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MODEL COMPOUNDS FOR FLUORINATED POLYMERS AND FLUIDS

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UNIVERSITY OF DURHAM, DURHAM CITY, ENGLAND

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FOREWORD

This report was prepared by the University of Durham, Durham City, England, on Air Force Contract No. F61052-69-C-0010. The contract was initiated under Project 7342 "Fundamental Research on Macromolecular Materials and Lubrication", Task 734201 "Basic Factors in the Synthesis of Macromolecular Materials" and was administered by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433, with Dr. Christ Tamborski (AFML/MBP) as Project Scientist.

This report covers work from 1 January 1969 to 31 December 1971.

This technical report has been reviewed and is approved.

R L Van Deusen

R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

This work is concerned with the preparation of model compounds based on the reactions of tetrafluoropyridazine and pentafluoropyridine with fluorinated olefins, acetylenes or ketones. The compounds which have been synthesized have been tested as to their thermal and oxidative stability.

TABLE OF CONTENTS

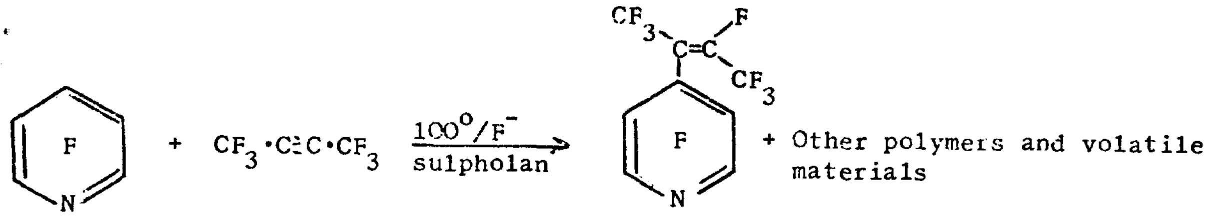
A. Introduction

The object of this work is to make model compounds based on the reactions of tetrafluoropyridazine and pentafluoropyridine with fluorinated olefins, acetylenes, or ketones to see whether they, and consequently any higher molecular weight derivatives are thermally and oxidatively stable.

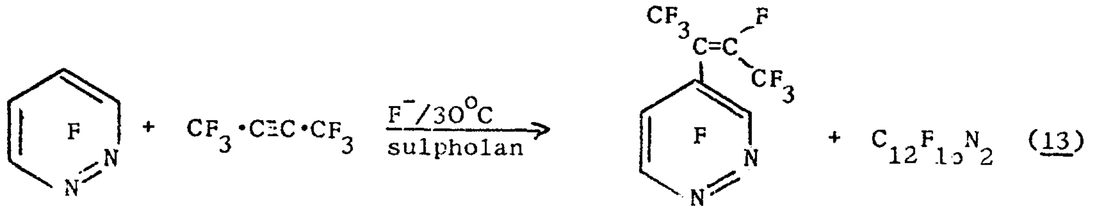
B. Summary

Alkenyl Compounds.

We have previously found that low yields of perfluoro-4-(2'-butenyl)-pyridine (12) and perfluoro-4-(2'-butenyl)-pyridazine were obtained when hexafluorobut-2-yne reacted with the corresponding heterocycle in a fluoride-ion process.



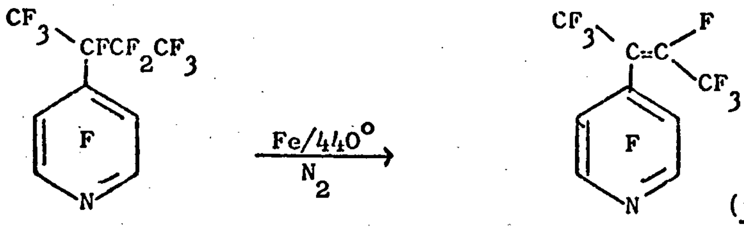
(12) 10%



(10) 10%

We now report the preparation of (10) and (12) by defluorination techniques of the corresponding perfluoro-4-(sec.butyl)-heterocycle, in high yield

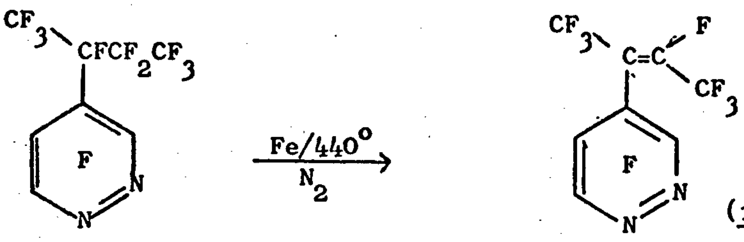
(30)



(12) 80%

and

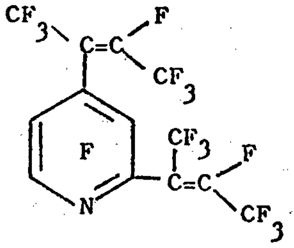
(31)



(10) 45%

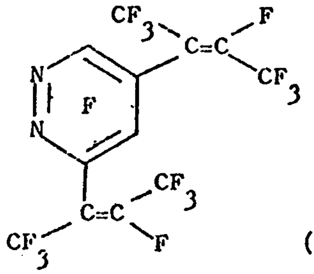
The preparation of the perfluoro sec.butyl compounds is also described as well as their ^{19}F n.m.r. spectra.

Preliminary defluorination experiments involving the di-substituted perfluoro sec.butyl compounds (39) and (40), to give the corresponding perfluoro-di-(2'butenyl) compounds, have been carried out, but extensive decomposition and the formation of mixtures occurred. Nevertheless, the i.r. spectra of the defluorination mixtures contain an absorption at 5·8μ, corresponding to C=C, showing that compounds of the type



(32)

and

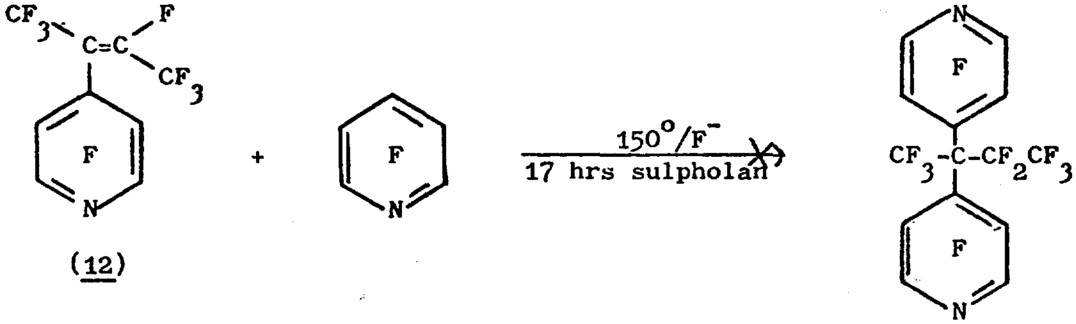


(33)

may be formed.

Perfluoro-4-(2'-butenyl)-pyridine (12) does not react with hexafluorobut-2-yne in the presence of fluoride-ion in a chain extension process. This indicates that the formation of the polyfluoropolyene derivatives of pentafluoropyridine, isolated from the fluoride-ion initiated reaction of pentafluoropyridine with hexafluorobut-2-yne, does not occur via perfluoro-4-(2'-butenyl)-pyridine.

Pentafluoropyridine has been reacted with perfluoro-4-(2'-butenyl)-pyridine in an attempt to produce the perfluoro bipyridyl ethane (34)

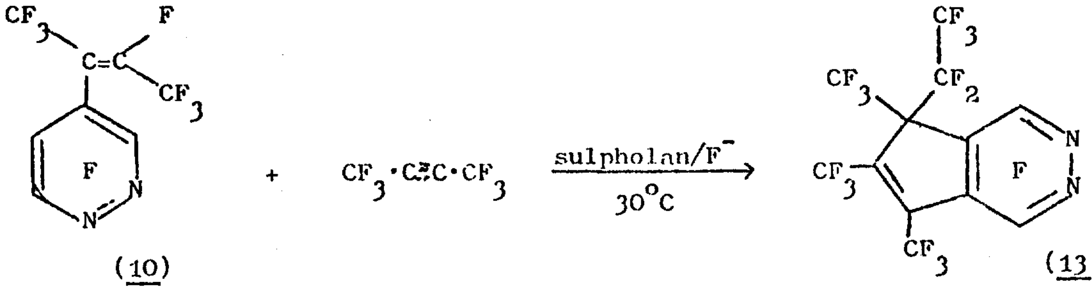


(12) (34)

Under the condition used so far no evidence for the formation of (34) has been found.

Attempts to polymerise perfluoro-4-(2'-butenyl)-pyridine (12) alone, and in the presence of hexafluoroprop-2-ene to form a co-polymer, by means of high energy radiation have been unsuccessful.

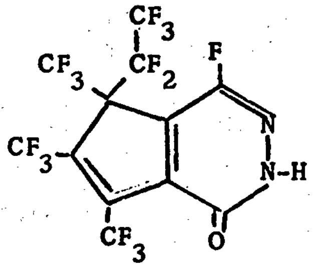
Perfluoro-4-(2'-butenyl)-pyridazine (10) reacts with hexafluorobut-2-yne, in contrast with (12), to form the cyclic compound (13) in good yield.



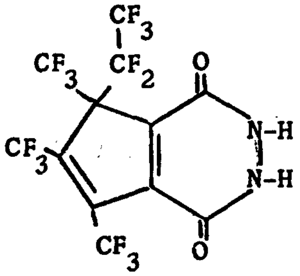
(10) (13)

This indicates that for this system the perfluoro butenyl pyridazine (10) is an intermediate in the formation of the cyclic structure in the fluoride-ion catalysed reaction between hexafluorobut-2-yne and tetrafluoropyridazine.

The structure of (13) has been established using structural data obtained from the two hydrolysis products (25) and (26).

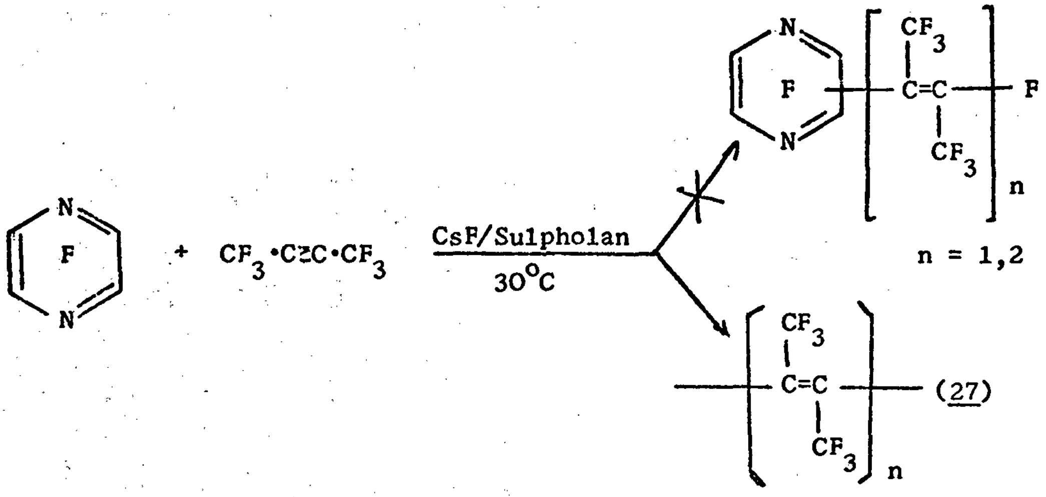


(25)



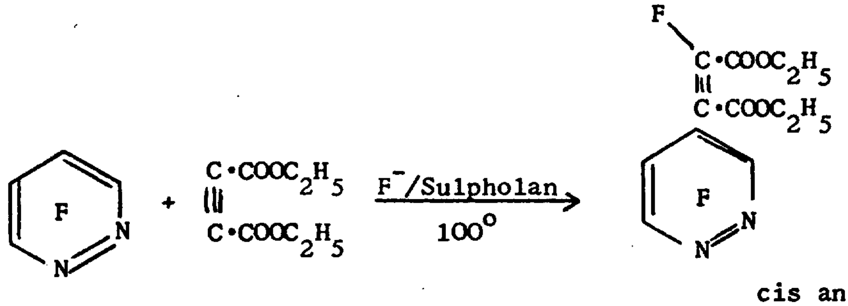
(26)

The use of tetrafluoropyrazine, rather than perfluoropyridine and tetrafluoropyridazine, in fluoride-ion-initiated reactions of hexafluorobut-2-yne, has yielded the polymer (27).



(27)

Diethyl acetylene dicarboxylate reacts with tetrafluoropyridazine, in the presence of caesium fluoride to give a mixture of cis and trans 1-fluoro-1,2-(biscarbethoxy)-2-(3,5,6-trifluoropyridazyl)ethylene.



(28)

cis and trans

Polyethers

A number of reactions between $(CF_3)_2CFOM$ (M = K or Cs) and perfluoropyridazine, have given ill-defined, high molecular-weight, hydrolysis products which we have been unable to characterize.

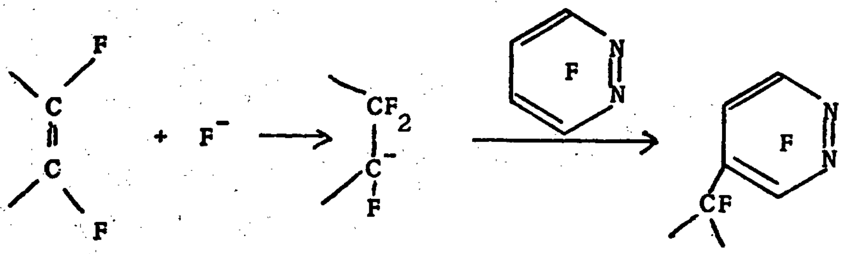
Perfluoro(methylpyridines).

Electron withdrawing groups in the 3,5-positions of pentafluoropyridine should enhance nucleophilic attack in the ortho- and para-positions so producing substrates for polymer formation more active than pentafluoropyridine. Perfluoro(3-methylpyridine) and perfluoro(3,5-dimethylpyridine) have been prepared and their reactivities to attack by the heptafluoroisopropyl anion have been compared with that of pentafluoropyridine. The order of reactivity is pentafluoropyridine   perfluoro(3,5-dimethylpyridine)   perfluoro(3-methylpyridine) and is rationalised in terms of the steric as well as electronic factor associated with the trifluoromethyl-group.

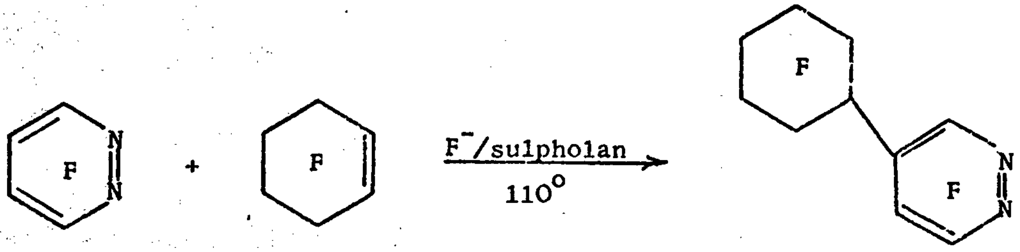
Perfluorocycloalkyl Derivatives of Fluorinated Nitrogen Heterocycles.

Work so far has indicated that these compounds can be synthesised by fluoride ion-induced reactions but the molecular weights of the systems produced have not been sufficiently high. One approach to increasing molecular weight lies in using more reactive heterocycles so that either (a) poly-substitution occurs directly or (b) reactive sites remain which can be exploited by reaction with other nucleophiles to increase molecular weight e.g. formation of poly-ether derivatives.

This report contains a preliminary survey of reactions of perfluorocycloalkenes with tetrafluoropyridazine, which is the most reactive of the nitrogen heterocycles synthesised in these laboratories.



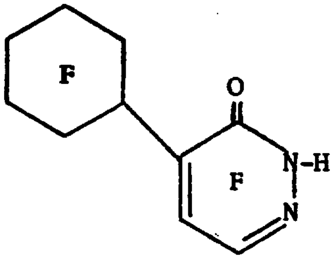
Perfluoro-(4-cyclohexylpyridazine) (XXIX) was isolated in 70% yield when equimolar amounts of tetrafluoropyridazine and perfluorocyclohexene (I) were heated at 110° for 19 hours with caesium fluoride and sulpholan.



(I)

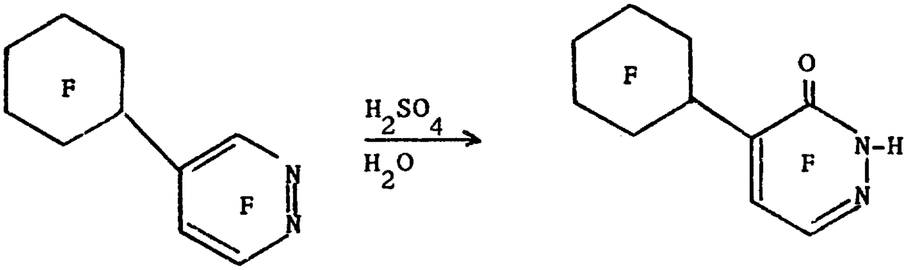
(XXIX)

The corresponding amino-derivative of (XXIX) was isolated but attempts to isolate higher substituted products were unsuccessful. In fact, solvent extraction of the involatile products from the reaction of tetrafluoropyridazine and an excess of perfluorocyclohexene (I) produced the corresponding pyridazone (XXX).



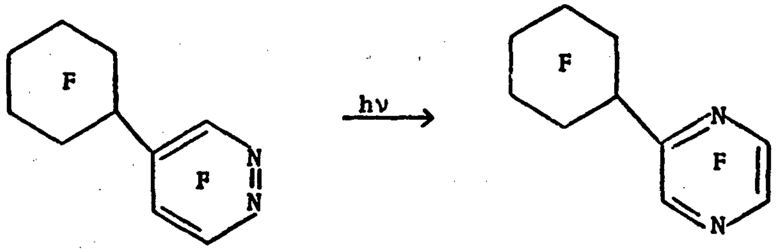
(XXX)

Also, hydrolysis of perfluoro-(4-cyclohexylpyridazine) (XXIX) with concentrated sulphuric acid gave (XXXII).



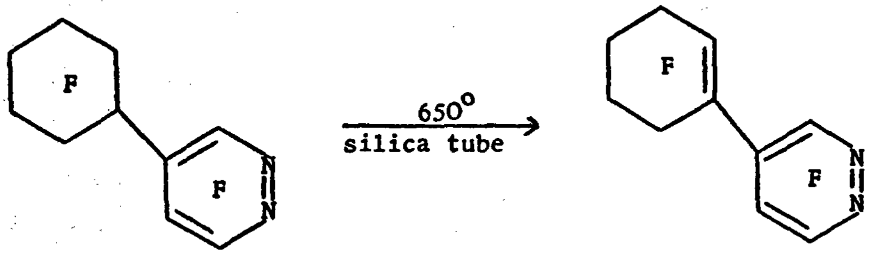
(XXIX) (XXXII)

Photolysis of perfluoro-(4-cyclohexylpyridazine) (XXIX) with u.v. light gave the pyrazine derivative (XXXV),



(XXIX) (XXXV)

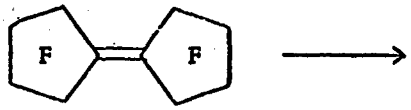
whereas the attempted pyrolysis of (XXIX) at 650° gave perfluoro-(4-cyclohexenylpyridazine) (XXXIII), and not a pyrimidine as expected.



