Fluorinated aza-alkenes and dienes

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UNIVERSITY OF DURHAM

A THESIS

ENTITLED

FLUORINATED AZA-ALKENES AND DIENES

SUBMITTED BY

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(ST. CUTHBERTS SOCIETY)

A CANDIDATE FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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I would also like to express my gratitude to the many technical and laboratory staff for their valuable advice and assistance and to Dr. S. Bartlett for typing this thesis.

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

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1978 and September 1981. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has been the subject of the following papers:

R.N. Barnes, R.D. Chambers, R.D. Hercliffe, and W.K.R. Musgrave, J. Chem. Soc. Perkin I, 1981, 2059

R.N. Barnes, R.D. Chambers, R.D. Hercliffe, and R. Middleton, J. Chem. Soc. Perkin I, submitted for publication.

R.N. Barnes, R.D. Chambers, and R.S. Matthews, J. Fluorine Chem., submitted for publication.

ABSTRACT

In this thesis the cobalt trifluoride fluorination of a series of perfluoroalkyl-pyridine, -pyrimidine, -pyrazine, -pyridazine, and -toluene derivatives is described. In general, these gave good yields of the corresponding cyclohexadiene and monoene derivatives.

The photochemistry of a number of the new dienes has been studied. Irradiations led to ring opening and fragmentation reactions which were analogous to those shown by corresponding hydrocarbon systems.

Various reactions with fluoride ion have been investigated. Addition of fluoride to perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene gave the stable perfluoro-1-aza-4-isopropylcyclohex-3-enyl anion. The reaction of N,N'-bis-1,3-diazacyclohex-2-enyl led to an interesting rearrangement involving internal nucleophilic attack at a saturated position.

Reactions of some of the new dienes with diazomethane are also described. These gave bicyclic products arising from 1,3-dipolar addition followed by elimination of either nitrogen or hydrogen fluoride.

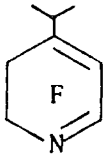
The chemistry of perfluoro-2,5-diazahexa-2,4-diene has also been studied. Reactions with fluoride ion in solution gave only dimers, but the reaction with caesium fluoride in the vapour phase provided a new and convenient route to perfluoro-1,3-diaza-1-methylcyclopent-2- and -3-enes. Defluorination over heated iron filings gave a new imidazole derivative, a reaction which represents the first synthetic route to a compound of this type. A series of similar reactions using iron, nickel, and platinum were only partially successful. Photochemical reactions were unsuccessful.

A preliminary investigation into the chemistry of perfluoro-1,3-diaza-1-methylcyclopent-2- and -3-enes is described. Reactions with caesium fluoride led to dimerization, but products arising from nucleophilic displacement of

vinylic fluorine were obtained on reaction with hexafluoropropene in the presence of fluoride ion. Hydrolysis led to a new diazacyclopentadione derivative arising from addition-elimination at both C2 and C4 positions.

NOMENCLATURE

1) The prefix 'perfluoro' is used before a name to denote that the compound or the part of the compound following the prefix is fully fluorinated.

2) A capital F in a ring (e.g. ) denotes that the ring and all its unspecified substituents are fully fluorinated.

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INTRODUCTION

General Introduction

The main differences in properties between fluorocarbon and hydrocarbon systems arise mainly from the difference in electronegativities of fluorine and hydrogen and the effects arising from the influence of non-bonded electron pairs on the fluorine atom. Consequently functional groups in fluorinated molecules are in completely different electronic environments in comparison with their hydrocarbon analogues, which leads to very different, though often complementary chemical reactions.

Owing to their high chemical and thermal stability fluorocarbons have found many industrial applications. For example, polytetrafluoroethylene has proved to be a very useful polymer which, apart from a high degree of chemical and thermal stability has a very low coefficient of friction and is used widely in the manufacture of dry bearings, as a coating for non-stick cooking utensils, etc.

The use of fluorine containing compounds in the pharmaceutical industry is becoming increasingly common and a major impact of fluorine chemistry on drugs is in the area of steroids. Methods have been developed to introduce fluorine into all of the available positions in the steroid nucleus resulting in fluorinated steroids, some of which exhibit considerably enhanced pharmacological activity. Many non-steroidal fluorinated compounds have also found medicinal applications. For example, fluorinated anaesthetics are now widely used, whilst 5-fluorouracil has been used successfully in the treatment of cancer.

Fluorinated compounds have also found many uses in agriculture, either for killing pests, or controlling disease.

Other uses of fluorocarbons include such diverse areas as surfactants, dyes, fire extinguishers, aerosol propellants, refrigerants, coolants for sealed electrical systems, etc.

This thesis intends to discuss the chemistry of fluorinated aza-alkenes, a class of compound which has been known for some time but has been subject to little more than superficial investigation.

CHAPTER 1

SYNTHESIS OF FLUORINATED AZA-ALKENES

1A GENERAL METHODS

1A.1 Pyrolysis of perfluoroalkylamines

The first examples of fluorinated aza-alkenes were prepared in 1953 by the pyrolysis of tri(perfluoroalkyl)amines.[1] Direct pyrolysis of tri(perfluoroethyl)amine gave perfluoro-2-azabut-1-ene (1).

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

The method can be used to prepare many higher homologues of (1), the structures of which depend upon the nature of the perfluoroalkyl group used.

i.e. $$[CF_3(CF_2)_3]_3N \xrightarrow{645\text{-}650^\circ C} CF_3(CF_2)_3N{=}CF_2$$

However, direct pyrolysis yields compounds which contain a terminal difluoromethylene group attached to nitrogen. Compounds containing internal imine groups have been obtained using various catalysts and pyrolyses over mixtures of AlF_3 and Al_2O_3 [1], and with Pt metal[2] have proved successful.

$$(C_2F_5)_3N \xrightarrow[AlF_3.Al_2O_3]{500\text{-}550^\circ C} CF_3CF_2N{=}CFCF_3$$

$$(C_3F_7)_3N \xrightarrow[AlF_3.Al_2O_3]{500\text{-}550^\circ C} CF_3CF_2CF_2N{=}CFCF_2CF_3$$

$$(n\text{-}C_4F_9)_3N \xrightarrow[650^\circ C]{Pt\ TUBE} CF_3CF_2CF_2CF{=}NCF_3 \quad (43\%)$$

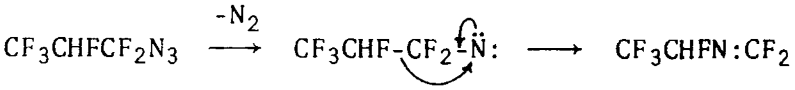
1A.2 Pyrolysis of polyfluoroalkylazides

The pyrolysis of the azide (2) has been reported to yield the aza-alkene (3).[3]

$$CF_3CF{=}CF_2 \xrightarrow[\substack{C_2H_5OH \\ 0^\circ C}]{NaN_3} \underset{(2)\ (36\%)}{CF_3CHFCF_2N_3} \xrightarrow[Pt]{270\text{-}280^\circ C} \underset{(3)\ (86\%)}{CF_3CFHN{=}CF_2}$$

This is one of the few examples of this type of reaction, however the presence of hydrogen as a functional group lends itself to various possibilities i.e. removal of HF to give a diene.

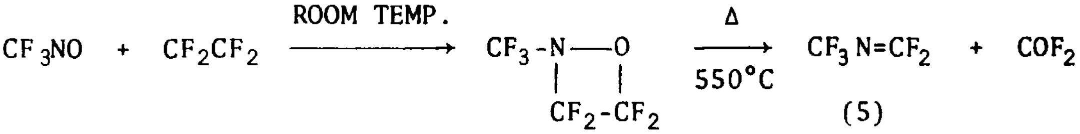
More recently, the conversion of (2) to (3) has been achieved photochemically[4], the mechanism of which is particularly interesting since it must invoke a nitrene intermediate and a 1,2-alkyl shift.



$$\underset{(2)}{CF_3CHFCF_2N_3} \xrightarrow{-N_2} CF_3CHF\text{-}CF_2\text{-}\ddot{N}: \longrightarrow \underset{(3)}{CF_3CHFN{:}CF_2}$$

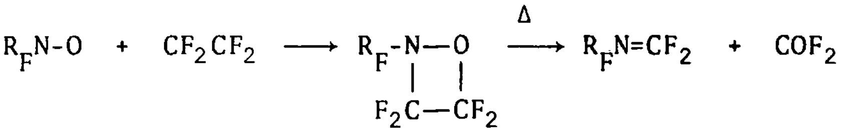
1A.3 Nitrosation of perfluoroalkenes

Trifluoronitrosomethane reacts quantitatively with tetrafluoroethylene to give mainly an oxazetidine derivative (4). Pyrolysis of (4) gives perfluoro-2-azapropene (5).[5]



(4)

Subsequent investigations[6] together with the ease of availability of perfluoronitrosoalkanes[5] have shown that this is a good general method for the preparation of fluorinated aza-alkenes.

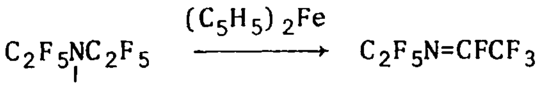


$R_F = C_2F_5,\ C_3F_7$

It must be noted that this method is restricted to the preparation of compounds containing a terminal difluoromethylene group since the ease of reactivity of perfluoronitrosoalkanes with perfluoroalkenes decreases with increasing numbers of substitutents on the alkene.

1A.4 Reductive defluorination of perfluoroalkyl-amines

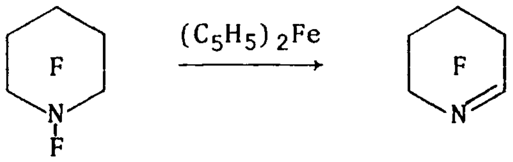
Dicyclopentadienyliron and dicumenechromium have been used successfully as reducing agents to introduce a $>C{=}N$ group into fluorocarbon structures in high yield.[7] Secondary fluoroamines give good yields of internal perfluoroaza-alkenes.



$$C_2F_5\underset{F}{N}C_2F_5 \xrightarrow{(C_5H_5)_2Fe} C_2F_5N{=}CFCF_3$$

(84%)

The method has also been used in the preparation of cyclic aza-alkenes.

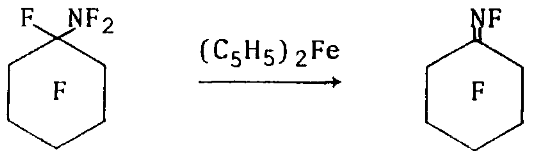


(94%)

More interesting is the application of the reaction to the preparation of compounds containing the $>C{=}NF$ group from difluoroamines.

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

(82%)



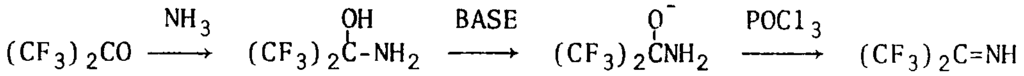
(78%)

Dienes have also been successfully prepared by reductive defluorination.

$$F_2NCF_2CF_2CF_2NF_2 \xrightarrow{(C_5H_5)_2Fe} FN{=}CFCF_2CF{=}NF$$

1A.5 Reaction of fluorinated ketones with primary amines

Methods of preparation discussed so far have included only those in which perfluoroaza-alkenes are synthesised. The reaction of fluorinated ketones with primary amines provides a method of obtaining aza-alkenes with hydrogen or an alkyl group attached directly to nitrogen.[8] Hexafluoroacetone (6) can be reacted with ammonia and the resultant product (7) dehydrated with a base and $POCl_3$ to give the aza-alkene (8).



$$(CF_3)_2CO \xrightarrow{NH_3} (CF_3)_2\overset{OH}{\overset{|}{C}}\text{-}NH_2 \xrightarrow{BASE} (CF_3)_2\overset{O^-}{\overset{|}{C}}NH_2 \xrightarrow{POCl_3} (CF_3)_2C{=}NH$$

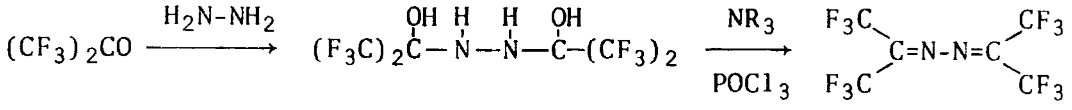
(6) (7) (8) (70%)

The reaction seems to be of a general nature and various primary amines have been used giving yields of 60-80%.

$$(CF_3)_2CO \xrightarrow[\substack{BASE \\ POCl_3}]{RNH_2} (CF_3)_2C{=}NR \qquad (60\text{-}80\%)$$

R = H, alkyl, aryl

Similar attempts to prepare aza-alkenes from fluorinated ketones and amines have only been partially successful.[9] An interesting application of the method has been found in the synthesis of perfluorinated azines.[10] Hexafluoroacetone azine (9) can be prepared from hexafluoroacetone (6) and hydrazine.

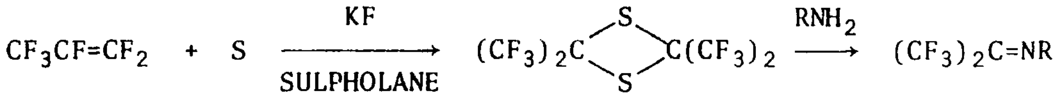


(6) (9) (65%)

Previously reported syntheses of fluorinated azines[11-13] are complicated and proceed in several steps. The chemistry of (9) is particularly interesting and is discussed later.

1A.6 Reaction of perfluorothioacetone dimer with primary amines

A novel method of synthesising fluorinated aza-alkenes with hydrogen, alkyl or aryl groups attached directly to nitrogen has involved the use of hexafluorothioacetone dimer (10).[14] Compound (10) can be prepared directly from hexafluoropropene and sulphur in sulpholane in the presence of KF, and will react with primary amines to give fluorinated aza-alkenes.



(10)

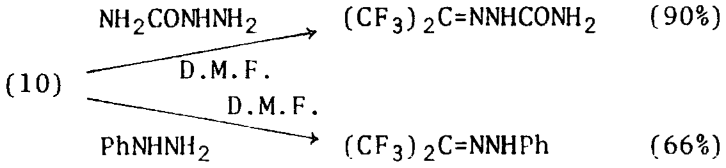
[R = H, C_3F_7, C_5H_9, C_6H_5, XC_6H_4 (X = *o*-Me, -Cl, -OMe, *m*-CH_3, -F, -CF_3, -C_3F_7, -Cl, *p*-Me, -F, -C_3H_7, -Cl, or -OMe)]

The dimer (10) can also be reacted with hydrazine to give hexafluoroacetone azine (9) but this is only present as the minor of two products.

$$(10) \xrightarrow{NH_2NH_2} (CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \quad + \quad (CF_3)_2C{=}NNH_2$$

(9) (11%) (43%)

A variation of this reaction using substituted hydrazines has provided convenient routes to fluorinated aza-alkenes containing additional functional groups.



1A.7 Photochemical syntheses

General synthetic methods discussed so far have mainly been concerned with the preparation of compounds containing a single C=N function. Fluorinated diaza-dienes have been prepared from the photolysis of perfluoro-2,3-diazabuta-1,3-diene (11).[15] Irradiation of (11) gave almost quantitative conversion to perfluoro-2,4-diazapenta-1,4-diene (12).

$$\underset{(11)}{CF_2{=}N{-}N{=}CF_2} \xrightarrow{h\nu} \underset{(12)}{CF_2{=}N{-}CF_2{-}N{=}CF_2} + N_2$$

This can be rationalized on the basis of the decomposition of (11) into $CF_2{=}\dot{N}$ radicals and difluorocarbene. Photolysis of (11) in the presence of difluorodiazomethane as a source of difluorocarbene resulted in the formation of the first four members of the series of diaza-dienes.

$$(11) \xrightarrow[CF_2N_2]{h\nu} CF_2{=}N{-}(CF_2)_{1-4}{-}N{=}CF_2$$

Additional members of the series were produced when photolysis of (11) was carried out in the presence of various fluorinated alkenes. This is summarized in Table 1.

CO-REACTANT	PRODUCT	% CONVERSION
$:CF_2$	$CF_2=N-CF_2-N=CF_2$	12
	$CF_2=N-(CF_2)_2-N=CF_2$	25
	$CF_2=N-(CF_2)_3-N=CF_2$	3
	$CF_2=N-(CF_2)_4-N=CF_2$	1
$CF_2=CF_2$	$CF_2=N-CF_2-N=CF_2$	13
	$CF_2=N-(CF_2)_2-N=CF_2$	57
	$CF_2=N-(CF_2)_3-N=CF_2$	10
$CF_3CF=CF_2$	$CF_2=N-CF_2-N=CF_2$	11
	$CF_2=N-CF(CF_3)-CF_2-N=CF_2$	66
$CF_3CF=CFCF_3$	$CF_2=N-CF_2-N=CF_2$	17
	$CF_2=N-CF(CF_3)-CF(CF_3)-N=CF_2$	30
$CF_2=CFCl$	$CF_2=N-CF_2-N=CF_2$	12
	$CF_2=N-CF_2-CFCl-N=CF_2$	25

TABLE 1 - FLUORINATED DIAZADIENES

1A.8 Miscellaneous

Silver(I) and silver(II) fluorides have been used to prepare fluorinated aza-alkenes from corresponding brominated derivatives.[16]

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

Dechlorinations, either thermal or by reaction with Hg have been used to prepare compounds containing the C=NF group.[17]

$$Cl_2C{=}NF \; + \; ClF \longrightarrow Cl_2FCNFCl \xrightarrow[\text{OR Hg}]{\Delta} ClFC{=}NF$$

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

Dehydrofluorination of fluorinated amines with KF has provided a comparatively simple synthetic route to various fluorinated aza-alkenes.[18] Perfluoro-2-azapropene (5) can be prepared by dehydrofluorination of hexafluorodimethylamine (13).

$$CCl_3N{=}CCl_2 \xrightarrow{HF} \underset{(13)}{(CF_3)_2NH} \xrightarrow[140\text{-}150°C]{KF} \underset{(5)}{CF_3N{=}CF_2} \quad (70\%)$$

Similarly the dehydrofluorination of phenyltrifluoromethylamine (14) provides an example of the general nature of the reaction.

$$\underset{(14)}{PhNHCF_3} \xrightarrow[140\text{-}150°C]{KF} PhN{=}CF_2$$

More recently the reaction has been used in the synthesis of perfluoro-2,5-diazahexa-2,4-diene (16).[19-21]

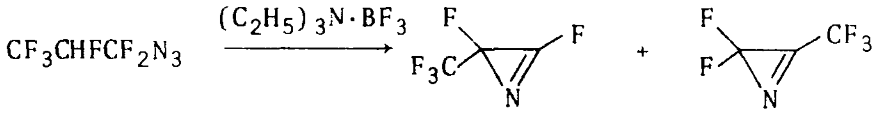
$$\begin{tikzcd}
Cl_2C{=}NCCl_2CCl_2N{=}CCl_2 \arrow[r, "HF", "70°C"'] & CF_3NHCF_2CF_2NHCF_3 \arrow[r, "NaF", "\text{ROOM TEMP.}"'] & \underset{(15)}{CF_2{=}NCF_2CF_2N{=}CF_2} \arrow[dl, shift left] \\
 & \underset{(16)}{CF_3N{=}CFCF{=}NCF_3} \arrow[ur, shift left] &
\end{tikzcd}$$

The presence of fluoride ion causes isomerization of the initial product (15) and (16) is obtained exclusively. The chemistry of (16) prepared by this method is discussed at some length in subsequent chapters.

1B HETEROCYCLIC COMPOUNDS

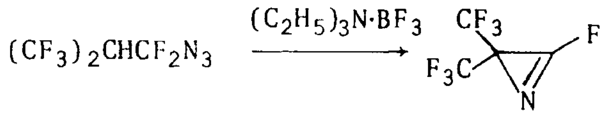
1B.1 Azacyclopropenes

The formation of fluorinated azacyclopropanes has been reported frequently.[22-24] Examples of fluorinated azacyclopropenes however are very rare. Perfluoro-2-methyl- (17) and -3-methyl-(18) azacyclopropenes have been prepared from the azide (19).[25]



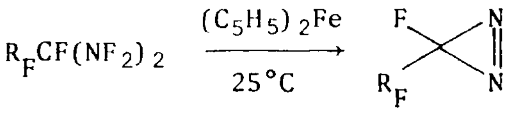
(19) (17) (18)

Perfluoro-2,2-dimethylazacyclopropene (20) has been prepared in a similar way[22].



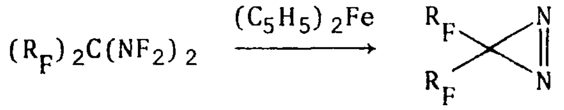
(20) (72%)

Examples of fluorinated diazacyclopropenes are more common. The reductive defluorination reaction with dicyclopentadienyliron (section 1A.4) has been used as a general method of preparation[26-28].



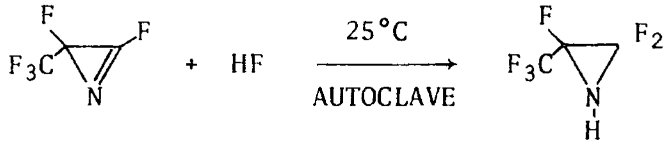
(R_F = F, C_2F_5, C_5F_{11}, $CF_2ClCFClCF_3$)

The reaction can also be used to prepare bis(perfluoroalkyl)diazacyclopropenes.



(R_F = CF_3, C_2F_5)

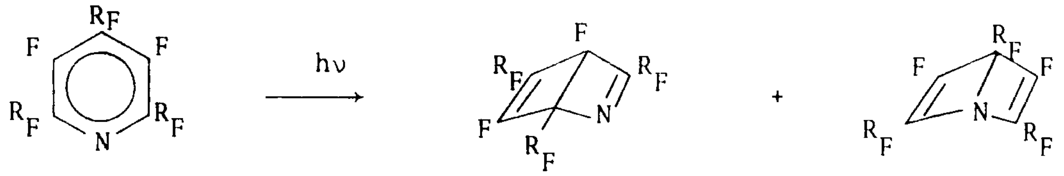
Further evidence for the stabilizing influence of fluorine in small ring systems is provided by the remarkable stability of fluorinated azacyclopropenes.[25] Direct reaction of (17) with HF leaves the 3-membered ring system intact.



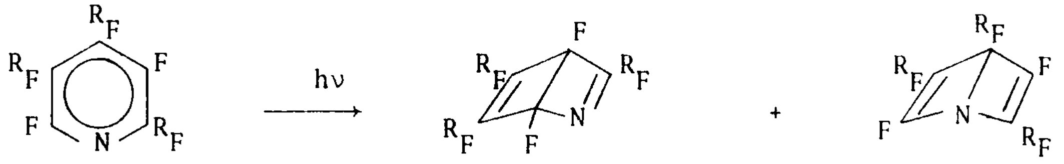
(17)

1B.2 Azacyclobutenes

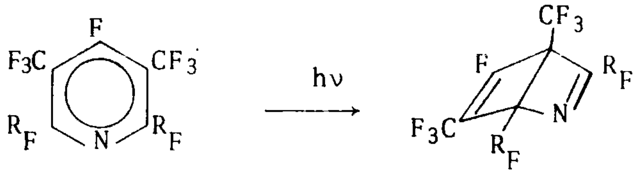
Four membered ring systems containing the C=N group are extremely rare. The only examples are those in which the azacyclobutane ring is part of bicyclic or polycyclic systems. The photolyses of various perfluoroalkylpyridines have given stable azabicyclo[2.2.0]hexa-2,5-diene derivatives.[29] Similarly the diazacyclobutadiene derivatives (21), (22), and (23) have been prepared from the photolysis of perfluoroalkylpyridazines.[30]



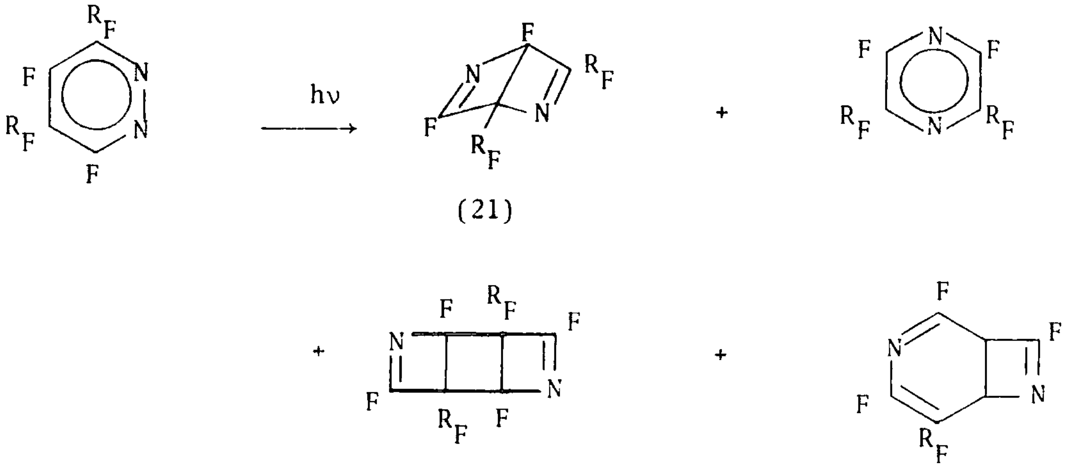
(99%) (1%)



(55%) (45%)



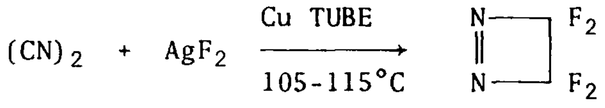
[R_F = $CF(CF_3)_2$]



(21)

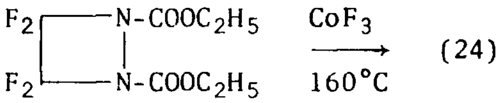
(22) (23)

The generation of an azacyclobutadiene intermediate is postulated to explain the formation of (22) and (23). The only example of a diazacyclobutene (24) has been prepared by two methods. Reaction of $(CN)_2$ with AgF_2 in a copper tube gives (24).[31]



(24)

Similarly (24) can be prepared by fluorination of the diethyl ester (25) with CoF_3.[32]

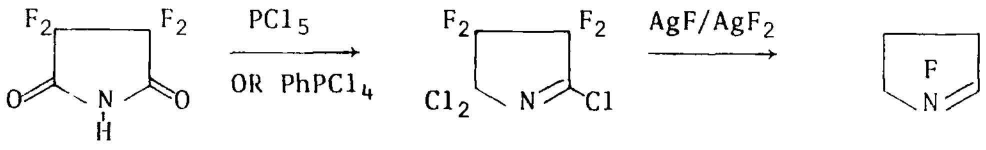


(25)

The nature of this reaction is interesting since compounds containing -N=N- groups have been shown to lead exclusively to loss of nitrogen on fluorination with CoF_3. (See Chapter 3 section E.)

1B.3 Azacyclopentenes

Perfluoro-1-azacyclopent-1-ene (26) was first prepared by reductive chlorination of tetrafluorosuccinimide (27) followed by reaction with an AgF/AgF_2 mixture.[33]

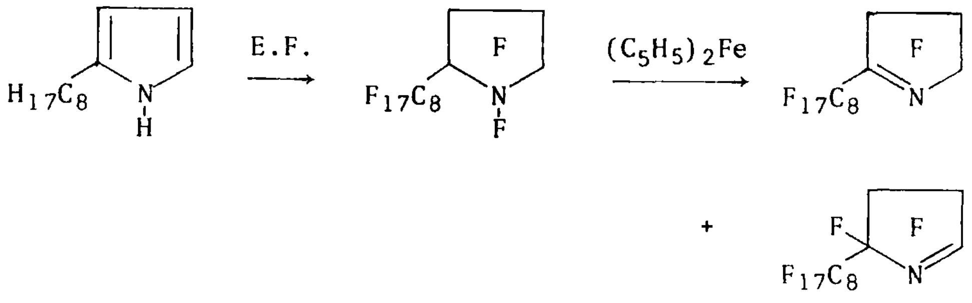


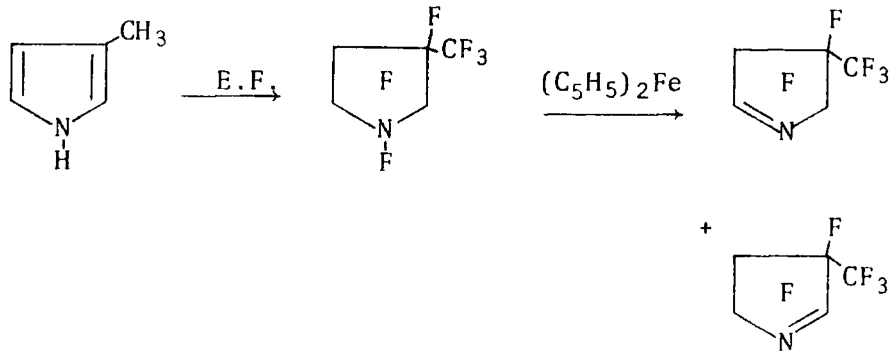
(27) (26)

A more convenient method was electrochemical fluorination of pyrrole followed by thermolysis to give (26).

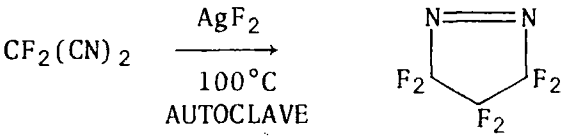
(26) (50%)

Electrochemical fluorination has also been used to prepare various substituted derivatives and reductive defluorination with dicyclopentadienyliron used to obtain the substituted perfluoroazacyclopentenes[34].



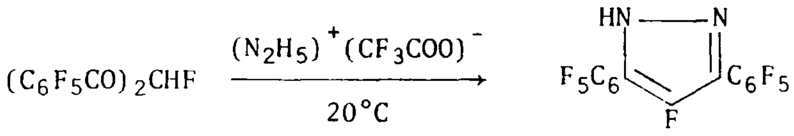


Examples of fluorinated 1,2-diazacyclopentenes are rare. Perfluoro-1,2-diazacyclopent-1-ene (28) can be prepared from the fluorination of $CF_2(CN)_2$ with AgF_2[35].



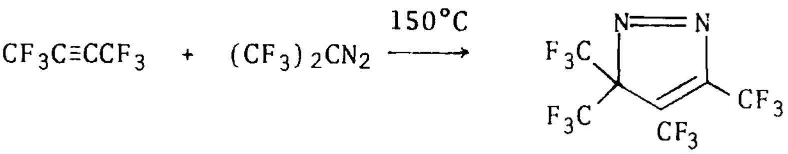
(28)

Various methods for the preparation of diazacyclopentadienes have been reported. The diketone (29) gives the perfluorinated diene (30) on reaction with $[N_2H_5^+][CF_3COO^-]$.[36]



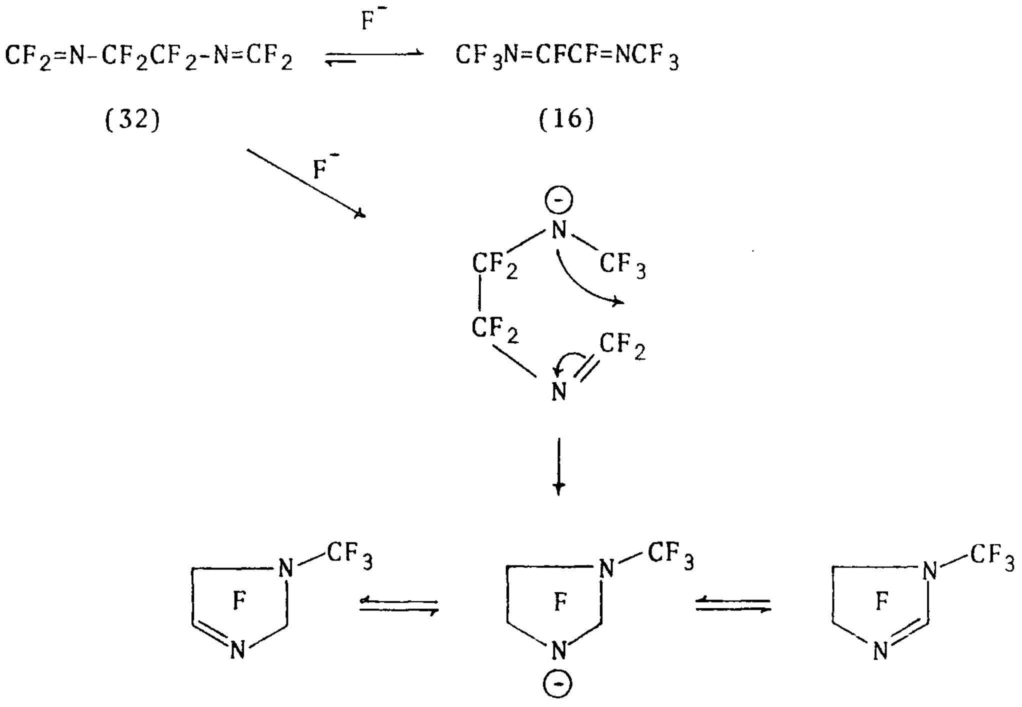
(29) (30) (100%)

Reaction of hexafluoro-2-butyne with $(CF_3)_2CN_2$ has been used to prepare the diazadiene (31).[37]



(31) (35%)

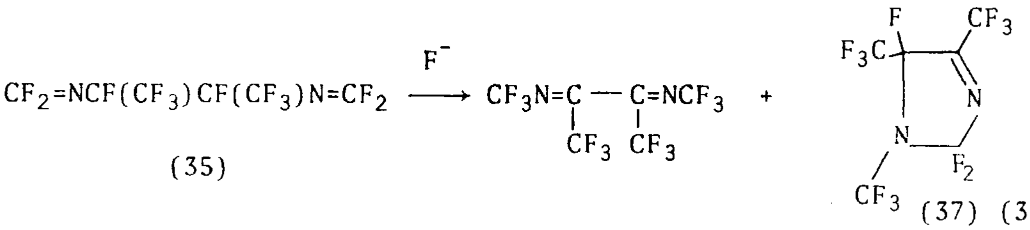
A convenient synthetic route to perfluoro-1,3-diazacyclopentenes involves the fluoride ion induced isomerization of perfluoro-2,5-diazahexadienes[38,39], the preparation of which was described in section 1A.7. The isomerization of perfluoro-2,5-diazahexa-1,5-diene (32) to perfluoro-2,5-diazahexa-2,4-diene (16) is accompanied by intramolecular cyclization to give the diazacyclopentenes (33) and (34).



(32) (16)

(33) (34)

Yields of (33) and (34) are low since cyclization is followed by dimerization. The chemistry of (32) and (16) with fluoride ion is discussed in more detail later. Similarly intramolecular cyclization occurs during the isomerization of perfluoro-2,5-diaza-3,4-dimethyl-hexa-1,5-diene (35) to give (37).



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

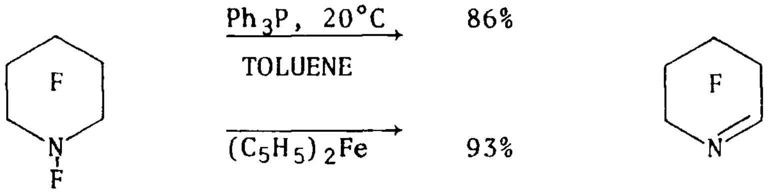
(35)

(37) (30%)

Interestingly dimerization does not occur in this system due to the 'blocking' effect of the vinylic CF_3 group.

1B.4 Azacyclohexenes

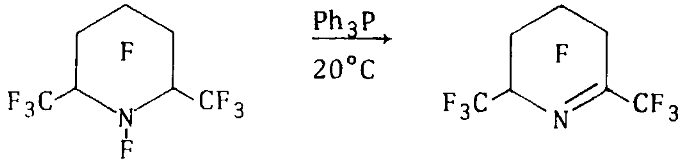
Perfluoro-1-azacyclohex-1-ene (38) has been prepared by numerous methods. Many of these involve thermolysis of perfluoropiperidine, (39) prepared by electrochemical fluorination of pyridine, in the presence of various metal catalysts.[40-42] Yields are generally low. Defluorination of (39) with Ph_3P[43] or dicyclopentadienyliron[44] gives excellent yields of (38).



(39)

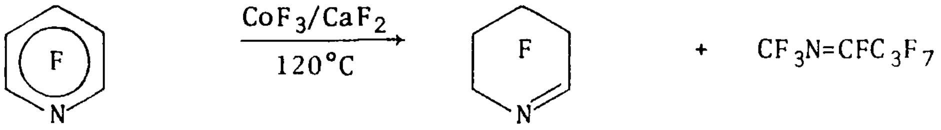
(38)

Electrochemical fluorination has provided a route to many perfluoroalkylpiperidines from pyridine precursors[45] and some of these have been successfully defluorinated to give substituted perfluoroazacyclohexenes. Perfluoro-2,6-dimethylpiperidine for example yields perfluoro-1-aza-2,6-dimethylcyclohex-1-ene on defluorination with Ph_3P.[43]



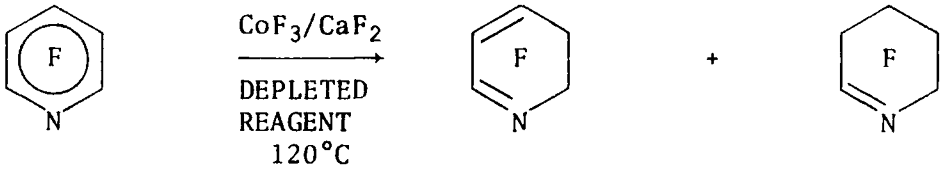
(86%)

Fluorination with high valency metal fluorides, particularly CoF_3, has provided an interesting synthetic route to fluorinated aza-alkenes from aromatic precursors. Compound (38) can be prepared by fluorination of pentafluoropyridine with a CoF_3/CaF_2 mixture.[46]



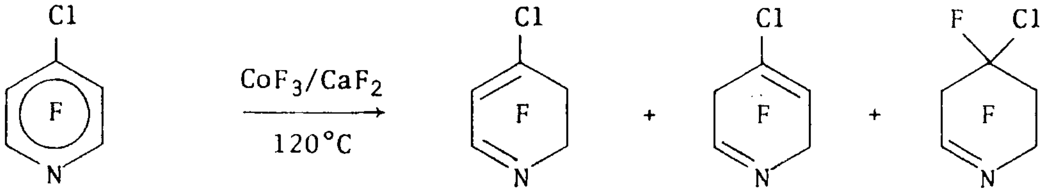
(38) (63%) (10%)

The reaction can be used to prepare fluorinated azacyclohexadienes, however the reaction with pentafluoropyridine, even under conditions of heavy CoF_3 depletion , gave only a small amount of a 1,3-diene (40).



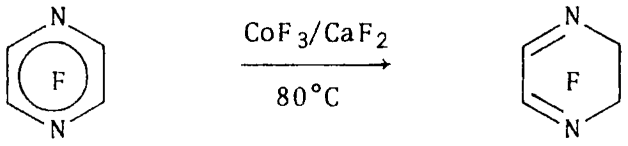
(40) (2%) (38) (61%)

Only when chlorine is introduced into the -4-position are substantial amounts of dienes observed in the product mixture.

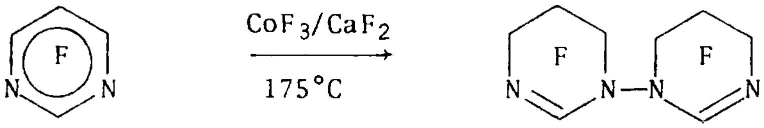


(45%) (2%) (12%)

The fluorination of tetrafluoropyrazine with CoF_3 gave a 1,4-diaza-1,3-diene (41) but, interestingly, tetrafluoropyrimidine gave a dimer (42).

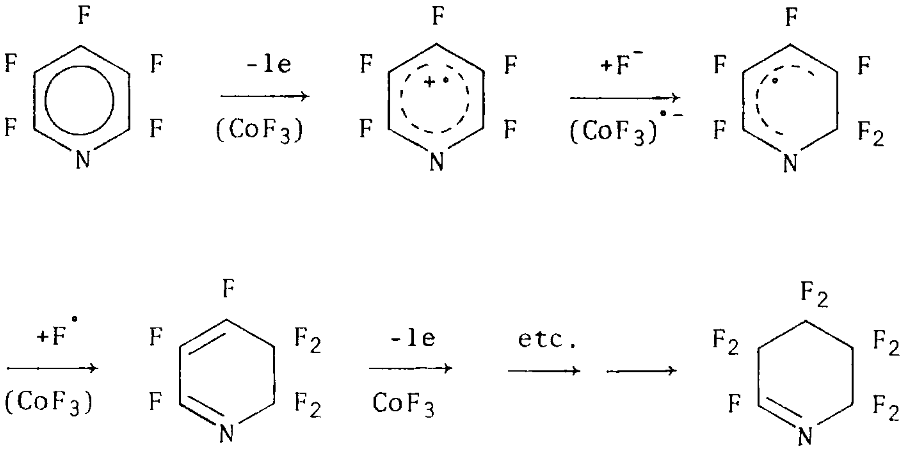


(41) (29%)



(42)

The proposed mechanism for CoF_3 fluorination involves the intermediacy of radical cations in the fluorination process[46,47] initiated by a 1-electron transfer.



(38)

The production of the dimer (42) from tetrafluoropyrimidine is strong support for this type of mechanism.

CHAPTER 2

THE CHEMISTRY OF FLUORINATED AZA-ALKENES

2A INTRODUCTION

The fluorine atom, although it has seven valence electrons, is only slightly larger than the hydrogen atom, and since it is also the most electronegative element the differences between the chemistry of fluorocarbon and hydrocarbon systems arise largely from electronic, rather than steric, effects.

In view of this it is possible to predict some of the properties of fluorinated aza-alkenes. The substitution of hydrogen in an aza-alkene by fluorine or perfluoroalkyl groups reduces the electron density at the C=N bond which makes the aza-alkene even more electrophilic in character and therefore very reactive towards nucleophilic attack.

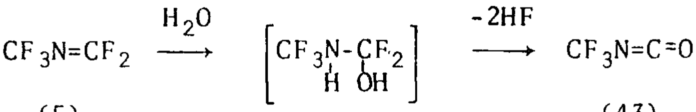
2B REACTIONS WITH NUCLEOPHILES

2B.1 O Nucleophiles

The affinity of fluorinated aza-alkenes towards nucleophiles is illustrated by the reaction of perfluoro-2-azapropene (5) with water.[5,6] Uncontrolled hydrolysis leads to complete degradation.

$$\underset{(5)}{CF_3N{=}CF_2} \xrightarrow{H_2O} CO_2 + NH_4F + HF$$

However the isocyanate (43) is obtained when (5) is reacted with a deficit of water.



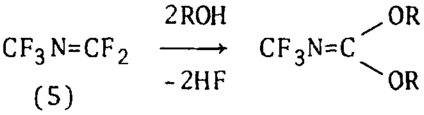
$$CF_3N{=}CF_2 \xrightarrow{H_2O} \left[CF_3\underset{H}{N}{-}\underset{OH}{C}F_2\right] \xrightarrow{-2HF} CF_3N{=}C{=}O$$

(5) (43)

Compounds not containing a terminal difluoromethylene group show a more moderate reaction with nucleophiles, which is illustrated by the hydrolysis of the diaza-diene (16) giving N,N'-bistrifluoromethyloxamide (44)[48].

$$\underset{(16)}{CF_3N{=}CFCF{=}NCF_3} \xrightarrow[-2HF]{2H_2O} \underset{(44)}{CF_3NHCOCONHCF_3}$$

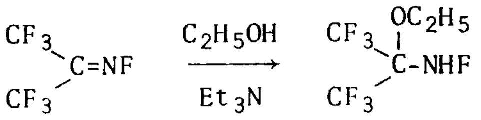
Reactions with alcohols also proceed via a similar addition-elimination mechanism, and reaction of (5) with alcohols in the presence of Et_3N leads to disubstituted products[49].



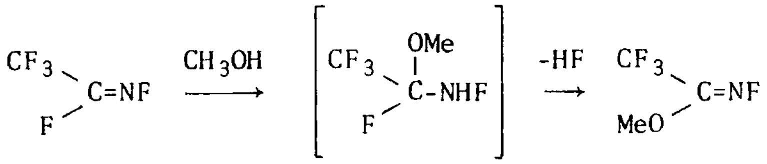
(5) (60-69%)

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

Addition of ROH followed by elimination of HF leads to a monosubstituted species which is itself activated towards further nucleophilic attack hence disubstitution occurs readily. Compounds containing the C=NF group tend to favour monosubstitution. Addition of ethanol to the imine (45) leads to (46) only since elimination of HF is impossible, however, compound (47) gives monosubstitution and elimination of HF to give (48)[50] on reaction with methanol.

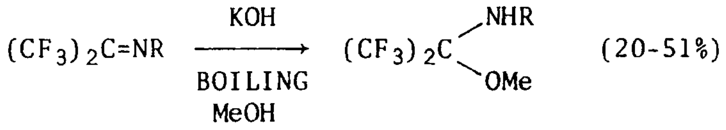


(45) (46)

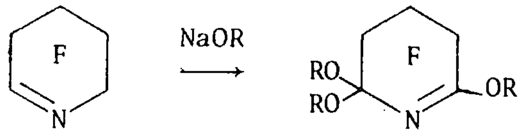


(47) (48)

Compounds containing the C=NR group (R = phenyl, substituted phenyl) react with alcohols but conditions are more harsh since the electron donating effect of the phenyl substituent renders the C=N bond less reactive towards nucleophiles.[51]



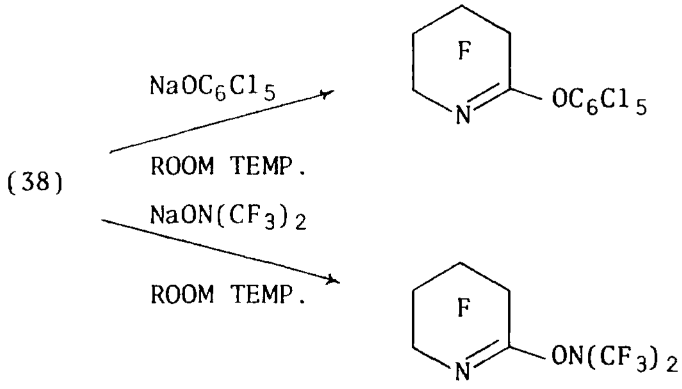
The reaction of perfluoro-1-azacyclohex-1-ene (38) with nucleophiles is interesting since loss of fluorine from both C2 and C6 sites occurs, indeed, addition of an excess of sodium methoxide or phenoxide to (38) leads to trisubstitution.[52,53]



(38)

(R = Me, Ph)

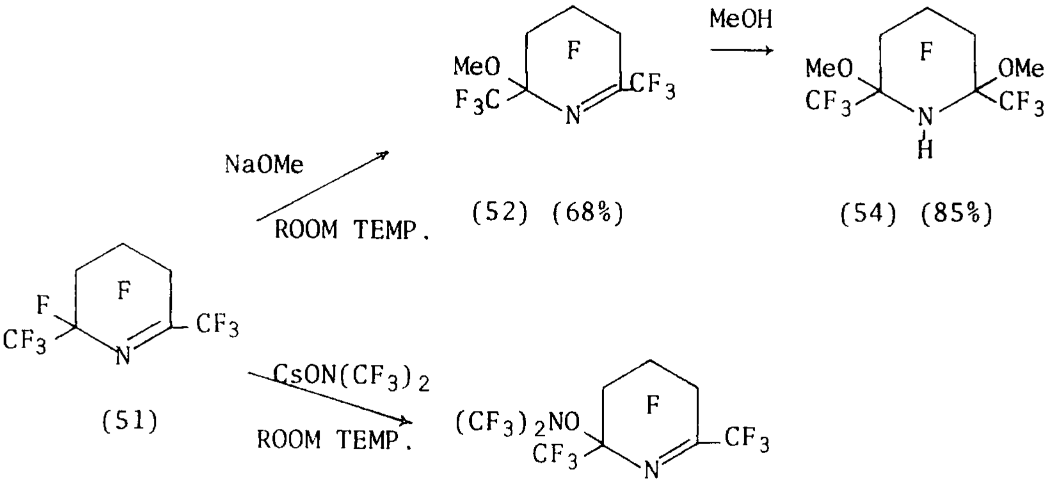
Monosubstitution can be achieved under mild conditions with a 1 molar proportion of a suitable nucleophile and reaction of sodium pentachlorophenoxide or sodium bistrifluoromethylnitroxide with (38) yields the imidic esters (49) and (50) respectively.[52]



(49) (79%)

(50) (70%)

An interesting example of elimination of fluorine from the C6 position only occurs when the substituted azacyclohexene (51) is reacted with sodium methoxide or caesium bistrifluoromethylnitroxide giving compounds (52) and (53) respectively.[54] Further reaction of (52) with an excess of methanol provides the piperidine derivative (54).



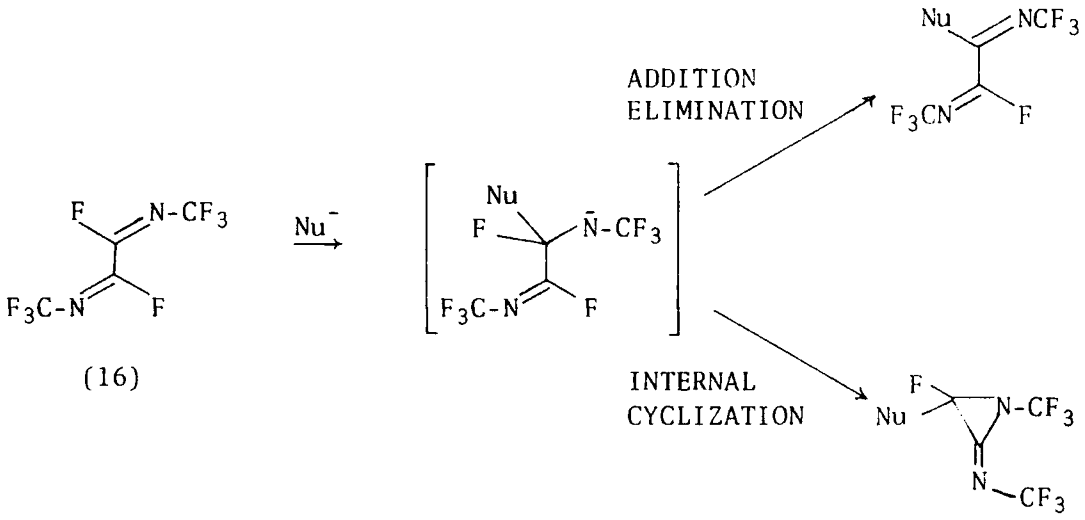
(51)

(52) (68%)

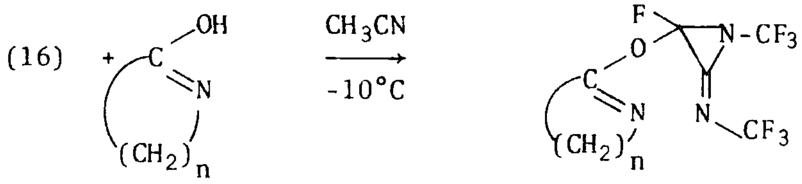
(54) (85%)

(53) (93%)

The reaction of perfluoro-2,5-diazahexa-2,4-diene (16) with nucleophiles has received much attention. Reaction can occur via standard addition-elimination or alternatively by internal cyclization giving an azacyclopropane derivative.



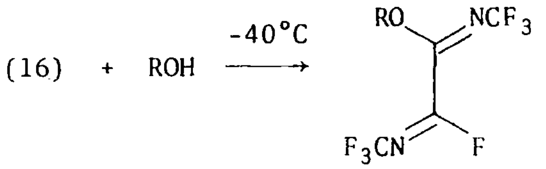
Products arising from internal cyclization have only been observed in reactions with lactams[55], in particular piperidine and caprolactam which react with (16) to give the azacyclopropane derivatives (55) and (56).



n = 4 (55) (77%)

n = 5 (56) (78%)

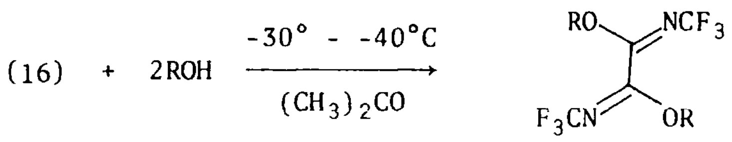
In all remaining reactions with alcohols and phenols internal cyclization does not occur and monosubstituted straight chain products are obtained in good yields[55].



(65-85%)

(R = Me, Et, Ph, 2,4-$C_6H_3Cl_2$, 4-C_6H_4Cl, 4-$C_6H_4NO_2$)

Substitution is achieved at both unsaturated sites in the molecule when a 2:1 excess of nucleophile is used.[56]

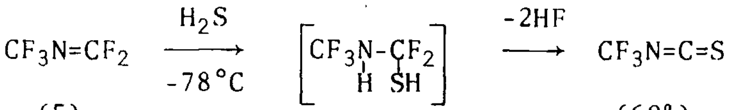


(75-100%)

(R = Me, Et, 2,4-$C_6H_3Cl_2$)

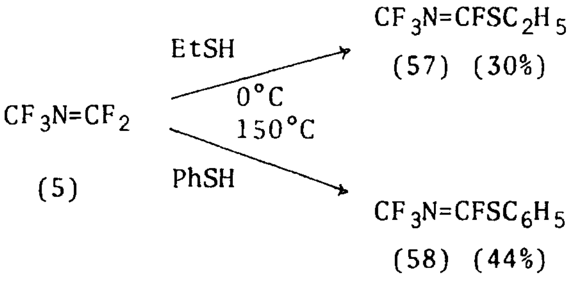
2B.2 S Nucleophiles

Reactions of fluorinated aza-alkenes with sulphur nucleophiles have been less widely exploited, however, the chemistry shows a parallel with that of oxygen nucleophiles with addition-elimination being the main mode of reaction. Perfluoro-2-azapropene (5) reacts with hydrogen sulphide to give trimethylisothiocyanate[57],



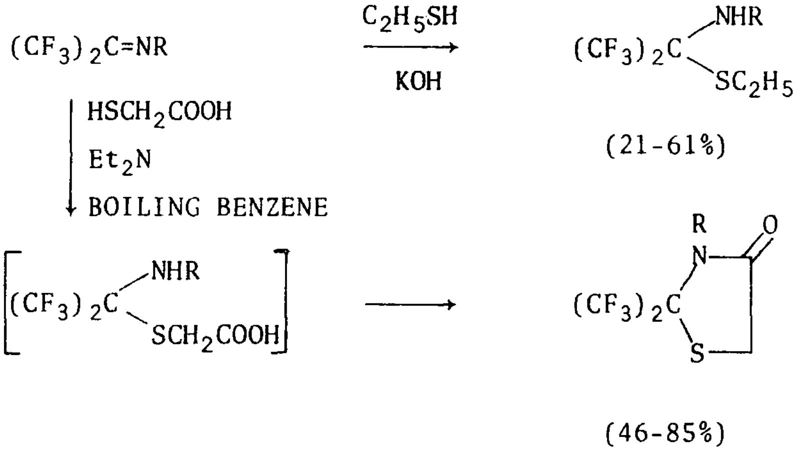
$$\underset{(5)}{CF_3N{=}CF_2} \xrightarrow[-78\,^{\circ}C]{H_2S} \left[CF_3\underset{H}{N}-\underset{SH}{C}F_2\right] \xrightarrow{-2HF} \underset{(60\%)}{CF_3N{=}C{=}S}$$

and reaction of (5) with thioethanol and thiophenol proceeds via a similar addition-elimination mechanism giving (57) and (58) respectively.[57]

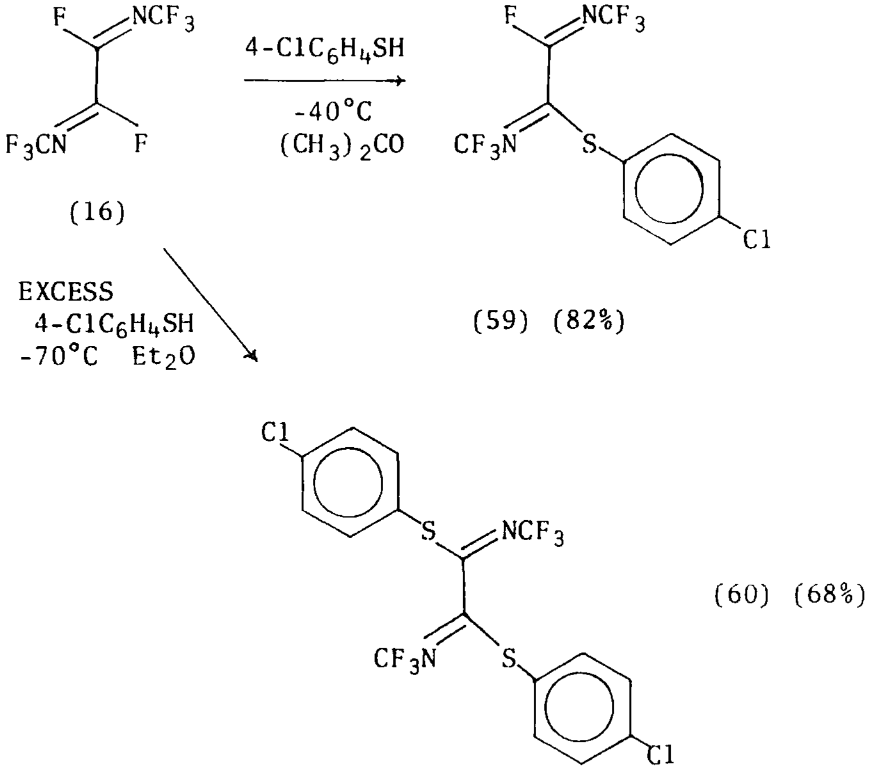


Interestingly, disubstituted products are not observed which indicates that (57) and (58) are not as susceptible to nucleophilic attack as their oxygen analogues.

Compounds containing the C=NR group (R = phenyl, substituted phenyl) also react with thiols[51] but conditions, as with corresponding alcohols, are more harsh and, interestingly, reaction with $HSCH_2COOH$ leads to an internal cyclization with elimination of water giving a novel series of five-membered heterocyclic compounds.



Perfluoro-2,5-diazahexa-2,4-diene (16) will react with thiophenols to give the corresponding addition elimination products and reaction of (16) with an equimolar amount of 4-chlorothiophenol gives the monosubstituted product (59).[55] Disubstitution occurs to give (60) when a 2:1 excess of 4-chlorothiophenol is used.[56]



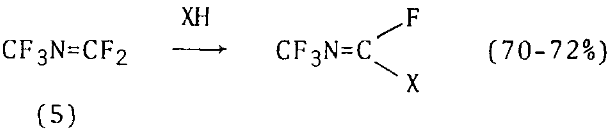
(16)

(59) (82%)

(60) (68%)

2B.3 N Nucleophiles

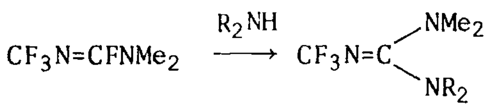
Reactions of amines with fluorinated aza-alkenes lead to a variety of products depending mainly on the nature of the amine. Perfluoro-2-azapropene (5) reacts with secondary amines to give monosubstituted or disubstituted products via elimination of HF.[49]



$$CF_3N{=}CF_2 \xrightarrow{XH} CF_3N{=}C\begin{matrix}F\\ X\end{matrix} \quad (70\text{-}72\%)$$

(5)

(X = NEt_2, NMe_2, piperidino, morpholino)



$$CF_3N{=}CFNMe_2 \xrightarrow{R_2NH} CF_3N{=}C(NMe_2)(NR_2) \quad (49\text{-}51\%)$$

(R = Me, Et)

Reactions with primary amines are more interesting since there are now two hydrogen atoms available for elimination, indeed, compound (5) reacts with aniline giving almost equimolar amounts of (61) and (62).[58] The formation of the carbodi-imide (62) is easily explained by the elimination of a second mole of HF from (61).

$$(5) \;+\; C_6H_5NH_2 \xrightarrow[-35\,^\circ C]{Et_2O} \underset{(61)}{CF_3N{=}CF\text{-}NHC_6H_5} \;+\; \underset{(62)}{CF_3\text{-}N{=}C{=}N\text{-}C_6H_5}$$

Similar reactions carried out in the presence of KF to facilitate removal of all available HF lead to the exclusive formation of carbodi-imides.

$$(5) \;+\; ArNH_2 \xrightarrow[-35\,^\circ C]{Et_2O\ 2KF} CF_3N{=}C{=}NAr \quad (70\text{-}80\%)$$

(Ar = C_6H_5, p-MeO-C_6H_4)

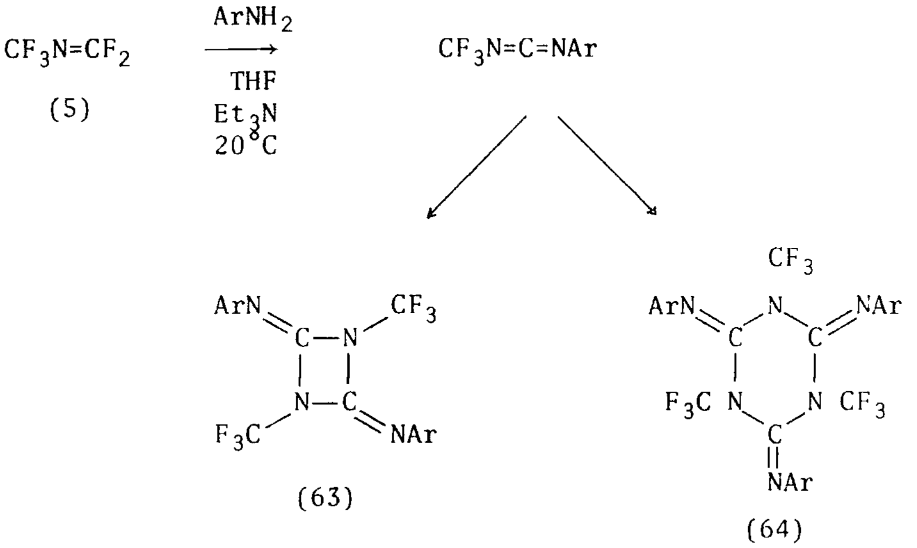
The removal of a second mole of HF is more difficult in reactions with aliphatic amines and further distillation from KF is required to obtain the carbodi-imides.[58]

$$(5) \;+\; RNH_2 \xrightarrow[-35\,^\circ C]{Et_2O\ KF} CF_3N{=}CFNHR \xrightarrow[DISTILLATION]{KF} \underset{(46\text{-}72\%)}{CF_3\text{-}N{=}C{=}N\text{-}R}$$

(R = C_2H_5, $C(CH_3)_3$, C_6H_{11}, $CH_2CH{=}CH_2$)

This is probably due to the different influence of alkyl and aryl groups on the proton elimination.

Reactions of (5) with various aniline derivatives in the presence of Et_3N lead to the formation of dimers and trimers of the carbodi-imide[59] and compound (5) reacts with 4-methoxyaniline to give the dimer (63a) (72%), whereas aniline gives the trimer (64a) (67%), and 2,6-dimethylaniline gives a mixture of (63b) and (64b).



(63)

(64)

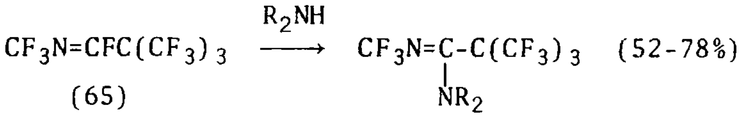
a: Ar = $4\text{-}MeOC_6H_4$

b: Ar = $2,6\text{-}Me_2C_6H_3$

a: Ar = Ph

b: Ar = $2,6\text{-}Me_2C_6H_3$

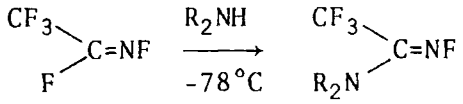
Elimination of two moles of HF to give carbodi-imides is only possible with aza-alkenes containing a terminal difluoromethylene group. Internal fluorinated aza-alkenes react with amines to give substituted products via the usual addition-elimination reaction which is shown with perfluoro-4-aza-2,2-dimethylpent-3-ene (65).



$$\underset{(65)}{CF_3N{=}CFC(CF_3)_3} \xrightarrow{R_2NH} CF_3N{=}\underset{NR_2}{\underset{|}{C}}\text{-}C(CF_3)_3 \quad (52\text{-}78\%)$$

(R = Me, Et)

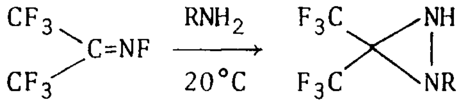
N-Fluoroimines behave differently in their reactions with amines. Compounds containing a vinylic fluorine atom react as expected, and compound (47) reacts with ammonia and dimethylamine giving products due to nucleophilic attack followed by elimination of HF[61],



(47)

(R = H, Me)

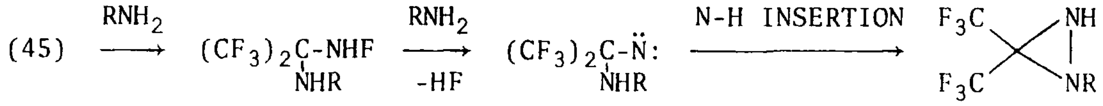
whereas compounds not containing a vinylic fluorine atom eliminate HF in a different manner leading to some interesting products. Compound (45) reacts with ammonia and primary amines to give novel diazacyclopropane derivatives.[62]



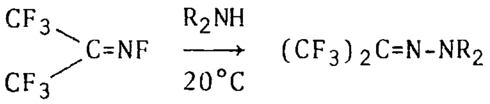
(45)

(R = H, Et, Ph)

The proposed mechanism for this involves elimination of HF to give a nitrene intermediate.



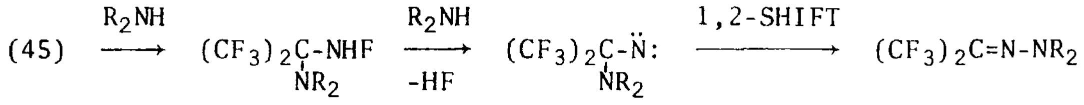
A different mode of behaviour is displayed in reactions with secondary amines, and the reactions of (45) with dimethylamine and diethylamine lead to the formation of products in which an N-N bond is formed.[61,62]



(45)

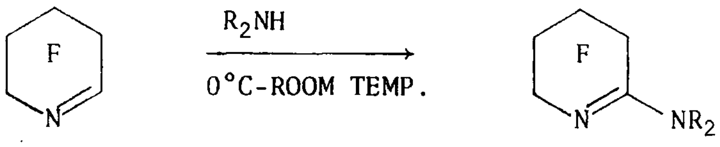
(R = Me, Et)

This is explained by a similar nitrene formation followed by a 1,2-shift.



$$(45) \xrightarrow{R_2NH} (CF_3)_2\underset{NR_2}{C}\text{-NHF} \xrightarrow[-HF]{R_2NH} (CF_3)_2\underset{NR_2}{C}\text{-}\ddot{N}: \xrightarrow{1,2\text{-SHIFT}} (CF_3)_2C{=}N\text{-}NR_2$$

The reaction of perfluoro-1-azacyclohex-1-ene (38) with secondary amines has been the subject of recent investigation[52], and mono-substituted products arising from replacement of the imino-fluorine atom are observed when a two molar proportion of amine is used.

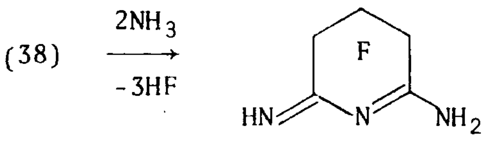


(38) (61-81%)

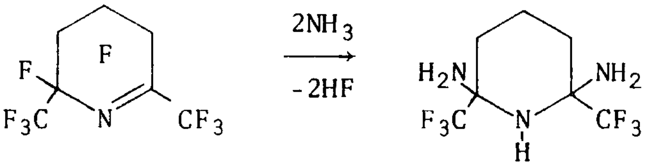
[R_2 = Me_2, Et_2, $(CH_2)_2O(CH_2)_2$, $CH_2(CH_2)_3CH_2$, XPh (X = Me, Et)]

(A two molar proportion of amine is required since HF reacts with amines to give alkyl ammonium fluorides.)

The reaction of (38) with excess ammonia leads to loss of fluorine from both C2 and C6 positions, however, this is not observed in reactions with other amines.



