Fluorinated aza-alkenes and related chemistry

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A THESIS

ENTITLED

FLUORINATED AZA-ALKENES AND RELATED CHEMISTRY

Submitted by

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A candidate for the degree of Doctor of Philosophy

Department of Chemistry

(1987)

To Mum, Dad, Mike, Jennie, and John

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Thanks are also due to Dr. Ray Matthews for help with the running and interpretation of n.m.r. spectra; Dr. M. Jones and Mr. V.J. McNeilly for running of mass spectra and help in their interpretation.

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Last, but by no means least, I would like to thank Bayer A.G. for generously supplying chemicals.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1982 and September 1986. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree. Part of this work has been the subject of the following papers:

R.N. Barnes, R.D. Chambers, C.D. Hewitt, M.J. Silvester, and E. Klauke, J,Fluorine Chem., 1984, 24, 211.

R.N. Barnes, R.D. Chambers, C.D. Hewitt, M.J. Silvester, and E. Klauke, J.Chem.Soc.Perkin Trans.I., 1985, 53.

R.D. Chambers, C.D. Hewitt, M.J. Silvester, and E. Klauke, J.Fluorine Chem., 1986, 32, 389.

R.N. Barnes, R.D. Chambers, and C.D. Hewitt, J.Fluorine Chem., 1986, 34, 59.

A paper presented at the 4th European Symposium on Organic Chemistry at Aix-en-Provence, France, August 1985.

SUMMARY

The fluoride ion catalysed reactions of perfluoro-2,5-diazahexa-2,4-diene were studied. Vapour phase reaction over CsF gave a mixture of perfluoro-1-methyl-1,3-diazacyclopent-2-ene and -3-ene. Reaction in solution gave a variety of dimers; product composition was dependent on fluoride source or reaction conditions and was due to kinetic or equilibrium control.

Prolonged stirring of perfluoro-1-methyl-1,3-diazacyclopent-2- and -3-ene with CsF in acetonitrile gave a stable nitranion, the perfluoro-3-methyl-1,3-diazacyclopentyl anion. Similarly, the perfluoro-2,4-bisisopropyl-1-azacyclohexl anion was formed from perfluoro-2,4-bisisopropyl-1-azacyclohex-1-ene.

Reaction of perfluoro-1,1'-bis-1,3-diazacyclohex-2-enyl with CsF at 150°C in the absence of solvent gave perfluoro-4-methyl-1,2,5,7-tetraazatricyclo[3.3.1.$0^{2.6}$]undec-4-ene via intramolecular elimination of fluoride from a saturated position by a nitranion in a step reminiscent of the Favorskii rearrangement.

The fluoride ion-induced co-oligomerisation reactions of perfluoro-1-methyl-1,3-diazacyclopent-2- and -3-ene with perfluoro-cyclobutene, -cyclopentene, and -cyclohexene were performed. Mono- and bis-(3-methylimidazolidin-1-yl)cyclobutene and -pentene derivatives were prepared but perfluorocyclohexane was less reactive and only the 1 : 1 adduct could be obtained.

The perfluoro-3-methyl-1,3-diazacyclopentyl anion could be trapped by fluorinated aromatic compounds. A number of mono- and di-substituted benzene, pyrimidine and pyridazine derivatives were prepared. Reaction with trifluoro-1,3,5-triazine gave a tri-substituted product. Kinetic and thermodynamic control was observed in product formation of disubstituted pyrimidines and pyridazines.

Comparisons of the ultraviolet spectra of perfluoropyridazine, perfluoro-4,5-bisisopropylpyridazine and perfluoro-4,5-bis-(3-methylimidazolidin-1-yl)pyridazine showed that the perfluoro-3-methylimidazolidin-1-yl substituent has an electron-withdrawing influence similar to that of perfluoroisopropyl.

Reactions of perfluoro-(3-methylimidazolidin-1-yl)-cycloalkenes showed them to be remarkably unreactive when compared to similar perfluorocycloalkylcycloalkenes. This finding was attributed to steric effects.

Reaction of p-nitrobenzylidene triphenylphosphorane with hexafluorobutyne gave a 1 : 1 adduct which reacted with hydrochloric acid or hexafluoroacetone to give a novel fluorinated alkene and diene respectively. Attempts to prepare higher adducts gave mixtures.

Reactions of p-nitrobenzylidene triphenylphosphorane and 9-fluorenylidene triphenylphosphorane with hexafluoroacetone gave novel trifluoromethylated alkenes in high yield.

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INTRODUCTION

CHAPTER 1 SYNTHESIS AND REACTIONS OF FLUORINATED IMINES

1A SYNTHESIS

1A.1 Via elimination reactions A. Pyrolysis

Pyrolysis of tris(perfluoroalkyl)amines gave the first examples of perfluoroaza-alkenes in 1953[1], perfluorotriethylamine reacting to produce perfluoro-2-azabut-1-ene (1).

$$(C_2F_5)_3N \xrightarrow[\text{GRAPHITE TUBE}]{745°C} \underset{(1)}{C_2F_5N{=}CF_2} + C_2F_4 + C_3F_6$$

This general method was extended to give other higher homologues, but is restricted to preparation of imines containing a terminal difluoromethylene group. Fluorinated internal aza-olefins were obtained by pyrolysis of the same amines over various catalysts; e.g. AlF_3/Al_2O_3[1] or Pt metal[2].

$$\text{e.g.}\quad (n\text{-}C_4F_9)_3N \xrightarrow[650°C]{\text{Pt metal}} CF_3CF_2CF_2CF{=}NCF_3 \quad (43\%)$$

Polyfluoroalkylazides can be readily prepared from fluoroolefins, and pyrolysis gives aza-alkenes in good yield. The pyrolysis of the azide (2) prepared from hexafluoropropene and ethanolic sodium azide gave imine (3)[3]. The presence of hydrogen leads to the possibility of

$$CF_3CF{=}CF_2 \xrightarrow[C_2H_5OH,\ 0°C]{NaN_3} \underset{(2)\ (36\%)}{CF_3CHFCF_2N_3}$$

$$(2) \xrightarrow[Pt]{270 - 280°C} \underset{(3)\ (86\%)}{CF_3CFHN{=}CF_2}$$

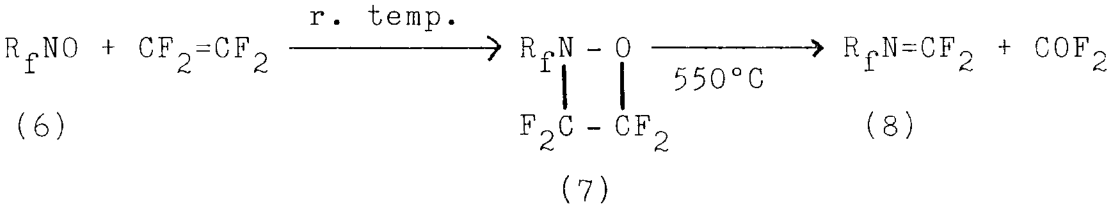
removal of HF to yield a diene. More recently pyrolysis of the polyfunctional azide (4) gave the imine (5)[4] containing a synthetically useful terminal acid fluoride function.

$$N_3CF_2CF_2C(CF_3)FO(CF_3CFCF_2O)_2CF(CF_3)COF \qquad (4)$$

$$\Big\downarrow \Delta$$

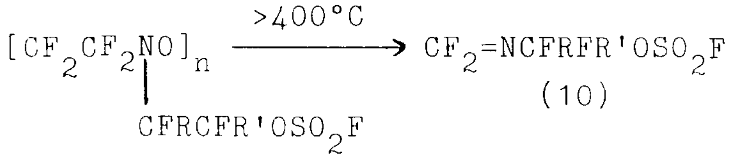
$$CF_3N{=}CFCF(CF_3)O(CF_3CFCF_2O)_2CF(CF_3)COF \quad (5)$$

Reaction of perfluoronitrosoalkanes (6) with perfluoroalkenes gave perfluorooxazetidine derivatives (7), pyrolysis of which proved a good general route to perfluoroimines (8)[5,6]. This route is limited to the synthesis of



imines containing a terminal difluoromethylene group since perfluoroalkyl-substitution of the fluoroolefins substantially reduces their reactivity towards perfluoronitrosoalkanes[6].

In a recent paper pyrolysis of the polymer (9) was shown to produce perfluoroazomethines (10) containing a terminal fluorosulphate group[7].



$$[CF_2CF_2\underset{CFRCFR'OSO_2F}{NO}]_n \xrightarrow{>400°C} CF_2{=}NCFRFR'OSO_2F$$

(10)

$(R{=}F,\ Cl;\ R'{=}F.\quad R{=}F;\ R'{=}OCF_3)$
(9)

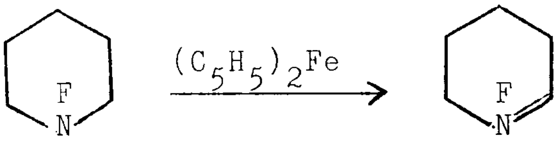
1A.1.B Defluorination reactions

Reductive defluorination using dicyclopentadienyliron and dicumenechromium has been used to prepare a wide range of cyclic and acyclic fluorocarbon imines in good yield[8].

Primary perfluoroamines react to produce N-fluoroimines, a rare and interesting class of compounds. Similarly, defluorination of secondary perfluoroamines, e.g.

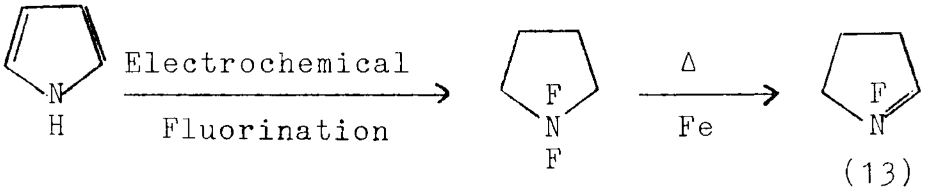
$$C_3F_7CF_2NF_2 \xrightarrow{(C_5H_5)_2Fe} \underset{(87\%)}{C_3F_7CF{=}NF}$$

perfluoropiperidine (11), readily gives the corresponding aza-alkenes.



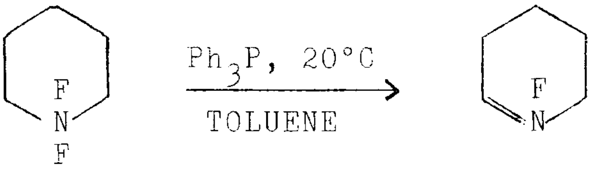
(11) (12)
(94%)

Defluorination over transition metal catalysts has also found use, for instance in the thermolysis of perfluorotetrahydropyrrole over iron to give perfluoro-1-azacyclopent-1-ene (13). Similar attempts to prepare perfluoro-1-azacyclohex-1-ene (12) from perfluoropiperidine (11) by thermolysis over various metal catalysts gave poor yields in general[9-11]. However, in addition to the route discussed earlier using dicyclopentadienyliron, defluorination



(13) (50%)

of (11) with triphenylphosphine gave (12) in good yield[12].

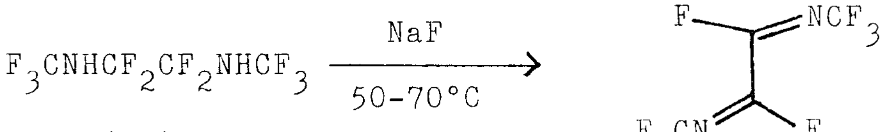


(11) (12)

1A.1.C Dehydrofluorination reactions

The strong inductive withdrawing influence of perfluoroalkyl groups causes the proton in bis(perfluoroalkyl) secondary amines to be very much more acidic than that in the corresponding hydrocarbon derivatives. One consequence of this is that such compounds can be readily dehydrofluorinated by mild base.

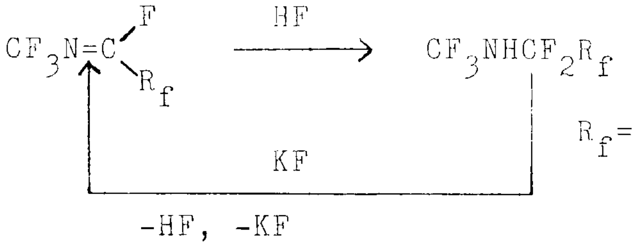
This methodology was applied in the synthesis of perfluoro-2,5-diazahexa-2,4-diene (15) from the ethylene diamine derivative (14) by dehydrofluorination over sodium fluoride in the absence of solvent[13]. This reaction which proceeds in quantitative yield, has been performed many



(14) (15)

times in this laboratory. Some chemistry of (15) is discussed in a later chapter.

Russian workers have recently used this method to purify fluoroazomethines, prepared by pyrolysis of perfluorotrialkylamines, containing 5-15% impurities which could not be separated by distillation. The impure imines were treated with HF, and after distillation of volatile impurities, the dialkylamines were dehydrofluorinated by KF to give analytically pure imines[14].

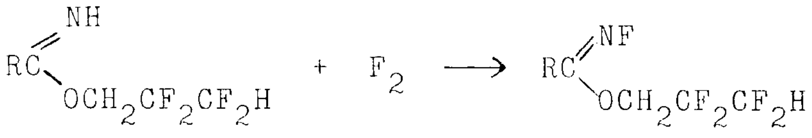


$R_f = CF_3$, C_2F_5, C_3F_7

1A.2 Via Halogenation

1A.2.A Elemental Fluorine

The use of elemental fluorine as a reagent has been demonstrated in the synthesis of N-fluoroiminoesters (17) from the 1,1,3-trihydroperfluoropropyl ester (16) of iminoperfluorocarboxylic acids[15].



(16) (17)

$R = CF_3$, $CF(NO_2)_2$

1A.2.B Hydrogen Fluoride

Reaction of perchloroimines with HF, with subsequent dehydrofluorination of the resulting secondary amines with alkali metal fluorides is a useful route to fluorinated imines. Examples include the synthesis of perfluoro-2-azapropene (18) and the diazadiene (15)[17-20].

$$CCl_3N{=}CCl_2 \xrightarrow{HF} (CF_3)_2NH \xrightarrow[140\text{-}150°C]{KF} CF_3N{=}CF_2 \quad (70\%)$$

(18)

$$\begin{tikzcd}
 & Cl_2C{=}NCCl_2CCl_2N{=}CCl_2 \arrow[r, "HF", "70°C"'] & CF_3NHCF_2CF_2NHCF_3 \arrow[d, "NaF", "\text{ROOM TEMPERATURE}"'] \\
\text{(15)} & CF_3N{=}CFCF{=}NCF_3 \arrow[r, shift right] & CF_2{=}NCF_2CF_2N{=}CF_2 \arrow[l, shift right, "F^-"']
\end{tikzcd}$$

1A.2.C Miscellaneous

Silver (I) and Silver (II) fluorides have been used to prepare fluorinated aza-alkenes from corresponding brominated derivatives[21].

$$\begin{tikzcd}
CBr_2{=}N{-}N{=}CBr_2 \arrow[r, "AgF_2", "100°C"'] \arrow[d, "AgF", "70°C"'] & CF_3N{=}NCF_3 \quad (92\%) \\
CF_2{=}N{-}N{=}CFBr \arrow[r, "{AgF,\ 125°C}"] & CF_2{=}N{-}N{=}CF_2 \quad (33\%)
\end{tikzcd}$$

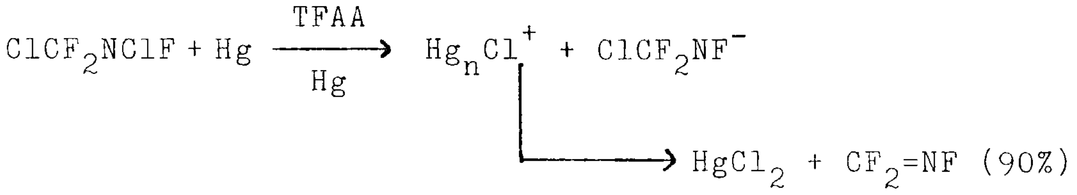
Similarly, reaction of the chloroazacyclopentene (19) with an AgF/AgF_2 mixture gave the first preparation of perfluoro-1-azacyclopent-1-ene (20)[22].

(19) (20)

Addition of ClF to chlorofluoroimines, followed by dechlorination, effected either over mercury or thermally, gave terminal N-fluoroimines[23]. A more recent report claims that large quantities of chlorotrifluoromethane are produced,

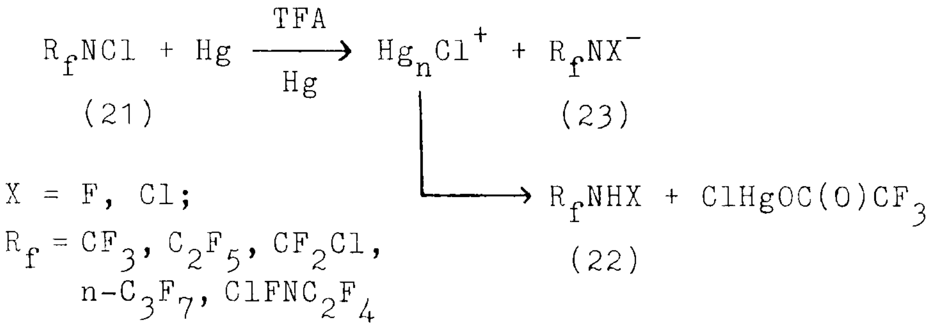
$$ClFC{=}NF + ClF \longrightarrow ClF_2CNFCl \xrightarrow[\text{or } \Delta]{Hg} F_2C{=}NF$$

possibly as a result of the exothermicity of the dechlorination reaction over mercury[24]. DesMarteau and co-workers have improved the yield of perfluoromethanimine by moderating the reaction in trifluoroacetic anhydride. Similarly dehalogenation of amines (21) in trifluoroacetic acid gave



$$ClCF_2NClF + Hg \xrightarrow[Hg]{TFAA} Hg_nCl^+ + ClCF_2NF^- \longrightarrow HgCl_2 + CF_2{=}NF\ (90\%)$$

the corresponding N-hydro amines (22) resulting from proton abstraction from the solvent by an intermediate nitranion (23). The amines (22) were readily dehydrofluorinated over



$$\underset{(21)}{R_fNCl} + Hg \xrightarrow[Hg]{TFA} Hg_nCl^+ + \underset{(23)}{R_fNX^-} \longrightarrow \underset{(22)}{R_fNHX} + ClHgOC(O)CF_3$$

$X = F, Cl;$

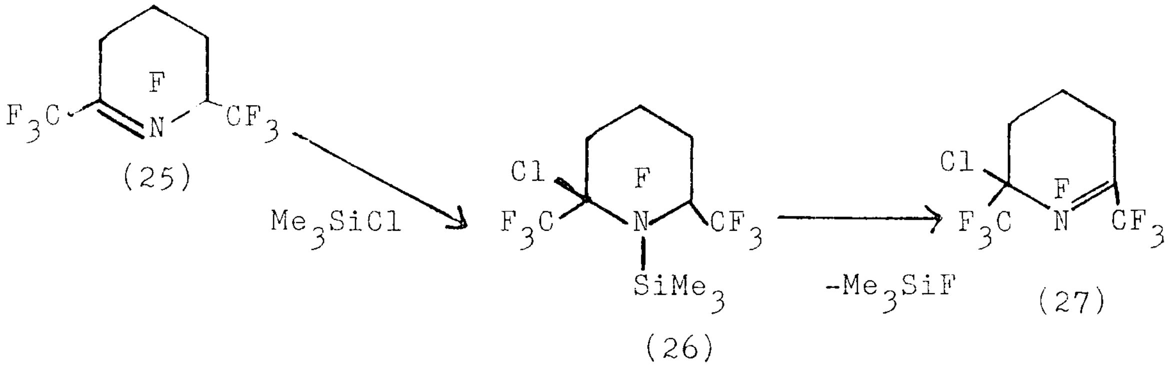
$R_f = CF_3, C_2F_5, CF_2Cl, n\text{-}C_3F_7, ClFNC_2F_4$

KF to give imines (24)[24].

$$\underset{(22)}{R_fCF_2NHX} \xrightarrow[25°C]{KF} \underset{(24)}{R_fCF{=}NX}$$

Substitution of chlorine for fluorine has been reported in reactions of perfluorocarbons with trimethylsilylchloride, the driving force being the formation of the extremely strong fluorine-silicon bond.

This chemistry is used in the conversion of the perfluoroazacyclohexene derivative (25) to the chlorinated compound (27) by trimethylchlorosilane[25]. The reaction



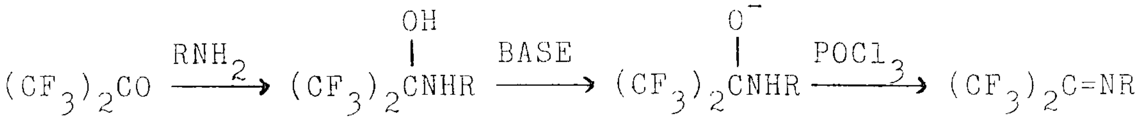
proceeds via intermediate (26) which readily eliminates trimethylfluorosilane under the reaction conditions to give (27). Imine (25) has also been converted to (27) using aluminium trichloride and in this case a bridged intermediate is proposed.

1A.3 CONDENSATION REACTIONS

The most common method for formation of a C=N bond in a hydrocarbon system is by condensation of a primary amine with a ketone, consequently it is not surprising that this methodology has found extensive application in the synthesis of fluorinated imines. This synthetic route has the additional advantage that it facilitates preparation of aza-alkenes with hydrogen or an alkyl group attached directly to nitrogen.

1A.3.A Hexafluoroacetone derivatives

Hexafluoroacetone (28) can be reacted with a variety of primary amines, and the resultant products (29) dehydrated with base and $POCl_3$ to give the aza-alkenes (30) in yields of 60 - 80% dependent on the substituent R[26].

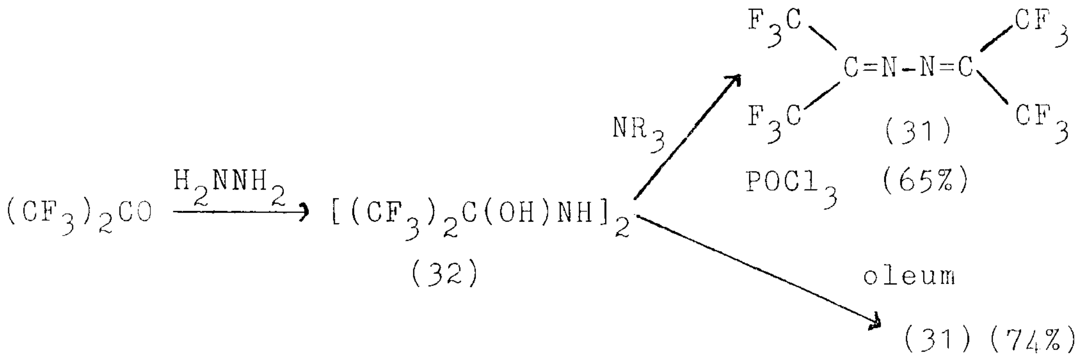


$$(CF_3)_2CO \xrightarrow{RNH_2} (CF_3)_2\overset{OH}{\overset{|}{C}}NHR \xrightarrow{BASE} (CF_3)_2\overset{O^-}{\overset{|}{C}}NHR \xrightarrow{POCl_3} (CF_3)_2C{=}NR$$

(28) R = H, alkyl, aryl (29) (30)

The reduced basicity of fluorinated amines makes this reaction less successful for the preparation of perfluoroimines[27].

Condensation of hexafluoroacetone with hydrazine yields hexafluoroacetone azine (31), the chemistry of which is particulary interesting, and will be discussed later in this chapter. Conventional use of base and phosphorus oxychloride to dehydrate intermediate (32) gave early workers the desired azine (31) in 65% yield[28], however more recently, workers in Russia have claimed improved yields for this step using oleum as the dessicant.



Condensation of the bisamides (33) with hexafluoroacetone gave the bis(perfluoroacyl)imines (34)[29].

$$\underset{(33)}{H_2NCO(CF_2)_nCONH_2} \xrightarrow[\text{(ii) POCl}_3\text{, pyridine}]{\text{(i) excess (CF}_3\text{)}_2\text{CO, sulpholane}}$$

$$\underset{(34)}{(CF_3)_2C{=}NCO(CF_2)_nC(O)N{=}C(CF_3)_2} \qquad (40\%)$$

Condensation of amides (35) with hexafluoroacetone gave the imines (36) in moderate yield[30].

$$\underset{(28)}{(CF_3)_2CO} + \underset{(35)}{H_2NCOR} \longrightarrow HOC(CF_3)_2NHCOR$$

$$[R = CF_3,\ nC_3F_7]$$

$$\xrightarrow[0 - 10^\circ C]{\text{oleum}} \underset{(36)}{(CF_3)_2C{=}NCOR}$$

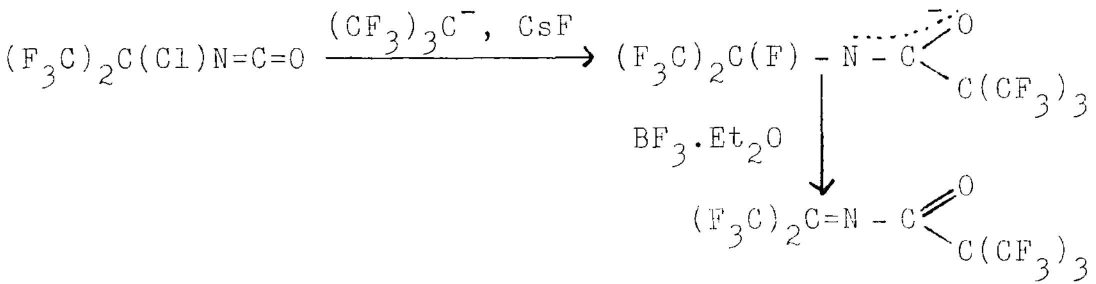
$$(54 - 65\%)$$

Likewise, reaction of diamide (37) with excess (28) gave the bis(perfluoroacyl)imine (38)[31].

$$\underset{(37)}{H_2NCO(CF_2)_nCONH_2} \xrightarrow[\text{(ii) POCl}_3\text{, pyridine}]{\text{(i) excess (CF}_3\text{)}_2\text{CO, sulpholane}}$$

$$\underset{(38)}{(CF_3)_2C{=}NCO(CF_2)_nCON{=}C(CF_3)_2} \qquad (40\%)$$

The similar N-perfluoropivaloylimine (39) of hexafluoroacetone has been prepared by an interesting route comprising nucleophilic attack by the perfluoro-t-butyl anion on the isocyanate shown, and subsequent BF_3-promoted

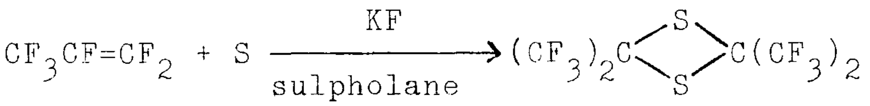


(39) (56%)

elimination of fluoride ion[32].

1A.3.B Reactions of Hexafluorothioacetone dimer

Hexafluorothioacetone dimer (40) can be prepared directly from hexafluoropropene and sulphur in sulpholane in the presence of KF, and has been found to react with a wide range of primary amines to give fluorinated aza-alkenes[33].



(40)

$$(40) \xrightarrow{RNH_2} (CF_3)_2C{=}NR$$

[R = H, C_3F_7, C_5H_9, XC_6H_4 (X = o-Me, -Cl, -OMe, m -CH_3, -F, -CF_3, -C_3F_7, -Cl, p -Me, -F, -C_3F_7, -Cl), or -Me]

Reaction of (40) with hydrazine gives aminoimine (41) with hexafluoroacetone azine (31) as a minor product.

$$(40) \xrightarrow{NH_2NH_2} \underset{(41)\ \ (43\%)}{(CF_3)_2C{=}NNH_2} + (31)\ \ (11\%)$$

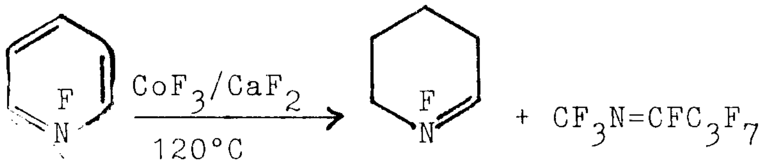
Correspondingly, reaction of substituted hydrazines leads to a range of imines containing additional functional groups.

e.g. $(40) \xrightarrow[DMF]{NH_2CONHNH_2} (CF_3)_2C{=}NNHCONH_2$ (90%)

1A.4 ADDITION REACTIONS

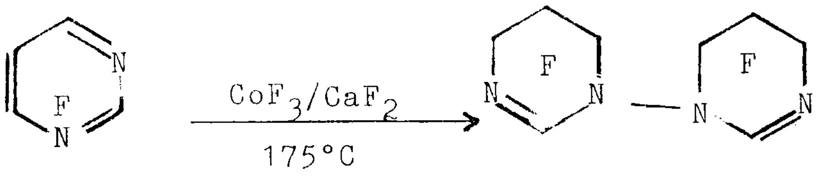
1A.4.A Fluorination 1. Cobalt Trifluoride

Indirect fluorination using high valency metal fluorides has found use for saturation of double bonds and aromatic systems as well as for replacement of hydrogen by fluorine. Cobalt trifluoride is the most versatile member of this class and has found widespread use in the preparation of fluorinated aza-alkenes. Fluorination of pentafluoropyridine using a CoF_3/CaF_2 mixture thus gave compound (12) with the ring-opened (42) as a side product[34].



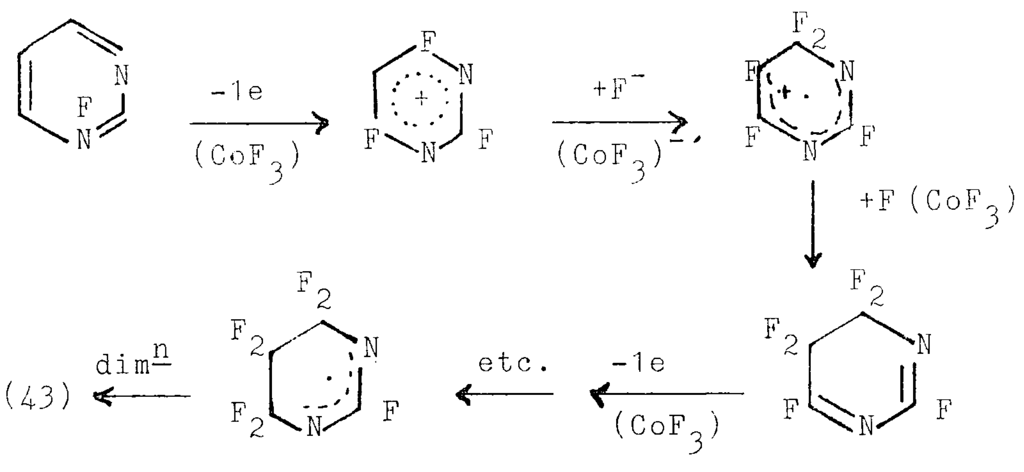
(12) (63%) (42) (10%)

Fluorination of tetrafluoropyrimidine interestingly gave the dimer (43). The proposed mechanism involves the intermediacy of radical cations in a process initiated by a



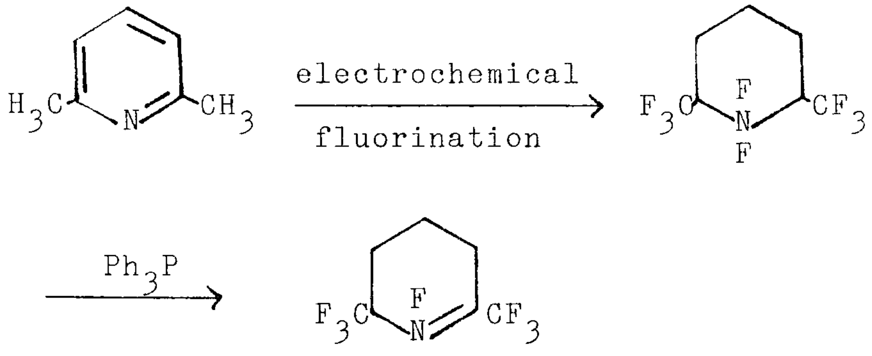
(43)

1-electron transfer to the metal complex[34].



1A.4.A.2 Electrochemical Fluorination

Electrochemical fluorination has found use in the synthesis of some perfluorinated imines. Examples are the synthesis of azacyclohexene derivative (44)[35], and in the preparation of perfluoroazacyclopentene (11) (see section 1A.1.B).



(44)

1A.4.B Addition to nitriles

It might appear at first that reduction of the carbon-nitrogen triple bond in fluorinated nitriles would provide a useful route to fluorocarbon imines but a search of the literature reveals an unexpected paucity in the use of this methodology for the preparation of fluoro-aza-alkenes.

Recently, American workers have found that pyrolysis of the N-bromoimine (45) gave pentafluoroethyl bromide and cyanogen fluoride. The nitrile could be converted to anion (46) by reaction with an alkali metal fluoride, and subsequent bromination gave N-bromodifluoromethanimine (47)[36]. This mixed halogen addition across the triple bond

$$\underset{(45)}{CF_3CF_2CF{=}NBr} \xrightarrow[450°C]{\Delta} C_2F_5Br + FC{\equiv}N \xrightarrow{MF} \underset{(46)}{[M^+F_2C{=}N^-]}$$

$$(46) \xrightarrow{Br_2} \underset{(47)}{F_2C{=}NBr}$$

of a perfluoronitrile has been utilised in an efficient synthesis of a range of N-bromoperhalo-1-alkanimines (48)[37].

$$R_fCN \xrightarrow[CsF]{Br_2} \underset{(48)}{R_fCF{=}NBr}$$

1A.5 PHOTOCHEMICAL REACTIONS

1A.5.A Photochemistry of perfluoro-2,3-diazabuta-1,3-diene

Irradiation of (49) gave almost quantitative conversion to perfluoro-2,4-diazapenta-1,4-diene (50).

$$\underset{(49)}{CF_2{=}N{-}N{=}CF_2} \xrightarrow{h\nu} \underset{(50)}{CF_2{=}NCF_2N{=}CF_2} + N_2$$

This can be rationalised on the basis of the decomposition of (49) into $CF_2{=}N^{\bullet}$ radicals and difluorocarbene. Photolysis of (49) in the presence of difluorodiazomethane as a source of difluorocarbene resulted in the formation of the first four members of the series of diazadienes[38].

$$(49) \xrightarrow[CF_2N_2]{h\nu} CF_2{=}N(CF_2)_{1-4}N{=}CF_2$$

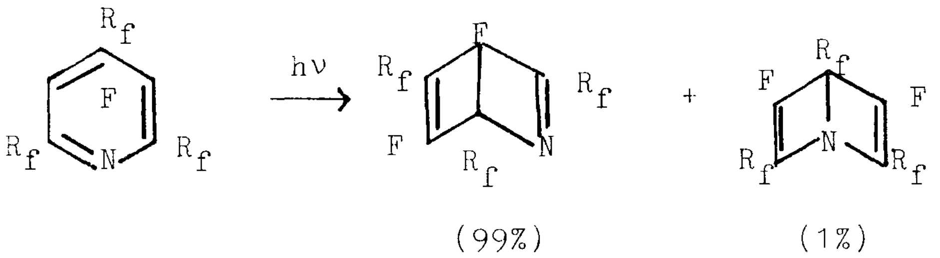
Additional members of the series were produced when photolysis of (49) was carried out in the presence of various fluorinated alkenes. These results are summarised in the Table.

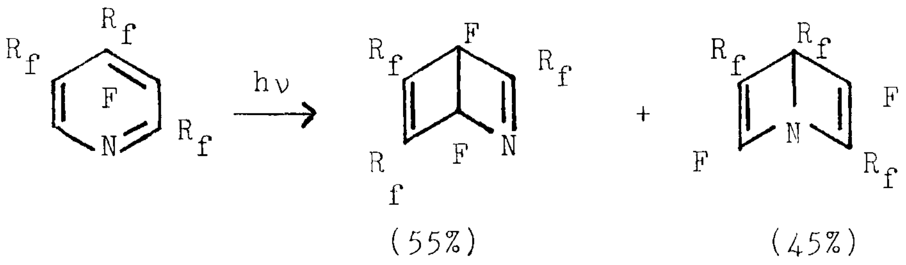
Co-reactant	Product	% Conversion
CF_2N_2	$CF_2{=}NCF_2N{=}CF_2$	12
	$CF_2{=}N(CF_2)_2N{=}CF_2$	25
	$CF_2{=}N(CF_2)_3N{=}CF_2$	3
	$CF_2{=}N(CF_2)_4N{=}CF_2$	1
$CF_2{=}CF_2$	$CF_2{=}NCF_2N{=}CF_2$	13
	$CF_2{=}N(CF_2)_2N{=}CF_2$	57
	$CF_2{=}N(CF_2)_3N{=}CF_2$	10
$CF_3CF{=}CF_2$	$CF_2{=}NCF_2N{=}CF_2$	11
	$CF_2{=}NCF(CF_3)CF_2N{=}CF_2$	66
$CF_3CF{=}CFCF_3$	$CF_2{=}NCF_2N{=}CF_2$	17
	$CF_2{=}NCF(CF_3)CF(CF_3)N{=}CF_2$	30
$CF_2{=}CFCl$	$CF_2{=}NCF_2N{=}CF_2$	12
	$CF_2{=}NCF_2CFClN{=}CF_2$	25

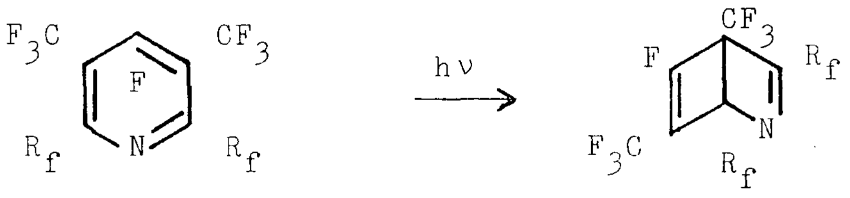
1A.5.B Photolysis of fluoroheteroaromatic compounds

The remarkable ability of perfluoroalkyl substituents to stabilise small ring compounds has facilitated the isolation of a number of valence isomers derived from polyfluoroalkyl substituted heteroaromatic compounds.

Four-membered ring systems containing the C=N group are extremely rare. The only isolated examples are those in which the azacyclobutene ring is part of a bicyclic or polycyclic system. The photolysis of various perfluoroalkylpyridines have given stable azabicyclo[2.2.0]hexa-2,5-diene derivatives[39]. Similarly the diazacyclohexadiene

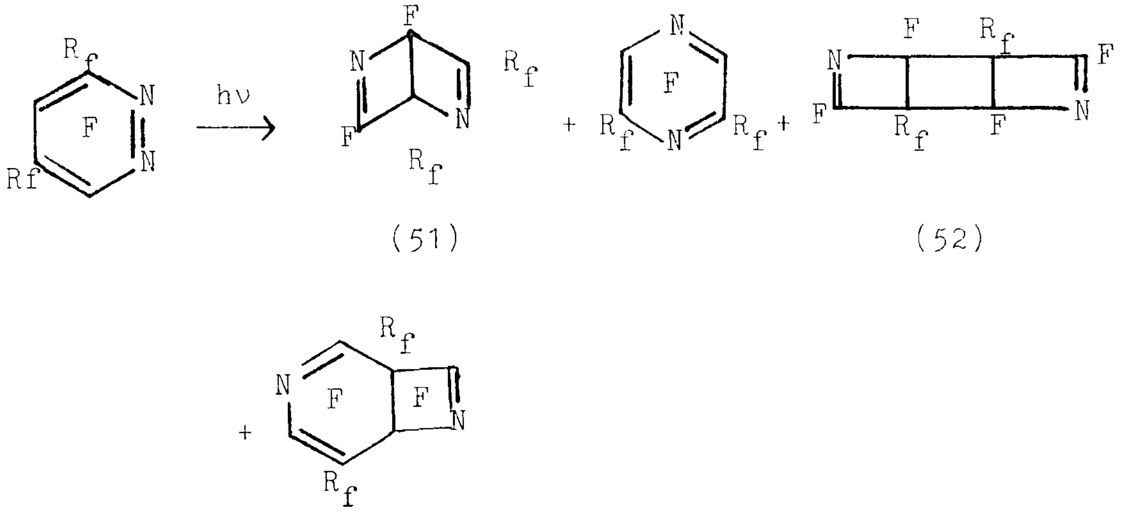






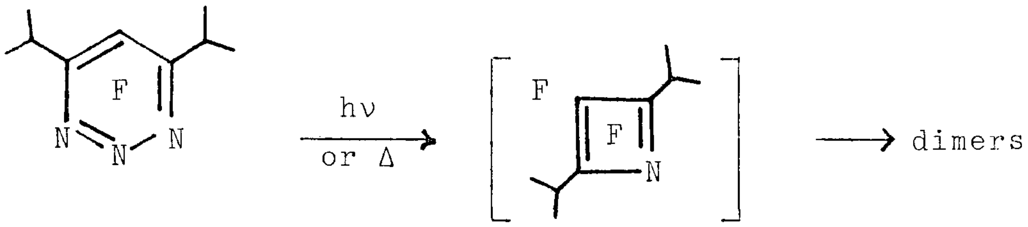
$R_f = CF(CF_3)_2$

derivatives (51), (52) and (53) have been prepared from the photolysis of perfluoroalkylpyridazines[40].



(51)
(52)
(53)

The generation of an azacyclobutadiene intermediate is postulated to explain the formation of (52) and (53). This highly reactive anti-aromatic system has also been generated by pyrolysis and photolysis of polyfluoroalkyl-1,2,3-triazines[41].



1A.5.C <u>Photolysis of polyfluoroalkyl azides</u>

The pyrolytic conversion of (2) to (3) has been discussed earlier in this chapter[3].

$$\underset{(2)}{CF_3CHFCF_2N_3} \xrightarrow[Pt]{270° - 280°C} \underset{(3)\ (86\%)}{CF_3CFHN{=}CF_2}$$

This conversion has also been achieved photochemically via an interesting mechanism which invokes a nitrene intermediate and a 1,2-alkyl shift[42].

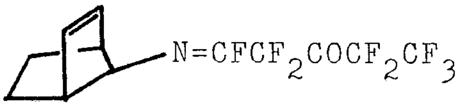
$$CF_3CHFCF_2N_3 \xrightarrow[-N_2]{h\nu} CF_3CHF\text{-}CF_2\text{-}\ddot{N}: \longrightarrow (3)$$

More recently, this reaction has been used in the preparation of a range of substituted fluoroimines[4]. An interesting rearrangement occurs on addition of fluoroalkyl azides to

$$N_3CF_2CF_2C(CF_3)(OMe)OCH_2CF_3 \xrightarrow{h\nu} CF_3N{=}CFC(CF_3)(OMe)OCH_2CF_3$$

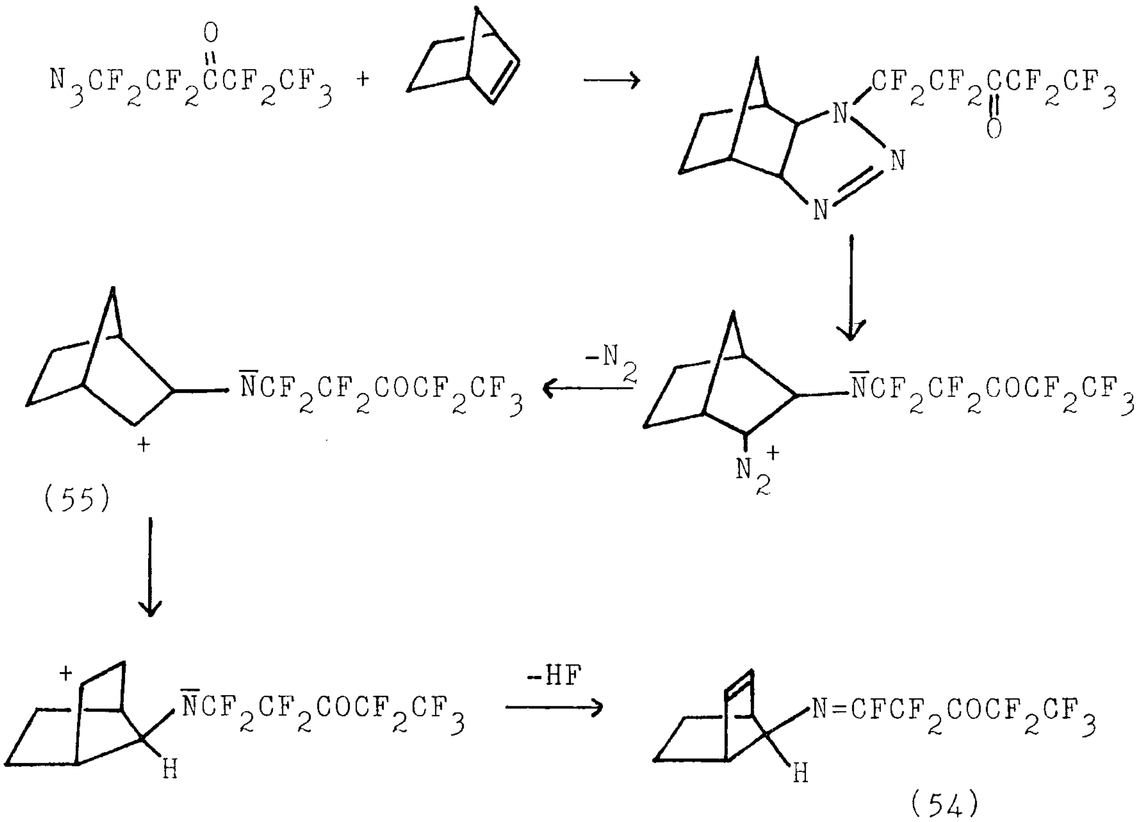
olefins. Simple olefins react so slowly at ordinary temperatures in the dark as to be considered unreactive, however reaction with the strained olefin norbornene proceeds with a mild exotherm to give the imine product (54)[4].

$$N_3CF_2CF_2COCF_2CF_3 \xrightarrow[\text{norbornene}]{h\nu}$$



(54)

The mechanism proposed involves 1,3-cycloaddition of the azide to the intermediate (55). Rather than collapse to the aziridine, (55) rearranges, and loses HF to give the observed imine product (54).


N3CF2CF2CCF2CF3
O
+
CF2CF2CCF2CF3
O
N
N
N
-N2
N̄CF2CF2COCF2CF3
+
N2+
(55)
-HF
N=CFCF2COCF2CF3
H
(54)

1B REACTIONS

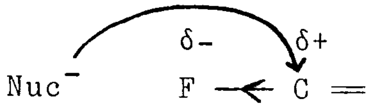
There exists between hydrogen and fluorine, a unique relationship in that fluorine is the only atom that can be substituted for hydrogen extensively throughout hydrocarbon systems. Consequently, as a result of the high electronegativity of fluorine a different, and sometimes complementary organic chemistry can be developed. This chemistry has been extensively studied by both theoreticians and experimental chemists with particular interest in Durham centred on the so-called "mirror image" chemistry of perfluoro-olefins and -aromatics. As a result, the electronic effects associated with nucleophilic attack on perfluoro-olefins are now well understood.

Nucleophilic attack on Fluorinated Alkenes

The double bond in a fluorinated alkene is susceptible to nucleophilic attack and a variety of factors influence this process.

(i) Polarisation effects

The electronegative fluorine atom has an inductive electron-withdrawing ability along the C-F σ-bond, which reduces electron density in the double bond to which it is attached, thus enhancing ion-dipole and dipole-dipole interactions.



(ii) Effect of β-fluorine on carbanion stability

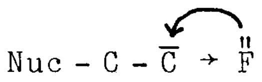
The inductive electron-withdrawing effect of fluorine β- to a position of developing negative charge will stabilise that charge with respect to a hydrogen atom at the same position. i.e. β-fluorines activate a double bond to

$$\mathrm{Nuc - CF - \overline{C}}$$

nucleophilic attack. Negative hyperconjugation may also have a contributory stabilising effect in this case[43-45], and is discussed later.

(iii) Effect of α-fluorine on carbanion stability

Where a fluorine is bonded directly to a centre of developing negative charge, the inductive electron-withdrawing influence is offset by electron-pair repulsions between the p-orbital on the carbanion and the non-bonding electron pairs on the fluorine. The result is that fluorine



$$\mathrm{Nuc - C - \overline{C} \rightarrow \overset{\shortparallel}{F}}$$

on this position has a net electronic effect dependent on the geometry of the carbanion.

(iv) Effect of perfluoroalkyl substituents on carbanion stability

In this case a strong stabilising effect is observed due to the powerful inductive electron-withdrawing effect of the substituent, possibly augmented by so-called negative hyperconjugation.

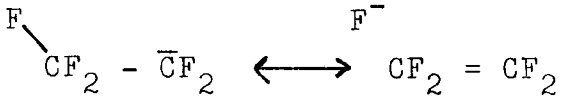
$$\mathrm{Nuc - C - \overline{C} \twoheadrightarrow R_f}$$

Negative hyperconjugation

The stability of perfluorocarbanions is, as discussed above, largely due to the inductive electron-withdrawing effect of the substituent perfluoroalkyl groups. The additional involvement of so-called negative hyperconjugation in the stabilisation of such anions has been the subject of some controversy[43,44].

Hyperconjugation involves the interaction of orbitals of π-symmetry present both in unsaturated and saturated groups[82]; $-CF_2-$ although considered to be a σ-system possesses orbitals of π-symmetry which can interact with p-orbitals on adjacent atoms.

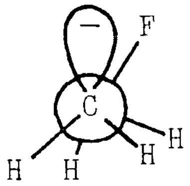
Thus negative hyperconjugation has been simply represented in terms of so-called "no-bond resonance" (56)↔(57) or MO formulations.



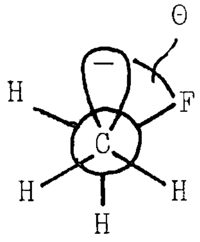
$$F-CF_2-\bar{C}F_2 \longleftrightarrow F^- \; CF_2=CF_2$$

(56) (57)

Since the interaction involves antisymmetric (π) orbitals, it must have, by implication, a tortional angle dependence. Negative hyperconjugation of the C-F bond should be at a maximum when this angle (θ) is zero (180°) and fall to zero when θ is 90° (see following diagram). Schleyer and Kos have shown[44] that for the fluoroethyl anion (58) the energy differences between (58a) and (58b) are large, that is of the order of 10 Kcal/mol, and indeed that the favoured configuration is that where the carbanionic p-oribitial is eclipsing fluorine, which without the involvement of hyperconjugation we would expect to be the least favoured.



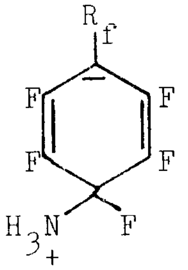
(58a)



(58b)

Schleyer and Kos, therefore argue that since theoretician's arguments against negative hyperconjugation fail to account for this tortional dependence[43], it must be accepted that this effect has energetic and geometrical consequences of general significance to organic chemistry.

Experimental chemists, however, have been unable to find physical support for the theoretical evidence for negative hyperconjugation in terms of rate enhancement. e.g. Chambers and co-workers[45] have studied the rates of reaction of various perfluoroalkyl-substituted benzenes with ammonia. Their results show that there is no significant difference in rate with increasing substitution of trifluoromethyl for fluorine in the substituent. If negative hyperconjugation has a significant stabilising effect on carbanionic intermediates generated in these systems we would expect stabilisation of the intermediate (59) to be at a maximum for $R_f = CF_3$, and to decrease with substitution of fluorines by trifluoromethyl unless the



(59)

$R_f = F, CF_3, C_2F_5, {}^iC_3F_7, {}^tC_4F_9$

combined inductive and negative hyperconjugative stabilising effects of fluorine and trifluoromethyl are of the same order. Consequently, this result cannot be interpreted as evidence for negative hyperconjugation.

Perfluoroaza-alkenes

Hydrocarbon imines possess an electron-deficient double bond due largely to the electronegativity of nitrogen, and are therefore susceptible to nucleophilic attack. The electronic effects of substitution of hydrogen by fluorine will further reduce the electron-density at the C=N bond and make the imine extremely electrophilic in character. Consequently the chemistry of fluorocarbon imines is dominated by their reactivity towards nucleophiles.

1B.1 Reactions with nucleophiles A. O.Nucleophiles

Reaction of perfluoro-2-azapropene (60) with an excess of water gives total decomposition.

$$\underset{(60)}{CF_3N{=}CF_2} \xrightarrow{H_2O} CO_2 + NH_4F + HF$$

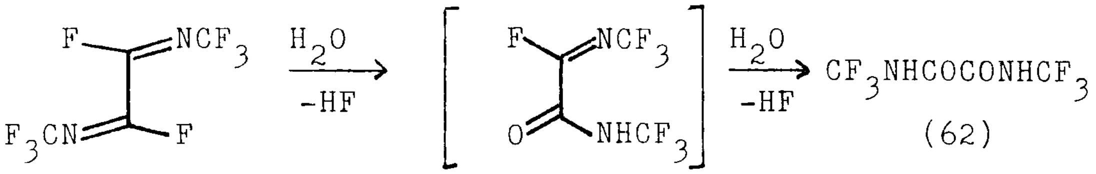
The reaction may be moderated by using a deficiency of water to yield trifluoromethyl isocyanate (61) via the intermediate shown[5,6].

$$\underset{(60)}{CF_3N{=}CF_2} \xrightarrow{H_2O} [CF_3NHCF_2OH] \xrightarrow{-2HF} \underset{(61)}{CF_3N{=}C{=}O}$$

Aza-alkenes which do not contain a terminal difluoromethylene group react more moderately, an example is the aqueous hydrolysis of perfluoro-2,5-diazahexa-2,4-diene (15) to yield the bistrifluoromethyl oxamide (62)[46].

$$\underset{(15)}{CF_3N{=}CF{-}CF{=}NCF_3} \xrightarrow[-2HF]{2H_2O} \underset{(62)}{CF_3NHCOCONHCF_3}$$

This reaction is particularly interesting since reaction of (15) with one equivalent of water gives only (62) and recovered (15), rather than the expected product (63)[47].



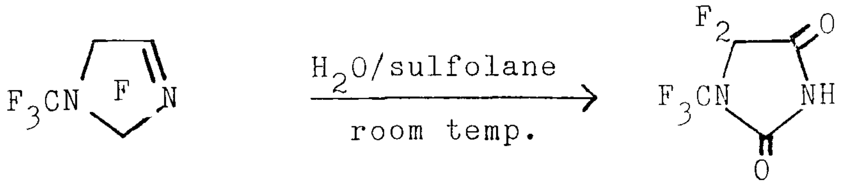
(15)

(63)

(62)

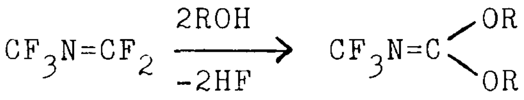
The carbonyl group in (63) is thought to increase the electrophilicity of the adjacent C=N bond to such an extent that (63) reacts with water in preference to (15), so that (62) is the only hydrolysis product isolated.

The aqueous hydrolysis of perfluoro-1,3-diaza-1-methylcyclopent-3-ene (64b) gives 1-trifluoromethyl-5,5-difluoro-1,3-diazacyclopenta-2,4-dione (65)[47].



(64b) (65)

Perfluoro-2-azapropene (60) reacts with excess alcohol in the presence of triethylamine via a similar addition-elimination mechanism to give disubstituted products[48].



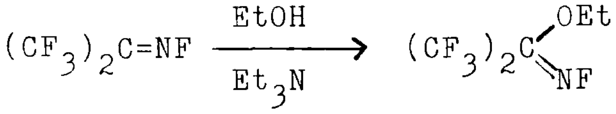
$$CF_3N{=}CF_2 \xrightarrow[-2HF]{2ROH} CF_3N{=}C(OR)_2$$

(60 - 69%)

(60)

$R = CH_3, C_2H_5, (CH_3)_2CH$

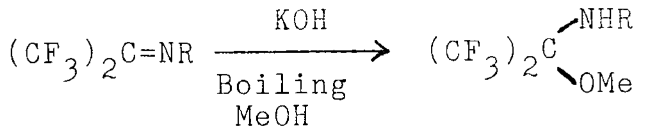
For compounds containing the C=NF group, monosubstitution is favoured. Addition of ethanol to imine (66) gives only (67), however where an imine contains a vinyl fluorine



$$(CF_3)_2C{=}NF \xrightarrow[Et_3N]{EtOH} (CF_3)_2C(OEt){-}NHF$$

(66) (67)

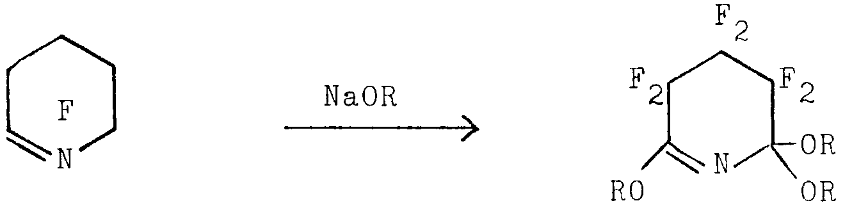
elimination of HF can occur and subsequent reaction to the disubstituted product is possible[49]. Compounds containing the -C=NR (R = aryl) function are less reactive to alcohols, since the electron-donating effect of the aryl substituent reduces the electrophilicity of the double bond. Consequently, considerably more forcing conditions are needed, and lower yields of products are obtained.[33]



$$(CF_3)_2C{=}NR \xrightarrow[\text{Boiling MeOH}]{KOH} (CF_3)_2C(NHR)(OMe) \qquad (20 - 51\%)$$

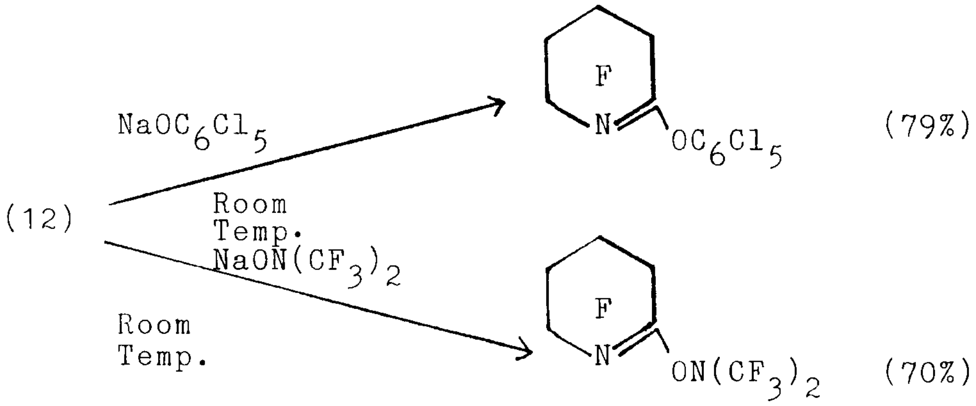
R = phenyl, substituted phenyl

Reaction of perfluoro-1-azacyclohex-1-ene (12) with nucleophiles is interesting since substitution occurs at both C2 and C6 sites leading to trisubstitution with an excess of alkoxide or phenoxide[8,26].

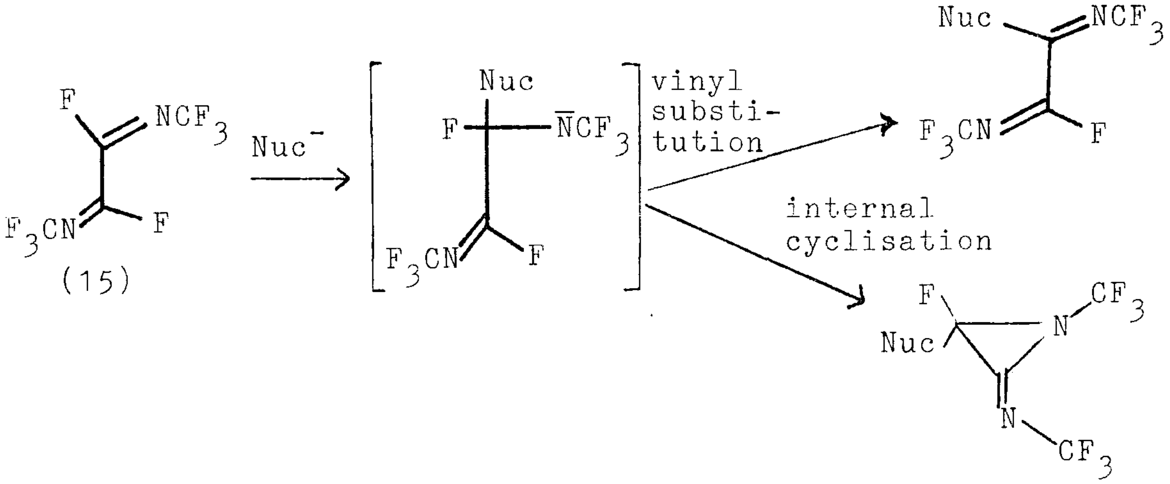


(12) (R = Me, Ph)

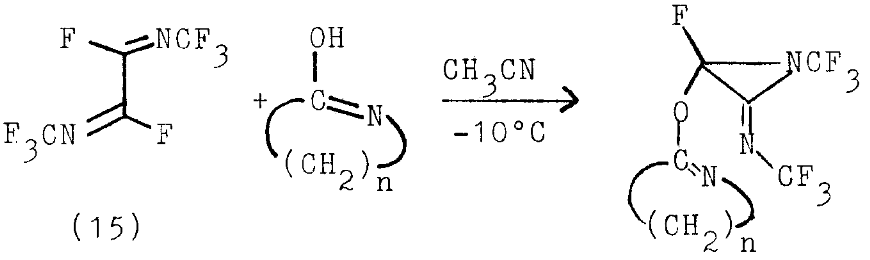
Monosubstitution can be achieved under mild conditions using a stoichiometric equivalent of a suitable nucleophile, examples being the reactions of sodium pentachlorophenoxide or sodium bis-trifluoromethylnitroxide with (12).



Reactions of perfluoro-2,5-diazahexa-2,4-diene (15) with nucleophiles have received much attention due to the utility of many of the products as agrochemicals. Reaction occurs to give the normal products of vinyl substitution, and also, in some cases via an interesting internal cyclisation to give azacyclopropane derivatives.

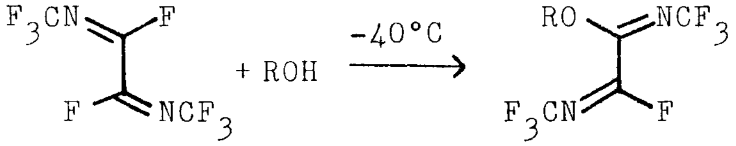


The internal cyclisation reaction has only been observed in those cases where the nucleophile is a lactam, as in the reactions with piperidine and caprolactam to give the azacyclopropane derivatives (68) and (69)[50].



n = 4 (68) (77%)
n = 5 (69) (78%)

All other reactions with alcohols and phenols give only straight chain substitution products in high yield[50], disubstitution being achieved when a 2:1 excess of



(15)

(65 - 85%)

R = Me, Et, Ph, $C_6H_3Cl_2$, 4-C_6H_4Cl, 4-$C_6H_4NO_2$

nucleophile is used[51].

1B.1.B N nucleophiles

Reaction of perfluoro-2-azapropene (60) with primary aliphatic amines proceeds via the normal addition-elimination mechanism to give the expected products (70) in high yield.

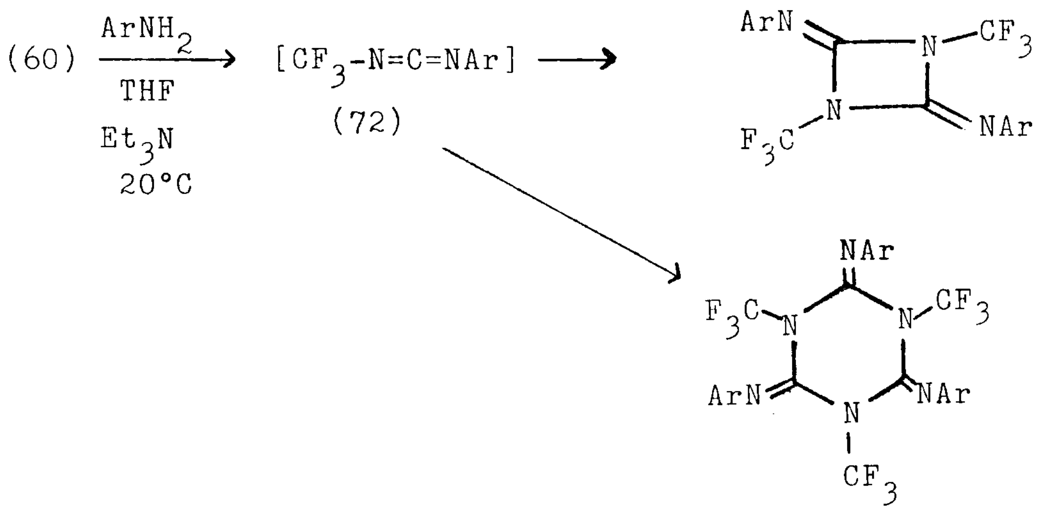
$$(60) + RNH_2 \longrightarrow \underset{(70)}{CF_3N{=}CFNHR}$$

$$R = C_2H_5,\ {}^tBu,\ C_6H_{11},\ CH_2CH{=}CH_2$$

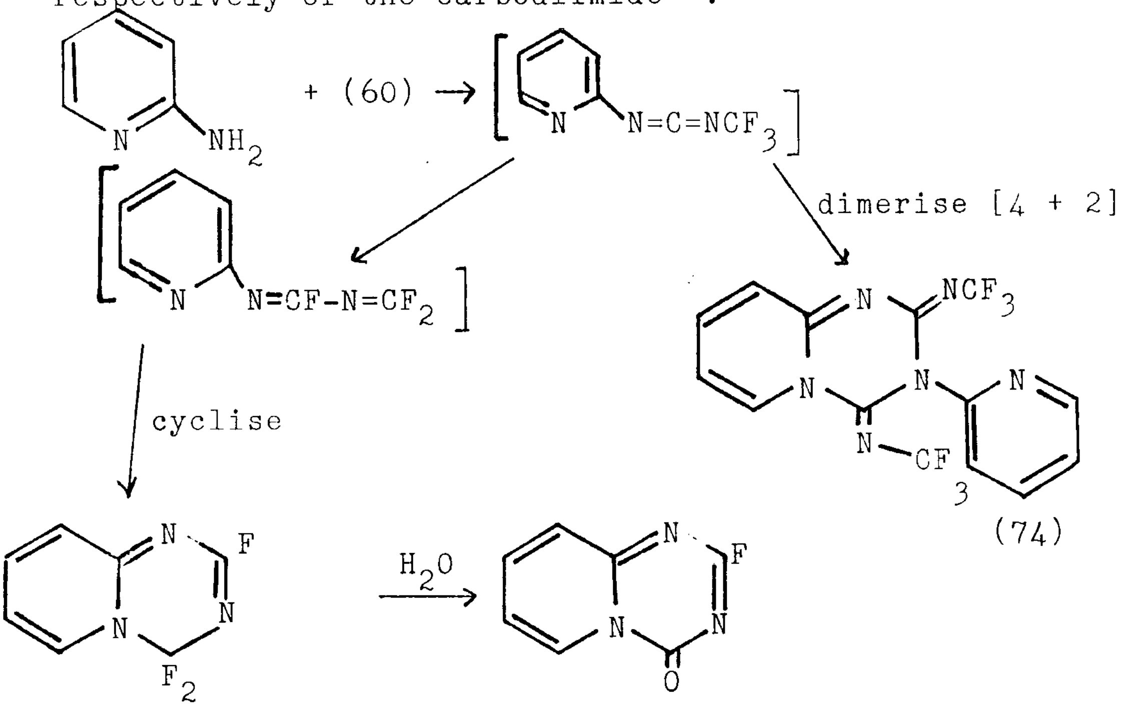
Dehydrofluorination of (70) using either KF or $BF_3.NEt_3$ gives the corresponding carbodiimides (71)[52].

$$\underset{(70)}{CF_3N{=}CFNHR} \xrightarrow[\text{or } BF_3.NEt_3]{KF} \underset{(71)}{CF_3N{=}C{=}NR} \quad (68.5 - 87\%)$$

Reaction of (60) with aromatic amines is more interesting. (60) reacts with primary aromatic amines in the presence of Et_3N to give the expected carbodiimide intermediates (72), which then dimerise or trimerise[53].



Reaction occurs with 2-aminopyridine to give the novel heterocyclic system 4H-pyrido-[1,2-α]-s-triazine (73) and its substituted dihydro derivative (74) via an intramolecular cyclisation and a [4 + 2] self-addition reaction respectively of the carbodiimide[53].



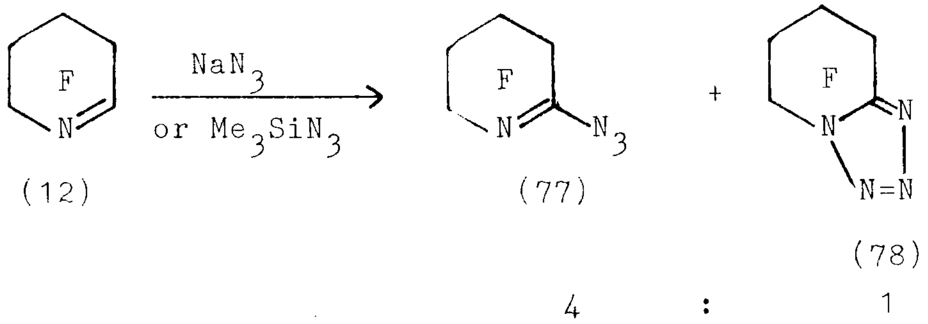
(74)

(73)

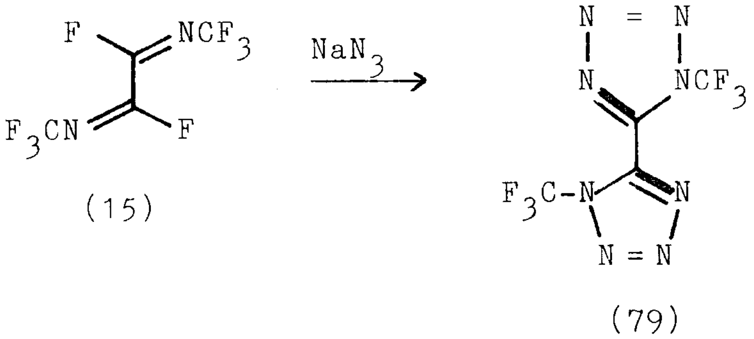
Azides react to give both the usual addition-elimination products, as in the reaction of (75) to form (76)[54], and also form tetrazoles in some cases.

$$\underset{(75)}{CF_3N{=}CFC(CF_3)_3} \xrightarrow[\text{PhNO}_2,\ \text{room temp.}]{\text{NaN}_3} \underset{(76)}{CF_3N{=}C(N_3)C(CF_3)_3}\ (32\%)$$

A particularly interesting example is the reaction of perfluoro-1-azacyclohex-1-ene (12) with trimethylsilylazide or a deficiency of sodium azide to give an equilibrium mixture of the azide (77) and tetrazole (78)[55].



Reaction of diazadiene (15) gives only the novel bistetrazole (79)[56].



Fluoride catalysed oligomerisation of fluorocarbon imines also comes into this category but will be discussed in more detail later.

An example is the addition of fluoride ion to perfluoro-2-azapropene (60) to give the nucleophilic bis(trifluoromethyl)aza anion (80) which readily reacts with a further molecule of (60) to give the amidine (81)[57].

$$\underset{(60)}{CF_3N{=}CF_2} \xrightarrow{F^-} \underset{(80)}{[(CF_3)_2N^-]} \xrightarrow[-F^-]{(60)} \underset{(81)}{(CF_3)_2NCF{=}NCF_3}$$

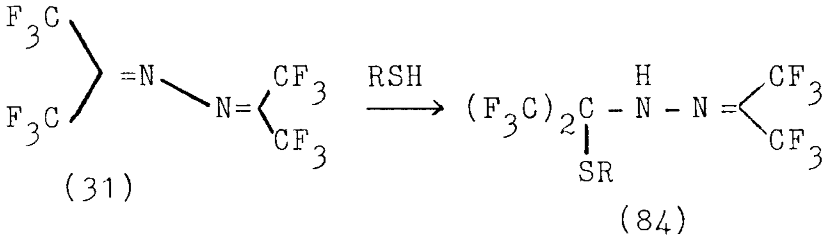
1B.1.C S Nucleophiles

The chemistry of sulphur nucleophiles parallels that of reactions between oxygen nucleophiles and fluorocarbon imines, being dominated by the addition-elimination mode of reaction. Perfluoro-2-azapropene (60) reacts with hydrogen sulphide to give the normal product (82), which may be further dehydrofluorinated using NaF to yield trifluoromethylisothiocyanate (83)[58].

$$\underset{(60)}{CF_3N{=}CF_2} + H_2S \longrightarrow [CF_3NHCF_2SH] \xrightarrow{(60)} \underset{(82)}{CF_3N{=}CFSH} + (CF_3)_2NH$$

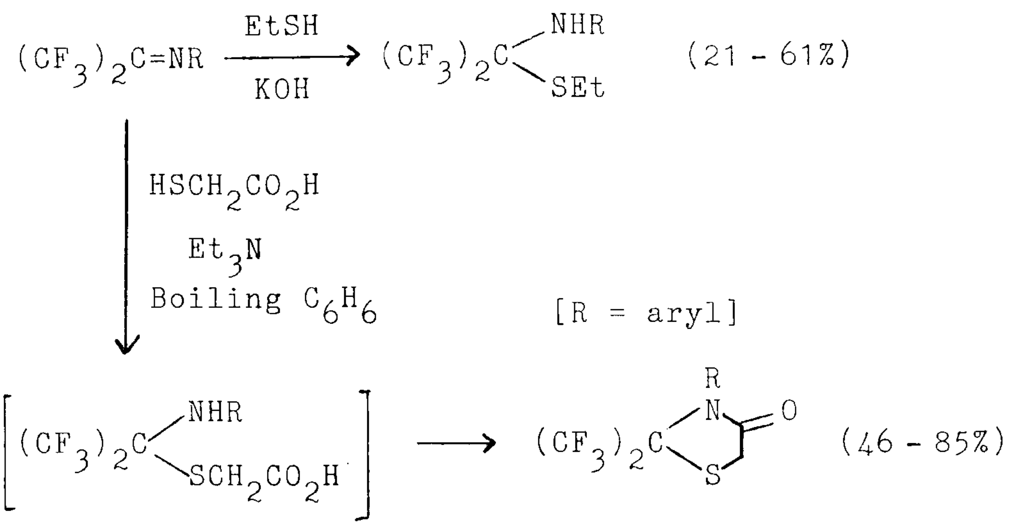
$$(82) + NaF \longrightarrow \underset{(83)}{CF_3N{=}C{=}S} \quad (60\%)$$

Mercaptans add to hexafluoroacetone azine (31) to give the expected hydrazones (84) in high yield[59].



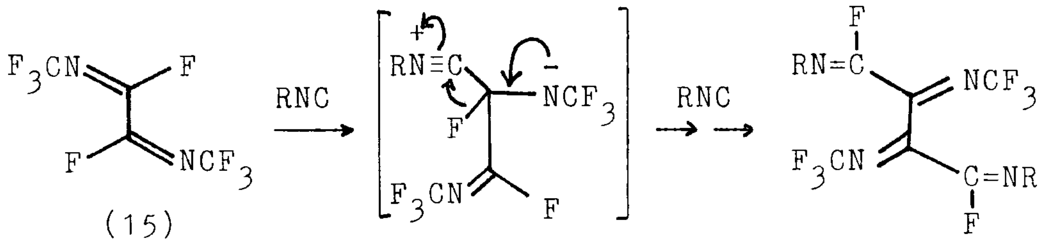
(31) (84)

Fluorocarbon imines of the type C=NR (R = aryl) require harsher conditions. Reaction of $HSCH_2CO_2H$ leads, interestingly, to a series of novel five-membered heterocycles via an internal cyclisation and condensation[60].



1B.1.D <u>C Nucleophiles</u>

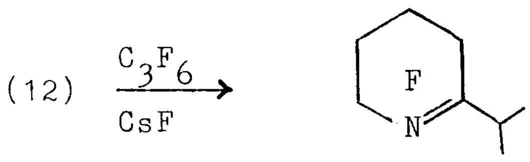
Reported reactions of carbon nucleophiles with fluorocarbon imines are rare although, interestingly, isonitriles add readily to (15) to give tetraazatetraenes (85) in moderate yield[61].



(85) (51 - 61%)

[R = ^tBu, 2,6-MeC_6H_3, cyclohexyl]

Alkylation of perfluoroimines with perfluoroalkyl anions has been exploited, for instance, in the preparation of the substituted azacyclohexene (86) from perfluoro-1-azacyclohex-1-ene (12)[62].



[$C_3F_7^-$] (86)

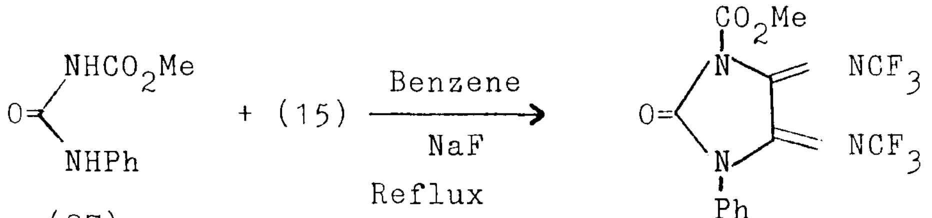
In general, however, this method is wasteful of the fluorinated alkene and imine starting materials many of which oligomerise readily in the presence of fluoride ion.

1B.1.E Bifunctional Nucleophiles

The reactions of perfluoro-2,5-diazahexa-2,4-diene (15) with bifunctional nucleophiles have been extensively studied and yield a number of interesting heterocycles[63-67] which have found use as agrochemicals. These reactions, for the purpose of illustration, may be described in three groups.

A. Reaction of (15) with urea derivatives readily gives heterocyclic ring systems with two ring nitrogens.

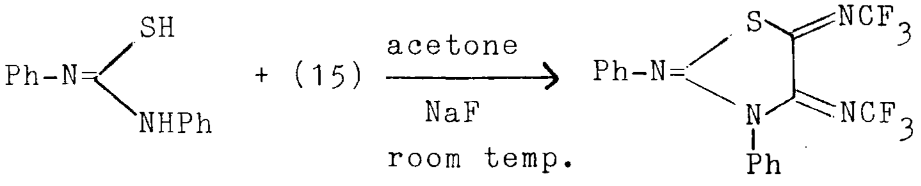
This is illustrated by the reaction of (87) with (15) to give imidazolone (88).



(87) (88)

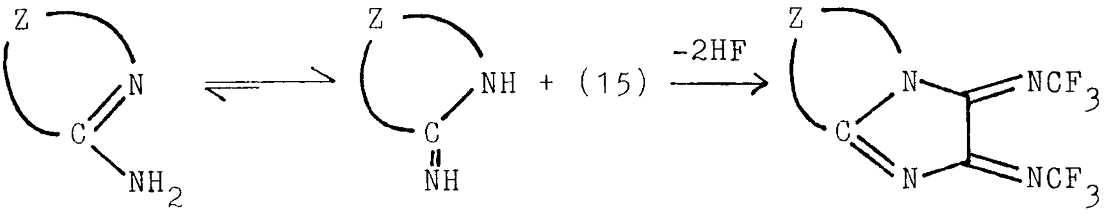
B. Thiourea derivatives react through their isomeric form to give heterocycles containing sulphur as a heteroatom.

Thus, the reaction of diphenylthiourea with (15) gives (89) in good yield.

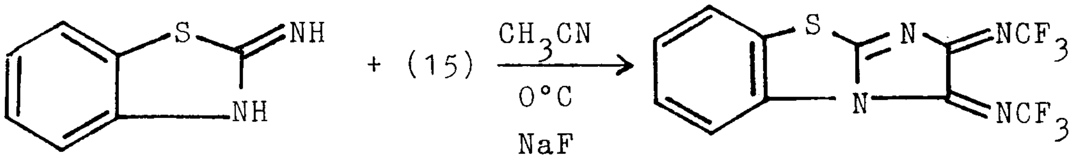


(89) (85%)

Amidines also react through their isomeric forms to give various polycyclic products.



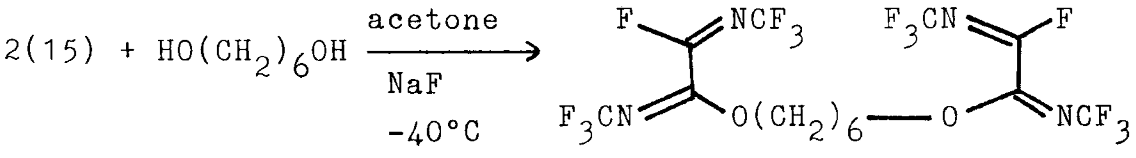
A good example is the reaction of (15) with 2-aminobenzothiazole to give (90).



