Novel chemistry of fluorinated carbanions

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Gray, William K. (1996) *Novel chemistry of fluorinated carbanions*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/5440/

UNIVERSITY OF DURHAM

Department of Chemistry

A THESIS
entitled

NOVEL CHEMISTRY OF FLUORINATED CARBANIONS

submitted by

WILLIAM K. GRAY B.Sc. (Hons)

A candidate for the degree of Doctor of Philosophy

1996

"...like those who drift down the stream of a deep and smooth river, we are not aware of the progress we have made until we fix our eye on the now distant point from which we have been drifted."

Sir Walter Scott
Waverley

Acknowledgements

I would like to thank Professor R. D. Chambers for his continuous help and encouragement throughout the course of this work, and the E.P.S.R.C. and Dr. S. R. Korn of Zeneca specialties for their financial support. Dr. J. F. S. Vaughan and Dr. G. Sandford are also acknowledged for their helpful advice.

I would also like to acknowledge the assistance of the technical staff without whom this thesis, and the work reported within, would not have been possible. Many thanks to Mr. L. W. Lauchlan (gas chromatography), Dr. M. Jones and Miss. L. M. Turner (mass spectrometry), Dr. R. S. Matthews, Dr. A. Kenwright and Mrs. J. Say (NMR spectroscopy), Mrs. J. Dorstal (elemental analysis), Mr. R. Hart and Mr. G. Haswell (glass blowing), Dr. A. Royston (computing), Mr. D. Hunter (high pressure laboratory and chemical policing), Mr. J. Lincoln (storekeeper), Mrs. E. M. Wood (artwork) and Professor J. A. K. Howard, Dr. C. W. Lehmann and Dr. A. S. Batsanov (x-ray crystallography).

The help of Dr. M. Médebielle (electrochemistry; Universite Denis Diderot, Paris), Professor F. G. N. Cloke (MVS apparatus; University of Sussex, Brighton) and Miss H. Swift (ultraviolet spectroscopy) is also greatly appreciated.

Particular thanks are due to *everyone* in lab 115 for a great time over the last three years, especially Andrew and Anwar for 'additional' computing facilities and Bob, Alex and Alan for a memorably unrememberable week in Slovenia. Thanks are also due to all the lads in Grad. Soc. AFC, especially, Shim, Sugar, Shortie, Kitten, Gazza, Scouse, Troll, Goat and Pav for more football related japery than one could ask for.

A special mention must go to the late Tom Holmes, who it was a pleasure to know and work with.

Memorandum

The work described in this thesis was carried out in the University of Durham between October 1993 and September 1996. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

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

Richard D. Chambers, William K. Gray and Stewart R. Korn, *Tetrahedron*, 1995, **51**, 48, 13167-13176.

Richard D. Chambers, William K. Gray, Julian F. S. Vaughan, Stewart R. Korn, Maurice Médebielle, Andrie S. Batsanov, Christian W. Lehmann and Judith A. K. Howard, accepted for publication in the *J. Chem. Soc., Perkin Trans. I.*

and has been presented at:

Anglo-Norman Organic Research Colloquia
Deauville, France
May, 1995.

11th European Symposium on Fluorine Chemistry
Bled, Slovenia
September 17th-22nd 1995.

I.C.I. Poster Session
University of Durham
December, 1995.

Nomenclature

Throughout this work, an 'F' in the centre of a ring denotes that all the unmarked bonds are to fluorine.

Abbreviations

The following are used throughout the thesis.

GLC-MS	gas-liquid chromatography-mass spectrometry
NMR	nuclear magnetic resonance
IR	infrared
FAB	fast atom bombardment
y.	yield

Abstract
Novel Chemistry of Fluorinated Carbanions
by William K. Gray

The research described within this thesis may be divided into four main subject areas:

I. The amine fluoride $TDAE^{2+}2F^{-}$ **(10)** has been used as a useful soluble source of fluoride ion in both C-F and C-C bond forming reactions. Methods of synthesis of **(10)** are described. This work led to the observation that TDAE **(8)**, and other amines, could be used as agents for the *in situ* generation of fluoride, by nucleophilic attack on fluoro-alkenes. Its use allows the effective isolation of the products of dimerisation, co-dimerisation and the perfluoroalkylation reactions for the first time.

II. Synthesis and reactions of perfluoro-3,4-dimethylhexa-2,4-diene **(14)** are described. Particular attention is paid to reactions with oxygen and carbon centred nucleophiles. The novel tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin ring system **(54)** so produced was extensively studied.

III. The synthetically useful cyclic diene hexakis(trifluoromethyl)cyclopentadiene **(96)** has been synthesised from diene **(14)**, by fluoride ion induced reaction with pentafluoropropene **(97)**. This diene can be reduced to the exceptionally stable pentakis(trifluoromethyl)cyclopentadienide anion **(84)** upon reaction with a range of alkali metal and tetralkylammonium iodides. The mechanism of this reaction appears to be a radical one and, indeed, electrochemical reduction is rapid. The intrinsic stability of **(84)** is borne out by the fact that concentrated sulphuric acid is required to synthesis its derived acid **(109)**.

IV. Diene **(96)** reacts with a variety of transition metal powders to give corresponding pentakis(trifluoromethyl)cyclopentadienide metal salts. The role of acetonitrile as a solvent in the reaction appears to be crucial to the formation and stabilisation of these species. The salt produced by reaction of **(96)** with copper powder, tetrakis(acetonitrile)copper (I) pentakis(trifluoromethyl)cyclopentadienide **(118)**, is remarkably stable and an x-ray crystal structure was obtained.

Table of Contents

CHAPTER ONE

CHAPTER TWO

CHAPTER FOUR

Formation of Pentakis(trifluoromethyl)cyclopentadienide Salts 91

CHAPTER FIVE

CHAPTER SIX

CHAPTER SEVEN

CHAPTER EIGHT

CHAPTER NINE

Appendix One

Appendix Two

Appendix Three

Appendix Four

CHAPTER ONE

The Role of Fluoride Ion in Organofluorine Chemistry

I. General Introduction

Fluorine is found in the earth's crust in relatively high abundance for a halogen (0.065% F : 0.055% Cl) and forms concentrated deposits in minerals such as fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapitite [$3Ca_3(PO_4)_2Ca(F,Cl)_2$].[1]

The first reported synthesis of a fluorine containing organic compound is attributed to Dumas and Peligot,[2] when in 1836 they reported fluoromethane. However, it was the pioneering work of Swarts,[3, 4] between the years of 1890 and 1938 on simple aliphatic fluorine containing compounds that established the foundations of organofluorine chemistry.

Since the Second World War our knowledge of the chemistry of fluorine containing compounds has increased markedly and the field has become a major area of research. One of the motivating forces behind development of the area is the interesting properties that compounds acquire on introduction of fluorine and fluorinated substituents. Some of the remarkable range of current applications include those listed in **Table 1.**

Table 1. Uses fluorinated materials

Area of Application	Compound
Components of Coolants and Refrigerants	$CFCl_3$, CF_2Cl_2, CF_3Br
Anaesthetics	$CF_3CHClBr$ (Halothane)
Components of Blood substituents	Perfluorodecalin
Drugs	5-fluorouracil
Plant protection	Trifluralin, Fusilade
Polymers, Elastomers and Membranes	$(CF_2CF_2)_n$ (PTFE)

The value of studying fluorocarbon systems lies not only in the industrial applications of new materials, but also in new areas of chemistry that display unusual types of reaction mechanism.

The unique chemistry of organofluorine systems is derived from a number of important factors:

1. the high electronegativity of the fluorine atom. The difference between fluorine and chlorine, the closest homologue, is substantially greater than the difference between any other two successive halogens, hence the term superhalogen;

2. the strong polarisation of the C-F bond. The difference in electronegativity between the two atoms gradually alters, and even inverts the reaction behaviour of adjacent centres;

3. fluorine is the halogen whose Van der Waals radius is most like that of hydrogen (F=1.35Å, H=1.10Å) leading to the possibility of perfluorination of long chains;

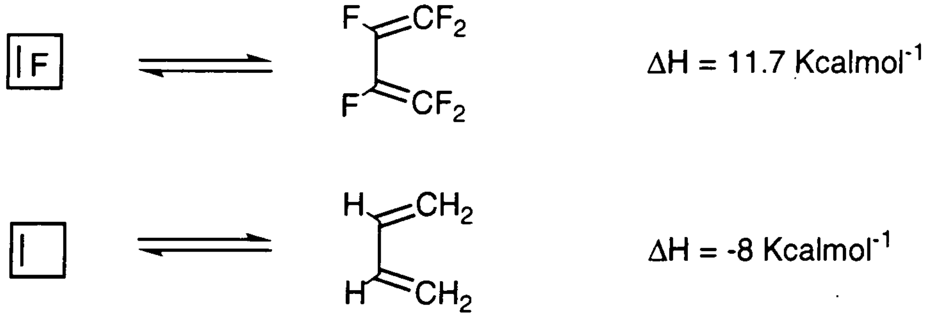
4. fluorine can be readily displaced from fluorocarbons as fluoride ion, this gives fluorine containing compounds a unique and potentially diverse nature- in perfluorinated species this can give rise to a complimentary chemistry in comparison with hydrocarbon systems;

5. the C-F bond is exceedingly strong (107Kcalmol^{-1}) leading to enhanced chemical utility due to thermal stability.

I.1. Fluoro-alkenes

This thesis is concerned with the chemistry of fluoro-alkenes and their derived anions. A brief review of the properties of such species is required.

If hydrogen is replaced by fluorine in an unsaturated system then its reactivity can be dramatically altered, and in many cases reversed. Most striking are thermochemical data relating to ring opening reactions of cyclobutenes in which the preference for butadiene in the parent compound is reversed on perfluorination.[5]

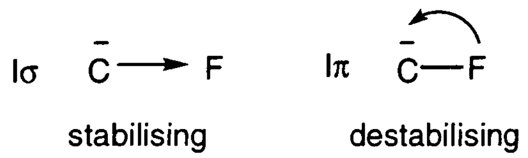


It would appear therefore that fluorine substitution destabilises a π system. This observation may at first seem strange given that fluorine is known to be highly electronegative and may therefore be expected to stabilise an electron rich system.

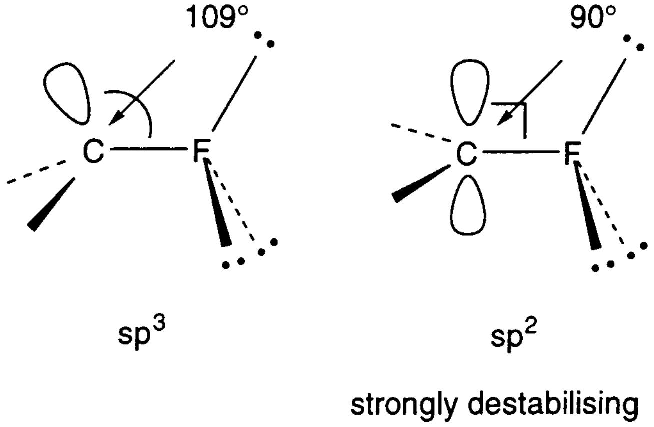
I.1.A. Effect of Fluorine on Carbanion Stability

A fluorine atom not only destabilises unsaturated systems, but has also been observed to be destabilising when directly attached to an anionic centre, and this provides the key to explaining many phenomena associated with fluorination of hydrocarbon systems.

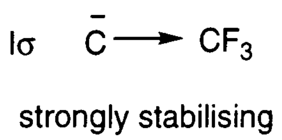
There is a competing effect to fluorine's inductive electron withdrawal, which is the return of electron density to the π system by the non-bonding *p*-orbitals of the fluorine atom.[6] This is the predominant factor when fluorine is directly attached to an anionic site.



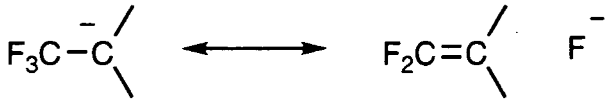
This effect is demonstrated by examining the effect of fluorine attached to sp^3 (tetrahedral) and sp^2 (planar) hybridised carbon.



Conversely, with perfluoroalkyl substitution, the effect is one of stabilisation since there are no π interactions.[7-9]

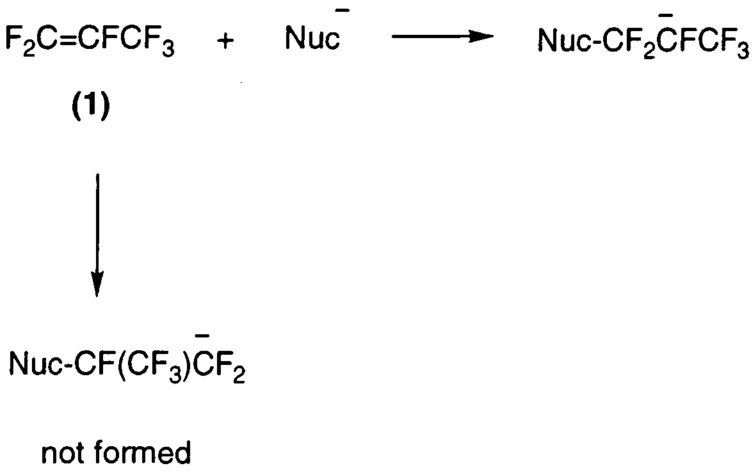


This stabilisation has also been explained in terms of 'C-F negative hyperconjugation'. This theory, which involves no-bond resonance, was first put forward by Roberts[10] in 1950 and arguments for and against its validity have raged ever since.[8, 11-13]



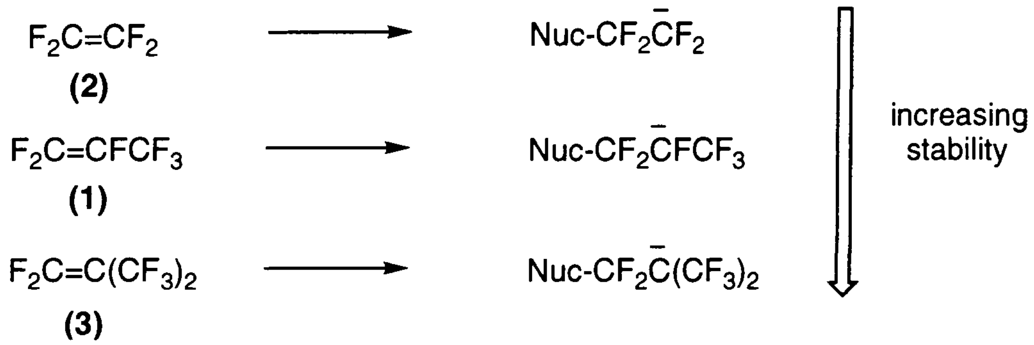
I.1.A.1. Nucleophilic Attack on Fluorinated Alkenes

There are two possible orientations in which a nucleophile can attack an unsymmetrical substituted polyfluorinated alkene:-[14]



One approach to explaining the observed orientation of attack is to consider the relative stabilities of the intermediates involved. It has been shown that fluorine directly attached to a carbanionic centre is strongly destabilising relative to hydrogen, whereas fluorine substitution at a position adjacent to a carbanion centre is stabilising. From these effects it can be deduced that attack of a nucleophile on a polyfluorinated alkene will take place at the end of the double bond with fewest perfluoroalkyl substituents in order to generate an anion at the site with the greatest number of stabilising groups around it.

Extrapolation of this principle leads to the observation that, as the number of perfluoroalkyl substituents adjacent to the resultant carbanion site increases, so the ability to support negative charge increases, thus leading to greater reactivity.



This order is well-established experimentally;[15] perfluoroisobutene (**3**) is readily attacked by neutral methanol,[16] hexafluoropropene (**1**) requires the presence of a base[17] and tetrafluoroethylene (**2**) only reacts in the presence of a strong base[15] or at elevated temperature.[18]

However, these simple 'ground rules' are not totally sufficient, because they do not explain the observation that (**1**) is much more reactive towards nucleophiles than octafluorobut-2-ene (**4**).

$$CF_2{=}CFCF_3 \quad + \quad \overset{-}{Nuc} \longrightarrow Nuc\text{-}CF_2\overset{-}{C}FCF_3$$

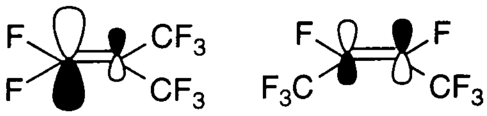
(1)

$$CF_3CF{=}CFCF_3 \quad + \quad \overset{-}{Nuc} \longrightarrow Nuc\text{-}CF(CF_3)\overset{-}{C}FCF_3$$

(4)

The intermediates formed in these two systems only have a small difference in stability, since fluorine and perfluoroalkyl groups exert a similar stabilising influence on an adjacent carbanionic centre. Consequently, a frontier molecular orbital approach has been used to account for the observed reactivity and orientation of attack. In general, substitution of a fluorine atom with an electronegative trifluoromethyl group reduces LUMO energy in an alkene, thus increasing reactivity towards nucleophiles.

This is true providing the trifluoromethyl groups are on the same side of the double bond, *i.e.* $CF_2{=}CF_2 < CF_2{=}CFCF_3 < CF_2{=}C(CF_3)_2$, which increases the coefficient of the LUMO of the carbon at the other end of the double bond. This effect is cumulative for two such groups attached geminally to the double bond, however, when the trifluoromethyl groups are at opposite ends of the double bond they effectively cancel each other out.

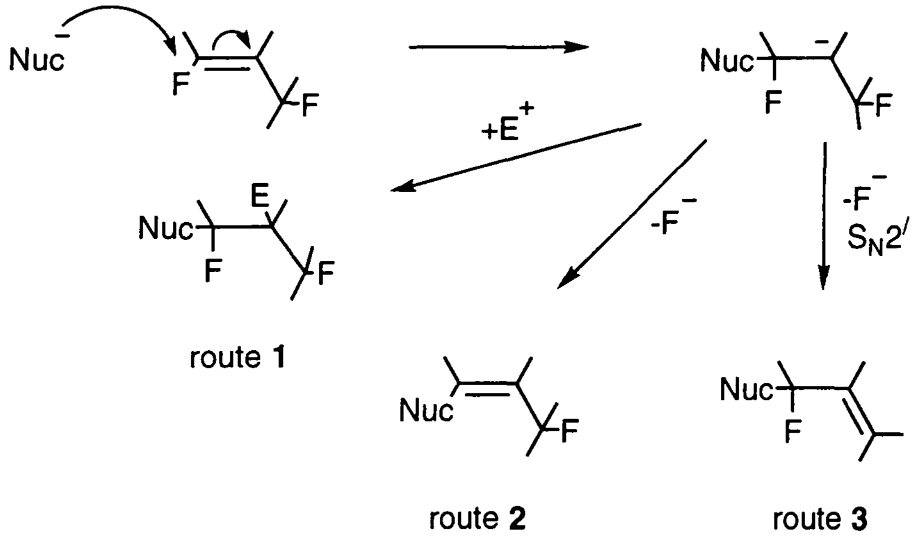


CF$_3$'s reinforce   CF$_3$'s in opposition

lowest unoccupied frontier molecular orbitals

I.1.B. Possible Products from Nucleophilic Attack on Perfluoroalkenes

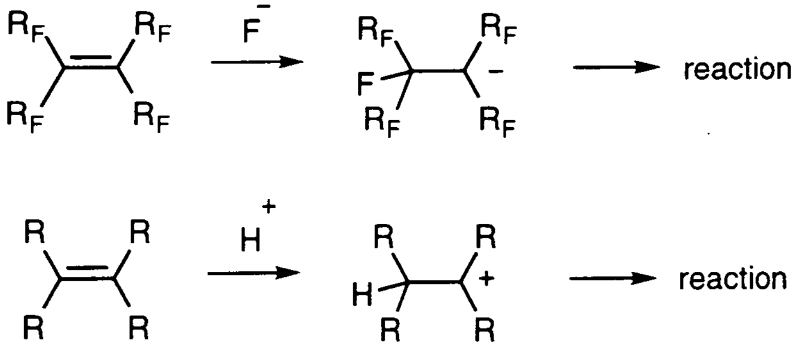
The intermediate carbanion derived from nucleophilic attack on a fluorinated alkene may react further in three main ways:-



There is considerable difficulty in assigning mechanistic preferences for any particular fluoro-alkene due to the huge variety of reaction conditions documented in the literature.[19] Addition of E$^+$ (route **1**) appears to be favoured by simpler, less electron deficient, fluoro-alkenes where the derived carbanions are more basic. Similarly, alkene precursors to more stable, less basic carbanions exhibit a greater propensity for substitution processes via either addition-elimination (route **2**) or allylic displacement (route **3**).

I.2 Fluoride Ion in Organofluorine Chemistry

The role of fluoride ion in fluorocarbon chemistry is analogous to the role of the proton in hydrocarbon chemistry. Thus, just as the chemistry of unsaturated hydrocarbons is dominated by carbocation intermediates, produced by electrophilic attack, so the chemistry of unsaturated fluorocarbons is dominated by carbanions and fluoride ion.[20] The two systems are complimentary in many ways and unsaturated fluorocarbon chemistry is often described as a mirror image chemistry.

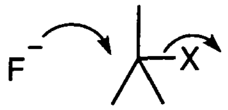


I.2.A. Fluoride Ion in C-F Bond Forming Reactions

I.2.A.1. Halogen Exchange Reactions

These reactions involve simple S_N2 substitution of a halogen atom for a fluorine atom at a carbon centre. Reactions of this type are one of the most popular methods of fluorination and will be discussed more fully in **Section 1.3.**

eg.



I.2.A.2. Rearrangement of Fluoro-alkenes

Reactions of this type are governed by S_N2' (allylic displacement) processes. Mechanistic work by Miller[21-24] established that attack by iodide ion occurs as predicted on the terminal difluoromethylene group and not on the α-carbon in the reactions shown below.

$$CF_2{=}CF{-}CF_2Cl + I^- \longrightarrow ICF_2{-}CF{=}CF_2 + Cl^-$$

$$CF_2{=}CCl{-}CF_2Cl + I^- \longrightarrow ICF_2{-}CCl{=}CF_2 + Cl^-$$

This may be deduced from the fact that under equivalent conditions $CClF{=}CF{-}CF_2Cl$ and $CCl_2{=}CCl{-}CF_2Cl$ are unreactive.

The relative order of reactivity, of halide ion with fluoro-alkenes in the S_N2' process is $F^- > Cl^- \gg I^-$, *eg*. for the reaction:[23, 24]

$$CF_2{=}CH{-}CFCl_2 + X^- \longrightarrow XCF_2{-}CH{=}CFCl + Cl^-$$

$$(X = F, Cl \text{ or } I)$$

This trend is in contrast to the known reactivity of halide ions with carbon in S_N2 processes and can be rationalised in terms of steric hindrance and the intrinsic strength of the new bond formed.

One of the first fluoride ion induced rearrangements studied was the reaction of fluoride ion with perfluorohept-1-ene.[23]

$$CF_3(CF_2)_4CF{=}CF_2 \xrightarrow{i} CF_3(CF_2)_3CF{=}CFCF_3 \quad 88\%\ y.$$

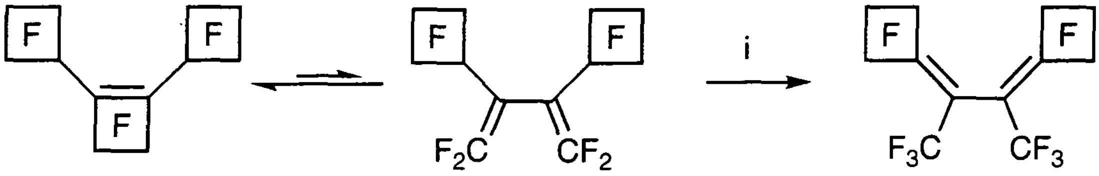
i. Et_4NF, $CHCl_3$, 5 min., r.t.

Perfluorodienes can be rearranged to acetylenes by a similar process.[25, 26]

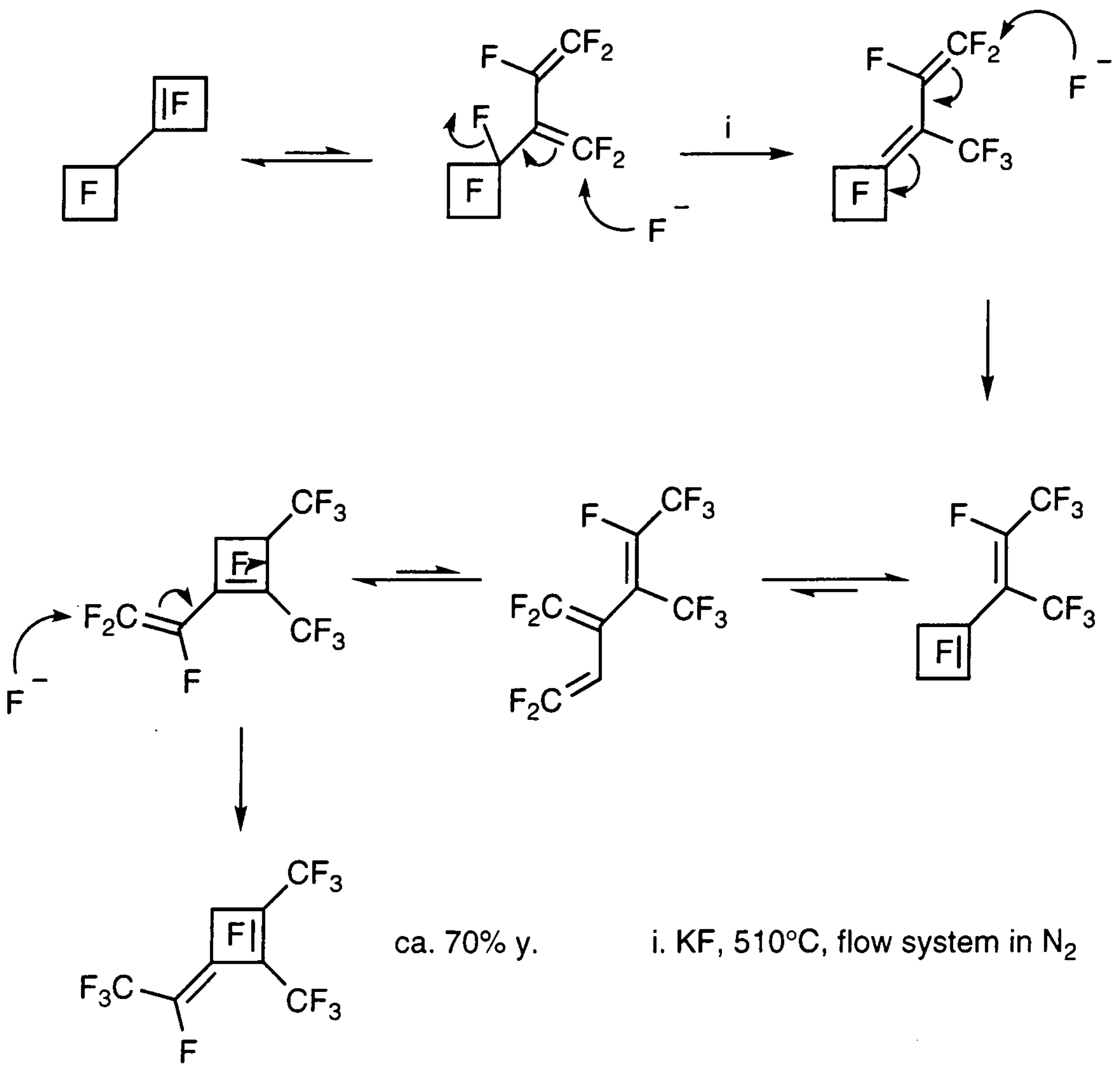
$$CF_2{=}CF{-}CF{=}CF_2 \xrightarrow{i} CF_3{-}C{\equiv}C{-}CF_3 \qquad 88\%\ y.$$

i. CsF, 100°C, no solvent

More recent work has led to some novel rearrangement of cyclic alkenes:[27, 28]



i. CsF, 300°C 100% y.



ca. 70% y.

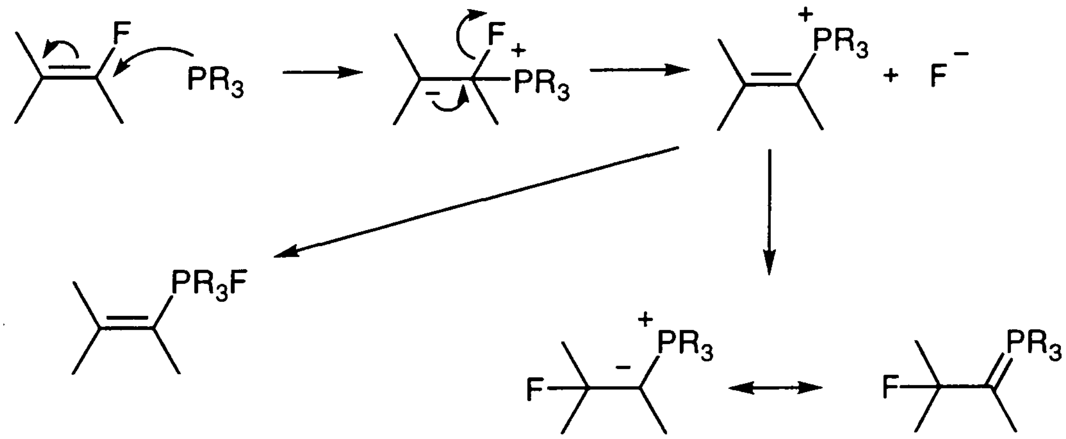
i. KF, 510°C, flow system in N_2

All of the above reaction can be explained in terms of the intrinsic instability of a fluorine atom directly attached to an unsaturated site.

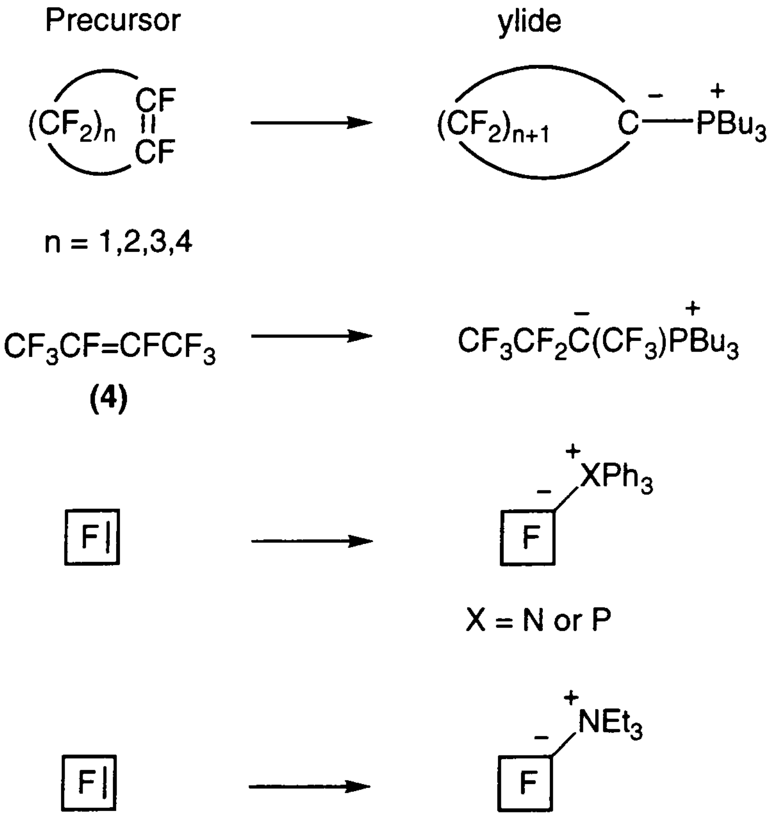
I.2.A.3. Production of Long Lived Carbanions

I.2.A.3.i. Ylides

Probably the largest class of highly fluorinated carbanionic species which have been directly observed are ylides.[29] The most common method of preparation of such systems is by reaction of fluorinated alkenes with tertiary amines and phosphines.



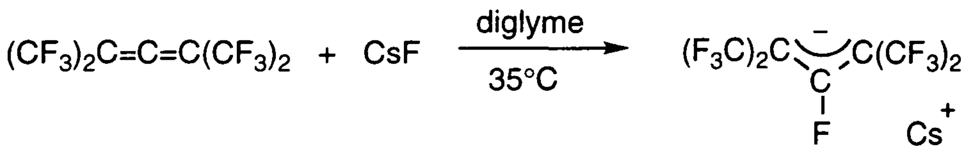
Some examples of stable ylides are shown below.[30-33]



In general, the phosphorous ylides go on to give fluorophosphoranes by attack of fluoride ion upon the positive centre.[34] This mode of stabilisation is not open to ammonium ylides and they are notably less stable than their phosphonium analogues. The triethylammonium perfluorocyclobutane ylide, shown above, has recently been used as a novel, if expensive, source of fluoride ion.[33]

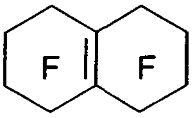
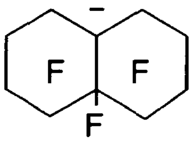
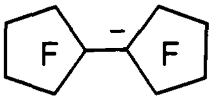
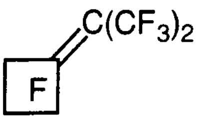
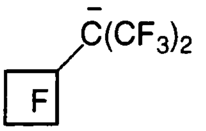
I.2.A.3.ii. Uncoordinated Carbanions

Knunyants and co-workers[35] claimed the first uncoordinated stable perfluorocarbanion by reaction of tetrakis(trifluoromethyl) allene with cesium fluoride.



The anion could not be isolated but was stable in solution up to 150°C.

In the last ten years work in these laboratories,[36, 37] and also by Smart,[38] has given a whole range of isolated perfluorocarbanions from their fluoro-alkene precursors using CsF and TAS-F (see later) as sources of fluoride ion.

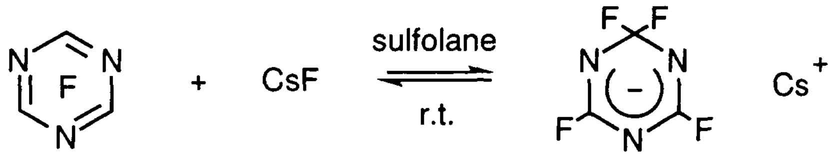
precursor	carbanion	counter ion
$(CF_3)_2C=CF_2$ **(3)**	$(CF_3)_3C^-$	TAS^+, Cs^+
$(CF_3)_2C=CFCF_2CF_3$ **(6)**	$(CF_3)_2\bar{C}CF_2CF_2CF_3$	TAS^+, Cs^+
		TAS^+
		TAS^+, Cs^+
		Cs^+

In all cases tetraglyme was found to be the most suitable solvent in which to perform these reactions, although some success was achieved using dimethylformamide.

It should be noted that in all the above systems the carbanions are significantly stabilised by bulky perfluoroalkyl groups, which can also act as a hindrance to attack of the carbanion on the precursor alkene giving oligomerisation. It is also worthy of note that no α-fluorocarbanions have ever been isolated and this tends to reiterate the known destabilising effect of fluorine directly bonded to an anionic site.

I.2.A.3.iii. σ-Complexes

Fluorinated hetroaromatic compounds are highly reactive towards nucleophiles and trifluoro-s-triazine has been shown by workers in these laboratories[39] to form a stable anion, at room temperature, by addition of caesium fluoride in sulfolane.



σ - complex

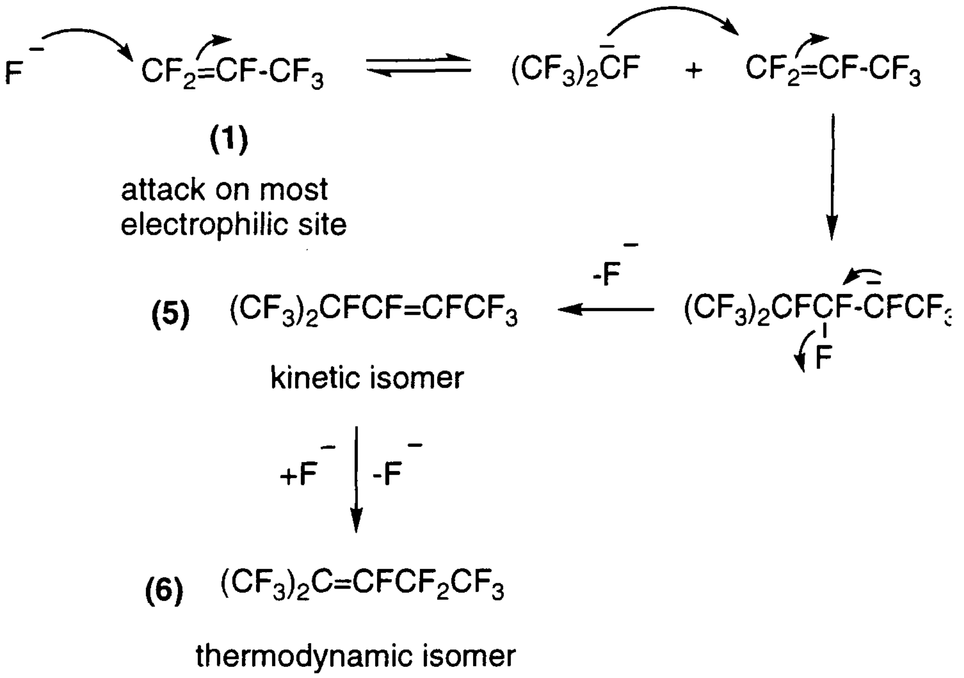
The σ-complex can be isolated by addition of toluene and cooling.

The mono- and di-alkylated derivatives of trifluoro-s-triazine also yielded stable anions under the same conditions.

I.2.B. Fluoride Ion in C-C Bond Forming Reactions

I.2.B.1. Dimerisation and Oligomerisation of Fluoro-alkenes

It was first shown by Miller[22] that carbanions could be generated by reaction of fluoride ion with fluorinated alkenes, and this observation has led to an extensive study of the nature of such processes. The regio-selectivity of addition is governed by the need to form the most stable carbanion as discussed previously. The fluoride ion induced dimerisation of hexafluoropropene (**1**) serves as example.



The dimer (**5**) rearranges to the more stable thermodynamic isomer (**6**) in which electron-electron repulsions between the fluorine lone pairs and the double bond are minimised. Higher oligomers of (**1**) are uncommon due to steric hinderance, although trimers are known, and this makes many fluoro-alkenes unsuitable for polymerisation processes.

