soc., 1968, 90, 2444.

33. D. T. Clark, J. N. Murrell and J. M. Tedder, J. Chem. Soc., 1963, 1250.

34. D. J. Cram, 'Fundamentals of Carbanion Chemistry', Academic Press, New York, 1965, page 71.

35. S. Andreades, J. A. Chem. Soc., 1964, 86, 2003.

36. (i) D. J. Cram, 'Fundamentals of Carbanion Chemistry', Academic Press, New Yorm, 1965, page 70.

    (ii) K. P. Butin, A. N. Kashin, I. P. Beletskaya, L. S. German and V. R. Polishchuk, J. Organometallic Chem., 1970, 25, 11.

37. I. L. Knunyants, L. S. German and I. N. Rozhkov, Izv. Akad. Nauk. SSSR Ser. Khim., 1966, 1062.

38. J. Hine, R. Wiesboeck and G. Ghirardelli, J. Amer. Chem. Soc., 1961, 83, 1219.

39. A. Streitwieser and D. Holtz, J. Amer. Chem. Soc., 1967, 89, 692.

40. R. D. Chambers, J. S. Waterhouse and D. L. H. Williams, Tetrahedron Lett., 1974, 743.

41. J. Hine and P. B. Langford, J. Org. Chem., 1962, 27, 4149.

42. W. T. Miller, E. W. Fager and P. H. Griswold, J. Amer. Chem. Soc., 1948, 70, 431.

43. D. W. Wiley, U.S.P. 2,988,537/1961.

44. R. D. Chambers, 'Fluorine in Organic Chemistry', Wiley Interscience, 1973, page 150.

45. I. L. Knunyants, A. I. Shchekotikhin and A. V. Fokin, Izv. Akad. Nauk. SSSR. Otdel, Khim. Nauk., 1953, 282.

46. R. N. Sterlin, V. E. Bagachev, R. D. Yatsenko and I. L. Knunyants, Izv. Akad. Nauk. SSSR. Otdel. Khim. Nauk., 1959, 2151.