(90) (92%)

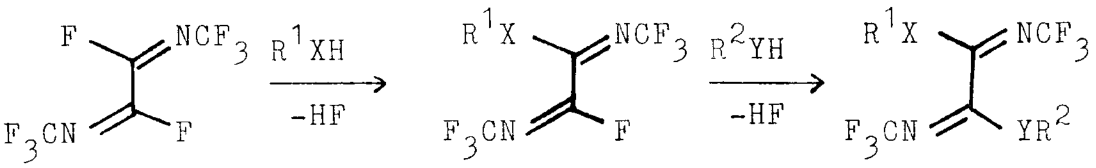
C. When the stereochemistry of the bifunctional nucleophile is not conducive to internal cyclisation, a different mode of reaction is observed, where two equivalents of the imine react with one of the nucleophile[68].

An example is the reaction of hexan-1,6-diol with two equivalents of (15) to give (91).



(91) (82%)

A variation of this type of reaction is in the action of two different nucleophiles on (15). This reaction has been exploited in the preparation of a variety of derivatives, generalised in the following scheme[65].



(15)

(X = O, S, NR^3) (Y = O, S, NR^4)

These reactions have the added benefit of being 'one pot' reactions which give good to excellent yields of the disubstituted products.

1B.2 With Fluoride ion

Many fluorocarbon imines readily isomerise or oligomerise in the presence of alkali metal fluorides, in much the same way as the well-known corresponding reactions of perfluoroolefins.

The diazadienes (92), (50), (94) and (96) were found to isomerise readily to the corresponding internal aza-olefins via a proposed S_N2' mechanism involving a nitranion intermediate[69].

$$\underset{(92)}{CF_2{=}NCF_2CF_2N{=}CF_2} \xrightarrow{F^-} \underset{(15)}{CF_3N{=}CF{-}CF{=}NCF_3}$$

$$\underset{(50)}{CF_2{=}NCF_2N{=}CF_2} \xrightarrow{F^-} \underset{(93)}{CF_3N{=}C{=}NCF_3}$$

$$\underset{(94)}{CF_2{=}NCF_2CF(CF_3)N{=}CF_2} \xrightarrow{F^-} \underset{(95)}{CF_3N{=}CFC(CF_3){=}NCF_3}$$

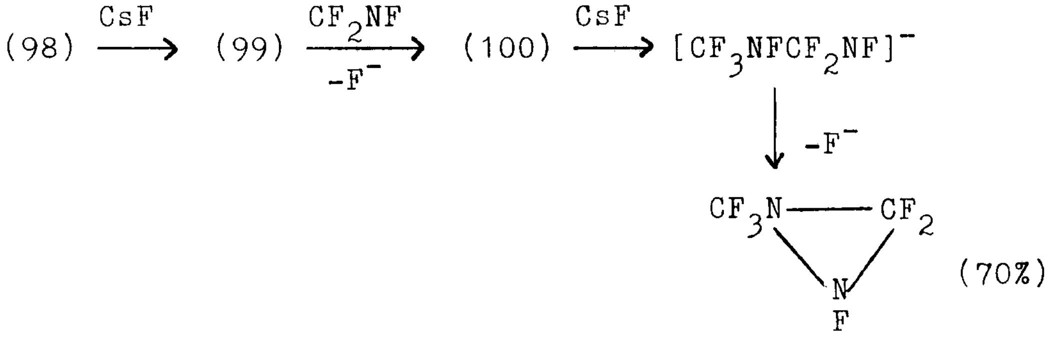
$$\underset{(96)}{CF_2{=}NCF(CF_3)CF(CF_3)N{=}CF_2} \xrightarrow{F^-} \underset{(97)}{CF_3N{=}C(CF_3)C(CF_3){=}NCF_3}$$

The solution and gaseous phase isomerisation and dimerisation reactions of (15) are particularly interesting and will be discussed in detail in Chapter 2.

Recently, the reactivity of the simplest perfluorinated imine, perfluoromethanimine (98) has been reported[70,71]. The perfluoromethanimine ion (99) is readily formed, and reacts with its precursor (98) to form dimers, or as a nucleophile to give novel fluorinated amines. Thus, the reaction of (98) with KF yields the dimer (100)[70].

$$\underset{(98)}{CF_2{=}NF} \xrightarrow[22^\circ C]{KF} \underset{(99)}{[CF_3NF]^-} \xrightarrow[-F^-]{CF_2NF} \underset{(100)}{CF_3NFCF{=}NF} \qquad (60\%)$$

Interestingly, reaction of (98) with the more active CsF gives (100) as an intermediate product which then undergoes CsF-catalysed isomerisation to form perfluoro-1-methyldiaziridine (101)[71], via internal nucleophilic attack at a saturated nitrogen.



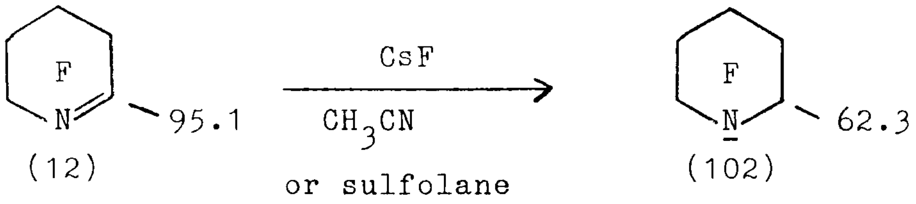
(101)

1B.2.A Stable nitranions

There has been interest in the preparation of more stable aza-anions and their observation by n.m.r. spectroscopy.

The first example of this rare class of intermediate was the bis(trifluoromethyl)aza anion, $(CF_3)_2N^-$ (80) prepared from perfluoro-2-azapropene (60) and CsF in acetonitrile. The ^{19}F n.m.r. was reported to show a broad singlet at 112.2 ppm (downfield positive from $CFCl_3$)[72].

Similarly, the perfluoro-1-azacyclohexyl anion (102) has been generated from perfluoro-1-azacyclohex-1-ene (12) and CsF in both acetonitrile[73] and sulfolane[74]. Anion (102) is remarkably stable, and the n.m.r. spectrum remains unchanged even on heating to 50°C[74]. The ^{19}F n.m.r. signals were found to be considerably sharper for anion (102) generated in sulpholane than for (102) in acetonitrile[74], and this is a good example of the solvent-dependent stability of intermediates in organic chemistry.



More recently, Russian workers have prepared a range of stable acyclic nitranions from the action of fluoride ion on internal perfluoroimines[75].

e.g. $CF_3N{=}CFCF_3 \xrightarrow[CH_3CN]{CsF} CF_3\bar{N}C_2F_5$

1B.2.B Reactions of nitranions

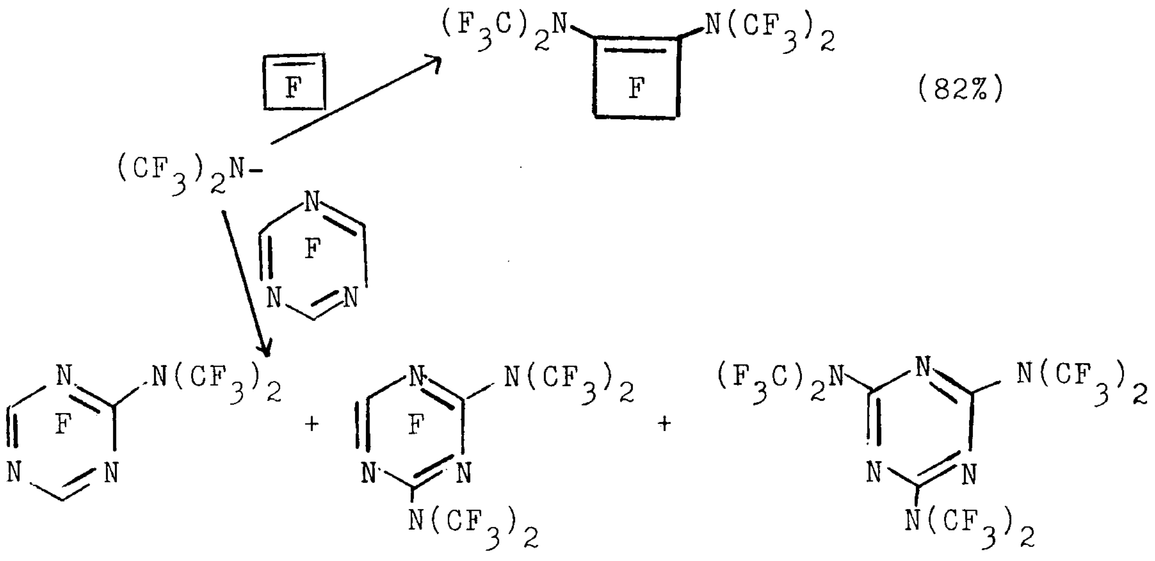
The chemistry of perfluorocarbanions, such as the heptafluoroisopropyl anion, has received extensive study over many years.

In contrast, the parallel chemistry of fluorinated nitranions has been less well explored, largely as a result of the paucity of suitable fluorinated imine precursors.

Trapping experiments have shown the reactivity of anion (80) as a nucleophile. An example is the substitution of bromine in allyl bromide[72].

$$CF_3N{=}CF_2 \xrightarrow[CH_3CN]{CsF} \underset{(80)}{(CF_3)_2N^-} \xrightarrow{BrCH_2CHCH_2} (CF_3)_2NCH_2CHCH_2$$

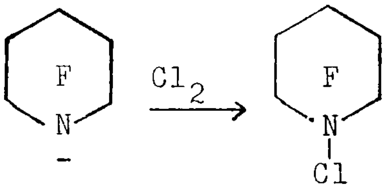
The aza-anion (80) also reacts readily with perfluorocyclobutene[72] and perfluoro-1,3,5-triazine[76] to give the corresponding derivatives in good yield.



(82%)

(39%) (51%) (5%)

Trapping of the perfluoro-1-azacyclohexyl anion (102) with chlorine gave a rare example of an N-chloroperfluoroamine (103)[77].



(102) (103)

(58%)

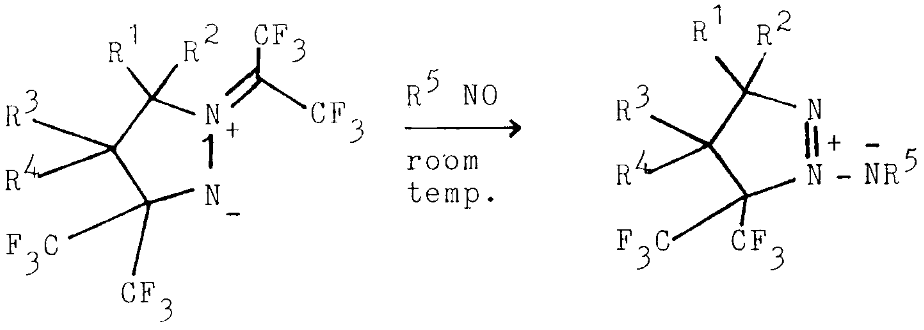
1B.3 Cycloaddition reactions

In general, organic compounds possessing an unsaturated π-system are susceptible to cycloaddition reactions. Fluorocarbon imines having substituents of strong electron-withdrawing ability, would be expected to be reactive to electron rich alkenes and alkynes.

1B.3.A Reactions of hexafluoroacetone azine

Hexafluoroacetone azine (31) reacts readily with a range of electron rich alkenes and alkynes to give novel heterocyclic products[78-84], according to scheme A, via a so-called "criss-cross" cycloaddition [(1,3-2,4)-addition]. The reaction has been shown to proceed via two (3 + 2) cycloadditions by the isolation of the intermediate 1,3-dipolar amines (104) and (105)[78].

An interesting metathesis reaction occurs on treating (104) (R^1, R^2, R^3, R^4 as below) with nitroso-alkanes and -arenes at room temperature[85], to give the azimines (112).

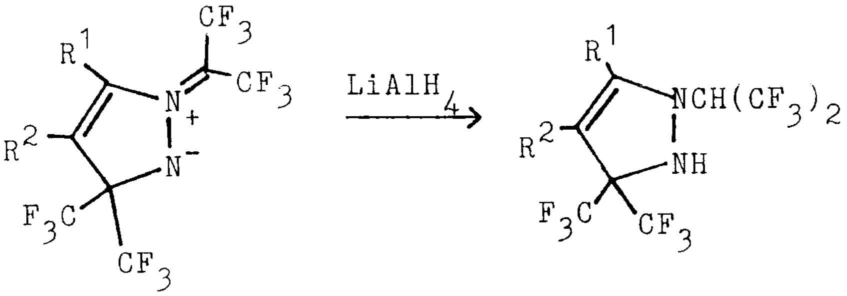


(104)

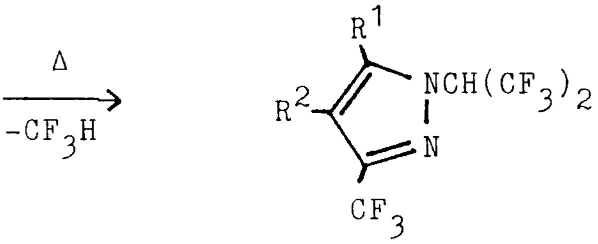
(112)

R^1 = Me, CMe=CH_2, Ph; R^2 = Me, R^3, R^4 = H; R^5 = CF_3, C_6F_5, Ph

Reduction of (105) with lithium aluminiumhydride and subsequent pyrolytic elimination of fluoroform gave the novel aromatic pyrazole derivatives (113)[86].



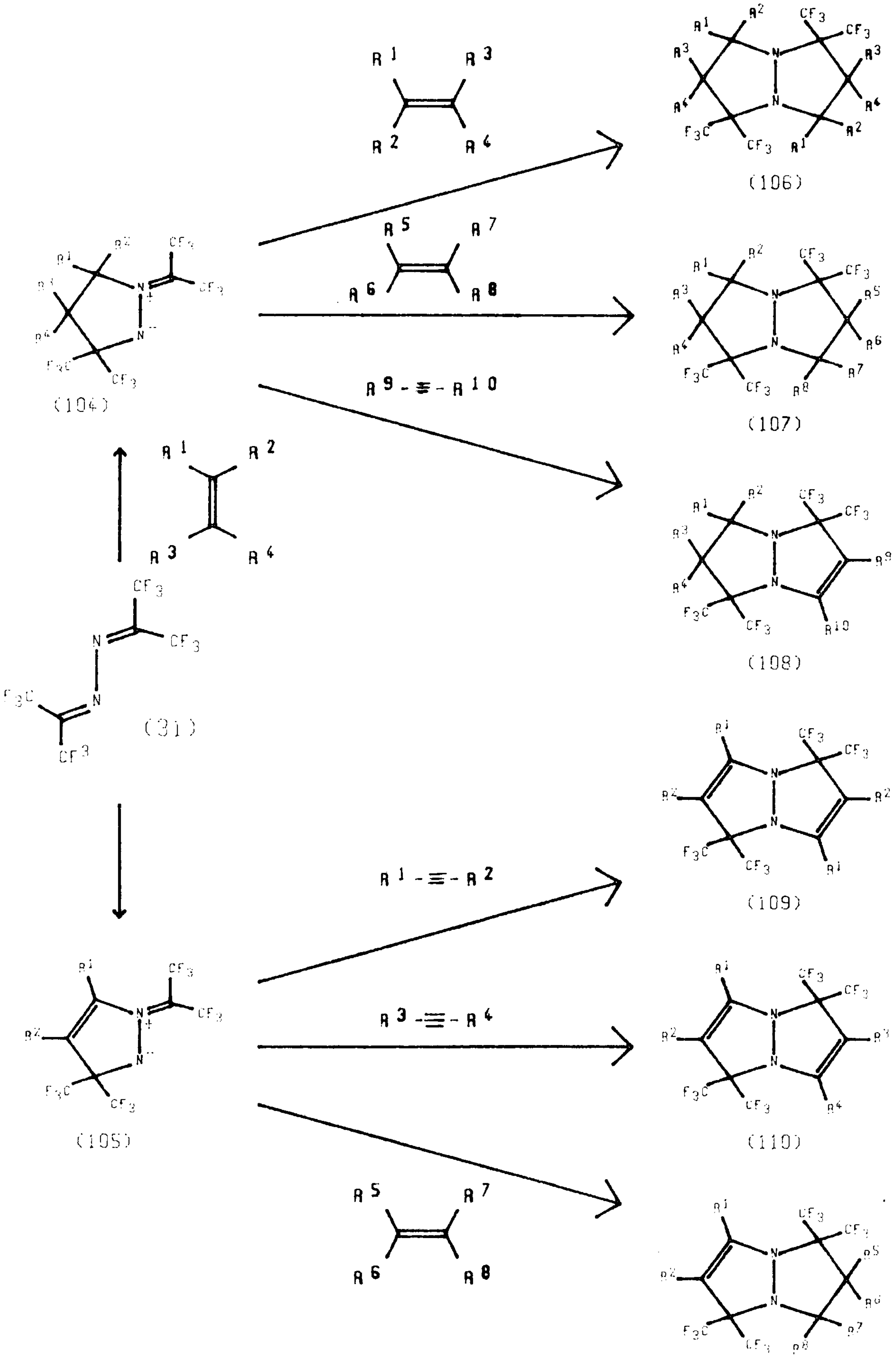
(105)



(113)

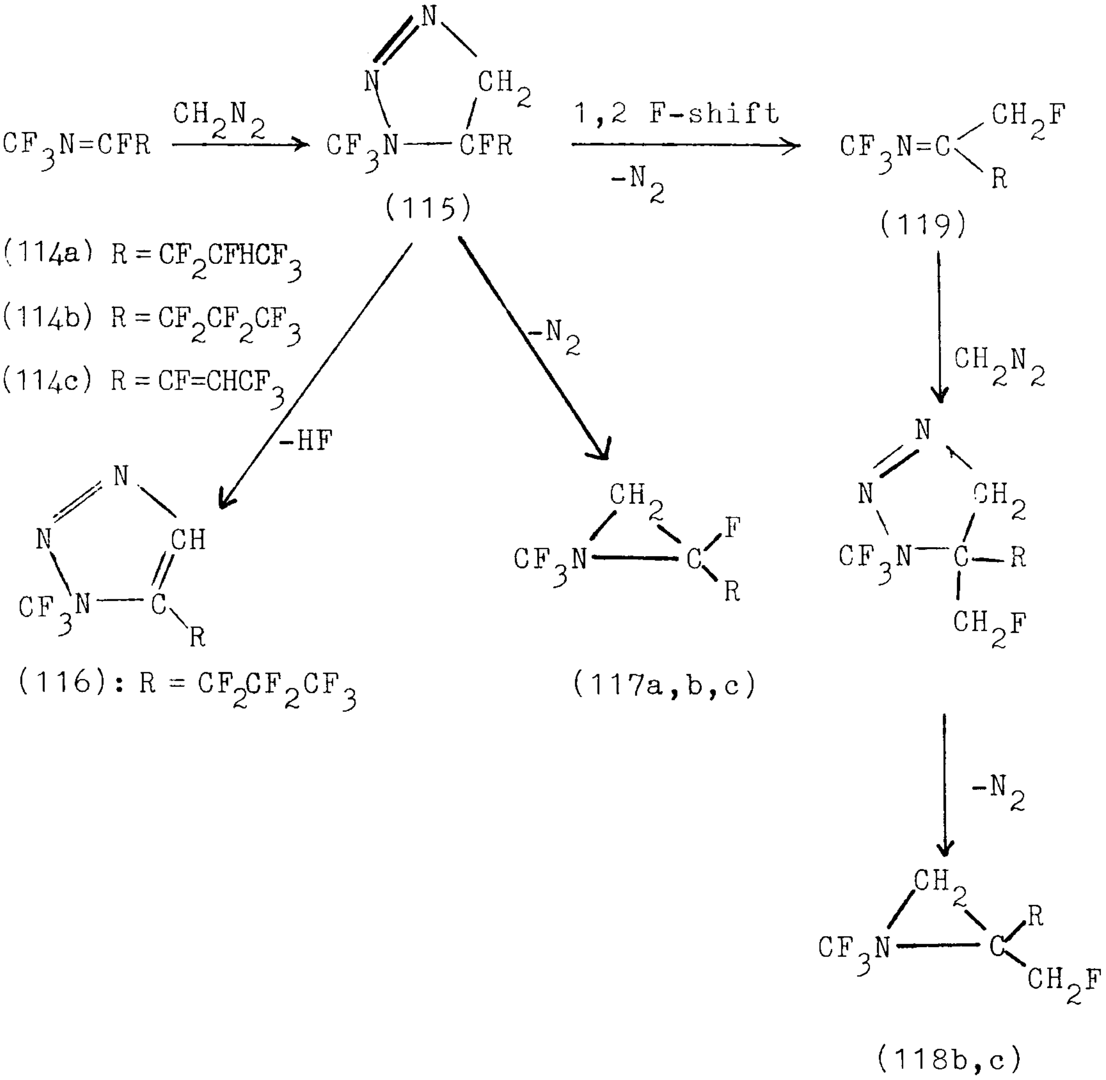
1B.3.B Cycloaddition reactions of diazomethane

Surprisingly, cycloaddition reactions of diazomethane with unsaturated fluorocarbon systems, and especially with fluorinated aza-olefins have not been well explored.


(104)
(31)
(105)
(106)
(107)
(108)
(109)
(110)
(111)
R1 — R3 / R2 — R4
R5 — R7 / R6 — R8
R9-≡-R10
R1 — R2 / R3 — R4
R1-≡-R2
R3-≡-R4
R5 — R7 / R6 — R8
CF3
F3C
N
N+
N−

Scheme A

Diazomethane ether azeotrope undergoes cycloaddition to azaalkenes to give a number of products via the three mechanistic pathways outlined in Scheme B[87]. The first step in all cases is addition of diazomethane to (114) to form pyrazolines (115).



Scheme B

Where the alkyl substituent, R, is strongly electron-withdrawing, as for (114b), elimination of HF may occur to give triazoles [e.g. (116)]. Less electronegative substituents, such as those on (114a) and (114c) favour loss of nitrogen to form aziridines, e.g. (117).

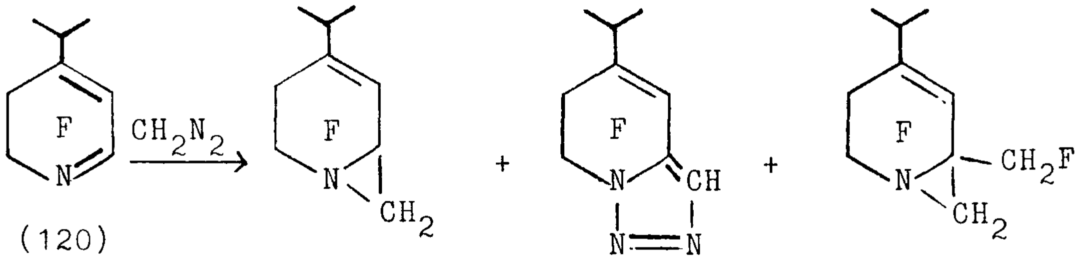
Elimination of nitrogen from (115), accompanied by a 1,2-fluorine shift gives insertion products (119), which are susceptible to further addition of diazomethane and loss of nitrogen to form aziridines (118).

The balance between effect of the alkyl group, R, and the mode of reaction is very fine, and can be seen from a comparison of the relative proportions of products (116) - (118) presented in the Table[87].

114	(116)%	(117)%	(118)%
a	-	100	-
b	56	38	6
c	-	79	21

Proportions expressed as percentages of isolated product mixture

All these modes of behaviour were displayed in the reaction of diazomethane with the fluorinated azacyclohexadiene (120)[47].



(120)

(121) (9%)

(122) (14%)

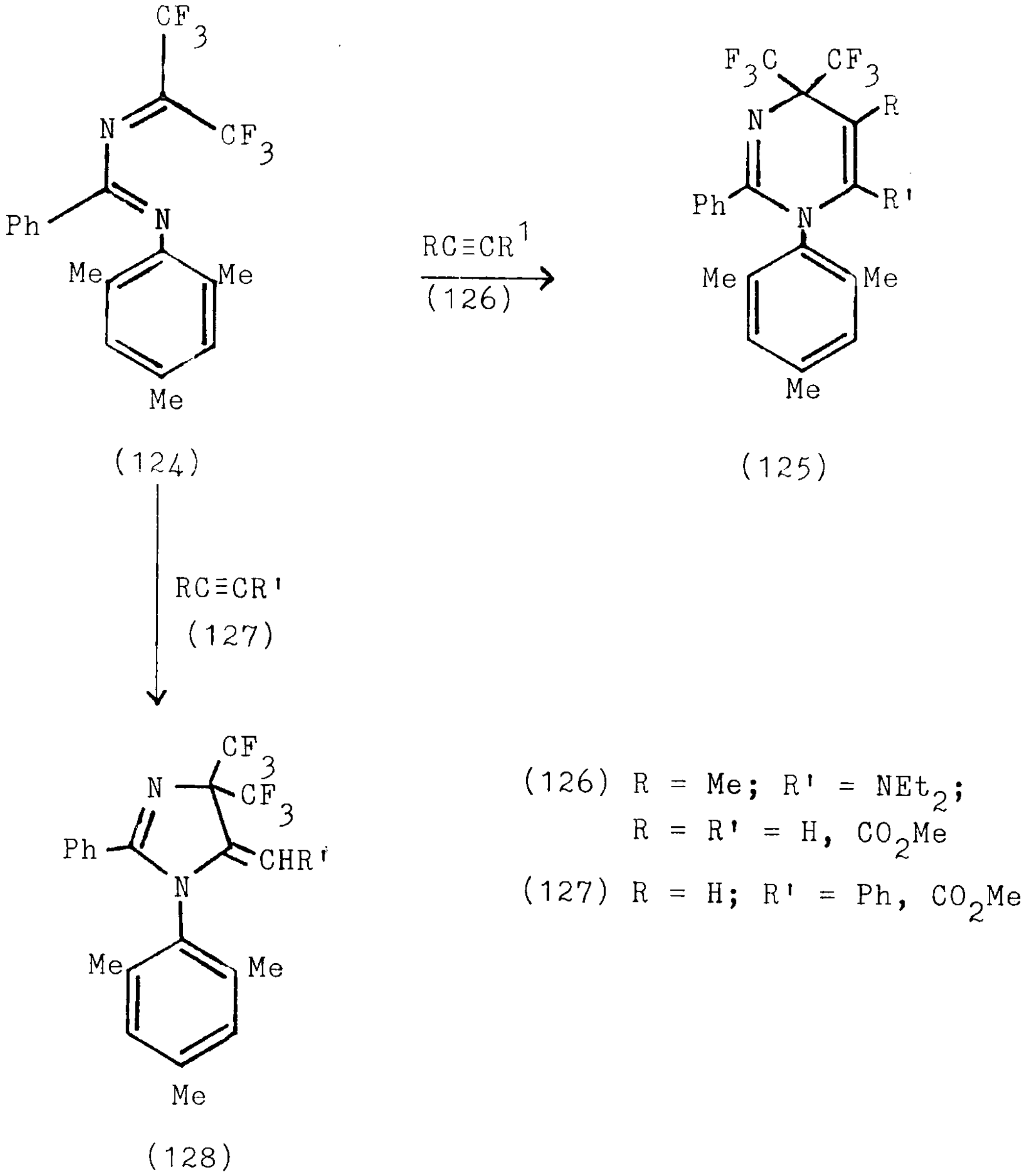
(123) (29%)

1B.3.C Reactions of hetero-1,3-dienes

Cycloaddition reactions of heterodienes have been studied recently as a source of a number of new heterocycles[88-92].

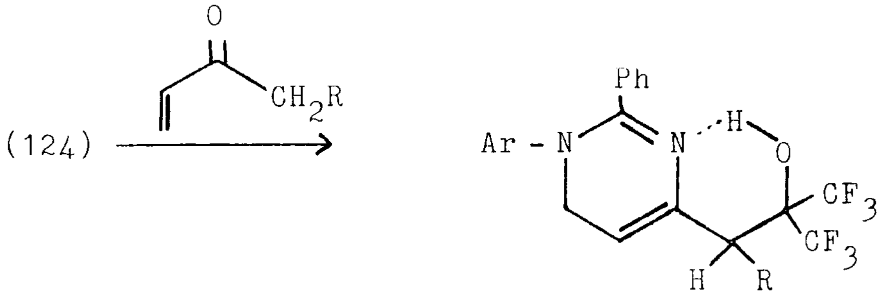
The chemistry of 1,3-butadiene derivatives is particularly interesting since in many cases the reactions deviate from the Diels-Alder scheme.

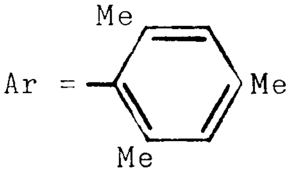
Butadiene (124) reacts with acetylenes (126) via a normal [4 + 2] cycloaddition process to give compound (125) but reacts with acetylenes (127) to give 2-imidazolines (128) only[88]. Similarly, (124) reacts with α,β-unsaturated ketones to give a number of pyrimidine derivatives (129)[89].



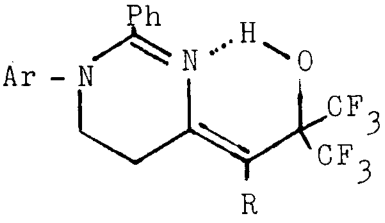
(126) R = Me; R' = NEt_2;
R = R' = H, CO_2Me

(127) R = H; R' = Ph, CO_2Me

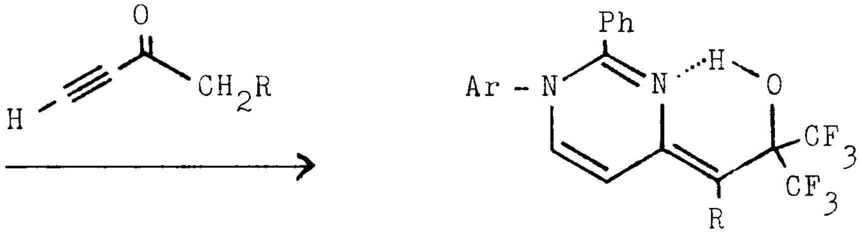




(129a) (R = H, Me)

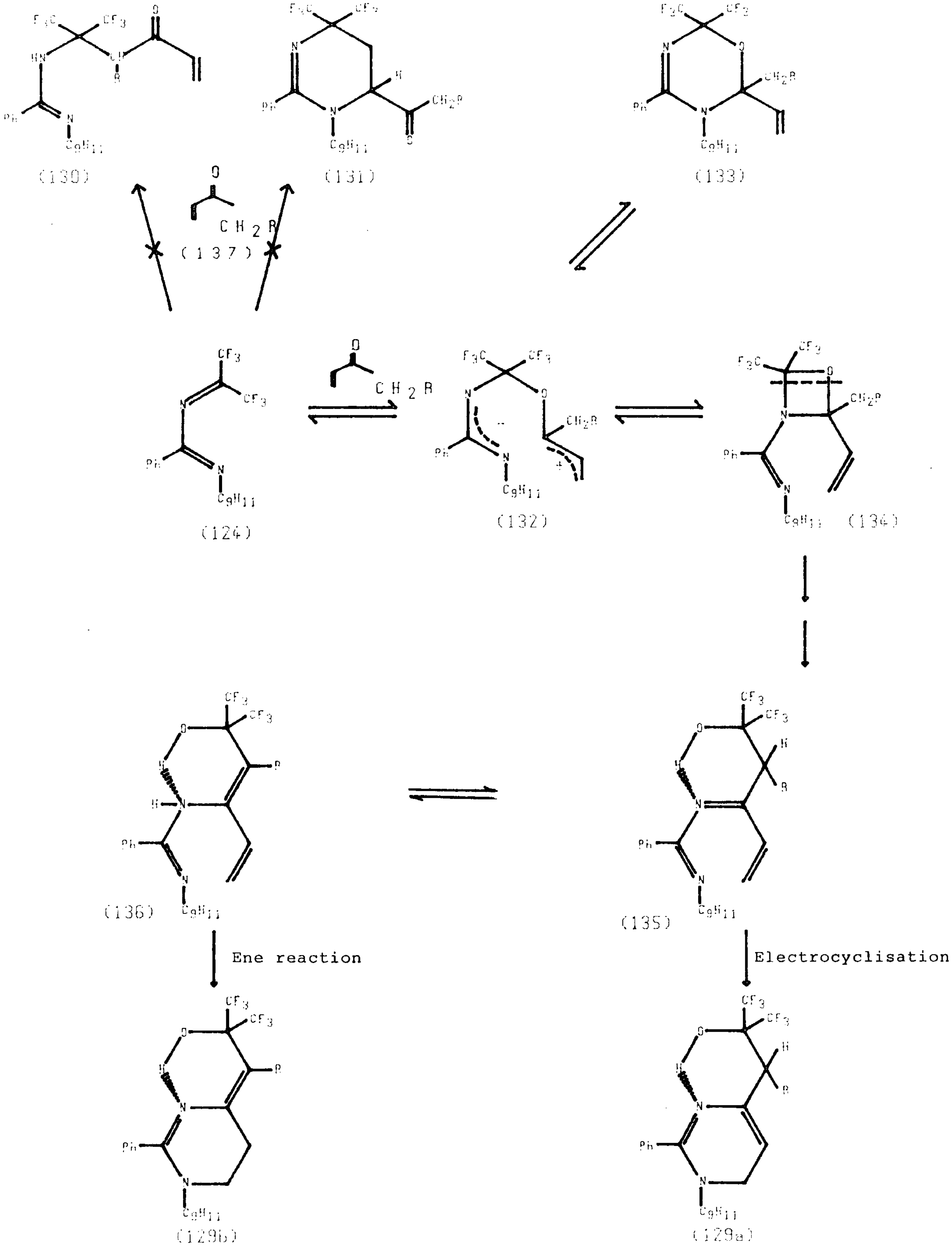


(129b) (R = H, Me)



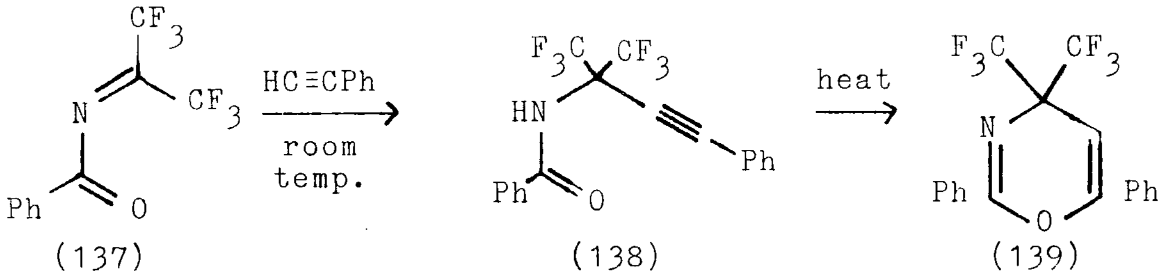
(129c) (R = H, Et)

Diene (124) does not react with enone (137) to give the normal nucleophilic addition (130) or [4 + 2] cycloaddition (131) products. The products obtained are consistent with formation of a dipolar intermediate (132), which collapses to the unstable (134). Retro-[2 + 2]-cycloaddition of (134) with subsequent aldol addition to the eliminated hexafluoroacetone gives (135) which can rearrange via an electrocyclisation process to yield (129a), or via an intramolecular ene reaction to produce (129b).


(130)
(131)
(133)
(137)
(124)
(132)
(134)
(136)
(135)
(129b)
(129a)
Ene reaction
Electrocyclisation

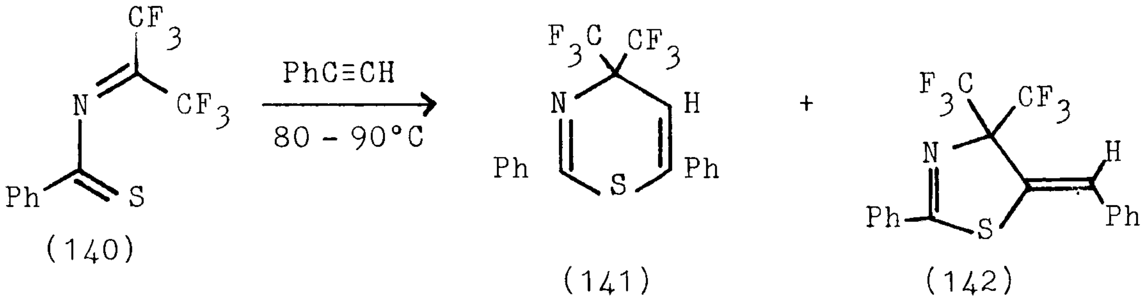
SCHEME C

Heterodiene (137) reacts with phenylacetylene at room temperature to give the Michael adduct (138), that can be transformed to the 4H-1,3-oxazine (139) on heating[92].

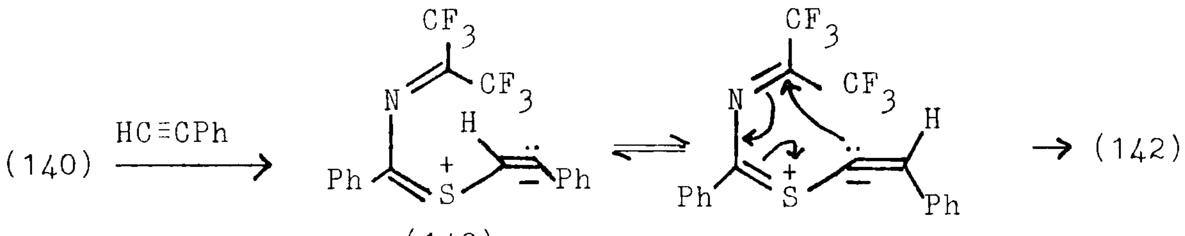


Reaction of the thia-analogue of (137) is more interesting, and is claimed to give the first example of a reaction in which the dienophile skeleton is only partially incorporated into the derived ring system[92].

Heating the thiaazabutadiene (140) in phenylacetylene gives both the [4 + 2]-cycloadduct (141), and a compound (142) formed via a novel cyclisation process.



Thiazole (142) is formed via initial attack of the acetylene on sulphur to form intermediate (143), which subsequent to a 1,2-hydrogen shift, ring closes to give the observed product.



(143)

1B.4 Miscellaneous

1B.4.A Addition of elemental fluorine

In spite of the extensive studies of addition of fluorine via electrochemical fluorination and high valency metal fluorides to a wide variety of organonitrogen compounds, there have been very few reports on reactions involving the simple addition of elementary fluorine across a carbon-nitrogen double bond. American workers have performed a systematic study of reaction of fluorine with nine perhaloimines. Results are presented in the table[93].

Imine	Time at 25°C	Products
$CF_3N=CF_2$ (60)	3h	$(CF_3)_2NF$ (87%)
$(CF_3)_2NCF=NCF_3$	7d	$(CF_3)_2NCF_2NFCF_3$ (98%)
$SF_5N=CF_2$	23h	SF_5NFCF_3 (57%)
$CF_2=NCl$	3h	CF_3NClF (89%)
$CF_2=NF$ (98)	4h	CF_3NF_2 (97%)
$CF_3CF=NF$ (148)	10h	recovered $CF_3CF=NF$ (93%)
$CF_3CF_2CF=NF$ (149)	4h	explosion C, CF_4, other
$(CF_3)_2C=NF$ (150)	5h	explosion C, CF_4, other
$(CF_2=NF)_2$ (151)	1d	recovered $(CF=NF)_2$ (91%)

The results were rationalised in the following way, as illustrated for $CF_2{=}NF$ (98).

$$CF_2{=}NF + F_2 \longrightarrow CF_3NF\cdot + F\cdot$$

$$CF_3NF\cdot + F\cdot + M \longrightarrow CF_3NF_2 + M$$

$$CF_3NF\cdot + F_2 \longrightarrow CF_3NF_2 + F\cdot$$

The authors have no explanation for the curious stability of (148) and (151), and attribute the explosive reactions of (149) and (150) to the instability of intermediate radicals $(CF_3)_2CFNF\cdot$ and $CF_3CF_2CF_2NF$.

1B.4.B Reactions with electrophiles

Reaction of perfluoro-2-azapropene (60) with fluoride ion leads only to dimer (81), since the stable $(CF_3)_2N$-group is easily displaced by subsequent nucleophilic attack.

$$\underset{(60)}{CF_3N{=}CF_2} \xrightarrow{F^-} \underset{(81)}{CF_3N{=}CF{-}N(CF_3)_2}$$

Recently, Russian workers have reported that treating (60) with SbF_5 gives a mixture of dimer (81) (23%) linear trimer (152) (36%) and a cyclotrimer (153) (18%), formed

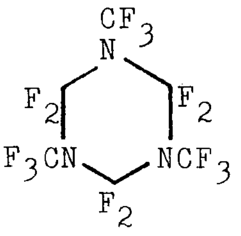
$$\underset{(60)}{CF_3N{=}CF_2} \xrightarrow{SbF_5} \underset{(154)}{[\overset{+}{CF_2{=}N{=}CF_2}]} \xrightarrow{(60)} \underset{(81)}{CF_3N{=}CF{-}N(CF_3)_2} \ (23\%)$$

$+$

$$\underset{(152)}{(CF_3)_2NCF_2N{=}CFN(CF_3)_2} (36\%)$$

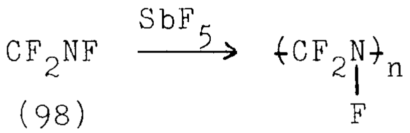
$+$

(153)

(18%)  (153)

via a common tetrafluoro-2-azapropenylium cation (154)[94].

Other workers have shown that reaction of perfluoromethanimine (98) with SbF_5 gives the first example of a polymer containing N-F bonds[95].



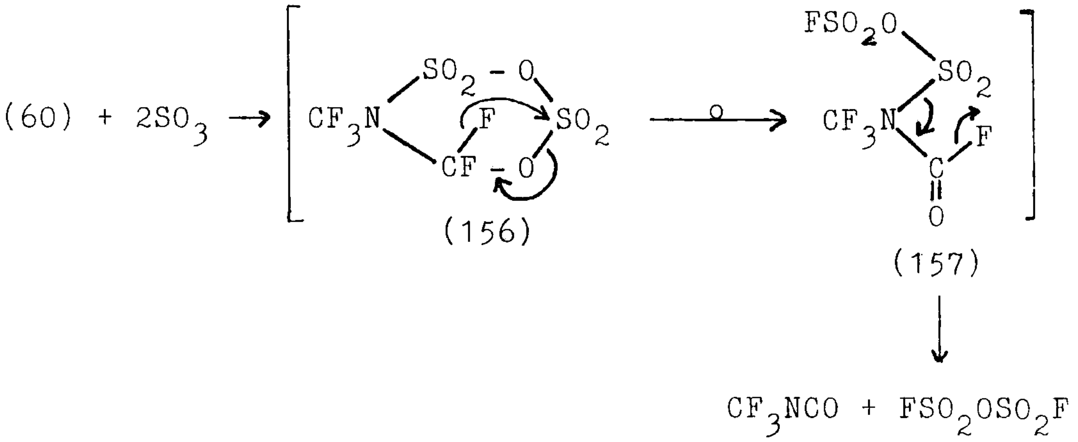
$$CF_2NF \xrightarrow{SbF_5} -(CF_2\underset{\displaystyle F}{\underset{|}{N}})-_n$$

(98)

Sulfotrioxidation of perfluoro-2-azapropene (60) gives trifluoromethyl isocyanate (155)[96].

$$\underset{(60)}{CF_3N{=}CF_2} + 2SO_3 \xrightarrow{100°C} \underset{(155)}{CF_3N{=}C{=}O} + FSO_2OSO_2F$$

The mechanism proposed is an initial attack of sulphur trioxide on the imine to give the β-pyrosultone (156), which then undergoes anionotropic isomerisation to the unstable carbamoyl fluoride (157) which decomposes under the reaction conditions to give pyrosulfuryl fluoride and isocyanate (155).



(156)

(157)

(155)

DISCUSSION

CHAPTER 2 FLUOROCARBON IMINES

2A SYNTHESIS AND REACTIONS OF PERFLUORO-2,5-DIAZAHEXA-2,4-DIENE AND RELATED AZA-OLEFINS

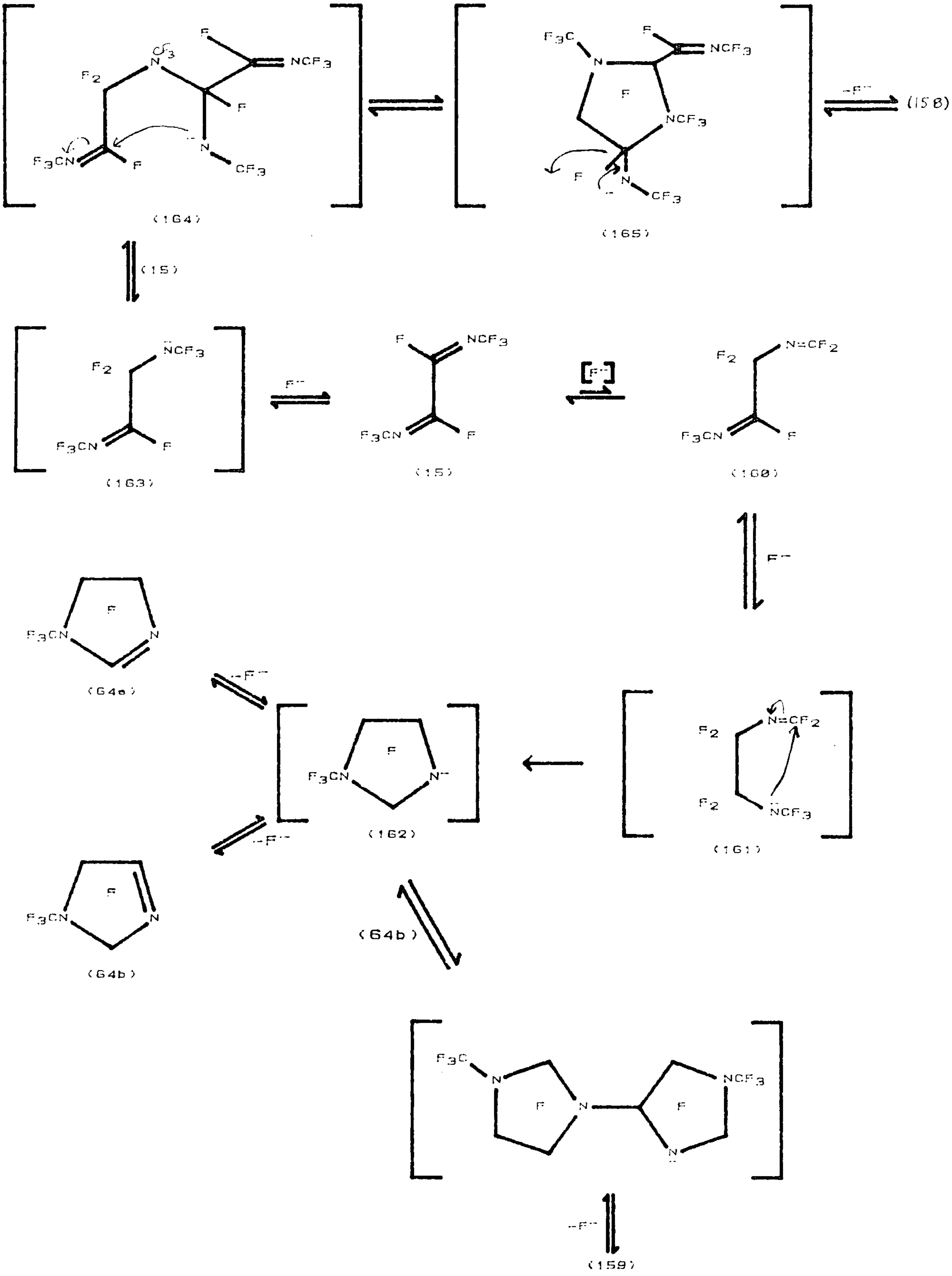
2A.1 Synthesis As can be seen from the previous chapter, good synthetic routes to perfluoroaza-olefins are comparatively few. One such route is to the di-imine perfluoro-2,5-diazahexa-2,4-diene (15)[13,97,20].

$$\begin{tikzcd}[column sep=huge, row sep=huge]
\mathrm{Me_2NCH_2CH_2NMe_2} \arrow[r, "\mathrm{Cl_2}", "\substack{\mathrm{1,2,4\text{-}Cl_3C_6H_3}\\ h\nu \\ 70\ -\ 200^\circ\mathrm{C}}"'] & \mathrm{Cl_2C{=}NCCl_2CCl_2N{=}CCl_2} \arrow[d, "\substack{\mathrm{HF,\ PhCl}\\ 110^\circ\mathrm{C}}"] \\
\substack{\mathrm{CF_3N{=}CFCF{=}NCF_3}\\ (15)} & \substack{\mathrm{CF_3NHCF_2CF_2NHCF_3}\\ (14)} \arrow[l, "\mathrm{NaF}"', "50\ -\ 70^\circ\mathrm{C}"]
\end{tikzcd}$$

We are grateful to the Bayer Co. for making available to our laboratory quantities of diamine (14). As a consequence of this available source of the perfluoro-imine (15) we have set out to explore the chemistry of (15) and oligomers derived from it. This thesis contains a survey of this chemistry.

2A.1.A Dimerisation reactions Workers at Bayer[19,98], and Barnes[47] in this laboratory, have demonstrated that dimers of (15) can be formed using NaF, KF and CsF. The mechanism proposed for forming these is shown in Scheme D.

We have explored the use of different fluoride ion sources at different temperatures with a view to:
(a) selectively producing particular dimers, (b) gaining more insight into the mechanism of fluoride-induced reactions



Scheme D

of these systems, and (c) comparing the characteristics of different fluoride sources. Chemistry involving fluoride sources is a topic of great current interest but there is little systematic comparison and understanding of the effect of the fluoride source on product distribution.

Results obtained from this series of reactions are shown in Table 1.

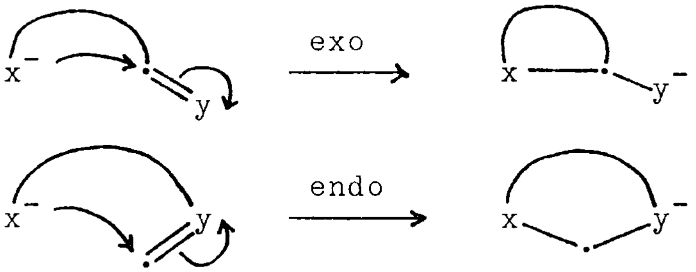
MF	(158)%	(159)%	(166)%	(169)%
NaF[a]	76	24	-	-
NaF[b]	35	65	-	-
KF[a]	43	50	7	-
CsF[c]	94	6	-	-
CsF[a]	37	57	6	-
CsF[b]	74	23	-	3

a: room temp, CH_3CN;[47] b: 120°C, sulfolane;
c: -23°C, CH_3CN

Table 1

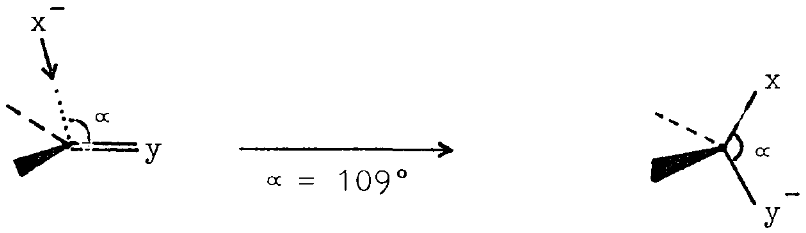
Comparison of the complete series of reactions yields a number of interesting mechanistic features. Probable mechanisms for the formation of dimers (158) and (159) are shown in Scheme D. It is important to note that the formation of (159) involves an intramolecular step, i.e. (161) → (162), and it might be anticipated that this unimolecular process would be preferred over the competing bimolecular step (163) → (164) involved in forming (158). However, from the tables, formation of (158) is preferred at lower temperatures, or using less reactive fluoride sources and this implies that the intramolecular cyclisation step (161) → (162) is not easy.

Baldwin has proposed three empirically based rules for prediction of the relative facility of ring forming reactions[99]. He describes a ring-forming process with the prefix Exo when the breaking bond is exocyclic to the smallest so formed ring, and Endo for the corresponding endocyclic case. Consideration of the stereochemical requirements of



transition states for the various tetrahedral, trigonal and digonal ring closure processes leads to an assessment of the facility of these reactions.

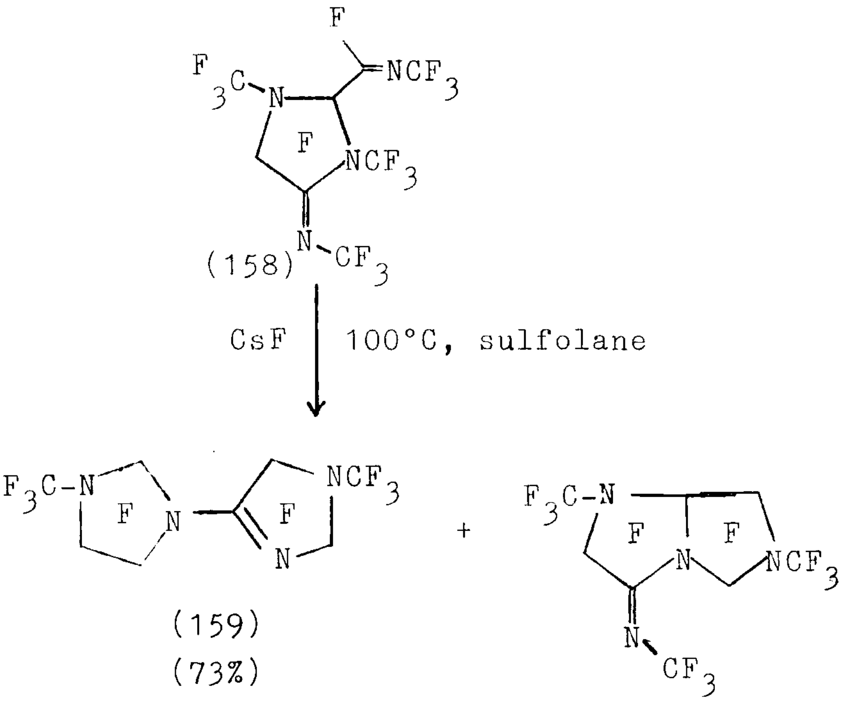
Thus, for trigonal systems, the favoured path will be that illustrated in the following Scheme. The subtended angle



α between the interacting atoms is maintained during the reaction pathway, and so favoured ring closures are those in which the nature of the linking chain enables the terminal atoms to achieve the required trajectories to form the final ring bond. Disfavoured cases, therefore require severe distortion of bond angles and distances to achieve such trajectories. Baldwin's rules for trigonal systems are therefore that (a) 3 to 7-Exo-Trig are all favoured processes and (b) 3 to 5-Endo-Trig are disfavoured; 6 to 7-Endo-Trig are favoured.

Thus, the observation that the bimolecular process (163)→(164) (Scheme D) is preferred over the cyclisation (161)→(162) is quite consistent with Baldwin's rules, since (161)→(162) is an example of a disfavoured 5-endo-Trig cyclisation. Formation of (158) also involves a cyclisation step (164)→(165), but this is an example of a favoured 5-exo-Trig process. Hence, from this argument and the experimental evidence presented earlier, the dimerisation occurs under a balance between kinetic and equilibrium control, (158) being the kinetically favoured product.

2A.1.B <u>Isomerisation reactions</u> The result of the reaction of (15) with CsF at 120°C, which was repeated many times is not easy to rationalise. We would expect, under the conditions employed, almost quantitative formation of (159) (see Scheme E and Table 1), however only a relatively low proportion of (159) was obtained and a new dimer (169) was isolated in 3% yield. Similarly, the preferred formation of (159) by NaF-catalysis at 100°C, reported by German workers[98] is at first slightly surprising since a mixture of (159) with (158), the "low temperature" product would have been anticipated. However, in a separate experiment, we have found that further heating of dimer (158) with caesium fluoride at 120°C gave (159) together with larger quantities of dimer (169).

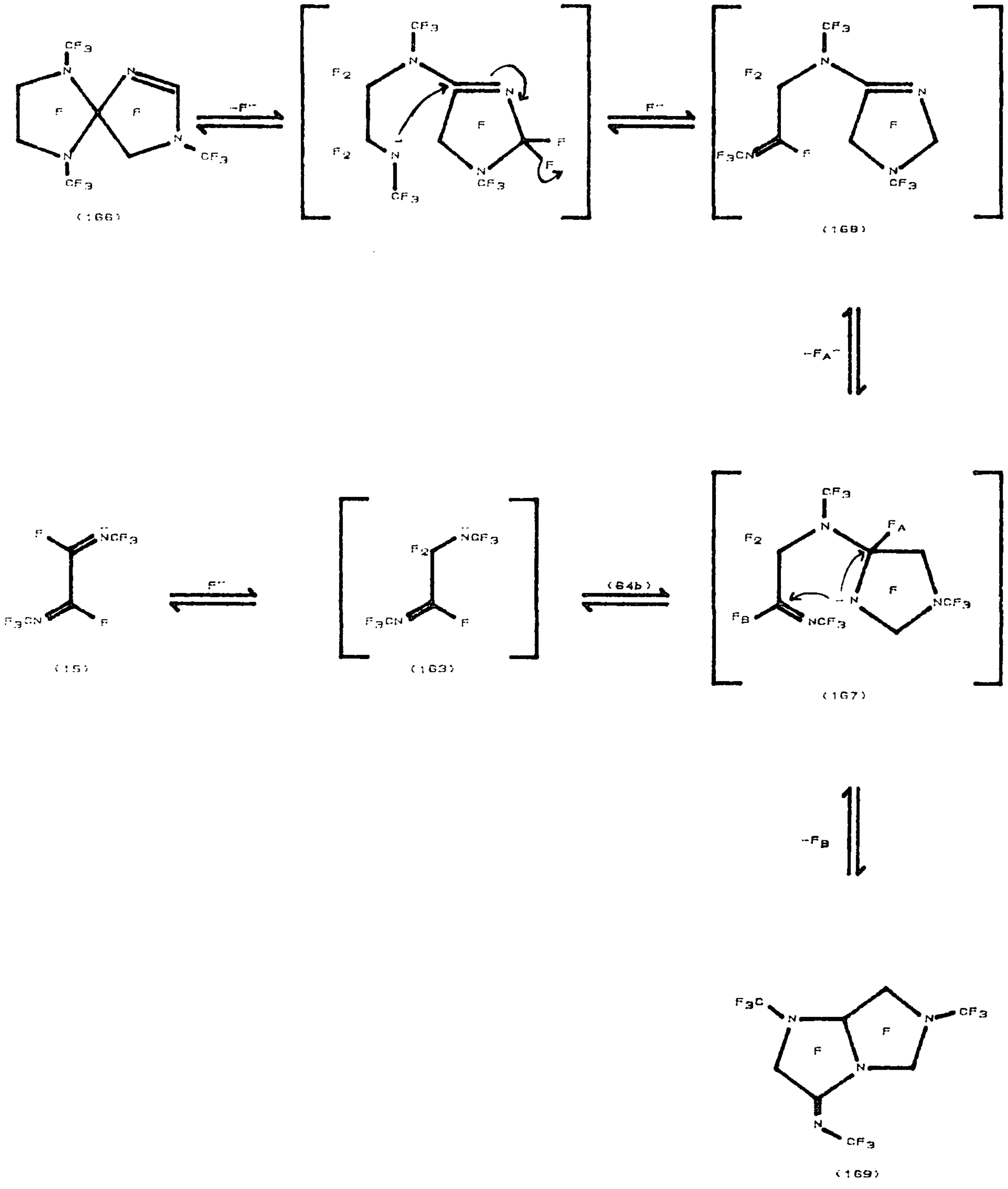


(158)

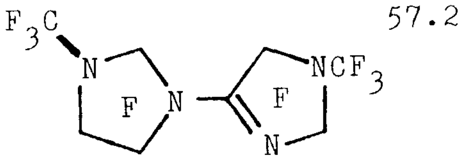
(159) (73%)

(169) (27%)

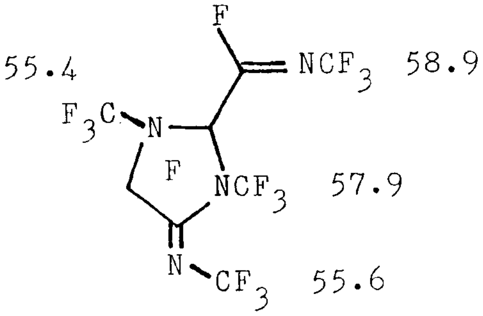
Probable mechanisms for the formation of the novel dimer (169), and spiro-compound (166) are shown in Scheme E. Addition of fluoride ion to di-imine (15) gives nitranion (163) which reacts with (64b) to give a common intermediate (167). Elimination of fluoride ion from (167) can occur in two ways, to give either the ring-closed isomer (169) or the open chain compound (168). Fluoride-catalysed isomerisation of (168) leads to the spiro-compound (166). Assignment of the structure of (169) was not easy. Mass spectra and elemental analysis showed it to be a dimer of (15) and the mass spectral fragmentation pattern showed the presence of CF_3 (m/e = 69) units. Significantly, there was no peak due to m/e = 100, indicating the absence of a C_2F_4 unit in the molecule. ^{19}F n.m.r. spectroscopy showed resonances at 57.7 and 58.3 ppm, characteristic of three trifluoromethyl



Scheme E



(159)

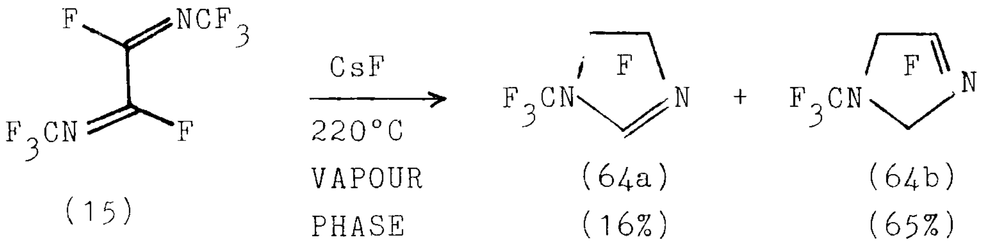


(158)

groups bonded to nitrogen, as well as two overlapping AB splitting patterns arising from CF_2 units, and a third resonance which integrated to two fluorines. A resonance integrating to a single fluorine at 102 ppm came at very low field for a tertiary position, but this downfield shift can be attributed to the influence of two adjacent nitrogens. The presence of a C=N bond was demonstrated by a ν_{max} in the infrared spectrum at 1760 cm^{-1}.

From Scheme E, it is likely that the formation of significant quantities of (169) can only occur if sufficient time has elapsed to set up an equilibrium mixture at high temperatures. The preferred formation of (169) over the spirodimer (166) at elevated temperatures is not easily explained but it may be that the necessary intramolecular cyclisation step (167)→(169) cannot occur quickly before elimination of fluoride ion from (167) at lower temperatures.

Barnes has reported that vapour phase reaction of (15) over CsF at 220°C is a good route to the cyclic isomers (64)[47].



(15) (64a) (16%) (64b) (65%)

Reaction of (15) using KF was attempted. Unfortunately, the use of this less active source of fluoride ion was found to be an unsatisfactory route to (64) and gave at best only around a 60% conversion.

$$(15) \xrightarrow[\text{VAPOUR PHASE}]{\text{KF}} \underset{(43\%)}{(64)} + \underset{(32\%)}{(15)}$$

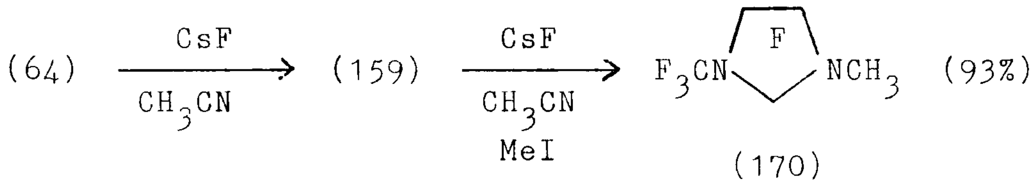
Recent examples in the literature of alkali metal fluorides on silica or alumina supports having a catalytic effect many orders of magnitude greater than that of the corresponding unsupported reagents[100,101] prompted an attempted conversion of (15) to (64) over KF on a silica support. The reaction gave a poor conversion, and overall recovery of fluorocarbon materials was very low.

$$(15) \xrightarrow[\text{VAPOUR PHASE } 220°\text{C}]{\text{KF/silica}} \underset{(16\%)}{(15)} + \underset{(5\%)}{(64)}$$

The best explanation for this disappointing result is that water is strongly physisorbed to the silica, and difficult to remove without overheating and changing the nature of the bonding between the metal fluoride and its support.

This water reacts rapidly with the extremely electrophilic imine to produce involatile hydrolysis products.

The lack of success with KF prompted a more careful use of the route employing CsF. Rigorous drying of the metal fluoride and the apparatus, and freshly distilling the imine from NaF before use (to remove traces of amine impurity) resulted in yields of (64) of greater than 90%. Stirring (64) in the presence of fluoride sources in solution gives rapid dimerisation to (159), obviously via nitranion (162), and indeed, stirring (159) with fluoride and iodomethane was found by a previous worker[47] to give the N-methyl derivative (170) in high yield.



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2A.1.C <u>New Fluoride ion sources</u> Tris(dimethylamino)-sulfonium trimethylsilyldifluoride (TAS-F), and "anhydrous" tetrabutylammonium fluoride (TBAF) are currently receiving a lot of attention as highly active sources of fluoride ion and significant claims are being made for their effectiveness. A study of their effect as catalysts for the dimerisation reactions of (15) was made in order to gauge the activity of these new fluoride ion sources in comparision with more conventional alkali metal fluorides.

Tetrabutylammonium fluoride can be readily prepared by neutralising an aqueous solution of the hydroxide with a solution of HF. We might anticipate that attempts to dry the material would result in decomposition to tributylamine,

$$^{n}Bu_4N^+OH^-_{(aq)} + HF_{(aq)} \longrightarrow {}^{n}Bu_4N^+F^-_{(aq)}$$

tetrabutylammonium bifluoride, and 1-butene and this is indeed the case when the salt is heated under high vacuum at 77°C[102]. However, American workers have claimed that when the salt is warmed to only 40°C under high vacuum, almost anhydrous TBAF can be obtained[102,103]. This "anhydrous" TBAF has been used by a number of workers both with[103,104] and without[103] solvent in various substitution reactions to give fluorine-containing compounds.

TAS-F was first prepared some time ago[105] as a polymerisation catalyst by reacting three or more equivalents of dimethylaminotrimethylsilane with sulphur tetrafluoride in an inert solvent. Recent reports claim its use as an extremely potent source of fluoride ion in the preparation of stable perfluorocarbanions from the corresponding olefins[106] and this claim is supported by findings in our own laboratory[107].

$$3Me_2NSiMe_3 + SF_4 \xrightarrow{Et_2O} (Me_2N)_3\overset{+}{S}Me_3SiF_2^- + 2Me_3SiF\uparrow$$

Reaction of di-imine (15) with catalytic quantities of TBAF and TAS-F in acetonitrile gave the results shown in the table. These results indicate an activity somewhere between NaF and KF for TBAF and considerably less than NaF for TAS-F. The low activity of TBAF in this type of reaction may be attributed to either, or both of two reasons. Firstly,

Catalyst	Yield (158%)	 (159%)
TBAF	56	31
TAS-F	78	8

the reaction with (15) is exothermic and, since it is known that the salt is sensitive to elevated temperatures, it may be that the catalyst is destroyed before significant quantities of (159) can be generated. Secondly, we have found that drying commercially obtained samples of TBAF.$3H_2O$ at 40°C leads to around a 75% weight loss which is indicative of decomposition of the salt. Consequently, in the reaction with (15), there may be significantly less TBAF, and more free tributylamine in the system than anticipated. Other workers have demonstrated that tertiary amines readily promote oligomerisation reactions of perfluoroolefins[107].

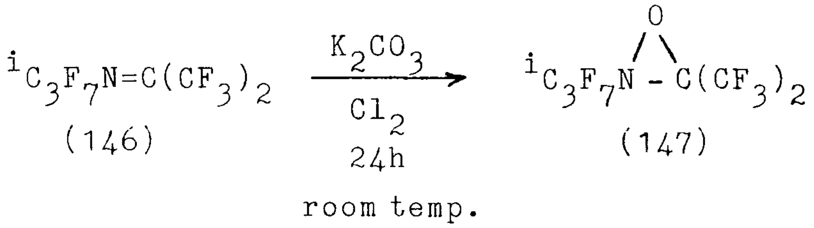
The reaction with TAS-F is more difficult to explain and it is probable that the mode of action of this reagent is significant. Since the reaction with (15) was performed another worker in our laboratory has shown that the action of TAS-F is not catalytic. The trimethylsilyldifluoride anion donates fluoride ion to the double bond in a fluoroolefin

$$(Me_2N)_3\overset{+}{S}Me_3SiF_2^- \;+\; {>}C=C{<} \xrightarrow{CH_3CN} (Me_2N)_3S^+ \;\; {>}CF-\overset{-}{C}{<} \;+\; Me_3SiF\uparrow$$

and the resulting anion is stabilised by the tris(dimethylamino)sulfonium cation[106,107]. Trimethylfluorosilane is eliminated from the system and hence no back reaction can occur. Thus, in the reaction with (15) intermediate anions (165) and (162) (Scheme D) will be formed and stabilised by the sulfonium cation. Since (164) is the kinetically preferred anion, (158) the product derived from this anion, is the predominant product.

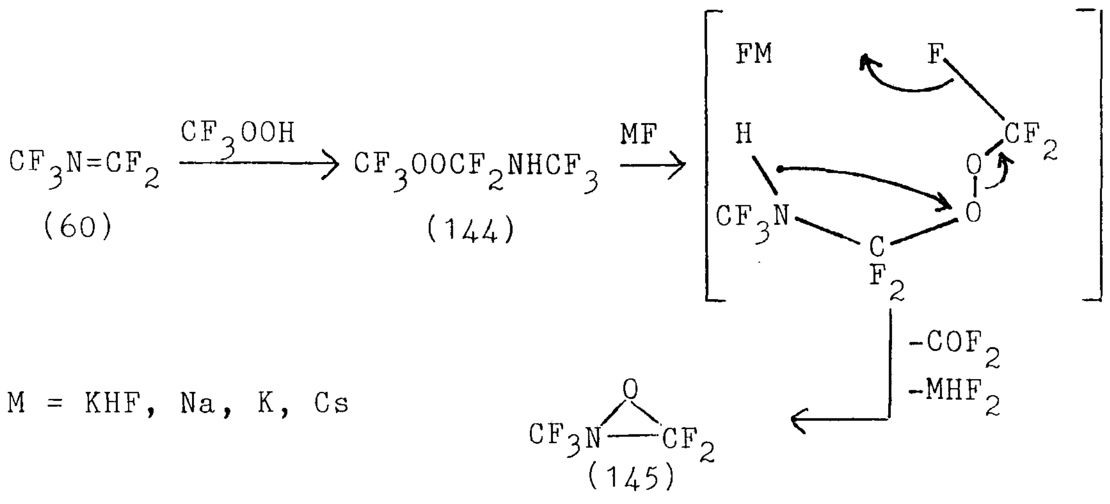
2A.2 Reactions A. Attempted synthesis of perfluorooxaziridines

Fluorinated oxaziridines are a little-known class of compounds to which two routes from aza-alkene starting materials have been proposed[108,109]. A report in the Patent literature[108] claims that contacting perhaloimines with one or more members of the group consisting of the carbonates, bicarbonates and oxides of the alkali and alkaline earth metals in the presence of elemental chlorine and an effective amount of moisture gives the oxaziridine products in high yield. An example is the oxidation of imine (146) to give oxaziridine (147). It is likely that the oxidising effect

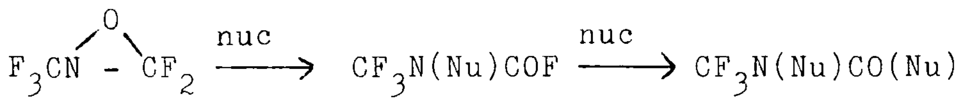


of this mixture is due to the formation of small quantities of inorganic hypochlorite on the surface of the metal oxide or carbonate.

In an alternative route reaction of perfluoro-2-azapropene (60) with trifluoromethylhydroperoxide gave intermediate (144), which on treatment with the fluoride, MF,



gave oxaziridine (145)[109]. This simple oxaziridine reacts readily through nitrogen to give a range of novel ketone derivatives[110,111].



$$F_3CN\overset{O}{-}CF_2 \xrightarrow{nuc} CF_3N(Nu)COF \xrightarrow{nuc} CF_3N(Nu)CO(Nu)$$

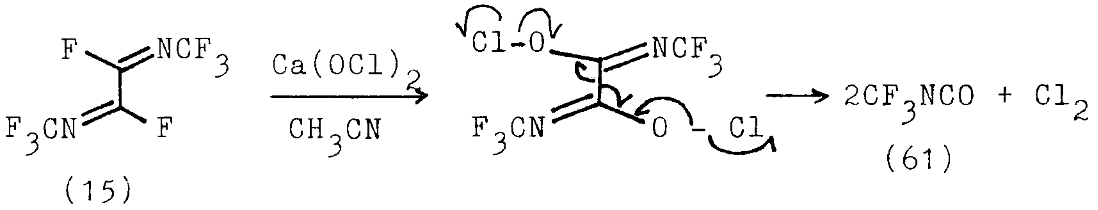
nuc = R^1OH, R^2CO_2H, R^3SH, R^4 R^5NH, KSCN, KCN

Nu = R^1O-, R^2CO_2-, R^3S-, R^4R^5N-, -SCN, -CN

Simple epoxides, especially hexafluoropropene oxide (HFPO) have found extensive use as synthons in the preparation of a wide range of organofluorine compounds[112]. The significant rôle played by compounds such as HFPO in the industrial manufacture of high-grade organofluorine products prompted an attempt to develop a synthetic route to similar oxaziridine derivatives. The method reported by Sekiya and DesMarteau[109], and described earlier was discounted as being unsuitable due to the relative inaccesibility of organic hydroperoxide reagents. Two approaches were made to the problem; firstly, a variation on work carried out in this laboratory on the preparation of fluorinated epoxides[113] and secondly, an extension of the route to epoxides and oxaziridines described in the patent literature by Ratcliffe[108].

Workers in Durham have used anhydrous calcium hypochlorite in epoxidation reactions of moisture-sensitive perfluoroolefins[113]. Since, in principle, the similarly electrophilic and moisture-sensitive imines (15), (158), and (159) should react in the same way to give perfluorooxaziridines a study of their reactions with anhydrous calcium hypochlorite was made.

In all cases no oxaziridine products were obtained. Diazadiene (15) reacted extremely vigorously to give trifluoromethyl isocyanate (61) and chlorine, possibly via the mechanism shown. Reaction did not occur at 0°C or in the absence of solvent.

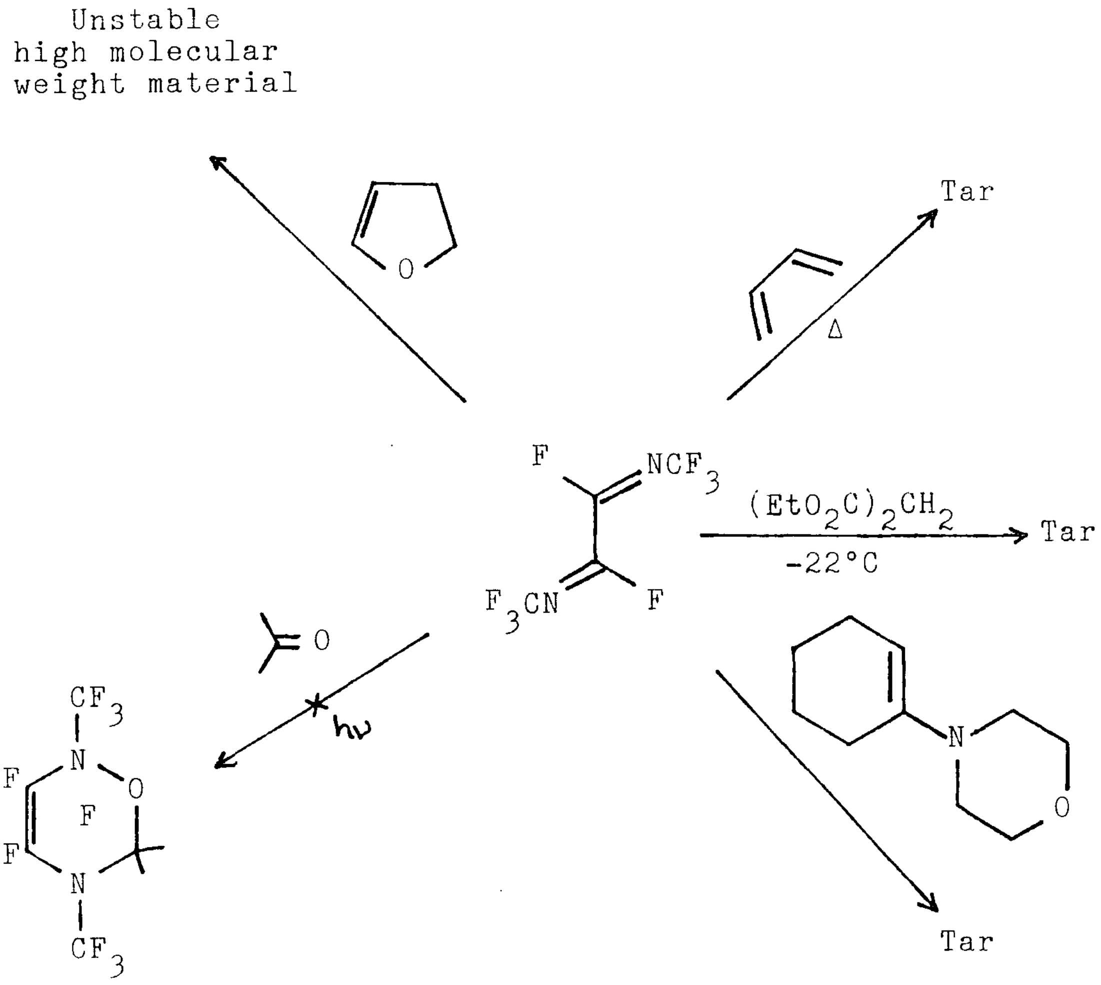


In an extension of work reported by Ratcliffe, both the tetramer of tetrafluoroethylene (for which the epoxide is known) and diazadiene (15) were reacted with potassium carbonate and chlorine in a nickel bomb. In both cases only starting materials were recovered. Repeated attempts gave the same results.

These results are disappointing in view of the potential utility of fluorinated oxaziridines in organic chemistry

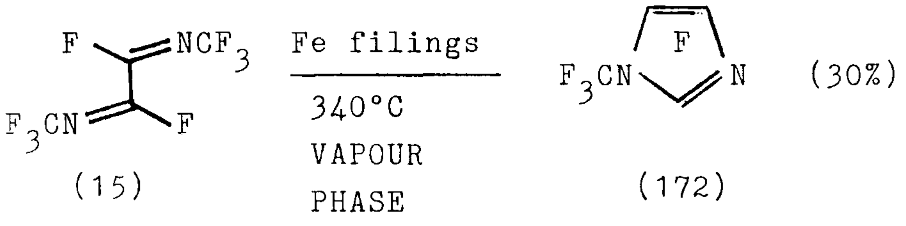
2A.2.B <u>Diazomethane additions</u> Addition of diazomethane to aza-olefins (15), (158) and (159) gave in all cases complex mixtures. Isolation of products was not attempted.

2A.2.C <u>Miscellaneous cycloaddition reactions</u> Cycloaddition reactions of (15) with electron-rich alkenes, 2,3-dimethyl buta-1,3-diene, an enolate anion and a photolytic reaction with acetone were all attempted unsuccessfully. The results are summarised in the scheme.



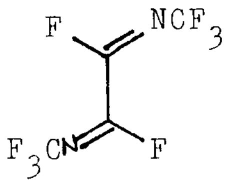
2A.2.D Attempted synthesis of perfluoro-1-methylimidazole

The defluorination of (15) over iron filings was claimed by a previous worker to give imidazole (172) in 30% yield[47]. The worker was unable to repeat the reaction, consequently

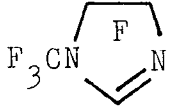


a careful study of the reaction of (15) and (64) with hot iron was made. The results are shown in the table and demonstrated that in all cases only recovered starting material or gaseous fragmentation products were obtained.