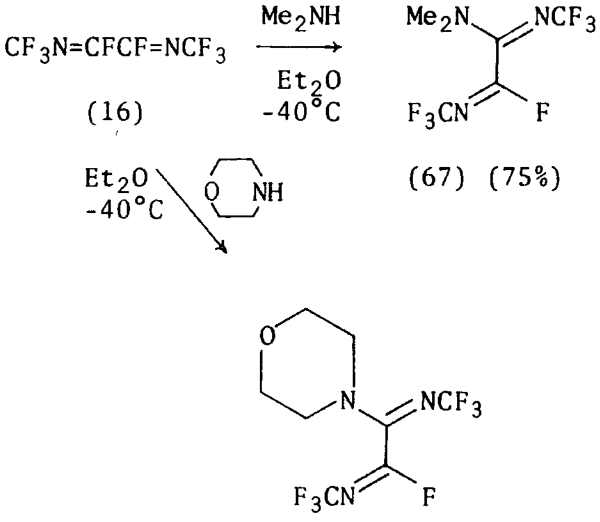
When the corresponding 2,6-disubstituted compound (51) is reacted with an excess of ammonia elimination of only two moles of HF is possible and the piperidine derivative (66) is formed.[54]



(51)

(66) (84%)

Perfluoro-2,5-diazahexa-2,4-diene (16) reacts with amines to give the expected addition-elimination products. Diethylamine and morpholine react with (16) to give the monosubstituted products (67) and (68) respectively.[55]

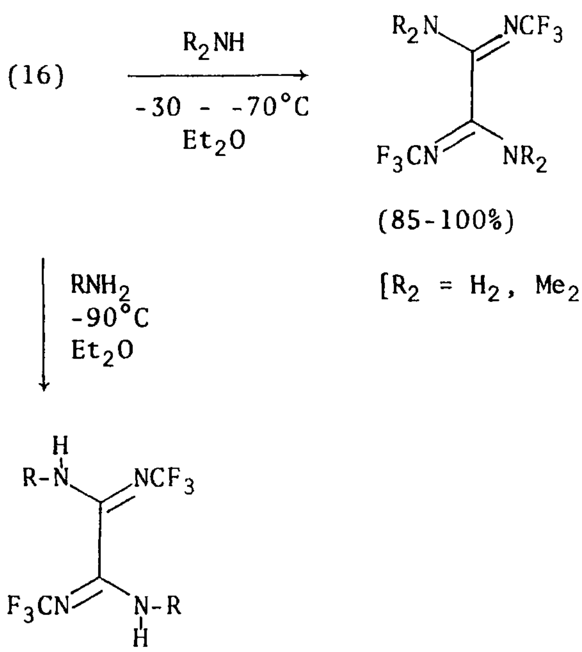


(16)

(67) (75%)

(68) (87%)

Reaction of (16) with an excess of amine leads to reaction at the second unsaturated site giving disubstituted products[56].

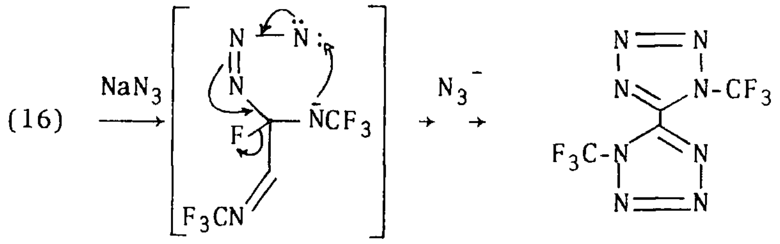


(85-100%)

[$R_2 = H_2$, Me_2, $(CH_2)_2O(CH_2)_2$]

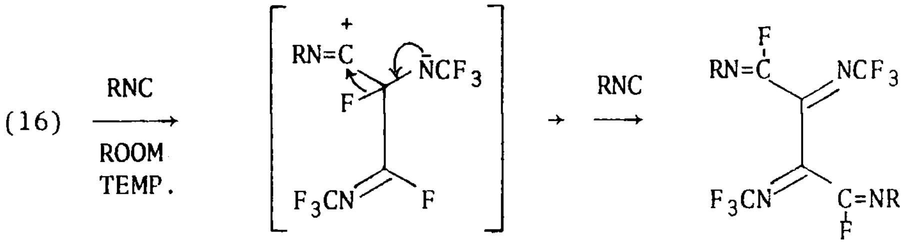
(65-85%) (R = Ph, Me)

The reactions of (16) with nucleophiles having electronic peculiarities are particularly interesting[63], and the novel bis-tetrazole (69) is formed when (16) is reacted with sodium azide.



(69)

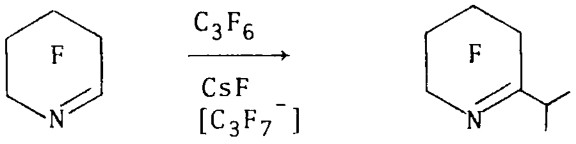
The reaction of (16) with isonitriles is even more interesting since this leads to compound (70) which is formed without elimination of HF.



[R = $(CH_3)_3C$, 2,6-MeC_6H_3, cyclohexyl] (70) (51-61%)

2B.4 C Nucleophiles

Reactions of fluorinated aza-alkenes with carbon nucleophiles have not been well exploited, however, the heptafluoroisopropyl anion, prepared from hexafluoropropene and fluoride ion, has been used to obtain the substituted azacyclohexene (71) from perfluoro-1-aza-cyclohex-1-ene (38).[64]



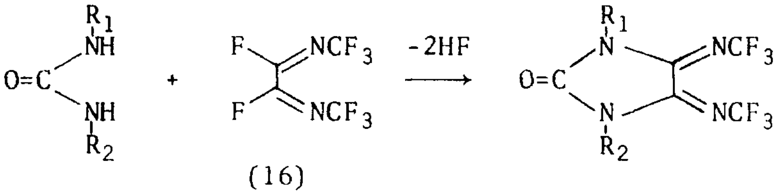
(38) (71)

In general this is not a good method since many fluorinated aza-alkenes and dienes readily oligomerize in the presence of fluoride ion (see Section 2C).

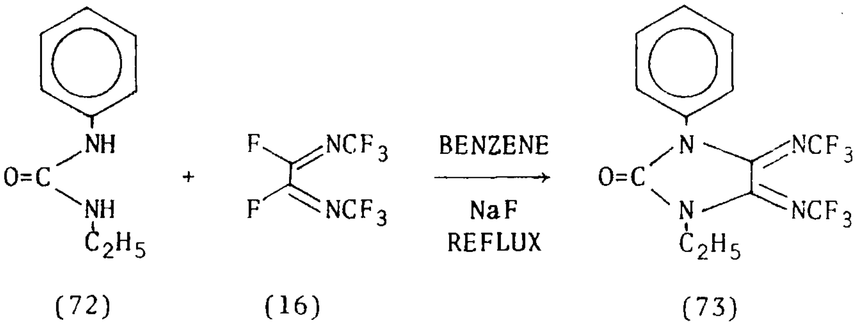
2B.5 Bifunctional nucleophiles

The reaction of perfluoro-2,5-diazahexa-2,4-diene (16) with bifunctional nucleophiles has been thoroughly investigated[65-69] since many of the products formed have been found useful as fungicides and insecticides. In view of the virtually unlimited number of bifunctional nucleophiles, an arbitrary break down into three groups is necessary. An example of each type of reaction is given.

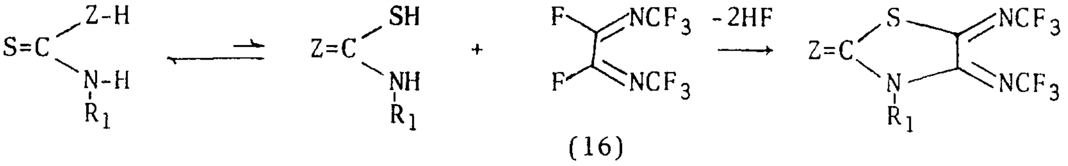
1) Urea derivatives react readily with (16) to form heterocyclic ring systems with two hetero atoms.



This is illustrated by the reaction of the urea derivative (72) with (16) to give imidazolone derivative (73).

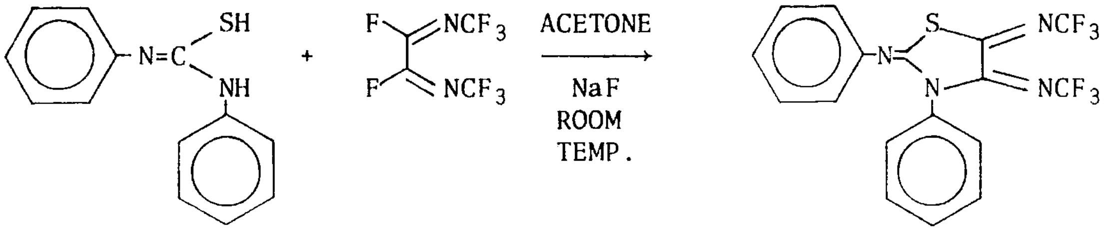


2) Thiourea derivatives react with (16) through their isomeric form to produce heterocyclic ring systems with two different hetero atoms.



(Z = O, NR)

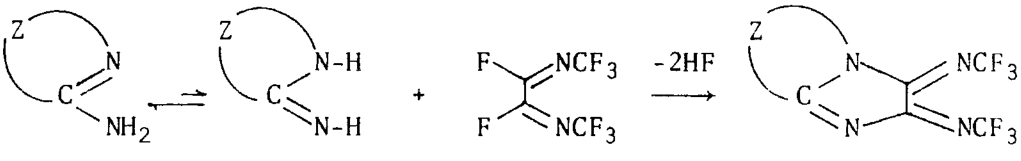
The reaction of diphenylthiourea with (16) to give (74) is a good example of this reaction.



(16)

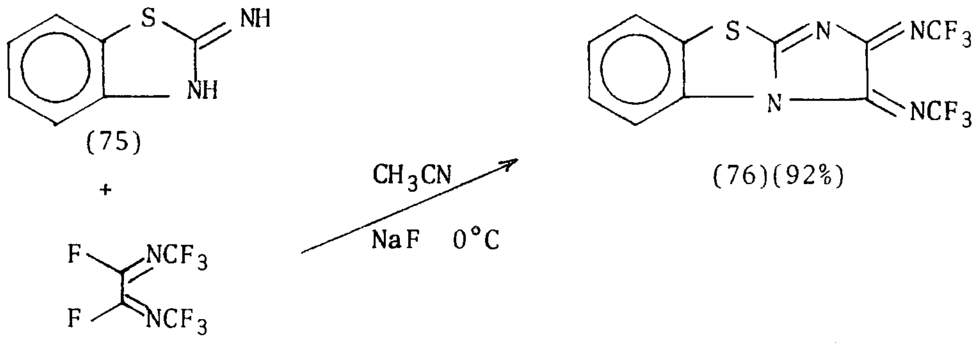
(74)(85%)

3) Amidines react with (16) through their isomeric form giving various polycyclic products.



(16)

An example of this is given by the reaction of (16) with 2-aminobenzothiazole (75) to give the tri-cyclic compound (76).

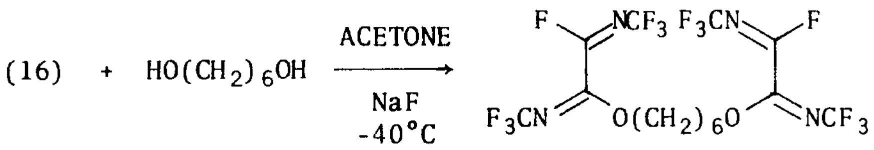


(75)

(16)

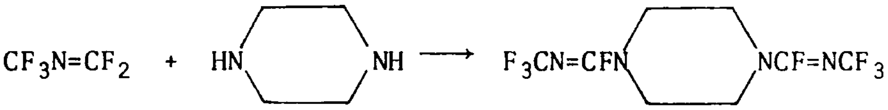
(76)(92%)

A different mode of reaction is shown when the stereochemistry of the bifunctional nucleophile is not ideal for internal cyclization[55], for example hexan-1,6-diol reacts with two moles of (16) to give compound (75a).



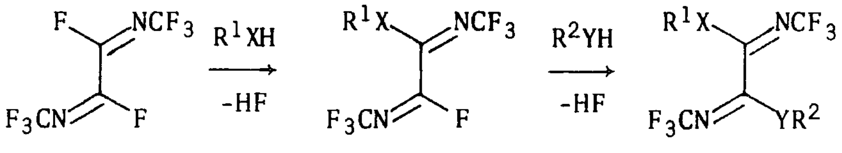
(75a) (82%)

An interesting example of this is provided by the reaction of perfluoro-2-azapropene (5) with the pyrazine derivative (76a) to give compound (77).[49]



(5) (76a) (77) (30%)

Interestingly, a variation on the reaction of perfluoro-2,5-diazahexa-2,4-diene (16) with bifunctional nucleophiles occurs when two different nucleophiles are used. This type of reaction has been well exploited[67] and can be generalized in the following sequence:

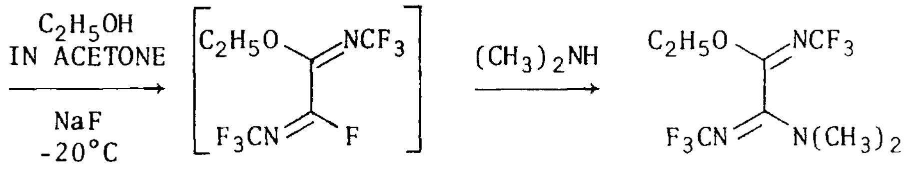


(16)

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

An example of this is provided by the 'one pot' reaction of (16) with ethanol followed by dimethylamine to give the disubstituted product (78).

(16)



(78) (68%)

2C REACTIONS WITH FLUORIDE ION

The fluorinated diazadienes (12), (32), (79), and (35) (see Section 1A.7 for synthesis) readily isomerize in the presence of alkali metal fluorides to give the corresponding internally unsaturated compounds.[39]

$$CF_2{=}NCF_2N{=}CF_2 \xrightarrow{F^-} CF_3N{=}C{=}NCF_3$$

(12)

$$CF_2{=}NCF_2CF_2N{=}CF_2 \xrightarrow{F^-} CF_3N{=}CFCF{=}CF_3$$

(32)

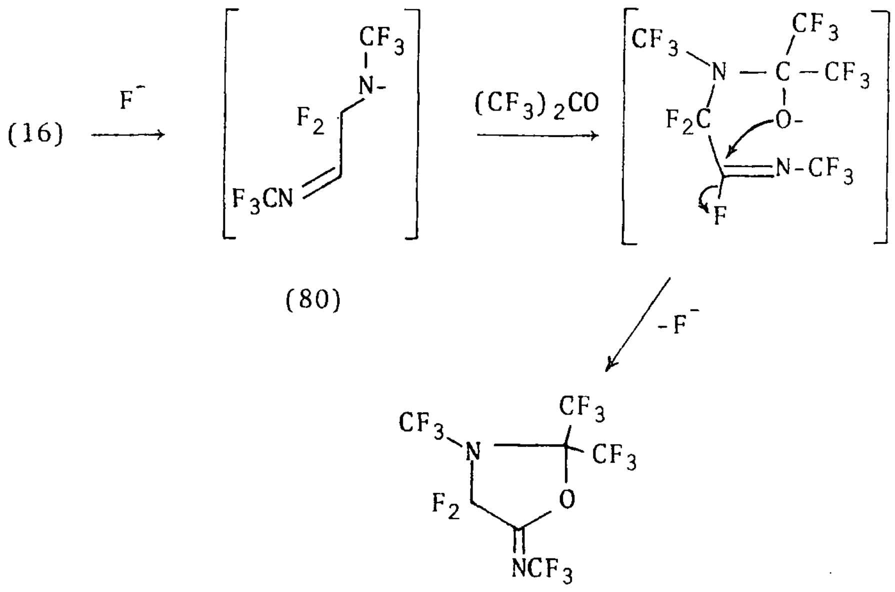
$$CF_2NCF_2CF(CF_3)N{=}CF_2 \xrightarrow{F^-} CF_3N{=}CFC(CF_3){=}NCF_3$$

(79)

$$CF_2NCF(CF_3)CF(CF_3)N{=}CF_2 \xrightarrow{F^-} CF_3N{=}C(CF_3)C(CF_3){=}NCF_3$$

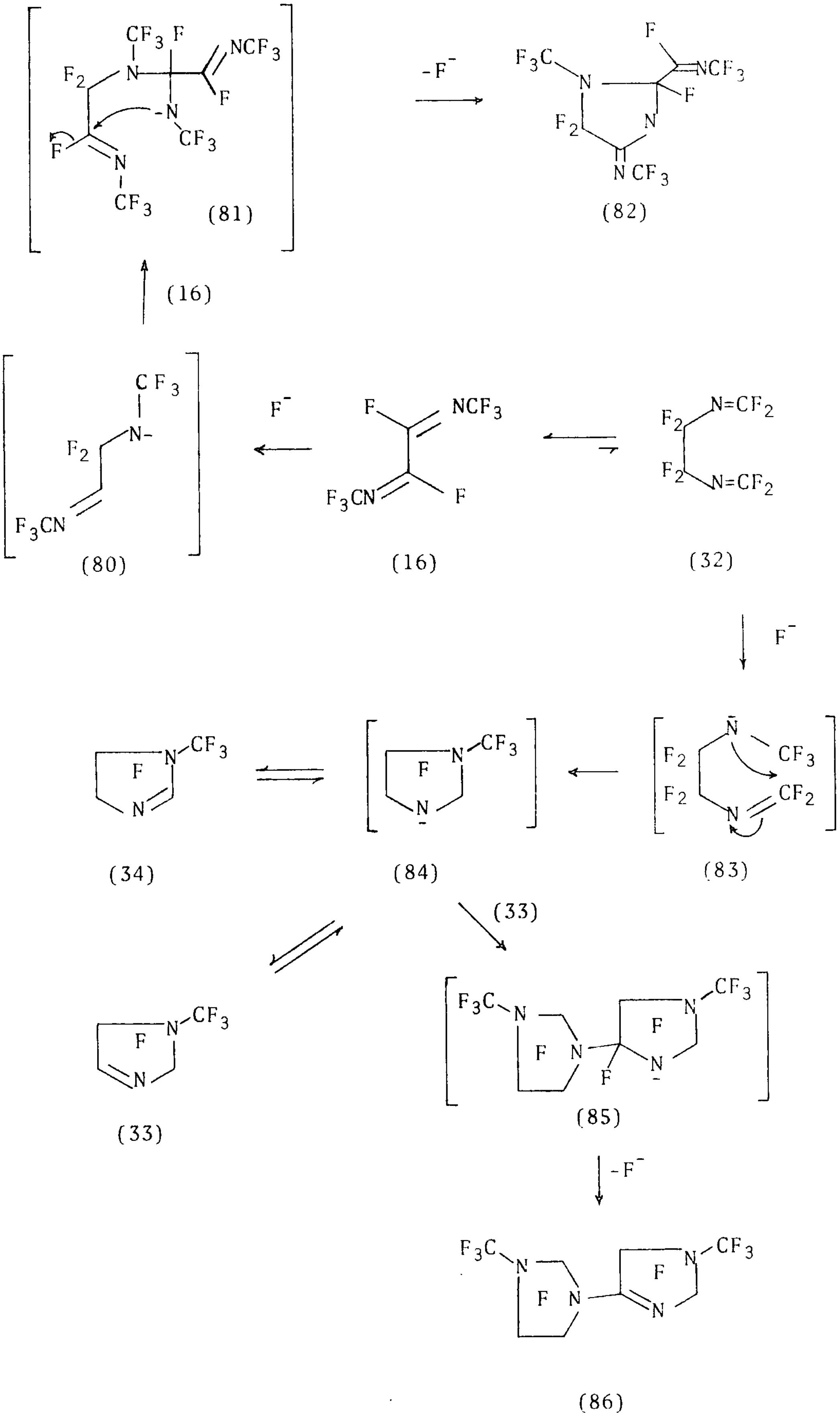
(35)

This was thought to occur via an S_N2' mechanism involving initial attack by fluoride ion leading to a nitranion intermediate. Perfluoro-2,5-diazahexa-2,4-diene (16) shows isomerization and dimerization in the presence of fluoride ion in sulpholane[21,38] according to scheme 1. Compound (16) reacts either directly with fluoride ion to give the anion (80) which further reacts with (16) followed by intramolecular cyclization to give (82), or via its isomeric form (32) which internally cyclizes to the anion (84) which on elimination of fluoride ion gives the diazacyclopentenes (33) and (34). Further reaction of (84) with (33) leads to the dimer (86), and the proportion of each product in the mixture depends upon reaction conditions. Although none of the nitranion intermediates could be observed, various trapping experiments have proved successful, indeed the extremely electrophilic hexafluoroacetone reacts with (80) followed by internal cyclization to give the novel heterocyclic compound (87).



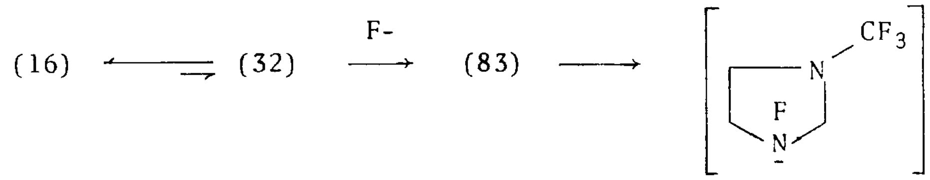
(80)

(87)

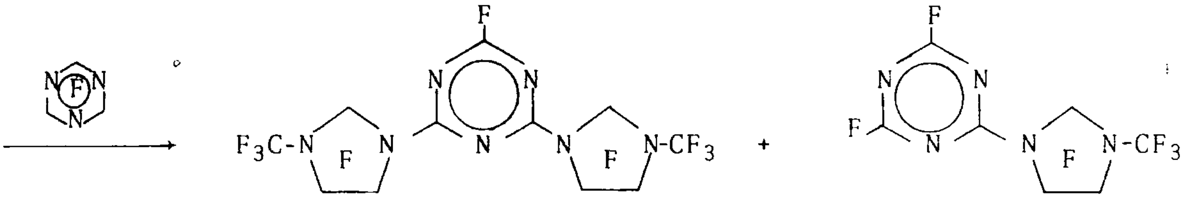


SCHEME 1

The less electrophilic cyanuric fluoride reacts with the nitranion (84) to give the triazine derivatives (88) and (89).

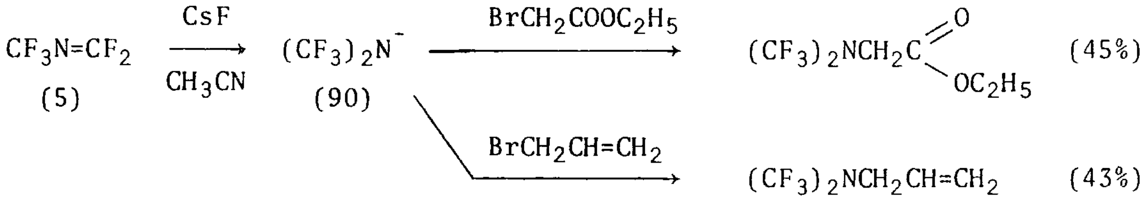


(84)

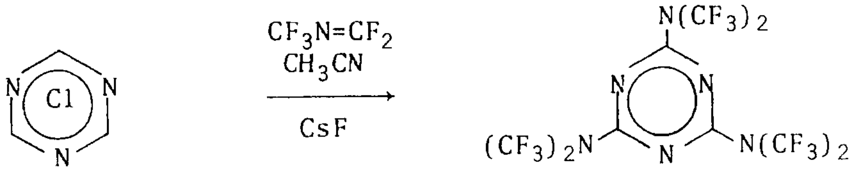


(88) (89)

There are examples of more stable nitranions which can be observed by n.m.r. spectrometry. The bistrifluoromethylaza anion, $(CF_3)_2N^-$ (90), prepared from perfluoro-2-azapropene (5) and CsF in acetonitrile, is reported to show a broad singlet at 112.2 p.p.m. ($CFCl_3$ reference).[70] The reactivity of (90) as a nucleophile has been demonstrated in various trapping experiments[70], and substitution of bromine occurs with ethyl bromoacetate and allyl bromide .

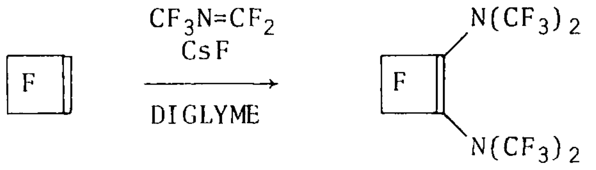


All three chlorine atoms are replaced when (90) is reacted with cyanuric chloride.[70]



(62%)

The aza-anion (90) is also very reactive towards fluoroalkenes, and reaction with perfluorocyclobutene gives the disubstituted product (91).



(91) (82%)

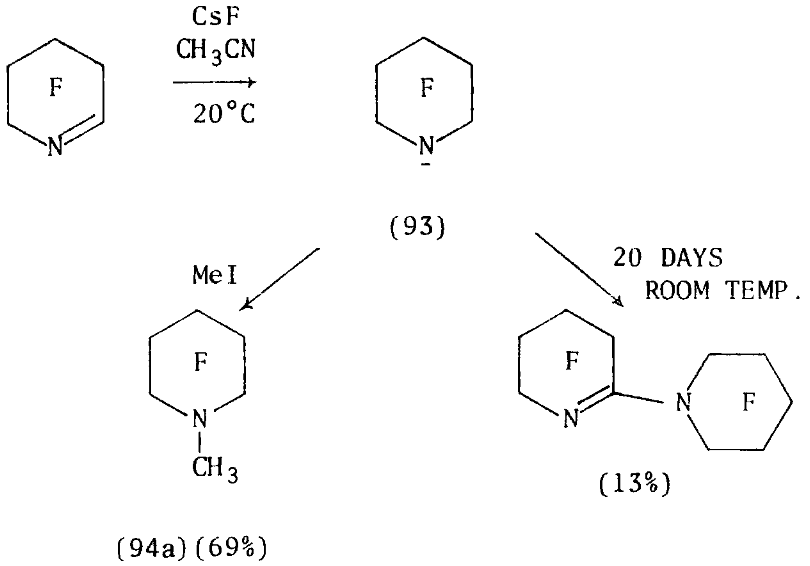
More recently (90) has been isolated as a stable salt from the reaction of bis(trifluoromethyl)amine with triethylamine.[71]

$$(CF_3)_2NH \ + \ Et_3N \longrightarrow (CF_3)_2\bar{N}\ \overset{+}{N}HEt_3$$

An interesting reaction between perfluoro-4-aza-2,2-dimethylpent-3-ene and CsF has been reported[60] to give the anion (90) together with the perfluoro tertiary butyl carbanion (92) which are trapped with $PhCH_2Br$.

$$CF_3N{=}CFC(CF_3)_2 \xrightarrow{CsF} \begin{bmatrix} (CF_3)_2N^- \\ + \ (CF_3)_3C^- \end{bmatrix} \begin{matrix} (90) \\ (92) \end{matrix} \xrightarrow{PhCH_2Br} \begin{matrix} PhCH_2N(CF_3)_2 \ (52\%) \\ + \ PhCH_2C(CF_3)_3 \ (39\%) \end{matrix}$$

The reaction of perfluoro-1-azacyclohex-1-ene (38) with caesium fluoride in acetonitrile has been reported to give the perfluoro-1-aza-cyclohexyl anion (93)[72], which can be observed by n.m.r. spectroscopy and shows broad signals at 66.1, 129.4, and 133.3 p.p.m. ($CFCl_3$ reference). The anion (93) seems to be a remarkably stable species since an appreciable amount of dimerization occurs only after a number of days which is in contrast to the more rapid dimerization of perfluoro-2-azapropene (5).[73] Trapping of (93) with methyl iodide gives the N-methyl derivative (94a).



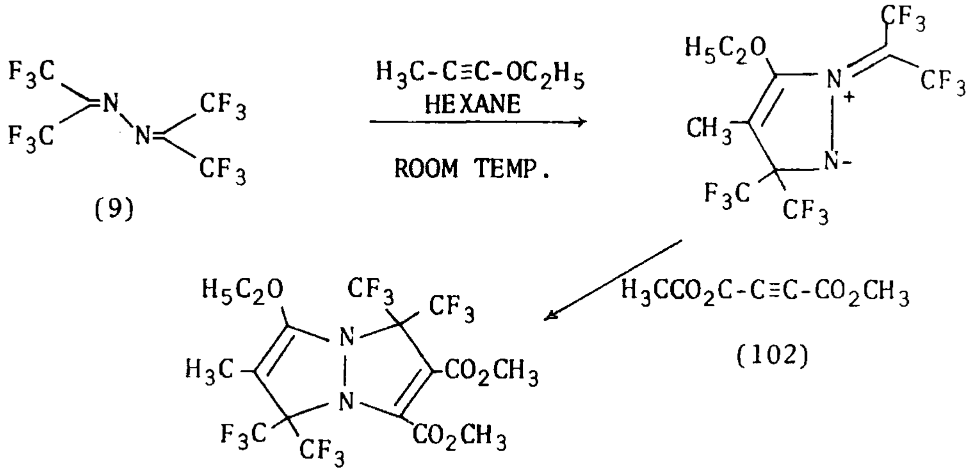
2D MISCELLANEOUS

2D.1 Cycloadditions of hexafluoroacetone-azine

Due to the structure of the molecule and the electron withdrawing effect of the trifluoromethyl groups, hexafluoroacetone azine (9) (see section 1A.5 for synthesis) would be expected to undergo cycloaddition reactions with electron rich alkenes and alkynes. Compound (9) reacts with numerous electron rich and electron deficient alkenes and alkynes[74-82], and in view of the virtually unlimited number of possibilities it is necessary to present a general reaction

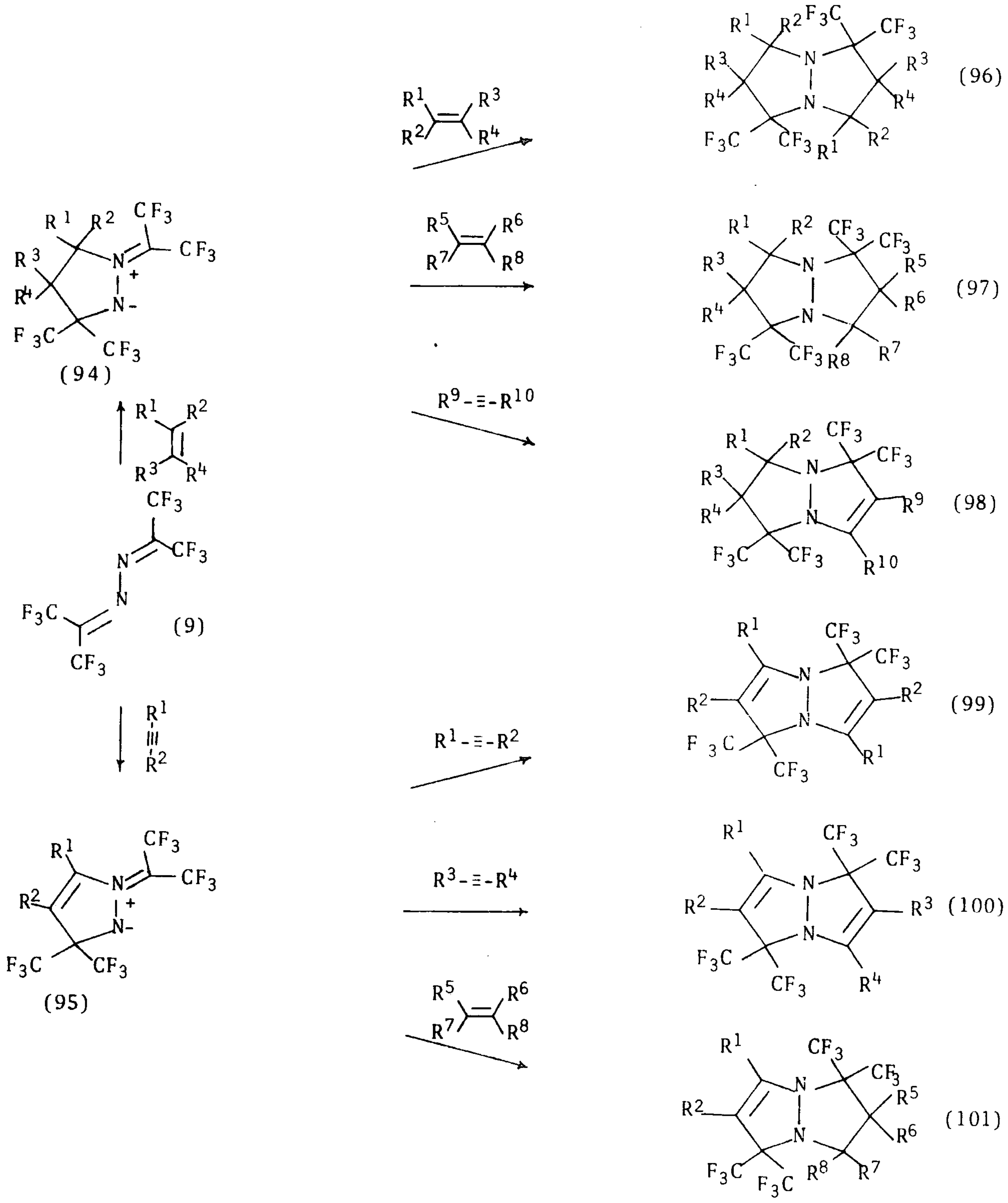
reaction scheme. This is shown in scheme 2.

Compound (9) will react with an alkene to give the 1,3-dipolar imine (94) which can be reacted with the same alkene to give (96), a different alkene to give (97), or an alkyne to give (98). Similarly (9) will react with an alkyne to give the eneimine (95) which can be reacted with the same alkyne to give (99), a different alkyne to give (100), or an alkene to give (101). The reaction is described as a "criss-cross" cycloaddition [(1,3-2,4)-addition] and has been shown to occur via two (3 + 2)-cycloadditions since the intermediate 1,3-dipolar imines (94) and (95) can in many cases be isolated.[77] The reaction is a versatile one since alkenes and alkynes containing a wide range of functional groups can be used, and this is illustrated by the reaction of (9) with 1-ethoxypropyne followed by reaction with the dimethyl ester (102) to give (103).



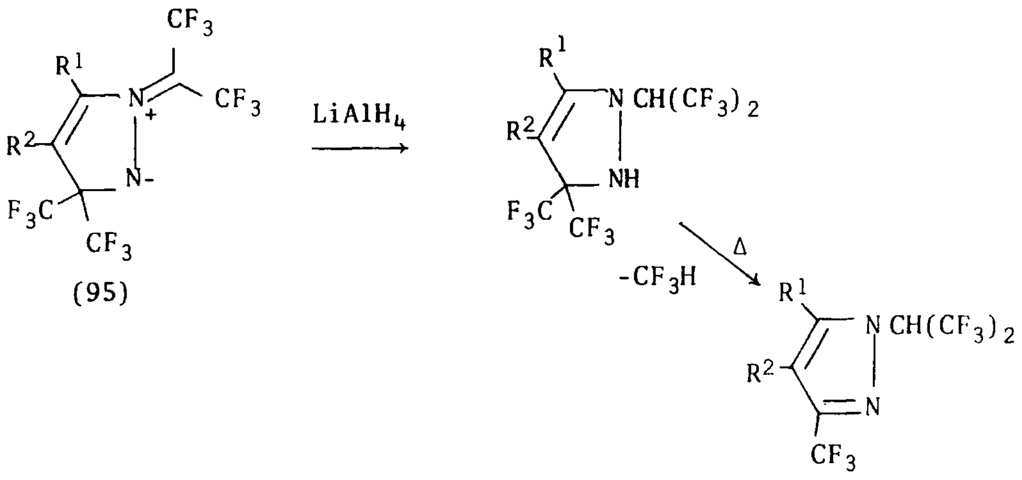
(103) (52%)

An interesting application of this reaction is in the synthesis of the aromatic pyrazole derivatives (104) from the reduction of the intermediates (95) by reaction with lithium aluminium hydride


(94)
(9)
(95)
(96)
(97)
(98)
(99)
(100)
(101)
R1 R2 R3 R4
R5 R6 R7 R8
R9-≡-R10
R1-≡-R2
R3-≡-R4
CF3
F3C
N
N-
N+

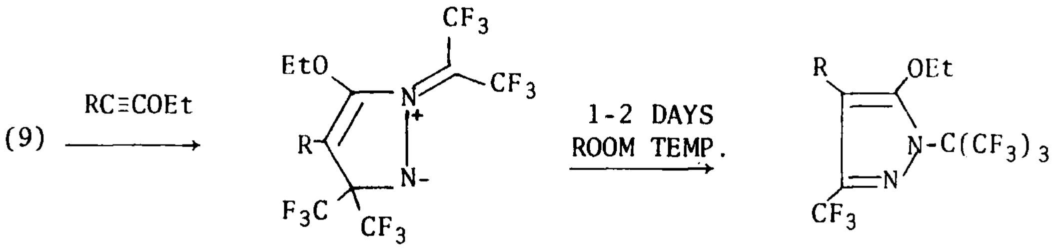
SCHEME 2

followed by pyrolysis.[83]



(95) (104)

A novel route to pyrazole derivatives has been found via the reaction of ethoxyalkynes with hexafluoroacetone azine (9) to give (105), which on standing at room temperature isomerize to give pyrazole derivatives (106).[84]



(105) (106)(52-87%)

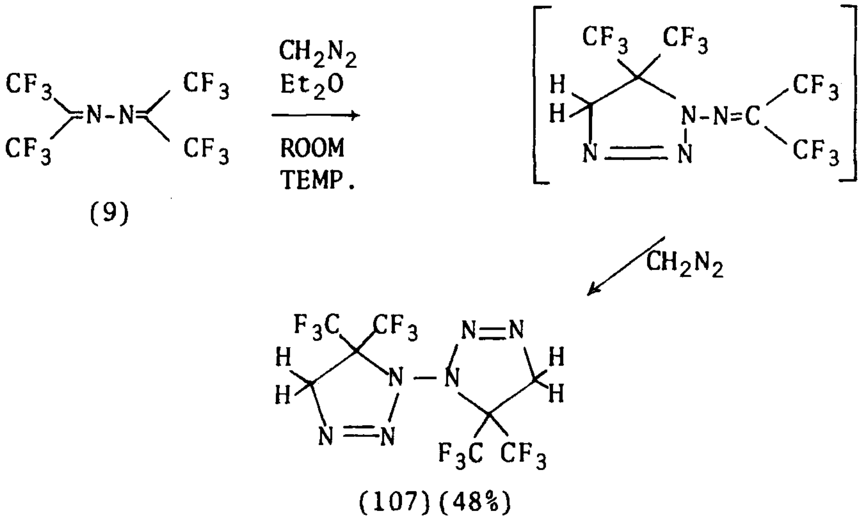
(R = H, Me)

An interesting feature of the reaction is that formation of (106) from (105) must involve a 1,4-migration of a trifluoromethyl group.

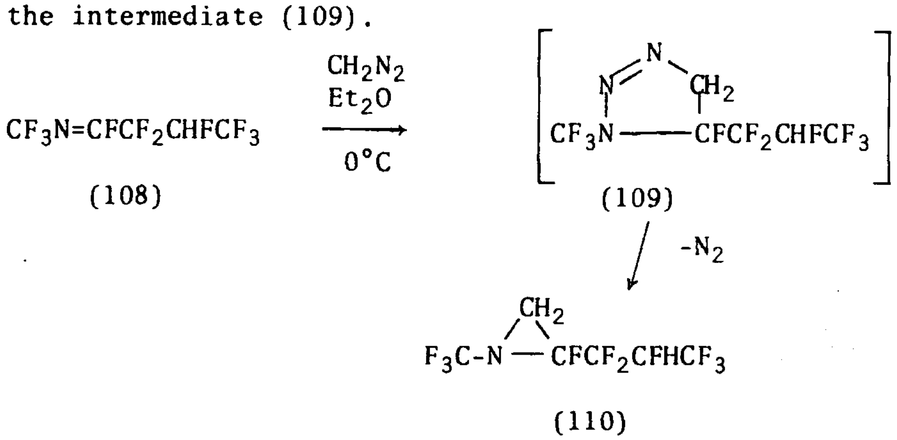
2D.2 Reactions with diazomethane

The dipolar addition of diazoalkanes to suitably activated alkenes has been well established in the hydrocarbon field for many years.[84a] Dipolar addition to fluoroalkenes has received little attention and there are few examples of addition to fluorinated aza-alkenes.

Hexafluoroacetone azine (9) reacts with CH_2N_2 to give the N,N'-bicyclic triazoline (107), however, the intermediate 1:1 adduct is not isolated.[85]



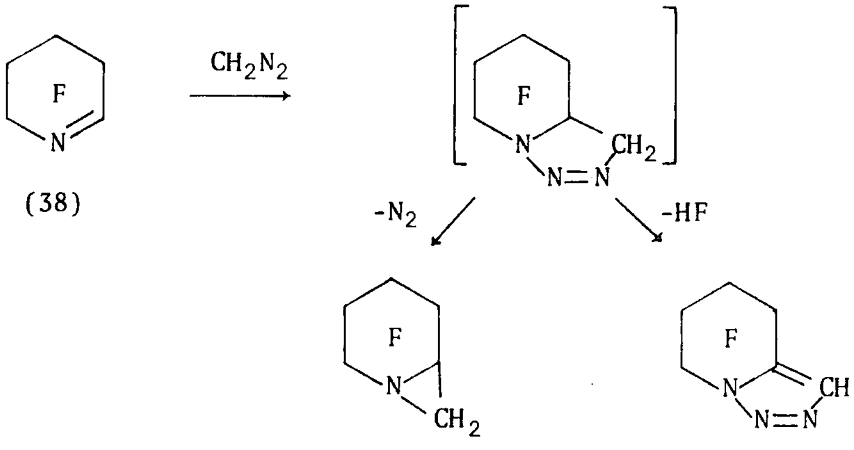
Reactions with other fluorinated aza alkenes have proved more complex.[86] The 2-azahex-2-ene derivative (108) reacts with CH_2N_2 to give the azacyclopropane derivative (110) via an elimination of nitrogen from the intermediate (109).



However, reaction of the octafluoro-2-azahexa-2,4-diene (111) with diazomethane is more complex; an azacyclopropane derivative (116) is the major product and this is accompanied by the corresponding derivative (115) but now containing a CH_2F group (ratio 71:29). This apparent CH_2 insertion into a C-F bond has been explained by a 1,2-fluorine shift with elimination of nitrogen from the intermediate (112) to give (113), which further reacts with CH_2N_2 giving (115) via elimination of nitrogen from (114) (see Scheme 3).

Perfluoro-2-azahex-2-ene (117) reacts with diazomethane giving three compounds, (118), (119), and (120), showing that all three types of reaction are taking place (see Scheme 4).

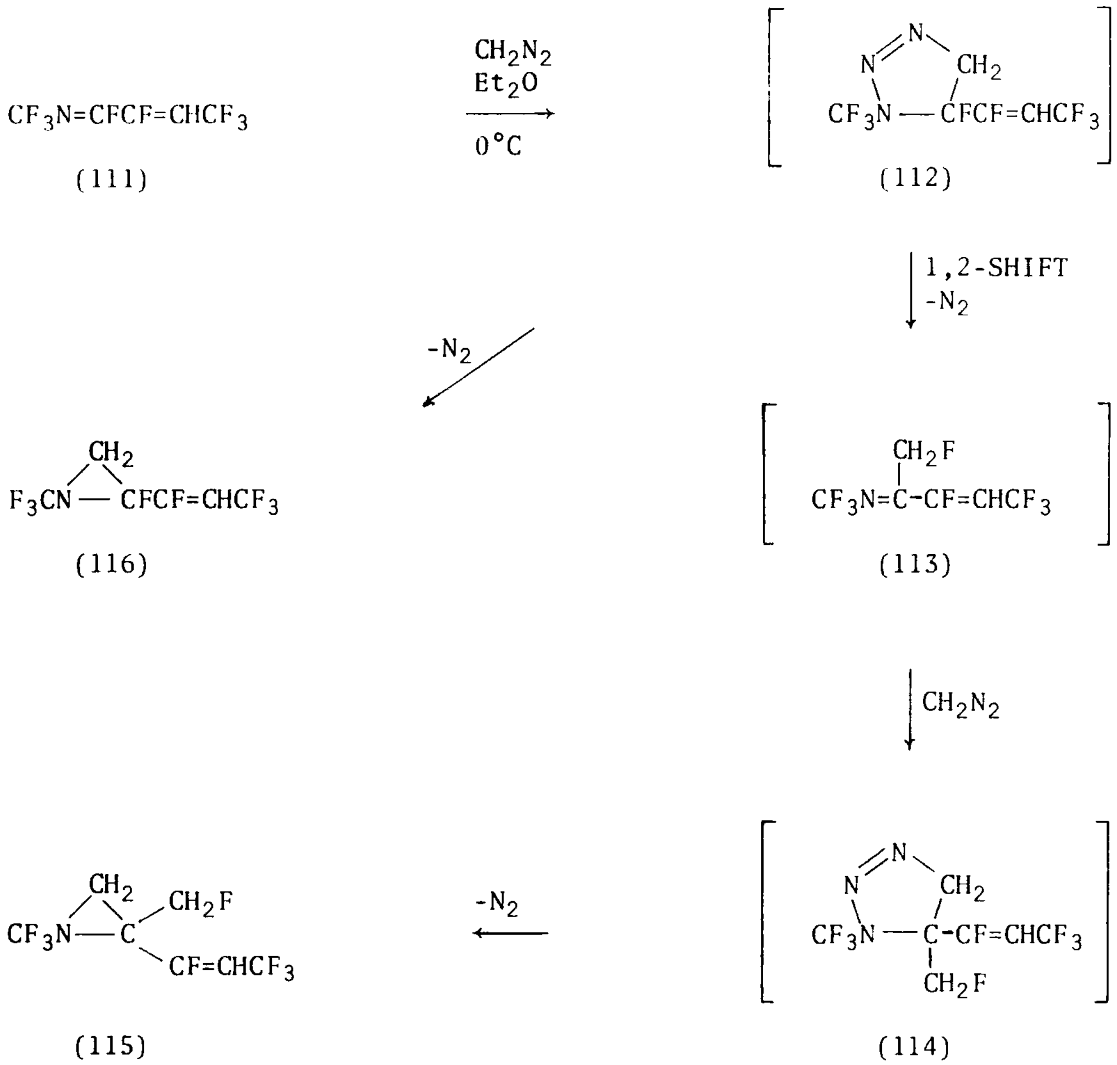
Interestingly, the reaction of perfluoro-1-azacyclohex-1-ene (38) with diazomethane gives products due to elimination of N_2 (121) and HF (122) (ratio 1:10) only and no product formed by a CH_2 insertion is observed.



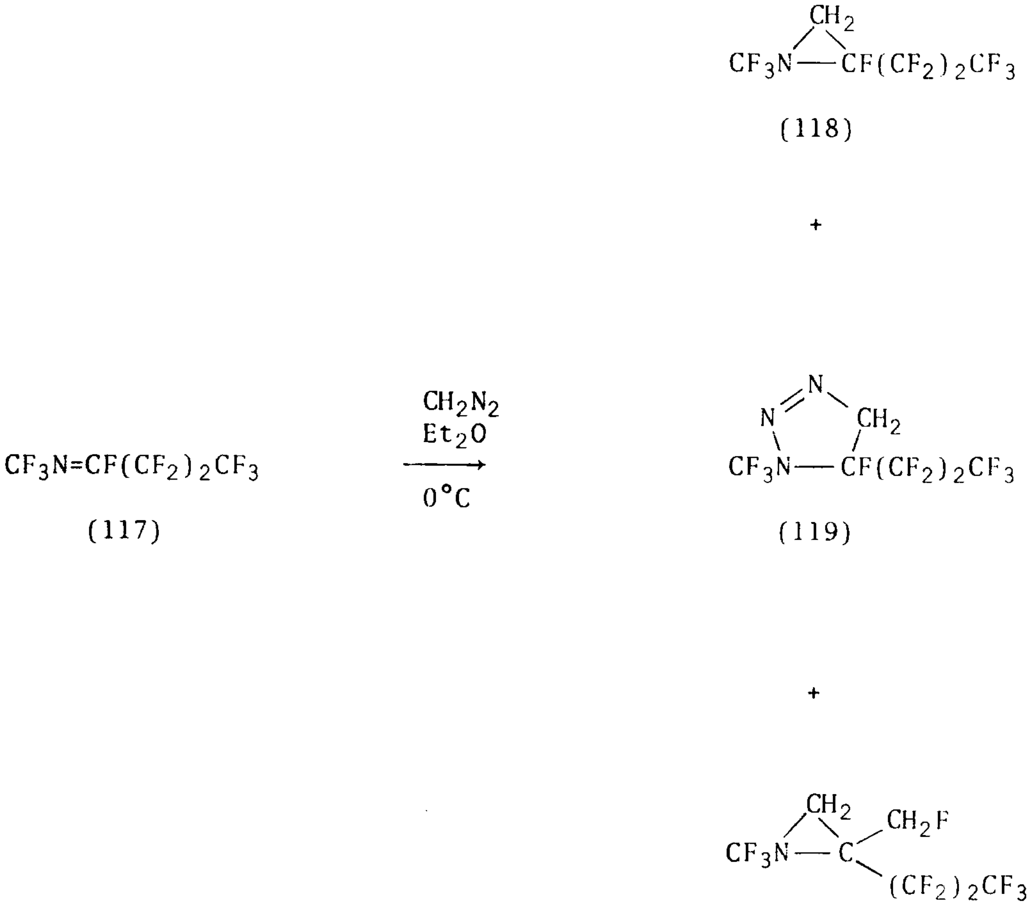
(38)

(121)

(122)


CF3N=CFCF=CHCF3
(111)
CH2N2
Et2O
0°C
N
N
CH2
CF3N
CFCF=CHCF3
(112)
1,2-SHIFT
-N2
CH2F
CF3N=C-CF=CHCF3
(113)
CH2N2
N
N
CH2
CF3N
C-CF=CHCF3
CH2F
(114)
-N2
CH2
CH2F
CF3N
C
CF=CHCF3
(115)
-N2
CH2
F3CN
CFCF=CHCF3
(116)

SCHEME 3



(117) (118) (119) (120)

[(118):(119):(120) = 6:2:1]

SCHEME 4

2D.3 Organometallics

Reactions of fluorinated aza-alkenes with organometallic compounds have not been well investigated. The synthetic use of perfluoroisopropenylimino lithium (123), prepared from n-butyllithium and perfluoroisopropylimine (8)[87], has however been demonstrated.

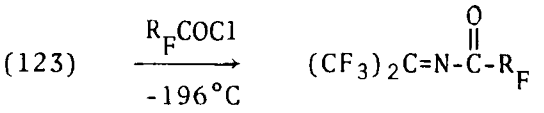
$$\underset{}{\mathrm{nBuLi}} + \underset{(8)}{(CF_3)_2C{=}NH} \longrightarrow \mathrm{nBuH} + \underset{(123)}{(CF_3)_2C{=}NLi}$$

The majority of the chemistry of (123) has been concerned with exchange reactions with various inorganic halides[88,89], however some interesting compounds containing N=S have been prepared.[90]

$$(123) \xrightarrow{CF_3SF_3} (CF_3)_2CFN{=}SFCF_3$$

$$(123) \xrightarrow{(CF_3)_2SF_2} (CF_3)_2CFN{=}S(CF_3)_2 + (CF_3)_2C{=}NC(CF_3)_2N{=}S(CF_3)_2$$

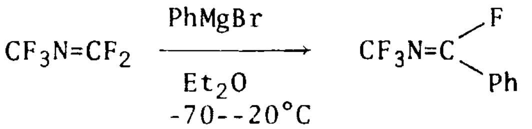
The reaction of (123) with fluorinated acid chlorides has provided a route to fluorinated aza-alkenes containing a carbonyl group.[91]



$$(123) \xrightarrow[-196^\circ C]{R_FCOCl} (CF_3)_2C{=}N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R_F$$

$(R_F = CF_3,\ C_2F_5)$

More recently the reaction of fluorinated aza-alkenes with Grignard reagents has been described.[92] Perfluoro-2-azapropene (5) reacts with phenyl magnesium bromide to give the substituted aza-alkene (124).



$$CF_3N{=}CF_2 \xrightarrow[\text{Et}_2\text{O},\ -70\text{--}-20^\circ\text{C}]{\text{PhMgBr}} CF_3N{=}C(F)Ph$$

(5) (124)(50%)

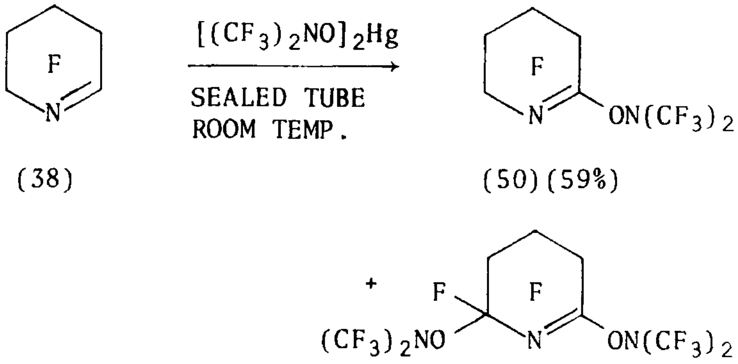
Under similar conditions the reaction of (5) with propyl and butyl magnesium bromides gave only the hydrolysis product of the intermediate substituted aza-alkene.

$$(5) \xrightarrow{\text{RMgBr}} [CF_3N{=}CFR] \xrightarrow{H_2O} CF_3NHCOR$$

(78-80%)

(R = Pr, Bu)

An interesting example of the use of a mercury derivative is in the reaction of perfluoro-1-azacyclohex-1-ene (38) with mercury(II)bis-trifluoromethylnitroxide to give the mono- and di-substituted products (50) and (125).

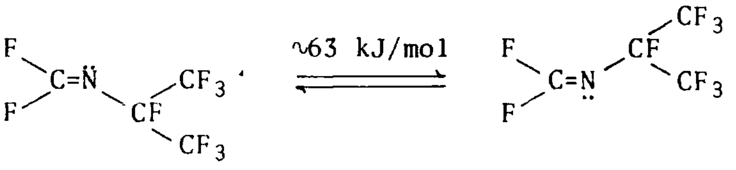


(38) (50)(59%)

(125)(6%)

2D.4 Stereochemistry

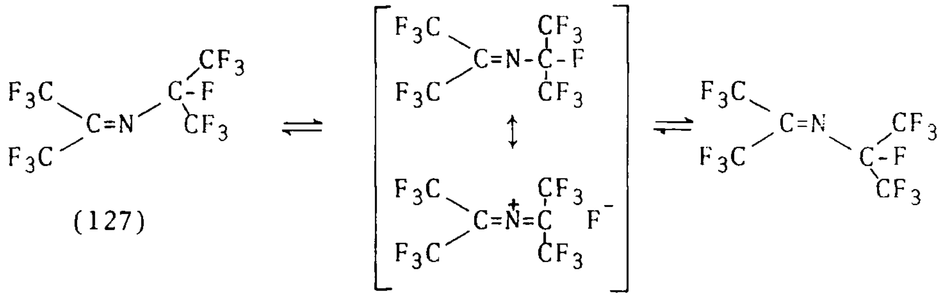
Stereochemistry about the C=N bond in fluorinated aza-alkenes has been the subject of much discussion.[93-96] Studies by n.m.r. spectroscopy have shown that compounds of the type CF_2=NR_F (R_F = branched perfluoroalkyl) show separate fluorine signals at low temperatures which, on warming, merge into a single broad signal due to rapid isomerization about the C=N bond. Perfluoro-2-aza-3-methylbut-1-ene (126) shows an AB type pattern in its ^{19}F n.m.r. spectrum at -42°C which collapses into a single broad peak on warming[94] consistent with rapid isomerization.



(126)

(The barrier to inversion estimated from the variation of peak widths with temperature.)

In contrast to these branched systems, compounds of the type F_2C=NR_F (R_F = n-perfluoroalkyl) do not display rapid isomerization at room temperature.[96] The heptafluoroisopropyl imine of hexafluoroacetone (127) has been of particular interest because of the low barrier to inversion (54 ± 12 kJ mol^{-1}).[93] It has been suggested that steric effects alone cannot account for this and a linear transition state stabilized by negative hyperconjugation has been proposed.[97]



(127)

This has led to a study of various N-fluoroalkyl and N-alkyl imines of the type $(CF_3)_2C{=}NR$ [$R = CF(CF_3)_2$, $CH(CF_3)_2$, $CCl(CF_3)_2$, CH_3, $CH(CH_3)_2$, $C(CH_3)_3$], the calculated barriers to inversion of which have been found to be more consistent with steric interactions than negative hyperconjugation.[98]

DISCUSSION

CHAPTER 3

SYNTHESIS OF PERFLUORO-AZA- AND -DIAZA-CYCLOHEXADIENE DERIVATIVES BY COBALT TRIFLUORIDE FLUORINATION

3A INTRODUCTION

In this chapter the fluorination of a series of perfluoroalkyl-pyridine, -pyrimidine, -pyrazine, and -pyridazine derivatives is described. For comparative purposes the fluorination of various perfluorotoluene derivatives is also described.

Precursors were prepared from alkylation reactions between the appropriate parent aromatic compound and hexafluoropropene in the presence of fluoride ion using an atmospheric pressure static gas system developed by workers at this[99,100] and other[101] laboratories.

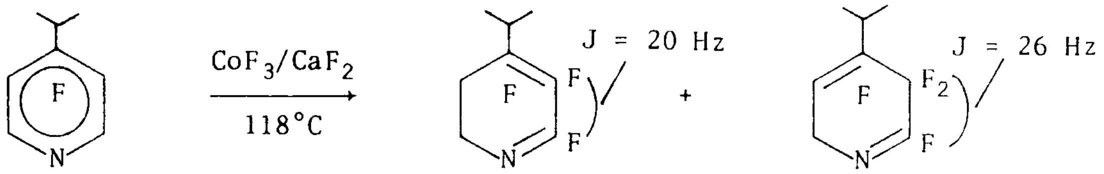
Fluorinations were carried out using cobalt trifluoride containing calcium fluoride in order to moderate the reactivity and it is possible that calcium tetrafluorocobaltate is formed in the system, since formation of similar salts and their use as fluorinating agents has been demonstrated.[102,103]

The proposed mechanism for fluorinations of this type involves a series of radical-cation intermediates (see Section 1B.4) and is well described in the literature.[46] In general the nature of the products described in this chapter are consistent with this type of mechanism.

3B PYRIDINE DERIVATIVES

3B.1 Fluorination of perfluoro-4-isopropylpyridine

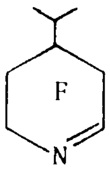
Fluorination of perfluoro-4-isopropylpyridine (128) with a 1:1 mixture of CoF_3 and CaF_2 at 118°C gave a complex mixture of products with two major components identified as perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129) and perfluoro-1-aza-4-isopropylcyclohexa-1,4-diene (130) from their n.m.r. spectra.



(128) (129) (60%) (130) (18%)

Compound (129) showed a signal at 52.5 p.p.m. (Int. 1), characteristic of an imino (-CF=N-) fluorine[46], which was strongly coupled (J = 20 Hz) with a signal at 107.2 p.p.m. (Int. 1), characteristic of a vinylic fluorine. The structure of (130) was deduced on the basis of a triplet (J = 26 Hz) at 57.8 p.p.m. (Int. 1) (-CF=N-) due to coupling with an adjacent $-CF_2-$ group. The i.r. spectra of (129) and (130) showed both compounds to contain two unsaturated sites. Remaining n.m.r. and other spectroscopic data agreed with the assigned structures.

A third component was obtained from a mixture of the minor components collected from a series of similar reactions and was identified as perfluoro-1-aza-4-isopropylcyclohex-1-ene (131).

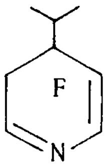


(131)

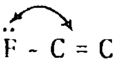
The n.m.r. spectrum of (131) showed a signal at 55.9 p.p.m. (Int. 1) and three AB type signals characteristic of CF_2 groups with non-equivalent fluorine atoms. The presence of signals at 181.3 (Int. 1) and 184.3 (Int. 1) p.p.m.. characteristic of 'tertiary' fluorine atoms confirmed this structure.

The formation of dienes as the major products is in contrast to the fluorination of pentafluoropyridine[46], where a 1,3-diene is formed as a minor product and only under conditions of heavy CoF_3 depletion. This is understandable since the replacement of fluorine by a perfluoroalkyl group would be expected to influence stability in such a way as to make the intermediate dienes more easily isolated.

It is interesting that a diene corresponding to the structure (132) was not observed although there is no reason to suggest any inherent difference in stability between the skeletal structures of (129) and (132), therefore the absence of (132) must be attributed to the effect of fluorine. It is well established[104,105] that an isomer having fluorine attached to an olefinic centre is less stable than isomers of the same compound, having only perfluoroalkyl groups attached to the centre, due to electron pair repulsions involving non-bonding electron pairs on fluorine and π-electrons.



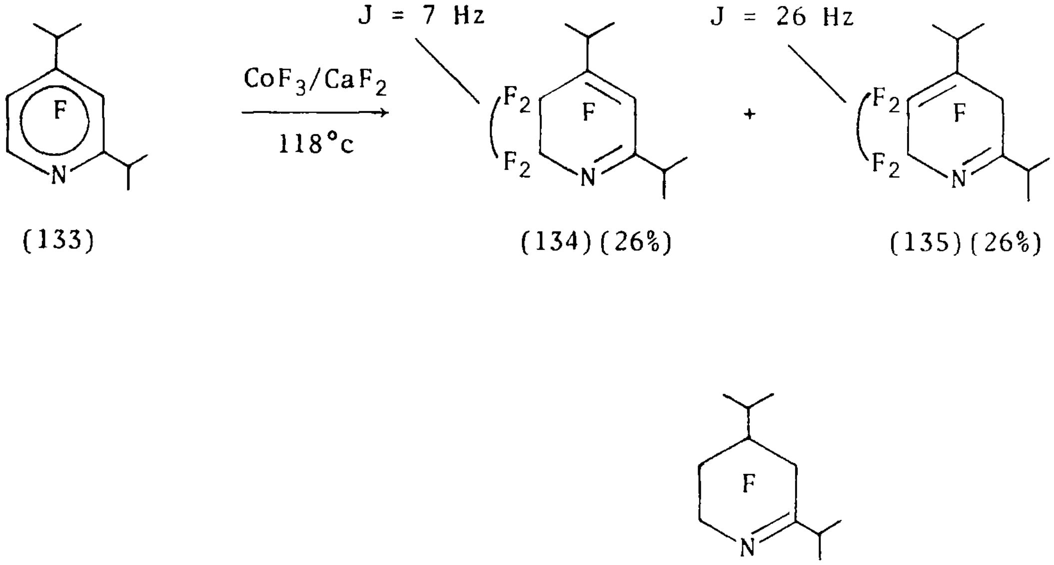
(132)



Isomer (132) has three vinylic fluorine atoms and, therefore, would be expected to be of higher energy than (129) and (130) which contain only two such fluorine atoms.

3B.2 Fluorination of perfluoro-2,4-di-isopropylpyridine

Fluorination of perfluoro-2,4-di-isopropylpyridine (133) at 118°C gave an inseparable mixture of perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,3-diene (134) and perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,4-diene (135) but, surprisingly, these were accompanied by perfluoro-1-aza-2,4-di-isopropylcyclohex-1-ene (136) as the major product. Fluorination of (133) at 170°C gave an excellent yield of (136) only.



(133)

(134)(26%)

(135)(26%)

(136)(45%)

$$(133) \xrightarrow[170^\circ C]{CoF_3/CaF_2} (136)\ (89\%)$$

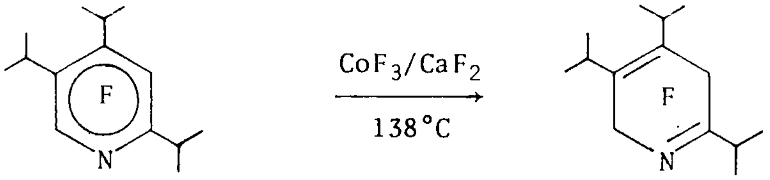
The structure of (136) followed from its n.m.r. spectrum; signals at 72.3 (Int. 6) and (76.1) (Int. 6) p.p.m. showed the presence of two perfluoroisopropyl groups and signals at 179.6 (Int. 1), 183.2 (Int. 1), and 191.0 (Int. 1) p.p.m. were characteristic of 'tertiary' fluorine atoms. The remaining three AB type signals between 90.8 and 130.2 p.p.m. confirmed the structure. Signals in the n.m.r. spectrum of (134) and (135) were more difficult to assign. Four multiplets, each of intensity 6, in the region 75 to 78 p.p.m., together with four 'tertiary' fluorine signals between 184 and 192 p.p.m. indicated the presence of four perfluoroisopropyl groups. The absence of signals in the low field region of the spectrum indicated that there were no imino fluorine atoms present. A doublet (J = 26 Hz) at 91.1 p.p.m. (Int. 2) was assigned to the 1,4-diene (135) since the fine structure indicated coupling to an adjacent vinylic fluorine atom. Similarly a triplet (J = 7 Hz) at 110.1 p.p.m. (Int. 2) was assigned to the 1,3-diene (134) since the fine structure indicated coupling to an adjacent CF_2 group. Signals at 101.2 (Int. 1) and 103.0 (Int. 1) p.p.m. were indicative of two vinylic fluorine atoms but could not be unambiguously assigned due to lack of fine structure. The infrared spectrum of the mixture showed absorptions at 1642, 1688, 1718, and 1740 cm^{-1} showing the presence of two compounds each containing two unsaturated sites.

The absence of an isomer of type (132) is further evidence of the stability gained by having a perfluoroisopropyl group, rather than a fluorine atom, attached to an olefinic centre.

The 1:1 ratio of (134) and (135) produced in this reaction is in contrast with the ratio of dienes produced from the fluorination of perfluoro-4-isopropylpyridine (128) where the 1,3-diene is the major isomer and it is not immediately clear why this should occur. It is possible that the reaction may simply involve kinetic, rather than thermodynamic, control.

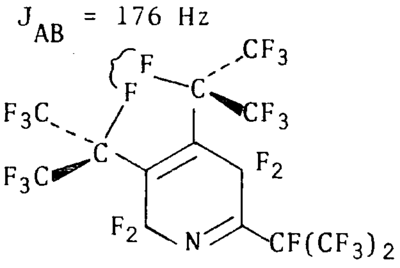
3B.3 Fluorination of perfluoro-2,4,5-tri-isopropylpyridine

Reaction of perfluoro-2,4,5-tri-isopropylpyridine (137) over CoF_3/CaF_2 at 138°C gave one major product identified as perfluoro-1-aza-2,4,5-tri-isopropylcyclohexa-1,4-diene (138). This is understandable on the basis of stability influences already discussed i.e. compound (138) contains no vinylic fluorine atoms and would therefore be expected to be the most stable isomer.

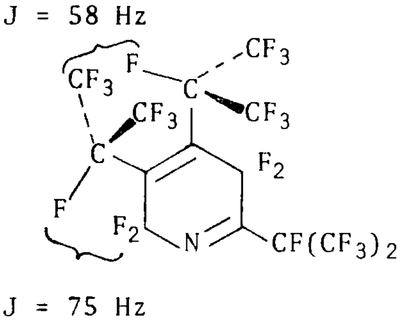


(137) (138)(62%)

The n.m.r. spectrum of (138) was complex and indicated a 2:1 ratio of rotational isomers at room temperature.



(138a)



(138b)

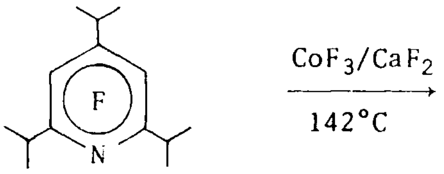
2:1 at room temperature

The structures were assigned on the basis of coupling constants of the 'tertiary' fluorine atoms attached to the two adjacent perfluoroisopropyl groups. A high field AB type signal centred at 159.6 and 164.7 p.p.m. (J_{AB} = 176 Hz) indicated the presence of two strongly interacting 'tertiary' fluorine atoms and was assigned to structure (138a), whereas a triplet at 161.8 p.p.m. (coupling with CF_2) and a septet at 170.9 p.p.m. (coupling with $C\underline{F}(CF_3)_2$) were assigned to the 'tertiary' fluorine atoms of structure (138b). A broad signal at 67.9 p.p.m. (Int. 2) indicated the presence of a CF_2 group adjacent to nitrogen and the remaining CF_2 group was observed as two separate signals at 98.9 and 99.9 p.p.m. (total intensity 2).