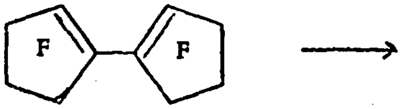
(XXIX) (XXXIII)

Reactions of the Oligomers of Perfluorocycloalkenes.

The derivatives of perfluorocyclopentene, $C_{10}F_{16}$ (VIII) and $C_{10}F_{14}$ (IX), were irradiated with u.v. light for extended periods, but there was no evidence of any rearrangement.

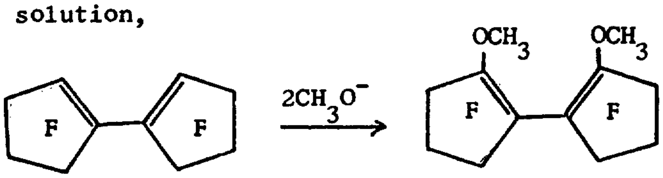


(VIII) u.v. No Change



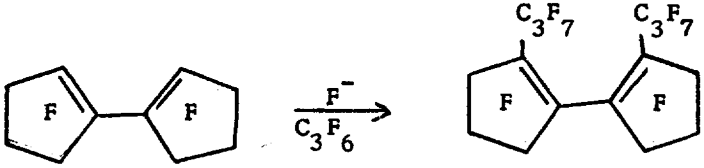
(IX)

The dimethoxy derivative (XXXVI) of perfluorobicyclopentenyl (IX) has been prepared by refluxing (IX) with two molecular proportions of sodium methoxide solution,



(IX) (XXXVI)

and the fluoride ion-initiated reaction of perfluorobicyclopentenyl (IX) with hexafluoropropene at atmospheric pressure gave the bisheptafluoroisopropyl derivative (XXXVII)

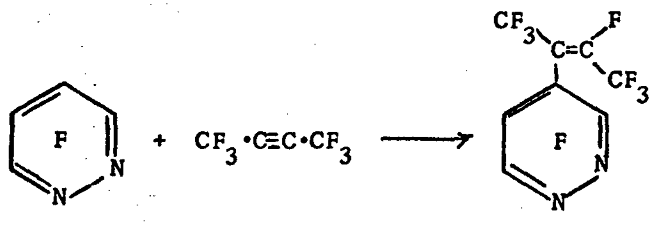


(IX) (XXXVII)

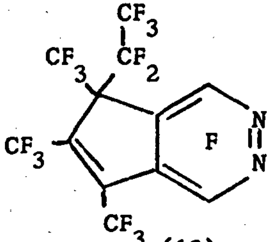
C. Discussion.

The reaction of tetrafluoropyridazine with hexafluorobut-2-yne.

The fluoride-ion-initiated reaction between hexafluorobut-2-yne and tetrafluoropyridazine has been reported previously[1] to give the monosubstituted compounds (10), and $C_{12}F_{16}N_2$ (13), i.e.

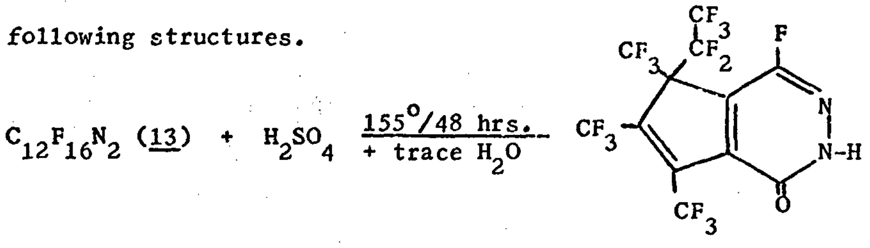


(10)



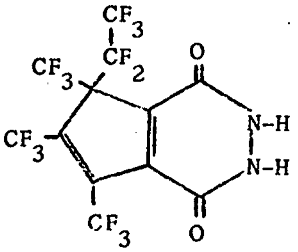
(13)

Reaction of (13) with conc. H_2SO_4 at 155° for 4 hrs. led to the formation of two hydrolysis products (25) and (26) which have been shown to have the following structures.



$$C_{12}F_{16}N_2\ (13) + H_2SO_4 \xrightarrow[+\ \text{trace}\ H_2O]{155^\circ/48\ \text{hrs.}}$$

(25)

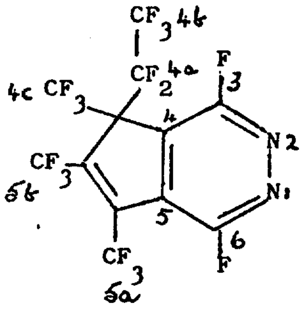
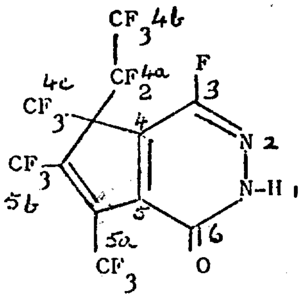


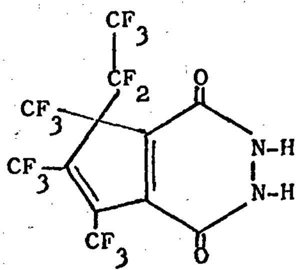
(26)

From careful studies of the ^{19}F n.m.r. of the hydrolysis products, it has been possible to elucidate the structure of the parent compound $C_{12}F_{16}N_2$ (13). It is interesting to note that whilst a cyclic product is obtained using perfluoropyridazine, pentafluoropyridine yields only straight chain compounds.[2]

^{19}F n.m.r. data on compounds (13), (25) and (26)

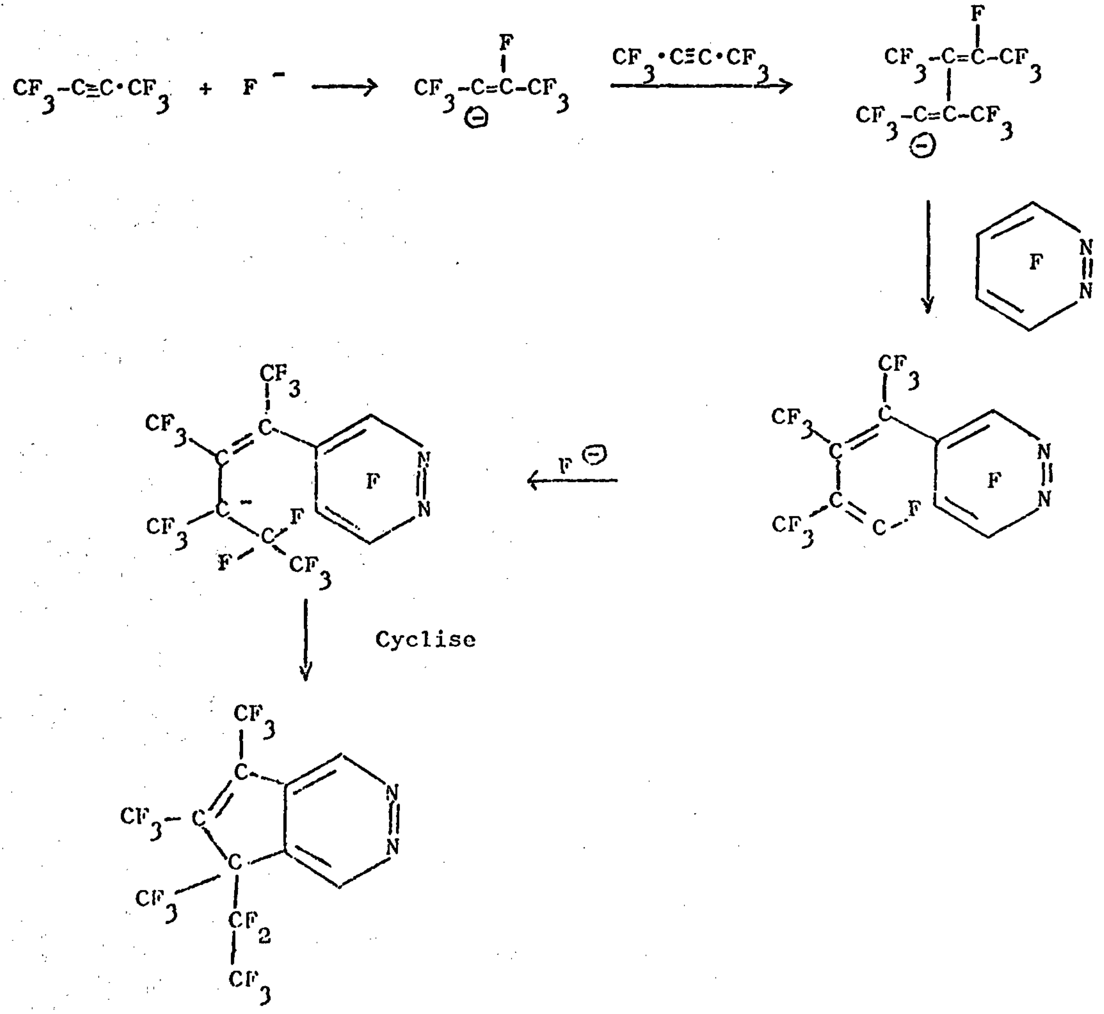
All shifts are measured upfield from $CFCl_3$ (external) reference using acetone as solvent

Compound	Chemical Shift p.p.m.	Coupling Constant Hz	Intensity	Assignment
 (13)	54·9	Broad multiplet J_{5b-4c} = 10, J_{5b-5a}=14	3	5b
	58·7	Hextet J_{5a-5b} = 14, J_{5a-6}=28	3	5a
	60·8	Octet J_{4c-5b} = 10, J_{4c-4a}=10 J_{4c-3} = 20	3	4c
	78·2	J_{6-5a} = 28, J_{3-4c}=20	2	3,6 Ring F's
	80·0	Singlet	3	4b
	106·8	J_{4a-4c} = 10	2	4a
 (25)	55·9	Broad multiplet J_{5b-5a}= 14, J_{5b-4c}= 11	3	5b
	60·1	Octet J_{4c-5b}= 11, J_{4c-3}= 22 J_{4c-4a} = 11	3	4c
	61·5	Quartet J_{5a-5b} = 14	3	5a
	82·0	Singlet	3	4b
	94·3	Broad unresolved multiplet J_{3-4a}= 22	1	3, (Ring F)
	100·8	Broad multiplet J_{4a-4c} = 11	2	4a

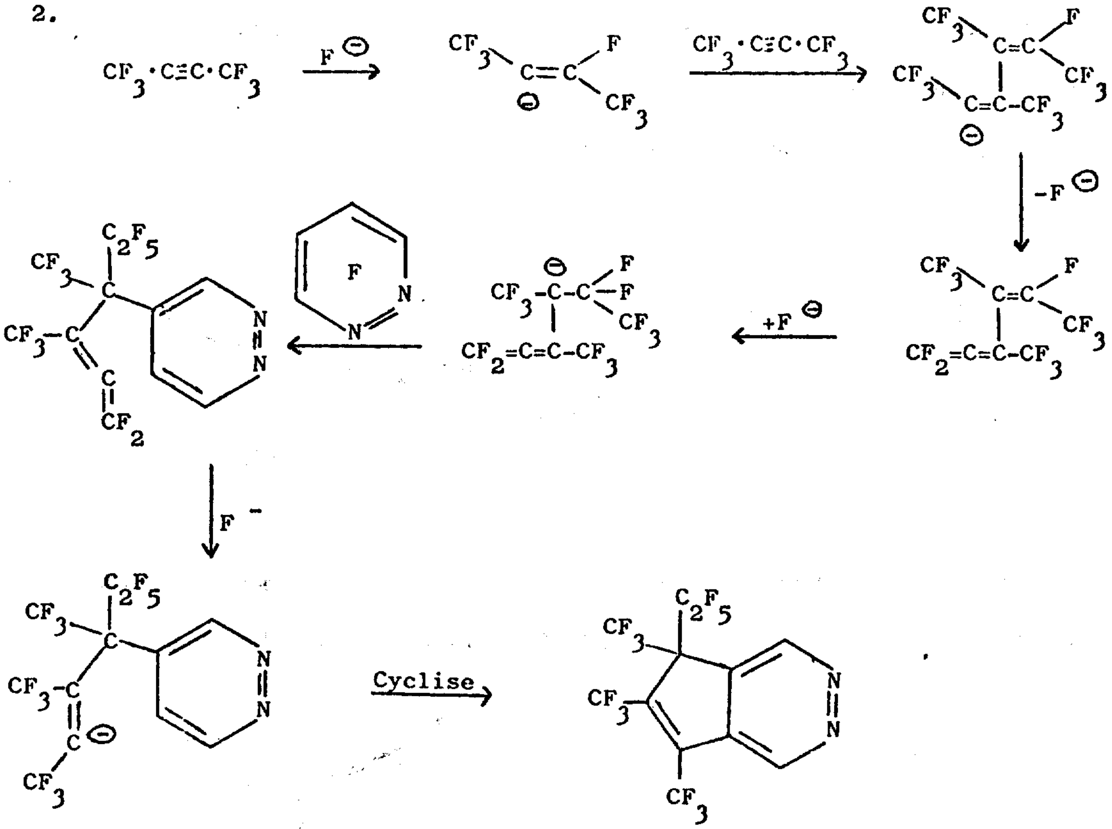
Compound	Chemical Shift p.p.m.	Coupling Constant Hz	Intensity	Assignment
 (<u>26</u>)	56·7	Broad multiplet $J_{5b-5a}=13{\cdot}5$, $J_{5b-4a}=10$	3	5b
	57·2	Hextet $J_{4c-4a}=10$, $J_{4c-5b}=10$	3	4c
	59·6	Quartet, $J_{5a-5b}=13{\cdot}5$	3	5a
	80·5	Singlet	3	4b
	104·3	Multiplet, $J_{4a-4c}=10$	2	4a

The formation of (<u>13</u>) can occur by the following three mechanisms:

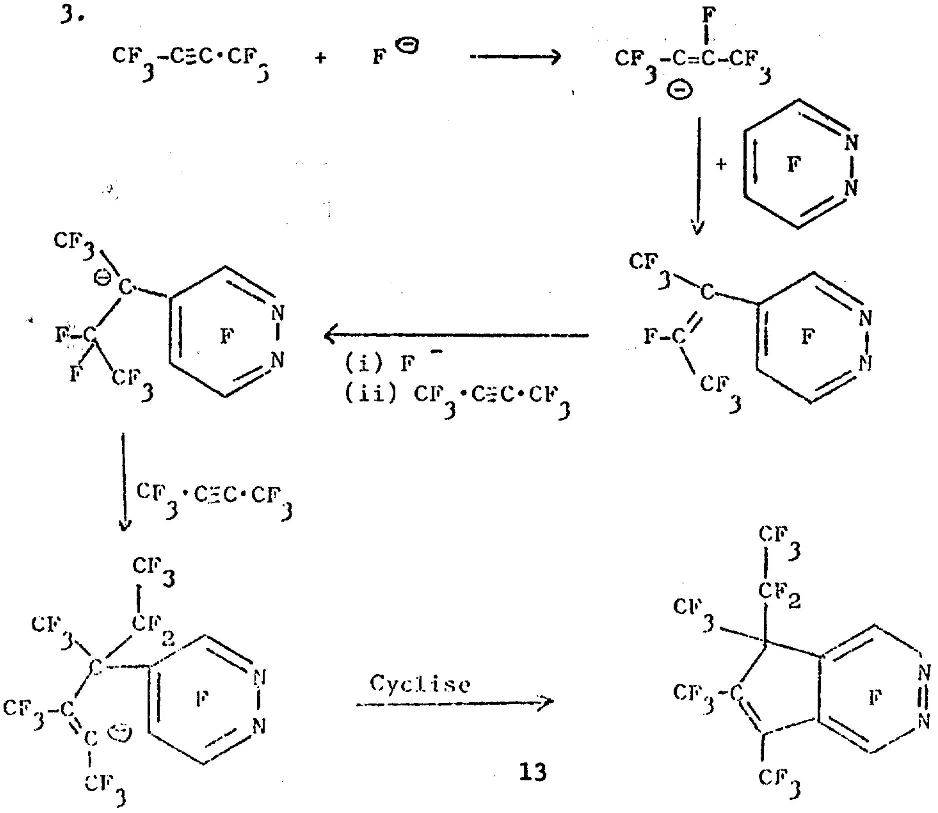
1.



2.


F⊖
CF3·C≡C·CF3
-F⊖
+F⊖
F
N
F−
Cyclise

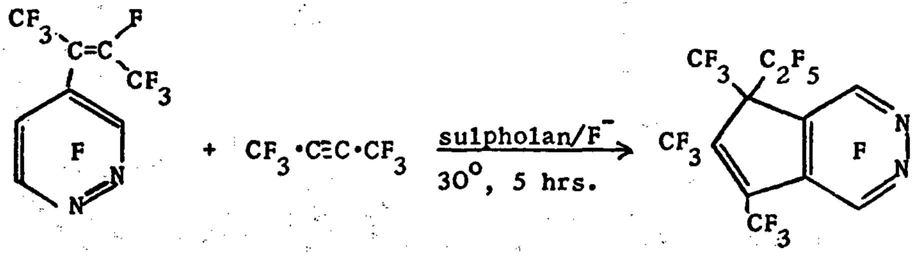
3.


+ F⊖
+
F
(i) F−
(ii) CF3·C≡C·CF3
CF3·C≡C·CF3
Cyclise

(10)

(13)

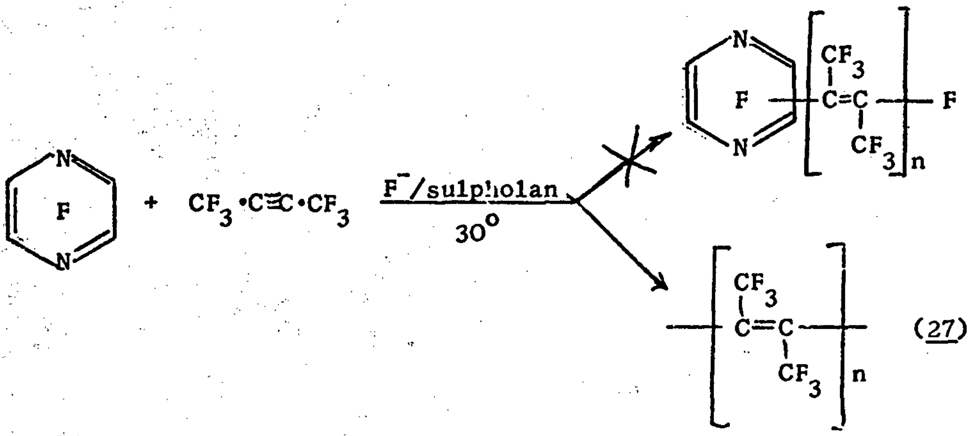
A separate reaction between the monosubstituted compound (10) and hexafluorobut-2-yne gave (13) in 50% yield, showing that a considerable part of (13) must arise from route No. 3.