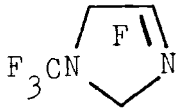
	Temp./°C	Product
(15)	340	(15) (72%)
(64)	400	(64) (81%)
(64)	450	(64) (72%)
(64)	500	(64) (42%)



(15)

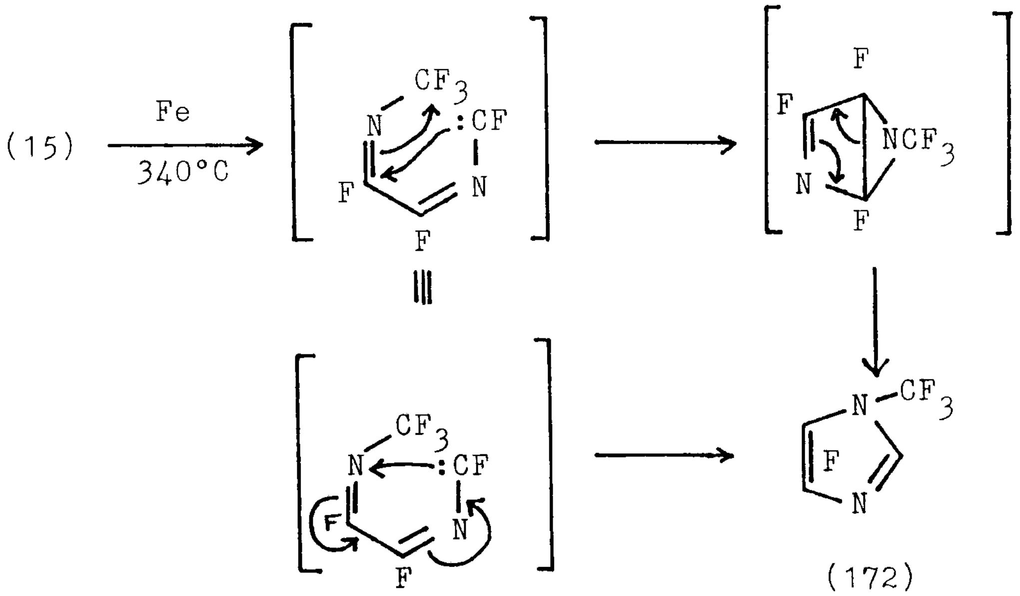


(64a)



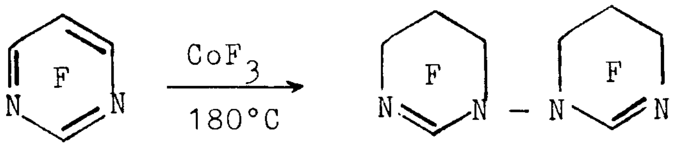
(64b)

The resistance of (64) to defluorination is consistent with the mechanisms proposed by Barnes for formation of (172) from (15), which do not involve (64) as an intermediate[47].



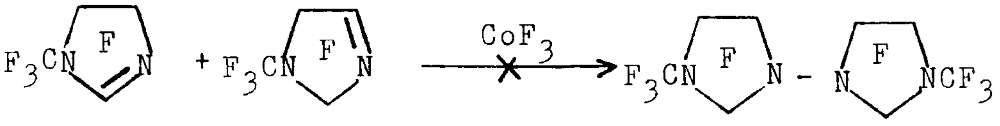
(172)

2A.2.E <u>Fluorination of (15) and (64)</u> The fluorination of tetrafluoropyrimidine by cobalt trifluoride is known to give the interesting bicyclohexenyl derivative (43) via a one-electron-transfer mechanism[34] (see Section 1A.4.A.1). It was thought that reaction of (64) with cobalt trifluoride



(43)

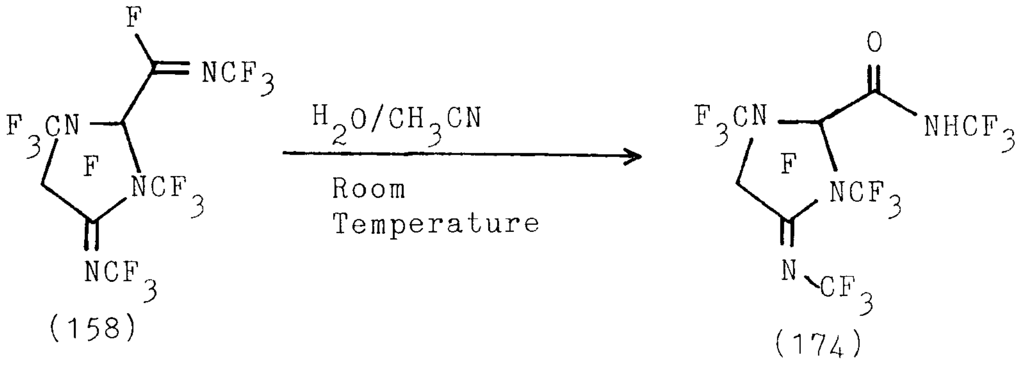
would, in a similar way, produce the bicyclopentanyl (173). However reaction of (64) with cobalt trifluoride at 180°C



(64a) (64b) (173)

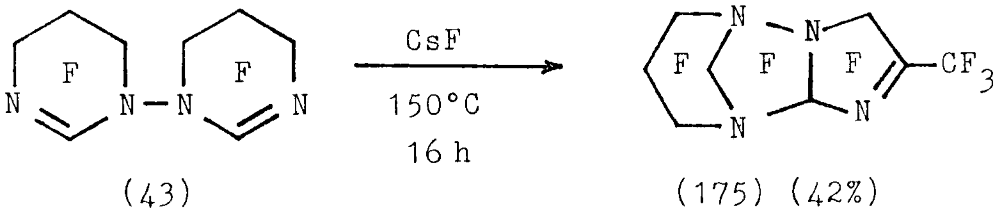
gave only recovered starting material (56%) and fragmentation products. Similarly, fluorination of (15) gave only recovered starting material and gaseous products.

2A.2.F <u>Aqueous hydrolysis of (158)</u> Workers in Durham[47,56] and elsewhere[46] have reported the aqueous hydrolysis reactions of (15)[46], (64)[47] and (159)[56]. The aqueous hydrolysis of dimer (158) is potentially more interesting as it has two C=N bonds. Stirring (158) with excess water at room temperature gave (174) only. The stability of the second C=N function under these conditions is understandable since hydrolysis would involve a ring-opening reaction with, in effect, $R_f - CF_2^-$ as a leaving group.



2B A NOVEL REARRANGEMENT OF PERFLUORO-1-1'-BIS-1,3-DIAZACYCLOHEX-2-ENYL (43)

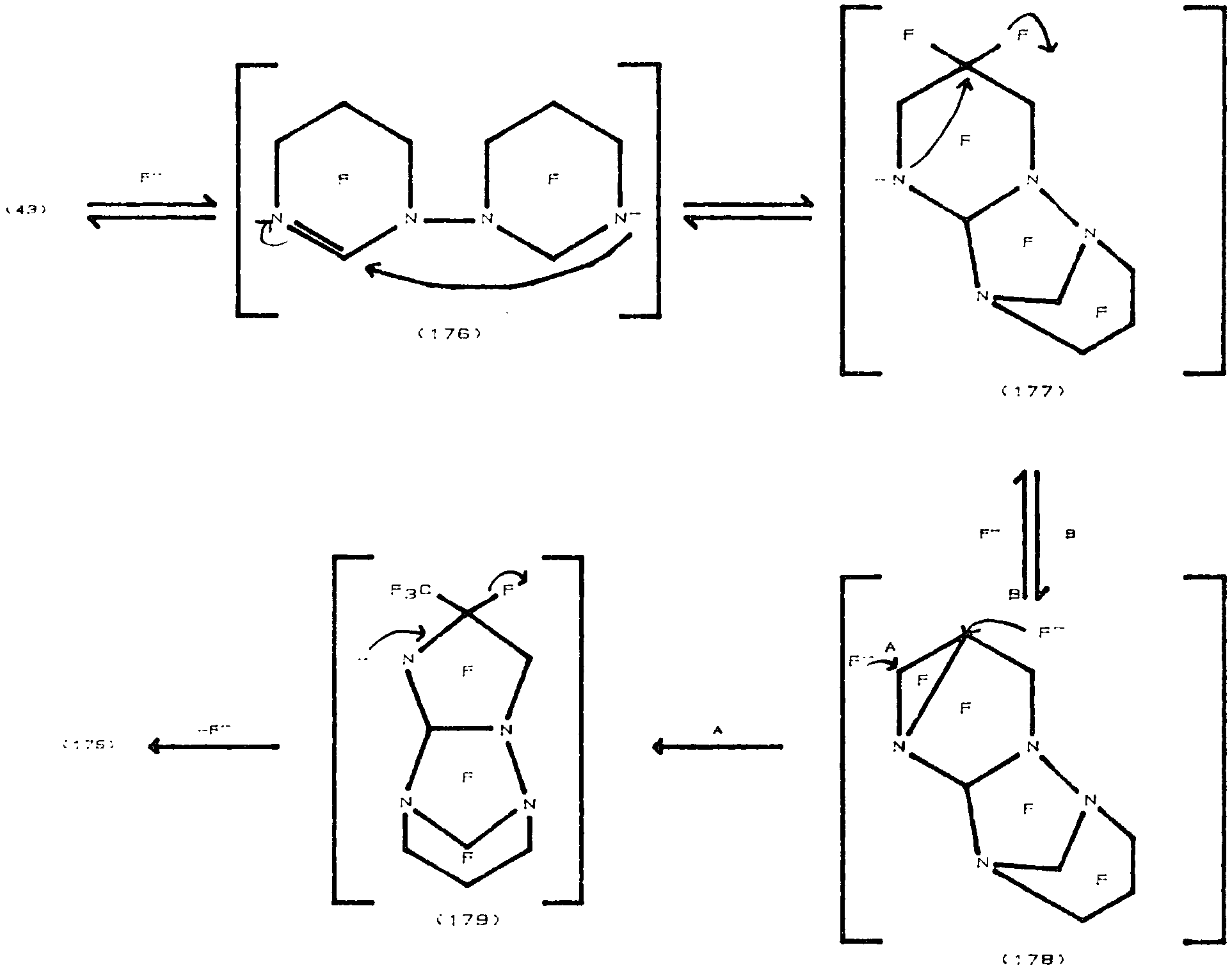
2B.1 Fluoride-catalysed isomerisation of (43) Barnes has reported that reaction of (43)[34] with CsF at 150°C in the absence of solvent gave a derivative isomeric with (43) and recovered starting material. He proposed structure (175) for this new isomer but spectroscopic evidence was not



sufficient to form any firm conclusion. We have reinvestigated this reaction with better spectroscopic tools available and with a view to obtaining a solid derivative for full X-ray analysis if necessary.

In fact the structure of (175) has now been fully confirmed from spectroscopic data; the parent ion in the mass spectrum (EI, CI and negative ion) and elemental analysis demonstrate that (175) is isomeric with the starting material (43) and a single absorption in the infrared spectrum at 1720 cm^{-1} indicates only one unsaturated site. High Field ^{19}F n.m.r. displays a series of AB signals between 89 and 118 ppm. (Intensity 8), together with a singlet at 127.1 ppm. (Intensity 2), showing that (175) contains five CF_2 groups. The presence of a singlet at 107.5 ppm. (Int. 1) is consistent with a 'tertiary' fluorine atom shifted downfield by the influence of adjacent nitrogen atoms. The remaining signal at 60.5 ppm. (Int. 3) is characteristic of a CF_3 group attached to an unsaturated site. The ^{13}C n.m.r. spectrum is very complex due to carbon-fluorine coupling but displays a quartet at 117.2 ppm. ($^1J_{CF}$ = 268 Hz) characteristic of CF_3[114] and a triplet at 147.1 ppm. ($^2J_{CF}$ = 14.6 Hz) characteristic of sp^2-hybridized carbon that is not bonded directly to fluorine[114,115]. The proven presence of a CF_3-group is a clear indication that ring contraction has taken place during the reaction and the absence of appropriate signals in the n.m.r. spectra indicate that there are no imino- or vinyl-groups attached directly to fluorine present, thus leaving (175) as the only reasonable structure consistent with the observed data and the structure of the starting material (43).

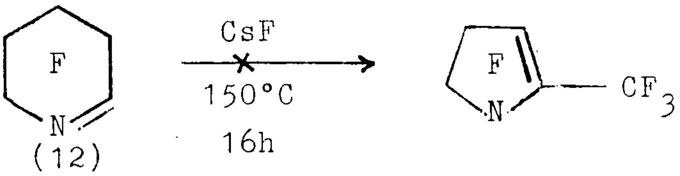
The proposed mechanism for this novel isomerisation is shown in Scheme F and involves internal nucleophilic attack at a saturated position, i.e. (177) → (178). The first stages of the isomerisation are obvious in that reaction must proceed via internal addition of fluoride ion to (43) to give nitrogen anion (176), followed by intramolecular nucleophilic addition to a double bond giving (177). More controversial, however, is the novel ring



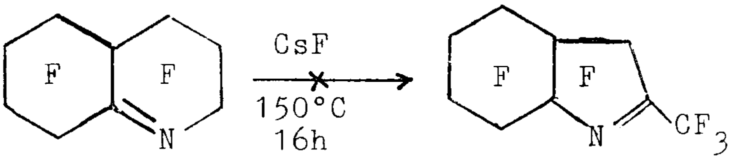
Scheme F

contraction of (177) to give (178), apparently via internal attack at a saturated position in a step reminiscent of the Favorskii rearrangement. Further attack of fluoride ion could then occur at position A or B in intermediate (178); attack at B would simply cause return to (43), whereas attack at A gives nitranion (179), from which, elimination of fluoride ion gives the observed product (175).

The unprecedented nature of the rearrangement (177) → (178) prompted model studies. Barnes has shown that heating perfluoroazacyclohexene (12) with caesium fluoride does not effect ring contraction but gives only starting material[47]. In a similar reaction, heating the octahydroquinoline derivative shown, under similar conditions, gave only recovered starting material. The reason for the difference in behaviour of these systems and of (43) is not obvious but it may be that the internal cyclisation of these compounds is a much higher energy process, or that the stereochemical requirements for the rearrangement (177) → (178) are very precise, and not achieved in the model compounds.

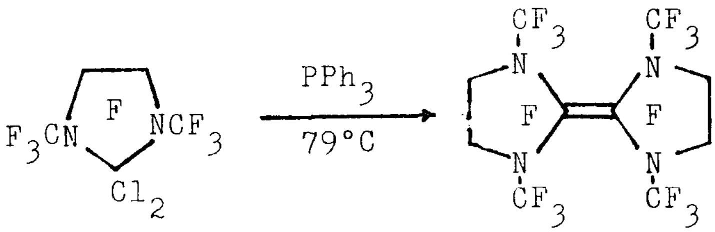


(12)



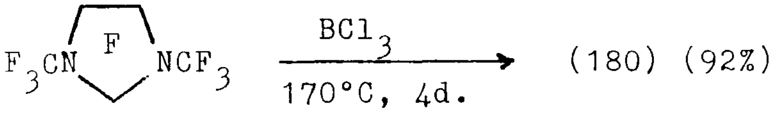
2B.2 <u>Reactions of (175)</u> In tandem with the spectroscopic investigation of the structure of (175) an attempt was made to prepare a solid derivative for X-ray crystallography. It was hoped that this would prove the presence of the interesting 1,2,5,7-tetraazatricyclo[3.3.1.0$^{2.6}$]undec-4-ene ring system.

A recent report[116] claims that reaction of the dichlorodiazacyclopentane (180) with triphenylphosphine at 79°C gives the coupled product (181) in near quantitative



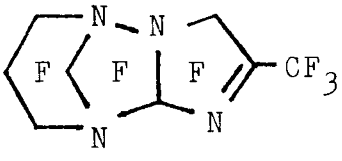
(180) (181)

yield. In an earlier report[117] CF_2 entities linked to two nitrogen atoms are selectively chlorinated by BCl_3 to form the corresponding N-CCl_2-N compounds. e.g. treatment of (182) with BCl_3 at 170°C gave (180) in high yield.

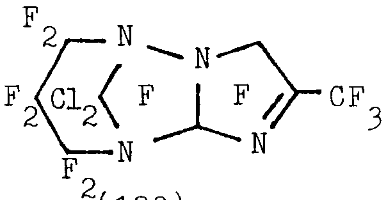


(182)

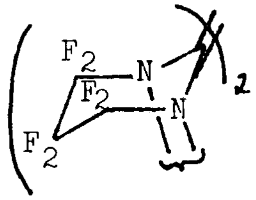
We envisaged that reaction of (175) with BCl_3 would give (183), which on treatment with PPh_3 would yield the solid (184).



(175)

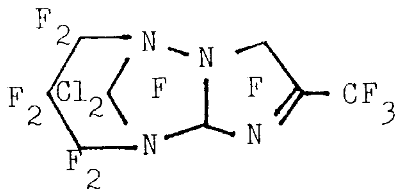


(183)



(184)

Chlorination of (175) with BCl_3 at 120°C gave a compound of probable structure (183). ^{19}F n.m.r. and infrared spectra and carbon nitrogen analyses were all consistent with this structure, however capillary g.c. mass spectroscocpy indicated a material of considerably higher molecular weight, and varied according to the sample



(183)

submitted. Reaction of (183) with BCl_3 at 170°C gave only recovered starting material and attempts at further substitution of chlorine for fluorine using $AlCl_3$ were also unsuccessful.

Assuming the ^{19}F n.m.r. assignment of the structure of (183) to be correct a sample was treated with PPh_3 and gave a crystalline solid (35%) which was difficult to identify. ^{19}F n.m.r. indicates the presence of only nine fluorines and the mass spectrum showed that the material contained one chlorine. We decided not to proceed with an X-ray analysis of the material since we were unsure of its chemical composition and geometry.

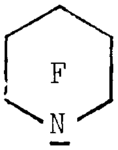
CHAPTER 3 PERFLUORINATED NITRANIONS

3A OBSERVABLE NITRANIONS

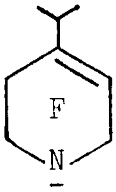
As described earlier (see Section 1.B.2) addition of fluoride ion to perfluoroimines readily occurs to give nitranion intermediates. However, examples of nitranions directly observable by nmr spectroscopy were limited to the anions (99)[57], (102)[73,74] and (185)[74] at the outset of this work, other perfluoroimines undergo oligomerisation. Nitranions (102) and (185) were generated by action of CsF on the corresponding imines (12) and (186) in aprotic solvents. In both cases a marked <u>downfield</u> shift in resonances arising from CF_2 <u>adjacent</u> to nitrogen was observed on formation of the nitranion, i.e. (12) → (102) and (186) → (185).

$(CF_3)_2N^-$

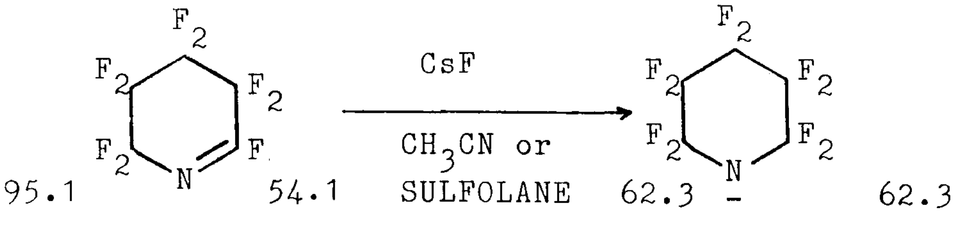
(99)



(102)

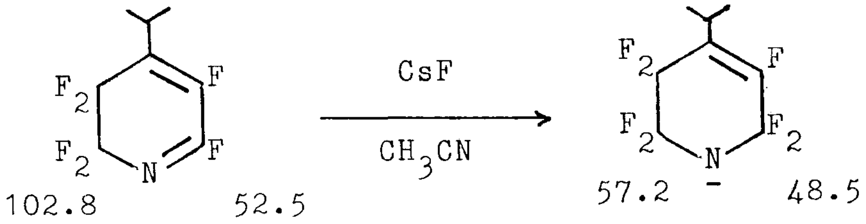


(185)



(12)

(102)

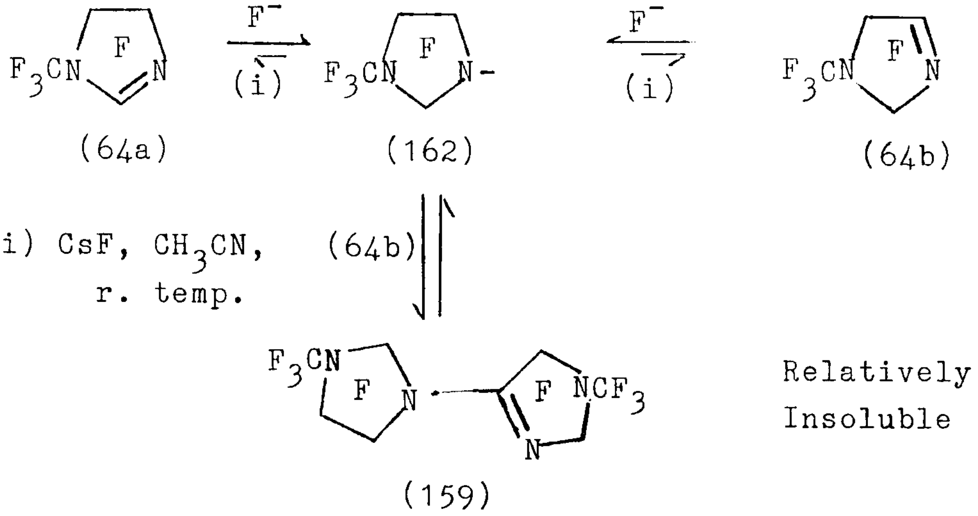


(186)

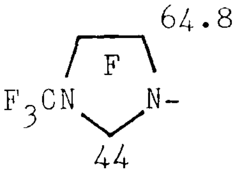
(185)

This observation is consistent with that made for perfluorocarbanions by other workers in Durham[118].

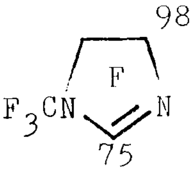
The ready formation of anions from perfluoroazacyclohexene derivatives (12) and (186) led us to propose that reaction of diazacyclopentenes (64) with CsF in acetonitrile would give a stable nitranion in much the same way. All early attempts to form anion (162) were unsuccessful, resulting only in rapid dimerisation to (159) which was largely insoluble in CH_3CN but prolonged stirring of (64) with CsF in acetonitrile gave slow formation of (162), gradually giving a stable homogeneous solution of the anion. This situation obviously arises from the much lower solubility of the dimer (159) compared with the monomers (64) or anion (162). The anion was observed by ^{19}F n.m.r. and



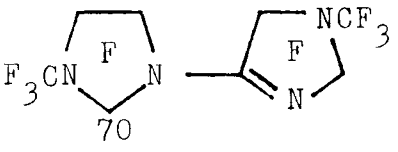
variable temperature studies showed little change in the spectrum between -40 and +50°C, indicating that reversible fluoride exchange involving anion (162) and precursors (64) does not occur rapidly on the n.m.r. time scale. The resonances arising from CF_2 groups are shifted <u>downfield</u>



(162)



(64a)



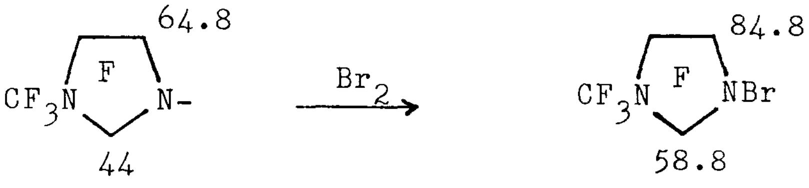
(159)

from the neutral precursors for positions adjacent to the nitrogen anion charge centre. This now characteristic change in the nmr spectrum has also been observed recently by Russian workers for positions adjacent to nitrogen in anion (187)[14], although in this case no shifts are quoted!

$$CF_3N{=}CFCF_3 \xrightarrow[CH_3CN]{CsF} CF_3\overline{N}C_2F_5$$

(187)

Quenching a solution of anion (162) with bromine resulted in an upfield shift of around 15 p.p.m. for resonances arising from CF_2 groups adjacent to the nitrogen bonded to bromine. However, the N-bromodiazacyclopentane (188) so-formed was too unstable for isolation and full

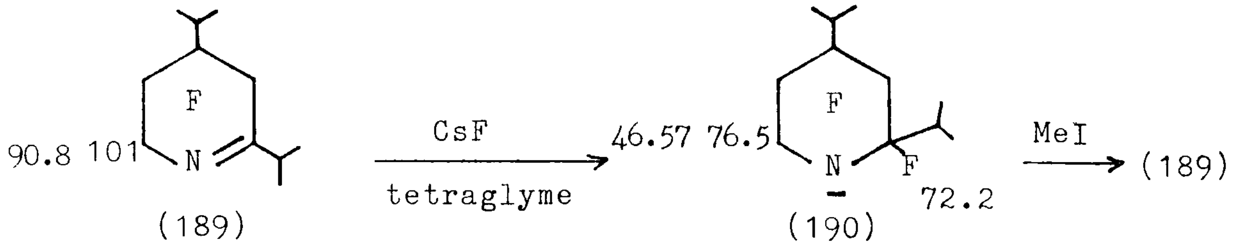


(162) (188)

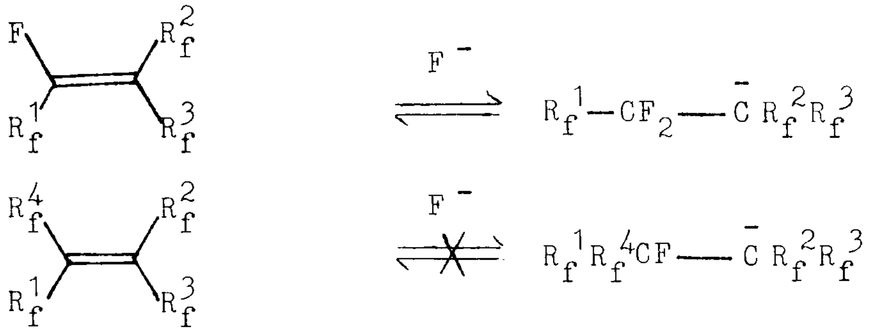
analysis. This result is consistent with the absence of examples of secondary N-bromoperfluoroalkylamines in the literature. Reports of N-bromoperfluoroalkyamines are limited to some recent examples prepared by DesMarteau and co-workers by mixed halogen addition to N-haloimines in the e.g. $CF_2{=}NCl \xrightarrow{Br_2/CsF} CF_3NBrCl + CF_3NBr_2$

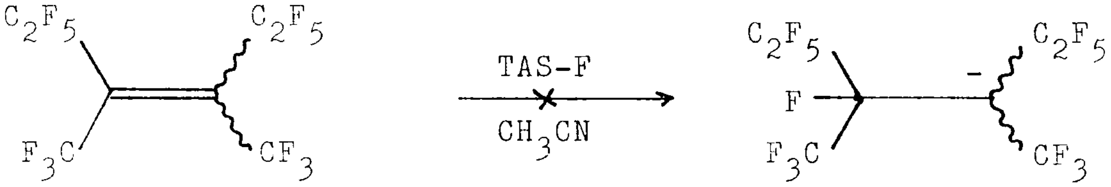
dark[119,120]. The N-bromoamines are stable in the dark at 22°C but readily decomposed under the influence of pyrex-filtered sunlight.

Examples of observable perfluoro-carbanions and -nitranions are limited to those prepared from unsaturated precursors containing a vinyl fluorine. We have been able to prepare an example of a perfluoronitranion from a precursor with a perfluoroalkyl group bonded to the imino-carbon. Stirring imine (189) with CsF in tetraglyme gave a yellow solution, ^{19}F n.m.r. spectroscopy of which showed downfield shifts for positions adjacent to nitrogen characteristic of formation of nitranions. Addition of MeI to the



solution of (190) gave none of the N-methyl derivative, instead the anion collapsed back to the imine (189). This result is consistent with observations made for other sterically demanding systems[107]. The stability of (190) is unprecedented. All previously reported observable nitranions and carbanions were prepared from precursors containing imino- or vinyl-fluorines respectively. Attempts to prepare carbanions from perfluoroolefins containing only perfluoroalkyl groups and no fluorines bonded directly to the double bond have been unsuccessful; for example tetrafluoroethylene tetramer, a perfluoroolefin analogue of (189), does not give a stable carbanion even on treatment with the extremely potent fluoride ion source TAS-F[107].

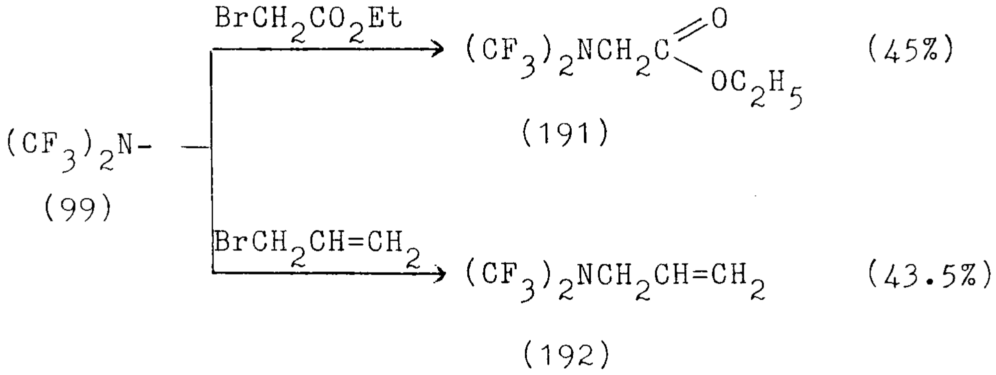




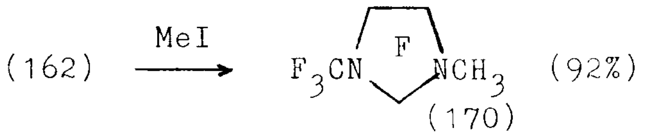
3B REACTIONS OF THE PERFLUORO-3-METHYL-1,3-DIAZACYCLOPENTYL ANION

1. With alkyl halides

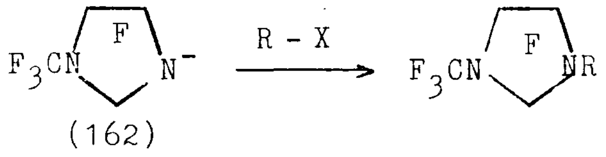
Reaction of the stable nitranion (99) with ethylbromoacetate and allyl bromide has been reported to give amino-acetate (191) and allylamine (192)[57]. Similarly, reaction of (162) with MeI was found by a previous worker



in our laboratory to give the amine (170) in excellent yield[47].

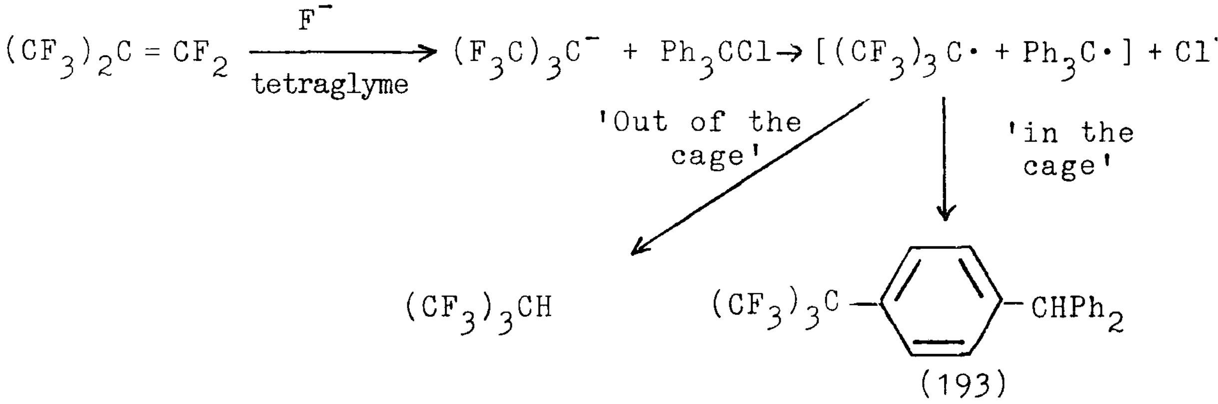


We have found that reaction of (162) with benzyl bromide and allyl iodide also leads to efficient N-alkylation.



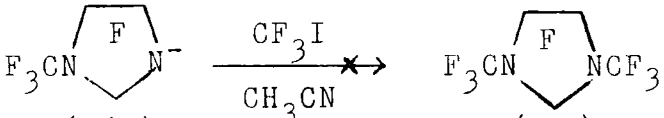
R = CH_2Ph, X = Br.
R = $CH_2{=}CHCH_2$, X = I.

Substitution reactions of benzyl halides are known to proceed in general via either S_N2 or single-electron-transfer pathways. Thus, (162) might, in principle, be reacting through either path. Published work shows that reaction of the perfluoro-t-butyl anion with triphenylchloromethane gives compound (193) in high yield via the single-electron-transfer (S.E.T.) reaction shown[121].



Reaction of (162) with trityl chloride gave only dimer (159) (48%) with no evidence for reaction with the aryl chloride having occurred. Anion (162) was similarly resistant to undergoing a S.E.T. reaction with trifluoroiodomethane to give the amine (180). Again dimer (159)

(61%) was isolated. These results indicate that anion (162) probably reacts with benzyl bromide via an S_N2 rather than



(162) (180)

a S.E.T. pathway. In a recent report[122] American workers have found that fluorinated carbanions react with perfluoroiodoalkanes and pentafluoroiodobenzene to give remarkable hypervalent species (see scheme). The resistance of (162) to forming a similar iodinanide complex with CF_3I may be

$$\mathrm{TAS}^+\ (CF_3)_3C^- + (CF_3)_3C-I \longrightarrow \mathrm{TAS}^+\ (CF_3)_3C-\overset{-}{I}-C(CF_3)_3$$

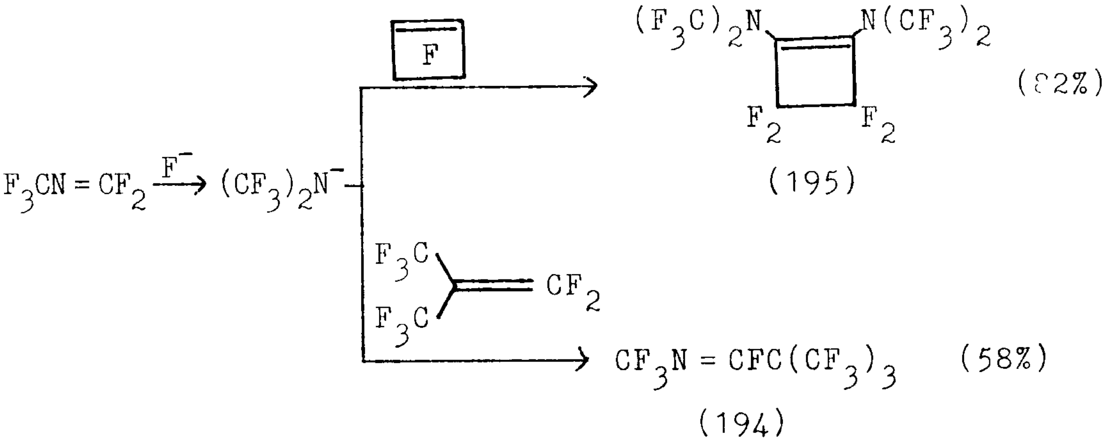
Scheme

due to one of two reasons. Firstly, the counter-ion in all reactions of (162) is Cs^+ which is less stabilising than TAS^+ in acetonitrile. Secondly, the nitrogen anion charge centre is probably harder than that in carbanions, since nitrogen is more electronegative and therefore less likely to coordinate to the soft iodine to form the complex.

3B.2 With perfluorocycloalkenes

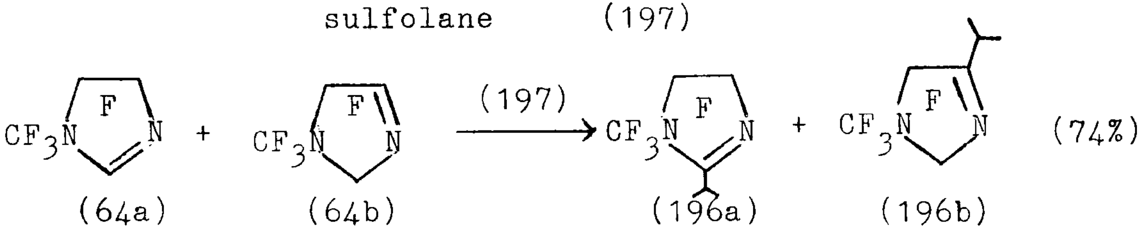
Oligomerisation reactions of perfluorocycloalkenes have been extensively studied in our laboratory[123,124] and, from the known reactions of perfluorocyclo-butene and -pentene, it appears likely that (162) could be trapped with cyclic fluoroalkenes and that a novel series of cyclic oligomers would result. This was supported by reported fluoride-induced reactions of perfluoro-2-azapropene with perfluoro-isobutene and -cyclobutene to give (194) and

(195) respectively[57]. Similarly, Barnes has reported that



reaction of (64) with hexafluoropropene gave diazacyclopentenes (196)[47].

$$CF_3CF=CF_2 \xrightarrow[\substack{50°C \\ \text{sulfolane}}]{KF} (CF_3)_2CF^- \quad (197)$$



(64a) (64b) (196a) (196b)

4 : 1 3 : 1

We need to remember that, in these reactions, the overall rate constant for the reaction of an anion, generated by fluoride, with an olefin derivative, will be the product of an equilbrium constant and a rate constant.

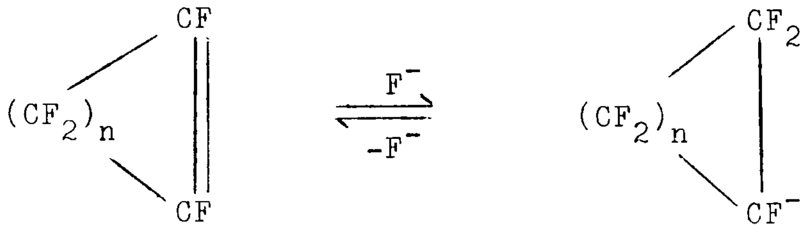
$$\text{Olefin derivative} + F^- \overset{K}{\rightleftharpoons} \text{anion}$$

$$\text{Anion} + \text{olefin derivative} \xrightarrow{k} \text{product.}$$

Overall rate = Kk.

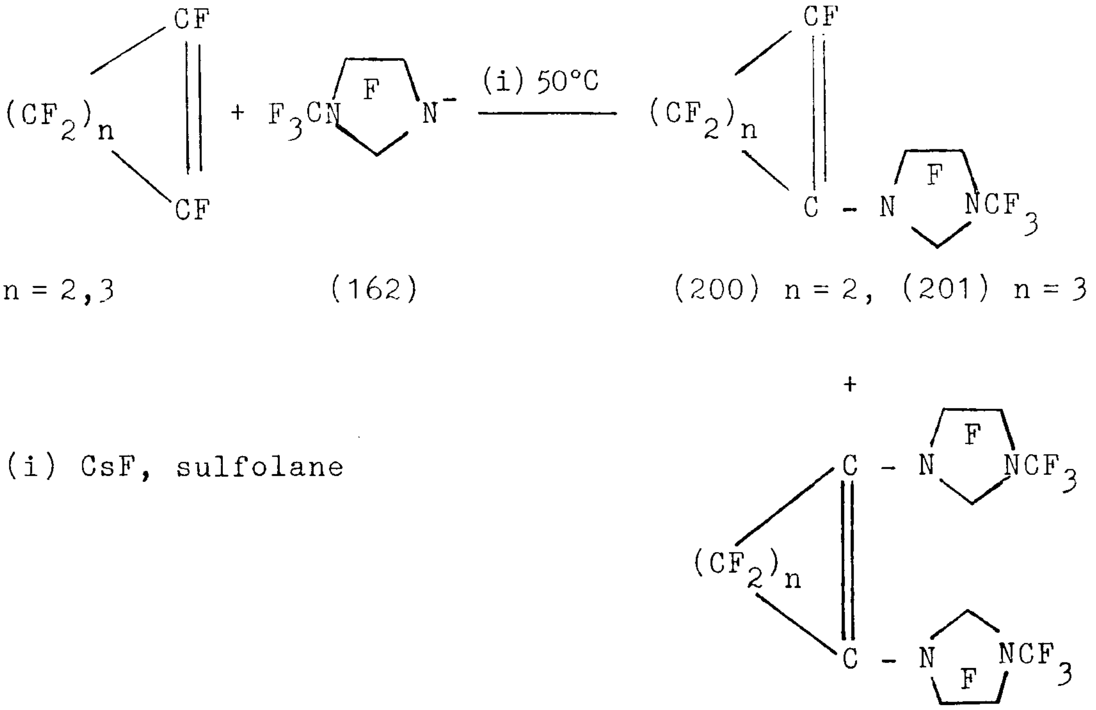
While it is almost certain that the equilibrium constant for forming the nitranion (162) is greater than for formation of the carbanion (197), the overall rate is, obviously, in favour of products derived from (197). Thus, the very stability of the nitranion (162) prevents reaction with hexafluoropropene and reaction occurs via (197).

In contrast, we have found that reaction occurs between anion (162) and perfluorocyclo-butene and -pentene and this most probably reflects the lower equilibrium constant for forming the cyclic carbanions (198) and (199)[123,124]. In forming these anions from the perfluorocycloalkenes, we



(198) n = 2, (199) n = 3

have increased eclipsing interactions, which will be especially important in fluorinated systems[123]. Consequently, reactions of the nitranion (162) now complete successfully with reactions that would involve the cyclic carbanions. By varying the ratio of the starting materials, 1 : 1 and 2 : 1 products could be isolated in high yield from reactions at 50°C by preparative scale g.l.c. (see Table). Their formation can readily be ascribed to attack of (162) on the fluorinated alkene with successive loss of fluoride ion.



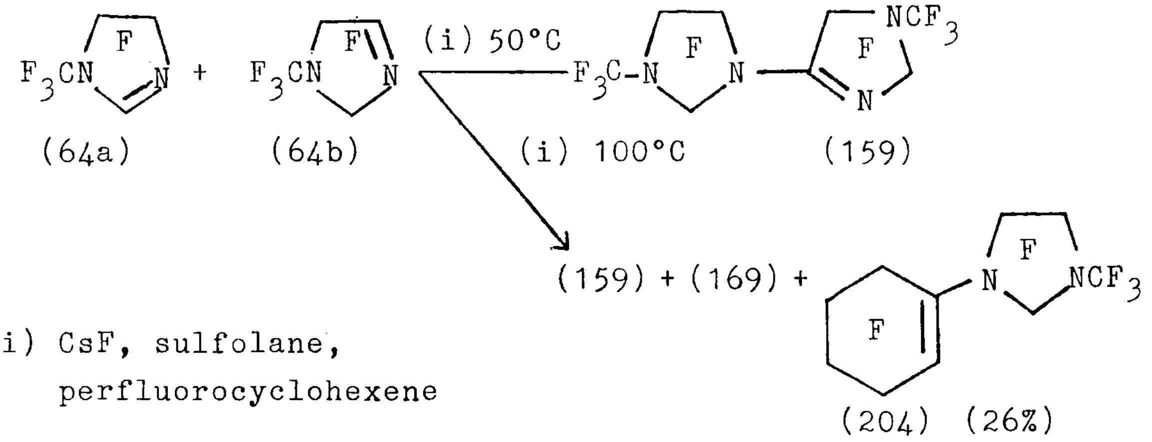
n = 2,3 (162) (200) n = 2, (201) n = 3

(202) n = 2, (203) n = 3

(i) CsF, sulfolane

Cycloalkene	Proportion (162) : alkenes	Products
F-cyclobutene	1 : 1	(200) (26%) (202) (37%)
	2 : 1	(159) (4%) (200) (4%) (202) (66%)
F-cyclopentene	1 : 1	(201) (60%) (203) (1%)
	2 : 1	(201) (20%) (203) (16%)

Perfluorocyclohexene proved to be the least reactive olefin and a higher reaction temperature was necessary in order to give even the 1 : 1 product. At 50°C the anion (162) reacted with (64b) to give the dimer (159) in preference to reaction with perfluorocyclohexene; at 100°C a 1 : 1 product (204) was, however, isolated together with dimers (159), (169), and recovered perfluorocyclohexene. It is

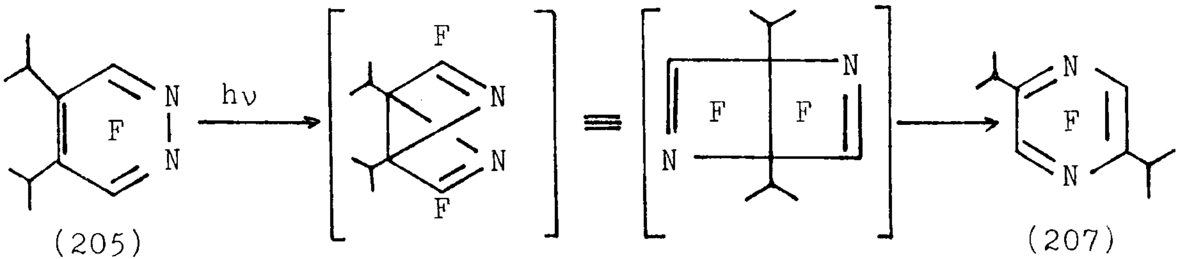


(i) CsF, sulfolane, perfluorocyclohexene

known from other reactions that perfluorocyclohexene is less reactive than perfluorocyclo-butene or -pentene towards nucleophiles[125] and we can reasonably conclude, therefore, that this lower reactivity accounts for the different behaviour of (162) with perfluorocyclohexene, as compared with perfluoro-cyclobutene or -cyclopentene.

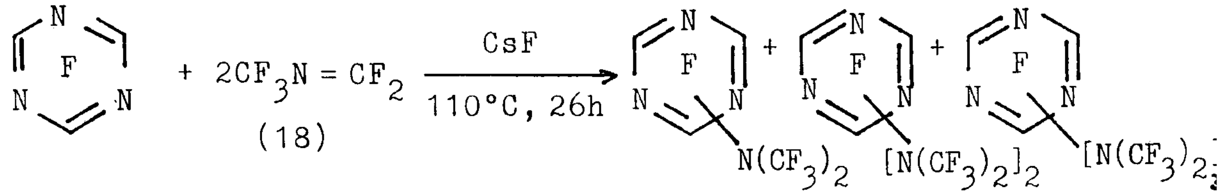
3B.3 With perfluoroaromatics

Polyfluorocarbanions generated by reaction of fluoride ion with fluoro-alkenes react with perhalohetero-aromatics to yield polyfluoroalkylated products[126]. These compounds have displayed a rich and varied chemistry, especially in their photolytic and pyrolytic rearrangement reactions which often occur via remarkably long-lived valence isomers[127,128]. An example is the photolytic rearrangement of the alkylated pyridazine (205) via Dewar



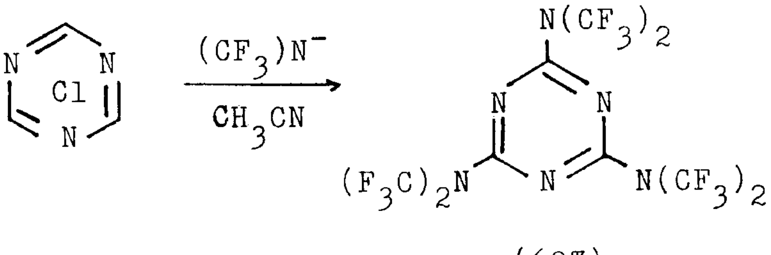
pyrazine (206) to give pyrazine (207)[128].

Reports in the literature of perfluoroalkylation reactions of halogenated aromatics by aza-anions are limited to the fluoride ion catalysed reactions of perfluoro-2-azapropene with perhalotriazines. American workers have reported that caesium fluoride promoted reaction of cyanuric fluoride with perfluoro-2-azapropene (18) gave a mixture of mono-, di-, and tri-substituted compounds[76]. Similarly, reaction of a solution of anion (99) with cyanuric chloride leads to replacement of all three chlorine

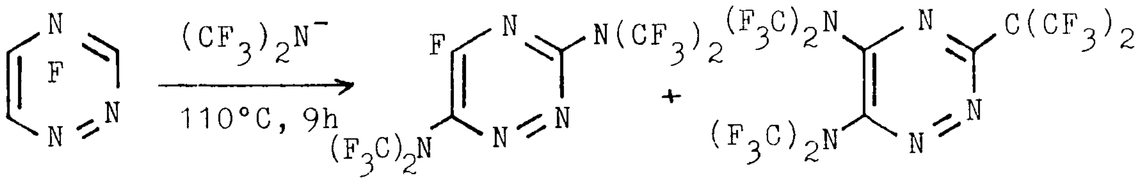


(19%) (29%) (16%)

atoms[57]. More recently, Haszeldine and co-workers demonstrated the easy substitution of fluorine in trifluoro-1,2,4-triazine by the bistrifluoromethylamino-anion[129].

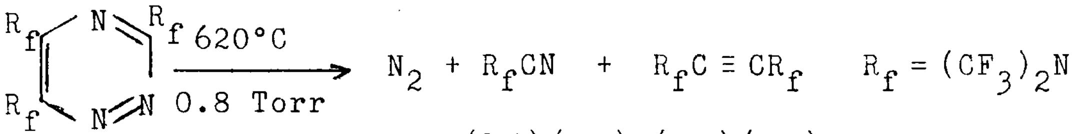


(62%)



(35%) (208) (37%)

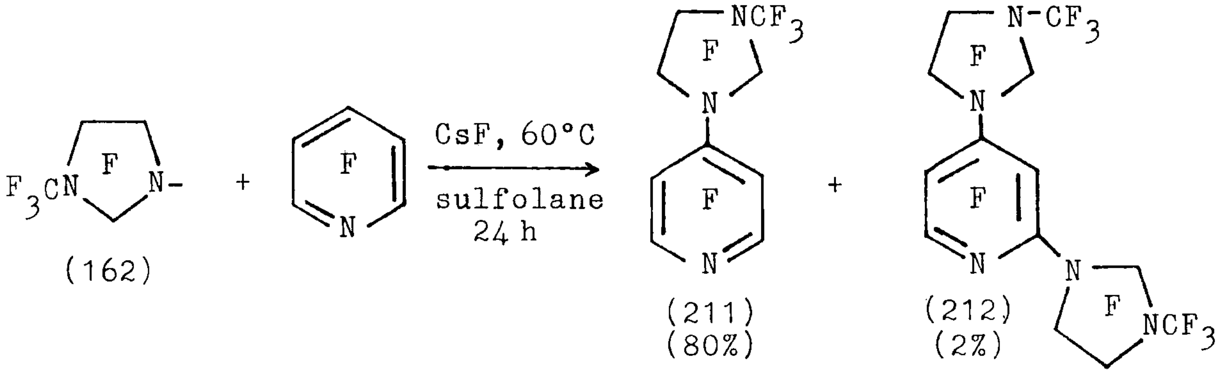
Pyrolysis of the trisubstituted derivative (208) gave the nitrile (209) and the acetylene (210) shown[129].



(208) (209) (73%) (210) (27%)

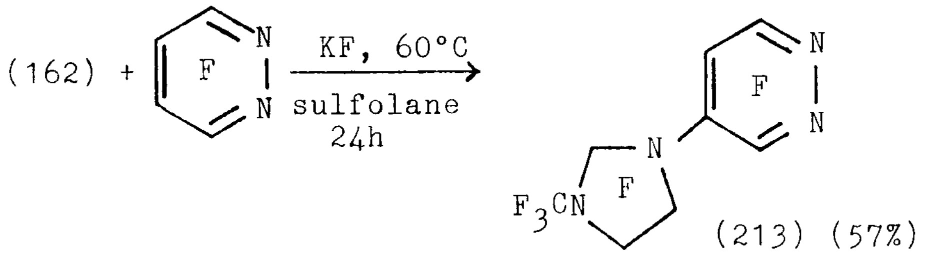
From this precedent, and the known chemistry of perfluorocarbanions, we proposed that reaction of activated perfluoroaromatics with anion (162) would lead to a range of novel substituted aromatic compounds and allow a comparison of the influence of a polyfluoroalkyl group with that of a polyfluoroalkylamino group on the chemistry of these systems.

Previous work in our laboratory[56] has demonstrated that reaction of (162) with pentafluoropyridine gave principally the 4-substituted product (211), together with a small amount of the 2,4-product (212). Reaction of (162) with an equimolar quantity of tetrafluoropyridazine gave the



(162) (211) (80%) (212) (2%)

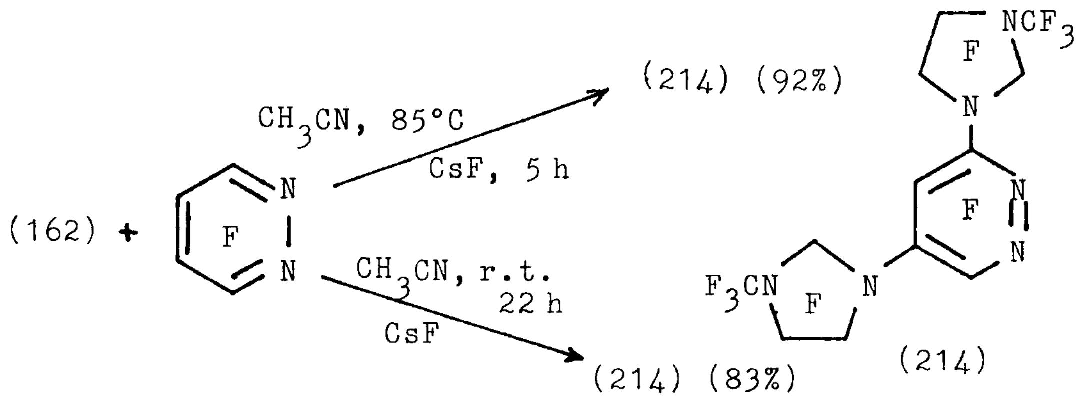
4-substituted product (213)[56]. The orientation of substitution



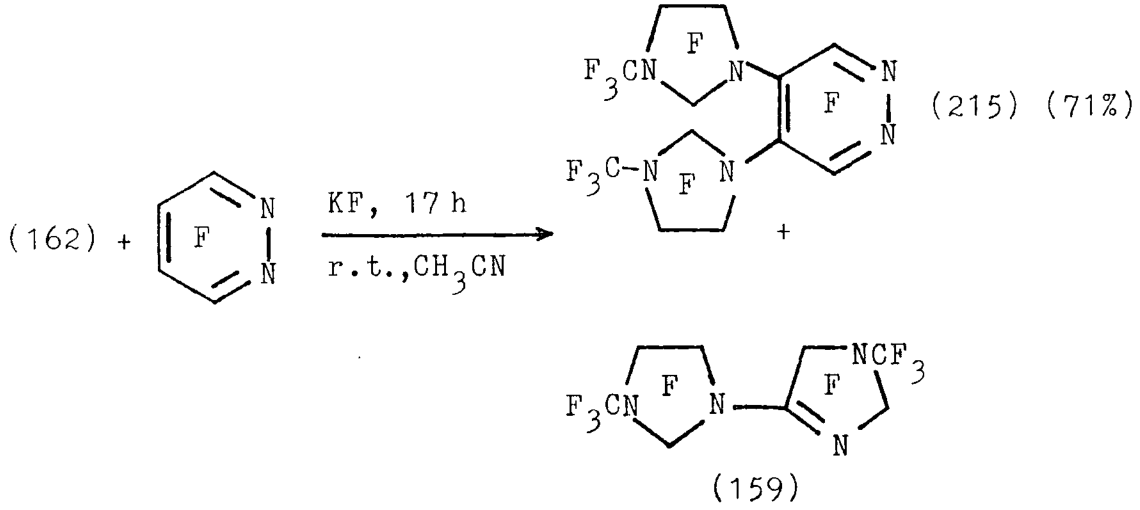
was determined by ^{19}F n.m.r. spectroscopy and followed a pattern observed previously for carbanions[127].

We have found that reactions of excess of anion (162) with tetrafluoro-pyridazine and -pyrimidine are more complex and clearly indicate the importance of kinetic and thermodynamic control.

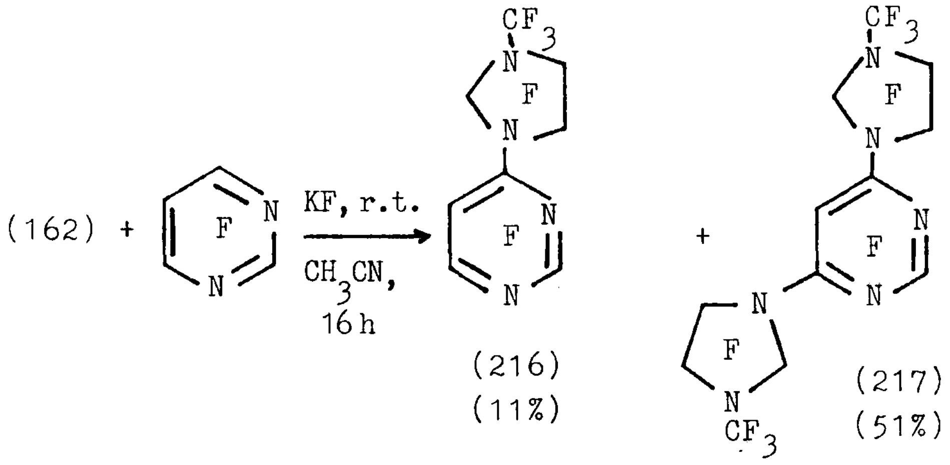
When caesium fluoride was used as the fluoride ion source with two mole equivalents of (162) disubstitution of tetrafluoropyridazine occurred to give a high yield of the 3,5-disubstituted pyridazine (214) and none of the expected 4,5-isomer was observed in marked contrast to polyfluoro-



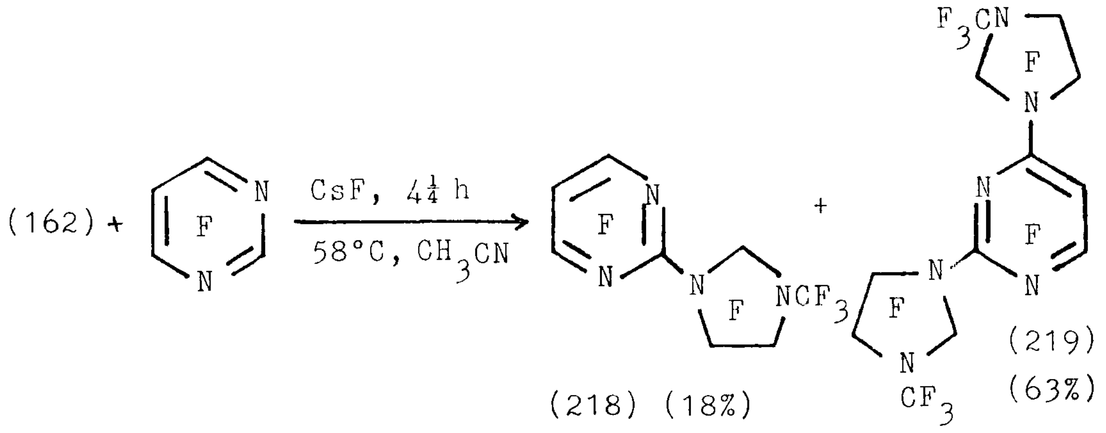
alkylation processes[126]. In order to obtain the 4,5-isomer (215) it was necessary to use potassium fluoride, which is a less active source of fluoride ion than caesium fluoride. A significant amount of dimer (159) was formed.



Similarly, mono- and di-substitution was observed by reaction of (162) with tetrafluoropyrimidine. Reaction of (162), generated using potassium fluoride, with tetrafluoropyrimidine at room temperature gave the expected 4- and 4,6-substituted products (216) and (217). In contrast,



when caesium fluoride was used as the fluoride ion source, and at higher temperature, 2- and 2,4-substituted pyrimidines (218) and (219) were obtained. This unusual substitution pattern is a result of fluoride ion catalysed isomerisations[130].



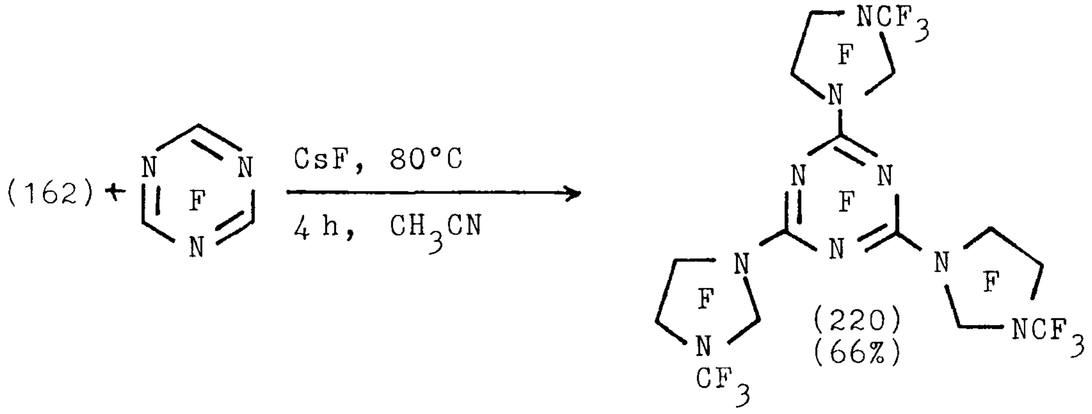
(218) (18%)

(219) (63%)

and this was confirmed by the observation that (217) could be transformed to (219) by caesium fluoride.

$$(217) \xrightarrow[22h,\ CH_3CN]{CsF,\ room\ temp.} (219)\ (49\%)$$

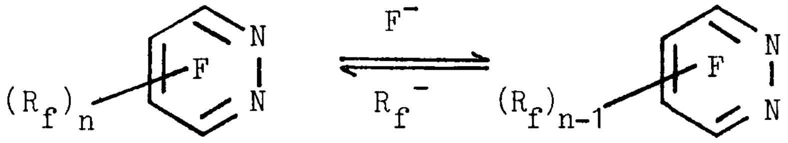
The highly activated nature of the triazine ring system is well illustrated by the formation of the tri-substituted compound as the only product in the reaction of (162) with trifluoro-1,3,5-triazine. Reactions carried out in acetonitrile, with a stoichiometry aimed at the



(220) (66%)

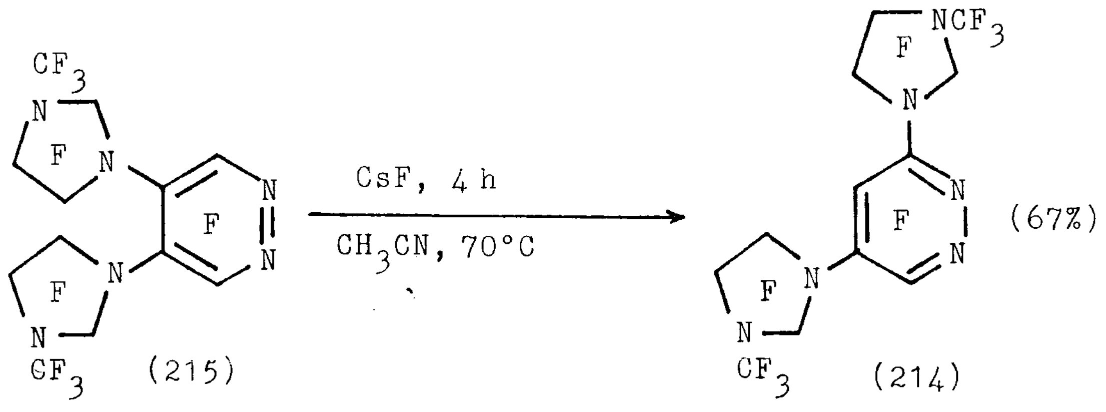
mono-substituted product, still led to (220) as the sole isolated product.

The ready formation of polysubstituted products in the reaction of nitranion (162) with fluorinated diazines and triazines is a consequence of the highly activated nature of these heteroaromatics. From other work[131], it has been shown that ring nitrogen is the dominant influence activating ortho- and para-positions. The orientation on substitution of, for example, the heptafluoroisopropyl anion in reaction with tetrafluoropyrimidine is in the order $4 > 6 > 2$. It has been previously noted however that thermodynamic control can have an influence on the final outcome of polyfluoroalkylation reactions[130]. The rearrangement of perfluoroalkylpyridazines can be used to illustrate this. Consider the equilibrium between (215) and (213); the ease with which this is set up will be primarily dependent on the stability of R_f^- and, to a lesser extent, on the activity of F^-. It has been found that for perfluoroalkyl anions of



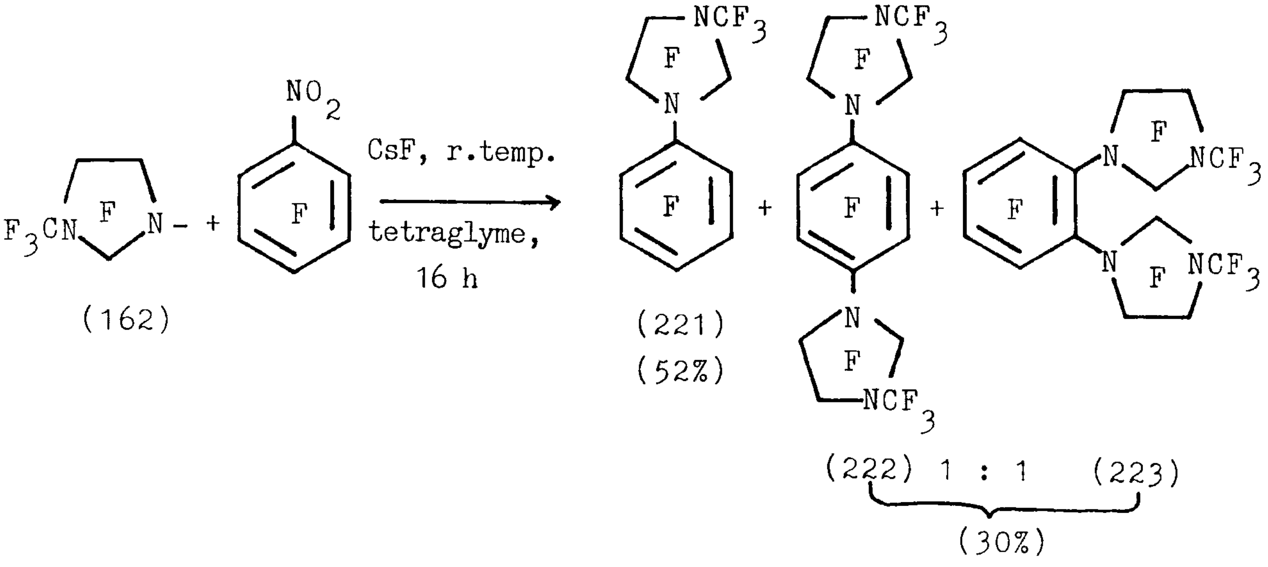
(215) (213)

low stability, e.g. $C_2F_5^-$, kinetic control predominates, whereas for relatively stable anions, e.g. $(CF_3)_3C^-$, the equilibrium is more readily established and thermodynamic control becomes important. However, we now find that, with nitranion (162), the nature of the product depends on the activity of the fluoride ion source i.e. it is possible to obtain the kinetically controlled product, using KF, and convert it to the thermodynamic product with CsF. For example (217) to (219) and, similarly, (215) to (214). It is clear that (162) is a member of the group of more stable



anions and consequently the orientation of substitution observed in the isolated product is due to competition between kinetic and thermodynamic control. Indeed, we have discussed the stability of (162), as an observable anion earlier in this chapter and the results obtained here are a consequence of this stability and the associated ease of displacement from an aromatic ring.

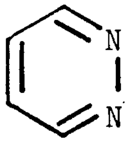
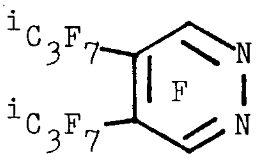
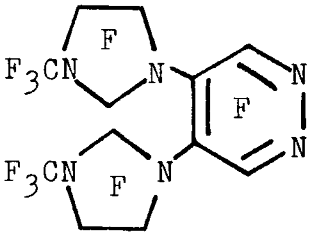
Previous work has shown that pentafluoronitrobenzene is susceptible to alkylation by perfluorocarbanions[132,133]. We have demonstrated that anion (162) readily alkylates pentafluoronitrobenzene at room temperature to give a mixture of 1 : 1 and 2 : 1 adducts. The reaction probably proceeds via initial alkylation para to the nitro-group with subsequent



substitution of the nitro-group by fluoride ion or (162) to give (221) and (222) respectively. The disubstituted compound (223) is probably formed from initial alkylation ortho- to the nitro-group and subsequent denitration by (162).

Ultraviolet spectroscopy is a probe for comparisons of the electronic influence of substituents on an aromatic ring. A comparison of the λ_{max} of substituted pyridazines allows, therefore, an assessment to be made of the electron-donating ability, or otherwise, of the perfluoro-(3-methylimidazolidin-1-yl) group (see Table 2). The results indicate that the bathochromic shift due to the perfluoro-(3-methylimidazolidin-1-yl) group is only slightly less than that arising from the perfluoroisopropyl group.

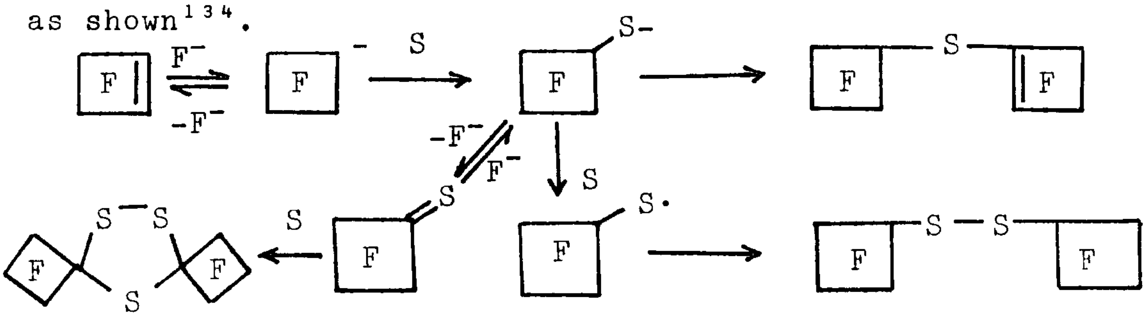
<u>U.V. Spectra in Cyclohexane</u>

	$\lambda_{max}(\varepsilon)$	
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
	246 (1400)	334 (360)
	248 (4160)	283 (900)
	278 (4100)	340 (370)
	273 (3460)	337 (310)

It follows, therefore, that the electron-donating ability of nitrogen is almost entirely overcome by the inductive electron-withdrawing effect of the fluorocarbon substituents. Clearly the chemistry of the perfluoro(3-methylimidazolidin-1-yl) substituted heteroaromatics will be similar to that of perfluoroalkyl substituted analogues, although in the former instance, steric effects will become important.

3B.4 Miscellaneous

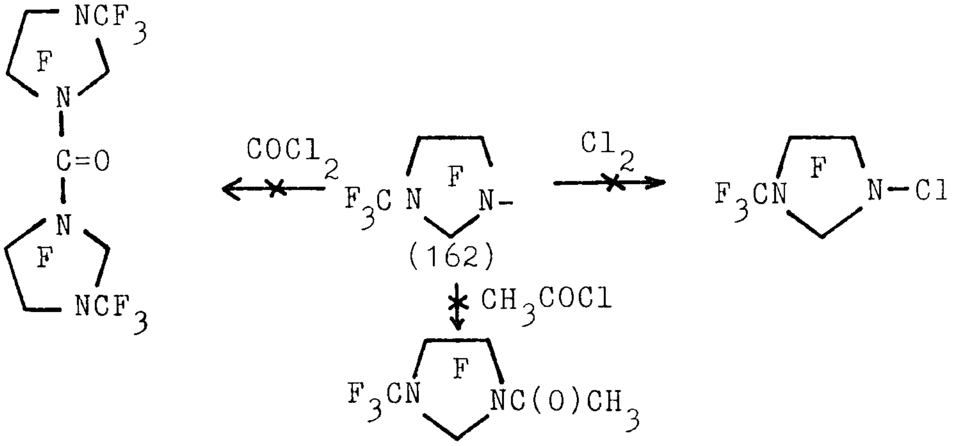
Reaction of the perfluorocyclobutyl anion with elemental sulfur gives a mixture of organosulfur compounds as shown[134].



Attempted reaction of aza-anion (162) at room temperature, 70°C, and 150°C gave only dimer (159), and none of the desired products.

Mercuric halides have been used as reagents in the preparation of a large number of organometallic compounds from perfluorocarbanions[135]. Reaction of anion (162) with mercuric chloride and iodide gave, in both cases, only dimer (159).

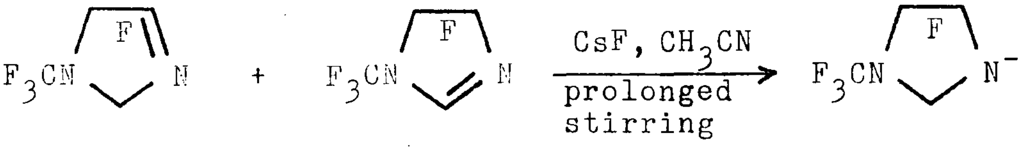
Reaction of (162) with chlorine, phosgene, and acetyl chloride gave in all cases only dimer (159) and none of the desired products (see Scheme).



We can conclude, therefore, that the chemistry of perfluoronitranions parallels that of perfluorocarbanions with one or two important differences. Firstly, the higher electronegativity of nitrogen facilitates the preparation of observable perfluoronitranions from tris(perfluoroalkyl)imine precursors, whilst analogous perfluorocarbanions are too short-lived even to be trapped by electrophiles. Secondly, the slightly harder nature of the charge centre makes nitranions resistant to single-electron-transfer reaction and the formation of hypervalent iodinanide complexes and mercury (II) salts, which are readily facilitated using the softer perfluorocarbanions. It should be noted, however, that anion (162) still behaves essentially as a soft nucleophile as demonstrated in the high yield of the substitution reaction with benzyl bromide.

CHAPTER 4 REACTIONS OF PERFLUORO-3-METHYLIMIDAZOLIDIN-1-YL DERIVATIVES

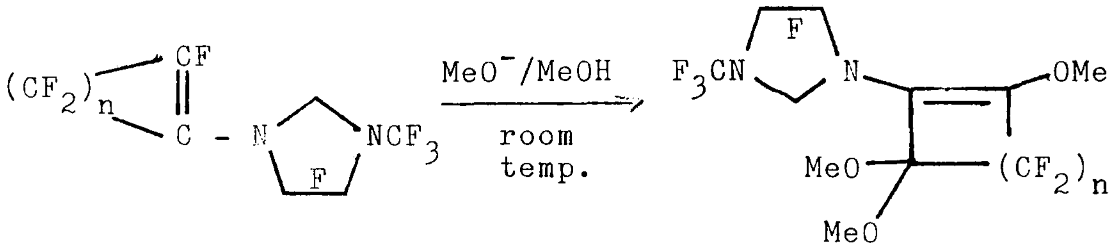
Investigations into the chemistry of the perfluoro-3-methyl-1,3-diazacyclopentyl anion (162), as described in the previous Chapter, have yielded a series of novel bisperfluoroalkylamino-substituted derivatives and this development prompted a comparative study between their chemistry and the known chemistry of perfluoroalkyl-substituted analogues[136].



(162)

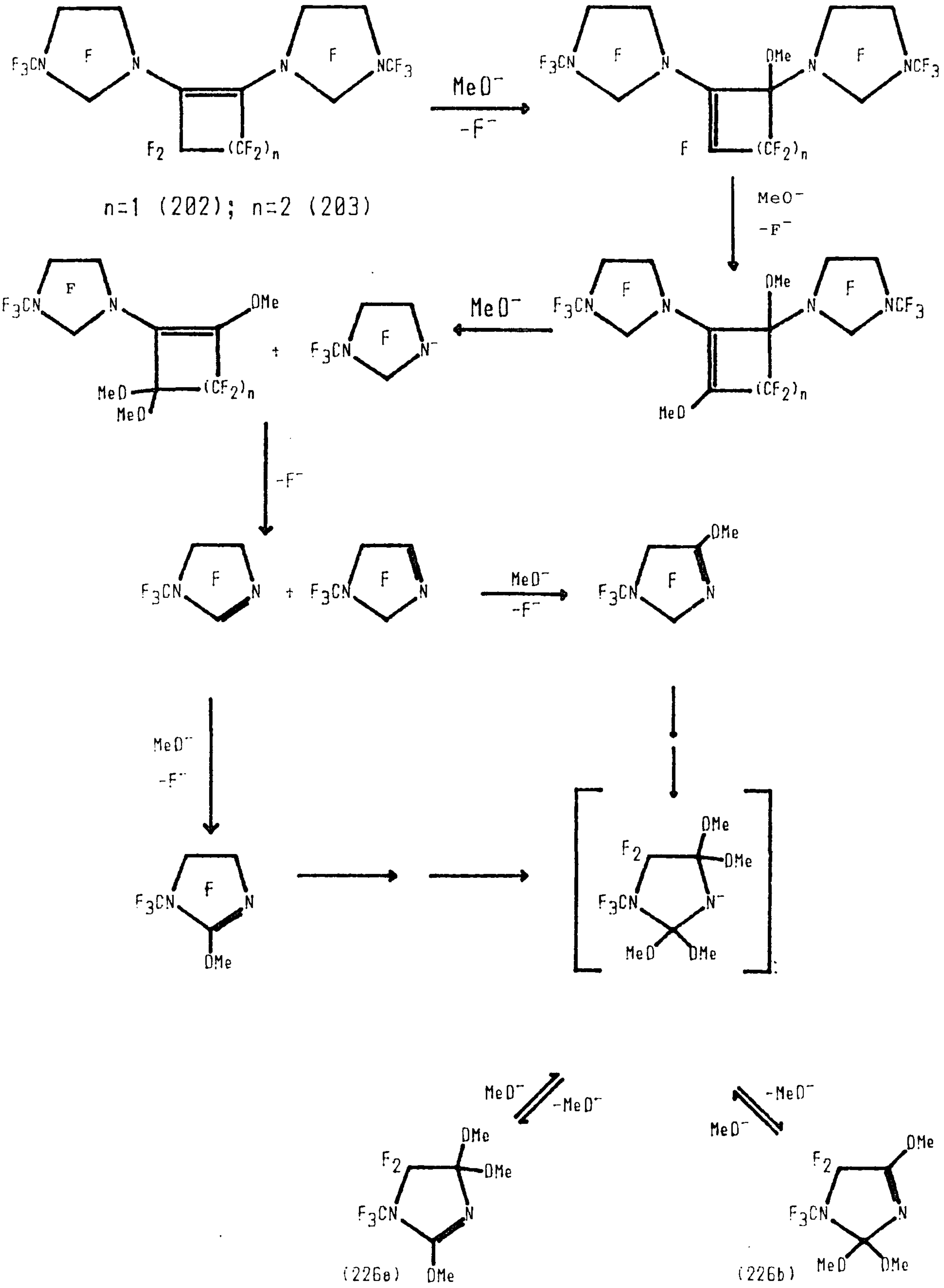
4A.1 Cycloalkene derivatives. A. Reactions with methoxide

Perfluoro-1-(3-methylimidazolidin-1-yl)-cyclobut-1-ene (200) and -cyclopent-1-ene (201) reacted with sodium methoxide in methanol at room temperature to give the trimethoxy derivatives (224) and (225) respectively. The bisimidazolidinyl derivatives (202) and (203) did not react under these conditions but heating under reflux with methoxide in methanol gave (224) and (225) respectively. The mechanism of this reaction is interesting (see Scheme G) since it must involve

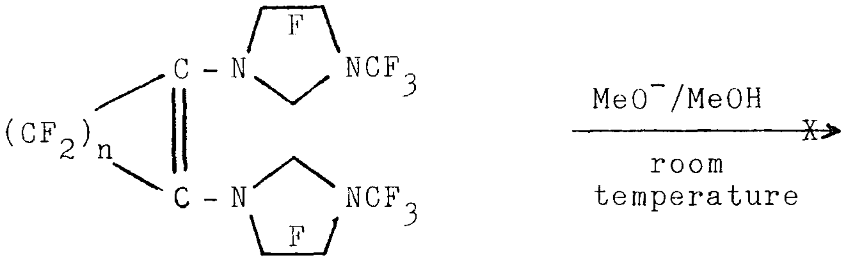


n = 2 (200); n = 3 (201)

n = 1 (224); n = 2 (225)


n=1 (202); n=2 (203)
MeO⁻
-F⁻
MeO⁻
-F⁻
MeO⁻
-F⁻
MeO⁻
-F⁻
MeO⁻
-F⁻
MeO⁻
-MeO⁻
-MeO⁻
MeO⁻
(226a)
(226b)

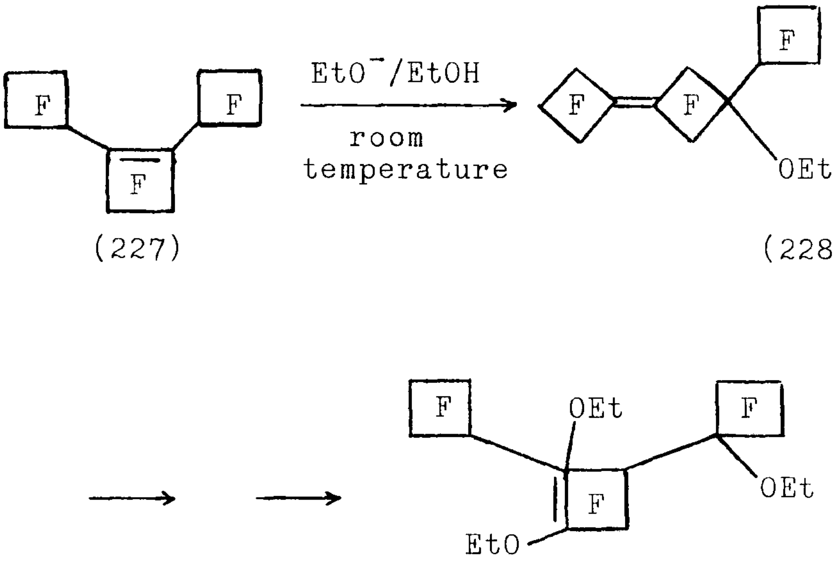
Scheme G



n = 2 (202); n = (203)

substitution of methoxy for a diazacyclopentane group. Once eliminated this group is itself susceptible to loss of fluoride and nucleophilic attack to give the trimethoxy derivatives (226) which we have been unable to distinguish by available spectroscopic techniques.