The presence of rotational isomers of (138) is not surprising as steric interactions between perfluoroisopropyl groups attached to positions C4 and C5 must be considerable, indeed, the parent compound (137) has also been shown to display rotational isomerism.[106]

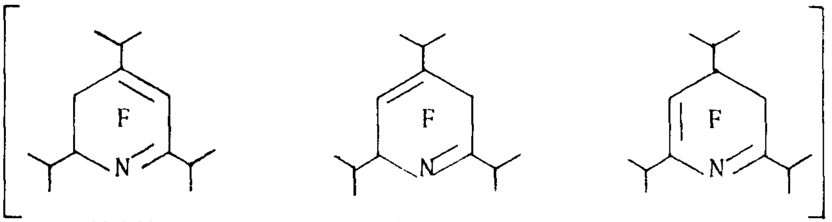
3B.4 Fluorination of perfluoro-2,4,6-tri-isopropylpyridine

Fluorination of perfluoro-2,4,6-tri-isopropylpyridine (139) at 145°C gave a complex mixture of products from which no single compound could be isolated, however, a study by g.l.c.-m.s. indicated that the mixture contained a mono-ene derivative (M^+ = 695) and several diene derivatives (M^+ = 657).



(139)

Complex mixture containing mono-ene and various dienes



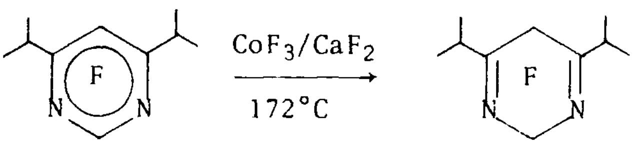
(140) (141) (142)

It is likely that all three dienes (140), (141), and (142) were present since each contains one vinylic fluorine atom and therefore, on the basis of stability influences already discussed, have very little difference in stability.

3C PYRIMIDINE DERIVATIVES

3C.1 Fluorination of perfluoro-4,6-di-isopropylpyrimidine

Fluorination of perfluoro-4,6-di-isopropylpyrimidine (143) at 172°C gave an excellent yield of perfluoro-1,3-diaza-4,6-di-isopropylcyclohexa-3,6-diene (144).

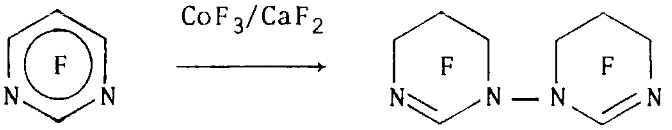


(143) (144)(83%)

The structure of (144) followed simply from its n.m.r. spectrum. A sharp singlet at 73.2 p.p.m. (Int. 2) was assigned to the CF_2 group adjacent to both nitrogen atoms. The remaining CF_2 group appeared as a triplet (J = 30 Hz) indicating coupling to two equivalent fluorine atoms and, interestingly, the same coupling constant was shown by a signal at 193.5 p.p.m. (Int. 2) attributable to two equivalent 'tertiary' fluorine atoms.

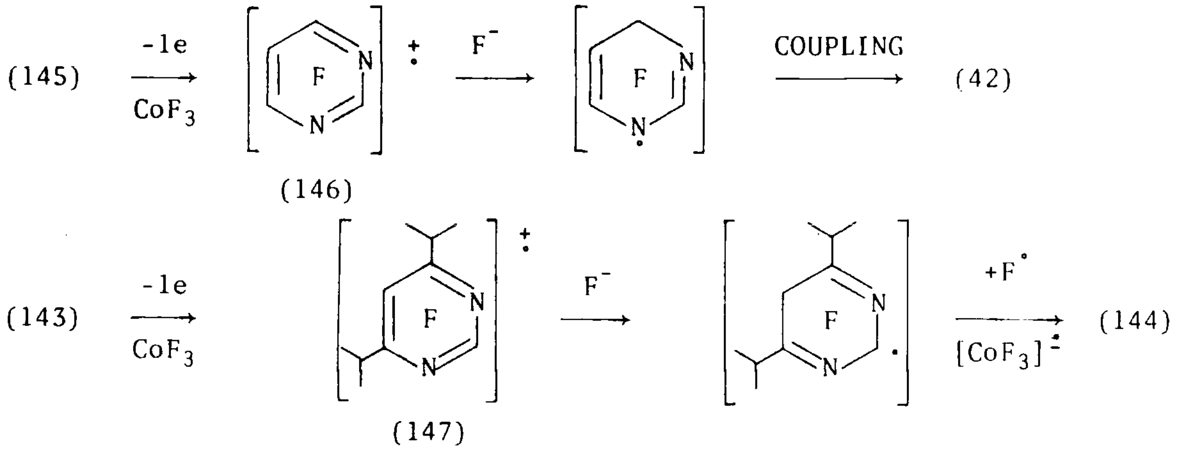
The exclusive formation of (144) provides further evidence for the preference of a perfluoroalkyl group, rather than a fluorine atom, attached to an olefinic centre.

The reaction is interesting because of the striking difference in the nature of the product formed i.e. (144), in comparison with the dimer (42), which is obtained from the fluorination of the parent compound tetrafluoropyrimidine (145).[46]



(145) (42)

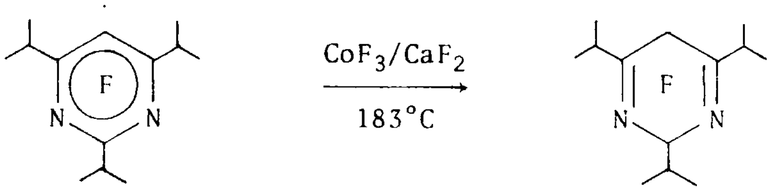
The difference can be accounted for by a consideration of the nature of the radical cation intermediates (146) and (147).



Transfer of fluoride ion to the radical cation intermediate (146) can occur at a position para to nitrogen leading to coupling through nitrogen-stabilized delocalized radicals. However, transfer of fluoride ion to the radical cation (147) at a position para to nitrogen is obviously inhibited by perfluoroisopropyl groups, therefore transfer meta to nitrogen is more likely.

3C.2 Fluorination of perfluoro-2,4,6-tri-isopropylpyrimidine

Fluorination of perfluoro-2,4,6-tri-isopropylpyrimidine (148) at 183°C gave only one major product identified as perfluoro-1,3-diaza-2,4,6-tri-isopropylcyclohexa-3,6-diene (149).

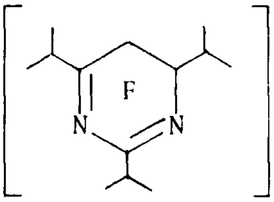


(148)

(149)(63%)

The structure of (149) was obvious from its n.m.r. spectrum which showed remarkable similarity to that of the di-isopropyl derivative (144). Signals at 76.5 (Int. 12), 110.6 (Int. 2), and 191.7 (Int. 2) p.p.m. indicated the presence of two equivalent perfluoroisopropyl groups and a CF_2 group and signals at 73.7 (Int. 6) and 184.7 (Int. 1) p.p.m. confirmed a third perfluoroisopropyl group. The remaining 'tertiary' fluorine atom was observed at 113.0 p.p.m. which at first sight seems at very low field, however, this can be attributed to the presence of two adjacent nitrogen atoms.

The exclusive formation of (149) is interesting since a 1,3-diene of the type (150) should now be possible as neither (149) nor (150) have fluorine atoms attached to an unsaturated site.


not observed

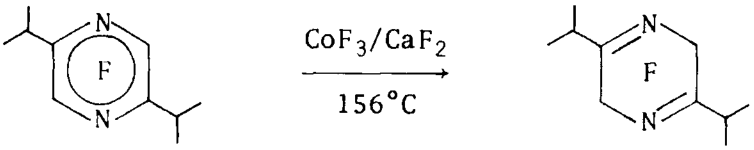
(150)

This striking selectivity, therefore, reveals another factor which almost certainly governs the choice between these two isomers. Isomer (150) would have severe eclipsing interactions which are obviously minimized in isomer (149).

3D PYRAZINE DERIVATIVES

3D.1 Fluorination of perfluoro-2,5-di-isopropylpyrazine

Reaction of perfluoro-2,5-di-isopropylpyrazine (151) over CoF_3/CaF_2 at 156°C gave perfluoro-1,4-diaza-2,5-di-isopropylcyclohexa-1,4-diene (152) exclusively.

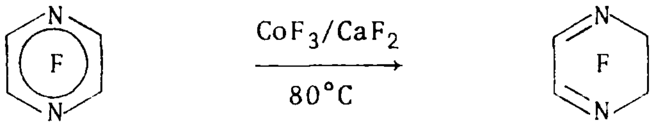


(151) (152)(87%)

The n.m.r. spectrum of (152) was simple showing only three signals. A triplet (J = 29 Hz) of septets (J = 6 Hz) at 191.7 p.p.m. indicated tertiary fluorine atoms coupled to both CF_2 and $(CF_3)_2$ groups and a doublet (J = 29 Hz) at 88.5 p.p.m. was assigned to ring CF_2 groups.

A remarkable feature of the spectrum is the complex fine structure exhibited by the 'tertiary' fluorine atoms indicating that the perfluoroisopropyl groups must be in a fixed position with the CF_3 groups orientated towards nitrogen. This phenomenon is not observed in the majority of the dienes already discussed where 'tertiary' fluorine atoms usually appear as high field broad signals, however, it is not unknown since the perfluorotri-isopropylpyridine derivatives (137) and (139) also exhibit this behaviour.[106]

The formation of (152) is in contrast with the product formed from the fluorination of tetrafluoropyrazine itself since this is reported to yield a 1,3-diene (41).[46]



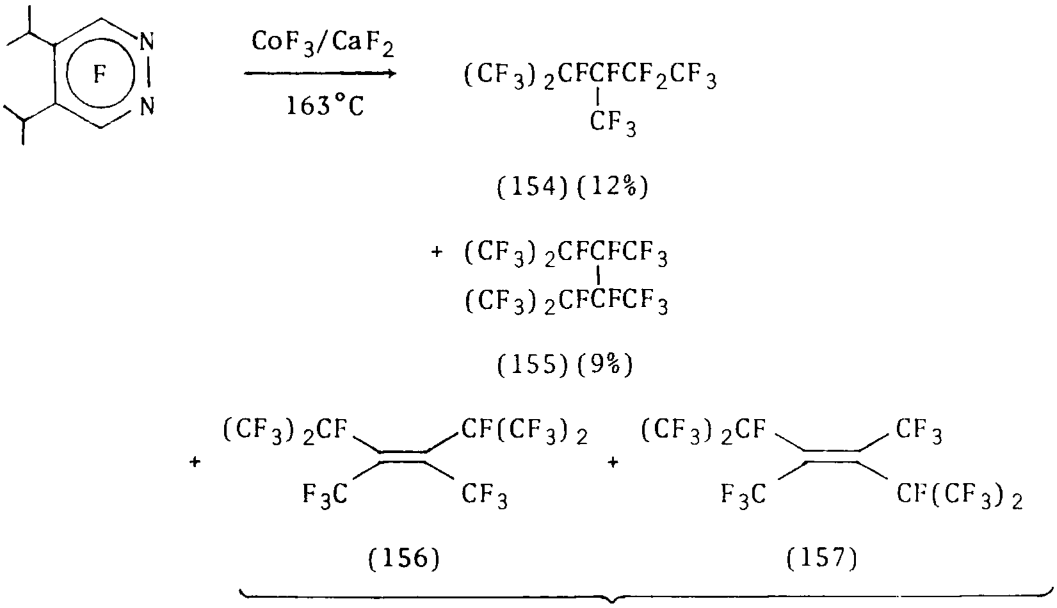
(41)(29%)

The effect of substitutents in the C2 and C5 positions thus provides further evidence that products which minimize the number of fluorines directly bonded to an unsaturated site are preferred.

3E PYRIDAZINE DERIVATIVES

3E.1 Fluorination of perfluoro-4,5-di-isopropylpyridazine

Fluorination of perfluoro-4,5-di-isopropylpyridazine (153) showed a marked contrast to the reactions of related systems. Four products were obtained, the formation of which involved loss of nitrogen from (153). These were identified as perfluoro-2,3-dimethylpentane (154), perfluoro-2,3,4,5-tetramethylhexane (155), and a mixture of *cis*(156)- and *trans*-perfluoro-2,3,4,5-tetramethylhex-3-ene (157).



(154)(12%)

(155)(9%)

(156) (157)

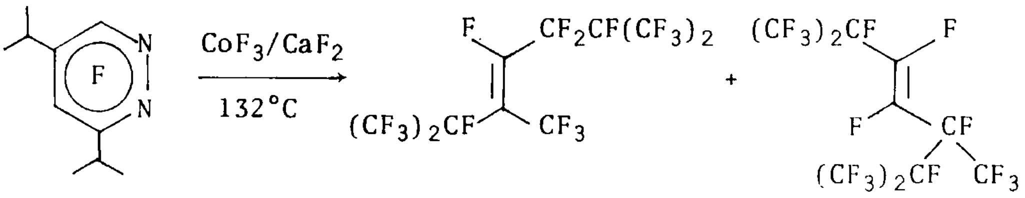
Inseparable 1:2.5 mixture (53%)

The n.m.r. spectrum of (154) showed a broad signal at 71.9 p.p.m. (Int. 9) indicating three trifluoromethyl groups in similar chemical environments. Signals at 82.4 (Int. 3), and 115.1 (Int. 2) p.p.m., characteristic of a perfluoroethyl group, and signals at 177.9 (Int. 1) and 181.8 (Int.1) p.p.m., characteristic of two 'tertiary' fluorine atoms, were in agreement with the proposed structure. The mass spectrum (M-F = 369) and the absence of absorptions above 1300 cm^{-1} in the infrared spectrum showed (154) to be a perfluoroheptane derivative.

The n.m.r. spectrum of (155) showed four signals at 69.0 (Int. 6), 72.1 (Int. 12), 166.6 (Int 2), and 170.3 (Int. 2) p.p.m. in agreement with the proposed structure, which was confirmed as a perfluorodecane derivative from its infrared and mass (M-F = 519) spectra.

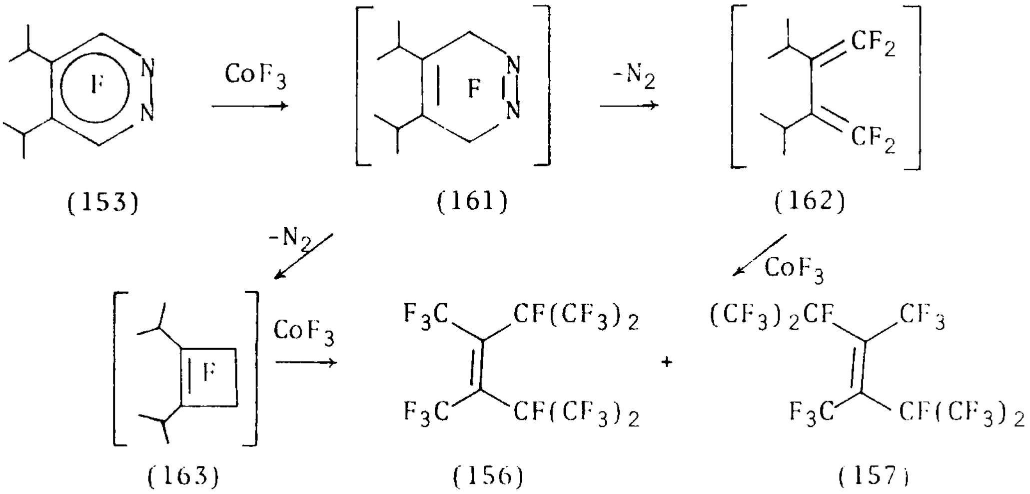
Isomers (156) and (157) were inseparable and were characterized as a mixture. A quartet at 161.4 p.p.m. (J = 50 Hz) was assigned to the 'tertiary' fluorine atoms of the *trans* isomer (157) due to the magnitude of the coupling with adjacent CF_3 groups, whereas the 'tertiary' fluorine atoms of the *cis* isomer (156) were observed as a broad signal at 159.3 p.p.m. Signals at 56.6 and 57.6 p.p.m. (total intensity 6) were assigned to the *cis*(156) and *trans*(157) isomers respectively on intensity grounds. Assignments are supported by a consideration of stability since the *trans* isomer (157) should be the preferred form on stereochemical grounds. Absorptions in the infrared spectrum at 1725 and 1740 cm^{-1} indicated that two different unsaturated compounds were present.

The reaction obviously provides a novel synthetic route to some unusual fluorinated alkenes; indeed the fluorination of perfluoro-3,5-di-isopropylpyridazine (158) leads to the alkenes (159) and (160) via a similar loss of nitrogen.[107]



(158) (159)(25%) (160)(25%)

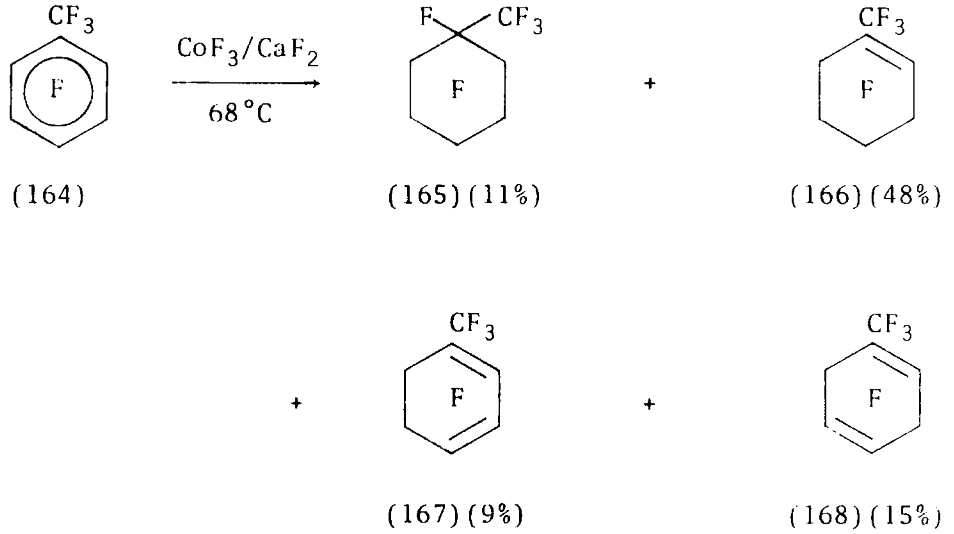
It is reasonable to assume the formation of the diene (161) as an intermediate during the fluorination of (153), since this would be the preferred isomer on the grounds that it contains no vinylic fluorine atoms. Thermal elimination of nitrogen from 1,2-diazines is well known in hydrocarbon chemistry[109,110] and can lead to either ring opened or cyclic products; therefore loss of nitrogen from (161) could give the cyclobutene derivative (163), or the diene (162), either of which would give compounds (156) and (157) on further fluorination.



3F TOLUENE DERIVATIVES

3F.1 Fluorination of perfluorotoluene

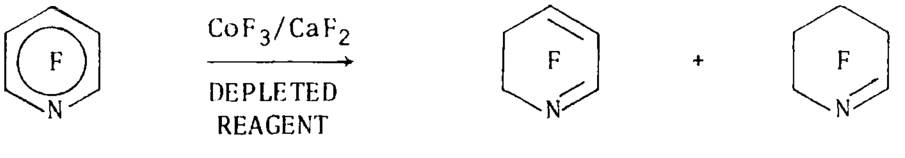
Fluorination of perfluorotoluene (164) at 68°C gave a mixture containing one major and three minor components. The major component was identified as perfluoro-1-methylcyclohexene (166) and the minor components as perfluoromethylcyclohexane (165), perfluoro-1-methylcyclohexa-1,3-diene (167), and perfluoro-1-methylcyclohexa-1,4-diene (168).



The structure of (165) was obvious from its n.m.r. spectrum; signals observed at 71.8 (Int. 3) and 190.8 (Int. 1) were characteristic of a trifluoromethyl group and a 'tertiary' fluorine atom respectively. The remainder of the ring CF_2 groups showed three distinct AB type signals (4:4:2) between 122 and 145 p.p.m. Similarly the structure of (166) followed from its n.m.r. spectrum which showed a doublet (J = 21 Hz) of triplets (J = 8 Hz) (Int. 3) at 61.2 p.p.m., indicating a CF_3 group coupled to both CF_2 and CF, confirming the position of the unsaturated site. This is further confirmed by the fact that the chemical shift occurs at $\sim$10 p.p.m. to lower field than that of the corresponding CF_3 group in the saturated compound (165). A single absorption at 1710 cm^{-1} in the infrared spectrum showed (166) to contain only one unsaturated site.

Identification of the dienes (167) and (168) was more difficult. Both gave six distinct signals in the ratio 3:2:2:1:1:1 in their n.m.r. spectra but fine structure was complicated and assignments could not be made on this basis. The fact that both showed two absorptions between 1680 and 1780 cm^{-1} in their infrared spectra and both showed parent ions at M^+ = 274 in their mass spectra was enough to eliminate all structures other than (167) and (168). Structures were finally assigned on the basis of ultraviolet spectra in which the 1,3-diene (167) showed a strong absorption ($\log\varepsilon$ = 3.68) at 255 nm, indicating the presence of conjugation, whereas the 1,4-diene (168) showed a much weaker absorption ($\log\varepsilon$ = 2.08) at 264 nm.

Interestingly the effect of a trifluoromethyl group attached to the ring seems to be very similar to the effect of a hetero-atom in the ring since the reaction is somewhat parallel to that of pentafluoropyridine, which gives a mono-ene (38) as the major product, together with a minor amount of the 1,3-diene (40) under mild conditions.[46]

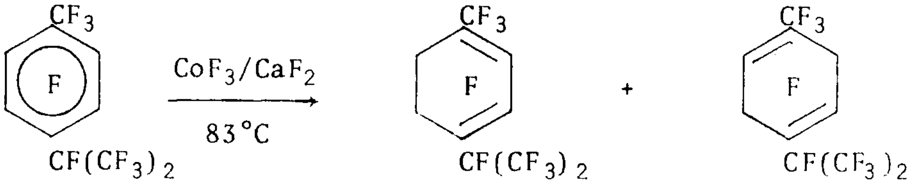


(40)(2%) (38)(50%)

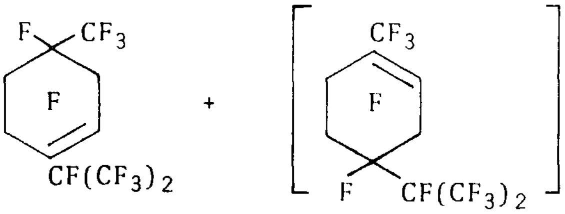
The formation of a fully saturated derivative (165) from the fluorination of perfluorotoluene (164) and no saturated derivative from pentafluoropyridine is understandable since the latter would involve a relatively weak[111] N-F bond.

3F.2 Fluorination of perfluoro-4-isopropyltoluene

Reaction of perfluoro-4-isopropyltoluene (169) over CoF_3/CaF_2 at 83°C gave a mixture containing two minor and two major components. The major components were identified as perfluoro-1-methyl-4-isopropylcyclohexa-1,3-diene (170) and perfluoro-1-methyl-4-isopropylcyclohexa-1,4-diene (171). Only one of the minor products was isolated and was identified as perfluoro-1-methyl-4-isopropylcyclohex-3-ene (172).



(169) (170)(25%) (171)(25%)



(172)(10%) (173)(3%)

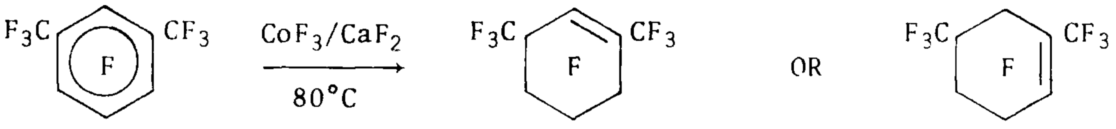
The identification of the dimers (170) and (171) was again difficult. Both displayed seven distinct signals in the ratio 6:3:2:2:1:1:1 in their n.m.r. spectra but examination of fine structure gave little information. Both compounds showed two absorptions between 1670 and 1750 cm^{-1} in their infrared spectra and each gave a parent ion of M^{+} = 424 in their mass spectra; information which was enough to exclude all structures other than (170) and (171). Structures were assigned on the basis of ultraviolet spectra in which the 1,3-diene (170) showed a strong absorption (logε = 3.84) at 251 nm indicating conjugation, whereas the 1,4-diene (171) showed a much weaker absorption (logε = 2.24) at 275 nm. The structure of the mono-ene (172) followed from its n.m.r. spectrum. A shift at 73.1 p.p.m. (Int. 3), indicative of a CF_3 group attached at a saturated position, confirmed the location of the double bond. A broad signal at 106.6 p.p.m. (Int. 1) and three AB type signals between 100 and 137 p.p.m. showed the presence of a vinylic fluorine atom and three CF_2 groups and a multiplet at 188.7 p.p.m. (Int. 1) was characteristic of a 'tertiary' fluorine atom. The presence of only one unsaturated site was confirmed by an absorption at 1702 cm^{-1} in the infrared spectrum. The fourth and most minor component, although not formally identified, was probably perfluoro-1-methyl-4-isopropylcyclohex-1-ene (173) since examination of the product mixture by g.l.c.-m.s. showed a parent ion at M = 462 and a mass spectrum similar to that of the isomer (172).

In this case the reaction shows a parallel with the fluorination of perfluoro-4-isopropylpyridine (128) in that dienes are produced as the major products with mono-enes present in only minor amounts. Moreover, the preference of perfluoroalkyl groups over fluorine atoms attached to unsaturated sites is again demonstrated.

The fact that (172) is formed in preference to its isomer (173) is probably due to the greater steric barrier presented by the perfluoroisopropyl group to addition of a fluorine atom.

3F.3 Fluorination of perfluoro-*m*-xylene

Perfluoro-*m*-xylene (174), prepared by defluorination of perfluoro-1,3-dimethylcyclohexane over heated iron filings[112], gave one major component on fluorination at 80°C. This was not unambiguously identified as spectroscopic data were consistent with either perfluoro-1,3-dimethylcyclohex-1-ene (175) or perfluoro-1,3-dimethylhex-3-ene (176).

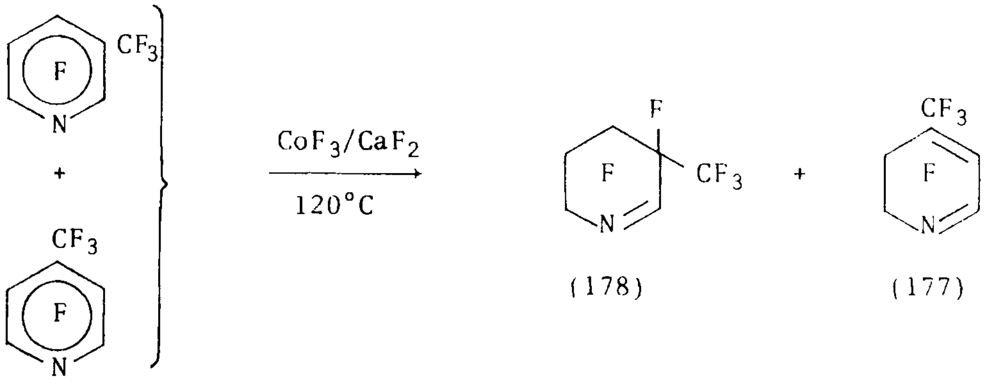


(174) . (175) (176)

(66%)

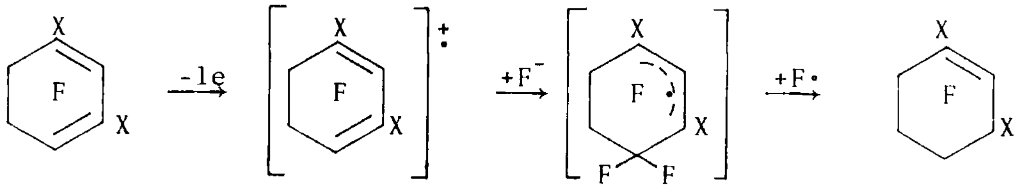
The n.m.r. spectrum showed signals at 62.3 (Int. 3) and 74.4 (Int. 3) p.p.m. indicating the presence of a CF_3 group attached to an unsaturated position and a CF_3 group attached to a saturated position; a broad signal at 176.3 p.p.m. (Int. 1) showed the presence of a 'tertiary' fluorine atom. A signal at 103.6 p.p.m. (Int. 1) and three AB type signals between 104 and 149 p.p.m. indicated the presence of a vinylic fluorine atom and three CF_2 groups respectively. Distinction between either structure could not be made on the basis of an examination of the fine structure. An absorption at 1704 cm^{-1} in the infrared spectrum and a parent ion of M^+ = 343 (M-F) in the mass spectrum was consistent with both (175) and (176).

It is not immediately obvious why dienes are not produced in this reaction, however, a parallel does occur in the fluorination of a mixture of 3- and 4-substituted pyridine derivatives to give the diene (177) and the mono-ene (178).[107]

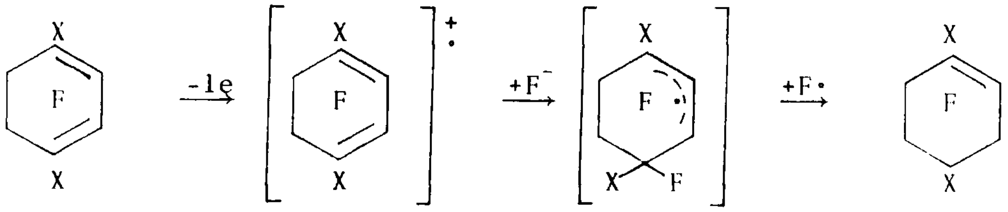


(178) (177)

Obviously a trifluoromethyl group at the 4-position has inhibited reaction. This is consistent with the radical cation mechanism since it is established that an olefinic position with fluorine attached is much more susceptible to nucleophilic attack than a corresponding position attached to perfluoroalkyl.[105] Clearly, on this basis, transfer of fluoride ion to the intermediate (179) would occur more readily than a similar transfer to intermediate (179a).



(179)



(179a)

(X = perfluoroalkyl)

CHAPTER 4

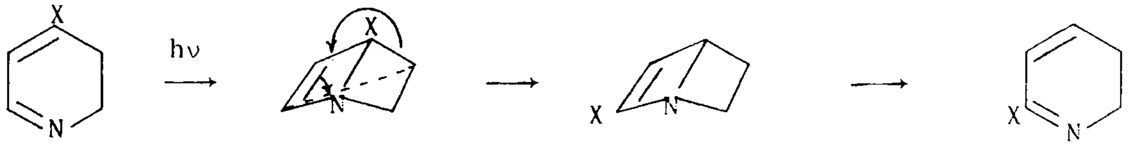
THE CHEMISTRY OF SOME PERFLUORO-AZA- AND -DIAZA-CYCLOHEXADIENE DERIVATIVES

4A PHOTOCHEMISTRY

4A.1 Introduction

Fluorine and perfluoroalkyl groups have been used successfully as substituent labels for the study of skeletal rearrangements in aromatic systems[113,114] and an unusual mechanism has been established to explain the photochemically induced 1,3-shifts in fluorinated pyridines and pyridazines[115], involving the intermediacy of para-bonded species.

The formation of para-bonded species could, in principle, occur during the irradiation of aza- and diazacyclohexadiene derivatives in an analogous manner.

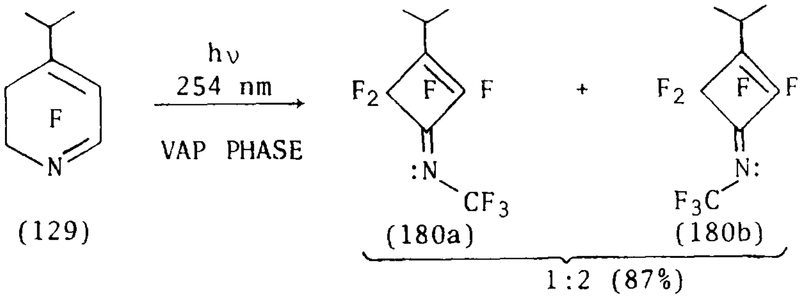


The photochemistry of the new fluorinated aza- and diazacyclohexadiene derivatives was, therefore, of considerable interest. Surprisingly, irradiations lead to a different group of rearrangements which were analogous to those shown by corresponding hydrocarbon systems.

4A.2 Irradiation of perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene

Irradiation of perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129) gave one major component identified as perfluoro-1-(methylimino)-3-isopropylcyclobut-2-ene (180), present as a 1:2 mixture of isomers

(180a, b), which were assigned on the basis of chemical shifts and



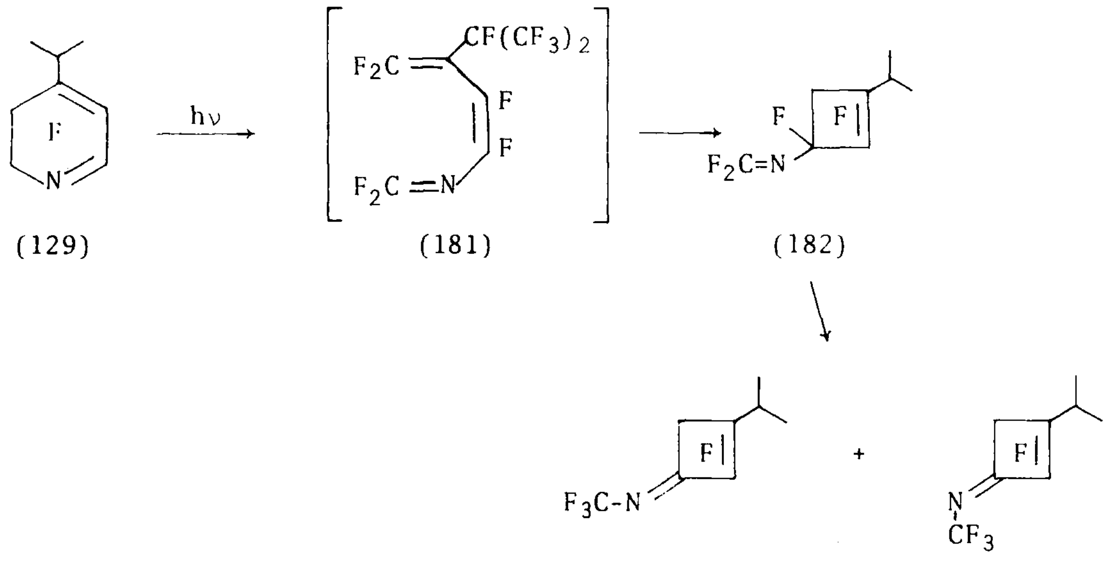
(129)

(180a) (180b)

1:2 (87%)

coupling constants. The n.m.r. spectrum of the mixture showed a triplet (J = 8 Hz) at 62.7 p.p.m. and a doublet (J = 18 Hz) at 62.1 p.p.m. (total intensity 3) indicating the presence of two CF_3 groups, in slightly different chemical environments, coupled to adjacent CF_2 and =CF groups and were assigned to structures (180b) and (180a) respectively. Four signals at 80.9 and 112.2 p.p.m. (180a), and at 89.8 and 104.4 p.p.m. (180b) displayed indistinct fine structure but were assigned on intensity grounds. Geometric isomers arising from the stereochemical integrity of nitrogen in fluorocarbon imines is well known[98] and was discussed in section 2D.4. Barriers to inversion are thought to be mainly influenced by steric effects but heating the mixture of (180a) and (180b) up to 90°C did not reveal any degree of coalescence between the n.m.r. signals. It is not surprising that the barrier to inversion would be affected by incorporation of the carbon of the imine group into a 4-membered ring.

In an earlier experiment[116] the irradiation of (129) gave a compound, to which the structure (181) was originally assigned, but it now seems more likely that this was in fact compound (182). However, in subsequent repeats of this experiment the major product has always been (180) together with (182) in minor proportions.

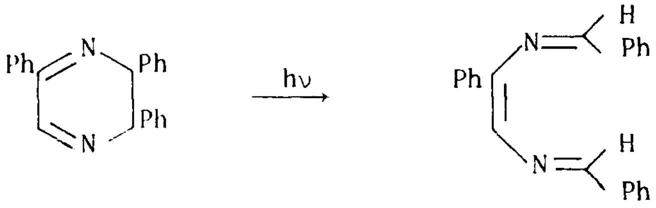


(129) (181) (182)

(180b) (180a)

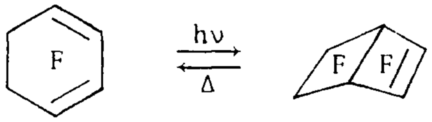
The structure of (182) has now been assigned on the basis of a signal at 136.7 p.p.m. (Int. 1) in the n.m.r. spectrum which is consistent with a 'tertiary' fluorine atom that has been shifted to lower field, due to the presence of adjacent nitrogen. The fact that the signal displays a doublet (J = 19 Hz) of triplets (J = 7.5 Hz) is also more consistent with structure (182) since it shows coupling to CF_2 and =CF groups which would be unlikely for any fluorine atom in structure (181). Two very broad signals at 32.9 p.p.m. (Int. 1) and 51.2 p.p.m. (Int. 1) were characteristic of an $N{=}CF_2$ group and signals at 96.1 p.p.m. (Int. 1) and 114.0 p.p.m. (Int. 2) were assigned to ring fluorine atoms.

The ring opening of cyclohex-1,3-dienes, giving trienes is well known[117,118] and analogous processes involving some heterocyclic systems have also been reported.[119]



Clearly, analogous ring opening of (129) to the triene (181) occurs, followed by ring closure to give (182). Further conversion of (182) to (180) could involve an allylic rearrangement induced by the presence of 'adventitious' fluoride ion, or a photochemically induced 1,3-shift of fluorine. The latter seems more likely since the conversion of (182) to (180) occurs very readily and the amounts of fluoride ion available could only be very small. The ready ring closure of (181) to give (182) is understandable, in view of the known propensity of fluorinated dienes to give corresponding cyclobutenes.[120]

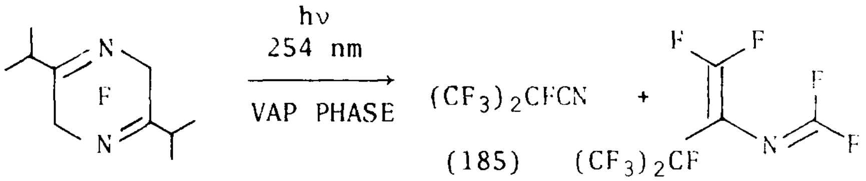
The behaviour of (129) upon irradiation is thus understandable, although in contrast to the irradiation of perfluorocyclohexa-1,3-diene (183), where formation of the para-bonded species (184) has been observed.[121]



(183) (184)

4A.3 Irradiation of perfluoro-1,4-diaza-2,5-diisopropylcyclohexa-1,4-diene

In contrast, irradiation of perfluoro-1,4-diaza-2,5-diisopropylcyclohexa-1,4-diene (152) gave > 90% conversion into a mixture containing equimolar amounts of perfluoroisobutyronitrile (185) and a compound identified as perfluoro-2-aza-3-isopropylbutadiene (186). No products arising from rearrangement of (152) were observed.



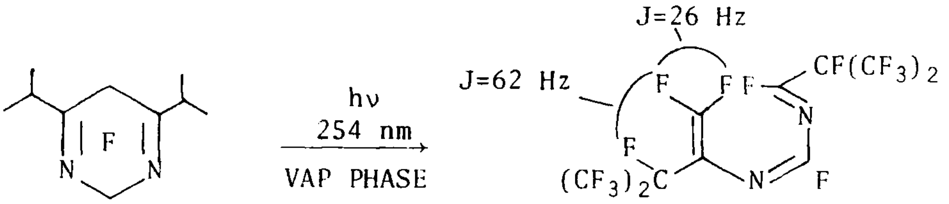
(152) (185) (35%) (186) (58%)

The structure of (186) followed simply from spectroscopic data; two very broad signals at 42.6 p.p.m. (Int. 1) and 55.9 p.p.m. (Int. 1) showed the presence of $N{=}CF_2$ and signals at 83.1 (Int. 1) and 93.0 (Int. 1) p.p.m., characteristic of vinylic fluorine atoms, were observed. Two absorptions at 1732 and 1805 cm^{-1} in the infrared spectrum and a parent ion of $M^+ = 295$ in the mass spectrum confirmed this structure.

Formation of (185) and (186) from (152) represents a rare example of a photochemically induced retro-Diels-Alder reaction.

4A.4 Irradiation of perfluoro-1,3-diaza-4,6-diisopropylcyclohexa-3,6-diene

Irradiation of perfluoro-1,3-diaza-4,6-diisopropylcyclohexa-3,6-diene (144) gave both perfluoroisobutyronitrile (185) and perfluoro-2-aza-3-isopropylbutadiene (186) together with a third product, identified as perfluoro-3,5-diaza-2-isopropyl-7-methylocta-1,3,5-triene (187).



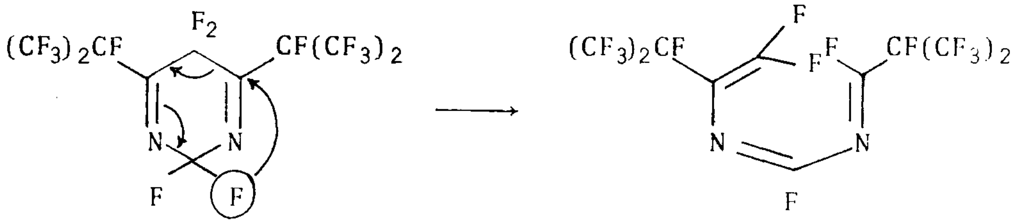
(144) (187) (48%)

+ (185) (11%) + (186) (17%)

The structure of (187) was deduced from spectroscopic data. Absorptions at 1678, 1731, and 1799 cm^{-1} in the infrared spectrum and a parent ion of M^+ = 490 in the mass spectrum showed it to be a triene derivative which was isomeric with the starting material (144).

Two signals at 77.7 (Int. 1) and 91.3 (Int. 1) p.p.m., which could be distinguished on the basis of observed coupling constants, were assigned to the $=CF_2$ group and a very broad signal at 41.8 p.p.m. (Int. 2) was assigned to both iminofluorine atoms. It is not surprising that these should be coincidentally equivalent due to the nature of their chemical environment and the broad nature of the signal.

Obviously a retro-Diels-Alder reaction is taking place similar to that which occurred during the irradiation of (152), however, (187) must be formed in a competing reaction which is particularly interesting since it must involve ring opening incorporating a 1,3-fluorine shift.

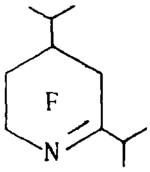


(144) (187)

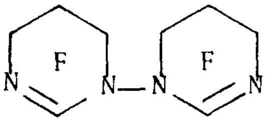
The nature of the stereochemistry about the imine groups is a point of particular interest but no information on this was available from the n.m.r. spectrum.

4A.5 Irradiation of other related compounds

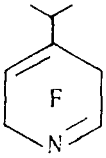
Irradiation of the related fluorinated aza-alkenes (136), (42), and (130) under similar conditions did not lead to product formation and in all cases > 95% recovery of starting material was obtained.



(136)



(42)



(130)

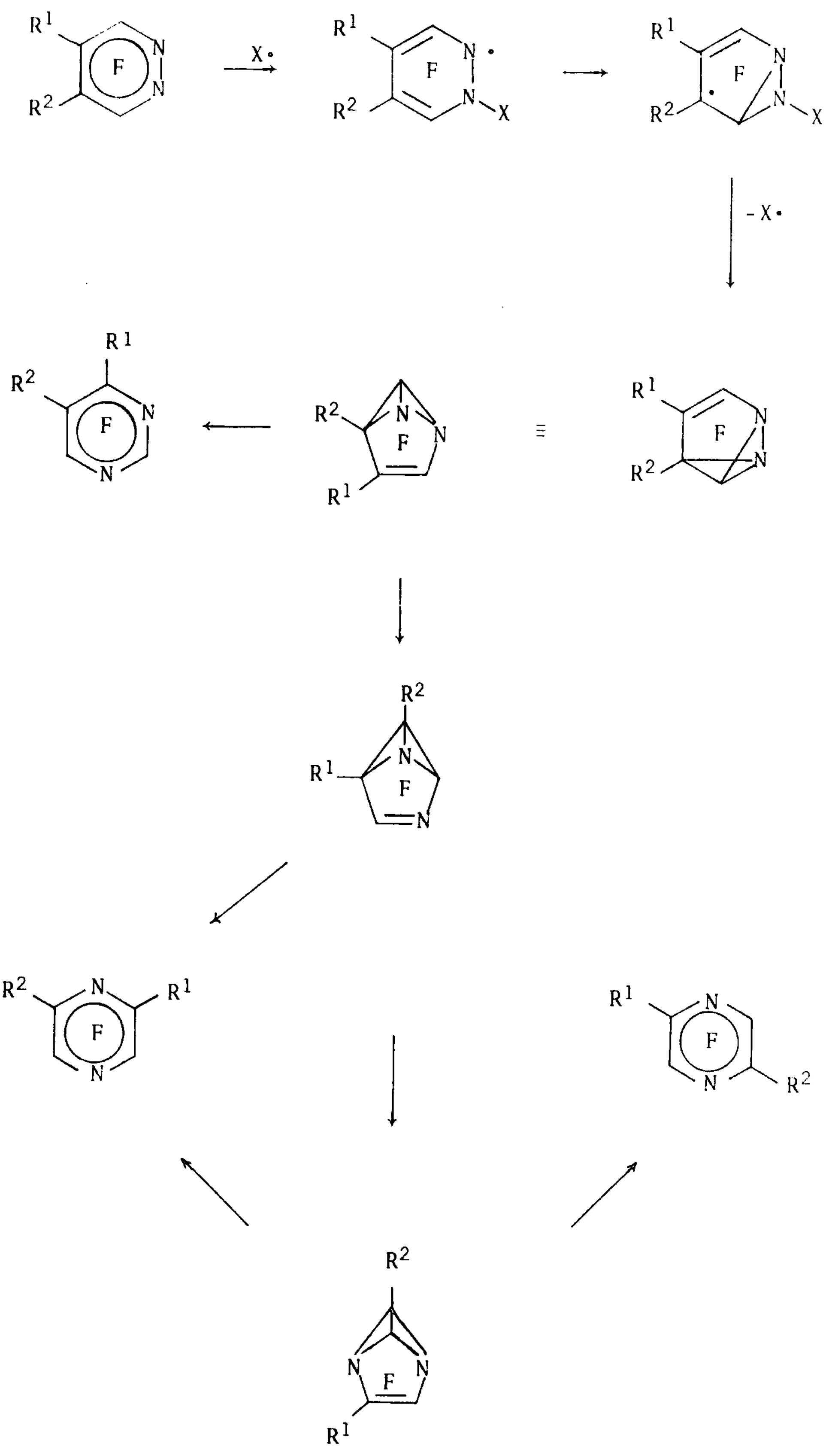
The fact that (136) and (42) do not react is understandable since quite different retro-Diels-Alder reactions would need to occur. A comparable retro-Diels-Alder reaction could, in principle, occur with (130) but this would involve the elimination of a fluoro-alkyne, which are known to be high energy species.[122]

4B THERMAL REACTIONS

4B.1 Introduction

The thermal rearrangement of perfluoroalkyl substituted pyridazine derivatives, giving pyrimidine and pyrazine derivatives, has been recently reported.[123] Various crowded fluorinated compounds, used as a source of free radicals, were found to promote these rearrangements and a free radical promoted formation of valence isomers has been proposed. (See overleaf)

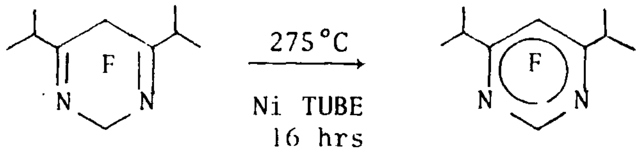
Similar thermal reactions were attempted with the fluorinated diazacyclohexadienes (144) and (152) in order to promote analogous rearrangement. This, however, did not occur.



(R^1, R^2 = F, various perfluoroalkyl)

4B.2 Pyrolysis of perfluoro-1,3-diaza-4,6-di-isopropylcyclohexa-3,6-diene

Pyrolysis of perfluoro-1,3-diaza-4,6-di-isopropylcyclohexa-3,6-diene (144) at 275°C in a sealed nickel tube gave a mixture containing mainly starting material and a minor amount of one other component, identified spectroscopically as the defluorination product (143).



(144) (143) (~10% conversion)

A similar experiment using perfluoro-3,4-dimethylhexane as a source of radical was found to give ~50% conversion to (143). It is not surprising that this type of reaction should occur since defluorination of saturated and partially saturated cyclic fluorocarbon systems over hot metal surfaces is well known[112], but it is not obvious why a greater conversion was achieved with perfluoro-3,4-dimethylhexane. It is more likely that this is simply a result of unobserved differences in reaction conditions.

4B.3 Pyrolysis of perfluoro-1,4-diaza-2,5-di-isopropylcyclohexa-1,4-diene

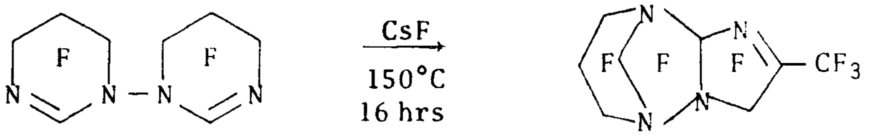
Pyrolysis of perfluoro-1,4-diaza-2,5-di-isopropylcyclohexa-1,4-diene (152) gave a 72% recovery of starting material only. No products due to rearrangement or defluorination were observed.

4C REACTIONS WITH FLUORIDE ION

4C.1 Reaction of perfluoro-1,1'-bis-1,3-diazacyclohex-2-enyl with fluoride ion

The reaction of fluorinated aza-alkenes with fluoride ion, giving isomerization and oligomerization via nitranion intermediates, is well known and is described in section 2C.

The reaction of perfluoro-1,1'-bis-1,3-diazacyclohex-2-enyl (42) with caesium fluoride in the absence of a solvent at 150°C gave, apart from recovered starting material, one other product which has been identified as perfluoro-4-methyl-1,2,5,7-tetraazatricyclo[3.3.1.$0^{2,6}$]undec-4-ene (188).

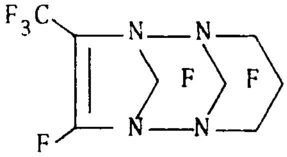


(42)

(188)(42%)

Identification of (188) was difficult due to the unusual and unexpected nature of the molecule. A parent ion at $M^+ = 418$ in the mass spectrum and elemental analysis showed it to be isomeric with the starting material (42) and a single absorption at 1720 cm^{-1} in the infrared spectrum indicated the presence of only one unsaturated site. The n.m.r. spectrum displayed a series of AB type signals between 89 and 118 p.p.m. and a singlet at 127.1 p.p.m. (Int. 2) showing (188) to contain five CF_2 groups. A singlet at 107.5 p.p.m. (Int. 1) was consistent with a 'tertiary' fluorine atom shifted downfield by the influence of three adjacent nitrogen atoms and the remaining signal at 60.5 p.p.m. (Int. 3) was characteristic of a CF_3 group attached to an unsaturated site. The presence of a CF_3 group is a clear indication that ring contraction has taken place during the reaction and the absence of any other signals in the low field region of the spectrum indicated that there were no imino-fluorines present.

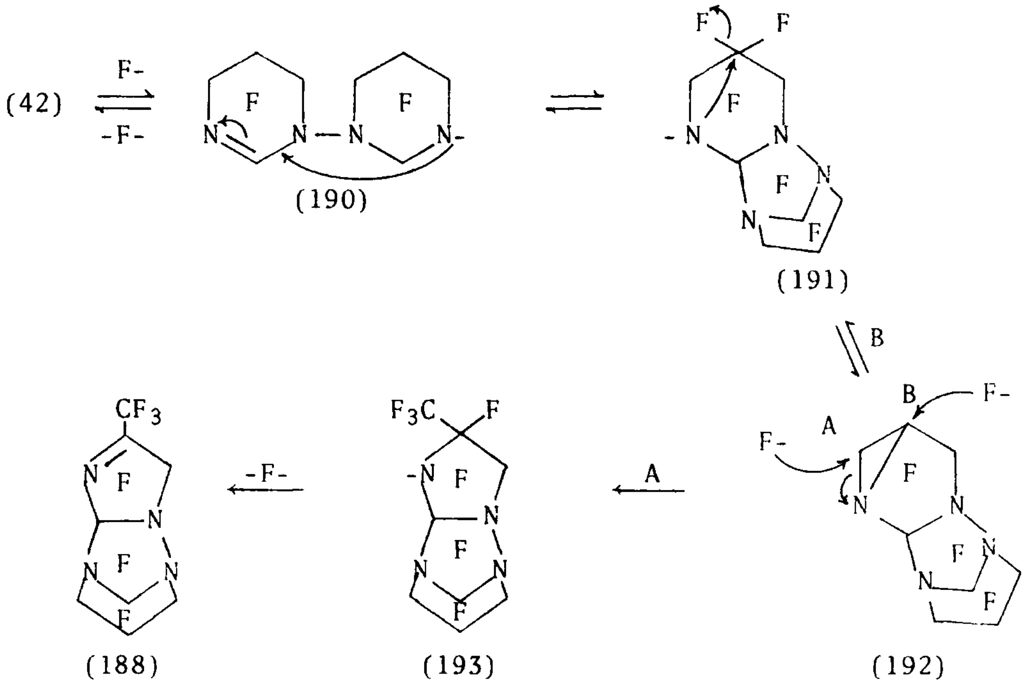
Spectroscopic evidence alone, however, does not discount the possibility of other similar structures. The signal at 107.5 p.p.m. could be interpreted as being due to a vinylic fluorine atom and a structure of the type (189) could, in principle, be a possibility. However, this would



(189)

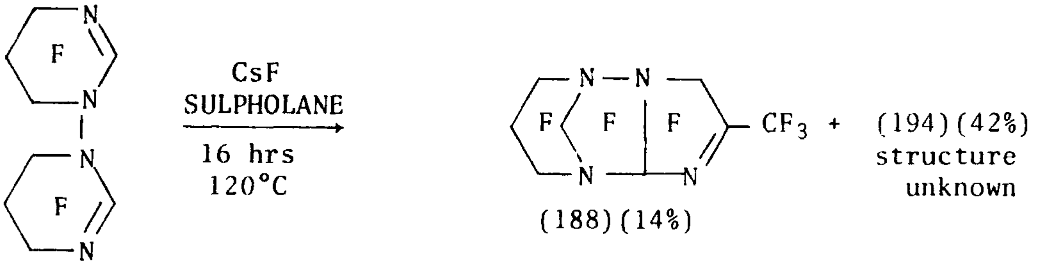
imply the presence of four bridgehead nitrogen atoms and it is difficult to see how such compounds could have formed from the starting material (42).

The proposed mechanism for the formation of (188) is unusual in that it involves internal nucleophilic attack at a saturated position.



The reaction must proceed via initial addition of fluoride ion to (42), giving the nitranion (190), followed by internal nucleophilic attack to give (191) since this is the only possible reaction pathway other than return to (42). The ring contraction of (191) to give (192) apparently occurs via an internal attack at a saturated position. Clearly, further attack by fluoride ion could occur at position A or B in the intermediate (192), but attack at position B would simply cause return to (191), whereas attack at A would give the nitranion (193). Both processes could clearly be taking place simultaneously, but conversion of (192) to (193) is non-reversible. Elimination of fluoride ion from (193) would give the observed product (188).

A similar reaction carried out using sulpholane as a solvent proved even more remarkable giving a product mixture containing three components, two of which were readily identified as starting material (42) and the product obtained previously (188). The third and most major product (194) was not identified.



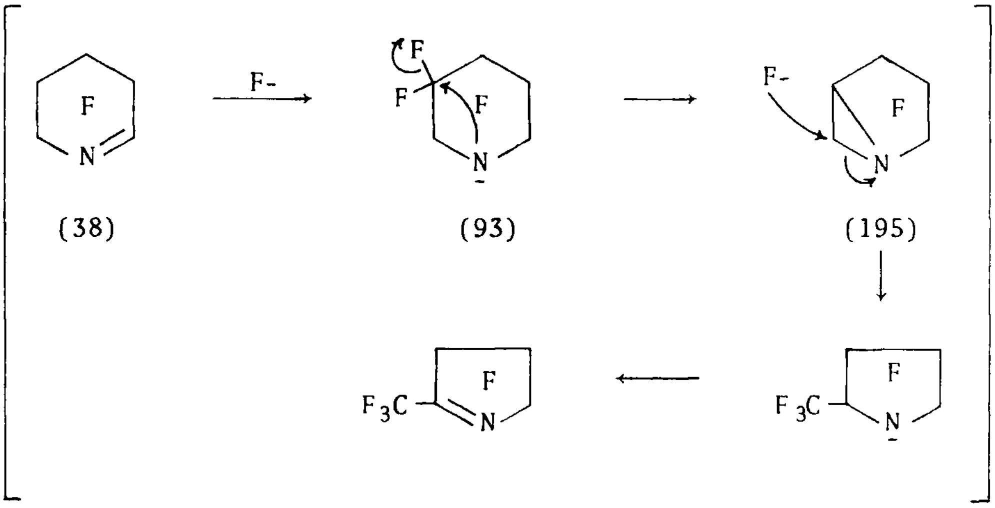
(42)

(188)(14%)

(194)(42%) structure unknown

The mass spectrum of (194) showed a parent ion of $M^+ = 423$ which is consistent with a molecular formula $C_8N_3F_{15}$. This is remarkable since it would involve addition of a fluorine atom to, and elimination of a nitrogen atom from, the starting material (42) ($C_8N_4F_{14}$), moreover, elemental analysis and chemical-ionization mass spectrometry agreed with this molecular formula. The n.m.r. spectrum of (194) showed six separate signals in the ratio 3:2:2:4:2:2. A triplet (J = 13 Hz) at 56.9 p.p.m. (Int. 3), characteristic of a CF_3 group attached to either an unsaturated site or a nitrogen atom, was the only signal showing any fine structure; all other signals were fairly sharp singlets. This indicated that compound (194) contained a CF_3 group and six CF_2 groups only. An absorption at 1688 cm^{-1} in the infrared spectrum indicated the presence of only one unsaturated site. It is difficult to see how such a compound could be produced from (42) hence no structure is proposed.

Perfluoro-1-azacyclohex-1-ene (38) was also heated to 150°C with caesium fluoride since this is related to (42) and could, in principle, show a similar ring contraction via internal attack at a saturated position.

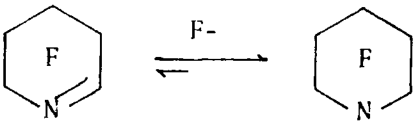


This did not occur and > 95% recovery of (38) was obtained. It is not obvious why reaction did not occur since compounds (42) and (38) are closely related species, however, it may be that the internal cyclization of (93) is a higher energy process and may be simply achieved by an increase in reaction temperature.

4C.2 Reaction of perfluoro-1-azacyclohex-1-ene with fluoride ion

The reaction of perfluoro-1-azacyclohex-1-ene (38) with fluoride ion has been reported to give the stable perfluorocyclohexyl anion (93).[56] The reaction was carried out in acetonitrile and an n.m.r. spectrum of the solution showed three broad signals at 66.1 (Int. 4), 129.4 (Int. 4), and 133.2 (Int. 2) p.p.m. indicating that the product was in equilibrium with its precursors.

A similar reaction was carried out using sulpholane as a solvent and, after stirring a solution of (38) in sulpholane with an excess of caesium fluoride for 38 hours, an n.m.r. spectrum of the solution showed three fairly sharp signals at 62.3, 127.1, and 131.1 p.p.m. Clearly, chemical shifts are within experimental error of those reported by Banks and co-workers[56] but, in contrast, the sharp nature of the signals indicates that the equilibrium is in favour of the nitranion (93). This provides an example of the influence of solvent on the stability of anionic species.

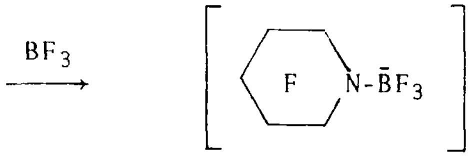


(38) (93)

Even on warming to 50°C, signals in the n.m.r. spectrum of (93) did not show any marked broadening.

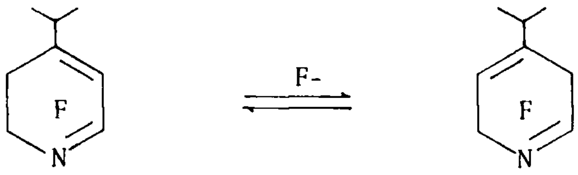
A further indication of the stability of (93) was given when BF_3-etherate was added to a sample of this solution. An n.m.r. spectrum showed that only a small amount of the starting material (38) had been regenerated and the presence of new signals between 51 and 135 p.p.m. indicated that (93) had reacted with BF_3, possibly giving the perfluoroazacyclohexyltrifluoroborate anion, in preference to elimination of fluoride ion.

(93)



4C.3 Reaction of perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene with fluoride ion

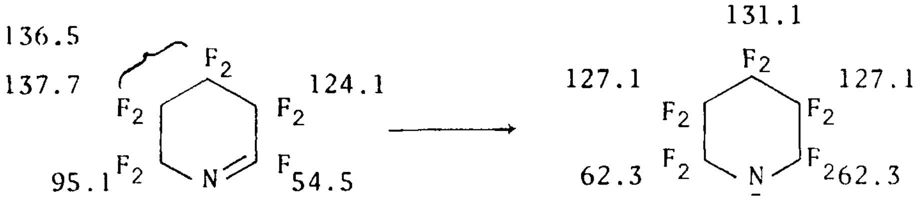
Perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129), on stirring with caesium fluoride for 20 hours at room temperature in the absence of a solvent, gave a mixture containing both the 1,3-diene (129) and the 1,4-diene (130).



(129) (83%) (130) (17%)

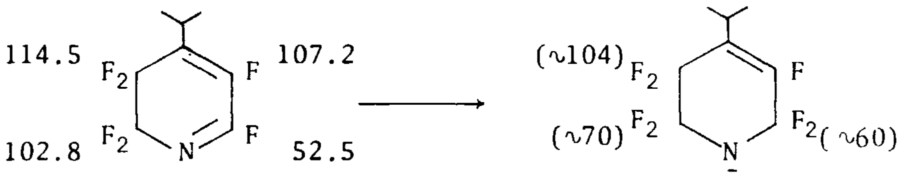
The position of the equilibrium is not surprising since the stability gained by conjugation would make (129) the favoured form. More interesting is the mechanism of isomerization, since this must involve a nitranion intermediate which, in principle, could be observed by n.m.r.

Stirring perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129) in acetonitrile with an excess of caesium fluoride gave a homogeneous solution from which a sample was removed and n.m.r. spectra were recorded at temperatures between -50°C and 50°C. At -30°C a series of fairly sharp signals were observed at 48.5 (Int. 2), 57.7 (Int. 2), 74.0 (Int. 6), 101.2 (Int. 1), 108.3 (Int. 2) and 183.9 (Int. 1) p.p.m. It was possible to assign these signals to the anion (196) on the basis of the differences in chemical shifts between perfluoro-1-azacyclohex-1-ene (38) and its corresponding anion (93).



(38) (93)

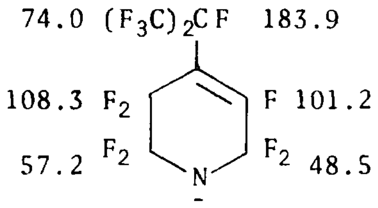
Taking into account the change in chemical shift on going from (38) to (93) it is possible to calculate a series of expected chemical shifts for the anion (196).



(129) (196)

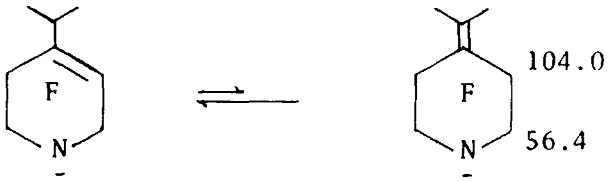
calculated shifts

It is clear that the chemical shifts observed are not far removed from those calculated and can be assigned to (196) on this basis.



(196)

On raising the temperature, exchange broadening was observed which was more significant in the signal at 48.5 p.p.m. and was accompanied by the appearance of two additional signals at 56.4 and 104.0 p.p.m. of equal intensity. Total integrations showed that these were due to a species which did not contain a 'tertiary' fluorine atom, but did contain CF_3 groups, which can only be consistent with the formation of the isomeric ion (197).

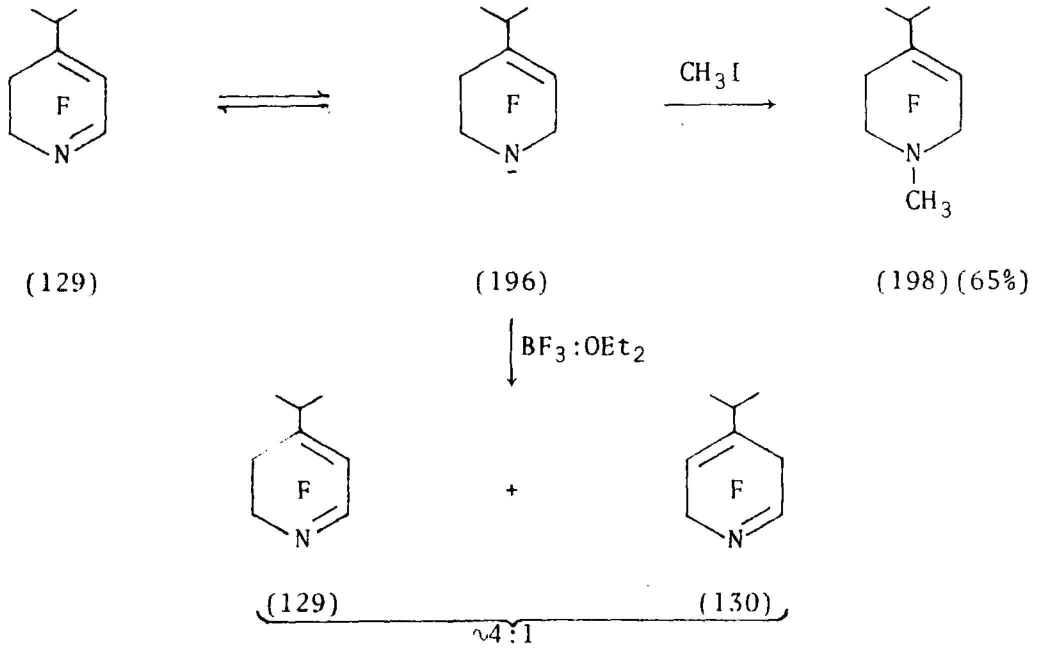


(196) (197)

Further increase in temperature was accompanied by increased exchange broadening but further reactions occurring meant that the anion (196) was not observed on cooling back to room temperature.

Addition of BF_3-etherate to a sample of the solution gave an equilibrium mixture of the 1,3- and 1,4-dienes (129) and (130) which were easily identified from their n.m.r. spectra.

Addition of methyl iodide to the remainder of the solution, followed by stirring for a further 24 hours, gave one product which was identified as N-methyl-1-aza-4-perfluoroisopropyl-2,2,3,5,5,6,6-heptafluorocyclohex-3-ene (198).



Signals in the ^{19}F n.m.r. spectrum of (198) at 89.5 (Int. 2), 103.7 (Int. 2), 105.7 (Int. 1), and 111.5 (Int. 2) p.p.m. were characteristic of three CF_2 groups and a vinylic fluorine atom and were assigned to ring fluorines. A singlet at 1.9 p.p.m., characteristic of a CH_3 group, was observed in the ^1H n.m.r. spectrum and absorptions in the infrared spectrum at 1723 and 2970 cm^{-1} indicated the presence of a single unsaturated site and C-H bonds respectively. The structure was confirmed by a parent ion of $M^+ = 391$ in the mass spectrum.