50%

(10) (13)

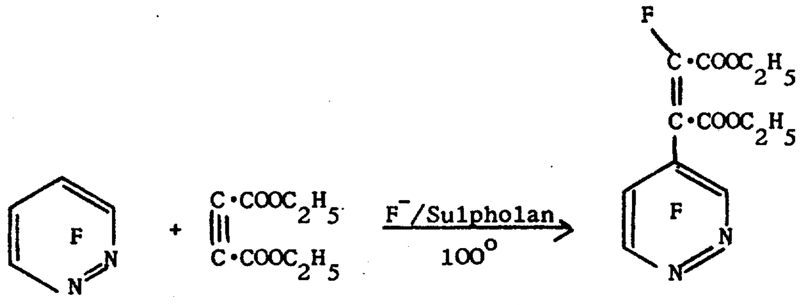
Fluoride ion induced reactions involving tetrafluoropyrazine and hexafluorobut-2-yne at ambient temperature yielded only the polymer material (27).



n = 1,2

(27)

Diethyl acetylene dicarboxylate reacts with tetrafluoropyridazine in a fluoride-ion process to give 1-fluoro-1,2-(biscarbethoxy)-2-(3,5,6-trifluoropyridazyl)ethylene (28)

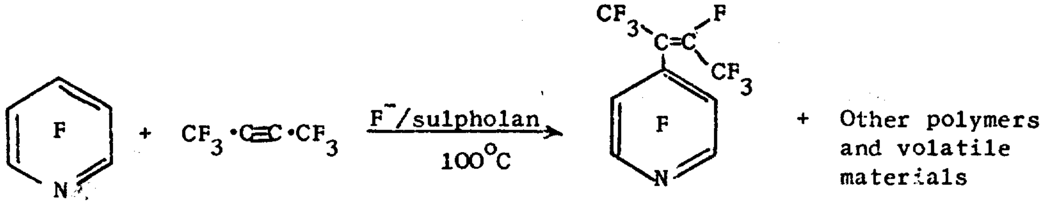


($\underline{28}$); 65%

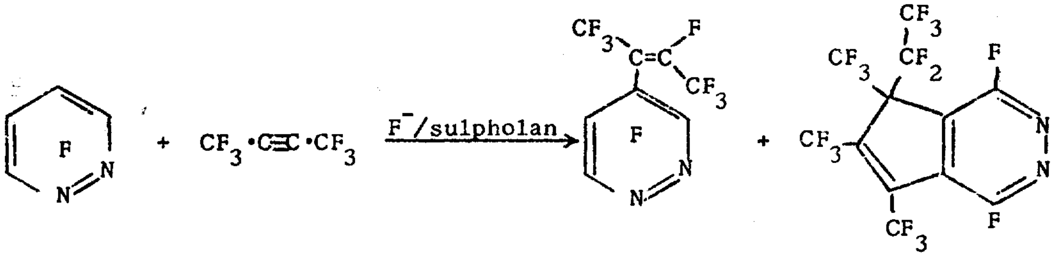
Vapour phase chromatography (G.D.B., Col. 'O' 180°) indicated a single component. However, preliminary ^{19}F n.m.r. evidence, suggested that in fact cis and trans isomers of ($\underline{28}$) had been formed in approximate ration 40:60.

Reactions of octafluorobut-2-ene with tetrafluoropyridazine.

Previous reports described the preparation of the polyfluoro-alkene derivative of pentafluoropyridine ($\underline{12}$)[3] and tetrafluoropyridazine ($\underline{10}$)[1] by a fluoride-ion process.



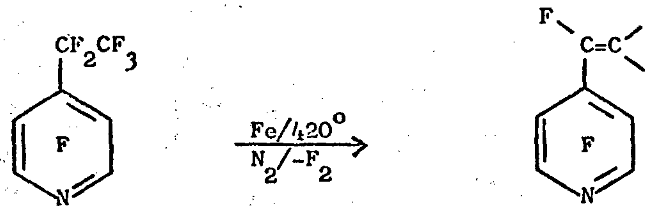
($\underline{12}$)



($\underline{10}$) ($\underline{13}$)

However, the yields of ($\underline{10}$) and ($\underline{12}$) have been low and have involved the separation of complex mixtures of volatile materials by varpour phase chromatography.

Recent work[4] carried out in this laboratory has led to the synthesis of perfluoro-4-(vinyl) and perfluoro-4-(α-trifluoromethyl vinyl)-pyridines, ((37) and (38) respectively), using defluorination techniques.

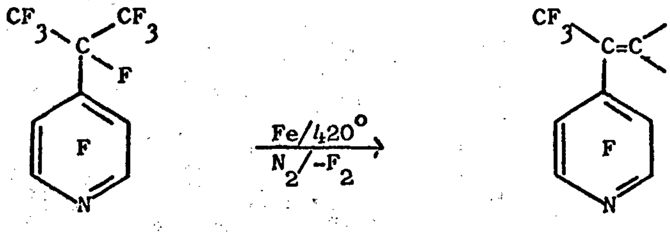


(35) (37)

40% yield

60% conversion

and

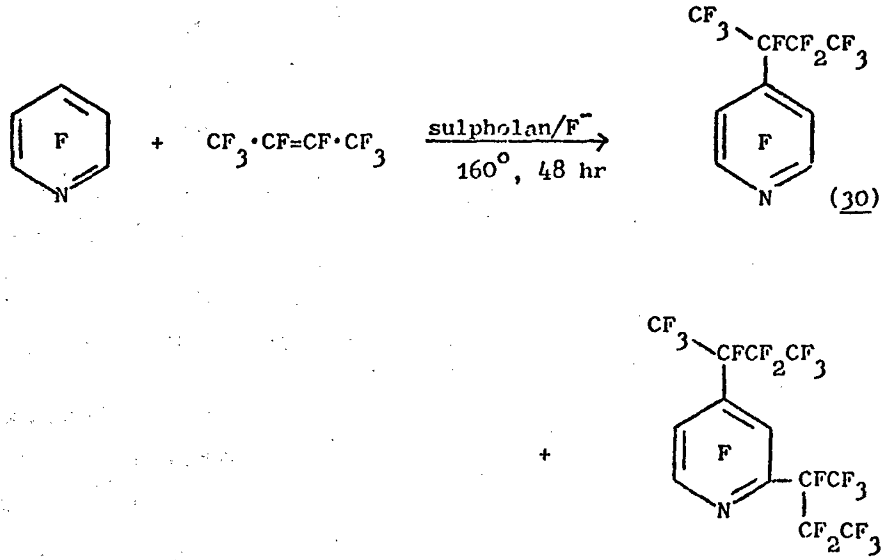


(36) (38)

45% yield

100% conversion

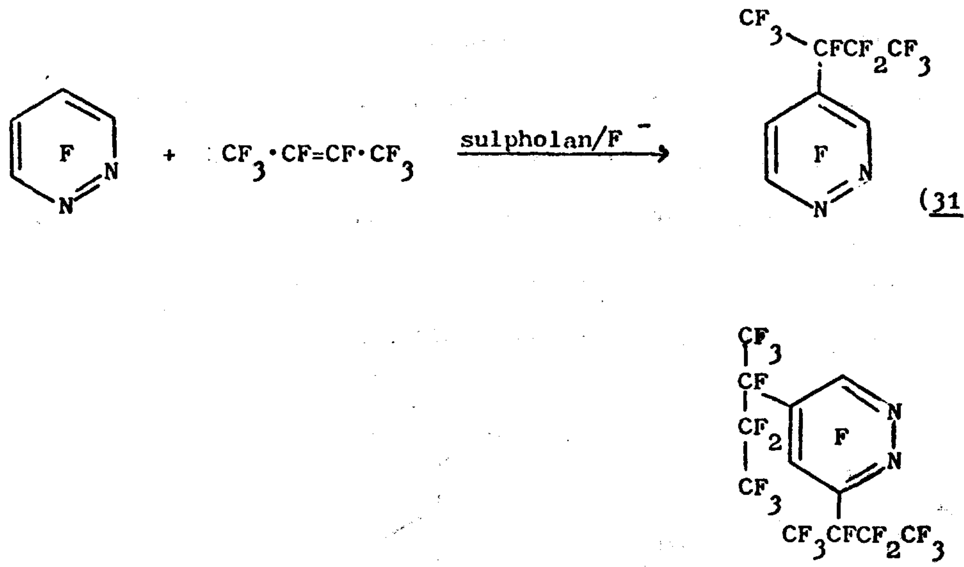
The possibility of extending the scope of these reactions to prepare (12) and (10) respectively has been investigated. The starting materials, perfluoro-4-(sec.butyl)-pyridine and perfluoro-4-(sec.butyl)-pyridazine, for defluorination, were prepared by reacting octafluorobut-2-ene with the corresponding heterocycle under pressure, in the presence of caesium fluoride.



(30) 50%

(39) 30%

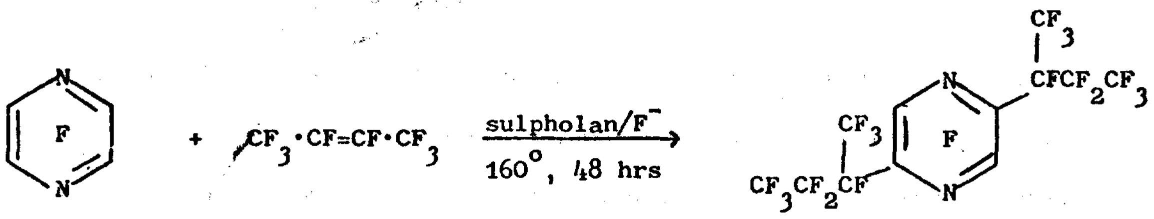
and



(31) 30%

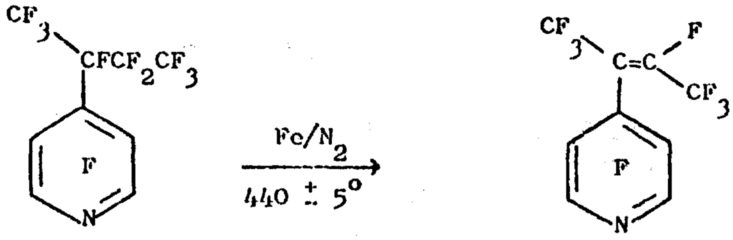
(40) 30%

In a similar reaction, tetrafluoropyrazine has been reacted with octafluorobut-2-ene. Only the 2,5 disubstituted product (41) has been isolated.



(41) 71%

Several defluorination reactions were then carried out using perfluoro-4-(sec.butyl)-pyridine (30) to optimise the yield of perfluoro-4-(2'-butenyl)-pyridine. In these reactions, (30) was passed through a silica tube packed with coarse iron filings, using dry nitrogen as a carrier, at temperatures between 380 and 450°C. The highest yield and conversion of (30) occurred at 440°.



(12)

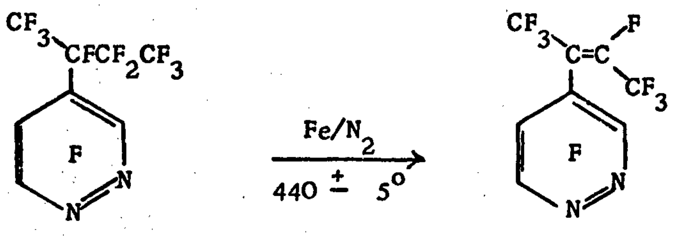
80% yield

75% conversion

+ unchanged (30)

The perfluoro-4-(2'-butenyl)-pyridine obtained, had an identical i.r. and ^{19}F n.m.r. spectrum with that of the trans product formed previously[3] by a fluoride-ion process. Re-cycling the reaction mixture through the tube failed to give a 100% conversion of (<u>30</u>) to the perfluoro-4-(2'-butenyl)-pyridine (<u>12</u>).

Under similar conditions, defluorination of perfluoro-4-(sec.butyl)-pyridazine (<u>31</u>) yielded the trans perfluoro-4-(2'-butenyl)-pyridazine (<u>10</u>).



(<u>31</u>)

(<u>10</u>)

45% yield conversion

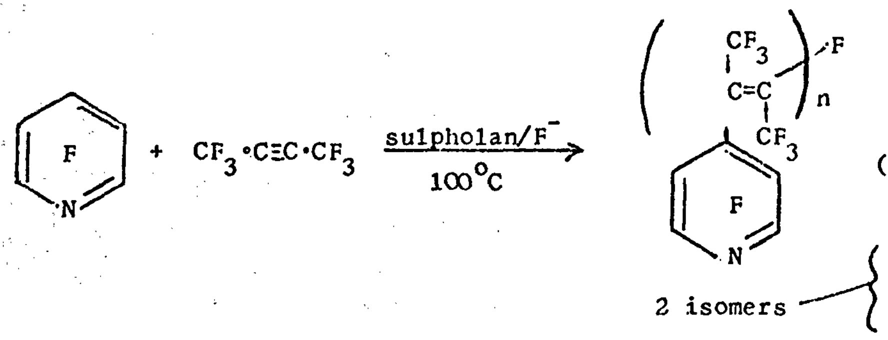
+ unchanged (<u>31</u>)

Defluorination experiments carried out on the two disubstituted products (<u>39</u>) and (<u>40</u>) have so far yielded complex mixtures of products with a low recovery of materials. However, weak absorptions at 5·8μ in the i.r. spectrum of the mixtures, indicate the presence of a $\rangle C=C \langle$ group.

<u>Derivatives of pentafluoropyridine.</u>

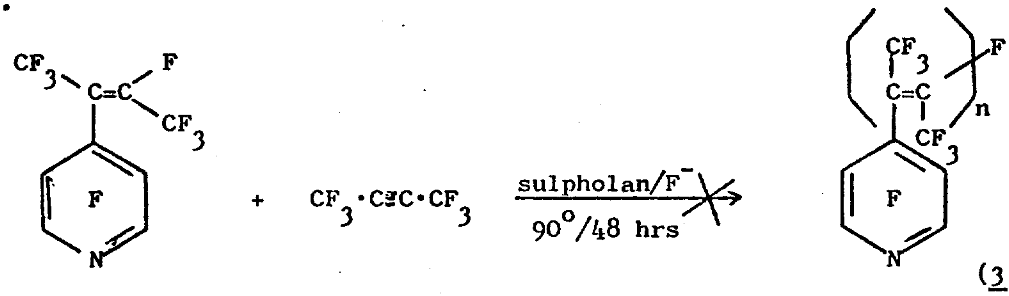
1. <u>With hexafluorobut-2-yne in the presence of fluoride ion</u>

In the fluoride-ion catalysed reaction between pentafluoropyridine and hexafluorobut-2-yne, several products (<u>3</u>), (<u>4</u>), (<u>5</u>) and (<u>12</u>), were reported.[3]



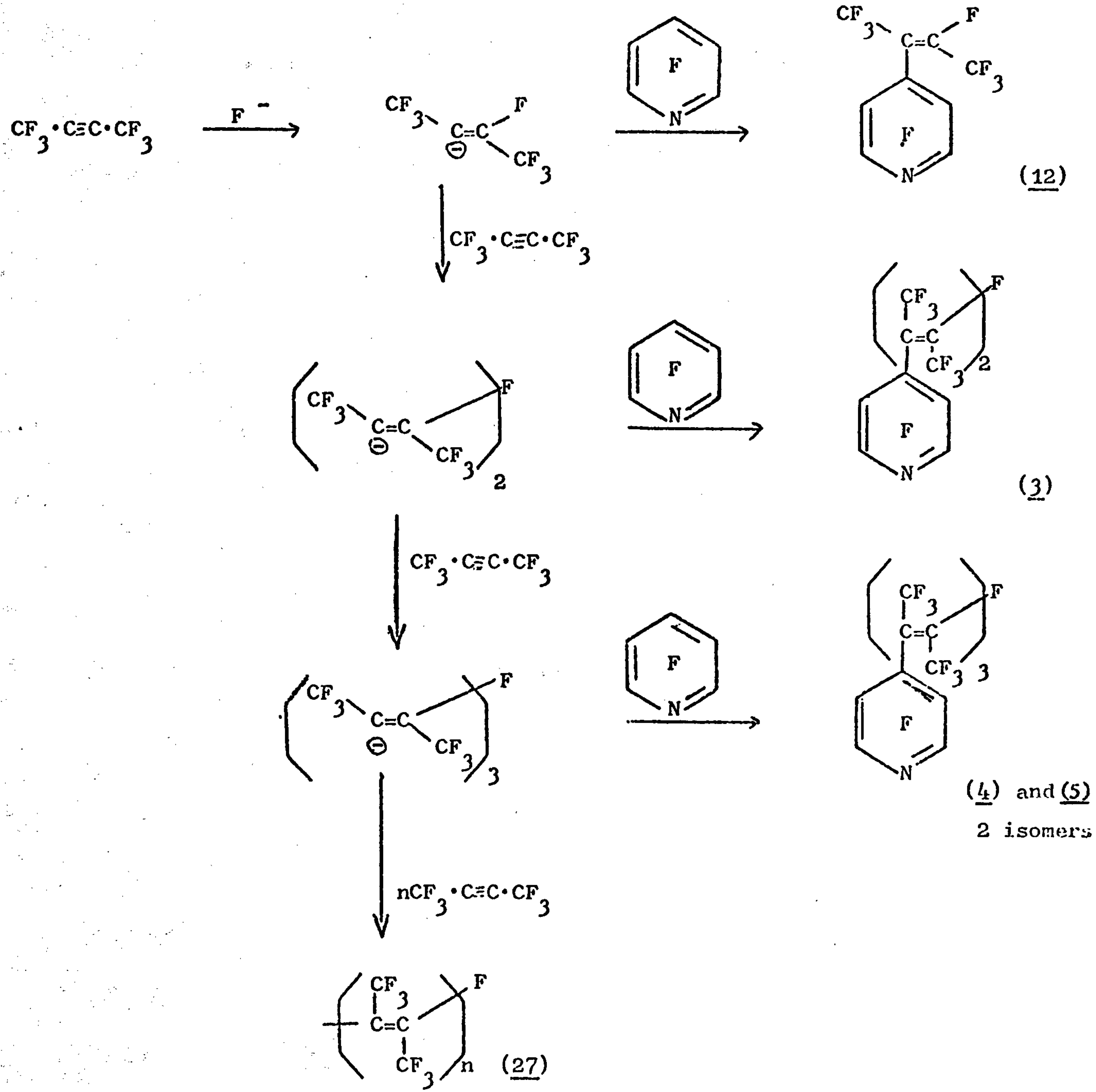
(<u>12</u>) n = 1
(<u>3</u>) n = 2
(<u>4</u>) n = 3
(<u>5</u>) n = 3

In order to determine the mode of formation of these products, perfluoro-4-(2'-butenyl)-pyridine was reacted with perfluorobut-2-yne in an attempt to form (3), (4) and (5) by chain extension. After 24 hours no evidence for the formation of (3), (4) or (5) could be found, recovering only the starting material (12) and a small quantity of polymer (27) derived from the perfluorobut-2-yne.



(3) n = 2
(4) and (5) n = 3

This would suggest that the formation of the polyfluoroalkene and polyfluoropolyene derivatives of pentafluoropyridine are formed by successive reactions of the perfluorobutenyl anion with hexafluorobut-2-yne, leading ultimately to polymer formation, with competing nucleophilic substitution reactions by the perfluoro carbanions with pentafluoropyridine to give (12), (3), (4) and (5).