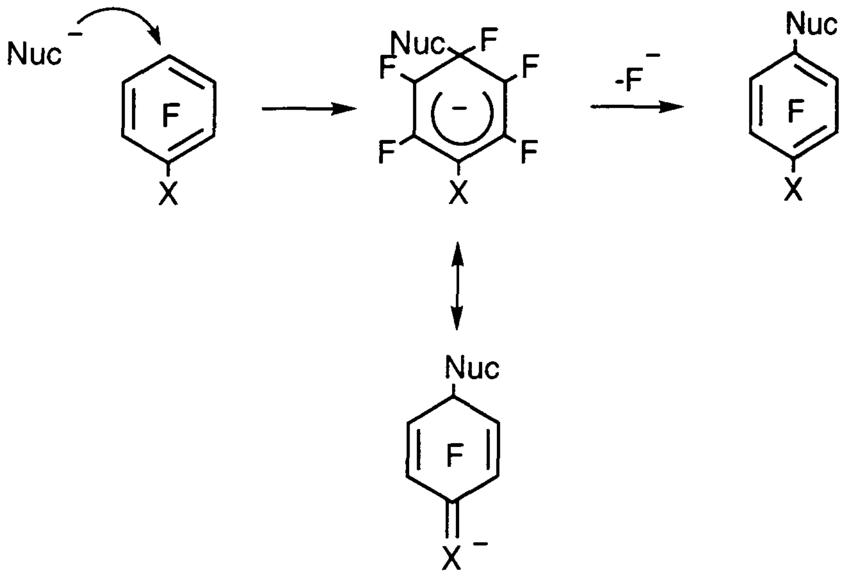
Although tetrafluoroethylene (**2**) is less reactive towards fluoride ion, and other nucleophiles, than hexafluoropropene (**1**) it can be oligomerised quite successfully at elevated temperatures.[40, 41]

$$\underset{\textbf{(2)}}{C_2F_4} \xrightarrow[100^\circ C]{CsF,\ triglyme} C_8F_{16} + C_{10}F_{20} + C_{12}F_{24} + C_{14}F_{28}$$

I.2.B.2. Fluoroalkylation of Aromatics

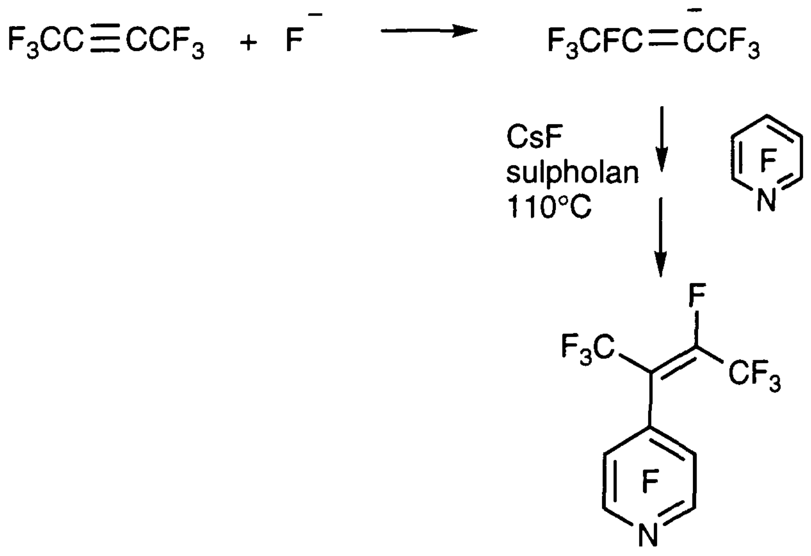
Fluoro-aromatics extend the mirror image relationship discussed above and their reactions with nucleophiles are often described as negative Friedel-Crafts processes.[42-47] Whilst hydrocarbon aromatics are activated towards attack from electrophiles, by electron donating groups at the ortho and para positions, fluoro-aromatics are activated to attack at these positions by electron withdrawing groups.

The orientation of attack can be understood in terms of the destabilising influence of the fluorine atom lone pairs on the ring.

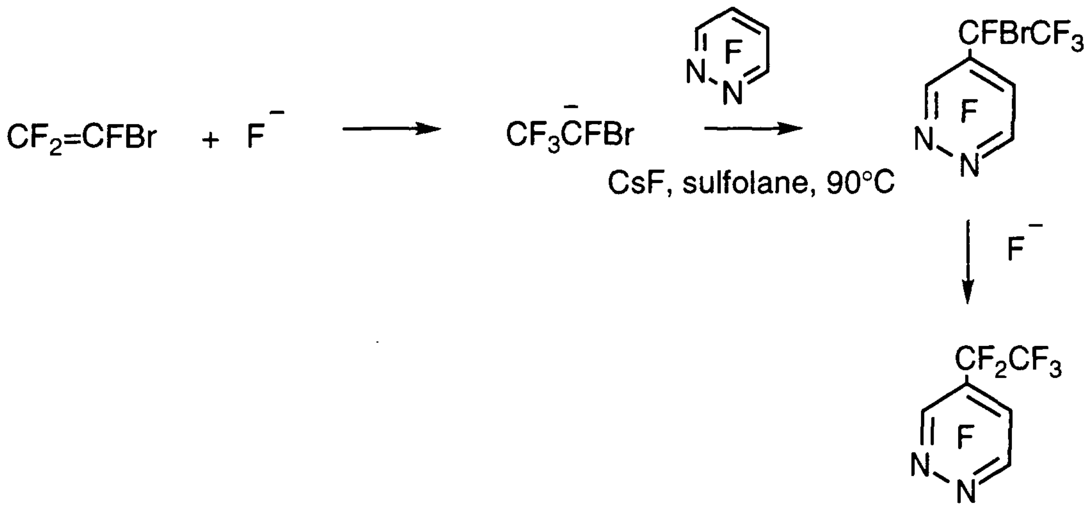


X = R_F, NO_2, SO_3H, Cl, Br, etc.

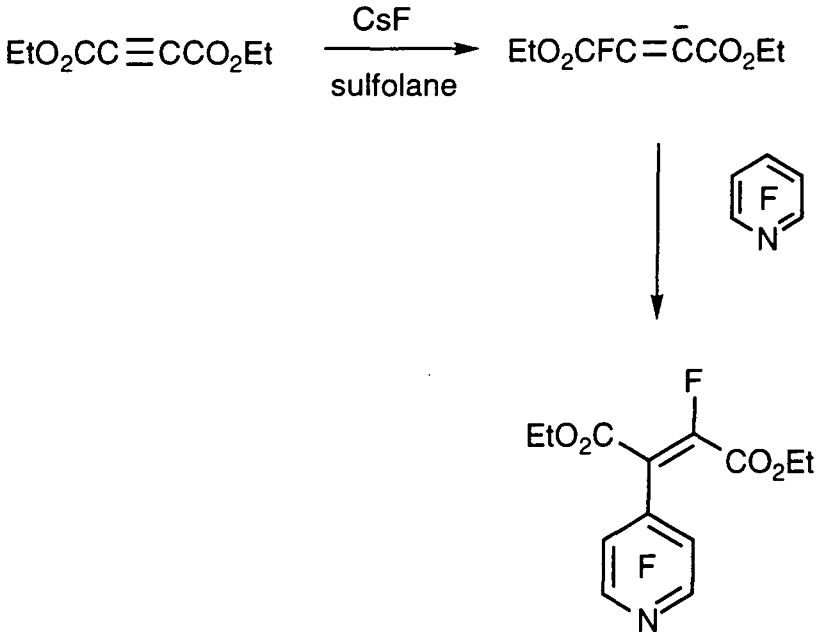
The intermediate anion places most electron density on the position para to the site of attack and so any substituent which can displace electron density away from this site will have a strong activating influence. Thus, fluorocarbanions produced in the reaction of fluoro-alkenes with fluoride ion can be used as a means of perfluoroalkylating suitably activated systems.[48-50]



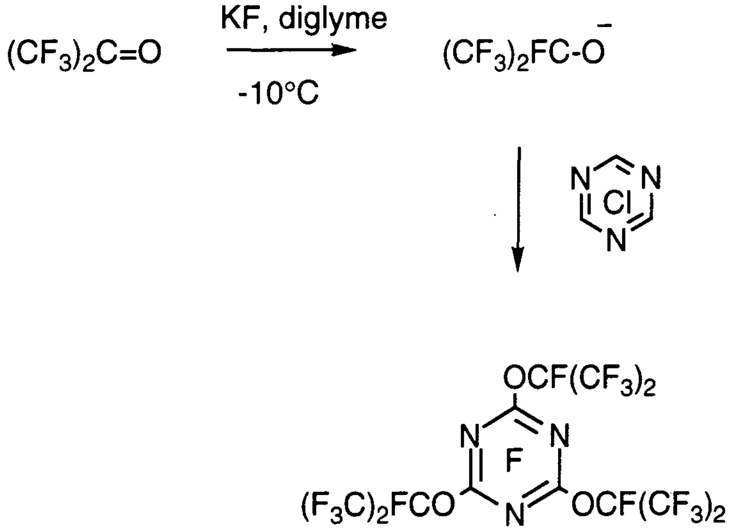
Fluorohalocarbanions can also be used as perfluoroalkylating agents.



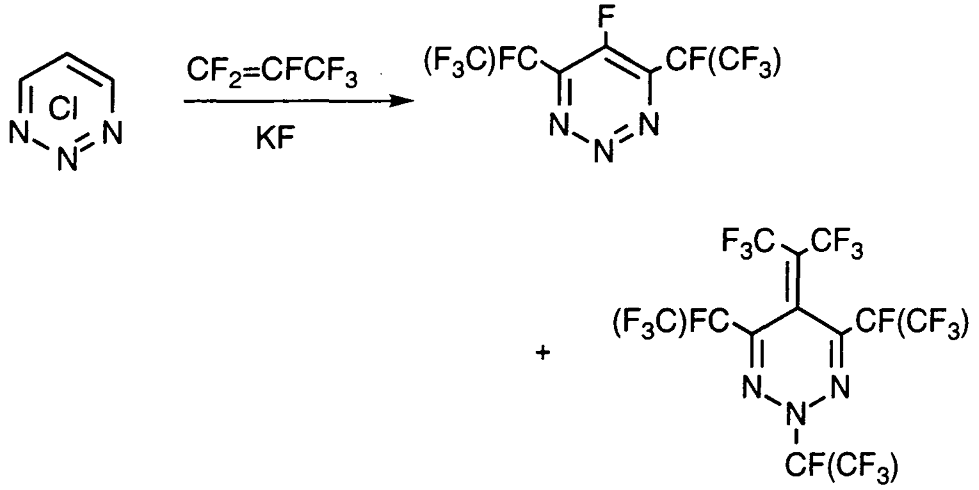
Non-perfluorinated carbanions can also be generated by reaction of fluoride ion with a suitable substrate and subsequently trapped by an aromatic.[50]



Cyanuric chloride rather than fluoride is used in the formation of perfluoroalkoxy derivatives in order to limit re-attack of the displaced halide ion on the aromatic ring.[51]



Similarly, trichloro-1,2,3-triazine is such a reactive system that fluorination and perfluoroalkylation can be carried out simultaneously.[52, 53] This reaction also gives a rare example of nucleophilic attack on a ring nitrogen.



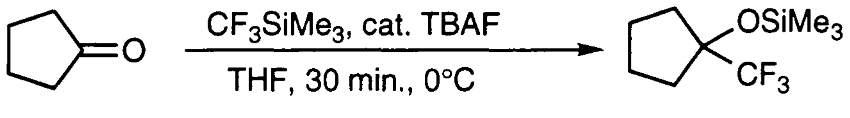
I.2.B.3. Perfluoroalkyltrialkylsilanes as Perfluoroalkylating Agents

Trifluoromethyltrimethylsilanes were first synthesised by Marchenko in 1980,[54] and later by Ruppert in 1984,[55] by the process shown below.

$$Me_3SiCl + CF_3Br + (Et_2N)_3P \xrightarrow{PhCN} Me_3SiCF_3$$

The method has been refined by other workers to give a range of perfluoroalkylsilanes.[56, 57]

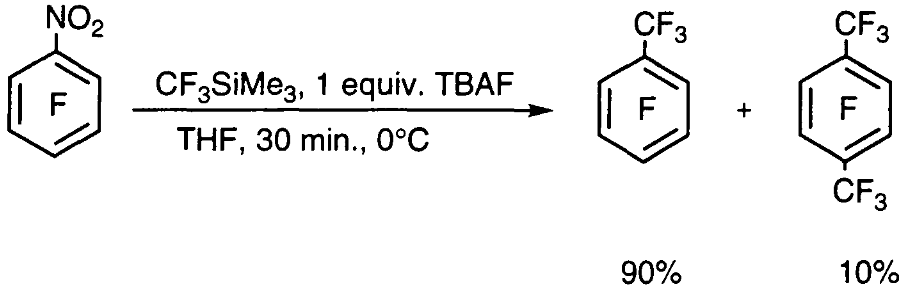
Although many reagents exist for perfluoroalkylation processes, most are complicated, expensive and give low yields of products. Over the years trimethylsilyl compounds substituted with electron withdrawing groups, such as CN, I, Cl, NCO and so on, have been used as synthetic reagents for the introduction of these substituents in electron deficient centres.[58, 59] The use of this methodology for perfluoroalkylation was first investigated by Olah and co-workers[60, 61] who utilised the intrinsic strength of a silicon-oxygen bond allied to the fact that perfluoroalkyl-silyl bonds are strongly polarised to effect the trifluoromethylation of ketones.



Hydrolysis of the product gives the corresponding alcohol in *ca.* 80% yield.

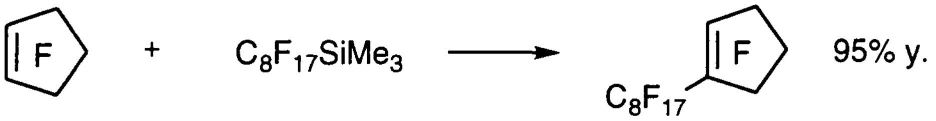
These reactions appear to proceed via an initial fluoride ion attack on silicon followed by transfer of the CF_3 group to the carbonyl in a nucleophilic process.

The use of such reagents in perfluoroalkylation of aromatics and alkenes has also been investigated.[61] Suitably activated aromatics, such as pentafluoronitrobenzene can be trifluoromethylated. Such reactions are thought to proceed via Meisenheimer complexes.

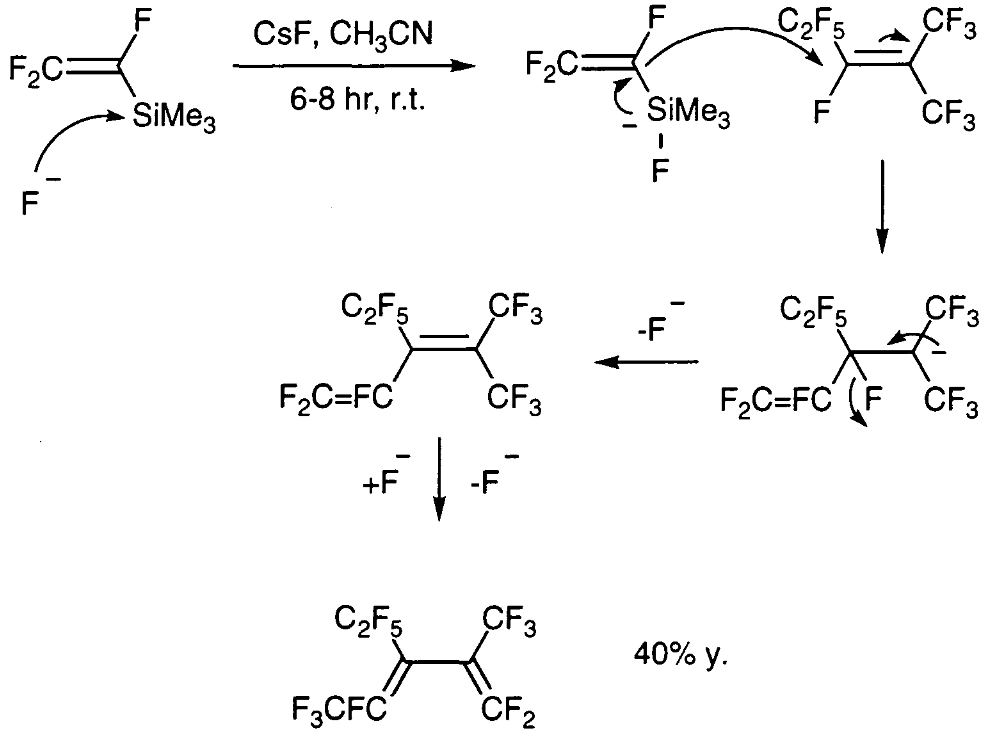


Substitution of systems baring activated hydrogens can lead to formation of trifluoromethane.

Farnham[61] has also reported nucleophilic addition of *n*-perfluoro-octyl groups to perfluorocyclopentene involving a simple addition-elimination mechanism.



Extension of this work has led to the formation of some novel dienes by Russian workers[62] who have employed trifluorovinyltrimethyl silane as a perfluorinating agent.



Interest in these remarkable perfluoroalkylating agents is now an important area of research and their simplicity suggests that such systems will become useful synthetic reagents in the future.

I.2.C. Fluoride Ion as a Base

The potential ability of fluoride ion to act as a base might be predicted on considering the relative strength of the H-F bond (~569 $KJmol^{-1}$, *cf.* H-Cl ~432 $KJmol^{-1}$, H-O ~428 $KJmol^{-1}$, H-N ~314 $KJmol^{-1}$). On this basis nucleophilic attack of fluoride ion on other nuclei might also be expected;

Si-F	~540 $KJmol^{-1}$
P-F	~439 $KJmol^{-1}$
C-F	~536 $KJmol^{-1}$

Fluoride ion attack on silicon is a long established method of removing silyl protecting groups and its attack on carbon forms the basis for some of the most fundamental reactions in fluoro-organic chemistry - halogen exchange.[44]

I.2.C.1. The Strength of Fluoride Ion as a Base

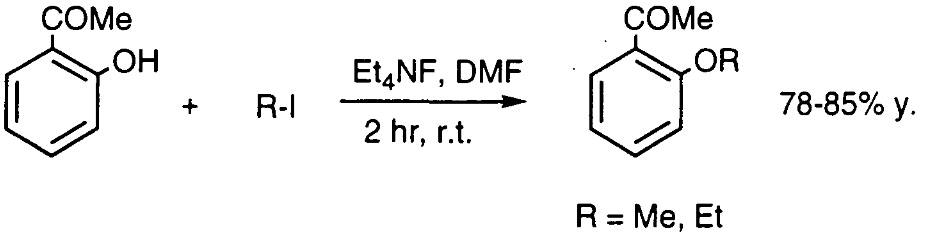
The base strength of an ionic fluoride is intrinsically dependent on the countercation used, the amount of water present and the solvent (see **Section I.3**). These factors lead to some huge inconsistencies in the reported basicity of fluoride ion. Some of the more reliable measurements place its potential between trialkylamines and alkoxides for Micheal addition reactions,[63] *ca.* 10^3 times more reactive than alkoxides on the basis of dehydrohalogenation reactions[64] and comparable to organomagnesium and organolithium species based on its ability to generate carbanions.[65]

Nesmeyanov[66] first reported the use of fluoride ion as a base for the decarboxylation of simple carboxylic acids in 1948 and in the last thirty years it has become a useful reagent in a number of common base induced processes.

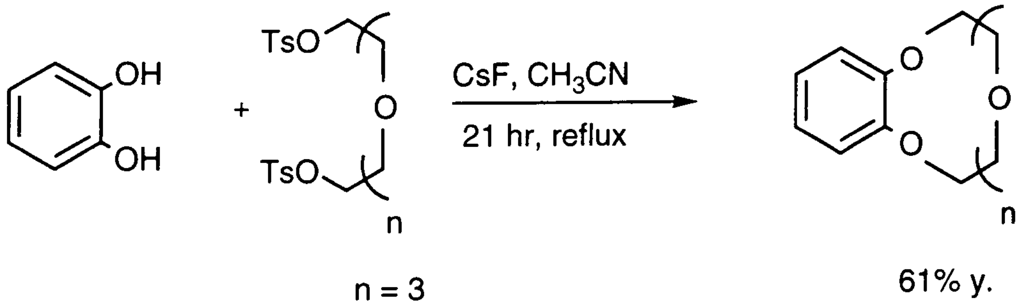
A few examples are given here, but more extensive reviews of the uses of fluoride ion in esterification, intermolecular condensations, dehydrations, dehydrohalogenations and cyclisations can be found elsewhere.[67]

I.2.C.2. Alkylation and Arylation

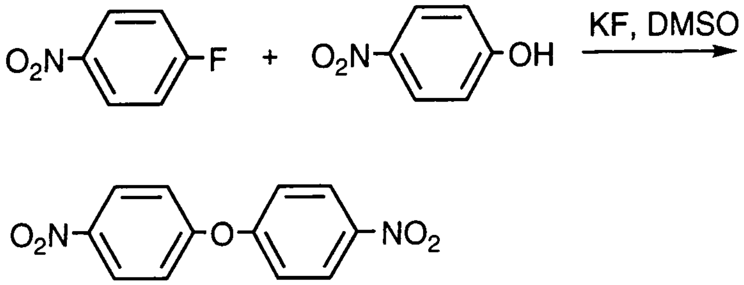
Fluoride ion induced alkylation of phenols has been thoroughly studied by Miller and co-workers[68] using tetraethylammonium fluoride in dimethylfomamide.



Reinhoudt[69] has extended this methodology to the synthesis of crown ethers.



Ishikawa has also reported a synthetically useful route to aryl-aryl ethers.[70]



I.3. Fluoride Ion Sources

Some of the simplest reactions in organofluorine chemistry are catalysed by fluoride ion and as the number of fluorine containing compounds grows the variety of fluorinating reagents also increases. This thesis is concerned with the study of new fluorinating systems and so an overview of some of the fluoride ion sources currently available is required.

I.3.A. Alkali Metal Fluorides

Much work in this area has involved use of alkali metal fluorides as fluoride ion sources. A general order of reactivity of these salts has been established.

$$CsF > KF > NaF > LiF$$

As lattice energy decreases, reactivity of the fluoride ion increases.

The alkali metal fluorides are appreciably soluble in only a few solvents such as diols, carboxylic acids and some fluorinated alcohols.[67, 71] In all the above cases, however, there is significant hydrogen bonding of fluoride ion and subsequent lowering of its nucleophilicity. Use of polar aprotic solvents does tend to avoid hydrogen bonding, but the solubility of alkali metal fluorides in such media is so low as to limit their reactivity. (*eg*. a saturated solution of KF in DMSO at 25°C contains 8mg of fluoride/100g solvent).

The most commonly used alkali metal fluorides are KF and CsF, with the former being less reactive but easier to dry and less expensive. Reactions involving alkali metal fluorides in polar aprotic solvents are thought to proceed via reaction at the surface of the undissolved fluoride. Alkali metal fluorides are still widely used, despite the alternatives available, owing to their high thermal stability and relative inexpensiveness. They are, however, unsatisfactory in many cases due to their low solubility and low reactivity. The quest for a reactive source of fluoride ion that is soluble in organic solvents has been an important objective for many years.

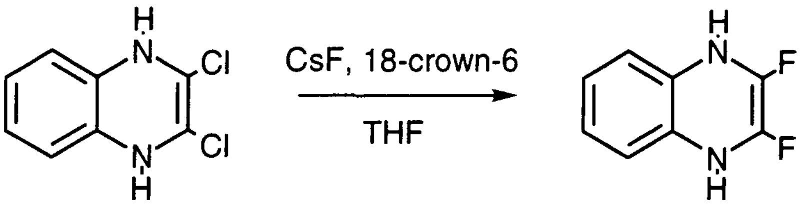
I.3.B. Increasing the Solubility of the Alkali Metal Fluorides

A variety of systems have been used to try to increase the solubility of the alkali metal fluorides.

I.3.B.1. Crown Ethers

The ability of an electron rich macrocycle to chelate an appropriately sized cation in solution, and so release the anion is a phenomenon that has been studied in many systems. The cyclic polyether 18-Crown-6 can bind potassium and so, theoretically, release the fluoride counter ion. However, studies have shown that this system only increases the reactivity of the fluoride ion to the level of that found in CsF. The system has found some use in halogen exchange processes.[72, 73]

$$CH_3(CH_2)_7Br \xrightarrow[\text{18-crown-6}]{\text{KF, }CH_3CN} CH_3(CH_2)_7F \quad \text{92\% y.}$$



18-crown-6 can also be used as a chelate for CsF,[74] despite the fact that the cavity in the centre of the ether ring is too small to fully accommodate a cesium cation. There is enhanced reactivity compared to normal CsF which has been accounted for in terms of sandwich chelation.

I.3.B.2. Phase Transfer Catalysts

The concentration of fluoride ion in the organic phase may be increased by use of a phase transfer catalyst (PTC) in conjunction with KF. Reactions of the following type have been studied.[75]

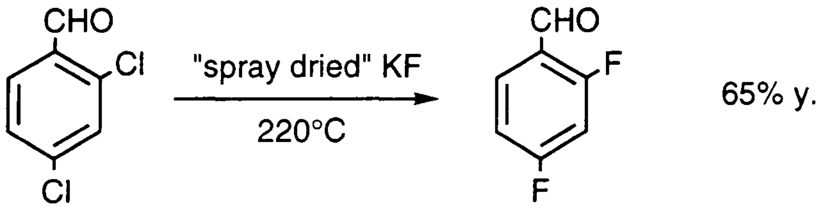
$$n\text{-}C_8H_{17}Cl_{(org)} + KF_{(s\text{ or }aq)} \xrightarrow{\text{PTC}} n\text{-}C_8H_{17}F_{(org)} + KCl_{(s\text{ or }aq)}$$

84% y.

The role of the PTC is to transfer the fluoride ion from the aqueous/solid phase to the organic phase. These types of phase transfer processes are known to be highly moisture dependent and in the above reaction it was found that maximum conversion was obtained with a KF/H_2O ratio of 3:1.

I.3.B.3. Spray Dried Potassium Fluoride

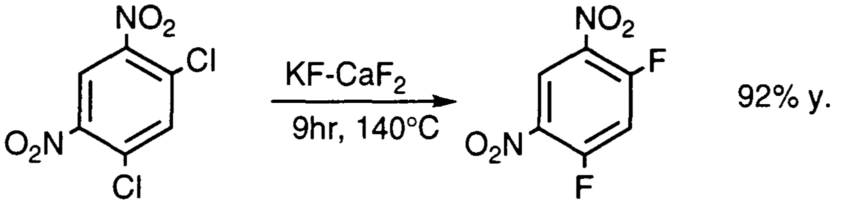
The surface area of normal KF ($0.1m^2/g$) is much less than that of Spray Dried KF ($1.3m^2/g$) and so the latter shows much greater reactivity than normal KF.[76]



Spray dried KF also has the significant advantage of being much less hygroscopic than normal KF. Using normal KF *p*-chloronitrobenzene can undergo halogen exchange in *ca.* 55% yield over 5 hours in DMSO, whereas using spray dried KF the same reaction proceeds to *ca.* 85% yield under similar conditions.

I.3.B.4. Supported Potassium Fluoride

Supported reagents have been used to increase the reactivity of KF in solution. Systems such as KF-CaF_2 have been successfully used as a source of fluoride ion.[77, 78] The greater reactivity of fluoride ion under these conditions is thought to be due to increasing the surface area of the KF.



In comparison with other methods of enhancing the reactivity of KF this method appears to be extremely useful.

The yields of reactions of various fluoride ion sources with benzyl bromide are listed in **Table 2.**

Table 2. Yields of fluorination of benzyl bromide

Fluoride ion source	Yield of benzyl fluoride after 10 hr under reflux (%)
KF	0.6
CaF_2	0.3
KF-CaF_2	89
Spray dried KF	68
KF 18-crown-6	50

Powder x-ray analysis of KF-CaF_2 reveals no chemical interaction between the two fluorides and study of the inorganic reaction products revealed KBr, KF and CaF_2 to be present but no $CaBr_2$. Thus, CaF_2 appears to be acting as a simple support to the KF and increasing its nucleophilicity by physical interaction. Support on other media such as alumina, silica and celite has been found to be of surprisingly little use in enhancing the reactivity of KF.[79] Crosslinked co-polymers as support reagents have been found to be of some use, however, and the styrene-divinylbenzene system has been used extensively to promote a variety of reactions.[80]

$$PhCOCl \xrightarrow[\text{r.t., 10 min.}]{\text{KF-polymer}} PhCOF \qquad 95\%\ y.$$

I.3.B.5. Anion Exchange Resins

Anion exchange resins are useful in halide exchange reactions involving fluoride ion. Amberite IRA 900 is of particular use in this area and acts by increasing the reactivity and solubility in the organic phase.

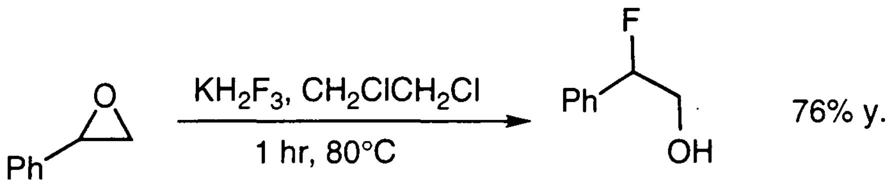
$$\text{Ⓟ}\!-\!CH_2\overset{+}{N}Me_3\overset{-}{F} \qquad P = \text{polymer}$$

The system has been used in a variety of reactions.[81]

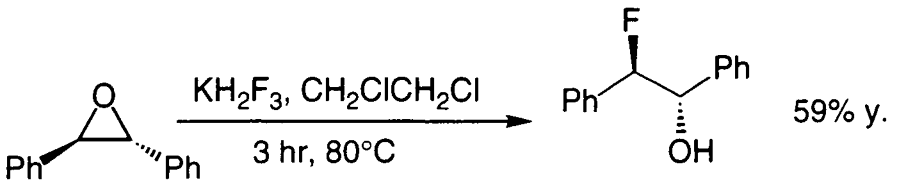
$$PhCOCH_2Br \xrightarrow{\text{Amberite-F}} PhCOCH_2F \qquad 61\%\ y.$$

I.3.B.6. Potassium Dihydrogen Trifluoride

Tamura[82] has recently found potassium dihydrogen trifluoride to be an effective regio-selective and stereo-selective reagent for the ring opening of epoxides.



The regio-selectivity has been explained in terms of the predisposition of benzylic sites to nucleophilic attack. Study of other less symmetrical systems led to the observation that the reaction proceeds via *cis* addition of an HF molecule giving rise to a high degree of steric control.



100% *threo* isomer

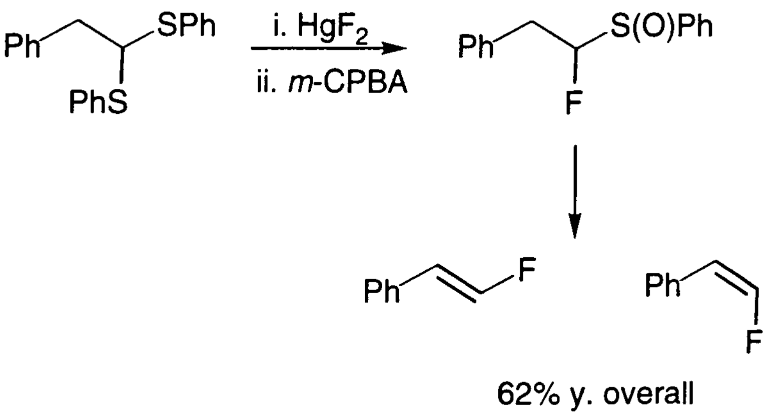
Other poly(hydrogen fluoride) salts have been used to halofluorinate alkenes.[83]

I.3.C. Covalent Metal Fluorides

Use of transition metal fluorides, such as SbF_5, as fluorinating agents is common. Such reagents cannot readily be described as fluoride ion sources since their mode of action often involves complex radical intermediates.[84] A few examples of recent developments in this area are given here, but more extensive reviews can be found elsewhere.[61, 84]

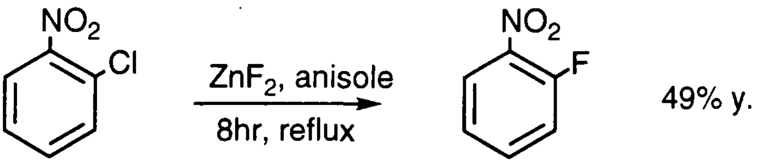
I.3.C.1. Mercury Fluorides

Mercury(II) fluoride is commonly used for the replacement of bromine by fluorine in organic halides,[85, 86] but has found use in the last few years in the generation of α-fluorosulphoxides and subsequently vinyl fluorides.[87]



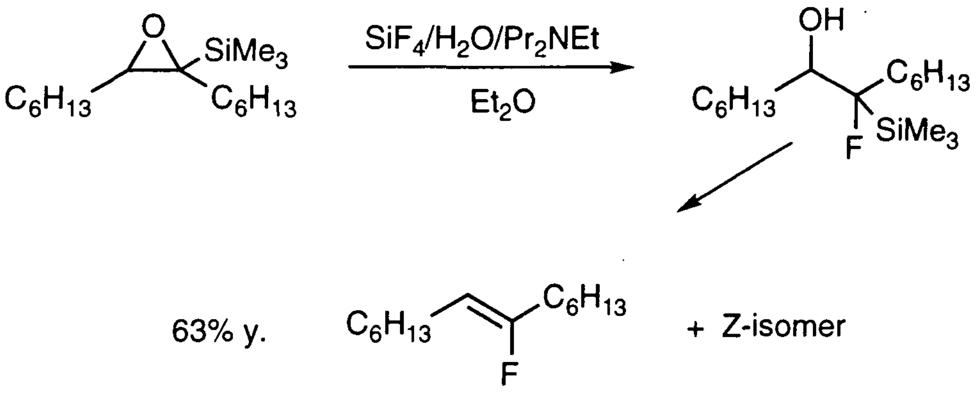
I.3.C.2. Zinc (II) Fluoride

Although not a common fluorinating agent, due to its high toxicity, ZnF_2 has recently found use in halogen exchange reactions.[88]



I.3.C.3. Silicon Fluorides

This relatively new fluorinating system, developed by Shimizu and Yoshioka,[89] has been used extensively to effect the ring opening fluorination of epoxides in conjunction with Bu_4NF and can give remarkable selectivity in comparison with other fluoride ion sources. In reaction with α,ß-epoxysilanes, the ring opened ß-fluoro-ß-silyl alcohol was produced without elimination of the silicon moiety, in contrast to $Et_3N{\cdot}3HF$, PPHF and KHF_2 which gave desilylated products.[90] The silyl alcohol produced can then undergo Peterson olefination to give the desired product.



I.3.D. Organic Sources of Fluoride Ion

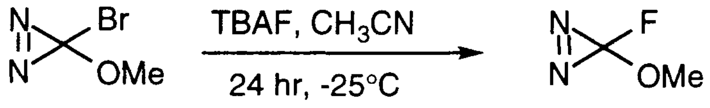
Use of an organic source of fluoride ion would enhance reactivity due to its solubility in organic systems. There are, however, many problems associated with such systems, including cost and hygroscopicity, and there is much room for improvement. Several systems have been investigated to try to overcome these effects.

I.3.D.1. Tetraalkylammonium Salts

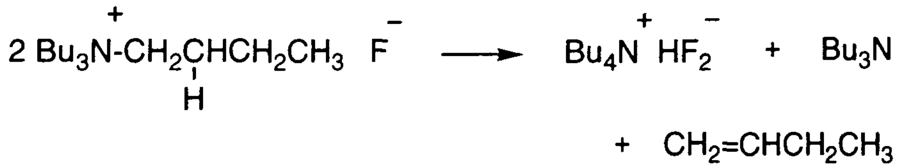
One of the simplest methods of increasing fluoride ion solubility is to use an organic counter ion.

The tetraalkylammonium fluorides, such as tetrabutylammonium fluoride (TBAF), can be used in halogen exchange reactions and can give high yields of products.[91]

$$CH_2{=}CHCH_2Br \xrightarrow[\text{8 hr}]{\text{TBAF}} CH_2{=}CHCH_2F \qquad \text{85\% y.}$$

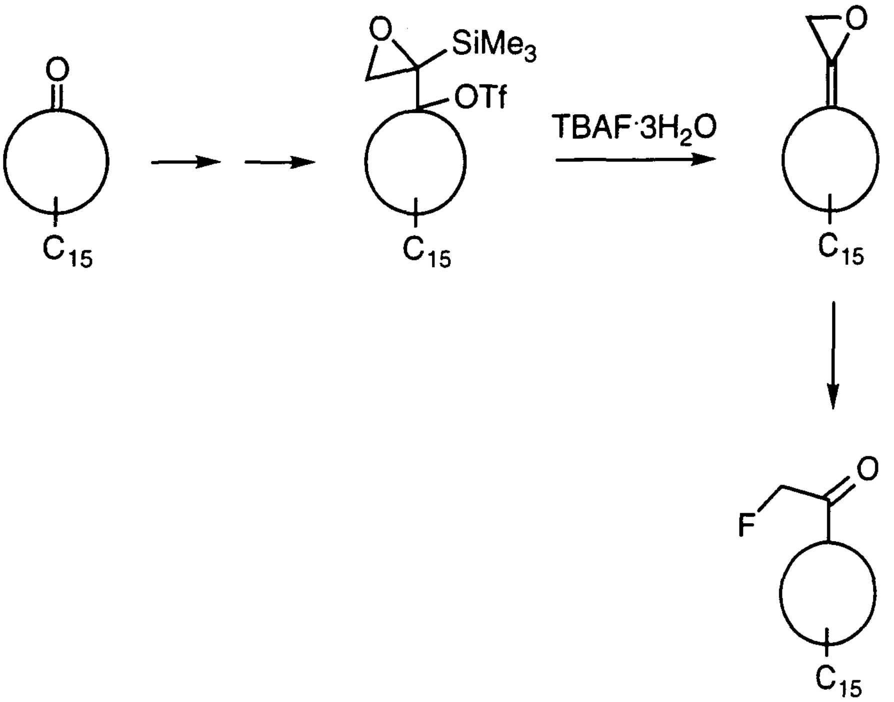


TBAF is a commercially available, extremely hygroscopic substance. Its major disadvantage is that trace amounts of water can drastically affect its reactivity and great care must be taken to dry such compounds. Even when the salt is 'comparatively dry' there is the possibility of Hoffmann elimination, which can occur more readily when the system is dehydrated. The success of the TBAF system as a fluoride ion source is due to the reactivity of the hydrated salt $But_4N^+HF_2^-$ produced in the elimination process shown below.[92]

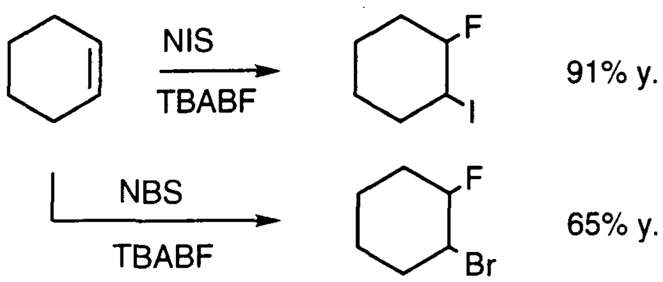


$$2\,Bu_3\overset{+}{N}\text{-}CH_2\underset{H}{C}HCH_2CH_3\;\overset{-}{F} \longrightarrow Bu_4\overset{+}{N}\;\overset{-}{HF_2} + Bu_3N + CH_2{=}CHCH_2CH_3$$

Despite efforts to produce the anhydrous material, 'wet' TBAF has recently been used to make a range of fluoro-methyl ketones via allene epoxides.[93]

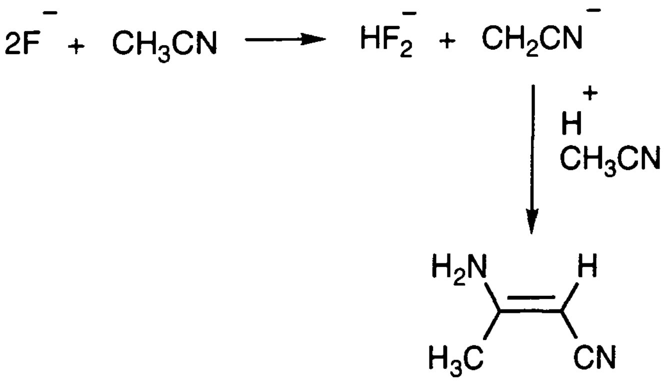


Tetrabutylammonium hydrogen bifluoride (TBABF) has been used as a source of fluoride ion, with particular attention being paid to its usefulness in halofluorination of alkenes.[94]

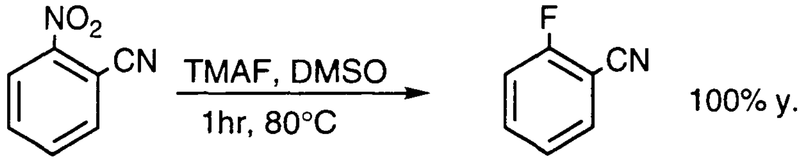


In systems where the quaternary ammonium moiety is not prone to β-elimination decomposition occurs on drying to give the tertiary amine and the alkylfluoride.