47. J. D. Park, R. J. McMurtgy and J. H. Adams, Fluor. Chem. Rev., 2, 55.

48. J. Hutchinson, Fette Seifen Anstrichm., 1974, 76, 4, 158.

49. R. D. Chambers, 'Fluorine in Organic Chemistry', Wiley Interscience, 1973, page 151 and references therein.

50. R. D. Chambers, 'Fluorine in Organic Chemistry', Wiley Interscience, 1973, page 1952.

51. H. F. Koch and A. J. Kielbania, J. Amer. Chem. Soc., 9970, 92, 729.

52. D. R. Sayers, R. Stephens and J. C. Tatlow, J. Chem. Soc., 1964, 3035.

53. D. C. England, L. R. Melby, M. A. Dietrich and R. V. Lindsey, J. Amer. Chem. Soc., 1960, 82, 5116.

54. R. C. Terrel, T. Ucciardi and J. F. Vitcha, J. Org. Chem., 1965, 30, 4011.

55. D. J. Burton, R. L. Johnson and R. T. Bogan, Canad. J. Chem., 1966, 44, 635.

56. W. T. Miller and A. H. Fainberg, J. Amer. Chem. Soc., 1957, 79, 4164.

57. J. H. Fried and W. T. Miller, J. Amer. Chem. Soc., 1959, 81, 2078.

58. H. Goldwhite and C. M. Valdez, Chem. Comms., 1969, 7.

59. J. D. Park, J. R. Lacher and J. R. Dick, J. Org. Chem., 1966, 31, 1116 and references therein.

60. J. A. Young, Fluor. Chem. Rev., 1967, 1, 359 and references therein.

61. C. G. Krespan, J. Org. Chem., 1962, 27, 1813.

62. F. S. Fawcett, C. W. Tullock and D. D. Coffman, J. Amer. Chem. Soc., 1962, 84, 4275.

63. D. P. Graham and W. B. McCormack, J. Org. Chem., 1966, 31, 958.

64. D. P. Graham and V. Weinmayr, J. Org. Chem., 1966, 31, 957.

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

66. R. D. Chambers, 'Fluorine in Organic Chemistry', Wiley Interscience, 1973, page 296 and references therein.

67. R. D. Chambers, R. P. Corbally and W. K. R. Musgrave, J. Chem. Soc. (Perkin I), 1972, 1281.

68. R. D. Chambers, M. Y. Gribble and E. Marper, J. Chem. Soc. (Perkin I), 1973, 1710.

69. W. T. Miller, W. Frass and P. R. Resnick, J. Amer. Chem. Soc., 1961, 83, 1767.

70. R. D. Dresdner, F. N. Tlumac and J. A. Young, J. Org. Chem., 1965, 30, 3524.

71. P. H. Ogden and R. A. Mitsch, J. Amer. Chem. Soc., 1967, 89, 5007.

72. R. E. Banks, M. G. Barlow, W. R. Deem, R. N. Haszeldine and D. R. Taylor, J. Chem. Soc. (C), 1966, 981.

73. D. P. Graham, J. Org. Chem., 1966, 31, 955.

74. H. C. Fielding and A. J. Rudge, B.P. 1,082,127/1967.

75. W. Brunskill, W. T. Flowers, R. Gregory and R. N. Haszeldine, J. Chem. Soc. (D), 1970, 1444.

76. T. Martini and S. P. Van Halasz, Ger. Tetrahedron Lett., 1974, 24, 2129.

77. D. L. Miller, U.S.P. 3,389,187/1968.

78. R. L. Pruett, C. T. Bahner and H. A. Smith, J. Amer. Chem. Soc., 1952, 74, 1638.

79. M. J. R. Fraticelli, Ph.D. Thesis, Cornell University, Ithica N.Y., 1965.

80. D. T. Clark, R. D. Chambers and D. B. Adams, J. Chem. Soc., Perkin Trans. 1, 1975, 647.

81. A. L. Henne and R. C. Arnold, J. Amer. Chem. Soc., 1948, 70, 758.

82. D. D. Coffman, R. Gramer and G. W. Rigby, J. Amer. Chem. Soc., 1949, 71, 979.

83. D. C. England, M. A. Dietrich and R. V. Lindsey, J. Amer. Chem. Soc., 1960, 82, 6181.

84. A. V. Fokin, Yu. N. Studnev and L. D. Kuznetsova, Izv. Akad. Nauk. SSSR. Ser. Khim., 1974, 471.

85. I. L. Knunyants, L. S. German and I. N. Rohkov, Izv. Akad. Nauk. SSSR. Ser. Khim., 1963, 1946.

86. G. G. Belen'kii and L. S. German, Izv. Akad. Nauk. SSSR. Ser. Khim., 1974, 942.

87. R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 1957, 2800.

88. J. F. Harris and F. W. Stacey, J. Amer. Chem. Soc., 1961, 83, 840.

89. R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 1957, 2193.

90. F. W. Stacey and J. F. Harris, Organic Reactions, 13, 150.

91. D. S. Ashton, D. J. Shand, J. M. Tedder and J. C. Walton, *J. Chem. Soc. (Perkin II)*, 1975, 320 and references therein.

92. R. N. Haszeldine, J. R. McAllister and A. E. Tipping, J. Chem. Soc. (Perkin I), 1974, 1303.

93. G. L. Fleming, R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc. (Perkin I)*, 1973, 575.

94. H. Muramatsu, S. Mariguchi and K. Inukai, *J. Org. Chem.*, 1966, *31*, 1306.

95. J. D. LaZerte and R. J. Koshar, *J. Amer. Chem. Soc.*, 1955, *77*, 910.

96. G. W. Parshall, D. C. England and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1959, *81*, 4801.

97. G. Haran and D. W. A. Sharp, *J. Chem. Soc. (Perkin I)*, 1972, 34.

98. R. D. Chambers, J. Hutchinson, R. H. Mobbs and W. K. R. Musgrave, *Tetrahedron*, 1964, 497.

99. H. G. Bryce, *Fluor. Chem.*, 1964 *5*, 297.

100. J. Harmon, *U.S.P.* 2,404,374/1946.

101. R. B. Woodward and R. Hoffman, '*The Conservation of Orbital Symmetry*', Academic Press, 1970, page 67.

102. E. E. Lewis and M. A. Naylor, *J. Amer. Chem. Soc.*, 1947, *69*, 1968.

103. J. D. Park, H. V. Holler and J. R. Lacher, *J. Org. Chem.*, 1960, *25*, 990.

104. R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1764.

105. P. D. Bartlett, L. K. Montgomery and B. Seidel, *J. Amer. Chem. Soc.*, 1964, *84*, 616.

106. P. D. Bartlett, G. M. Cohen, S. P. Elliot, K. Hummel, R. A. Minns, C. M. Sharts and J. Y. Fukunaga, J. Amer. Chem. Soc., 1972, 94, 2899.