(12)

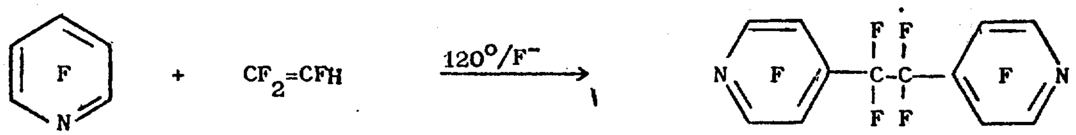
(3)

(4) and (5)
2 isomers

(27)

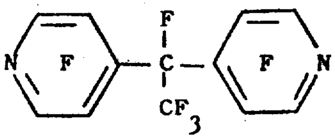
2. With pentafluoropyridine in the presence of caesium fluoride

The fluoride-ion induced reaction between trifluoroethylene and pentafluoropyridine, was reported[1] to give the perfluoro-1,2-bipyridyl ethane.



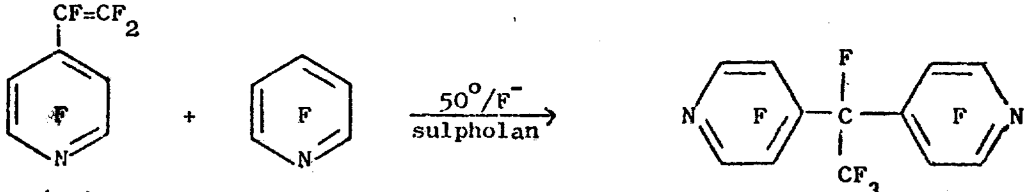
(15)

Recent ^{19}F n.m.r. studies[4] have indicated however, that in fact a perfluoro-1,1-bipyridyl ethane is formed, i.e.



(41)

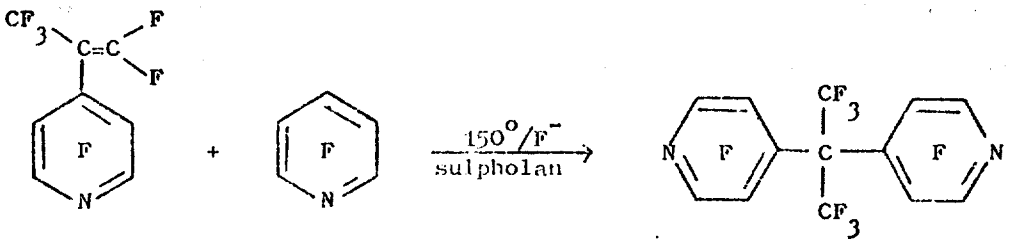
Reaction of the perfluoro-4-(vinyl)- and perfluoro-4-(α-trifluoromethyl-vinyl)-pyridines, (37) and (38), with pentafluoropyridine under fluoride-ion conditions, has led to the formation of the substituted 1,1-bipyridyl ethanes.



(37)

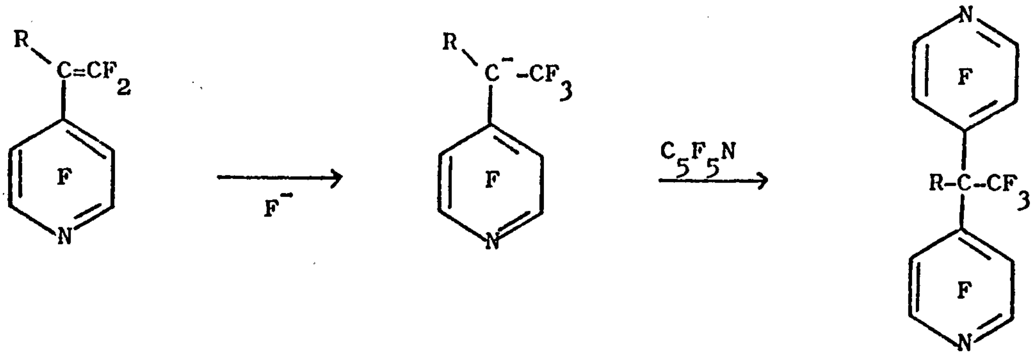
(42)

and



(43)

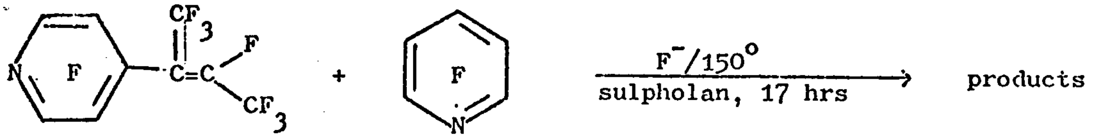
mechanism:



(42) R = F

(43) R = CF_3

As this type of process is potentially valuable as a cross-linking reaction for polymer preparation, a similar reaction has been carried out involving perfluoro-4-(2'-butenyl)-pyridine (12). Under the reaction conditions employed so far, only starting materials were recovered.



Further reactions are in hand using more forceful conditions.

Attempted polymerisation of perfluoro-4-(2'-butenyl)pyridine

Attempts to polymerise perfluoro-4-(2'-butenyl)pyridine in sealed tubes by means of high energy ^{60}Co radiation have so far failed to produce high molecular weight materials. Co-polymerisation reactions of perfluoro-4-(2'-butenyl)-pyridine and an excess of perfluoroprop-2-ene have given similar results.

^{19}F n.m.r. studies of some perfluoro alkyl and alkenyl heterocycles

In the fluoride-ion initiated reaction between octafluorobut-2-ene and tetrafluoropyridazine mono- and di-substituted products (31) and (40) respectively, were obtained. The orientation of substitution in these, and the corresponding di-substituted pyrazine (41), was determined by ^{19}F n.m.r. data, reported in Table 1.

The mono-substituted perfluoropyridazine (31), exhibited absorptions at 71·2 p.p.m. and 97·8 p.p.m. which were assigned to the 3 and 6 ring fluorines respectively, indicating perfluoro-4-(sec.butyl)-pyridazine. This is in agreement with the data[5] for the perfluoro mono isopropylpyridazine which reports that mono-substitution of the perfluoropyridazine ring occurs exclusively at the 4-position.

For the di-substituted perfluoro(sec.butyl)pyridazine (40), resonances at 69·1 p.p.m. and 102·9 p.p.m., attributed to the 6 and 4 ring fluorines respectively, indicate a 3,5-di-substitution pattern. In both the mono- and di-substituted pyridazines, (31) and (40), resonances attributed to CF, CF_2 and CF_3 groups confirmed the presence of perfluoro sec.butyl group(s).

The di-substituted perfluoropyrazine (41), exhibited a single resonance at 76·7 p.p.m., intensity 2, which was assigned to the 3,6 ring fluorines, by comparison of this value with that of 76·66 p.p.m. obtained for the 3,6 ring fluorines in perfluoro-2,5-bis(isopropyl)-pyrazine[6].

Recent ^{19}F n.m.r. data (Table 1) obtained for 1-fluoro-1,2-(Biscarbethoxy)-2-(2',3',5',6'-tetrafluoropyridyl)ethylene (1) reported previously[3], has shown that a mixture of cis and trans-isomers (50:50) is formed. This is in contrast to the perfluoro-4-(2'-butenyl)pyridine which exists only in the trans configuration.[1]

TABLE 1

^{19}F n.m.r. data

All chemical shifts are measured upfield from an external $CFCl_3$ reference.

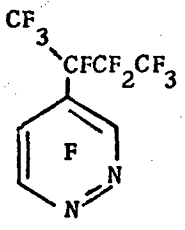
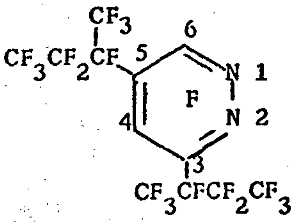
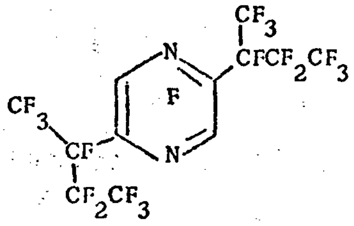
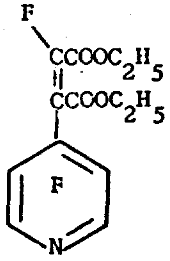
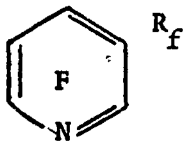
COMPOUND	CHEMICAL SHIFT (P.P.M.)	INTENSITY	ASSIGNMENT
 (31) (NEAT)	71·2	1	3-ring F
	72·7	3	$\underline{CF}_3\text{-}CF\text{-}$
	82·2	3	$CF_3\backslash CFCF_2\underline{CF}_3$.
	97·8 J = 33 cps	1	6 Ring F
	121·15	2	$CF_3\backslash CF\underline{CF}_2CF_3$
	182·5	1	$CF\text{-}CF_2CF_3$
 (40) (IN ACETONE)	69·1	1	6-Ring F
	73·9	6	$\underline{CF}_3\backslash CFCF_2CF_3$
	82·3	6	$CF_3CFCF_2\underline{CF}_3$
	102·9	1	4-ring F
	121·0	4	$CF_3\cdot CF\underline{CF}_2CF_3$
	181·5	1)	$CF_3\underline{CF}\cdot CF_2CF_3$
	187·0	1)	
 (41)	74·6	6	$\underline{CF}_3\backslash CFCF_2CF_3$
	76·7 J = 12 Hz	2	3,6 Ring F's
	82·5	6	$CF_3\backslash CFCF_2\underline{CF}_3$
	122·0	4	$CF\underline{CF}_2CF_3$
	188·4	2	$CF_3\backslash \underline{CF}\text{-}CF_2CF_3$

Table 1 (cont.)

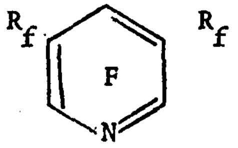
COMPOUND	CHEMICAL SHIFT (P.P.M.)	INTENSITY	ASSIGNMENT
 (1) 50:50 cis/trans	94·0	4	2,6 ring F
	98·5	2	CF
	141·6	5	3,5 ring F

Perfluoro(trifluoromethylpyridines) and derivatives.

Substitution of pentafluoropyridine in the 3,5-positions by electron withdrawing perfluoroalkyl-groups would be expected to lead to enhanced reactivity of the 2-, 4-, and 6-positions to nucleophilic attack but preparation of compounds of the types (XXXVIII) and (XXXIX) have not been hitherto practicable.



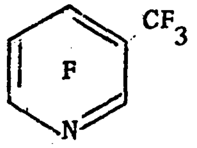
(XXXVIII)



(XXXIX)

R_f = perfluoroalkyl-group

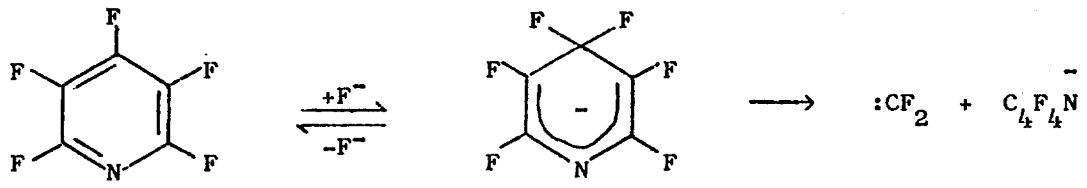
However, we have found that perfluoro(3-methylpyridine) (XL) and perfluoro(3,5-dimethylpyridine) (XLI) are formed in low yield during the preparation of pentafluoropyridine from pentachloropyridine and potassium fluoride at 480°.



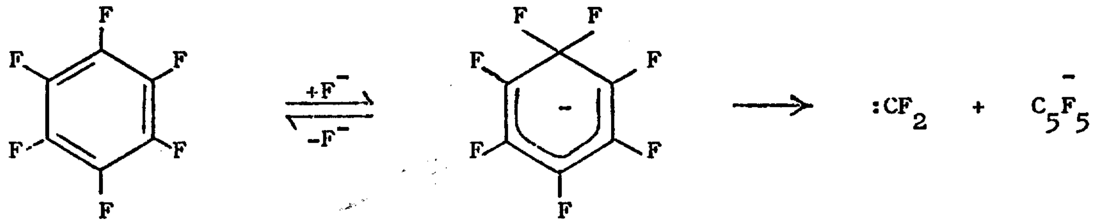
(XL)

(XLI)

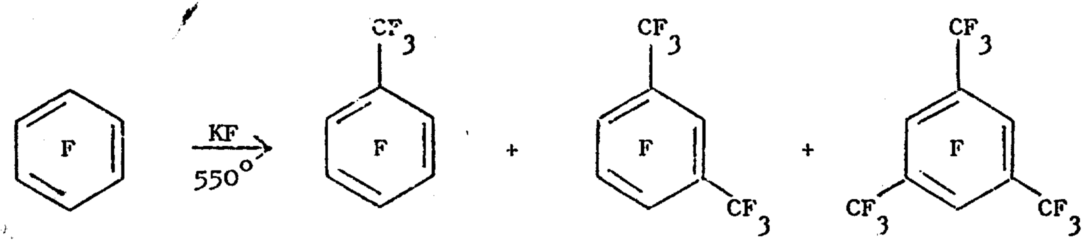
It is thought these compounds arise by electrophilic attack on pentafluoropyridine by difluorocarbene produced by the potassium fluoride catalysed breakdown of pentafluoropyridine.



This is analogous to the mechanism postulated by Platonov et al.[7] to explain the formation of perfluorotoluene (XLII), perfluoro-m-xylene (XLIII) and perfluoromesitylene (XLIV) on heating hexafluorobenzene (XLV) with potassium fluoride at 550°.

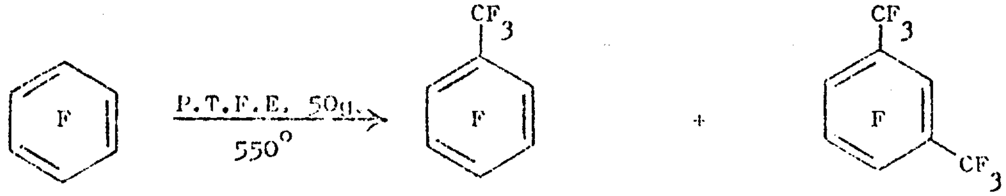


(XLV)



(XLV) (XLII) (XLIII) (XLIV)

Indirect confirmation for the above postulate was reported by Vorozhtsov et al.[8] who heated P.T.F.E. and hexafluorobenzene in a bomb at 550°.

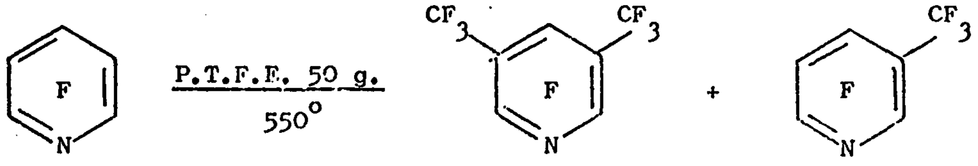


300g. 140g. 30g.

It seemed worthwhile, therefore, to study the reaction between P.T.F.E. and pentafluoropyridine at 550° in order to prepare perfluoro(3,5-dimethylpyridine) and perfluoro(3-methylpyridine) and examine their relative reactivities to nucleophilic attack in the hope that these systems would be more reactive than pentafluoropyridine and hence better substrates for the preparation of polymers.

Preparation of perfluoro(3-methylpyridine) and perfluoro(3,5-dimethylpyridine)

As anticipated, heating P.T.F.E. and pentafluoropyridine at 550° produces a major product of perfluoro(3,5-dimethylpyridine) together with a small amount of perfluoro(3-methylpyridine).



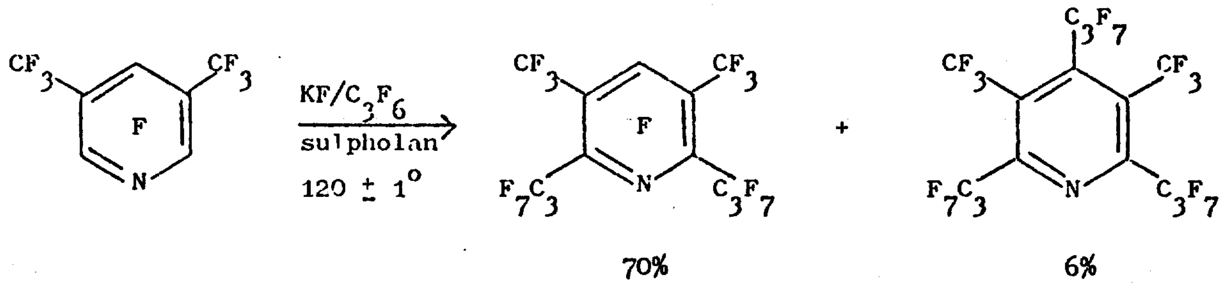
(XLI) (XL)

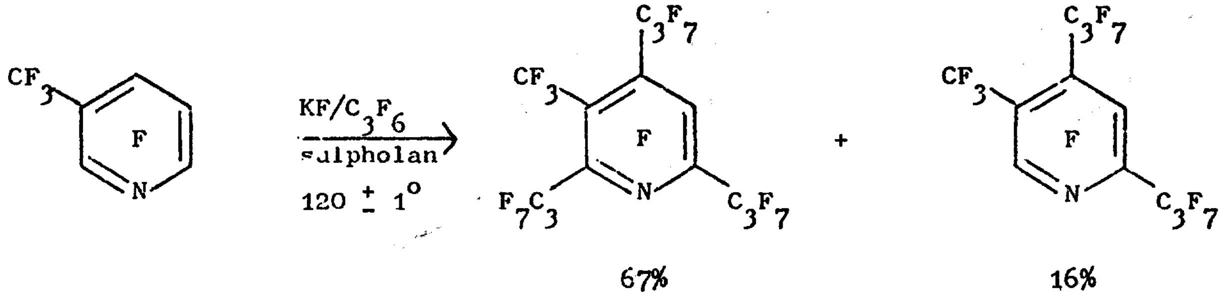
25g. 60% 5%

If, however, the reaction temperature is lowered to 500° or the ratio of weights of starting materials is reversed whilst the reaction temperature is maintained at 550°, the major product is now perfluoro(3-methylpyridine)in yields of 35 and 30%, respectively. Both products were isolated in reasonable purity by fractional distillation.

Polyperfluoroisopropylation of perfluoro(3-methylpyridine) and perfluoro(3,5-dimethylpyridine)

The polyperfluoroisopropylation reactions were carried out initially at 120° in a flow process. The major products were isolated, characterised and their substitution patterns were elucidated by ^{19}F n.m.r. spectroscopy.





In order to acquire an approximate estimate of the relative reactivities of pentafluoropyridine, perfluoro(3-methylpyridine) and perfluoro(3,5-dimethylpyridine) to nucleophilic attack, the polyperfluoroisopropylation of all three compounds were carried out, by the method described for perfluoro(3,5-dimethylpyridine), at 102 ± 1° over 45 minutes.