Tetramethylammonium fluoride (TMAF) has been used to perform many halogen exchange reactions, but drying must be rigorous, with reaction thought to be due to a $-(HF_2)_n-$ moiety.[92, 95] TMAF was first synthesised in 1888 by reaction of tetramethylammonium hydroxide with HF[96] and, although many methods are now available for its production, Christie[97] has modified this method to produce the first example of fully anhydrous TMAF. By using scrupulously dry reagents and re-crystalising from isopropyl alcohol, production of TMAF with a water content of 0.06 wt. % was achieved. Although the product was extremely anhydrous, it was so reactive as to dimerise its solvent, acetonitrile, by proton abstraction.[98]



TMAF has recently been used in fluorodenitration reactions of aromatics.[99, 100] Use of alkali metal fluorides for such processes can lead to significant amounts of phenolic and diarylic ethers as by-products due to re-attack of the displaced NO_2 group on the initial product. When TMAF is used as the fluorinating agent this does not occur due to formation of stable tetramethylammonium nitrite.



I.3.D.2. Tetraalkylphosphonium Salts

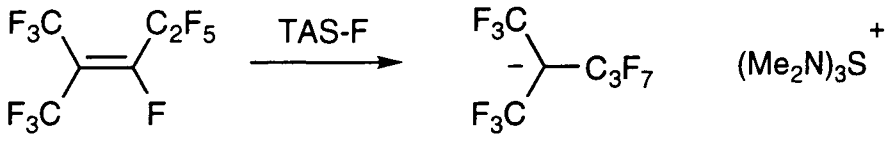
Phosphoranes, such as methyltributyl phosphorane, have been extensively studied in tosyl displacement reactions, but present the same problems of preparation as the tetraalkylammoniums.[101]

I.3.D.3. Trisdimethylaminosulphonium Difluorotrimethylsilicate (TAS-F)

TAS-F is probably the most useful currently available fluoride ion source due to its high reactivity. Preparation of the salt utilises the strength of the Si-F bond.

$$(Me_2N)_2SF_2 + Me_2NSiMe_3 \longrightarrow \underset{\text{TAS-F}}{[(Me_2N)_3S]^{+}\,[Me_3SiF_2]^{-}}$$

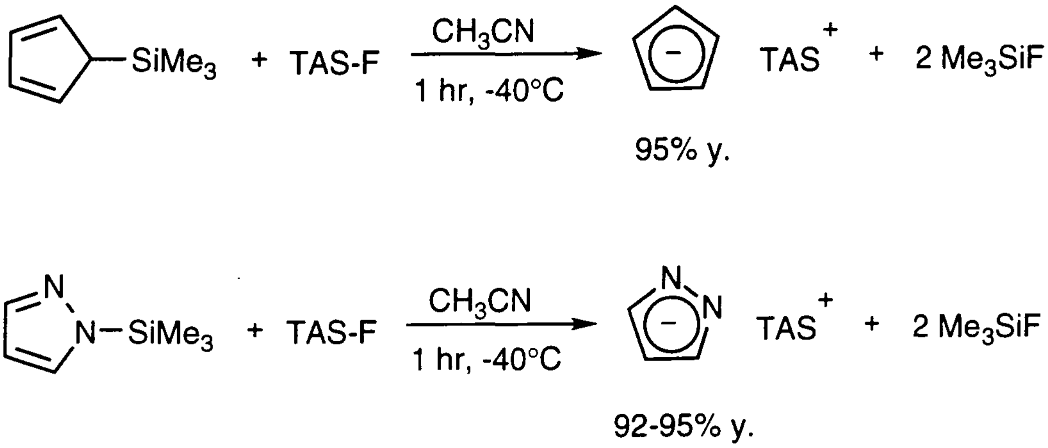
It was first investigated by Middleton[102] in 1976 as a highly nucleophilic source of fluoride ion and can be used to form fluorides from some otherwise unreactive halides. It has also been used to prepare stable perfluorocarbanions.[36-38, 103, 104]



(6)

The process is in effect irreversible due to loss of fluorotrimethylsilane from the counter ion.

TAS-F has also been used to prepare a range of cyclopentadienide and corresponding cyclic azolide salts by reaction of TAS-F with the parent trimethylsilane cyclopentadienes and azodienes.[105] These compounds were found to be surprisingly stable and afforded 'naked' anions.

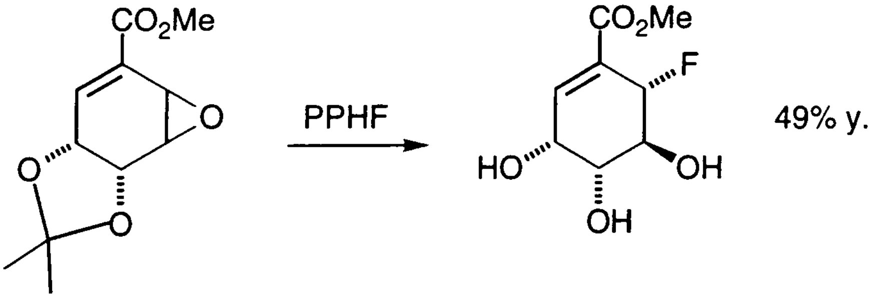


I.3.D.4. Hydrogen Fluoride

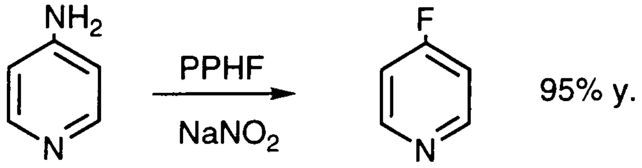
Anhydrous hydrogen fluoride is one of the cheapest and most popular fluorinating agents[106] but, due to its highly corrosive nature and low boiling point (19°C), methods of moderating it have been sought. Solvents such as amines and pyridines have been used with a view to solvating the proton and so releasing fluoride ion. A general review of this approach to obtaining reactive fluoride ion was published in 1991.[107]

I.3.D.4.i. Polypyridinium Hydrogen Fluoride (PPHF)

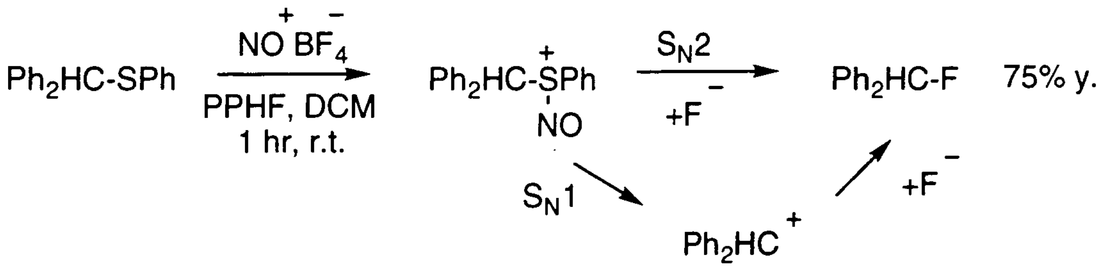
Polypyridinium hydrogen fluoride (PPHF), commonly known as Olah's reagent, is a commercially available stable liquid with molecular composition 1py:9HF. It has been used in a variety of reactions over the last twenty years including, fluorination of secondary and tertiary alcohols, alkenes and alkynes and halogen exchange reactions.[61, 108-110] It has recently been used to incorporate fluorine into shikimic acid.[111]



PPHF has also been used by Yoneda[112] in a modification of the Balz-Schiemann reaction.

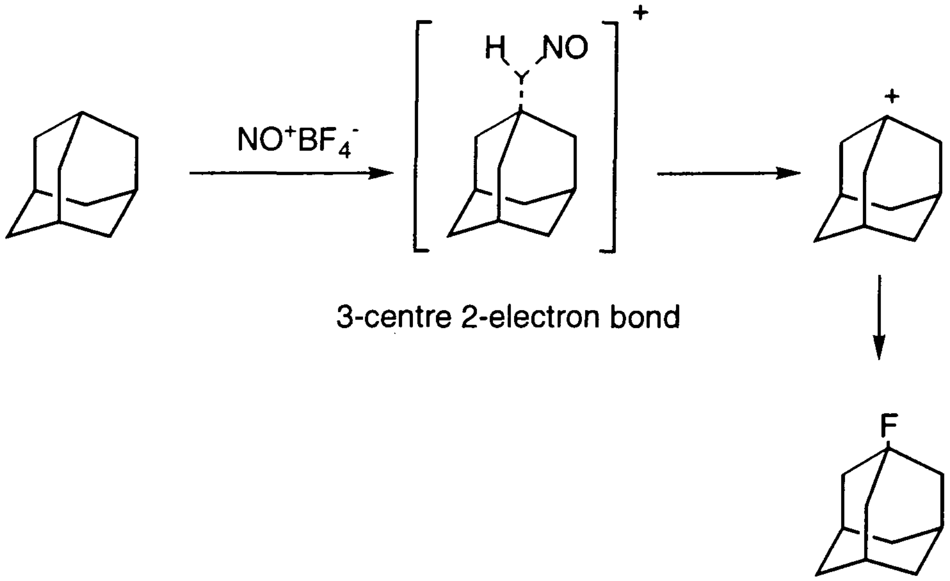


PPHF in conjunction with nitrosonium tetrafluoroborate has been used by Olah and co-workers[113] as a desulphurative fluorinating agent.

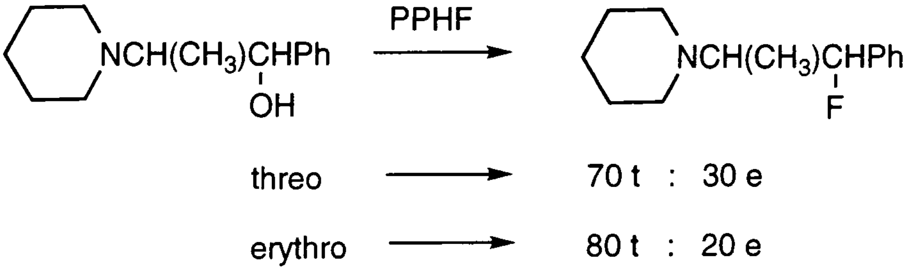


The reaction involves initial production of a sulphonium ion by attack of NO^+ upon sulphur, followed by nucleophilic displacement of sulphur by fluoride ion in either an S_N1 or an S_N2 process.

Direct fluorination of saturated hydrocarbons can be achieved using PPHF in conjunction with $NO^+BF_4^-$ in reactive systems such as adamantane or triphenyl methane.[114]

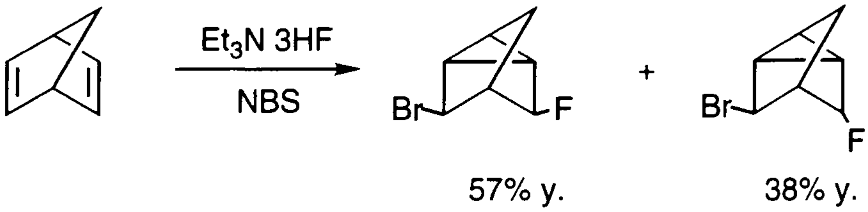


PPHF used in the fluorination of secondary and tertiary amine alcohols displays a high degree of stereo-selectivity.[115]

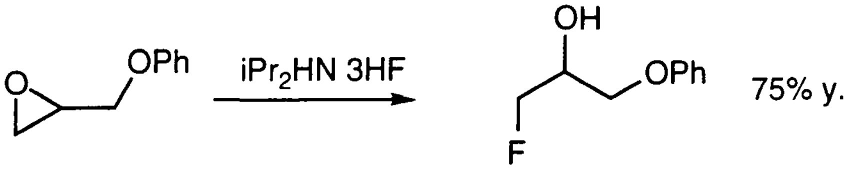


I.3.D.4.ii. Alkylamine Hydrogen Fluorides

Reagents such as $Et_3N{\cdot}3HF$ were first used by Franz in the early eighties and, because they are less corrosive than PPHF, continue to be used extensively.[84, 116-119] Use with NCS and NBS gives remarkably clean halofluorination.[120]



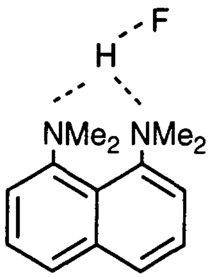
$Et_2NH{\cdot}3HF$ is also a good fluorinating agent and has been used with great success in the regio-selective ring opening of epoxides to give predominantly *trans* addition.[121]



The success of these reagents in performing regio-selective transformations means they are being used increasingly in bio-organic chemistry.[116, 117]

I.3.D.4.iii. Proton Sponge-HF

Work in these laboratories has revealed 1,8-bis(dimethylamino)napthalene, or Proton Sponge, to be a useful chelating agent for HF providing enhancement of reactivity by release of fluoride ion.[122, 123]



This system, and other aromatic amine-HF complexs, have been used in halogen exchange reactions.

$$CH_3(CH_2)_7I \xrightarrow[\text{24 hr, reflux}]{\text{proton sponge-HF}} CH_3(CH_2)_7F$$

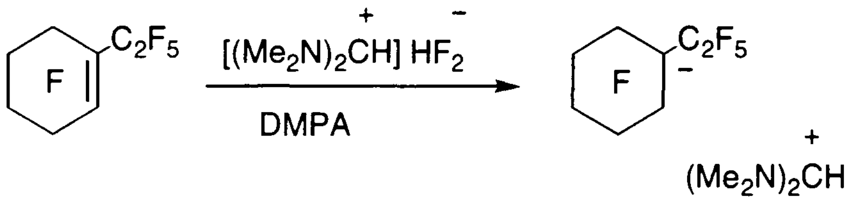
65% y.

I.3.D.5. α-Fluoroalkylamines

α-Fluoroalkylamines have been investigated by Knunyants and co-workers as potential sources of fluoride ion. The reactivity of the system depends on the equilibrium;

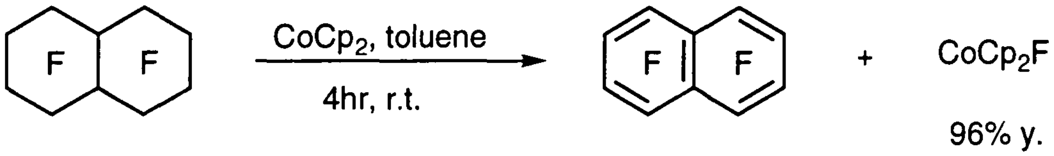
$$R_2N\text{-}CH_2F \rightleftharpoons R_2\overset{+}{N}{=}CH_2 \quad \overset{-}{F}$$

Bis(dimethylamino)fluoromethane is a particularly reactive system with the positive charge dispersed over the two nitrogen lone pairs. It has been used to produce stable perfluorocarbanions.

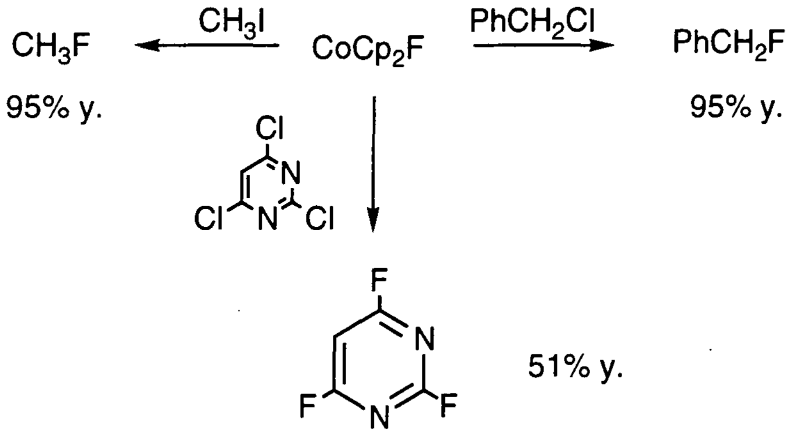


I.3.D.6. Cobaltocenium Fluoride

In the last few years Richmond and co-workers[124] have discovered cobaltocenium fluoride (Cp_2CoF) to be a highly effective source of fluoride. It is prepared by reaction of perfluorodecalin with cobaltocene to give octafluoronapthalene and the salt.

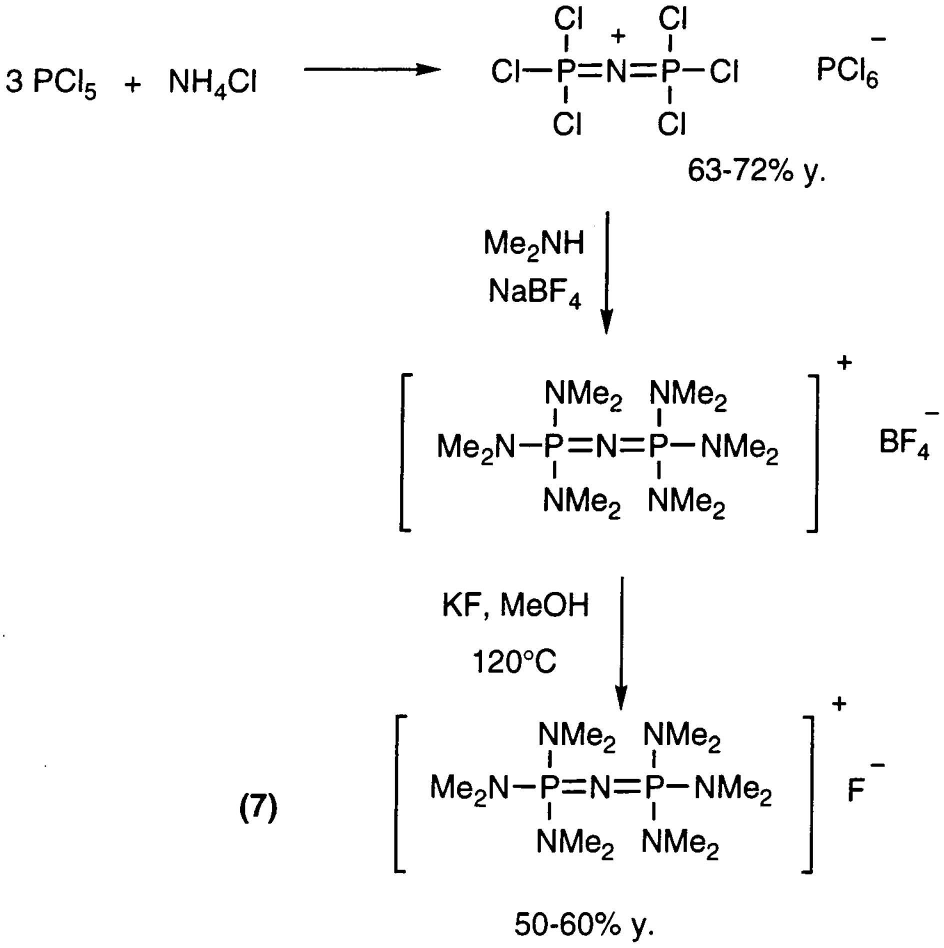


The product appears to be an exceedingly nucleophilic source of fluoride ion, although the esoteric nature of production and its hygroscopic nature mean that further work will have to be done if it is going to become commercially useful.



I.3.D.7. Phosphazenium Fluoride

Schwesinger[125] has reported synthesis of the potentially reactive phosphazenium fluoride shown below.



(7)

The salt (7) is soluble in THF and has the largest cation-anion distance observed in any solvent free fluoride, indicating it to be highly reactive.

(7)	6.30 Å
KF	2.67 Å
CsF	3.01 Å
TMAF	4.20 Å

Preliminary investigation of (7) reveal it to have surprisingly low nucleophilicity, but its ready dehydrohalogenation of alkyl halides suggests that its ability to act as a powerful base warrants further study.

$$n\text{-}C_{11}H_{23}I \xrightarrow[-70^{\circ}C]{THF} \underset{9}{C_{11}H_{22}} \; + \; \underset{1}{n\text{-}C_{11}H_{23}F} \qquad 9 : 1$$

I.4. Conclusions

Fluoride ion has a central role in fluoro-organic chemistry and, although sources of fluoride ion currently available are many and varied, fundamental problems of solubility, reactivity and purity still have to be addressed. Despite claims by many authors of 'naked' fluoride ion formation, the production of such a species still remains an important target.

CHAPTER TWO

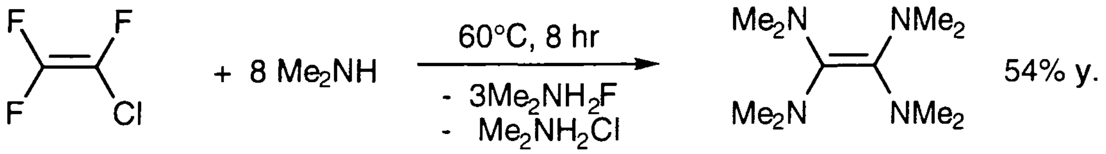
Amines as Initiators of Fluoride Ion Induced Reactions

II.1. Introduction

The types of reagent that are effective sources of fluoride ion which are currently available have been discussed in **Chapter One**. However, there remains a need for a source of fluoride ion that is soluble in organic media, since reagents such as the alkali metal fluorides are largely insoluble, limiting their use in organic synthesis. In this chapter a new fluoride ion source $TDAE^{2+}2F^-$ (**10**), produced by oxidation of tetrakis(dimethylamino)ethene (TDAE) (**8**), will be discussed. Investigation of this novel salt opened up the possibility of using TDAE, and other amines, as initiators of *in situ* fluoride ion formation.

II.1.A. TDAE (8) as an Electron Rich Base

Tetrakis(dimethylamino)ethene (TDAE) (**8**) is the first of the series of electron rich bases the tetra-aminoethenes.[126] It was first synthesised by Pruett in 1950.[127]

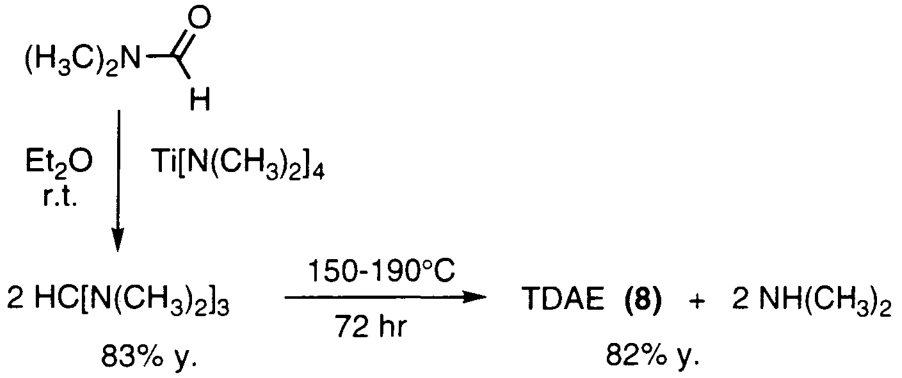


TDAE

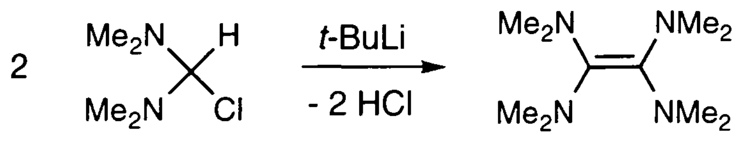
(8)

Pruett reported TDAE to be a clear slightly yellow, mobile liquid which was strongly luminescent in contact with air and reacted with oxygen to give a white solid.

A second synthesis was reported by Weingarten in 1966 which involved the pyrolysis of tris(dimethylamino)methane.[128, 129]



The titanium species used in the reaction is converted into an insoluble oxide. The only other reported synthesis of TDAE was also by Weingarten, who in 1971 reported it as a minor by-product in reaction between N,N,N',N'-tetramethylformamidium chloride and *t*-butyl lithium.[130]



(8)

When Pruett first synthesised TDAE he noted its extreme reactivity towards water, alcohols and bromine and iodine solutions, in each case giving a white powder, thought to be a salt produced by the oxidation of TDAE. The reduction potential of TDAE has been likened to that of the alkali metals (Ionisation Energies; Li 5.04 V, Na 5.14 V, TDAE 6.13 V).[131] Redox cells of TDAE and various metals have established that in such a system its reducing power lies between zinc and copper. More importantly, however, the behaviour of TDAE in these cells indicated that the oxidation of TDAE to its dication was reversible and that a true redox process was in operation. This led to TDAE being described as 'quasi-metallic' by Wiberg.[131, 132]

$$\mathrm{TDAE} \underset{\text{red.}}{\overset{\text{oxid.}}{\rightleftharpoons}} \mathrm{TDAE}^{2+} + 2e$$

$$\mathrm{M} \underset{\text{red.}}{\overset{\text{oxid.}}{\rightleftharpoons}} \mathrm{M}^{2+} + 2e$$

M = Mg, Cu, Zn, Sn, etc.

It is well known that many members of the tetra-aminoethenes can donate electrons and so reduce halogenated systems via single electron transfer processes.[133]

$$CCl_3\text{-}CCl_3 \quad + \quad \mathbf{(8)} \xrightarrow[125^\circ C]{\text{heptane}} CCl_2{=}CCl_2$$

64% y.

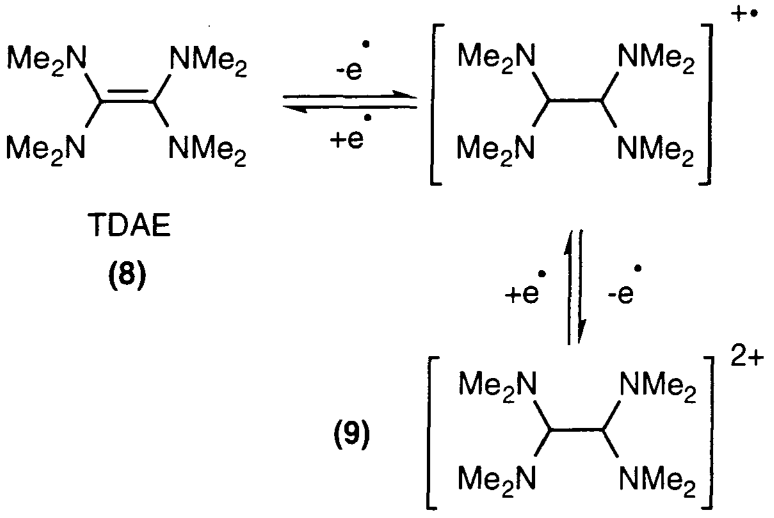
$$CHBr_2\text{-}CHBr_2 \quad + \quad \mathbf{(8)} \xrightarrow[175^\circ C]{\text{pentane}} CHBr{=}CBr_2 \quad + \quad CHBr{=}CBrH$$

70% y. 30% y.

$$CF_3CCl_2\text{-}CCl_2CF_3 \quad + \quad \mathbf{(8)} \xrightarrow[125^\circ C]{\text{heptane}} CF_3CCl{=}CClCF_3$$

97% y.

In all these reactions the by-product is the stable octamethyloxamidinium dication (**9**), which is formed by single electron oxidation of (**8**).



TDAE
(8)

(9)

The intermediate radical cation has been observed by ESR spectroscopy,[134, 135] the results of which suggest that the positive charge may be unevenly distributed over the two halves of the molecule. The high stability of the TDAE dication (**9**) can be explained upon considering its electronic structure. TDAE has ten π electrons arranged as shown in **Figure 1**. Two electrons occupy a high energy antibonding orbital b_{1u}, and can therefore be readily removed from the system. The dication so produced can, thus, be thought of as having a 'stable octet'[132] of π electrons.

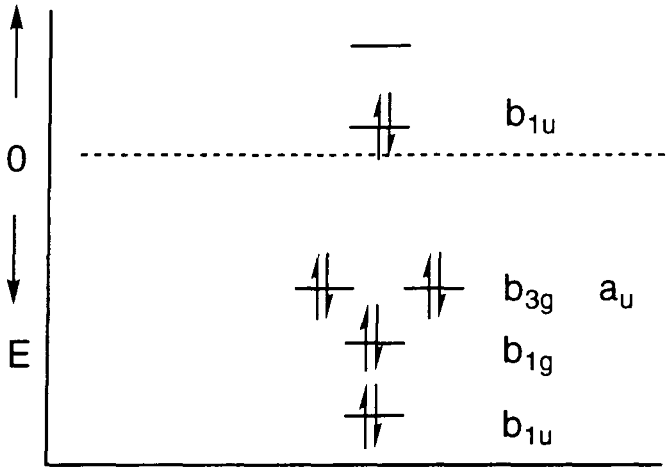


Figure 1. π energy level scheme of TDAE

Iodide and bromide salts of (**9**) can be produced by direct reaction between TDAE and iodine or bromine respectively.[131, 132]

$$\text{TDAE} + X_2 \longrightarrow \text{TDAE}^{2+}2X^- \qquad X = \text{Br, I}$$

The chloride salt of (**9**) has only previously been reported on reaction of (**8**) with organochlorines, notably tetrachloromethane, or by reduction of copper (I) chloride.[131, 132]

$$\text{TDAE} + 2\text{CuCl} \longrightarrow \text{TDAE}^{2+}2\text{Cl}^- + 2\text{ Cu}$$

$$\text{TDAE} + \text{CCl}_4 \longrightarrow \text{TDAE}^{2+}2\text{Cl}^- + \{2\text{ CCl}_3 \longrightarrow ?\}$$

TDAE can also be used as a novel trifluoromethylating agent.[56]

$$\underset{\textbf{(8)}}{\text{TDAE}} + \text{CF}_3\text{I} + \text{R-Cl} \longrightarrow \text{TDAE}^{2+}\ \text{Cl}^-\ \text{I}^- + \text{R-CF}_3$$

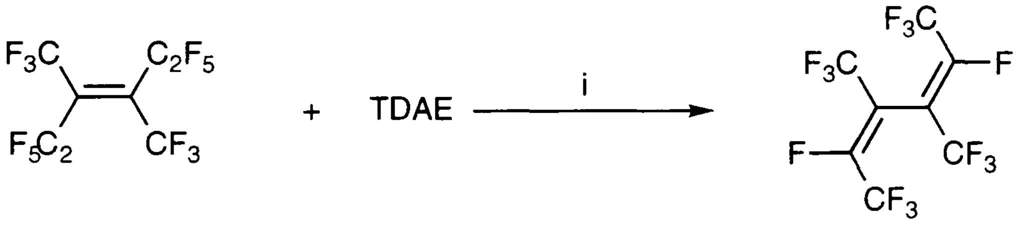
$$\text{R} = (\text{CH}_3)_3\text{Si}$$

II.1.B. Reduction of Organofluorine Compounds with TDAE (8)

TDAE can reduce perfluoroalkenes to their diene analogues by two electron reduction.[136-138] Reduction is accompanied by formation of the difluoride salt of (**9**), $\text{TDAE}^{2+}2\text{F}^-$ (**10**).

(11) **(8)** **(12)**

+ $\text{TDAE}^{2+}2\text{F}^-$ **(10)**

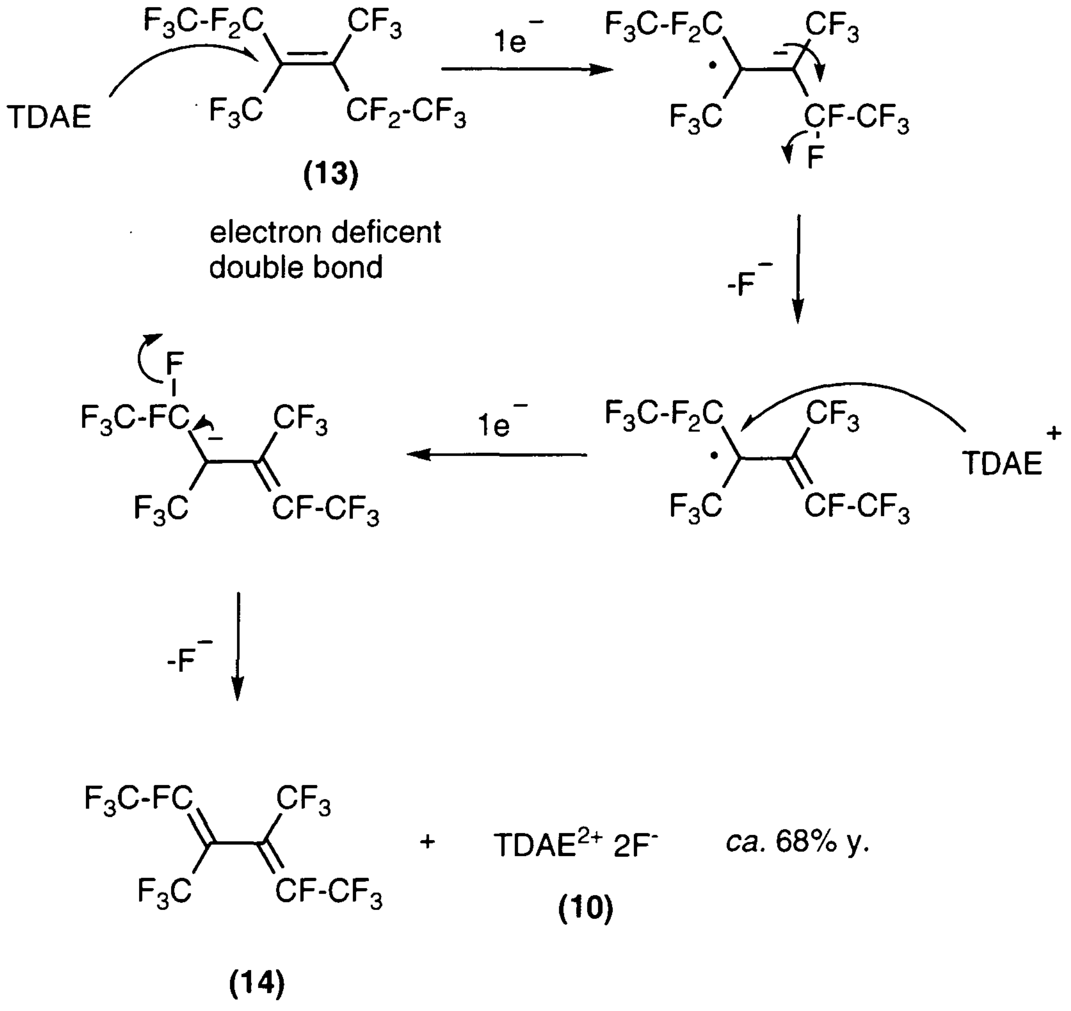


(13) **(8)** **(14)**

i. CH_2Cl_2, 0°C, 30 min

+ $\text{TDAE}^{2+}2\text{F}^-$ **(10)**

The reduction of perfluoro-3,4-dimethylhex-3-ene (**13**) occurs by the mechanism shown in **Scheme 1**.



ca. 88% y., with *Z,Z-* isomer predominant

Scheme 1

The *Z,Z-* isomer predominates in the product mixture, although a small amount of *Z,E-* isomer is also formed. Diene **(14)** has some novel chemistry associated with it and this will be discussed in **Chapter Three**.

The reduction of both **(11)** and **(13)** yields the difluoride salt TDAE^{2+}2F^{-} **(10)** as a by-product and in the reduction of **(13)** the salt can be isolated from the solvent as a white precipitate.

This difluoride salt has been investigated as a possible source of soluble fluoride ion, and the results are discussed here. Study of **(10)** led to considering the possibility of using TDAE as an agent for the formation of fluoride ion *in situ*.

II.2. TDAE^{2+}2F^{-} (10) as a Soluble Source of Fluoride Ion

As we have seen, reduction of the perfluoroalkenes **(11)** and **(13)** yields the difluoride salt **(10)**.[136-138] The dication is known to be susceptible to attack by water and bases,[131] but the chemistry of the difluoride **(10)** is not well known and it has only recently been prepared in these laboratories.

II.2.A. Physical Properties of TDAE^{2+}2F^{-} (10)

II.2.A.1. ^{19}F NMR Analysis

Accurate ^{19}F NMR study of fluoride ion salts is notoriously difficult and firm conclusions are hard to draw. The literature covering the NMR spectra of fluoride ion in solution is very confused. Early reports use different solvents and fluoride concentrations, often arbitrarily, which can drastically effect the fluorine shifts. Recent literature is more informative however, and a brief list of some fluoride ion chemical shifts is given in **Table 1**.[139]

Table 1. ^{19}F NMR chemical shifts of fluoride ion sources.

Species	F^{-}	HF	HF$_2^-$
KF$_{(aq)}$	-117.5 to -124.8		
KF$_{(EtOH)}$	-136.7		
KF$_{(dichloromethane)}$	-97		
Pr$_4$NF	-114.6		
HF$_{(aq)}$		-204.0	
HF$_{(anhyd.)}$		-196.0	
Bu$_4$NHF$_2$			-144.0
Pr$_4$NHF$_2$			-149.4
Me$_4$NF	-73.2		
CsF$_{(solid\ state)}$	-79		

From these results we can make the general observation that fluoride ion has a shift between δ_F -73ppm and δ_F -125ppm; HF between δ_F -190ppm and δ_F -200ppm and HF$_2^-$ between δ_F -144ppm and δ_F -149ppm.