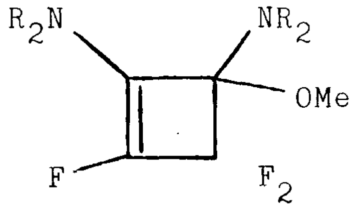
A previous worker in this laboratory has demonstrated that the cyclobutene trimer (227) reacts readily with sodium ethoxide at room temperature via successive allylic and vinylic displacement of fluoride[137]. Compounds (202) and (203) are less reactive and we know from u.v. studies of



(227)

(228)

substituted pyridazines that the electronic effect of the diazacyclopentyl group is roughly equivalent to perfluoroalkyl (see Section 3B.3). Consequently, it may be concluded that this lower reactivity results from either steric factors or, less probably, from the higher energy of intermediate (229), which contains a vinyl fluorine atom, when compared to (228).



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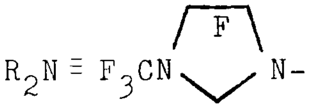
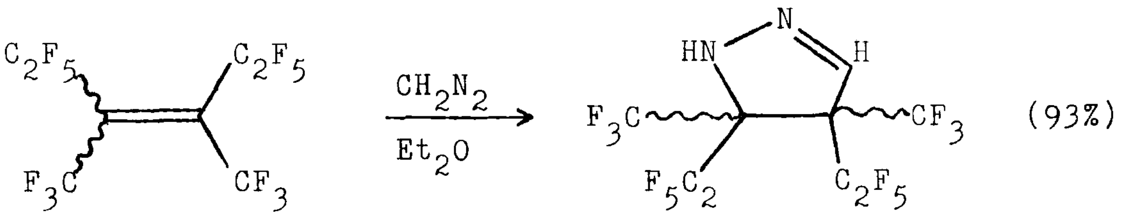


4A.1.B Further chemistry of bisimidazolidinylcyclobutene (202)

4A.1.B.1 Reaction with diazomethane

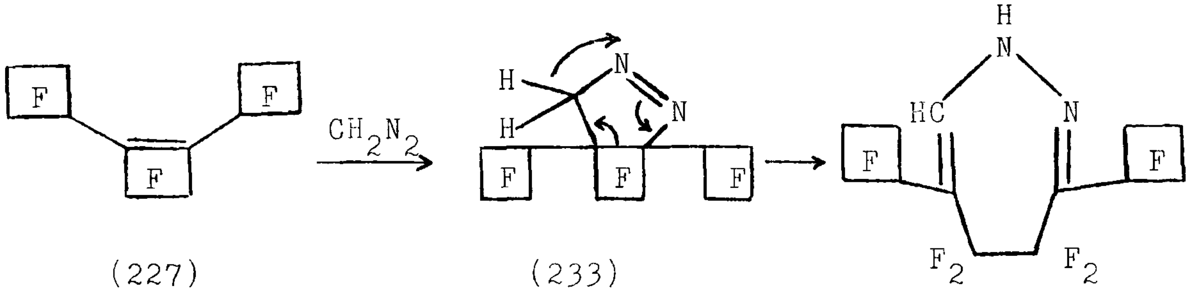
Previous workers have shown that electron-withdrawing substituents activate double bonds to attack by diazomethane and similar dipoles[138]. For example, tetrafluoroethylene tetramer (230) reacts smoothly in high yield to give the Δ^2-pyrazoline (231)[138]. More interestingly, cyclobutene



(230) (231)

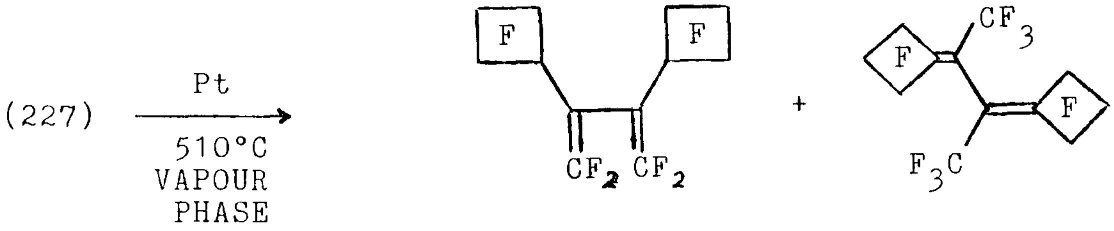
trimer (227) reacts readily with diazomethane to give the novel ring-opened product (232)[139].

However, disubstituted derivative (202) was inert to diazomethane, and again, this lack of reactivity can be attributed to the large steric requirement of the diazacyclopentyl substituents.



(227) (233) (232)

4A.1.B.2 Pyrolysis Taylor has shown that pyrolysis of cyclobutene trimer (227) gives the novel dienes (234) and (235)[136]. Many attempts to prepare novel dienes from (202)



(234) (15%)

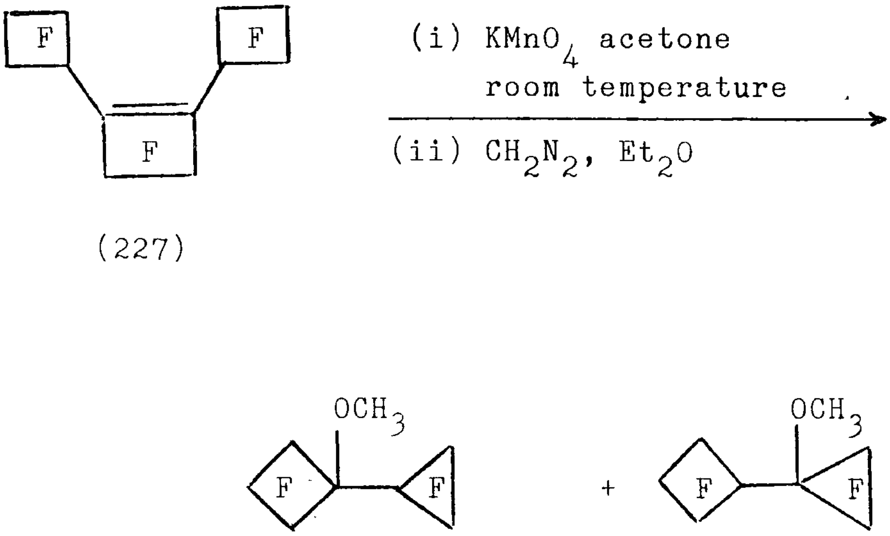
(235) (40%)

$$(227) \xrightarrow[\text{VAPOUR PHASE}]{\text{CsF/510°C}} (234) + (235)\ (90\%)$$

$$(227) \xrightarrow[\text{300°C}]{\text{Static}} (234)\ (20\%) + (227)\ (80\%)$$

by static and vapour phase pyrolysis reactions resulted only in recovery of starting material or decomposition. This reluctance of (202) to undergo isomerisation may be due to the weakness of the C - N bond between the diazacyclopentyl substituent and the cyclobutene ring, which results in decomposition under conditions too mild to effect ring-opening.

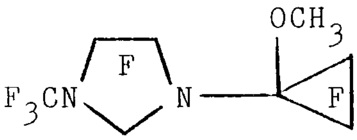
4A.1.B.3 <u>Oxidation</u> The oxidation of trimer (227) by potassium permanganate, and subsequent methylation was found by Taylor to give the two isomeric methyl ethers (236)[140]. A similar oxidation of (202) would be expected



(227)

(236a) (236b)

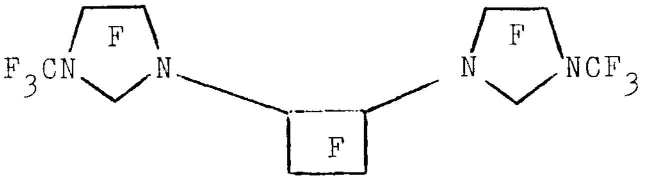
to give (237) only, however the reaction gave only recovered (202) (47%) and some decomposition. The lack of reactivity of (202) is, again, best explained in



(237)

terms of steric factors.

4A.1.B.4 Fluorination Attempted synthesis of the cyclobutane derivative (238) by fluorination of (202) over CsF_3 at 200°C gave only gaseous products.

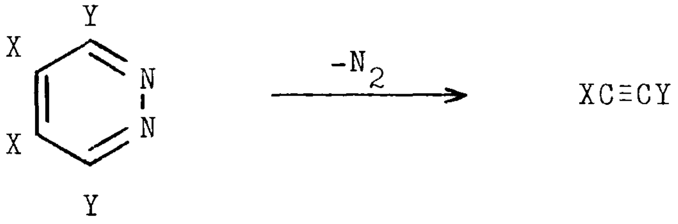


(238)

4A.2 Perfluoroaryl derivatives

4A.2.A Attempted preparation of a stable cyclobutadiene

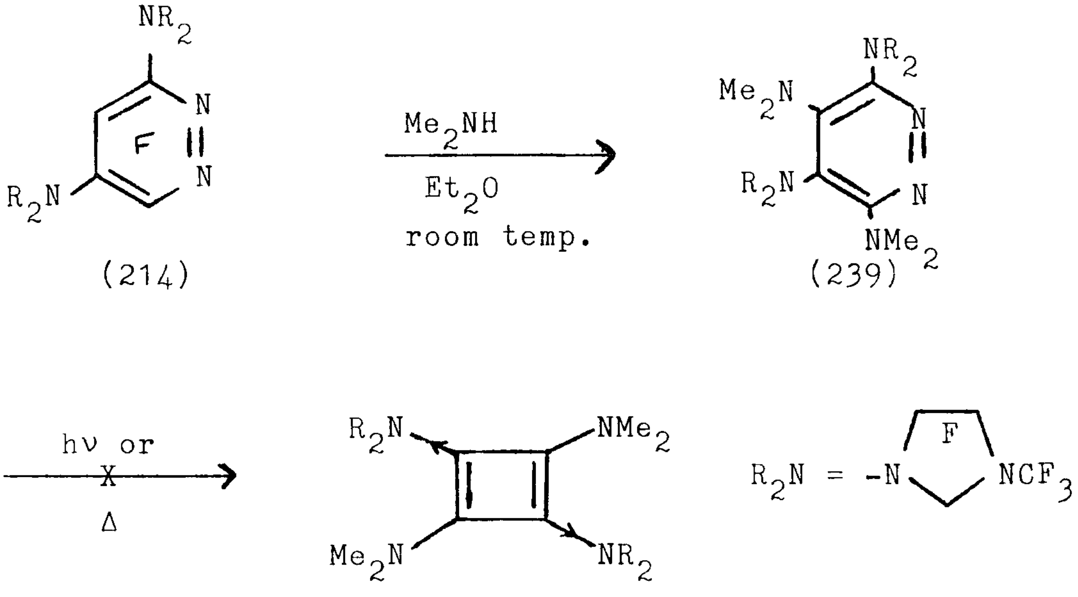
There is a continuing interest in our laboratory in the preparation of small-ring compounds stabilised by perfluoroalkyl substitutuents. Previous workers demonstrated that pyrolysis of perfluoroalkylpyridazines under flow conditions or vacuum gave acetylenes in excellent yields[141]. The absence of symmetrical acetylene products, e.g. XC≡CX, is consistent with



X, Y = C_6F_5, $CF(CF_3)_2$, $4\text{-}C_5F_4N$

the intermediacy of diradical rather than tetrahedral or cyclobutadiene intermediates.

The availability of the 3,6-disubstituted pyridazine (214) prompted a further attempted preparation of a cyclobutadiene derivative. Reaction of (214) with dimethylamine in diethyl ether gave the bisdimethylamino derivative (239) in good yield. However, photolysis and flash vacuum pyrolysis of (239) gave none of the cyclobutadiene (240) or products derived from it (see Table).

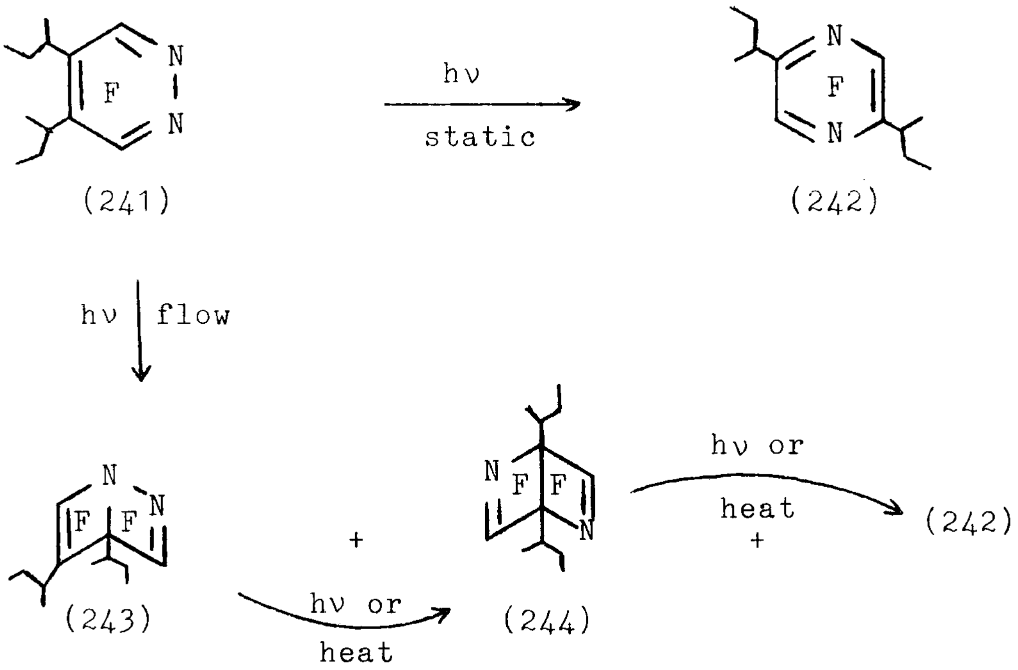


(214) (239) (240)

Reaction Conditions	Product
hν, 254 nm, 6h, $CF_2ClCFCl_2$	(239) (100%)
f.v.p. 600°C	(239) (100%)
f.v.p. 700°C	tar (complex by ^{19}F nmr)

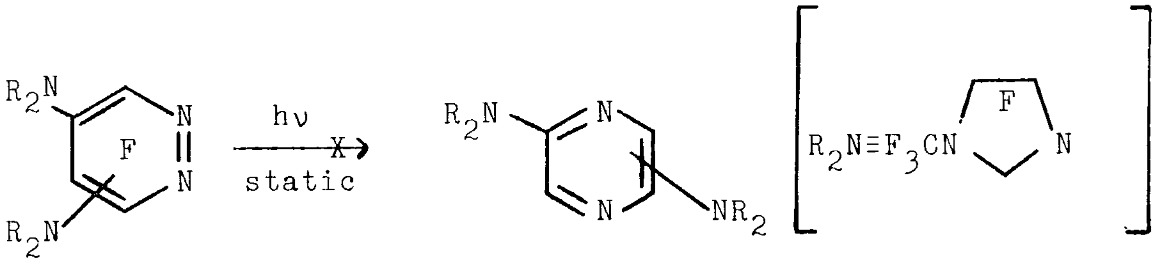
4A.2.B Photochemical and Thermal Isomerisation reactions

Photolysis of perfluoroalkyl-pyridine and -pyridazine compounds is a good route to stable valence isomers[142,143]. These valence isomers have, in many cases been demonstrated as intermediates in photochemical rearrangement reactions. For example, ultraviolet irradiation of pyridazine (241) in a sealed tube led to a 1,3-shift in the position of the nitrogen atoms to give pyrazine (242)[144]. However, irradiation under flow conditions gave a mixture of valence isomers

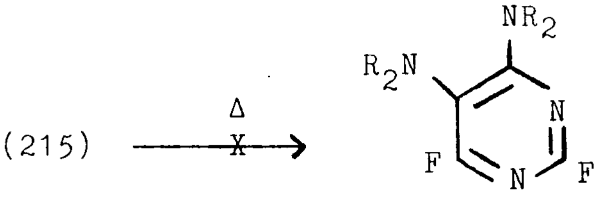


(243) and (244) as well as pyrazine (242)[145].

Disappointingly, photolysis of the bis(3-methylimidazolidin-1-yl)pyridazines (214) and (215) under static conditions gave only recovered starting materials. Pyridazine

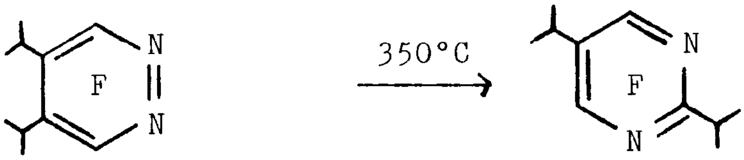


(215) was similarly resistant to thermal isomerisation and



Δ = 150, 200, 250, and 350°C

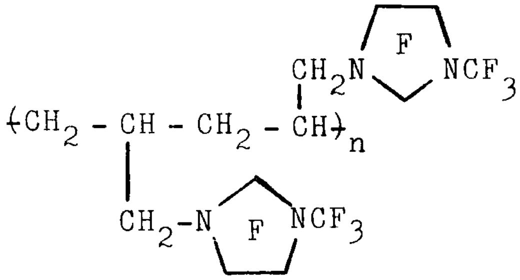
disappointingly decomposed at 350°C, at the temperature at which the analogue (205) rearranges to pyrimidine (245)[146].



(205) (245)

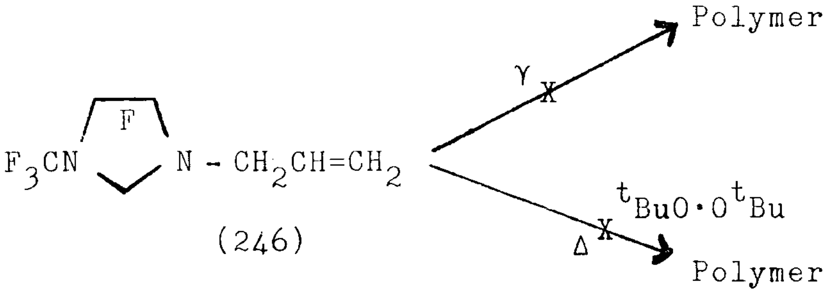
4A.3 Attempted polymerisation of 1-allyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (246)

4A.3.A Homopolymerisation There is considerable current interest in the synthesis of new fluorine-containing polymers as a result of the novel properties that they exhibit. Attempts to generate the homopolymer (247) of (246) were made. It is known that simple fluorinated alkenes generally



(247)

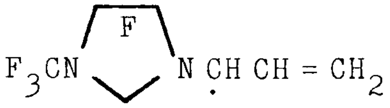
polymerise readily under free-radical initiation but attempts to polymerise (246) using thermally generated tertiary butoxy radicals or gamma irradiation were unsuccessful, giving in both cases only recovered starting material.



(246)

4A.3.B Copolymerisation Similar γ-ray initiated attempts to copolymerise (246) with styrene and methylmethacrylate gave only polystyrene and polymethylmethacrylate respectively with a virtually quantitative recovery of (246). The γ-ray initiated reaction of (246) with vinylidene fluoride gave an involatile, sticky, insoluble solid material the precise nature of which could not be determined.

The resistance of (246) to polymerisation can be attributed to two factors. Firstly, the bulk of the diazacyclopentane substituent and secondly, the stability of the radical (248) which will make the predominant reaction proton



(248)

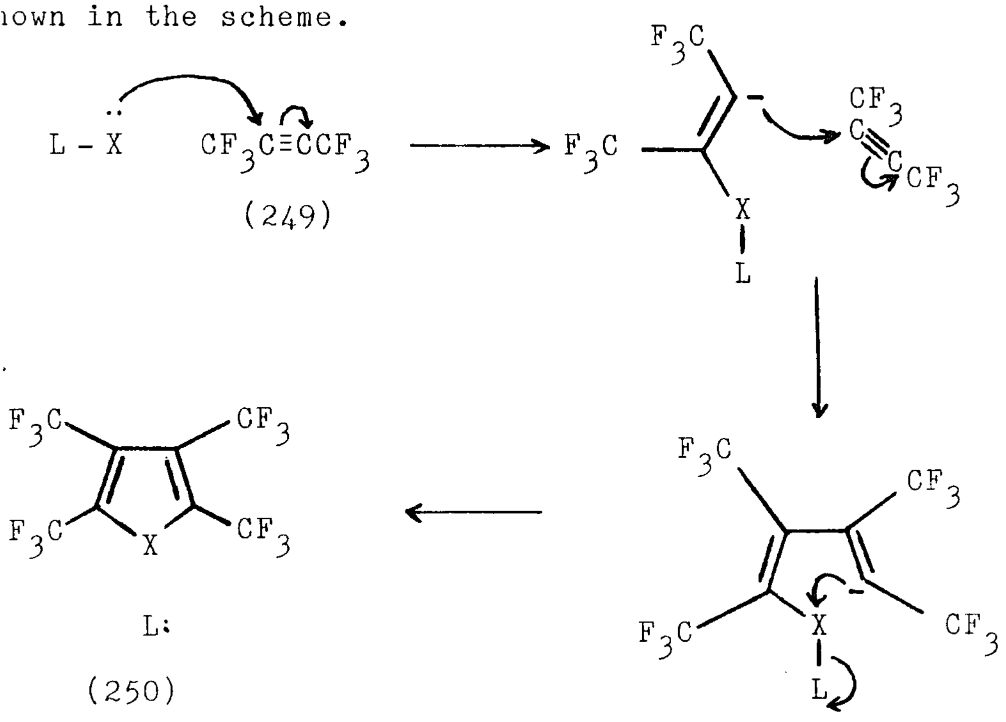
abstraction at the position α- to the fluorinated substituent rather than chain propagation to give the polymer.

CHAPTER 5 PHOSPHORUS YLIDES

5.A.1 General Introduction

Nucleophilic displacement reactions, involving fluorinated alkenes, that lead to heterocyclic products have been extensively studied both in Durham and elsewhere[147]. In contrast, studies of processes that lead to cyclic products from fluorinated acetylenes are rare. We were especially concerned to study those processes leading to heterocyclic and carbocyclic cyclopentadienes since a study of those reactions might lead to an efficient synthesis of the strongest carbon acid known, pentakis(trifluoromethyl)cyclopentadiene. This compound had only been prepared previously using relatively esoteric methodology[148].

Previous work in Durham[149] had shown that reaction of sulfur with hexafluorobut-2-yne (249) gave tetrakis(trifluoromethyl)thiophene (250a) in good yield probably via the route shown in the scheme.



a: X = S; b: X = $C(CF_3)_2$; c: X = $CHCF_3$

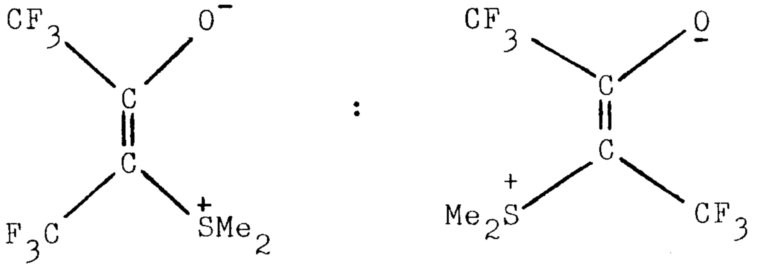
This reaction is particularly interesting because of the cisoid arrangement of the trifluoromethyl groups. For this arrangement to occur it is necessary that the attacking group, L - X, is sufficiently large, e.g. S_8, for syn addition to dominate and that L is a good leaving group. Similar products to the thiophene derivative e.g. (250b) $[X = C(CF_3)_2]$ have been obtained in lower yield from fluoride ion induced reactions of perfluorinated alkenes with (249)[150].

Early attempts by Jones[149] to prepare the target cyclopentadiene (250c) from reaction of trifluoroethyltosylate with LDA to generate an anion which was subsequently reacted with alkyne (249) gave only rapid polymerisation.

$$CF_3CH_2OTs \xrightarrow{\text{LDA}} CF_3\overset{-}{C}HOTs \xrightarrow{(249)} \text{polymer}$$

This result paralleled observations made in the reaction of (249) with other nucleophiles[149].

Jones also attempted reaction of (249) with dimethylsulphoxide[151], which is known to react as a weak nucleophile through oxygen. In this case an interesting reaction occurred to give a mixture of syn- and anti-products shown by ^{19}F n.m.r. spectroscopy to be in the proportions 70% syn- to 30% anti- at room temperature. The adducts did not react



70% : 30%

further with hexafluorobutyne even under quite forcing conditions.

Dimethylsulfoxide was thought to have reacted through the ylide-like structure (251) and accordingly reactions of

$$(CH_3)_2S=O \longleftrightarrow (CH_3)_2\overset{+}{S}-\overset{-}{O}$$

(251)

hexafluorobutyne (249) with a number of unstabilised phosphorus ylides - that is ylides without an electron-withdrawing group on the carbon atom adjacent to phosphorus - were attempted. In all cases[149] the fluorine-containing products formed resulted from anionic polymerisation of (249).

We decided that stabilised ylides, in which the nucleophilicity of the carbon is reduced, might prove a more fruitful class of reagent and a study of the reactions of one such ylide with (249) form the basis of this Chapter. Firstly, however, the background to the role of phosphorus ylides in fluorine chemistry will be discussed.

5A.2 Synthesis and reactions of phosphorus ylides

Throughout this section we will only consider those ylides containing fluorine in the 'alkylidene' component and on, or adjacent to, the carbanionic centre since only these systems have any relevance to the work discussed later. Fluorine-containing halogenomethylenephosphoranes are generally unstable and are reacted without isolation. In contrast, many other fluorine-containing phosphorus ylides are entirely stable and can be isolated and characterised[152]. The chemistry of hydrocarbon phosphorus ylides is dominated by their application in Wittig reactions. This reaction has been less well investigated for fluorine-containing phosphorus ylides than for hydrocarbon analogues although these compounds undergo many interesting and frequently unusual reactions.

5A.2.A Synthesis of fluorinated phosphorus ylides

Halogenomethylenephosphoranes have found utility in the preparation of terminal halogenomethylene olefins. The preparation of terminal difluoromethylene olefins has been facilitated by the reaction of difluoromethylenetriphenylphosphorane, $Ph_3P{=}CF_2$ (252), with aldehydes[153] and ketones[154]. The phosphorane intermediate (252) was first generated by decarboxylation of alkali metal salts of chlorodifluoroacetic acid.

$$C_6H_5COCF_3 + Ph_3P + CF_2ClCO_2Na \xrightarrow[\text{diglyme}]{100°C} \underset{(252)}{[Ph_3P{=}CF_2]}$$

$$\longrightarrow F_2C{=}C(C_6H_5)CF_3 + Ph_3PO + NaCl + CO_2$$

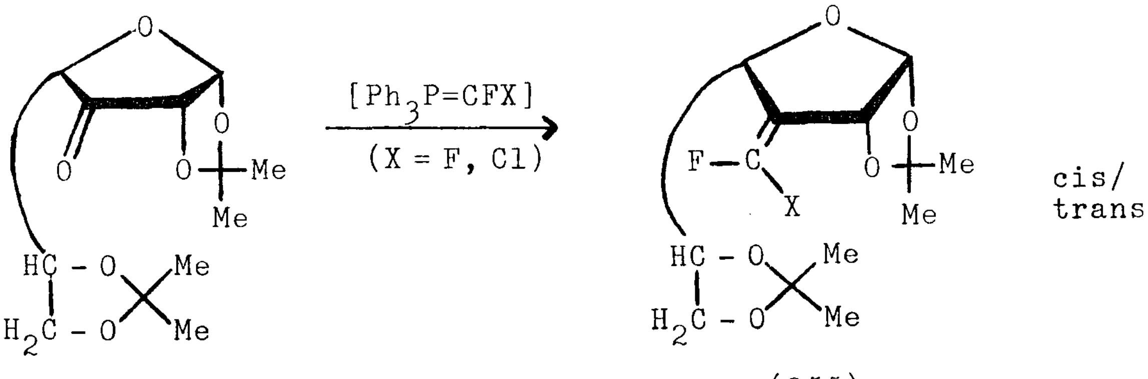
Burton and co-workers demonstrated that the mechanism does not involve trapping of a fluorocarbene but more likely involves formation of the phosphobetaine $[Ph_3\overset{+}{P}CF_2C\overset{-}{O_2}]$ with decomposition directly to the ylide (252)[154,155]. This method was severely limited in scope for a number of reasons. Firstly, the acid salts used were hygroscopic, secondly, the carboxylic acids used are expensive, and thirdly, and more importantly, isomerisation and/or HF addition[156,157] reactions occurred.

Generation of ylide (252) in situ from the reaction of dibromodifluoromethane, CF_2Br_2 (253), with triphenylphosphine gave a route for the preparation of difluoromethylene olefins which completely avoided any fluoride ion isomerisation or addition reactions[157]. Similarly, reaction of fluorotribromomethane with triphenyl phosphine in dry

$$\underset{(253)}{CF_2Br_2} + 2Ph_3P + RCOR_f \xrightarrow[\text{diglyme}\\ \text{24h}]{70°C} F_2C = C(R)R_f + Ph_3PBr_2 + Ph_3PO$$

glyme solvents at 70°C gave bromofluoromethylenetriphenylphosphorane, $[Ph_3P{=}CFBr]$ (254), in solution[158]. Remarkably, the solution of (254) did not decompose even on warming to 37 - 38°C for 21 h. This is in marked contrast to solutions of $Ph_3P{=}CFCl$ which show stability for only ¼ - ½ h at ambient temperature[155] and $Ph_3P{=}CFH$ which show stability at low temperatures but decompose rapidly on warming to room temperature[158,159].

More recently, treatment of furanos-3-ulose derivatives with halogenomethylenetriphenylphosphoranes generated by the action of triphenylphosphine on fluorohalocarbene produced in situ gave the corresponding halogeno sugars in good yield[160]. Subsequent reaction of the chlorofluoromethylene derivatives,



(255)

(255) (X = Cl), with lithium aluminium hydride gave stereospecifically the corresponding fluoromethylene derivatives with inversion of configuration at the double bond.

Methods of preparation and properties of longer-carbon-chain fluorine-containing alkylidene phosphoranes have been described by Russian workers in a recent review[152]. These compounds have been prepared by four general methods.

1. Interaction of tertiary phosphines with fluoroolefins

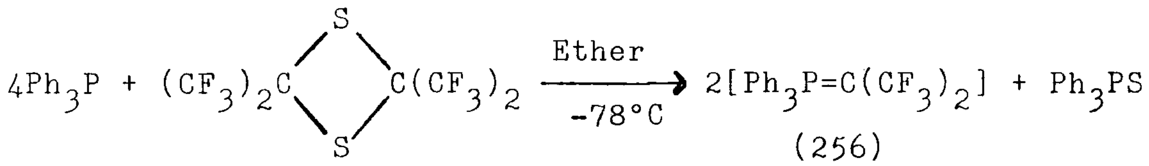
The electrophilic nature of fluoroolefins renders them susceptible to attack by nucleophilic tertiary phosphines. Tributylphosphine reacts readily with terminal fluoroolefins to give substituted vinylfluorophosphoranes[161]. Perfluorocycloalkenes[152,162] and internal fluoroolefins[161] react with tertiary phosphines to give perfluoroalkylidenetriphenylphosphoranes. It has been suggested[161] that alkenylfluorophosphoranes are obtained in those cases where the intermediate phosphonium cation contains a fluorine atom in the α-position, while phosphorus ylides are produced when there is no α-fluorine atom.

2. Interaction of tertiary phosphines with other organofluorine compounds

The method most widely used for preparation of hydrocarbon phosphorus ylides is dehydrohalogenation of the corresponding phosphonium salt. This synthetic route has also found use in preparation of fluorine-containing phosphorus ylides[163,164]. Phosphonium halides prepared by reactions of tertiary phosphines with fluorinated alkyl halides can subsequently undergo a base-induced dehydrohalogenation.

e.g. $$Ph_3P + BrCH_2C_6F_5 \longrightarrow Ph_3\overset{+}{P}CH_2C_6F_5.Br^- \xrightarrow[\text{or MeONa}\ (-HBr)]{BuLi} Ph_3P{=}CHC_6F_5$$

Triphenylphosphine was used as the base in the reaction with α-bromopentafluoroacetophenone[152]. This so-called "salt method"[152] is frequently unsuitable for the synthesis of fluorinated phosphorus ylides and tertiary phosphines are unreactive with compounds of the type $(R_f)_2CHX$. Various alternative methods have been described[152], one of the most promising of which involves interaction of tertiary phosphines with fluorine-containing thioketones. Thus, the unstable ylide (256) has been obtained from triphenylphosphine and thiohexafluoroacetone dimer[165].



(256)

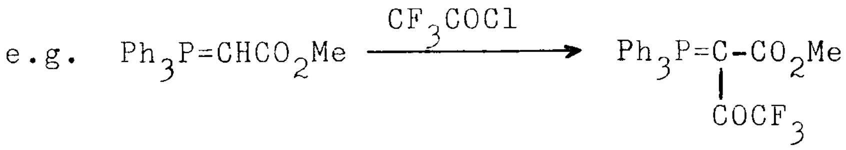
3. Interaction of phosphorus ylides with fluorine-containing compounds

Hydrocarbon phosphorus ylides are readily acylated[152]. Thus, reaction of methylenetriphenylphosphorane with ethyltrifluoroacetate readily gives the stable ylide (257)[166]. Similarly, stabilised ylides are acylated by perfluorocarboxylic

$$Ph_3P{=}CH_2 \xrightarrow[-70\ -\ 25°C]{CF_3CO_2Et} Ph_3P{=}CHCOCF_3$$

(257)

acid chlorides[152]. Pentafluorophenyl ylides have been prepared



$$\text{e.g.}\quad Ph_3P{=}CHCO_2Me \xrightarrow{CF_3COCl} Ph_3P{=}\underset{\displaystyle COCF_3}{\underset{|}{C}}{-}CO_2Me$$

from the reaction of active phosphorus ylides with hexafluorobenzene[167].

$$\text{e.g.}\quad Ph_3P{=}CH_2 + C_6F_6 \xrightarrow[\text{ether}]{\sim 20°C} [Ph_3\overset{+}{P}CH_2C_6F_5.F^-] \xrightarrow{Ph_3P=CH_2}$$

$$Ph_3P{=}CHC_6F_5$$

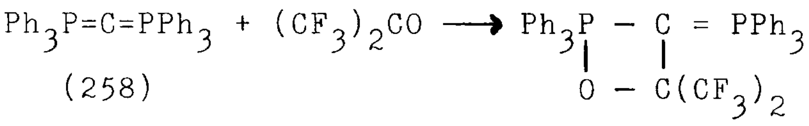
4. The preparation of Wittig-Horner reagents

These reagents are outside the scope of this discussion but can be considered as analogues of phosphorus ylides.

5A.2.B Reactions of phosphorus ylides with fluorocarbons

1. Carbonyl compounds

Hexaphenylcarbodiphosphorane (258) reacts with hexafluoroacetone to give the [2 + 2]-cycloadduct (259). This extremely stable oxaphosphetane was isolated and characterised[168]. The stability of (259) is a result of

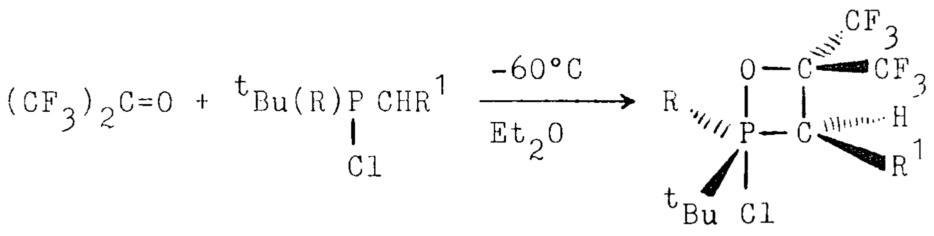


$$\underset{(258)}{Ph_3P{=}C{=}PPh_3} + (CF_3)_2CO \longrightarrow \begin{matrix} Ph_3P & - & C & = & PPh_3 \\ | & & | & & \\ O & - & C(CF_3)_2 & & \end{matrix}$$

(259)

the electron-withdrawing influence of the trifluoromethyl groups and the high electron density of the adjacent sp^2-hybridized carbon, which discourage dissociation of the

C - P bond[169]. Similar derivatives have been prepared more recently from chlorophosphoniumalkylidenes[170]. The

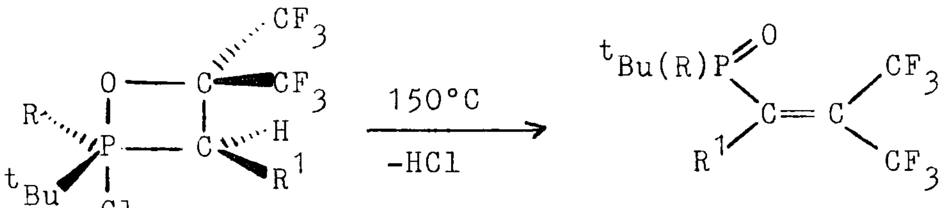


(260)

$R = {}^tBu$, $R^1 = H$

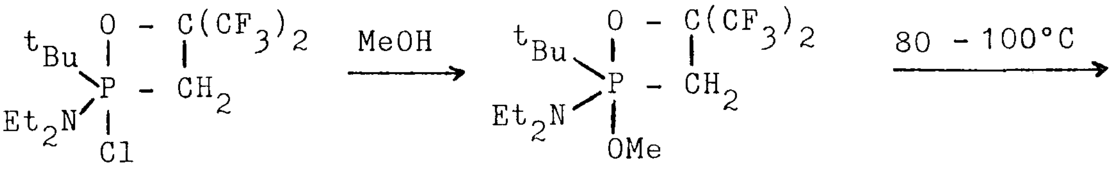
$R = Et_2N$, $R^1 = H$, Me

oxaphosphetanes (260) were formed as mixtures of two diastereoisomers. When heated above 150°C (260) decomposed via loss of hydrogen chloride to the phosphorus-containing olefins (261) (Same R as R^1). This contrasts with the reaction which occurs on heating the similar methoxy-derivative



(260) (261)

(262) which proceeds in accordance with the "normal" course of the Wittig reaction to give alkene (263)[170].



(262)

${}^tBu(Et_2N)(MeO)PO + (CF_3)_2C{=}CH_2$

(263)

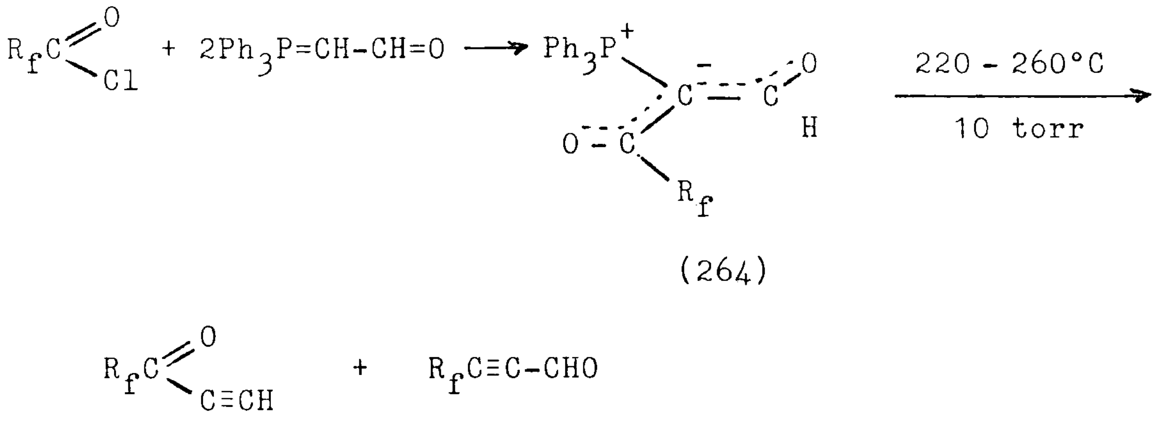
With the exception of halogenomethylenephosphoranes, fluorine-containing phosphorus ylides exhibit a moderate or even low reactivity towards carbonyl compounds[152]. The ylide (256) reacts in situ with various aldehydes under mild conditions but decomposes before reaction can occur with the less reactive ketones[165].

$$[Ph_3P{=}C(CF_3)_2] + RCHO \xrightarrow[Et_2O]{-78\ -20°C} RCH{=}C(CF_3)_2 + Ph_3PO$$

(256) (26 - 62%)

R = Ph, p-MeC_6H_4, p-$MeOC_6H_4$, $O_2NC_6H_4$, C_6F_5, PhMeCH, n-C_6H_{13}, PhCH=CH, 2-furfuryl, 2-pyridyl, or m-$CF_3C_6H_4$.

Perfluoroacylacetylenes and perfluoroalkynals have been prepared via intramolecular Wittig reaction of a range of perfluoroacylated phosphoranes (264)[171].



(264)

$R_f = CF_3, C_2F_5$, n-C_3F_7

2. Others

The lack of a suitable, cheap method to recycle the phosphine oxide produced in the Wittig reaction has limited its use to small scale laboratory reactions. In an attempt to circumvent this problem, American workers have reported a novel route to 1,1-difluoro-1-alkenes which avoids the formation of phosphine oxides[172]. Previous workers had demonstrated that halocarbenes generated via haloform/base reactions may be trapped with nitrogen[173] and phosphorus[174],[175] ylides to give halogenated olefins. Burton and Wheaton[172] used non-stabilised phosphonium ylides as bifunctional reagents in the reaction with chlorodifluoromethane to give 1,1-difluoro-1-alkenes.

Thus, non-stabilised alkylidene- and (arylalkylidene)-triphenylphosphoranes, in which the negative charge on the ylidene carbon is not extensively delocalised by resonance or inductive effects, react readily with chlorodifluoromethane to give the corresponding alkenes. The reaction gives excellent yields except when R^1 or R^2 are extensively

$$2Ph_3P^+ - C^-R^1R^2 + HCF_2Cl \longrightarrow [Ph_3P^+CHR^1R^2]Cl^- + Ph_3P + F_2C = CR^1R^2$$

electron-withdrawing. Benzhydrylidenetriphenylphosphorane (265a) and isopropylidenetriphenylphosphorane (265b) gave the alkenes (266a) and (266b) respectively in moderate to high

$$Ph_3\overset{+}{P} - \overset{-}{C}R_2 \xrightarrow{HCF_2Cl} F_2C = CR_2$$

R = Ph (265a) R = Ph (266a) (83%)

R = Me (265b) R = Me (266b) (62%)

yield; whereas (p-nitrobenzylidene)triphenylphosphorane was essentially unreactive.

Fluoroolefins are known to be highly electrophilic and to readily undergo nucleophilic substitution reactions[176]. Phosphorus ylides may be viewed as stabilised nucleophiles and have been shown to react with fluoroolefins via an addition-elimination mechanism to produce unsaturated phosphonium salts[177]. Hydrolysis of the phosphonium salts (267) provided a route to new unsaturated organofluorine compounds[177].

$$Ph_3P\text{-}CR^1R^2 + F_2C = CR^3R^4 \longrightarrow [Ph_3\overset{+}{P}CR^1R^2 - CF_2\overset{-}{C}R^3R^4]$$

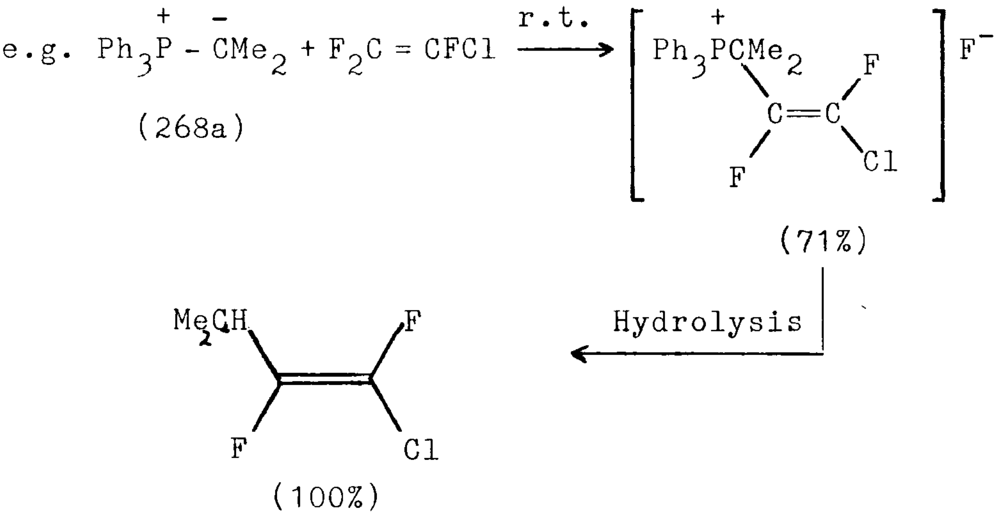
(268)

$$\xrightarrow{-F^-} [Ph_3\overset{+}{P}CR^1R^2CF = CR^3R^4]F^-$$

(267)

When the ylide (268) contains no α-hydrogen the allylic phosphonium salt (267) can be hydrolysed to give the corresponding alkene in high yield. When the ylide (268) contains an α-hydrogen reaction is much more complex. The initially formed phosphonium salt reacts with additional

e.g.



ylide (268b) to ultimately form an allenic phosphonium salt (269).

e.g. $$\underset{(268b)}{\mathrm{Ph_3\overset{+}{P}-\overset{-}{C}HMe}} + \mathrm{F_2C=C(CF_3)Ph} \xrightarrow{\mathrm{r.t.}} \mathrm{[Ph_3\overset{+}{P}CH(Me)-CF=C(CF_3)Ph]F^-}$$

$$\xrightarrow{(268b)} \mathrm{[Ph_3\overset{+}{P}-\overset{-}{C}(Me)-CF=C(CF_3)Ph]} + \mathrm{[Ph_3\overset{+}{P}CH_2Me]F^-}$$

$$\xrightarrow{-F^-} \underset{(269)}{\mathrm{[Ph_3\overset{+}{P}-C(Me)=C=C(CF_3)Ph]F^-}}$$

Hydrolysis of the resulting phosphonium salt (269) gives a mixture of three products. The predominance of acetylenic

$$\underset{(269)}{\mathrm{[Ph_3\overset{+}{P}-C(Me)=C=C(CF_3)Ph]F^-}} \xrightarrow{\mathrm{Hyd.}} \mathrm{MeCH=C=C(CF_3)Ph}\ (270)$$

$$+\ \mathrm{MeC{\equiv}C-C(CF_2)Ph}\ (271)$$

$$+\ \mathrm{MeC{\equiv}C-CH(CF_3)Ph}\ (272)$$

(270) : (271) : (272) = 1 : 1.4 : 1.6

products is consistent with the formation of an intermediate anion (273).

$$\underset{(273a)}{\mathrm{Me\overset{-}{C}=C=C(CF_3)Ph}} \longrightarrow \underset{(273b)}{\mathrm{MeC{\equiv}\overset{-}{C}C(CF_3)Ph}} \xrightarrow[\text{or } -F^-]{+H^+} \text{products}$$

5B Reaction of p-nitrobenzylidene triphenylphosphorane with hexafluorobut-2-yne

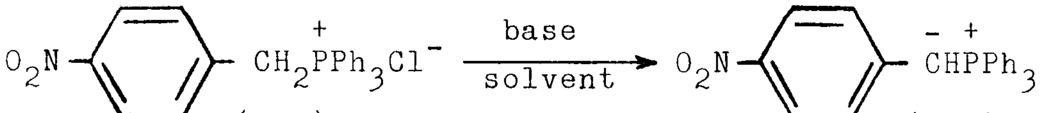
We were concerned to explore reactions of stabilised nucleophiles with hexafluorobut-2-yne (249) with a view to preparing cyclopentadienoid species (see Section 5A.1). As a part of this investigation it was decided to attempt reactions of stabilised phosphorus ylides with (249).

It was known that dimethylacetylene dicarboxylate (276) reacts readily with methylene phosphoranes in aprotic solvents to give stable ylides (277)[179]. In similar work Jones found that reaction of hexafluorobut-2-yne (249) with

$$Ph_3P{=}CHCOR + \underset{(276)}{MeO_2CC{\equiv}CCO_2Me} \longrightarrow \underset{(277)}{Ph_3P{=}C(CO_2Me)(MeO_2C)C{=}CHCOR}$$

unstabilised ylides led only to rapid anion polymerisation[151]. In an interesting reaction with the pseudo-ylide dimethylsulphoxide he was able to isolate a mixture of 1 : 1 adducts[151] and this result prompted us to study reactions of hexafluorobutyne with stabilised ylides.

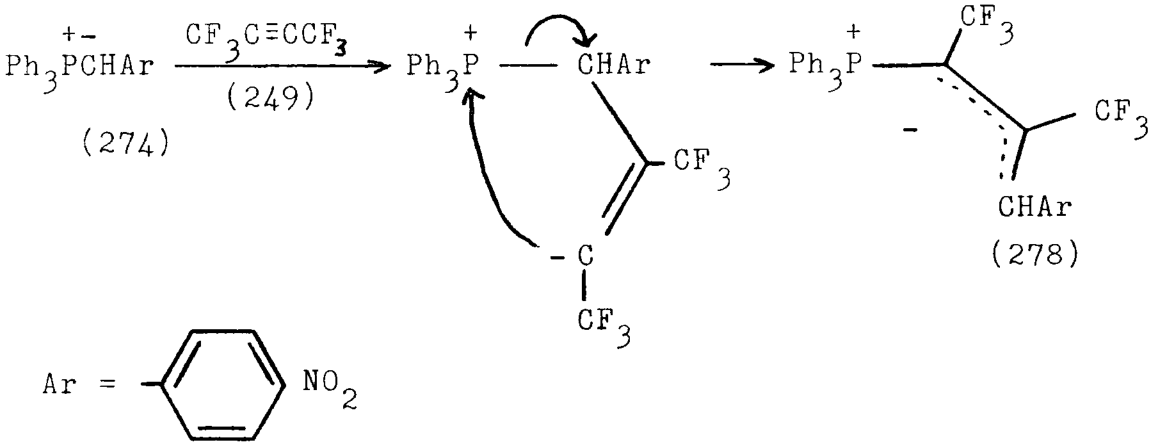
We were fortunate in having a readily available source of the stabilised ylide p-nitrobenzylidene triphenylphosphorane (274) as the corresponding hydrochloride (275)[178]. The ylide (274) was generated in situ by treatment with mild base in a suitable solvent.



(275) (274)

5B.1 Preparation of 1:1 adducts

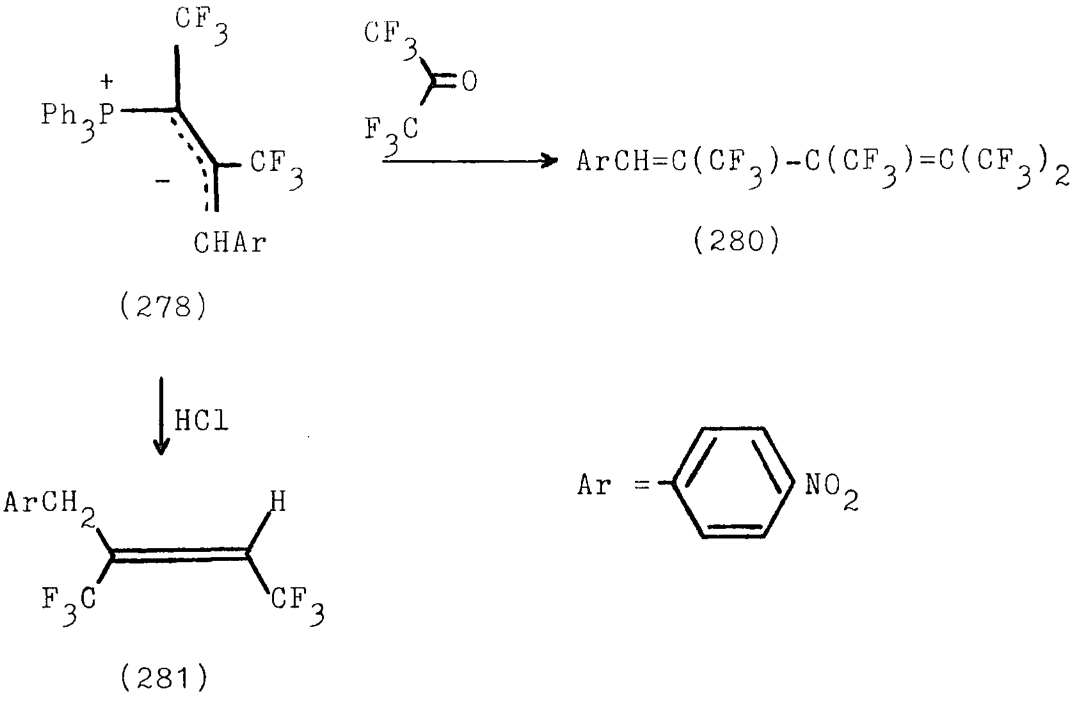
We have found that (249) reacts with the stabilised ylide (274) to give insertion products. Reaction of ylide (274), generated in situ using sodium carbonate, with alkyne (249) gave the insertion product (278). Our aim was to extend this reaction in an attempt to prepare ylides of the type (279) as possible precursors to novel trifluoromethylated cyclopentadienes.



$$\overset{+}{Ph_3P}[(CF_3CCCF_3)_nCHAr]^- \quad (n > 1)$$

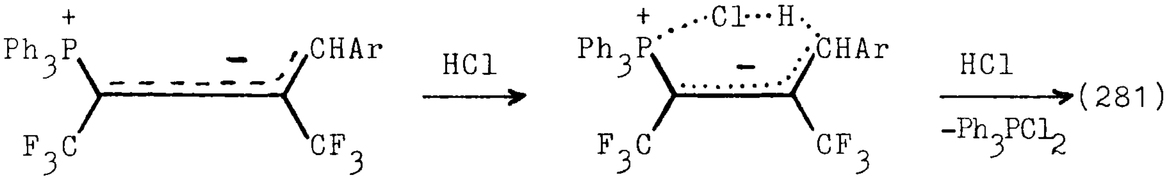
(279)

In order to prepare the carbocyclic target compounds it was necessary to explore ways of removing the phosphorus from the ylides (278) and (279) to give stable unsaturated products. Reaction of (278) with hexafluoroacetone under mild conditions gave the diene (280) via a Wittig reaction. Ylide (278) was also readily hydrolysed by hydrochloric acid to give the cis-alkene (281). The specific formation of the Z-isomer of the product was demonstrated by the presence of a quartet (J = 7.5 Hz) splitting pattern, in the ^{19}F n.m.r.



(278) (280) (281)

spectrum. This specificity is probably introduced through reaction of (278) with HCl in a cyclic process via (282).

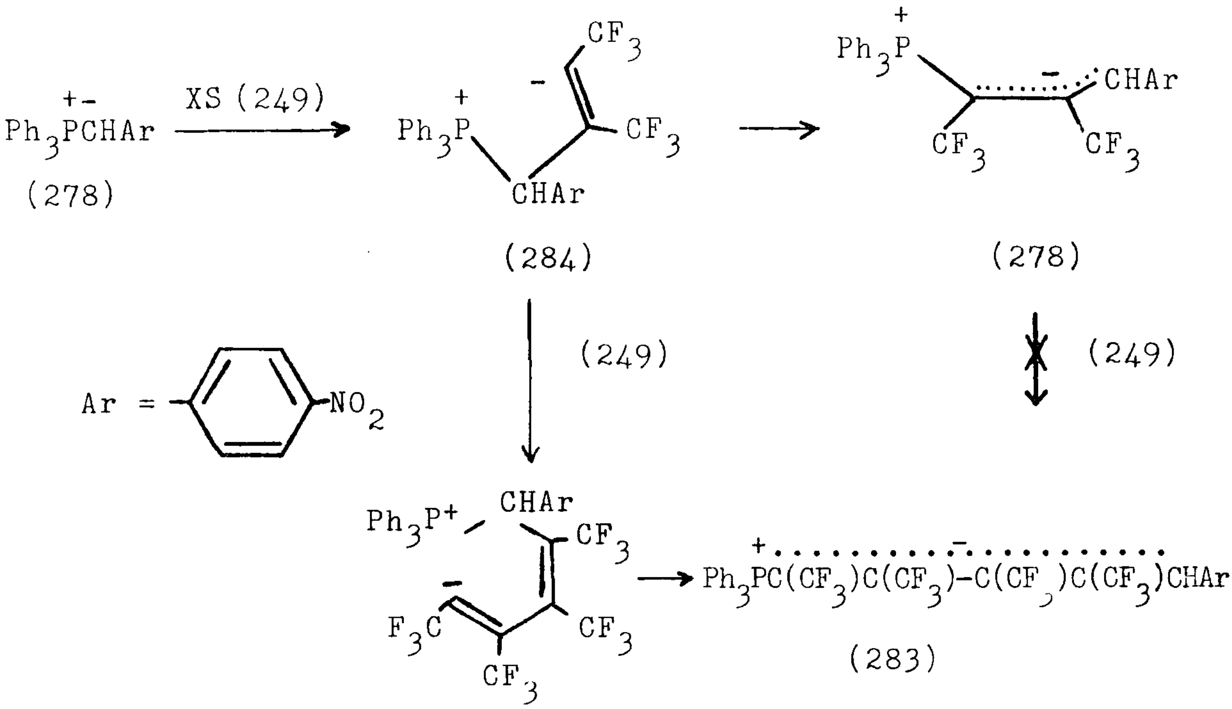


(282)

5B.2 Preparation of higher adducts

p-Nitrobenzylidene triphenylphosphorane (274) reacted with more than one mole-equivalent of hexafluorobut-2-yne (249) under autogenous pressure to give mixtures. Mass spectra showed M^+ peaks due to the 1 : 1 adduct (278) and 2 : 1 adduct (283) as well as a large number of impurities. Interestingly, (278) was essentially unreactive to (249) under the same conditions. This must be a result of the negative charge in (278) being stabilised to such an extent as to make it unreactive to the highly electrophilic alkyne

(249). It is, therefore, likely that (283) and (278) are formed via the common intermediate (284). Mixtures of (278) and (283) were also obtained from reaction of (278) with

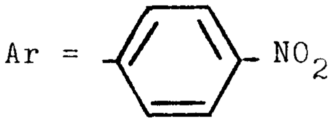


(249) at atmospheric pressure and elevated temperatures. Unfortunately, the products were not stable to chromatography and could not be separated.

Our initial intent had been to isolate the 2 : 1 adduct (283) and remove the triphenylphosphine group by reaction with hexafluoroacetone or hydrochloric acid to obtain alkenes (285) and (286) respectively.

$ArCH{=}C(CF_3)(CF_3)C{=}C(CF_3)C(CF_3){=}C(CF_3)_2$

(285)



$ArCH_2C(CF_3){=}C(CF_3)(CF_3)C{=}CHCF_3$

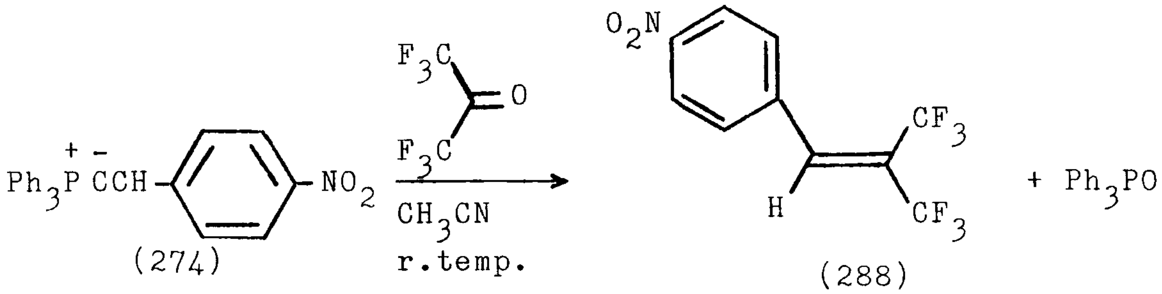
(286)

Note: Pages 125 and 126 are in incorrect sequence

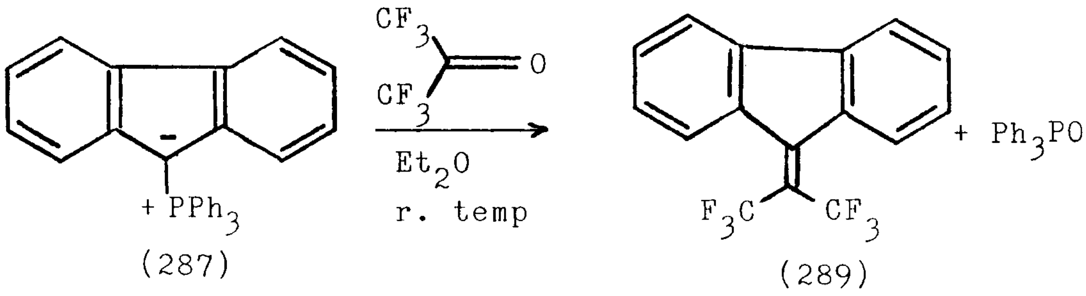
The mixture containing (278) and (283) was reacted with hexafluoroacetone in acetonitrile. The reaction was monitored by observing the disappearance of the signals at around 66 p.p.m. due to CF_3 on the carbon adjacent to phosphorus in (278). Attempted chromatographic isolation of (285) was unsuccessful due to contamination with unstable impurities. Similarly, the products of reaction of the mixture containing (283) and (278) showed significant changes in the ^{19}F n.m.r. spectrum from the starting materials but proved unstable to the separation techniques used. Clearly, further work is required on this system.

5C Synthesis and reactions of fluorinated alkenes via stabilised phosphorus ylides

Comparatively few reactions of hexafluoroacetone with ylides have been reported[168-170,180,181] but we have found that the stabilised phosphorus ylides (274) and (287) react readily with hexafluoroacetone at room temperature to give the novel alkenes (288) and (289) respectively. These alkenes are particularly interesting since they contain



(274) (288)



(287) (289)

Note: Pages 125 and 126 are in incorrect sequence

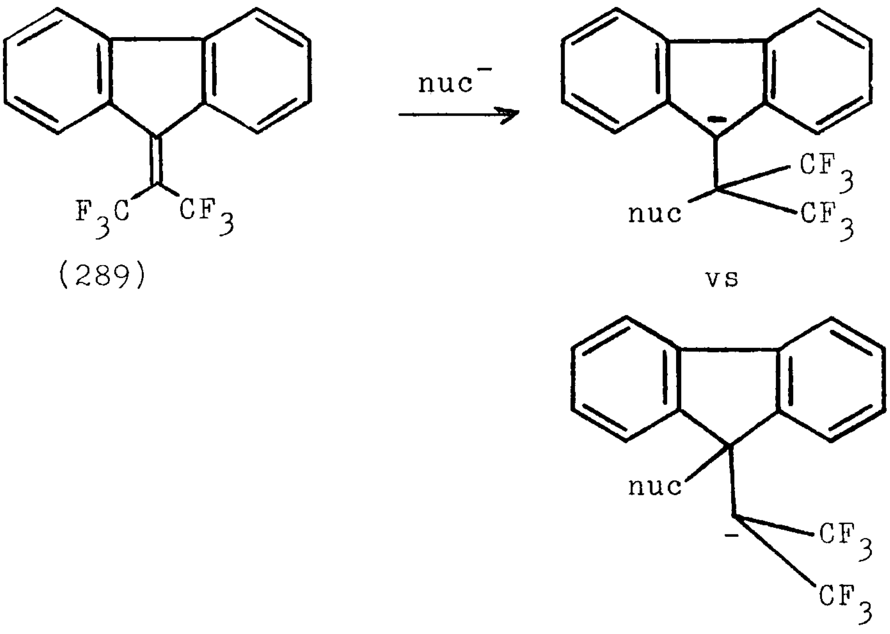
strong electron-withdrawing substituents at both ends of the double bond and we would anticipate, therefore, that, as for perfluorinated alkenes, they would be highly susceptible to nucleophilic attack, and may give stable anionic intermediates.

Neither (288) or (289) formed stable anions on treatment with CsF in Tetraglyme and (289) did not form an anion on treatment with the extremely reactive fluoride source TAS-F (see Section 2A.1.C). These observations parallel those made for tetra(perfluoroalkyl)alkenes by Bayliff[147]. He has found that to prepare stable fluorocarbanions from fluoroolefin precursors it is necessary for the fluoroolefins to contain at least one fluorine on the double bond [147] as well as electron-withdrawing perfluoroalkyl substituents.

Reactions with sodium methoxide in methanol

Since both ends of the carbon-carbon double bond in (288) and (289) have electron-withdrawing substituents we might envisage a competition for orientation of substitution in reaction with nucleophiles. Consequently, the orientation of substitution in the products from reaction of (288) and (289) with methoxide will give an indication of the stabilising

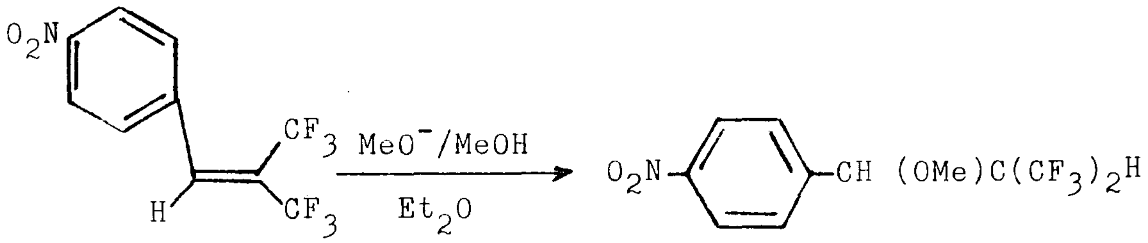
e.g.



(289)

effect of the 4-nitrobenzyl and fluorenyl substituents in competition with hexafluoroisopropyl.

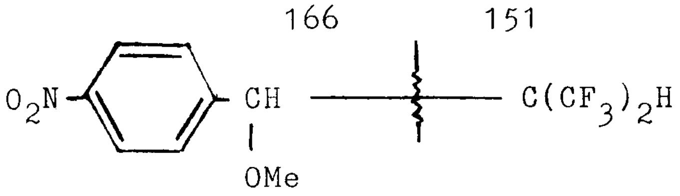
Reaction of (288) with sodium methoxide in methanol and ether gave (290) in moderate yield. The orientation of substitution was deduced by examination of the mass spectra.



(288)

(290)

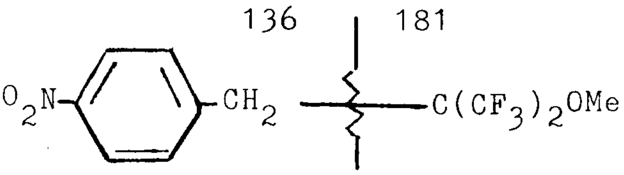
The base peak in the E.I. spectrum came at m/e 166 corresponding to a fragmentation at the bond shown. The complementary fragment of m/e 151 had a relative intensity of 46.8%. Similar fragmentation of the alternative isomer



Observed

(290)

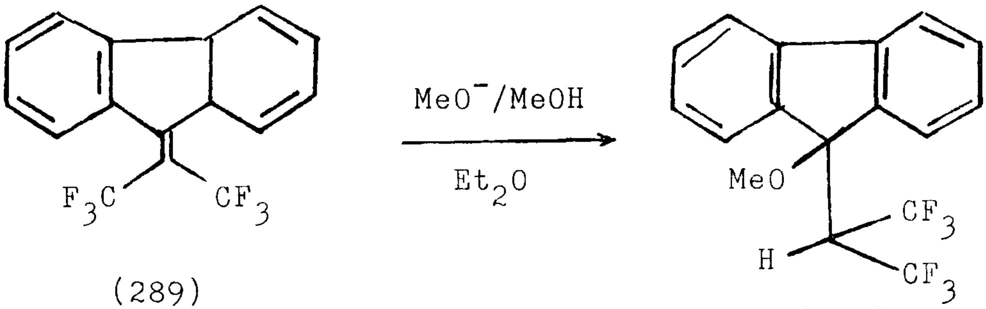
(291) would give peaks at m/e 181 and 136 neither of which are observed in the spectrum obtained.



Not Observed

(291)

The corresponding reaction of (289) with methoxide gave (292). The orientation was again deduced by examination



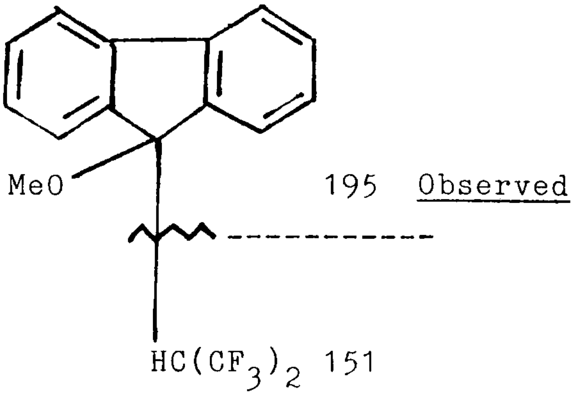
(289)

(292)

(40%)

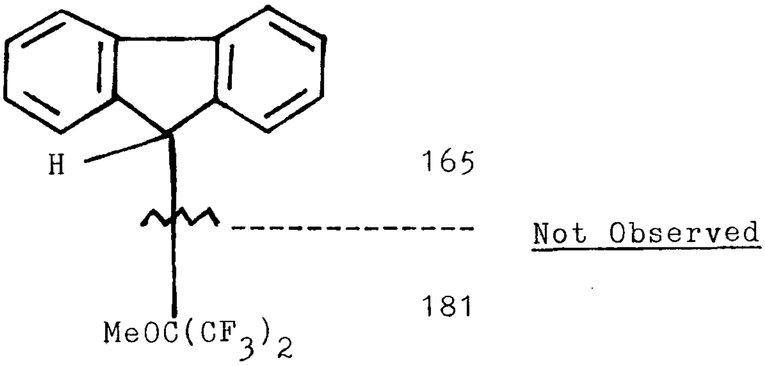
of the mass spectra. The base peak in the E.I. Spectrum came at 195 corresponding to fragmentation at the bond shown.

(292)



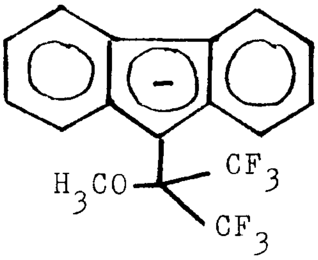
The complementary fragment had a relative intensity of 10.58%. Similar fragmentation of the alternative isomer (293) would give peaks at m/e 181 and 165. The peaks are found in the E.I. spectrum with %HT base of 7.51 and 20.59 respectively.

(293)

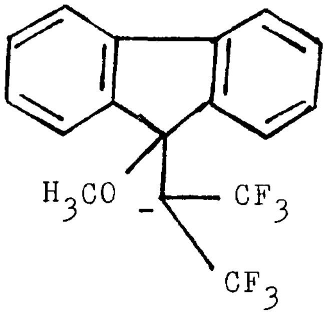


There is, however, no evidence for a mixture in the ^{19}F n.m.r. spectrum which shows a singlet at 57 p.p.m. and the structure assigned is (292) only.

These results are interesting since from consideration of steric factors and the stabilities of the anionic intermediates we would expect to obtain (291) and (293). Anion (294) which would give isomer (293) is a cyclopentadienyl anion and it seems unlikely that this anion is less stable than the alternative, (295), stabilised by CF_3 groups.



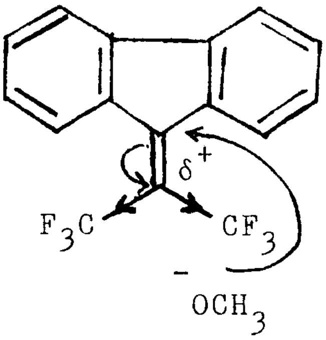
(294)



(295)

Therefore the factor controlling orientation of nucleophilic attack in compounds (288) and (289) may be polarisation of the initial state which would favour

i.e.



formation of the observed products.

EXPERIMENTAL

INSTRUMENTATION

N.m.r. Spectra were recorded on the following instruments:

Spectrometer	Nucleus	Frequency/MHz	Reference
Varian EM360L	^{1}H	60	TMS
Varian EM360L	^{19}F	56.45	$CFCl_3$
Brüker HX90E (with FT facility)	^{19}F	84.68	$CFCl_3$
Brüker WH-360 (with FT facility)	^{13}C	90.6	TMS
Hitachi R-24B	^{1}H	60	TMS
Brüker AC250 (with FT facility)	^{1}H	250	TMS
Brüker AC250 (with FT facility)	^{19}F	235	$CFCl_3$
Brücker AC250 (with FT facility)	^{13}C	62	TMS

Ultraviolet spectra were recorded on a Pye-Unicam SP8-100 ultraviolet spectrometer using cyclohexane as the solvent.

Infrared spectra were recorded on a Perkin Elmer 457 grating infrared spectrophotometer using KBr discs or plates as appropriate. Gaseous samples were condensed into a cylindrical cell with KBr windows.

Elemental Analysis Carbon, hydrogen and nitrogen analyses were obtained using a Perkin Elmer 240 Elemental Analyser. Analysis for halogens was performed as described in the literature[198].

Mass spectra Mass spectra of mixtures were run on a VG Micromass 12B Spectrometer fitted with a Pye 104 Gas Chromatograph or a VG 7070E Spectrometer fitted with a Hewlett Packard 5790A Capillary Column Gas Chromatograph (25 m fused silica column with O_{v1} coating). Spectra of solid or one component liquid samples were run on VG 7070E or A.E.I. MS9 Spectrometers.

Gas Liquid Chromatographic Analysis was carried out using a Varian Aerograph Model 920 (Gas Density Balance detector) Chromatograph with packed columns. The column packings were as follows:

Col A. 20% Diisodecylphthalate on Chromosorb P.

Col K. 20% Krytox[199] 143AD fluid on Chromosorb W.

Col F. 20% Fomblin[200] fluid on Phasesep P N.A.W.

A Hewlett Packard 5890 A Gas Chromatograph fitted with a 25 m fused silica column with O_{v1} coating was also used. Preparative scale g.l.c. was performed on a Varian Aerograph Model 920 with packed columns.

Fractional Distillation of product mixtures was carried out using a Fischer spaltrohr MMS 202 System.

Melting and Boiling Points were determined at atmospheric pressure and are uncorrected.

CHAPTER 6

EXPERIMENTAL FOR CHAPTER 2

6A Reagents and Solvents

Sulfolane was distilled under reduced pressure and the fore-fraction discarded. The remainder was stored over molecular sieve (4A) and under dry nitrogen.

Acetonitrile was distilled from P_2O_5 and stored on molecular sieve (4A) under dry nitrogen.

Diethyl ether was distilled from sodium and stored on molecular sieve (4A) under dry nitrogen.

Potassium and Caesium Fluoride were dried by heating to 150°C under high vacuum (10^{-3} mm Hg) for 24 hours, grinding under a nitrogen atmosphere and repeating the process twice. The dry powders were stored under dry nitrogen.

Sodium Fluoride was dried by heating over a gas burner and stored in an oven (180°C).

Perfluoro-2,5-diazahex-2,4-diene was prepared by NaF-induced dehydrofluorination of N,N-bis(trifluoromethyl)tetrafluoroethylenediamine[13].

TAS-F was prepared by the literature method[105] and generously donated by A.E. Bayliff.

Diazomethane was prepared according to the literature method[183].

Perfluoro-2,3,4,5,6,7,8,9-octahydroquinoline was prepared by Cobalt trifluoride fluorination of F-quinoline and was kindly donated by Dr. M.J. Silvester.

Tetrabutylammonium fluoride triydrate was purchased from Aldrich Chemical Co. Ltd.

6B Synthesis and Reactions of Perfluoro-2,5-diazahexa-2,4-diene and related aza-olefins

6B.1.A Dimerisation reactions

6B.1.A.1 At 120°C using NaF

A mixture containing perfluoro-2,5-diazahexa-2,4-diene (15) (8.7 g, 38.4 mmol), sodium fluoride (1.1 g, 26.7 mmol), and sulfolane (25 ml) was heated at 120°C for three days in a Carius tube. Volatile material was transferred under vacuum into a trap cooled in liquid air. The resultant liquid (7.9 g, 91% recovery) was shown by g.l.c.-m.s. (Column K, 100°C) to consist of (158) (35%) and (159) (65%) by comparison with authentic spectra[47].

6B.1.A.2 At 120°C using CsF

A mixture containing perfluoro-2,5-diazahexa-2,4-diene (15) (9.6 g, 42.1 mmol) caesium fluoride (1.7 g, 11.1 mmol), and sulfolane (25 ml) was heated to 120°C for three days in a Carius tube. Volatile material was transferred under vacuum to a trap cooled in liquid air. The resultant liquid (7.5 g, 79% recovery) was shown by g.l.c.-m.s. (Column K, 100°C) to consist of (158) (74%), (159) (23%) and a new dimer (169) (3%). (see 6B.1.B.1 for identification).

6B.1.A.3 At -23°C using CsF

A mixture of perfluoro-2,5-diazahexa-2,4-diene (15) (8.8 g, 38.8 mmol), caesium fluoride (0.8 g, 5.3 mmol), and acetonitrile (25 ml) was stirred at -23°C for 23 hours. Volatile material was transferred under vacuum into a trap cooled in liquid air and the lower fluorocarbon layer removed. The resultant liquid (6.8 g) was shown by g.l.c.-m.s. (Column K, 95°C) to contain dimers (158) (94%) and (159)(6%).

6B.1.B Isomerisation reactions

6B.1.B.1 Isomerisation of dimer (158)

A mixture of dimers containing (158) (94%) and (159) (6%) (4.7 g, 10.3 mmol), caesium fluoride (0.8 g, 5.39 mmol), and sulfolane (20 ml) was heated at 100°C for three days. Volatile material was transferred under vacuum to a trap cooled in liquid air. The resultant liquid (2.1 g) was shown by g.l.c.-m.s. (Column K, 100°C) to contain (159) (73%) and (169)(27%). A sample of (169) was isolated and shown to be perfluoro-1,6-dimethyl-4-methylimino-1,3,6-triazabicyclo-[3.3.0.$^{3.7}$]octane. Spectra No. 1.

6B.1.B.2 Vapour phase reaction of (15) with potassium fluoride

Compound (15) (9.1 g, 40.1 mmol) was passed through a silica tube containing potassium fluoride at 230°C in a flow of nitrogen (contact time ∿70 s). The product was collected in a liquid air cooled trap. The resultant liquid (7.7 g, 84% recovery) was shown by g.l.c. (Column A, 60°C) to consist of recovered (15) (32%) and the cyclic isomers (64) (43%), identified by comparison of spectroscopic details with authentic spectra[47].

6B.1.B.3 Vapour phase reaction of (15) with potassium fluoride on silica

Potassium fluoride (29 g) and 60 - 220 mesh silica (50 g) were added to water (100 ml) and shaken to form a slurry. Water was removed under reduced pressure, and the resulting powder was dried by heating under high vacuum at 75°C for two days.