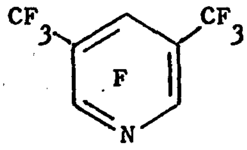
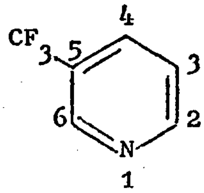
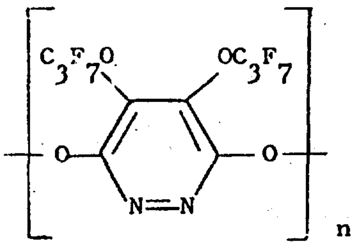
Substrate	Position and % yields of substitution products			% recovery of starting materials	Total
	Mono-	Di-	Tri-		
	4- 54·3	2,4- 8·2	2,4,5-/2,4,6- 19·6	2·3	85
	-	2,6- 70·6	2,4,6- 5·4	12·5	88·5
	-	2,4- 51·3	2,4,6- 30·2	1·4	82·9

Table II. Polyperfluoroisopropylation reactions at 102 ± 1° over 45 minutes in a flow system

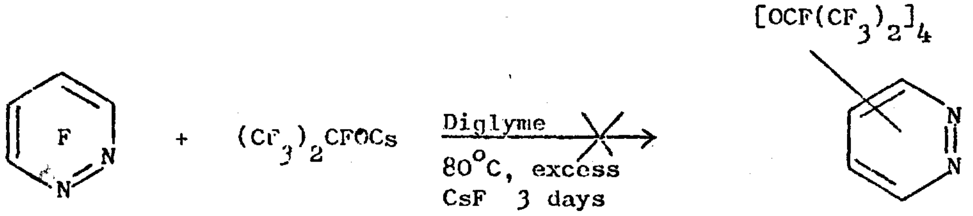
The results indicate that the trifluoromethyl-groups in the 3- and 5- positions do enhance nucleophilic substitution in the ortho- and para-positions but that their electronic effect is offset by the increased steric crowding which occurs in the formation of products, so much so that in the case of perfluoro(3,5-dimethylpyridine) the 4-position shows little affinity for substitution by the heptafluoroisopropyl anion although smaller anions e.g. SH^-, $CF_3CF_2^-$, $R_FCF_2O^-$ may react much more readily.

Attempted preparations of perfluoropolyethers containing heterocyclic rings.

Preliminary experiments using pre-formed $(CF_3)_2CFOCs$ in diglyme with tetrafluoropyridazine, reported previously,[1] indicated that products can be obtained but that hydrolysis reactions led to high molecular-weight materials, possibly of the type:

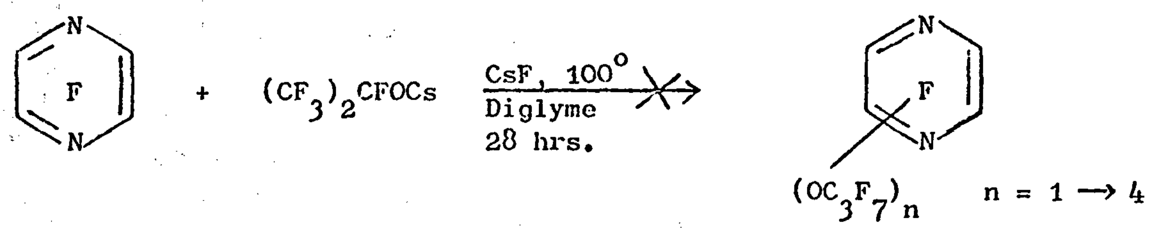


In an attempt to increase the degree of substitution in the pyridazine nucleus by the perfluoroisopropoxide anion, $(CF_3)_2CFO^-$ to yield tetra-substituted products, a reaction was carried out in which the complex, $(CF_3)_2CFOCs$, was prepared in situ and at such a rate that caesium fluoride was always present in the reaction mixture. After 3 days however, only a high melting solid (>300°C), similar to the hydrolysis products obtained previously, was observed.



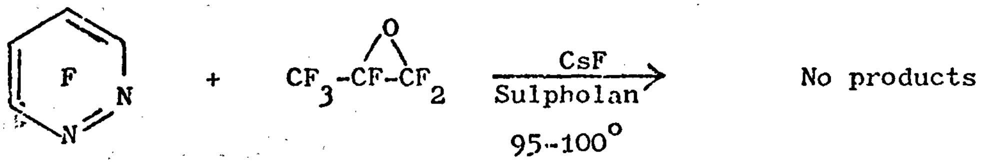
It is now believed that some reaction is occurring with the glass and that it may be possible to avoid this process by using metal apparatus.

Tetrafluoropyrazine is known to be less reactive than tetrafluoropyridazine, both towards nucleophilic attack and also to hydrolysis. Under the conditions attempted so far, no reaction has been achieved between tetrafluoropyrazine and $(CF_3)_2CFO^-$.



Epoxides

Initially, the fluoride-ion induced reaction of hexafluoropropene epoxide with tetrafluoropyridazine using reported[9] conditions, failed to give any ring substituted compounds. Furthermore, homopolymers and oligomers of the perfluoro epoxide were not formed to any appreciable extent in these reactions. Thus, a 'static' reaction carried out at 95-100°C for 8 hrs between the perfluoro epoxide and tetrafluoropyridazine gave no identifiable products and only low recovery of starting materials.

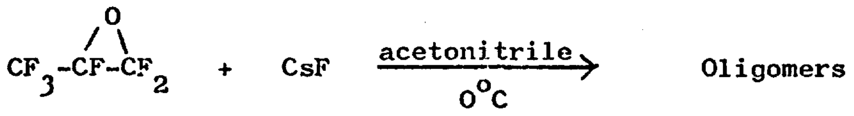


In an attempt to increase the solubility of the epoxide in the reaction mixture, a flow reaction was carried out, initially at 80°C for 5 hrs and then 30°C for 48 hrs. Again, only the volatile starting materials could be isolated from the reaction. Solvent extraction of the residues failed to reveal the presence of any highly substituted involatile materials.

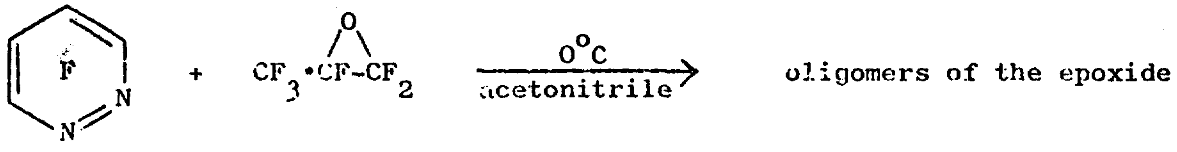
It was thought that if a mixture of hexafluoropropene epoxide and hexafluoropropene was circulated through a suspension of caesium fluoride in sulpholan and pyridazine, then the perfluoroisopropyl carbanion formed from the hexafluoropropene might initiate the perfluoropropene epoxide reaction. However after 20 hrs, the only volatiles collected were starting materials.

Similar results were obtained using tetraglyme as solvent.

Attempts to oligomerise hexafluoropropene epoxide in the presence of caesium fluoride using reported conditions[9], were successful however, when the epoxide, caesium fluoride and acetonitrile were sealed in a Carius tube at 0°C for 3 days.



Using acetonitrile as solvent, a 'flow reaction' was then carried out at 0°C in the presence of tetrafluoropyridazine and caesium fluoride, using perfluoro epoxide diluted with nitrogen. Reaction was extremely rapid and after 5 hrs a colourless fluorocarbon layer formed which was readily separated. Analytical v.p.c. indicated a four component mixture, whilst elemental analysis confirmed the absence of any nitrogen in the mixture i.e. the mixture was derived from the hexafluoropropene epoxide only.



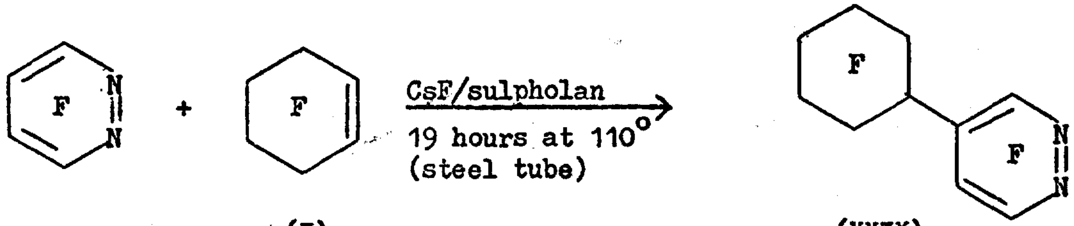
Infrared spectroscopy indicated a -COF group present (5•3μ).

It is hoped to carry out a fluoride-ion induced reaction with this mixture and pyridazine at higher temperatures in a nickel tube, to remove any reaction involving glass, to prepare substituted pyridazine derivatives.

Another flow reaction at higher temperatures in acetonitrile is planned so that the substitution reaction can compete more strongly with the oligomerisation reactions of the perfluoro epoxide.

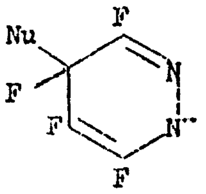
Fluoride Ion-initiated Reactions of Perfluorocycloalkenes with Tetrafluoropyridazine

Initial reactions were carried out using perfluorocyclohexene (I) to generate the fluorocarbanion. When equimolar proportions of tetrafluoropyridazine and perfluorocyclohexene (I) were heated in a stainless-steel tube with caesium fluoride and sulpholan for 19 hours at 80°, some unchanged starting materials were recovered in addition to the formation of the monosubstituted pyridazine (XXIX). When the reaction was repeated by heating the reactants for 19 hours at 110°, no unchanged starting materials were recovered and perfluoro-(4-cyclohexylpyridazine) (XXIX) was obtained as the only product in 70% yield.

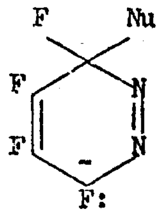


(I) (XXIX)

It has been shown[13] that nucleophilic substitution in tetrafluoropyridazine occurs initially at the 4- and 5-positions. Attack at these positions is preferred since in the transition state charge density is probably greatest at the position para to the point of entry of the nucleophile,[14] and while it is energetically favourable to generate charge on nitrogen, as in (A), charge on a carbon atom bearing fluorine, as in (B), is unfavourable due to repulsion by electron pairs on fluorine.



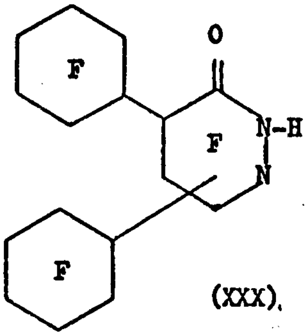
(A)



(B)

The ^{19}F n.m.r. spectrum of (XXIX) showed that the cyclohexyl group was substituted at the 4-position giving the expected orientation of substitution.

The reaction of tetrafluoropyridazine with two molecular proportions of perfluorocyclohexene (I) gave, in addition to the monosubstituted pyridazine (XXIX) (45% yield), a high melting-point solid which was obtained by solvent extraction of the involatile products from an aqueous solution. Although no information on the composition of this solid could be obtained from chromatography, it was obvious from mass spectrometry that it contained products corresponding to the hydrolysis of the substituted pyridazine. Recrystallisation of the crude solid from hot benzene afforded a small quantity of a yellow crystalline solid which was shown to correspond to the dicyclohexyl-substituted pyridazone (XXX) below,



(XXX),

by elemental analysis and i.r. and mass spectrometry. Absorptions due to the $\rangle$C=O and $\rangle$N-H were present in the i.r. spectrum of (XXX), but the small amount of product prevented the confirmation of the structure by n.m.r. spectroscopy.

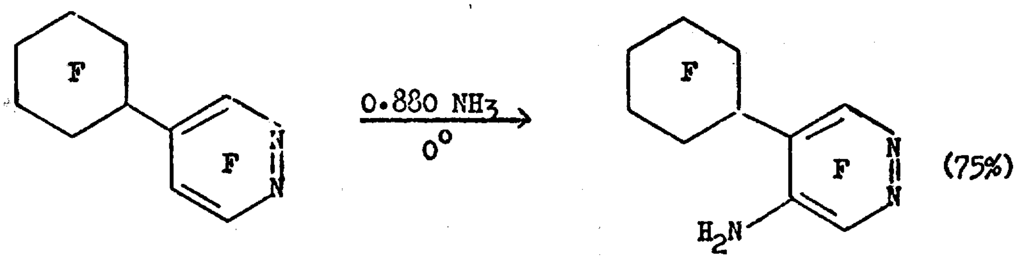
Hence, although optimum conditions were found for the preparation of perfluoro-(4-cyclohexylpyridazine) (XXIX) in relatively high yield, the isolation of higher substituted products was made more difficult by the hydrolysis of these products during solvent extraction from aqueous solution. Further work is required on the reaction between tetrafluoropyridazine and perfluorocyclohexene, but the isolation of the pyridazone (XXX) does indicate that the preparation of more highly substituted pyridazines may be possible. The main problem would appear to be the extractions of these products from the reaction mixture and not the relative reactivity of the olefin

Reactions of Perfluoro-(4-cyclohexylpyridazine)

Perfluoro-(4-cyclohexylpyridazine) (XXIX) was the only compound isolated in reasonable yield from the preliminary fluoride ion-initiated reactions of tetrafluoropyridazine and perfluorocycloalkenes. It was found to be a fairly stable, colourless, viscous liquid, and several reactions were carried out with this compound, the most interesting of these being photolysis and pyrolysis.

Nucleophilic substitution with ammonia

Perfluoro-(4-cyclohexylpyridazine) (XXIX) was found to be very reactive towards aqueous ammonia, and 5-amino-4-perfluorocyclohexyl-3,6-difluoropyridazine (XXXI) was obtained in fairly high yield by addition of (XXIX) to aqueous ammonia at 0°.

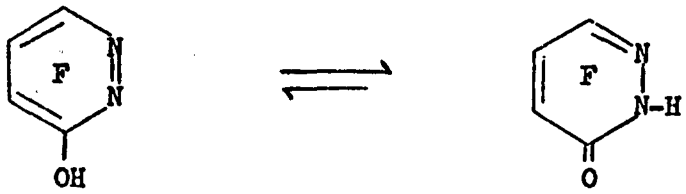


(XXIX) (XXXI)

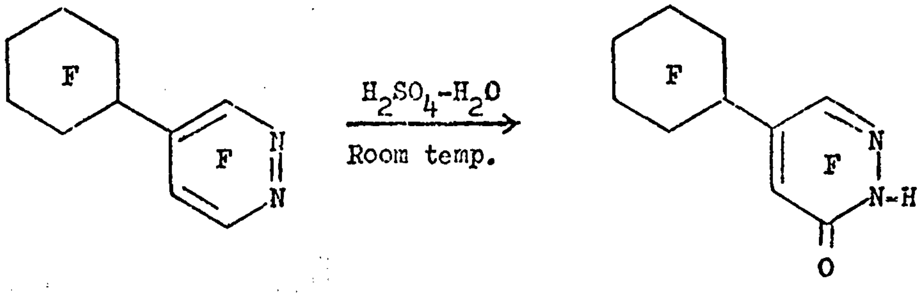
The orientation of substitution of the amino group in (XXXI) was determined from ^{19}F n.m.r. data, and the normal mode of substitution was followed, the 4- and 5-positions of tetrafluoropyridazine having been shown to be the most reactive to nucleophilic attack by several nucleophiles.[13] Thus the presence of the perfluorocyclohexyl group did not have any unusual directive effect and the amino group was substituted for the remaining fluorine atom para to a nitrogen atom.

Reaction with sulphuric acid

Under strongly acidic conditions, nucleophilic attack on tetrafluoropyridazine by water leads to substitution of the fluorine atoms at C-3 and C-6[5] in preference to those at C-4 and C-5 which were previously shown to be more reactive towards nucleophilic reagents under basic conditions.[13] Also, the hydroxylation product of tetrafluoropyridazine has been shown to exist as the pyridazinone tautomer, rather than the hydroxypyridazine, the principal evidence for this being the presence of an N-H stretching band and a carbonyl band in the i.r. spectrum.



When water was added slowly to perfluoro-(4-cyclohexylpyridazine (XXIX) in concentrated sulphuric acid, 3,4-difluoro-5-perfluorocyclohexyl-1H-pyridazin-6-one (XXXII) was obtained in quantitative yield.

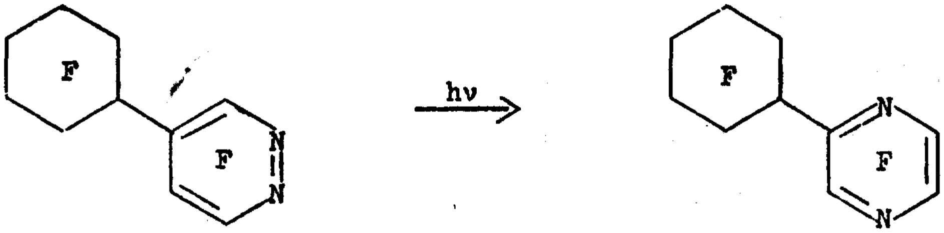


(XXIX) (XXXII)

The existence of (XXXII) as the pyridazinone tautomer was shown by the presence of N-H and carbonyl bands in the i.r. spectrum, and the structure of (XXXII) was confirmed by n.m.r. spectroscopy. The same pyridazone was also produced, autocatalytically, when perfluoro-(4-cyclohexylpyridazine) (XXIX) was exposed to atmospheric moisture.

Photolysis of perfluoro-(4-cyclohexylpyridazine)

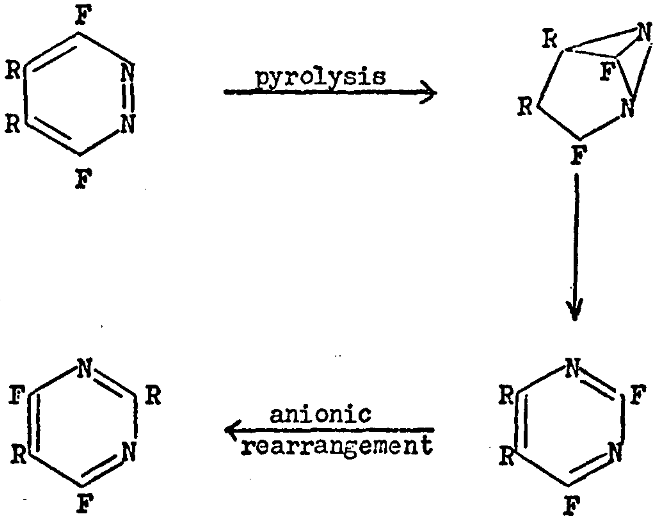
It has been shown that tetrafluoropyridazine and its substituted derivatives rearrange to the corresponding isomeric tetrafluoropyrazine and its substituted derivatives when irradiated with u.v. light.[6,15] In order to see if a similar rearrangement occurred with perfluorocycloalkylated pyridazines, perfluoro-(4-cyclohexylpyridazine) was irradiated in a silica tube with u.v. light for several days. A colourless liquid, with a shorter retention time than the starting material (from v.p.c.), was obtained, and i.r. and ^{19}F n.m.r. data show this to be the corresponding perfluoro-(6-cyclohexylpyrazine) (XXXV).