The validity of these results as an accurate reflection of where anhydrous fluoride ion appears in the ^{19}F NMR spectrum is questionable, however, since many of the results were recorded in aqueous or aqueous organic solution and so the shifts are not really those of fluoride ion alone, due to hydrogen bonding (e.g.. δ_F -136.7ppm in ethanol and δ_F -97ppm in dichloromethane).[140]

Christie[98] synthesised anhydrous tetramethylammonium fluoride in 1990 (see **Section I.3.D.1.**) and reported a peak at δ_F -73.2ppm in the ^{19}F NMR spectrum and it was concluded that the large up field shift previously noted for other fluoride ion salts was probably due to the presence of HF or HF_2^-.

The lowfield shift of anhydrous Me_4NF is supported by solid state measurements on cesium fluoride by Clark,[141] who reports a shift of δ_F -79ppm for anhydrous samples.

We can, therefore, tentatively conclude that anhydrous fluoride ion has a peak in the range δ_F -73ppm to δ_F -79ppm and that as the shift moves to lower field so the degree of solvation of the fluoride ion decreases. This observation is at first surprising since one would assume that anhydrous fluoride would have more electrons shielding the nucleus than if it were solvated, and thus appear at higher field. It is possible, however, that in a tight anhydrous lattice the fluoride is in closer contact with cationic electron withdrawing species than if it were slightly solvated, resulting in a distinct lowfield shift.

Previous reports[137, 138] of $TDAE^{2+}2F^-$ have recorded a peak, assigned as fluoride ion, in the ^{19}F NMR spectrum anywhere between δ_F -110 and δ_F -130 depending on its moisture content. In order to try to record the ^{19}F NMR spectrum of anhydrous $TDAE^{2+}2F$ samples, freshly prepared under dry nitrogen, were placed in sealable NMR tubes and solvent added to each tube by vacuum transfer. The tubes were sealed and shaken at 40°C until a degree of solvation had occurred. Analysis revealed a peak in the ^{19}F NMR spectrum at δ_F -104.3ppm, a value which stayed remarkably constant in a wide variety of solvents (see later). On heating to 80°C the salt appears to decompose slightly to give a peak at δ_F -130ppm.

It can be tentatively concluded that **(10)** is a potentially reactive source of soluble fluoride ion.[139]

II.2.A.2. Solubility

$TDAE^{2+}2F^-$ is soluble in a range of solvents.

Soluble	Insoluble
Acetonitrile	Dichloromethane
Dimethylformamide	
Sulfolane	
Tetrahydrofuran	
Tetraglyme	
Dimethylsulphoxide	

II.2.B. Reactions of $TDAE^{2+}2F^-$ (10)

In order to ascertain whether **(10)** is a reactive source of fluoride ion in solution, a series of standard experiments were carried out. The salt was used to catalyse C-F bond forming reactions, involving nucleophilic displacement, and C-C bond forming reactions, via perfluorocarbanions. The reactions were repeated using cesium fluoride as the fluoride ion source for comparison.

II.2.B.1. $TDAE^{2+}2F^-$ (10) in C-F Bond Forming Reactions

II.2.B.1.i. Halogen Exchange Reactions

Simple halogen exchange reactions have in the past been used to quantify the reactivity of fluoride ion sources.[124, 142] The reactions detailed in **Table 2** were all performed in sulfolane and stirred for 48 hours at room temperature.

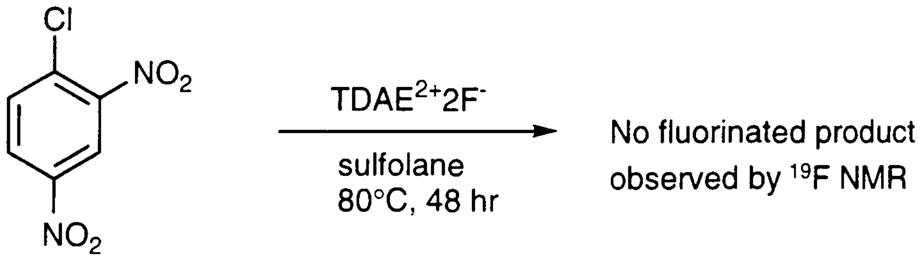
Table 2. Halogen exchange reactions using $TDAE^{2+}2F^-$ as a fluoride ion source

Substrate	Product	Yield (%)	Yield using CsF (%)
PhCOCl	PhCOF	100	90
$PhCH_2Br$	$PhCH_2F$	54	66
$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2F$	16	21
$CH_3(CH_2)_7I$	$CH_3(CH_2)_7F$	12	25
CH_3PhSO_2Cl	CH_3PhSO_2F	66	51
$CH_3(Ch_2)_6OSO_2PhCH_3$	$CH_3(CH_2)_6F$	47	53

All yields are calculated by ^{19}F NMR integration against fluorobenzene as an internal marker, characterisation was by comparison of ^{19}F NMR chemical shifts with literature values (see experimental section). From these preliminary results $TDAE^{2+}2F^-$ appears to be of similar potency as cesium fluoride as a fluoride ion source.

II.2.B.1.ii. Nucleophilic Substitution at Aromatic Carbon

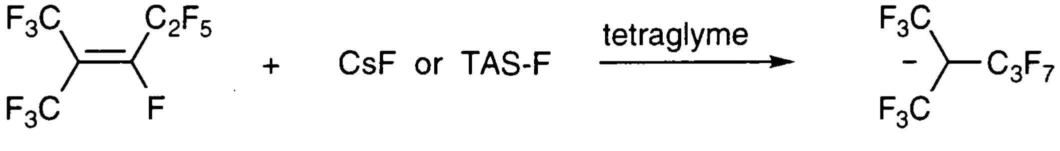
The success of **(10)** at performing halogen exchange reactions at both saturated and unsaturated sites suggested that it may be able to act in the same way in aromatic systems. Fluorination of 2,4-dinitrochlorobenzene involves attack at a highly activated aromatic site.



This result is surprising and possibly a result of interaction between **(10)** and the aromatic ring. $TDAE^{2+}2F^-$ also failed to fluorinate any of the ring positions of pentachloropyridine, tetrachloropyrimidine and trichloro-s-triazine.

II.2.B.1.iii. Anion Formation

Formation of stable fluorocarbanions from fluoro-alkenes is possible using cesium fluoride or TAS-F as the fluoride ion source.[36, 38]

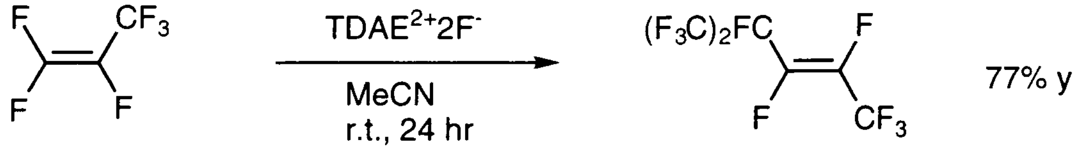


(6) **(15)**

Salt **(10)** has potential to act in the same way. However, despite the use of a variety of solvents (acetonitrile, DMSO, sulfolane, tetraglyme, DMF) anion **(15)** was not formed upon ^{19}F NMR analysis after stirring **(6)** with **(10)** first at room temperature and then at 60°C for 4 days.

II.2.B.2. $TDAE^{2+}2F^-$ (10) in C-C Bond Forming Reactions

It is well established that fluoride ion can catalyse the oligomerisation of perfluoro-alkenes.[44, 45, 143, 144] Alkali metals can be used as catalysts for these processes[145, 146] and **(10)** acts in an analogous way.



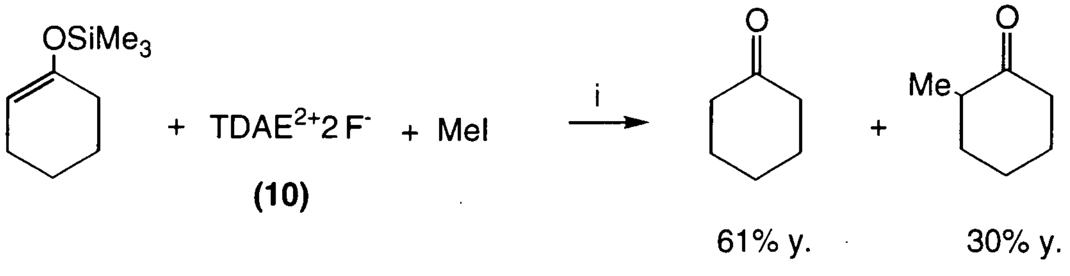
(1) **(5)**

kinetic isomer of **(6)**

The kinetic isomer **(5)** of hexafluoropropene dimer was formed. This is a consequence of the fact that the reaction was performed at room temperature and other authors have found that with alkali metal fluoride catalysis temperatures in excess of 100°C are required for effective conversion to the thermodynamic isomer **(6)**.[145-147] The fact that **(10)** can catalyse the dimerisation of **(1)**, via anionic intermediates, yet we do not observe the anion **(15)** from **(6)** is confusing. A possible reason for this apparent contradiction shall be discussed in **Section II.3.B.1.**

II.2.B.3. $TDAE^{2+}2F^-$ (10) as a Reagent for Desilylation

There is a continued interest by organic chemists in novel method of desilylation[148-151] and, indeed, we found that the salt **(10)** generates an enolate anion from silyl ether, even at 0°C, and trapping with iodomethane was carried out.



(10)

i. CH_3CN, 48 hr, 0°C

+ Me_3SiF

II.2.C. A Direct Route to $TDAE^{2+}2F^-$ (10) (With Dr. J. F. S. Vaughan)

Since the results detailed above were obtained a new direct method of $TDAE^{2+}2F^-$ production has been found. If 10% elemental fluorine gas in dry nitrogen is bubbled at a rate of 5ml min^{-1} of fluorine through a solution of TDAE in anhydrous acetonitrile, then a white precipitate, resembling that obtained in the reaction between perfluoroalkene **(13)** and TDAE, falls out of solution. The solid material was filtered and washed with dichloromethane to leave a powder, which upon ^{19}F NMR analysis revealed a single peak at δ_F -130ppm which was attributed to $TDAE^{2+}2F^-$ contaminated with a small amount of HF, probably produced by attack of F_2 on either TDAE or the solvent.

$$\underset{\textbf{(8)}}{TDAE} \quad + \quad F_2 \quad \xrightarrow{i} \quad \underset{\textbf{(10)}}{TDAE^{2+}2F^-} \quad 73\%\ y.$$

i. CH_3CN, r.t.

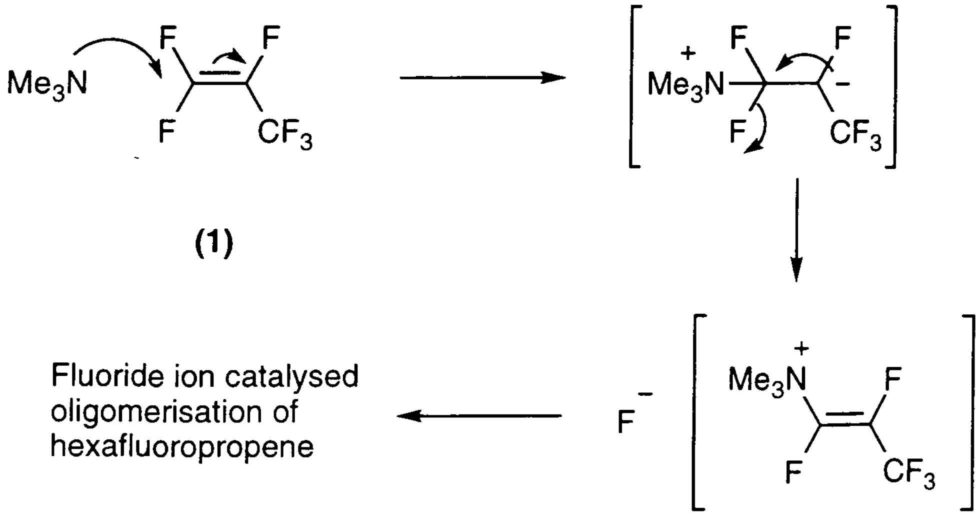
Whether this new source of $TDAE^{2+}2F^-$ is more reactive than that used in the reactions discussed above is not yet clear, although the possibility of using the salt without need for isolation is attractive. What is apparent, however, is that we now have a direct and simple route to a new soluble fluoride ion source and that which was previously a rather serendipitous compound may now become a viable fluorinating agent.

II.3. TDAE as an Agent for *In Situ* Fluoride Ion Generation

All of the fluoride ion sources discussed so far are used as preformed salts and many of the problems associated with these compounds could be avoided if they could be formed from a fluorinated precursor *in situ*.

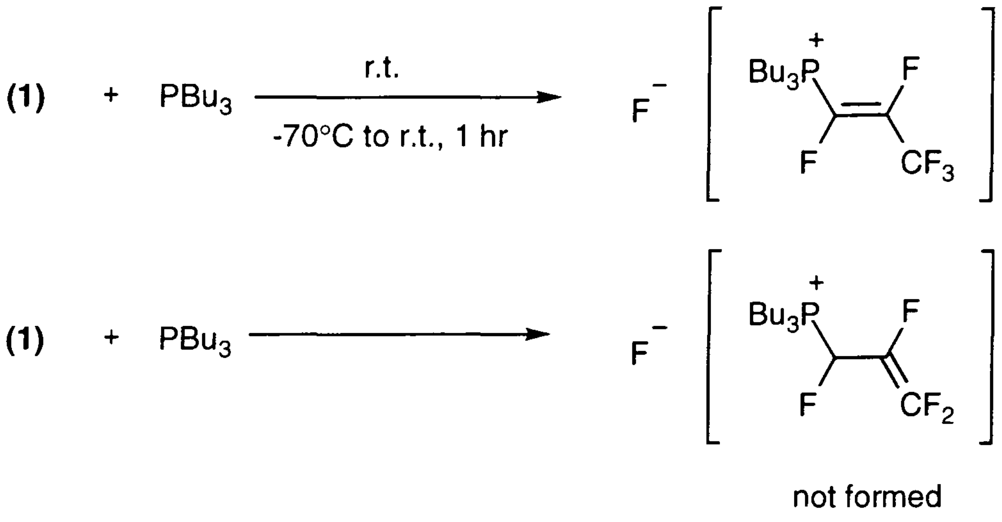
II.3.A. Fluoride Ion Generation by Reaction of Fluoro-alkenes with Tertiary Amines and Phosphines

Haszeldine and other workers[147, 152] have found that hexafluoropropene (**1**) can be oligomerised by adding a small amount of the base trimethylamine to the monomer in an aprotic solvent. The reaction is thought to proceed by the addition-displacement mechanism shown in **Scheme 2**.

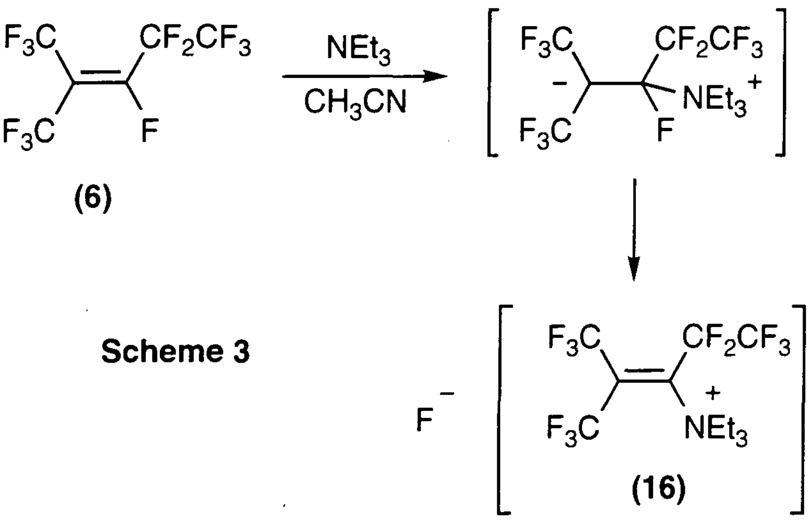


Scheme 2

A phosphonium analogue of the cation shown in **Scheme 2** was characterised by Burton[30] when (**1**) was reacted with tributylphosphine. There was no evidence of formation of the less stable isomeric product of S_N2' substitution.



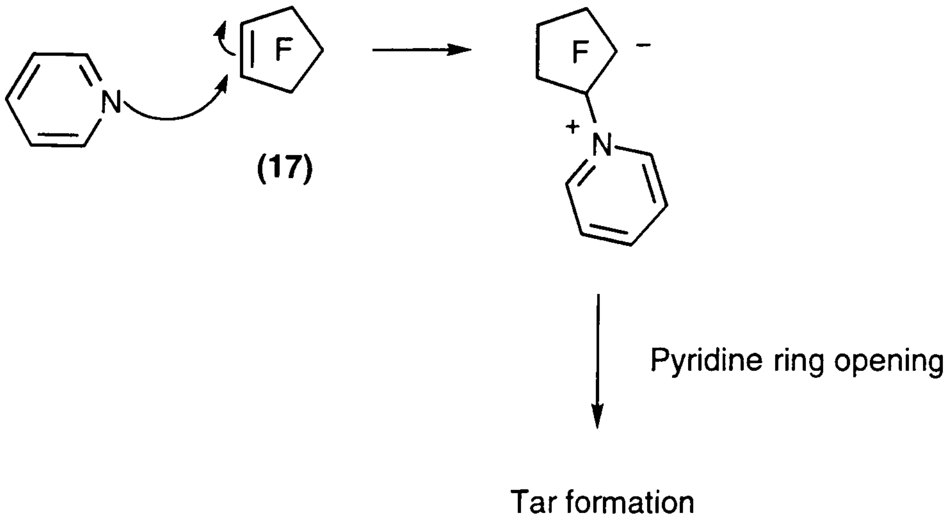
Ishikawa[153] has reported an analogous reaction between hexafluoropropene dimer **(6)** and triethylamine. In this case the intermediate fluoride ion salt **(16)** was observed by ^{19}F NMR.



Scheme 3

The formation of other stable fluorocarbon ylides is discussed more extensively in **Section I.2.A.3.i.**

In all of these cases the base can be thought of as a promoter of *in situ* fluoride ion formation. Other studies using pyridine as the catalyst in oligomerisation of hexafluorocyclobutene tend to confirm this.[28, 143] The use of pyridine as a catalyst in the dimerisation of octafluorocyclopentene **(17)** has also been investigated and provides an example of the limitations of such processes, the formation of stable ylides between the amine and the fluorocarbon, thus, stopping further reaction since no fluoride ion is produced.[34]



(17)

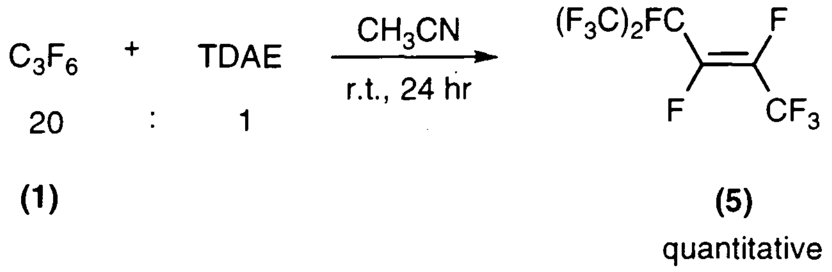
It is possible that other bases may not form stable ylides with perfluorocyclo-alkenes and so be of greater use.

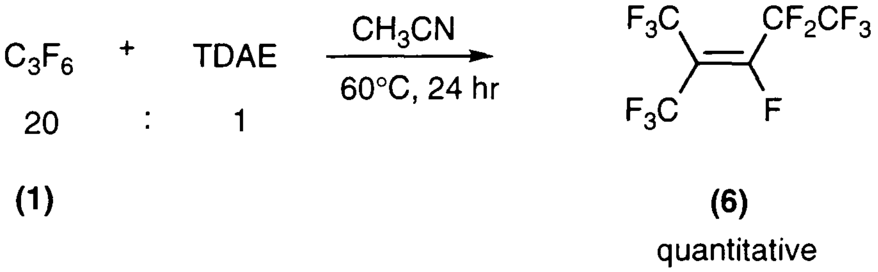
II.3.B. Reactions of TDAE with Perfluoro-alkenes

The indication that $TDAE^{2+}2F^{-}$ **(10)** may act as a useful source of soluble fluoride ion prompted investigation into TDAE itself as a potential initiator of *in situ* fluoride ion formation. It was hoped that a fluoride ion salt could be formed and used *in situ* without the need for isolation. In order to assess what types of reaction may be possible using such a system, a few simple oligomerisation reactions were performed.

II.3.B.1. Dimerisation of Hexafluoropropene (1)

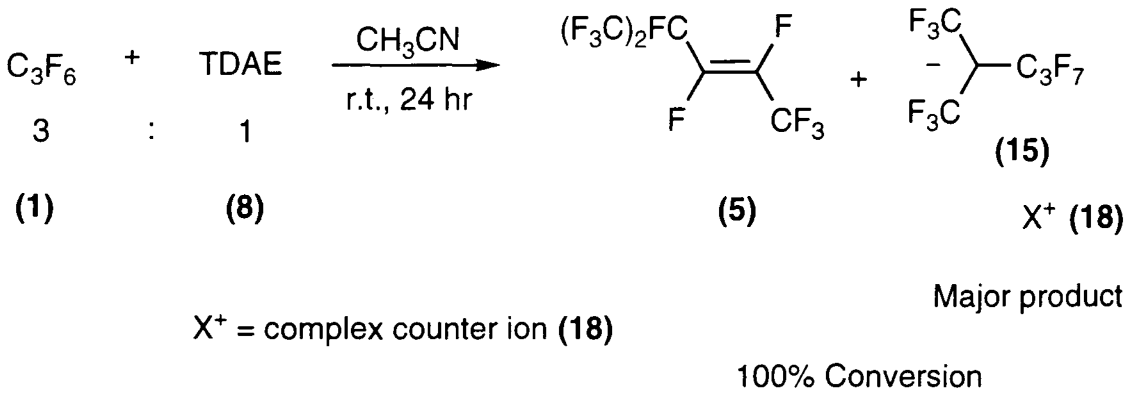
If TDAE is to be of use in preparing fluoride ion *in situ* it must be able to oligomerise **(1)**, via a similar mechanism to that used in other amine systems.[147] A catalytic amount of TDAE was added to a Carius tube containing **(1)** and acetonitrile, the tube sealed under vacuum and stirred for 48 hours at room temperature with formation of the kinetic dimer **(5)** in high yield as a lower clear layer. If the reaction is performed at 60°C the thermodynamic dimer **(6)** is formed exclusively.





The reaction can occur just as readily in the absence of solvent, allowing isolation of the pure product by flash distillation.

Use of a higher ratio of TDAE to alkene in the reaction mixture gives a high yield of anion (**15**) in the upper solvent layer of the reaction mixture. The yield of (**15**) is dependant on the amount of TDAE used.

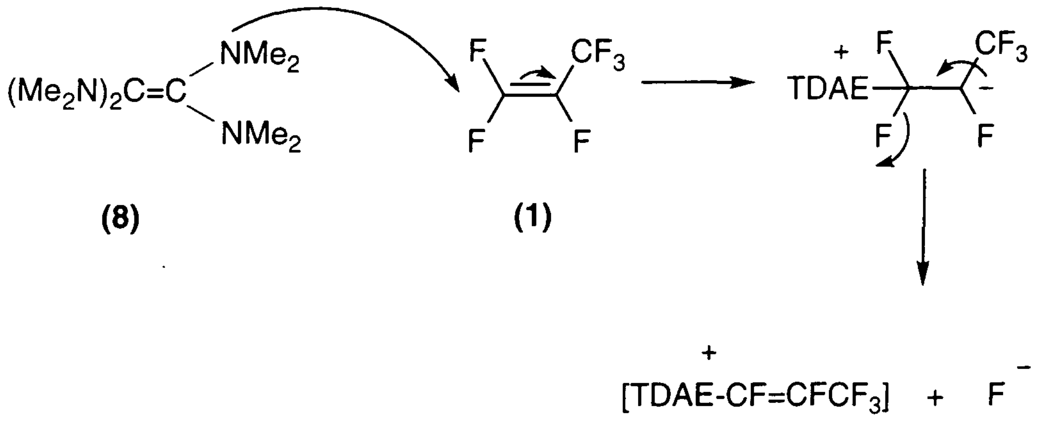


A separate experiment was carried out to assess the potency of cesium fluoride in producing anion (**15**) from dimer (**6**) and only an 11% yield was recorded after stirring for 4 days at room temperature. It can be concluded that TDAE has potential to act as a promoter of *in situ* formation of very active fluoride ion.

The nature of the counter cation (**18**) to the anion (**15**) is not clear, although from the ^{19}F NMR spectrum it appears to be a mixture of TDAE-fluorocarbon salts. It is also apparent that this new source of fluoride ion is *not* $TDAE^{2+}2F^-$ since its ability to yield anion (**15**) marks it out as a far more potent source of nucleophilic fluoride.

The ^{19}F NMR spectrum of (**15**) is remarkably similar to that of the corresponding caesium salt,[36] and demonstrates that fluorocarbon anion salts are most likely to be relatively 'free' carbanions, quite unlike many other such systems, whose structure in solution is often highly associated.

In these reactions TDAE may be acting as a simple ionic catalyst, in a similar way to trimethylamine, or as a single electron donor, and this adds further confusion as to the nature of (**18**).

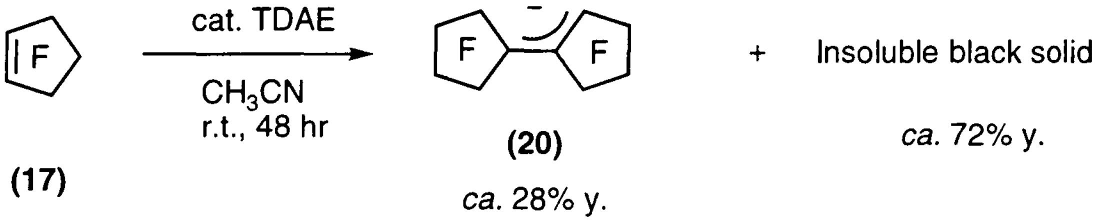


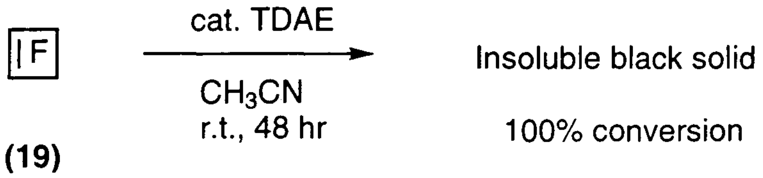
(18)

Interestingly, in view of the results discussed so far, a German patent in 1993[154] described work in which TDAE was reacted with potassium fluoride in dry acetonitrile, and the uncharacterised salt so produced used to dimerise hexafluoropropene. It was clearly assumed that, in the initial reaction between TDAE and KF, a salt of the type TDAE^{2+}2F^{-} had been produced and this was corroborated by the observation that it was soluble in acetonitrile. It now seems apparent, however, that dimerisation of (**1**) may have been catalysed by residual TDAE in solution, rather than by a fluoride ion salt.

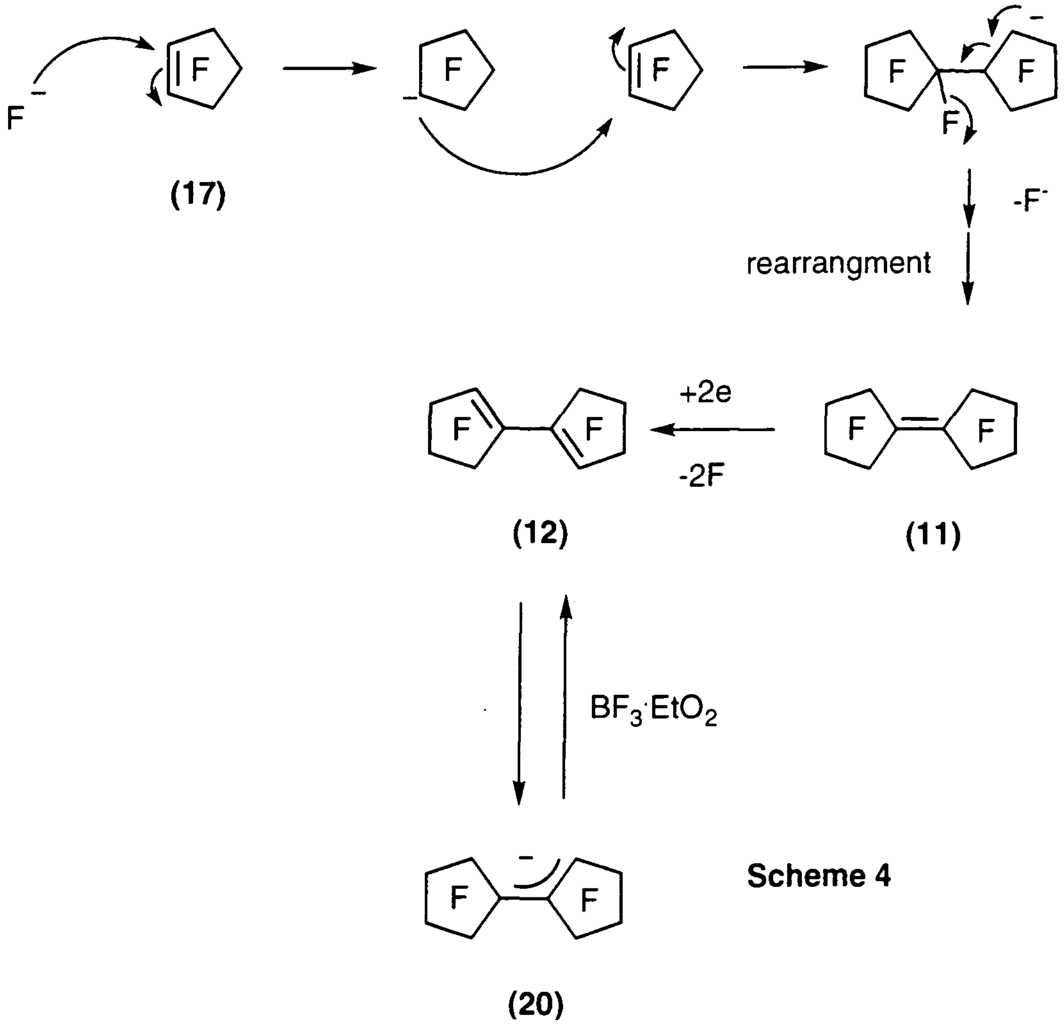
II.3.B.2. Reaction of TDAE with Perfluorocycloalkenes

TDAE reacts with the cyclic fluoroalkenes octafluorocyclopentene (**17**) and hexafluorocyclobutene (**19**).





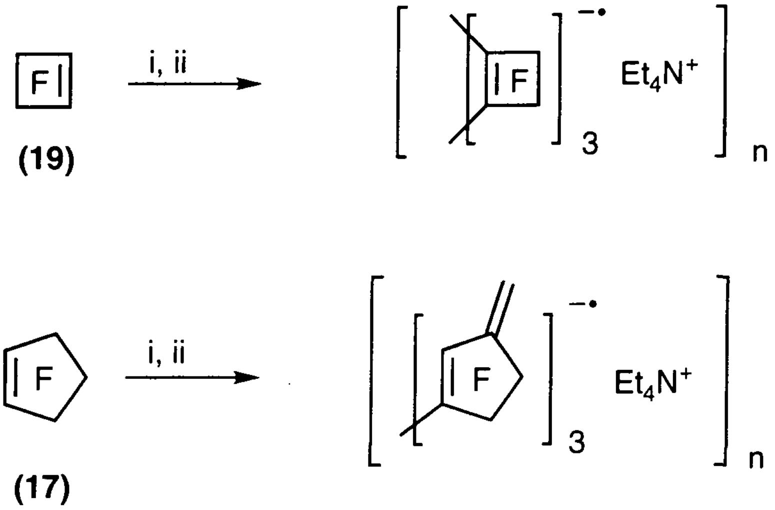
Anion (**20**) was characterised by reference to a previous synthesis of the cesium salt in these laboratories by Nakamura.[137] It is thought to be formed by the route shown in **Scheme 4**.



Scheme 4

Addition of BF_3 etherate to the anion (**20**) in solution gave the diene (**12**).

The black solid isolated in reaction of TDAE with both cyclic alkenes was difficult to identify. Its insolubility and likely ionic character made study by ^{19}F NMR and mass spectroscopy impossible, and elemental analysis proved an unreliable method of characterisation upon repetition. It was thought that the material could be an ionic long chain fluorocarbon, such as those isolated by the analagous electrochemical reduction[155] shown in **Scheme 5** and, given their insolubility this is perhaps more likely than that they are ylides analogous to those isolated by Burton.[30, 31, 156]



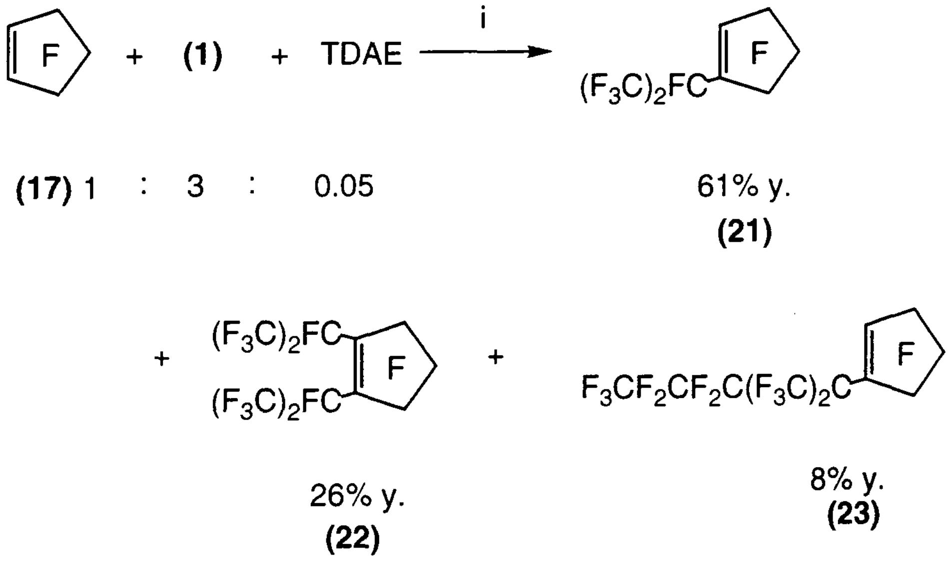
i. Pt or Hg cathode, divided cell, CH_3CN, Et_4NBF_4
ii. -1.9 V

Scheme 5

II.3.B.3. Co-dimerisation Reactions

The success of the TDAE/hexafluoropropene system at generating fluoride ion, and subsequently reactive fluorocarbanions *in situ*, prompted investigation into other common fluoride ion mediated processes.[34, 157]

TDAE can catalyse co-dimerisation of hexafluoropropene (**1**) and octafluorocyclopentene (**17**). Characterisation was by ^{19}F NMR and GLC-MS upon comparison with previous syntheses.[34]



i. no solvent, 48 hr, 60°C

Calculation of product yields was by ^{19}F NMR integration and compare favourable with those obtained under cesium fluoride catalysis.[34]

Co-dimerisation of hexafluorocyclobutene **(19)** with **(1)** yielded an insoluble black solid which could not be identified.

II.3.B.4. TDAE as a Catalyst for Perfluoroalkylation of Aromatics

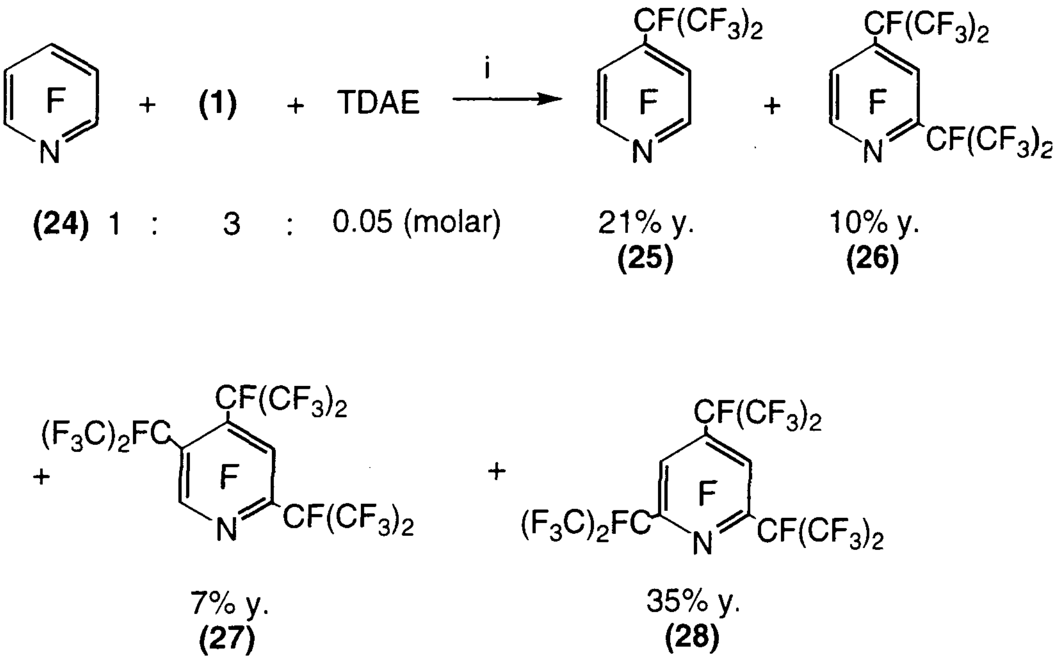
Perfluoroalkylation of the perfluoro-azoaromatics, pentafluoropyridine, tetrafluoropyrimidine and trifluoro-s-triazine has been extensively studied by various authors,[39, 42, 122, 144, 158-162] as discussed in **Section I.2.B.2.** Just as for their hydrocarbon analogues, these systems provide an excellent basis for mechanistic study of the alkylation process. In general, all the fluoro-azabenzenoids are activated towards nucleophilic attack relative to hexafluorobenzene, with trifluoro-s-triazine the most activated.[44] The alkylation of these species with perfluoroalkyl anions using TDAE as an initiator of fluoride ion formation is discussed below.

In all cases product characterisation was by comparison of ^{19}F NMR and mass spectroscopy data with those obtained from previous studies using cesium fluoride as the catalyst. Unusual and interesting features in the ^{19}F NMR spectra of the various compounds formed in these reactions are discussed at lenght in papers relating to the original synthetic route and will not be discussed here. A comprehensive list of references is given.

II.3.B.4.i. Pentafluoropyridine (24)

The simplest and most comprehensively studied perfluoroalkylating group is the perfluoroisopropyl anion produced by attack of fluoride ion on hexafluoropropene

(**1**).[43-45, 160, 161, 163] Pentafluoropyridine (**24**) was alkylated by stirring with (**1**) at 60°C in a sealed Carius tube using a catalytic amount of TDAE.