Compound (15) (5.5 g, 24 mmol) was passed through a silica tube containing potassium fluoride on silica (prepared by the method outlined above) at 220°C in a flow of nitrogen (contact time ∿70 s). The product was collected in a liquid air cooled trap. The resultant liquid (1.2 g, 21% recovery) was shown by g.l.c. (Column A, 60°C) to consist of recovered (15) (16%) and the cyclic isomers (64) (5%).

6B.1.B.4 Vapour phase reaction of (15) with caesium fluoride

Compound (15) (7.6 g, 33.2 mmol) was passed through a silica tube containing caesium fluoride at 220°C in a flow of nitrogen (contact time ∿70 s). The product was collected in a liquid air cooled trap. The resultant liquid (6.8 g, 90% recovery) was shown by g.l.c. (Column A, 60°C) to consist of two components, identified by g.l.c.-m.s. (same conditions) as (64a) (72%) and (64) (18%).

6B.1.C New Fluoride ion sources

6B.1.C.1 Reactions of (15) with anhydrous TBAF

Tetrabutylammonium fluoride trihydrate (0.5 g) was heated at 40°C under high vacuum (0.001 mm Hg) for 48 hours to remove water. At the end of this time the remaining oil had a mass of 0.2 g.

Dry acetonitrile (2 ml) was added to give a homogeneous solution and then perfluoro-2,5-diazahexa-2,4-diene (15) (1.9 g, 8.16 mmol) was added. A highly exothermic reaction occurred. The mixture was stirred for 23 hours and then volatiles were transferred under vacuum to a trap cooled in liquid air. The lower layer (1.6 g, 86% recovery) was shown by g.l.c.-m.s. (Column K, 90°C) to consist of dimers (158) (65%) and (159) (35%).

6B.1.C.2 Reaction of (15) with TAS-F

TAS-F (50 mg) was dissolved in dry acetonitrile (2 ml) and compound (15) (1.8 g, 7.7 mmol) was added. The mixture was stirred for 23 hours and then volatiles were transferred under vacuum to a trap cooled in liquid air. The lower layer (1.5 g, 85% recovery) was shown by g.l.c.-m.s. (Column K, 100°C) to comprise dimers (158) (90%) and (159) (10%).

6B.2.A Attempted synthesis of perfluorooxaziridines

6B.2.A.1 Reaction of (15) with calcium hypochlorite

Compound (15) (6.1 g, 27 mmol) was added dropwise to a mixture of calcium hypochlorite (17.2 g, 120 mmol), 18-crown-6 polyether (0.1 g) and acetonitrile (4 ml) stirred at room temperature in a round-bottomed flask fitted with a condenser. The gaseous products evolved were collected in two liquid air cooled traps and then transferred to a gas storage bulb. Infrared analysis showed, by comparison with the literature[184], the presence of trifluoromethyl isocyanate. No oxaziridine products were detected in the remaining liquid.

6B.2.A.2 Reaction of dimer (158) with calcium hypochlorite

Calcium hypochlorite (1.3 g, 8.8 mmol), dimer (158) (2.0 g, 4.4 mmol) and acetonitrile (2 ml) were stirred for 72 hours at room temperature in a round-bottomed flask fitted with a gas bladder.

A small quantity of gas evolved was identified by comparison of its infrared spectrum with the literature as trifluoromethyl isocyanate.

Volatile components in the remaining mixture were transferred under vacuum to a trap cooled in liquid air and n.m.r. analysis of the lower, fluorocarbon, layer showed only recovered (158).

6B.2.A.3 Reaction of dimer (159) with calcium hypochlorite

Calcium hypochlorite (1.2 g, 8.3 mmol), dimer (159) (1.7 g, 3.8 mmol) 18-crown-6 polyether (50 mg) and acetonitrile (4 ml) were stirred under nitrogen for 72 hours at room temperature. Volatile components were transferred under vacuum to a trap cooled in liquid air and the lower, fluorocarbon, layer (0.7 g, 55% recovery) was shown by n.m.r. to be recovered (159).

6B.2.A.4 Reaction of (15) with potassium carbonate and chlorine

Potassium carbonate (10 g, 72 mmol) and compound (15) (6.9 g, 30 mmol) were sealed in a nickel tube and chlorine (7.7 g, 108 mmol) was added at -196°C. The tube was allowed to warm to ambient temperature for 21 hours. After venting excess chlorine volatile material was transferred under vacuum to a trap cooled in liquid air and was shown by n.m.r. to be unchanged (15) (3.6 g, 52% recovery).

6B.2.A.5 Reaction of tetrafluoroethylene tetramer with potassium carbonate and chlorine

Potassium carbonate (10 g, 72 mmol) and TFE tetramer (12.2 g, 305 mmol) were sealed in a nickel tube and chlorine (9 g, 126.8 mmol) was added at -196°C. The tube was left at ambient temperature for 16½ hours and after venting excess chlorine volatile material was transferred to a trap cooled in liquid air and was shown by infrared spectroscopy to be unchanged tetramer (10.8 g, 88.5% recovery).

6B.2.B Diazomethane additions

Diazomethane was prepared by the method of T.J. de Boer and H.J. Backer[183].

A 250 ml round-bottomed 2-necked flask fitted with a 250 ml long-stemmed dropping funnel, still head and condenser was connected to a 500 ml round-bottomed flask fitted with a dreschel head. The receiver was cooled in an ice-salt bath.

In the receiver was placed potassium hydroxide pellets (12 g) and diethyl ether (20 ml). Potassium hydroxide (12 g) in water (20 ml) was placed in the reaction flask with digol (70 ml) and ether (20 ml). The reaction flask was heated to ca. 75°C in a water bath, and a solution of 'Diazald' (p-tolysulphonylmethyl nitrosamide) (35.4 g) in ether (250 ml) was added slowly (∿60 mins) to the stirred solution in the reaction flask, followed by a further ∿150 ml of ether until the distillate was colourless (CH_2N_2 in Et_2O is yellow).

Note: Apparatus should be clean and dry and free from cracks or sharp edges. Ideally rubber stoppers and tubes should be used and ground glass joints avoided.

6B.2.B.1 Reaction of (15) with CH_2N_2 at 0°C

Diazomethane ether azeotrope was added dropwise to compound (15) (1.1 g, 4.8 mmol) at 0°C until a permanent yellow colour was attained and the mixture was stirred overnight at room temperature.

Removal of ether gave a white solid, shown by I.R. spectroscopy to be hydrolysed (15), and a yellow oil, shown by g.l.c.-m.s. (Column K, 100°C) to be a complex mixture.

6B.2.B.2 Reaction of dimer (158) with CH_2N_2 at 0°C

Diazomethane ether azeotrope was added dropwise to dimer (158) (4.5 g, 9.9 mmol) at 0°C until a permanent yellow colour was attained. After warming to room temperature and stirring for an hour ether was removed by distillation and the remaining pale yellow liquid was transferred under vacuum to a trap cooled in liquid air.

Gas chromatography (Column K, 110°C) showed a complex mixture and no further separation and analysis were attempted.

6B.2.B.3 Reaction of dimer (159) with CH_2N_2 at 0°C

Excess diazomethane ether azeotrope was added dropwise to dimer (159) (0.9 g, 2.0 mmol) at 0°C, and the mixture was left stirring overnight at room temperature. After removal of ether the resulting yellow oil was transferred under vacuum to a trap cooled in liquid air and shown by gas chromatography (Column K, 125°C) to be a multicomponent mixture.

Further separation and analysis were not attempted.

6B.2.C Miscellaneous cycloaddition reactions

6B.2.C.1 Reaction of (15) with 2,3-dihydrofuran

2,3-Dihydrofuran (13.8 g, 196 mmol) was added to compound (15) (36.4 g, 159.6 mmol) at room temperature. An exothermic reaction occurred which was controlled using an ice bath. Volatile material was transferred under vacuum to a trap cooled in liquid air and on warming decomposed to give a sticky material assumed to be a polymer which was not analysed further.

6B.2.C.2 Reaction of (15) with 2,3-dimethylbuta-1,3-diene

Compound (15)(3.3 g, 41.2 mmol) and 2,3-dimethylbuta-1,3-diene (3.1 g, 13.6 mmol) were heated to 120°C for 48 hours in a sealed glass tube and gave an involatile black tar which was not further analysed.

6B.2.C.3 Reaction of (15) with diethylmalonate

Compound (15) (8.9 g, 39 mmol) was added dropwise to a mixture of diethylmalonate (23.7 g, 143.7 mmol) and potassium carbonate (15 g) at -22°C. After stirring at this temperature for two hours the mixture was allowed to warm to ambient temperature overnight. Volatile materials were transferred under vacuum to a trap cooled in liquid air and were shown by n.m.r. to contain no fluorinated material. The remaining involatile tarry material was not analysed further.

6B.2.C.4 Photolytic reaction of (15) with acetone

Compound (15) (1.7 g, 7.6 mmol) and acetone (1.0 g, 16.5 mmol) were sealed under vacuum in a quartz tube and irradiated using a high pressure ultraviolet lamp for three days. The resulting liquid was shown by n.m.r. to comprise only unchanged starting materials.

6B.2.C.5 Reaction of (15) with 1-(N-morpholino)cyclohex-1-ene

1-(N-morpholino)cyclohex-1-ene (4.6 g, 27.7 mmol) in acetonitrile (3 ml) was added dropwise to a stirred mixture of compound (15) (2.2 g, 9.7 mmol) and sodium fluoride ($\sim$5 g) in acetonitrile (10 ml) at -22.5°C under dry nitrogen. The mixture was allowed to warm to room temperature with stirring and 10 ml water was added. The lower layer was isolated and filtered and was shown by n.m.r. to be a complex mixture. The material rapidly decomposed to form a viscous tar. Further analysis was not attempted.

6B.2.D Attempted synthesis of perfluoro-1-methylimidazole

General procedure. A silica tube was packed with coarse iron filings and was heated to 250°C under high vacuum (0.001 mm Hg) for six hours and after cooling was left overnight under an atmosphere of dry nitrogen. Imine starting materials were passed through the tube at the desired temperature in a flow of dry nitrogen (contact time ∿30 s) and the products were trapped in two vessels cooled in liquid air. Analysis was by g.l.c.-m.s. (Column A, 60°C).

6B.2.D.1 Defluorination of (15) at 340°C

Compound (15) (3.5 g, 15.2 mmol) was passed through a tube containing iron filings at 340°C according to the general procedure above. An analysis of the trapped material (2.7 g) showed it to be unchanged starting material.

6B.2.D.2 Defluorination of (64)

Reactions of (64) were carried out according to the same procedure at the temperatures shown in the Table. Unchanged starting material was isolated in the proportions shown.

Starting Material (64)	Reaction Temperature (°C)	Recovery
4.7 g, 20.6 mmol	400	3.8 g, 81%
4.5 g, 19.7 mmol	450	3.2 g, 72%
3.2 g, 14 mmol	500	1.3 g, 42%

6B.2.E Fluorination reactions - General Procedure

Fluorinations were carried out in a small stirred nickel reactor containing cobalt trifluoride (150 g) and calcium fluoride (150 g). Reactants were dropped from a suitably modified burette directly into the reactor, through which a steady stream of nitrogen was flowing. Products were collected in a trap cooled in liquid air.

6B.2.E.1 Fluorination of (15)

Compound (15) (2.6 g, 11.5 mmol) was fluorinated at 130°C and gave gaseous products and unchanged starting material (1.6 g, 59%). A repeat reaction at 180°C gave a reduced recovery (42%) of starting material.

6B.2.E.2 Fluorination of (64)

Compounds (64) (1.9 g, 8.2 mmol) were fluorinated at 180°C and gave gaseous products and unchanged starting material (1.0 g, 56%).

6B.2.F. Aqueous hydrolysis of (158)

Dimer (158) (4.6 g, 10 mmol), water (1.0 g, 55.6 mmol) and acetonitrile (2 ml) were stirred at room temperature for 72 hours. Unreacted water and acetonitrile were removed under vacuum and the residue was sublimed to give 4.2 g (92% yield) of a white solid identified as N-trifluoromethyl(perfluoro-1,3-dimethyl-4-methylimino-trihydroimidazolindin-2-yl)methanamide (174). [Found: C, 20.8; H, 0.0; N, 12.1; F, 62.6%. $C_8F_{15}HN_4O$ requires C, 21.15; H, 0.2; N, 12.35; F, 62.80%]. Spectra No. 2.

6C A novel rearrangement of Perfluoro-1,1'-bis-1,3-diaza-cyclohex-2-enyl (43)

6C.1 Fluoride-catalysed isomerisation of (43)

Compound (43) (3.3 g, 7.9 mmol) was transferred under vacuum to a Carius tube (volume 10 ml) containing dry CsF (∿0.5 g). This was sealed under high vacuum and then heated to 150°C for 16 h. Volatile material was transferred under vacuum to a trap cooled in liquid air and the resultant liquid (2.3 g) was shown by g.l.c. (Column A, 80°C) to comprise two components. Separation by preparative scale g.l.c. gave (43) and perfluoro-4-methyl-1,2,5,7-tetraazatricyclo[3.3.1.0$^{2.6}$]undec-4-ene (175) (42%): [Found: C, 23.0; F, 64.0; N, 13.2%. $C_8F_{14}N_4$ requires C, 23.0; F, 63.6; N, 13.4%]. Spectra No. 3.

6C.2 Reaction of Perfluoro-2,3,4,5,6,7,8,9-octahydroquinoline with fluoride

Perfluoro-2,3,4,5,6,7,8,9-octahydroquinoline (0.30 g, 0.7 mmol) and dry caesium fluoride (∿0.5 g) were sealed under high vacuum in a Carius tube (volume 10 ml) and heated to 150°C for 17 hours. Volatile material was transferred under vacuum to a trap cooled in liquid air and the resultant liquid (0.2 g) was shown by ^{19}F n.m.r. to be unchanged starting material.

6C.3 Reaction of (175) with BCl_3 at room temperature

Imine (175) (0.8 g, 2 mmol) and BCl_3(0.2 g, 2 mmol) were heated in a sealed tube at 120°C for 48 hours. Gaseous products were vented off to leave 1.0 g of a material comprising one major component. A sample was isolated by preparative scale g.l.c. (Column F, 175°C) and is thought to be 11,11-dichloro-4-(trifluoromethyl)nonafluoro-1,2,5,7-tetraazatricyclo[3.3.1.0$^{2.6}$]undec-4-ene (183) (92%): [Found: C, 21.3; N, 12.5%. $C_8Cl_2F_{12}N_4$ requires C, 21.3; N, 12.4%]. Spectra 4. Mass spectra were not reproducible.

6C.4 Reaction of (183) with BCl_3 at 170°C

Compound (183) (0.3 g, 0.75 mmol) and BCl_3 (0.3 g, 2.5 mmol) were heated at 170°C for four days in a sealed tube. Gaseous products were vented off to leave 0.28 g of a material identified by ^{19}F n.m.r. as unchanged starting material.

6C.5 Reaction of (183) with PPh_3 at 120°C

Compound (183) (0.4 g, 0.9 mmol) and PPh_3 (0.5 g, 1.8 mmol) were heated at 120°C for four days. Volatiles were transferred under vacuum to a liquid air cooled trap to leave a solid material shown by ^{19}F n.m.r. to contain no fluorocarbon products.

Fractional vacuum distillation of the volatiles gave 0.14 g of starting material and 0.15 g of a solid material which was recrystallised from hexane. The structure of this material was difficult to assign. Spectra No.5.

CHAPTER 7

EXPERIMENTAL FOR CHAPTER 3

7A Reagents and Solvents

Solvents Tetraglyme was distilled under vacuum from sodium and stored under nitrogen over molecular sieve (4A). For others see Section 6A.

Perfluoro-2,4-bisisopropyl-1-azacyclohex-1-ene was prepared by cobalt trifluoride fluorination of perfluoro-2,4-bisisopropylpyridine and kindly donated by Dr. M.J. Silvester.

Perfluorocyclo-butene[185] and -pentene[186] were prepared by the departmental technical facility according to literature methods.

Perfluoroheteroaromatics were prepared by the departmental technical facility according to the literature methods[187-191].

Pentafluoronitrobenzene was prepared by nitration of pentafluorobenzene according to the literature method[192].

Perfluoro-1-methyl-1,3-diazacyclopent-2- and -3-ene were prepared by the method outlined in 6.B.2.

7B Observable Nitranions

7B.1 The perfluoro-3-methyl-1,3-diazacyclopentane anion (162)

7B.1.A Preparation of (162)

A mixture containing (64) (0.2 g, 0.8 mmol), caesium fluoride (0.5 g, 3.4 mmol), and [$^2H_3$]acetonitrile (1 ml) was stirred at ambient temperature for *ca*. 30 s. The ^{19}F n.m.r. spectrum of the mixture showed only dimer (159). However, after the mixture had been stirred for a further 72 h a pale yellow colour was observed and the ^{19}F n.m.r. spectrum of the mixture showed only the perfluoro-3-methyl-1,3-diazacyclopentane anion (162). Spectrum No. 6. Variable temperature studies on the solution containing (162) showed no significant changes between 233 and 323 K.

7B.1.B Reaction of (162) with bromine

Addition of a drop of bromine to a sample of a solution of (162) in an n.m.r. tube caused the spectrum to collapse instantly showing a mixture of dimer (159) and another compound, probably 1-bromo-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (188). Spectrum No. 7.

7B.2 The perfluoro-2,4-bisisopropyl-1-azacylopentane anion (190)

7B.2.A Preparation of (190)

A mixture containing perfluoro-2,4-bisisopropyl-1-azacyclohex-1-ene (189) (0.6 g, 1.1 mmol), caesium fluoride (∿1 g) and tetraglyme (1 ml) was stirred overnight at ambient temperature to give a pale yellow solution. The ^{19}F n.m.r. of the mixture showed only anion (190). Spectrum No. 8.

7B.2.B Reaction of (190) with iodomethane

Iodomethane (0.2 g, 1.4 mmol) was added to the stirred solution of (190) and after stirring overnight at room temperature volatile material was transferred under vacuum to a trap cooled in liquid air. The resultant liquid (0.4 g) was shown by g.l.c.-m.s. (Column K, 150°C) to consist of iodomethane and azacyclohexene (189) only.

7C Reactions of anion (162)

7C.1 With Alkyl halides

7C.1.A Benzyl bromide

A mixture containing (64) (1.4 g, 6.7 mmol), caesium fluoride (1.6 g, 10.3 mmol) and benzyl bromide (1.1 g, 6.1 mmol), in acetonitrile (3 ml) was stirred at room temperature for 41 h. Volatile material was transferred under vacuum to a trap cooled in liquid air. G.l.c. (Column K, 150°C) showed only one product. A sample was separated from the solvent by preparative-scale g.l.c. (Column K, 150°C) and shown to be 1-benzyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane. [Found C, 39.1; H, 1.7; N, 8.1 %. $C_{11}H_7F_9N_2$ requires C, 39.0; H, 2.1; N, 8.3 %] Spectra No. 9.

7C.1.B With Allyl Iodide

A mixture containing (64) (7.7 g, 33.8 mmol), caesium fluoride (7.0 g, 46 mmol) and allyl iodide (5.7 g, 33.8 mmol) in sulpholane (15 ml) was stirred at 30°C for 6 h. Volatile material (9.6 g, 99%) was transferred under vacuum to a trap cooled in liquid air. G.l.c. (Column K, 90°C) showed it to be pure product, identified as 1-allyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane. [Found: C, 29.4; H, 2.1; N, 9.9 %. $C_7H_5F_9N_2$ requires C, 29.2; H, 1.7; N, 9.7 %]. Spectra No. 10.

7C.1.C With Trityl chloride

Compound (64) (1.2 g, 5.2 mmol), caesium fluoride (1.4 g, 9.1 mmol), and tetraglyme (5 ml) were stirred for 10 minutes at room temperature and a pale yellow colour, possibly due to anion (162) was observed. Trityl chloride (2.2 g, 8.1 mmol) was added and the mixture was stirred at ambient temperature overnight. Volatile material was transferred under vacuum to a trap cooled in liquid air to give a liquid identified by g.l.c.-m.s. (Column A, 50°C) as dimer (159) (48% yield).

7C.1.D With trifluoroiodomethane

Compound (64) (3.3 g, 14.4 mmol), caesium fluoride (2.3 g, 15.1 mmol), trifluoroiodomethane (4.7 g, 24 mmol), and acetonitrile (5 ml) were sealed in a carius tube and shaken at room temperature for 67¼ hours. Volatiles were transferred under vacuum to a trap cooled in liquid air and trifluoroiodomethane was allowed to evaporate. The lower layer of the remaining 2-phase mixture was separated and shown by ^{19}F n.m.r. to be dimer (159).

7C.2 With F-cycloalkenes

7C.2.A F-cyclobutene

7C.2.A.1 Equimolar mixture

A mixture containing (64) (2.3 g, 10 mmol), caesium fluoride (0.6 g, 3.6 mmol), and sulpholane (10 ml) was stirred at 50°C for 24 h under an atmosphere of perfluorocyclobutene (1.6 g, 10 mmol). Volatile material was transferred under vacuum to a trap cooled in liquid air. After removal of recovered perfluorocyclobutene (0.5 g) the lower layer (2.50 g) was isolated and shown by g.l.c. (Column K, 110°C) to contain two components. Separation by preparative scale g.l.c. (Column K, 100°C) gave perfluoro-1-(3-methylimidazolidin-1-yl)cyclobut-1-ene (200) 26%). [Found: C, 24.6; F, 68.0; N, 7.3 %. $C_8F_{14}N_2$ requires C, 24.6; F, 68.2; N, 7.2 %]. Spectra No. 11; and perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)cyclobut-1-ene (202) (37%) b.p. 179 - 181°C. [Found: C, 23.15; F, 67.3; N, 8.8 %: $C_{12}F_{22}N_4$ requires C, 23.3; F, 67.6; N, 9.0 %]. Spectra No. 12.

7C.2.A.2 Excess of (64)

A mixture containing (64) (3.8 g, 16.8 mmol), caesium fluoride (0.5 g, 3.3 mmol), and sulfolane (5 ml) was stirred under an atmosphere of perfluorocyclobutene (1.3 g, 8.4 mmol) at 50°C for 24 h. Volatile material was transferred under vacuum to a trap cooled in liquid air and after removal of unchanged cyclobutene (0.3 g) the lower layer (3.8 g) was isolated and shown by g.l.c. (Column K, 150°C) to contain three components. Separation by preparative scale g.l.c. gave dimer (159) (4.2%), (200) (4.2%) and (202) (65.8%).

7C.2.B F-cyclopentene

7C.2.B.1 Equimolar mixture

A mixture containing compound (64) (2.6 g, 11 mmol), caesium fluoride (0.56 g, 3.6 mmol), and sulpholane (10 ml) was stirred at 50°C for 24 h under an atmosphere of perfluorocyclopentene (2.4 g, 11.0 mmol). Volatile material was transferred under vacuum to a trap cooled in liquid air. After removal of unchanged perfluorocyclopentene (1.0 g), the lower layer (3.0 g) was isolated and shown by g.l.c. (Column K, 180°C) to contain two components. Separation by preparative scale g.l.c. (Column K, 150°C) gave _perfluoro-1-(3-methylimidazolidin-1-yl)cyclopent-1-ene_ (201) (60%), b.p. 123 - 125°C. [Found: C,24.5; F, 68.7; N, 6.4 %; $C_9F_{16}N_2$ requires C, 24.5; F, 69.1; N, 6.3 %: Spectra No. 13; and _perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)-cyclopent-1-ene_ (203) (1%).

7C.2.B.2 Excess (64)

A mixture containing (64) (4.0 g, 17.5 mmol) caesium fluoride (1.9 g, 6.6 mmol), and sulfolane (20 ml) was stirred at 50°C for 18.5 h under an atmosphere of perfluorocyclopentene (2.3 g, 14.7 mmol). Volatile material was transferred under vacuum to a trap cooled in liquid air. The lower layer (5.6 g) was shown by g.l.c. (Column K, 140°C) to consist of two components. Separation by preparative scale g.l.c. gave (201) (20%) and perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)cyclopent-1-ene (203) (16%). [Found: C, 23.1; F, 68.6; N, 8.2 %: $C_{13}F_{24}N_4$ requires C, 23.3; F, 69.2; N, 8.4 %]. Spectra No. 14.

7C.2.C F-cyclohexene

7C.2.C.1 At 50°C

A mixture of compound (64) (4.7 g, 20.6 mmol), caesium fluoride (0.6 g, 3.9 mmol), perfluorocyclohexene (2.7 g, 10.3 mmol) and sulfolane (10 ml) were stirred at 50°C for 67 hours. Volatile material was transferred under vacuum to a trap cooled in liquid air and the lower layer (4.8 g) was shown by g.l.c. (Column K, 80°C) to consist of four components. These were separated by preparative scale g.l.c. and shown by ^{19}F n.m.r. to be unchanged (64) (3.9%) (two isomers), perfluorocyclohexane and dimer (159) (63%).

7C.2.C.2 At 100°C

A mixture containing (64) (3.4 g, 15 mmol), caesium fluoride (1.0 g, 6.6 mmol), sulfolane (10 ml), and perfluorocyclohexene (2.0 g, 7.5 mmol) was heated at 100°C for 67 h in a Carius tube. Volatile material was transferred under vacuum into a trap cooled in liquid air. The lower layer (3.9 g) was isolated and shown by g.l.c. (Column K, 140°C) to consist of five components. Separation by preparative scale g.l.c. (Column K, 150°C and Column A, 40°C) gave unchanged perfluorocyclohexene (0.7 g), dimers (159) (1.8 g) and (169) (0.4 g), and perfluoro-1-(3-methylimidazolidin-1-yl)-cyclohex-1-ene (204) (26%). b.p. 143 - 145°C. [Found: C, 24.4; F, 70.1; N, 6.0 %. $C_{10}F_{18}N_2$ requires C, 24.5; F, 69.8; N, 5.7 %]. Spectra No. 15.

7C.3 With perfluoroaromatics

7C.3.A With F-pyridazine

7C.3.A.1 CsF-catalysed reaction at 85°C

A mixture containing (64) (6.3 g, 27.6 mmol), tetrafluoropyridazine (2.0 g, 13.2 mmol), caesium fluoride (∿1 g), and acetonitrile (3 ml) was stirred at 85°C for 5 h. Volatile material was transferred under vacuum into a trap cooled in liquid air and the lower layer (8.2 g) was isolated and shown to be predominantly one compound by g.l.c. Preparative scale g.l.c. (Column F, 200°C) gave perfluoro-3,5-bis-(3-methylimidazolidin-1-yl)pyridazine (214) (92%). [Found: C, 23.9; F, 62.0; N, 13.6 %. $C_{12}F_{20}N_6$ requires C, 23.7; F, 62.5; N, 13.8 %]. Spectra No. 16.

7C.3.A.2 CsF-catalysed reaction at room temperature

A mixture containing (64) (3.6 g, 15.8 mmol), tetrafluoropyridazine (1.2 g, 7.9 mmol), caesium fluoride (∿1 g), and acetonitrile (3 ml) was stirred at room temperature for 22 h. Volatile material was transferred under vacuum into a trap cooled in liquid air and the lower layer (4.7 g, 99%

recovery) was shown by g.l.c.-m.s. (Column F, 160°C) and ^{19}F n.m.r. spectroscopy to be (214) (83%).

7C.3.A.3 KF-catalysed reaction at room temperature

A mixture containing (64) (3.8 g, 16.6 mmol), tetrafluoropyridazine (1.30 g, 8.6 mmol), potassium fluoride (∿1 g), and acetonitrile (4 ml) was stirred at room temperature for 17 h. Volatile material was transferred into a trap cooled in liquid air to leave a white solid from which sublimation under vacuum gave perfluoro-4,5-bis-(3-methylimidazolidin-1-yl)pyridazine (215) (2.0 g, 71%). m.p. 76 - 78°C. [Found: C, 23.4; F, 62.9; N, 13.9 %. $C_{12}F_{20}N_6$ requires C, 23.68; F, 62.5; N, 13.8 %]. Spectra No. 17. The lower layer of the volatile component was isolated and shown by g.l.c.-m.s. (Column K, 110°C) to be dimer (159) (1.65 g).

7C.3.A.4 CsF-catalysed isomerisation of (215)

A mixture containing (215) (0.2 g, 0.4 mmol), caesium fluoride (∿0.5 g), and acetonitrile (1 ml) was stirred at 70°C for 4 h. Volatile material was transferred under vacuum into a trap cooled in liquid air and added to water. The lower layer (0.2 g, 67%) was isolated and shown by ^{19}F n.m.r. spectroscopy to be (214).

7C.3.B F-pyrimidine

7C.3.B.1 KF-catalysed reaction at room temperature

A mixture containing (64) (3.3 g, 14.5 mmol), tetrafluoropyrimidine (1.2 g, 8.2 mmol), potassium fluoride (∿1 g), and acetonitrile (3 ml) were stirred under nitrogen at room temperature for 16 h. Volatile material was transferred under vacuum into a trap cooled in liquid air and the lower fluorocarbon layer (3.5 g) was isolated. Separation by preparative scale g.l.c. (Column F, 170°C) gave perfluoro-4-(3-methylimidazolidin-1-yl)pyrimidine (216) (11%). [Found: F, 59.4; N, 15.2 %. $C_8F_{12}N_4$ requires F, 60.0; N, 14.7 %]; Spectra No. 18 and perfluoro-4,6-bis-(3-methylimidazolidin-1-yl)pyrimidine (217) (51%). [Found: C, 23.5; F, 61.7; N, 13.8 %. $C_{12}F_{20}N_6$ requires C, 23.7; F, 62.5; N, 13.8 %]; Spectra No. 19.

7C.3.B.2 CsF-catalysed reaction at 58°C

A mixture containing tetrafluoropyrimidine (2.9 g, 18.8 mmol), caesium fluoride (∿1 g), acetonitrile (7 ml), and (64) (7.7 g, 33.5 mmol) was stirred at 58°C for 4¼ h. Volatiles were transferred under vacuum at room temperature into a trap cooled in liquid air to leave a white solid. Sublimation under vacuum gave perfluoro-2,4-bis-(3-methylimidazolidin-1-yl)pyrimidine (219) (6.6 g, 63%). m.p. 123 - 125°C. [Found: C, 23.8; F, 62.0; N, 13.6 %. $C_{12}F_{20}N_6$ requires C, 23.7; F, 62.5; N, 13.8 %].

The volatile components of the product mixture were poured into water and the lower layer (2.4 g) was isolated and separated by preparative scale g.l.c. (Column K, 100°C) to give perfluoro-2-(3-methylimidazolidin-1-yl)pyrimidine (218) 18%). [Found: C, 25.3; F, 60.4; N, 14.6 %. $C_8F_{12}N_4$ requires C, 25.3; F, 60.0; N, 14.7 %]. Spectra No. 21.

7C.3.B.3 CsF-catalysed isomerisation of (217)

A mixture containing (217) (0.4 g, 0.7 mmol), caesium fluoride (∿0.5 g), and acetonitrile (1 ml) were stirred at room temperature for 22 h. Volatile material was transferred under vacuum into a trap cooled in liquid air. The fluorocarbon product (0.2 g, 49%) was isolated and shown to be (219) by ^{19}F n.m.r.

7C.3.C Trifluoro-1,3,5-triazine

A mixture containing (64) (3.8 g, 16.7 mmol), trifluoro-1,3,5-triazine (1.0 g, 7.4 mmol), caesium fluoride (1.1 g, 7.2 mmol), and acetonitrile (5 ml) was stirred under nitrogen at 80°C for 4 h. Volatile material was transferred under vacuum into a trap cooled in liquid air, and acetonitrile and unchanged trifluoro-1,3,5-triazine were removed by molecular distillation to leave a white solid. Vacuum sublimation (120 - 122°C, 0.004 mm Hg) gave perfluoro-2,4,6-tris-(3-methylimidazolidin-1-yl)-1,3,5-triazine (220) (3.0 g, 66%). m.p. 164 - 166°C. [Found: C, 22.1; F, 63.0. $C_{15}F_{27}N_9$ requires C, 22.0; F, 62.5 %]. Spectra No. 22.

7C.3.D Pentafluoronitrobenzene

Compound (64) (2.3 g, 10.3 mmol) was added to a stirred mixture of pentafluoronitrobenzene (1.8 g, 8.5 mmol), caesium fluoride (2.8 g, 18.8 mmol) and tetraglyme (5 ml). An exothermic reaction occurred and a brown gas was evolved.

The mixture was stirred overnight and volatiles were transferred under vacuum to a trap cooled in liquid air. The lower layer (3.0 g, 82% recovery) was shown by g.l.c. (Column F, 150°C) to consist of two components. Separation by preparative scale g.l.c. gave perfluoro-(3-methylimidazolidin-1-yl)benzene (221) (52%). [Found: C, 29.2; F, 63.9; N, 7.0 %. $C_{10}F_{14}N_2$ requires C, 29.0; F, 64.2; N, 6.7 %].

Spectra No. 23 and an inseparable mixture of perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)benzene (222) and perfluoro-1,4-bis-(3-methylimidazolidin-1-yl)benzene (223) (30%). [Found: C, 26.2; F, 64.6; N, 8.6 %. $C_{14}F_{22}N_4$ requires C, 26.1; F, 65.1; N, 8.7 %]. Spectra No. 24.

7C.4 Miscellaneous

7C.4.A Reaction with sulphur

7C.4.A.1 Reaction at room temperature

Compound (64) (3.1 g, 13.7 mmol), caesium fluoride (2.1 g, 13.6 mmol), sulphur (0.6 g, 18.1 mmol), and acetonitrile (3 ml) were stirred at room temperature for 50¼ hours. Volatile material was transferred under vacuum to a trap cooled in liquid air and the lower fluorocarbon layer (2.7 g) was separated and shown by g.l.c.-m.s. (Column K, 90°C) to be dimer (159).

7C.4.A.2 Reaction at 70°C

Dimer (159) (1.7 g, 3.8 mmol), caesium fluoride (1.5 g, 9.9 mmol), sulphur (0.8 g, 25 mmol), and acetonitrile (5 ml) were stirred at 70°C for 66 hours. Volatile material was transferred under vacuum to a trap cooled in liquid air and the lower fluorocarbon layer was shown by g.l.c.-m.s. (Column K, 150°C) to be unchanged (159).

7C.4.A.3 Reaction at 150°C

Compound (64) (1.8 g, 7.9 mmol), caesium fluoride (1.4 g, 9 mmol), sulphur (0.4 g, 13.5 mmol), and acetonitrile were heated at 150°C for 66 hours in a Carius tube. Volatile material was transferred under vacuum to a trap cooled in liquid air to leave a black involatile residue.

The volatile component was allowed to warm up to room temperature and a gas evolved was collected in a bulb and shown by comparison of infrared spectrum with the literature[193] to be silicon tetrafluoride. The remaining material was shown by infrared spectroscopy to be acetonitrile.

7C.4.B Reactions with mercuric halides

7C.4.B.1 Mercuric chloride

A mixture of (64) (5.1 g, 22.5 mmol), caesium fluoride (7.0 g, 45.8 mmol), mercuric chloride (3.0 g, 11.2 mmol), and acetonitrile (5 ml) were stirred at room temperature for 24 hours. Volatile components were transferred under vacuum to a trap cooled in liquid air leaving a white solid material. ^{19}F n.m.r. analysis of the volatiles showed only dimer (159) in the lower layer. Attempted vacuum sublimation of the solid material resulted only in charring.

7C.4.B.2 With mercury (II) iodide

A mixture of compound (64) (2.5 g, 11 mmol), caesium fluoride (2.4 g, 15.8 mmol) and acetonitrile (5 ml) were stirred at room temperature for two hours. Mercury (II) iodide (2.0 g, 4.5 mmol) was added and the mixture was stirred for a further 40 h. Volatile material was transferred under vacuum to a trap cooled in liquid air and separation of the lower layer gave dimer (159) (82% yield).

7C.4.C Reaction with phosgene

A mixture of compound (64) (3.8 g, 16.7 mmol), caesium fluoride (5.0 g, 21.8 mmol), and acetonitrile (4 ml) were stirred at room temperature in an atmosphere of phosgene (0.6 g, 6.1 mmol) for 5½ d. Volatile material was transferred under vacuum to a trap cooled in liquid air and unchanged phosgene was removed by distillation. The lower layer (3.1 g) of the remaining liquid was separated and shown by ^{19}F n.m.r. to be dimer (159).

7C.4.D Reaction with acetyl chloride

A mixture of compound (64) (4.2 g, 18.3 mmol), caesium fluoride (3.2 g, 21.6 mmol), and acetonitrile (3 ml) were stirred at room temperature for 30 m and acetyl chloride (1.4 g, 18.1 mmol) in acetonitrile (5 ml) was added dropwise over 30 m. After stirring overnight the volatile components were transferred under vacuum to a trap cooled in liquid air and the lower layer (3.1 g) was isolated and shown by g.l.c. (Column K, 110°C) and infrared spectroscopy to be dimer (159).

7C.4.E Reaction with chlorine

A mixture of compound (64b) (2.7 g, 11.8 mmol), caesium fluoride (2.1 g, 14.1 mmol) and acetonitrile (3 ml) were stirred at room temperature in an atmosphere of chlorine (10.7 g, 10.4 mmol) for 24 h. Volatile material was transferred under vacuum to a trap cooled in liquid air and the lower layer was isolated. ^{19}F n.m.r. of the upper layer showed that no fluorocarbon products were present. The lower layer (1.9 g) was shown by g.l.c. (Column K, 125°C) to be a two-component mixture. Separation by preparative scale g.l.c. gave dimer (159) (65%) and another compound which was too unstable for further analysis.

CHAPTER 8

EXPERIMENTAL FOR CHAPTER 4

8A Reagents and Solvents

Solvents Methanol was dried over sodium and then distilled under nitrogen and used immediately. For other solvents see previous Chapter.

Ozone was generated from oxygen using a Towers ozone generator.

8B.1 Cycloalkene derivatives

8B.1.A Reactions with methoxide

8B.1.A.1 Reaction of (200)

Sodium (0.3 g, 13.1 mmol) was dissolved in methanol and, after cooling, perfluoro-1-(3-methylimidazolidin-1-yl)-cyclobut-1-ene (200) (2.0 g, 5.1 mmol) was added. The mixture was stirred at room temperature for 21 h. Volatile components were transferred under vacuum to a trap cooled in liquid air and methanol was removed by distillation. Preparative scale g.l.c. (Column K, 120°C) of the remaining liquid gave methanol and 1-(perfluoro-3-methyl-1-imidazolidin-1-yl)-3,3-difluoro-2,4,4-trimethoxycyclobutene (224), identified by comparison of n.m.r. and mass spectra with an authentic sample.

8B.1.A.2 Reaction of (201)

Sodium (0.1 g, 3.9 mmol) was dissolved in methanol (2 ml) and, after cooling, perfluoro-1-(3-methylimidazolidin-1-yl)cyclopent-1-ene (201) (0.1 g, 0.2 mmol) was added and the mixture stirred at room temperature for three days. Volatile components were then transferred under vacuum to a trap cooled in liquid air and shown by g.l.c.-m.s.

(Column K, 145°C) and ^{19}F n.m.r. to contain only methanol and 1-(perfluoro-3-methylimidazolidin-1-yl)-3,3,4,4-tetrafluoro-2,5,5-trimethoxycyclopent-1-ene (225) by comparison with authentic spectra. (Section 8B.1.A.4).

8B.1.A.3 Reaction of (202)

Sodium (0.3 g, 12.2 mmol) was dissolved in methanol (15 ml) and, after cooling, perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclobut-1-ene (202) (1.7 g, 2.7 mmol) was added and the mixture stirred under reflux for 20 h. Volatile components were transferred under vacuum to a trap cooled in liquid air and the lower layer (1.4 g) was isolated and shown by g.l.c. (Column K, 140°C) to contain two components. Separation by preparative scale g.l.c. (Column K, 140°C) gave 1-trifluoromethyl-5,5-difluoro-2,4,4-trimethoxy-1,3-diazacyclopent-2-ene (226a) or 1-trifluoromethyl-5,5-difluoro-2,2,4-trimethoxy-1,3-diazacyclopent-3-ene (226b) (28%). [Found: C, 31.6; H, 3.6; F, 36.4; N, 10.2 %. $C_7F_5H_9N_2O_3$ requires C, 31.8; H, 3.4; F, 36.0; N, 10.6 %]. Spectra No. 25, and <u>1-(perfluoro-3-methylimidazolidin-1-yl)-3,3-difluoro-2,4,4-trimethoxycyclobut-1-ene</u> (224) (45%). [Found: C, 31.2; H, 2.3; F, 48.6; N, 6.6 %. $C_{11}H_9F_{11}N_2O_3$ requires C, 31.0; H, 2.1; F, 49.0; N, 6.5 %]. Spectra No. 26.

8B.1.A.4 Reaction of (203)

Sodium (0.5 g, 21.7 mmol) was dissolved in methanol (10 ml) and, after cooling, perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclopent-1-ene (203) (2.0 g, 3 mmol) was added and the mixture stirred under reflux for 20 h. Volatile components were transferred under vacuum to a trap cooled in liquid air and methanol was subsequently removed by distillation. The resulting liquid was shown by g.l.c. (Column F, 200°C) to contain two components which were separated by preparative scale g.l.c. (Column K, 200°C) to give methanol and 1-(perfluoro-3-methylimidazolin-1-yl)-3,3,4,4-tetrafluoro-2,5,5-trimethoxycyclopent-1-ene (225) (75%). [Found: C, 30.5; H, 1.6; F, 52.2; N,6.1 %. $C_{12}H_9F_{13}N_2O_3$ requires C, 30.3; H, 1.9; F, 51.9; N, 5.9 %]. Spectra No. 27.

8B.1.B Further Chemistry of (202)

8B.1.B.1 Reaction with diazomethane

Diazomethane ether azeotrope, prepared by the literature method[183], was added to compound (202) (0.5 g, 0.8 mmol) and stirred at room temperature for 168 h. After removal of ether analysis of the remaining liquid (0.4 g) by n.m.r. showed it to be unchanged (202).

8B.1.B.2 Pyrolysis reactions

8B.1.B.2.A Static

(a) Compound (202) (0.7 g, 1.2 mmol) was sealed in an n.m.r. tube and heated at 300°C for 24 hours. ^{19}F n.m.r. analysis of the slightly charred products showed only unchanged compound (202).

(b) Repeated reactions at 350°C for one hour gave no change in n.m.r. spectrum with gradual charring. Heating a sample of compound (202) at 400°C for one hour gave complete decomposition.

8B.1.B.2.B Flow over CsF

Compound (202) (1.4 g, 2.3 mmol) was passed in a stream of nitrogen through a silica tube packed with caesium fluoride at 515°C. No liquid products were isolated from the two liquid air cooled traps and all the starting material was found to have charred and stuck to the fluoride packing.

8B.1.B.2.C Flash pyrolysis

Flash pyrolysis of compound (202) (1.3 g, 2.2 mmol) at 500°C and 0.001 mm Hg through a quartz tube gave 1.2 g (90%) of unchanged starting material.

8B.1.B.3 Oxidation

Compound (202) (1.0 g, 1.7 mmol) was dissolved in acetone (10 ml) and added dropwise to a solution of potassium permanganate (0.3 g, 2 mmol) in acetone (30 ml). The mixture was stirred at room temperature for 1¾ h and then added to water and decolourised with SO_2. After removing acetone on a rotary evaporator, the fluorocarbon remaining was extracted with 4 x 20 ml of ether and the ether extracts combined and reduced to ∿20 ml on the rotary evaporator. After drying with P_2O_5 and decanting, the remainder of the ether was removed and diazomethane ether azeotrope[183] was added until a permanent yellow colour was obtained. After stirring for ½ hour excess diazomethane and ether were removed by distillation. Volatile material was transferred from the remaining liquid to a trap cooled in liquid air to give a two phase mixture. The lower layer (0.5 g) was isolated and shown by ^{19}F n.m.r. to be unchanged (202) (47%).

8B.1.B.4 Fluorination

Fluorination of compound (202) (1.9 g, 3.2 mmol) by cobalt trifluoride at 200°C gave only gaseous products.

8B.2 Perfluoroaryl derivatives

8B.2.A Attempted preparation of a stable cyclobutadiene

8B.2.A.1 Reaction of (214) with dimethylamine

Dimethylamine (2.3 g, 52.2 mmol) was transferred under vacuum onto a mixture of perfluoro-3,5-bis(3-methylimidazolidin-1-yl)pyridazine (214) (0.8 g, 1.3 mmol) in ether (3 ml) at -196°C and sealed in a glass tube. The tube was allowed to warm to room temperature with shaking and then unreacted amine and diethyl ether were removed by vacuum transfer. Water was added and then extracted with 4 x 20 ml chloroform. After drying with $MgSO_4$ and filtering chloroform was removed to leave a yellow oil. Vacuum micro-distillation gave a yellow solid (0.6 g, 69% yield) identified as 3,5-bis(dimethylamino)-4,6-bis(perfluoro-3-methylimidazolidin-1-yl)pyridazine (239). [Found: C, 29.5; H, 1.9; F, 51.7; N, 17.2 % $C_{16}H_{12}F_{18}N_8$ requires C, 29.2; H, 1.8; F, 52.0; N, 17.0 %]. Spectra No. 28.

8B.2.A.2 Photolysis of (239)

Compound (239) (0.1 g, 0.1 mmol) and 1,1,2-trichlorotrifluoroethane (2 ml) were degassed and sealed in a quartz tube. After irradiation by a high pressure ultraviolet lamp for six hours the solvent was removed under vacuum and the remaining yellow solid was dissolved in $CDCl_3$ and identified by n.m.r. as unchanged starting material.

8B.2.A.3 Pyrolysis of (239)

(a) Flash vacuum pyrolysis of compound (239) (0.2 g, 0.3 mmol) at 600°C and 0.005 mm Hg through a quartz tube packed with platinum foil gave recovered (239) (100%).

(b) Flash vacuum pyrolysis of compound (239) (0.3 g, 0.5 mmol) at 700°C and 0.005 mm Hg through a quartz tube packed with platinum foil gave gaseous products and 0.02 g of a material shown by ^{19}F n.m.r. to be a complex mixture.

8B.2.B Photochemical and Thermal Isomerisation Reactions

8B.2.B.1 Photolysis. (a) of (215)

Perfluoro-4,5-bis(3-methylimidazolidin-1-yl)pyridazine (215) (0.4 g, 0.7 mmol) was sealed in a quartz tube at 0.003 mm Hg and irradiated at 254 nm using a high pressure mercury lamp for 280 h. The product was recovered from the tube and shown by ^{19}F n.m.r. to be unchanged (215) (0.3 g, 85%).

(b) of (214) Perfluoro-4,6-bis(3-methylimidazolidin-1-yl)-pyridazine (214) (0.4 g, 0.7 mmol) was sealed in a quartz tube at 0.004 mm Hg and irradiated at 254 nm using a high pressure mercury lamp for 283 h. The product was recovered from the tube and shown by ^{19}F n.m.r. to be unchanged starting material (0.3 g, 75%).

8B.2.B.2 Pyrolysis of (215)

Samples of (215) were sealed in 10 ml Carius tubes and heated at the temperatures and for the times shown in the Table. Material was recovered and analysed by ^{19}F n.m.r.

(215)	Reaction temperature /°C	Reaction time /h	Product g/%
0.6 g, 1.0 mmol	150	72	(215) (0.5 g, 93%)
0.5 g, 0.8 mmol	200	3	(215) (0.5 g, 91%)
0.4 g, 0.7 mmol	250	6	(215) (0.4 g, 92%)
1.4 g, 2.3 mmol	350	16	Carbonaceous Material

8B.3 Attempted polymerisation of 1-allyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (246)

8B.3.A Homopolymerisation (a) Peroxide-induced

Compound (246) (0.8 g, 2.8 mmol) and ditertiarybutyl peroxide (0.1 g, 0.3 mmol) were degassed and sealed in a pyrex tube. After heating at 140°C for 23 h vacuum transfer gave 0.6 g of a liquid shown by g.c. retention time not to be starting material. No acetone or butanol were found in the product mixture indicating that the reaction was not straight forward. Since the desired high molecular weight material was not obtained this reaction was not investigated further.

(b) γ-ray induced

Compound (246) (0.2 g, 1.1 mmol) was degassed and sealed in a pyrex tube (vol. 10 ml) and irradiated using a ^{60}Co source for 5 d. The liquid recovered was identified by comparison of infrared spectra as unchanged (214) (100% recovery).

8B.3.B Copolymerisation (a) With methyl methacrylate

Compound (246) (1.8 g, 6.1 mmol) and methyl methacrylate (0.6 g, 6.1 mmol) were degassed and sealed in a 10 ml pyrex tube. After γ-ray irradiation for 91 h vacuum transfer gave 1.7 g of unchanged (246) (96% recovery) and a residue of white polymeric material.

(b) With styrene

Compound (246) (1.3 g, 4.7 mmol) and styrene (0.5 g, 4.9 mmol) were degassed and sealed in a 10 ml pyrex tube. After γ-ray irradiation for 91 h vacuum transfer gave 1.3 g of unchanged (246) (96% recovery) and a residual white polymeric material.

(c) With 1,1-difluoroethene

Degassed compound (246) (1.0 g, 3.6 mmol) and vinylidene fluoride (0.3 g, 4.4 mmol) were sealed in a 10 ml pyrex tube. After γ-ray irradiation for 34 d an involatile, sticky material (1.0 g) was isolated and shown to be probably an oligomer of (246). Spectra No. 29.

CHAPTER 9

EXPERIMENTAL FOR CHAPTER 5

9A Reagents and solvents

Solvents were dried as described previously.

p-Nitrobenzyltriphenylphosphonium bromide was prepared by the literature method[194] and dehydrobrominated in situ using potassium carbonate to generate p-nitrobenzylidene triphenyl phosphorane[195].

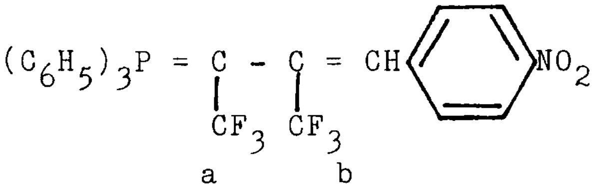
9-Fluorenylidenetriphenylphosphine was prepared by the literature method[196].

9B Attempted preparation of polyfluoroalkylated cyclopentadiene derivatives

9B.1 Via p-nitrobenzylidene triphenylphosphorane (274)

9B.1.A Reaction of (274) with hexafluorobut-2-yne at 0°C[197]

Potassium carbonate (0.8 g) was added to a stirred solution of p-nitrobenzylphenylphosphonium bromide (1.8 g, 3.8 mmol) in 20 ml ether at 0°C. The mixture was stirred in an atmosphere of hexafluorobut-2-yne (3.9 g, 24 mmol) for 24 h at 0°C. Volatile material was distilled from the mixture to leave a solid residue. Ether (10 ml) and water (5 ml) were added and the ether phase isolated and dried with magnesium carbonate. The solution was filtered and the ether removed to leave red crystals shown to be 1,2-bis(trifluoromethyl)-3-(4-nitrophenyl)propanyliden-1-enyl triphenylphosphorane (278) (1.4 g, 66%, m.p. 60 - 61°C. [Found: C, 64,4; H, 3.6; N, 2.8; $C_{29}H_{20}F_6NO_2P$ requires C, 64.4; H, 3.6; N, 2.5 %]; δ_F 60.4 (3F, d, J = 7.5 Hz, F_a), 66.0 (3F, s, F_b); δ_H 7.5 - 6.8; δ_P -27.5.



(278)

9B.1.B <u>Reaction of (278) with hexafluoroacetone</u>[197]

Ylide (278) (1.68 g, 3 mmol), ether (5 ml) and hexafluoroacetone (0.8 g, 4.6 mmol) were sealed in a Carius tube and reacted for 36 h at room temperature. Volatile material was removed by distillation to leave an oily residue. Microdistillation (100°C, 0.001 mm Hg) gave an oil shown to be 1,1,1-trifluoro-2,3,4-tris(trifluoromethyl)-5-(4-nitrophenyl)-penta-2,4-diene (0.4 g, 31% yield). (M^+ - NO_2, 401; M^+ - CF_3, 378; $C_{14}H_5F_{12}$ NO_2 requires M 447). δ_F 59.2 (6F), 60.5 (3F), 65.0 (3F), 66.5 (6F), and 68.7 (3F).

9B.1.C <u>Hydrolysis of (278) with hydrochloric acid</u>[197]

Ylide (278) (1.3 g, 2.3 mmol) was dissolved in ether (10 ml) and concentrated hydrochloric acid was added dropwise at room temperature with stirring until the red colour disappeared. The ether phase was separated and dried over P_2O_5. The ether phase was decanted and then the ether was evaporated and the residue sublimed (100°C, 0.001 mn Hg) to give (Z)-3-trifluoromethyl-1,1,1-trifluoro-4-(4-nitrophenyl) but-2-ene (0.4 g, 56%). [Found: M^+, 299. $C_{11}H_7F_6NO_2$ requires M 299]; δ_F 63.3 (3F, m, F_a) and 66.6 (3F, q, J = 7.5 Hz, F_b).

9B.1.D Reaction of (278) with hexafluorobut-2-yne at 70°C

The ylide (278) was generated by reaction of potassium carbonate (0.26 g, 1,9 mmol) with p-nitrobenzyltriphenylphosphonium bromide (1.8 g, 3.8 mmol) in acetonitrile (100 ml). Reaction was carried out at 70°C for 24 h at atmospheric pressure in the presence of molecular sieve 4A (6 g) to absorb water produced in the reaction. Hexafluoro-2-butyne (249) was introduced from a flexible reservoir. ^{19}F n.m.r. spectroscopy of the resulting solution showed a complex mixture which was not further analysed.

9B.1.E Reaction of (274) with (249) in a sealed tube

Potassium carbonate (0.26 g, 1.9 mmol), p-nitrobenzyltriphenylphosphonium bromide (1.8 g, 3.8 mmol), acetonitrile (32 ml) and compound (249) (1.49 g) were sealed in a Carius tube and shaken vigourously for 48 h. ^{19}F n.m.r. spectroscopy of the solution showed a complex mixture the mass spectrum indicated the presence of the 1 : 1 adduct (278) and 2 : 1 adduct (283).

9B.1.F Reaction of the product from 9B.1.D with (249)

Volatile materials were removed under vacuum from the solution obtained in 9B.1.D and toluene (20 ml) was added to the resulting solid. The solution was sealed in a Carius tube with hexafluoro-2-butyne (1.01 g) and heated at 100°C for 24 h. Analysis of the ^{19}F n.m.r. spectrum showed it to be identical to that obtained in 9B.1.D. A repeat reaction at 150°C for 48 h resulted in decomposition of the starting materials.

9B.1.G Reaction of product from 9B.1.D with hydrochloric acid

Concentrated hydrochloric acid (10 ml) was added dropwise to a solution of the products (0.79 g) from 9B.1.E in ether (50 ml) at room temperature and stirred for 4 h. The organic later was isolated, neutralised using sodium carbonate, and dried ($MgSO_4$). After filtration and removal of ether the residue (0.75 g) was analysed by ^{19}F n.m.r. and shown to be a complex mixture which would not be purified.

9B.1.H Reaction of product from 9B.1.D with hexafluoroacetone

A solution of the product from 9B.1.D in acetonitrile was stirred in an atmosphere of hexafluoroacetone (1.32 g, 9.2 mmol) at 50°C for 48 h. After this time ^{19}F n.m.r. signals due to starting materials were absent. The solvent was removed under vacuum to leave a solid which was distilled under vacuum (90°C, 0.03 mm Hg) to give a yellow oil (0.50 g), shown by ^{19}F n.m.r. to be a complex material. Attempts at purification by column chromatography were unsuccessful.

9C Synthesis of fluorinated alkenes via stabilised phosphorus ylides

9C.1 Synthesis of (288)

p-Nitrobenzyltriphenylphosphonium bromide (4.77 g, 10 mmol), potassium carbonate (2.5 g, 18 mmol) and acetonitrile

(100 ml) were stirred in an atmosphere of hexafluoroacetone (8.6 g, 52 mmol) at 0°C for 12 h. Acetone and unreacted hexafluoroacetone were removed by distillation to leave a residue, careful sublimation of which gave 1,1,1-trifluoro-2-trifluoromethyl-3-(4-nitrophenyl)prop-2-ene (288) (1.7 g, 31% yield) m.p. 52 - 54°C. [Found: C, 42.3; H, 1.5; N, 5.2 % $C_{10}H_5F_6NO_2$ requires C, 42.1; H, 1.7; N, 4.9 %]. Spectra No. 30.

9C.2 Synthesis of (289)

9-Fluorenylidene triphenylphosphorane (1.28 g, 3 mmol) was stirred in dry ether (100 ml) in an atmosphere of hexafluoroacetone (1.0 g, 6 mmol) at room temperature for 48 h. Solvent and recovered hexafluoroacetone were removed by distillation to leave an orange residue. Sublimation twice (50°C, 0.03 mm Hg) gave 1,1,1,3,3,3-hexafluoro-2-fluoren-9-ylidinylpropen-2-ylidene (289) (0.9 g, 95%) m.p. 110 - 112°C. [Found: C, 61.0; H, 2.5; $C_{16}H_8F_6$ requires C, 61.15; H, 2.55]. Spectra No.31.

9C.3 Reactions with fluoride ion

9C.3.A Reaction of (288)

Alkene (288) (0.34 g, 1.2 mmol), caesium fluoride (2.50 g, 16.4 mmol), and tetraglyme (5 ml) were stirred overnight at room temperature. ^{19}F n.m.r. analysis of the solvent showed only alkene (288).

9C.3.B.1 Reaction of (289) with CsF

Alkene (289) (0.13 g, 0.4 mmol), caesium fluoride (∿0.5 g) and tetraglyme (5 ml) were stirred at room temperature for 2 d. ^{19}F n.m.r. analysis of the solvent showed only alkene (289).

9C.3.B.2 Reaction of (289) with TAS-F

Alkene (289) (0.7 g, 2.2 mmol) was dissolved in acetonitrile (3 ml) and a solution of TAS-F (0.1 g) in acetonitrile (0.5 ml) was added. ^{19}F n.m.r. analysis of the solution showed only alkene (289) and decomposition products of TAS-F.

9C.4 Reactions with methoxide

(C.4.A Reaction of (288)

A mixture of alkene (288) (0.9 g, 3.2 mmol), sodium methoxide (1.14 g, 21 mmol), methanol (1 ml) and ether (10 ml) were stirred at room temperature for 2 d. Solvent was removed under vacuum and then water (20 ml) was added to the residue. The organic product was extracted into ether (5 x 50 ml) and the ether fractions combined and dried ($MgSO_4$). After filtering and removal of ether using a rotary evaporator the residue was recrystallised from 60 - 80 petroleum ether to give 1,1,1-trifluoro-2-trifluoromethyl-3-methoxy-3-(4-nitrophenyl)propane (290) (0.31 g, 31% yield). [Found: M^+ 317; $C_{11}H_9F_6NO_3$ requires M 317]; Spectra No. 32.

9C.4.B Reaction of (289)

A mixture of alkene (289) (1.0 g, 3.2 mmol), sodium methoxide (1.16 g, 21.5 mmol), methanol (1 ml) and ether (10 ml) was stirred at room temperature for 2 d. Solvent was removed under vacuum and then water (20 ml) was added to the residue. The organic product was extracted into ether (5 x 50 ml) and the ether fractions combined and dried. After filtering and removal of ether using a rotary evaporator the residue was recrystallised from 60 - 80 petroleum ether to give 9-(1,1,1,3,3,3-hexafluoroisopropyl)-9-methoxyfluorene (292) (0.43 g, 40%). [Found: M^+ 346; $C_{17}H_{12}F_6O$ requires M 346]. Spectra No. 33.

APPENDICES

APPENDIX I

N.M.R. Spectra

1. Perfluoro-1,6-dimethyl-4-methylimino-1,3,6-triazabicyclo-[3.3.0.$^{3.7}$]octane (169) : (^{19}F).
2. N-Trifluoromethyl(perfluoro-1,3-dimethyl-4-methylimino-trihydroimidazolidin-2-yl)methanamine (174) : (^{19}F and ^{1}H).
3. Perfluoro-4-methyl-1,2,5,7-tetraazatricyclo[3.3.1.0.$^{2.6}$]-undec-4-ene (175) : (^{19}F and ^{13}C).
4. 11,11-Dichloro-4-trifluoromethylnonafluoro-1,2,5,7-tetraazatricyclo[3.3.1.0.$^{2.6}$]undec-4-ene (183) : (^{19}F).
5. Unknown : (^{19}F).
6. Perfluoro-3-methyl-1,3-diazacyclopentane anion (162) : (^{19}F)
7. 1-Bromo-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (188) : (^{19}F).
8. Perfluoro-2,4-bisisopropyl-1-azacyclopentane anion (190) : (^{19}F).
9. 1-Benzyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (^{19}F and ^{1}H).
10. 1-Allyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (^{19}F and ^{1}H).
11. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclobut-1-ene (200) : (^{19}F).
12. Perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)cyclobut-1-ene (202) : (^{19}F).
13. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclopent-1-ene (201) : (^{19}F).
14. Perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)cyclopent-1-ene (203) : (^{19}F).

15. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclohex-1-ene (204) : (^{19}F).

16. Perfluoro-3,5-bis-(3-methylimidazolidin-1-yl)pyridazine (204) : (^{19}F).

17. Perfluoro-3,4-bis-(3-methylimidazolidin-1-yl)pyridazine (215) : (^{19}F).

18. Perfluoro-4-(3-methylimidazolidin-1-yl)pyrimidine (216) : (^{19}F).

19. Perfluoro-4,6-bis-(3-methylimidazolidin-1-yl)pyrimidine (217) : (^{19}F).

20. Perfluoro-2,4-bis-(3-methylimidazolidin-1-yl)pyrimidine (219) : (^{19}F).

21. Perfluoro-2-(3-methylimidazolidin-1-yl)pyrimidine (218) : (^{19}F).

22. Perfluoro-2,4,6-tris-(3-methylimidazolidin-1-yl)triazine (220) : (^{19}F).

23. Perfluoro-(3-methylimidazolidin-1-yl)benzene (221) : (^{19}F).

24. Perfluoro-1,4-bis-(3-methylimidazolidin-1-yl)benzene (223) and Perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)-benzene (222) : (^{19}F).

25. 1-Trifluoromethyl-5,5-difluoro-2,4,4-trimethoxy-1,3-diazacyclopent-2-ene (226a) or 1-Trifluoromethyl-5,5-difluoro-2,2,4-trimethoxy-1,3-diazacyclopent-3-ene (226b) : (^{1}H and ^{19}F).

26. 1-(Perfluoro-3-methylimidazolidin-1-yl)-3,3-difluoro-2,4,4-trimethoxycyclobut-1-ene (224) : (^{1}H and ^{19}F).

27. 2-(Perfluoro-3-methylimidazolidin-1-yl)-3,3,4,4-tetrafluoro-2,5,5-trimethoxycyclopent-1-ene (225) : (^{1}H and ^{19}F).

28. 3,5-Bis(dimethylamino)-4,6-bis(perfluoro-3-methylimidazolidin-1-yl)pyridazine (239) : (^{1}H and (^{10}F).

29. 1-Allyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane/vinylidene fluoride copolymer (^{1}H and ^{19}F).

30. 1,1,1-Trifluoro-2-trifluoromethyl-3-(4-nitrophenyl)-prop-2-ene (288) : (^{1}H, ^{19}F, and ^{13}C).

31. 1,1,1,3,3,3-Hexafluoro-2-fluoren-9-ylidinylpropen-2-ylidene (289) : (^{1}H and ^{19}F).

32. 1,1,1-Trifluoro-2-trifluoromethyl-3-methoxy-3-(4-nitrophenyl)propane (290) : (^{1}H and ^{19}F).

33. 9-(1,1,1,3,3,3-hexafluoroisopropyl)-9-methoxyfluorene (292) : (^{1}H and ^{19}F).

The following abbreviations are used in this appendix: s, singlet; d, doublet; t, triplet; q, quartet; sx, sextet; m, multiplet; br, broad.

Unless otherwise stated spectra were recorded at 40°C as neat liquids.

CFCl$_3$, TMS, and TMS were used as reference for ^{19}F, ^{1}H, and ^{13}C spectra respectively.

For ^{1}H spectra, downfield shifts are quoted as positive, whilst for ^{19}F spectra, upfield shifts are quoted as positive.

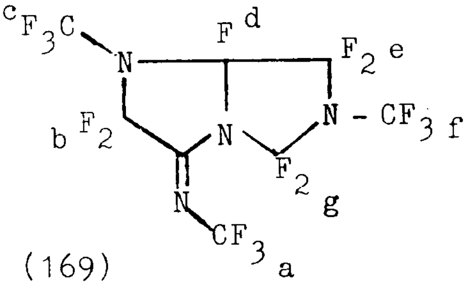
For ^{13}C spectra, "downfield" shifts are quoted as postive where downfield is the direction of increasing the absolute values.

Relative intensities in ^{13}C spectra are approximate values.

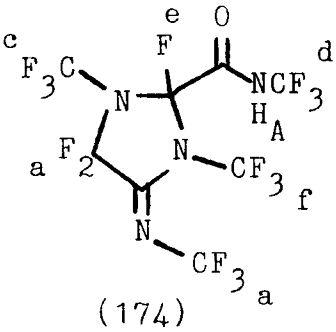
Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign-ment

1. Perfluoro-1,6-dimethyl-4-methylimino-1,3,6-triazabicyclo-$[3.3.0^{3.7}]$octane (169).

57.7	br	-	3	a
58.3	br	-	6	c or f
61,4, 76.3	AX	J_{AX} = 127	2	b or g
78.5	br	-	2	e
85.1, 106	AX	J_{AX} = 166	2	b or g
101.9	s	-	1	d



(169)



(174)

2. N-trifluoromethyl(perfluoro-1,3-dimethyl-4-methyliminotri-hydroimidazolidin-2-yl)methanamine (174). (d^6 acetone).

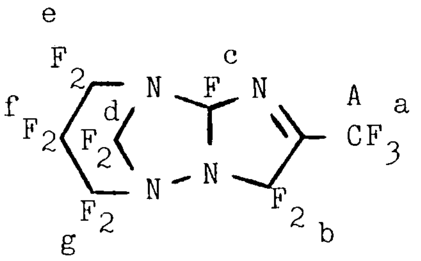
^{19}F

61.5	T	15.6	3	a
62.5	Q	10.4	3	c
65.3	D	7	3	f
66.6	s	-	3	d
85.8	brm	-	2	b
109.9	brm	-	1	e

^{1}H

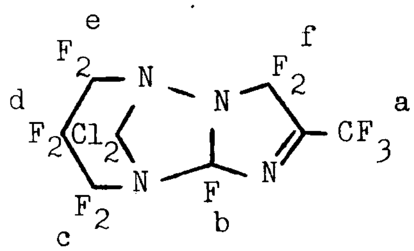
3.6	brs	-	-	A

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
3. Perfluoro-4-methyl-1,2,5,7-tetrazatricyclo[3.3.1.$0^{2.6}$]-undec-4-ene (175)				
^{19}F				
60.5	s	-	3	a
89.9, 100.5	AB	230	2	d
105.8, 108.7	AB	186	2	b, e, f, and g.
132.2, 141.0	AB	259	2	
94.6	d	146	1	
117.5	d	146	1	
127.1	s	-	2	
107.5	s	-	1	c
^{13}C				
117.2	q	268		A
147.1	t	14.6		B



(175)

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign-ment
4. 11,11-dichloro-4-trifluoromethylnonafluoro-1,2,5,7-tetra-azatricyclo[3.3.1.$0^{2.6}$]undec-4-ene (183)				
59.2	m	-	3	a
91.6, 101.9	AB	173	2	e
93.1, 115.5	AB	136	2	f
118.4, 123.9	AB	234	2	c
106.5	hp	7.5	1	b
122.5	m	-	2	d



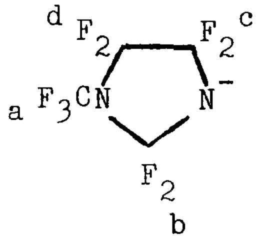
(183)

5. (166S) Unknown

57.4	br	-	3	
90.5, 112.3	AB	145	2	
101	br	-	1	
120.0, 124.9	AB	211	2	
145	br	-	1	

6. Perfluoro-3-methyl-1,3-diazacyclopentane anion (162)

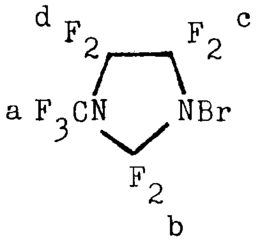
Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign-ment
58.3	br	-	3	a
44.0	br	-	2	b
64.8	br	-	2	c
94.1	br	-	2	d



(162)

7. 1-Bromo-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (188).

58.0	P	7.5	3	a
58.8	br	-	2	b
84.5	br	-	2	c
94.0	br	-	2	d

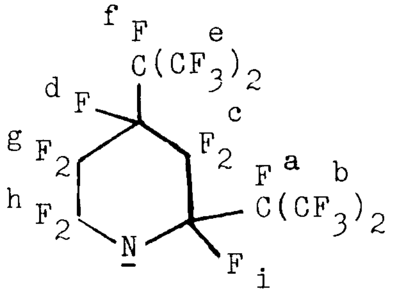


(188)

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment

8. The F-2,4-bisisopropyl-1-azacyclopentane anion (190)

46.5, 76.5	AB	119	2	h
68.1	br	-	6	b and e
69.5	br	-	6	
72.2	br	-	1	i
107.3, 112.1	AB	158	2	c and g
114.3, 120.1	AB	186	2	
175.1	br	-	1	a, d and f
180	br	-	1	
182.6	br	-	1	



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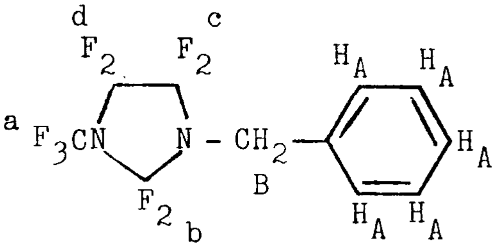


9. 1-Benzyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane

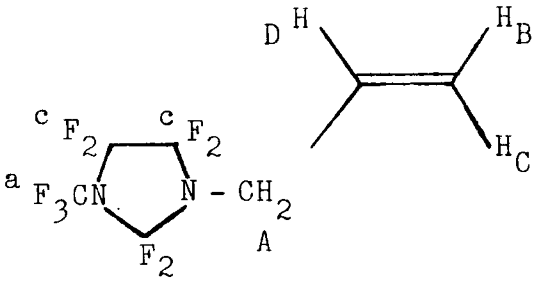
^{19}F

56.0	p	7.4	3	a
64.7	m	-	2	b
91.8	t	8	2	c
93	m	-	2	d

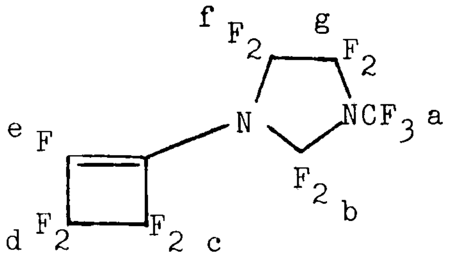
^{1}H

4.4	brs	-	2	B
7.4	brs	-	5	A

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign-ment
10. 1-Allyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (246).				
^{19}F				
59.5	p	7.5	3	a
68.7	m	-	2	b
97	brm	-	4	c
^{1}H				
4.05	brd	5.6	2	A
5.45	brm	-	1	B
5.65	brs	-	1	C
5.95	m	-	1	D



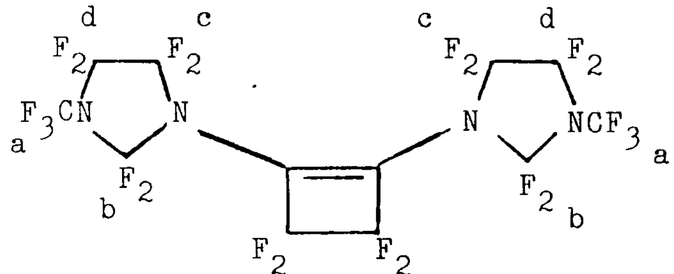
(246)



(200)

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign-ment
11. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclobut-1-ene (200)				
58.0	m	7.5	3	a
64.7	brs	-	2	b
93.8	brm	-	4	f and g
117.3	m	-	2	c
119.2	m	-	2	d
123.3	m	-	1	e

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign-ment
12. Perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclobut-1-ene (202)				
58.4	br	-	6	a
64.5	br	-	4	b
94.4	br	-	4	c and d
95.1	br	-	4	
116.8	br	-	4	e



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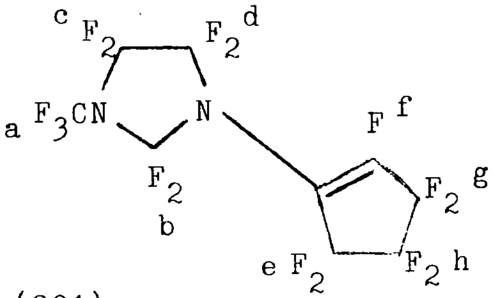
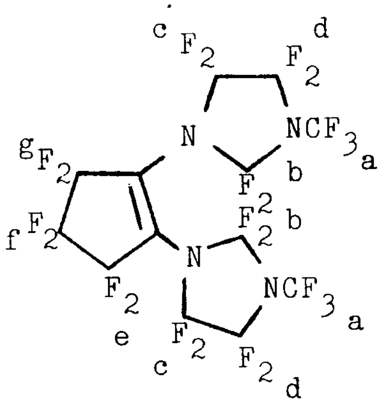


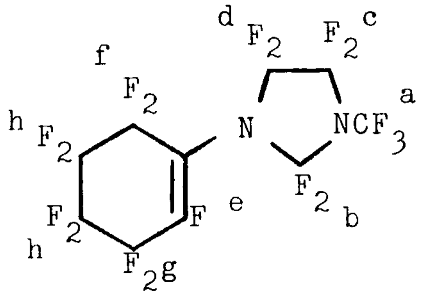
(201)

13. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclopent-1-ene (201)				
59.0	m	7.8	3	a
65.0	m	-	2	b
94.0	m	-	2	c
95.8	sp	2.9	2	d
115.5	m	-	2	e
122.1	m	-	1	f
124.1	m	-	2	g
134.2	m	-	2	h

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign-ment
14. Perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclopent-1-ene (203)				
58.5	br	-	6	a
63.9	br	-	4	b
93.7	br	-	4	c and d
96.0	br	-	4	
115.6	br	-	4	e
134.1	br	-	2	f



(203)



(204)

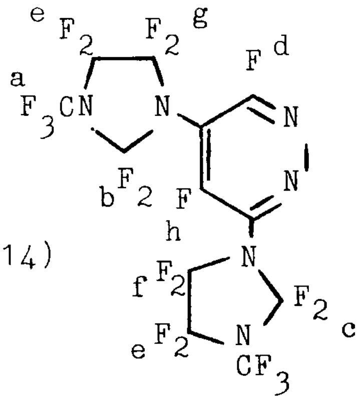
15. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclohex-1-ene (204)

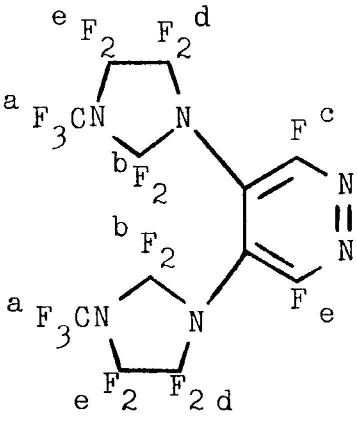
58.3	m	8	3	a
64.3	br	-	2	b
92.5	br	-	2	c
94.1	br	-	2	d
112.6	brm	-	1	e
113.6	br	-	2	f
121.9	d	21.6	2	g
135.5	br	-	4	h

16. Perfluoro-3,5-bis-(3-methylimidazolidin-1-yl)pyridazine (214).

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
56.7	p	6.9	6	a
62.5	m	-	2	b and c
63.2	m	-	2	
79.0	m	-	1	d
90.5	m	-	4	e
92.3	m	-	2	f and g
93.2	m	-	2	
112.2	m	-	1	h

(214)



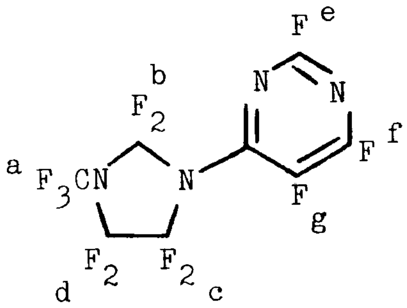


(215)

17. Perfluoro-3,4-bis-(3-methylimidazolidin-1-yl)pyridazine (215) in acetone

56.0	br	-	3	a
61.3	br	-	2	b
80.2	br	-	1	c
90.0	br	-	2	d
92.7	br	-	2	e

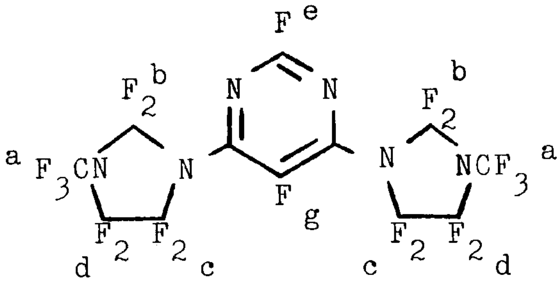
Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign-ment
18. Perfluoro-4-(3-methylimidazolidin-1-yl)pyrimidine (216).				
47.5	d	29.3	1	e
58.6	br	-	3	a
63.9	br	-	2	b
73.9	d	19.6	1	f
93.8	d	29.3	2	c
95.5	br	-	2	d
163.8	m	-	1	g



(216)

19. Perfluoro-4,6-bis-(3-methylimidazolidin-1-yl)pyrimidine (217) in acetone

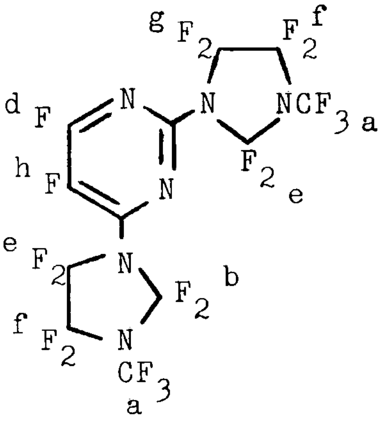
46.9	br	-	2	e
55.8	br	-	6	a
61.2	br	-	4	b
90.7	d	29.3	4	c
93.2	br	-	4	d
147.1	m	-	1	f



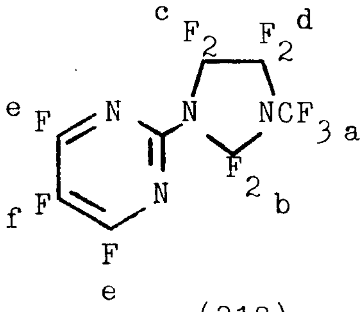
(217)

20. Perfluoro-2,4-bis-(3-methylimidazolidin-1-yl)pyrimidine (219) in acetone.

Shift (p.p.m.)	Mulitplicity	Coupling Constant Hz	Relative Intensity	Assign-ment
57.3	p	7.5	6	a
62.7	dsx	24.5 and 7.5	2	b
66.3	m	7.5	2	c
75.7	d	21.6	1	d
92.7	dt	26.8 and 6.5	2	e
94.5	m	-	4	f
96.8	t	16	2	g
162.7	m	-	1	h



(219)

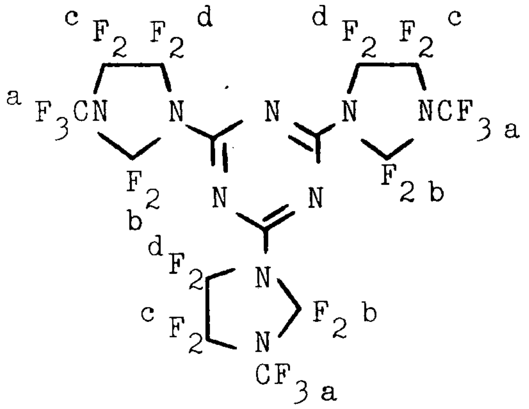


(218)

21. Perfluoro-2-(3-methylimidazolidin-1-yl)pyrimidine (218)

58.3	p	7.5	3	a
67.5	m	7	2	b
75.3	d	19	2	e
94.8	sx	7	2	d
97.8	t	7	2	c
176.6	t	19	1	f

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
22. Perfluoro2,4,6-tris-(3-methylimidazolidin-1-yl)-1,3,5-triazine (220) in C_6F_6				
54.8	p	7.5	3	a
63.1	m	-	2	b
90.7	m	-	2	c
93.7	t	6	2	d



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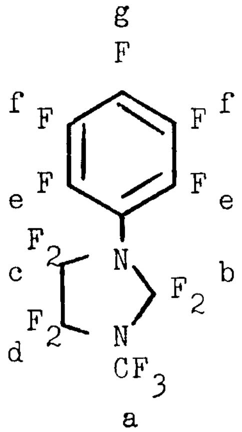


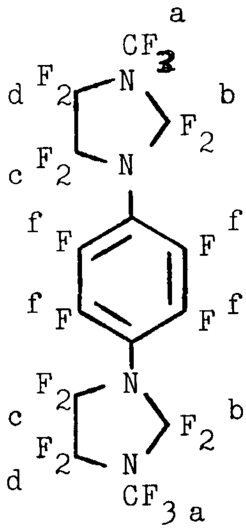
(221)

23. Perfluoro-(3-methylimidazolidin-1-yl)benzene (221)

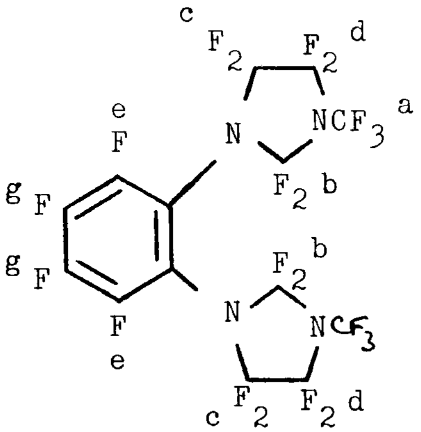
58.2	p	7.5	3	a
66.0	sx	7.5	2	b
93.2	p	7.5	2	d
94	q	7.2	2	c
140.7	m	-	2	e
150	t	19.8	1	g
163.7	t	17.4	2	f

24. Perfluoro-1,4-bis-(3-methylimidazolidin-1-yl)benzene (223) and Perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)benzene (222) in acetone.