(XXIX) (XXXV)

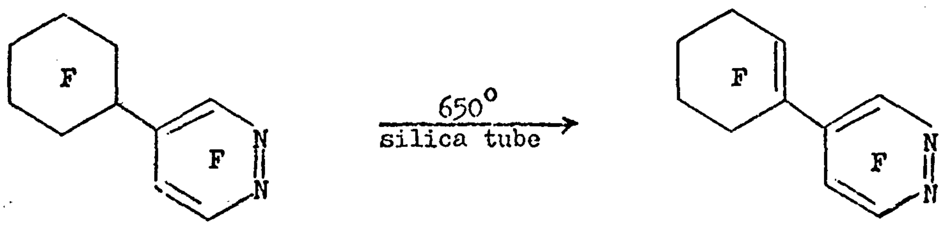
Attempted pyrolysis of perfluoro-(4-cyclohexylpyridazine)

In contrast to the isomerisation of tetrafluoropyridazine and its perfluoroalkyl derivatives to the corresponding pyrazine derivative by u.v. irradiation, tetrafluoropyrimidine and its derivatives are obtained on pyrolysis.[4] It was suggested that this thermal isomerisation proceeds through a diazabenzvalene intermediate by fission of the N-N bond and re-aromatisation to the corresponding pyrimidine.



(R = F or iso-C_3F_7)

When perfluoro-(4-cyclohexylpyridazine) (XXIX) was passed over silica wool at 650°, this temperature being chosen as optimum after a series of small-scale preliminary reactions, a brown liquid was recovered and shown to consist of two components. Separation of the mixture afforded unchanged perfluoro-(4-cyclohexylpyridazine) and a white crystalline solid of which i.r. and ^{19}F n.m.r. data only were obtained before decomposition occurred. An attempt to recover any pure product, after decomposition, by vacuum distillation resulted in recovery of a small quantity of a colourless liquid which exhibited a strong molecular ion peak at $^m/e$ =376 in the mass spectrum. This corresponds to perfluoro-(cyclohexenylpyridazine), and the previously obtained i.r. and ^{19}F n.m.r. data support this.



(XXIX) (XXXII)

The structure given above for (XXXIII) is in accord with the n.m.r. spectrum. Thus the pyrolysis of perfluoro-(4-cyclohexylpyridazine) (XXIX) at 650° did not produce the corresponding pyrimidine derivative as expected, but instead the pyridazine ring remained intact, the cyclohexyl ring being partially defluorinated.

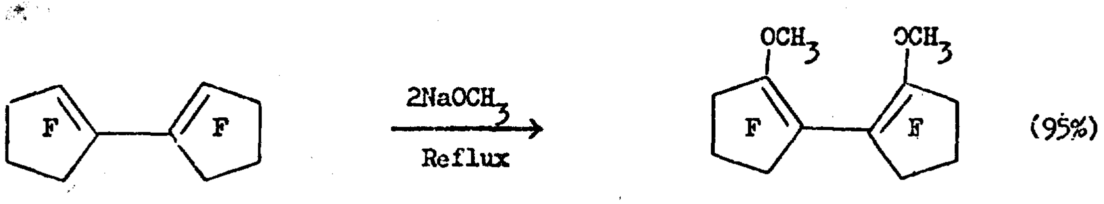
Reactions of the Oligomers of Perfluorocycloalkenes

Nucleophilic substitution

Investigations into the nucleophilic attack of perfluorobicyclopentenyl (IX) were carried out initially using methoxide ion as the nucleophile, but the perfluoroisopropyl anion was also used as the nucleophile since any products resulting from the 'polyfluoroalkylation' of perfluorobicyclopentenyl would be interesting.

Reaction of perfluorobicyclopentenyl with methoxide ion

Perfluorobicyclopentenyl (IX) was found to be very reactive towards nucleophilic attack by methoxide ion and, when (IX) was stirred with an equimolecular proportion of sodium methoxide in methanol, a mixture of the mono- and di-methoxy derivatives was obtained. The dimethoxy derivative was isolated in 95% yield when (IX) was refluxed with two molecular proportions of sodium methoxide in methanol.



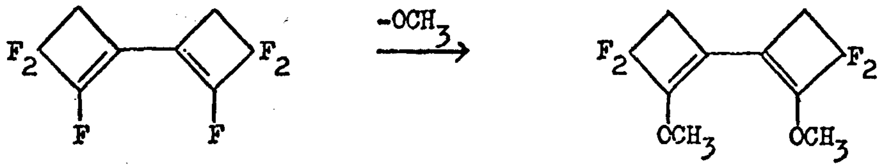
(IX) (XXXVI)

The structure given for (XXXVI) is in accord with the ^{19}F n.m.r. spectrum which contained three broad singlets of equal intensity and with the following chemical shifts:

107•2 116•3 131•9 p.p.m. (Ref: $CFCl_3$)

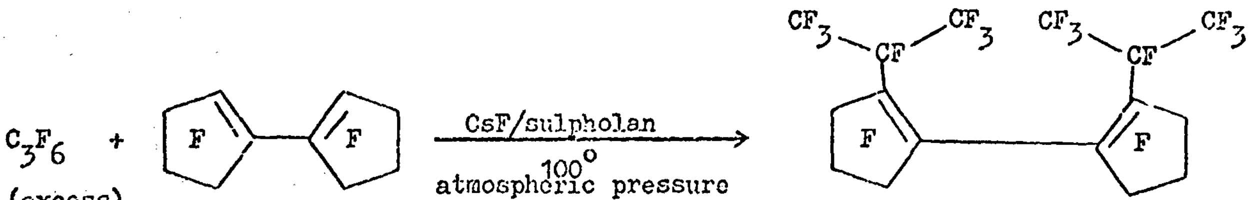
The non-planarity of (XXXVI) was indicated by the absence of any absorption in the u.v. spectrum of this compound.

The formation of a dimethoxy derivative of perfluorobicyclopentenyl (IX) under relatively mild conditions is indicative of the vinylic fluorine atoms being very reactive to nucleophilic attack. Park and co-workers[16] obtained similar results with hexafluorobicyclobutenyl and found that, as with perfluorocyclobutene, attack by alkoxide tends to give a diether at room temperature.



<u>Fluoride ion-initiated reaction of perfluorobicyclopentenyl with hexafluoroprop</u>

When perfluorobicyclopentenyl (IX) was stirred in the presence of caesium fluoride and sulpholan under an atmosphere of hexafluoropropene for 4-5 hours at 100°, a white crystalline solid was isolated from the reaction mixture by solvent extraction and shown to be perfluoro-(2,2'-diisopropylbicyclopentenyl) (XXXVII)

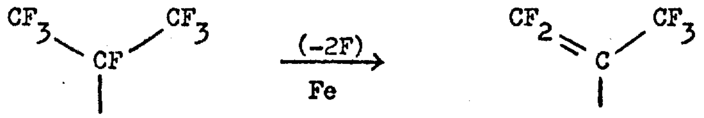


(IX)

(XXXVII)

(35% yield

The di-isopropyl compound (XXXVII) is interesting since the removal of fluorine from the side chain could lead to a vinyl derivative or even cyclisation. The following conversion was effected when the side-chain was attached to a heterocyclic substrate.[4]

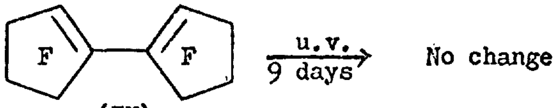


by passage over heated iron. When (XXXVII) was passed over iron at 480°, however, a 25% recovery of the starting material was obtained with no other products.

Other Reactions of the Oligomers of Perfluorocycloalkenes

Irradiation with u.v. light

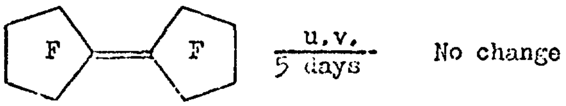
In order to establish whether perfluorobicyclopentenyl (IX) would rearrange on photolysis, a sample of (IX) was irradiated in a silica tube from a medium pressure u.v. lamp for 18 hours. No change occured and the starting material was recovered. When this was repeated using a little benzophenone as photosensitizer and irradiating the compound for a much longer time (9 days), (IX) was recovered unchanged.



(IX)

This further substantiates the stability of the diene (IX), which was shown earlier to be stable to defluorination.

No change was observed when perfluorocyclopentene dimer (VIII) was irradiated with u.v. light under similar conditions



It was also shown that perfluoro-(1-cyclohexylcyclohexene) (VI) and perfluorocyclobutene trimer (X) were stable to irradiation with u.v. light for 100 hours, and the recovered starting materials were confirmed by i.r. spectroscopy.

D. Experimental.

Hydrolysis of Perfluoro-(1,2,3-trimethyl)-1-ethyl-5,6-diazaindene, $C_{12}F_{16}N_2$ (13)

$C_{12}F_{16}N_2$ (13), (1·5 g., 3·16 m.mole) in concentrated sulphuric acid (10 ml.) to which a few drops of water had been added, was heated to 150°C for 48 hrs. The reaction was cooled and the sulphuric acid solution added dropwise to water (50 ml.). The resulting precipitate (1·3 g.) was filtered, washed, dried in vacuo, and crystallised from aqueous methanol several times. Analytical scale v.p.c. (G.D.B. 'O' 200°C) showed a two component mixture.

The mixture (ca. 1 g.) was then dissolved in chloroform (5 ml.) plus a few drops of methanol and eluted down a silica column (1' x ½"; 'Silicar' CC7, 100-120 mesh neutral silica) with chloroform. Two main fractions were collected and on removal of solvent yielded:

(a) a white solid (0·2 g.). This was identified as 1,2,3-tris-(trifluoromethyl)-1-pentafluoroethyl-7-fluoro-4-hydroxy-5,6-diazaindene, m.pt. 163-5°. (Found: C, 29·9; H, 0·2; F, 60·2; N, 6·0%; M, 474. $C_{12}HF_{15}N_2O$ requires: C, 30·4; H, 0·2; F, 60·0; N, 5·9; M, 474).

(b) a pale yellow solid (0·3 g.). This was identified as 1,2,3-tris-trifluoromethyl)-1-pentafluoroethyl-4,7-dihydroxy-5,6-diazaindene, m.pt. 207-9. (Found: C, 30·7; H, 0·4; F, 56·6; N, 6·1; M, 472. $C_{12}H_2F_{14}N_2O_2$ requires: C, 30·6; H, 0·4; F, 56·5; N, 5·94; M, 472)

Reactions of Hexafluorobut-2-yne with Tetrafluoropyridazine.

(a) In acetonitrile at 0°C.

Caesium fluoride (4 g., 26·4 m.mole) and acetonitrile (30 ml.) were introduced into a 100 ml. flask under dry nitrogen. The flask was then evacuated at room temperature. When degassing of the solvent had ceased, hexafluorobut-2-yne (4 g., 24·64 m.mole) was allowed into the system until atmospheric pressure had been reached. Tetrafluoropyridazine (5 g., 33·0 m.mole) was introduced into the flask which was then cooled to 0-5°C and rapidly stirred at this temperature. After 3 hrs., the stirring was stopped and, on standing, two layers were observed in the reaction vessel. These were separated and the lower layer (1·1 g.) was shown to consist of oligomers of hexafluorobut-2-yne by I.R. spectroscopy. The upper layer was shown (v.p.c. G.D.B. 'A' 78°C) to consist of acetonitrile and unreacted tetrafluoropyridazine (3 g.).

(b) In acetonitrile at -40°C.

Acetonitrile (30 ml.), caesium fluoride (3 g., 19·8 m.mole) and tetrafluoropyridazine (3 g., 19·8 m.mole) were introduced into a 100 ml. flask (equipped with a dry ice condenser) under dry nitrogen. The flask was then cooled to -120° and evacuated. Hexafluorobut-2-yne (4 g., 24·64 m.mole) was then condensed into the system and the whole allowed to warm up to -40°C. The reaction was then stirred at this temperature. After 5 hrs. vacuum transfer of the volatile materials and subsequent analysis (v.p.c. col. 'A' 78°C G.D.B.) indicated acetonitrile and pyridazine only. Polymeric material (4 g.) was recovered from the residues which had an identical i.r. spectrum with that of an authentic sample of the polymer, formed between the reaction of hexafluorobut-2-yne with caesium fluoride.

Reaction of Hexafluorobut-2-yne with Tetrafluoropyrazine at 30°C.

Sulpholan (30 ml.) and caesium fluoride (19·8 m.mole) were introduced into 100 ml. flask under dry nitrogen. The flask was then evacuated at room temperature. When degassing of the solvent had ceased, hexafluorobut-2-yne (4 g., 24·64 m.mole) was allowed into the system until atmospheric pressure had been reached. Tetrafluoropyrazine (3 g., 19·8 m.mole) was then introduced into the flask, and the reaction was stirred at room temperature. After 12 hrs. transfer under vacuum yielded a white solid (2·2 g.) which had an i.r. spectrum which was identical with that of an authentic sample of pyrazine. Polymeric material (4 g.) was recovered from the residues.

Reaction of Diethyl Acetylene Dicarboxylate with Tetrafluoropyridazine at 90·95°C.

Sulpholan (50 ml.), caesium fluoride (26·4 m.mole) and tetrafluoropyridazine (6·0 g., 39·6 m.mole) were introduced into a 100 ml. flask under dry nitrogen. The mixture was then stirred at 90-95°C and diethyl acetylene dicarboxylate (7·5 g., 39·4 m.mole) was added dropwise over 30 mins. at 90-95°C. After a further 1½ hrs. vacuum transfer of volatile material to a cold trap gave tetrafluoropyridazine (3 g.).

The residue was cooled to room temperature and poured into water and the ether extracted (3 x 50 ml.). The ether extracts were combined, washed and dried ($MgSO_4$). Removal of the solvent left an oil (5·9 g.) which was distilled under high vacuum collecting the main fraction (2·0 g.) boiling at 112-114°C at 0·015 mm. Yield, 65%. Preliminary ^{19}F n.m.r. (and mass spectral) data indicated that the product was a cis/trans mixture of 1-fluoro-1,2-(biscarbethoxy)-2-(3,5,6-trifluoropyridazyl)ethylene (28). Full elemental analysis is awaited.

Reaction of Tetrafluoropyridazine with Caesium Fluoride in Nickel Apparatus.

(a) Using sulpholan as solvent.

Caesium fluoride (1 g., 6•6 m.mole), sulpholan (30 ml.) and tetrafluoropyridazine (3 g., 19•8 m.mole) were sealed in a nickel tube under dry nitrogen. The tube was then rotated in an oil bath at 140°. After 48 hrs. the tube was cooled and perfluoropyridazine (2 g.) was transferred under vacuum to a cold trap (66% recovery). No other materials could be recovered from the residue.

(b) Using diglyme as solvent.

Diglyme (30 ml.), caesium fluoride (1•0 g., 6•6 m.mole) and tetrafluoropyridazine (3 g., 19•8 m.mole) were sealed in a nickel tube under dry nitrogen. The tube was rotated in an oil bath at 140°C. After 48 hrs., the tube was cooled and perfluoropyridazine (40% recovery) was recovered (1•2 g., 40%). Treatment of the residue with water yielded a high melting solid (0•4 g.) which had an i.r. spectrum similar to that obtained previously.[10]

Reaction of perfluoro-4-(2'-butenyl)pyridazine with hexafluorobut-2-yne at 30°C.

Sulpholan (5 ml.) and caesium fluoride (0·5 g., 3·3 m.mole) were introduced into a 10 ml. flask under dry nitrogen at 30°C. The flask was evacuated and when de-gassing of the solvent had ceased, hexafluorobut-2-yne (1·0 g., 6·1 m.mole) was allowed into the system until atmospheric pressure had been reached. Perfluoro-4-(2'-butenyl)pyridazine (0·3 g., 0·96 m.mole) was added to the stirred suspension with the immediate formation of an intense yellow colour.

After 6 hrs., vacuum transfer of the volatile material to a cold trap, gave a small quantity of material which crystallised from toluene to give a white solid (0·2 g.), m.pt. 56-58°C; the i.r. spectrum of the solid was identical with that of an authentic sample of perfluoro-(1,2,3-trimethyl)-1-ethyl-5,6-diaza indene.

Reaction of perfluoro-4-(2'-butenyl)pyridine with hexafluorobut-2-yne at 90 ± 5°C.

Using a similar procedure to that described above, caesium fluoride (0·5 g., 3·3 m.mole), sulpholan (5 ml.) and perfluoro-4-(2'-butenyl)pyridine (1·0 g., 1·9 m.mole) were stirred together under an atmosphere of perfluorobut-2-yne. After 24 hrs., vacuum transfer of the volatile materials to a cold trap yielded a colourless liquid (0·6 g.) which was shown by v.p.c. measurements (Col. 'A' 100°C) and i.r. studies to be essentially starting material. No evidence was found for the formation of perfluoro-2-(2',3',5',6'-tetrafluoropyridyl)-3,4-bistrifluoromethyl heptafluorohexa-2,4-diene (3) and the higher polyenes (4) and (5).

Reaction of pentafluoropyridine with octafluorobut-2-ene in a nickel tube.

In a typical reaction, pentafluoropyridine (12 g., 72·9 m.mole), octafluorobut-2-ene (15·6 g., 78·0 m.mole), sulpholan (15 ml.) and caesium fluoride (6 g., 39·6 m.mole) were sealed in a nickel tube under dry nitrogen. The tube was rotated in an oil bath at 160°C.

After 48 hrs., the tube was cooled, vented and the vacuum transfer of the volatile materials to a cold trap gave a colourless liquid (21·5 g.) which was separated (Aerograph Col. 'O' at 110°C) into two fractions:

(i) a colourless liquid 7·1 g. This was identified by i.r. spectroscopy, as perfluoro-4-(sec. butyl pyridine) (30), B.pt. 147°C, 50% yield.

(ii) a colourless liquid 5·9 g., identified as perfluoro-2,4-di-(sec. butyl)-pyridine, B.pt. 194°, 30% yield.

Reaction of tetrafluoropyridazine with octafluorobut-2-ene.

Tetrafluoropyridazine (8·9 g., 58·6 m.mole), caesium fluoride (6·0 g., 39·6 m.mole), octafluorobut-2-ene (11·7 g., 58·6 m.mole) and sulpholan (15 ml.) were sealed in a nickel tube. The tube was then rotated in an oil bath at 160°C. After 24 hrs. the tube was cooled and vacuum transfer of the volatile material gave a colourless liquid (13·4 g.). V.p.c. (G.D.B. Col. 'O' 78°C) showed a two component mixture. Separation of the mixture (Aerograph Col. 'A' at 130°C) gave:

(1) a colourless liquid (4·0 g.). This was identified as perfluoro-(3,5-di-[sec. butyl]pyridazine), B.pt. 182-4°C. M, 552. Yield 30%.

(2) a colourless liquid (4·3 g.). This was identified as perfluoro-4-(sec. butyl)pyridazine, B.pt. 149-50°C. M, 352. Yield: 30%. ^{19}F nuclear magnetic resonance data are consistent with the assigned structures. Elemental analyses are awaited.

Reaction of tetrafluoropyrazine with octafluorobut-2-ene.

Tetrafluoropyrazine (5·0 g., 33·0 m.mole), caesium fluoride (4·0 g., 26·4 m.mole), octafluorobut-2-ene (8·0 g., 40·0 m.mole) and sulpholan (15 ml.) were sealed in a nickel tube. The tube was then rotated in an oil bath at 160°C. After 48 hrs., careful vacuum transfer of the volatile materials gave:

(1) a white solid (1·2 g.). This was identified as tetrafluoropyrazine, having an identical i.r. spectrum with that of an authentic sample.

(2) a colourless liquid (10 g.). This was identified as perfluoro-(2,5-di-[sec. butyl]pyrazine), B.pt. 165°C, M, 552. Elemental analysis is awaited.

Attempted defluorination of perfluoro-4-(sec. butyl)pyridine.