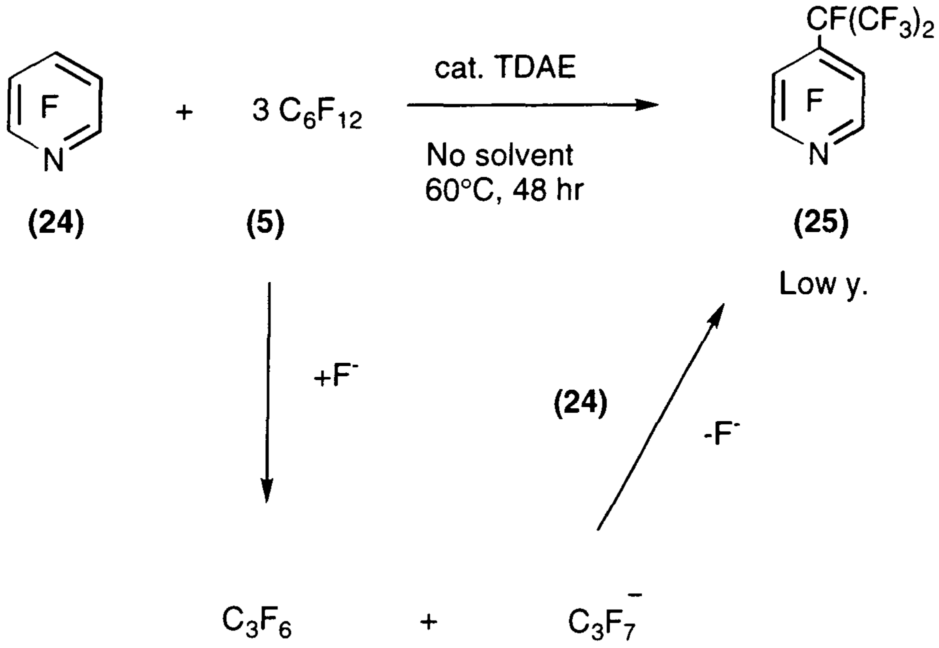


i. no solvent, 48 hr, 60°C

The excess hexafluoropropene, not used in the alkylation process, is dimerised to the thermodynamic isomer (**6**). The various perfluoroalkylated products were isolated by transfer to a cold trap under reduced pressure and so characterisation was possible without separation of the different adducts.

The 2,4,5-adduct (**27**) is the kinetically favoured trialkylated product,[160] due to the activation of the 5 position to attack by the two isopropyl groups, and predominates when cesium fluoride is used as the fluoride ion source. The formation of the less crowded thermodynamic 2,4,6-isomer (**28**) as the major isomer in this case when fluoride ion is produced *in situ* suggests the system to be remarkably potent.

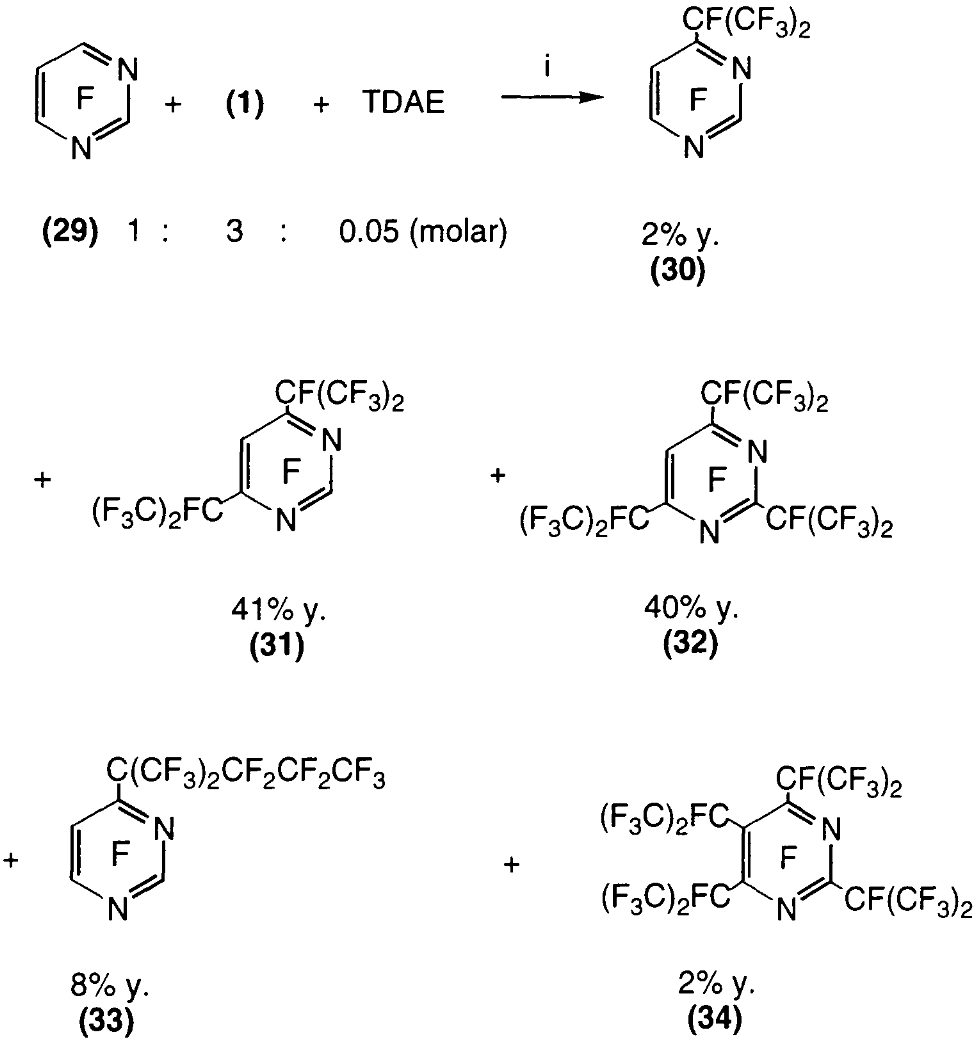
Reaction of (**24**) with the more bulky anion (**15**), derived from hexafluoropropene dimer (**5**), was also attempted.



The dimer (**5**) is cleaved by fluoride ion to give an isopropyl anion which goes on to form (**25**) by attack on the aromatic ring. This does, however, indicate that the anion (**15**) is produced *in situ* in such a system and it may be possible to add (**15**) to a more activated system.

II.3.B.4.ii. Tetrafluoropyrimidine (29)

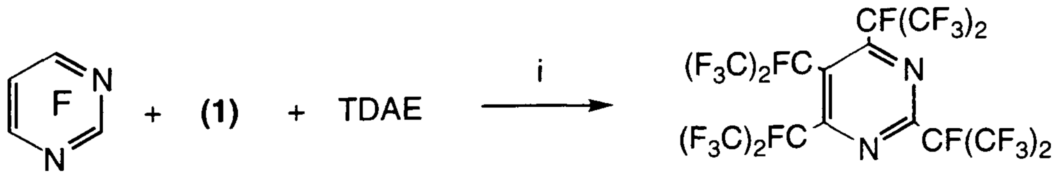
Tetrafluoropyrimidine (**29**) is considerably more activated towards nucleophilic attack than (**24**), due to the influence of a second nitrogen atom in the ring *meta* to the first.



i. no solvent, 48 hr, 60°C

Isolation and identification techniques were as for the perfluoroalkylation of (**24**). The addition pattern is similar to that found using cesium fluoride,[158] although yields are higher and conditions milder. The formation of (**34**) again indicates the potency of TDAE as an initiator of fluoride ion formation, since it is not observed using cesium fluoride as a catalyst at 80°C.

It is important to note in this study that the duration of the reaction, the molar equivalents of (**1**) to substrate and the temperature at which alkylation is carried out are all arbitrary and by way of illustration the tetra-adduct (**34**) produced in the reaction of (**29**) with (**1**) can be formed in quantitative yield when excess (**1**) is present. The reaction was performed by allowing slow diffusion of (**1**) into the reaction mixture from a gas bladder, thus making the competing hexafluoropropene dimerisation reaction less likely to occur (see experimental section).

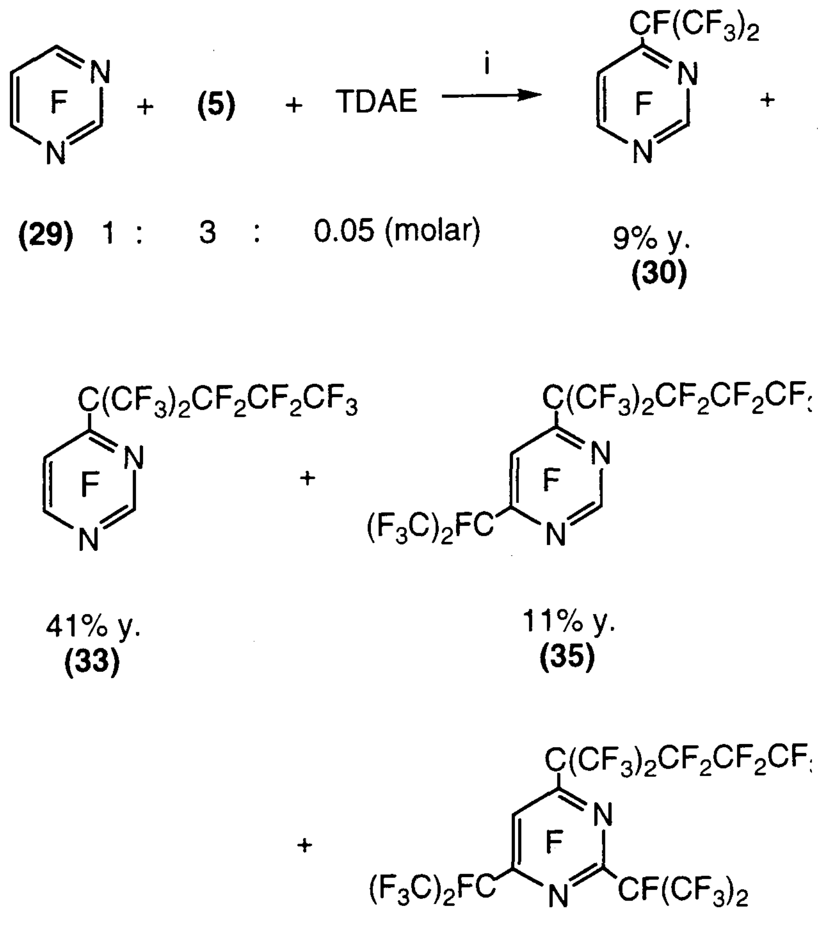


(29) 1 : excess : 0.1 (molar)

quantitative
(34)

i. CH_3CN, 48 hr, r.t.

Direct reaction between (**5**) and (**29**) is also possible.



(29) 1 : 3 : 0.05 (molar)

9% y.
(30)

41% y.
(33)

11% y.
(35)

i. no solvent, 48 hr, 60°C

19% y.
(36)

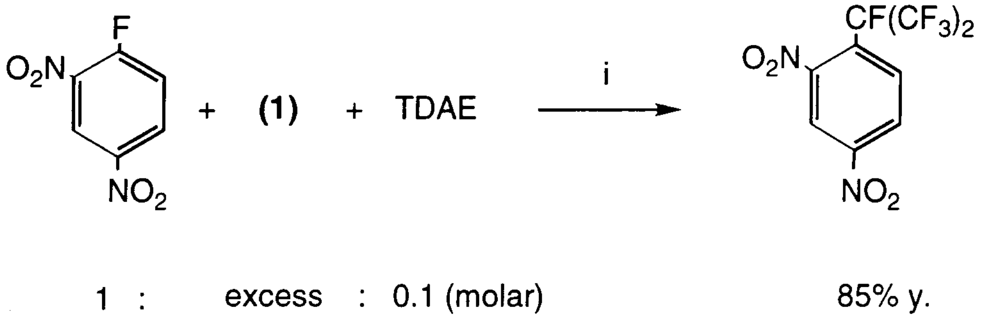
Compounds (**33**), (**35**) and (**36**) have not been reported using cesium fluoride as the fluoride ion source.[158] A small amount of (**33**) was isolated by preparative scale GLC and the compound fully characterised. NMR spectral assignment was made facile by comparison with related systems.

II.3.B.4.iii. Trifluoro-s-triazine (37)

The highly reactive triazine (**37**) reacts with TDAE directly to give amination of the ring. No alkylation products were observed by GLC-MS using either (**1**) or (**5**) as the alkene.

II.3.B.4.iv. 2,4-Dinitrofluorobenzene (38)

Metal fluorides have previously been used to perfluoroalkylate 2,4-dinitrofluorobenzene (**38**),[43] but the high temperatures required (120°C) led to competing, fluoride ion induced loss of the nitro groups to give fluorobenzene derivatives. Reaction of excess (**1**) with (**38**) at 60°C gave the mono-alkylated product (**39**) in high yield, with no evidence of denitration.



(38) **(39)**

i. CH_3CN, 3 days, 60°C

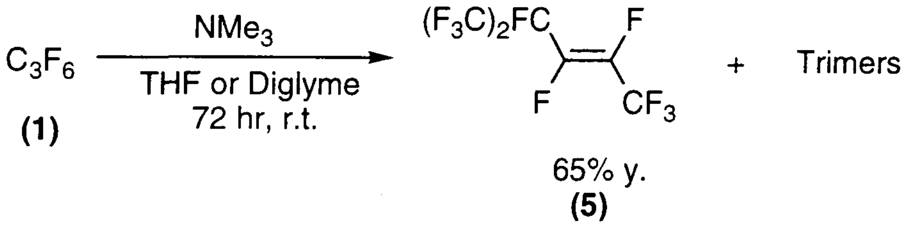
Hexafluoropropene failed to react with the less activated *p*-nitrofluorobenzene even at elevated temperatures.

II.4. Trimethylamine as a Reagent for *In Situ* Fluoride Ion Formation

II.4.A. Oligomerisations and Co-oligomerisations

II.4.A.1. Dimerisation of Hexafluoropropene (1)

The following reaction was performed by Haszeldine and co-workers[147] in polar aprotic solvents (see **Section II.3.A.**).



To assess the comparative reactivity of trimethylamine and tributylamine as catalysts for perfluorocarbanion formation a Carius tube was charged with hexafluoropropene and a catalytic amount of amine with acetonitrile as the solvent. The tube was sealed and stirred at room temperature for 48 hours. Using trimethylamine as the base dimer (**5**) was isolated in 60% yield, and in 50% yield using tributylamine as a clear lower layer.

Trimethylamine appears to be a slightly better initiator of fluoride ion formation than tributylamine, possibly due to steric effects and the potential for Hoffmann elimination in ammonium salts with β carbons.[97, 98]

The interaction of trimethylamine with perfluoroalkenes as a means of producing fluoride ion *in situ* was explored further.

II.4.A.2. Oligomerisation of Tetrafluoroethene (2)

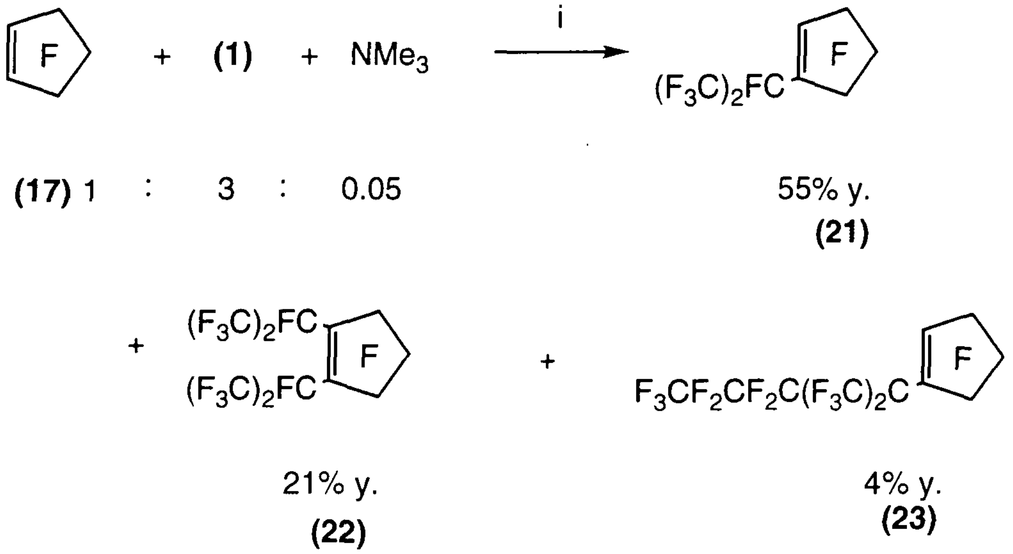
Tetrafluoroethene (**2**) is much more difficult to oligomerise than (**1**), due to the relative instability of the intermediate pentafluoroethyl anion. The structure of the oligomers have been well described in the literature[40, 41] but relatively high temperatures (100°C) are required for conversion. Alkene (**2**) could not be oligomerised without use of DMF as a solvent, however, with this solvent oligomerisation occurred, even at 60°C, under pressure to give the normal range of products with the pentamer predominating (see **Section I.2.B.1.**).

$$\underset{\textbf{(2)}}{CF_2{=}CF_2} \xrightarrow{\text{i}} (C_2F_4)_n\text{, where } n = 2,\ 6\%\text{ y.; } 3,\ 8\%\text{ y.; } 4,\ 11\%\text{ y.; } 5,\ 58\%\text{ y.; } 6,\ 12\%\text{ y.}$$

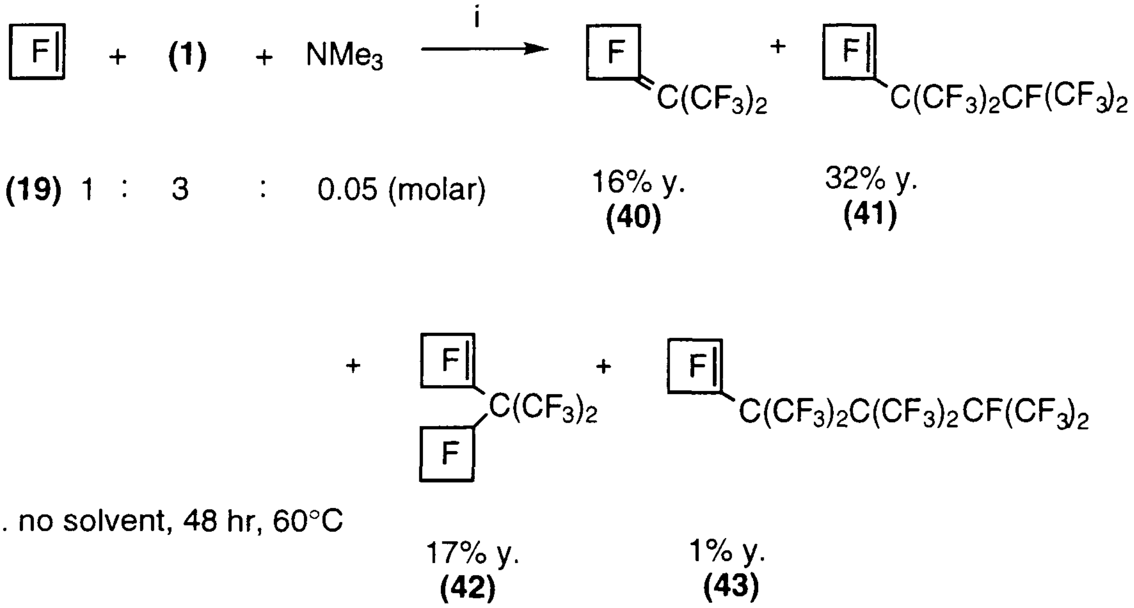
i. cat. NMe_3, DMF, 60°C.

II.4.A.3. Co-dimerisations of Hexafluoropropene (1)

Co-dimerisation of hexafluoropropene (**1**) with octafluorocyclopentene (**17**) and hexafluorocyclobutene (**19**) was achieved using trimethylamine as a catalyst.



i. no solvent, 48 hr, 60°C



i. no solvent, 48 hr, 60°C

The yields of reaction and ratios of products vary little regardless of whether a solvent is used or not, but yields are slightly lower than when TDAE is used as the base under the same conditions.

II.4.B. Perfluoroalkylation of Aromatics

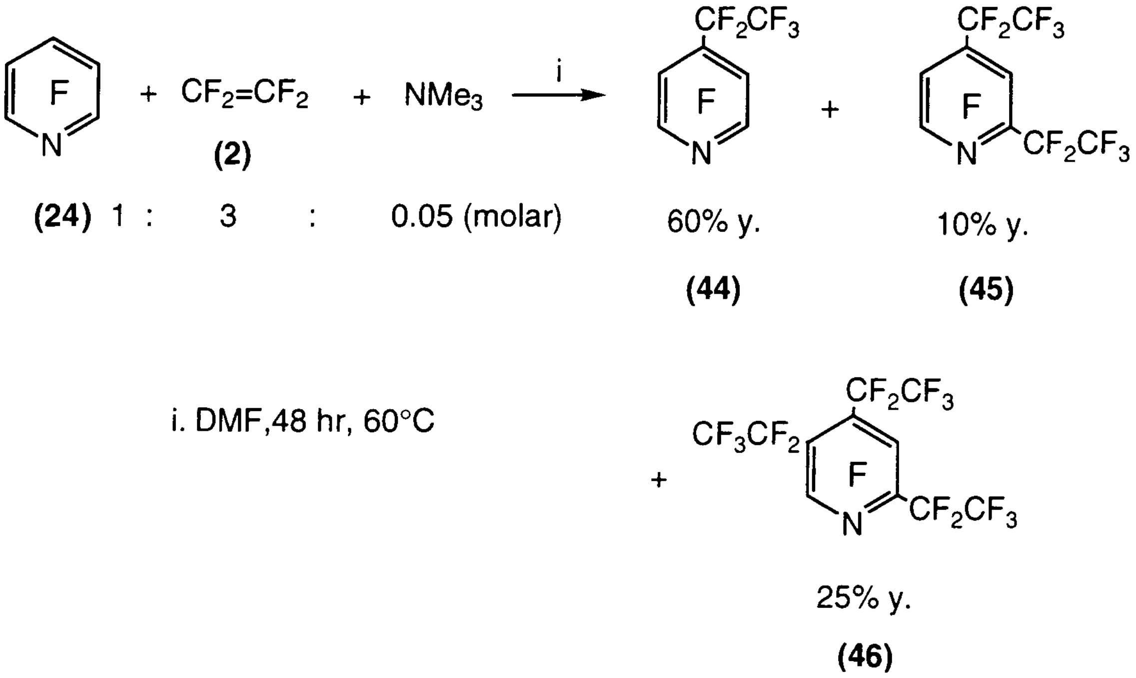
TDAE was able to catalyse the perfluoroalkylation of aromatics, and so similar reactions were carried out using trimethylamine. In all cases a 3:1 excess of perfluoroalkenes (**1**) or (**5**) to substrate was used and the system heated to 60°C for 48 hours.

II.4.B.1. Pentafluoropyridine (24)

Trimethylamine was able to initiate perfluoroalkylation of pentafluoropyridine (**24**).

Alkene	Yield (%)
(**1**)	(**25**) 20%
	(**26**) 8%

Using (**2**) with pentafluoropyridine it was found that, as with oligomerisation (see above), DMF was essential to the success of the process. Excellent yields were obtained even at 60°C. [164]



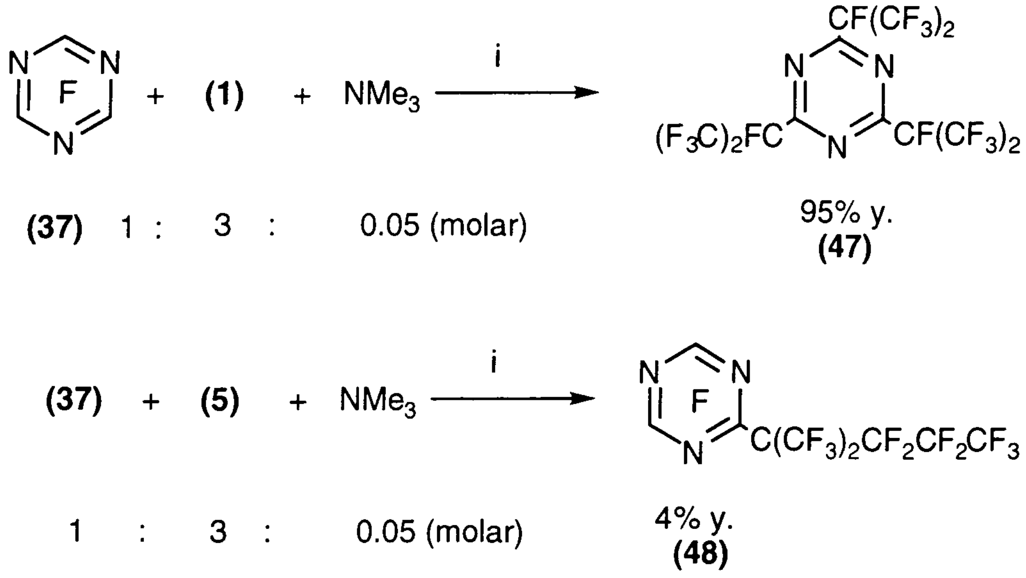
II.4.B.2. Tetrafluoropyrimidine (29)

Similarly, perfluoroalkylation of tetrafluoropyrimidine (**29**) was achieved.

Alkene	Yield (%)
(**1**)	(**31**) 42%
	(**32**) 44%
	(**34**) 2%
(**5**)	(**33**) 48%

II.4.B.3. Trifluoro-s-triazine (37)

TDAE was unable to perfluoroalkylate trifluoro-s-triazine (**37**), due to direct interaction with the aromatic ring. Trimethylamine does not react with the substrate, however, and can promote addition in high yield.

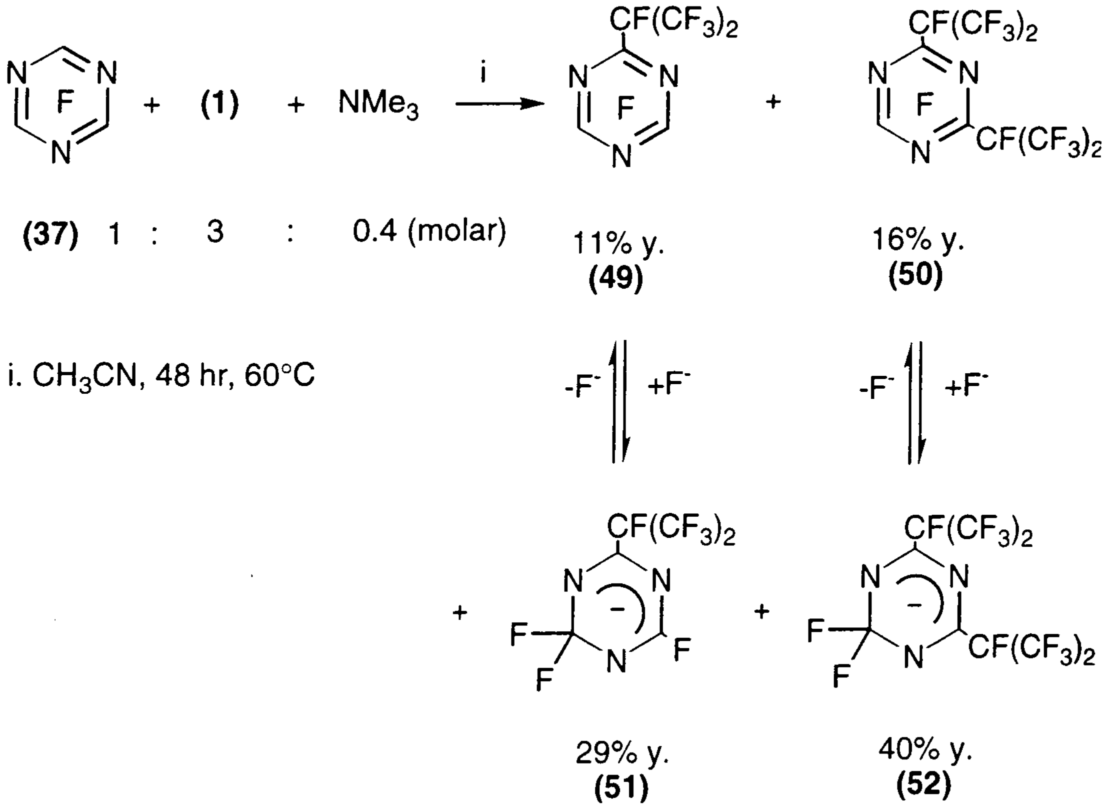


(37) **(47)** **(48)**

i. no solvent, 48 hr, 60°C

Formation of the tri-adduct (**47**) gives a ready illustration of an important practical significance of performing these reactions in the absence of solvent. Synthesis of (**47**) was previously notoriously difficult, since production of σ-complexes (**51**) and (**52**) acts as a competing process to trialkylation. In the absence of solvent such σ-complexes are much less likely to form, with nothing to solvate them, and so (**47**) is formed in high yield. The compound was isolated by distillation of the volatile unreacted starting materials to give (**47**) as a fluffy white powder. As a consequence full analysis, including ^{13}C NMR, was obtained for the first time.

When a solvent is used stable σ-complexes were observed by ^{19}F NMR. These anions have been previously observed when cesium fluoride is used as the catalyst.[39]



The ring fluorines undergo an equilibrium exchange process which is slow enough for the individual anions to be seen on the NMR timescale. Addition of a small amount of BF_3-etherate to the mixture converts the σ-complexes to their mono- and di-adduct analogues to give an overall product yield.

$$\textbf{(49), (50), (51), (52)} \xrightarrow{BF_3\text{-}EtO_2} \textbf{(51)}\ 38\%\ \text{y.};\ \textbf{(52)}\ 45\%\ \text{y.}$$

II.5. Amines as Catalysts in C-F Bond Forming Reactions

So far we have seen that TDAE and tertiary amines can initiate fluoride ion formation by nucleophilic attack on fluoro-alkenes and so catalyse processes such as oligomerisation and perfluoroalkylation.

If this methodology can be used to promote C-F bond forming reactions, by nucleophilic displacement of halogens, then it will be a useful general method of fluorination.

II.5.A. Halogen Displacement

II.5.A.1. TDAE (8) with Hexafluoropropene (1)

To an evacuated round bottomed flask containing benzoyl chloride and TDAE in acetonitrile, was attached an expandable gas bladder, fitted with a tap and charged with hexafluoropropene (**1**). The bladder was opened to the flask, allowing slow diffusion of (**1**), and the mixture stirred for 48 hours at 80°C.

A lower layer of dimer (**6**) was pipetted off and the upper organic layer shown to contain, by ^{19}F NMR, benzoyl fluoride in 49% yield. The ^{19}F NMR spectrum also revealed a number of other peaks between δ_F -40ppm and δ_F -150ppm, which may be part of the fluoride ion salt.

The reaction was repeated with benzyl bromide as the substrate. The results are given in **Table 3**.

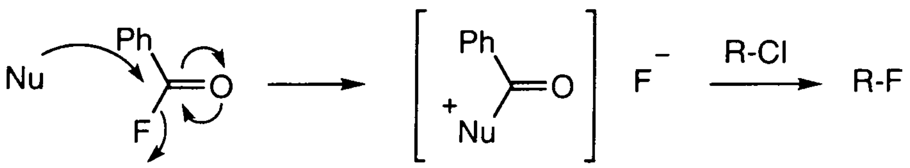
Table 3. Halogen exchange reactions using TDAE/hexafluoropropene as a fluoride ion source.

Substrate	Product	Yield (%)	Yield using $TDAE^{2+}2F^-$ as the fluoride ion source (%)	Yield using cesium fluoride as the fluoride ion source (%)
PhCOCl	PhCOF	49	100	90
$PhCH_2Br$	$PhCH_2F$	36	54	66

Despite the low yields halogen exchange is possible with such a system. Hexafluoropropene is, however, too expensive to be of any practical use as a fluoride ion donor. With this in mind cheaper potential donors were investigated.

II.5.A.2. TDAE with Benzoyl Fluoride

Benzoyl fluoride is a potential source of fluoride ion upon nucleophilic attack, since the fluorine atom in acid fluorides is known to be a good leaving group.[157, 165-168]



An equivalence of benzyl bromide was added to a stirred solution of benzoyl fluoride and TDAE in acetonitrile. The reaction procedure was as in **Section II.5.A.1.**

The reaction was repeated with allyl bromide and octyl iodide as the substrate. The results are given in **Table 4.**

Table 4. Halogen exchange reactions using TDAE/benzoyl fluoride as a fluoride ion source.

Substrate	Product	Yield (%)
$PhCH_2Br$	$PhCH_2F$	30
$CH_2=CHCH_2Br$	$CH_2=CHCH_2F$	16
$C_8H_{17}I$	$C_8H_{17}F$	17

The product yields did not increase upon stirring over a longer period and in the case of benzyl bromide maximum yield was obtained after 5 hours.

One possible reason for these surprisingly low yields could be that the fluoride ion, which is evidently being produced in this system re-attacks the carbonyl group to form stable ylides.

II.5.A.3. Trimethylamine and Pyridine with Benzoyl Fluoride

Use of either pyridine or trimethylamine as a promoter of fluoride ion formation from benzoyl fluoride failed to yield any fluorinated products. This is possibly due to formation of either stable ylides or aminoalkenones, similar to those observed by Platoshkin upon reaction of acid fluorides with triethylamine.[168]

$$CF_3COF + NEt_3 \longrightarrow CF_3COCH=CHNEt_2 + CF_3CHO + Et_3NHF$$

II.6. Conclusions

The difluoride salt of the tetrakis(dimethylamino)ethene dication $TDAE^{2+}2F^-$ **(10)** is a nucleophilic source of fluoride ion and can effect C-C and C-F bond forming reactions in yields comparable with those obtained using cesium fluoride as the fluorinating agent.

TDAE (**8**) can act as a promoter of fluoride ion formation *in situ*. The system has the advantage of being homogeneous, easy to handle and work up and is high yielding at moderate temperature. Such reactions can occur *without the need for a solvent* and this is a major advantage over previous methods, in which reactions were often performed in highly ionic media, such as sulfolane or glyme. Without a solvent flash distillation is an effective and simple method of isolation, making further study of these novel systems possible.

Trimethylamine can also act as an initiator of *in situ* fluoride ion formation and appears to be an excellent promoter of perfluoroalkylation and oligomerisation. Although it is a slightly less prolific reagent than TDAE, it is of great used for systems where TDAE will react with the substrate.

Attempts to use this new amine/fluoro-organic system as general source of fluoride ion were successful. Yields are, however, low and appear to be affected by formation of stable ylides and salts.

CHAPTER THREE

Synthesis and Reactions of Perfluoro-2,3-dimethylhexa-2,4-diene

III. Introduction

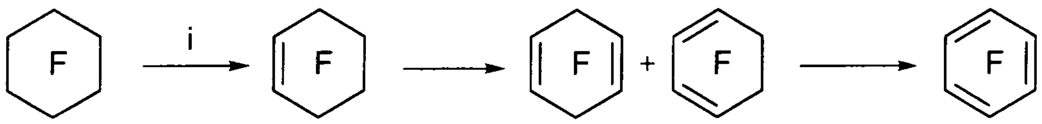
Perfluorinated diene systems have been much studied and provide important examples of the mirror image chemistry which exists when one compares the chemistry of unsaturated hydrocarbon and fluorocarbon systems. The delocalisation of two double bonds in a conjugated system gives far greater synthetic utility than a simple alkene. Some chemistry of the novel diene perfluoro-2,3-dimethylhexa-2,4-diene (**14**) will be discussed in this chapter and so a review of some of the more common methods of synthesis of fluorinated dienes is presented here.

III.1. Diene Synthesis by Reductive Defluorination

There are several methods concerned with the reductive defluorination of fluorocarbons described in the literature. Most involve single electron transfer.

III.1.A. Hot Metals

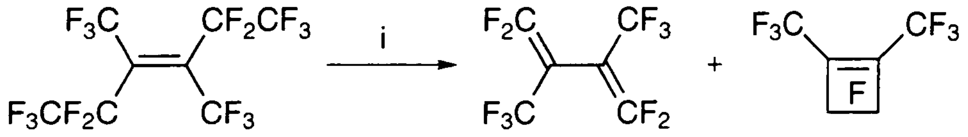
The defluorination of perfluorocyclohexanes, over iron at 300-600°C, to give the corresponding aromatic and diene products has been described by Tatlow.[169-172]



i. Fe, 500°C, N_2 flow

major product

Related work in these laboratories[173] has detailed the defluorination of perfluoroalkenes, over platinum or iron, at elevated temperatures, to give fluorinated dienes and cyclobutenes.



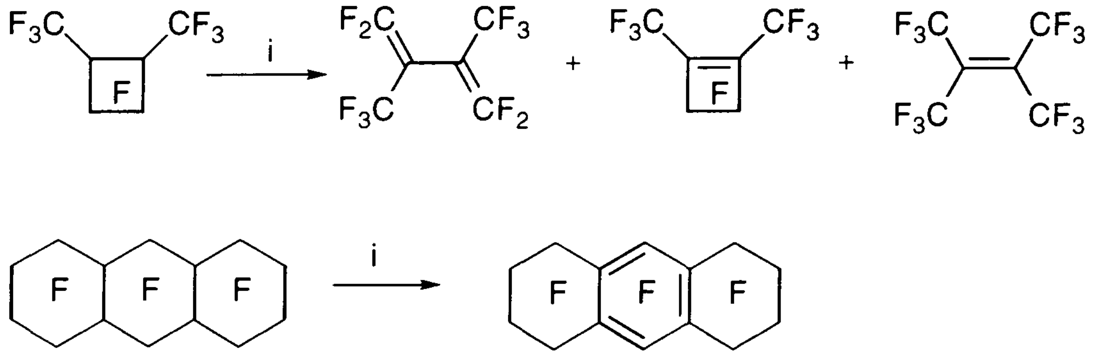
i. Pt, 670°C

59% y.

14% y.

III.1.B. Activated Carbon

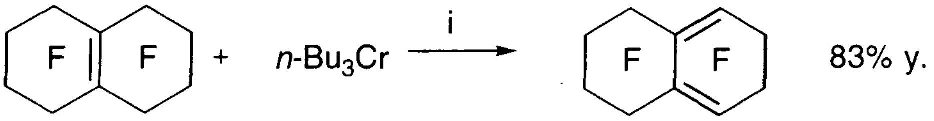
Weigert[174, 175] has shown that perfluorocarbons can be defluorinated over activated (i.e. high surface area) carbon at temperatures below those required for the hot metal defluorinations detailed above.