An identical experiment was carried out using sulpholane as a solvent. N.m.r. studies showed that spectra were not significantly different from those obtained using acetonitrile at corresponding temperatures.

4D REACTIONS WITH DIAZOMETHANE

4D.1 Introduction

Reactions between fluorinated aza-alkenes and diazomethane were described fully in section 2D.2.

In general, products are obtained via one or more of three mechanistic pathways[86]:

a) addition of CH_2N_2 followed by elimination of HF giving a triazacyclopentadiene derivative,

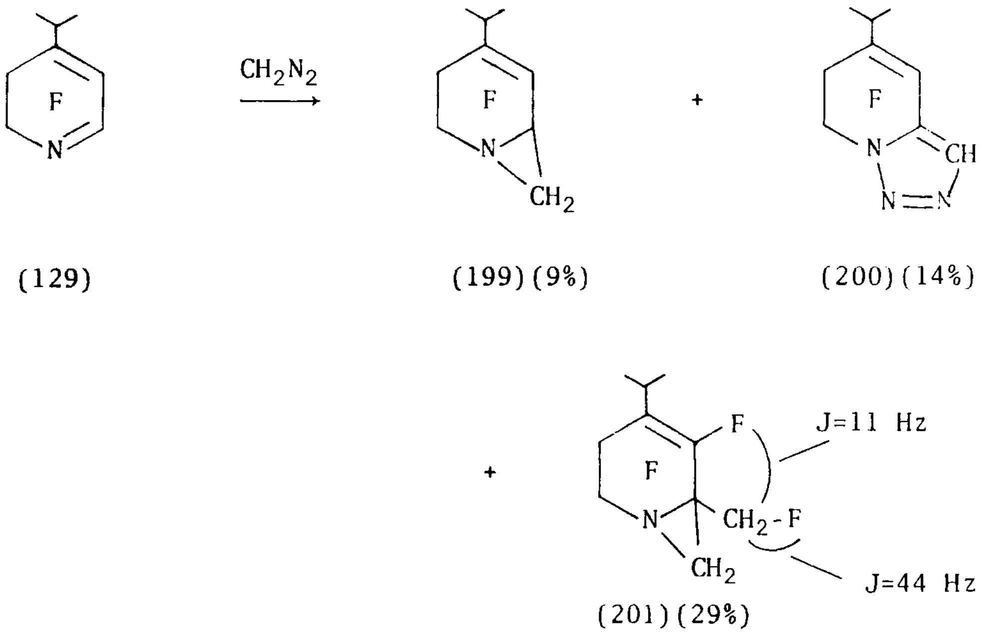
b) addition of CH_2N_2 followed by elimination of N_2 giving an azacyclopropane derivative,

c) addition of CH_2N_2 accompanied by elimination of N_2 and a 1,2-fluorine shift, followed by further addition-elimination giving an azacyclopropane derivative containing a CH_2F group.

All three modes of behaviour are displayed in the reactions of diazomethane with the various fluorinated azacyclohexadienes described in this section.

4D.2 Reaction of perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene with diazomethane

The reaction of diazomethane with perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129) gave a complex mixture of viscous liquids containing five components but only three of these were separated. These were identified as 4-(perfluoroisopropyl)-2,2,3,3,5,6-hexafluoro-1-azabicyclo[4.1.0]hept-4-ene (199), 4-(perfluoroisopropyl)-2,2,3,3,5-pentafluoro-1,8,9-triazabicyclo[4.3.0]nona-4,6,8-triene (200), and 4-(perfluoroisopropyl)-6-(fluoromethyl)-2,2,3,3,5-pentafluoro-1-azabicyclo[4.1.0]-hept-4-ene (201).



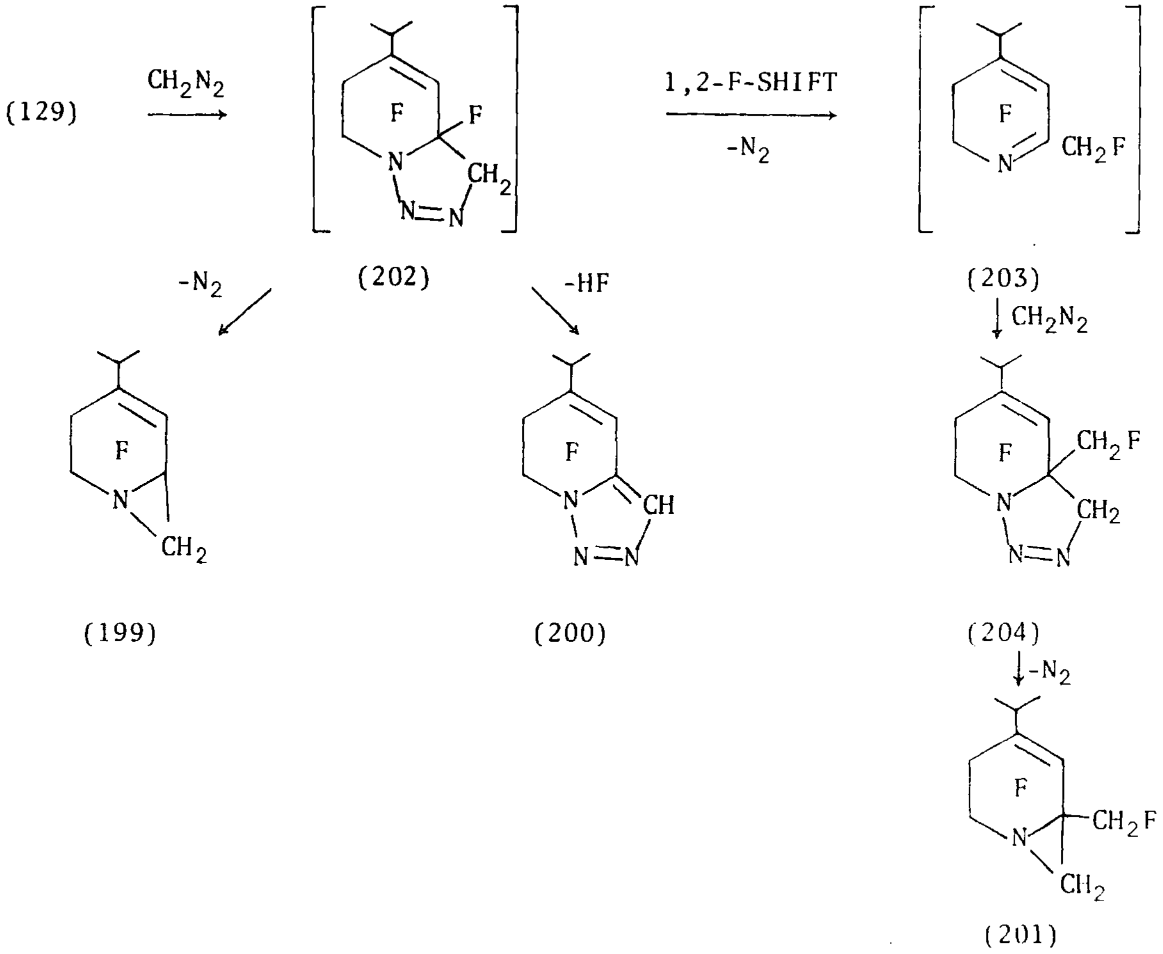
(129) (199)(9%) (200)(14%) (201)(29%)

The structure of (199) followed from spectroscopic data. A high field signal at 169.5 p.p.m. (Int. 1) indicated the presence of a second 'tertiary' fluorine atom showing that addition across a double bond had occurred and the presence of a signal at 88.6 p.p.m. (Int. 1), due to a vinylic fluorine atom was enough to confirm addition had taken place across the C=N bond, since addition across the C=C bond would have left an imino-fluorine atom (N=CF), the chemical shift of which would be expected to occur at much lower field. The ^{1}H n.m.r. spectrum showed two singlets at 2.47 and 2.63 p.p.m. indicative of a CH_2 group. Absorptions at 1692, 3030, and 3120 cm^{-1} in the infrared spectrum and a parent ion of $M^+ = 271$ in the mass spectrum confirmed this structure.

The ^{19}F n.m.r. spectrum of (200) was similar to that of (199), the main difference being the absence of a second 'tertiary' fluorine type signal indicating that this had been eliminated. The ^{1}H n.m.r. spectrum showed only one signal at 7.88 p.p.m. characteristic of a vinylic hydrogen atom. The structure was confirmed by the mass spectrum (M^+ = 379) and absorptions at 1458 (C=C), 1677 (C=C) and 3150 (C-H) cm^{-1} in the infrared spectrum.

The n.m.r. spectra of (201) were more complex. The ^1H n.m.r. spectrum gave signals at 2.48 and 2.63 p.p.m. which were assigned to the bridging CH_2 group and a doublet (J = 44 Hz) of doublets (J = 11 Hz) at 4.40 p.p.m. indicative of a CH_2 group coupled to two separate fluorine atoms. The ^{19}F n.m.r. spectrum showed a triplet (J = 44 Hz) at 225.6 p.p.m. (Int. 1) which was obviously assigned to the fluorine belonging to the CH_2F group. Absorptions at 1688 (C=C) and 2975 (C-H) cm^{-1} in the infrared spectrum and a parent ion of M^+ = 385 in the mass spectrum confirmed this structure.

The reaction of (129) with diazomethane thus behaves in an analogous manner to reactions of similar fluorinated aza-alkenes reported by Coe and Holton[86] (section 2D.2). The first step seems to be the 1,3-dipolar addition of CH_2N_2 to give the intermediate (202).

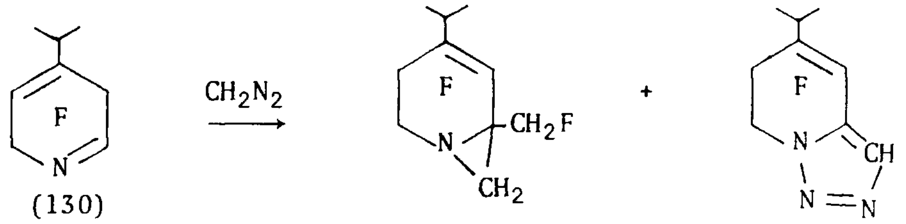


This then follows three different competing reaction pathways; elimination of N_2 to give (199), elimination of HF to give (200), or elimination of N_2 with a 1,2-fluorine shift to give the intermediate (203), which then further reacts with CH_2N_2 to give (201) via elimination of N_2 from (204).

Interestingly, products due to addition across the C=C bond are not observed. This is probably an indication of the lower energy of the LUMO of the C=N bond, in comparison with that of the C=C bond, since the mechanism of the initial 1,3-dipolar addition involves interaction between the HOMO of CH_2N_2 and the LUMO of the alkene.[84a]

4D.3 Reaction of perfluoro-1-aza-4-isopropylcyclohexa-1,4-diene with diazomethane

The reaction of perfluoro-1-aza-4-isopropylcyclohexa-1,4-diene (130) with diazomethane gave a complex mixture containing two major, and at least five minor, components. Only the two major products could be separated and were identified from their n.m.r. spectra as the derivatives (200) and (201) observed in the previous experiment.



(130)

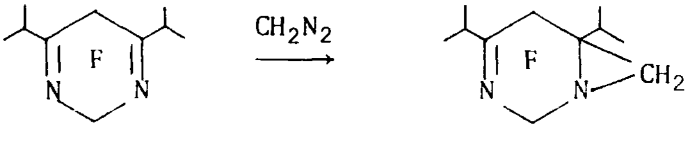
(201) (15%)

(200) (7%)

Obviously compounds (200) and (201) must be formed from the 1,3-diene (129), which is understandable since the formation of HF in any reaction of (130) would cause equilibration to take place giving the 1,3-diene (129) and, since this is the dominant isomeric form, the formation of (200) and (201) would follow. However, the nature of the remaining product mixture was unknown and it could well be that this contained small amounts of addition-elimination products derived from the 1,4-diene (130).

4D.4 Reaction of perfluoro-1,3-diaza-4,6-diisopropylcyclohexa-3,6-diene with diazomethane

Perfluoro-1,3-diaza-4,6-diisopropylcyclohexa-3,6-diene (144) reacted with diazomethane to give one product which was identified as 4,6-bis-(perfluoroisopropyl)-2,2,5,5-tetrafluoro-1,3-diazabicyclo[4.1.0]hept-3-ene (205).



(144) (205)(53%)

The ^{19}F n.m.r. spectrum of (205) contained an AB type signal centred at 63.3 and 71.1 p.p.m. which was assigned to the CF_2 group adjacent to the nitrogen atoms due to its low field position. Remaining signals indicated the presence of a second CF_2 group and two non-equivalent perfluoroisopropyl groups. The ^1H n.m.r. spectrum displayed two singlets at 1.73 and 2.37 p.p.m. characteristic of a bridging CH_2 group. Confirmation of the structure was given by a parent ion of $M^+ = 504$ in the mass spectrum and an absorption at 1700 cm^{-1} (C=N) in the infrared spectrum.

The fact that reaction did not take place at the second unsaturated site is surprising, however, there is no reason to believe that this would not occur in the presence of an excess of diazomethane.

CHAPTER 5

THE CHEMISTRY OF PERFLUORO-2,5-DIAZAHEXA-2,4-DIENE

5A INTRODUCTION

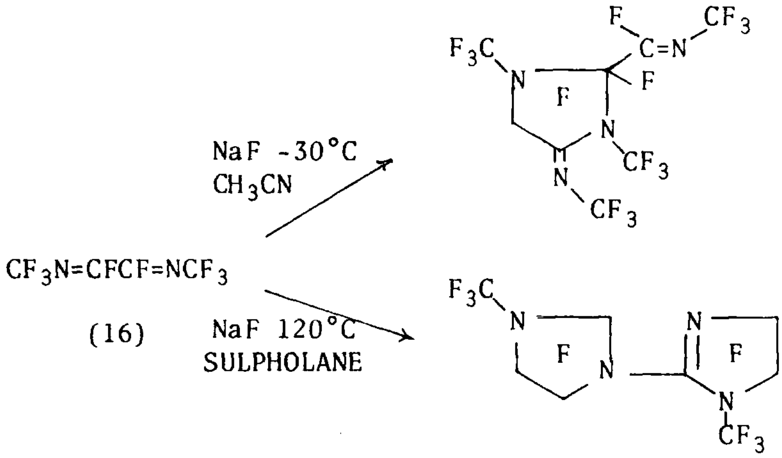
The chemistry of perfluoro-2,5-diazahexa-2,4-diene (16) that has been developed so far is described in Chapter 2, but this is concerned exclusively with nucleophilic reactions and fluoride ion induced dimerizations.

In this chapter the chemistry of (16), prepared by dehydrofluorination of N,N-bis(trifluoromethyl)tetrafluoroethylenediamine using sodium fluoride[21], is further investigated. Reactions with fluoride ion are described, together with a preliminary investigation into photochemical and thermal reactions.

5B REACTIONS WITH FLUORIDE ION

5B.1 Reaction with alkali metal fluorides in sulpholane

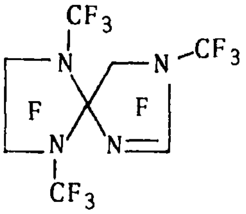
Perfluoro-2,5-diazahexa-2,4-diene (16) reacts with sodium fluoride giving the dimers (82) and (86) as major products.[21,38] The proportion of each in the product mixture depends on reaction conditions, indeed at -30°C compound (82) is formed exclusively[21], whereas at 120°C compound (86) is the preferred product.[38]



(82) (85%)

(86) (88%)

Reactions of (16) with NaF, KF, and CsF in sulpholane at room temperature were carried out since, in principle, this is an ideal system for an investigation into the effect of alkali metal cation on the activity of fluoride ion. In all cases dimers (82) and (86) were produced as the major products, but a third dimer, identified as perfluoro-spiro-1,3,6,9-tetra-aza-3,6,9-trimethylnon-1-ene (206), has now been observed in reactions with KF and CsF.



(206)

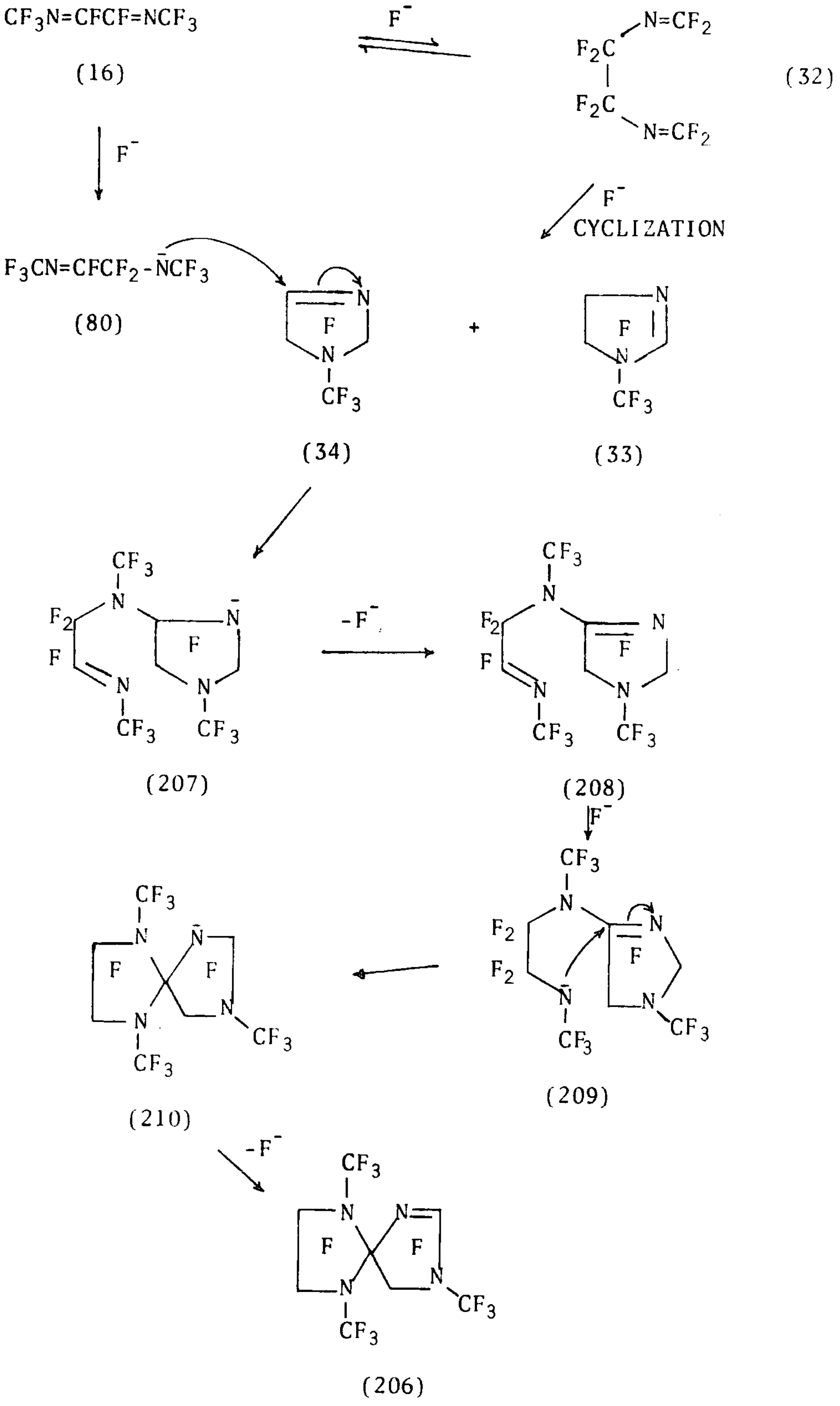
The proportion of products from each reaction is shown in Table 2.

MF	(82)%	(86)%	(206)%
NaF	76	24	0
KF	43	50	7
CsF	37	57	6

TABLE 2

The structure of compounds (82) and (86) followed from spectroscopic data which were consistent with those reported in the literature[21,38], but identification of the third and previously unknown dimer (206) was more difficult. A parent ion in the mass spectrum at $M^+ = 456$ and an absorption at 1742 cm^{-1} in the infrared spectrum indicated a dimeric species with only one unsaturated site. A broad multiplet at 57.8 p.p.m. (Int. 6) and two signals at 90.7 (Int. 2) and 91.2 (Int. 2) p.p.m. in the n.m.r. spectrum were consistent with two CF_3 groups and two CF_2 groups in similar chemical environments. This is consistent with structure (206) due to the symmetrical nature of the saturated part of the molecule.

The mechanism of formation of dimers (82) and (86) is described in detail in section 2C, but the proposed mechanism for the formation of (206) is more interesting (Scheme 5), since it must involve attack by the anion (80) on the cyclic derivative (34) giving the anion (207), which on elimination of fluoride ion gives the intermediate (208). Addition of fluoride ion to (208) gives (209) which isomerizes to (210), via an interesting intramolecular cyclization, and elimination of fluoride ion from (210) gives the dimer (206).


CF3N=CFCF=NCF3
(16)
F⁻
(32)
N=CF2
F2C
F2C
N=CF2
F⁻
F⁻
CYCLIZATION
F3CN=CFCF2-N̄CF3
(80)
(34)
(33)
+
CF3
(207)
-F⁻
(208)
F⁻
(209)
(210)
-F⁻
(206)

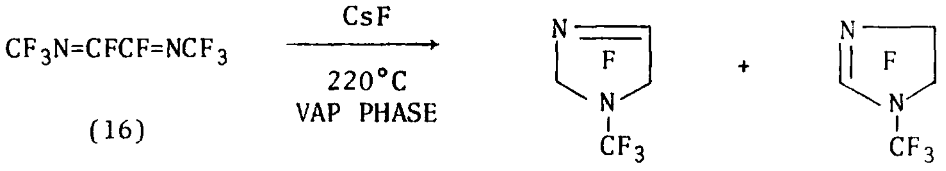
SCHEME 5

The formation of (206) has therefore occurred via reaction of (16) in its straight chain form with the cyclic analogue (34), which is reasonable since both compound (34) and the straight chain anion (80) are involved in the formation of dimers (82) and (86) and must be present in significant amounts.

It is not clear why (206) was not observed in the reaction of (16) with NaF, but the change in activity in fluoride ion with differing alkali metal cation has been demonstrated and indicates CsF > KF > NaF.

5B.2 Vapour phase reaction with caesium fluoride

The cyclic products perfluoro-1,3-diaza-1-methylcyclopent-3-ene (33) and perfluoro-1,3-diaza-1-methylcyclopent-2-ene (34) were obtained exclusively when compound (16) was passed over caesium fluoride at 220°C in a flow of nitrogen.



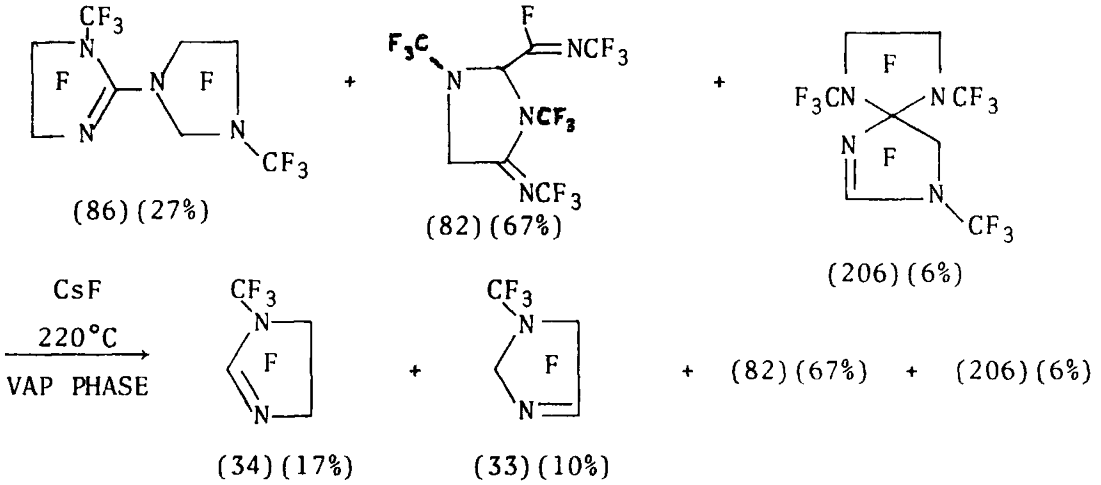
(16)

(33)(16%) (34)(65%)

The structure of (33) and (34) followed from spectroscopic data which were consistent with those reported in the literature[38], but this represents a new and convenient method of preparation since these compounds were previously isolated only as minor products during the dimerization of (16).[38] It is not surprising that (33) and (34) are formed exclusively, since reaction in the vapour phase would be expected to inhibit dimerization.

5B.3 Vapour phase reaction of a mixture of dimers with caesium fluoride

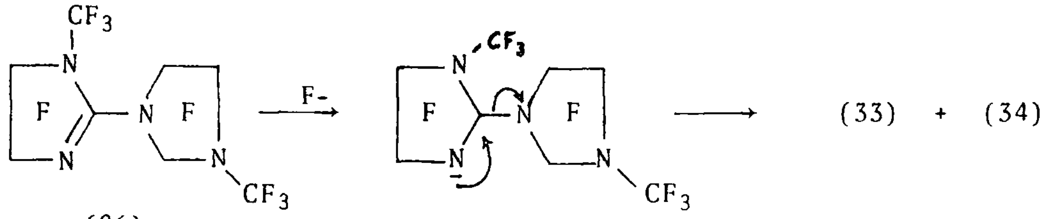
A mixture of dimers of compound (16) containing (86) (27%), (82) (67%), and (206) (6%) gave a four component mixture when passed over CsF at 220°C in a flow of nitrogen. These were spectroscopically identified as dimers (82) (67%) and (206) (6%), together with the diazacyclopentene derivatives (33) (10%) and (34) (17%).



(86) (27%) + (82) (67%) + (206) (6%)

(34) (17%) + (33) (10%) + (82) (67%) + (206) (6%)

Clearly the dimers (82) and (206) have remained unchanged, whereas dimer (86) has been converted to a mixture of monomers (33) and (34). This is understandable since the nature of compounds (82) and (206) obviously makes simple conversion to monomers impossible, whereas a simple process is available for conversion of (86).



(86)

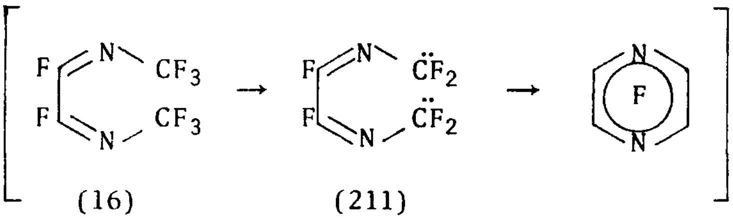
The reaction therefore provides another convenient route to the diazacyclopentene derivatives (33) and (34), since compound (86) can be obtained exclusively from the dimerization of (16) (section 5B.1).

5C DEFLUORINATION REACTIONS

5C.1 Introduction

Reactions of fluorocarbon systems over heated metal surfaces have been mainly concerned with the formation of aromatic species from saturated and partially saturated cyclic systems[112], although successful defluorinations using acyclic precursors have been reported.[123a]

The defluorination of perfluoro-2,5-diazahexa-2,4-diene (16) could, in principle, give a convenient synthesis of tetrafluoropyrazine via the carbene intermediate (211).

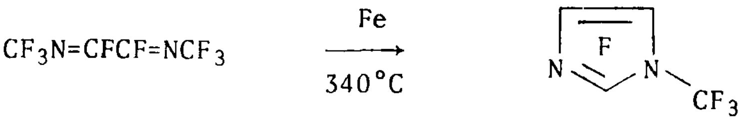


(16) (211)

Nevertheless, various reactions with heated iron, nickel, and platinum, described in the following section, did not achieve this.

5C.2 Reactions over hot metal surfaces

The vapour phase reaction of perfluoro-2,5-diazahexa-2,4-diene (16) over Fe filings at 340°C in a flow of nitrogen gave, together with unreacted starting material, one other compound identified as perfluoro-N-methylimidazole (212).

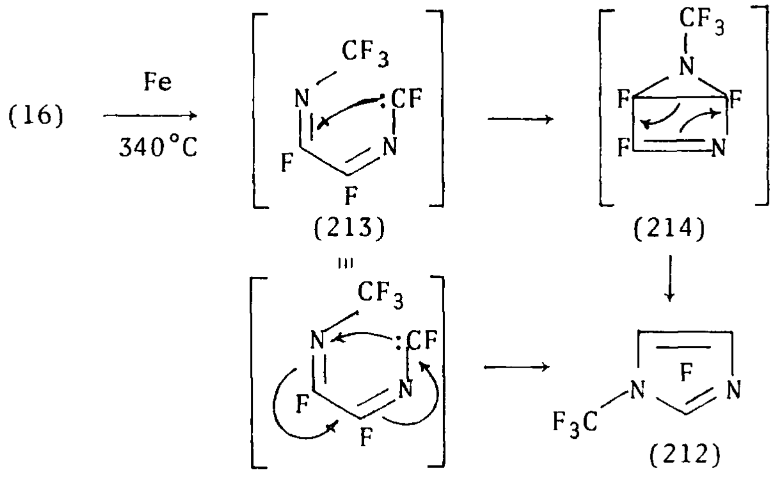


(16) (212)(30%)

The structure of (212) followed from spectroscopic data. Confirmation that defluorination had taken place was given by a parent ion of M^{+} = 190 in the mass spectrum and absorptions in the infrared spectrum at 1622 and 1730 cm^{-1} indicated that two unsaturated sites were present. The n.m.r. spectrum contained a signal at 58.6 p.p.m. (Int. 3) characteristic of N-CF_3, but the remaining three signals at 107.8 (Int. 1), 153.0 (Int. 1), and 165.2 (Int. 1) p.p.m. were more characteristic of fluorine atoms attached to an aromatic nucleus.[124]

This reaction therefore represents the first synthetic route to a perfluorinated imidazole derivative.

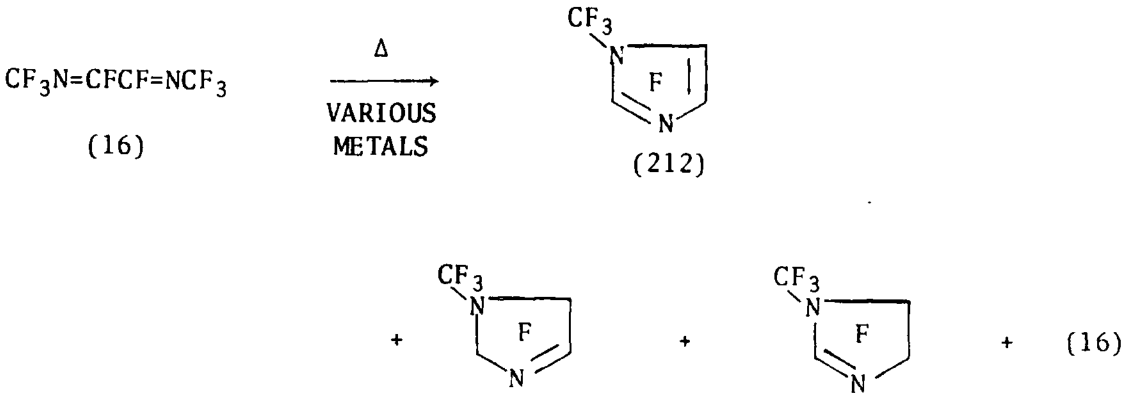
The formation of (212) could occur via the carbene intermediate (213) which could undergo intramolecular cyclization giving (212), via the intermediate (214), or via internal nucleophilic attack at nitrogen.



It is not immediately obvious why (212) is formed in preference to tetrafluoropyrazine, but formation of the latter would imply the di-carbene intermediate (211), and since this requires removal of four fluorine atoms from (16) would inherently be a much higher energy species than the intermediate (213).

Another possible mechanism for the formation of (212) could involve isomerization of (16) to the diazacyclopentene derivatives (33) and (34) as the first step, followed by defluorination, however, the reaction of (33) and (34) over Fe filings at 340°C was attempted and led only to recovery of starting materials, a result which does not support this mechanism.

Although conversion to (212) was reasonable (∿60%), recovery was low (∿50%), and in view of this a series of reactions were attempted using Fe, Ni and Pt under various conditions, the results of which are summarised in Table 3. In most cases compound (212) was obtained but only in minor amounts, together with significant amounts of recovered starting material (16) and diazacyclopentene derivatives (33) and (34).



(16) (212) (33) (34)

Reaction conditions	% recovery	% in product mixture			
		(212)	(33)	(34)	(16)
Pt metal, 480°C, N_2 flow system	88	0	11	6	83
Ni turnings, 380°C, N_2 flow system	93	0	0	0	100
Sealed Ni tube, 290°C, 18 hours	83	9	14	38	39
Sealed Ni tube with Ni turnings, 300°C, 18 hours	42	5	9	20	66
Sealed Ni tube with Fe filings, 300°C, 18 hours	67	6	13	28	53

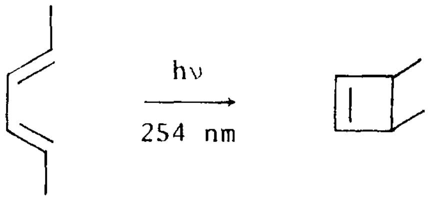
TABLE 3

5D PHOTOCHEMISTRY

5D.1 Introduction

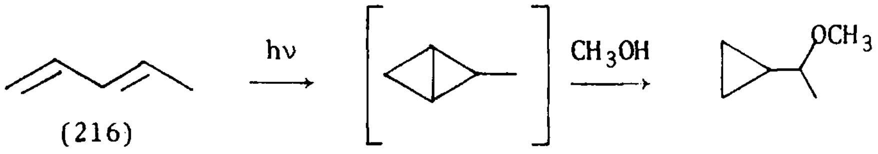
The photochemistry of conjugated 1,3-dienes has been well investigated and various products are obtained, depending on the nature of the substrate and reaction conditions.

In many cases irradiation of dienes and polyenes leads to *cis-trans* isomerization about one or more unsaturated site[125] but the most common reaction is ring closure giving cyclobutene derivatives[126,127], as illustrated by the irradiation of hexa-2,4-diene (215):



(215)

Bicyclobutanes are also formed[128], although these are mostly observed as minor by-products of ring closure reactions and, since such compounds are generally unstable, a suitable trapping agent must be used cf. the irradiation of penta-1,3-diene (216).



(216)

The potential photochemistry of perfluoro-2,5-diazahexa-2,4-diene (16) is therefore interesting since reactions of the fluorinated aza- and diaza-cyclohexadiene derivatives, described in section 4A, have shown a parallel with reactions of their hydrocarbon analogues. Another interesting possibility is the occurrence of 1,3-fluorine shifts giving the isomer (15).

$$\left[\begin{array}{ccc} CF_3N{=}CFCF{=}NCF_3 & \rightarrow & CF_2{=}NCF_2CF_2N{=}CF_2 \\ (16) & & (15) \end{array}\right]$$

So far, however, none of these processes has been observed.

5D.2 Irradiations of perfluoro-2,5-diazahexa-2,4-diene

The ultraviolet spectrum of compound (16) displayed a broad but fairly weak band between 210 and 290 nm (λ_{max}, 228 nm; log ε_{max}, 2.54), but vapour phase irradiation of (16) at 254 nm gave a 93% recovery of starting material and no other product was observed. A similar irradiation using a medium pressure broad band Hg lamp and n-pentane as a solvent also failed to promote reaction, and even on addition of a 4:1 molar excess of *p*-xylene as a potential sensitizer, products were not observed.

It is not clear why compound (16) should be photochemically inert, but a possible explanation could be an initial $n \rightarrow \pi^*$ transition giving an unreactive intermediate which, upon decay, returns to (16) exclusively.

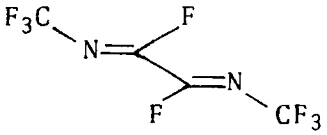
5D.3 Irradiations in the presence of ketones

Cycloadditions between ketones and alkenes giving oxetene derivatives are well known and has been observed in fluorinated systems[129], but vapour phase irradiations of perfluoro-2,5-diazahexa-2,4-diene (16) at 300 nm in the presence of acetone and hexafluoroacetone respectively did not lead to product formation and in both cases ∿95% recovery of starting materials was obtained.

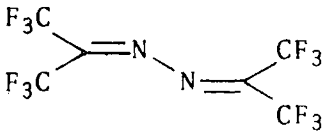
5E THERMAL REACTIONS WITH ALKENES

5E.1 Introduction

The possibility of cycloadditions of perfluoro-2,5-diazahexa-2,4-diene (16) with alkenes is interesting since the carbon-nitrogen skeleton of the molecule is isoelectronic with that of hexafluoroacetone azine (9) and could, in principle, undergo similar [3 + 2] cycloadditions (see section 2D.1).

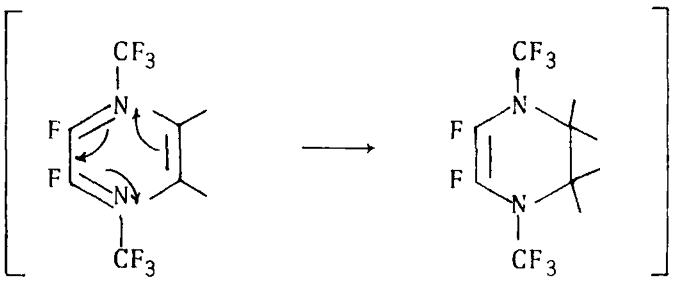


(16)



(9)

Alternatively, since compound (16) is an electron deficient 1,3-diene, [4 + 2] cycloadditions with electron rich alkenes should be possible, in an inverse electron demand Diels-Alder reaction.



In practice, however, neither of these reactions was observed.

5E.2 Attempted cycloadditions

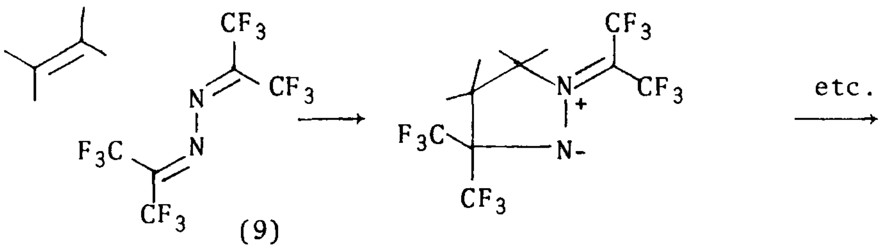
An equimolar mixture of compound (16) and cyclohexene gave a product mixture consisting of two layers when heated to 80°C for 100 hours. The lower layer was identified as unreacted (16) only, more interestingly the upper layer was shown to contain one major component, the mass spectrum of which was consistent with a dimer of cyclohexene, ($M^+ = 164$). No other products were observed.

A similar reaction of (16) with 2-methylbut-2-ene at 80°C for 140 hours showed parallel behaviour in that a lower layer, consisting of unreacted (16) only, and an upper layer were observed. The latter contained several components, the mass spectra of which were consistent with dimers of 2-methylbut-2-ene, ($M^+ = 140$).

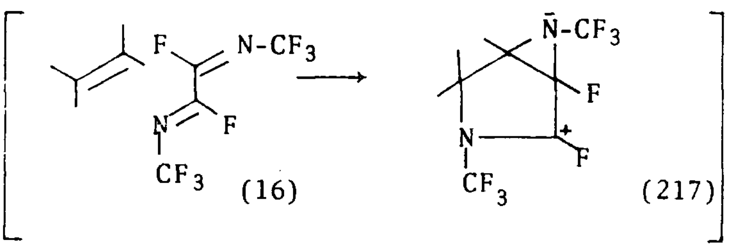
Obviously cycloaddition reactions have not occurred and the formation of the hydrocarbon products can be explained by an acid catalysed dimerization, since compound (16) is very susceptible to hydrolysis with subsequent elimination of HF, and even a minor amount of water would produce enough HF to promote dimerization.

Both reactions were repeated at 150°C for 24 hours using carefully dried precursors and, in both cases, a dry black residue was obtained from which no products could be isolated.

It is understandable that compound (16) does not behave in a manner similar to hexafluoroacetone azine (9) in its reactions with alkenes since this would involve the formation of an unusual intermediate (217), but it is not clear why [4 + 2] cycloadditions do not occur.



(9)



(16) (217)

5F HYDROLYSES

5F.1 Reaction with a 2:1 molar ratio of water

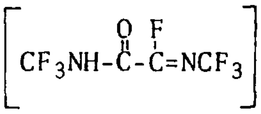
The reaction of compound (16) with a 2:1 molar ratio of water in sulpholane gave one product identified as N,N'-histrifluoromethyloxamide (44) from spectroscopic data, which were consistent with those reported in the literature.[48]

$$\underset{(16)}{CF_3N{=}CFCF{=}NCF_3} \xrightarrow[\substack{\text{SULPHOLANE} \\ \text{ROOM TEMP.}}]{2H_2O} \underset{(44)(82\%)}{CF_3NHCOCONHCF_3}$$

5F.2 Reaction with a 1:1 molar ratio of water

A similar reaction of (16) with a 1:1 molar ratio of water again gave compound (44) as the only product.

The hydrolysis of fluorinated aza-alkenes is well known (see section 2B.1) and proceeds via initial attack of H_2O followed by elimination of HF. Clearly the formation of (44) from (16) is quite consistent with this, although it is not immediately obvious why reaction with an equimolar amount of water does not lead to the partially hydrolysed product (218). It is probable, however, that the electron withdrawing effect of the adjacent carbonyl group in the intermediate (218) makes the remaining C=N bond even more susceptible to nucleophilic attack.



$$(16)\ \xrightarrow[-HF]{H_2O}\ \left[CF_3NH-\overset{\overset{O}{\|}}{C}-\overset{\overset{F}{|}}{C}=NCF_3\right]\ \xrightarrow{H_2O}\ (44)$$

(218)

CHAPTER 6

THE CHEMISTRY OF PERFLUORO-1,3-DIAZA-1-METHYLCYCLOPENT-2-ENE AND PERFLUORO-1,3-DIAZA-1-METHYLCYCLOPENT-3-ENE

6A INTRODUCTION

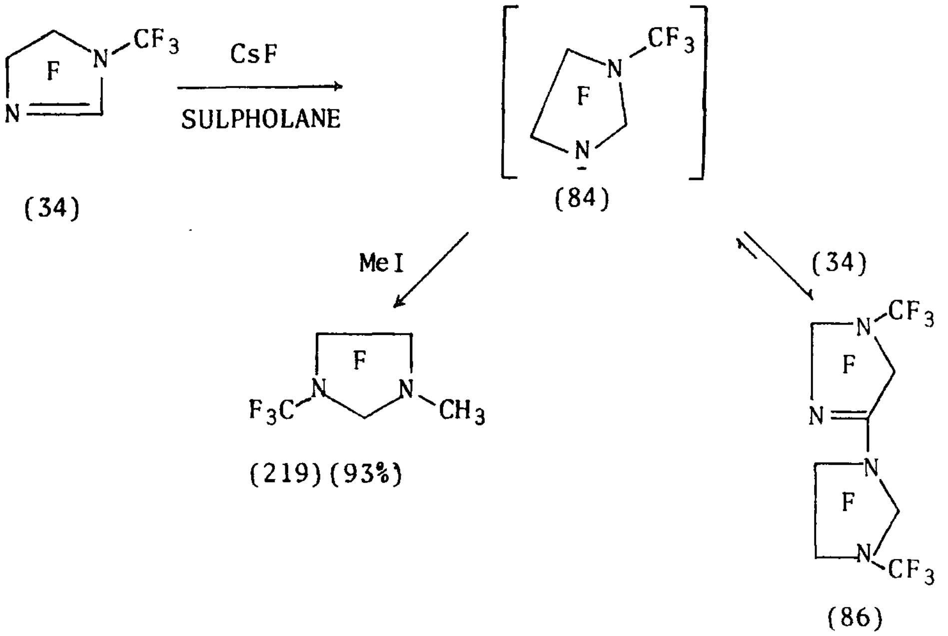
The diazacyclopentene derivatives (33) and (34) were previously only obtained as minor products from the dimerization of perfluoro-2,5-diazahexa-2,4-diene (16) (see section 1B.3) and consequently, their chemistry has not been explored. However, the new route to (33) and (34) via the vapour phase reaction of (16) with CsF (see section 5B.2) now makes this study possible.

In this chapter a preliminary investigation into the chemistry of compounds (33) and (34) is described.

6B FLUORIDE ION INDUCED REACTIONS

6B.1 Reaction of perfluoro-1,3-diaza-1-methylcyclopent-2-ene with caesium fluoride

The reaction of compound (34) with caesium fluoride in sulpholane gave complete conversion to a single dimer (86). An examination of the solvent layer by ^{19}F n.m.r. gave no indication of the intermediate nitranion (84), but addition of methyl iodide gave one product which was identified as 1-methyl-3-trifluoromethyl-2,2,4,4,5,5-hexafluoro-1,3-diazacyclopentane (219).

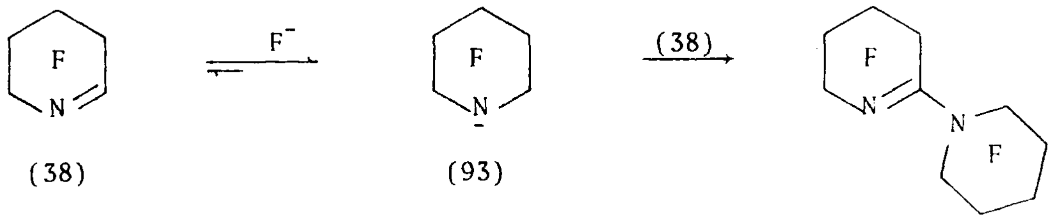


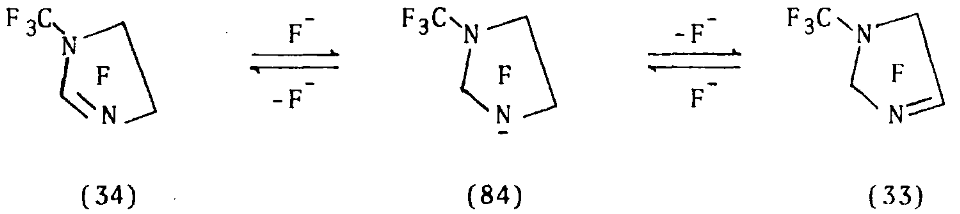
(34) (84) (219) (93%) (86)

The structure of (219) followed simply from spectroscopic data. Four signals in the ^{19}F n.m.r. spectrum in the ratio 3:2:2:2 and a singlet in the ^{1}H n.m.r. spectrum at 2.43 p.p.m., characteristic of a CH_3 group, were observed. A parent ion at $M^+ = 262$ in the mass spectrum and a single absorption at 2960 cm^{-1} in the infrared spectrum confirmed the structure.

The formation of (219) clearly demonstrates the existence of the nitranion intermediate (84), but the fact that this was not observed due to the rapid formation of the dimer (86) is in contrast to the related perfluoroazacyclohexyl anion (93) (see section 4C.2), where significant dimerization occurs only after a number of days.

The reason for this difference is not obvious, but it may be an indication of the difference in position of equilibrium between the two systems, since this was shown (section 4C.2) to be greatly in favour of the anion (93), which would make dimerization difficult as the amount of (38) present must be minimal.



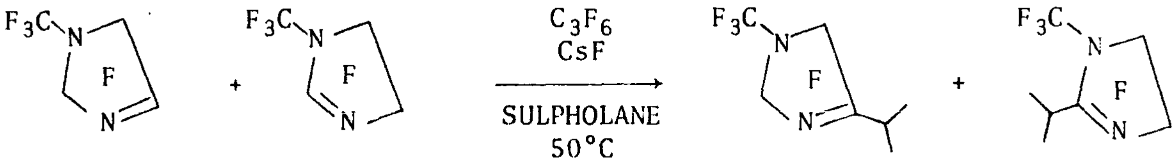


Similar differences in stability have been observed in cyclic carbanion systems and are attributed to eclipsing interactions.[130] Clearly, such interactions would be minimised in the nitranion (93).

Interestingly, the reaction has further demonstrated the use of dimer (86) as a convenient source of compounds (33) and (34) in fluoride ion induced reactions.

6B.2 Reaction of a mixture of perfluoro-1,3-diaza-1-methylcyclopentenes with hexafluoropropene in the presence of caesium fluoride

A 1:4 mixture of compounds (33) and (34) gave a complex mixture of products when reacted with an excess of hexafluoropropene, in the presence of caesium fluoride in sulpholane at 50°C. Separation gave dimers and trimers of hexafluoropropene, together with two other components identified from spectroscopic data as perfluoro-1,3-diaza-1-methyl-2-isopropylcyclopent-2-ene (220) and perfluoro-1,3-diaza-1-methyl-4-isopropylcyclopent-3-ene (221).

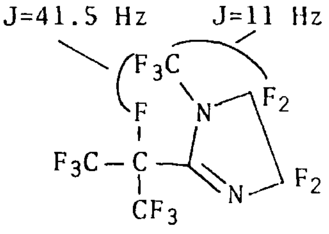


(33) (34) 1 : 4

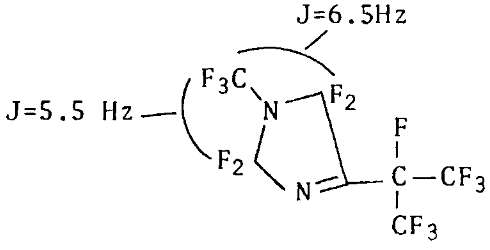
(221) (220) 1 : 3

(74% total yield)

The n.m.r. spectrum of (220) was similar to that of the parent compound (34). The absence of any signal due to a vinylic fluorine atom and the presence of signals at 77.0 (Int. 6) and 189.6 (Int. 1) p.p.m. indicated that this had been replaced by a perfluoroisopropyl group. A parent ion of $M^+ = 378$ in the mass spectrum and an absorption at 1648 cm^{-1} in the infrared spectrum supported this structure. These data could also be consistent with the isomer (221), however, the structure was unambiguously assigned on the basis of coupling constants in the n.m.r. spectrum.



(220)



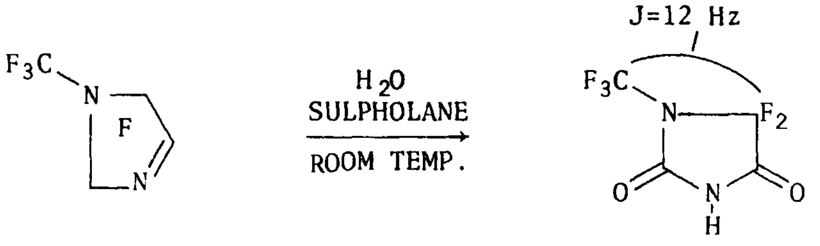
(221)

Similarly, the n.m.r. spectrum of (221) was not significantly different from that of the parent compound (33). Signals at 78.5 (Int. 6) and 196.6 (Int. 1) p.p.m. again indicated that the vinylic fluorine atom had been replaced by a perfluoroisopropyl group. Observed coupling constants, together with a parent ion of $M^+ = 378$ in the mass spectrum and an absorption at 1680 cm^{-1} in the infrared spectrum confirmed the structure.

6C HYDROLYSES

6C.1 Hydrolysis of perfluoro-1,3-diaza-1-methylcyclopent-3-ene

The reaction of perfluoro-1,3-diaza-1-methylcyclopent-3-ene (33) with an excess of water in sulpholane at room temperature gave one product identified as 1-trifluoromethyl-5,5-difluoro-1,3-diazacyclopenta-2,4-dione (222).

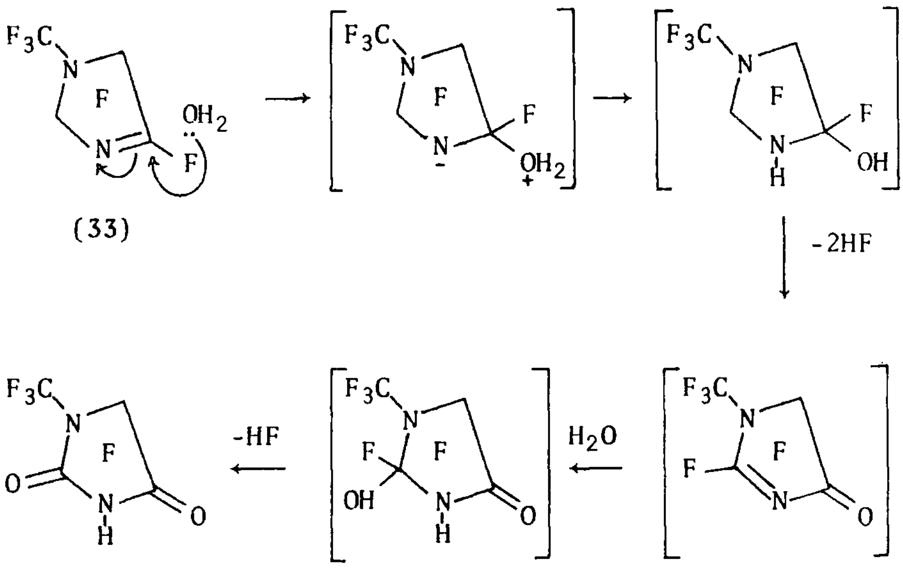


(33)

(222) (42%)

The structure of (222) followed simply from spectroscopic data, indeed the ^{19}F n.m.r. spectrum showed only two coupled signals at 58.3 (Int. 3) and 95.1 (Int. 2) p.p.m. and the ^{1}H n.m.r. spectrum showed only one broad signal at 4.9 p.p.m., characteristic of an N-H group. The structure was confirmed by a parent ion of M^+ = 204 in the mass spectrum and strong absorptions at 1788, 1844 and 3100 cm^{-1} in the infrared spectrum.

The probable mechanism for the reaction must involve initial attack by H_2O, followed by elimination of HF giving the intermediate (223), clearly this is further activated towards nucleophilic attack by a second molecule of water followed by further elimination of HF giving (222).



(33)

(222)

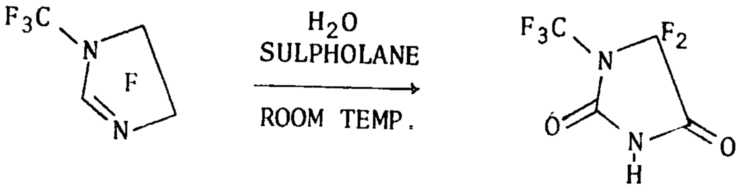
(223)

Interestingly the reaction has demonstrated addition-elimination involving loss of fluorine from both C2 and C4 positions, behaviour which is also shown by perfluoro-1-azacyclohex-1-ene (38) in its reactions with nucleophiles^{52} (see section 2B).

6C.2 Hydrolysis of perfluoro-1,3-diaza-1-methylcyclopent-2-ene

Similarly, the reaction of perfluoro-1,3-diaza-1-methylcyclopent-2-ene (34) with an excess of water in sulpholane at room temperature gave one product which was identified spectroscopically as compound (222), previously obtained from the hydrolysis of (33).

It is understandable that the same product is obtained from the hydrolysis of (33) and (34), since addition-elimination at both C2 and C4 positions in compound (34) would be expected to lead to (222) via a similar mechanism.



(34) (222) (38%)

EXPERIMENTAL

INSTRUMENTATION

Spectroscopic data were obtained using the following spectrometers: i.r., Perkin-Elmer 457 or 577; u.v., Pye Unicam S.P. 800; mass, A.E.I. MS9 or V.G. Micromass 12B linked with g.l.c.; n.m.r., Varian A56/60D, EM 360L, or Brüker HX90E. Chemical shifts are quoted relative to external trichlorofluoromethane and tetramethylsilane. G.l.c was carried out using a Varian Aerograph 920 fitted with a gas density balance detector or a Pye 104 fitted with a flame ionization detector. Three columns were used: Column O, 30% SE30 on Chromosorb G60-80; Column A, 20% di-isodecylphthalate on Chromosorb P; and Column Z, 17% 2-cyanoethylmethylsilicone on Chromosorb P. Fischer-Spaltrohr MMS 200 and HMS 500 columns were used for fractional distillation. Carbon, hydrogen, and nitrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Fluorine analyses were obtained using the literature method.[131]

CHAPTER 7

EXPERIMENTAL TO CHAPTER 3

7A COBALT TRIFLUORIDE FLUORINATIONS - GENERAL PROCEDURE

All 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 liquid air cooled trap.

7B PYRIDINE DERIVATIVES

7B.1 Perfluoro-4-isopropylpyridine (128)

Compound (128) (20.0 g, 62.7 mmol) was fluorinated at 118°C. The product (22.5 g) was shown by g.l.c. (Column A at 80°C) to consist of a complex mixture of liquids with two major components. Separation by preparative scale g.l.c. gave perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129) (60%) (Found: C, 26.9; F, 68.9; N, 4.2%. $C_8F_{13}N$ requires C, 26.9; F, 69.2; N, 3.9%). λ_{max}(cyclohexane) 231 nm (ε 5060), spectra no. 1, and perfluoro-1-aza-4-isopropylcyclohexa-1,4-diene (130) (18%) (Found: C, 26.7; F, 68.9; N, 4.3%. $C_8F_{13}N$ requires C, 26.9; F, 69.2; N, 3.9%). Spectra no.2. Minor components from a series of similar reactions were collected and separation by preparative scale g.l.c. gave perfluoro-1-aza-4-isopropyl-cyclohex-1-ene (131) (Found: C, 23.7; F, 71.8; N, 5.9%. $C_8F_{15}N$ requires C, 24.3; F, 72.2; N, 3.5%). Spectra no. 3.

7B.2 Perfluoro-2,4-di-isopropylpyridine (133)

(a) at 118°C

Compound (133) (9.5 g, 20.3 mmol) was fluorinated at 118°C. The product (10.5 g) was not completely separable by g.l.c. (Column A at 80°C and Column O at 120°C) but fractional distillation gave a mixture of perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,3-diene (134) (26%) and perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,4-diene (135) (26%), b.p. 142°C. (Found: C, 25.9; F, 70.7; N, 3.1%. Calculated for $C_{11}F_{19}N$: C, 26.0; F, 71.2; N, 2.8%.) Spectra no. 5, and perfluoro-1-aza-2,4-di-isopropylcyclohex-1-ene (136) (45%), b.p. 153°C. (Found: C, 23.9; F, 73.7; N, 2.9%. $C_{11}F_{21}N$ requires C, 24.2; F, 73.2, N, 2.6%.) Spectra no. 4.

(b) at 170°C

Compound (133) (17.1 g, 36.5 mmol) was fluorinated at 170°C. The product (17.5 g) was shown by g.l.c. (Column A at 80°C) to consist of one major component. Purification by fractional distillation gave perfluoro-1-aza-2,4-di-isopropylcyclohex-1-ene (136) (89%), identified by comparison of spectroscopic data with those of a sample obtained in a).

7B.3 Perfluoro-2,4,5-tri-isopropylpyridine (137)

Compound (137) (8.1 g, 13.1 mmol) was fluorinated at 138°C. The product (6.3 g) was shown by g.l.c. (Column A at 80°C) to consist of one major component. Purification by preparative scale g.l.c. gave perfluoro-1-aza-2,4,5-tri-isopropylcyclohexa-1,4-diene (138) (62%) (Found: F, 73.3%. $C_{14}F_{25}N$ requires F, 73.8%). Spectra no. 6.

7B.4 Perfluoro-2,4,6-tri-isopropylpyridine (139)

Compound (139) (7.0 g, 11.3 mmol) was fluorinated at 145°C. The product (4.8 g) was not completely separable by g.l.c. (Columns O and A at various temperatures) and fractional distillation proved unsuccessful. A detailed study by g.l.c.-m.s. showed two major components, the first of which (M^+, 657) was consistent with any of the dienes (140), (141), and (142), but the complexity of the mass spectrum suggested a mixture of all three. The second component (M^+, 695) was consistent with a mono-ene.

7C PYRIMIDINE DERIVATIVES

7C.1 Perfluoro-4,6-di-isopropylpyrimidine (143)

Compound (143) (13.4 g, 29.6 mmol) was fluorinated at 172°C. The product (13.5 g) was shown by g.l.c. (Column A at 60°C) to consist of one major component. Separation by fractional distillation gave perfluoro-1,3-diaza-4,6-di-isopropylcyclohexa-3,6-diene (144) (83%) b.p. 129°C, (Found: C, 24.8; F, 69.2; N, 5.6%. $C_{10}F_{18}N_2$ requires C, 24.5; F, 69.8; N, 5.7%). λ_{max}(cyclohexane) 263 nm (ϵ 380), spectra no.7.

7C.2 Perfluoro-2,4,6-tri-isopropylpyrimidine (148)

Compound (148) (20.2 g, 33.6 mmol) was fluorinated at 183°C. The product (18.5 g) was shown by g.l.c. (Column A at 90°C) to consist of a complex mixture of liquids with one major component. Separation by fractional distillation gave perfluoro-1,3-diaza-2,4,6-tri-isopropylcyclohexa-3,6-diene (149) (63%) (Found: F, 70.9%. $C_{13}F_{24}N$ requires F, 71.2%). λ_{max}(cyclohexane) 257 nm (ϵ 500), spectra no. 8.

7D PYRAZINE DERIVATIVES

7D.1 Perfluoro-2,5-di-isopropylpyrazine (151)

Compound (151) (12.8 g, 28.3 mmol) was fluorinated at 156°C. The product (11.6 g) was collected as a low melting white crystalline solid. Recrystallization (60°-80° petroleum ether) gave perfluoro-1,4-diaza-2,5-di-isopropylcyclohexa-1,4-diene (152) (87%) (Found: C, 24.5; F, 69.3; N, 6.3%. $C_{10}F_{18}N_2$ requires C, 24.5; F, 69.8; N, 5.7%). λ_{max}(cyclohexane) 256 nm (ε 220), spectra no. 9.

7E PYRIDAZINE DERIVATIVES

7E.1 Perfluoro-4,5-di-isopropylpyridazine (153)

Compound (153) (21.2 g, 46.9 mmol) was fluorinated at 163°C. The product (17.8 g) was shown by g.l.c. (Column A at 60°C) to be a mixture containing one major and two minor components. Fractional distillation gave perfluoro-2,3-dimethylpentane (154) (12%) b.p. 83°C. (Found: C, 21.9; F, 78.2%. C_7F_{16} requires C, 21.6; F, 78.4%), spectra no. 10, and perfluoro-2,3,4,5-tetramethylhex-3-ene (156, 157)(*cis* + *trans* isomers, 1:2.5) (53%) b.p. 126°C. (Found: C, 23.8; F, 76.2. Calculated for $C_{10}F_{20}$, C, 24,0; F, 76.0%). Spectra no. 12. Separation of the pot residue by preparative scale g.l.c. gave perfluoro-2,3,4,5-tetramethylhexane (155) (9%) (Found: C, 22.4; F, 77.3%. $C_{10}F_{22}$ requires C, 22.3; F, 77.7%). Spectra no. 11.

7F TOLUENE DERIVATIVES

7F.1 Perfluorotoluene (164)

Compound (164) (16.1 g, 68.2 mmol) was fluorinated at 68°C. The product (18.0 g) was shown by g.l.c. (Column Z at 60°C) to contain one major and three minor components. Separation by preparative scale g.l.c.

gave perfluoromethylcyclohexane (165) (11%), (Found: C, 24.2; F, 75.7%. C_7F_{14} requires C, 24.0; F, 76.0%), spectra no. 13, perfluoro-1-methylcyclohexene (166) (48%), (Found: C, 27.0; F, 73.2%. C_7F_{12} requires C, 26.9; F, 73.1%), spectra no. 14, perfluoro-1-methylcyclohexa-1,3-diene (167) (9%), (Found: C, 30.6; F, 69.2%. C_7F_{10} requires C, 30.7; F, 69.3%), λ_{max}(cyclohexane) 255 nm (ε 4833), spectra no.15, and perfluoro-1-methylcyclohexa-1,4-diene (168) (15%) (Found: C, 30.5; F, 69.1%. C_7F_{10} requires C, 30.7; F, 69.3%), λ_{max}(cyclohexane) 264 nm (ε 120), spectra no. 16.

7F.2 Perfluoro-4-isopropyltoluene (169)

Compound (169) (20.1 g, 52.1 mmol) was fluorinated at 83°C. The product (12.5 g) was shown by g.l.c. (Column Z at 95°C) to consist of two major and two minor components. Separation by preparative scale g.l.c. gave perfluoro-1-methyl-4-isopropylcyclohex-3-ene (172) (10%) (Found: C, 26.0; F, 73.7%. $C_{10}F_{18}$ requires C, 26.0; F, 74.0%), spectra no. 17, perfluoro-1-methyl-4-isopropylcyclohexa-1,3-diene (170) (25%) (Found: C, 28.5; F, 71.8%. $C_{10}F_{16}$ requires C, 28.3; F, 71.7%), λ_{max} (cyclohexane) 251 nm (ε 6871), spectra no. 18, and perfluoro-1-methyl-4-isopropylcyclohexa-1,4-diene (171) (25%) (Found: C, 28.3; F, 71.7%. $C_{10}F_{16}$ requires C, 28.3; F, 71.7%), λ_{max}(cyclohexane) 275 nm (ε 172), spectra no. 19. The fourth and most minor component was not isolated, however the mass spectrum was consistent with perfluoro-1-methyl-4-isopropylcyclohex-1-ene (173) (3%) (M^+, 462).

7F.3 Perfluoro-*m*-xylene (174)

Compound (174) (5.4 g, 18.9 mmol) was fluorinated at 80°C. Products (5.0 g) were shown by g.l.c. (Column A at room temperature) to consist of one major component. Purification by preparative scale g.l.c. gave a compound which was not unambiguously identified but spectroscopic data were consistent with perfluoro-1,3-dimethylcyclohex-1-ene (175) or perfluoro-1,3-dimethylcyclohex-3-ene (176) (66%) (Found: C, 25.1; F, 73.8%. Calculated for C_8F_{14}, C, 26.5; F, 73.5%). Spectra no. 20.

CHAPTER 8

EXPERIMENTAL TO CHAPTER 4

8A PHOTOCHEMISTRY

8A.1 Irradiations - General Procedure

All irradiations were carried out using a Rayonet R.P.R. 208 reactor equipped with eight 15 W low pressure mercury lamps emitting at 253.7 nm. Starting materials were transferred under vacuum into a 34 x 4 cm silica tube, degassed and sealed under high vacuum. After irradiation products were similarly transferred into a liquid air cooled trap attached to an inflatable bladder.

8A.2 Perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129)

Compound (129) (4.3 g, 12.0 mmol) was irradiated for 72 hours. The product (3.9 g) was shown by g.l.c. (Column A at 80°C) to consist of a mixture of liquids with one major component. Preparative scale g.l.c. gave perfluoro-1-(2-aza-allyl)-3-isopropylcyclobut-2-ene (182) (70%) (Found: C, 27.0; F, 69.3; N, 4.1%. $C_8F_{13}N$ requires C, 26.9; F, 69.2; N, 3.9%). Spectra no. 21.

In all subsequent experiments compound (182) could not be obtained in any significant quantity, and a new product (180) was obtained. A typical example is as follows:

Compound (129) (3.8 g, 10.6 mmol) was irradiated for 72 hours. The product (3.5 g) was shown by g.l.c. (Column A at 80°C) to consist of one major component. Preparative scale g.l.c. gave perfluoro-1-methylimino-3-isopropylcyclobut-2-ene (180) (87%) (Found: C, 27.2; F, 68.7; N, 4.1%. $C_8F_{13}N$ requires C, 26.9; F, 69.2; N, 3.9%). Spectra no. 22.

8A.3 Perfluoro-1,4-diaza-2,5-diisopropylcyclohexa-1,4-diene (152)

Compound (152) (3.2 g, 6.5 mmol) was irradiated for 340 hours. Products consisted of a gas (1.1 g), identified as perfluoroisobutyronitrile (185) (35%), by comparison of spectroscopic data with those of an authentic sample, and a liquid (1.9 g), shown by g.l.c. (Column A at 60°C) to consist of a minor amount of (185) and one major component. Preparative scale g.l.c. gave perfluoro-2-aza-3-isopropylbuta-1,3-diene (186) (58%) (Found: C, 24.2; F, 70.5; N, 4.7%. $C_6F_{11}N$ requires C, 24.4; F, 70.8; N, 4.7%). Spectra no. 23.