Shift) (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign- ment
57.5	p	7.5	6	a
65	brm	-	4	b
92.2	brm	-	4	d
93.5	q	6.9	4	c
123.3	sx	7.5	1	e
128.2	dm	22.6	2	f
159.8	td	21.6, 9.4	1	g



(223)

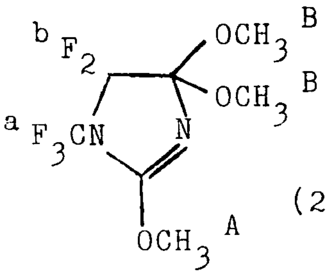


(222)

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment

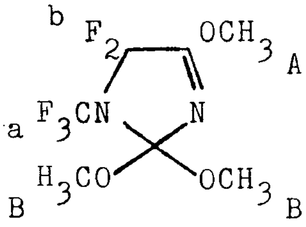
25. 1-Trifluoromethyl-5,5-difluoro-2,4,4-trimethoxy-1,3-diazacyclopent-2-ene (226a) OR 1-trifluoromethyl-5,5-difluoro-2,2,4-trimethoxy-1,3-diazacyclopent-3-ene (226b)

^{19}F				
58.2	t	8	3	a
96.5	q	8	2	b
^{1}H				
3.62	s	-	2	B
4.22	s	-	1	A



(226a)

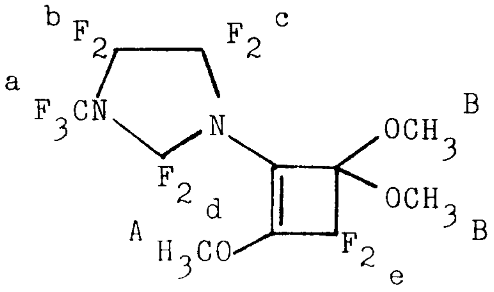
OR



(226b)

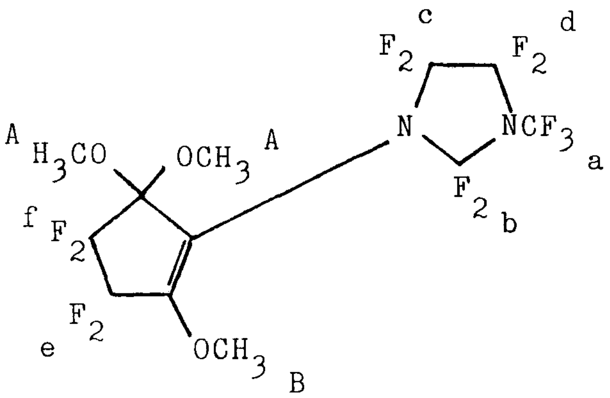
26. 1-(Perfluoro-3-methylimidazolidin-1-yl)-3,3-difluoro-2,4,4-trimethoxycyclobut-1-ene (224)

^{19}F				
58.2	qu	7.5	3	a
64.2	se	7.2	2	d
92.2	m	-	2	b and c
95.0	m	-	2	
115.7	s	-	2	e
^{1}H				
3.68	s	-	2	B
4.18	s	-	1	A



(224)

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
27. 2-(Perfluoro-3-methylimidazolidin-1-yl)-3,3,4,4-tetrafluoro-2,5,5-trimethoxycyclopent-1-ene (225).				
^{19}F				
57.3	br	-	3	a
62.3	br	-	2	b
90.5	br	-	2	c
94.2	br	-	2	d
117.2	br	-	2	e
127.3	br	-	2	f
^{1}H				
3.6	s	-	2	A
4.2	brs	-	1	B

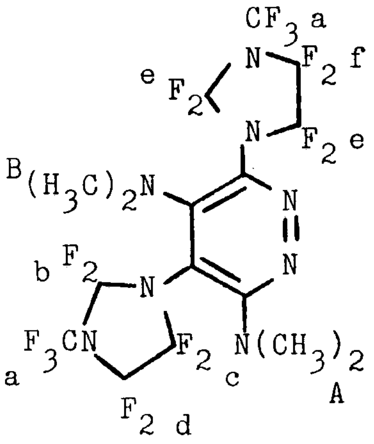


(225)

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assign-ment

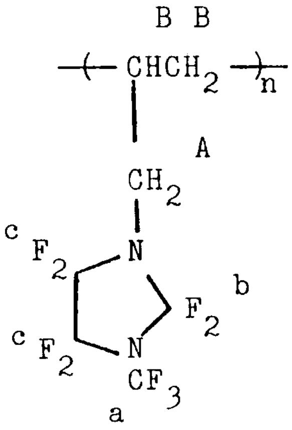
28\. 3,5-bis(dimethylamino)-4,6-bis(perfluoro-3-methylimidazolidin-1-yl)pyridazine (239) in $CDCl_3$.

^{19}F				
55.9	br	-	6	a
63.4	br	-	4	b
88.1	br	-	1	c, d, e, and f
89.7	br	-	1	
92.3	br	-	4	
94.7	br	-	2	
^{1}H				
2.8	br	-	1	A and B
3.1	br	-	1	

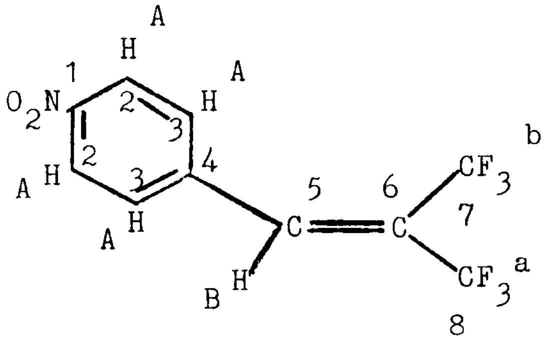


(239)

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
29. 1- Allyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane/vinylidene fluoride "copolymer", in d^6-acetone.				
^{19}F				
58	br	-	3	a
66.7	br	-	2	b
95.3	br	-	4	c
^{1}H				
3.16	br	-	2	A
1.8	br	-	3	B

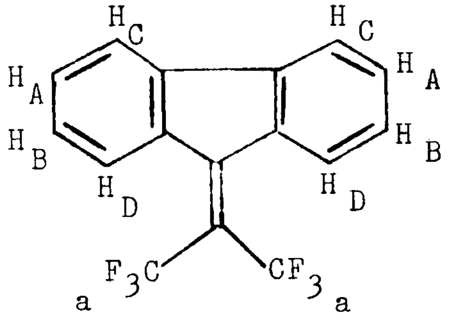


Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
30. 1,1,1-Trifluoro-2-trifluoromethyl-3-(4-nitrophenyl)prop-2-ene (286) in $CDCl_3$.				
^{19}F				
58.0	q	7	1	a
64.8	dq	2, 7	1	b
^{1}H				
7.62, 8.31	AB	9	4	A
7.74	br	-	1	B
^{13}C - proton decoupled				
120.9	qd	270, 31		7 and 8
124.0	br	-		2 and 3
129.8	br	-		
137.7	s	-		4
141.2	br	-		5
149	s	-		1



(286)

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
31. 1,1,1,3,3,3-hexafluoro-2-fluoren-9-ylidinylpropen-2-ylidene (287) in $CDCl_3$.				
^{19}F				
56.6	s	-	-	a
^{1}H				
7.25	t	7.7	1	A and B
7.40	t	7.45	1	
7.55	d	7.45	1	C and D
7.8 - 7.85	d	7.9	1	



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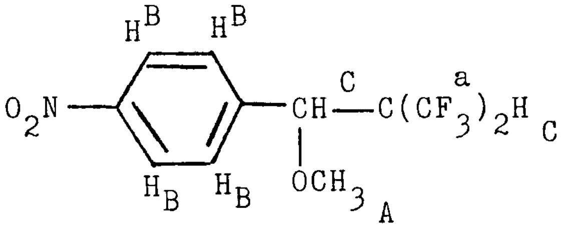
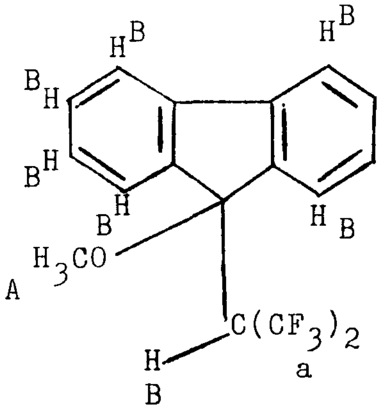


(289)

32. 1,1,1-trifluoro-2-trifluoromethyl-3-methoxy-3-(4-nitrophenyl)propane in $CDCl_3$.				
^{19}F				
57.8	s	-	-	a
^{1}H				
3.83	s	-	3	A
7.41, 8.14	AB	8	4	B
8.0	brs	-	2	C

Shift (p.p.m.)	Multiplicity	Coupling Constant Hz	Relative Intensity	Assignment
33. 9-(1,1,1,3,3,3-hexafluoroisopropyl)-9-methoxy-fluorene				
^{19}F				
57	s	-	-	a
^{1}H				
3.8	s	-	3	A
7 - 7.9	br	-	9	B



(289)

APPENDIX II

I.R. Spectra

1. Perfluoro-1,6-dimethyl-4-methylimino-1,3,6-triazabicyclo-[3.3.$0^{3.7}$]octane (169).
2. N-Trifluoromethyl(perfluoro-1,3-dimethyl-4-methyliminotrihydroimidazolidin-2-yl)methanamide (174).
3. Perfluoro-4-methyl-1,2,5,7-tetraazatricyclo[3.3.1.$0^{2.6}$]-undec-4-ene (175).
4. 11,11-Dichloro-4-(trifluoromethyl)nonafluoro-1,2,5,7-tetraazatricyclo[3.3.1.$0^{2.6}$]undec-4-ene (183).
5. Unknown.
9. 1-Benzyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane.
10. 1-Allyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (246).
11. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclobut-1-ene (200).
12. Perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)cyclopent-1-ene (202).
13. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclopent-1-ene (201).
14. Perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclopent-1-ene (203).
15. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclohex-1-ene (204).
16. Perfluoro-3,5-bis(3-methylimidazolidin-1-yl)pyridazine (204).
17. Perfluoro-4,5-bis(3-methylimidazolidin-1-yl)pyridazine (215).

18. Perfluoro-4-(3-methylimidazolidin-1-yl)pyrimidine (216).

19. Perfluoro-4,6-bis(3-methylimidazolidin-1-yl)pyrimidine (217).

20. Perfluoro-2,4-bis(3-methylimidazolidin-1-yl)pyrimidine (219).

21. Perfluoro-2-(3-methylimidazolidin-1-yl)pyrimidine (218).

22. Perfluoro-2,4,6-tris(3-methylimidazolidin-1-yl)-1,3,5-triazine (220).

23. Perfluoro-(3-methylimidazolidin-1-yl)benzene (221).

24. Perfluoro-1,2-bis(3-methylimidazolidin-1-yl)benzene (222) and perfluoro-1,4-bis(3-methylimidazolidin-1-yl)benzene (223).

25. 1-Trifluoromethyl-5,5-difluoro-2,4,4-trimethoxy-1,3-diazacyclopent-2-ene (226a) OR 1-Trifluoromethyl-5,5-difluoro-2,2,4-trimethoxy-1,3-diazacyclopent-3-ene (226b).

26. 1-(Perfluoro-3-methylimidazolidin-1-yl)-3,3-difluoro-2,4,4-trimethoxycyclobut-1-ene (224).

27. 2-(Perfluoro-3-methylimidazolidin-1-yl)-3,3,4,4-tetrafluoro-2,5,5-trimethoxycyclopent-1-ene (225).

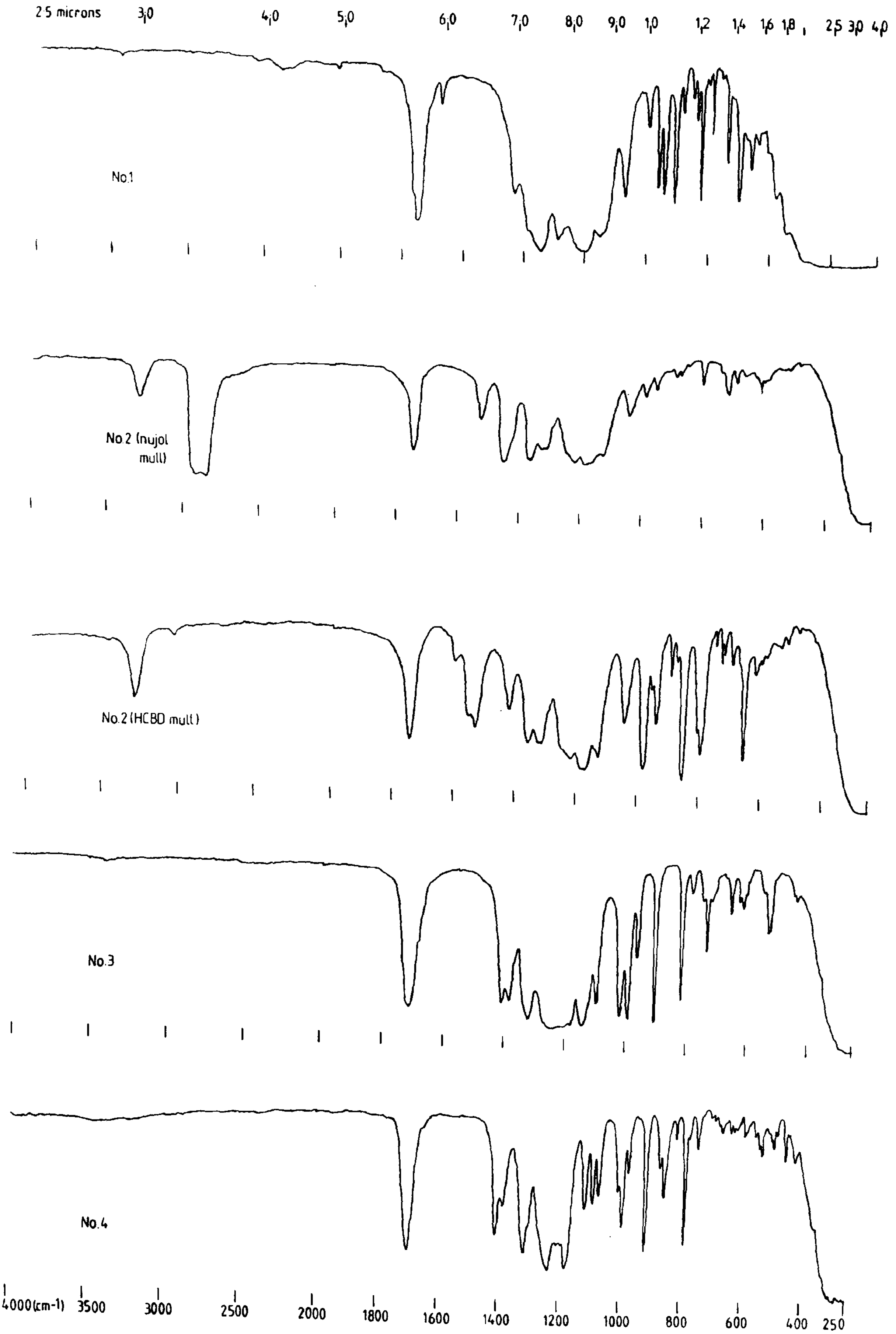
28. 3,5-Bis(dimethylamino)-4,6-bis(perfluoro-3-methylimidazolidin-1-yl)pyridazine (239).

30. 1,1,1-Trifluoro-2-trifluoromethyl-3-(4-nitrophenyl)prop-2-ene (288).

31. 1,1,1,3,3,3-Hexafluoro-2-fluoren-9-ylidinylpropen-2-ylidene (289).

32. 1,1,1-Trifluoro-2-trifluoromethyl-3-methoxy-3-(4-nitrophenyl)propane (290).

33. 9-(1,1,1,3,3,3-Hexafluoroisopropyl)-9-methoxyfluorene (292).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4,0
5,0
6,0
7,0
8,0
9,0
1,0
1,2
1,4
1,6
1,8
2,5
3,0
4,0
No.1
No.2 (nujol mull)
No.2 (HCBD mull)
No.3
No.4
4000(cm-1)
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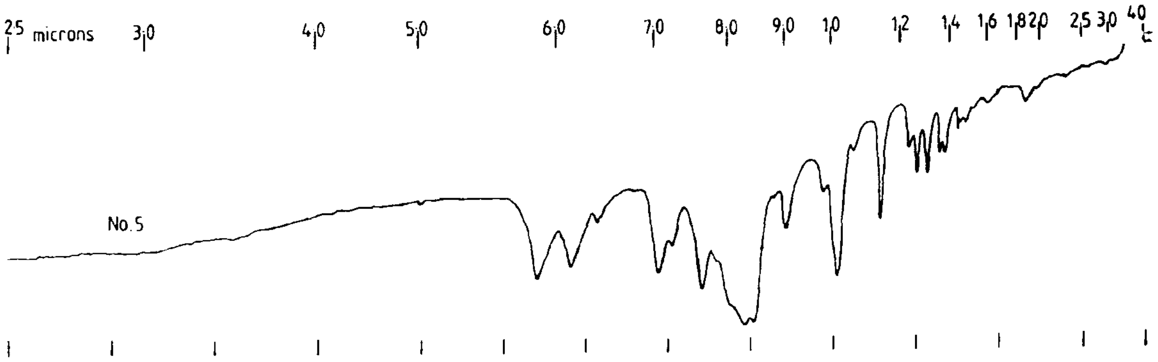
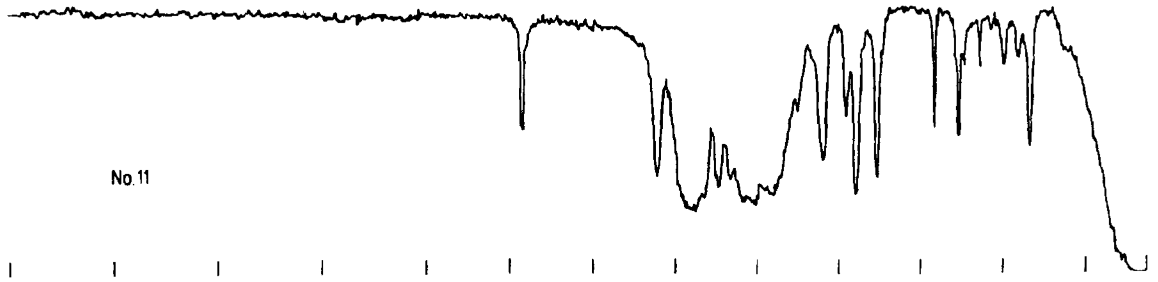
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250



No.5

No.9

No 10



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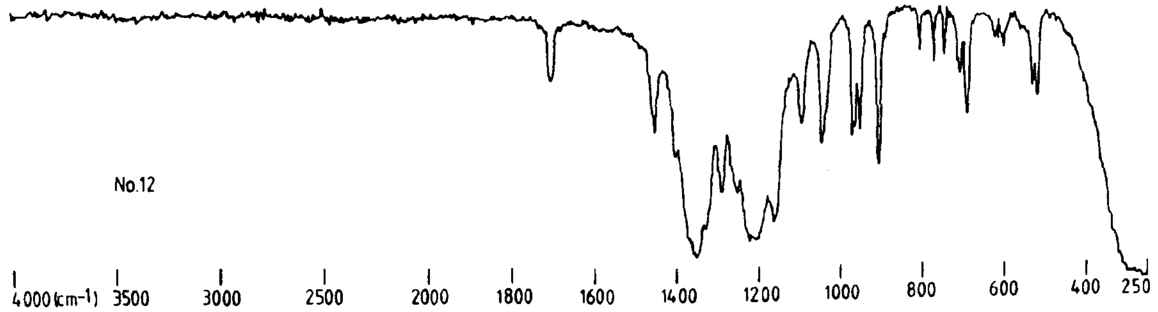

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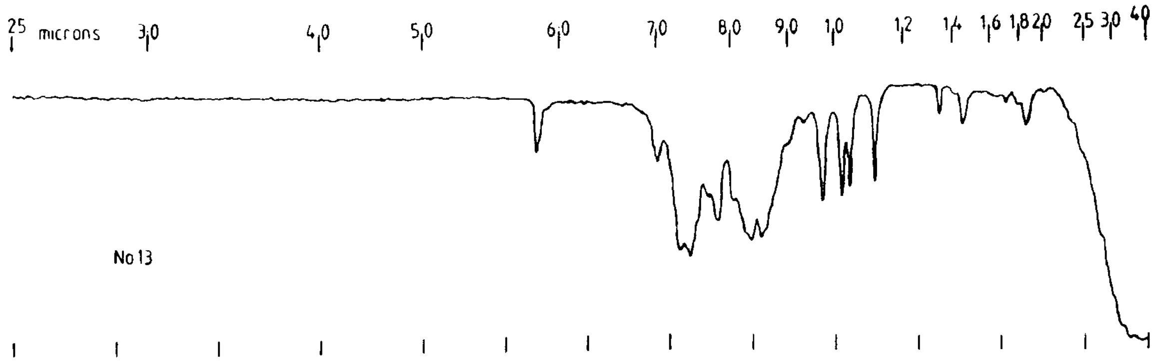

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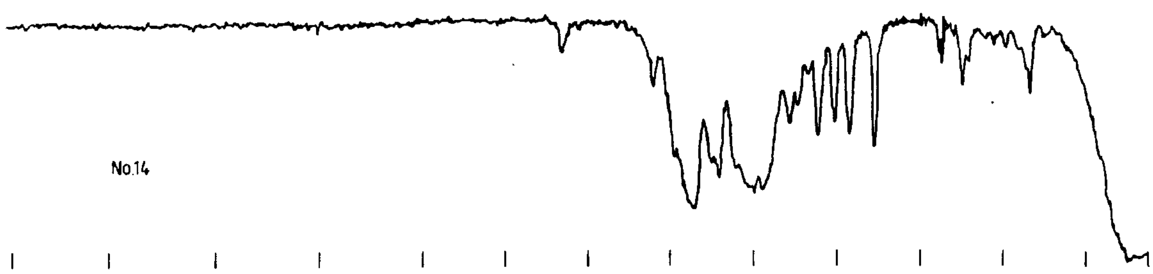

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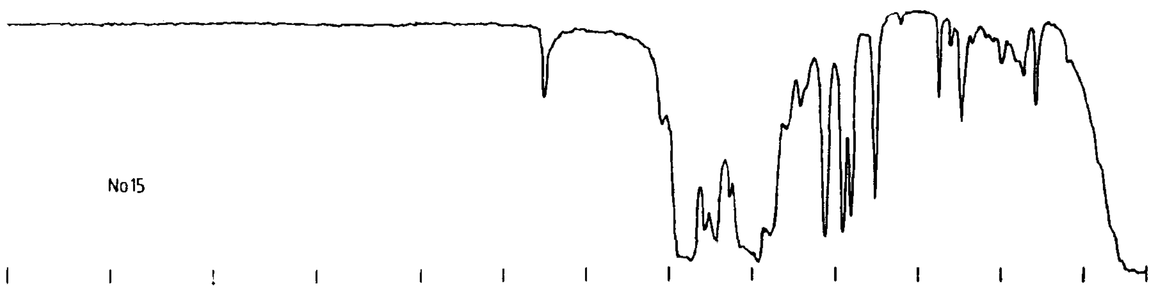

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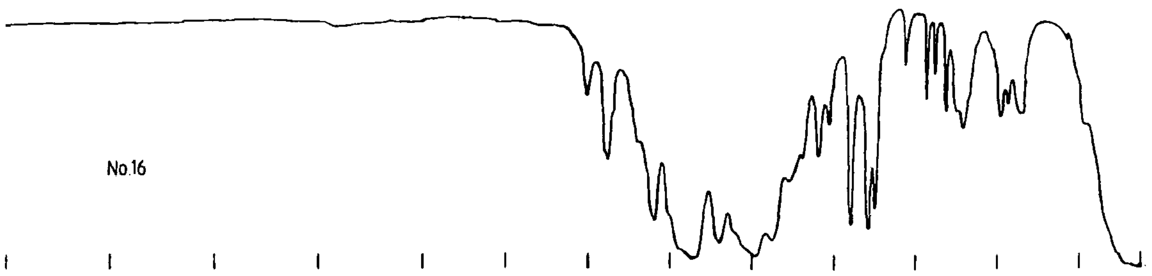

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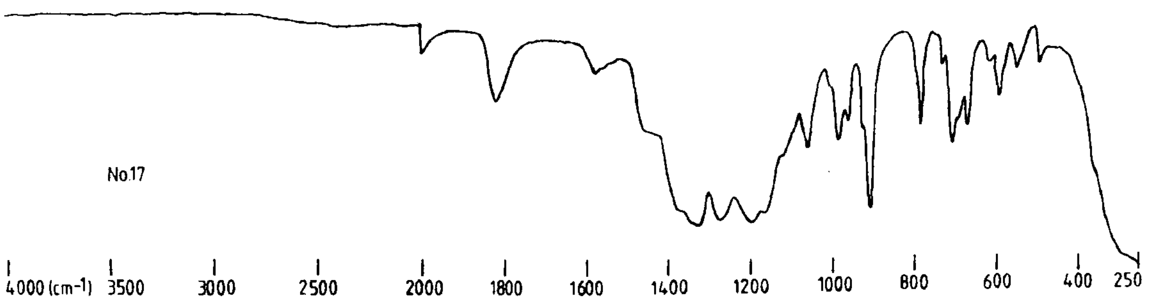

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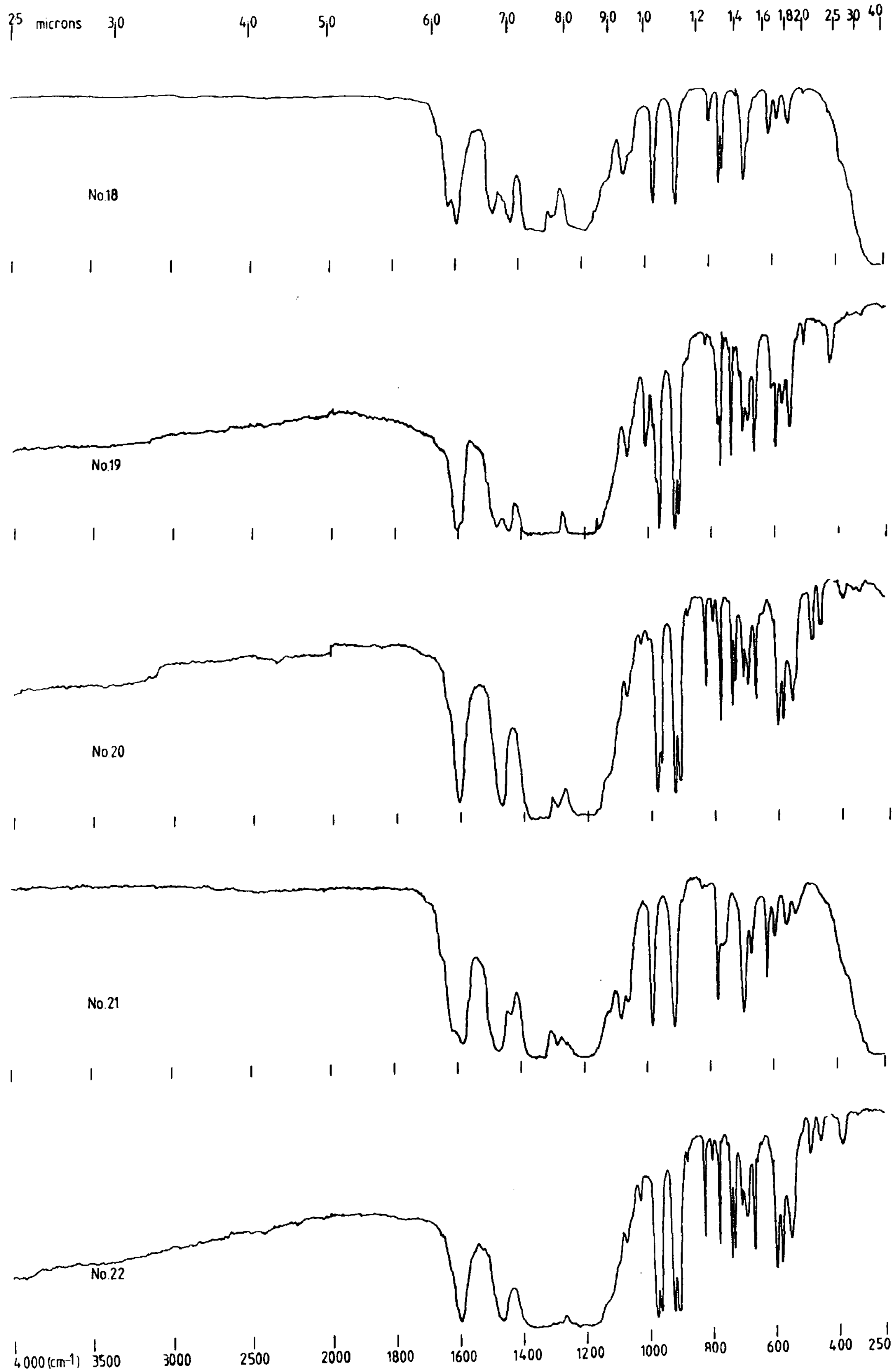
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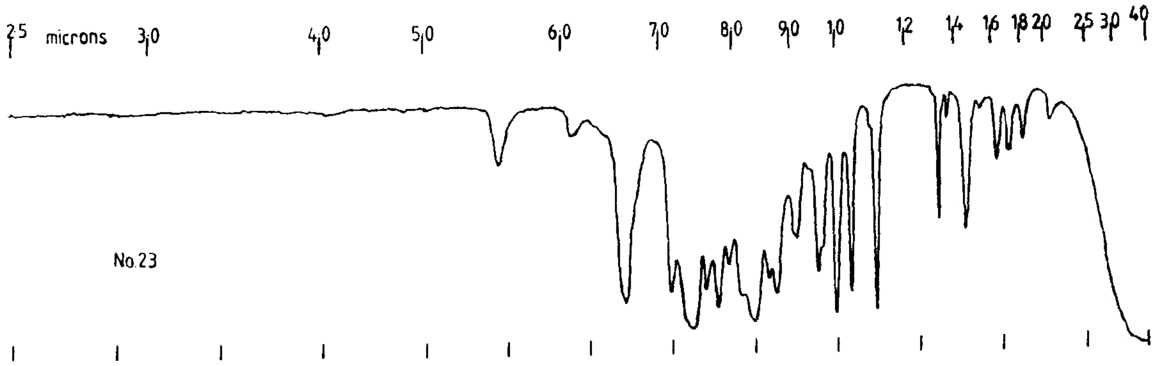
No.18
No.19
No.20
No.21
No.22
4000 (cm-1) 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250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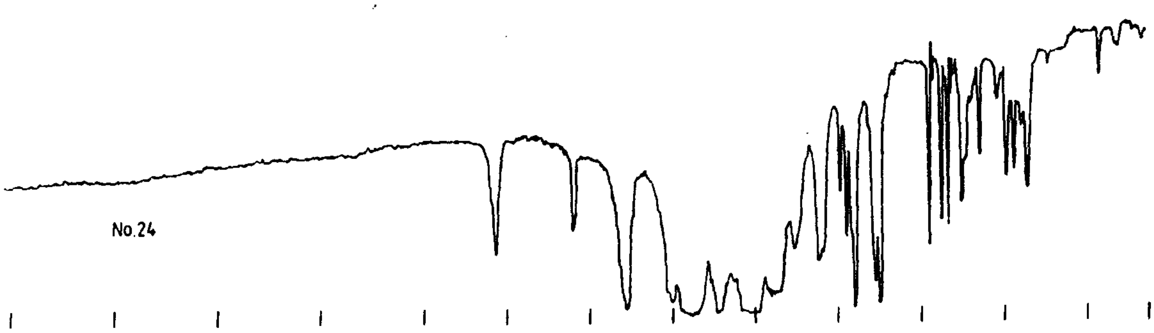
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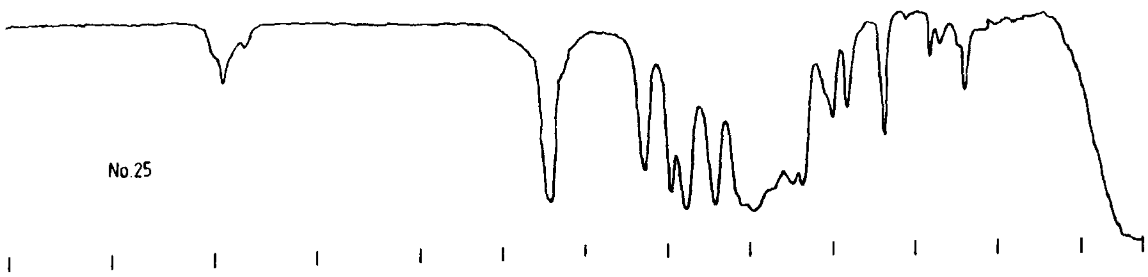
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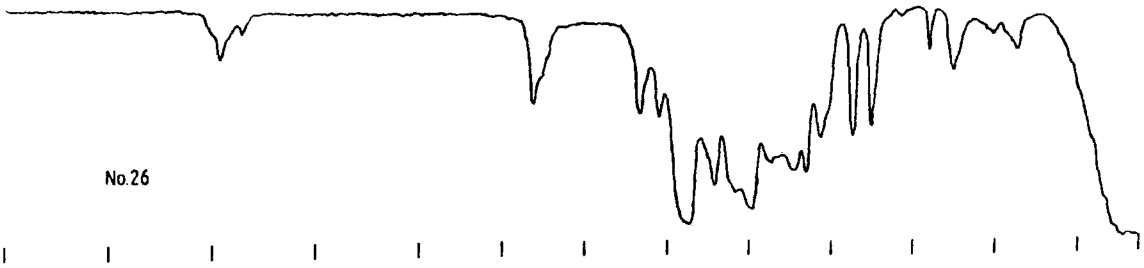
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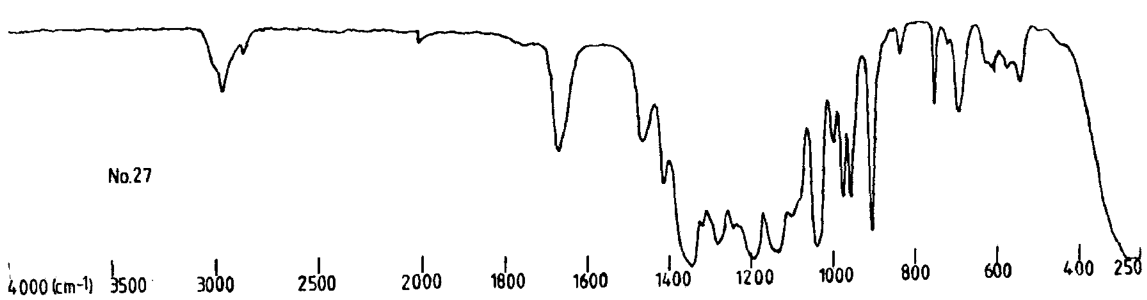
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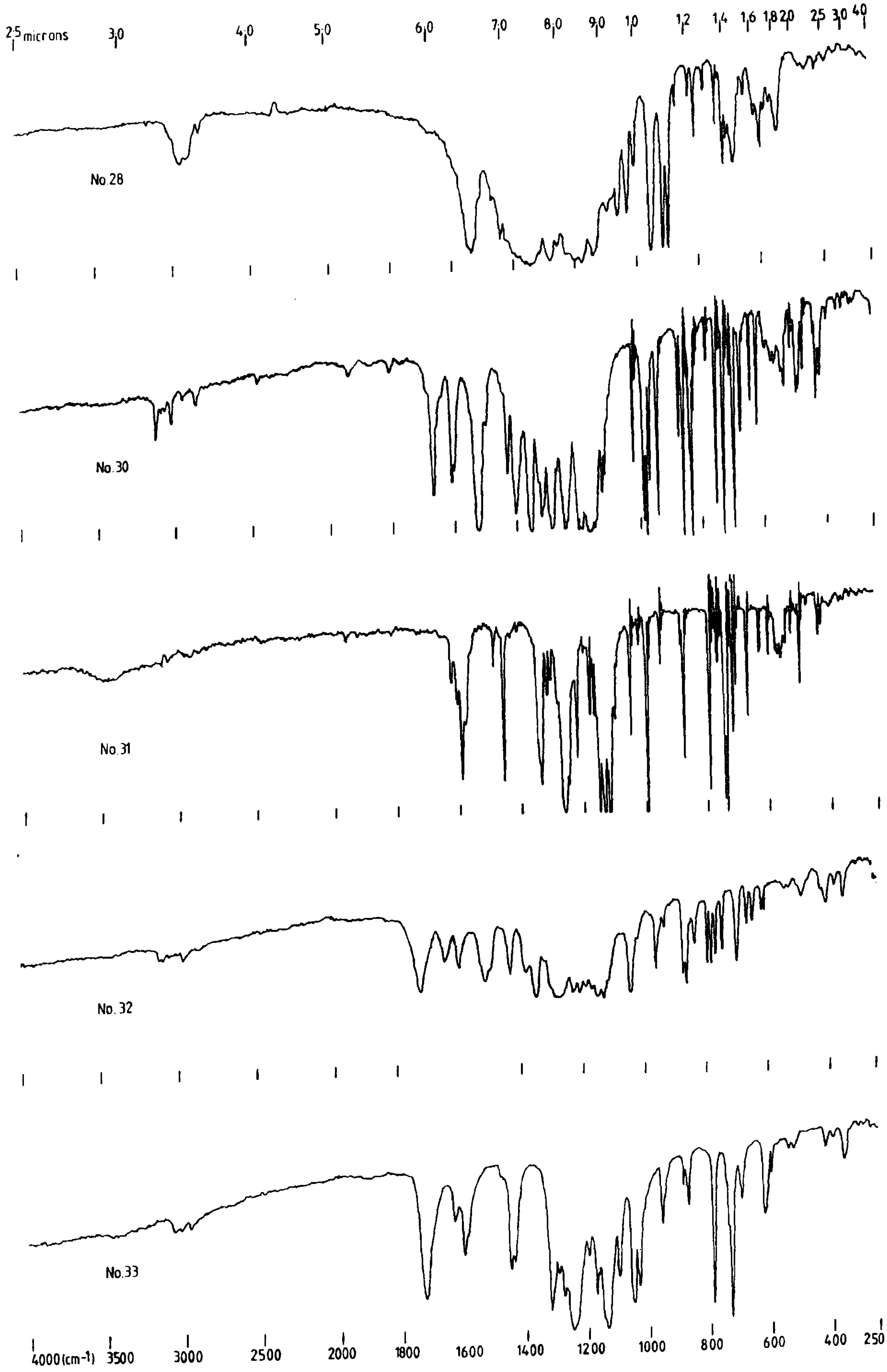

2.5 microns
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
40
No.28
No.30
No.31
No.32
No.33
4000(cm-1)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

APPENDIX III

Mass Spectra

1. Perfluoro-1,6-dimethyl-4-methylimino-1,3,6-triazabicyclo-$[3.3.0^{3.7}]$octane (169) : (EI).
2. N-Trifluoromethyl(perfluoro-1,3-dimethyl-4-methylimino-trihydroimidazolidin-2-yl)methanamide (174) : (EI).
3. Perfluoro-4-methyl-1,2,5,7-tetraazatricyclo$[3.3.1.0^{2.6}]$-undec-4-ene (175) : (EI, CI, and NH_3 NEG).
9. 1-Benzyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (EI).
10. 1-Allyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane (246) : (EI).
11. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclobut-1-ene (200) : (EI).
12. Perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclobut-1-ene (202) : (EI).
13. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclopent-1-ene (201) : (EI).
14. Perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclopent-1-ene (203) : (EI).
15. Perfluoro-1-(3-methylimidazolidin-1-yl)cyclohex-1-ene (204) : (EI).
16. Perfluoro-3,5-bis(3-methylimidazolidin-1-yl)pyridazine (214) : (EI).
17. Perfluoro-4,5-bis-(3-methylimidazolidin-1-yl)pyridazine (215) : (EI and NEG I.Bu).
18. Perfluoro-4-(3-methylimidazolidin-1-yl)pyrimidine (216) : (EI).
19. Perfluoro-4,6-bis-(3-methylimidazolidin-1-yl)pyrimidine (217) : (EI).

20. Perfluoro-2,4-bis-(3-methylimidazolidin-1-yl)pyrimidine (219) : (EI, CI, NEG NH_3 and NEG ARGON).

21. Perfluoro-2-(3-methylimidazolidin-1-yl)pyrimidine (218) : (EI).

22. Perfluoro-2,4,6-tris-(3-methylimidazolidin-1-yl)-1,3,5-triazine (220) : (EI).

23. Perfluoro-(3-methylimidazolidin-1-yl)benzene (221) : (EI).

24. Perfluoro-1,2-bis-(3-methylimidazolidin-1-yl)benzene (222) and perfluoro-1,4-bis-(3-methylimidazolidin-1-yl)benzene (223) : (EI, CI, and NEG ARGON).

25. 1-Trifluoromethyl-5,5-difluoro-2,4,4-trimethoxy-1,3-diazacyclopent-2-ene (226a) or 1-Trifluoromethyl-5,5-difluoro-2,2,4-trimethoxy-1,3-diazacyclopent-3-ene (226b) : (EI).

26. 1-(Perfluoro-3-methylimidazolidin-1-yl)-3,3-difluoro-2,4,4-trimethoxycyclobut-1-ene (224) : (EI).

27. 2-(Perfluoro-3-methylimidazolidin-1-yl)-3,3,4,4-tetrafluoro-2,5,5-trimethoxycyclopent-1-ene (225) : (EI).

28. 3,5-Bis(dimethylamino)-4,6-bis-(perfluoro-3-methylimidazolidin-1-yl)pyridazine (239) : (EI).

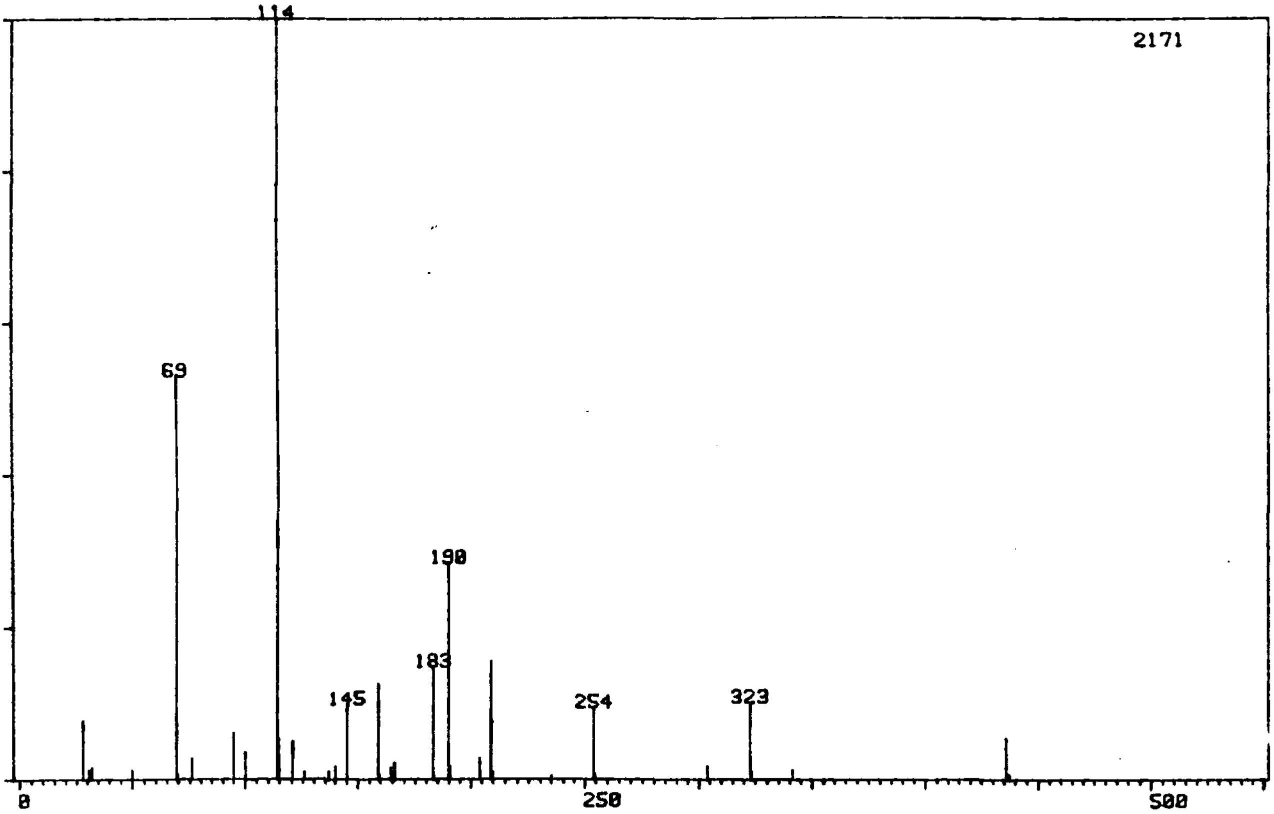
30. 1,1,1-Trifluoro-2-trifluoromethyl-3-(4-nitrophenyl)-prop-3-ene (288) : (EI).

31. 1,1,1,3,3,3-Hexafluoro-2-fluoren-9-ylidinylpropen-2-ylidene (289) : (EI).

32. 1,1,1-Trifluoro-2-methoxy-2-trifluoromethyl-3-(4-nitrophenyl)propane (290) : (EI, CI, and NEG).

33. 9-(1,1,1,3,3,3-Hexafluoro-2-methoxyisopropyl)fluorene (292) : (EI, CI, and NEG).

CH612 6 C.D.HEWITT 26-NOV-82
CAL:CAL25A

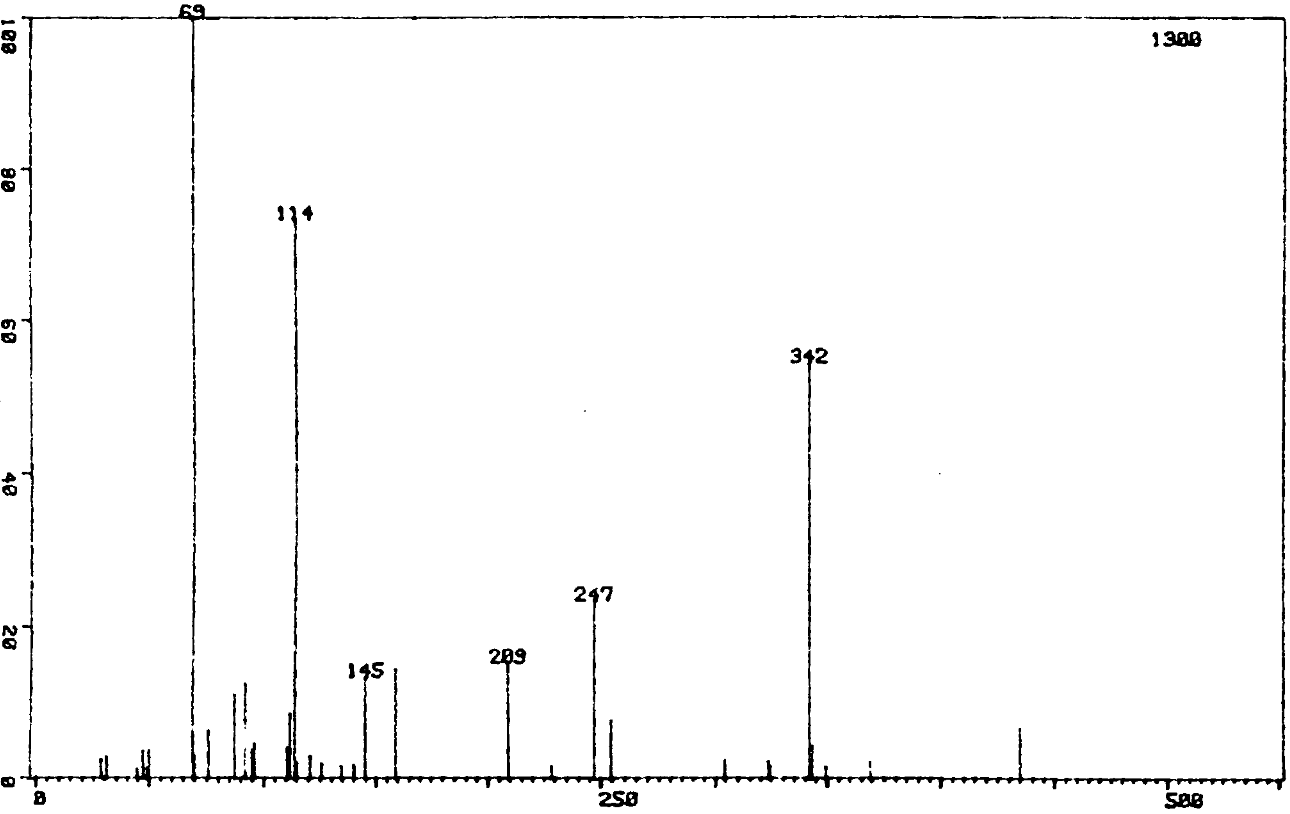


PEAK NO.	MASS	%HT BASE
1	28.05	7.83
2	30.83	1.34
3	31.93	1.66
4	49.82	1.24
5	68.90	53.11
6	69.07	8.52
7	69.85	0.78
8	76.02	2.81
9	94.96	6.13
10	99.87	3.59
11	113.94	100.00
12	114.24	5.30
13	114.87	3.18
14	120.84	5.02
15	125.95	1.01
16	136.89	1.11
17	139.84	1.75
18	144.93	9.95
19	158.83	12.67
20	159.39	0.55
21	163.94	1.70
22	165.89	2.21
23	182.84	14.97
24	183.47	0.60
25	189.85	28.74
26	190.26	0.69
27	190.78	1.84
28	203.81	2.81
29	208.75	15.75
30	208.95	7.69
31	209.32	0.88
32	209.80	1.01
33	234.80	0.46
34	253.74	9.53
35	254.75	0.78
36	303.66	1.80
37	322.56	10.23
38	323.65	1.06
39	341.53	1.29
40	436.21	5.53
41	437.30	0.69

No. 1.

CHS8 4 C.D.HEWITT
CAL:CAL10

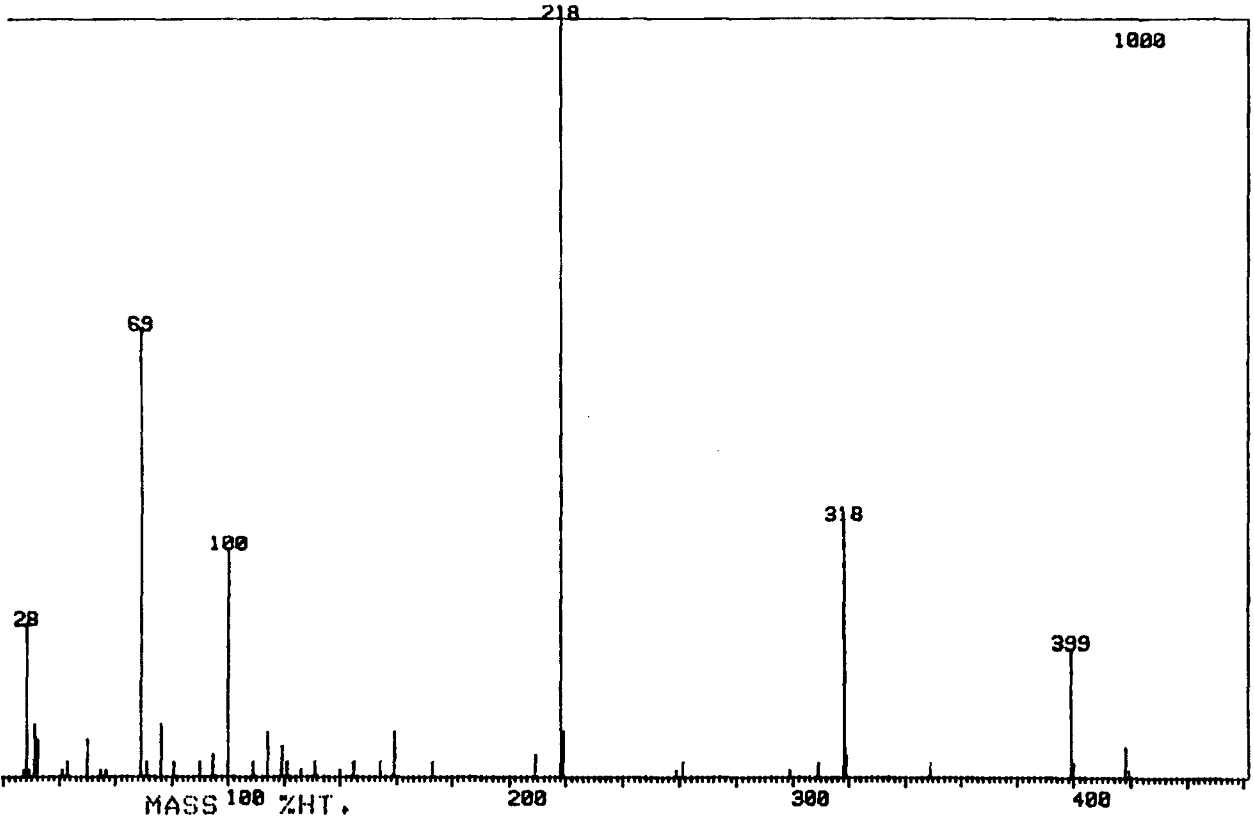
10-MAY-83



1	28.13	2.38
2	30.92	2.85
3	44.16	1.15
4	47.13	3.54
5	49.02	1.38
6	49.91	3.54
7	69.04	100.00
8	70.00	3.00
9	76.14	6.15
10	87.24	10.85
11	92.01	12.31
12	95.08	3.69
13	96.09	4.54
14	111.01	4.00
15	112.03	8.38
16	114.05	73.54
17	115.11	2.00
18	121.05	2.85
19	126.11	1.92
20	134.10	1.62
21	140.02	1.77
22	145.05	13.31
23	159.02	14.23
24	209.08	15.08
25	228.27	1.62
26	247.07	23.38
27	254.13	7.54
28	304.15	2.38
29	323.19	2.23
30	324.19	1.62
31	341.94	54.77
32	343.05	4.15
33	349.09	1.62
34	369.06	2.08
35	434.76	6.62

No. 2

131EI 0 08-SEP-86
AL:LIB STA: 0:0



MASS	%HT. BASE
27.15	0.41
28.03	19.46
28.93	0.41
30.77	7.00
31.88	4.61
39.73	0.41
40.86	0.71
41.96	0.41
43.03	1.60
49.82	4.39
55.11	0.67
56.11	0.41
57.03	0.67
57.09	1.00
61.98	0.41
68.96	59.17
69.91	0.86
70.97	1.30
71.05	0.48
76.06	6.33
80.95	1.79
89.92	1.45
93.02	0.74
95.04	3.16
99.91	29.59
100.96	0.78
105.11	0.41
107.02	0.86
108.97	2.01
111.99	0.78
114.02	5.81
118.97	3.68
120.97	1.49
126.04	1.08
130.98	2.01
139.95	1.19
145.03	1.64
154.03	2.23
158.98	5.47
164.01	0.48
170.97	0.60
173.00	1.38
177.99	0.37
189.96	0.60
208.96	2.57
217.99	100.00
218.97	6.07
248.97	0.93
253.98	0.56
258.96	1.04
260.98	1.75
298.94	1.19
308.94	2.16
310.94	0.37
317.96	33.64
318.93	2.38
348.93	1.49
398.89	16.75
399.91	1.67
417.95	3.98
418.91	0.41

No. 3. EI

131CI 0
CAL:LIB STA:

16-SEP-86
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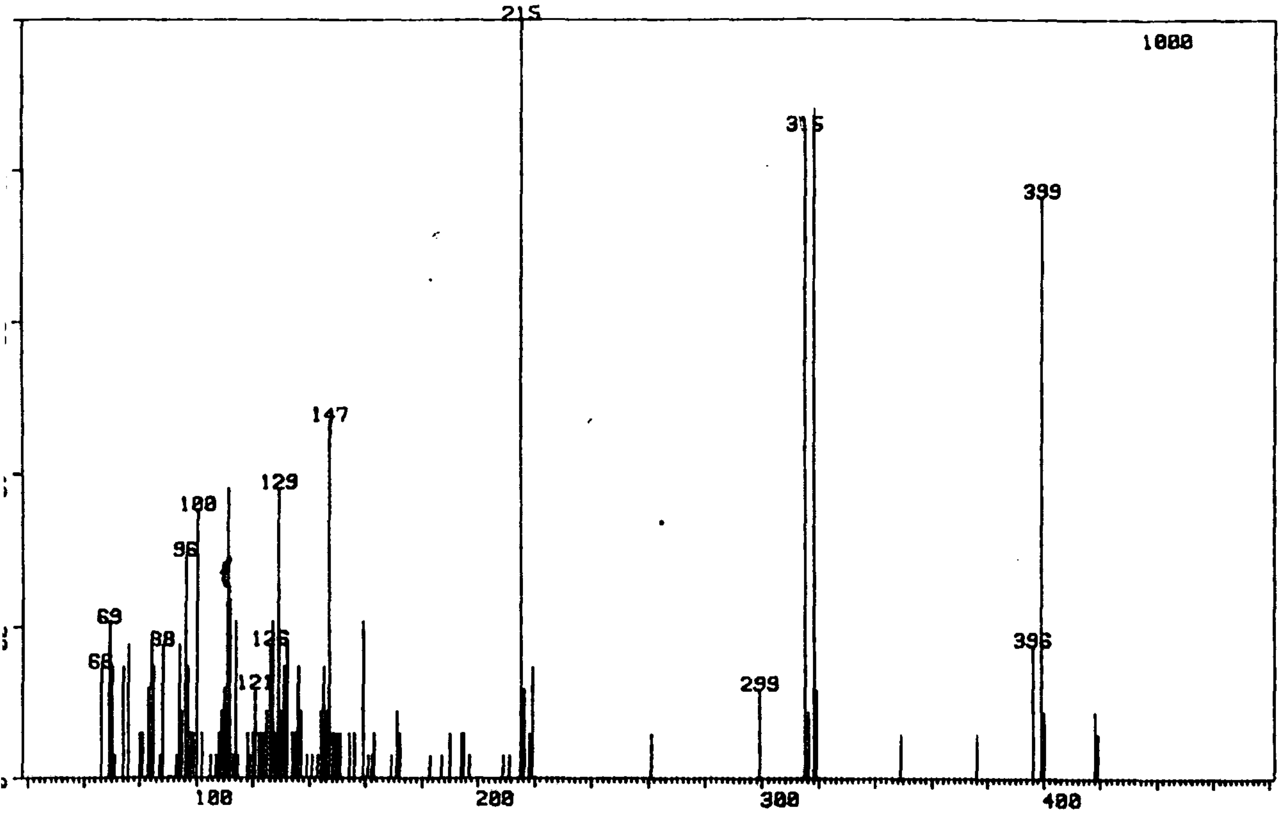

MASS	%HT. BASE
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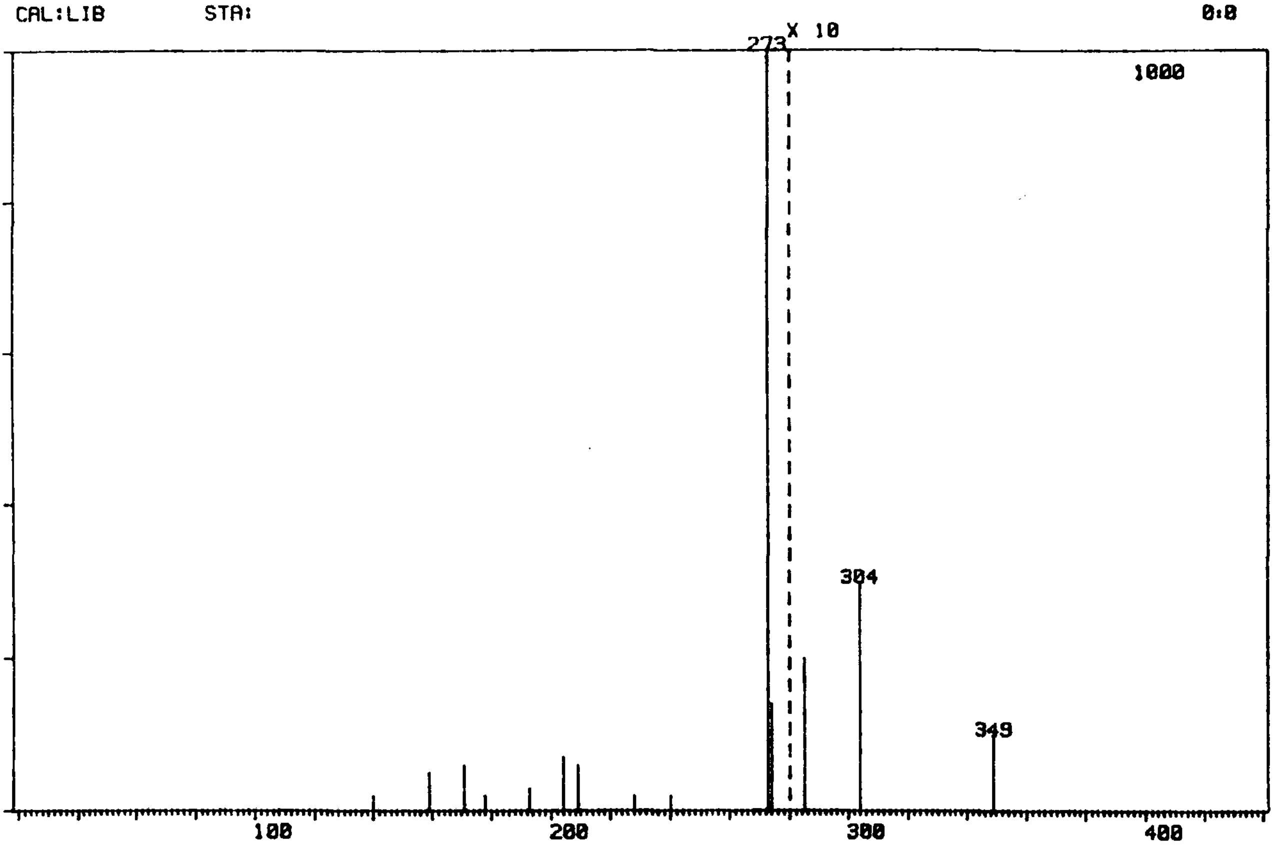
66.14	4.89
67.13	0.47
68.07	0.97
68.97	6.54
69.92	5.22
70.98	1.42
74.10	4.75
75.98	1.98
76.05	5.93
79.86	2.27
80.94	1.59
83.04	4.10
84.06	6.22
85.07	5.42
87.05	1.30
88.06	5.98
93.06	1.03
94.11	6.28
95.09	3.24
96.08	9.88
97.08	4.92
98.07	2.09
99.04	1.74
99.93	12.47
102.07	2.03
105.10	1.15
107.07	1.03
108.05	1.98
109.01	2.86
109.99	4.07
111.03	13.33
112.06	8.20
113.07	1.39
114.07	6.57
115.07	1.47
118.04	1.59
119.01	1.42
119.96	2.12
121.00	3.74
122.04	2.00
123.07	1.62
124.09	1.98
125.09	2.80
126.09	6.10
127.07	6.60
128.04	2.36
129.02	13.21
129.98	3.39
130.97	4.51
132.03	5.57
134.09	1.56
135.10	2.21
136.08	4.92
137.07	3.12
139.04	1.15
141.05	1.00
143.09	1.06
144.10	2.83
145.01	4.81
146.05	2.59
147.05	16.19
148.05	1.80
148.99	2.27
150.01	1.98
151.04	2.39
154.05	2.36
156.05	1.83
158.98	7.13
161.05	1.15
162.08	1.21
163.13	2.03
169.03	1.15
171.00	2.51
172.04	1.77
183.10	1.42
187.06	1.06
189.96	1.89
194.04	1.89
195.06	1.74
197.04	1.03
208.96	1.33
211.07	1.36
215.03	33.96
216.03	4.48
218.00	2.06
218.98	4.86
261.03	1.56
299.09	3.71
315.11	28.60
316.09	2.71
318.07	30.19
319.05	4.33
349.09	2.27
376.17	1.92
396.12	6.37
399.07	26.39
400.07	2.65
418.08	2.65
419.08	1.71

No.3. CI

131NEG 0
CAL:LIB STA:

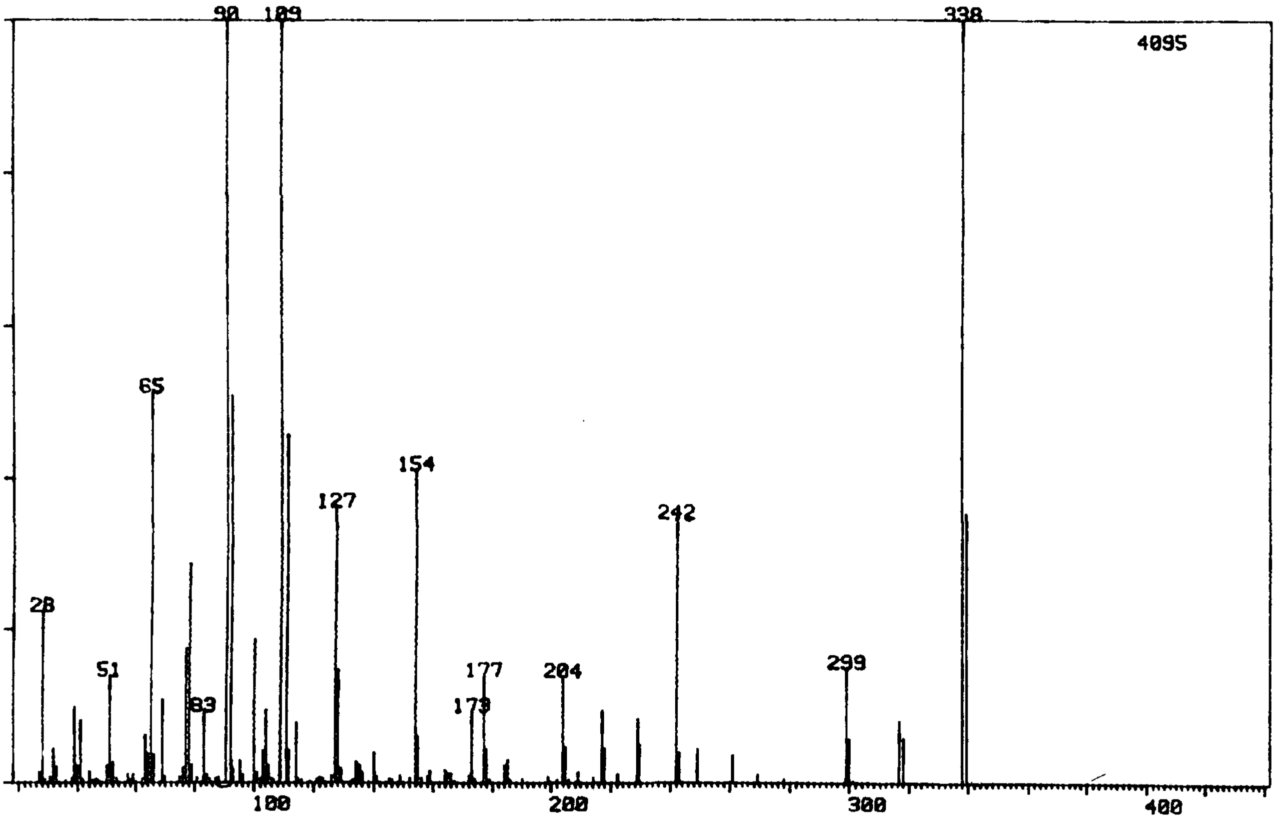
08-SEP-86
0:0



MASS	%HT. BASE
133.08	0.52
140.04	1.94
152.11	0.87
159.09	4.72
160.06	0.32
171.08	5.96
172.10	0.43
178.07	2.08
193.01	2.63
203.94	7.03
204.96	0.41
208.88	5.82
209.87	0.32
228.10	2.17
240.08	1.91
254.10	0.90
266.08	0.55
273.08	100.00
274.10	13.43
275.07	0.38
285.10	1.50
304.07	3.27
305.08	0.35
349.06	0.81
354.09	0.29

No. 3. NEG

CH110 19 C.D.HEWITT 09-MAR-84
CAL:CALM6

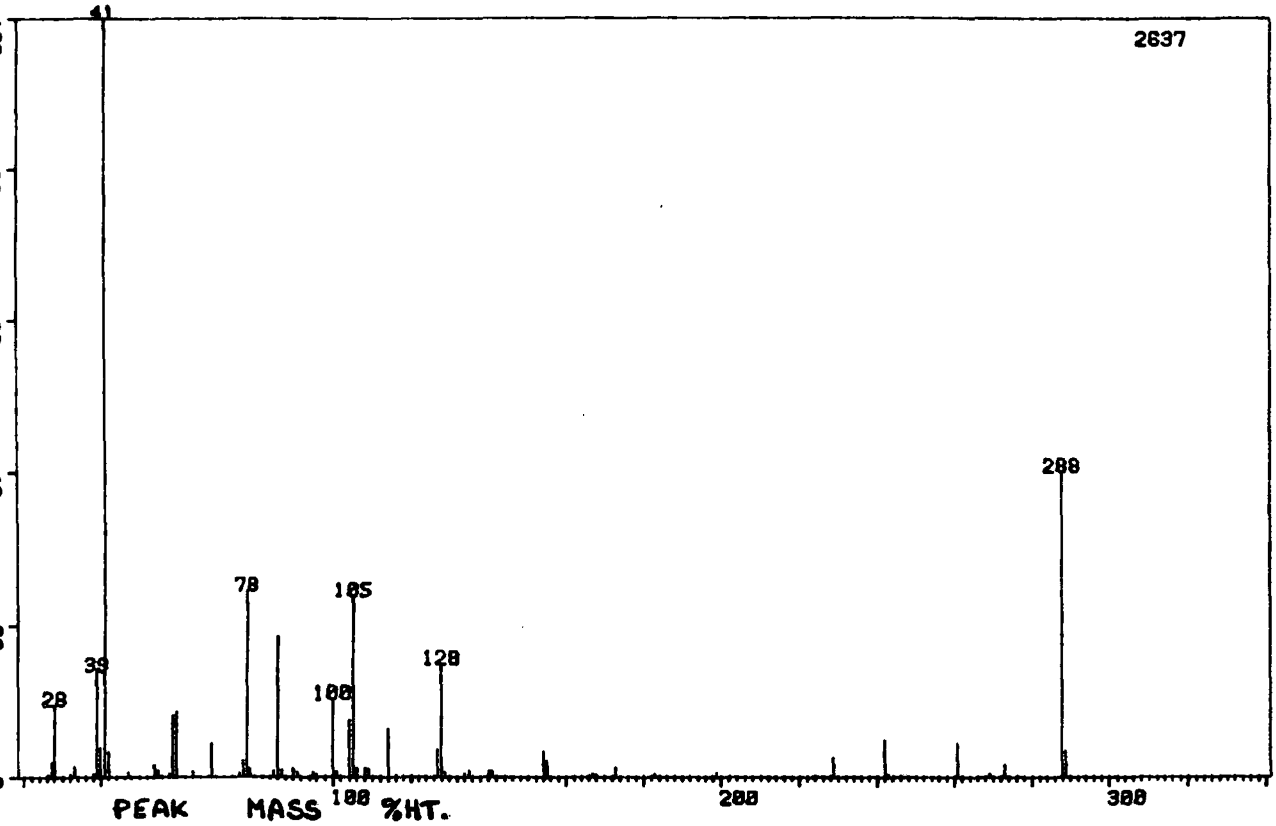


PEAK NO.	MASS	%HT. BASE
1	27.17	1.42
2	28.06	22.49
5	31.94	4.47
6	33.05	2.15
10	38.95	9.91
11	39.84	2.30
12	40.92	8.08
14	44.08	1.44
24	49.86	2.32
25	50.92	13.97
26	52.00	2.64
28	57.06	1.07
30	58.96	1.12
32	63.03	6.18
33	64.06	3.83
34	65.09	51.48
35	66.07	3.69
36	68.93	10.84
39	76.05	1.95
40	77.03	17.61
41	77.98	28.74
42	78.97	2.37
44	83.02	9.35
45	84.05	1.00
49	90.37	100.00
50	91.97	51.06
51	92.34	2.95
53	93.04	1.83
54	95.00	2.83
55	96.02	1.05
56	99.86	18.83
57	100.94	1.42
60	103.04	4.20
61	104.05	9.45
62	104.24	3.79
63	104.99	2.32
67	108.88	100.00
68	110.91	45.86
69	111.67	4.27
70	113.96	7.89
78	126.99	36.48
79	127.91	14.85
80	128.94	1.88
82	133.98	2.66
83	135.00	2.30
84	136.03	1.39
85	139.90	3.91
91	153.96	41.29
92	154.90	6.03
95	158.93	1.51
96	163.95	1.61
97	164.98	1.25
98	165.99	1.15
101	172.92	9.23
103	176.94	13.97
104	177.71	4.40
106	184.04	2.30
107	185.01	3.05
112	203.93	13.87
113	204.87	4.66
115	208.96	1.39
117	216.98	9.38
118	217.71	4.54
119	222.07	1.07
120	228.92	8.40
121	229.53	4.98
122	242.02	34.99
123	242.97	3.88
124	249.17	4.47
125	260.92	3.59
126	269.03	1.07
128	298.80	15.21
129	299.85	5.84
131	316.63	8.28
132	317.95	5.98
133	337.76	100.00
134	339.22	35.43

No. 9.

H96 S C.D.HEWITT
CAL:CALM18 STA:

24-JAN-84
8:57

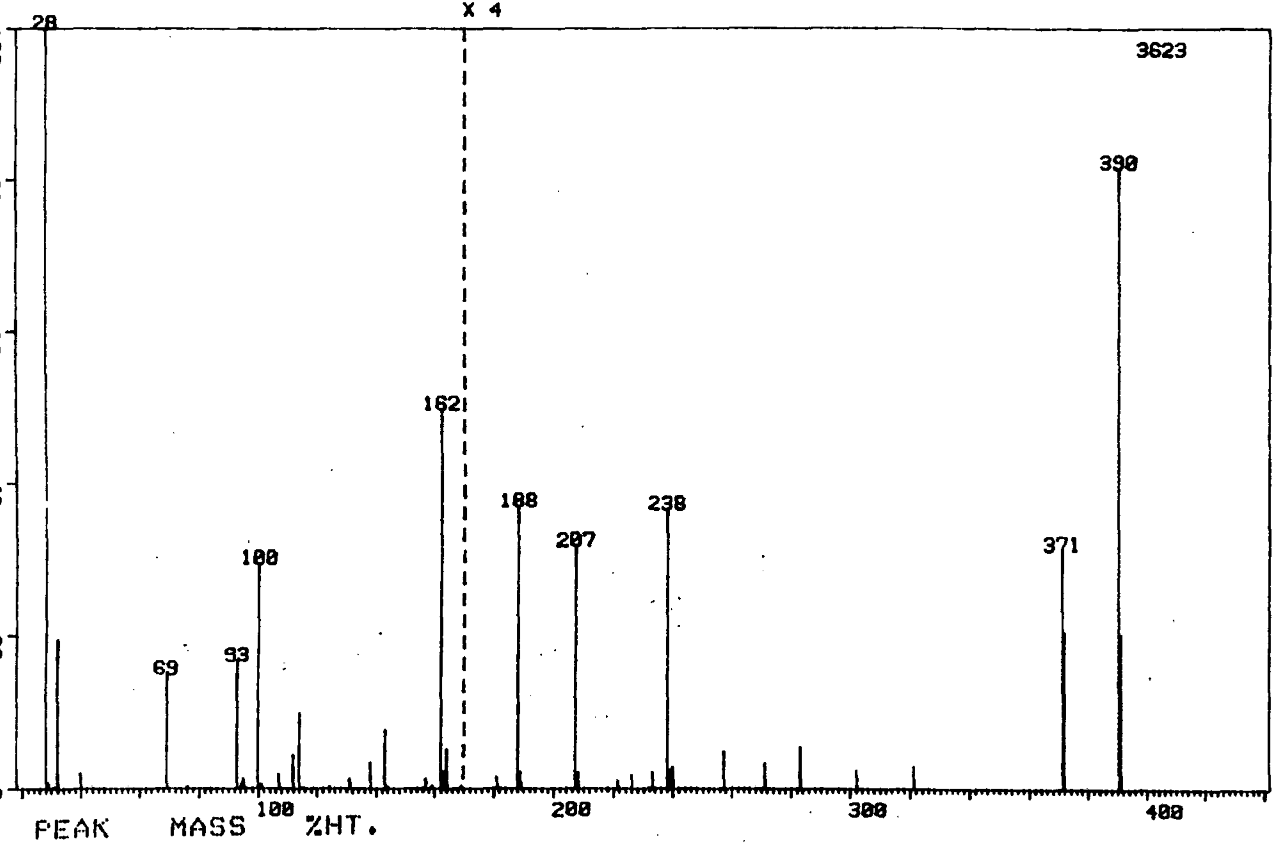


PEAK NO.	MASS	%HT. BASE
1	26.30	0.38
2	27.24	1.93
3	28.12	9.63
4	31.99	0.42
5	33.10	1.40
6	38.06	0.38
7	38.98	14.11
8	39.87	3.79
9	40.95	100.00
10	42.05	3.34
11	47.10	0.68
12	54.11	1.63
13	55.12	0.83
14	58.04	0.42
15	58.99	8.15
16	59.92	8.65
17	64.07	0.72
18	68.94	4.44
19	75.99	0.38
20	76.99	2.01
21	77.96	24.73
22	78.91	1.10
23	85.00	0.87
24	86.02	18.70
25	87.01	0.95
26	89.87	1.14
27	90.96	0.68
28	95.01	0.68
29	96.03	0.42
30	99.89	10.43
31	100.96	0.72
32	104.06	7.58
33	105.08	24.00
34	106.08	1.18
35	108.02	1.21
36	109.00	1.14
37	114.03	6.37
38	116.04	0.34
39	126.99	3.68
40	127.95	14.94
41	128.94	0.64
42	134.00	0.46
43	135.00	0.87
44	139.88	0.83
45	140.92	0.83
46	153.99	3.45
47	155.01	2.12
48	166.99	0.42
49	167.88	0.34
50	172.96	1.25
51	182.90	0.34
52	198.90	0.57
53	228.84	2.54
54	241.87	4.85
55	242.89	0.30
56	260.84	4.51
57	269.00	0.49
58	272.88	1.59
59	287.78	40.08
60	288.81	3.45

No. 10.