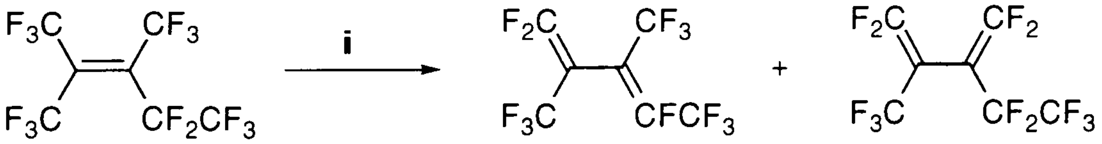
i. autoclave, 400°C, activated carbon, 4 hr

III.1.C. Organometallics

Various organometallic reagents have been used to activate C-F bonds towards reduction. Huang[176] has demonstrated that 'Cr-H' species, derived from *n*-Bu_3Cr or *i*-Bu_3Cr, can give dienes from alkenes, and Watson[177] has used lanthanoid species for the reduction of simple acyclic perfluoroalkenes.



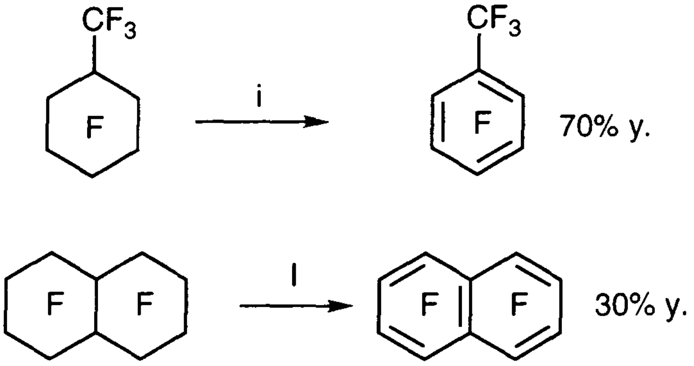
i. THF, -78°C-20°C, 12 hr



ii. $YbMCp_2$, THF, r.t.

III.1.D. Other Methods of Reductive Defluorination

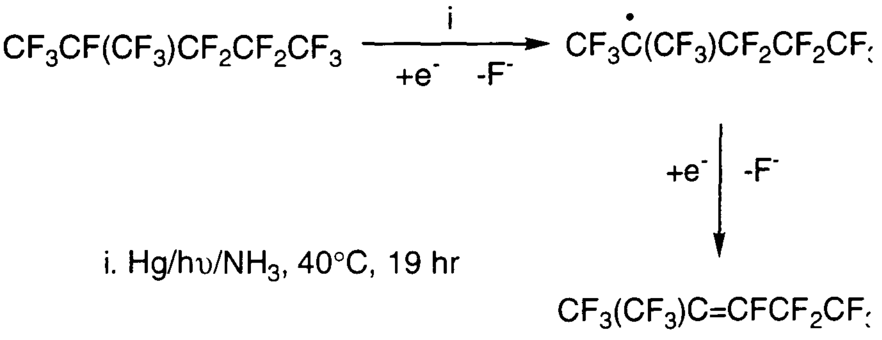
Recent research into the field of reductive defluorination by Crabtree and co-workers[178] has led to the discovery that powdered sodium oxalate ($Na_2C_2O_4$) can effect the defluorination of cyclic perfluoroalkanes to yield perfluoroarenes at 230°C.



i. $Na_2C_2O_4$, 230°C

The exact reaction mechanism is not clear, but it has been suggested that sodium oxalate acts as a two electron reducing agent whilst Na^+ is a fluoride ion acceptor.

Crabtree[179] has also reported the formation of perfluoro-2-methylpent-2-ene by reduction of its saturated precursor, upon ultraviolet irradiation, in the presence of mercury and under a flow of gaseous ammonia.



$$\begin{tikzcd} CF_3CF(CF_3)CF_2CF_2CF_3 \arrow[r, "i", "+e^- \quad -F^-"'] & CF_3\dot{C}(CF_3)CF_2CF_2CF \arrow[d, "+e^-"', "-F^-"] \\ & CF_3(CF_3)C{=}CFCF_2CF \end{tikzcd}$$

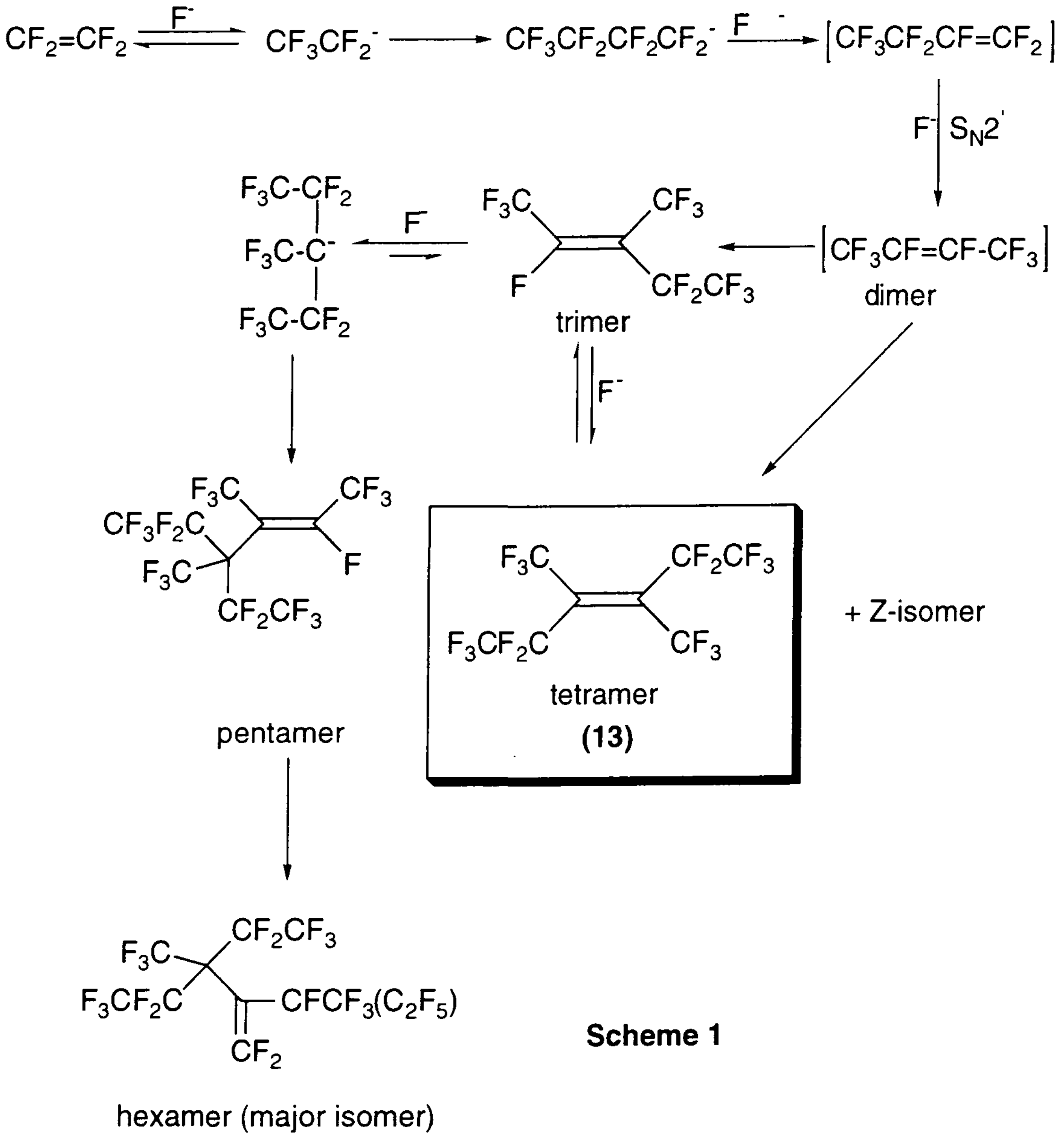
i. $Hg/h\nu/NH_3$, 40°C, 19 hr

Again, the exact reaction mechanism is not clear, but the single electron transfer mechanism shown above has been postulated.

Whether these two new methods can be used to produce fluorinated dienes from saturated precursors warrants investigation.

III.2. Synthesis of Perfluoro-3,4-dimethylhex-3-ene (13)

The title diene (**14**) can be formed by reductive defluorination of (**13**), the tetrameric product of fluoride ion induced oligomerisation of tetrafluoroethene (**2**),[40] as shown in **Scheme 1**. Such oligomerisations are more fully described in **Chapter One**.



Scheme 1

III.3. Defluorination of Perfluoro-3,4-dimethylhexa-3-ene (13)

Diene (**14**) is formed by reductive defluorination of (**13**). There are three common methods of effecting this:-

i. electrochemical reduction;

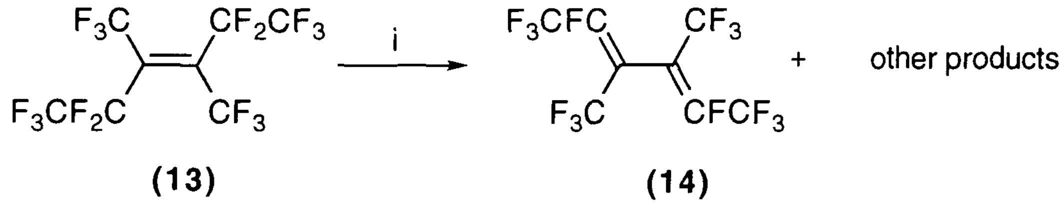
ii. sodium or potassium amalgam reduction; and

iii. tetrakis(dimethylamino)ethene induced reduction.

In each case the defluorination process occurs via single electron transfer, the mechanism of which is discussed in **Chapter Two**. Route **iii.** is currently the method of choice.

III.3.A. Electrochemical Reduction

When tetramer (**13**) is added to the cathodic electrode compartment of an electrochemical cell, and a potential of -1.70V applied to the system for five and a half hours, diene (**14**) is produced in a yield of 15 %.[136, 180]



i. divided cell, CH_3CN, tetraethylammonium tetrafluoroborate

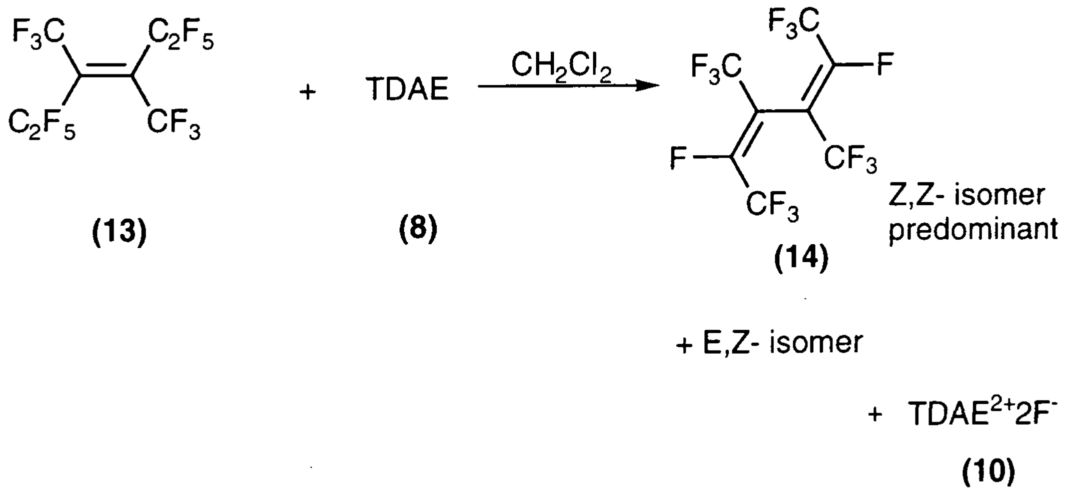
A degree of starting material decomposition appears to occur in the reaction, and this may limit the yield.

III.3.B. Sodium and Potassium Amalgams

Freshly prepared sodium/mercury and potassium/mercury amalgams can reduce (**13**) after shaking vigorously under dry nitrogen to give 85% and 39% yields of (**14**) respectively. The low yield for the K/Hg system is thought to be due to the difficulty of dissolving potassium in mercury.[136]

III.3.C. Tetrakis(dimethylamino)ethene (TDAE) Reduction

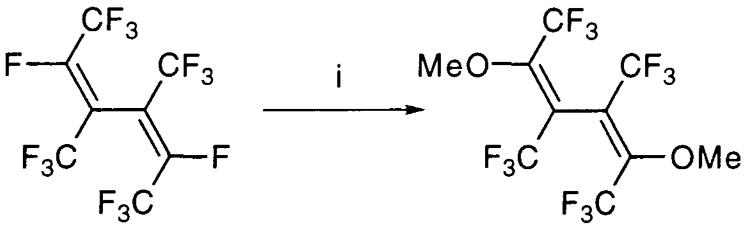
This reaction is discussed briefly in **Chapter Two** and is the simplest and most effective way of synthesising (**14**). Reduction of (**13**) by stirring with TDAE (**8**) for 30 minutes, at 0°C, in dichloromethane gives (**14**) in *ca.* 88% yield as a lower layer.[136, 138, 181]


(13)
+ TDAE
(8)
CH2Cl2
(14)
Z,Z- isomer predominant
+ E,Z- isomer
+ TDAE2+2F-
(10)

III.4. Reaction of (14) with Oxygen Nucleophiles

Reactions which replace the vinylic fluorine atoms in diene **(14)** with oxygen atoms by nucleophilic displacement have been studied extensively by various workers.[61, 137, 180, 182-184]

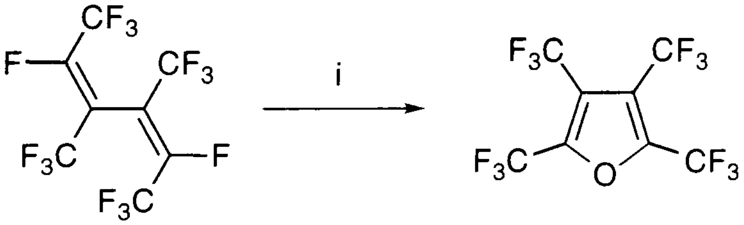
Reactions with alcohols and phenols[181, 183] give mono- and di-substituted products in high yield. They are generally base catalysed at room temperature.



(14) quantitative y.

i. Na_2CO_3, MeOH, r.t.

Diene **(14)** is an excellent synthon for the formation of heterocycles, and hydrolysis occurs readily to give the furan derivative **(53)**.[181, 183]



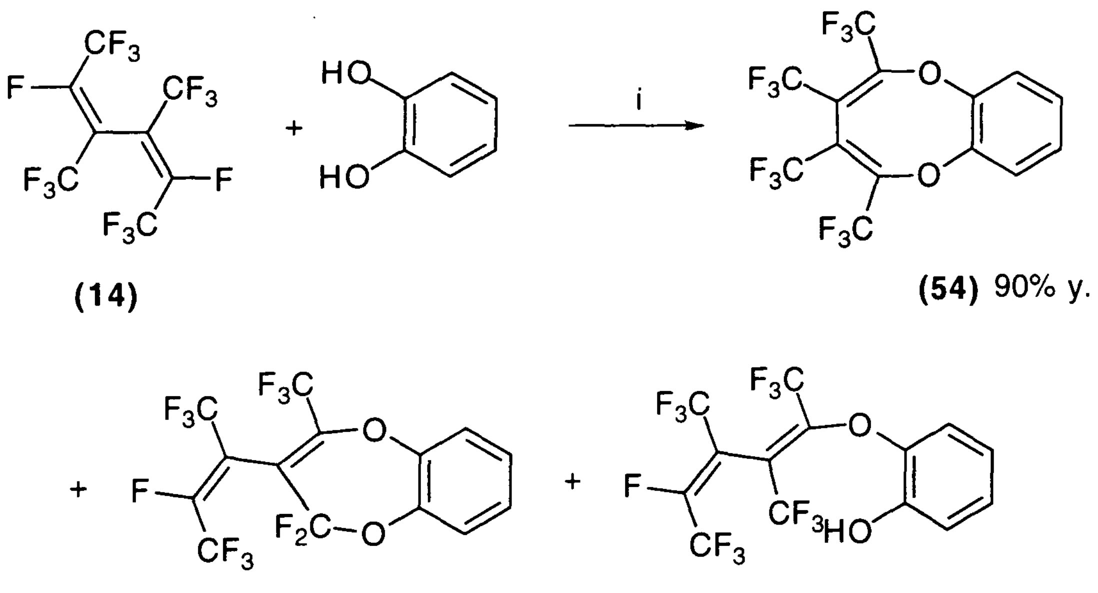
(14) **(53)**

i. H_2O, K_2CO_3, CH_3CN, r.t. quantitative y.

III.4.A. Formation of Tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin (54)

The majority of work presented in this chapter will be concerned with the formation and reactions of the novel bicyclic **(54)** and the chemistry of related systems.

A round bottomed flask was charged with diene **(14)**, catechol and cesium fluoride in acetonitrile and stirred for seven days at room temperature. Filtration, followed by addition of a small amount of water to the product solution gave the novel benzodioxocin **(54)** as a lower layer. Side products **(55)** and **(56)** were also observed, although never isolated.



(14) (54) 90% y.

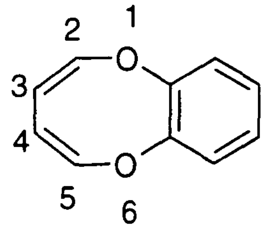
(55) (56)

i. CsF, CH_3CN, 7 days, r.t.

Compound **(54)** showed distinguishing peaks in the ^{19}F NMR spectrum at δ_F -56.4ppm and δ_F -65.0ppm corresponding to the two distinct CF_3 environments in the molecule. Mass spectroscopy revealed the molecular ion [M^+ 432] as well as a major peak at 69 (CF_3). ^{13}C and ^1H NMR, together with micro-analysis, also confirmed the structure.

III.4.A.1. Aromaticity of (54)

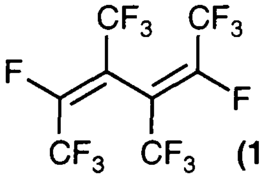
Although the benzodioxocin ring system **(54)** has 14π electrons, and as such conforms to the Hückel rules, both experimental and theoretical calculations on a hydrocarbon analogue **(57)**[185-187] of **(54)** tend to suggest that the system is not aromatic. The ^1H NMR signals of the dioxocin ring protons in **(57)** lie in the olefinic region; δ_H 5.35ppm (dd, *J* 2Hz, 5Hz) and δ_H 6.95ppm (dd, *J* 2Hz, 5Hz). This is in contrast to the benzene ring protons which occur in the distinctive aromatic region at δ_H 7.60ppm.



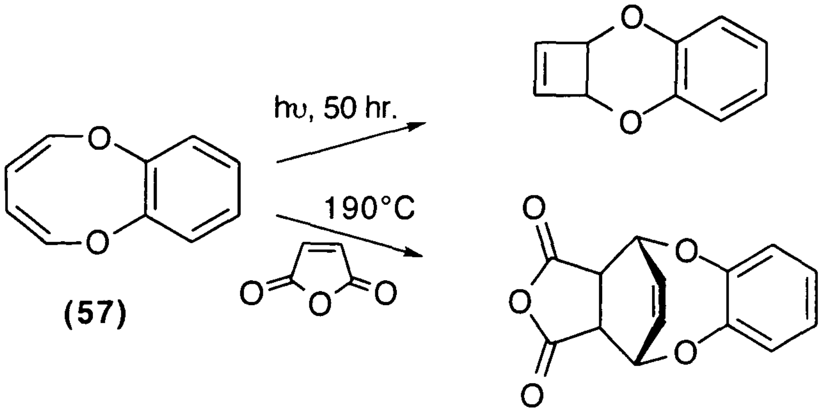
(57)

The ultraviolet spectra of both **(54)** (λ_{max} 229nm and 272nm in dichloromethane) and **(57)** (λ_{max} 277nm and 272nm in cyclohexane) are also revealing, see **Table 1**. The with aromatic systems, relative to simple conjugated dienes (235nm-253nm) or substituted aromatics (184nm-278nm).[188] Hückel type theoretical studies of **(57)**[185] indicate it to be a non-aromatic non-planar system, since the two oxygen atoms make planarity almost impossible. Also, by considering the electronegativity of the oxygen atoms, it is possible to draw analogy with the strong diene character of furan.

Table 1. Ultraviolet data for some conjugated dienes and aromatics.

Compound	$\Pi \rightarrow \Pi^*$ Transition	
	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
(54)	229	25 425
	273	12 075
(57)	272	2 951
	277	3 090
$CH_2{=}CH{-}CH{=}CH_2$	217	21 000[189]
	256	8 000[189]
$CF_2{=}CF{-}CF{=}CF_2$	206	2 800[190]
 **(14)**	234	272[191]
Benzene	184	60 000[188]
Phenol	210	6 200
	270	1 450[188]
Catechol	214	6 000
	278	2 630[188]

Compound **(57)** will undergoes pericyclic reactions commonly associated with conjugated dienes.[192] It is capable of a [4+2] Diels-Alder reaction with maleic anhydride and can also electrocyclise under ultraviolet irradiation.



(57)

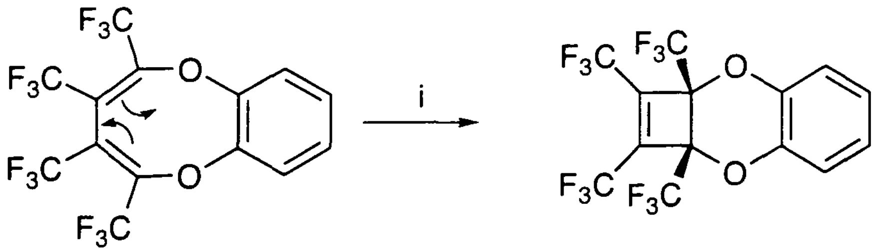
III.4.B. Reactions of Tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin (54)

A number of reactions were performed with **(54)**, firstly to investigate its chemical reactivity and secondly with a view to producing simple solid derivatives suitable for x-ray analysis in order to obtain structural information on such an interesting ring system.

III.4.B.1. Pericyclic Reactions of (54)

Compound **(57)** undergoes photochemical electrocyclisation[192] and so, given that $-CF_3$ groups tend to stabilise strained rings,[44] an attempt was made to cyclise **(54)**.

A quartz Carius tube was charged with a solution of **(54)** in acetonitrile and irradiated with broad band ultraviolet light for 24 hours. Compound **(58)** was formed in quantitative yield via an electrocyclisation process and isolated as a semi-solid gel by removal of solvent.



(54) **(58)**

i. hν, CH_3CN, 24 hr quantitative

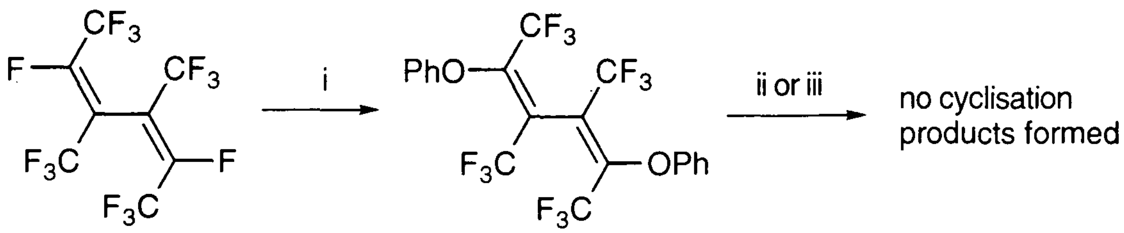
Compound **(58)**, like its precursor, has two distinct peaks in its ^{19}F NMR spectrum. The chemical shift of the trifluoromethyl groups on positions 3 and 4, δ_F -63.9ppm, remains almost unchanged from those of the corresponding positions on **(54)**, this is not surprising since they are in a similar vinylic environment. The shift of the trifluoromethyl groups on positions 2 and 5 is, however, dramatically shifted upfield by almost 20ppm, relative to **(54)**, to δ_F -73.4ppm, indicative of a CF_3 moiety attached to a secondary or tertiary saturated site.

The stereochemistry shown for **(58)**, with the two tertiary trifluoromethyl groups *cis* to one another, would result from a disrotatory ring closure as predicted by the Woodward-Hoffmann rules. It is supported by the simplicity of the ^{19}F NMR spectrum which shows only two CF_3 resonances, indicating the molecule to be completely symmetrical.

Compound **(54)** decomposes at 180°C before it will undergo thermal electrocyclisation. This is not unexpected given that **(57)** also decomposes under similar conditions.

III.4.B.2. Attempted Electrocyclisation of Tetrakis(trifluoromethyl)-2,5-dipenoxyhexa-2,4-diene (59)

The diphenoxy analogue of diene **(14)** was formed in high yield by reaction of **(14)** with phenol. The *Z,Z*-isomer **(59)** was the major stereo-isomer and is the thermodynamically favoured product, if one considers the preference for the stereochemically demanding phenoxy groups to be as far apart as possible. It was discernible from the other isomers present by its distinctive ^{19}F NMR fluorine-fluorine couplings, as described by Mullins.[184]



(14) **(59)**

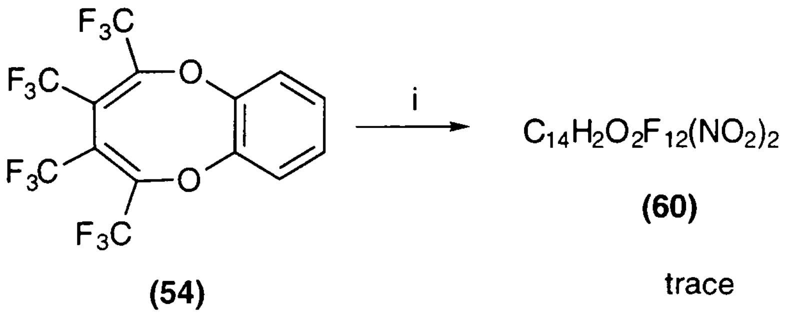
i. CsF, PhOH, 48 hr, r.t.

ii. $h\nu$, CH_3CN, 24 hr
iii. 80°C, CH_3CN, 48 hr

Electrocyclisation of **(59)** was attempted in order to try to build up a pattern of reactivity in such systems. Despite both heating in acetonitrile under reflux and irradiation under broad band ultraviolet light **(59)** would not cyclise and only starting material was observed by ^{19}F NMR spectroscopy. Bearing in mind that **(14)** readily undergoes both photochemical and thermal electrocyclisation at 50°C,[184] it can be concluded that the bulky aromatic side chains hinder cyclisation by making the *cisoid* conformation less likely to form as an intermediate in the reaction.

III.4.B.3. Reaction of (54) with Electrophiles

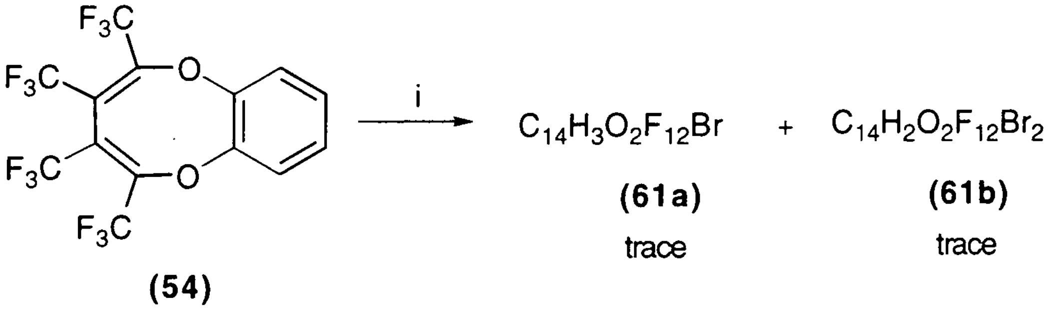
The benzodioxocin derivative (**54**) is remarkably resistant to electrophilic attack. Addition of concentrated nitric acid to (**54**) gave a low yield, by GLC, of the di-nitro derivative (**60**). The mass spectrum of the product revealed the molecular ion [M^+ 522], but due to the low yield the compound could not be isolated and, consequently, the positions of nitration was not ascertained. The molecular ion corresponding to mono-substitution was not observed. The reaction was repeated with a catalytic amount of fuming sulphuric acid, in dimethylformamide and the reaction mixture gently heated, however, the yield did not increase significantly.



(54) $\xrightarrow{i}$ $C_{14}H_2O_2F_{12}(NO_2)_2$ **(60)** trace

i. HNO_3, CH_3CN, 3 days, r.t.

It is likely that nitric acid is too reactive an electrophile, since decomposition of the starting material occurs under the conditions described, with none remaining in the product mixture by GLC. To test this hypothesis (**54**) was stirred with bromine.

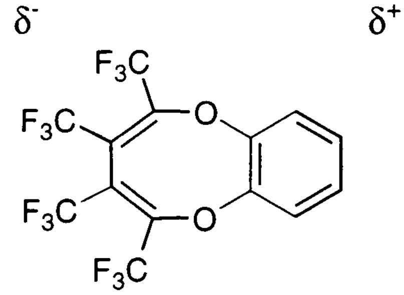


(54) $\xrightarrow{i}$ $C_{14}H_3O_2F_{12}Br$ **(61a)** trace + $C_{14}H_2O_2F_{12}Br_2$ **(61b)** trace

i. Br_2, CH_2Cl_2, 3 days, r.t.

Once again a low product yield was observed by GLC, with both mono- and di-substitution products present. The mass spectrum revealed both molecular ions, [M^+ 511] and [M^+ 590], each showing the distinctive bromine isotope pattern. Repetition of the reaction at various temperatures and in different solvents (acetonitrile, diethyl ether) failed to increase the yield significantly.

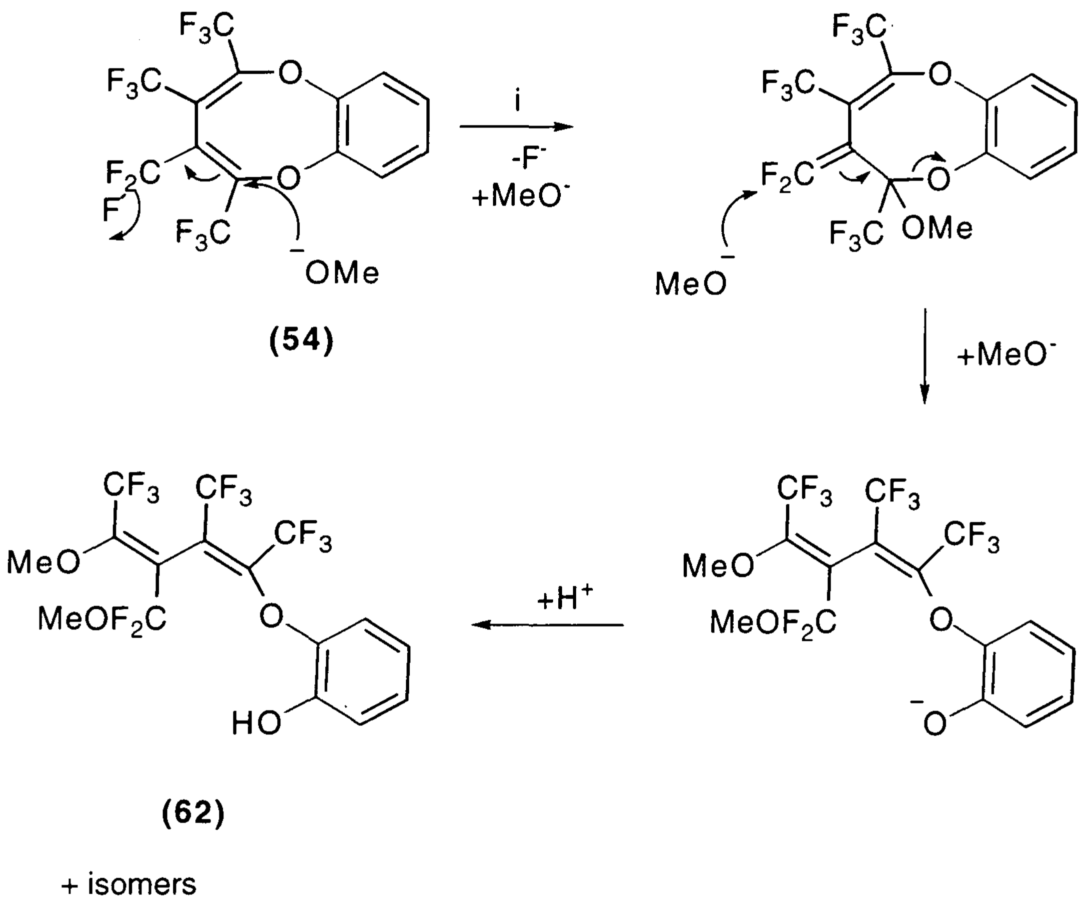
It can only be concluded that the electron withdrawing effect of the fluorinated end of the molecule upon the benzenoid ring is more significant than would appear to be the case based on theoretical calculations, making the system deactivated towards electrophilic attack.



(54)

III.4.B.4. Reaction of (54) with Nucleophiles

In contrast to the reactions of **(54)** with electrophiles, vigorous reaction with nucleophiles was observed. A round bottomed flask was charged with **(54)** and freshly prepared sodium methoxide in methanol. Immediate reaction occurred with formation of an intense blue colour, which faded after a few minutes. The mixture was stirred for a further five minutes, the product extracted into diethyl ether and isolated by removal of solvent under vacuum. GLC-MS analysis of the viscous residue revealed two main products as well as a large number of side products of similar retention time. The mass spectra of the two main components both showed a molecular ion peak at [M^+ 476] and they are thus thought to be isomers of one another formed by attack of methoxide on the electrophilic double bond. A probable mechanism is shown in **Scheme 2**.



(54)

(62)

+ isomers

i. MeONa, MeOH, 5 min, r.t.

Scheme 2

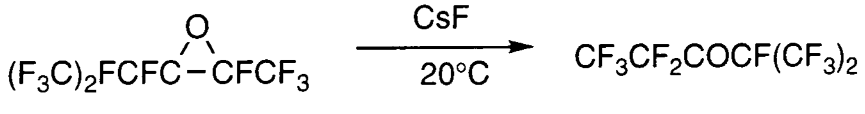
The ^{19}F NMR spectrum of the crude mixture shows four major peaks in a ratio of 3:3:3:2, which would support the proposed structure of **(62)**. The three 3F resonances appear in the typical region for vinylic trifluoromethyl groups at δ_F -57.2ppm, δ_F -64.2ppm and δ_F -64.3ppm. The CF_2 resonance, however, occurs at surprisingly low field, δ_F -65.0ppm, and this can only be attributed to the electron withdrawing effect of the geminal methoxy group, as described by other authors.[138] The other major product is probably a stereo-isomer of **(62)** and the minor products structural isomers and products of further methoxide attack.

Attempts to isolate the products by column chromatography and preparative scale GLC were only partly successful and the ^{19}F NMR remained complicated, consequently full analysis was not possible.

III.4.B.5. Epoxidation Reactions

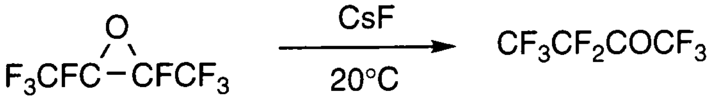
Perfluoroalkylation is well known to confer stability to epoxides.[138, 193, 194] As an example, the epoxides of perfluoro-5-methylpent-2-ene **(63)** and octafluorobut-2-ene **(64)**, with only two perfluoroalkyl groups attached to the epoxide ring, react with cesium fluoride at 20°C,[195, 196] whereas the fully perfluoroalkylated perfluoro-3,4-

dimethylhex-3-ene epoxide (**65**) only ring opens at 200°C.[194] It therefore seems likely that the epoxide of (**54**) will be stable and resistant to nucleophilic attack.



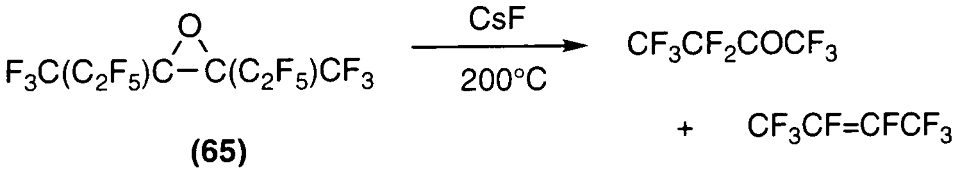
$$(F_3C)_2FCFC(O)CFCF_3 \xrightarrow[20°C]{CsF} CF_3CF_2COCF(CF_3)_2$$

(63)



$$F_3CFC(O)CFCF_3 \xrightarrow[20°C]{CsF} CF_3CF_2COCF_3$$

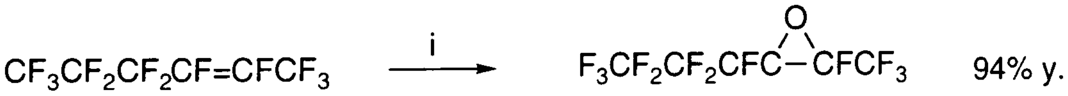
(64)



$$F_3C(C_2F_5)C(O)C(C_2F_5)CF_3 \xrightarrow[200°C]{CsF} CF_3CF_2COCF_3 + CF_3CF{=}CFCF_3$$

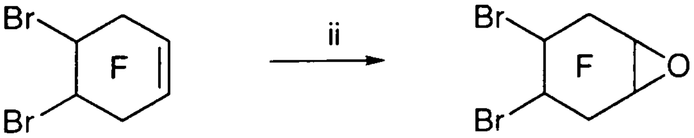
(65)

Workers in these laboratories[138, 184, 193, 194] have shown that calcium hypochlorite [$Ca(ClO)_2$] can be used as an effective agent for nucleophilic epoxidation in systems with internal perfluoroalkylated double bonds. The method was first described by Kolenko[195, 196] in 1979 for the epoxidation of perfluorohex-2-ene and has proved to be a remarkably versatile system.[197, 198]

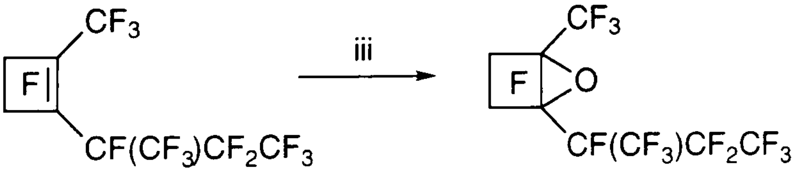


$$CF_3CF_2CF_2CF{=}CFCF_3 \xrightarrow{i} F_3CF_2CF_2CFC(O)CFCF_3 \quad 94\%\ y.$$

i. $Ca(ClO)_2$, CH_3CN



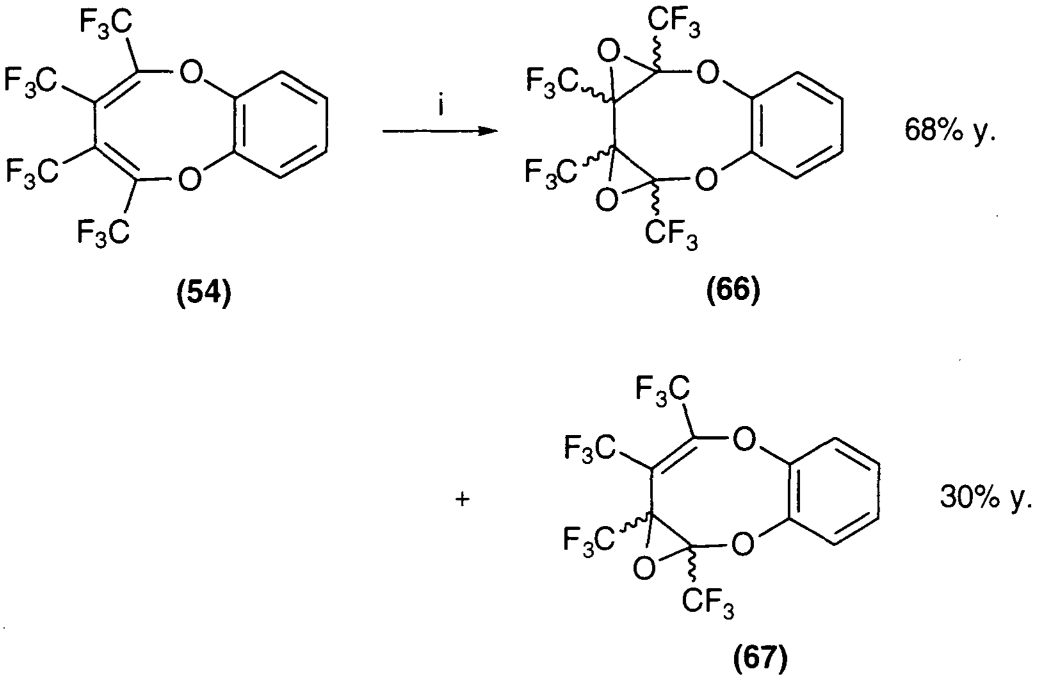
ii. NaOCl, CH_3CN, 50°C, 1 hr



iii. NaOCl, CH_3CN, 18°C, 1 hr

III.4.B.5.i. Epoxidation of Benzodioxocin Derivative (54)

Compound (**54**) was epoxidised using this procedure in high yield by $Ca(ClO)_2$ to give a mixture of the mono- and diepoxides. The ^{19}F NMR spectrum showed resonances in the CF_3 region corresponding to both compounds. Diepoxide (**66**) showed only two peaks, at δ_F -65.3ppm and δ_F -69.1ppm, whereas (**67**) showed four peaks, two corresponding to the vinylic sites, at δ_F -56.7ppm and δ_F -65.1ppm, and a further two, at δ_F -65.7ppm and δ_F -70.7ppm, corresponding to the epoxidised sites. GLC-MS analysis gave both molecular ions [M^+ 448] and [M^+ 464].