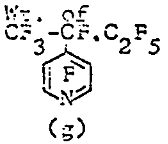
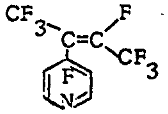
Several reactions were carried out at different temperatures and flow rates to find an optimum temperature for the defluorination of perfluoro-4-(sec. butyl)pyridine. A quantity of perfluoro-4-(sec. butyl pyridine) was passed through a silica tube (20" x $\frac{1}{2}$") packed with coarse iron filings using a steady flow of dry nitrogen and the products collected in a cold trap (for quantities, conditions and yields see Table III). An attempt to effect complete defluorination of the perfluoro-4-(sec. butyl)pyridine by re-cycling the volatile materials from the cold trap (Table III, experiment 8) was unsuccessful.

The volatile materials obtained from the defluorination reactions were combined (20 g.) and separated using preparative scale chromatography (Aerograph Col. 'O' at 90 ± 5°C) into two fractions:-

(1) a colourless liquid (7·0 g.), which had an identical i.r. spectrum with that of an authentic sample of perfluoro-4-(2'-butenyl)pyridine (12).

(2) starting material (4·0 g.).

TABLE III

Expt. No.	Wt. of 	Tube °C Temp.	Time hrs.	Flow Rate mls./min.	Total wt. of Recovered material	Wt. of 	Yield %	Conversion %
1	3·0	385 ± 5°	9		2·3	0·8	59	50
2	2·8	410 ± 5	48		2·4	0·9	75	47
3	5·0	420 ± 5	20		3·2	2·2	62	80
4	5·0	440 ± 5	25		3·9	2·69	80	75
5	7·0	450 ± 5	24		4·3	2·15	50(b)	-
6	3·0	450 ± 5	48		1·0	0·7	25	-
7	8·0	420 ± 5	48		5·0	3·3	60	78
8	1·0(a)	440 ± 5	24		0·25	-		

a = The weight of volatile material obtained from experiment 5.

b = The low recovery of material due to mechanical losses.

Defluorination of perfluoro-4-(sec. butyl)pyridazine.

Perfluoro-4-(sec. butyl)pyridazine (2•9 g., 8•2 m.mole) was passed through a silica tube packed with coarse iron filings at 440 ± 5°C using a steady flow of dry nitrogen and collecting the product (1•3 g.) in a cold trap. Analytical scale v.p.c. (Col. 'O' 78°C) showed a two component mixture which was separated (Aerograph Col. 'A', 100°C) into:

(a) a colourless liquid 0•6 g., whose i.r. was identical with that of an authentic sample of perfluoro-4-(2'-butenyl)pyridazine, Estimated yield: 45%.

(b) starting material 0•3 g.

Attempted defluorination of perfluoro-2,4-di-(sec. butyl)pyridine.

In a similar experiment, perfluoro-2,4-di-(sec. butyl)pyridine (1•5 g., 2•56 m.mole) was passed through a silica tube packed with coarse iron filings at 440°C using a flow of dry nitrogen. A colourless liquid (1•0 g.) was recovered from the cold trap and shown by v.p.c. (Col. 'A' G.D.B. 78°C) to consist of a 5 component mixture. The presence of a weak absorption in the i.r. at 5.8μ indicates a $\rangle C=C \langle$ group.

Attempted defluorination of perfluoro-3,5-di-(sec. butyl)pyridazine.

Using a similar procedure, perfluoro-3,5-di-(sec. butyl)pyridazine (1•7 g.) was defluorinated at 420°C. Only a small quantity (0•2 g.) of a colourless liquid was recovered indicating that extensive decomposition of the starting material had occurred. V.p.c. measurements (Col. 'O', 78°C) indicated a 4 component mixture. An absorption at 5•8μ in the i.r. indicated the presence of a C=C group.

Reaction of perfluoro-4-(2'-butenyl)-pyridine with pentafluoropyridines.

Pentafluoropyridine (0·5 g., 2·96 m.mole), caesium fluoride (0·3 g., 3·3 m.mole), sulpholan (5 ml.) and perfluoro-4-(2'-butenyl)-pyridine (1·0 g., 1·9 m.mole) were sealed in a Carius tube. The tube was rotated in an oil bath at 150°C. After 17 hrs., vacuum transfer of volatile materials to a cold trap yielded a colourless liquid (1·3 g.). This was shown (v.p.c. G.D.B. 'A' 78°) to be a mixture of starting materials.

Attempted polymerisation of perfluoro-4-(2'-butenyl)-pyridine.

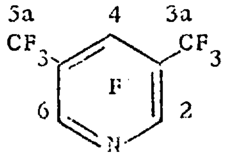
Perfluoro-4-(2'-butenyl)-pyridine (0·5 g., 0·95 m.mole) was sealed in a Carius tube under vacuum. The tube was irradiated in a ^{60}Co source for 5 days. Volatile material (0·4 g.) was recovered which was shown to be unchanged starting material (i.r.).

Attempted co-polymerisation of perfluoro-4-(2'-butenyl)-pyridine with hexafluoroprop-2-ene.

Perfluoro-4-(2'-butenyl)-pyridine (0·5 g., 0·95 m.mole) was placed in a Carius tube and the tube cooled. Hexafluoroprop-2-ene (2·(g., 13·3 mm.) was condensed into the tube which was then sealed. The tube was irradiated in a ^{60}Co source for 5 days. Volatile material (2·4 g.) was recovered and the gaseous fraction allowed to escape. The residual liquid (0·4 g.) had an identical i.r. with that of the starting material.

Preparation of perfluoro(3,5-dimethylpyridine).

Pentafluoropyridine (25 g.) and P.T.F.E. turnings (50 g.) were sealed in an autoclave (550 ml. capacity) which was heated at 550° for 15½ hours. The volatile products were distilled from the hot autoclave under vacuum and collected in a trap immersed in liquid air. Vapour phase chromatography on the distillate showed it to contain perfluoro(3,5-dimethylpyridine) (23·9 g., 60% yield), perfluoro(3-methylpyridine) (1·6 g., 5% yield), perfluoromesitylene and other, unidentified, products. The products from two preparations were combined and twice fractionated using a spinning band column. Perfluoro(3,5-dimethylpyridine) (30 g., 38% yield, 96% pure), containing approximately equal amounts of perfluoromesitylene and perfluoro(3-methylpyridine) as impurities, was obtained as a colourless liquid, b.p. 119-121/775 mm. A small sample of perfluoro(3,5-dimethylpyridine) was further purified by preparative vapour phase chromatography on a column of di-<u>n</u>-decylphthalate at 70°, b.p. 119/776 mm. (Found: C, 31·1; N, 5·0; F, 63·1. C_7F_9N requires: C, 31·3; N, 5·2; F, 63·5%). The mass spectrum shows a parent peak at M269 and the ultra-violet spectrum shows λ_{max} (cyclohexane) at 214, 247 and 250mμ. The ^{19}F n.m.r. spectrum of perfluoro(3,5-dimethylpyridine is shown below.

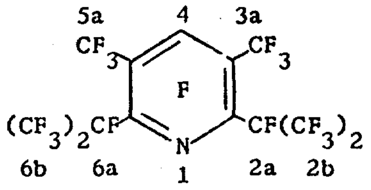


Peak	Chemical Shift ($CFCl_3$) Hz	p.p.m.	Integration	Shape	J Values Hz	Assignment
A	3193	56·54	2	broad quartet	$J_{2,3a}$ 20	2,6 F's
B	3383	59·91	6	d.o.d.	$J_{3a,2}$ $_{3a,4}$ = 21·5	3a and 5a F's
C	5152	91·24	1	heptet of triplets	$J_{4,3a}$ = 20·3 $J_{4,2}$ = 2·7	4F

Polyperfluoroisopropylation of Perfluoro-(3,5-dimethylpyridine).

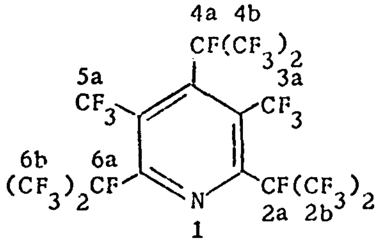
The apparatus consisted of a 250 ml., 3-necked flask fitted with an air-tight, ground glass stirrer. One side arm was connected to two consecutive reflux condensers and a lead from the top of the second condenser passed to a trap which was immersed in ice/water. The outlet of the trap passed to a small electric pump which circulated the gases in the system by way of a sintered glass lead placed in the second side arm of the flask. There were also connections for evacuating the system and introduction of hexafluoropropene, a bypass tap for the sinter to prevent suck back, and a bladder which was used as a reservoir for hexafluoropropene and ensured the automatic maintenance of atmospheric pressure inside the closed circuit apparatus. The 3-necked flask was heated in a thermostated oil bath.

Potassium fluoride (20 g.) and sulpholan (150 ml.) were placed in the flask and the apparatus was evacuated (10^{-2} mm. Hg) and then let down to hexafluoropropene until the bladder was inflated. Perfluoro-(3,5-dimethylpyridine) (9·7 g.) was injected into the flask through a serum cap and the mixture was stirred rapidly and the flask heated at $120 \pm 1^{\circ}$. The electric pump was switched on and the circulating gases were bubbled through the preparative mixture for 2 hours, after which the volatile products were transferred under high vacuum to a trap immersed in liquid-air. The product was analysed quantitatively (using a gas-density balance and an internal marker of toluene) and consisted of perfluoro(2,6-di-isopropyl-3,5-dimethylpyridine) (14·4 g., 70% yield), perfluoro(2,4,6-tri-isopropyl-3,5-dimethylpyridine) (1·6 g., 6% yield), perfluoro(3,5-dimethylpyridine) (0·97 g., 10% recovery), and small amounts of other, unidentified, substitution products together with dimers and trimers of hexafluoropropene. After fractionation and fractional freezing of higher boiling fractions at room temperature and below, perfluoro(2,6-di-isopropyl-3,5-dimethylpyridine) was obtained as a colourless solid, m.p. 37°. (Found: C, 27·2; N, 2·3; F, 69·7. $C_{13}F_{21}N$ requires: C, 27·4; N, 2·5; F, 70·1%). The mass spectrum shows a parent peak at M569 and the ^{19}F n.m.r. spectrum is set out below.



Peak	Chemical Shift (CFCl$_3$) Hz	p.p.m.	Integration	Shape	J Values Hz	Assignment
A	3128	55·40	6	d.o.d.o.h.	$J_{3a,4}$ = 39·5 $J_{3a,2a}$ = 50 $J_{3a,2b}$ = 3	3a and 5a F's
B	4210	74·56	12	d.o.q.	J = 3 and 3	2b and 6b F's
C	5049	89·41	1	heptet	$J_{4,3a}$ = 39·5	4F
D	10,219	181·0	2	q.o.h.	$J_{2a,3a}$ = 50 $J_{2a,2b}$ = 3	2a and 6a F's

Perfluoro(2,4,6-tri-isopropyl-3,5-dimethylpyridine) was isolated as a colourless oil from the residual liquors of the above preparation by repeated preparative vapour phase chromatography on a column of di-n-decylphthalate at 110°. (Found: C, 27·0; N, 2·15; F, 70·9. $C_{16}F_{27}N$ requires: C, 26·7; N, 1·94; F, 71·3%). The mass spectrum shows a parent peak at M719 and the ^{19}F n.m.r. spectrum is set out below.



Peak	Chemical Shift ($CFCl_3$) Hz		Inte-gration	Shape	J Values Hz	Assignment
	Hz	p.p.m.				
A	2968	52·57	6	broad complex		3a,5a F's
B	4016	71·11	6	broad		4b F's
C	4206	74·47	12	broad		2b,6b F's
D	8107	143·5	1	quartet	J = 40	4a F
E	10,257	181·7	2	over-lapping quartets	J 50 and 60	2a,6a F's

Preparation of Perfluoro(3-methylpyridine).

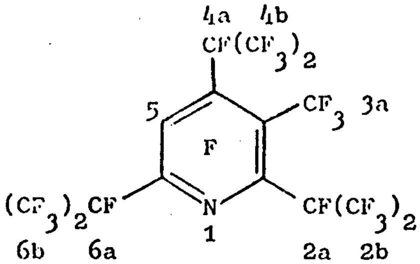
Pentafluoropyridine (25 g.) and P.T.F.E. turnings (50 g.) were sealed in an autoclave (550 ml. capacity) which was heated at 500° for 15½ hours. The volatile products were distilled from the hot autoclave under vacuum and collected in a trap immersed in liquid air. Vapour phase chromatography on the distillate showed it to contain perfluoro(3-methylpyridine) (11·3 g., 35% yield), perfluoro(3,5-dimethylpyridine) (5·6 g., 14% yield), pentafluoropyridine (1·8 g., 7% recovery), perfluoromesitylene and other, unidentified, products.

In a similar preparation, pentafluoropyridine (50 g.) and P.T.F.E. turnings (25 g.) were heated at 550° for 15½ hours and the major products were perfluoro(3-methylpyridine) (19·4 g., 30% yield), perfluoro(3,5-

dimethylpyridine) (8·8g., 11% yield) and pentafluoropyridine (0·55g., 11% recovery). The products of reaction were combined and twice fractionated, using a spinning band column, to give perfluoro(3-methylpyridine) (95% pure) as a colourless oil, b.p. 102-103°/746 mm. A small sample of perfluoro(3-methylpyridine) was further purified by preparative vapour phase chromatography on a column of di-n-decylphthalate at 70°, b.p. 102°/747 mm. (Found: C, 32·7; N, 6·2; F, 61·0. Calc. for C_6F_7N: C, 32·9; N, 6·4; F, 60·7%). The ^{19}F n.m.r. spectrum is identical with that reported by Lee and Orrell[11] and the boiling point and λ_{max} in the ultra-violet spectrum are the same as those reported by Barks et al.[12] The mass spectrum shows a parent peak at M219.

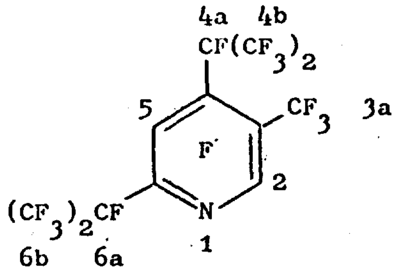
Polyperfluoroisopropylation of Perfluoro(3-methylpyridine)

The polyperfluoroisopropylation of perfluoro(3-methylpyridine) was carried out exactly as described for the polyperfluoroisopropylation of perfluoro(3,5-dimethylpyridine) using 7·7g. of perfluoro(3-methylpyridine) instead of 9·7g. of perfluoro(3,5-dimethylpyridine). The product consisted of perfluoro(2,4,6-tri-isopropyl-3-methylpyridine) (15·8g., 67% yield), perfluoro(2,4-di-isopropyl-5-methylpyridine) (3·0g., 16% yield) and small amounts of other, unidentified, products together with trimers and dimers of hexafluoropropene. After fractionation to remove volatiles, the major products were isolated by preparative vapour phase chromatography on a column of di-n-decylphthalate at 110°. Perfluoro(2,4,6-tri-isopropyl-3-methylpyridine) was obtained as a colourless oil. (Found: C, 26·9; N, 2·1; F, 71·0%). The mass spectrum shows a parent peak at M669 and the ^{19}F n.m.r. spectrum is set out below.



Peak	Chemical Shift (CFCl$_3$) Hz	Chemical Shift (CFCl$_3$) p.p.m.	Integration	Shape	J Values Hz	Assignment
A	2962	52·46	3	overlying d.o.d.	J = 48	3a F's
B	4185	74·11	6	d.o.h.	$J_{4b,5}$ 30 $J_{4b,4a}$ 3·5	4b F's
C	4204	74·44	6	d.o.d.?	$J_{2b,2a}$ 4	2b F's
D	4305	76·25	6	d.o.d.	$J_{6b,6a}$ = 6	6b F's
E	6179	109·4	1	broad heptet	J 30	5F
F	9715	172·0	1	q.o.h.	$J_{4a,3a}$ = 53 $J_{4a,4b}$ 3	4a F
G	10,153	179·8	1	q.o.h.	$J_{2a,3a}$ = 45 $J_{2a,2b}$ 3·5	2a F
H	10,537	186·5	1	d.o.h.	$J_{6a,5}$ = 58 $J_{6a,6b}$ = 6	6a F

Perfluoro(2,4-di-isopropyl-5-methylpyridine) was also obtained as a colourless oil. (Found: C, 28·0; N, 2·5; F, 69·0. $C_{12}F_{19}N$ requires: C, 27·8; N, 2·7; F, 69·5%). The mass spectrum shows a parent peak at M519 and the ^{19}F n.m.r. spectrum is set out below.



Peak	Chemical Shift (CFCl$_3$) Hz	Chemical Shift (CFCl$_3$) p.p.m.	Integration	Shape	J Values Hz	Assignment
A	3120	55·26	3	overlapping d.o.d.o.h.	J 53 J = 4	3a F's
B	3241	57·38	1	complex		2F
C	4213	74·61	6	overlapping d.o.d.o.q.	J 30	4b F's
D	4293	76·03	6	overlapping d.o.d.	J = 6	6b F's
E	6611	117·0	1	broad doublet		5F
F	9814	173·8	1	overlapping quartets	$J_{4a,5}$ = 60	4a F
G	10,487	185·8	1	overlapping d.o.h.	$J_{6a,5}$ = 60 $J_{6a,6b}$ = 6	6a F

Reactions of Caesium Isopropoxide with Tetrafluoropyridazine

(a) At 80-85°C

Diglyme (40 ml.) and caesium fluoride (6g., 39·6 mm.) were introduced into a 250 ml. conical flask under dry nitrogen. The flask was evacuated at room temperature. When de-gassing of the solvent had ceased, hexafluoroacetone was allowed into the system until atmospheric pressure was reached. Tetrafluoropyridazine (2·5g., 16·5 mm.) was introduced into the flask from a syringe through a serum cap at $80-85^{\circ}$C. The rapidly stirred mixture was heated at this temperature for 36 hours, adding hexafluoroacetone but maintaining caesium fluoride in excess.

The volatile materials were transferred under vacuum to a cold trap. Analytical scale v.p.c. indicated a mixture of tetrafluoropyridazine and diglyme. Treatment of the residue with dry methanol yielded a brown solid (0·5g., m.pt. $>300^{\circ}$).

(b) In a sealed tube

Diglyme (10 ml.), caesium fluoride (2g., 13·2 mm.) and tetrafluoropyrazine (2g., 13·2 mm.) were introduced into a carius tube under dry nitrogen. The tube was cooled and evacuated. Hexafluoroacetone (3g., 18·0 mm.) was condensed into the tube which was then sealed and rotated in an oil bath at 100-110

After 28 hrs., the tube was cooled and opened. The volatile materials were transferred under vacuum to a cold trap. Analytical scale v.p.c. showed these to consist of diglyme and traces of lower retention time material. The residue was treated with water and ether extracted (3 x 25 ml.). The extracts were combined, washed with water, dried ($MgSO_4$) and the solvent removed to yield a colourless liquid (0·8g.) which was shown to consist of a mixture of hexafluoroacetone hydrates by v.p.c., i.r., n.m.r. and mass spectroscopy.