107. P. D. Bartlett, K. Hummel, S. P. Elliot and R. A. Minns, J. Amer. Chem. Soc., 1972, 94, 2898.

108. R. Wheland and P. D. Bartlett, J. Amer. Chem. Soc., 1973, 95, 4003.

109. J. D. Roberts and C. M. Sharts, Organic Reactions, 12, 1.

110. P. L. Barrick, U.S.P. 2,427,116/1947.

111. M. Hauptschein, A. H. Fainberg and M. Braid, J. Amer. Chem. Soc., 1958, 80, 842.

112. D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, J. Amer. Chem. Soc., 1949, 71, 490.

113. M. Y. Gribble, Ph.D. Thesis, Durham, 1972.

114. R. D. Chambers and M. Y. Gribble, J. Chem. Soc. (Perkin I), 1973, 1411.

115. R. A. Storey, Ph.D. Thesis, Durham, 1967.

116. J. A. Jackson, Ph.D. Thesis, Durham, 1968.

117. R. D. Chambers, R. P. Corbally, J. A. Jackson and W. K. R. Musgrave, Chem. Comm., 1969, 271 and references therein

118. R. D. Chambers and M. Y. Gribble, J. Chem. Soc. (Perkin I), 1973, 1405.

119. R. D. Chambers, R. A. Storey and W. K. R. Musgrave, Chem. Comm., 1966, 384.

120. C. J. Drayton, W. T. Flowers and R. N. Haszeldine, J. Chem. Soc. (C), 1971, 2750.

121. D. B. Speight, Ph.D. Thesis, Durham, 1974.

122. J. S. Waterhouse, Personal Communication.

123. E. M. Smolin and L. Rapoport, '<u>S-Triazines and Derivatives</u>', Interscience Publishers Inc., 1959, page 24.

124. J. A. Young and R. L. Dressler, <u>U.S.P.</u> 3,525,746/1970.

125. A. C. Young, Personal Communication.

126. R. D. Hercliffe, Personal Communication.

127. J. W. Emsley, J. Feeney and L. H. Sutcliffe, '<u>High Resolution Nuclear Magnetic Resonance Spectroscopy</u>' <u>Vol. 2</u>, Pergamon Press, 1966, page 891.

128. R. D. Chambers, '<u>Fluorine in Organic Chemistry</u>', Wiley Interscience, 1973, page 103.

129. R. D. Chambers, Personal Communication.

130. R. D. Chambers, '<u>Fluorine in Organic Chemistry</u>', Wiley Interscience 1973, page 263 and references therein.

131. C. Tamborski, E. J. Soloski and R. J. De Pasquale, <u>J. Organometallic Chem</u>. 1968, <u>15</u>, 494.

132. J. W. Emsley, J. Feeney and L. H. Sutcliffe, '<u>High Resolution Nuclear Magnetic Resonance Spectroscopy</u>', <u>Vol. 2</u>, Pergamon Press, 1966, page 908.