CH70A 8 C.HEWITT
CAL:CALM1A

17-JUN-83

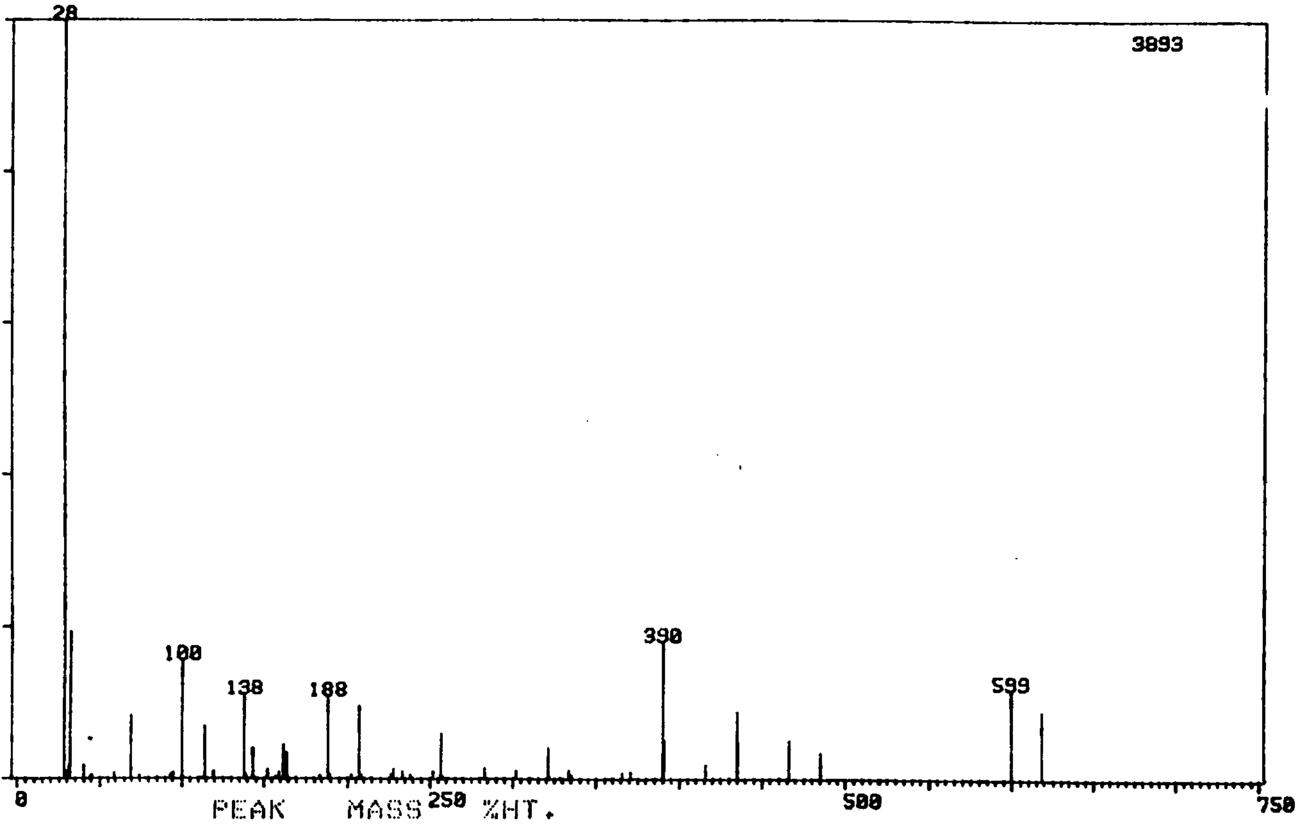


PEAK NO.	MASS	%HT. BASE
1	28.13	100.00
2	28.99	0.80
3	30.92	0.30
4	32.01	19.51
5	39.84	2.04
6	44.13	0.28
7	69.06	15.04
8	76.16	0.33
9	93.13	16.84
10	94.13	0.52
11	95.11	1.21
12	99.94	29.70
13	101.02	0.63
14	107.09	1.90
15	112.08	4.39
16	114.11	9.88
17	115.09	0.25
18	119.02	0.28
19	124.11	0.30
20	131.04	1.35
21	138.08	3.39
22	143.11	7.65
23	144.09	0.30
24	157.10	1.30
25	159.07	0.41
26	162.06	50.04
27	163.09	2.26
28	164.10	5.11
29	169.10	0.36
30	181.10	0.39
31	188.14	9.33
32	189.10	0.55
33	207.13	8.03
34	208.10	0.52
35	221.15	0.28
36	226.13	0.47
37	233.16	0.52
38	238.11	9.22
39	239.10	0.63
40	240.12	0.72
41	257.19	1.24
42	271.22	0.86
43	283.22	1.38
44	302.16	0.63
45	321.31	0.77
46	371.33	7.87
47	372.03	5.19
48	390.34	20.40
49	391.25	5.11

No. 11.

CH70B 8 C.HEWITT
CAL:CALM1A

17-JUN-83



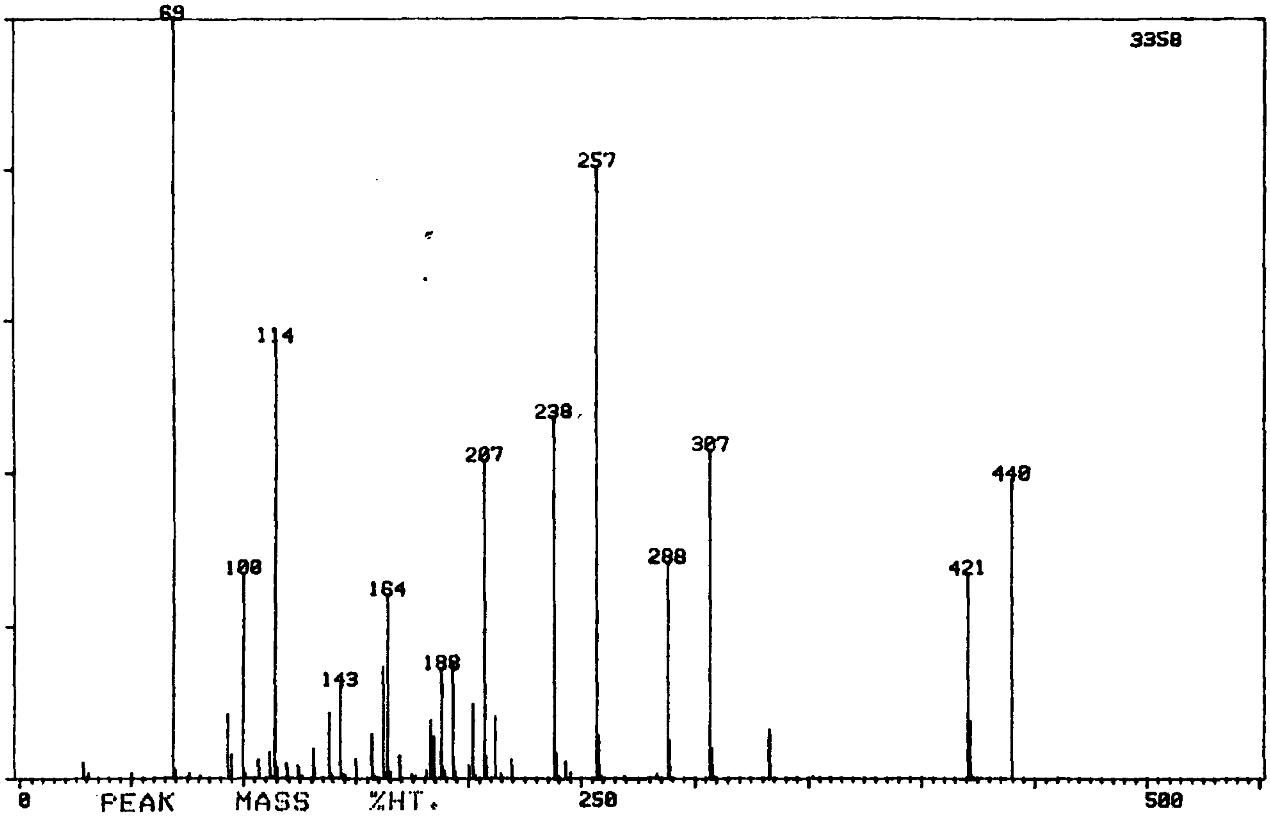
PEAK NO.	MASS	%HT. BASE			
1	28.13	100.00	36	233.13	0.98
2	29.01	1.03	37	238.06	0.54
3	30.92	1.62	38	252.11	0.95
4	32.01	19.39	39	257.11	5.91
5	39.84	1.85	40	258.08	0.39
6	44.14	0.28	41	283.15	1.49
7	45.20	0.57	42	302.08	1.13
8	59.08	0.74	43	321.24	4.11
9	69.05	8.32	44	322.21	0.41
10	74.24	0.49	45	328.14	0.26
11	93.14	0.54	46	333.13	1.10
12	95.14	0.82	47	335.22	0.49
13	99.96	15.75	48	366.23	0.80
14	101.03	0.36	49	371.18	0.95
15	112.08	0.28	50	390.07	18.19
16	114.13	6.91	51	390.98	5.06
17	119.04	0.95	52	416.24	1.90
18	138.09	11.17	53	435.02	8.86
19	139.08	0.54	54	435.73	4.75
20	143.11	3.96	55	466.29	5.01
21	152.12	1.16	56	485.28	3.54
22	157.11	0.33	57	599.32	11.97
23	159.05	0.90	58	618.39	9.02
24	162.07	4.44			
25	164.11	3.42			
26	169.08	0.23			
27	183.15	0.49			
28	188.12	10.94			
29	189.06	0.59			
30	202.14	0.54			
31	207.11	9.56			
32	208.09	0.57			
33	214.15	0.26			
34	226.14	0.64			
35	229.08	1.34			

No. 12.

CH71AR 3 C.D.HEWITT

CAL:CALM28

01-JUL-83

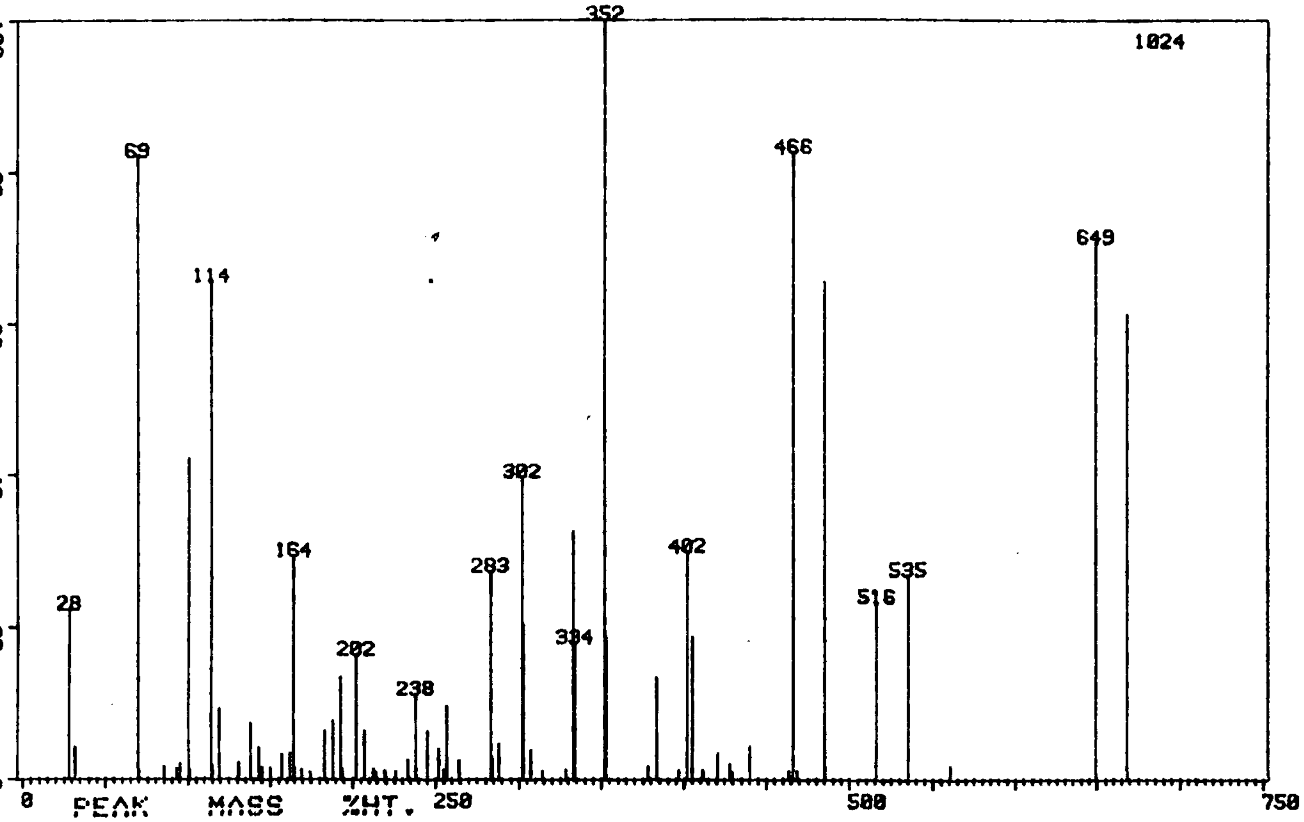


PEAK NO.	MASS	%HT. BASE
1	28.13	2.08
2	30.91	0.74
3	49.89	0.83
4	68.55	0.30
5	68.98	100.00
6	69.92	1.04
7	76.10	0.66
8	80.95	0.42
9	93.00	8.46
10	94.03	0.36
11	95.03	3.19
12	99.89	27.04
13	100.97	0.63
14	107.03	2.47
15	112.00	3.54
16	113.02	0.27
17	114.05	57.50
18	115.06	1.46
19	118.99	1.94
20	124.04	1.70
21	126.06	0.36
22	130.98	3.96
23	138.00	8.64
24	138.98	0.51
25	143.01	12.24
26	144.03	0.57
27	145.04	0.45
28	149.90	2.50
29	157.01	5.93
30	158.00	0.36
31	159.03	0.30
32	161.98	14.71
33	163.01	0.77
34	164.01	24.21
35	165.01	0.92
36	168.97	3.13
37	174.02	0.57
38	176.04	0.36
39	180.97	1.07
40	182.97	7.71
41	184.41	5.57
42	186.72	0.27
43	187.97	14.47
44	189.00	1.01
45	192.99	15.37
46	194.01	0.95
47	199.94	1.58
48	201.94	9.86
49	202.99	0.48
50	206.98	41.69
51	207.88	2.83
52	211.99	8.28
53	214.38	0.66
54	218.98	2.53
55	237.98	47.35
56	238.88	3.45
57	239.90	0.33
58	240.14	0.30
59	243.00	2.14
60	245.08	0.77
61	257.01	80.46
62	257.96	5.72
63	258.94	0.36
64	269.03	0.45
65	283.04	0.68
66	287.99	28.38
67	288.86	5.06
68	306.97	43.03
69	307.94	4.02
70	308.86	0.30
71	332.95	6.43
72	333.45	5.99
73	352.01	0.33
74	389.90	0.24
75	420.93	27.07
76	421.83	7.59
77	423.05	0.33
78	439.92	39.28

No. 13.

CH712 25 C.D.HEWITT
CAL:CALMS

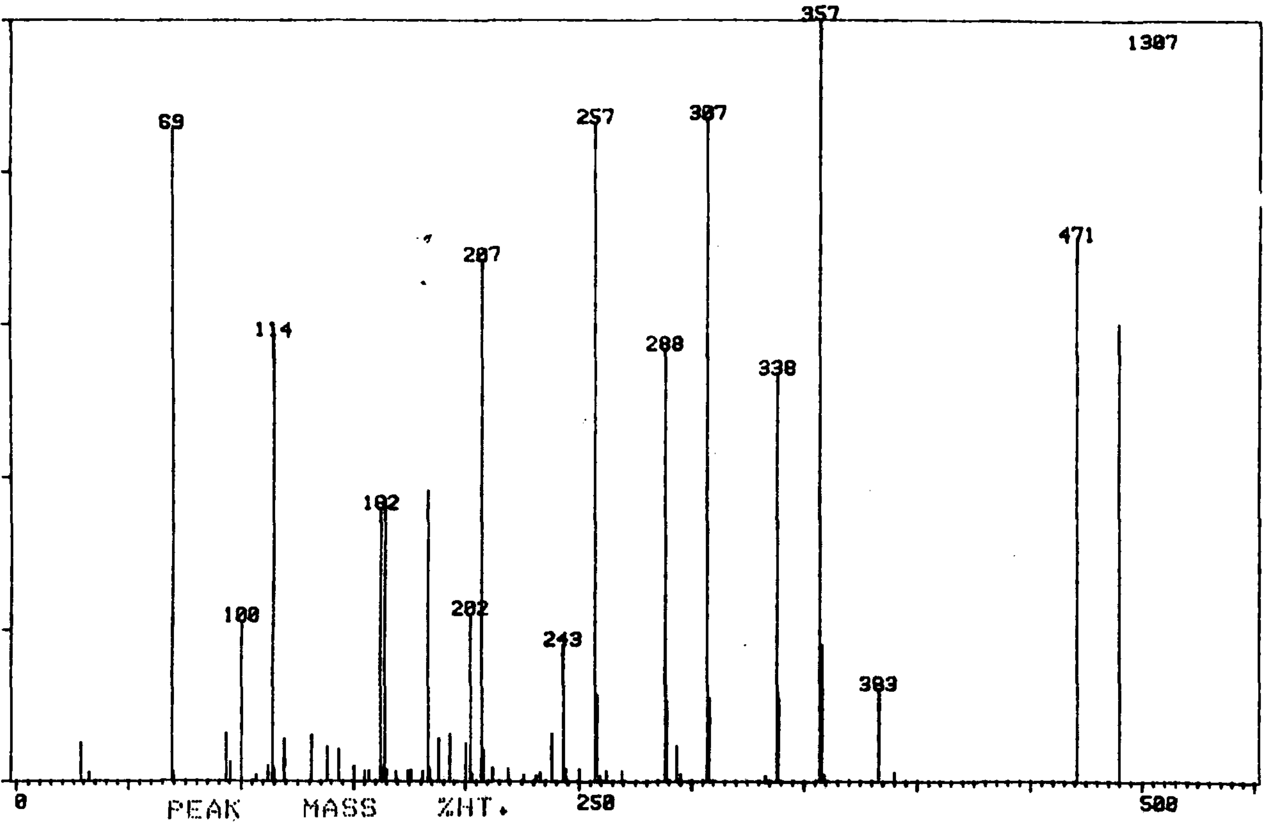
22-SEP-83



PEAK NO.	MASS	%HT. BASE
1	28.12	22.36
2	32.01	4.20
3	69.01	82.13
4	69.96	1.17
5	85.09	1.66
6	93.09	1.37
7	95.10	2.05
8	99.97	42.29
9	101.03	1.27
10	114.11	65.72
11	115.08	1.86
12	119.00	9.28
13	131.04	2.15
14	138.04	7.32
15	143.08	4.10
16	145.13	1.56
17	150.02	1.46
18	157.07	3.22
19	162.04	3.42
20	164.08	29.39
21	165.11	1.46
22	169.05	1.27
23	174.10	0.98
24	183.04	6.35
25	188.02	7.62
26	193.02	13.38
27	194.07	1.27
28	202.05	16.31
29	207.08	6.35
30	212.18	1.37
31	214.02	0.98
32	218.98	1.17
33	226.09	1.07
34	233.07	2.64
35	238.07	11.13
36	245.11	6.25
37	252.11	4.00
38	255.08	1.27
39	257.01	9.57
40	264.09	2.44
41	283.08	27.34
42	284.09	2.83
43	288.08	4.69
44	302.02	39.84
45	302.69	20.21
46	307.04	3.81
47	314.12	1.07
48	328.05	1.27
49	333.05	32.62
50	333.78	17.87
51	352.15	100.00
52	353.12	18.65
53	378.15	1.76
54	383.21	13.38
55	397.01	1.27
56	401.92	29.98
57	405.14	18.65
58	411.16	1.27
59	412.18	0.98
60	421.01	3.42
61	428.07	2.05
62	429.68	0.98
63	439.98	4.30
64	463.33	1.17
65	466.13	82.52
66	468.29	1.17
67	484.98	65.53
68	516.07	23.34
69	535.02	26.86
70	561.00	1.76
71	648.97	70.80
72	668.11	61.43

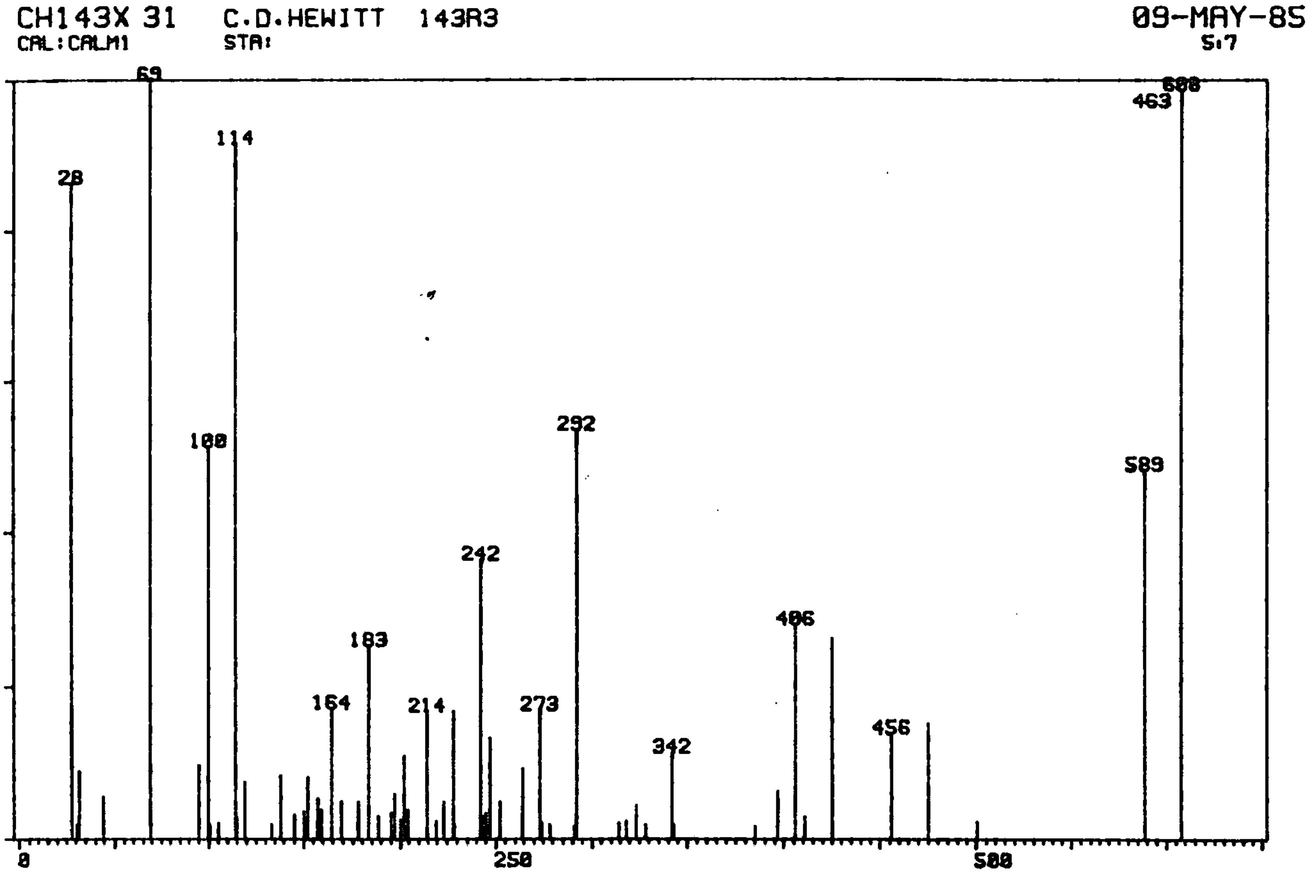
No. 14.

CH73CD 14 C.D.HEWITT 73CDE 30-JUN-83
CAL:CALM28



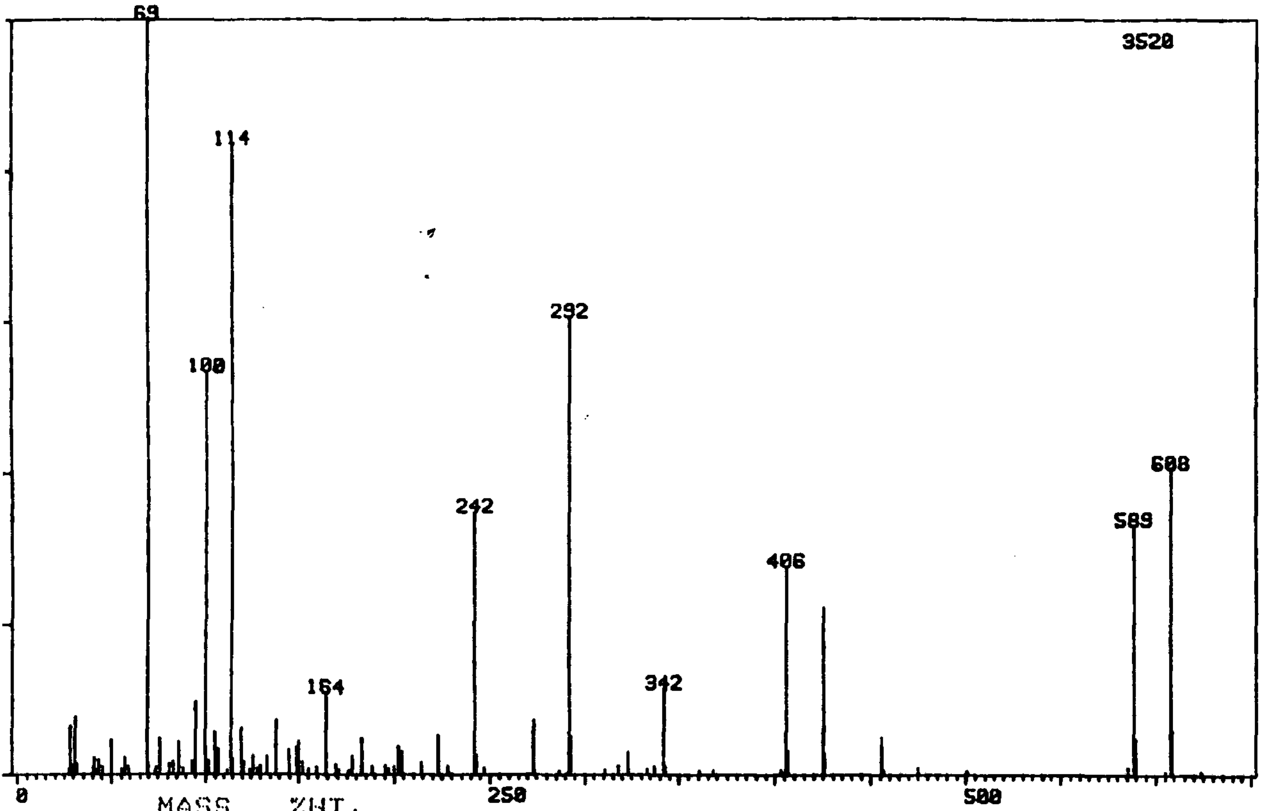
PEAK NO.	MASS	%HT. BASE
1	28.13	5.13
2	32.01	1.15
3	68.98	85.77
4	69.92	1.15
5	93.03	6.35
6	95.07	2.45
7	99.93	21.19
8	107.07	0.84
9	112.03	2.07
10	114.05	58.76
11	115.08	1.68
12	118.99	5.59
13	131.00	6.20
14	138.02	4.51
15	143.03	4.21
16	149.95	1.99
17	155.06	1.30
18	157.06	1.38
19	162.03	35.96
20	163.06	1.76
21	164.06	37.03
22	165.07	1.53
23	169.02	1.22
24	174.08	1.38
25	176.09	1.53
26	181.03	1.30
27	183.06	38.41
28	184.06	1.76
29	188.06	5.66
30	193.06	6.27
31	200.00	4.97
32	202.01	22.04
33	203.09	0.99
34	207.05	68.55
35	208.05	4.21
36	212.06	1.76
37	219.02	1.61
38	226.07	0.92
39	231.18	0.77
40	232.80	1.15
41	238.03	6.35
42	243.03	17.98
43	244.07	1.68
44	250.05	1.61
45	257.04	86.53
46	257.90	11.40
47	259.14	0.77
48	262.03	1.30
49	269.03	1.38
50	288.04	56.85
51	288.86	10.64
52	293.07	4.67
53	295.10	0.99
54	307.00	86.99
55	307.92	10.94
56	333.05	0.77
57	338.02	53.63
58	338.86	10.79
59	357.02	100.00
60	357.98	17.98
61	358.93	0.84
62	383.09	12.09
63	390.01	1.15
64	471.17	71.23
65	490.05	60.21

No. 15.


CH143X 31
C.D.HEWITT 143R3
09-MAY-85
CAL:CALM1
STA:
S:7
69
608
463
114
28
100
292
589
242
406
183
164
214
273
456
342
0
250
500

No. 16.

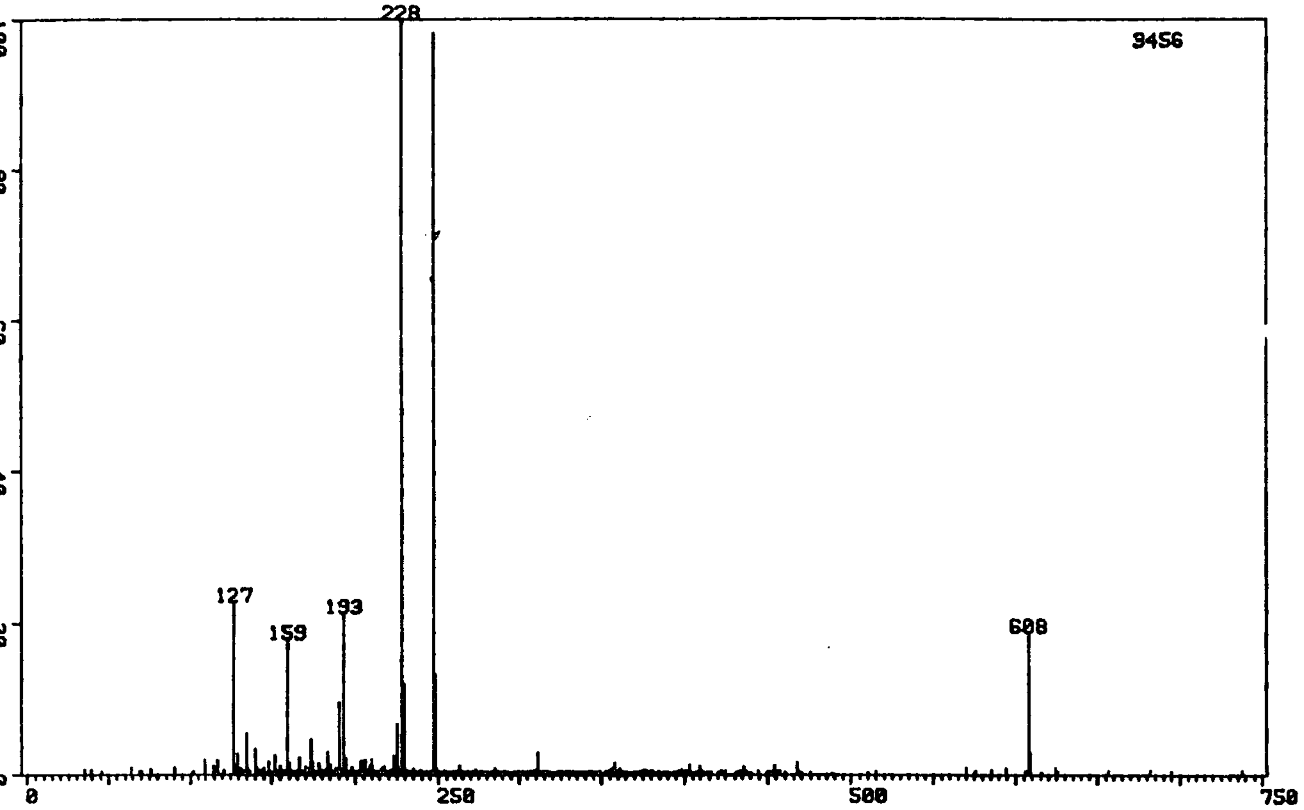
C169SX 4 C.D.HEWITT 24-JUL-85
CAL:CALT1 STA: 8:42



MASS	%HT. BASE
27.30	0.77
28.17	6.48
29.05	1.22
30.93	7.78
30.95	0.88
32.03	1.45
39.82	0.94
40.97	2.24
43.13	1.96
45.15	1.14
49.87	4.69
55.14	0.82
56.14	0.65
57.12	2.30
59.00	1.11
68.95	100.00
69.02	1.62
69.89	1.22
74.07	0.94
76.08	4.83
80.98	1.45
83.06	1.68
86.07	4.32
88.03	0.85
93.05	1.73
95.07	9.77
99.95	53.64
100.98	1.59
102.03	1.82
105.06	5.65
107.04	3.49
112.00	0.60
114.03	83.64
115.03	2.10
118.96	6.19
120.95	1.65
123.99	0.71
126.01	2.50
127.99	0.85
129.89	1.16
133.03	2.47
138.00	7.24
145.03	3.32
149.00	3.69
149.94	4.40
151.99	1.68
155.02	0.74
158.97	0.97
164.00	10.91
168.95	1.42
170.95	0.74
177.97	2.44
182.96	4.80
187.96	1.14
194.97	1.28
196.96	0.88
199.90	1.11
201.93	3.72
203.97	3.10
213.96	1.59
222.93	5.31
227.93	1.16
241.91	34.97
242.92	2.70
246.92	0.99
272.90	7.27
273.90	0.65
286.91	0.60
291.86	60.88
292.91	5.20
310.87	0.65
317.91	1.25
322.91	3.04
332.88	0.77
336.91	1.16
341.90	11.45
342.92	1.14
360.88	0.60
367.88	0.62
402.88	0.68
405.94	27.70
406.94	3.24
424.91	22.24
425.93	2.84
455.89	5.03
456.92	0.62
474.88	0.94
500.87	0.54
585.77	1.05
588.77	33.21
589.83	4.83
607.87	40.68
608.85	5.88

No.17. EI.

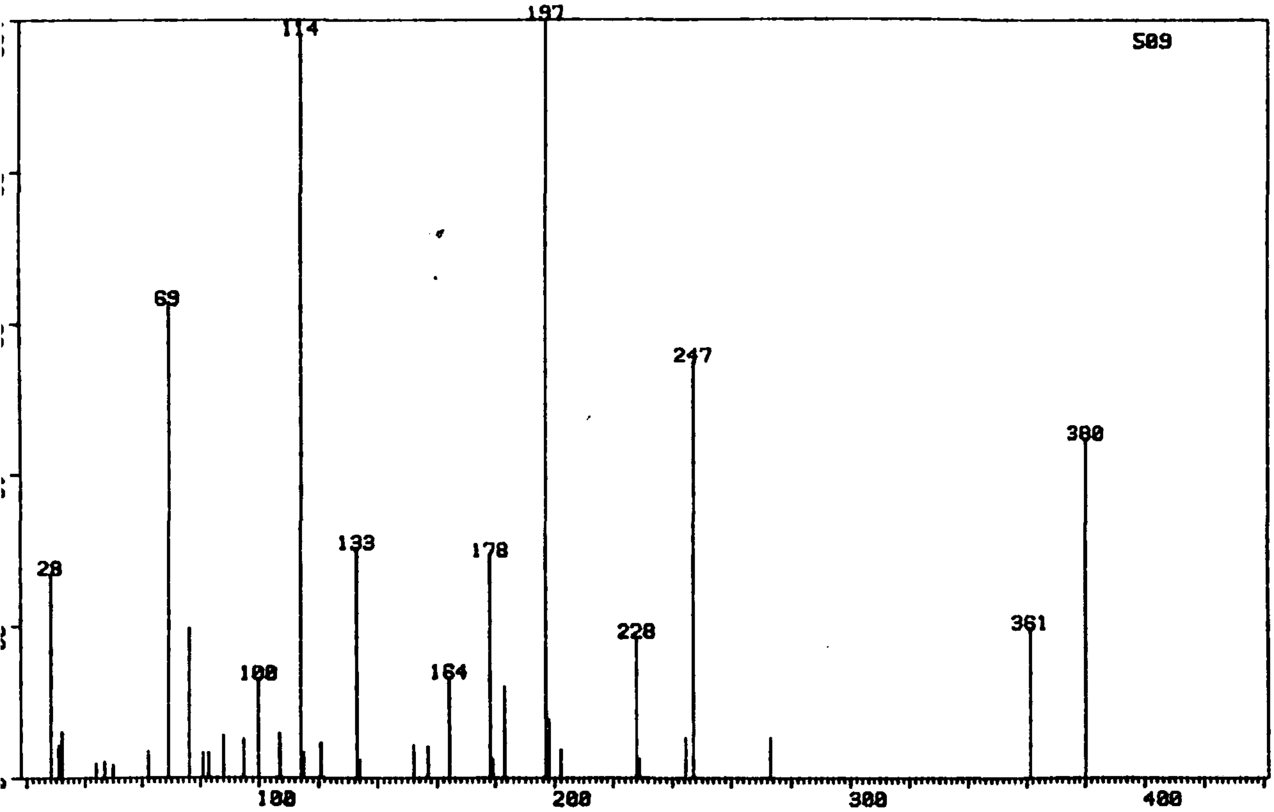
C169SX 5 C.D.HEWITT NEG. I.BU 24-JUL-85
CAL:CALN1 STA: 0:51



MASS	%HT. BASE
126.93	22.97
135.06	5.56
158.99	18.06
189.96	9.58
193.02	21.47
225.03	6.74
228.00	100.00
229.00	12.04
247.04	98.12
248.04	13.25
608.05	18.95

No. 17. NEG

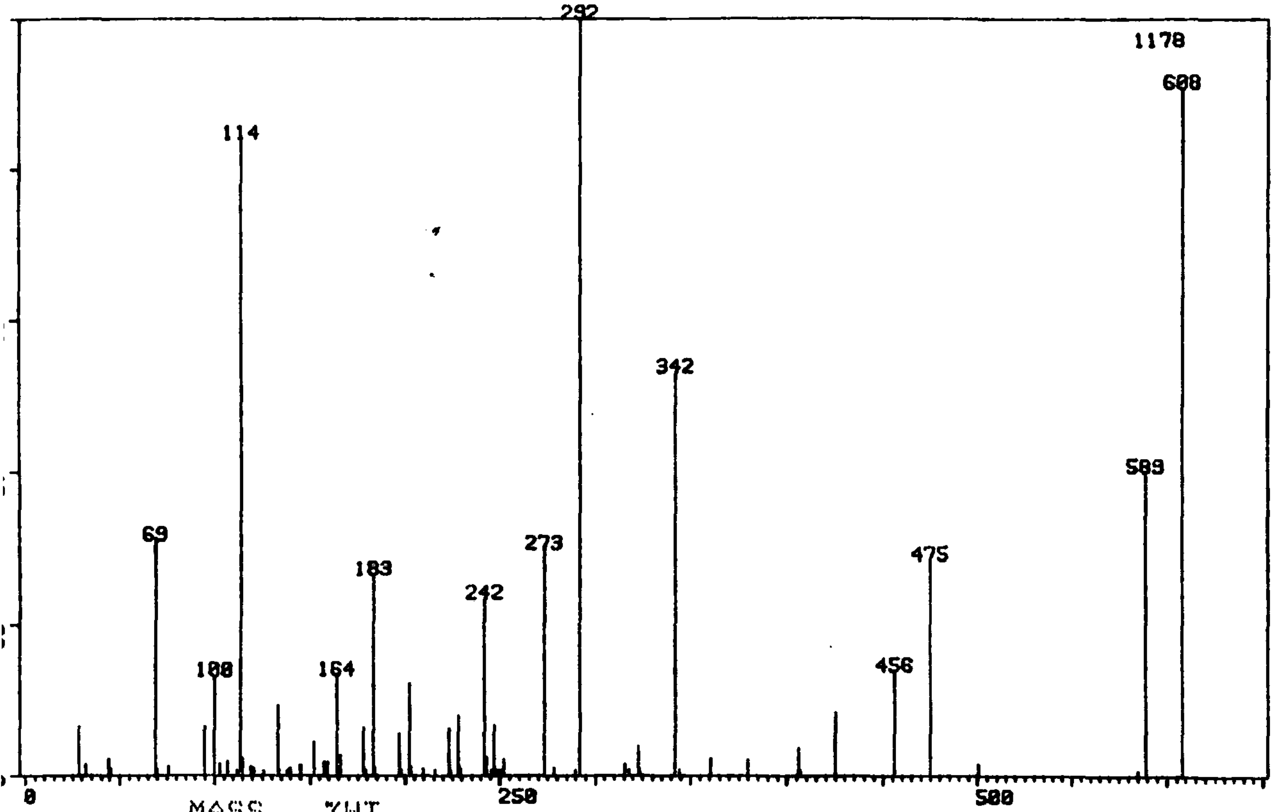
CH174X 32 C.D.HEWITT 04-JUN-85
CAL:CALM30 STA: S:21



MASS	%HT. BASE
28.13	26.92
30.91	4.32
32.02	6.09
44.14	1.96
47.12	2.16
49.88	1.77
62.05	3.54
69.00	62.67
76.12	19.84
80.99	3.34
83.08	3.34
88.05	5.50
95.07	5.11
99.92	12.97
107.04	5.89
114.06	98.04
115.07	3.34
121.02	4.52
133.07	30.26
134.12	2.36
152.03	4.32
157.04	4.13
164.06	13.16
178.08	29.27
179.05	2.55
183.09	11.98
197.05	100.00
198.03	7.66
202.05	3.73
228.11	18.47
229.00	2.55
244.75	5.30
247.25	55.21
273.11	5.30
361.28	19.65
380.14	44.79

No. 18

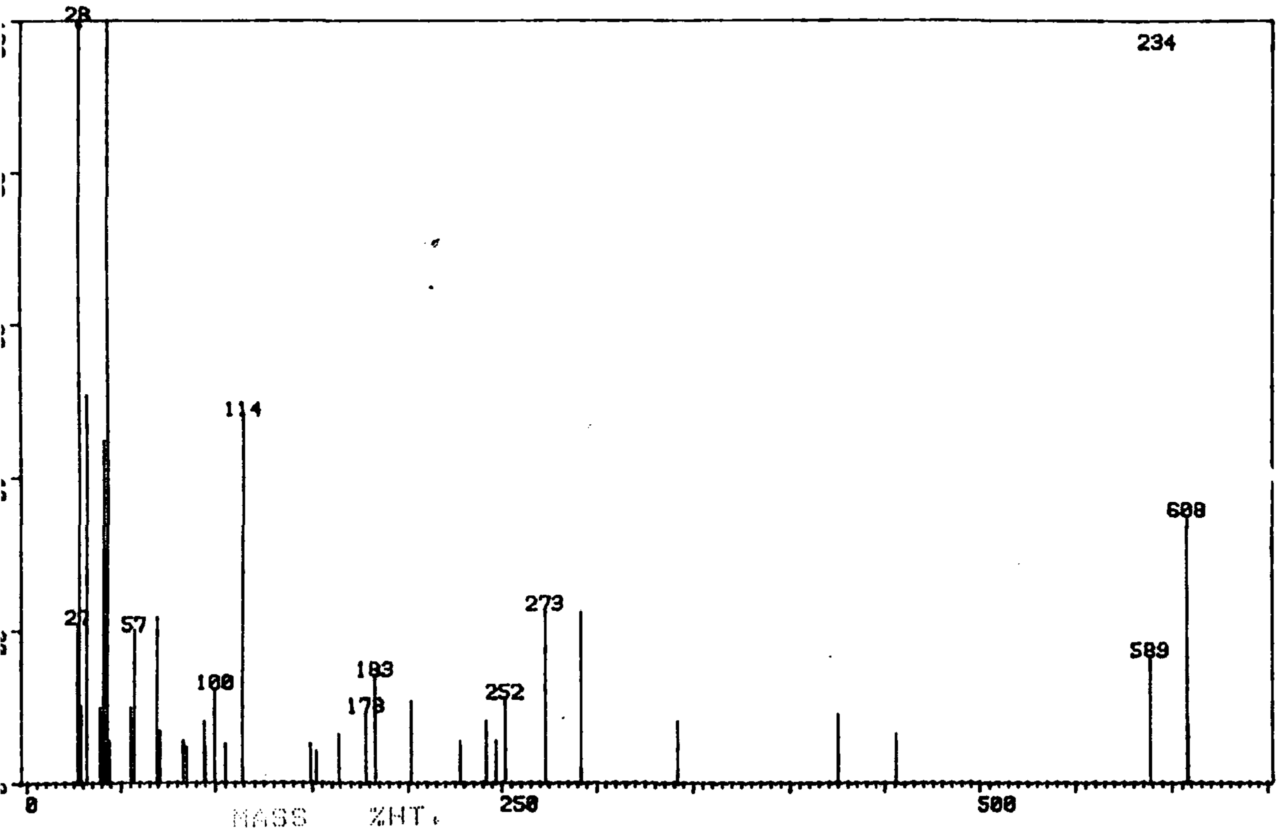
CH174X 82 C.D.HEWITT 04-JUN-85
CAL:CALM30 STR: 13:29



MASS	%HT. BASE
28.13	6.62
32.02	1.53
44.12	2.29
45.16	1.02
68.99	31.15
69.93	0.93
76.11	1.27
95.06	6.54
99.91	13.33
102.90	1.61
107.01	1.95
111.95	0.76
112.01	0.76
114.02	84.21
115.05	2.29
118.98	1.27
120.98	1.02
126.06	0.76
133.02	9.34
134.05	0.85
138.03	0.68
139.95	1.02
145.06	1.44
152.01	4.50
157.05	1.87
158.98	1.87
164.04	13.50
165.04	0.93
166.04	2.80
178.02	6.37
179.05	0.85
183.02	26.74
184.05	1.10
197.01	5.60
198.00	0.85
201.98	12.22
202.98	1.19
209.00	0.93
216.04	0.85
223.05	6.28
224.00	0.76
228.03	7.98
229.06	1.02
242.00	23.51
242.99	2.46
245.59	0.76
247.12	6.71
248.58	0.76
248.83	0.68
249.08	0.76
249.90	0.76
251.01	0.76
252.04	2.21
273.13	30.14
278.01	1.10
289.28	0.76
292.02	100.00
315.97	1.61
317.98	0.85
322.98	3.99
324.01	0.93
342.06	53.40
344.08	0.85
360.97	2.29
379.88	2.21
405.98	3.74
407.04	0.76
425.12	8.49
456.10	14.01
475.05	28.78
500.89	1.61
585.01	0.76
589.03	40.24
607.97	90.83

No. 19.

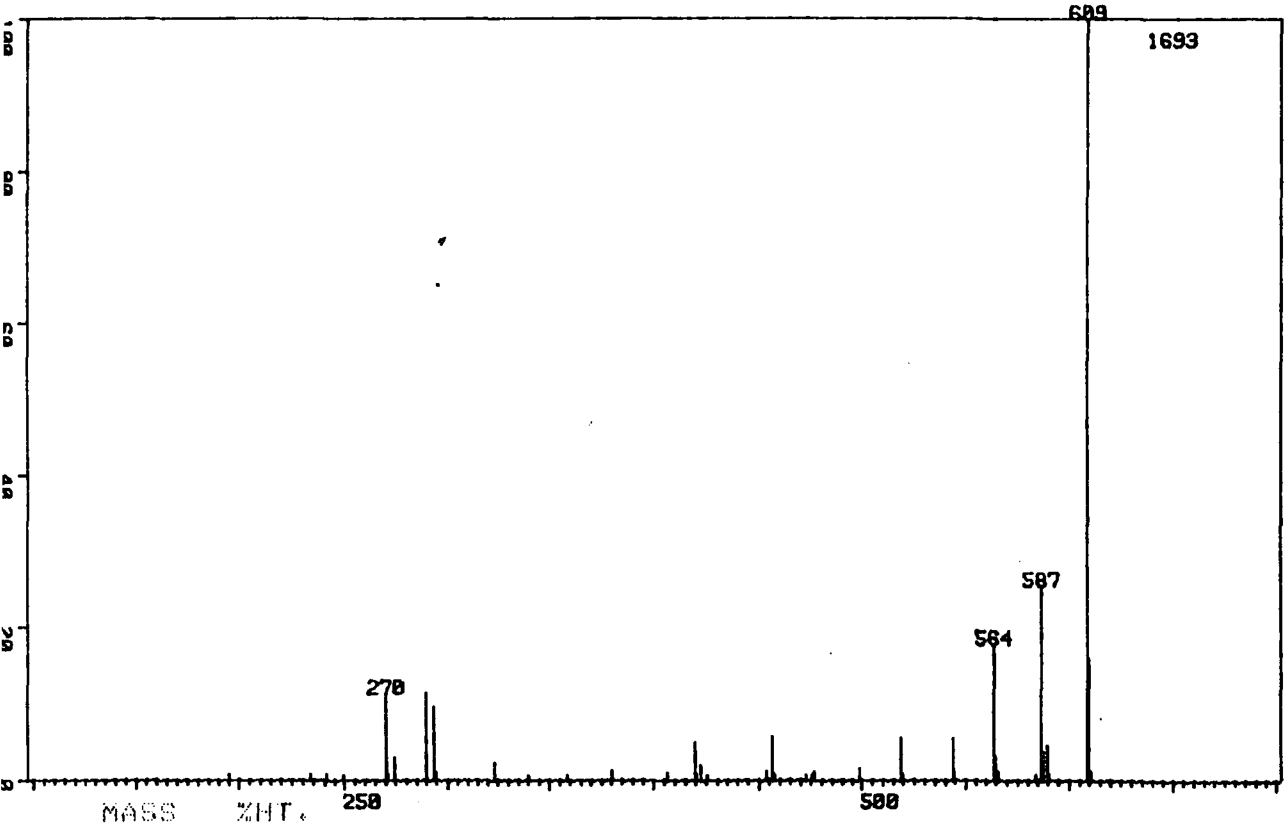
129B1X 2 C.D.HEWITT 09-OCT-84
CAL:CALTS STA:2 0:24



MASS	%HT. BASE
27.15	7.72
28.03	100.00
28.90	1.73
28.93	3.78
31.87	18.74
38.89	3.62
39.73	2.99
40.86	16.54
41.95	11.18
43.03	36.65
44.00	2.05
55.09	3.62
56.07	2.99
57.08	7.40
66.95	8.03
69.02	3.62
69.97	2.20
71.03	2.52
83.09	2.05
85.13	1.73
94.00	2.99
94.97	1.73
99.86	4.57
105.07	1.89
113.98	17.80
148.92	1.89
151.93	1.57
163.93	2.36
177.90	3.46
182.89	5.20
201.89	3.94
227.91	2.05
241.87	2.99
246.90	2.05
251.90	4.09
272.94	8.35
291.86	8.19
341.88	2.99
424.81	3.31
455.82	2.36
588.63	6.14
607.60	12.91
608.53	2.83

No. 20. EI.

129B1X 13   C.D.HEWITT   NH3   C.I.GAS   09-OCT-84
CAL:CALTS   STA: 1:55

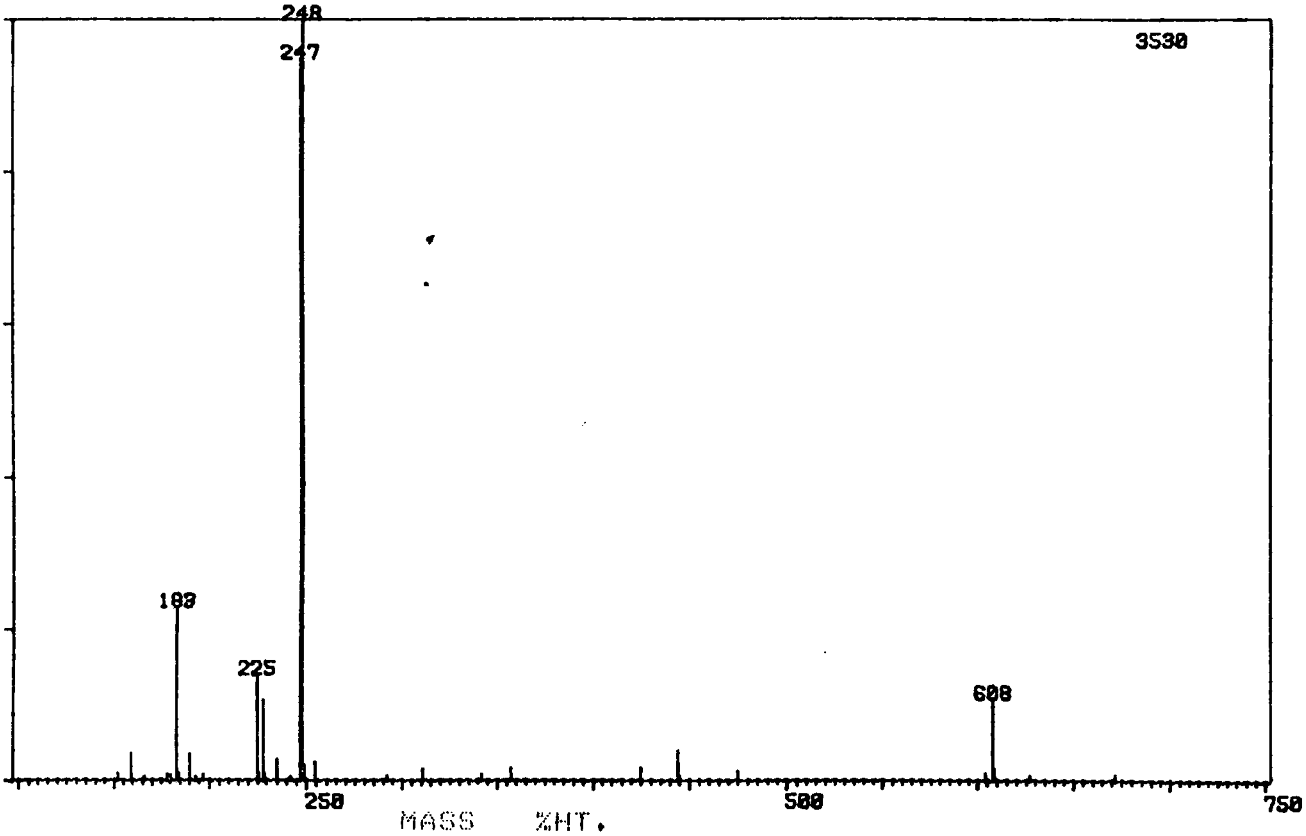


```
   MASS     %HT.
            BASE

  195.16    0.83     586.74   25.58
  233.27    0.77     587.75    3.78
  241.23    0.71     589.66    4.61
  249.17    0.59     590.69    0.89
  270.24   11.40     608.83  100.00
  271.23    0.89     609.82   16.01
  274.26    3.01     610.82    1.24
  289.28   11.46
  293.31    9.69
  294.31    1.06
  323.33    2.30
  339.35    0.65
  340.37    0.59
  358.41    0.65
  380.48    1.30
  406.51    0.95
  419.52    4.90
  420.49    0.89
  422.51    1.95
  425.47    0.71
  453.55    1.18
  456.53    5.79
  457.54    0.83
  472.58    0.65
  475.57    0.65
  476.59    1.12
  498.66    1.59
  518.71    5.61
  519.70    0.89
  543.68    5.49
  544.74    1.18
  563.82   17.96
  564.81    3.13
  565.79    1.12
  583.71    0.59
```

No. 20. CI

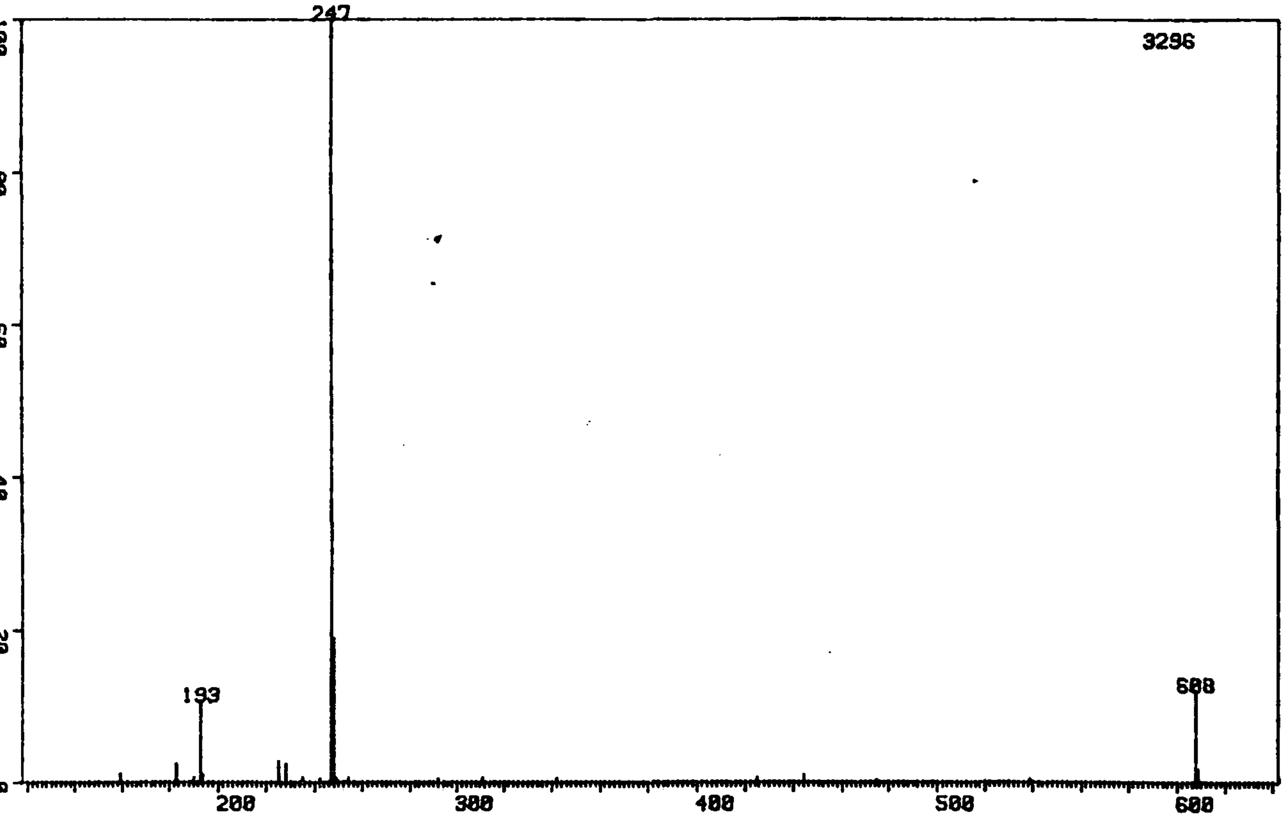
129B1X 7 C.D.HEWITT NH3 NEG.GAS 09-OCT-84
CAL:CALTS STA: 1:5



MASS	%HT. BASE
152.11	0.96
159.10	3.51
166.14	0.42
178.10	0.79
180.03	0.65
183.07	23.03
184.08	0.99
189.98	3.37
193.01	0.48
196.99	0.85
225.04	14.02
226.04	0.96
228.07	10.62
229.06	0.76
235.10	2.69
242.04	0.48
247.00	94.90
248.00	100.00
249.02	1.95
254.04	2.41
292.04	0.48
311.01	1.47
342.02	0.88
357.05	1.67
425.04	1.67
444.04	3.85
445.08	0.54
475.11	1.16
603.98	0.93
607.96	10.88
609.01	1.44

No. 20. NEG. NH_3.

CDH129 4 C.D.HEWITT 129B1 NEG. ARGON 193 REF 11-OCT-84
CAL:CALN18 STA: 0:40

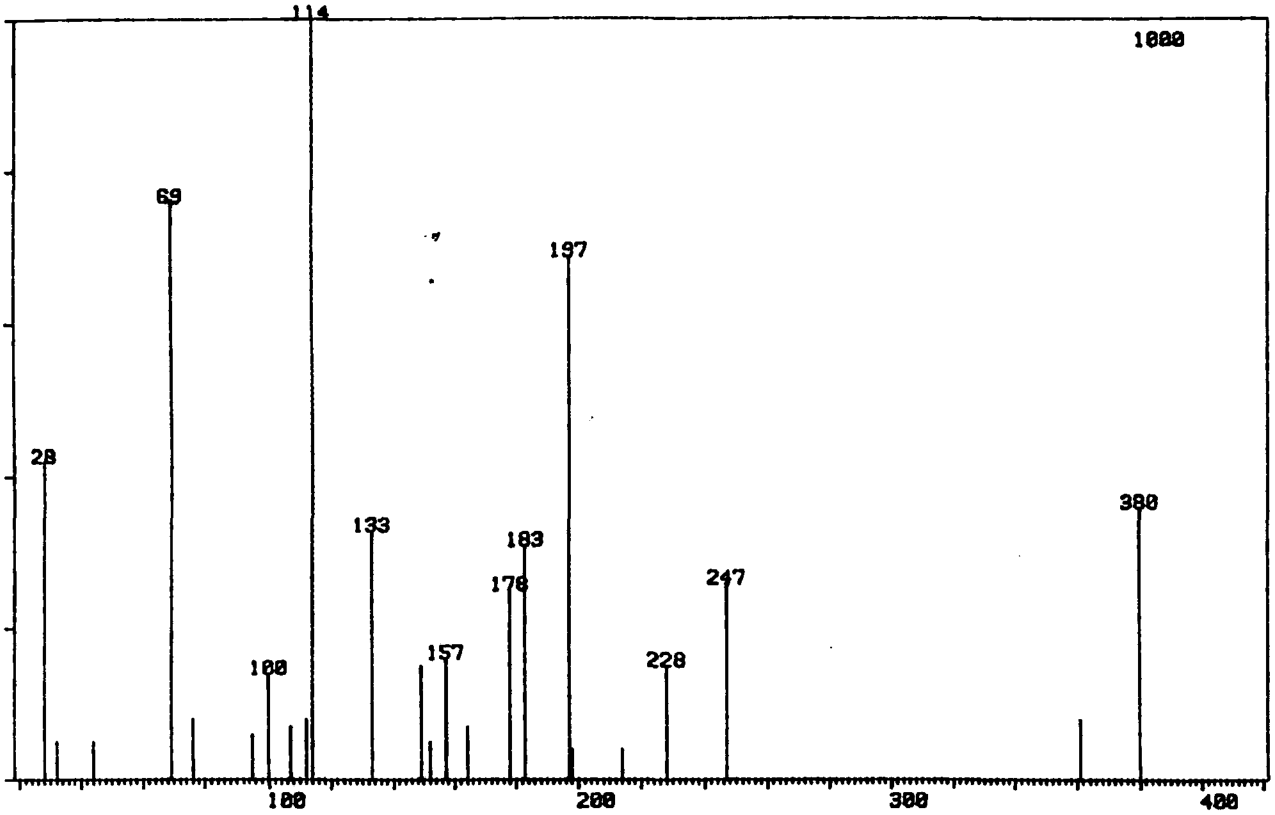


MASS	%HT. BASE
159.12	1.12
183.07	2.46
189.98	0.67
193.01	10.77
194.01	0.91
225.02	2.67
228.04	2.46
235.08	0.64
242.05	0.46
247.05	100.00
248.02	18.96
249.02	0.46
254.04	0.58
292.00	0.49
310.98	0.55
341.98	0.46
424.94	0.70
443.94	1.00
474.95	0.39
538.75	0.42
607.78	12.14
608.83	1.85

No. 20. NEG. ARGON.

129EI 0
CAL:LIB STA:

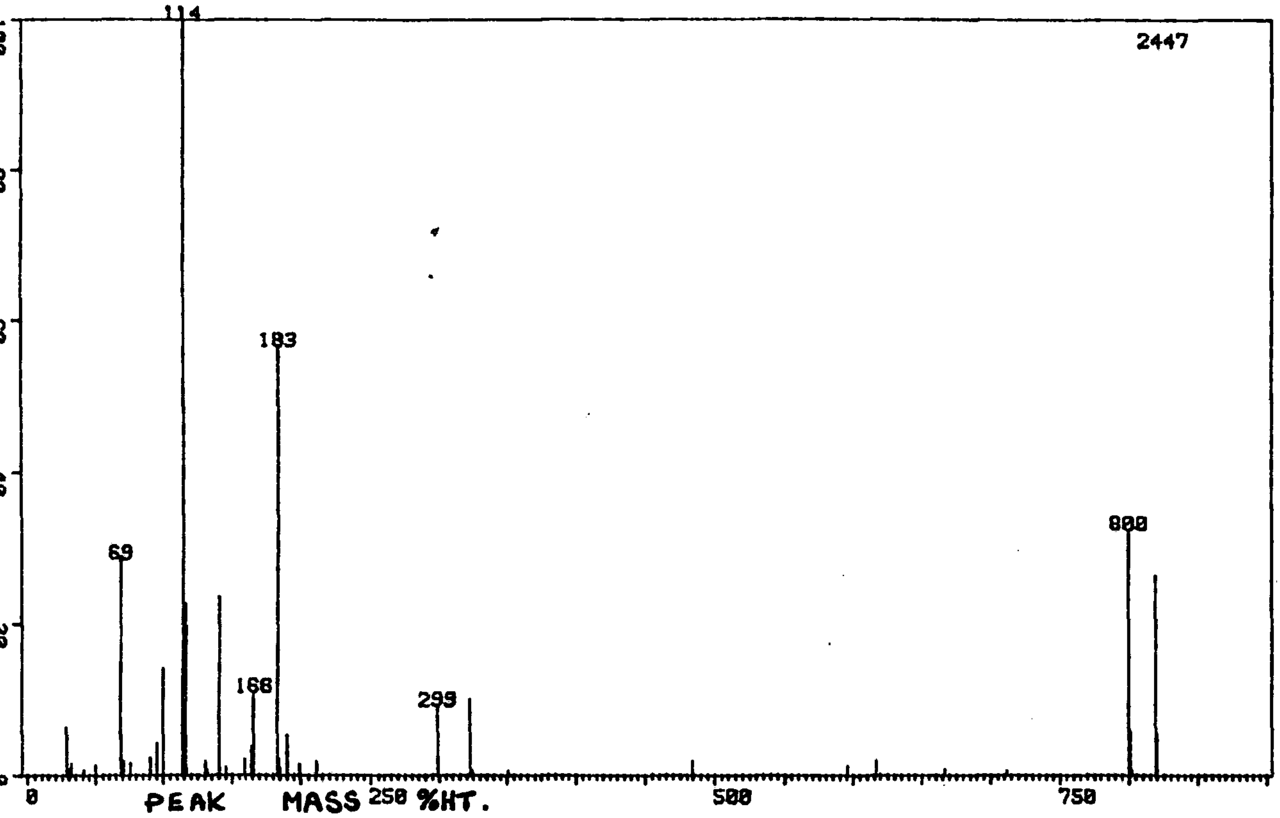
08-SEP-86
0:0



MASS	%HT. BASE
28.06	42.01
31.96	4.83
44.10	5.20
68.99	75.46
76.10	7.81
95.11	5.95
99.96	13.38
107.07	6.32
112.04	7.81
114.07	100.00
133.09	33.09
146.70	14.50
152.16	5.20
157.11	15.61
164.13	6.69
178.09	24.54
183.09	31.23
197.08	68.77
198.14	4.09
214.12	4.09
228.03	14.50
247.08	26.02
361.16	8.18
380.16	35.69

No. 21.

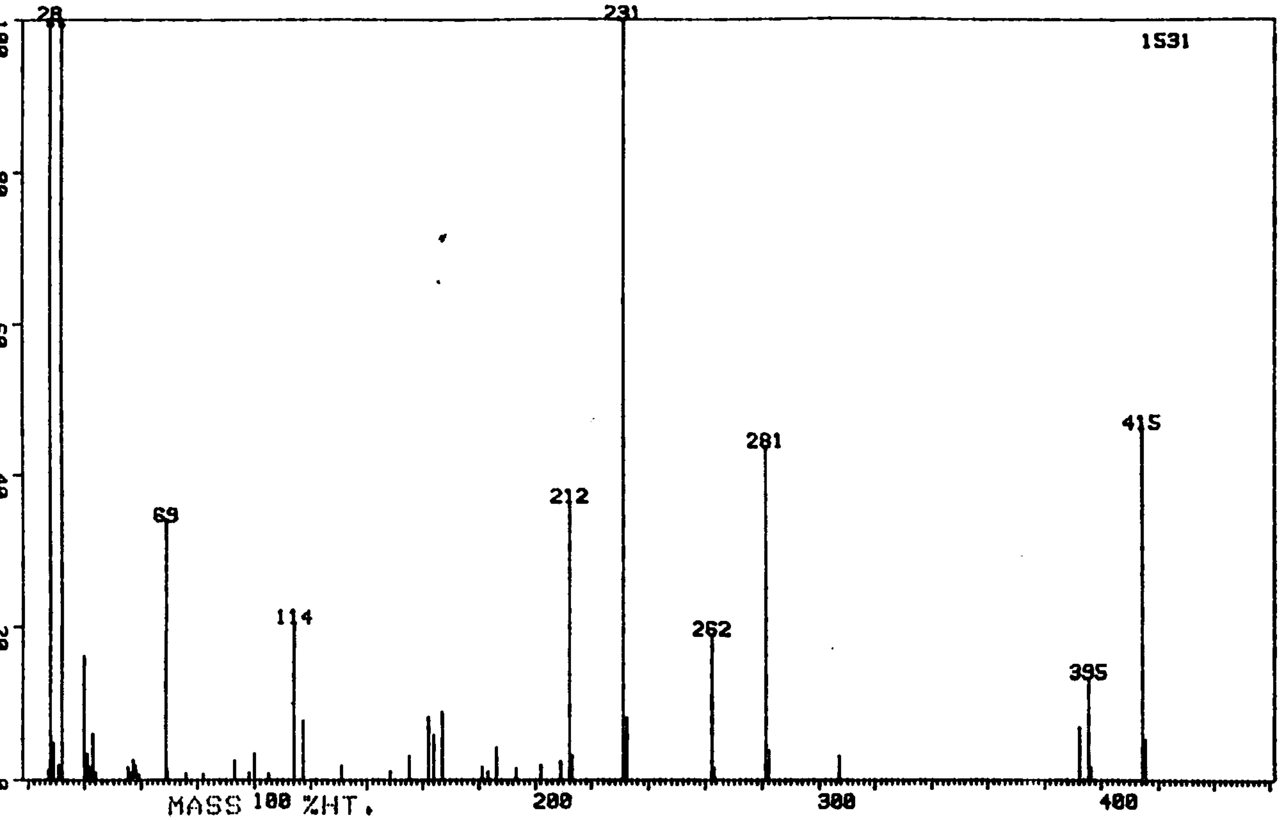
CH87RX 26 C.D.HEWITT 16-JUL-84
CAL:CAL16M STA: 9:24



PEAK NO.	MASS	%HT. BASE
1	28.10	6.38
2	30.85	0.94
3	31.96	1.51
4	40.94	0.69
5	49.86	1.39
6	68.97	28.77
7	70.96	1.92
8	76.06	1.51
9	89.91	2.29
10	95.04	4.29
11	99.92	14.18
12	114.04	100.00
13	115.06	2.62
14	116.05	22.84
15	117.04	0.98
16	129.92	1.92
17	131.96	0.61
18	139.95	23.66
19	140.99	0.94
20	145.01	1.10
21	158.97	2.21
22	164.00	3.76
23	166.00	11.07
24	183.00	56.85
25	184.01	2.08
26	185.02	1.02
27	189.96	5.27
28	198.93	1.43
29	211.00	1.92
30	298.97	9.24
31	323.02	10.01
32	324.02	0.74
33	350.96	0.65
34	483.92	1.88
35	595.98	1.19
36	616.90	1.96
37	666.92	0.86
38	711.92	0.61
39	800.00	32.69
40	800.92	5.68
41	802.00	0.57
42	818.89	26.60
43	820.03	5.56

No. 22.

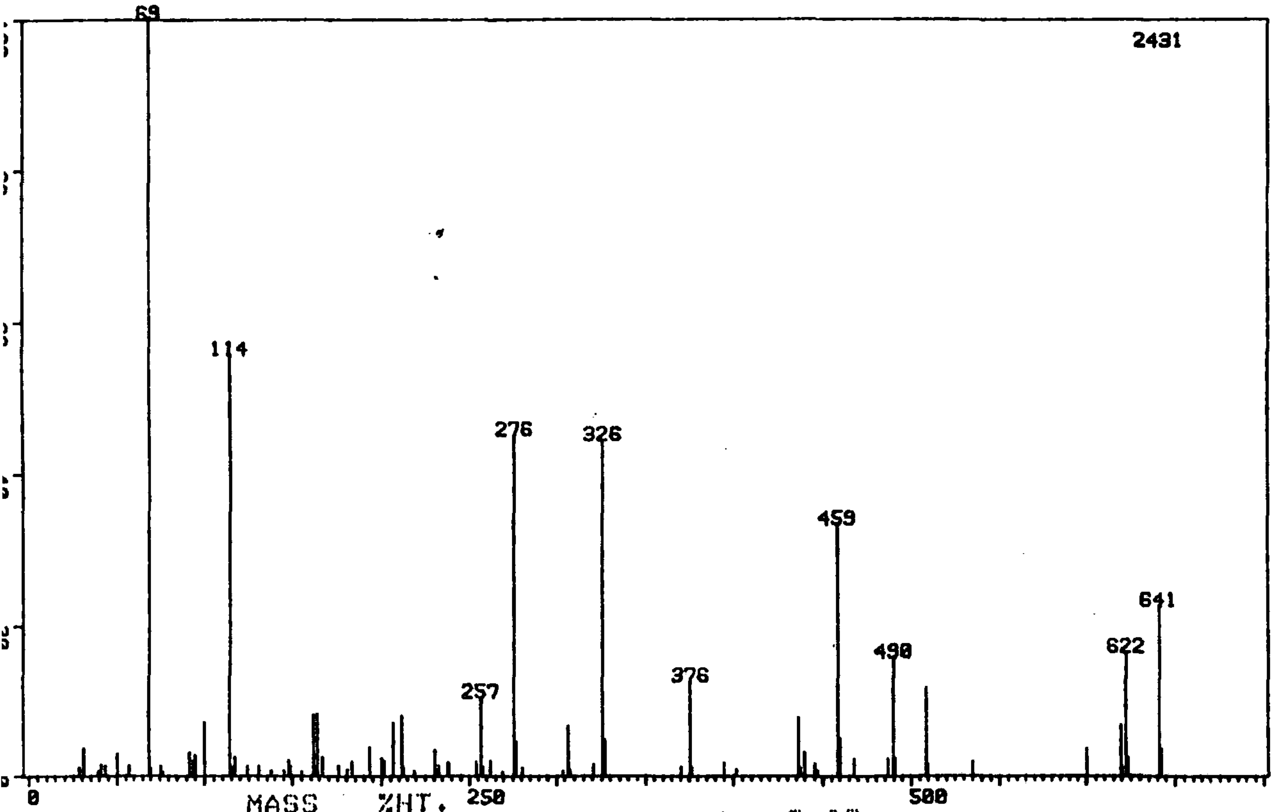
C1772X 4 C.D.HEWITT E.I. 10-SEP-86
CAL:CALT9 STA: 0:43



MASS	%HT. BASE
27.22	0.59
28.10	100.00
28.96	2.09
28.99	0.62
30.86	0.85
30.88	0.59
31.97	54.69
39.81	7.01
40.96	1.47
42.05	0.71
43.08	1.67
43.12	2.63
44.09	0.45
55.18	0.76
56.18	0.42
57.17	1.13
58.10	0.82
59.06	0.34
69.03	14.71
69.10	0.51
76.13	0.40
82.13	0.37
93.14	1.10
98.09	0.42
100.01	1.47
105.21	0.40
114.15	8.91
117.09	3.34
131.08	0.82
148.14	0.51
155.16	1.39
162.10	3.54
164.10	2.52
167.07	3.82
181.08	0.76
183.11	0.48
186.12	1.84
193.09	0.68
202.10	0.85
209.09	1.05
212.13	15.81
213.11	1.39
231.09	43.30
232.11	3.51
262.15	8.20
263.13	0.68
281.12	18.98
282.13	1.70
307.18	1.39
392.45	2.97
395.47	5.80
396.49	0.68
414.53	20.05
415.55	2.29

No. 23.