8A.4 Perfluoro-1,3-diaza-4,6-diisopropylcyclohexa-3,6-diene (144)

Compound (144) (3.7 g, 7.6 mmol) was irradiated for 140 hours. The product (3.5 g) was shown by g.l.c. (Column A at 60°C) to consist of four components. Preparative scale g.l.c. gave compounds (185) (11%) and (186) (17%) identified by comparison of spectroscopic data with samples obtained in 8A.3, and perfluoro-3,5-diaza-7-methyl-2-isopropylocta-1,3,5-triene (187) (48%) (Found: C, 24.7; F, 69.2; N, 6.2%. $C_{10}F_{18}N_2$ requires C, 24.5; F, 69.8; N, 5.7%). Spectra no. 24. The fourth component was identified as starting material (144) by comparison of spectroscopic data (yields based on amount of (144) consumed).

8A.5 Related compounds

(a) Perfluoro-1-aza-2,4-diisopropylcyclohex-1-ene (136)

Compound (136) (4.6 g, 8.4 mmol) was irradiated for 137 hours. The product (4.5 g) was shown by g.l.c. (Column A at 60°C) to consist of one component, identified spectroscopically as starting material (136) (98% recovery).

(b) Perfluoro-N,N'-bis-1,3-diazacyclohex-2-enyl (42)

Compound (42) (2.7 g, 6.5 mmol) was irradiated for 235 hours. The product (2.6 g) was shown by g.l.c. (Column A at 80°C) to consist of one component, identified spectroscopically as starting material (42) (96% recovery).

(c) Perfluoro-1-aza-4-isopropylcyclohexa-1,4-diene (130)

Compound (130) (2.0 g, 5.6 mmol) was irradiated for 70 hours. The product (1.9 g) was shown by g.l.c. (Column A at 60°C) to consist of one component, identified spectroscopically as starting material (130) (95% recovery).

8B THERMAL REACTIONS

8B.1 General procedure

Starting materials were added to a 30 x 2.5 cm oven dried nitrogen purged nickel tube which was sealed and heated to the required temperature in a Carius furnace. Products were obtained by transferring under vacuum into a liquid air cooled trap.

8B.2 Perfluoro-1,3-diaza-4,6-diisopropylcyclohexa-3,6-diene (144)

(a) at 275°C

Compound (144) (3.3 g, 6.7 mmol) was heated to 275°C for 16 hours. The product (2.4 g) was shown by g.l.c. (Column A at 60°C) to consist of two components, identified as starting material (144) and perfluoro-4,6-diisopropylpyrimidine (143) ($\sim$10% conversion) by comparison of g.l.c.-m.s. data.

(b) at 275°C with perfluoro-3,4-dimethylhexane

Compound (144) (2.9 g, 5.9 mmol) and perfluoro-3,4-dimethylhexane (∿0.2 g) were heated to 275°C for 16 hours. The product (2.0 g) was shown by g.l.c. (Column A at 60°C) to consist of two components similarly identified as starting material (144) and perfluoro-4,6-diisopropylpyrimidine (143) (∿50% conversion).

8B.3 Perfluoro-1,4-diaza-2,5-diisopropylcyclohexa-1,4-diene (152)

Compound (152) (3.3 g, 6.7 mmol) was heated to 275°C for 16 hours. The product (2.4 g) was shown by g.l.c. (Column A at 60°C) to consist of one component, identified spectroscopically as starting material (152) (72% recovery).

8C REACTIONS WITH FLUORIDE ION

8C.1 Perfluoro-1,1'-bis-1,3-diazacyclohex-2-enyl (42)

(a) in the absence of a solvent

Compound (42) (3.3 g, 7.9 mmol) was transferred under vacuum into a 10 ml Carius tube containing dry CsF (∿0.5 g). This was sealed under high vacuum and heated to 150°C for 16 hours with vigorous shaking. Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (2.3 g) was shown by g.l.c. (Column A at 80°C) to consist of two components. Separation by preparative scale g.l.c. gave starting material (42) and perfluoro-4-methyl-1,2,5,7-tetraazatricyclo[3.3.1.0$^{2\cdot6}$]undec-4-ene (188) (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. 25.

(b) in sulpholane

Compound (42) (1.1 g, 2.63 mmol) was transferred under vacuum into a 10 ml Carius tube containing dry CsF (∿0.5 g) and sulpholane (3 ml). This was sealed under high vacuum and heated to 120°C for 16 hours with vigorous shaking. Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (0.9 g) was shown by g.l.c. (Column A at 80°C) to consist of three components. Separation by preparative scale g.l.c. gave starting material (42), compound (188) (14%), and a new product (194) (42%) which was not identified. (Found: C, 22.8; F, 66.6; N, 9.9%. Calculated for $C_8N_3F_{15}$, C, 22.7; F, 67.3; N, 9.9%). Spectra no. 26.

8C.2 Perfluoro-1-azacyclohex-1-ene (38)

(a) in the absence of a solvent

Compound (38) (2.0 g, 8.2 mmol) was transferred under vacuum into a 5 ml Carius tube containing dry CsF (∿1.0 g). This was sealed under high vacuum and heated to 150°C for 64 hours with vigorous shaking. Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (1.9 g) was shown by g.l.c. (Column A at room temperature) to consist of one component, identified spectroscopically as starting material (38) (95% recovery).

(b) in sulpholane

Compound (38) (1.45 g, 5.9 mmol) was added to a 10 ml flask containing dry CsF (1.0 g, 6.6 mmol) and sulpholane (5 ml). This was stirred at room temperature for 38 hours. An n.m.r. spectrum of the homogeneous solution showed fairly sharp signals at 62.3, 127.1, and 131.1 p.p.m. which were assigned to the perfluoroazacyclohexyl anion (93). Exchange broadening was not observed on heating to 50°C. Addition of BF_3 etherate gave a solution which was shown by n.m.r. to contain only a small amount of (38). Other signals between 51 and 135 p.p.m. indicated that another species was present but these were not assigned.

8C.3 Perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129)

(a) in the absence of a solvent

Compound (129) (1.0 g, 2.8 mmol) was stirred with dry CsF (∿0.5 g) at room temperature for 20 hours. Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (0.9 g) was shown by n.m.r. to consist of a mixture of starting material (129) (83%) and the isomeric 1,4-diene (130) (17%).

(b) in acetonitrile

Compound (129) (2.0 g, 5.6 mmol) was added to a 10 ml flask containing dry CsF (1.0 g, 6.6 mmol) and acetonitrile (5 ml). This was stirred at room temperature for 25 hours and a sample of the resultant homogeneous solution was taken for subsequent n.m.r. experiments.

N.m.r. spectra were recorded at various temperatures betweem -30° and 50°C and observed signals were assigned to the nitranion (196) (section 4C.3). Addition of BF_3 etherate gave a solution which was shown by n.m.r. to contain an equilibrium mixture of starting material (129) and the isomeric 1,4-diene (130).

Methyl iodide (0.92 g, 6.5 mmol) was added to the remainder of the solution followed by stirring for 24 hours. Water (5 ml) was added and the lower fluorocarbon layer separated. The resultant liquid (1.7 g) was shown by g.l.c. (Column A at 70°C) to consist of one major component. Purification by preparative scale g.l.c. gave N-methyl-1-aza-4-perfluoroisopropyl-2,2,3,5,5,6,6-heptafluorocyclohex-3-ene (198) (65%) (Found: C, 27.4; H, 0.6; F, 67.7; N, 4.0%. $C_9F_{14}H_3N$ requires: C, 27.6; H, 0.8;

F, 68.0; N, 3.6%). Spectra no. 27.

(c) in sulpholane

An experiment identical to that described in (b) was carried out using sulpholane as solvent. N.m.r. studies showed that spectra were not significantly different from those obtained using acetonitrile at corresponding temperatures.

8D REACTIONS WITH DIAZOMETHANE

8D.1 General procedure

Diazomethane ether azeotrope, prepared from *p*-tolylsulphonylmethylnitrosamide by the literature method[132], was added slowly to a neat sample of the substrate at room temperature until a permanent yellow colour was established. Excess diazomethane and ether were allowed to evaporate off and products were obtained from the residual oil by vacuum sublimation.

8D.2 Perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129)

Compound (129) (2.6 g, 7.3 mmol) gave a yellow viscous liquid (1.8 g) on reaction with diazomethane. This was shown by g.l.c. (Column O at 200°C) to consist of five components. Separation by preparative scale g.l.c. gave only three pure components identified as 4-(perfluoroisopropyl)-2,2,3,3,5,6-hexafluoro-1-azabicyclo[4.1.0]hept-4-ene (199) (9%) (Found: C, 29.3; H, 0.25; F, 66.2; N, 3.9%. $C_9H_2F_{13}N$ requires: C, 29.1; H, 0.54; F, 66.6; N, 3.8%), spectra no. 28, 4-(perfluoroisopropyl)-2,2,3,3,5-pentafluoro-1,8,9-triazabicyclo[4.3.0]nona-4,6,8-triene (200) (14%) (Found: C, 28.5; H, 0.4; F, 60.6; N, 10.9%. $C_9HF_{12}N_3$ requires: C, 28.5; H, 0.26; F, 60.2; N, 11.1%), spectra no. 29, and 4-(perfluoroisopropyl)-

6-(fluoromethyl)-2,2,3,3,5-pentafluoro-1-azabicyclo[4.1.0]hept-4-ene (201) (29%) (Found: C, 31.3; H, 1.0; F, 63.8; N, 3.5%. $C_{10}H_4F_{13}N$ requires: C, 31.2; H, 1.04; F, 64.2; N, 3.6%), spectra no. 30.

8D.3 Perfluoro-1-aza-4-isopropylcyclohexa-1,4-diene (130)

Compound (130) (2.6 g, 7.3 mmol) gave a yellow viscous liquid (1.6 g) on reaction with diazomethane. This was shown by g.l.c. (Column O at 200°C) to be a complex mixture containing two major and at least five minor components. Separation by preparative scale g.l.c. gave two major components which were identified as compounds (201) (15%) and (200) (7%) previously obtained from the 1,3-diene (129).

8D.4 Perfluoro-1,3-diaza-4,6-diisopropylcyclohexa-3,6-diene (144)

Compound (144) (1.5 g, 5.7 mmol) gave a pale yellow viscous liquid (1.1 g) on reaction with diazomethane. This was shown by g.l.c. (Column O at 150°C) to consist of two components. Separation by preparative scale g.l.c. gave starting material (144) and 4,6-bis-(perfluoroisopropyl)-2,2,5,5-tetrafluoro-1,3-diazabicyclo[4.1.0]hept-3-ene (205) (53%) (Found: C, 26.3; H, 0.3; F, 68.2; N, 5.3%. $C_{11}H_2F_{18}N_2$ requires: C, 26.2; H, 0.4; F, 67.9; N, 5.5%). Spectra no. 31.

CHAPTER 9

EXPERIMENTAL TO CHAPTER 5

9A REACTIONS WITH FLUORIDE ION

9A.1 Reaction of perfluoro-2,5-diazahexa-2,4-diene (16) with alkali metal fluorides in sulpholane

(a) NaF

Compound (16) (3.2 g, 14.0 mmol) was stirred with NaF (∿1.0 g) in sulpholane (5 ml) for 70 hours at room temperature. Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (2.9 g) was shown by g.l.c. (Column A at 60°C) to contain two components. Separation by preparative scale g.l.c. gave the known dimers (82) (76%) (spectra no. 36) and (86) (24%) (spectra no. 35), identified by comparison of spectroscopic data with those reported in the literature.[21,38]

(b) KF

A similar experiment using KF gave the dimers (82) (43%) and (86) (50%) together with a third component identified as perfluorospiro-1,3,6,9-tetra-aza-3,6,9-trimethylnon-1-ene (206) (7%) (Found: C, 21.0; F, 66.6; N, 12.1%. $C_8F_{16}N_4$ requires: C, 21.1; F, 66.7; N, 12.3%). Spectra no. 37.

(c) CsF

Similarly, an experiment using CsF gave a mixture of dimers (82) (37%), (86) (57%), and (206) (6%).

9A.2 Vapour phase reaction of perfluoro-2,5-diazahexa-2,4-diene (16) with caesium fluoride

Compound (16) (10.9 g, 47.8 mmol) was passed through a silica tube containing caesium fluoride at 220°C in a flow of nitrogen (contact time $\sim$70s). The product was collected in a liquid air cooled trap. The resultant liquid (8.8 g) (81% recovery) was shown by g.l.c. (Column A at room temperature) to consist of two components. Separation by preparative scale g.l.c. gave the known compounds (33) (16%) (spectra no. 33) and (34) (65%) (spectra no. 34), identified by comparison of spectroscopic data with those reported in the literature.[38]

9A.3 Vapour phase reaction of a mixture of dimers with caesium fluoride

A mixture of dimers of compound (16) containing (86) (27%), (82) (67%), and (206) (6%) (5.5 g) was passed through a silica tube containing caesium fluoride at 220°C in a flow of nitrogen (contact time $\sim$15 s). The product was collected in a liquid air cooled trap. The resultant liquid (4.5 g) was shown by g.l.c. (Column A at 65°C) to consist of four components, identified as compounds (33) (10%), (34) (17%), (82) (67%) and (206) (6%) by comparison of g.l.c.-m.s. data.

9B DEFLUORINATION REACTIONS

9B.1 Reactions of perfluoro-2,5-diazahexa-2,4-diene (16) over hot metal surfaces

(a) with Fe filings in a flow system

Compound (16) (4.7 g, 20.6 mmol) was passed through a silica tube containing Fe filings at 340°C in a flow of nitrogen (contact time $\sim$30 s). The product was collected in a liquid air cooled trap. The resultant liquid (2.3 g) was shown by g.l.c. (Column A at 70°C) to consist of two components. Separation by preparative scale g.l.c. gave starting material (16) and perfluoro-N-methylimidazole (212) (30% based on g.l.c. analysis) (Found: C, 25.2; F, 59.7; N, 14.6%. $C_4F_6N_2$ requires: C, 25.3; F, 60.0; N, 14.8%). Spectra no. 39.

(b) with Pt metal in a flow system

Compound (16) (6.0 g, 26.3 mmol) was passed over Pt metal at 480°C in a similar flow system (contact time ∿35 s). The resultant liquid (5.3 g) (88% recovery) was shown by g.l.c. (Column A at 60°C) to consist of three components, identified as compounds (33) (11%), (34) (6%), and (16) (83%) by comparison of g.l.c.-m.s. data.

(c) with Ni turnings in a flow system

Compound (16) (4.5 g, 19.7 mmol) was passed over Ni turnings at 380°C in a similar flow system (contact time ∿40 s). The resultant liquid (4.2 g) (93% recovery) was shown by g.l.c. (Column A at 60°C) to consist of one component, identified spectroscopically as starting material (16).

(d) in a sealed Ni tube

Compound (16) (5.4 g, 23.7 mmol) was added to a 30 x 2.5 cm dry Ni tube, sealed and heated to 290°C for 18 hours. Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (4.5 g) (83% recovery) was shown by g.l.c. (Column A at 60°C) to consist of four components, identified as compounds (212) (9%), (33) (14%), (34) (38%), and (16) (39%) by comparison of g.l.c.-m.s. data.

(e) in a sealed Ni tube with Ni turnings

A similar reaction of compound (16) (5.5 g, 24.1 mmol) in a sealed Ni tube with Ni turnings (∿21 g) at 300°C for 18 hours, gave a product mixture (2.3 g) (42% recovery) containing compounds (212) (5%), (33) (9%), (34) (20%), and (16) (66%).

(f) in a sealed Ni tube with Fe filings

Similarly, compound (16) (5.5 g, 24.1 mmol) was heated to 300°C for 18 hours in a sealed Ni tube containing Fe filings (∿18 g). The product mixture (3.7 g) (67% recovery) was shown to contain compounds (212) (6%), (33) (13%), (34) (28%) and (16) (53%).

9C PHOTOCHEMISTRY

9C.1 Irradiation of perfluoro-2,5-diazahexa-2,4-diene (16)

(a) in the vapour phase

Compound (16) (4.2 g, 18.4 mmol) was transferred under vacuum into a 34 x 4 cm silica tube, degassed and sealed under high vacuum. This was irradiated for 46 hours (253.7 nm, low pressure Hg lamp). Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (3.9 g) (93% recovery) was shown by g.l.c. (Column A at 70°C) to consist of one component, identified spectroscopically as starting material (16).

(b) in n-pentane

Compound (16) (4.0 g, 17.5 mmol) was dissolved in n-pentane (100 ml) and irradiated using a broad band medium pressure Hg lamp. Samples were removed at 30 minute intervals and analysed by g.l.c. (Column A at 60°C). After 12.5 hours no significant decrease in the concentration of (16) could be observed. Examination of the resultant solution by n.m.r. confirmed that reaction had not taken place.

(c) in n-pentane with *p*-xylene

A similar irradiation of compound (16) with a 4:1 molar excess of *p*-xylene was carried out. The resultant solution was shown by n.m.r. to contain only starting materials.

9C.2 Irradiation of perfluoro-2,5-diazahexa-2,4-diene (16) in the presence of ketones

(a) with acetone

Compound (16) (4.7 g, 20.6 mmol) and dry acetone (1.2 g, 20.7 mmol) were transferred under vacuum into a 34 x 4 cm silica tube, degassed and sealed under high vacuum. This was irradiated for 29 hours (300 nm, Hg phosphor lamp). Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (5.6 g) was shown by g.l.c.-m.s. to contain only starting materials (95% recovery).

(b) with hexafluoroacetone

A similar irradiation of compound (16) with hexafluoroacetone was carried out. This led to a 94% recovery of starting material.

9D THERMAL REACTIONS WITH ALKENES

9D.1 with cyclohexene

(a) at 80°C

Perfluoro-2,5-diazahexa-2,4-diene (16) (4.0 g,17.5 mmol) was transferred under vacuum into a 50 ml Carius tube containing cyclohexene (1.44 g, 17.6 mmol). This was sealed under high vacuum and heated to

80°C for 100 hours. Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (4.4 g) consisted of two layers, the lower of which was shown by g.l.c. (Column A at 60°C) to consist of one component, identified spectroscopically as starting material (16). The upper layer was similarly shown to consist of one major component, the mass spectrum of which was consistent with a dimer of cyclohexene (M^+ = 164).

(b) at 150°C

A similar reaction of compound (16) (4.1 g, 18.0 mmol) with cyclohexene (1.5 g, 18.3 mmol) at 150°C using carefully dried precursors gave a dry black residue (4.0 g) from which products were not obtained.

9D.2 with 2-methylbut-2-ene

(a) at 80°C

A reaction similar to that described in 9D.1 (a) was carried out using compound (16) (4.3 g, 18.9 mmol) and 2-methylbut-2-ene (1.33 g, 19.0 mmol). The resultant liquid (4.5 g) consisted of two layers, the lower of which was again identified as unreacted (16) only. The upper layer was shown by g.l.c. (Column A at 100°C) to consist of several components, the mass spectra of which were consistent with dimers of 2-methylbut-2-ene (M^+ = 140)

(b) at 150°C

A similar reaction of compound (16) (4.1 g, 18.0 mmol) with 2-methylbut-2-ene (1.3 g, 18.6 mmol) at 150°C using carefully dried precursors gave a dry black residue (3.9 g) from which products were not obtained.

9E HYDROLYSES

9E.1 Reaction with a 2:1 molar ratio of water

Perfluoro-2,5-diazahexa-2,4-diene (16) (2.1 g, 9.2 mmol) was stirred with water (0.34 g, 18.9 mmol) in sulpholane (10 ml) at 15°C for 85 hours. The solution was extracted with ether (2 x 10 ml). Ether was allowed to evaporate off leaving a white solid (1.7 g) which, on vacuum sublimation, gave N,N'-bistrifluoromethyloxamide (44) (82%) (M^+, 224) (spectra no. 40), identified by comparison of spectroscopic data with those reported in the literature.[48]

9E.2 Reaction with a 1:1 molar ratio of water

A similar reaction of compound (16) (2.1 g, 9.2 mmol) with water (0.17 g, 9.4 mmol) again gave compound (44) (77%) as the only product.

CHAPTER 10

EXPERIMENTAL TO CHAPTER 6

10A FLUORIDE ION INDUCED REACTIONS

10A.1 Reaction of perfluoro-1,3-diaza-1-methylcyclopent-2-ene (34) with caesium fluoride

Compound (34) (2.1 g, 9.2 mmol) was stirred with dry caesium fluoride (1.35 g, 9.5 mmol) in sulpholane (3 ml) at room temperature. After ∿30 minutes a lower fluorocarbon layer was observed which was shown by n.m.r. to contain the dimer (86) only. Examination of the upper solvent layer by n.m.r. gave no indication of the intermediate nitranion (84). Methyl iodide (1.35 g, 9.5 mmol) was added and the solution stirred for a further 22 hours. Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (2.2 g) was shown by g.l.c. (Column A at 80°C) to consist of one major component. Purification by preparative scale g.l.c. gave <u>1-methyl-3-trifluoromethyl-2,2,4,4,5,5-hexafluoro-1,3-diazacyclopentane</u> (219) (93%) (Found: C, 23.1, H, 1.3; F, 64.8; N, 10.6%. $C_5H_3F_9N_2$ requires: C, 22.9; H, 1.2; F, 65.3; N, 10.7%). Spectra no. 38.

10A.2 Reaction of a mixture of perfluoro-1,3-diaza-1-methylcyclopentenes (33) and (34) with hexafluoropropene in the presence of fluoride ion

Caesium fluoride (∿1 g) and sulpholane (5 ml) were added to a nitrogen purged 25 ml flask which was evacuated and exposed to an atmosphere of hexafluoropropene (3.8 g, 25.3 mmol) stored in a bladder. The mixture was heated to 50°C with stirring. After ∿15 minutes a 1:4 mixture of compounds (33) and (34) (1.5 g) was injected through a septum and stirring was continued for a further 20 hours. Volatile material was vacuum transferred into a liquid air cooled trap. The resultant liquid (3.4 g) was shown by g.l.c. (Column A at room temperature) to consist of a complex mixture of liquids with six components. Separation by preparative scale g.l.c. gave dimers and trimers of hexafluoropropene, together with perfluoro-1,3-diaza-1-methyl-4-isopropylcyclopent-3-ene (221) (Found: C, 22.2; F, 70.2; N, 7.8%. $C_7F_{14}N_2$ requires: C, 22.2; F, 70.4; N, 7.4%), spectra no. 41, and perfluoro-1,3-diaza-1-methyl-2-isopropylcyclopent-2-ene (220) (Found: C, 22.3; F, 70.6; N, 7.7%. $C_7F_{14}N_2$ requires: C, 22.2; F, 70.4; N, 7.4%), spectra no. 42. (1:3 ratio, total yield 74%).

10B HYDROLYSES

10B.1 Hydrolysis of perfluoro-1,3-diaza-1-methylcyclopent-3-ene (33)

Compound (33) (0.80 g, 3.51 mmol) was stirred with water (0.2 g, 11.1 mmol) in sulpholane (3 ml) at 15°C for 60 hours. The solution was extracted with ether (2 x 3 ml). Ether was allowed to evaporate off leaving a white solid (0.3 g). Purification by vacuum sublimation gave 1-trifluoromethyl-5,5-difluoro-1,3-diazacyclopenta-2,4-dione (222) (42%) (Found: C, 23.7; H, 0.6; F, 46.3; N, 13.6%. $C_4HF_5N_2O_2$ requires: C, 23.5; H, 0.5; F, 46.6; N, 13.7%). Spectra no. 43.

10B.2 Hydrolysis of perfluoro-1,3-diaza-1-methylcyclopent-2-ene (34)

A similar reaction of compound (34) (1.16 g, 5.1 mmol) with water (0.2 g, 11.1 mmol) gave compound (222) (38%), identified by comparison of spectroscopic data, as the only product.

APPENDICES

COMPOUND INDEX

Spectra no.

1) Perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129)

2) Perfluoro-1-aza-4-isopropylcyclohexa-1,4-diene (130)

3) Perfluoro-1-aza-4-isopropylcyclohex-1-ene (131)

4) Perfluoro-1-aza-2,4-di-isopropylcyclohex-1-ene (136)

5) Perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,3-diene (134) and perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,4-diene (135)

6) Perfluoro-1-aza-2,4,5-tri-isopropylcyclohexa-1,4-diene (138)

7) Perfluoro-1,3-diaza-4,6-di-isopropylcyclohexa-3,6-diene (144)

8) Perfluoro-1,3-diaza-2,4,6-tri-isopropylcyclohexa-3,6-diene (149)

9) Perfluoro-1,4-diaza-2,5-di-isopropylcyclohexa-1,4-diene (152)

10) Perfluoro-2,3-dimethylpentane (154)

11) Perfluoro-2,3,4,5-tetramethylhexane (155)

12) *Cis*(156)- and *trans*(157)-perfluoro-2,3,4,5-tetramethylhex-3-ene

13) Perfluoromethylcyclohexane (165)

14) Perfluoro-1-methylcyclohexene (166)

15) Perfluoro-1-methylcyclohexa-1,3-diene (167)

16) Perfluoro-1-methylcyclohexa-1,4-diene (168)

17) Perfluoro-1-methyl-4-isopropylcyclohex-3-ene (172)

18) Perfluoro-1-methyl-4-isopropylcyclohexa-1,3-diene (170)

19) Perfluoro-1-methyl-4-isopropylcyclohexa-1,4-diene (171)

20) Perfluoro-1,3-dimethylcyclohex-1-ene (175) or perfluoro-1,3-dimethylcyclohex-3-ene (176)

21) Perfluoro-1-(2-aza-allyl)-3-isopropylcyclobut-2-ene (182)

22) Perfluoro-1-(methylimino)-3-isopropylcyclobut-2-ene (180)

23) Perfluoro-2-aza-3-isopropylbutadiene (186)

24) Perfluoro-3,5-diaza-2-isopropyl-7-methylocta-1,3,5-triene (187)
25) Perfluoro-4-methyl-1,2,5,7-tetra-azatricyclo[3.3.1.$0^{2\cdot 6}$]undec-4-ene (188)
26) Compound (194). Structure unknown
27) N-Methyl-1-aza-4-(perfluoroisopropyl)-2,2,3,5,5,6,6-heptafluorocyclohex-3-ene (198)
28) 4-(Perfluoroisopropyl)-2,2,3,3,5,6-hexafluoro-1-azabicyclo[4.1.0]-hept-4-ene (199)
29) 4-(Perfluoroisopropyl)-2,2,3,3,5-pentafluoro-1,8,9-triazabicyclo-[4.3.0]nona-4,6,8-triene (200)
30) 4-(Perfluoroisopropyl)-6-(fluoromethyl)-2,2,3,3,5-pentafluoro-1-azabicyclo[4.1.0]hept-4-ene (201)
31) 4,6-Bis(perfluoroisopropyl)-2,2,5,5-tetrafluoro-1,3-diazabicyclo-[4.1.0]hept-3-ene (205)
32) Perfluoro-2,5-diazahexa-2,4-diene (16)
33) Perfluoro-1,3-diaza-1-methylcyclopent-3-ene (33)
34) Perfluoro-1,3-diaza-1-methylcyclopent-2-ene (34)
35) Perfluoro-4-(3-methyl-1-imidazolidinyl)-1-methyl-2,5-dihydroimidazole (86)
36) Perfluoro-1,3-dimethyl-2-methyliminomethyl-5-methyliminotetrahydroimidazole (82)
37) Perfluorospiro-1,3,6,9-tetra-aza-3,6,9-trimethylnon-1-ene (206)
38) 1-Methyl-3-trifluoromethyl-2,2,4,4,5,5-hexafluoro-1,3-diazacyclopentane (219)
39) Perfluoro-N-methylimidazole (212)
40) N,N'-Bistrifluoromethyloxamide (44)
41) Perfluoro-1,3-diaza-1-methyl-4-isopropylcyclopent-3-ene (221)
42) Perfluoro-1,3-diaza-1-methyl-2-isopropylcyclopent-2-ene (220)
43) 1-Trifluoromethyl-5,5-difluoro-1,3-diazacyclopenta-2,4-dione (222)

APPENDIX I

N.M.R. SPECTRA

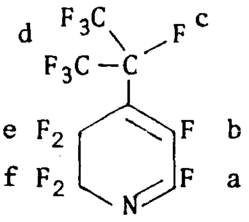
The following abbreviations are used in this appendix:

S, singlet; D, doublet; T, triplet; Q, quartet; Qu, quintet; Sp, septet; M, multiplet.

Unless otherwise stated spectra were recorded as neat liquids using $CFCl_3$ and TMS as external references for ^{19}F and ^{1}H spectra respectively.

For ^{19}F spectra upfield shifts are quoted as positive whilst for ^{1}H spectra, downfield shifts are quoted as positive (delta scale).

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
1. Perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (129)			
52.5	D, $J_{ab} = 20$	1	a
76.8	Broad M	6	d
102.8	Broad S	2	f
107.2	D, $J_{ba} = 20$ of M	1	b
114.5	D, $J_{ec} = 35$ of M	2	e
185.0	Broad	1	c



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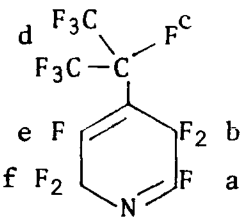
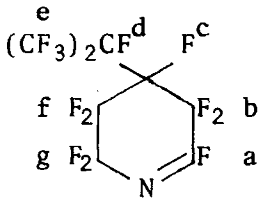


(130)

2. Perfluoro-1-aza-4-isopropylcyclohexa-1,4-diene (130)

57.8	T, $J_{ab} = 26$	1	a
77.6	Broad M	6	d
88.6	D, $J_{ec} = 20$	2	f
100.2	Broad M	1	e
103.0	Broad M	2	b
188.2	Broad M	1	c

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
3. Perfluoro-1-aza-4-isopropylcyclohex-1-ene (131)			
55.9	T, J_{ab} = 29	1	a
73.2	M	6	e
89.9, 98.0	J_{AB} = 249	2	g
112.1, 117.7	J_{AB} = 317	2	b or f
120.1, 129.8	J_{AB} = 308	2	f or b
181.3	Broad	1	c or d
184.3	Broad	1	d or c
4. Perfluoro-1-aza-2,4-di-isopropylcyclohex-1-ene (136)			
72.3	Broad M	6	b or f
76.1	M	6	f or b
90.8, 101.0	J_{AB} = 258	2	h
103.5, 112.8	J_{AB} = 336	2	c or g
119.6, 130.2	J_{AB} = 290	2	g or c
179.6	Broad	1	d or e
183.2	Broad	1	e or d
191.0	Broad M	1	a



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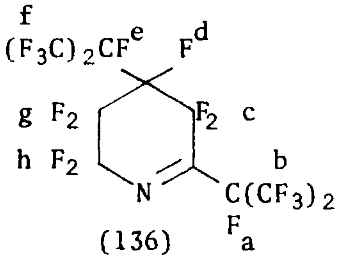
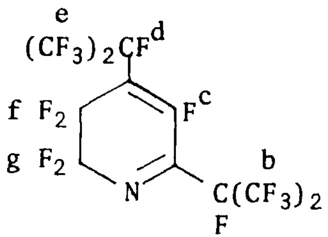


(136)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
5. Perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,3-diene (134) and perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,4-diene (135)			
75.5	M	6	b, e, b' or e'
76.5	M	6	b, e, b' or e'
76.8	M	6	b, e, b' or e'
77.6	M	6	b, e, b' or e'
91.1	D, $J_{g'f'}$ = 26	2	g'
98.4	Broad	2	c'
101.2	Broad M	1	c or f'
103.0	Broad	1	c or f'
110.1	T, J_{gf} = 7	2	g
119.2	Broad M	2	f
184.3	Broad	1	d or d'
186.6	Broad	1	d or d'
187.9	Broad	1	a or a'
191.6	Broad	1	a or a'



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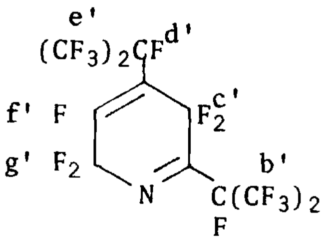
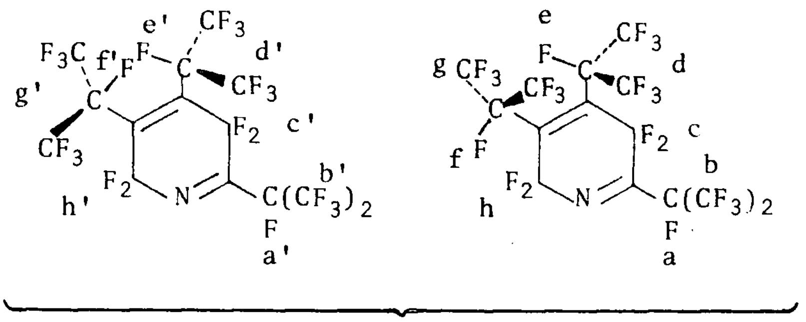


(135)

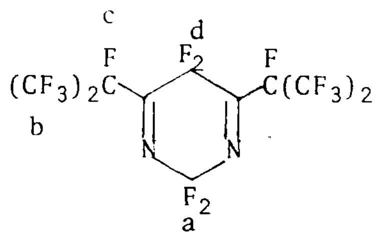
Recorded as an inspeparable 1:1 mixture of isomers.

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
6. Perfluoro-1-aza-2,4,5-tri-isopropylcyclohexa-1,4-diene (138)			
67.9	Broad	2	h and h'
70.8	Broad M	12	d, g, d' and g'
74.7	Broad M	6	b and b'
98.9	D, $J_{a'c'}$ = 38	2	c'
99.9	D, J_{ac} = 38		c
159.6, 164.7	J_{AB} = 176	-	e' and f'
161.8	T, J_{fh} = 75	-	f
170.9	Sp, J_{eg} = 58	-	e
190.3	T, $J_{aca'c'}$ = 38	1	a and a'

Recorded as a 2:1 mixture of rotational isomers at room temperature



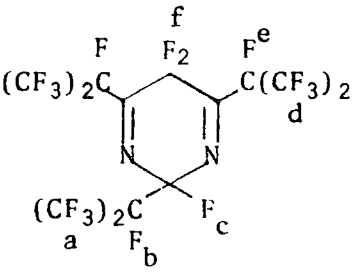
(138) 2:1 at room temperature



(144)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
7. Perfluoro-1,3-diaza-4,6-di-isopropylcyclohexa-3,6-diene (144)			
73.2	S	2	a
77.2	M	12	b
113.9	T, J_{dc} = 30	2	d
193.5	T, J_{cd} = 30 of Sp, J_{cb} = 6	2	c

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
8. Perfluoro-1,3-diaza-2,4,6-tri-isopropylcyclohexa-3,6-diene (149)			
73.7	Broad M	6	a
76.5	Broad M	12	d
110.6	Q, J_{fe} = 32	2	f
113.0	Broad	1	c
184.7	Broad	1	b
191.7	T, J_{ef} = 32 of Sp, J_{ed} = 6	1	e



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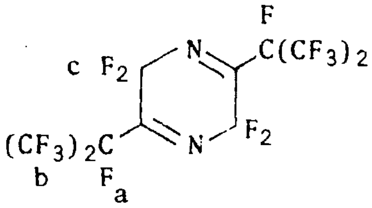

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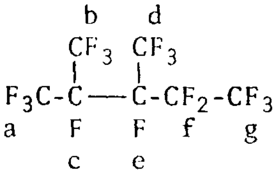

$F_3C-C(CF_3)F-C(CF_3)F-CF_2-CF_3$

(154)

9. Perfluoro-1,4-diaza-2,5-di-isopropylcyclohexa-1,4-diene (152)

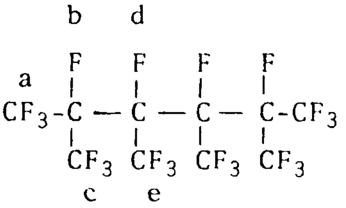
Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
76.6	M	12	b
88.5	D, J_{ca} = 29	4	c
191.3	T, J_{ac} = 29 of Sp, J_{ab} = 6	2	a

Recorded as a solution in d_6-acetone

10. Perfluoro-2,3-dimethylpentane (154)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
71.9	Broad M	9	a, b, and d
82.4	D, J_{gf} = 19	3	g
115.1	Broad M	2	f
177.9	Broad	1	c or e
181.8	Broad	1	e or c

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
11. Perfluoro-2,3,4,5-tetramethylhexane (155)			
69.0	Broad	6	e
72.1	Broad	12	a and c
166.6	Broad	2	b or c
170.3	Broad	2	d or b



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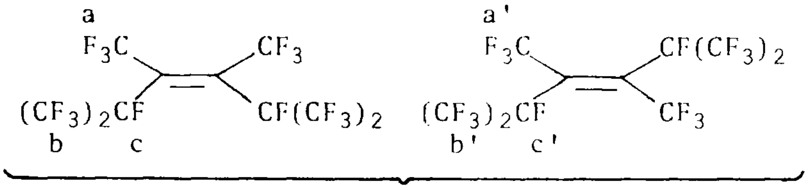

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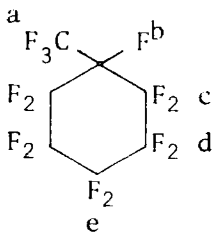
(156) (157)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
12. *Cis*(156)- and *trans*(157)-perfluoro-2,3,4,5-tetramethylhex-3-ene			
56.6	Broad	6	a
57.6	Broad		a'
72.3	Broad M	12	b and b'
159.3	Broad	2	c
161.4	Q, $J_{a'c'} = 50$		c'

Recorded as a 1:2.5 mixture of isomers

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
13. Perfluoromethylcyclohexane (165)			
71.8	D, $J_{ab} = 6$ of T, $J_{ac} = 14$	3	a
122.8, 133.6	$J_{AB} = 295$	4	c or d
125.2, 142.5	$J_{AB} = 289$	4	d or c
126.7, 144.6	$J_{AB} = 292$	2	e
190.8	Broad	1	b



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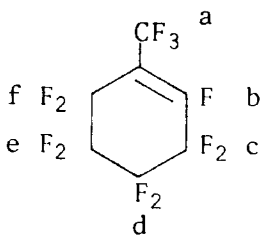
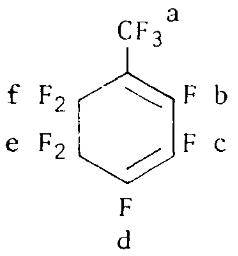


(166)

14. Perfluoro-1-methylcyclohexene (166)			
61.2	D, $J_{ab} = 21$ of T, $J_{af} = 8$	3	a
112.5	Broad	2	f
114.4	Broad	1	b
123.3	D, $J_{cb} = 19$	2	c
137.1	S	4	d and e

15. Perfluoro-1-methylcyclohexa-1,3-diene (167)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
56.9	D, J_{ab} = 24 of T, J_{ac} = 7	3	a
108.0	Broad M	1	b
116.6	Broad	2	f
124.3	T, J_{ef} = 17	2	e
149.1	M	1	c or d
151.0	M	1	d or c



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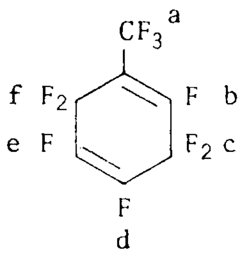
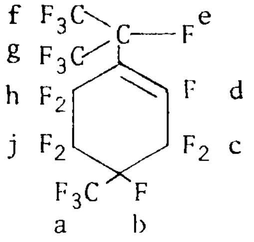


(168)

16. Perfluoro-1-methylcyclohexa-1,4-diene (168)

61.2	D, J_{ab} = 18 of T, J_{af} = 8	3	a
106.4	Broad M	2	f
115.9	Broad M	2	c
117.8	Broad M	1	b
155.6	M	1	e or d
161.4	M	1	d or e

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
17. Perfluoro-1-methyl-4-isopropylcyclohex-3-ene (172)			
73.1	M	3	a
76.9	D, J_{gh} = 28 of M	3	g
78.2	M	3	f
106.6	Broad	1	d
100.3, 117.2	J_{AB} = 286	2	h
114.2, 119.9	J_{AB} = 314	2	c
120.7, 136.4	J_{AB} = 296	2	j
185.5	D, J_{ed} = 52	1	e
188.7	M	1	b



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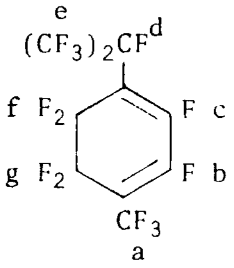

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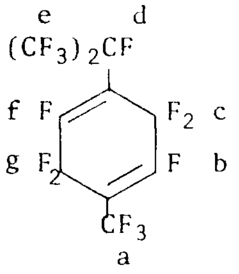
Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
18. Perfluoro-1-methyl-4-isopropylcyclohexa-1,3-diene (170)			
61.0	D, J_{ab} = 24 of T, J_{af} = 7	3	a
77.0	D, J_{ec} = 18 of M	6	e
105.5	M	1	c
112.4	M	1	b
118.1	Broad	2	f
120.2	Broad	2	g
184.2	Broad	1	d

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
19. Perfluoro-1-methyl-4-isopropylcyclohexa-1,4-diene (171)			
60.7	D, J_{ab} = 19 of T, J_{ag} = 8	3	a
77.3	D, J_{ef} = 24	6	e
103.5	Broad	2	c
105.6	Broad	2	g
106.0	V. Broad	1	f
113.1	Broad M	1	b
187.4	T, J_{dc} = 37 of M	1	d



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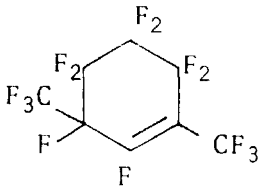

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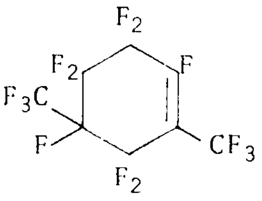
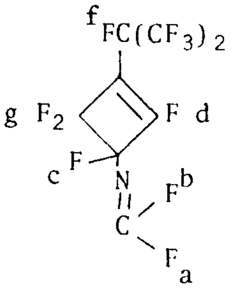


(176)

20. Perfluoro-1,3-dimethylcyclohex-1-ene (175) or perfluoro-1,3-dimethylcyclohex-3-ene (176)

62.3	M	3	-
74.4	M	3	-
103.6	M	1	-
104.9, 123.8	J_{AB} = 293	2	-
127.4, 137.0	J_{AB} = 304	2	-
128.7, 148.6	J_{AB} = 298	2	-
176.3	Broad	1	-

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
21. Perfluoro-1-(2-aza-allyl)-3-isopropylcyclobut-2-ene (182)			
32.9	V. Broad	1	a or b
51.2	V. Broad	1	b or a
78.2	M	6	e
96.1	Broad	1	d
114.0	Broad M	2	g
136.7	D, J_{cd} = 19 of T, J_{cg} = 7.5	1	c
186.4	Broad	1	f



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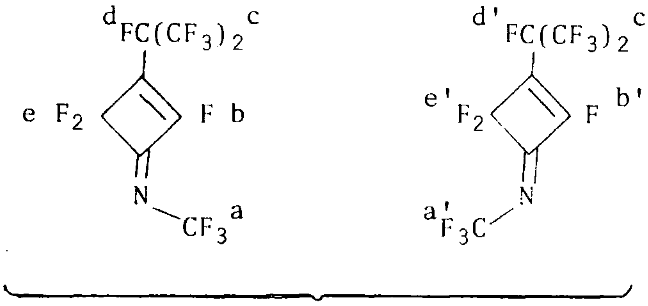


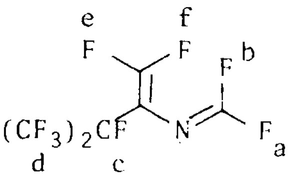
(180) 1:2

22. Perfluoro-1-(methylimino)-3-isopropylcyclobut-2-ene (180)

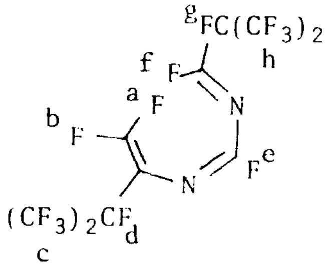
62.1	D, J_{ab} = 18	3	a
62.7	T, $J_{a'e'}$ = 8		a'
79.9	M	6	c and c'
80.9	Broad	1	b
89.8	Broad		b'
104.4	Broad M	2	e'
112.2	M		e
187.7	Broad M	1	d and d'

Recorded as an inseparable mixture of isomers

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
23. Perfluoro-2-aza-3-isopropylbutadiene (186)			
42.6	V. Broad	1	a or b
55.9	V. Broad	1	b or a
78.9	S	6	d
83.1	D, J_{fe} = 29 of T, J_{fab} = 15	1	f
93.0	D, J_{ec} = 59 of D, J_{fe} = 29	1	e
187.0	D, J_{ce} = 59	1	c



(186)

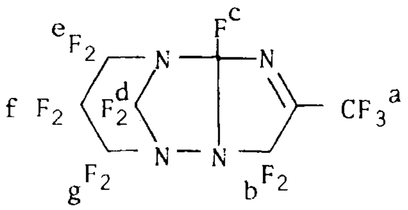


(187)

24. Perfluoro-3,5-diaza-2-isopropyl-7-methylocta-1,3,5-triene (187)

41.8	Broad	2	e and f
76.6	Broad M	6	c or h
77.7	D, J_{ab} = 26	1	a
77.9	Broad M	6	h or c
91.3	D, J_{bd} = 62 of D, J_{ba} = 26	1	b
182.2	Broad M	1	g
185.9	D, J_{db} = 62	1	d

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
25. Perfluoro-4-methyl-1,2,5,7-tetra-azatricyclo[3.3.1.$0^{2\cdot6}$]undec-4-ene (188)			
60.5	S	3	a
89.9, 100.5	J_{AB} = 230	2	d
105.8, 108.7	J_{AB} = 186	2	b, e, f and g
132.2, 141.0	J_{AB} = 259	2	
94.6	D, J = 146	1	
117.5	D, J = 146	1	
127.1	S	2	
107.5	S	1	c

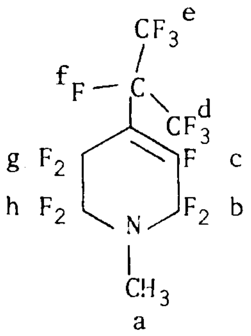


(188)

26. Compound (194). Structure unknown

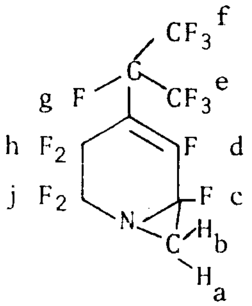
56.9	T, J = 13	3	-
95.3	S	2	-
99.5	S	2	-
101.8	S	4	-
139.0	S	2	-
141.6	S	2	-

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
27. N-Methyl-1-aza-4-(perfluoroisopropyl)-2,2,3,5,5,6,6-heptafluorocyclohex-3-ene (198)			
^{19}F			
76.9	Q, J_{de} = 5	3	d or e
77.3	Q, J_{ed} = 5	3	e or d
89.5	D, J_{gf} = 22 of T, J_{gh} = 7	2	g
103.7	Broad	2	h
105.7	Broad M	1	c
111.5	D, J_{bc} = 28	2	b
186.1	Broad M	1	f
^{1}H			
1.90	S	-	a



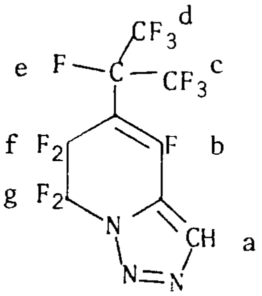
(198)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
28. 4-(Perfluoroisopropyl)-2,2,3,3,5,6-hexafluoro-1-azabicyclo[4.1.0]-hept-4-ene (199)			
^{19}F			
76.4	M	3	e or f
77.7	M	3	f or e
88.4, 109.7	$J_{AB} = 207$	2	j
88.6	Broad M	1	d
103.2	Broad	2	h
169.5	D, $J_{cd} = 23$	1	c
183.9	Broad	1	g
^{1}H			
2.47	S	1	a or b
2.63	S	1	b or a



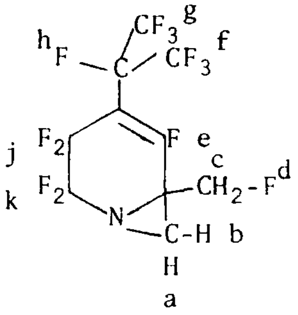
(199)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
29. 4-(Perfluoroisopropyl)-2,2,3,3,5-pentafluoro-1,8,9-triazabicyclo-[4.3.0]nona-4,6,8-triene (200)			
^{19}F			
75.8	Q, J_{cd} = 5.5	3	c or d
76.2	Q, J_{dc} = 5.5	3	d or c
101.1	Broad M	1	b
101.7	T, J_{gf} = 4	2	g
109.1	D, J_{fe} = 30 of M	2	f
182.9	T, J_{ef} = 30	1	e
^{1}H			
7.88	S	-	a



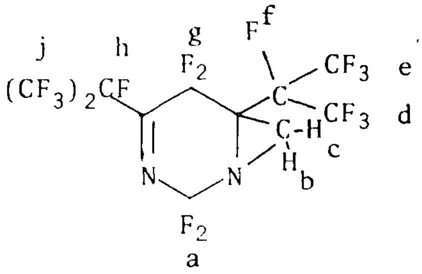
(200)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
30. 4-(Perfluoroisopropyl)-6-(fluoromethyl)-2,2,3,3,5-pentafluoro-1-azabicyclo[4.1.0]hept-4-ene (201)			
^{19}F			
75.3	M	3	g or f
77.2	M	3	f or g
80.8	Broad	1	e
84.8, 106.1	J_{AB} = 207	2	k
96.9, 101.6	J_{AB} = 284	2	j
183.3	Broad	1	h
225.6	T, J_{dc} = 44	1	d
^{1}H			
2.48	S	1	a or b
2.63	S	1	b or a
4.40	D, J_{cd} = 44 of D, J_{ce} = 11	2	c

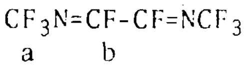


(201)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
31. 4,6-Bis(perfluoroisopropyl)-2,2,5,5-tetrafluoro-1,3-diazabicyclo[4.1.0]-hept-3-ene (205)			
^{19}F			
63.3, 71.1	J_{AB} = 211	2	a
74.5	M	3	d or c
76.4	M	6	j
76.6	M	3	e or d
99.5	Broad	2	g
184.7	Broad M	1	f
189.6	Broad M	1	h
^{1}H			
1.73	S	1	c or b
2.37	S	1	b or c



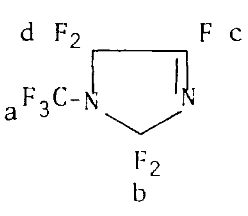
(205)


$$\underset{a}{CF_3}N{=}\underset{b}{CF}{-}CF{=}NCF_3$$

(16)

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
32. Perfluoro-2,5-diazahexa-2,4-diene (16)			
27.5	Q, J_{ba} = 14	2	b
59.7	D, J_{ab} = 14	6	a

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
33. Perfluoro-1,3-diaza-1-methylcyclopent-3-ene (33)			
59.9	M	3	a
73.7	Broad	2	b
84.8	T, J_{cd} = 15	1	c
93.6	Broad M	2	d



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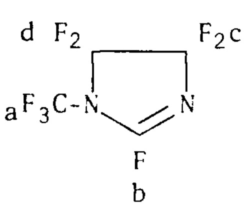

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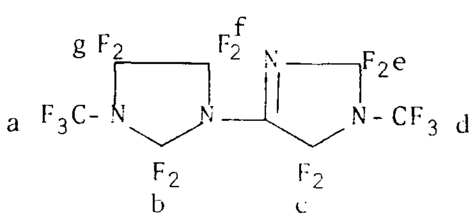
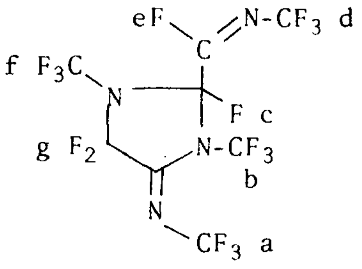


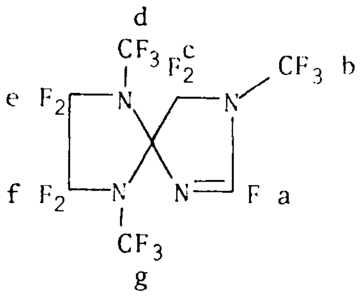
(86)

34. Perfluoro-1,3-diaza-1-methylcyclopent-2-ene (34)			
59.7	D, J_{ab} = 11 of T, J_{ad} = 7	3	a
75.2	Broad S	1	b
98.8	Broad S	2	c
102.0	Q, J_{da} = 7	2	d
35. Perfluoro-4-(3-methyl-1-imidazolidinyl)-1-methyl-2,5-dihydroimidazole (86)			
57.2	Qu, J_{d-ec} = 7.5	3	d
58.1	Qu, J_{a-bg} = 6.5	3	a
63.9	Broad S	2	e
70.4	Q, J_{ba} = 6.5	2	b
83.9	Broad M	2	c
93.6	M	4	f and g

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
36. Perfluoro-1,3-dimethyl-2-methyliminomethyl-5-methyliminotetrahydro-imidazole (82)			
24.2	Q, J_{ed} = 14	1	e
55.4	D, J_{fe} = 3 of Q, J_{f-cg} = 7.5	3	f
55.6	T, J_{ag} = 16	3	a
57.9	D, J_{bc} = 6.5	3	b
58.9	D, J_{de} = 14	3	d
78.6	Broad M	2	g
99.6	Broad M	1	c



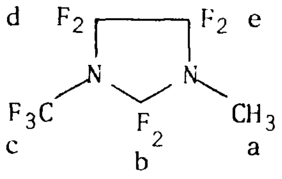
(82)



(206)

37. Perfluorospiro-1,3,6,9-tetraaza-3,6,9-trimethylnon-1-ene (206)			
57.8	Broad M	6	d and g
58.5	Broad S	3	b
71.4	Broad S	2	c
83.4	Broad S	1	a
90.7	M	2	e
91.2	Q, J_{fg} = 8.5	2	f

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
38. 1-Methyl-3-trifluoromethyl-2,2,4,4,5,5-hexafluoro-1,3-diazacyclopentane (219)			
^{19}F			
59.7	T, J_{cb} = 7 of T, J_{cd} = 6	3	c
72.3	Q, J_{bc} = 7	2	b
96.6	Q, J_{dc} = 6 of T, J_{de} = 8	2	d
100.0	T, J_{ed} = 8	2	e
^{1}H			
2.43	S	-	a



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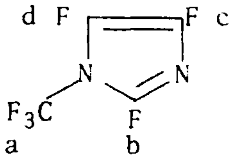

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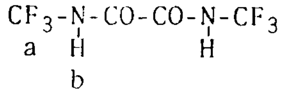


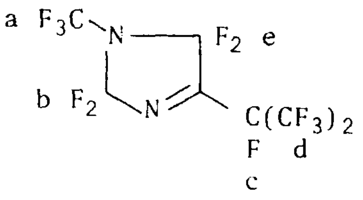
$CF_3\text{-}\underset{\text{H}}{\text{N}}\text{-}CO\text{-}CO\text{-}\underset{\text{H}}{\text{N}}\text{-}CF_3$

(44)

39. Perfluoro-N-methylimidazole (212)			
58.6	T, $J_{a\text{-}bd}$ = 15	3	a
107.8	Q, J_{ba} = 15	1	b
153.0	Broad M	1	c or d
165.2	Broad M	1	d or c
40. N,N'-Bistrifluoromethyloxamide (44)			
^{19}F			
59.1	S	-	a
^{1}H			
10.05	Broad S	-	b

Recorded as a solution in d_6-acetone

Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
41. Perfluoro-1,3-diaza-1-methyl-4-isopropylcyclopent-3-ene (221)			
60.0	T, J_{ae} = 6.5 of T, J_{ab} = 5.5	3	a
75.2	Q, J_{ba} = 5.5	2	b
78.5	D, J_{dc} = 6.5 of T, J_{de} = 2.5	6	d
98.0	Broad	2	e
196.6	Sp, J_{cd} = 6.5	1	c



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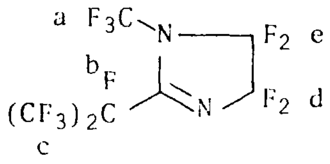
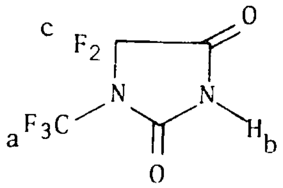


(220)

42. Perfluoro-1,3-diaza-1-methyl-2-isopropylcyclopent-2-ene (220)

56.9	D, J_{ab} = 41.5 of T, J_{ae} = 11	3	a
77.0	D, J_{cb} = 5.5 of Q, J_{ca} = 2	6	c
102.6	S	2	d
103.9	Q, J_{ea} = 11	2	e
189.6	Q, J_{ba} = 41.5 of Sp, J_{bc}=5.5	1	b

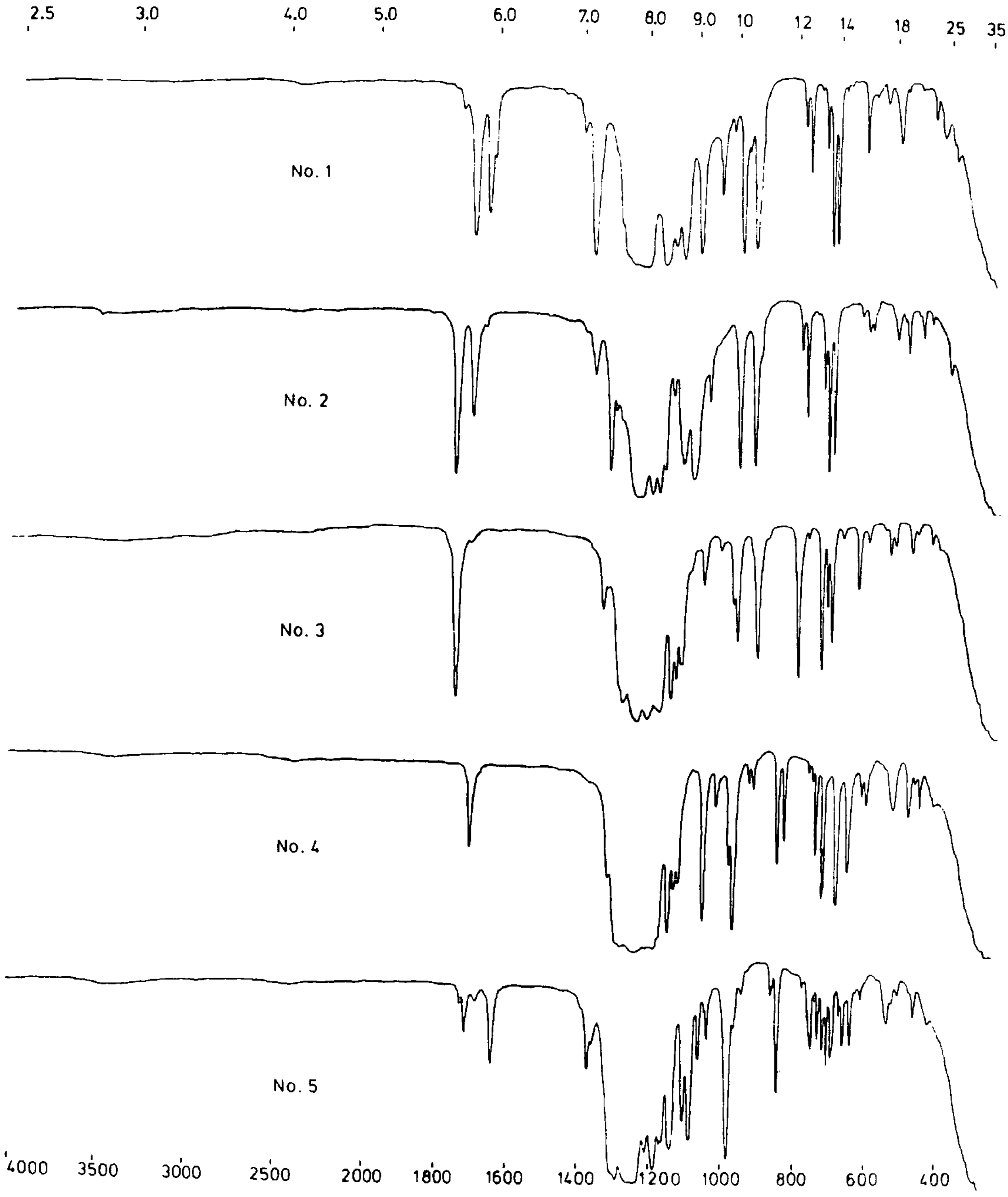
Shift p.p.m.	Fine structure J values in Hz	Relative intensity	Assignment
43. 1-Trifluoromethyl-5,5-difluoro-1,3-diazacyclopenta-2,4-dione (222)			
^{19}F			
58.3	T, J_{ac} = 12	3	a
95.1	Q, J_{ca} = 12	2	c
^{1}H			
4.90	Broad S	-	b



(222)