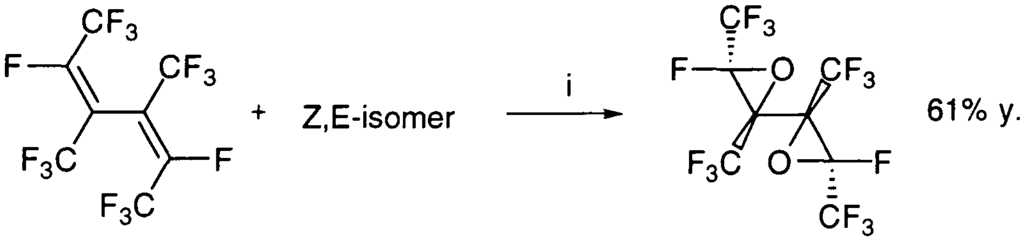


i. $Ca(ClO)_2$, CH_3CN, 4 days, 80°C

The reaction was repeated, but left over seven days, yielding the diepoxide (**66**) almost exclusively. Filtration of unreacted calcium hypochlorite followed by removal of solvent and low temperature precipitation (-15°C) from diethyl ether gave a white powder in 72% isolated yield, allowing full characterisation. The ^{13}C NMR spectrum reveals resonances for the epoxidised carbons (positions 2, 3, 4, and 5) as quartets centred at δ_C 63.7ppm and δ_C 82.8ppm. This is a dramatic shift upfield relative to the corresponding positions in (**54**); δ_C 107.5ppm and δ_C 144.4ppm, clearly indicating that the sites are no longer unsaturated.

Although the stereochemistry of (**66**) cannot be ascertained directly from NMR data the reaction appears to be remarkably clean, with one stereo-isomer predominant.

Interestingly, the structurally similar acyclic diene (**14**) appeared also to give only one stereo-isomer (**68**) upon diepoxidation.[193]

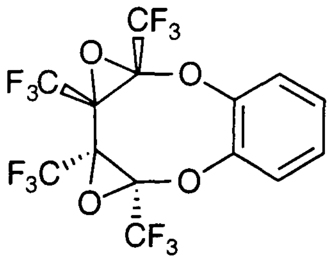


(14) **(68)**

i. Ca(OCl)$_2$, CH$_3$CN, 24 hr, r.t.

The ^{19}F NMR spectrum of **(68)** showed only three sharp resonances, corresponding to the all *trans* isomer shown. This high level of diastereo-selectivity is due to the need to minimise the interaction between adjacent trifluoromethyl groups, facilitated by adoption of the observed stereochemistry. The reaction is, thus, under thermodynamic control. It seems likely that the thermodynamically most stable isomer is also produced upon diepoxidation of **(54)**.

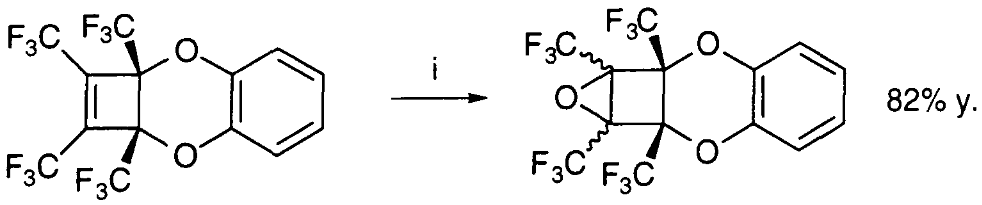
Since **(66)** is cyclic formation of an all *trans* isomer is not possible in this case. Thus, the most likely conformation for **(66)** to adopt is the *cis, trans, cis* structure shown below.



(66)

III.4.B.5.ii Epoxidation of Electrocyclisation product (58)

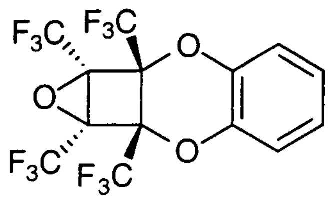
The tricyclic mono-ene **(58)**, was epoxidised and isolated using the same methodology described for the epoxidation of **(54)**.



(58) **(69)**

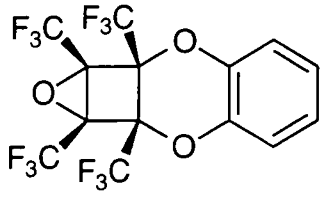
i. Ca(ClO)$_2$, CH$_3$CN, 4 days, 80°C

The ^{19}F NMR spectrum revealed the presence of two stereo-isomers of **(69)** in a 2:3 ratio. This is surprising since the two tertiary CF_3 groups in **(58)** would be expected to exert a high degree of stereo-control upon the geometry of epoxidation of the neighbouring double bond. Thus, the *cis,trans,cis* - isomer **(69a)**, with $CF_3...CF_3$ interactions minimised, would be expected to be formed almost exclusively. Also surprising is the lack of any CF_3-CF_3 coupling in the spectrum, a phenomena that has been observed in other similarly arranged systems.[138]



cis,trans,cis-isomer

(69a)



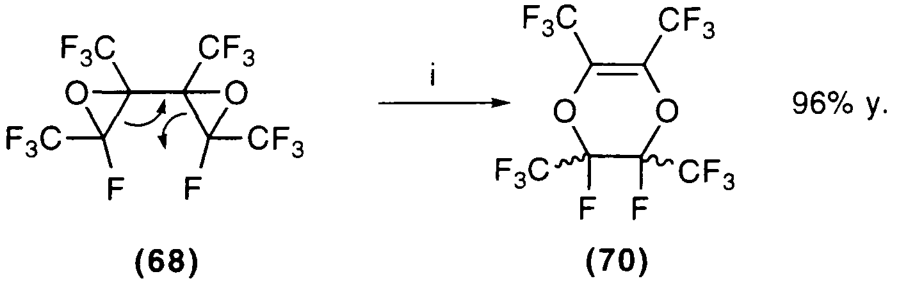
cis,cis,cis-isomer

(69b)

The reason both diastereomers of **(69)** are formed is not clear, although bearing in mind that the molecule is far from planar, other stereo-chemical factors may be influencing the thermodynamic stability of the product.

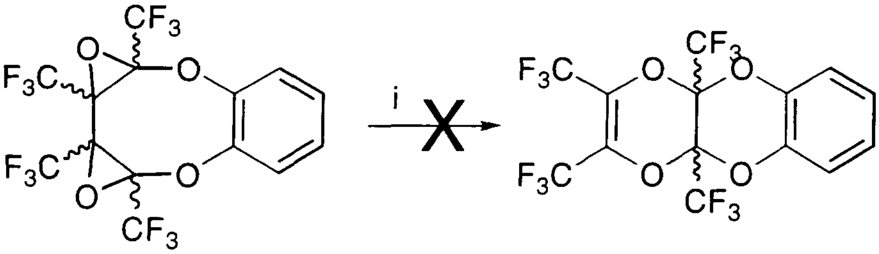
III.4.B.6. Attempted Ring Opening Reactions with Diepoxide (66)

As described earlier workers in these laboratories have diepoxidised diene **(14)** to give the novel diepoxide **(68)** in good yield.[193] Upon heating **(68)** rearranged to give the perfluorinated dioxin **(70)**.[193]



i. sealed tube, 200°C, 24 hr

Attempt was made to ring open **(66)** and so provide further basis for the postulation of structure **(70)** as the ring opened isomer of **(68)**.



(66) **(71)**

i. sealed tube, Δ, 24 hr

Diepoxide (**66**) was dissolved in a small amount of diethyl ether, sealed in a quartz NMR tube and heated first at 100°C and then in 50°C increments up to 350°C for 24 hours at a time. At 300°C ^{19}F NMR revealed a small degree of decomposition of the starting diepoxide, and at 350°C most of (**66**) had decomposed, with no formation of (**71**).

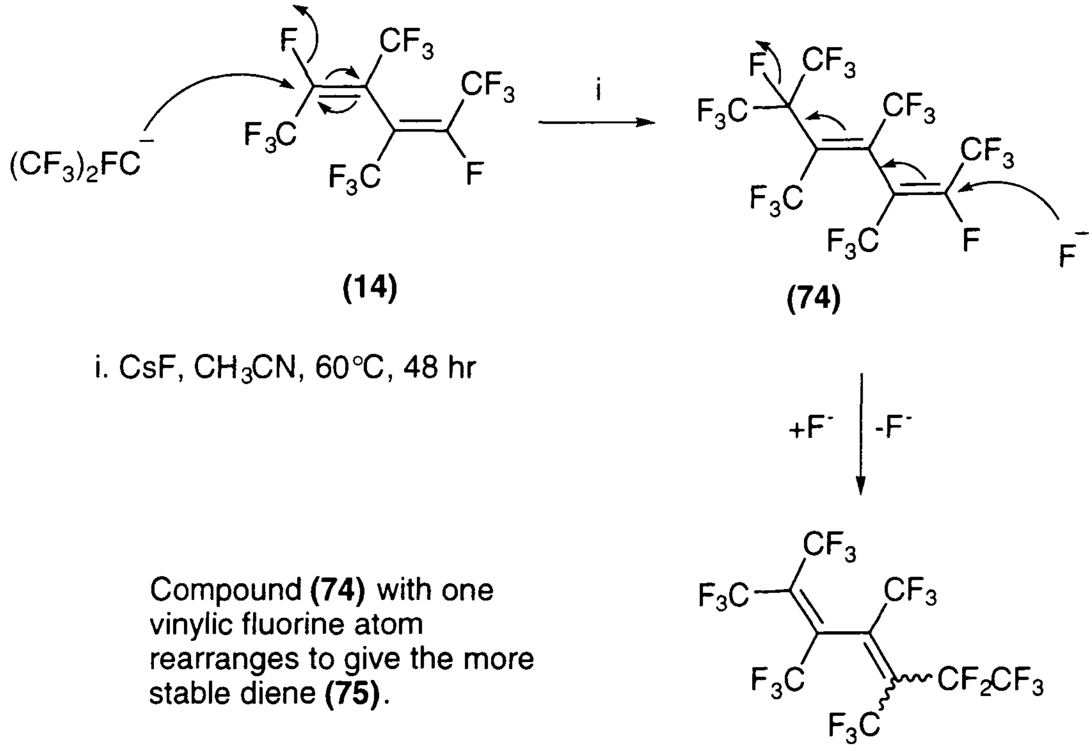
This result is puzzling, bearing in mind the ready rearrangement of (**68**) at 200°C, and may be due to the constraint placed on the system by being held in an eight membered ring.

III.5. Reaction of (14) with Perfluorocarbanions

In **Chapter Two** it was shown that the perfluoroisopropyl anion can be generated by attack of fluoride ion on hexafluoropropene **(1)**. It was attempted to add this carbanion to **(14)** via a vinylic addition-displacement mechanism.

III.5.A. Cesium Fluoride Catalysis

A Carius tube was charged with cesium fluoride, diene **(14)**, hexafluoropropene **(1)** and acetonitrile and stirred in a rotating oil bath at 60°C for 2 days. A mixture of the rearranged product **(75)** and recovered **(14)** were isolated as a lower fluorocarbon layer, with a 84% crude yield of **(75)**, based on **(14)** consumed. Compound **(75)** was isolated pure by preparative scale GLC as a volatile liquid. The interesting rearrangement of the presumed initial product **(74)** to **(75)** is consistent with the general situation that 'internal' isomers of fluoro-alkenes are more stable than terminal isomers.



(14)

(74)

i. CsF, CH_3CN, 60°C, 48 hr

Compound **(74)** with one vinylic fluorine atom rearranges to give the more stable diene **(75)**.

(75)

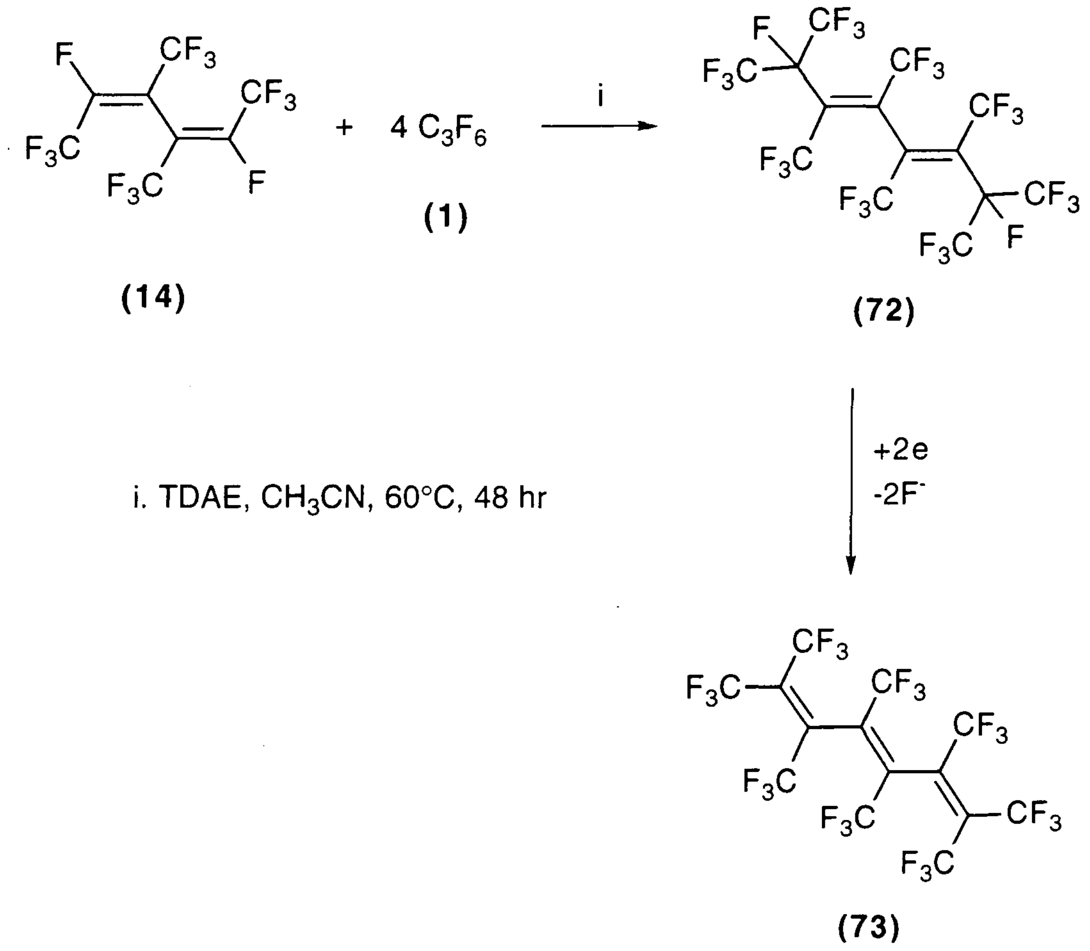
84% y.

The ^{19}F NMR spectrum of **(75)** showed five vinylic trifluoromethyl groups resonating between δ_F -56.2ppm and δ_F -59.6ppm. The CF_3 and CF_2 of the pentafluoroethyl moiety resonate at δ_F -79.0ppm (t, *J* 7.5Hz) and δ_F -106.8ppm (br.s) respectively. There were no resonances in the vinylic region, as would be expected if **(74)** were present. Structure **(75)** is supported by the mass spectrum cracking pattern which shows a large peak at [M^+ 119, 23%] corresponding to the pentafluoroethyl fragment.

The ultraviolet spectrum of **(75)** is interesting since the compound is a unique example of a fully perfluoroalkylated diene. The spectrum of **(75)**, and other fluorinated dienes shall be discussed in **Chapter Four**.

III.5.B. TDAE Catalysis

TDAE is known to catalyse *in situ* formation of the perfluoroisopropyl anion from **(1)**. Formation of the di-addition product **(72)** from **(14)** would then give the possibility of reductive defluorination to the triene **(73)**.



(14) **(1)** **(72)** **(73)**

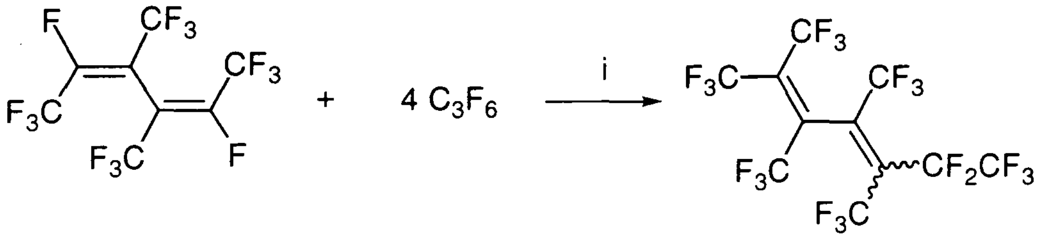
i. TDAE, CH_3CN, 60°C, 48 hr

A Carius tube was charged with diene **(14)**, hexafluoropropene **(1)**, TDAE and acetonitrile, sealed *in vacuo* and stirred for 2 days at 60°C. Analysis of the product material suggested that **(14)** interacts with TDAE directly under these conditions to give a mixture of defluorination and addition products, since no adducts of **(14)** were observed by either ^{19}F NMR of GLC-MS.

III.5.C. Trimethylamine Catalysis

Trimethylamine can also promote fluoride ion formation *in situ* and so may be able to catalyse formation of **(72)**. Initial investigation, using a sealed Carius tube as the reaction vessel, revealed that dimerisation of **(1)** was a strong competing force to perfluoroalkylation. The reaction was, therefore, performed by allowing slow diffusion of **(1)** and trimethylamine from a gas bladder into a two-neck flask containing the diene.

The mixture was stirred for 48 hour at 60°C after which time the bladder had deflated and an 8% yield of mono-adduct **(75)** was observed by GLC. The major component in the fluorocarbon layer was hexafluoropropene dimer **(5)**. The di-adduct was not observed.



(14)

(75) 8% y.

i. NMe_3, CH_3CN, 60°C, 48 hr

III.6. Conclusion

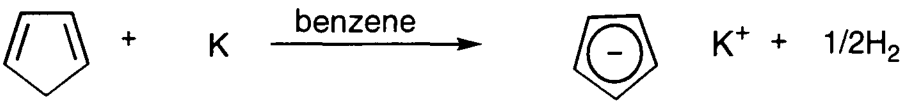
Reaction of oxygen and carbon centred nucleophiles with perfluoro-2,3-dimethylhexa-2,4-diene **(14)** has been shown to yield interesting products with potentially novel properties. The benzodioxocin derivative **(54)** readily reacts with nucleophiles and can be epoxidised in high yield. The addition of perfluorinated groups to dienes such as **(14)** has the potential to substantially improve our understanding of perfluorinated systems.

CHAPTER FOUR

Formation of Pentakis(trifluoromethyl)cyclopentadienide Salts

IV.1. Introduction

The first reported synthesis of an ionic derivative of cyclopentadiene was by Johannes Thiele in 1901.[199] Reaction of potassium with cyclopentadiene in benzene evolved hydrogen gas and produced an off white solid with the proposed potassium cyclopentadienide structure shown below.



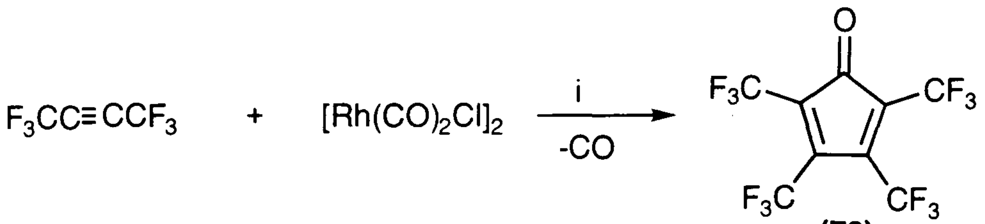
This still remains the most general method of cyclopentadienide formation, and salts derived from reaction of sodium with cyclopentadiene are widely used in the synthesis of transition metal complexes.[1]

The synthesis and reactions of a range of polytrifluoromethylated cyclopentadienides will be discussed in the next two chapters. An excellent review of the literature pertaining to cyclopentadienides bearing trifluoromethyl groups and other electron withdrawing substituents was published by Macomber in 1982.[200] A comprehensive update of the work detailed in that review is presented here.

IV.1.A. Trifluoromethylated Cyclopentadienides

IV.1.A.1. Tetrakis(trifluoromethyl)cyclopentadienone (76)

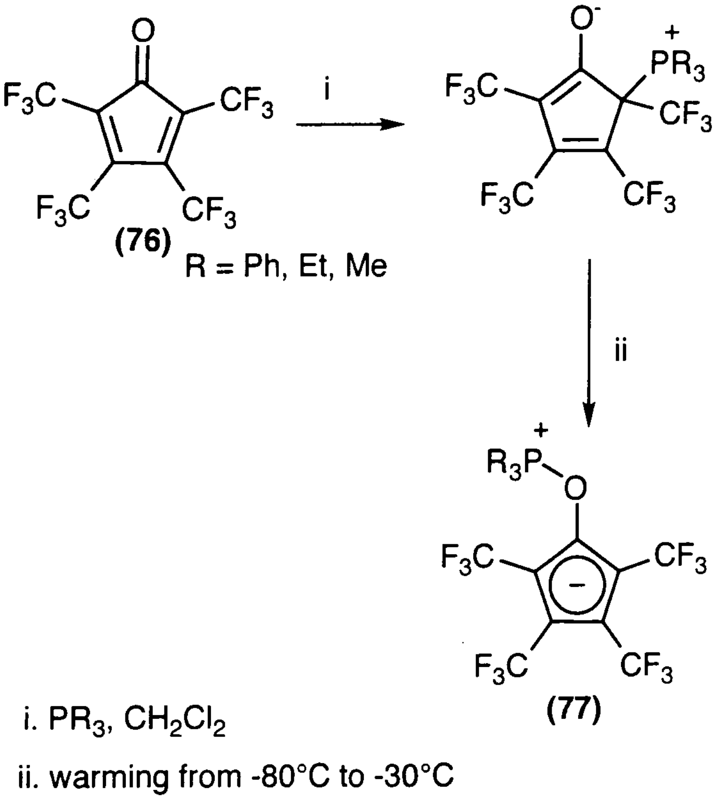
Tetrakis(trifluoromethyl)cyclopentadienone (**76**) was first synthesised by Dickson and Wilkinson in the early sixties.[201]



i. 150°C

(76)

Reactions of the dienone (**76**) with simple nucleophiles gives addition to both the ring and to the carbonyl oxygen, depending on the nature of the reactant. Trialkyl phosphines add to the carbon adjacent to the carbonyl carbon in a Michael type process and this species can then be isomerised to the thermodynamic oxygen substituted ylide (**77**) upon warming.[202]



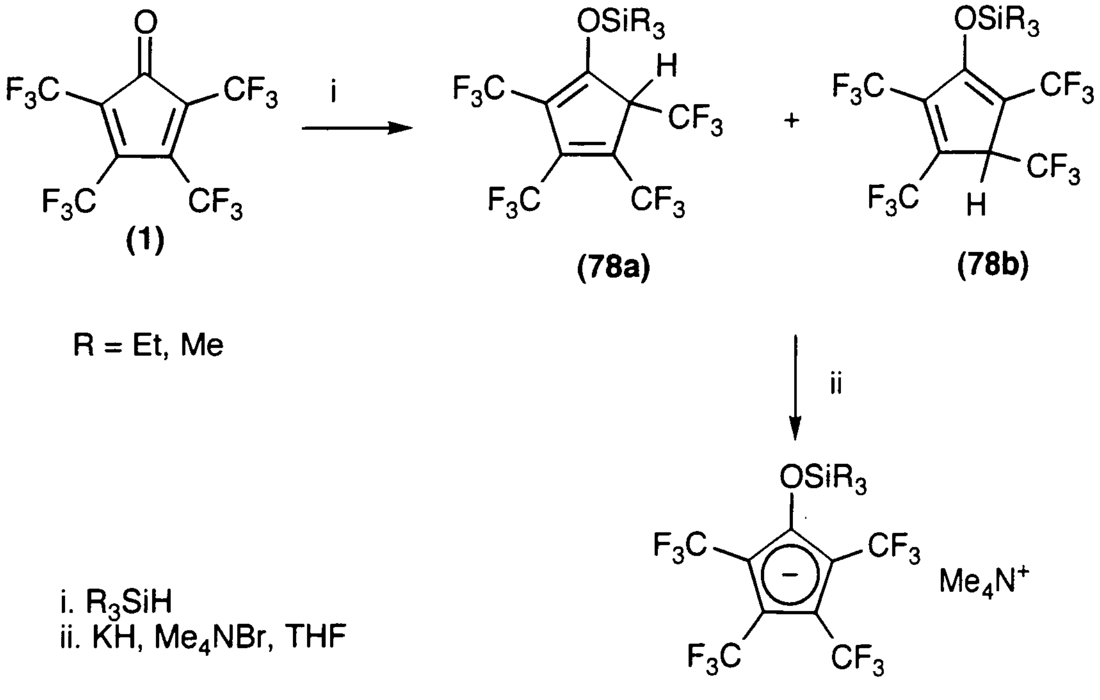
(76) R = Ph, Et, Me

(77)

i. PR_3, CH_2Cl_2

ii. warming from -80°C to -30°C

Reaction of (**76**) with trialkylsilane gave the expected siloxy derivative (**78**) and further treatment with strong base, such as potassium hydride, gave the novel polytrifluoromethylated cyclopentadienide anion. (**79**).



(1) (78a) (78b)

R = Et, Me

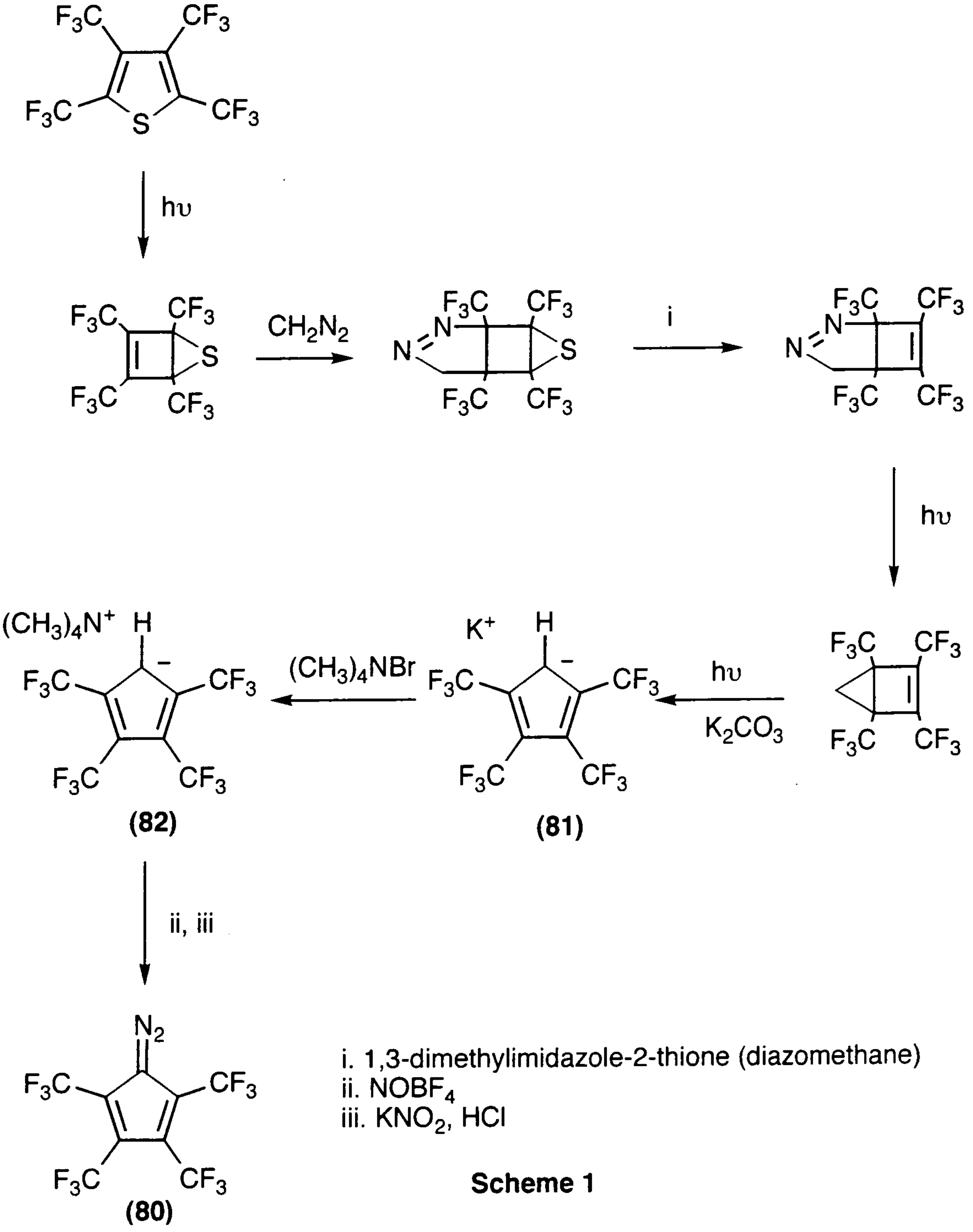
i. R_3SiH

ii. KH, Me_4NBr, THF

(79)

IV.1.A.2. Diazotetrakis(trifluoromethyl)cyclopentadiene (80)

Janulis and Arduengo[203] have synthesised diazotetrakis(trifluoromethyl)cyclopentadiene (**80**), as shown in **Scheme 1.**

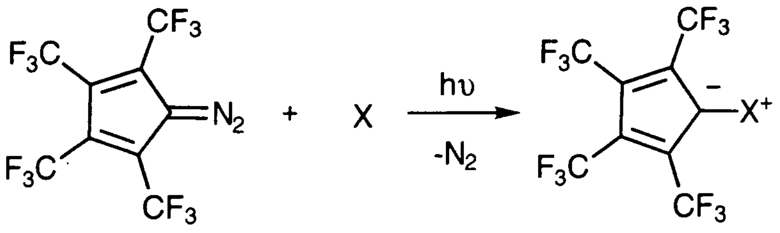


i. 1,3-dimethylimidazole-2-thione (diazomethane)
ii. $NOBF_4$
iii. KNO_2, HCl

Scheme 1

Formation of the tetramethyl ammonium salt (**82**) from the potassium salt (**81**) was necessary because of the difficulty of isolation of the potassium salt compared to the relatively stable tetraalkyl ammonium salt.

Although (**80**) is thermally stable, it can undergo a photochemical loss of nitrogen and subsequently react with a variety of nucleophiles.

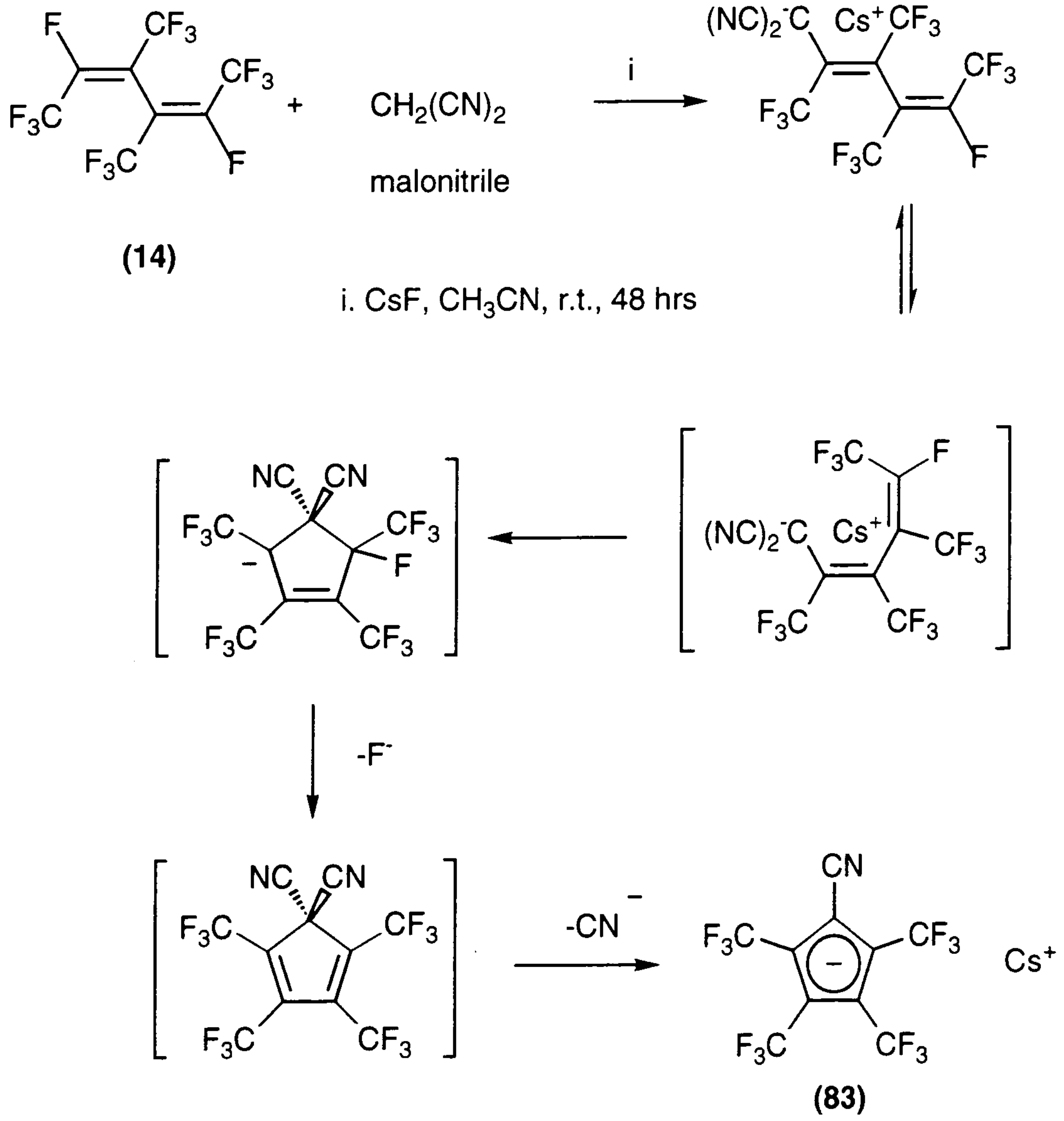


(80)

X = $O(CH_3)_2$, or $S(CH_3)_2$, or $ClC_6H_4CH_3$, or $BrC_6H_4CH_3$ or $CNC_6H_4CH_3$

IV.1.A.3. Tetrakis(trifluoromethyl)cyclopentadienides

Work in these laboratories[204] has shown that reaction between perfluoro-3,4-dimethyl-2,4-hexadiene **(14)** and malonitrile under reflux gives tetrakis(trifluoromethyl)cyanocyclopentadienide **(83)** via the mechanism shown in **Scheme 2.**

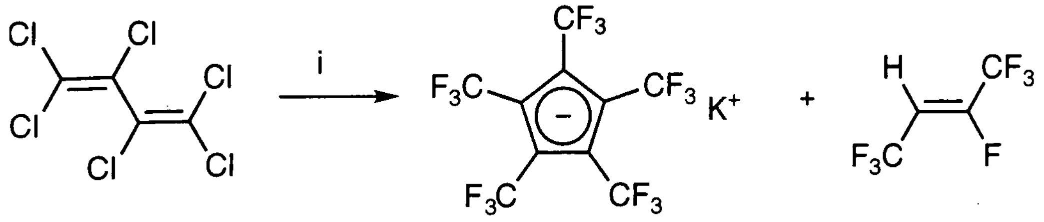


Scheme 2

If the reaction is performed at room temperature then the intermediate anions can be observed by ^{19}F NMR spectroscopy.

IV.1.A.4. Pentakis(trifluoromethyl)cyclopentadienide (84)

Roche^{205} recently synthesised the potassium salts of pentakis(trifluoromethyl)cyclopentadienide (**84**) from hexachlorobutadiene and potassium fluoride.