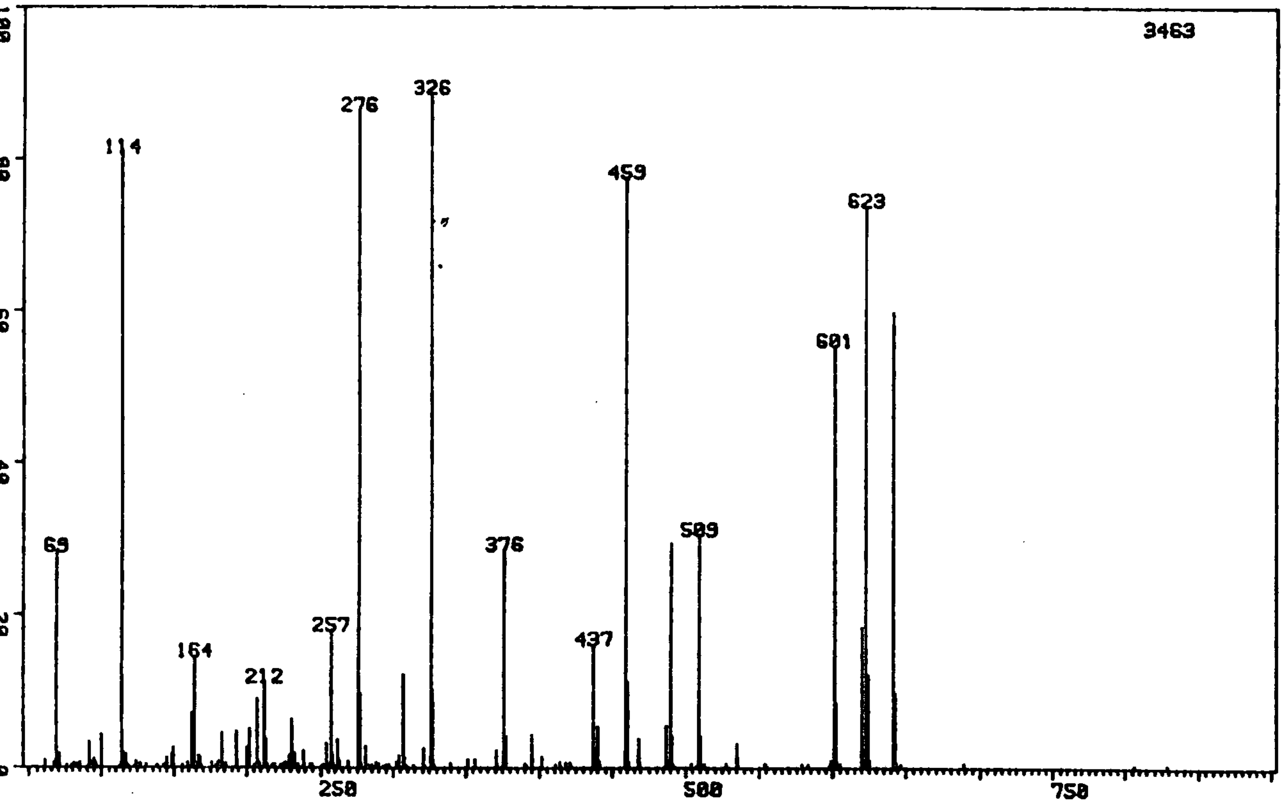
CH52XX 5 C.D.HEWITT 02-JUL-85
CAL:CALT1 STR: 0:50



MASS	%HT. BASE
28.17	1.19
29.05	0.78
30.93	3.74
38.98	0.66
40.96	1.52
43.12	1.36
49.86	3.04
57.11	1.44
68.93	100.00
69.87	1.03
76.05	1.40
77.08	0.53
91.98	3.21
93.01	2.06
95.03	2.84
99.91	7.24
113.97	55.94
114.98	1.19
116.95	2.55
123.94	1.40
130.87	1.36
137.93	0.78
144.95	0.78
147.91	2.10
148.91	1.40
154.94	0.58
161.90	8.14
162.94	0.82
163.93	8.23
166.92	2.47
175.92	1.44
180.86	0.95
182.91	1.97
192.90	3.83
199.83	2.39
201.89	2.02
206.96	7.12
211.93	7.98
212.94	1.11
218.89	0.78
230.90	3.50
232.93	1.44
237.90	1.85
253.90	1.97
256.92	10.49
257.90	1.19
261.90	2.14
268.90	0.53
275.92	45.37
276.92	4.61
280.87	1.11
303.89	0.74
304.89	6.71
307.94	0.86
320.88	1.52
325.91	44.71
326.91	4.90
370.77	1.28
375.81	12.63
376.86	1.28
394.86	1.85
401.87	0.90
436.79	7.77
437.79	1.19
439.80	3.17
445.99	1.69
446.96	0.78
458.78	33.57
459.83	5.06
467.82	2.30
486.81	2.34
489.87	15.80
490.82	2.43
508.75	11.81
509.78	1.69
534.73	1.93
600.55	3.74
619.49	6.87
620.48	1.19
622.50	16.58
623.51	2.51
641.39	22.83
642.44	3.78

No. 24. EI

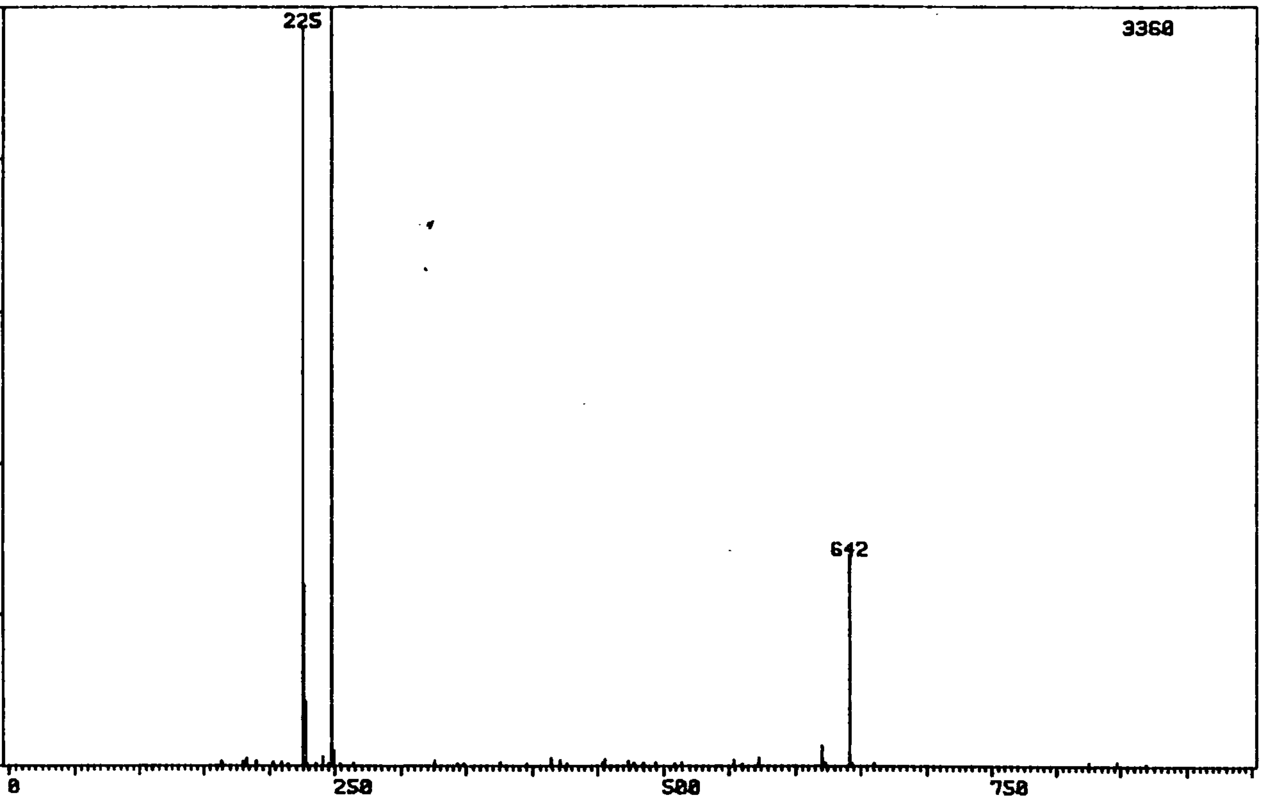
CH1S2X 2   C.D.HEWITT   152L2   I.BU   CI   22-MAY-85
CAL:CALT1   STA: 8:25



MASS	%HT. BASE
60.89	1.04
68.89	28.18
68.99	1.41
70.99	1.91
91.90	3.47
94.96	1.18
99.83	4.36
113.93	80.83
114.93	2.11
116.91	1.82
144.92	1.36
147.88	1.88
148.92	2.69
161.91	7.22
163.93	14.52
166.92	1.59
167.91	1.39
182.92	4.56
192.91	4.85
193.93	1.01
199.84	2.66
201.89	5.11
206.96	9.04
211.91	11.15
212.94	3.75
228.92	1.73
230.89	6.41
232.95	1.99
237.94	2.22
253.91	3.23
256.93	17.99
257.91	1.91
261.88	3.73
262.95	1.07
275.93	86.40
276.91	9.64
280.88	2.86
303.92	1.70
306.90	12.24
307.91	1.44
320.88	2.60
325.94	88.68
326.94	10.25
351.87	1.16
356.92	1.21
370.83	2.40
375.89	28.62
376.92	4.16
394.91	4.42
395.93	1.76
401.89	1.47
436.93	16.14
437.93	2.40
439.88	5.46
458.91	77.62
459.87	11.32
467.90	3.84
486.87	5.54
489.91	29.54
490.88	4.16
508.90	30.55
509.93	4.24
534.90	3.23
598.85	1.04
600.87	55.50
601.94	8.63
619.85	18.57
620.88	4.07
622.93	73.90
623.94	12.24
624.95	1.07
641.83	60.06
642.92	9.90

No. 24. CI.

CH152X S   C.D.HEWITT   152L2   NEG. ARGON   21-MAY-85
CAL:CALN0   STA: 0:51

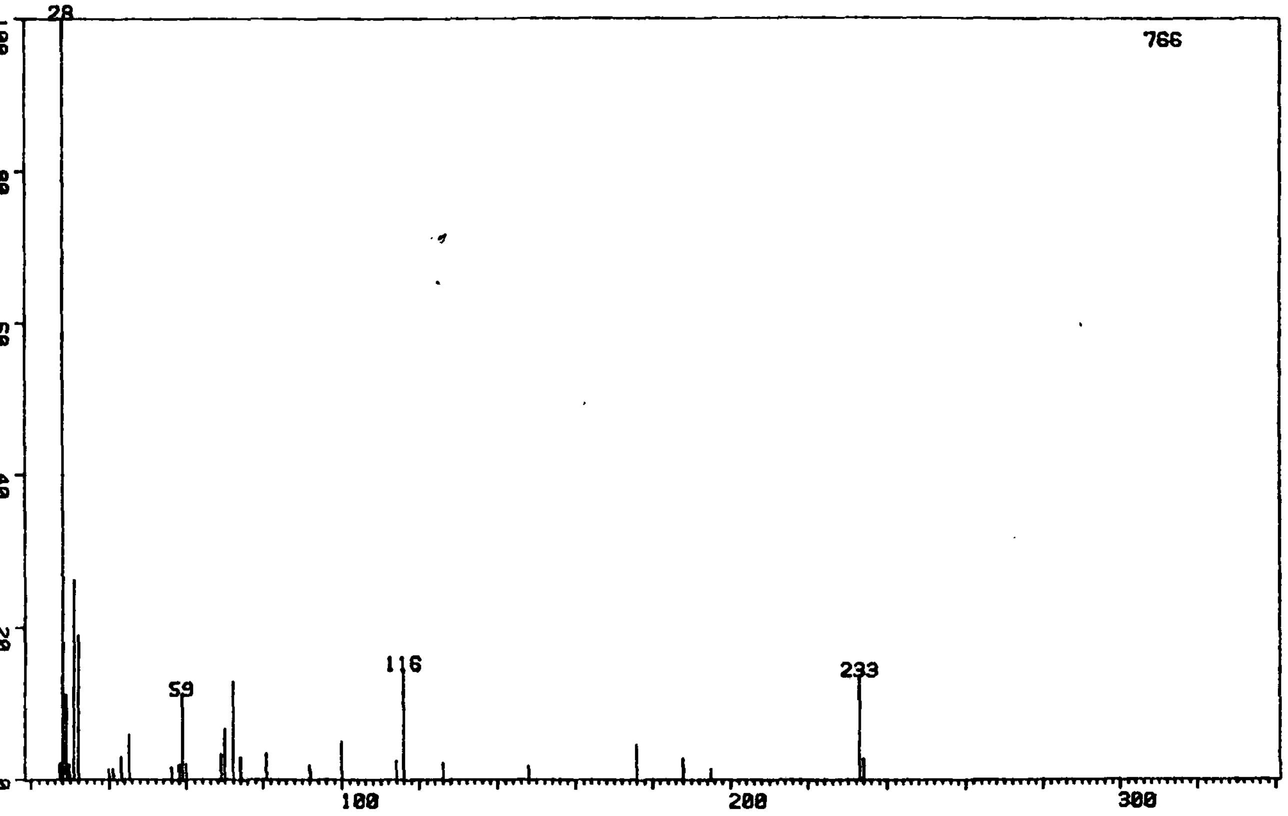


MASS	%HT. BASE
163.96	0.65
179.90	0.68
182.95	1.07
189.91	0.68
202.93	0.54
208.93	0.45
213.93	0.27
224.93	97.38
225.26	0.27
225.93	24.05
226.93	1.46
227.93	8.54
228.91	0.57
234.92	0.33
240.90	1.34
245.00	0.30
246.93	100.00
247.92	88.81
248.54	0.30
248.94	2.02
253.95	0.33
263.98	0.42
325.94	0.74
342.95	0.33
347.95	0.30
375.93	0.54
394.90	0.36
413.93	1.13
420.90	0.80
426.86	0.33
453.91	0.51
455.91	0.86
473.95	0.65
477.91	0.45
484.86	0.33
493.88	0.57
508.84	0.36
513.94	0.51
553.94	0.86
560.05	0.30
572.91	1.16
619.88	2.77
620.90	0.71
622.93	0.48
642.02	28.21

No. 24. NEG.

CH86B1 0 C.D.HEWITT
CAL:CALM12

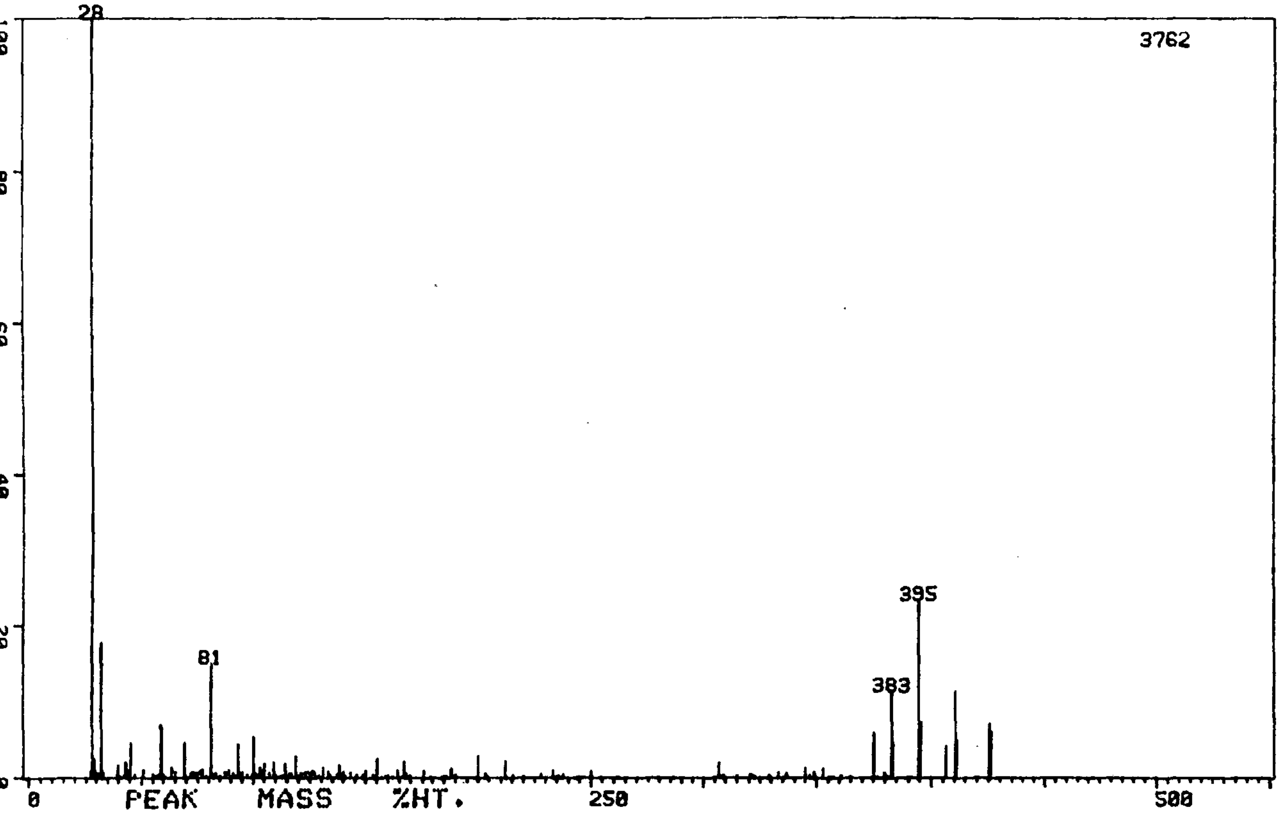
12-OCT-83
0:7



PEAK NO.	MASS	%HT. BASE
1	27.18	2.22
2	28.06	100.00
3	28.94	11.10
4	29.78	1.96
5	30.85	26.24
6	31.96	19.06
7	39.80	1.44
8	40.95	1.44
9	43.09	3.13
10	45.15	6.01
11	56.13	1.70
12	58.07	1.96
13	59.00	11.10
14	59.92	2.09
15	68.98	3.39
16	69.92	6.66
17	72.07	12.92
18	74.15	3.00
19	80.95	3.39
20	91.97	1.96
21	99.93	4.96
22	114.02	2.48
23	116.05	14.49
24	126.05	2.35
25	148.01	1.83
26	176.03	4.70
27	188.00	2.74
28	195.06	1.44
29	233.02	13.58
30	234.01	2.74

No. 25.

CH86B2 3 C.D.HEWITT 26-OCT-83
CAL:CALM12

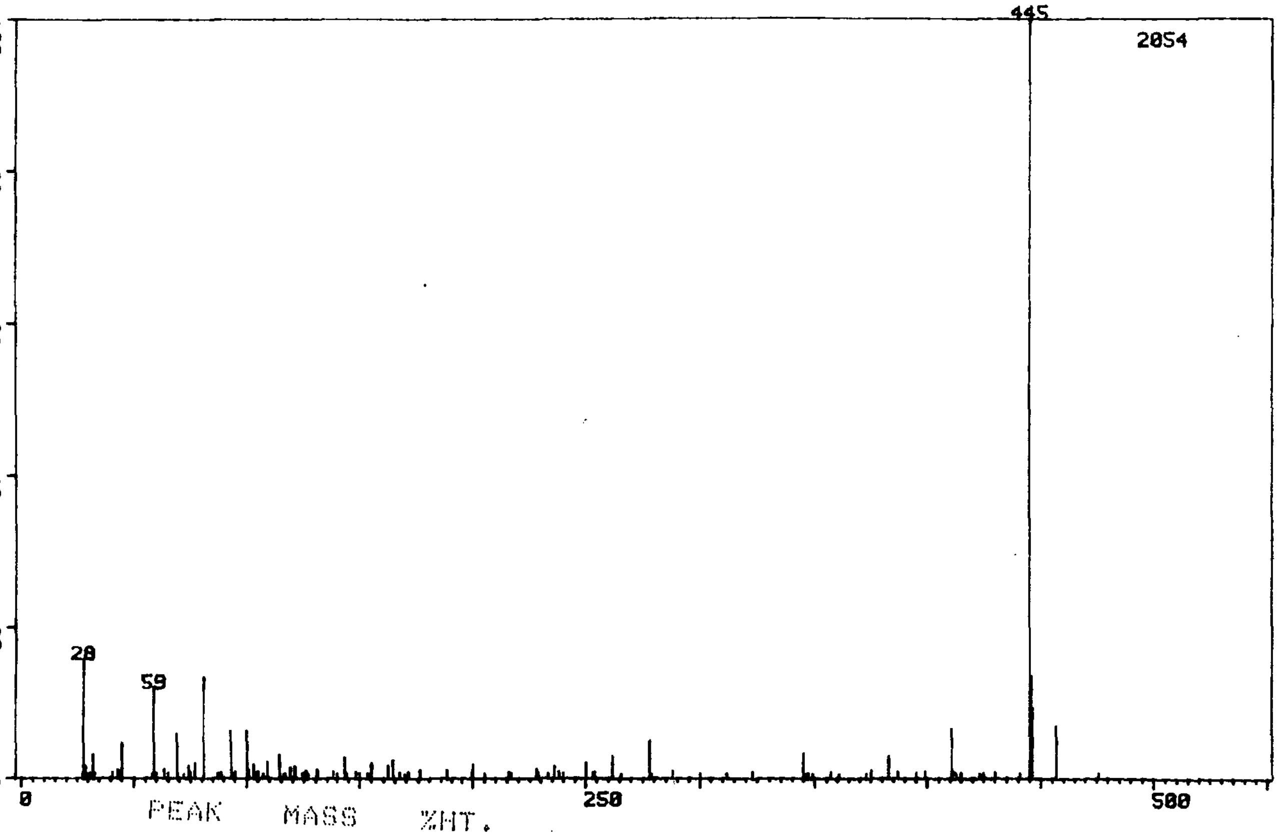


PEAK NO.	MASS	%HT. BASE
2	28.06	100.00
3	28.93	2.45
6	31.94	17.78
9	39.79	1.75
12	43.05	1.99
14	45.12	4.60
16	50.89	1.06
21	58.93	6.88
24	63.02	1.30
26	68.91	4.65
34	76.99	1.06
37	80.88	15.02
43	88.92	1.01
47	92.99	4.39
52	99.85	5.29
55	103.02	1.36
57	105.04	1.81
59	108.94	2.05
63	113.97	1.81
66	118.94	2.76
77	130.92	1.25
81	137.93	1.73
92	154.99	2.55
99	166.93	2.21
108	187.88	1.14
112	199.86	2.95
113	202.92	0.64
114	203.92	0.40
115	211.89	2.23
116	212.93	0.29
117	215.87	0.45
118	219.89	0.35
119	227.86	0.51
120	232.90	1.04
121	233.93	0.29
122	234.93	0.32
123	235.92	0.48
124	237.90	0.53
125	243.88	0.32
126	249.87	0.90
127	254.01	0.27
128	261.88	0.27
129	286.82	0.24
130	306.83	1.99
131	307.95	0.29
132	308.87	0.48
133	314.78	0.43
134	320.69	0.56
135	321.72	0.45
136	322.82	0.40
137	328.77	0.45
138	332.83	0.85
139	336.81	0.69
140	344.87	1.28
141	346.89	0.45
142	348.84	0.82
143	352.77	1.22
144	356.59	0.35
145	357.43	0.27
146	360.83	0.45
147	364.79	0.32
148	374.60	6.01
149	375.15	5.69
150	376.73	0.29
151	379.51	0.66
152	380.63	0.40
153	382.55	11.46
154	383.32	4.55
155	391.82	0.27
156	394.52	23.58
157	395.64	7.31
158	406.73	4.17
159	410.62	11.48
160	411.44	4.97
161	425.45	7.18
162	426.15	6.09

No. 26.

CH97C 4 C.D.HEWITT
CAL:CALM10

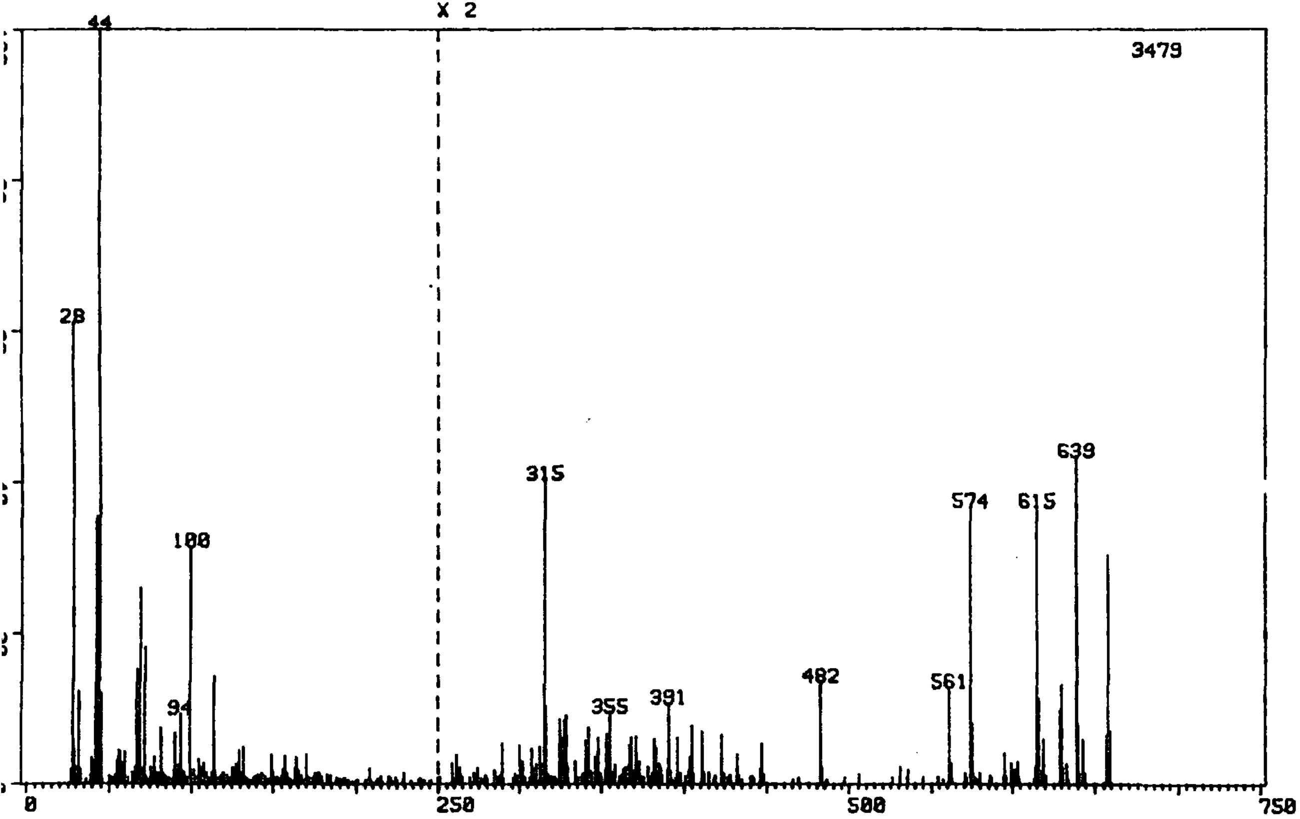
10-JAN-84



PEAK NO.	MASS	%HT. BASE
2	28.07	15.82
3	28.93	1.61
6	31.95	3.21
9	43.08	1.12
11	45.14	4.63
13	58.96	11.93
15	63.06	1.22
17	68.96	5.94
19	74.09	1.61
21	77.05	2.00
22	80.96	13.39
26	93.03	6.18
29	99.90	6.13
30	100.95	1.12
31	103.06	1.85
35	108.96	2.09
36	114.02	3.02
39	118.95	1.41
40	120.95	1.46
43	126.01	1.02
45	130.96	1.22
48	142.99	2.68
54	155.00	2.04
55	161.98	1.66
56	163.96	2.39
60	175.94	1.12
61	187.93	1.12
63	199.87	1.80
67	227.94	1.31
70	235.97	1.51
73	249.91	2.14
76	261.94	2.87
78	277.88	4.87
84	344.92	3.26
91	374.90	1.07
92	382.91	2.97
96	410.89	6.62
97	411.94	0.88
98	412.96	0.54
99	414.93	0.73
100	422.92	0.54
101	425.03	0.54
102	429.96	0.83
103	440.89	0.73
104	444.90	100.00
105	445.92	13.58
106	446.57	9.25
107	457.08	6.91
108	475.96	0.78

No. 27.

CH179 11 C.D.HEWITT E.I. 22-SEP-86
CAL:CALT9 STA: 1:43

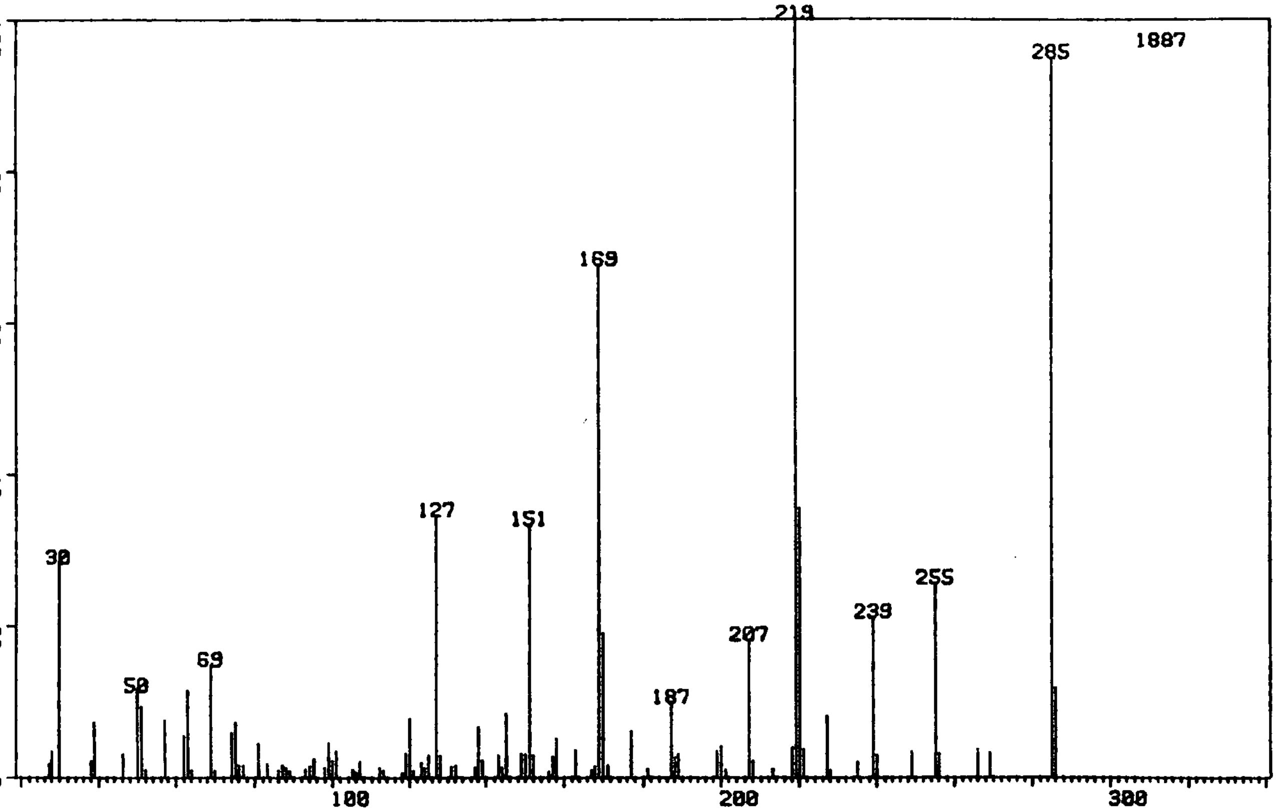


MASS	%HT. BASE
27.23	1.98
28.10	61.17
28.12	5.89
28.96	2.10
28.99	4.43
29.82	2.16
31.97	12.27
33.07	1.87
39.80	3.36
42.03	35.47
43.10	11.21
44.08	8.94
44.14	100.00
45.17	11.96
55.16	3.13
56.16	4.46
57.14	4.28
59.94	4.28
67.07	15.18
68.97	25.98
72.05	18.14
78.04	3.48
82.07	7.36
90.98	6.78
94.08	9.26
99.88	31.50
105.07	3.28
114.02	14.26
128.99	4.46
132.05	4.83
149.03	3.79
157.08	3.65
164.06	3.48
170.05	3.88
289.10	2.67
300.07	2.56
315.10	20.24
316.07	5.09
324.08	4.28
325.08	3.08
327.06	4.20
328.09	4.51
342.10	3.68
348.05	3.05
353.10	3.25
355.10	4.71
368.05	3.08
371.10	3.13
391.04	5.35
396.10	3.08
405.08	3.82
411.16	3.48
423.06	3.19
482.15	6.81
561.20	6.41
574.10	18.40
575.08	4.00
595.10	2.07
599.06	1.38
603.11	1.44
614.09	1.18
615.09	18.40
616.08	5.66
619.07	3.02
620.08	0.60
629.08	4.89
630.11	6.58
631.11	1.09
633.08	1.32
634.05	0.34
639.15	21.73
640.09	4.05
641.08	0.69
643.10	2.99
644.08	0.75
657.12	3.25
658.09	15.15
659.09	3.54

No. 28.

C1753X 9 C.D.HEWITT E.I.
CAL:CALT9 STA:

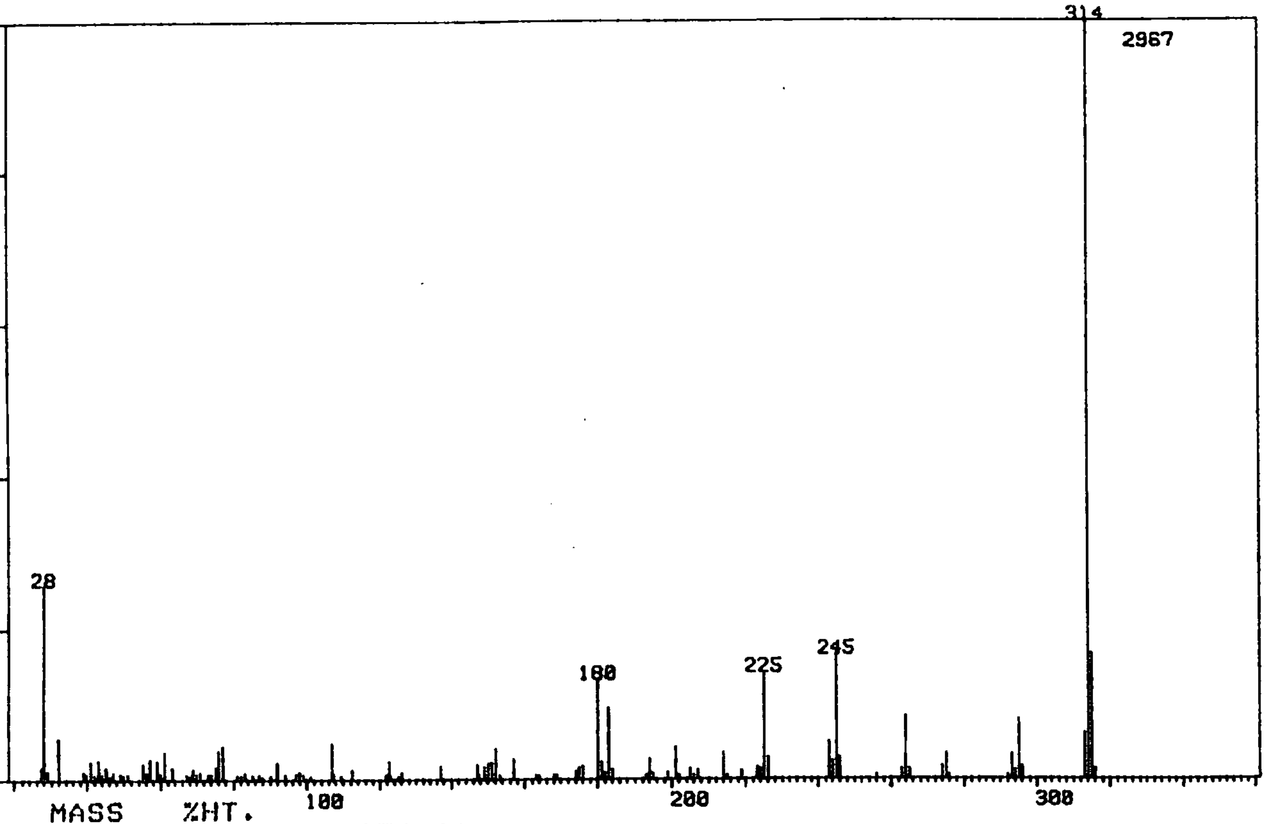
10-SEP-86
1:26



MASS	%HT. BASE
27.22	1.80
28.10	3.50
29.79	28.35
38.04	2.17
38.97	7.31
46.11	3.07
49.90	11.39
50.98	9.33
52.06	1.06
57.12	7.53
62.08	5.46
63.13	11.45
64.13	1.01
68.98	14.84
69.94	0.95
74.10	5.88
75.09	7.26
76.10	1.59
77.08	1.64
81.01	4.45
83.10	1.80
86.08	1.01
87.06	1.54
88.04	1.27
89.03	0.90
93.07	1.11
94.10	1.54
95.10	2.49
98.06	1.27
99.01	4.56
99.98	2.23
101.04	3.55
105.11	1.11
106.08	0.74
107.09	2.12
112.05	1.22
113.08	1.06
118.06	0.58
119.03	3.18
120.03	7.74
121.07	0.95
123.08	1.96
124.10	1.22
125.09	2.97
127.09	34.71
128.07	2.81
131.05	1.48
132.07	1.64
137.10	1.38
138.06	6.62
139.04	2.28
143.09	2.91
144.12	1.32
145.08	8.37
149.03	3.13
150.03	3.13
151.07	33.49
152.10	2.91
156.10	0.79
157.08	2.76
158.07	5.19
163.08	3.66
167.09	1.06
168.06	1.48
169.05	67.78
170.05	19.02
171.09	1.64
177.13	6.20
181.05	1.17
187.10	9.91
188.10	2.65
189.08	3.13
199.08	3.55
200.09	4.08
201.12	1.11
207.12	18.18
208.08	2.17
213.12	1.17
218.08	3.97
219.07	100.00
220.08	35.61
221.10	3.66
227.12	8.21
228.09	1.06
235.12	2.01
239.07	21.20
240.09	2.91
249.07	3.44
255.14	25.65
256.11	3.18
266.10	3.76
269.07	3.34
285.16	94.97
286.10	11.92

No. 30.

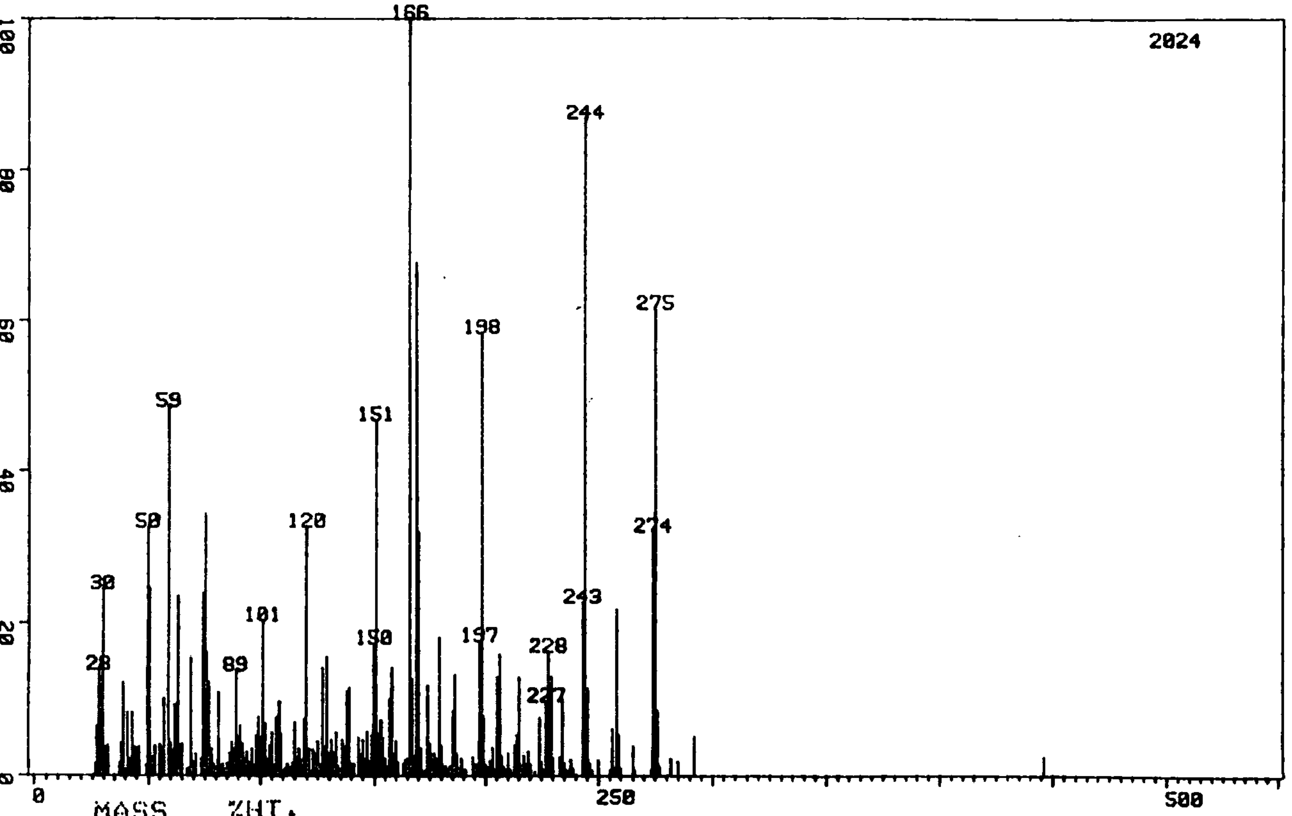
C1752X 6 C.HEWITT E.I. 10-SEP-86
CAL:CALT9 STA: 1:0



MASS	%HT. BASE
27.22	1.52
28.10	25.85
28.96	1.11
28.99	1.18
31.97	5.46
38.97	1.11
43.12	2.63
45.11	1.55
45.16	1.38
47.09	1.01
55.18	2.12
57.17	2.70
59.02	2.56
61.03	3.67
63.13	1.55
69.04	1.48
71.07	1.04
75.10	1.58
76.07	3.81
77.04	4.48
91.48	2.06
92.01	2.22
98.04	1.11
107.04	4.79
112.54	1.28
122.56	2.43
126.10	1.01
137.09	1.85
147.12	1.99
149.05	1.58
150.05	2.12
151.10	2.26
152.10	4.04
157.06	2.70
174.10	1.08
175.10	1.55
176.11	1.82
180.05	13.25
181.06	2.33
183.09	9.47
184.11	1.35
194.08	2.66
201.07	4.25
205.10	1.42
207.09	1.21
214.13	3.54
219.05	1.18
223.08	1.69
224.10	1.38
225.09	14.26
226.11	2.90
243.11	4.99
244.09	2.49
245.11	16.62
246.09	2.80
263.09	1.35
264.11	8.39
265.10	1.42
274.07	1.75
275.10	3.44
293.11	3.34
294.10	1.15
295.09	7.95
296.09	1.72
313.15	6.20
314.11	100.00
315.11	16.62
316.08	1.38

No. 31.

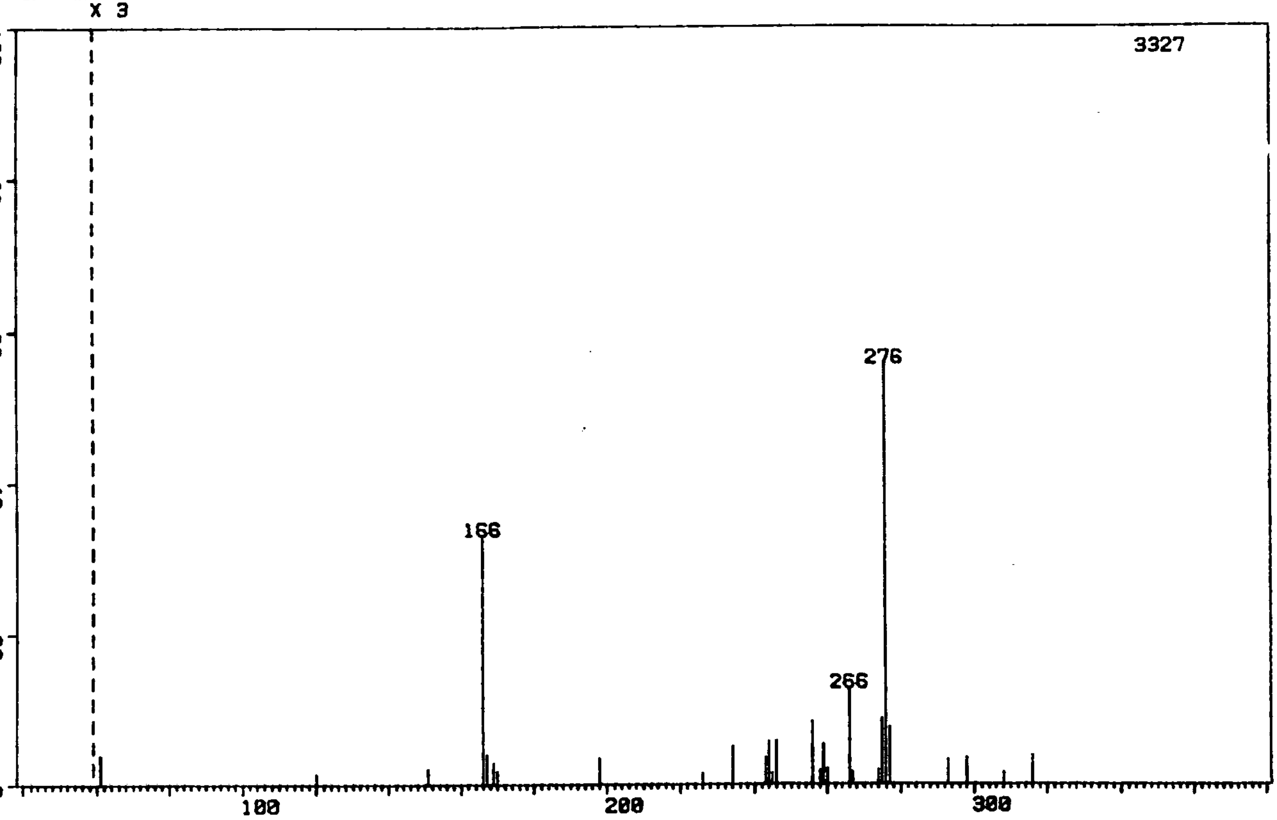
CH221X 6 C.D.HEWITT E.I. 10-JUN-86
CAL:CALT9 STA: 0:56



MASS	%HT. BASE
27.23	6.47
28.10	13.88
28.96	12.75
29.79	24.46
38.96	12.20
40.94	8.35
43.11	8.35
49.88	32.56
50.96	24.46
57.14	10.03
58.99	48.62
62.04	9.34
63.09	23.57
68.94	15.32
74.08	23.86
75.10	34.34
76.09	16.16
77.09	12.30
80.99	10.87
88.93	13.78
90.98	6.52
97.98	5.24
98.94	7.71
100.96	20.36
102.00	6.87
105.04	5.68
107.01	7.56
108.01	9.73
108.97	5.43
115.07	7.11
118.97	7.36
119.95	32.66
127.03	14.08
128.98	15.56
133.04	5.68
138.02	11.02
139.00	11.51
147.04	5.78
148.99	5.29
149.96	17.34
151.01	46.84
152.03	5.48
153.02	7.26
157.04	9.93
158.03	14.18
166.04	100.00
167.05	12.65
168.97	67.69
169.96	31.97
174.03	11.81
179.00	18.13
185.03	8.45
186.03	13.19
197.02	17.64
198.01	58.50
198.99	7.91
205.05	12.90
206.04	15.81
214.03	5.29
215.02	12.85
224.01	7.56
227.01	9.73
228.01	16.25
229.00	12.99
234.05	9.98
243.01	22.68
244.02	86.91
245.04	11.46
256.04	6.18
258.02	21.84
259.00	5.39
274.02	32.07
275.05	61.66
276.05	8.55

No. 32. EI

CH221X 10 C.D.HEWITT C.I. I-BU 10-JUN-86
CAL:CALT9 STA: 1:30

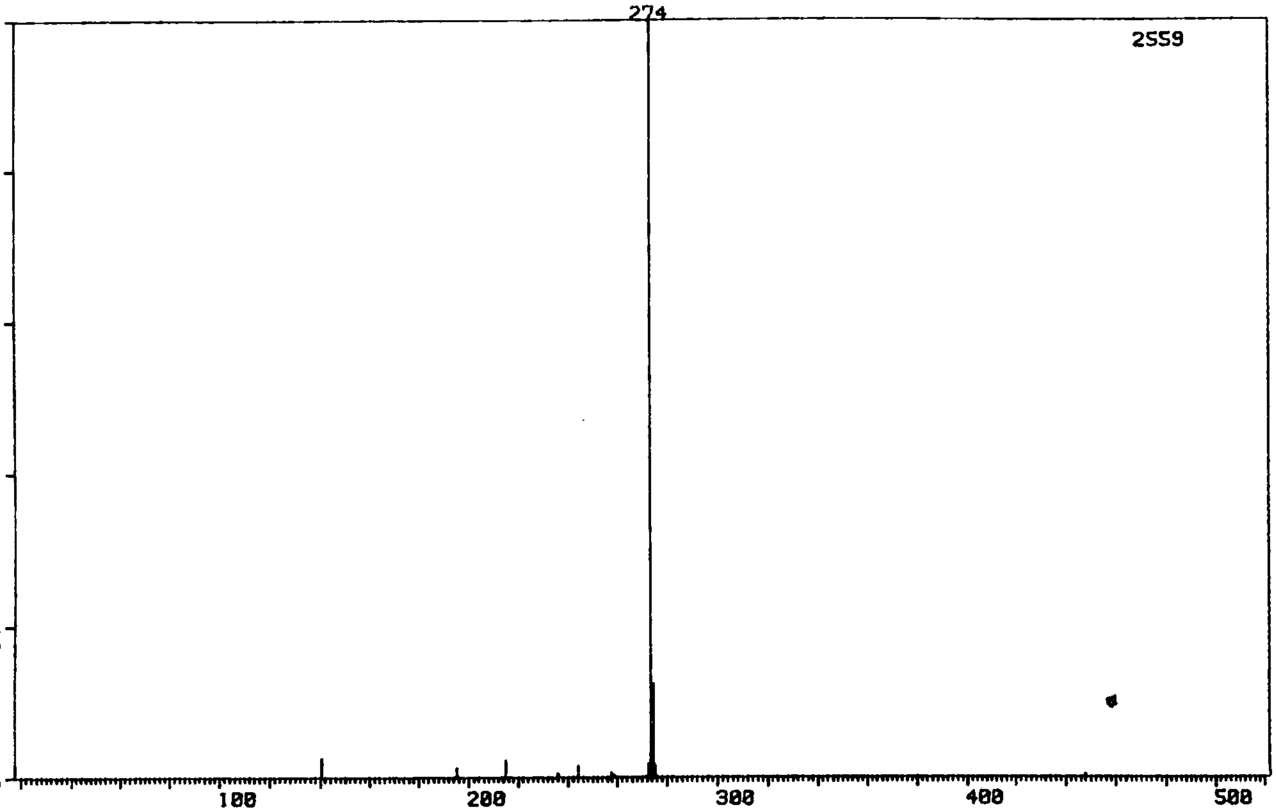


MASS	%HT. BASE
60.95	1.29
119.92	0.48
150.94	0.69
165.97	11.03
166.97	1.32
168.90	0.99
169.91	0.60
197.92	1.17
225.94	0.51
233.91	1.71
242.92	1.20
243.91	1.92
244.92	0.54
245.95	1.92
255.89	2.80
257.90	0.63
258.93	1.80
259.90	0.69
265.95	4.30
266.97	0.57
273.93	0.66
274.93	2.95
275.93	18.61
276.94	2.52
292.94	1.11
297.98	1.20
307.97	0.54
315.97	1.29

No. 32. CI

CH221X 3 C.D.HEWITT NEG.
CAL:CALN22 STA:

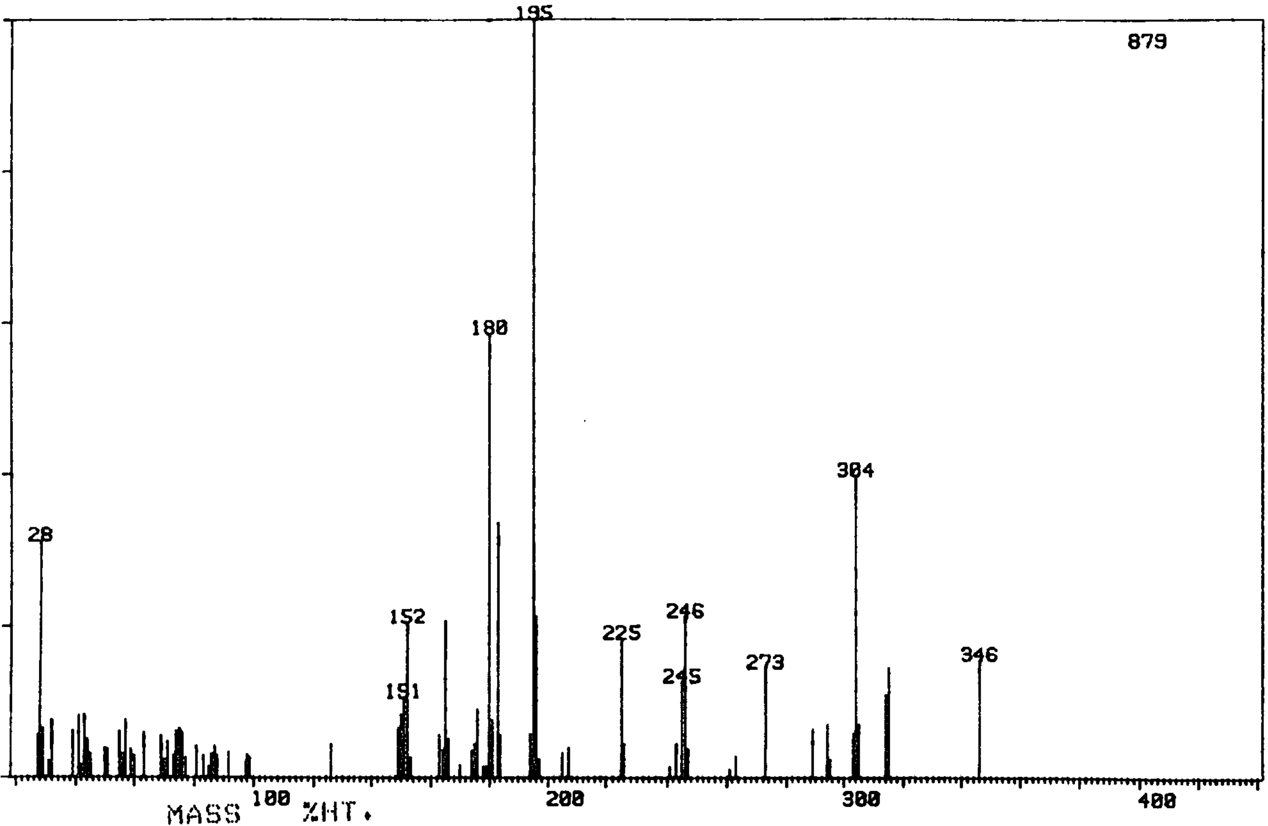
10-JUN-86
0:35



MASS	%HT. BASE
140.55	2.58
195.22	1.33
215.07	2.31
235.86	0.63
243.86	1.60
257.70	0.70
272.56	1.91
273.56	100.00
274.56	12.43
275.54	1.60
447.84	0.47

No. 32. NEG

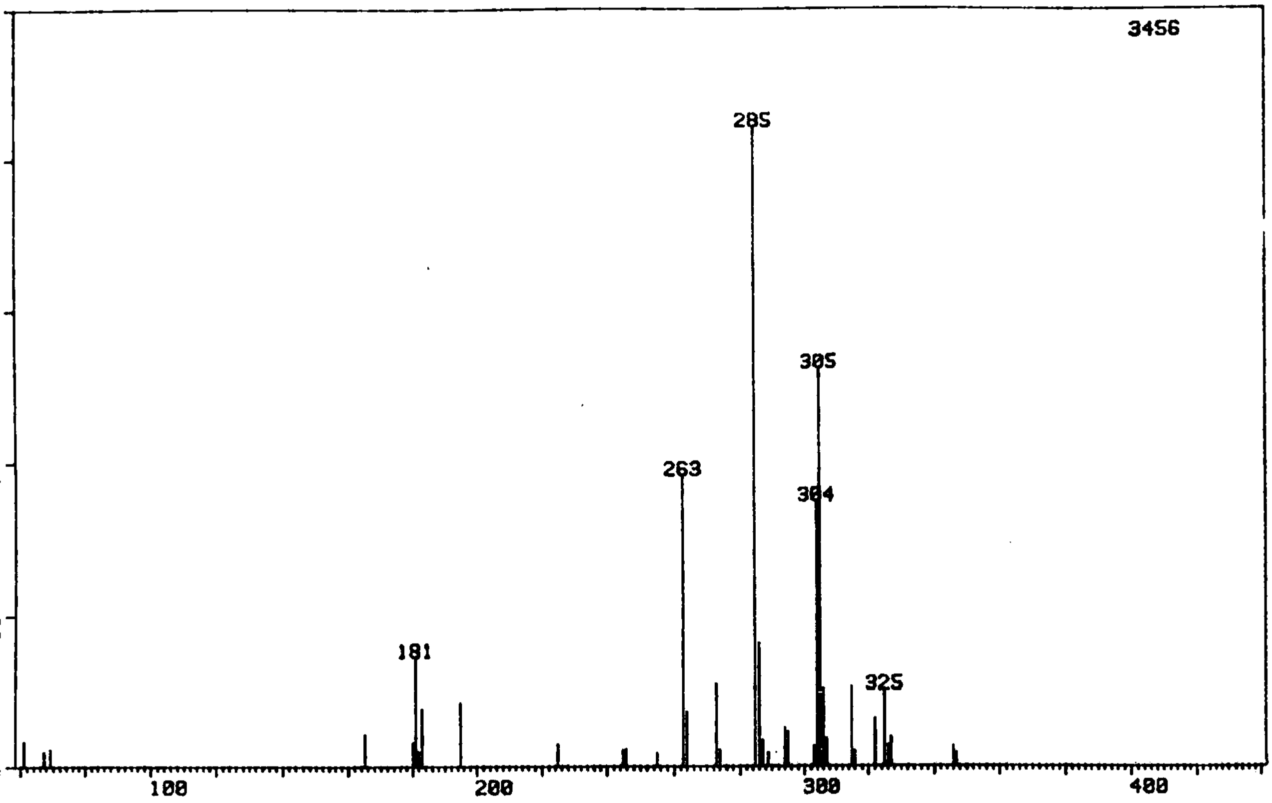
CH220X 2 C.HEWITT E.I. 30-MAY-78
CAL:CALT9 STA: 0:25



MASS	%HT. BASE
27.23	5.69
28.10	31.29
28.96	6.48
28.99	5.12
30.88	2.16
31.97	7.62
38.96	6.14
40.94	8.19
42.03	1.71
43.06	2.62
43.11	8.30
44.07	5.01
45.13	3.07
49.88	3.87
50.95	3.75
55.15	6.14
56.15	3.07
57.13	7.62
58.98	3.75
59.92	2.84
63.08	6.03
68.98	5.46
69.05	4.10
70.00	2.39
71.06	4.66
73.09	2.96
74.09	6.14
75.11	6.48
76.09	5.80
77.08	2.62
80.98	4.10
83.13	2.96
85.05	1.48
86.04	3.07
87.04	4.21
88.02	2.84
91.50	3.30
97.53	2.16
98.00	3.07
98.97	2.62
126.04	4.44
148.97	6.48
149.97	8.30
151.00	10.58
152.04	20.48
153.06	2.62
163.03	5.57
164.05	3.64
165.07	20.59
166.07	5.01
169.96	1.71
174.03	3.53
175.03	4.44
176.05	8.99
178.04	1.48
179.02	1.48
179.97	58.70
181.01	7.51
183.04	33.67
184.04	5.57
194.04	5.69
195.05	100.00
196.05	21.27
197.04	2.39
205.04	3.19
207.04	3.87
225.01	18.32
226.03	4.44
241.00	1.37
243.00	4.44
245.02	12.63
246.03	21.27
247.02	3.75
260.98	1.14
263.02	2.73
273.00	14.45
288.98	6.37
294.05	7.05
295.04	2.39
303.04	5.92
304.03	39.93
305.06	7.05
314.02	10.81
315.05	14.56
346.08	15.59

No. 33. EI.

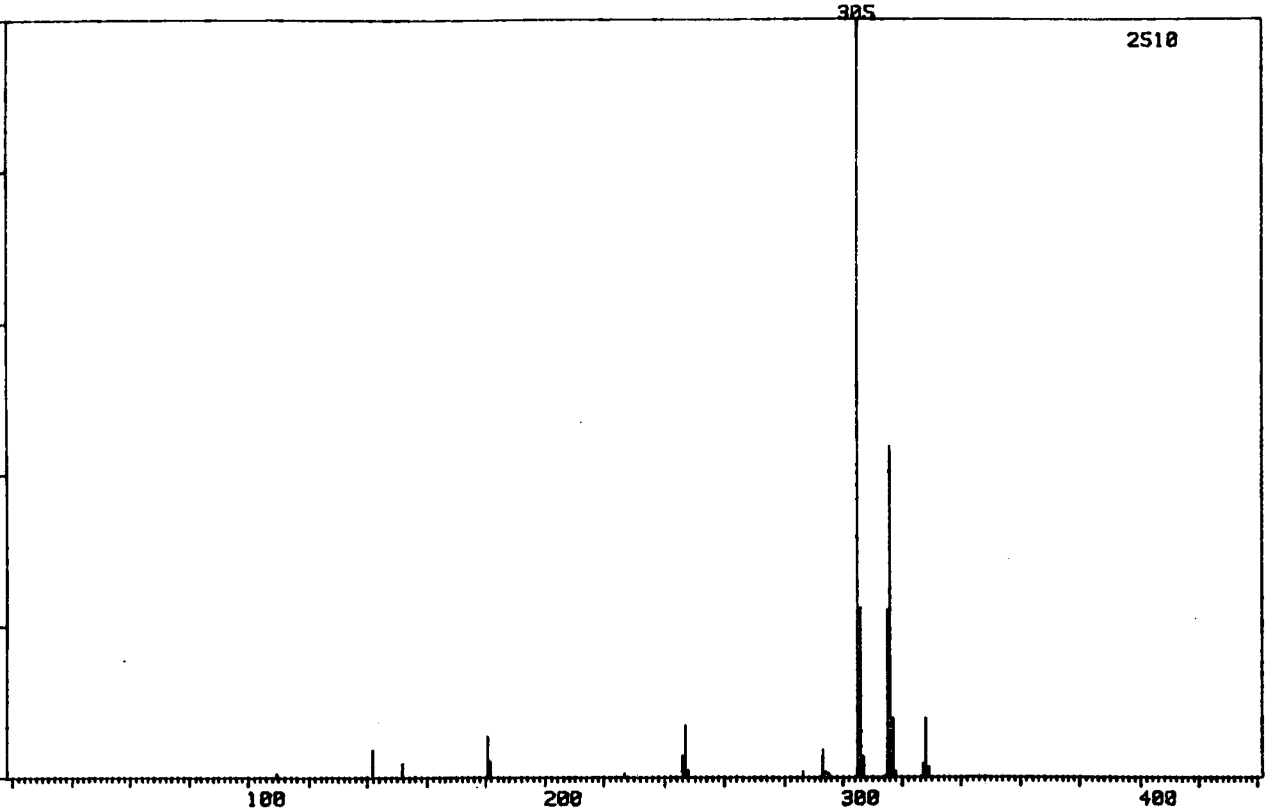
CH220X 7 C.D.HEWITT C.I. I-BU 30-MAY-78
CAL:CALT9 STA: 1.5



MASS	%HT. BASE
60.95	3.36
67.08	2.00
69.01	2.34
165.01	4.34
179.92	3.18
180.95	14.44
181.97	2.00
182.97	7.49
194.97	8.39
224.94	2.89
244.93	2.20
245.92	2.34
254.90	1.85
262.89	38.40
263.94	7.26
272.95	10.88
273.95	2.17
284.94	84.37
285.95	16.17
286.96	3.41
288.90	1.82
293.96	5.06
294.98	4.54
302.97	2.60
303.97	34.95
304.96	52.52
305.99	10.19
306.98	3.70
314.98	10.53
315.97	2.00
321.97	6.25
324.99	10.16
325.98	2.75
326.97	3.85
345.96	2.60
346.98	1.85

No. 33. CI

CH220X 1 C.D.HEWITT NEG 30-MAY-78
CAL:CALN22 STA: 0:17



MASS	%HT. BASE
109.40	0.48
141.58	3.63
151.61	1.87
180.70	5.42
181.68	2.07
226.85	0.44
245.90	2.79
246.91	6.85
247.90	0.96
285.97	0.84
292.97	3.71
293.99	0.76
294.99	0.56
305.01	100.00
306.01	22.27
307.04	2.67
315.01	22.03
316.01	43.75
317.04	7.77
318.03	0.72
327.06	1.75
328.06	7.69
329.06	1.31

No. 33. NEG.

COLLOQUIA AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate thesis contains an appendix listing;

a) all research colloquia, seminars, and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

b) all research conferences attended and papers presented by the author during the period in which the research for the thesis was carried out;

c) details of the postgraduate induction course.

a) Research Colloquia, Seminars and Lectures

1982

13 October	*Dr. W.J. Feast (University of Durham), "Approaches to the synthesis of conjugated polymers".
14 October	Prof. H. Suhr (University of Tubingen, FRG), "Preparative Chemistry in Non-equilibrium plasmas".
14 October	Mr. F. Shenton (County Analyst, Durham), "There is death in the pot".
27 October	*Dr. C.E. Housecroft (Oxford High School/ Notre Dame University), "Bonding capabilities of butterfly-shaped Fe_4 units. Implications for C-H bond activiation in hydrocarbon complexes".
28 October	Prof. M.F. Lappert, F.R.S. (University of Sussex), "The Chemistry of some unusual

	subvalent compounds of the main group IV and V Elements".
4 November	*Dr. D.H. Williams (University of Cambridge), "Studies on the structures and modes of action of antibiotics".
11 November	Dr. J. Cramp (ICI Ltd.), "Lasers in Industry".
15 November	Dr. G. Bertrand (University of Toulouse, France), "Curtius rearrangement in organometallic series. A route for hybridised species".
24 November	*Prof. G.G. Roberts (Applied Physics, University of Durham), "Langmiur - Blodgett films: solid state polymerisation of diacetylenes".
25 November	*Dr. D.H. Richards, (P.E.R.M.E., Ministry of Defence), "Terminally Functional Polymers, their synthesis and uses".
2 December	*Dr. G.M. Brooke, (University of Durham), "The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoroaryl and -heteroaryl systems".
8 December	Dr. G. Wooley (Trent Polytechnic), "Bonds in transition-metal cluster compounds".

<u>1983</u>

12 January	*Dr. D.C. Sherrington (University of Strathclyde), "Polymer-supported phase transfer catalysts".
27 January	*Prof. D.W.A. Sharp (University of Glasgow), "Some Redox reactions in Fluorine Chemistry".

3 February	Dr. R. Manning (Department of Zoology, University of Durham), "Molecular mechanisms of hormone action".
9 February	Dr. P. Moore (University of Warwick), "Mechanistic studies in solution by stopped-flow F.T.-N.M.R. and high pressure N.M.R. line broadening".
10 February	Sir Geoffrey Allen, F.R.S. (Unilever Ltd.), "UK Research Ltd.".
17 February	*R.S.C. Centenary Lecture. Prof. A.G. MacDiarmid (University of Pennsylvania), "Metallic covalent polymers: $(SN)_x$ and $(CH)_x$ and their derivatives".
21 February	*Dr. Lynden-Bell (University of Cambridge), "Molecular motion in the cubic phase of NaCN".
2 March	Dr. D. Bloor (Queen Mary College, University of London), "The solid-state chemistry of diacetylene monomers and polymers".
3 March	Prof. A.C.T. North (University of Leeds), "The use of a computer display system in studying molecular structures and interaction".
8 March	*Prof. D.C. Bradley, F.R.S. (Queen Mary College, University of London), "Recent developments in organo-imido-transition metal chemistry".
9 March	*Dr. D.M.J. Lilley (University of Dundee), "DNA, Sequence, Symmetry, Structure and Supercooling".

11 March	*W.K.R. Musgrave Lecture. Prof. H.G. Viehe (University of Louvain, Belgium), "Oxidations on Sulphur".
	*"Fluorine substitutions in radicals".
16 March	*Dr. I. Gosney (University of Edinburgh), "New extrusion reactions: Organic synthesis in a hot-tube".
25 March	Prof. F.G. Baglin (University of Nevada, U.S.A.), "Interaction induced Raman spectroscopy in supra-critical ethane".
21 April	Prof. J. Passmore (University of New Brunswick, Canada), "Novel selenium-iodide cations".
4 May	Prof. P.H. Plesh (University of Keele), "Binary ionisation equilibria between two ions and two molecules. What Ostwald never though of".
10 May	*Prof. K. Burger (Technical University of Munich, F.R.G.), "New reaction pathways from trifluoromethyl-substituted heterodienes to partially fluorinated heterocyclic compounds".
11 May	*Dr. N. Isaacs (University of Reading), "The Application of high pressures to the theory and practice of organic chemistry".
13 May	*Dr. R. de Koch (Calion College, Grand Rapids, Michigan/Free University Amsterdam), "Electronic structural calculations in organometallic cobalt cluster molecules. Implications for metal surfaces".

16 May	*Prof. R.J. Lagow (University of Texas, U.S.A.), "The chemistry of polylithium organic compounds. An unusual class of matter".
18 May	Dr. D.M. Adams, (University of Leicester), "Spectroscopy at very high pressures".
25 May	*Dr. J.M. Vernon (University of York), "New heterocyclic chemistry involving lead tetraacetate".
15 June	Dr. A. Pietrzykowski (Technical University of Warsaw/University of Strathclyde), "Synthesis, structure and properties of Aluminoxanes".
22 June	Dr. D.W.H. Rankin (University of Edinburgh), "Floppy molecules - the influence of phase and structure".
5 July	*Prof. J. Miller (University of Camfinas, Brazil), "Reactivity in nucleophilic substitution reactions".
5 October	Prof. J.P. Maier (University of Basel, Switzerland), "Recent approaches to spectroscopic characterisation of cations".
12 October	Dr. C.W. McLeland (University of Port Elizabeth, Australia), "Cyclisation of aryl alcohols through the intermediacy of alkoxy radicals and aryl radical cations".
19 October	Dr. N.W. Alcock (University of Warwick), "Aryl Tellurium (IV) compounds, patterns of primary and secondary bonding".

20 October	*Prof. R.B. Cundall (University of Salford), "Explosives".
26 October	*Dr. R.H. Friend (Cavendish Laboratory, University of Cambridge), "Electronic properties of conjugated polyments".
3 November	Dr. G. Richards (University of Oxford), "Quantum pharmacology".
10 November	*Dr. G. Thorpe (Sterling Organics), "Applied Chemistry and the pharmaceutical industry".
24 November	*Prof. D.A. King (University of Liverpool), "Chemistry in two dimensions".
30 November	Prof. I. Cowie (University of Stirling), "Molecular interpretation of non-relaxation processes in polymer glasses".
1 December	*Dr. J.D. Coyle (The Open University), "The problem with sunshine".
14 December	Prof. R.J. Donovan (University of Edinburgh), "Chemical and physical processes involving ion pair states of the halogen molecules".

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10 January	Prof. R. Hester (University of York), "Nano second laser spectroscopy of reaction intermediates".
18 January	*Prof. R.K. Harris (University of East Anglia), "Multi-nuclear solid state magnetic resonance".
26 January	Prof. T.L. Blundell (Birbeck College, London), "Biological recognition: interactions of macromolecular surfaces".

2 February	*N.B.H. Jonathon (University of Southampton), "Photoelectron spectroscopy - a radical approach".
8 February	Dr. B.T. Heaton (University of Kent), "Multi-nuclear n.m.r. studies".
15 February	*Dr. R.M. Paton (University of Edinburgh), "Heterocyclic synthesis using nitrile sulphides".
16 February	Prof. D. Phillips (The Royal Institution), "Luminescence and the photochemistry - a light entertainment".
23 February	Prof. F.G.A. Stone (University of Bristol), The use of carbene and carbyne groups to synthesise metal clusters".
1 March	*Prof. A.J. Leadbetter (Rutherford Appleton Laboratories), "Liquid crystals".
7 March	*Dr. R.T. Walker (University of Birmingham), "Synthesis and biological properties of some 5-substituted uracil derivatives; yet another example of serendipity in antiviral chemistry".
8 March	Prof. D. Chapman (Royal Free Hospital School of Medicine, University of London), "Phospholipids and biomembranes: basic structure and future techniques".
21 March	Dr. P. Sherwood (University of Newcastle), "X-Ray photoelectron spectroscopic studies of electrode and other surfaces".

23 March	Dr. A. Ceulemans (Catholic University of Leuven), "The development of field type models of bonding in molecular clusters".
28 March	R.S.C. Centenary Lecture. Prof. H. Schmidbaur (Technical University of Munich F.R.G.), "Ylides in the coordination sphere of metals; synthetic, structural, and theoretical aspects".
2 April	*Prof. K. O'Driscoll (University of Waterloo), "Chain ending reactions in free radical polymerisation ".
3 April	Prof. C.H. Rochester (University of Dundee), Infrared studies of adsorption at the solid-liquid interface".
25 April	*Dr. R.M. Acheson (Department of Biochemistry, University of Oxford), "Some heterocyclic detective stories".
27 April	Dr. T. Albright (University of Houston), "Sigmatropic rearrangements in organometallic chemistry".
14 May	*Prof. W.R. Dolbier Jr. (University of Florida), "Cycloaddition reactions of fluorinated allenes".
16 May	*Dr. P.J. Garrett (University College, London), "Syntheses with dilithiated vicinal diesters and carboximides".

31 May	Dr. A. Haaland (University of Oslo), "Electron diffraction studies of some organometallic compounds".
11 June	*Dr. J.B. Street (I.B.M. San Jose), "Conducting polymers derived from pyrolles".
19 September	Dr. C. Brown (I.B.M. San Jose), "New super-base reaction - organic compounds".
21 September	*Dr. H.W. Gibson (Signal UOP Research Centre, Des Plaines, Illinois), "Isomerisation of polyacetylene".
18 October	Dr. N. Logan (University of Nottingham), "N_2O_4 and rocket fuels".
19 October	*Dr. A. Germain (University du Languedoc, Montpelier), "Anodic oxidation of perfluoro organic compounds in perfluorosulphonic acids".
24 October	*Prof. R.K. Harris (University of Durham), "N.m.r. of solid polymers".
1 November	Prof. B.J. Aylett (Queen Mary College, University of London), "Silicon - dead common or refined".
7 November	Dr. H.S. Munro (University of Durham), "New information from E.S.C.A. data".
7 November	*Prof. W.W. Porterfield (Hampden Sidney College, U.S.A.), "There is no borane chemistry, only geometry".
15 November	*Prof. B.T. Golding (University of Newcastle-upon-Tyne), "The vitamin B_{12} mystery".
21 November	Dr. W.J. Feast (University of Durham), "A plain man's guide to polymeric organic metals".

22 November	Prof. D.T. Clark (I.C.I. New Science Group), "Structure, bonding, reactivity and synthesis as revealed by E.S.C.A.".
28 November	Dr. T.A. Stephenson (University of Edinburgh), "Some recent studies in platinum metal chemistry".
29 November	*Prof. C.J.M. Sterling (University College of North Wales), "Molecules taking the strain".
6 December	*Prof. R.D. Chambers (University of Durham), "The unusual world of fluorine chemistry".

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24 January	*Dr. A.K. Covington (University of Newcastle-upon-Tyne), "Chemistry with chips".
31 January	Dr. M.L.H. Green (University of Oxford), "Naked atoms and negligee ligands".
7 February	Prof. A. Ledwith (Pilkington Brothers), "Glass as a high technology material".
13 February	Dr. G.W.J. Fleet (University of Oxford), "Synthesis of some alkaloids from carbohydrates".
14 February	*Dr. J.A. Salthouse (University of Manchester), "Son et Lumiere, (a chemical energy show)".
19 February	*Dr. D.J. Mincher (University of Durham), "Stereoselective syntheses of some novel anthracyclinones related to the anti-cancer drug adriamycin and to the steffimycin antibiotics".
21 February	Prof. P.M. Maitlis, F.R.S. (University of Sheffield), "What use is rhodium".

27 February	*Dr. R.E. Mulvey (University of Durham), "Some unusual lithium complexes".
7 March	Dr. P.J. Rodgers (I.C.I. plc Agricultural Division, Billingham), "Industrial polymers from bacteria".
7 March	Dr. P.W. Atkins (University of Oxford), "Magnetic reactions".
12 March	*Prof. K.J. Packer (BP Research Centre), "N.m.r. investigations of the structure of solid polymers".
14 March	*Prof. A.R. Katritzky, F.R.S. (University of Florida), "Some adventures in heterocyclic chemistry".
21 March	*Dr. M. Poliakoff (University of Nottingham), "New methods for detecting organometallic intermediates in solution".
28 March	*Prof. H. Ringsdorf (Organic Chemistry Institute, University of Mainz), "Polymeric liposomes as models for biomembranes and cells".
24 April	*Dr. M.C. Grosel (Bedford College, University of London), "Hydroxypyridone dyes - bleachable one dimensional metals".
1 May	*Dr. D. Parker (I.C.I. plc Petrochemicals and Plastics Division, Wilton), "Applications of radioisotopes in industrial research".
7 May	Prof. G.E. Coates (formerly of the University of Wyoming, U.S.A.), "Chemical education in Britain and America: successes and deficiencies".

8 May	Prof. D. Tuck (University of Windsor, Ontario), "Lower oxidation state chemistry of indium".
8 May	Prof. G. Williams (University College of Wales, Aberyswyth), "Liquid crystalline polymers".
9 May	*Prof. R.K. Harris (University of Durham), "Chemistry in a spin".
14 May	Prof. J. Passmore (University of New Brunswick), "The synthesis and characterisation of some novel selenium-iodine cations, aided by ^{77}Se n.m.r. spectroscopy".
15 May	*Dr. J.E. Packer (University of Auckland, New Zealand), "Studies of free radical reactions in aqueous solution using ionising radiation".
17 May	Prof. I.D. Brown (Institute for Materials Research, McMaster University, Canada), "Bond valence as a model for inorganic chemistry".
21 May	Dr. D.L.H. Williams (University of Durham), "Chemistry in colour".
22 May	*Dr. R. Grimmett (University of Otago, Dunedin, New Zealand), "Some aspects of nucleophilic substitution in imidazoles".
22 May	*Dr. M. Hudlicky (Virgina State University, Blacksburg), "Preferential elimination of hydrogen fluoride from vicinal bromofluorocarbons".
13 June	Dr. D. Woollins (Imperial College, University of London), "Metal-sulphur-nitrogen complexes".
14 June	*Prof. Z. Rappoport (The Hebrew University of Jerusalem), "The rich mechanistic world of nucleophilic vinylic substitution".

19 June	Dr. T.N. Mitchell (University of Dortmund), "Some synthetic and n.m.r.-spectroscopic studies of organotin compounds".
26 June	*Prof. G. Shaw (University of Bradford), "Some synthetic studies in imidazole nucleosides and the antibiotic coformycin".
12 July	Dr. K. Laali (Hydrocarbon Research Institute, University of Southern California), "Recent developments in superacid chemistry and mechanistic considerations in electrophilic aromactic substitutions; a progress report".
13 September	*Dr. V.S. Palmer (University of Delhi), "Enzyme Assisted ERC Synthesis".
17 October	Dr. C.J. Ludman (University of Durham), "Some Thermochemical Aspects of Explosions".
24 October	Dr. J. Dewing (U.M.I.S.T.), "Zeolites - Small Holes, Big Opportunities".
30 October	Dr. S.N. Whittleton (University of Durham), "An Investigation of a Reaction Window".
31 October	Dr. P. Timms (University of Bristol), "Some Chemistry of Fireworks".
5 November	*Prof. M.J. O'Donnell (Indiana-Perdue University), "New Methodology for the Synthesis of Amino Acids".
7 November	Prof. G. Ertl (University of Munich), "Heterogeneous Catalysis".
14 November	*Dr. S.G. Davies (University of Oxford), "Chirality Control and Molecular Recognition".

20 November	*Dr. J.A.H. Macbride (Sunderland Polytechnic), "A Heterocyclic Tour on a Distorted Tricycle - Biphenylene".
21 November	Prof. K.H. Smith (University of Newcastle), "Chemistry of Si-Al-O-N Engineering Ceramics".
28 November	Dr. B.A.G. Clark (Kodak Ltd.), "Chemistry and Principles of Colour Photography".
28 November	Prof. D.J. Waddington (University of York), "Resources for the Chemistry Teacher".

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15 January	Prof. N. Sheppard (University of East Anglia), "Vibrational and Spectroscopic Determinations of the Structures of Molecules Chemisorbed on Metal Surfaces".
23 January	Prof. Sir Jack Lewis (University of Cambridge), "Some more Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls".
29 January	*Dr. J.H. Clark (University of York), "Novel Fluoride Ion Reagents".
30 January	Dr. N.J. Phillips (University of Technology, Loughborough), "Laser Holography",
12 February	Dr. J. Yarwood (Univeristy of Durham), "The Structure of Water in Liquid Crystals".
12 February	*Prof. O.S. Tee (Concordia University, Montreal), "Bromination of Phenols".
13 February	*Prof. R. Grigg (Queens University, Belfast), "Thermal Generation of 1,3-Dipoles".
19 February	Prof. G. Procter (University of Salford), "Approaches to the Synthesis of some Natural Products".

20 February	Dr. C.J.F. Barnard (Johnson Matthey Group), "Platinum Anti-Cancer Drug Development".
26 February	Miss C. Till (University of Durham), "ESCA and Optical Emission Studies of the Plasma Polymerisation of Perfluoroaromatics".
27 February	*Prof. R.K. Harris (University of Durham), "The Magic of Solid State N.M.R.".
5 March	*Dr. D. Hathaway (University of Durham), "Herbicide Selectivity".
5 March	Dr. D.M. Schroder (University of Edinburgh), "Studies on Macrocycle Complexes".
6 March	*Dr. B. Iddon (University of Salford), "The Magic of Chemistry".
12 March	Dr. J.M. Brown (University of Oxford), "Chelate Control in Homogeneous Catalysis".
14 May	Dr. P.R.R. Langridge-Smith (University of Cambridge), "Naked Metal Clusters - Synthesis, Characterisation and Chemistry".
9 June	Prof. R. Schmutzler (University of Braunschweig), "Mixed Valence Diphosphorus Compounds".
23 June	*Prof. R.E. Wilde (Texas Technial University), "Molecular Dynamic Processes from Vibrational Bandshapes".

Lectures starred were attended.

(B) RESEARCH CONFERENCES ATTENDED

Graduate Symposium, Durham, April 1983.

17th Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, December 1983.

Graduate Symposium, Durham, April 1984.

International Symposium on "Chemistry of Carbanions", Durham, July 1984.

Autumn Meeting, Royal Society of Chemistry, Kingston-upon-Hull, September 1984.

Graduate Symposium, Durham, April 1985.

Fourth European Symposium on Organic Chemistry, Aix-en-Provence, France, September 1985.

General Poster Meeting, Newcastle-upon-Tyne, December 1985.

19th Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, December 1985.

Graduate Symposium, Durham, April 1986.

Postgraduate Heterocyclic Symposium, Aston, July 1986.

International Symposium to celebrate the "Centenary of the discovery of Fluorine", Paris, France, September 1986.

(C) POSTGRADUATE INDUCTION COURSE

In each part of the course, the uses and limitations of the various services available were explained.

Departmental Organisation:- Dr. E.J.F. Ross.

Safety Matters:- Dr. M.R. Crampton.

Electrical Appliances and Infrared Spectroscopy:- (the Late) Mr. R.N. Brown.

Chromatography and Micro Analysis:- Mr. T.F. Holmes.

Atomic Adsorption Spectrometry and Inorganic Analysis:- Mr. R. Coult.

Library Facilities:- Mr. R.B. Woodward.

Mass Spectrometry:- Dr. M. Jones.

Nuclear Magnetic Resonance Spectroscopy:- Dr. R.S. Matthews.

Glassblowing Techniques:- Mr. R. Hart and Mr. G. Haswell.

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