APPENDIX II

INFRARED SPECTRA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6.0
7.0
8.0
9.0
10
12
14
18
25
35
No. 1
No. 2
No. 3
No. 4
No. 5
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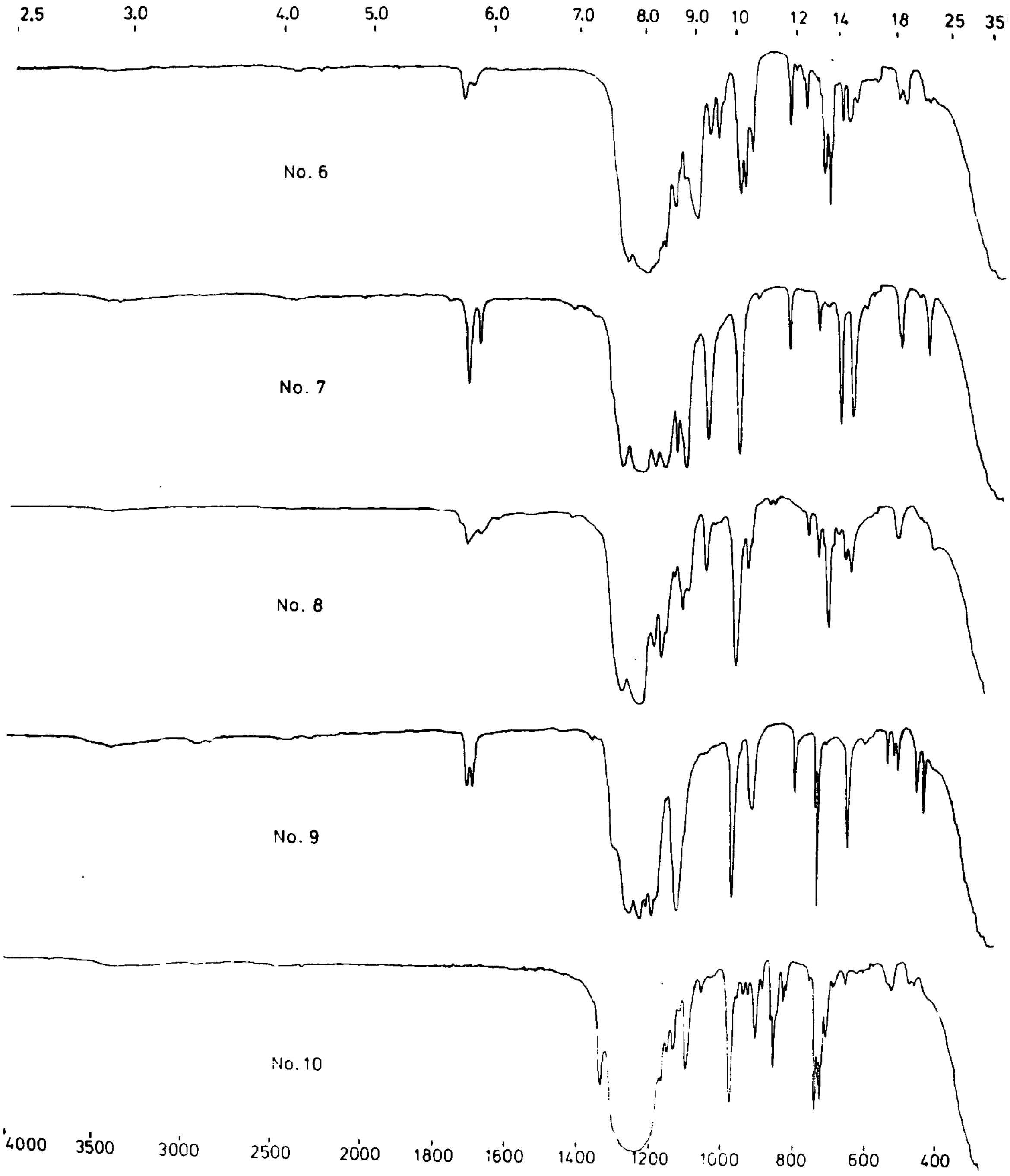
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400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35
No. 6
No. 7
No. 8
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1800
1600
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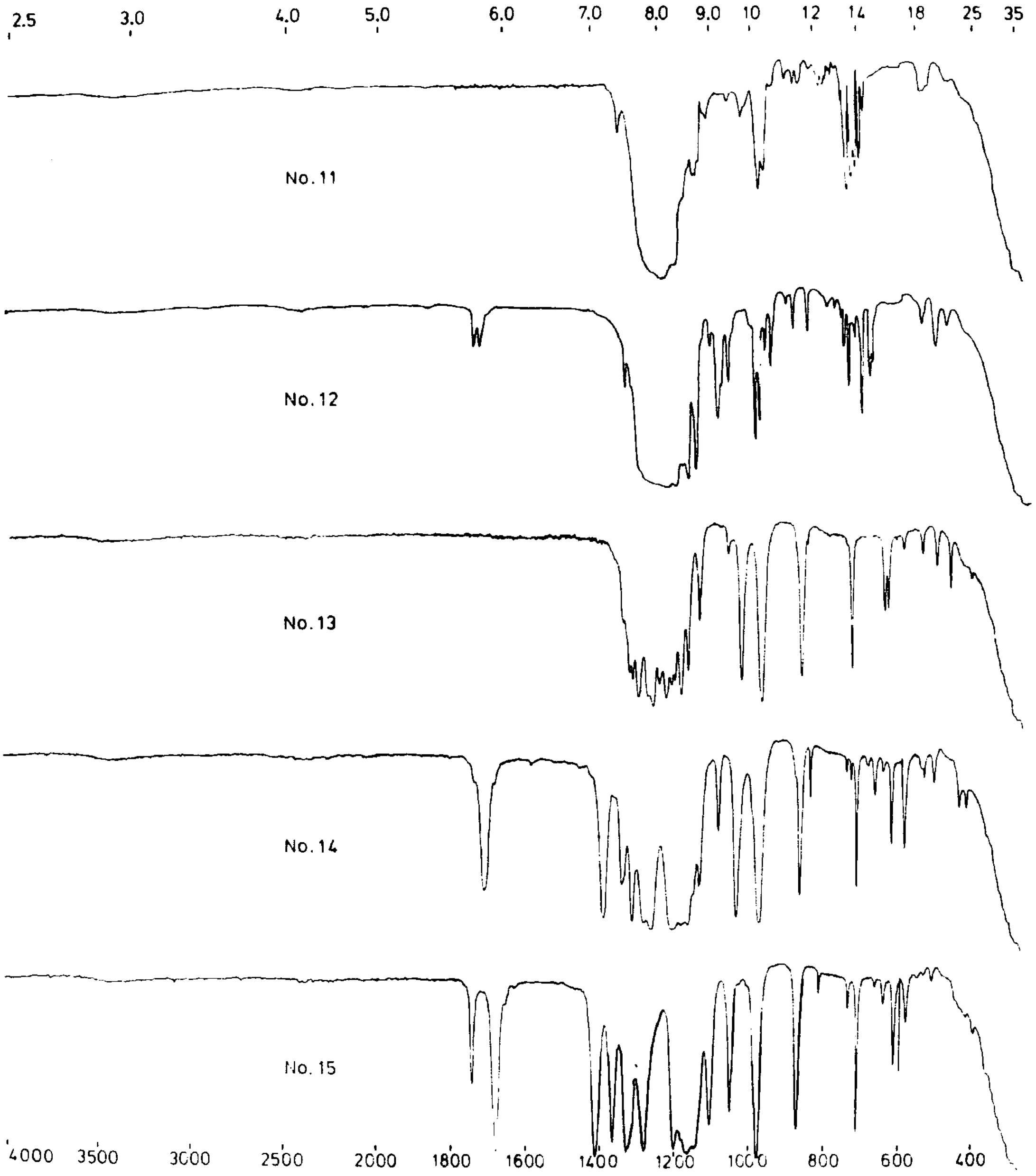
600
400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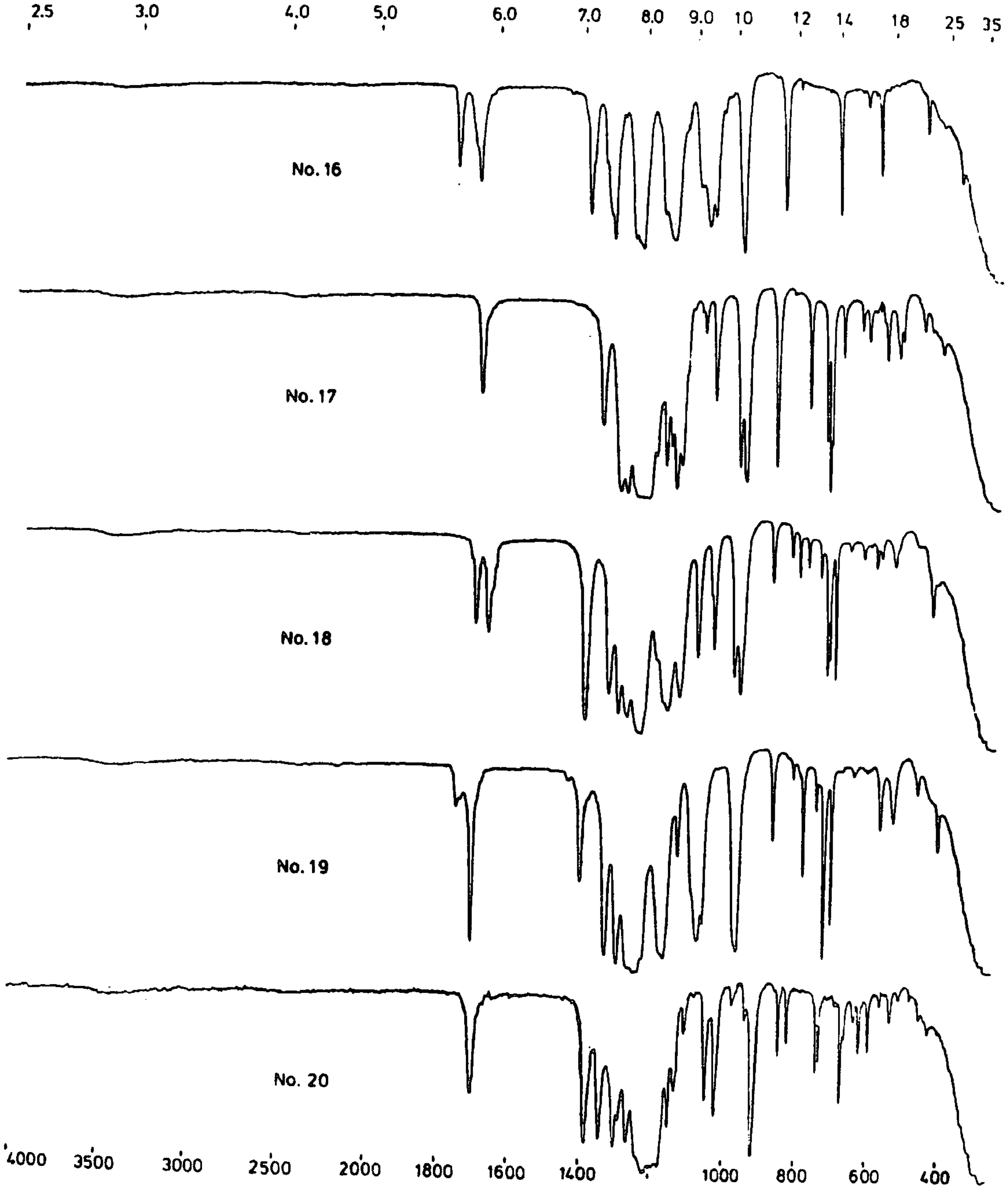
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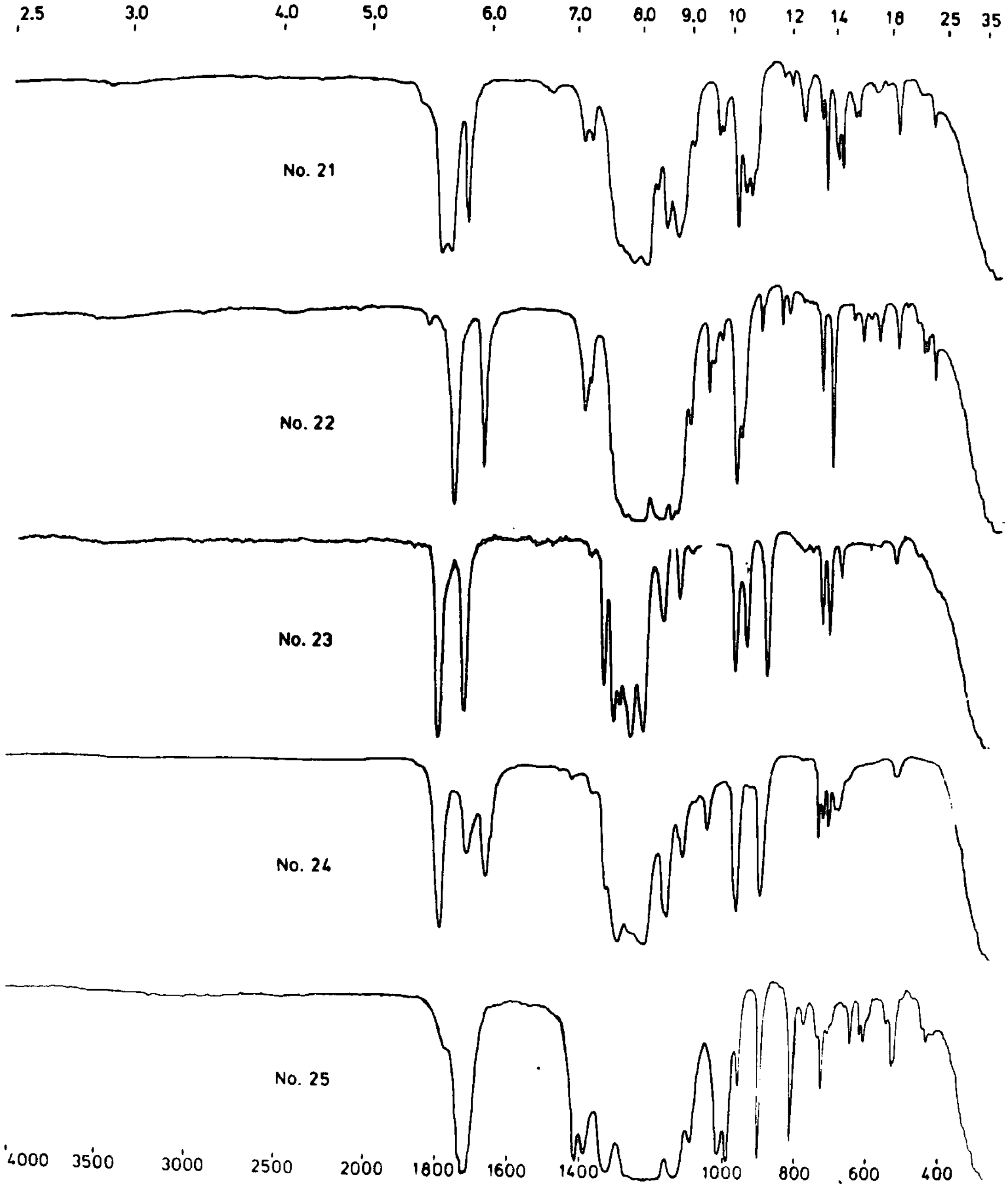
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No. 24
No. 25
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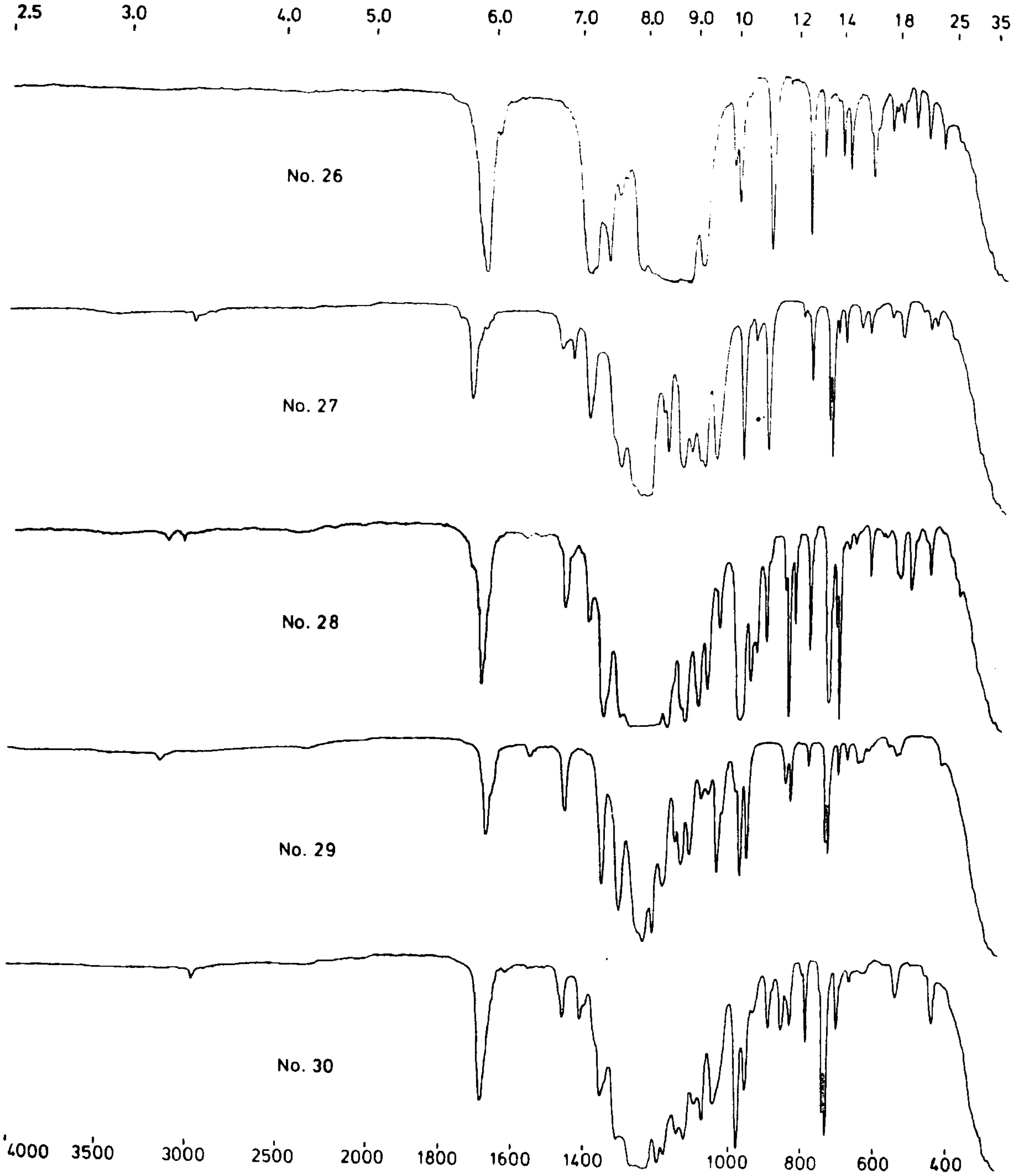
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No. 27
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No. 29
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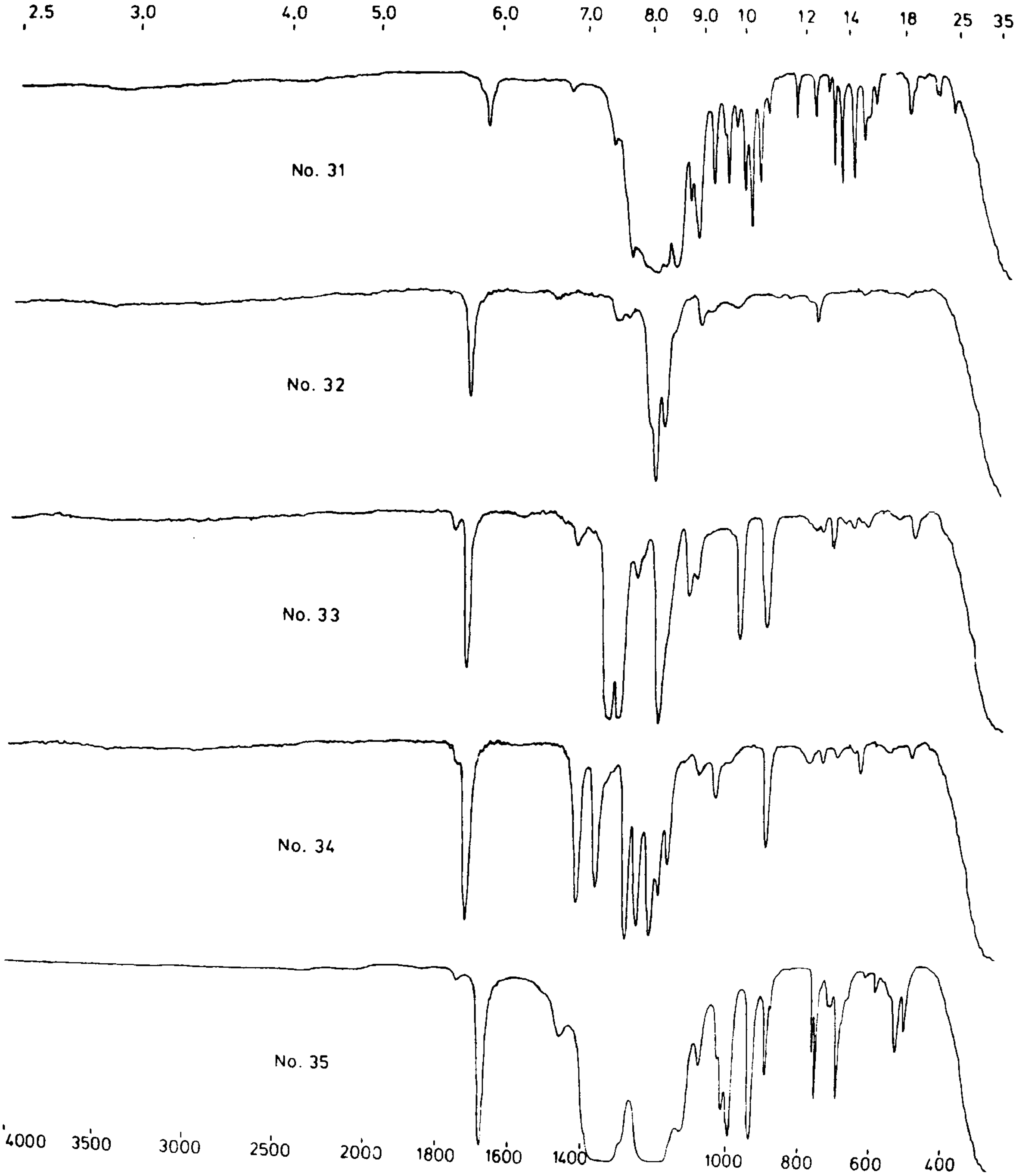
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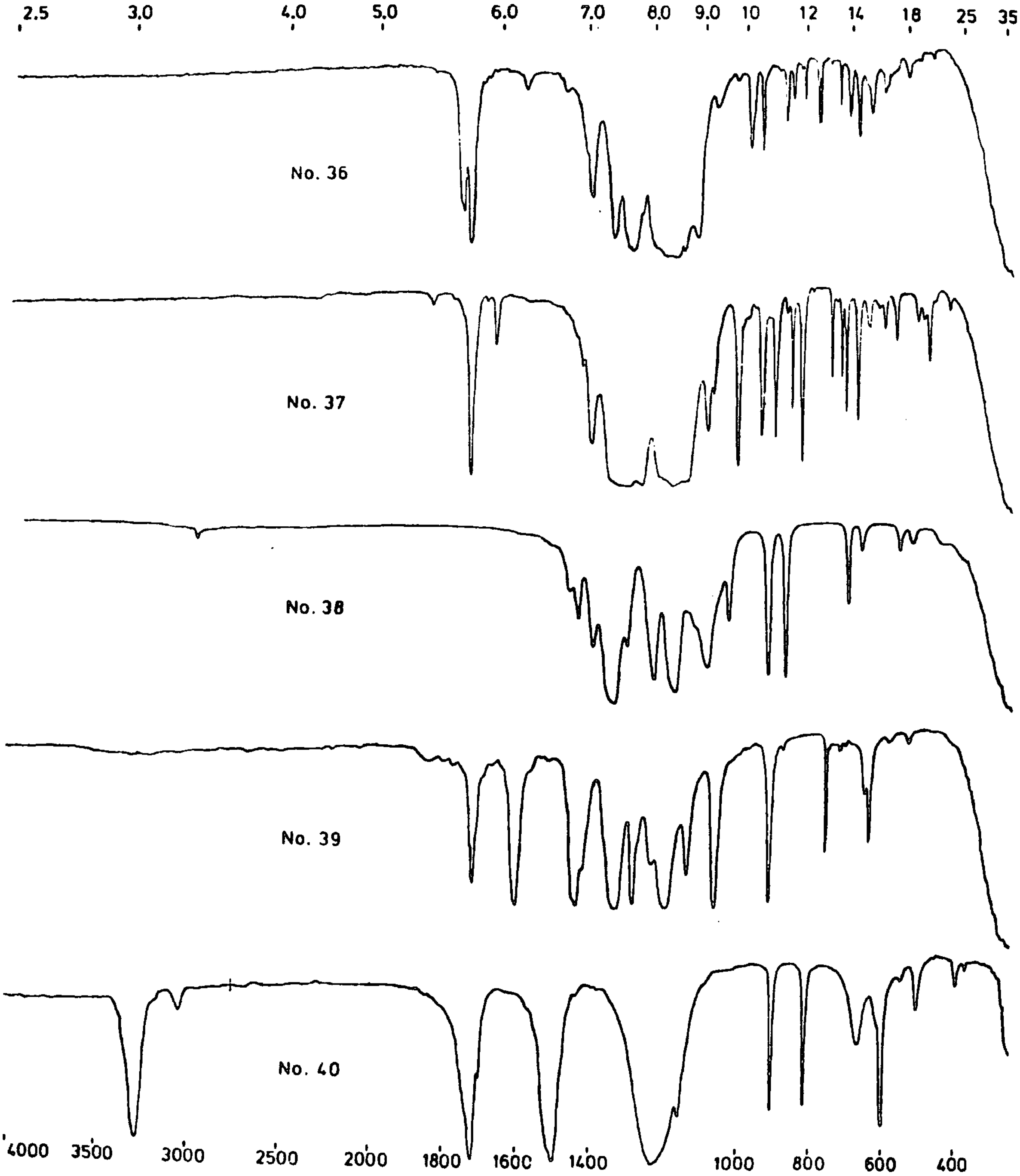
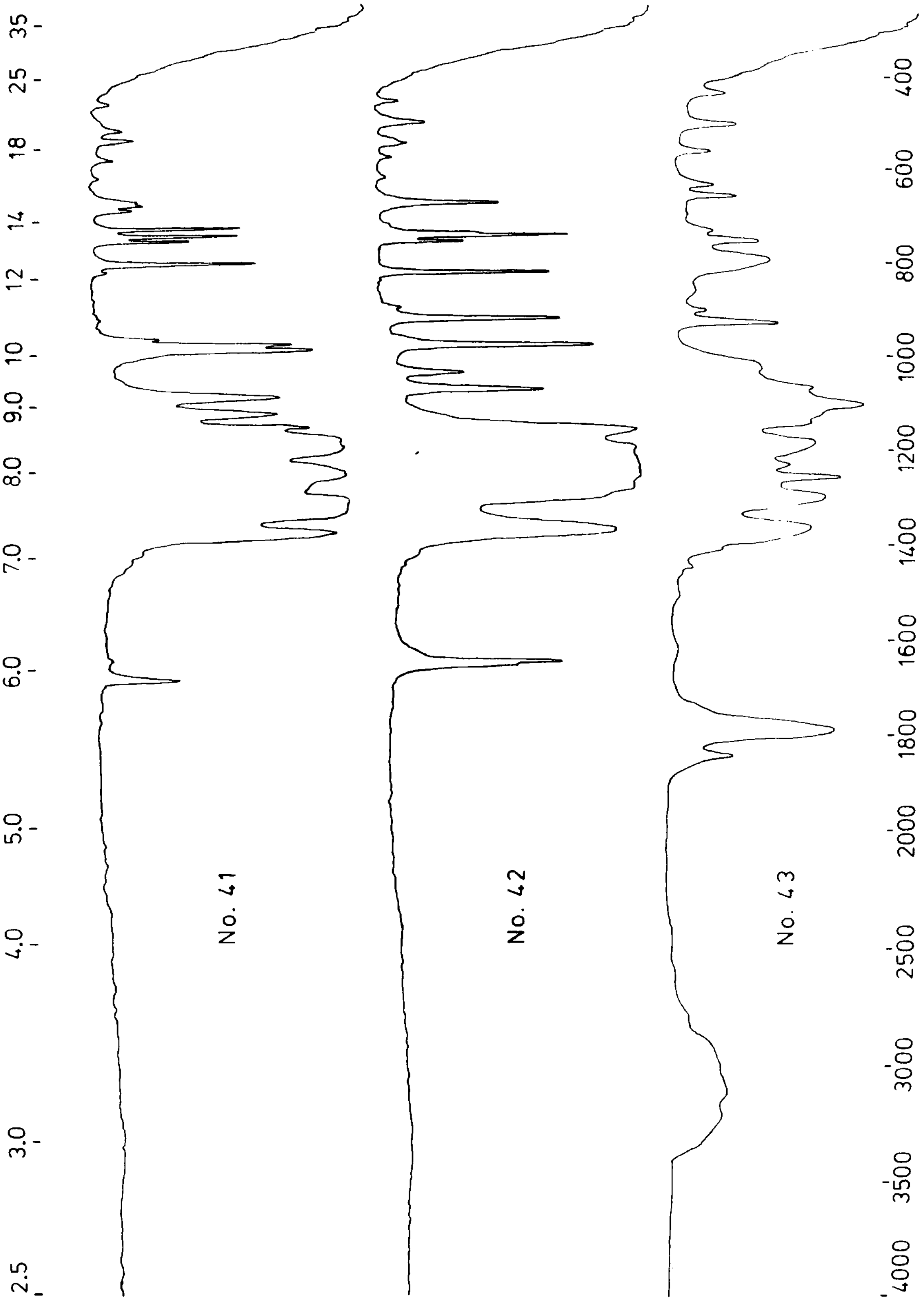
No. 31
No. 32
No. 33
No. 34
No. 35
4000
3500
3000
2500
2000
1800
1600
1400
1000
800
600
400


2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
18
25
35
No. 36
No. 37
No. 38
No. 39
No. 40
4000
3500
3000
2500
2000
1800
1600
1400
1000
800
600
400


2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
18
25
35
No. 41
No. 42
No. 43
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400

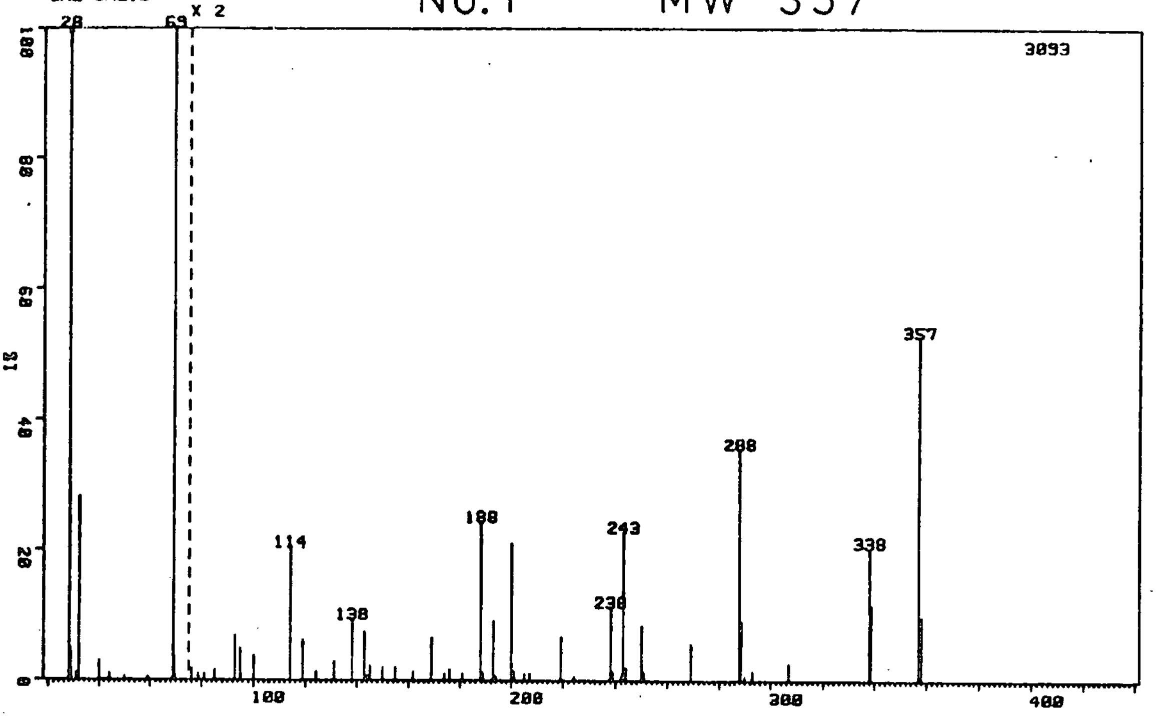
APPENDIX III

MASS SPECTRA

RNB7 71 R.N.BARNES
CAL:CAL19

No.1 MW 357

20-JAN-81

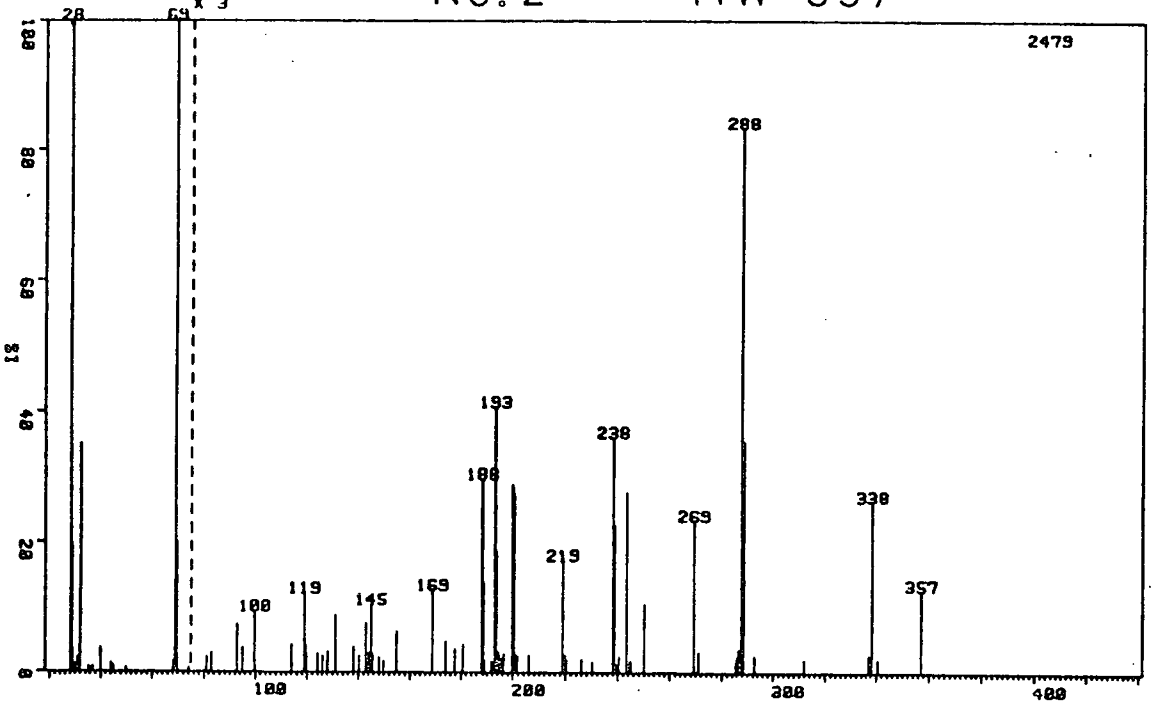


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	100.00	54	250.99	0.54
2	28.22	3.69	55	268.95	2.12
3	29.00	1.25	56	287.92	13.41
4	30.92	0.85	57	288.63	3.44
5	32.02	21.29	58	289.82	0.27
6	32.08	4.08	59	293.02	0.59
7	39.84	2.22	60	306.93	1.00
8	44.12	0.73	61	338.00	7.67
9	49.86	0.39	62	338.61	4.37
10	59.06	0.34	63	356.91	19.88
11	68.58	0.29	64	357.96	3.69
12	68.98	75.53			
13	69.18	2.71			
14	69.88	0.63			
15	76.02	0.68			
16	78.88	0.39			
17	80.90	0.37			
18	84.96	0.61			
19	92.98	2.56			
20	95.02	1.86			
21	95.20	0.32			
22	99.90	1.42			
23	114.02	7.69			
24	118.95	2.32			
25	124.02	0.54			
26	130.95	1.10			
27	137.97	3.52			
28	142.98	2.81			
29	143.92	0.24			
30	145.01	0.90			
31	149.94	0.78			
32	155.02	0.78			
33	161.97	0.51			
34	168.94	2.52			
35	173.99	0.39			
36	176.01	0.63			
37	180.97	0.42			
38	187.98	9.16			
39	188.90	0.46			
40	192.94	3.44			
41	194.01	0.27			
42	199.89	7.89			
43	200.94	0.59			
44	205.01	0.37			
45	207.00	0.42			
46	218.97	2.54			
47	224.03	0.27			
48	230.00	4.22			
49	230.95	0.51			
50	242.30	0.29			
51	242.99	8.57			
52	243.97	0.26			
53	249.93	3.20			

RNB7 41 R.N.BARNES
CAL:CAL19

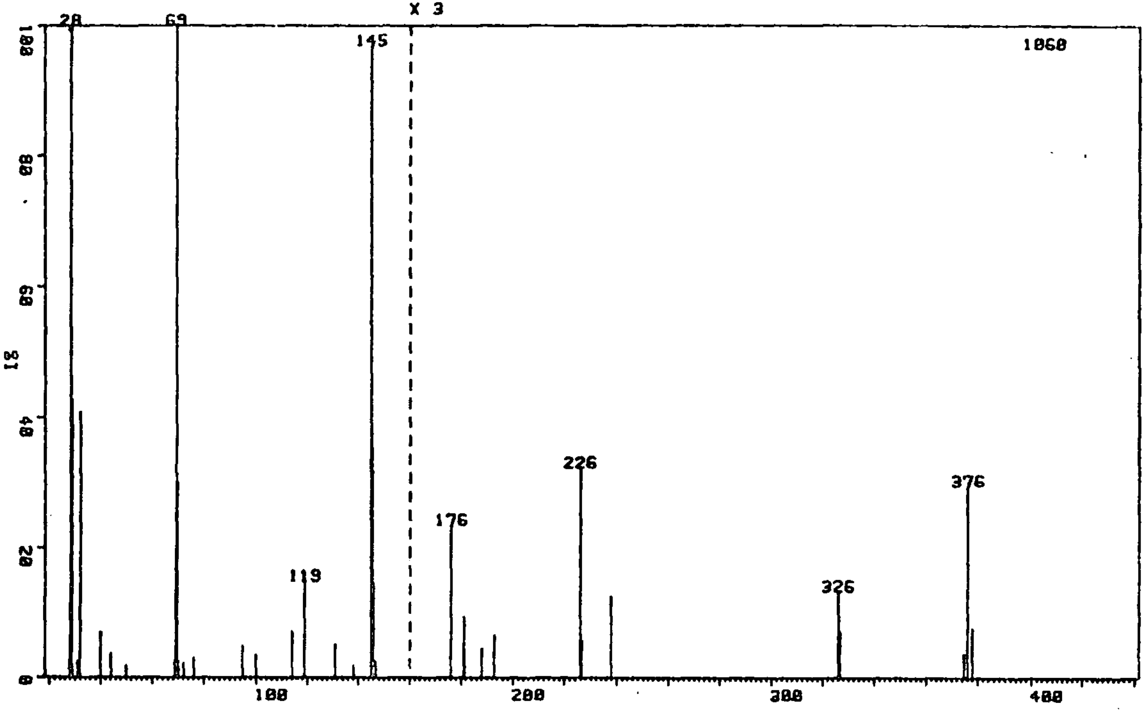
No. 2 MW 357

20-JAN-81



PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	100.00	54	149.76	0.41
2	28.19	13.45	55	154.82	1.44
3	28.25	5.36	56	155.02	0.41
4	28.34	0.99	57	168.89	2.87
5	29.00	2.37	58	173.86	1.08
6	29.06	0.41	59	177.52	0.83
7	29.09	0.50	60	180.82	0.99
8	29.83	0.86	61	187.93	6.76
9	29.98	0.86	62	188.21	3.15
10	30.93	1.55	63	188.84	0.47
11	31.52	0.69	64	191.64	0.39
12	32.02	23.96	65	192.84	9.28
13	32.08	6.60	66	193.24	4.20
14	35.39	0.52	67	193.92	0.58
15	36.99	0.58	68	194.44	0.72
16	39.85	2.51	69	194.83	0.64
17	44.13	1.02	70	195.91	0.52
18	45.18	0.61	71	196.53	0.66
19	49.90	0.44	72	199.78	6.57
20	68.06	0.47	73	200.20	6.27
21	68.22	0.64	74	201.25	0.64
22	68.45	1.13	75	201.77	0.58
23	68.94	68.44	76	206.11	0.64
24	69.06	13.64	77	218.89	3.92
25	69.25	5.72	78	219.80	0.64
26	69.77	1.68	79	220.51	0.47
27	69.94	0.61	80	226.11	0.47
28	70.04	0.52	81	230.14	0.36
29	74.01	0.44	82	237.97	8.23
30	81.20	0.55	83	238.56	5.16
31	82.93	0.69	84	239.70	0.30
32	92.95	1.68	85	240.59	0.58
33	94.96	0.86	86	243.24	6.29
34	99.83	2.13	87	244.69	0.41
35	113.97	0.97	88	245.18	0.39
36	114.22	0.30	89	250.17	2.40
37	118.98	2.76	90	269.20	5.33
38	119.49	0.97	91	271.01	0.72
39	119.86	0.64	92	285.58	0.36
40	124.05	0.66	93	286.15	0.52
41	126.04	0.58	94	286.64	0.83
42	127.70	0.41	95	287.78	19.02
43	128.02	0.75	96	288.69	8.09
44	130.96	2.02	97	292.79	0.58
45	131.29	0.72	98	311.78	0.47
46	137.92	0.91	99	336.97	0.61
47	138.42	0.64	100	338.37	5.99
48	140.28	0.58	101	340.39	0.47
49	142.97	1.74	102	357.19	2.87
50	144.17	0.69			
51	144.93	2.37			
52	145.68	0.66			
53	148.09	0.52			

RN87 27 R.N.BARNES No.3 MW 395 20-JAN-81
CAL:CAL19

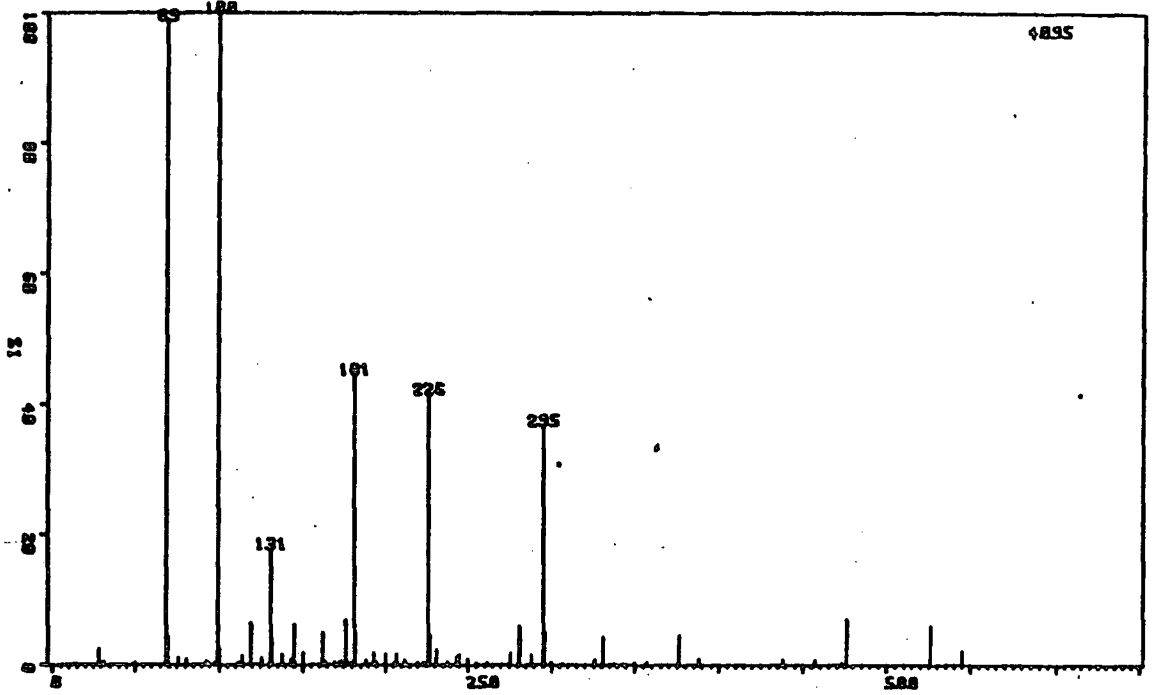


PEAK NO.	MASS	%HT. BASE
1	27.86	0.78
2	27.99	1.19
3	28.06	0.86
4	28.13	100.00
5	28.19	18.48
6	28.24	8.22
7	28.34	1.23
8	29.06	0.78
9	30.91	1.10
10	32.02	17.70
11	32.08	7.15
12	39.86	3.03
13	44.12	1.59
14	49.88	0.78
15	49.99	0.53
16	68.73	1.14
17	69.06	43.34
18	69.18	12.96
19	69.32	7.15
20	69.96	0.70
21	70.13	1.14
22	72.35	0.94
23	76.02	1.31
24	95.11	2.09
25	99.92	1.51
26	100.12	0.49
27	114.04	3.07
28	119.03	6.42
29	131.04	2.25
30	138.08	0.82
31	144.99	42.03
32	145.28	15.33
33	145.81	6.26
34	146.99	1.02
35	176.08	3.39
36	181.02	1.35
37	181.36	0.61
38	188.06	0.65
39	192.93	0.94
40	225.99	4.66
41	226.52	0.82
42	237.93	1.80
43	326.08	1.92
44	326.73	1.02
45	374.88	0.53
46	376.33	4.25
47	377.94	1.10

RNB9 28 R.N.BARNES
CAL:CALN23

No.4 MW 545

28-APR-81

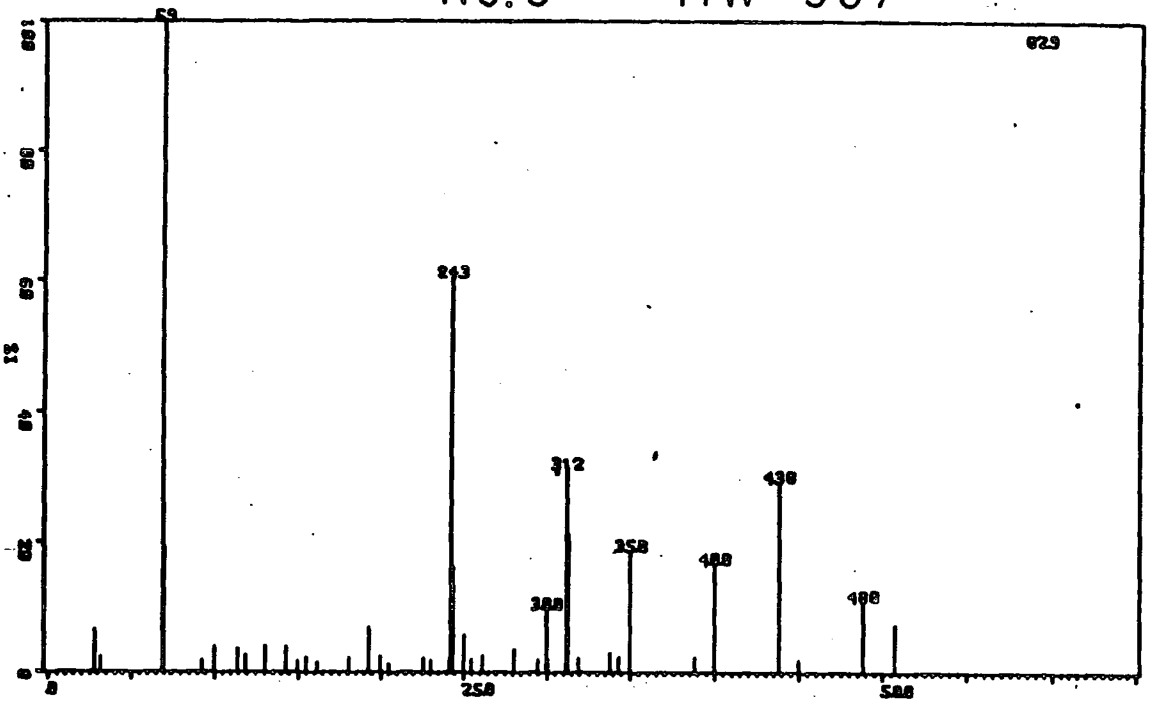


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	2.42	54	213.33	0.32
2	30.92	0.34	55	219.23	0.37
3	32.02	0.56	56	223.03	0.37
4	49.89	0.37	57	224.01	0.39
5	68.47	0.29	58	226.11	41.56
6	69.00	98.83	59	226.90	4.66
7	69.21	4.37	60	231.09	2.22
8	69.44	0.49	61	238.05	0.44
9	69.88	1.20	62	243.19	1.25
10	76.10	1.07	63	245.07	1.56
11	80.97	0.85	64	250.08	0.88
12	93.07	0.61	65	255.14	0.42
13	95.09	0.32	66	262.09	0.39
14	98.15	0.27	67	276.21	1.90
15	98.37	0.37	68	281.06	5.98
16	98.62	0.39	69	281.64	3.93
17	99.96	100.00	70	288.15	1.54
18	101.00	2.59	71	295.03	36.75
19	112.07	0.49	72	296.06	5.03
20	114.12	1.47	73	300.09	0.44
21	119.01	6.40	74	307.27	0.24
22	126.12	0.98	75	326.07	0.81
23	130.99	17.73	76	331.13	4.22
24	131.24	3.93	77	338.11	0.34
25	131.61	0.32	78	343.13	0.24
26	132.01	0.49	79	350.14	0.46
27	137.99	1.64	80	357.32	0.49
28	143.02	0.93	81	376.30	4.57
29	145.03	6.18	82	388.14	0.93
30	146.04	0.32	83	438.26	0.81
31	149.93	1.93	84	457.19	0.76
32	162.01	4.86	85	473.05	0.37
33	163.14	0.27	86	476.28	7.01
34	164.03	0.44	87	526.28	5.98
35	169.03	0.44	88	544.09	2.17
36	172.11	0.29			
37	172.37	0.44			
38	173.80	0.61			
39	176.08	6.86			
40	177.01	0.51			
41	178.73	0.32			
42	179.61	0.44			
43	181.05	44.57			
44	181.82	4.79			
45	188.16	0.61			
46	193.13	1.86			
47	194.14	0.32			
48	195.15	0.42			
49	200.05	1.68			
50	205.32	0.32			
51	207.10	1.66			
52	208.14	0.32			
53	212.06	0.71			

RNB15 13 R.N.BARNES
CAL:CALM23

No.5 MW 507

28-APR-81

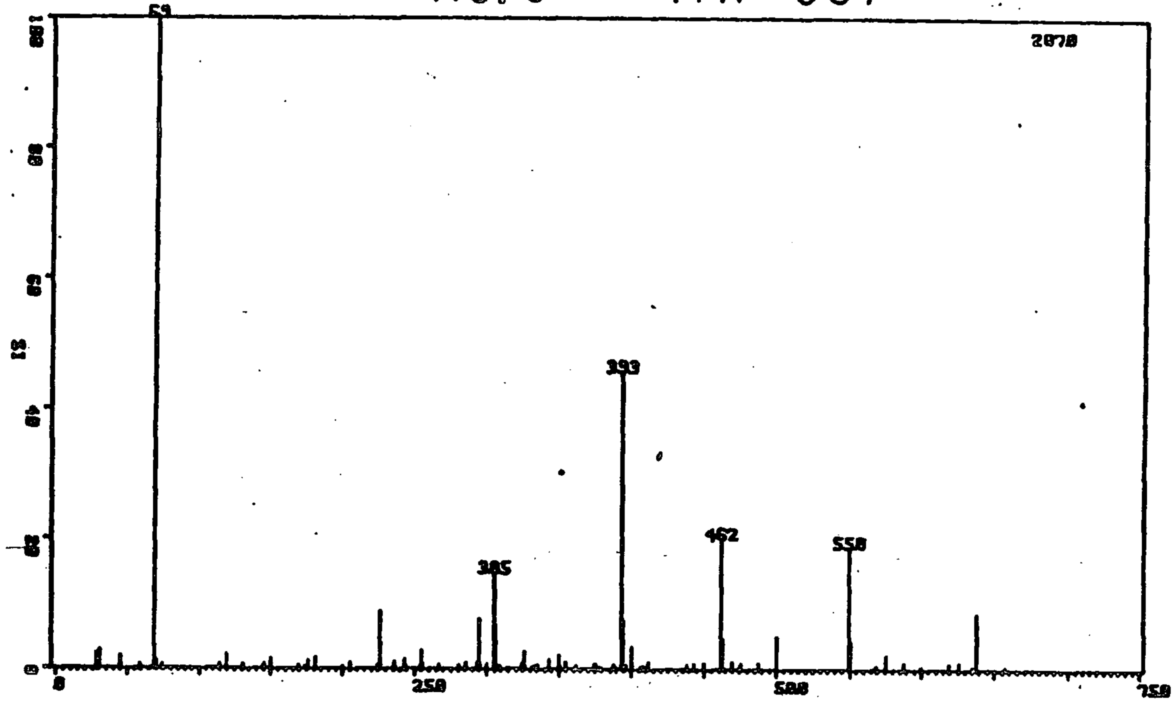


PEAK NO.	MASS	%HT. BASE
1	28.13	6.63
2	32.02	2.29
3	69.01	100.00
4	69.13	19.18
5	69.90	1.93
6	93.06	1.81
7	99.99	3.98
8	114.11	3.62
9	119.02	2.65
10	131.04	4.10
11	143.13	3.98
12	150.11	1.81
13	155.12	2.29
14	162.06	1.57
15	181.02	2.17
16	193.07	6.88
17	200.09	2.53
18	205.09	1.33
19	226.25	2.17
20	231.09	1.81
21	241.03	2.05
22	243.15	60.55
23	243.81	16.28
24	250.18	5.79
25	255.11	2.05
26	262.08	2.53
27	281.21	3.50
28	295.16	1.93
29	300.19	9.65
30	301.05	2.05
31	312.01	31.24
32	312.58	21.35
33	319.11	2.17
34	338.06	3.14
35	343.03	2.41
36	350.16	18.70
37	388.00	2.29
38	400.12	16.65
39	430.34	29.31
40	450.23	1.93
41	488.42	10.98
42	507.30	7.48

RNB22 9 R.N.BARNES
CAL:CAL23M

No. 6 MW 657

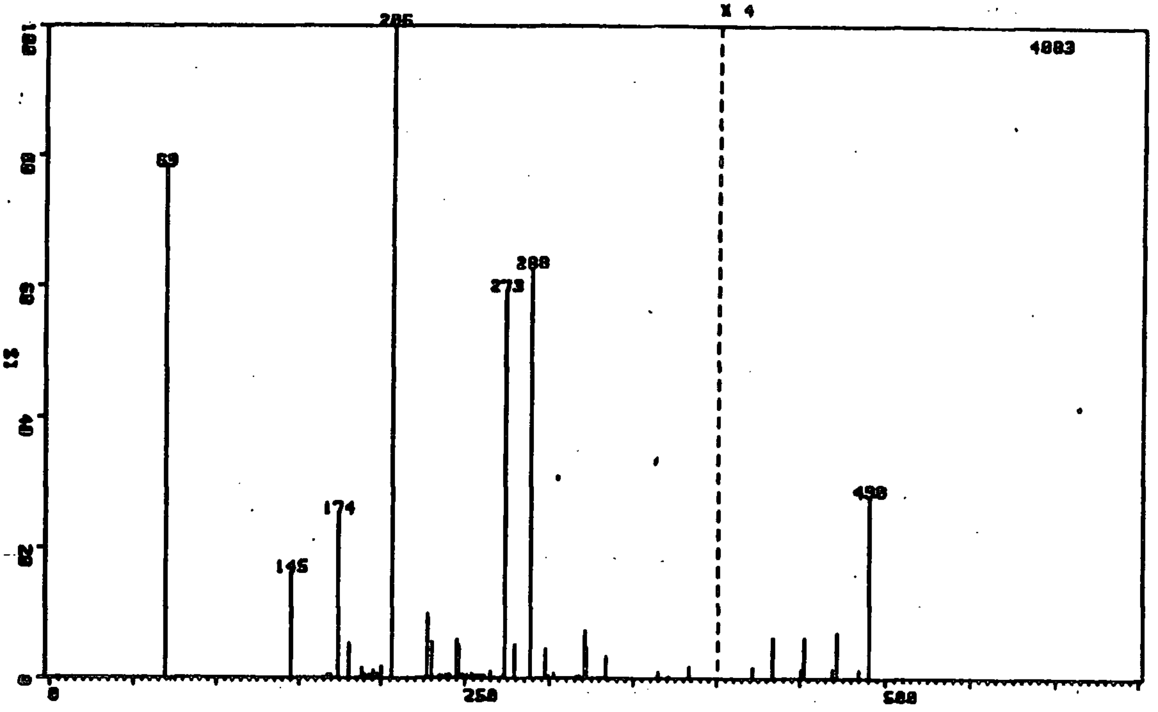
23-JUN-81



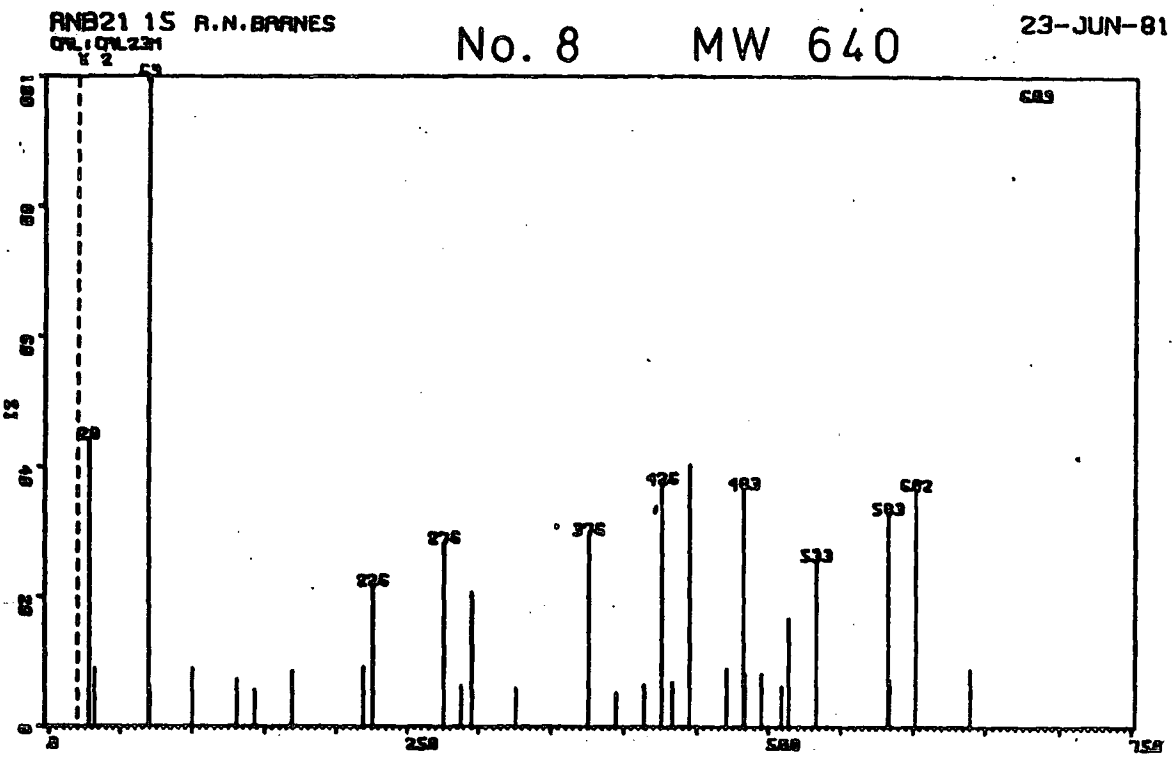
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	2.33	54	342.93	1.46
2	29.02	1.18	55	349.94	2.13
3	30.93	2.82	56	351.06	0.45
4	44.59	1.88	57	354.90	1.01
5	45.18	0.66	58	361.07	0.56
6	59.02	0.70	59	374.22	0.73
7	68.57	1.01	60	375.96	0.70
8	68.97	100.00	61	378.49	0.38
9	69.40	0.45	62	387.08	0.66
10	69.89	1.25	63	389.49	0.45
11	74.17	0.59	64	392.79	45.71
12	113.98	0.66	65	394.20	7.49
13	118.95	2.20	66	396.62	0.63
14	130.93	0.66	67	399.87	3.41
15	144.97	0.66	68	400.89	0.91
16	149.09	1.57	69	406.32	0.45
17	168.96	0.59	70	408.30	0.56
18	173.52	0.42	71	409.83	0.49
19	175.98	1.22	72	412.01	1.11
20	180.91	1.67	73	438.04	0.66
21	199.98	0.45	74	442.92	0.80
22	205.01	0.98	75	450.02	1.05
23	223.97	0.52	76	461.90	20.03
24	225.97	8.82	77	462.82	4.70
25	226.99	0.73	78	464.00	0.35
26	236.00	1.08	79	469.11	1.22
27	237.06	0.52	80	473.92	0.49
28	242.96	1.57	81	475.97	0.80
29	244.93	0.52	82	487.96	0.94
30	253.75	0.45	83	500.13	5.12
31	254.95	2.82	84	549.85	18.71
32	256.01	0.59	85	550.98	4.25
33	266.91	0.63	86	568.85	0.52
34	280.87	0.56	87	575.99	2.20
35	285.98	0.80	88	587.90	1.01
36	293.03	0.91	89	600.03	0.56
37	293.82	0.49	90	619.05	0.87
38	294.99	7.77	91	626.01	1.05
39	295.97	0.70	92	634.94	0.52
40	299.94	0.66	93	637.88	8.64
41	304.87	14.67	94	638.54	6.93
42	305.51	6.79	95	657.32	0.52
43	306.88	0.59			
44	309.04	0.52			
45	314.10	0.42			
46	324.05	0.80			
47	326.00	2.61			
48	327.08	0.45			
49	332.05	0.42			
50	333.61	0.38			
51	334.22	0.52			
52	334.66	0.42			
53	335.44	0.53			

RNB6 7 R.N.BARNES
CAL:CAL25

No. 7 MW 490 25-FEB-81



PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	69.05	78.35	54	297.24	4.53
2	145.21	16.26	55	299.41	0.39
3	167.39	0.54	56	302.33	0.76
4	167.75	0.44	57	316.40	0.42
5	167.91	0.27	58	316.88	0.29
6	168.76	0.56	59	317.72	0.27
7	169.78	0.56	60	318.31	0.37
8	173.72	25.23	61	320.97	7.30
9	180.21	5.34	62	322.15	4.58
10	188.18	1.52	63	328.82	0.24
11	189.60	0.39	64	331.28	0.27
12	190.16	0.51	65	333.39	3.33
13	190.71	0.47	66	364.43	0.98
14	191.04	0.44	67	371.32	0.29
15	191.46	0.39	68	383.29	1.79
16	191.78	0.29	69	421.66	0.44
17	192.24	0.49	70	433.62	1.57
18	192.69	0.39	71	450.81	0.34
19	193.44	0.56	72	452.52	1.54
20	195.32	1.22	73	468.80	0.37
21	197.66	0.71	74	471.32	1.76
22	198.64	0.29	75	484.33	0.34
23	200.24	1.89	76	490.23	6.98
24	206.15	100.00			
25	227.11	9.87			
26	229.89	5.63			
27	234.05	0.32			
28	234.80	0.49			
29	235.63	0.42			
30	236.26	0.49			
31	238.23	0.56			
32	239.88	0.47			
33	240.70	0.59			
34	241.60	0.34			
35	244.59	5.93			
36	246.06	4.95			
37	248.03	0.64			
38	249.51	0.34			
39	250.51	0.56			
40	251.27	0.51			
41	253.44	0.69			
42	255.10	0.47			
43	256.25	0.39			
44	257.49	0.49			
45	258.68	0.44			
46	259.66	0.42			
47	260.09	0.32			
48	260.49	0.42			
49	261.46	0.47			
50	264.56	1.00			
51	272.92	59.27			
52	278.67	5.17			
53	288.14	62.75			



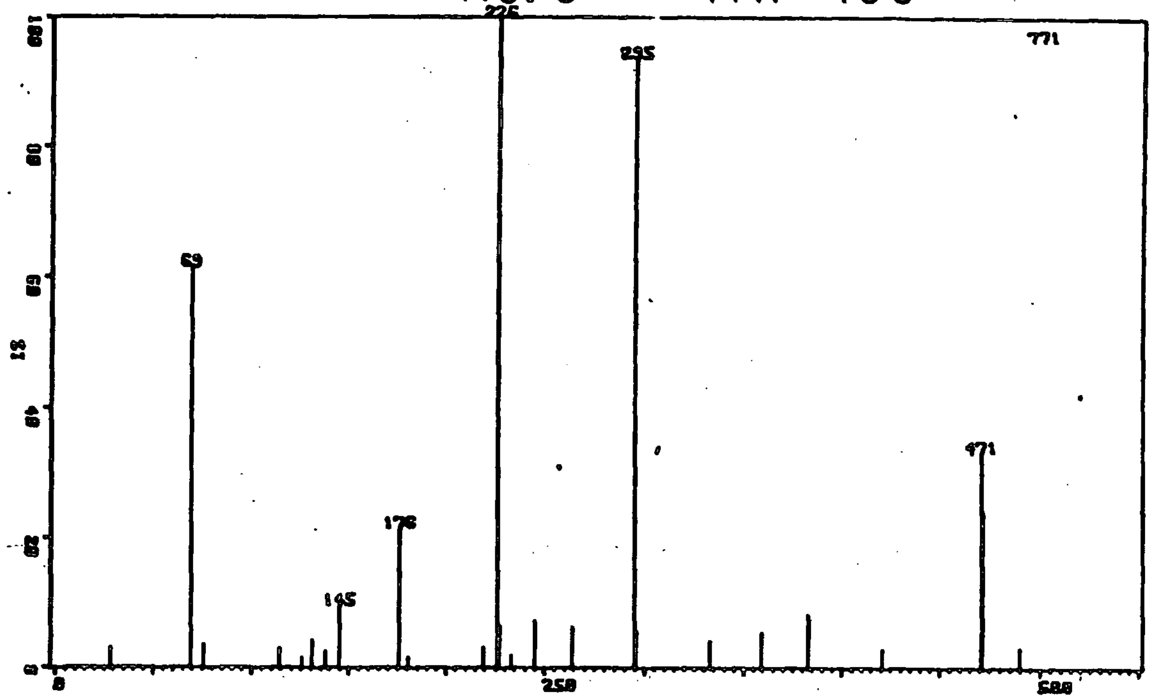
No. 8 MW 640

PEAK NU.	MASS	%HT. BASE
1	28.13	22.17
2	32.02	4.43
3	68.97	100.00
4	69.91	3.12
5	99.94	4.43
6	130.97	3.61
7	143.10	2.79
8	168.98	4.27
9	218.99	4.60
10	226.04	10.84
11	275.99	14.12
12	287.99	3.12
13	295.00	10.34
14	326.05	2.96
15	375.99	14.78
16	394.93	2.63
17	413.90	3.28
18	425.94	18.72
19	432.98	3.45
20	444.93	20.20
21	470.91	4.43
22	482.87	18.39
23	483.83	4.11
24	494.96	4.11
25	508.96	3.12
26	513.98	8.37
27	533.05	12.81
28	582.88	16.42
29	583.96	3.61
30	602.14	18.23
31	639.80	4.43

RNB200 1 R.N.BARNES
CAL:CAL23M

No. 9 MW 490

24-JUN-81



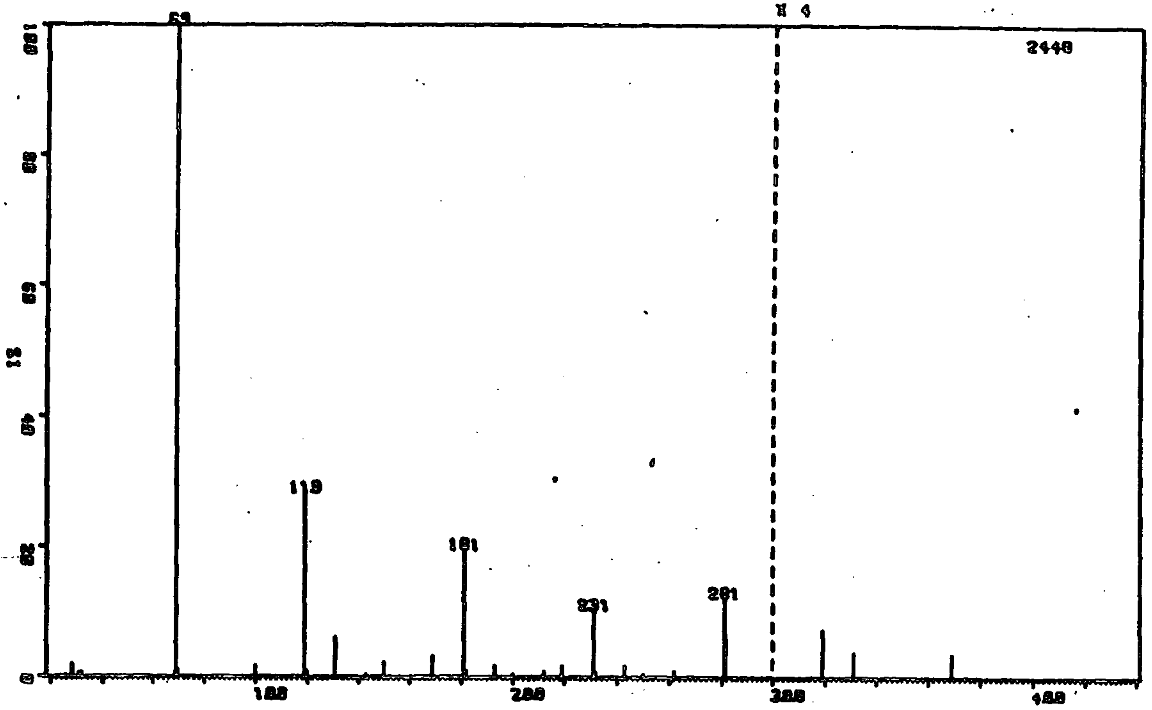
PEAK NO.	MASS	%HT. BASE
1	28.13	3.11
2	69.01	61.61
3	76.12	3.50
4	114.09	2.98
5	126.10	1.56
6	131.02	4.15
7	138.07	2.46
8	145.08	9.60
9	176.11	21.53
10	181.06	1.56
11	219.12	3.11
12	226.15	100.00
13	227.09	6.49
14	233.15	1.95
15	245.14	7.26
16	264.07	6.36
17	295.12	93.77
18	296.12	5.71
19	333.16	4.15
20	359.20	5.45
21	383.11	8.17
22	421.17	2.98
23	471.21	33.33
24	471.80	24.25
25	490.26	3.11

RNB13 6 R.N.BARNES
CAL:CALM23

No. 10

MW 388

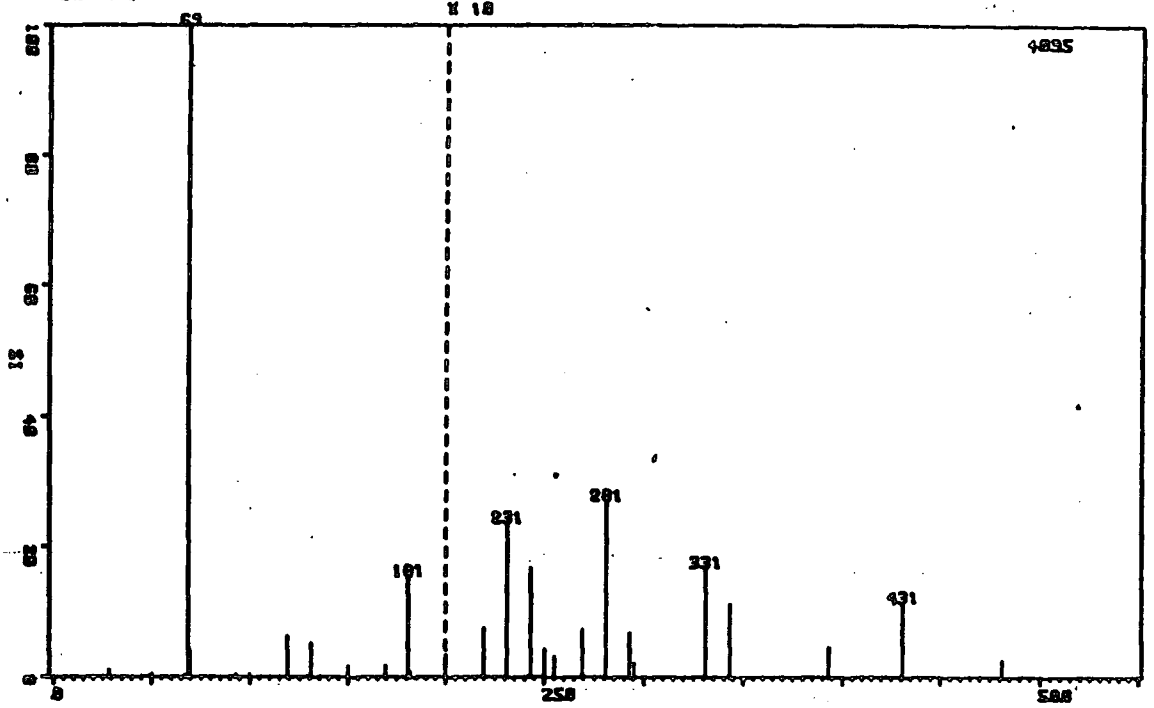
28-APR-81



PEAK NO.	MASS	%HT. BASE
1	28.13	1.92
2	30.92	0.53
3	32.03	0.61
4	69.00	100.00
5	69.93	1.10
6	100.00	1.67
7	119.06	28.31
8	120.02	0.90
9	131.08	6.13
10	143.12	0.45
11	150.10	2.25
12	169.12	3.23
13	181.12	19.57
14	182.07	0.82
15	193.11	1.72
16	200.13	0.53
17	212.10	0.82
18	219.07	1.72
19	231.09	10.29
20	232.04	0.74
21	243.11	1.76
22	250.06	0.53
23	262.11	0.90
24	281.07	12.21
25	281.64	6.66
26	319.14	1.84
27	331.12	0.94
28	369.17	0.90