133. T. F. Holmes, Personal Communication.

134. R. D. Chambers, Yu. A. Cheburkov, J. A. H. Macbride and W. K. R. Musgrave, <u>J. Chem. Soc. (C)</u>, 1971, 532.

135. R. D. Chambers, Personal Communication.

136. J. Dyer and J. Lee, <u>Trans. Farad. Soc</u>., 1966, <u>62</u>, 257.

137. A. L. Henne and R. P. Ruh, <u>J. Amer. Chem. Soc</u>., 1947, <u>69</u>, 279.

138. T. F. Holmes, Personal Communication.

139. B. Atkinson and M. Stedman, J. Chem. Soc., 1962, 512.

140. R. D. Chambers, D. T. Clark, T. F. Holmes, W. K. R. Musgrave and I. Ritchie, J. Chem. Soc. (Perkin I), 1974, 114.

141. R. D. Chambers, 'Fluorine in Organic Chemistry', Wiley Interscience, 1973, page 183.

142. B. Atkinson and P. B. Stockwell, J. Chem. Soc. (B), 1966, 740.

143. E. R. Bissel and D. B. Fields, J. Org. Chem., 1964, 29,

144. P. D. Bartlett and G. M. Cohen, J. Amer. Chem. Soc., 1973, 95, 7923.

145. H. C. Fielding, B.P. 1,151,601/1969.

146. H. C. Fielding, B.P. 1,176,492/1970.

147. R. D. Chambers, J. A. Jackson, S. Partington, P. D. Philpot, and A. C. Young, J. Fluor. Chem., 1975, 6, 5.

148. Unpublished results obtained from these laboratories.

149. E. W. Schlag and E. W. Kaiser, J. Amer. Chem. Soc., 1964, 86, 1676.

150. R. D. Chambers, S. Partington and D. B. Speight, J. Chem. Soc. (Perkin I), 1974, 2673.

151. G. Tsukamoto and N. Ishikawa, Chem. Letts., 1972, 577.

152. W. T. Flowers, R. N. Haszeldine, C. R. Owen and A. Thomas, Chem. Comm., 1974, 134.

153. H. H. Evans, R. Fields, R. N. Haszeldine and M. Illingworth, J. Chem. Soc. (Perkin I), 1973, 649.

154. J. Hutchinson, B.P. 1,370,024/1974.

155. J. W. Emsley, J. Feeney and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Vol. 2, Pergamon Press, 1966, page 881.

156. D. W. Brown, J. M. Antonucci and L. A. Wall, *Polym. Prep. Amer. Chem. Soc., Div. Polym. Chem.*, 1968, *9*, 1278.

157. J. F. Harris and D. D. Coffman, *J. Amer. Chem. Soc.*, 1962, *84*, 1553.

158. A. H. Lovelace, W. Postelnek and D. A. Rausch, '*Aliphatic Fluorine Compounds*', Reinhold, New York, 1958.

159. R. D. Chambers, J. Hutchinson and W. K. R. Musgrave, *J. Chem. Soc.*, 1964, 3573.

160. R. D. Chambers, J. A. H. MacBride and W. K. R. Musgrave, *Chem. and Ind.*, 1966, 1721.

161. R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1968, 2116.

162. R. E. Banks, F. Cuthbertson and W. K. R. Musgrave, *Anal. Chim. Acta.*, 1955, *13*, 442.

163. (i) P. L. Coe, A. E. Jukes and J. C. Tatlow, *J. Chem. Soc. (C)*, 1966, 2323.

     (ii) P. L. Coe and A. E. Jukes, *Tetrahedron*, 1968, *24* 5913.

diene.

$$\underset{45\%}{(179)} + \underset{12\%}{(184)} + \underset{15\%}{(180)} \xrightarrow[\text{Reflux}]{\text{CsF/Sulpholane}} \underset{65\%}{(179)} + \underset{13\%}{(184)} + \underset{22\%}{(180)}$$

+ others

The compound (180) was probably formed via a fluoride ion-initiated reaction rather than an intramolecular cycloaddition. Further evidence against a cycloaddition reaction was obtained when no increase in the percentage of (180) was observed on heating a mixture of dienes and (180) in a Carius tube.

$$\text{Dienes} + (180) \xrightarrow[\text{Carius Tube}]{300^{\circ}} \text{No change}$$

VII.B.1.a Determination of Structures

The mass spectrum of the defluorinated (176) showed a large peak at $^{M}/e$ 343, consistent with P-19 for the dienes, and the structure of the two dienes, (179) and (184), plus the cyclobutene (180) were determined from the n.m.r. spectra of enriched samples.

The n.m.r. spectrum of the diene (179) showed the presence of two different $CF_3{>}C{=}$ groups and a vinylic fluorine, with the lowfield $CF_3{>}C{=}$ peak consisting of a doublet, having a coupling constant expected for $CF_3{>}C{=}C{<}^{F}$ (Table 35), a spectrum consistent with structure (179).