Reaction of hexafluoropropene epoxide with pyridazine

(a) At $95-100^{\circ}$

Caesium fluoride (6g., 39·6 mm.) and sulpholan (50 ml.) were introduced under dry nitrogen into a 250 ml. flask fitted with a water condenser. The flask was then evacuated at room temperature. When degassing of the solvent had ceased, hexafluoropropene epoxide was allowed into the system until atmospheric pressure was reached and a bladder attached to the top of the condenser was partially inflated. Tetrafluoropyridazine (3•5 g., 22•9 mm.) was introduced into the flask when the reaction temperature had reached 95-100°C. The mixture was then heated with stirring at this temperature under an atmosphere of hexafluoropropene epoxide. After 8 hrs. the volatile materials (6 g.) were transferred under vacuum to a cold trap. Analytical v.p.c. showed these to consist of tetrafluoropyridazine, unreacted hexafluoropropene epoxide and traces of highly volatile material. Solvent extraction (ether) of the residues gave no further products. Unreacted hexafluoropropene epoxide was recovered from the reservoir.

(b) At 30°C

Caesium fluoride (3 g., 19•8 mm.) and sulpholan (30 ml.) were introduced into a 100 ml. flask under dry nitrogen. The flask was then evacuated at room temperature. When degassing of the solvent had ceased, a mixture containing hexafluoropropene epoxide (5 g., 30•0 mm.) and hexafluoropropene (0•5 g., 3•0 mm.) was allowed into the system until atmospheric pressure had been reached. Tetrafluoropyridazine (2 g., 13•2 mm.) was introduced into the flask at 30°C. The mixture was rapidly stirred at 30°C and the epoxide-propene mixture was circulated through the system.

After 20 hrs., volatile material (1·5g.) was transferred under vacuum to a cold trap. Analytical v.p.c. showed these to consist of unchanged perfluoropyridazine, perfluoropropene epoxide and traces of other materials. Solvent extraction of the residues gave no further products.

Reactions of hexafluoropropene epoxide with fluoride ion in acetonitrile at 0°C

(i) Caesium fluoride (0·5g.), and acetonitrile, were introduced into a small Carius tube under dry nitrogen. The tube was evacuated, cooled, and hexafluoropropene epoxide (1·5g., 9·0 mm.) was condensed into the tube which was then sealed and allowed to stand at 0-5°C.

After 3 days, the tube was cooled, opened and a white solid was collected (0·7g.). Mass spectrometry indicated a molecular weight of approximately 330.

(ii) Caesium fluoride (0·5g.) and acetonitrile were introduced into a small Carius tube under dry nitrogen. The tube was evacuated, cooled and a mixture of hexafluoropropene (0·2g., 0·6 mm.) and hexafluoropropene epoxide (1·5g., 9·0 mm.) was condensed into the tube. After sealing it was allowed to stand at 0-5°C.

After 3 days, the tube was cooled, opened and a white solid collected (0·6g.). Mass spectrometry indicated a molecular weight of approximately 330.

Reaction of hexafluoropropene epoxide with pyridazine in acetonitrile at 0°C

Acetonitrile (25 ml.) and caesium fluoride (1g., 6·6 mm) were introduced under dry nitrogen into a 100 ml. flask fitted with a water condenser. The flask was then evacuated at room temperature. When degassing of the solvent had ceased, dry nitrogen was allowed into the system until atmospheric pressure was almost reached. Tetrafluoropyridazine (3·0g., 19·8 mm.) was introduced into the flask and the flask cooled to 0-5°C. The reaction mixture was then stirred at 0-5°C and hexafluoropropene epoxide circulated through the system.

After 5 hrs., the stirring was stopped and the fluorocarbon layer (2·2g.) was readily separated. Analytical v.p.c. indicated a four component mixture containing no pyridazine. An i.r. spectrum of the mixture indicated the presence of a -COF group (5·3μ). Pyridazine (2·8g.) was recovered from the solvent layer.

Fluoride Ion-initiated Reactions of Tetrafluoropyridazine and Perfluorocycloalkenes

Reactions involving perfluorocyclohexene

(a) Using 1 molecular proportion of perfluorocyclohexene

Two reactions were carried out in which equimolar quantities of tetrafluoropyridazine and perfluorocyclohexene were heated in the presence of caesium fluoride and sulpholan in a stainless-steel autoclave (for quantities and reaction conditions, see Table IV).

The products were recovered by vacuum transfer from the autoclave into a cold trap. Examination by v.p.c. (column 'O' at 200°) showed that in reaction (i) a mixture of unchanged perfluorocyclohexene and tetrafluoropyridazine and a product of longer retention time was obtained. In the mass spectrum of this mixture there was a peak at $^{m}/e$, 414 which corresponds to the monosubstituted derivative of pyridazine. The material recovered from reaction (ii) was shown by v.p.c. to be one component (a colourless viscous liquid), and identified as perfluoro-(4-cyclohexylpyridazine), b.pt. 200°/760 mm. (Found: C, 29·1; F, 64·7%; M, 414. $C_{10}F_{14}N_2$ requires C, 29·0; F, 64·3%; M, 414). $\lambda_{max.}$ (cyclohexane) = 230 and 272 mμ, (ε = 7403 and 6963). Yield of product, 70% (100% conversion of tetrafluoropyridazine).

When reaction (ii) was repeated, the materials remaining after vacuum transfer of the volatile product were poured into water and extracted in the usual way with ether. In this way a yellow-brown solid (1·0g.) was recovered, and this was dissolved in hot benzene with a little ethanol added.

Table IV

Reaction	$C_4F_4N_2$	C_6F_{10}	CsF	Sulpholan	Temp. (°C)	Time	Wt of products recovered
(i)	2·0g. (13·2 m.moles)	3·5g. (13·4 m.moles)	2g.	25 mls.	80°	19 hours	4·3g.
(ii)	1·5g. (9·9 m.moles)	2·8g. (10·7 m.moles)	2g.	25 mls.	110°	19 hours	2·8g.

On cooling a pale brown solid crystallised out, and this was shown by i.r. spectroscopy to be the corresponding dicyclohexylpyridazone which was characterised fully in the following reaction.

(b) Using 2 molecular proportions of perfluorocyclohexene

Tetrafluoropyridazine (1·0g., 6·6 m.moles), perfluorocyclohexene (3·7g., 14·1 m.moles), caesium fluoride (2g.) and sulpholan (25 mls.) were introduced into a stainless-steel autoclave which was then shaken for 22 hours at 120°. The autoclave was opened and the volatile materials transferred under vacuum to a cold trap. The product mixture (1·8g.) was shown by v.p.c. to consist of unchanged C_6F_{10}, a trace amount of tetrafluoropyridazine, and the monosubstituted pyridazine (45% yield) (from retention times). The remaining materials were poured into water and extracted with ether, the extract dried ($MgSO_4$), and removal of the solvent left a brown solid (1·5g.). Sublimation of the solid at 200° and 0·005 mm. gave a yellow crystalline solid which melted at ca. 260°. No chromatographic analysis was possible but, in the mass spectrum of the solid, molecular ion peaks were present at $^m/e$ = 676, 674 and 938 corresponding to the disubstituted pyridazine, its monohydroxy derivative, and the trisubstituted pyridazine respectively. The solid was dissolved in hot benzene (containing a little ethanol) and, on cooling, a pale yellow crystalline solid (0·2g.) was obtained. This was filtered from the mother liquid, dried by pumping under vacuum, and shown to be a,b-perfluorodicyclohexyl-c-fluoro-1H-pyridazin-d-one, m.pt. 302°. (Found: N, 4·00; H, 0·49; F, 65·1%; M, 674. $C_{16}HF_{23}N_2O$ requires N, 4·15; F, 64·8%). $\lambda_{max.}$ (ethanol) = 243 and 305 (broad) mμ, (ε = 8243 and 5707).

Absorptions due to the $\rangle$C=O and $\rangle$N-H vibrations were present at 3·3 and 6·3μ respectively in the i.r. spectrum of the solid, but a correct elemental analysis for carbon could not be obtained. Insufficient of this compound was obtained for n.m.r. studies.

Reaction of Perfluoro-(4-cyclohexylpyridazine)

Reaction with ammonia

5 mls. 0·880 ammonia was stirred in a small conical flask which was immersed in ice. Perfluoro-(4-cyclohexylpyridazine) (2·0g.) was added slowly to the ammonia solution. A yellow-brown solid was precipitated almost immediately, and this was filtered, washed with water, and recrystallised from aqueous ethanol to give a pale brown crystalline solid (1·5g.). This was identified as 4-perfluorocyclohexyl-5-amino-3,6-difluoropyridine, m.pt 191°. (Found: C, 29·6; H, 0·79; F, 60·5%; M, 411. $C_{10}H_2F_{13}N_3$ requires C, 29·2; H, 0·5; F, 60·1%; M, 411). $\lambda_{max.}$ (ethanol) = 241 and 286·5 (broad) mμ (ε = 7911 and 6360). The yield of the amino-derivative was 75%.

Reaction with sulphuric acid

Perfluoro-(4-cyclohexylpyridazine) (0·5g.) in concentrated sulphuric acid (10 mls.) was treated dropwise with water (40 mls.) during 40 mins. with vigorous stirring; the addition was regulated to keep the temperature below 60°. The mixture was stirred for a further 2·5 hours at ca. 25° and then extracted with 2 x 50 ml. portions of ether. The extract was washed with saturated sodium sulphate solution and dried ($MgSO_4$), and removal of the solvent left a white powdery solid (0·50g.). This was recrystallised from benzene to give a white crystalline solid which was identified as 3,5-difluoro-4-perfluorocyclohexyl-1H-pyridazin-6-one, m.pt. 251° (d). (Found: C, 28·8; H, 0·34; F, 59·9%; M, 412. $C_{10}HF_{13}N_2O$ requires C, 29·1; H, 0·24; F, 60·0%; M, 412). $\lambda_{max.}$ (ethanol) = 241 and 276 (broad) mμ, (ε = 8900 and 5600). Yield of pyridazone 100%.

Photolysis of perfluoro-(4-cyclohexylpyridazine)

Perfluoro-(4-cyclohexylpyridazine) (0·6g.) was placed in a small silica tube and irradiated with u.v. light for 138 hours. The resulting brown liquid (0·4g.) was removed from the tube with a pipette and purified by vacuum distillation to give a colourless liquid. The product was shown to be pure by v.p.c. (column 'O' at 170°), having a shorter retention time than that of the starting material, and identified as perfluoro-(6-cyclohexylpyrazine), (Found: C, 28·7; F, 64·4%; M, 414. $C_{10}F_{14}N_2$ requires C, 29·0; F, 64·3%; M, 414). $\lambda_{max.}$ (ethanol) = 276 mμ (ε = 7478). Yield of monosubstituted pyrazine, 70%. The structure was confirmed by ^{19}F n.m.r. spectroscopy.

Attempted pyrolysis of perfluoro-(4-cyclohexylpyridazine)

Three preliminary reactions were carried out at different temperatures in order to find an optimum temperature for the pyrolysis of perfluoro-(4-cyclohexylpyridazine). A small quantity of perfluoro-(4-cyclohexylpyridazine) was passed through a silica tube packed with silica wool using a steady flow of dry nitrogen and the products collected in a cold trap (for quantities and conditions, see Table V).

Table V

Temp. (°C)	Wt. of $C_{10}F_{14}N_2$	N_2 flow (mls./min.)	Wt. of products	Composition of products (from analytical v.p.c.)
500°	0.5g.	100	0.2g.	(i) Unchanged $C_{10}F_{14}N_2$ + (ii) major product with slightly shorter retention time + (iii) minor component (low b.pt.)
600°	0.5g.	50	0.25g.	No unchanged $C_{10}F_{14}N_2$ + two components with shorter retention times + component (iii) as in above
700°	0.5g.	100	0.15g.	No unchanged $C_{10}F_{14}N_2$ + two major components of shorter retention times

Perfluoro-(4-cyclohexylpyridazine) (3·1g.) was passed through the silica tube at 650° using a flow of nitrogen (50-100 mls./min.). The product, a brown liquid (1·4g.), was collected in a cold trap and shown by v.p.c. to consist of two components having slightly different retention times. Separation of the mixture by prep. scale v.p.c. (Aerograph: column 'O' at 120°) gave a colourless liquid, which was shown to be recovered perfluoro-(4-cyclohexylpyridazine) by i.r. spectroscopy, and a white crystalline solid, m.pt. 37-38°. I.r. and ^{19}F n.m.r. spectra of the solid were obtained but it decomposed to a brown liquid before elemental analysis and mass spectral data could be acquired. A small quantity of a colourless liquid was recovered after decomposition by vacuum distillation. (Found: M, 376. $C_{10}F_{12}N_2$ requires M, 376). $\lambda_{max.}$ (ethanol) = 242·5 and 292 (infl.) mμ (ε = 5926 and 1995). The i.r., n.m.r. and mass spectral data obtained showed the product to be perfluoro-(4-cyclohexenylpyridazine).

Nucleophilic Substitution Reactions using Sodium Methoxide

Perfluorobicyclopentenyl, $C_{10}F_{14}$

(a) Reaction of $C_{10}F_{14}$ with 2 molecular proportions of methoxide ion

To a stirred solution of perfluorobicyclopentenyl (0·40g., 1·04 m.moles) in 25 mls. dry methanol at room temperature was added 25 mls. (2·5 m.moles) of a 0·1M solution of sodium methoxide over a period of 25 mins. The mixture was then stirred under reflux for a further 4 hours. After cooling, the solution was poured into water (500 mls.) and extracted with two portions of methylene chloride. The extracts were combined, dried ($MgSO_4$), and removal of the solvent left a pale yellow liquid (0·40g.) which solidified slowly on standing to give a white crystalline solid. This was shown to be 2,2'-dimethoxy-dodecafluorobicyclopentenyl, m.pt. 52-53°. (Found: C, 35·4; H, 1·00; F, 55·1%; M, 410. $C_{12}H_6F_{12}O_2$ requires C, 35·1; H, 1·46; F, 55·6%; M, 410). Yield of dimethoxy derivative 95%.

(b) Attempted preparation of the monomethoxy derivative of $C_{10}F_{14}$

Two reactions were carried out using one molecular proportion of sodium methoxide solution (for quantities and reaction conditions, see Table 5). In each case the requisite amount of sodium methoxide solution was added to a stirred solution of the fluorocarbon in dry methanol.

Table VI

Reaction	$C_{10}F_{14}$	0·1M sodium methoxide solution (mls.)	Reaction conditions
(i)	0·47g. (1·22 m.moles) in 30 mls. methanol	10 (1·00 m.moles)	NaOMe solution added over a period of 20 mins. to a stirred solution of $C_{10}F_{14}$ at room temp., and mixture stirred at room temp., for a further 90 mins.
(ii)	0·50g. (1·30 m.moles) in 30 mls. methanol	13 (1·30 m.moles)	NaOMe solution added over a period of 15 mins. to a stirred solution of $C_{10}F_{14}$ at room temp., and mixture stirred under reflux for a further 75 mins

After each reaction the methanol solution was poured into a large volume of water and extracted with methylene chloride in the usual way.

In reaction (i), 0·5g. pale yellow liquid was recovered and shown by analytical v.p.c. (column 'O' at 150°) to consist of the mono- and di-methoxy derivatives in approx. ratio 40:60 respectively with a trace of unreacted $C_{10}F_{14}$.

In reaction (ii), 0·5g. pale yellow liquid was recovered and this was shown by v.p.c. to be mainly the dimethoxy derivative (ca. 80% of the total area of the chromatogram) with small amounts of the monomethoxy compound and unreacted $C_{10}F_{14}$. On cooling, solidification occurred and it was possible to extract a white crystalline solid. This was confirmed as the dimethoxy derivative by i.r. and mass spectrometry.

Fluoride Ion-initiated Reaction of Perfluorobicyclopentenyl with Hexafluoropropene

Caesium fluoride (1g., 6·6 m.moles) and sulpholan (15 mls.) were introduced under dry nitrogen into a 50 ml. flask fitted with a water condenser. The flask was then evacuated at room temperature. When degassing of the solvent had ceased, hexafluoropropene was allowed into the system until atmospheric pressure was reached and a bladder attached to the top of the water condenser was partially inflated. Perfluorobicyclopentenyl (1·2g., 3·11 m.moles) was introduced into the flask from a pipette when the reaction mixture had reached the reaction temperature (100°). The mixture was then heated with stirring at this temperature, under an atmosphere of hexafluoropropene, for 4½ hours.

After this time the reservoir of hexafluoropropene had collapsed and a partial vacuum was indicated in the system. The volatile materials (0·7g.) were then transferred under vacuum to a cold trap. Analytical v.p.c. showed these to consist of hexafluoropropene dimers and trimers (ca. 90%), a trace of perfluorobicyclopentenyl, and a product of longer retention time (ca. 10%).

The remaining materials were extracted from water (150 mls.) with 3 x 50 ml. portions of ether. The extracts were dried ($MgSO_4$) and removal of the solvent left a yellow-orange solid. This was sublimed at 0·05 mm. and 50° to give a white solid (0·75g.), which was then recrystallised from ether/petroleum ether giving white needle-shaped crystals. The compound was identified as perfluoro(2,2'-diisopropylbicyclopentenyl), m.pt. 54-55°. (Found: C, 27·8; F, 71·7%; M, 686. $C_{16}F_{26}$ requires C, 28·0; F, 72·0%; M, 686). Yield of $C_{16}F_{26}$ was 35% (based on quantitative conversion of perfluorobicyclopentenyl).

The preparation of a further quantity of perfluoro-(2,2'-diisopropylbicyclopentenyl) in a subsequent experiment showed that the product with a longer retention time in the mixture of volatile products was perfluoro-(2,2'-diisopropylbicyclopentenyl).

Attempted defluorination of perfluoro-(2,2'-diisopropylbicyclopentenyl)

Perfluoro-(2,2'-diisopropylbicyclopentenyl) (0·4g.) was passed over iron filings heated to 480° in a silica tube. A white solid (0·1g.) was collected in a cold trap after 2 hours, and this was shown to be pure by v.p.c.

(column '0' at 125°). The i.r. spectrum of the product was identical to that of the starting material.

Photolytic Reactions

Perfluorocyclopentene dimer, $C_{10}F_{16}$

$C_{10}F_{14}$ (1·0g.) was placed in a small bore silica tube and a trace of benzophenone was added as photosensitiser. The tube was sealed and irradiated under a u.v. lamp for 113 hours, after which time the tube was cooled, opened, and the products transferred under vacuum to a cold trap. A colourless liquid (0·6g.) was obtained and shown to be unchanged $C_{10}F_{14}$ by v.p.c. and i.r. spectroscopy.

Perfluorobicyclopentenyl, $C_{10}F_{14}$

Three reactions were carried out in small bore silica tubes which were irradiated under a u.v. lamp (for quantities and reaction times, see Table (VII).

Table VII

Reaction	$C_{10}F_{14}$	Benzophenone	Time of irradiation with u.v. light
1	1·0g.	None	18 hours
2	1·0g.	Trace	14·5 hours
3	1·0g.	Trace	290 hours

It was shown by v.p.c. and i.r. spectroscopy that, in all three reactions, the material recovered was unchanged $C_{10}F_{14}$.

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13. ABSTRACT

This work is concerned with the preparation of model compounds based on the reactions of tetrafluoropyridazine and pentafluoropyridine with fluorinated olefins acetylenes or ketones. The compounds which have been synthesized have been tested as to their thermal and oxidative stability.

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