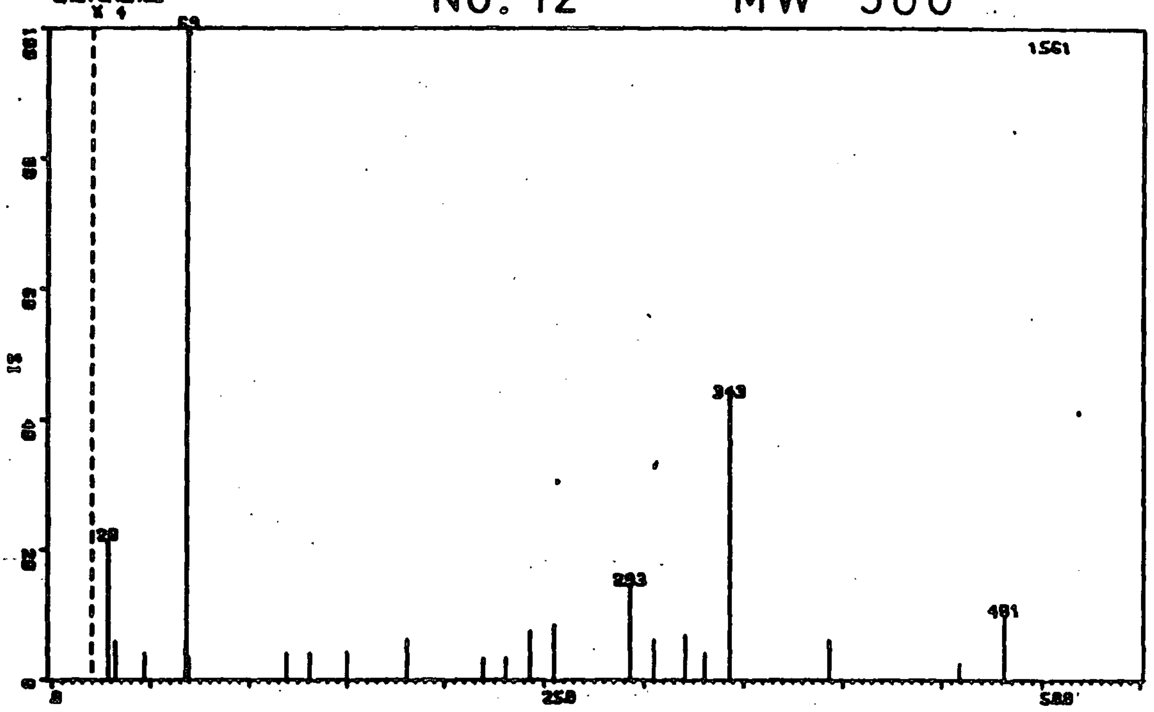
RNB12 18 R.N.BARNES
CAL:CALM23

No. 11 MW 538 28-APR-81

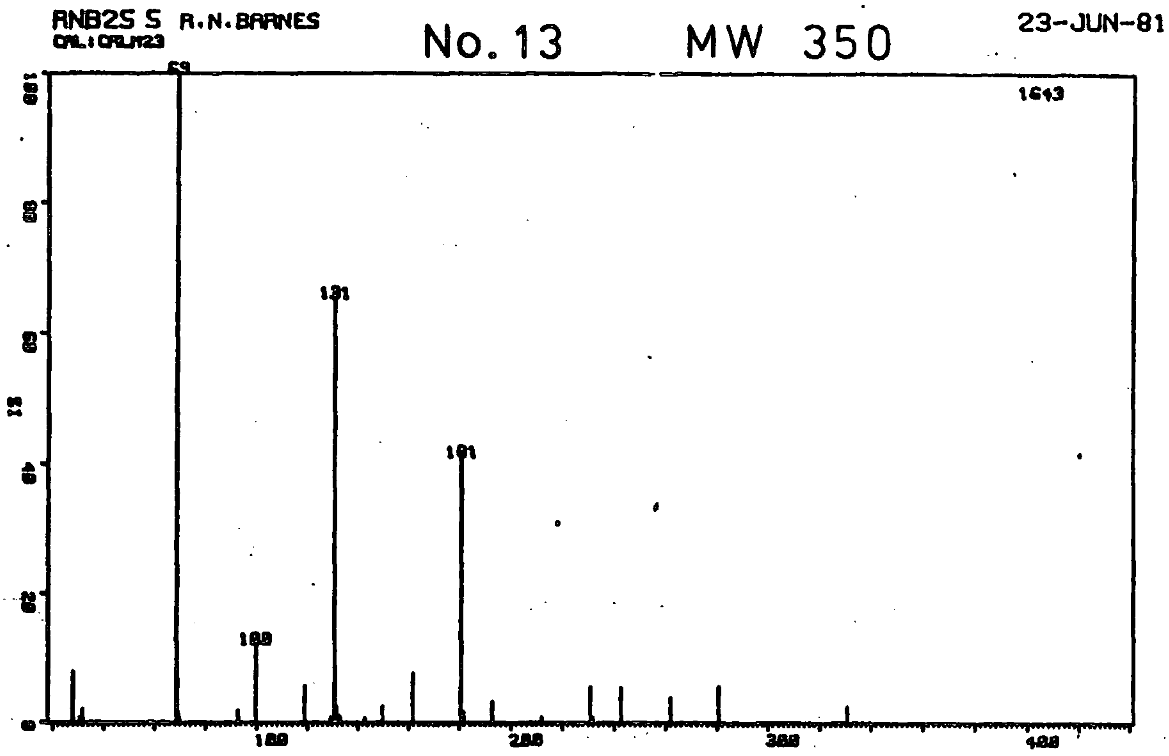


PEAK NO.	MASS	%HT. BASE
1	28.13	1.00
2	49.89	0.44
3	67.27	0.37
4	68.98	100.00
5	69.31	4.27
6	69.91	1.66
7	93.00	0.46
8	100.02	0.56
9	119.06	6.32
10	131.08	5.20
11	150.08	1.76
12	169.17	1.83
13	181.13	15.56
14	182.05	0.85
15	200.13	0.34
16	219.20	0.76
17	231.13	2.37
18	243.16	1.68
19	250.06	0.44
20	255.08	0.32
21	269.13	0.73
22	281.16	2.71
23	293.26	0.68
24	295.29	0.22
25	331.13	1.68
26	343.11	1.12
27	393.22	0.46
28	431.27	1.15
29	481.45	0.27

ANB14 11 A.N.BARNES No. 12 MW 500 28-APR-81
CAL:CALM23



PEAK NO.	MASS	%HT. BASE
1	28.13	5.38
2	32.01	1.47
3	47.10	1.02
4	67.91	1.22
5	68.28	1.15
6	68.45	0.83
7	68.94	100.00
8	69.35	0.64
9	69.89	0.90
10	119.06	1.02
11	131.10	1.02
12	150.06	1.09
13	181.14	1.54
14	219.28	0.83
15	231.05	0.83
16	243.19	1.86
17	255.10	2.11
18	293.21	3.65
19	305.23	1.54
20	321.13	1.73
21	330.85	1.02
22	343.08	10.89
23	393.27	1.54
24	459.16	0.64
25	481.36	2.50

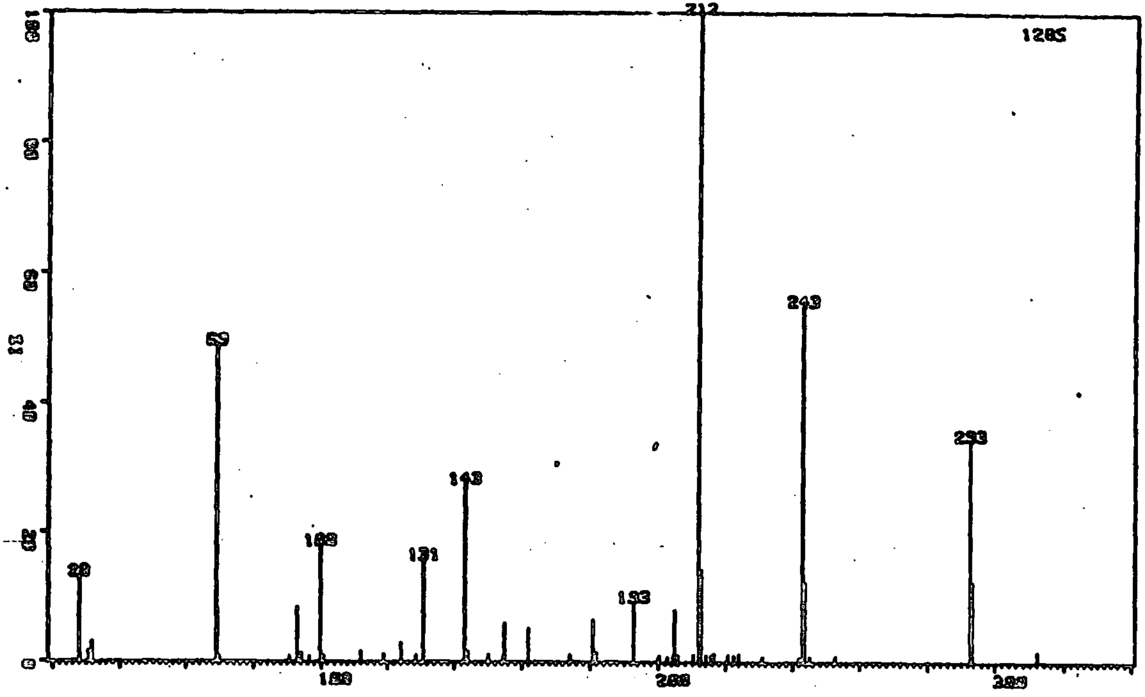


PEAK NO.	MASS	%HT. BASE
1	28.13	7.79
2	30.92	0.85
3	32.03	2.01
4	68.97	100.00
5	69.12	7.00
6	69.29	0.91
7	69.43	0.67
8	69.53	1.34
9	69.82	1.52
10	70.04	0.79
11	92.93	1.89
12	99.85	12.11
13	118.93	5.60
14	129.42	0.91
15	129.83	0.73
16	130.92	65.37
17	131.23	8.83
18	131.87	2.56
19	132.89	1.10
20	133.18	0.79
21	142.94	0.91
22	149.88	2.62
23	161.94	7.67
24	180.93	41.02
25	181.89	1.64
26	192.93	3.23
27	211.94	0.91
28	230.93	5.54
29	232.03	0.79
30	242.90	5.42
31	261.93	3.96
32	280.84	5.66
33	330.80	2.56

RNB26 7 R.N.BARNES
CRL1CRLM23

No 14 MW 312

23-JUN-81

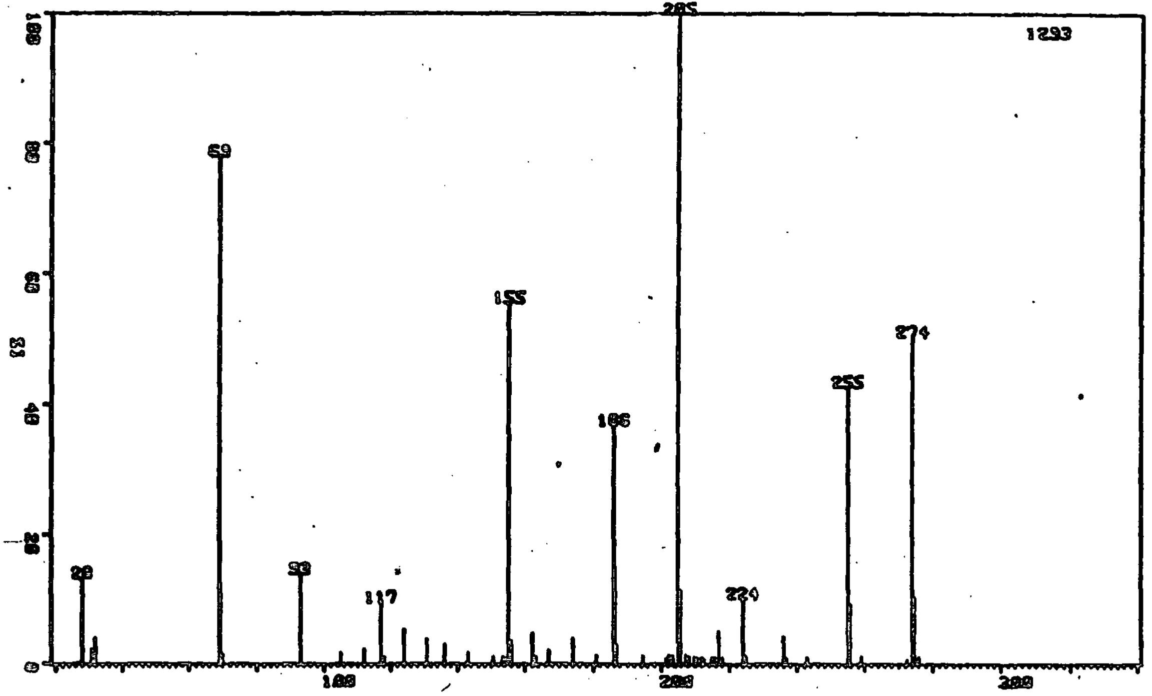


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	13.15	54	311.97	1.71
2	30.92	1.63			
3	32.02	3.11			
4	68.97	48.79			
5	69.06	8.09			
6	69.91	0.86			
7	90.65	0.86			
8	92.98	8.48			
9	94.04	1.40			
10	96.59	0.86			
11	99.90	17.98			
12	100.98	1.01			
13	112.00	1.63			
14	118.99	1.17			
15	124.02	2.88			
16	128.46	1.01			
17	130.94	15.80			
18	142.96	27.55			
19	143.42	1.01			
20	144.00	1.63			
21	149.95	1.17			
22	154.53	1.01			
23	155.00	5.99			
24	161.93	5.21			
25	173.99	1.17			
26	180.95	6.61			
27	181.98	1.56			
28	192.93	9.34			
29	200.17	0.78			
30	200.54	1.01			
31	202.84	0.86			
32	204.43	1.17			
33	204.91	8.02			
34	205.70	1.01			
35	206.01	1.17			
36	210.46	1.25			
37	211.90	100.00			
38	212.66	14.24			
39	214.13	1.17			
40	215.54	1.01			
41	216.51	1.40			
42	220.80	1.17			
43	222.55	1.01			
44	223.95	1.32			
45	230.91	0.70			
46	231.33	0.93			
47	241.80	0.78			
48	242.88	54.86			
49	243.60	12.37			
50	245.04	0.86			
51	252.61	0.93			
52	292.86	33.74			
53	293.59	12.37			

RNB28 14 R.N.BARNES
CAL:CALM23

No.15 MW 274

23-JUN-81

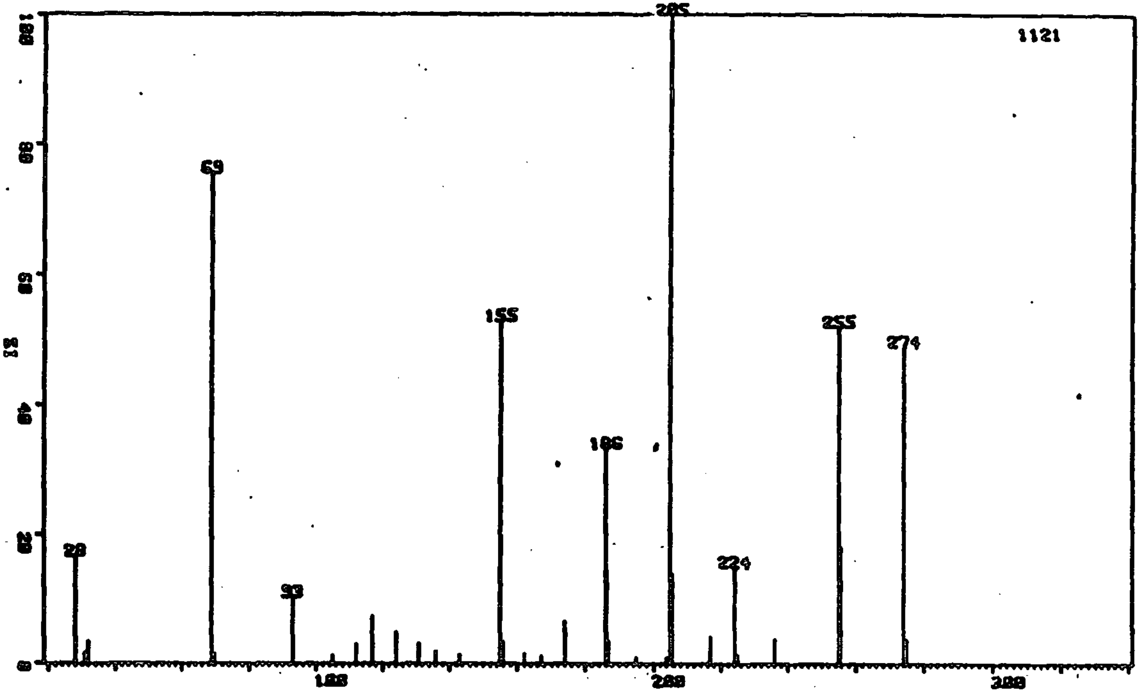


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	13.23	54	242.99	1.01
2	30.92	2.24	55	254.97	42.61
3	32.03	3.94	56	255.70	9.20
4	68.97	77.96	57	259.08	1.08
5	69.08	12.30	58	272.72	0.77
6	69.92	1.55	59	274.08	50.35
7	92.98	13.92	60	274.81	10.29
8	105.04	1.78	61	275.82	0.85
9	112.02	2.24	62	276.19	1.01
10	117.04	9.51			
11	118.07	1.16			
12	124.02	5.34			
13	130.94	3.79			
14	136.01	3.09			
15	142.96	1.78			
16	150.62	1.08			
17	153.47	0.93			
18	153.73	1.01			
19	154.00	0.77			
20	154.47	0.77			
21	155.07	55.45			
22	156.02	3.56			
23	162.03	4.72			
24	163.08	0.93			
25	163.27	1.24			
26	167.01	2.09			
27	173.96	3.94			
28	180.92	1.39			
29	185.92	36.74			
30	186.17	14.77			
31	186.90	3.02			
32	194.68	1.31			
33	201.43	0.93			
34	201.98	0.85			
35	202.46	1.39			
36	202.91	1.16			
37	203.67	1.31			
38	204.87	100.00			
39	205.69	11.37			
40	207.14	1.47			
41	208.24	1.24			
42	209.69	1.01			
43	210.73	1.01			
44	211.91	1.01			
45	212.66	0.85			
46	214.75	1.01			
47	215.64	1.01			
48	216.90	5.03			
49	217.89	1.01			
50	223.98	10.13			
51	225.00	1.31			
52	236.02	4.25			
53	237.03	0.93			

RNB27 12 R.N.BARNES
CAL:CALM23

No. 16 MW 274

23-JUN-81

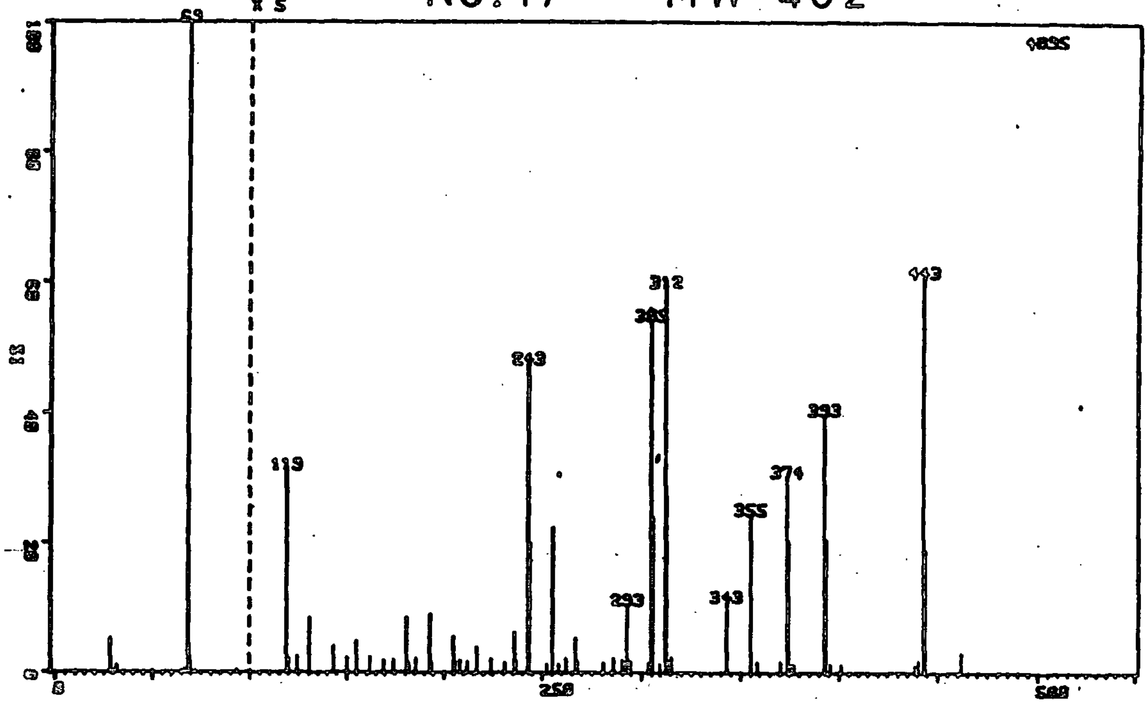


PEAK NO.	MASS	%HT. BASE
1	28.13	16.59
2	30.91	1.61
3	32.01	3.30
4	68.98	75.56
5	69.91	1.52
6	92.98	10.35
7	105.02	1.34
8	112.00	3.03
9	117.00	7.23
10	124.02	4.82
11	130.92	3.12
12	135.96	1.96
13	142.96	1.43
14	154.97	52.90
15	155.93	3.48
16	162.04	1.52
17	167.01	1.25
18	173.99	6.51
19	185.93	33.27
20	186.11	14.36
21	186.92	3.57
22	195.05	0.98
23	203.75	0.98
24	204.95	100.00
25	205.67	13.83
26	216.94	4.19
27	224.01	14.99
28	225.03	1.43
29	235.97	3.84
30	254.93	52.01
31	255.53	18.02
32	273.93	48.97
33	274.90	3.75

RNB29 6 R.N.BARNES
CAL:CALM23

No.17 MW 462

23-JUN-81

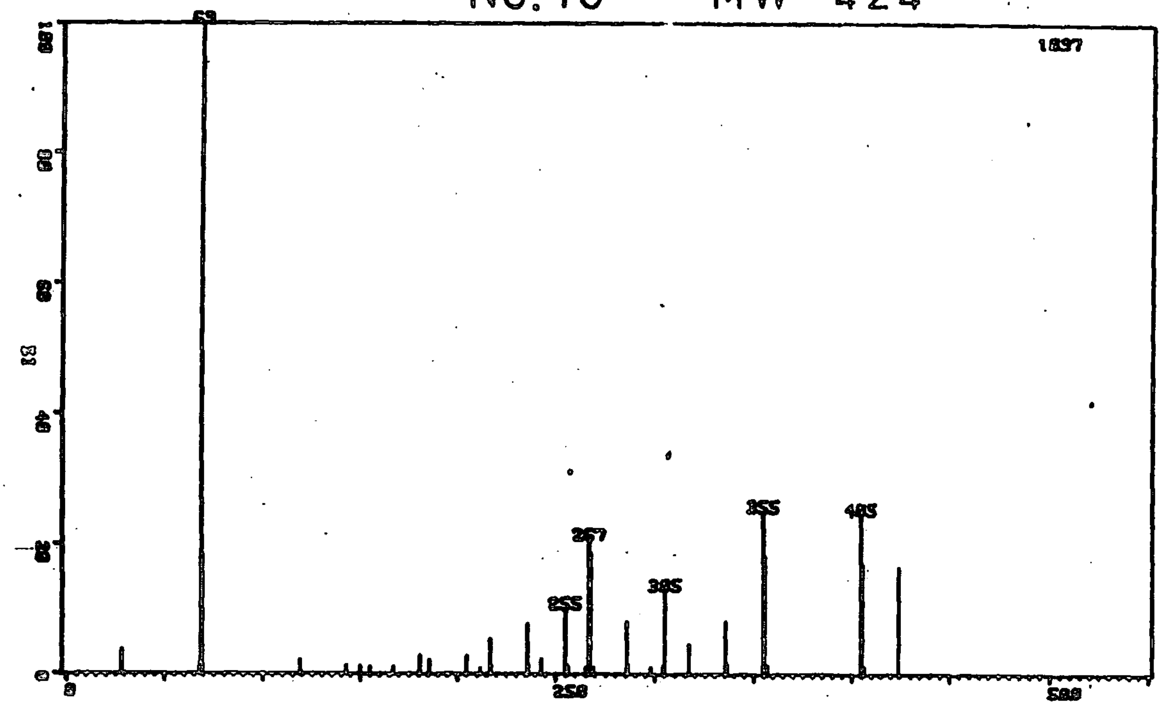


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	5.20	54	268.06	0.32
2	30.92	0.32	55	280.94	0.29
3	32.01	0.95	56	285.90	0.44
4	49.87	0.32	57	290.19	0.39
5	65.06	0.27	58	290.83	0.34
6	66.69	0.27	59	291.87	0.29
7	66.82	0.37	60	292.96	2.08
8	66.94	0.27	61	293.95	0.37
9	67.47	0.34	62	294.84	0.32
10	68.03	0.44	63	303.36	0.32
11	68.16	0.37	64	304.89	10.82
12	68.28	0.42	65	305.73	4.76
13	68.97	100.00	66	309.12	0.27
14	69.16	4.27	67	311.98	11.84
15	69.54	0.76	68	312.66	5.45
16	69.85	1.61	69	314.03	0.34
17	70.28	0.29	70	315.19	0.46
18	72.15	0.32	71	342.91	2.17
19	72.46	0.37	72	355.05	4.86
20	92.97	0.39	73	358.48	0.32
21	99.92	0.42	74	370.56	0.34
22	118.96	6.25	75	373.82	6.03
23	119.94	0.42	76	374.54	4.05
24	124.02	0.49	77	376.19	0.27
25	130.91	1.68	78	377.67	0.24
26	142.96	0.81	79	392.75	7.94
27	149.92	0.46	80	393.67	4.08
28	155.00	0.95	81	395.97	0.27
29	161.98	0.46	82	401.18	0.24
30	168.97	0.37	83	438.60	0.22
31	174.05	0.39	84	440.61	0.37
32	180.95	1.68	85	443.00	12.16
33	181.94	0.32	86	444.09	3.79
34	182.80	0.22	87	461.96	0.61
35	185.98	0.42			
36	192.93	1.78			
37	193.91	0.29			
38	204.94	1.10			
39	205.94	0.32			
40	208.24	0.37			
41	211.94	0.34			
42	216.90	0.78			
43	223.93	0.42			
44	230.97	0.29			
45	235.97	1.22			
46	236.91	0.34			
47	242.82	9.50			
48	243.69	4.98			
49	252.40	0.27			
50	255.06	4.47			
51	258.24	0.27			
52	261.98	0.42			
53	265.95	1.05			

RNB31 22 A.N.BARNES
CAL:CALM23

No. 18 MW 424

23-JUN-81

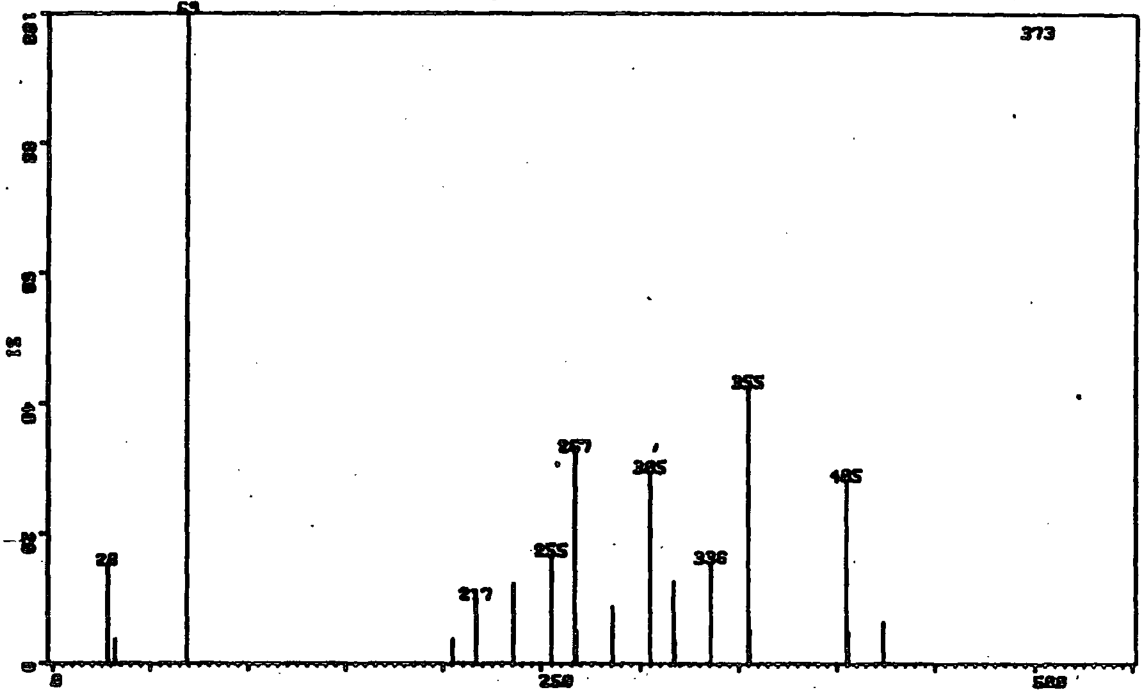


PEAK NO.	MASS	%HT. BASE
1	28.13	3.74
2	68.23	0.91
3	68.25	0.91
4	68.33	1.82
5	68.81	100.00
6	68.99	18.32
7	69.28	1.00
8	69.35	1.00
9	69.64	1.19
10	69.75	1.55
11	118.85	2.10
12	142.82	1.37
13	149.83	1.28
14	155.03	1.09
15	167.05	1.19
16	180.97	2.83
17	186.01	2.10
18	204.96	2.83
19	211.87	0.82
20	216.90	5.29
21	217.84	1.37
22	236.00	7.66
23	236.98	1.37
24	242.97	2.28
25	254.90	10.03
26	256.06	1.37
27	256.71	1.19
28	265.10	1.00
29	266.04	1.00
30	266.88	20.60
31	267.49	18.60
32	269.34	1.00
33	285.93	8.11
34	287.07	1.37
35	297.98	1.00
36	303.78	1.28
37	305.21	12.85
38	317.05	4.65
39	335.82	8.20
40	336.06	1.55
41	354.78	24.98
42	355.72	18.14
43	357.57	1.46
44	404.90	24.52
45	405.61	17.05
46	406.89	1.19
47	424.12	16.41

RNB30 15 R.N.BARNES
CAL:CALM23

No. 19 MW 424

23-JUN-81

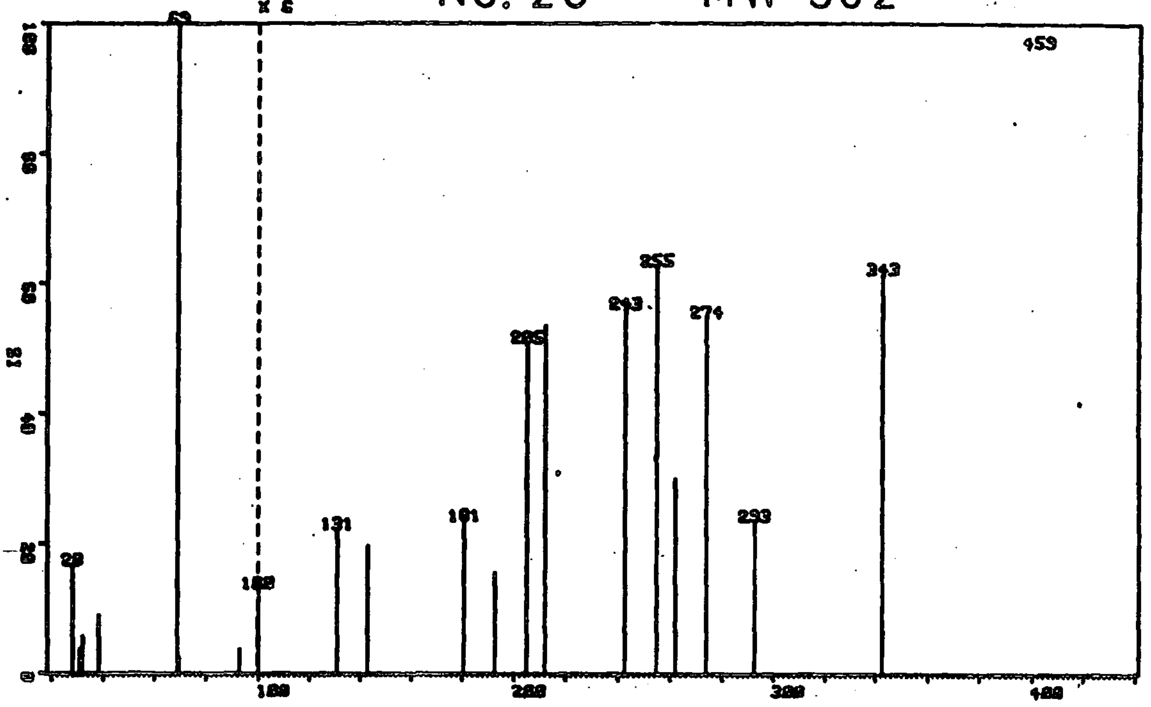


PEAK NO.	MASS	%HT. BASE
1	28.13	15.28
2	32.01	3.75
3	68.97	100.00
4	204.88	3.75
5	216.86	9.92
6	235.92	12.33
7	254.91	16.62
8	266.89	32.71
9	267.93	5.09
10	285.90	8.85
11	304.89	29.49
12	316.91	12.60
13	317.86	3.49
14	335.82	15.55
15	354.87	42.63
16	355.91	5.09
17	404.93	28.15
18	405.94	4.83
19	423.91	6.43

RNB34 11 R.N.BARNES
CAL:CAL123

No. 20 MW 362

23-JUN-81

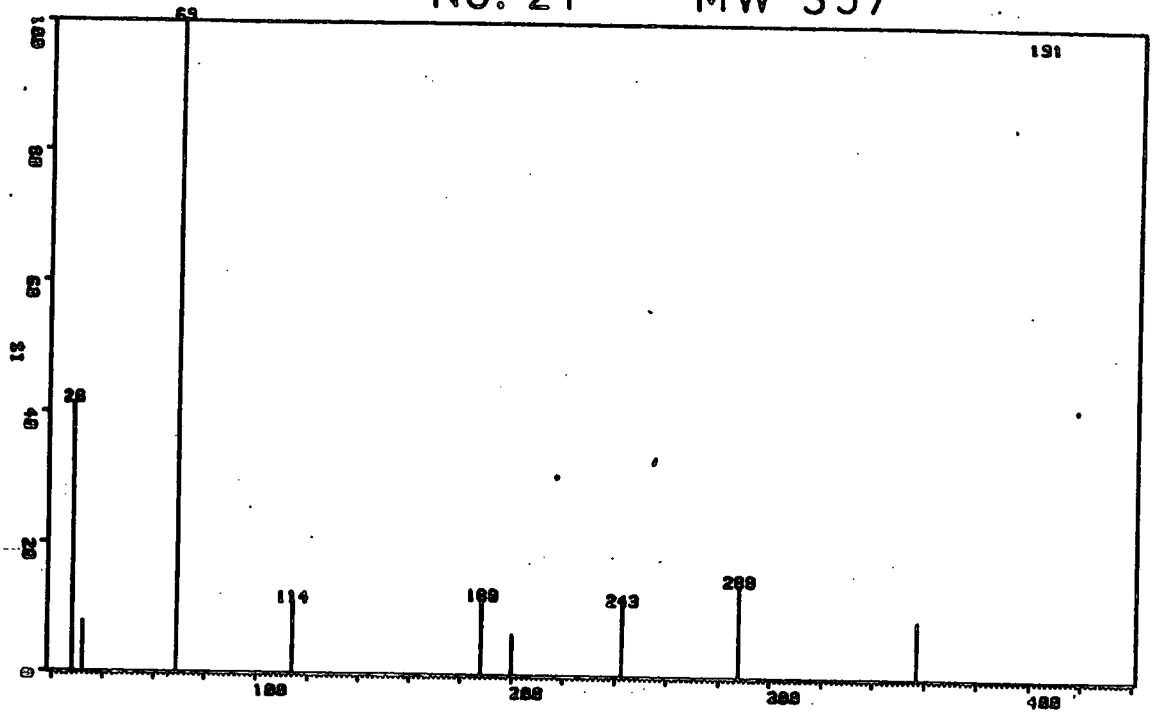


PEAK NO.	MASS	%HT. BASE
1	28.13	16.78
2	30.92	3.70
3	32.01	5.66
4	38.46	8.93
5	68.97	100.00
6	69.91	2.40
7	92.97	3.70
8	99.90	13.07
9	130.94	3.70
10	142.91	3.27
11	180.89	3.92
12	192.92	2.61
13	204.94	8.50
14	211.93	8.93
15	242.85	9.37
16	254.91	10.46
17	261.96	5.01
18	273.87	9.15
19	292.87	3.92
20	342.79	10.24

RNB134 6 A.N.BARNES
CAL:CAL13

No. 21 MW 357

13-JAN-81

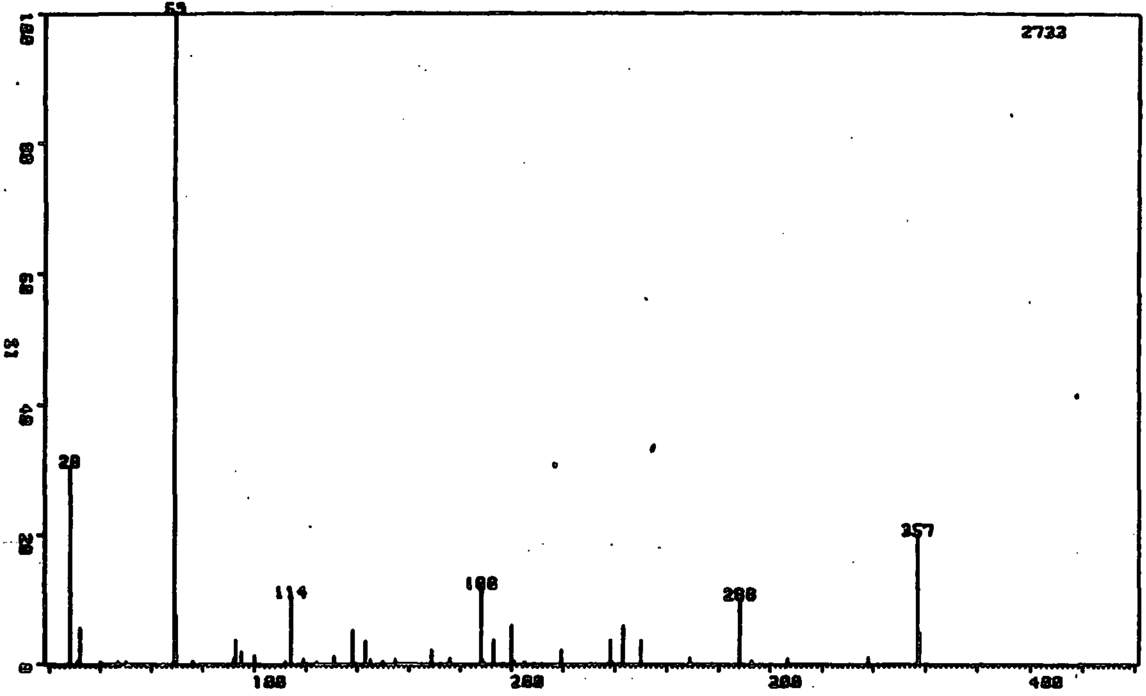


PEAK NO.	MASS	%HT. BASE
1	28.10	41.36
2	31.98	7.85
3	68.99	100.00
4	114.05	10.99
5	188.10	11.52
6	199.97	6.28
7	243.01	10.99
8	287.97	14.14
9	357.04	8.90

ANB134 S A.N.BARNES
CAL:CAL13

No. 22 MW 357

13-JAN-81

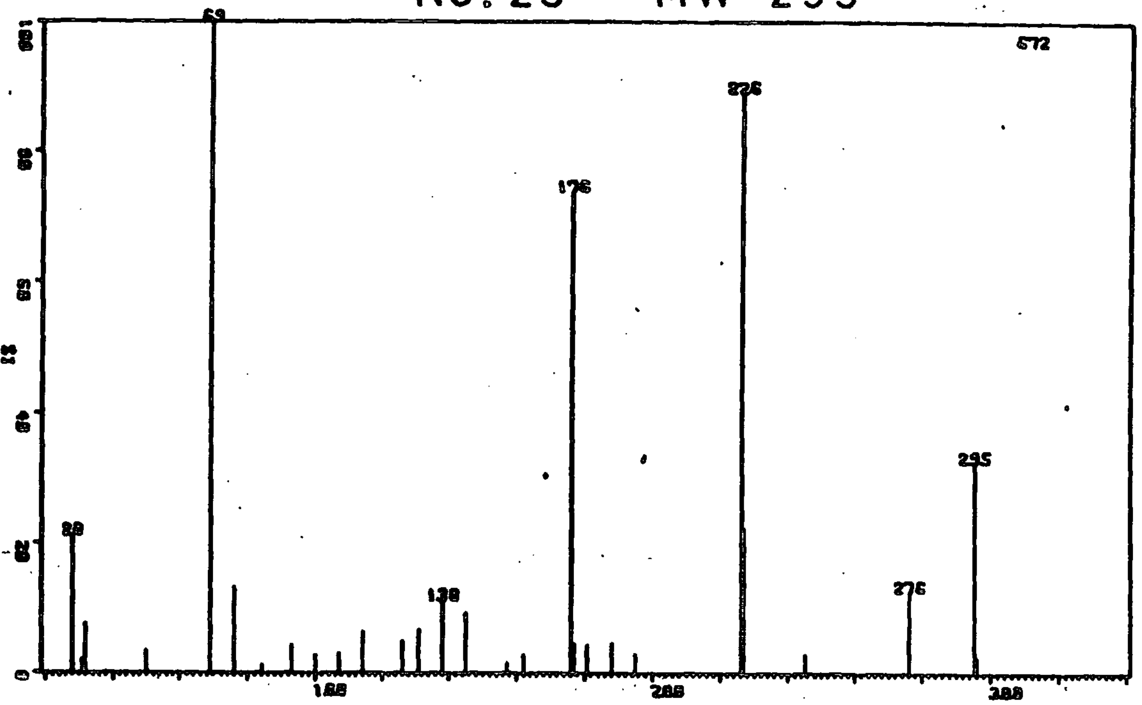


PEAK NO.	MASS	%HT. BASE
1	28.10	30.52
2	30.87	0.51
3	31.98	5.60
4	39.83	0.51
5	47.09	0.48
6	49.88	0.44
7	68.64	0.48
8	68.98	100.00
9	69.14	7.57
10	69.89	1.46
11	76.09	0.62
12	92.01	0.80
13	93.03	3.66
14	95.05	1.98
15	99.91	1.43
16	112.00	0.51
17	114.05	10.35
18	119.05	0.84
19	124.09	0.48
20	131.07	1.35
21	138.09	5.27
22	139.09	0.40
23	143.07	3.55
24	145.08	0.77
25	149.92	0.51
26	155.01	0.73
27	169.10	2.20
28	176.14	0.91
29	188.00	11.67
30	188.98	0.70
31	192.97	3.70
32	199.89	5.96
33	200.95	0.59
34	204.98	0.48
35	219.15	2.16
36	238.04	3.77
37	239.01	0.40
38	243.08	5.93
39	249.91	3.66
40	268.97	1.02
41	288.01	9.95
42	292.94	0.62
43	306.92	0.91
44	337.85	1.17
45	356.91	19.80
46	357.85	4.79

RNB19 7 R.N.BARNES
CAL:CALN23

No. 23 MW 295

28-APR-81

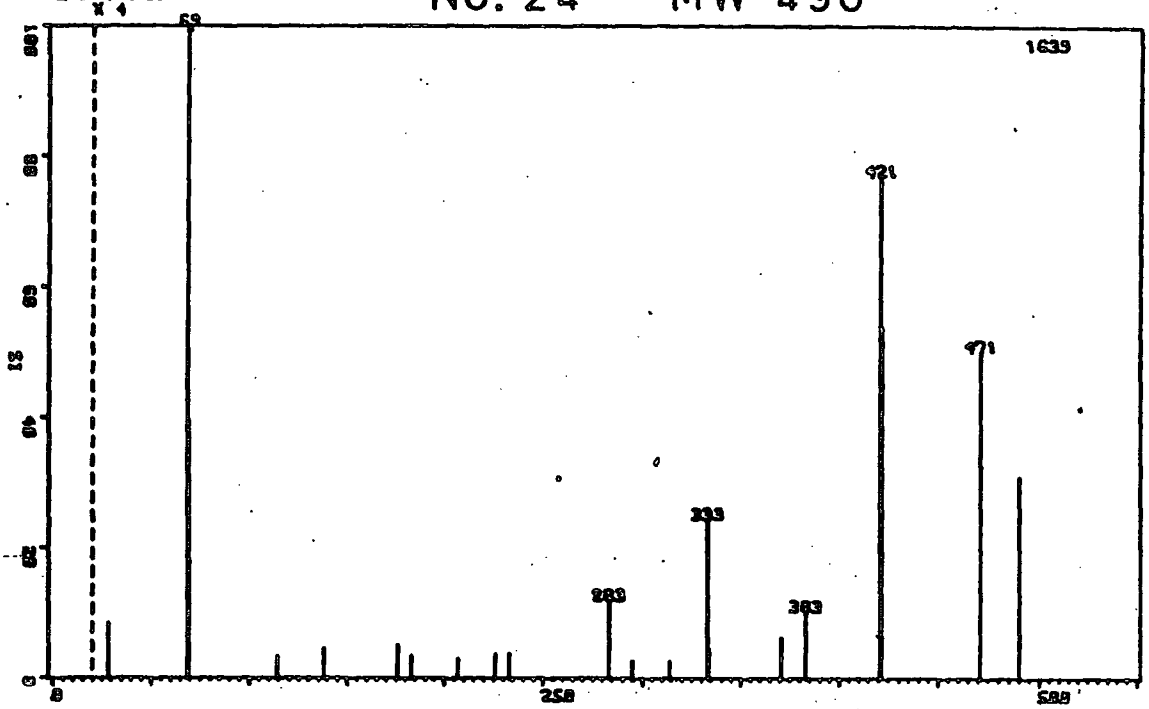


PEAK NO.	MASS	%HT. BASE
1	27.91	1.79
2	28.00	1.34
3	28.13	21.28
4	30.93	2.08
5	32.03	7.59
6	49.89	3.42
7	69.02	100.00
8	76.12	13.24
9	84.31	1.34
10	93.10	4.32
11	100.00	2.83
12	107.13	3.12
13	114.11	6.40
14	126.10	4.91
15	131.05	6.70
16	138.06	11.16
17	145.12	9.23
18	157.16	1.64
19	162.05	2.83
20	176.12	73.81
21	177.12	4.61
22	181.01	4.32
23	188.08	4.61
24	195.06	2.98
25	226.15	89.14
26	226.75	22.32
27	245.26	2.98
28	276.23	12.50
29	295.29	32.44
30	296.23	2.53

RNB8 23 R.N.BARNES
CAL:CALM23

No. 24 MW 490

28-APR-81

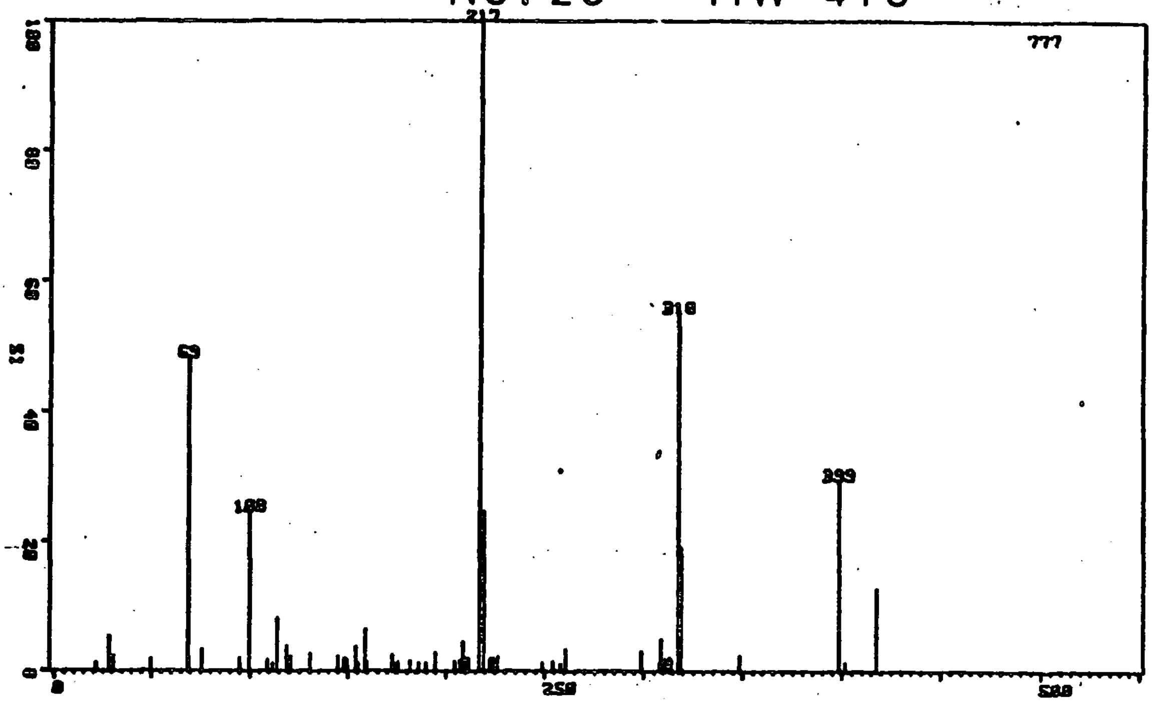


PEAK NO.	MASS	%HT. BASE
1	28.13	2.14
2	68.69	0.67
3	69.00	100.00
4	69.14	9.95
5	69.90	0.98
6	114.17	0.85
7	138.08	1.16
8	176.18	1.28
9	183.08	0.85
10	207.16	0.73
11	226.16	0.92
12	233.13	0.92
13	283.28	2.99
14	295.31	0.67
15	314.09	0.67
16	333.09	6.10
17	334.14	1.16
18	371.24	1.59
19	383.11	2.56
20	421.00	19.28
21	421.77	13.48
22	471.43	12.57
23	490.37	7.75

RNB32 11 R.N.BARNES
CAL:CALN23

No. 25 MW 418

23-JUN-81

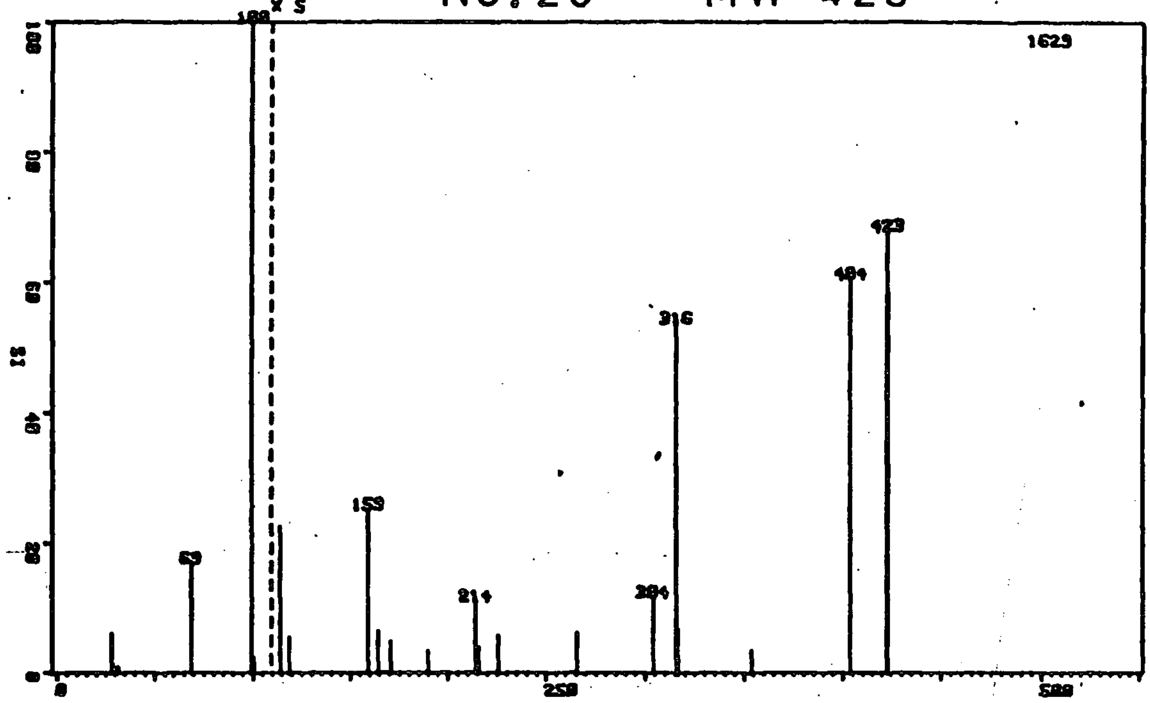


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	21.79	1.29	54	260.93	3.35
2	28.13	5.41	55	298.89	3.09
3	30.91	2.32	56	299.46	1.42
4	49.87	1.80	57	308.17	1.42
5	68.94	48.26	58	308.89	4.89
6	69.28	1.93	59	309.94	1.29
7	75.95	3.35	60	311.09	1.93
8	94.89	1.93	61	312.03	1.67
9	99.86	24.58	62	313.14	1.29
10	108.93	1.67	63	313.58	2.19
11	109.54	1.29	64	314.37	1.67
12	111.96	1.16	65	317.58	55.21
13	114.00	8.11	66	319.26	19.05
14	118.90	3.73	67	348.70	2.32
15	120.93	2.19	68	398.59	29.47
16	130.87	2.70	69	401.98	1.42
17	144.95	2.32	70	417.77	12.74
18	147.94	1.42			
19	148.35	1.93			
20	148.72	1.67			
21	149.08	2.06			
22	149.93	1.29			
23	150.15	1.67			
24	154.00	3.73			
25	155.76	1.16			
26	158.98	6.56			
27	159.91	1.42			
28	173.01	2.45			
29	174.14	1.16			
30	175.92	1.42			
31	181.07	1.54			
32	186.63	1.29			
33	190.02	1.29			
34	195.00	2.83			
35	204.65	1.54			
36	205.03	1.29			
37	207.40	1.67			
38	208.81	4.50			
39	209.99	1.93			
40	210.85	2.06			
41	212.22	1.93			
42	217.16	100.00			
43	219.24	24.58			
44	222.13	1.80			
45	222.51	1.93			
46	223.23	1.67			
47	223.72	1.29			
48	224.25	2.06			
49	224.74	1.93			
50	226.43	2.19			
51	240.91	1.29			
52	254.04	1.54			
53	258.03	1.16			

RNB33 10 R.N.BARNES
CAL:CALM23

No. 26 MW 423

23-JUN-81

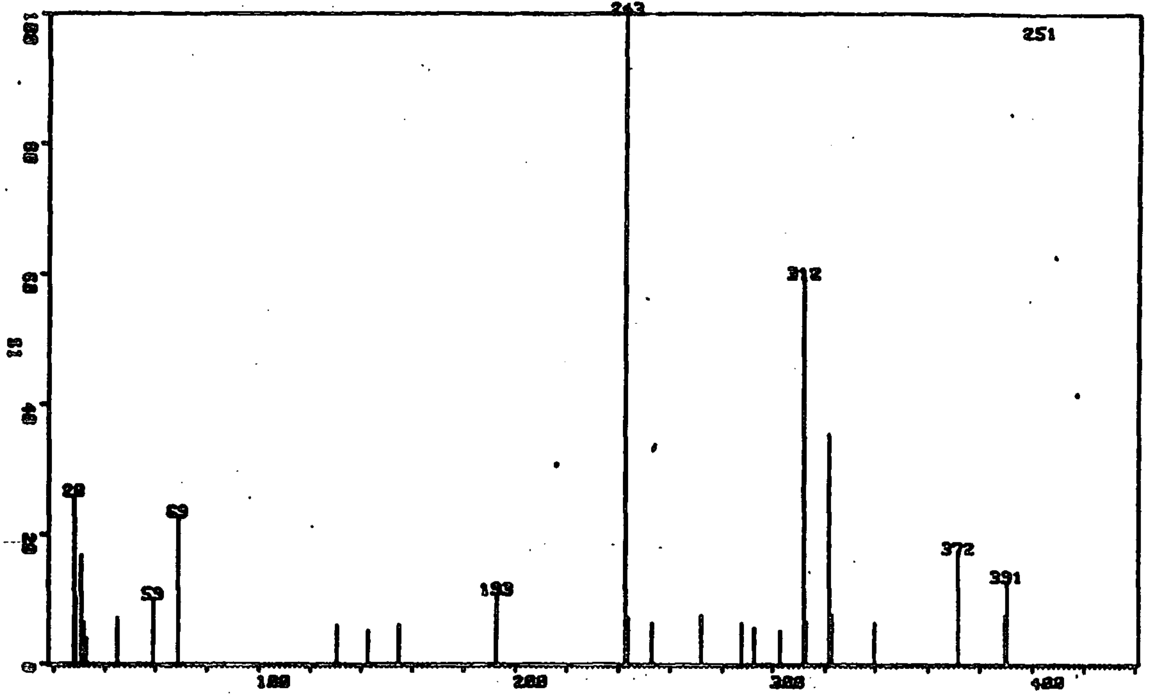


PEAK NO.	MASS	%HT. BASE
1	28.13	6.08
2	30.91	0.86
3	32.02	0.92
4	68.98	16.94
5	99.35	0.74
6	99.48	0.98
7	99.92	100.00
8	100.92	2.39
9	114.05	4.54
10	118.97	1.10
11	158.96	5.03
12	164.00	1.29
13	170.93	0.98
14	189.94	0.68
15	213.92	2.21
16	215.90	0.80
17	225.97	1.17
18	265.93	1.23
19	303.90	2.33
20	315.87	10.74
21	316.90	1.35
22	353.85	0.68
23	403.92	12.09
24	422.73	13.57
25	423.36	11.66

RNB37 7 R.N.BARNES
CAL:CAL/123

No. 27 MW 391

23-JUN-81

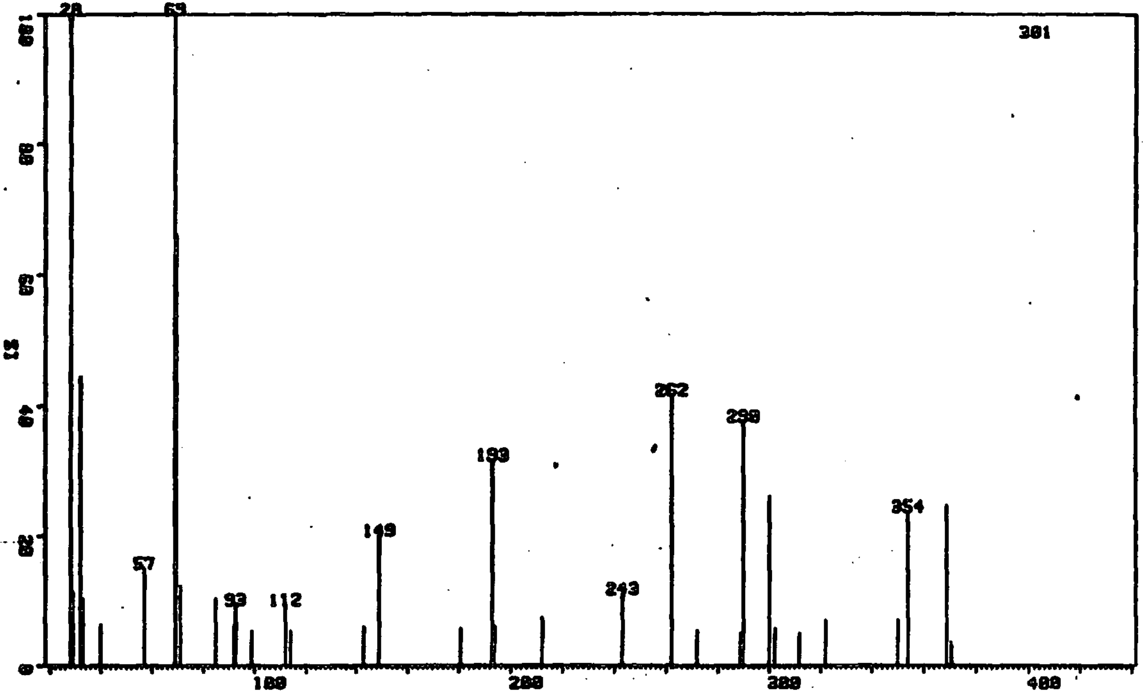


PEAK NO.	MASS	%HT. BASE
1	28.13	25.90
2	29.02	10.36
3	30.92	16.73
4	32.03	6.37
5	33.13	3.98
6	45.17	7.17
7	59.03	9.96
8	60.96	22.71
9	130.90	5.98
10	142.98	5.18
11	155.00	5.98
12	192.86	10.76
13	242.05	100.00
14	243.38	4.38
15	243.87	7.17
16	252.92	6.37
17	271.97	7.57
18	287.84	6.37
19	292.94	5.58
20	303.03	5.18
21	311.91	59.36
22	312.96	6.77
23	321.93	35.46
24	322.95	7.57
25	339.78	6.37
26	371.94	17.13
27	389.72	7.57
28	390.76	12.75

RNB149 25 R.N.BARNES
CAL:CAL19

No. 28 MW 371

19-JAN-81

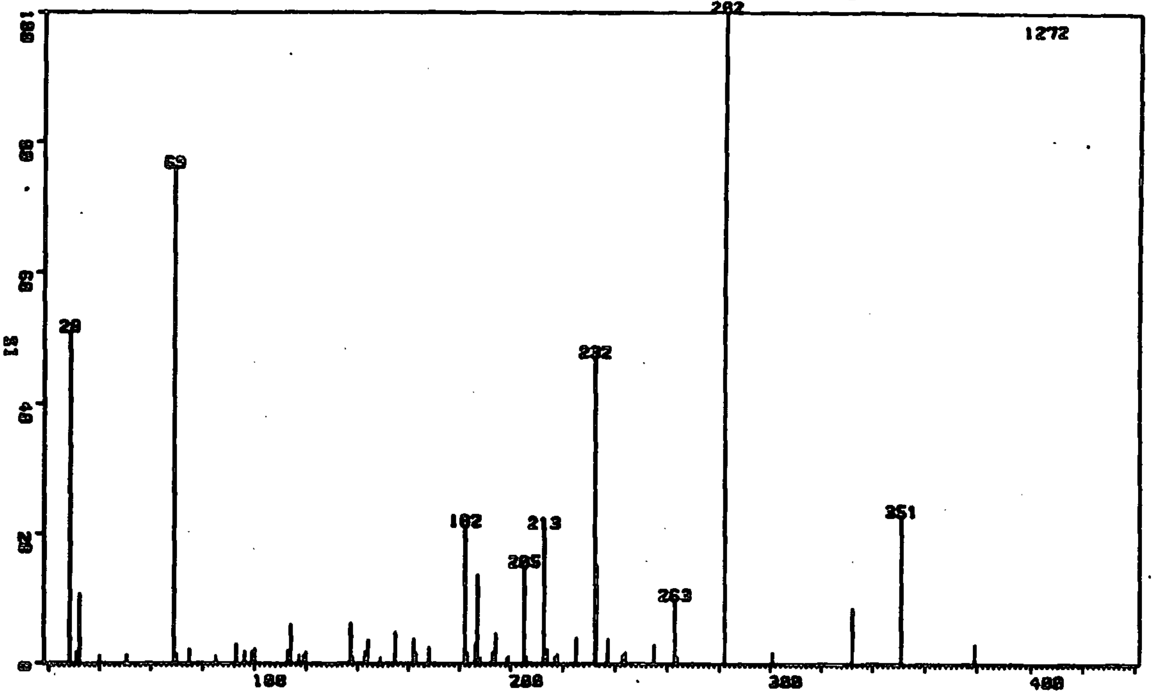


PEAK NO.	MASS	%HT. BASE
1	27.99	1.44
2	28.13	100.00
3	28.26	2.29
4	29.00	4.09
5	29.05	1.68
6	32.03	16.13
7	33.12	3.73
8	39.84	2.29
9	57.15	5.42
10	68.95	36.22
11	69.06	23.95
12	71.06	4.45
13	71.21	1.32
14	85.07	3.73
15	91.93	2.29
16	92.94	3.37
17	99.02	1.93
18	111.97	3.37
19	113.98	1.93
20	142.97	2.17
21	148.96	7.22
22	180.90	2.05
23	193.00	11.43
24	193.88	2.17
25	212.03	2.65
26	243.08	3.97
27	262.11	15.04
28	271.92	1.93
29	289.05	1.81
30	290.05	13.60
31	300.15	9.39
32	301.93	1.56
33	302.39	2.05
34	311.86	1.81
35	321.96	2.53
36	350.18	2.53
37	354.17	8.54
38	368.95	8.90
39	370.54	1.32
40	370.91	1.08

BG1493 8 R.N.BARNES
CAL:CAL3

No. 29 MW 379

03-FEB-81

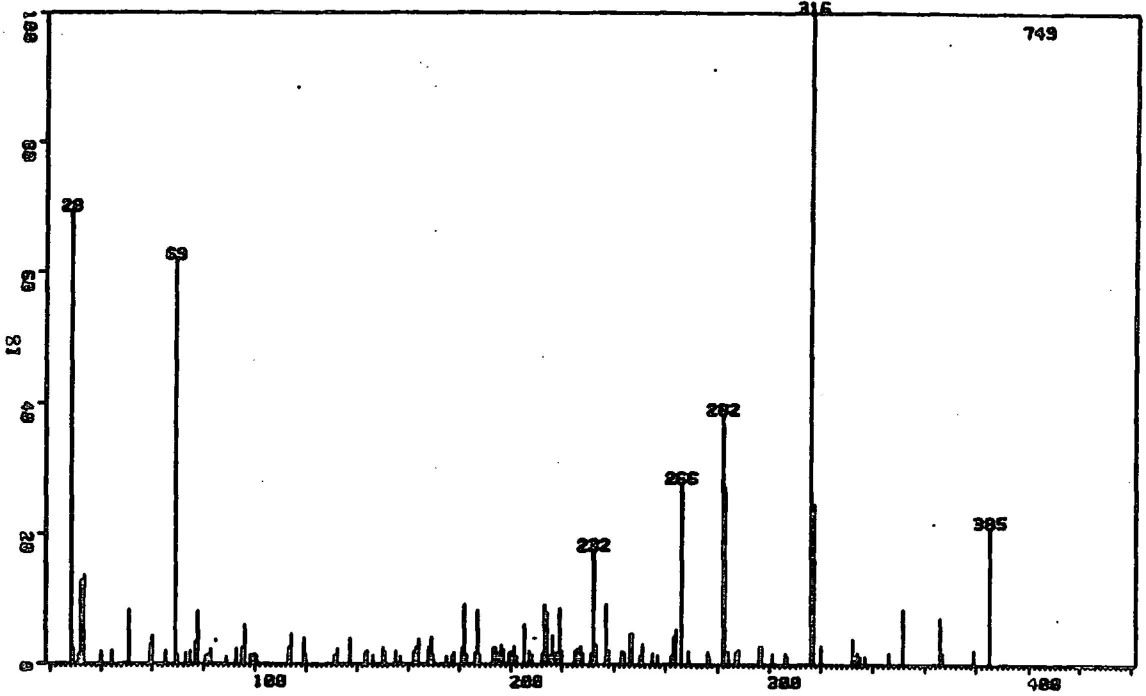


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.14	50.94	54	264.05	1.02
2	30.88	1.42	55	282.10	100.00
3	30.94	1.65	56	300.86	1.73
4	32.02	10.61	57	332.07	8.57
5	39.86	1.18	58	350.96	22.72
6	50.94	1.34	59	378.95	3.07
7	68.98	75.94			
8	69.91	1.49			
9	75.05	2.20			
10	85.01	1.18			
11	93.00	3.07			
12	96.04	1.81			
13	98.97	1.81			
14	99.95	2.20			
15	113.02	2.04			
16	114.03	5.97			
17	117.09	1.34			
18	118.93	1.26			
19	119.92	1.73			
20	136.97	6.13			
21	138.02	0.94			
22	142.86	1.81			
23	143.09	1.73			
24	144.01	3.54			
25	149.11	0.86			
26	154.95	4.80			
27	161.96	3.77			
28	162.84	1.73			
29	163.13	1.42			
30	167.92	2.44			
31	181.96	21.15			
32	183.02	1.65			
33	186.02	2.99			
34	186.98	13.60			
35	188.12	0.86			
36	193.00	1.73			
37	193.97	4.64			
38	198.75	0.86			
39	199.17	1.10			
40	204.92	14.86			
41	205.91	1.18			
42	212.74	20.83			
43	213.92	2.12			
44	216.83	0.94			
45	217.99	1.49			
46	225.02	3.93			
47	231.99	47.01			
48	232.82	15.02			
49	237.06	3.85			
50	243.03	1.42			
51	244.05	1.73			
52	255.03	3.07			
53	262.94	9.75			

RB1492 69 R.N.BARNES
CAL:CAL27

No.30 MW 385

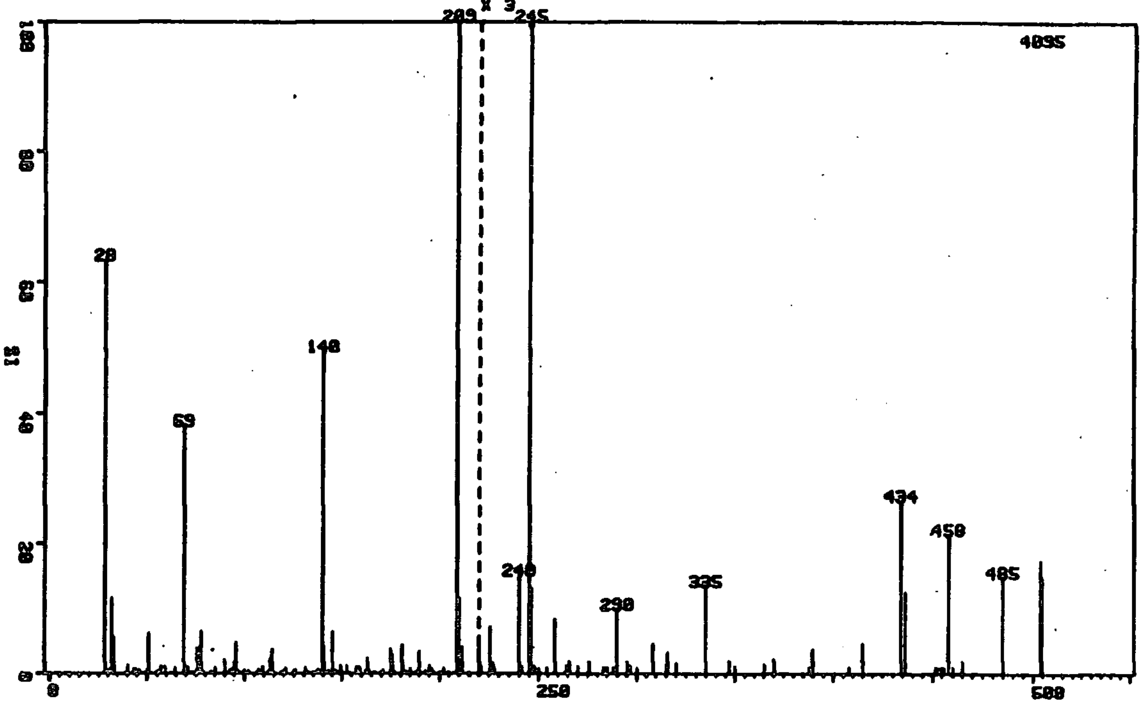
29-JAN-81



PEAK NO.	MASS	%HT. BASE
1	28.14	69.43
2	29.00	2.27
3	30.91	1.47
4	32.02	12.68
5	33.13	13.48
6	39.84	1.87
7	44.11	2.00
8	50.94	8.28
9	59.02	2.94
10	59.94	4.27
11	65.14	2.00
12	68.95	61.95
13	69.90	1.47
14	73.05	1.74
15	75.03	2.00
16	77.00	3.34
17	77.96	8.01
18	80.88	1.20
19	81.97	1.47
20	83.02	2.27
21	88.99	1.20
22	93.04	2.40
23	95.07	2.54
24	96.06	6.01
25	98.04	1.47
26	98.95	1.47
27	99.92	1.60
28	100.95	1.34
29	112.91	2.54
30	113.95	4.54
31	118.96	4.01
32	119.98	1.47
33	131.00	1.34
34	132.03	2.27
35	137.03	3.87
36	143.01	1.74
37	144.04	2.00
38	146.04	1.34
39	149.95	2.54
40	150.98	1.87
41	155.05	2.00
42	156.99	1.20
43	162.03	1.87
44	163.04	2.54
45	164.03	3.74
46	167.99	2.54
47	168.98	4.14
48	169.97	1.47
49	174.97	1.34
50	177.04	1.34
51	178.03	1.87
52	180.98	2.40
53	182.00	9.08
54	182.96	1.47
55	185.98	1.74
56	187.00	8.14
57	188.02	1.47
58	192.99	2.54
59	194.00	2.54
60	195.04	1.74
61	196.05	3.07
62	197.06	2.27
63	198.98	1.74
64	199.96	2.00
65	200.99	2.80
66	201.99	1.34
67	204.98	6.14
68	207.04	2.00
69	208.00	1.47
70	212.04	1.74
71	213.04	8.95
72	214.04	7.88
73	215.05	1.47
74	216.05	4.41
75	217.02	1.74
76	218.02	1.87
77	218.95	8.54
78	219.96	2.00
79	224.99	2.14
80	226.05	2.40
81	227.06	2.80
82	228.04	1.74
83	231.02	1.60
84	232.00	17.49
85	233.02	3.07
86	237.00	9.21
87	237.99	2.14
88	243.05	2.00
89	243.99	1.87
90	246.03	4.67
91	247.06	4.67
92	249.95	1.34
93	250.97	3.20
94	254.95	1.74
95	257.03	1.47
96	261.99	1.34
97	262.97	4.27
98	263.99	5.34
99	266.04	27.77
100	268.97	2.00
101	276.00	1.87
102	277.01	1.20
103	281.86	38.32
104	282.56	27.10
105	284.05	2.00
106	287.06	1.87
107	288.07	2.27
108	296.11	2.80
109	297.06	2.80
110	301.01	1.60
111	306.01	1.74
112	306.92	1.34
113	315.81	100.00
114	317.17	24.43
115	319.90	2.94
116	332.02	3.87
117	332.97	1.34
118	334.08	1.87
119	335.15	1.34
120	337.07	1.34
121	346.03	1.74
122	351.37	8.41
123	365.90	7.08
124	366.94	1.74
125	378.94	2.27
126	385.09	20.96

RNB153 14 R.N.BARNES
CAL:CAL19

No.31 MW 504 19-JAN-81

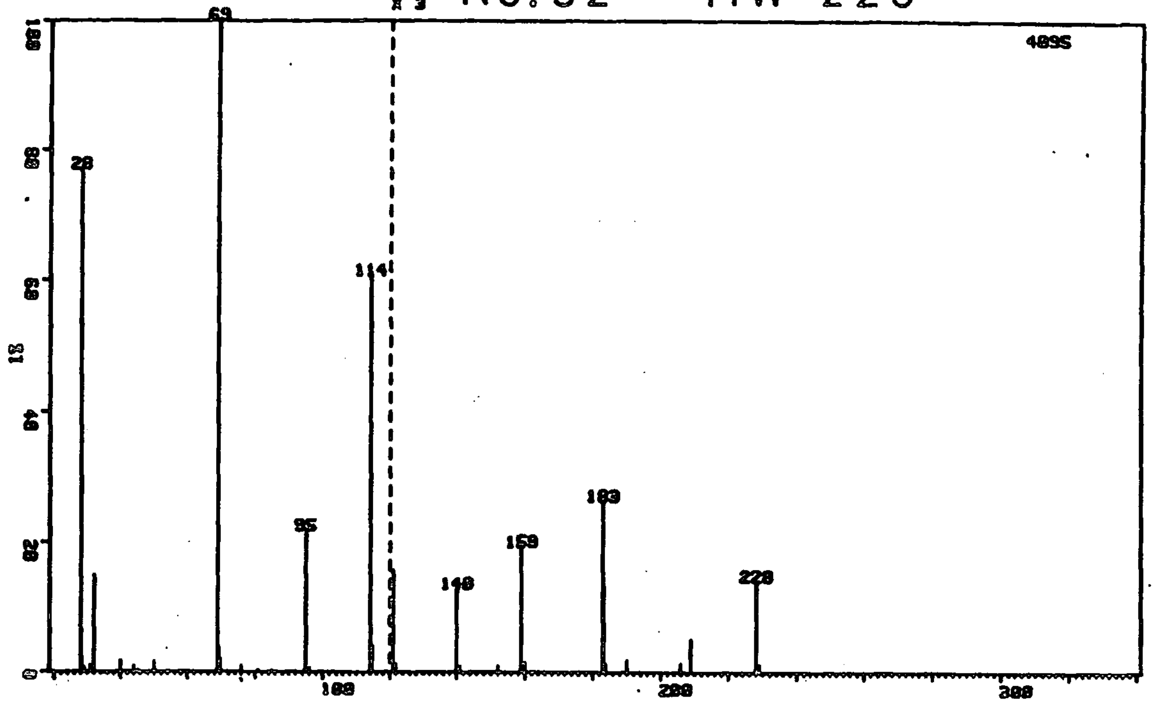


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	63.30	54	130.98	0.93	107	220.04	1.27
2	29.00	0.66	55	131.97	0.39	108	221.17	0.39
3	30.92	0.59	56	133.09	0.27	109	225.68	2.37
4	32.02	11.58	57	135.09	0.29	110	227.11	0.56
5	33.12	5.57	58	137.04	0.46	111	228.02	0.29
6	39.84	1.25	59	138.00	0.71	112	240.09	5.01
7	43.15	0.66	60	138.54	0.32	113	241.64	0.37
8	44.13	0.71	61	139.91	49.40	114	245.03	33.70
9	45.17	0.46	62	140.72	4.08	115	246.25	4.37
10	46.14	0.56	63	142.10	0.42	116	247.99	0.37
11	49.88	0.51	64	143.06	0.54	117	249.94	0.27
12	50.95	6.08	65	145.07	6.37	118	254.01	0.29
13	55.18	0.46	66	145.96	0.27	119	258.20	2.81
14	56.15	0.49	67	146.15	0.49	120	263.88	0.42
15	57.15	1.12	68	147.10	0.51	121	265.89	0.63
16	59.02	1.10	69	149.05	1.34	122	269.87	0.39
17	64.13	0.85	70	150.02	0.56	123	275.97	0.63
18	68.95	38.05	71	152.05	1.25	124	283.05	0.32
19	69.28	0.32	72	154.04	0.27	125	285.05	0.34
20	69.37	0.32	73	157.07	1.03	126	288.05	0.29
21	69.52	0.34	74	158.02	0.71	127	289.95	3.27
22	69.91	1.05	75	159.06	0.98	128	294.98	0.63
23	71.01	0.95	76	162.10	0.54	129	296.06	0.29
24	73.03	0.29	77	163.02	2.42	130	296.95	0.44
25	75.01	0.54	78	164.06	0.51	131	299.95	0.27
26	76.00	3.93	79	166.10	0.34	132	308.18	1.54
27	76.96	3.79	80	167.09	0.27	133	314.85	0.46
28	77.94	6.47	81	169.99	0.32	134	315.96	1.10
29	78.87	0.46	82	171.04	0.61	135	319.85	0.56
30	82.99	0.42	83	174.54	0.22	136	335.13	4.47
31	85.06	0.81	84	175.07	3.76	137	346.95	0.68
32	89.88	2.08	85	176.04	2.95	138	349.96	0.42
33	90.96	0.29	86	177.06	0.46	139	364.90	0.51
34	92.74	0.27	87	180.97	4.42	140	369.84	0.76
35	93.02	0.63	88	181.95	0.56	141	387.78	0.32
36	93.33	0.22	89	183.06	0.39	142	389.75	1.25
37	94.07	0.61	90	185.10	0.78	143	408.00	0.32
38	95.07	1.66	91	188.04	0.32	144	415.20	1.54
39	96.04	4.76	92	189.00	0.29	145	434.34	8.84
40	97.05	0.49	93	189.98	3.39	146	436.47	4.18
41	99.92	0.56	94	191.05	0.24	147	451.72	0.32
42	102.01	0.49	95	193.00	0.56	148	452.90	0.27
43	107.05	0.61	96	194.98	1.29	149	454.53	0.32
44	108.99	1.05	97	196.02	0.76	150	455.42	0.27
45	112.00	0.32	98	197.03	0.37	151	455.94	0.29
46	113.00	2.37	99	199.98	0.32	152	457.87	7.11
47	114.01	3.76	100	202.00	0.85	153	460.20	0.34
48	115.04	0.29	101	204.36	0.29	154	464.82	0.66
49	118.96	0.42	102	204.91	0.32	155	485.05	4.91
50	119.92	0.46	103	208.82	100.00	156	503.57	5.79
51	120.97	0.81	104	209.79	11.50	157	504.61	4.93
52	125.05	0.44	105	211.30	4.08			
53	126.07	0.63	106	215.20	0.22			

ANB144 32 A.N.BARNES
CAL:CAL19

No. 32 MW 228

21-JAN-81

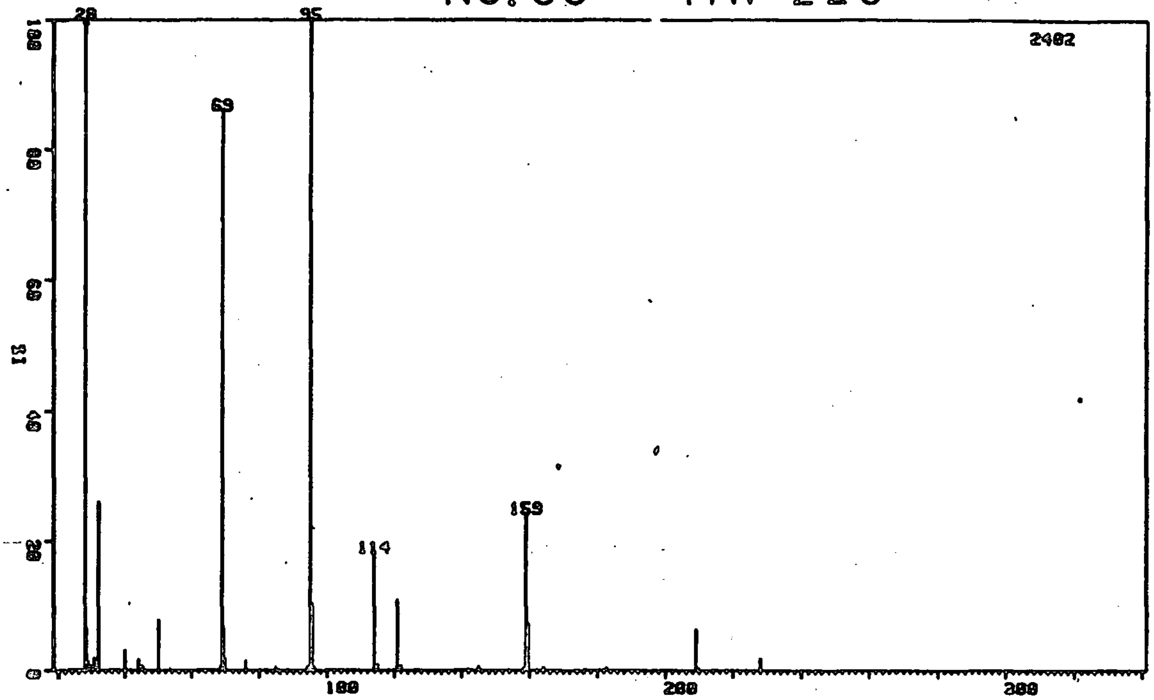


PEAK NO.	MASS	%HT. BASE
1	28.13	77.05
2	28.22	2.15
3	29.00	0.66
4	30.92	0.98
5	32.03	14.90
6	39.84	1.68
7	44.12	0.90
8	45.18	0.32
9	49.88	1.64
10	68.26	0.27
11	68.98	100.00
12	69.25	3.88
13	69.83	2.03
14	70.37	0.27
15	76.02	0.90
16	80.87	0.42
17	84.97	0.32
18	91.96	0.24
19	94.64	0.27
20	95.05	21.76
21	96.04	0.76
22	114.03	60.76
23	114.70	3.98
24	119.04	0.27
25	121.05	5.23
26	121.36	0.22
27	122.05	0.44
28	140.01	4.27
29	141.04	0.29
30	152.10	0.32
31	159.05	6.42
32	159.59	0.29
33	160.05	0.51
34	183.08	8.77
35	183.36	4.47
36	184.10	0.46
37	190.09	0.63
38	206.01	0.46
39	209.03	1.68
40	228.10	4.69
41	229.08	0.42

9NB144 S A.N.BARNES
CAL:CAL19

No. 33 MW 228

21-JAN-81

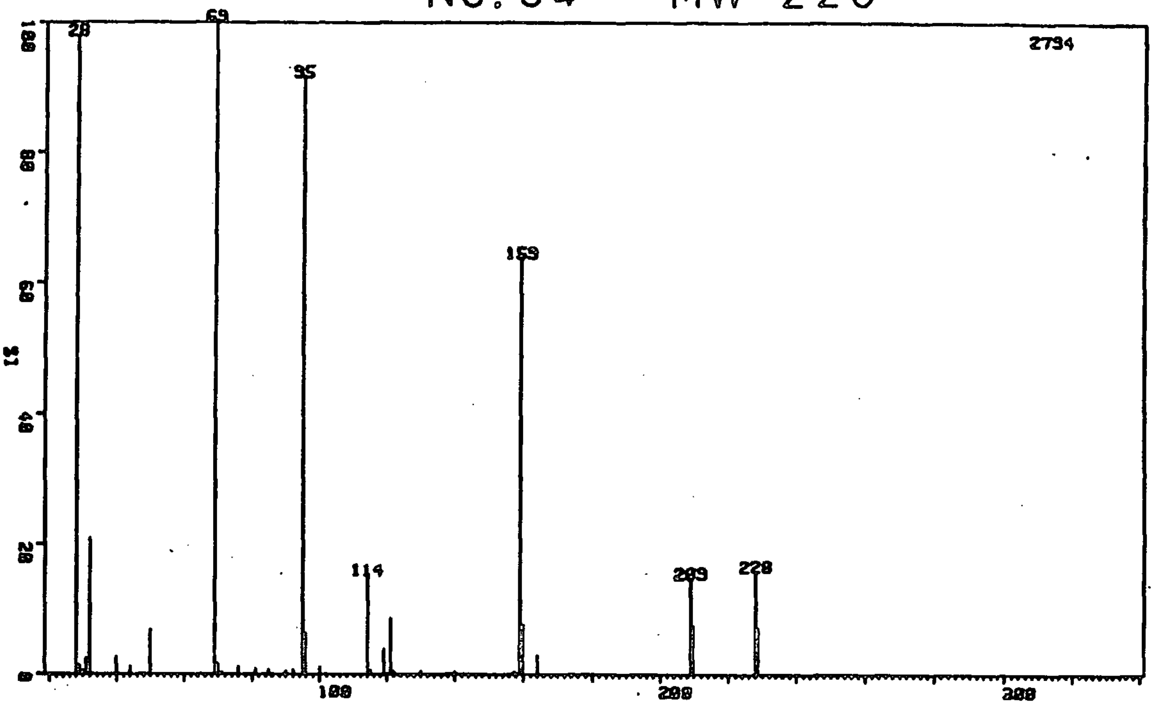


PEAK NO.	MASS	%HT. BASE
1	27.99	0.37
2	28.13	100.00
3	28.23	5.40
4	29.00	1.09
5	29.85	0.48
6	30.92	1.56
7	32.02	21.20
8	39.84	2.55
9	44.13	1.39
10	45.14	0.58
11	49.88	6.35
12	68.46	0.51
13	68.99	70.10
14	69.23	5.47
15	69.87	1.53
16	76.02	1.19
17	84.99	0.44
18	94.01	0.41
19	94.23	0.51
20	94.97	81.62
21	95.59	8.32
22	96.30	0.37
23	96.39	0.44
24	113.97	14.81
25	114.53	0.34
26	114.97	0.63
27	120.91	8.87
28	121.98	0.61
29	144.97	0.51
30	158.26	0.41
31	158.91	19.71
32	159.48	5.95
33	163.99	0.44
34	182.94	0.37
35	208.89	5.23
36	209.81	0.41
37	227.99	1.56

RNB144 8 R.N.BARNES
CAL:CAL19

No. 34 MW 228

21-JAN-81

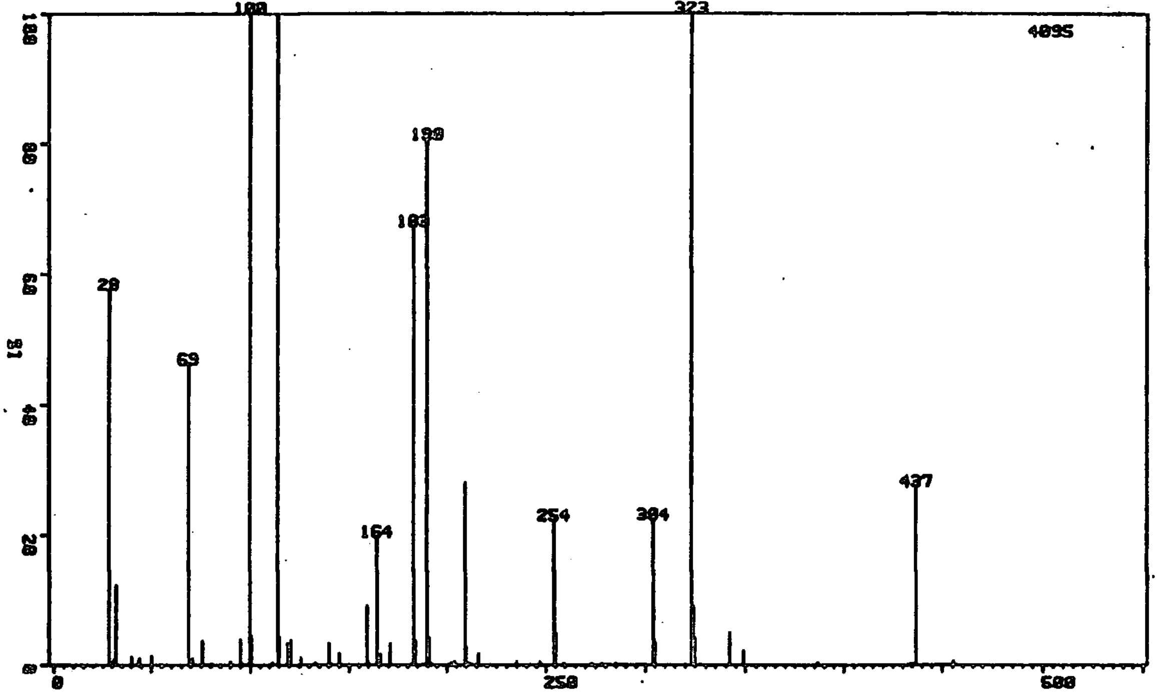


PEAK NO.	MASS	%HT. BASE
1	28.13	97.85
2	28.32	0.39
3	28.99	1.40
4	29.81	0.50
5	30.90	2.47
6	32.02	20.87
7	39.83	2.72
8	44.12	1.22
9	49.87	6.84
10	68.98	100.00
11	69.38	0.36
12	69.45	0.36
13	69.91	1.65
14	70.96	0.39
15	76.02	1.25
16	80.89	0.82
17	85.02	0.72
18	89.90	0.50
19	92.01	0.64
20	95.05	91.52
21	95.76	6.37
22	99.99	1.18
23	114.10	15.28
24	115.09	0.68
25	119.01	3.90
26	121.02	8.59
27	122.06	0.50
28	130.00	0.50
29	140.02	0.47
30	157.22	0.39
31	157.87	0.39
32	159.00	63.71
33	159.78	7.62
34	164.11	2.93
35	208.96	14.71
36	209.58	7.37
37	228.02	15.75
38	228.66	7.09

RNB136 S3 R.N.BARNES
CAL:CAL19

No. 35 MW 456

21-NOV-80

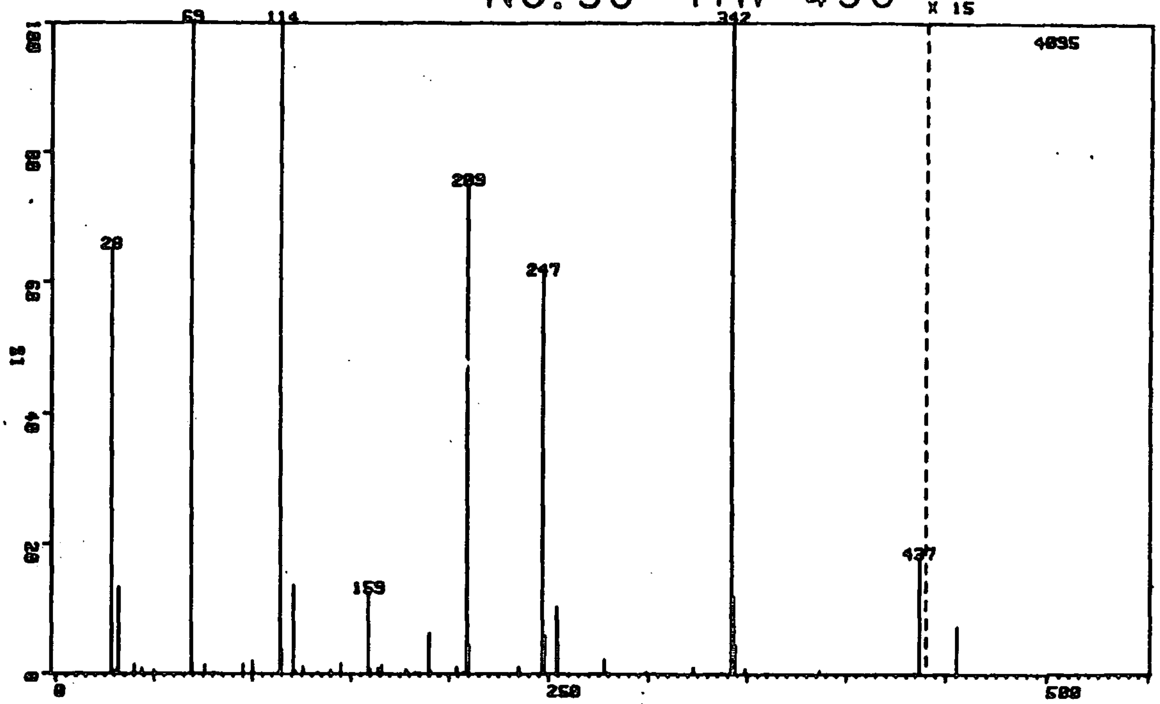


PEAK NO.	MASS	%HT. BASE
1	28.1348	57.70
2	28.9941	0.44
3	30.9033	0.83
4	32.0239	12.31
5	39.8364	1.29
6	43.1152	0.42
7	44.1089	1.00
8	49.8682	1.37
9	68.9575	46.25
10	69.5215	0.34
11	69.8828	0.78
12	70.9741	1.00
13	76.0669	3.69
14	80.9350	0.32
15	89.8608	0.51
16	95.0471	3.93
17	96.0383	0.29
18	98.8533	0.29
19	99.9055	100.00
20	100.7404	4.47
21	111.0421	0.27
22	111.1764	0.27
23	111.9943	0.46
24	114.0695	100.00
25	114.9460	4.30
26	119.0036	3.39
27	121.0006	3.91
28	126.0520	1.20
29	133.0270	0.46
30	139.9704	3.39
31	141.0666	0.29
32	145.0436	1.83
33	158.9914	9.06
34	159.9459	0.51
35	164.0011	19.71
36	164.9899	1.00
37	166.0079	1.66
38	170.9469	3.30
39	181.7331	0.27
40	182.9684	67.28
41	183.9065	3.74
42	187.9976	0.24
43	188.4006	0.24
44	189.9118	80.56
45	190.8444	4.22
46	191.7624	0.46
47	201.9821	0.49
48	204.0035	0.51
49	208.9352	27.94
50	209.8239	2.86
51	210.0911	0.42
52	211.7162	0.32
53	212.5756	0.27
54	216.0180	1.76
55	234.9560	0.59
56	246.9726	0.56
57	253.9550	22.15
58	254.8069	4.91
59	258.7690	0.24
60	259.1108	0.34
61	273.1025	0.29
62	277.9192	0.32
63	285.0677	0.37
64	299.1815	0.27
65	303.9642	22.34
66	304.8797	3.57
67	320.0269	0.27
68	322.9787	100.00
69	323.9991	9.06
70	324.9659	4.18
71	327.1168	0.24
72	342.0509	4.93
73	348.9820	2.27
74	386.8092	0.56
75	433.9542	0.24
76	436.9326	27.40
77	455.8926	0.59

RNB136 39 A.N.BARNES
CAL:CAL19

No. 36 MW 456

21-NOV-80

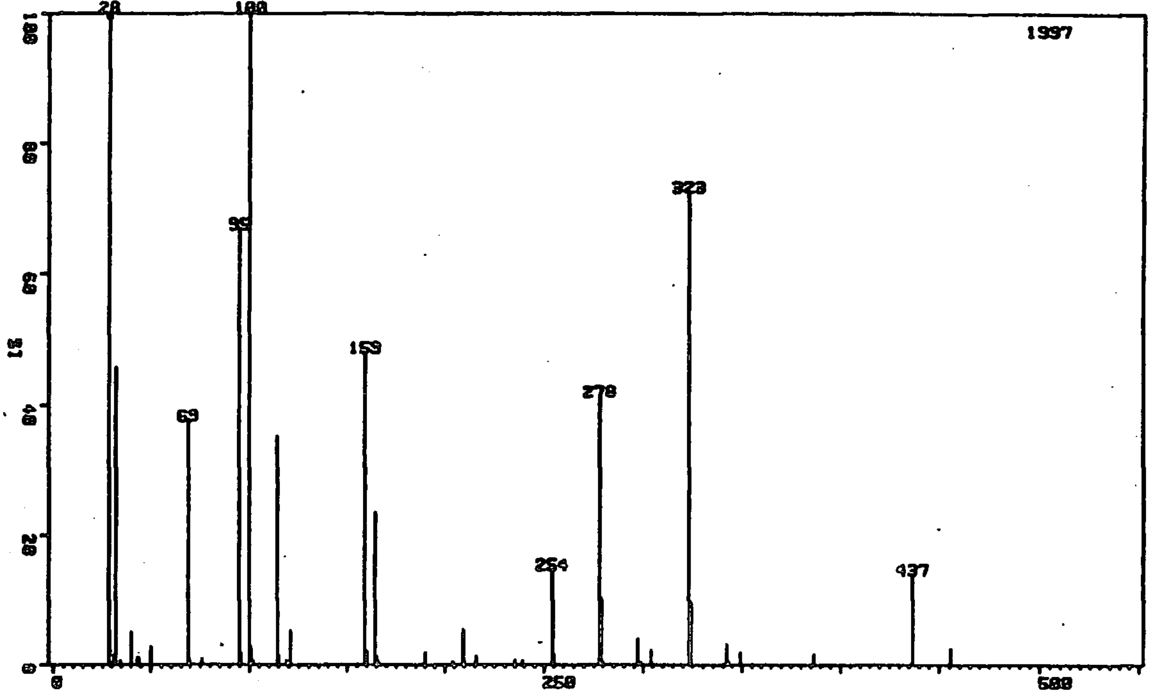


PEAK NO.	MASS	%HT. BASE
1	28.1348	65.08
2	28.3740	0.29
3	28.9990	0.66
4	30.9106	0.61
5	32.0190	13.33
6	39.8291	1.42
7	43.1152	0.27
8	44.1089	0.73
9	49.8608	0.56
10	68.9477	100.00
11	69.4775	0.49
12	69.8828	1.64
13	76.0669	1.42
14	80.8789	0.27
15	80.9912	0.27
16	95.0122	1.56
17	99.8559	1.93
18	100.3779	0.27
19	100.8124	0.29
20	113.0536	0.32
21	113.9887	100.00
22	114.8822	3.79
23	120.9470	13.65
24	121.9846	0.56
25	126.0397	1.07
26	133.0368	0.32
27	139.9362	0.61
28	144.9850	1.61
29	158.9304	12.43
30	159.9118	0.68
31	163.9670	0.81
32	165.9445	1.29
33	178.0759	0.71
34	179.0695	0.29
35	182.9636	0.32
36	189.8459	6.15
37	190.8171	0.51
38	203.9804	1.05
39	207.3348	0.32
40	207.6083	0.27
41	208.9462	74.90
42	209.9374	4.52
43	234.9227	1.07
44	246.9003	61.10
45	247.9232	5.79
46	253.8802	10.23
47	254.6329	4.52
48	277.8677	2.22
49	279.0482	0.24
50	298.8675	0.37
51	322.0763	1.10
52	337.4776	0.29
53	337.9244	0.22
54	341.8624	100.00
55	342.9757	11.99
56	344.2256	4.44
57	348.8861	0.81
58	386.7980	0.61
59	434.5118	0.22
60	436.8531	17.80
61	455.7719	0.49

RNB136 29 A.N.BARNES
CAL:CAL19

No.37 MW 456

21-NOV-80

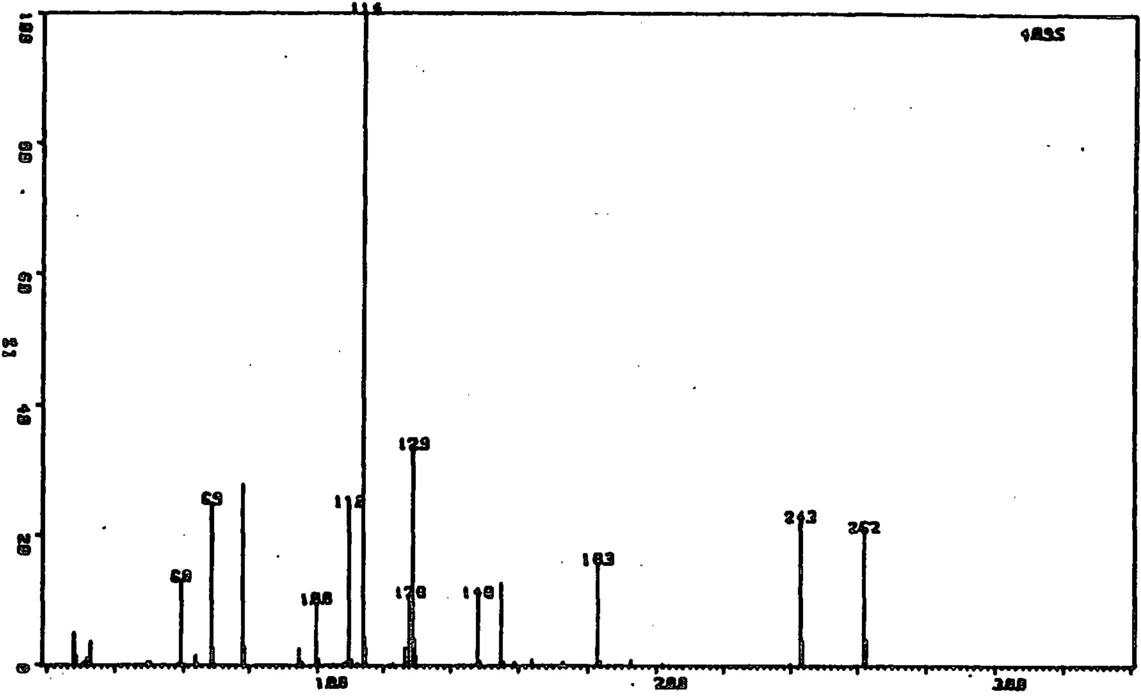


PEAK NO.	MASS	%HT. BASE
1	28.1348	100.00
2	28.1934	2.52
3	28.3374	0.24
4	28.9990	1.10
5	30.9033	0.73
6	32.0190	22.30
7	34.1553	0.34
8	39.8291	2.47
9	43.1079	0.59
10	44.1162	0.51
11	49.8682	1.37
12	68.9575	18.29
13	69.8926	0.39
14	76.0498	0.44
15	94.9829	32.50
16	95.9888	0.90
17	99.8584	48.77
18	100.9044	1.34
19	101.9641	0.32
20	113.9953	17.14
21	115.0060	0.71
22	118.8904	0.32
23	120.9069	2.56
24	158.8708	23.37
25	159.8846	1.03
26	163.9686	11.45
27	164.9843	0.66
28	165.9755	0.29
29	189.8792	0.93
30	204.0307	0.27
31	208.8940	2.61
32	210.0483	0.27
33	215.9589	0.63
34	235.0531	0.32
35	238.9764	0.32
36	253.8958	7.11
37	254.9450	0.76
38	277.8844	20.10
39	278.6922	5.01
40	279.7493	0.22
41	296.9222	1.98
42	298.8338	0.22
43	303.9120	1.10
44	322.8425	35.29
45	323.9562	4.66
46	341.8931	1.54
47	343.0577	0.27
48	348.9098	0.95
49	386.7297	0.78
50	436.9363	6.76
51	455.8963	1.25

RNB186 15 R.N.BARNES
CAL:CAL11

No.38 MW 262

14-MAY-81

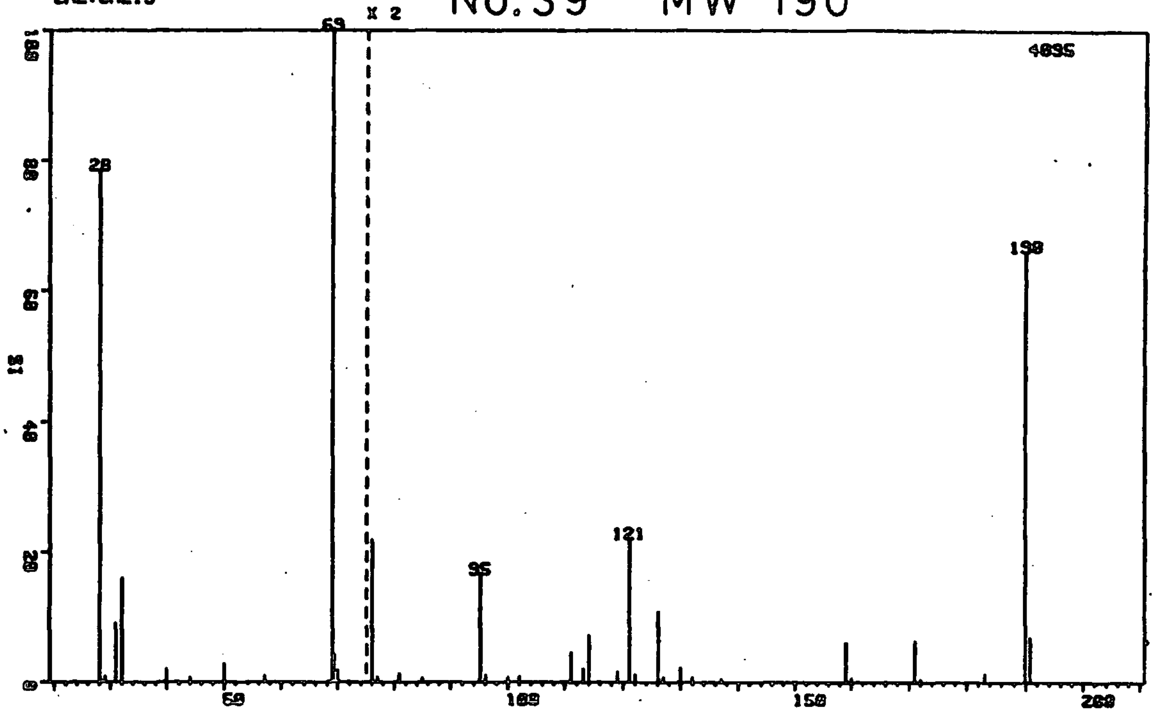


PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	4.93	54	193.01	0.73
2	29.02	1.51	55	202.00	0.39
3	30.93	0.46	56	240.11	0.49
4	32.03	1.03	57	242.98	22.15
5	33.14	3.69	58	243.76	3.83
6	49.90	0.56	59	260.10	0.27
7	50.98	0.56	60	261.93	20.63
8	59.03	0.37	61	262.77	4.03
9	59.95	12.87			
10	61.05	0.42			
11	64.15	1.51			
12	65.13	0.34			
13	68.98	24.79			
14	69.10	2.81			
15	69.92	0.44			
16	78.04	27.96			
17	78.17	3.35			
18	78.30	0.34			
19	78.96	2.91			
20	95.02	2.71			
21	96.01	0.56			
22	99.86	9.45			
23	100.03	3.83			
24	100.59	0.42			
25	100.99	0.90			
26	105.10	0.27			
27	107.86	0.39			
28	109.01	0.63			
29	109.93	24.49			
30	110.52	0.24			
31	110.96	0.90			
32	112.38	0.37			
33	112.78	0.34			
34	112.93	0.29			
35	114.03	100.00			
36	114.33	4.57			
37	115.04	2.91			
38	123.09	0.29			
39	126.56	0.24			
40	127.04	2.83			
41	128.04	10.48			
42	129.01	33.28			
43	129.24	4.13			
44	129.93	1.44			
45	147.98	10.45			
46	148.95	0.68			
47	155.01	12.77			
48	155.99	0.66			
49	158.96	0.63			
50	164.00	0.90			
51	173.04	0.59			
52	183.01	15.63			
53	184.05	0.68			

RNB144 19 R.N.BARNES
CAL:CAL19

No.39 MW 190

21-JAN-81

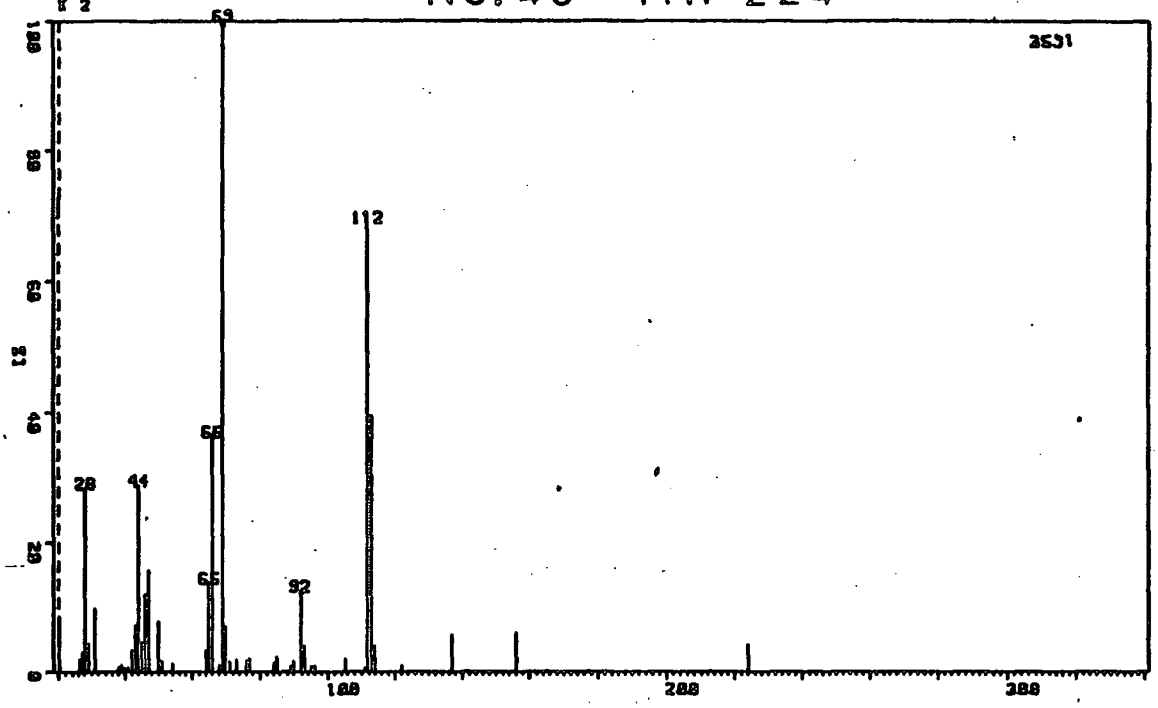


PEAK NO.	MASS	%HT. BASE
1	28.01	0.27
2	28.13	78.36
3	28.27	0.22
4	28.31	0.42
5	29.00	0.83
6	30.91	9.06
7	32.02	15.97
8	39.84	2.03
9	44.13	0.68
10	49.88	2.91
11	57.10	0.95
12	68.42	0.34
13	68.98	100.00
14	69.25	4.22
15	69.86	1.83
16	76.00	10.92
17	76.22	0.22
18	76.98	0.37
19	80.86	0.66
20	85.00	0.32
21	95.06	8.25
22	96.05	0.54
23	99.94	0.34
24	101.97	0.42
25	110.94	2.32
26	113.01	1.05
27	114.04	3.59
28	118.99	0.81
29	121.00	11.01
30	122.04	0.61
31	126.06	5.42
32	126.41	0.24
33	127.03	0.37
34	129.94	1.07
35	132.00	0.37
36	137.02	0.27
37	159.00	3.00
38	160.01	0.29
39	171.00	3.15
40	172.05	0.27
41	183.06	0.66
42	189.98	32.97
43	190.85	3.49

RB1712 8 R.N.BARNES
CAL:CAL6
% 2

No. 40 MW 224

06-MAR-81

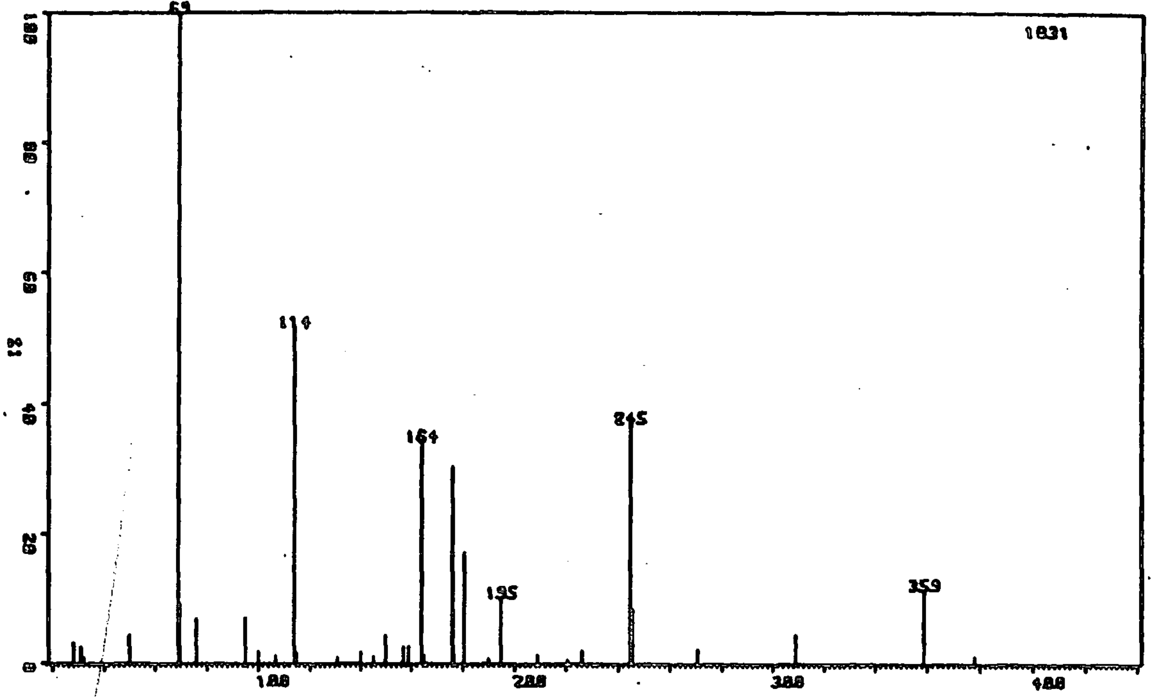


PEAK NO.	MASS	%HT. BASE
1	20.59	4.26
2	26.55	0.97
3	27.43	1.53
4	28.27	14.15
5	29.12	2.17
6	30.99	4.87
7	38.05	0.33
8	38.98	0.50
9	39.87	0.31
10	40.96	0.36
11	41.98	1.70
12	43.03	3.59
13	44.06	14.37
14	45.08	2.34
15	46.08	5.99
16	47.04	7.83
17	49.88	3.93
18	50.99	0.81
19	54.10	0.67
20	64.11	1.70
21	65.10	6.79
22	66.08	18.10
23	68.07	0.53
24	68.97	100.00
25	69.93	3.51
26	71.01	0.81
27	73.06	0.95
28	76.08	0.86
29	77.09	1.00
30	84.05	0.70
31	85.06	1.17
32	89.00	0.45
33	89.95	0.84
34	91.98	6.21
35	93.03	2.03
36	95.10	0.45
37	96.11	0.45
38	105.10	1.00
39	111.03	0.31
40	111.99	34.45
41	113.03	19.69
42	114.06	2.03
43	122.16	0.47
44	137.06	2.84
45	156.05	2.98
46	224.15	2.09

RNB183 11 A.N.BARNES
CAL:CALS

No.41 MW 378

05-MAY-81

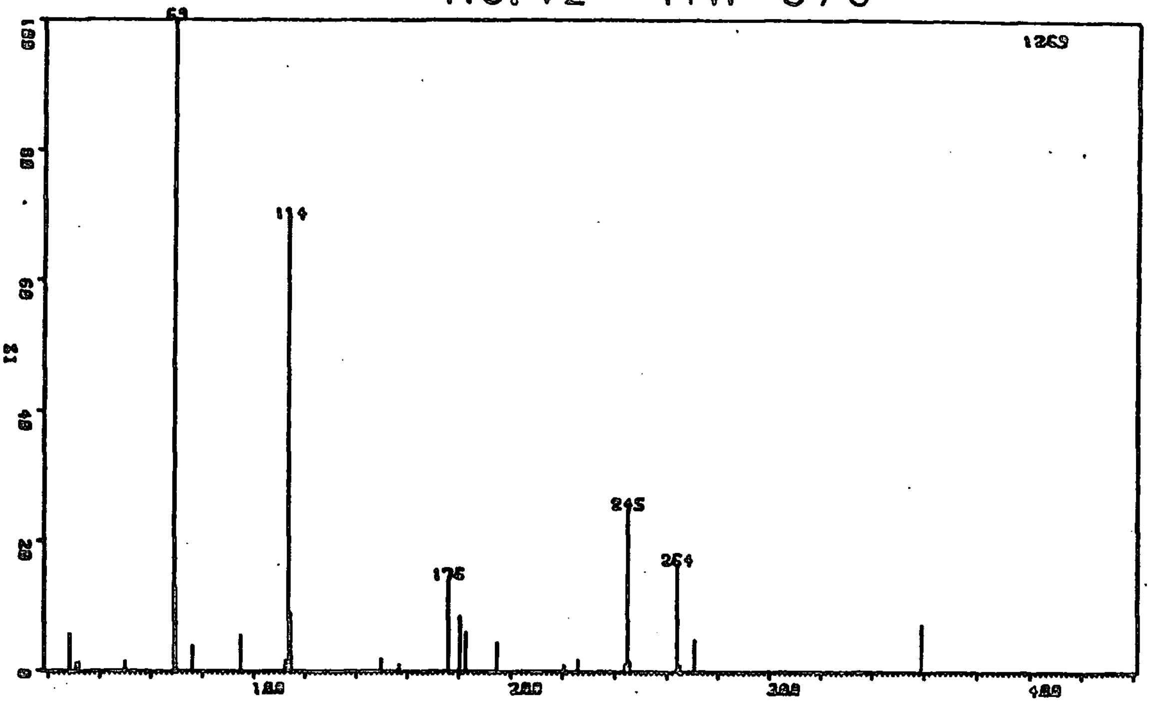


PEAK NO.	MASS	%HT. BASE
1	28.13	5.67
2	30.92	1.26
3	32.00	1.34
4	49.87	1.50
5	68.96	100.00
6	69.11	12.84
7	69.28	1.26
8	69.81	1.26
9	76.02	3.86
10	94.98	5.59
11	112.62	1.65
12	113.92	69.50
13	114.21	9.06
14	114.94	2.36
15	149.85	1.97
16	156.99	1.18
17	175.93	14.18
18	180.90	8.59
19	182.93	6.07
20	194.98	4.49
21	220.94	0.95
22	225.94	1.81
23	243.92	1.18
24	244.90	24.98
25	245.86	1.58
26	263.93	16.47
27	265.04	1.10
28	270.94	4.89
29	358.90	7.33

RNB183 B R.N.BARNES
CAL:CALS

No.42 MW 378

05-MAY-81

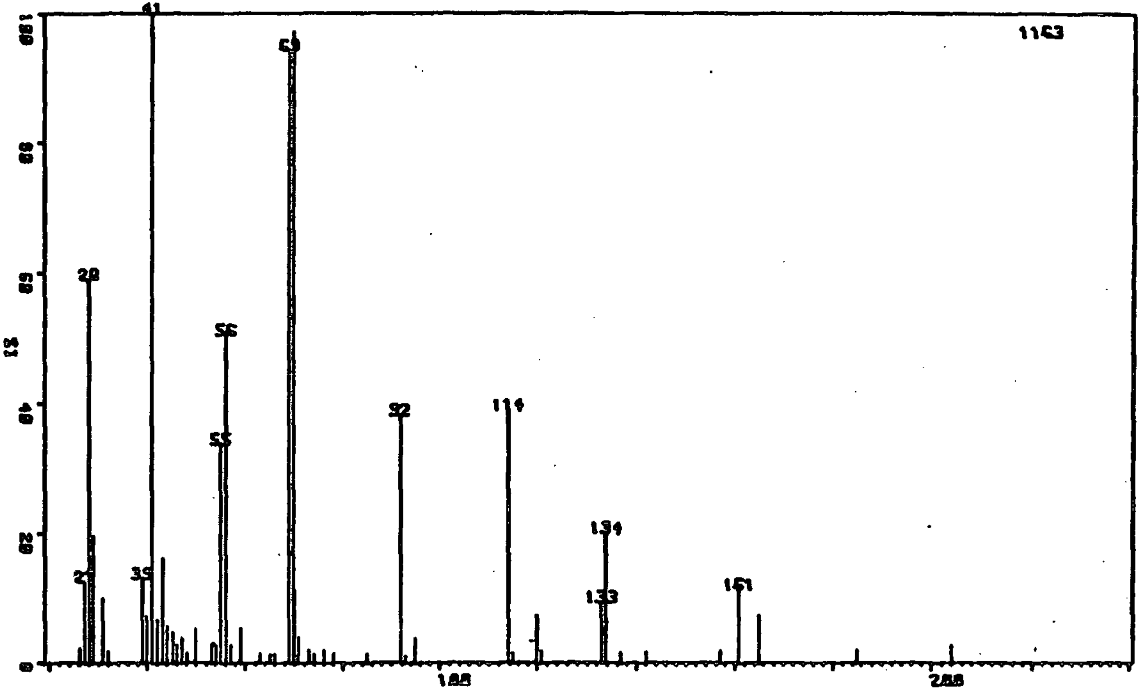


PEAK NO.	MASS	%HT. BASE
1	28.13	3.17
2	30.90	2.51
3	32.02	0.87
4	49.87	4.42
5	68.96	100.00
6	69.08	9.34
7	69.90	0.98
8	76.05	6.88
9	95.01	7.10
10	99.92	1.97
11	107.01	1.31
12	113.99	51.72
13	115.04	1.75
14	130.96	0.98
15	139.93	1.91
16	145.02	1.15
17	149.90	4.42
18	157.00	2.79
19	158.94	2.73
20	163.96	34.24
21	164.68	0.87
22	164.96	1.37
23	175.96	30.42
24	176.23	8.19
25	176.90	1.47
26	180.87	17.26
27	189.97	0.76
28	194.96	10.21
29	208.91	1.42
30	220.91	0.60
31	225.95	2.02
32	244.87	37.03
33	245.64	8.47
34	270.97	2.29
35	308.93	4.53
36	358.94	11.36
37	377.83	1.20

RNB18S 0 A.N.BARNES
CAL:CAL18

No. 43 MW 204

22-MAY-81
8:7



PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.30	2.24			
2	27.24	12.55			
3	28.13	58.99			
4	28.18	14.62			
5	29.01	19.60			
6	30.91	9.97			
7	32.01	1.81			
8	38.99	12.98			
9	39.88	7.22			
10	40.96	100.00			
11	42.04	6.62			
12	43.08	16.08			
13	44.11	5.67			
14	45.14	4.73			
15	46.12	2.92			
16	47.07	3.87			
17	47.99	1.55			
18	49.84	5.25			
19	53.09	2.84			
20	54.10	2.75			
21	55.13	33.71			
22	56.14	50.39			
23	57.11	2.84			
24	58.99	5.42			
25	63.03	1.38			
26	65.08	1.29			
27	66.04	1.29			
28	68.95	94.15			
29	69.87	97.16			
30	70.02	11.18			
31	70.23	1.20			
32	70.92	3.96			
33	73.01	1.98			
34	74.08	1.29			
35	76.02	1.98			
36	77.93	1.46			
37	84.98	1.38			
38	91.91	38.09			
39	92.95	1.03			
40	94.98	3.70			
41	113.93	38.95			
42	114.97	1.46			
43	119.80	7.31			
44	120.94	1.09			
45	132.96	9.37			
46	133.95	20.03			
47	136.93	1.63			
48	141.92	1.63			
49	156.96	1.01			
50	160.09	11.35			
51	164.99	7.39			
52	184.97	1.98			
53	203.95	2.84			

APPENDIX IV

DEPARTMENTAL COLLOQUIA AND INDUCTION COURSE FOR POSTGRADUATES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing

a) all research colloquia, research seminars and lectures arranged by the department of Chemistry during the period of the writer's residence as a postgraduate student;

b) all research conferences attended and papers read out by the writer of the thesis during the period when the research for the thesis was carried out; and

c) details of the postgraduate induction course.

Events in a) which were attended are marked *.

Research Colloquia, Seminars and Lectures

1. University of Durham Chemistry Colloquia

Academic Year 1978-1979

* 12 Dec. Professor C.J.M. Stirling (U. of Bangor), "Parting is such sweet sorrow - the leaving group in organic chemistry".

* 31 Jan. Professor P.D.B. de la Mare (U. of Auckland, New Zealand), "Some pathways leading to electrophilic substitution".

14 Feb. Professor B. Dunnel (U. of British Columbia), "The application of n.m.r. to the study of motions of molecules in solids".

* 14 Mar. Dr. J.C. Walton (U. of St. Andrews), "Pentadienyl radicals".

* 28 Mar. Dr. A. Reiser (Kodak Ltd.), "Polymer photography and the mechanism of cross link formation in solid polymer matrices".

* 25 Apr. Dr. C.R. Patrick (U. of Birmingham), "Chlorofluorocarbons and stratospheric ozone: an appraisal of the environmental problem".

* 1 May Dr. G. Wyman (European Research Office, U.S. Army), "Excited state chemistry of indigoid dyes".

* 2 May Dr. J.D. Hobson (U. of Birmingham), "Nitrogen-centred reactive intermediates".

8 May Professor A. Schmidpeter (Inst. of Inorg. Chem., U. of Munich), "Five-membered phosphorus heterocycles containing dicoordinate phosphorus".

* 9 May Professor G. Maier (Lahn-Geissen U.), "Tetra-tert-butyltetrahedrane".

9 May Dr. A.J. Kirkby (U. of Cambridge), "Structure and reactivity in intramolecular and enzymic catalysis".

* 16 May Dr. J.F. Nixon (U. of Sussex), "Some recent developments in platinum metal phosphine complexes".

23 May Dr. B. Wakefield (U. of Salford), "Electron transfer in the reaction of metals and organometallic compounds with polychloropyridine derivatives".

* 13 Jun. Professor I. Ugi (U. of Munich), "Synthetic uses of super nucleophiles".

* 25 Sep. Professor R. Soulen (Southwestern U., Texas), "Applications of HSAB theory to vinylic halogen substitution reactions and a few copper coupling reactions".

Academic Year 1979-1980

* 21 Nov. Dr. J. Müller (U. of Bergen), "Photochemical reactions of ammonia".

28 Nov. Dr. B. Cox (U. of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity".

* 5 Dec. Dr. G.C. Eastmand (U. of Liverpool), "Synthesis and properties of some multicomponent polymers".

12 Dec. Dr. C.I. Ratcliffe, "Rotor motions in solids".

* 18 Dec. Dr. K.E. Newman (U. of Lausanne), "High pressure multinuclear n.m.r. in the elucidation of mechanism of fast simple inorganic reactions".

* 30 Jan. Dr. M.J. Barrow (U. of Edinburgh), "The structures of some simple inorganic compounds of silicon and germanium - pointers to structural trends in group IV".

* 6 Feb. Dr. J.M.E. Quirke (U. of Durham), "Degradation of chlorophyll-a in sediments".

* 23 Apr. B. Grievson B.Sc. (U. of Durham), "Halogen radio-pharmaceuticals".

* 14 May Dr. R. Hutton (Waters Associates), "Recent developments in multi-milligram and multi-gram scale preparative high performance liquid chromatography".

* 21 May Dr. T.W. Bentley (U. of Swansea), "Medium and structural effects on solvolytic reactions".

* 10 Jul. Professor D. Des Marteau (U. of Heidelberg), "New developments in organonitrogen fluorine chemistry".

Academic Year 1980-1981

* 7 Oct. Professor T. Fehlner (Notre Dame U., Indiana), "Metalloboranes - cages orco-ordination compounds".

* 15 Oct. Dr. R. Alder (U. of Bristol), "Doing chemistry inside cages - medium ring bicyclic molecules".

12 Nov. Dr. M. Gerloch (U. of Cambridge), "Magneto-chemistry is about chemistry".

* 19 Nov. Dr. T. Gilchrist (U. of Liverpool), "Nitroso-olefines as synthetic intermediates".

3 Dec. Dr. J.A. Connor (U. of Manchester), "Thermochemistry of transition metal compounds".

18 Dec. Dr. R.F. Evans (U. of Brisbane), "Some recent communications to the editor of Australian Journal of Failed Chemistry".

* 18 Feb. Professor S.F.A. Kettle (U. of East Anglia), "Variations in the molecular dance at the crystal ball".

* 25 Feb. Dr. K. Bowden (U. of Essex), "The transmission of polar substituent effects".

4 Mar. Dr. S. Cradock (U. of Edinburgh), "Pseudo-linear pseudohalides".

* 18 Mar. Dr. P.J. Smith (Int. Tin Research Institute), "Organotin compounds - a versatile class of organometallic derivatives".

* 6 May Professor M. Szwarc, F.R.S., "Ions and ion pairs".

* 8 May Professor H.F. Koch (Bathaca College, U.S.A.), "Proton-transfer during elimination reactions".

13 May Professor H. Fritzer (U. of Graz), "Simple methods to construct representations for discrete symmetry groups".

14 May Professor H. Fritzer (U. of Graz), "The interplay of permutational and geometrical symmetry of certain electronic systems".

* 10 Jun. Dr. J. Rose (I.C.I. Plastics Division), "New engineering plastics".

* 17 Jun. Dr. P. Moreau (U. of Montpellier), "Recent results in perfluoro-organometallic chemistry".

* 24 Jun. Dr. S.A.R. Knox (U. of Bristol), "Coordination and reactivity of organic species at dinuclear metal centres".

26 Jun. Professor A.P. Schaap (U.S. Office of Naval Research, London), "Mechanisms of chemiluminescence and photooxygenation".

2. Durham University Chemical Society

Academic Year 1978-1979

* 10 Oct. Professor H.C. Brown (Purdue U.), "The tool of increasing electron demand in the study of cationic processes".

* 19 Oct. Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is death in the pot".

* 26 Oct. Professor W.J. Albery (Imperial College, London), "Photogalvanic cells for solar energy conversion".

* 9 Nov. Professor A.R. Katritsky (U. of East Anglia), "Some adventures in heterocyclics".

* 16 Nov. Dr. H.C. Fielding (I.C.I. Mond Division), "Fluorochemical surfactants and textile finishes".

* 23 Nov. Dr. C. White (U. of Sheffield), "The magic of chemistry".

* 18 Jan. Professor J.C. Robb (U. of Birmingham), "The plastics revolution".

* 8 Feb. Mr. C.G. Dennis (Vaux Ltd.), "The art and science of brewing".

* 1 Mar. Professor R. Mason (Govt. Scientific Advisor), "The scientist in defence policy".

10 May Professor G. Allen (Chairman S.R.C.), "Neutron scattering for polymer structures".

Academic Year 1979-1980

* 18 Oct. Dr. G. Cameron (U. of Aberdeen), "Synthetic polymers - twentieth century polymers".

25 Oct. Professor P. Gray (U. of Leeds), "Oscillatory combustion reactions".

* 1 Nov. Dr. J. Ashby (I.C.I. Toxicological Laboratory), "Does chemically-induced cancer make chemical sense ?"

* 8 Nov. Professor J.H. Turnbull (R.M.C. Shrivenham), "Luminescence of drugs".

15 Nov. Professor E.A.V. Ebsworth (U. of Edinburgh), "Stay still you brute: the shape of the simple silyl complexes".

* 24 Jan. Professor R.J.P. Williams (U. of Oxford), "On first looking into biology's chemistry".

14 Feb. Professor G. Gamlen (U. of Salford), "A yarn with a new twist - fibres and their uses".

* 21 Feb. Dr. M.L.H. Green (U. of Oxford), "Synthesis of highly reactive organic compounds using metal vapours".

* 28 Feb. Professor S.F.A. Kettle (U. of East Anglia), "Molecular shape, structure and chemical blindness".

* 6 Mar. Professor W.D. Ollis (U. of Sheffield), "Novel molecular rearrangements".

Academic Year 1980-1981

* 16 Oct. Dr. D. Maas (U. of Salford), "Reactions a go-go".

* 23 Oct. Professor T.M. Sugden (U. of Cambridge), "Some reactions of metals in high temperature flames".

* 30 Oct. Professor N. Grassie (U. of Glasgow), "Inflammability hazards in commercial polymers".

6 Nov. Professor A.G. Sykes (U. of Newcastle), "Metallo-proteins: An inorganic chemists approach".

* 13 Nov. Professor N.N. Greenwood (U. of Leeds), "Metalloborane chemistry".

* 4 Dec. Rev. R. Lancaster, "Fireworks".

* 22 Dec. Professor E.A. Dawes (U. of Hull), "Magic and mystery through the ages".

* 29 Jan. Mr. H.J.F. MacLean (I.C.I. Agricultural Division), "Managing the chemical industry in the 1980s".

* 5 Feb. Professor F.G.A. Stone (U. of Bristol), "Chemistry of carbon to metal triple bonds".

* 12 Feb. Dr. I. Fleming (U. of Cambridge), "Some uses of silicon compounds in organic synthesis".

17 Mar. Professor W.P. Jencks (Brandeis U., Massachusetts), "When is an intermediate not an intermediate?".

7 May Professor M. Gordon (U. of Essex), "Do scientists have to count?".

Research Conferences Attended

3rd Annual Congress of the Chemical Society, Durham, 9-11 April 1980.

7th European Symposium on Fluorine Chemistry, Venice, 15-19 September 1980.

Postgraduate Induction Course

In each part of the course, the uses and limitations of the various services available were explained by those responsible for them.

Departmental organisation - Dr. E.J.F. Ross

Electrical appliances and infrared spectroscopy - Mr. R.N. Brown

Chromatography and microanalysis - Mr. T.F. Holmes

Atomic absorption spectrometry and inorganic analysis - Mr. R. Coult

Mass spectrometry - Dr. M. Jones

N.m.r. spectrometry - Dr. R.S. Matthews

Glassblowing techniques - Mr. W.H. Fettis and Mr. R. Hart

Safety matters - Dr. D.L.H. Williams

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