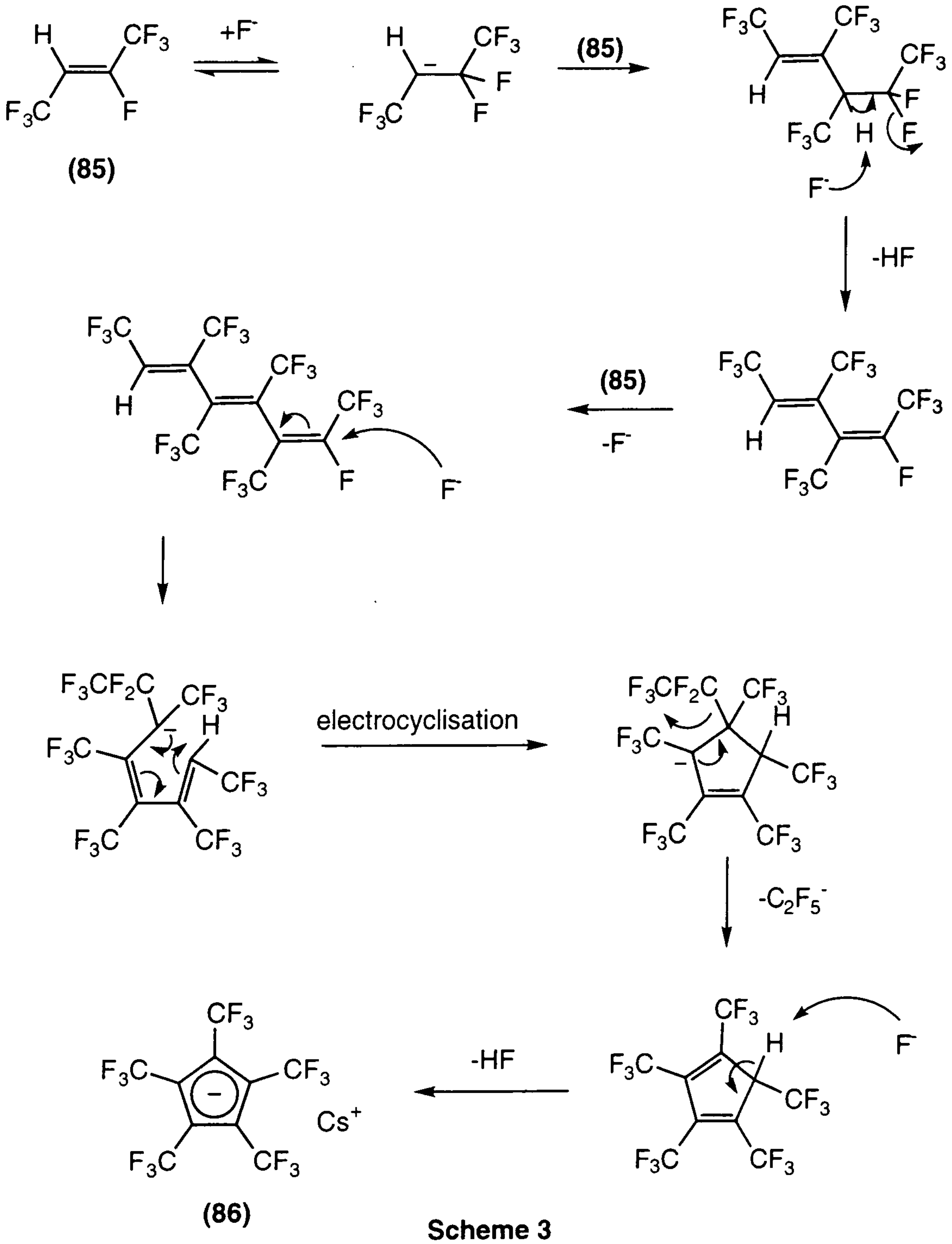


(84) 3% y.

(85) 45% y.

i. KF, 190°C, sulpholan

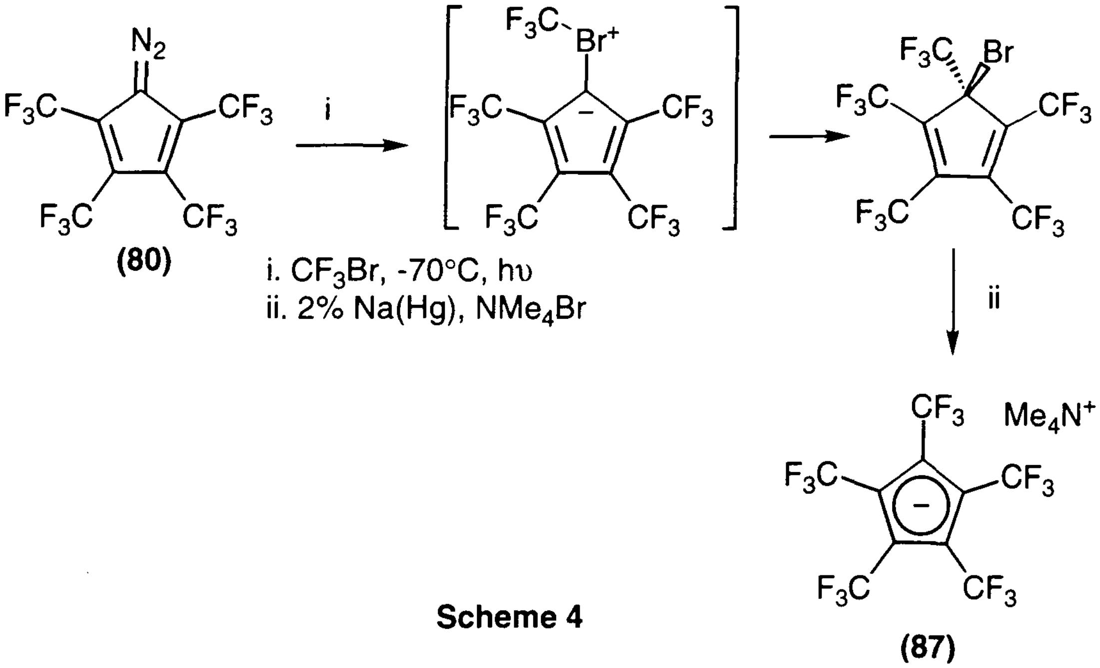
The reaction proceeds via 2*H*-heptafluoro-2-butene (**85**). The full mechanism is shown in **Scheme 3**



Scheme 3

There are only two other reported syntheses of **(84)**. The first was by Laganis and Lemal in 1980 who reported the H_3O^+ Salt on interaction of the carbon acid of **(84)** with water. This synthesis is discussed fully in **Section IV.4.B.**

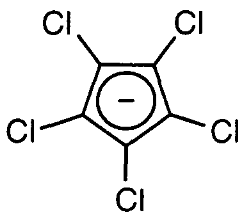
Janulis and Arduengo synthesised, but never isolated, **(84)** via the route shown in **Scheme 4**.[206]



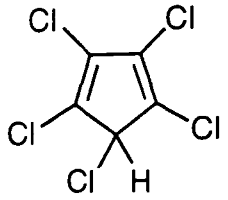
Scheme 4

IV.1.B. Polychlorocyclopentadienides

One of the first cyclopentadienide anions studied with electron withdrawing substituents was pentachlorocyclopentadienide (**88**). West[207] reported a range of thallium, tetraalkylammonium and phosphonium salts of (**88**). The thallium salts were prepared by reaction of hexachlorocyclopentadiene with thallium amalgam. Formation of ammonium and phosphonium salts was achieved by addition of the appropriate tetraalkylammonium or phosphonium halide to pentachlorocyclopentadiene (**89**). None of the compounds were thermally stable, e.g. $C_5Cl_5^-Tl^+$ ignites spontaneously at -15°C even under nitrogen. Anion (**88**) was observed to be an exceedingly poor nucleophile with significant charge delocalisation onto the chlorine atoms. Its derived acid (**89**) is surprisingly weak, however, with no apparent ionisation in solution.



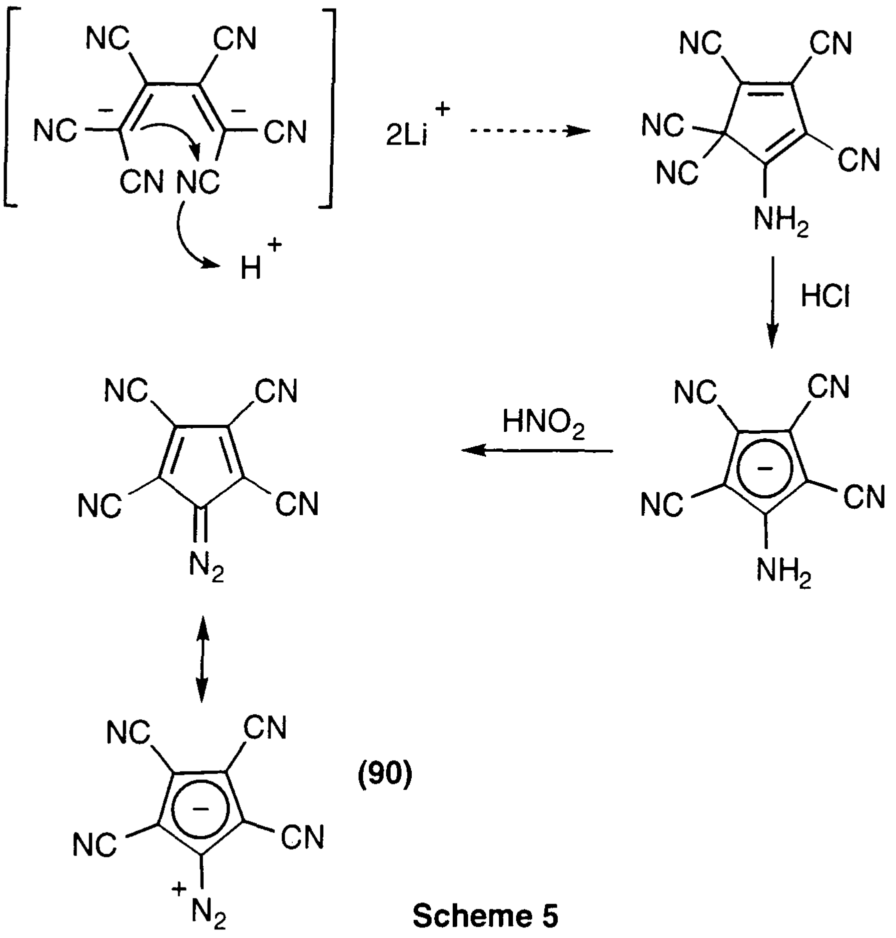
(88)



(89)

IV.1.C. Polycyanocyclopentadienides

A variety of tetracyanocyclopentadienides were synthesised by Webster[208] using the approach shown in **Scheme 5**.



(90)

Scheme 5

Compound **(90)** was then used as a synthon for a variety of polycyanocyclopentadienide derivatives, as shown in **Table 1**, including pentacyanocyclopentadienide **(91)**.

Table 1. Reaction of **(90)** with nucleophiles

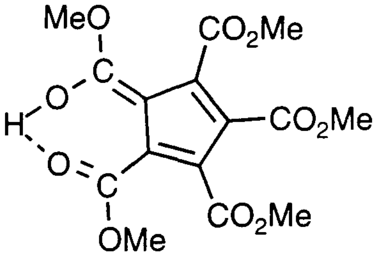
Reagent	Product
CuCN	$C_5(CN)_5^-$ **(91)**
I_2	$C_5(CN)_4I^-$
Br_2	$C_5(CN)_4Br^-$
Cl_2 (Cu)	$C_5(CN)_4Cl^-$
PhOH	$C_5(CN)_4OPh^-$
CO, Cu, H_2O	$C_5(CN)_4CO_2H^-$
NO_2	$C_5(CN)_4NO_2^-$

Salt **(91)** could not be protonated, even using perchloric acid in acetonitrile, and so the pK_a of its acid is unknown, although it should be significantly lower than -8, the estimated pK_a of tetracyanocyclopentadiene **(92)**.[208]

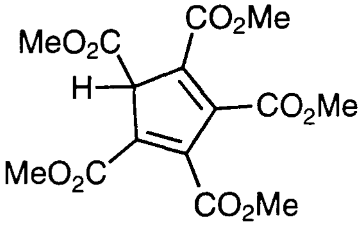
The ferrous salt of (**91**) has also been prepared and its air sensitivity and non-volatile nature indicate it to have a structure of the form $Fe^{2+}[C_5(CN)_5]^-{}_2$.[209] Full analytical data on this salt would have been interesting, in view of work which will be discussed later, and, as will become clear, it would be surprising if the ferrous cation was not solvated in some way.

IV.1.D. Pentakis(methoxycarbonyl)cyclopentadiene Derivatives

Pentakis(methoxycarbonyl)cyclopentadiene (**93**) has an acid strength in solution similar to that of hydrochloric acid. When it was first described in 1942 by Otto Diels,[210] and later by Cookson,[211] structure (**94**) was postulated. However, when Bruce and co-workers[212, 213] obtained a crystal structure in 1981 the hydrogen atom was found to be located between two of the carbonyl oxygens as shown.



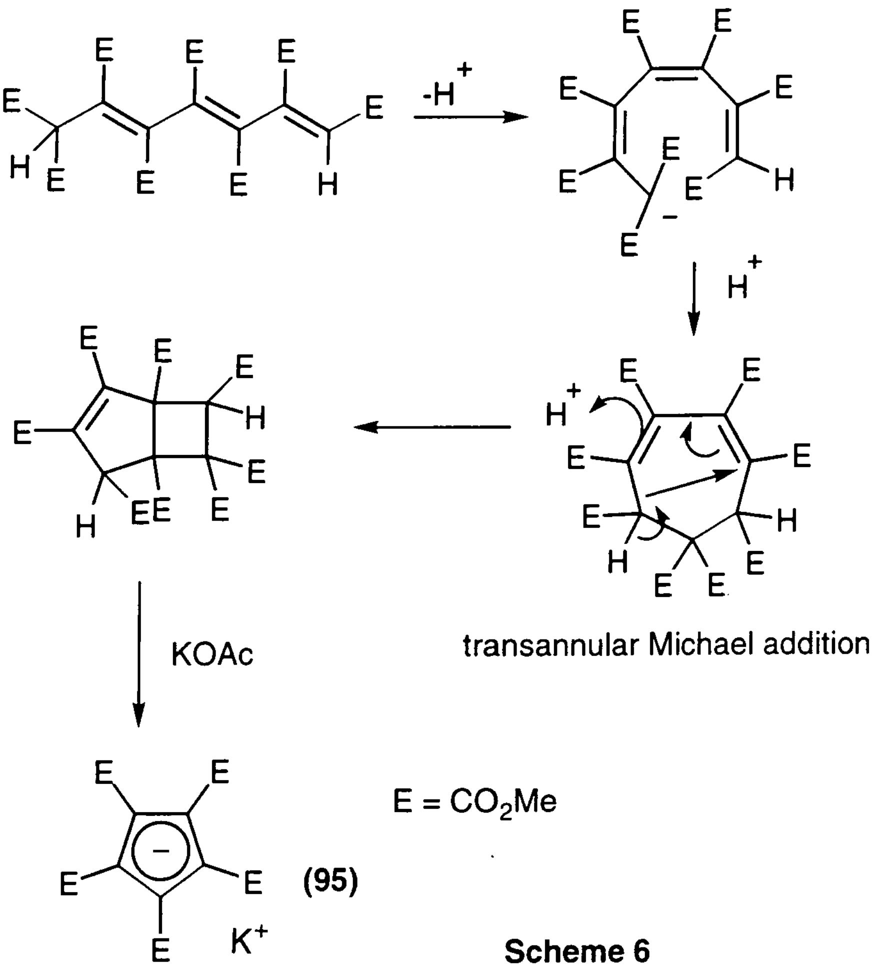
(93)



(94)

The derived cyclopentadienide anion (**95**) has been thoroughly studied and delocalisation of charge onto the methoxycarbonyl groups appears to be a major factor in stabilising the system. Indeed, x-ray analysis of the lithium salt shows the metal cation chelated between two carbonyl groups, rather than positioned directly below the plane of the ring as is observed in other cyclopentadienide salts.[213]

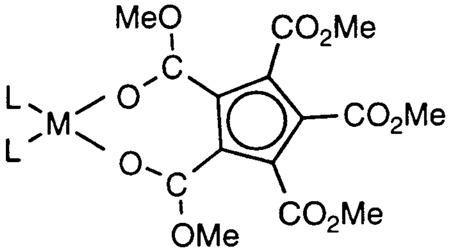
The potassium salt of (**95**) can be formed directly from acyclic precursors as shown in **Scheme 6**.[211, 214]



Scheme 6

Salts of **(95)** with a variety of alkali metal,[213] tetraalkylammonium[215] and tropylium[216] counter ions have been described over the years. Tetraalkylammonium salts can be synthesised by reaction of the potassium or thallous salts with the corresponding ammonium halides.

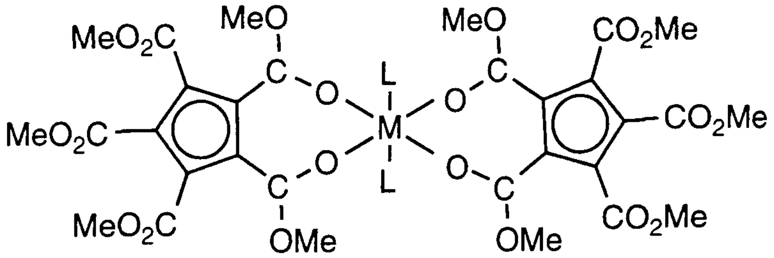
Bruce has prepared solvated gold (I) and silver (I) salts by heating **(94)** with silver and gold acetates.[217, 218]



M = Ag, Au
L = PPh$_3$, MeOH

Again, it is the carbonyl oxygens rather than the ring that ligate the metal.

Similarly, divalent manganese, iron, cobalt, nickel and copper salts were also synthesised, with the copper species the first example of a Copper (II) cyclopentadienide complex.[219]



M	L
Fe	MeOH
Co	H_2O
Cu	MeOH

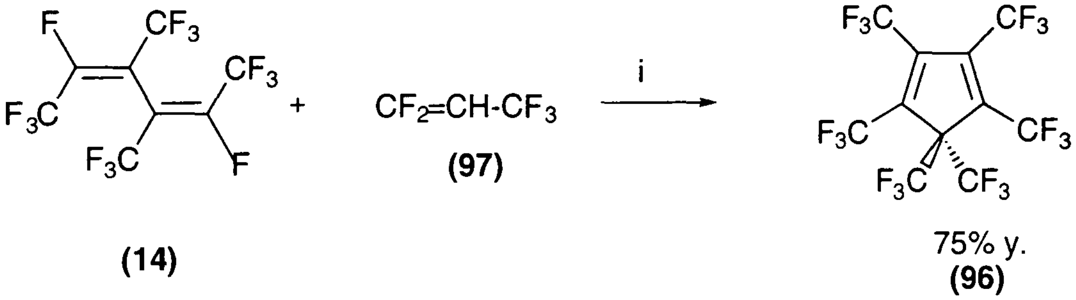
In aqueous solution the complexes behave as 2:1 electrolytes and were coloured as the corresponding aquo cations, $[M(H_2O)_6]^{2+}$, and were, thus, described in terms of ion pairs rather than π complexes.

Earlier work by Cookson[211] claimed formation of a ferrous salt by reaction of **(94)** with iron metal, although the product was ill characterised.

IV.2. Synthesis of Hexakis(trifluoromethyl)cyclopentadiene

This chapter and the succeeding one are concerned with the synthesis and reactions of the cyclic diene hexakis(trifluoromethyl)cyclopentadiene (**96**), which can be used as a synthon for the interesting pentakis(trifluoromethyl)cyclopentadienide anion (**84**).

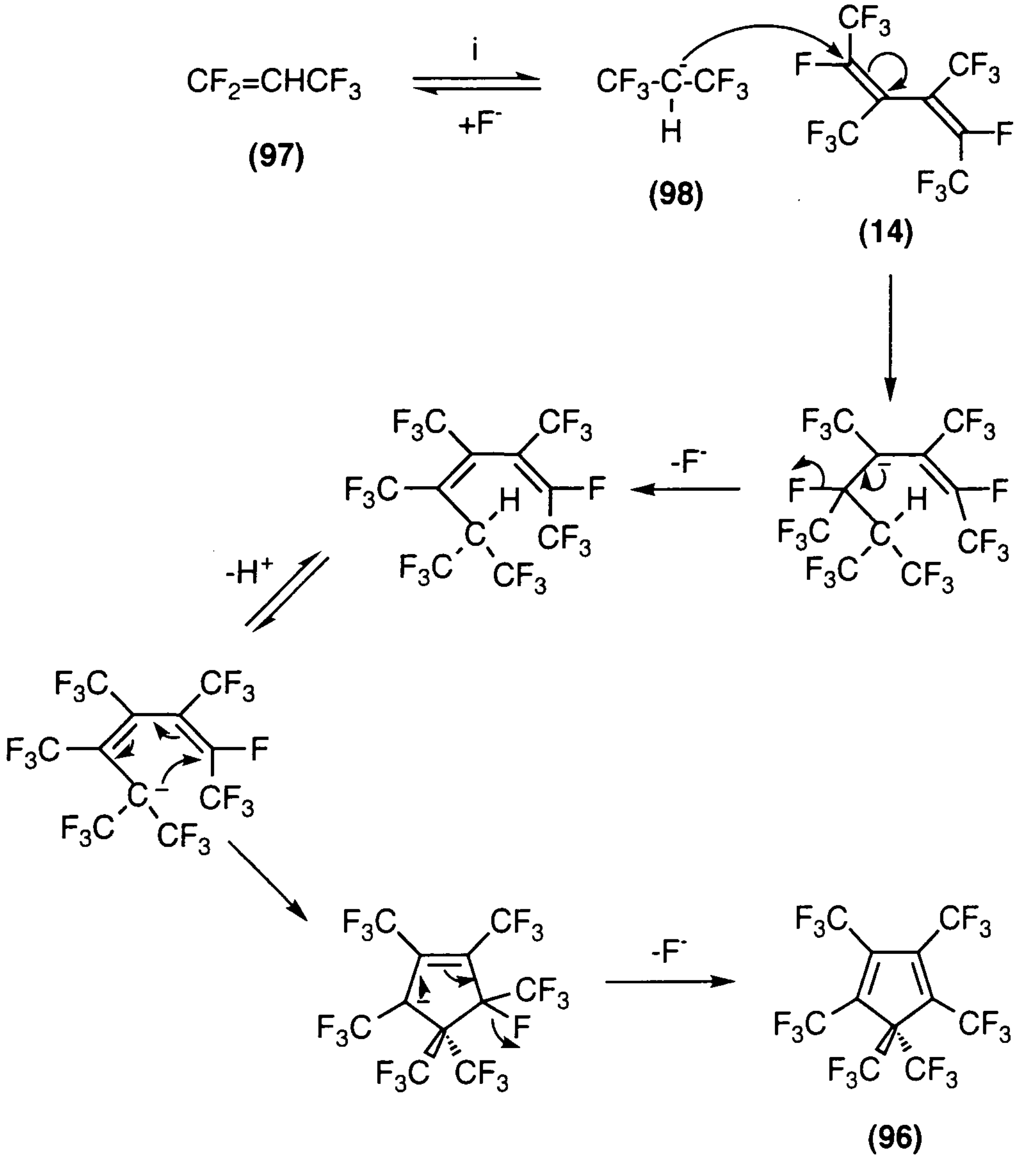
Preliminary work by Vaughan[138, 205] in these laboratories has yielded hexakis(trifluoromethyl)cyclopentadiene (**96**) by reaction of diene (**14**), pentafluoropropene (**97**) and cesium fluoride in acetonitrile.



(14) **(97)** **(96)**

i. CsF, CH_3CN, rotating arm, r.t., 48 hr

The reaction is remarkably clean with only one component observed by GLC upon flash distillation of the crude reaction mixture, allowing full characterisation. The ^{19}F NMR spectrum shows three distinct peaks of equal intensity at, δ_F -55.6ppm, δ_F -59.3ppm and δ_F -59.7ppm, corresponding to the three different fluorine environments in the molecule. The mechanism for the formation of (**96**) involves initial attack of fluoride ion on pentafluoropropene, generating a carbanion (**98**) which subsequently attacks the electrophilic double bond of diene (**14**)[182] and substitutes the vinylic fluorine via an addition-elimination process. Cesium fluoride then acts as a base removing the proton to give a second intermediate carbanion, which undergoes intramolecular ring closure and displacement of the second vinylic fluorine to give cyclopentadiene (**96**) . The full mechanism is given in **Scheme 7**.



i. CsF, MeCN, stirring, r.t.

Scheme 7

The final ring closure is interesting in that it is a 5-*endo*-trig process and so formally disallowed by Baldwin's rules.[220] It is, therefore, likely that the process is an entirely ionic one, rather than concerted. Reactions of this kind, although rare, have been noted previously.[16, 204, 221, 222]

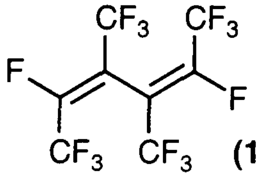
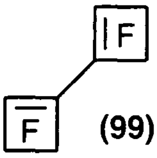
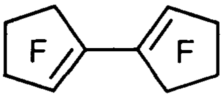
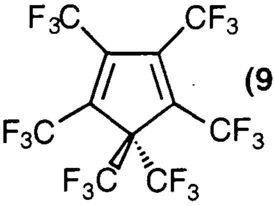
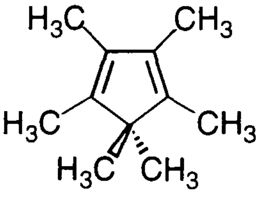
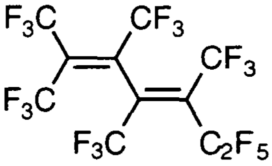
IV.2.A. Ultraviolet Spectrum of Cyclic Diene (96)

Ultraviolet spectroscopy is used to measure the molar abrosption, or extinction coefficient (ε), in unsaturated compounds. When the double bonds of a diene are conjugated, as in butadiene, then there is a relatively small energy difference between the HOMO and the LUMO, which is reflected in a high extinction coefficient and a longer wavelength of ultraviolet absorption.

The ultraviolet spectrum of **(96)** is contained in **Table 2**, together with the spectra of other fluorinated dienes for comparison.[136]

It is well established that homoannular conjugated dienes have lower extinction coefficients than analogous acyclic and heteroannular systems, due to the conjugation length being shorter[188, 189] and, consistent with these findings for various hydrocarbon systems, the extinction coefficient for the cyclic system **(96)** is, indeed, smaller than *e.g.* for **(12)** or **(99)**. Remarkably, however, if we assume that trifluoromethyl has an incremental effect on λ_{max} values that is approximately equivalent to that of chlorine or bromine,[188] *i.e.* inducing a bathochromic, or red, shift of *ca.* 5nm, then the λ_{max} values that are recorded in **Table 2** are very close to calculated values. Crowding probably causes the low extinction coefficient of **(14)** if one considers trifluoromethyl to be isosteric with an isopropyl, rather than a methyl, group.[223]

Table 2. Ultraviolet data for some conjugated dienes

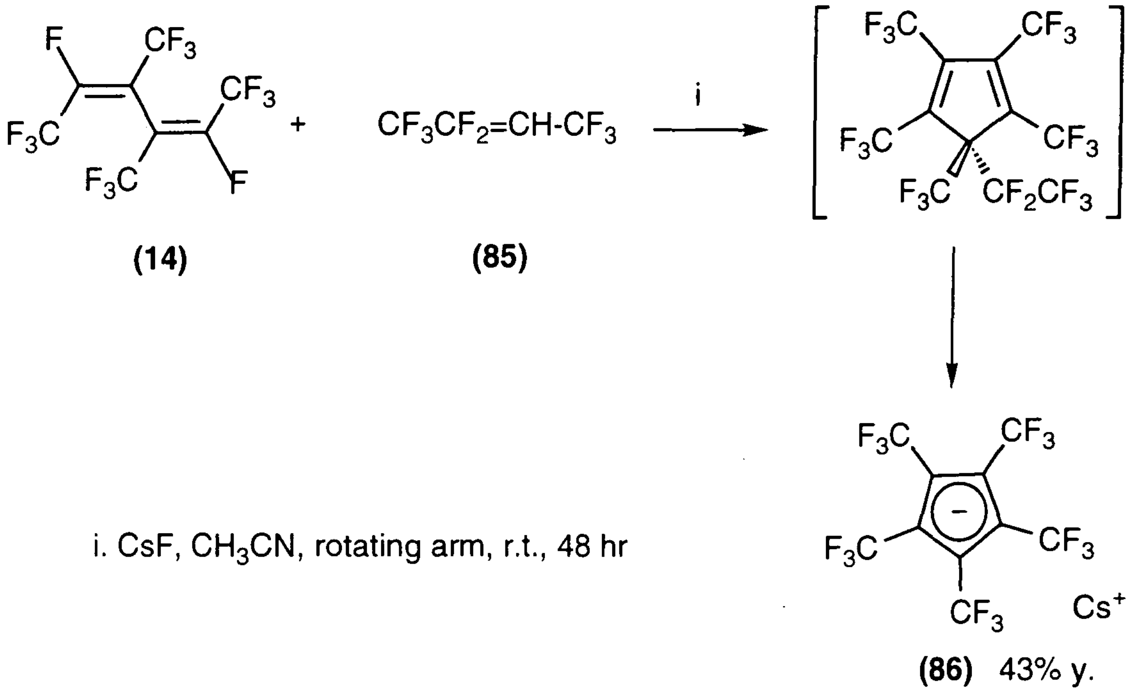
Diene	Π→Π* Transition	
	λmax/nm	ε/dm³ mol⁻¹ cm⁻¹
$CH_2=CH-CH=CH_2$	217	21 000[189]
	256	8 000[189]
$CF_2=CF-CF=CF_2$	206	2 800[190]
 **(14)**	234	272[191]
 **(99)**	277	18 800[191]
 **(12)**	278	10 900[191]
 **(96)**	253	1674[191]
	252	4140[224]
 **(75)**	253	500*

* For synthesis see **Section III.5**

The double bonds in butadiene are in the same plane, which allows maximum overlap of the *p* orbitals (*i.e.* conjugation). However, with hexafluoro-1,3-butadiene the double bonds are forced out of planarity into a skew-cis structure,[190] which decreases the *p* orbital overlap and, therefore, the conjugation. Diene **(14)** has four sterically demanding CF_3 groups and, as a result, may adopt an energy minimised *skew-cis* conformation. This is supported by an extremely low extinction coefficient, which stems from the fact that the double bonds are far less conjugated than in hexafluoro-1,3-butadiene. The high extinction coefficients of dienes **(99)** and **(12)** are due to the decreased bond angle causing a reduction in interaction between the cyclo-alkyl groups.[137] The exceedingly low extinction coefficient of **(75)** can also be explained in terms of energy minimisation by distortion of planarity.

IV.3. Synthesis of Pentakis(trifluoromethyl)cyclopentadienide Salts (With Dr. J. F. S. Vaughan)

Mullins[184, 205] has demonstrated that diene (**96**) will undergo a cesium fluoride catalysed reaction with 2*H*-heptafluoro-2-butene (**85**) to give a moderate yield of the cesium pentakis(trifluoromethyl)cyclopentadienide salt (**86**). Purification of the material was never possible and ^{19}F NMR data and FAB-MS of both the anion and the cation were the only method of characterisation. The reaction appears to proceeded via pentafluoroethylpentakis(trifluoromethyl)cyclopentadiene.

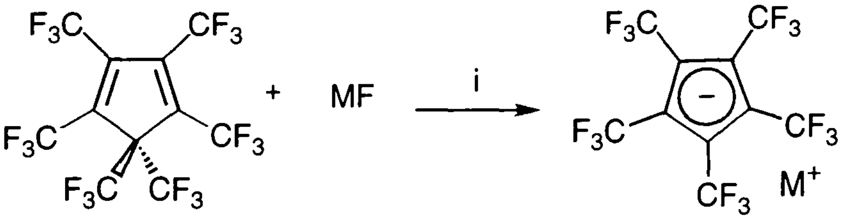


i. CsF, CH_3CN, rotating arm, r.t., 48 hr

IV.3.A. Reaction of Cyclic Diene (96) with Metal Fluorides

The proposed intermediate diene involved in the formation of (**86**) provides an indication of the methodology which may be required to synthesis cyclopentadienide derivatives of (**96**).

Cyclic diene (**96**) reacts with cesium fluoride and potassium fluoride to give the corresponding cyclopentadienide salts of (**84**) in moderate yield by ^{19}F NMR, with a single distinguishing pentakis(trifluoromethyl)cyclopentadienide anion peak at *ca.* δ_F -49ppm (s).



(96) i. CH_3CN, reflux, 48 hr (84)

M = K 39% y.
Cs 48% y.

An off-white solid was isolated from the reaction mixtures and FAB-MS revealed both potassium and cesium cations, as well as the characteristic anion peak at [M^+ 405], confirming the identity of both salts. The compounds were difficult to purify and were unstable over a period of days, making full analysis difficult.

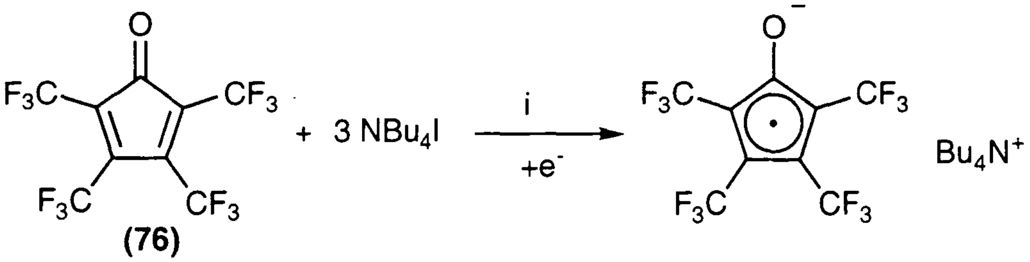
IV.3.B. Reaction of Cyclic Diene (96) with Tetraalkylammonium Iodides

In order to try to isolate pure salts of **(84)** an approach was required which took into consideration a number of factors:-

i. cyclopentadienide **(84)** should be quite stable since we have five symmetrically arranged trifluoromethyl groups to stabilise the negative charge; and

ii. large, organic, counter ions should provide the most stable salts of **(84)**.

Burk and co-workers[202] have described the synthesis of cyclopentadienide systems bearing multiple trifluoromethyl substituents. Reaction between tetrabutylammonium iodide and tetrakis(trifluoromethyl)cyclopentadienone **(76)** gave the tetrabutyl ammonium radical anion salt in good yield. The species can exist for up to two days in dry dichloromethane.

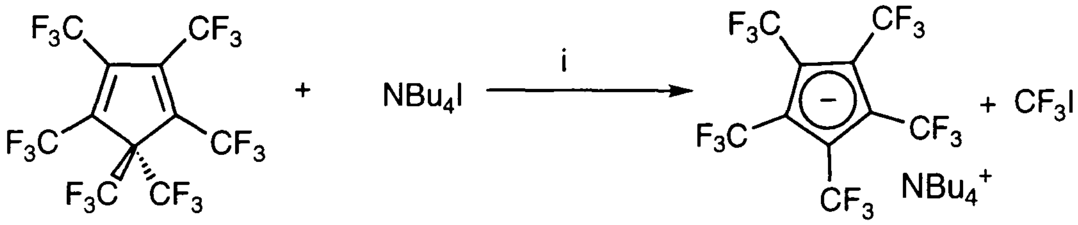


(76)

i. CH_2Cl_2, 25°C, 20 mins 62% y

Iodide ion is a powerful reducing agent (E^o for the couple I/I^- is 0.89 V),[225, 226] and so easily transfers an electron to the ketone to give the radical anion.

Reaction of **(96)** with tetrabutylammonium iodide, under reflux, provides a simple method of obtaining the corresponding tetrabutylammonium salt **(87)**.



(96) i. CH_3CN, reflux, 48 hr **(87)**

70% y.

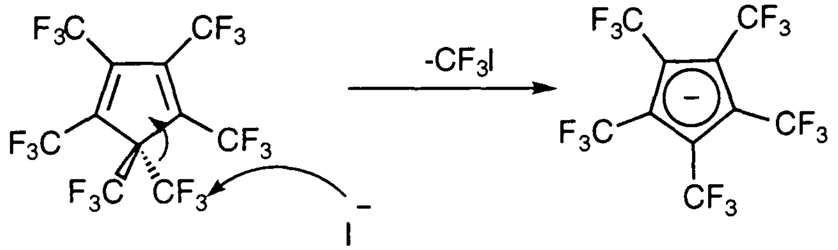
The by-product of the reaction, trifluoromethyl iodide, can be observed at δ_F -16ppm by ^{19}F NMR when the reaction is performed in a sealed quarts NMR tube, again the anion **(84)** shows a single peak at δ_F -49ppm (s). FAB-MS revealed both the anion [M^+ 405, 100%] and the cation [M^+ 242, 23%]. The salt was isolated by recrystalisation from dichloromethane and hexane to give the first isolated example of a pentakis(trifluoromethyl)cyclopentadienide salt in good yield. Full analysis, including microanalysis, was obtained.

Crystals of **(87)** were submitted for x-ray analysis and a full crystal structure obtained. Results pertaining to the crystallographic study of **(87)** will be discussed in **Chapter Five,** together with those of other salts.

111.3.C. Mechanism of Pentakis(trifluoromethyl)cyclopentadienide Salt Formation

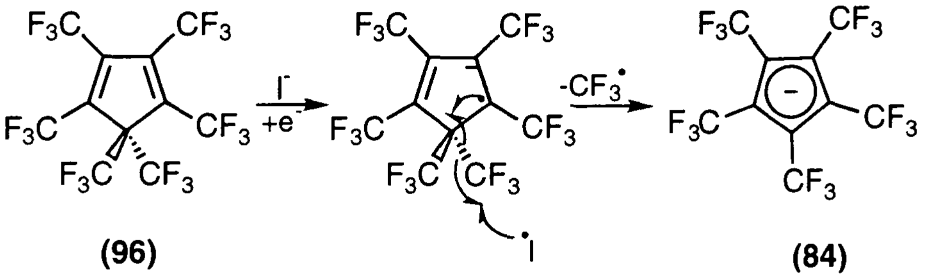
There are two possible mechanisms for this reaction of tetrabutylammonium iodide with **(96)**;

(a) Since the pentakis(trifluoromethyl)cyclopentadienide anion is exceedingly stable, it is a good leaving group and so a simple S_N2 nucleophilic displacement reaction mechanism does not seem unreasonable, and is supported by the fact that cesium fluoride can promote loss of CF_3 from **(96)**.



(96) **(84)**

(b) The second possible mechanism is a radical one and involves transfer of an electron from iodide ion to the diene to generate a radical anion and an iodine atom. The iodine atom then cleaves a geminal C-CF_3 bond, forming CF_3I and the aromatic pentakis(trifluoromethyl)cyclopentadienide anion **(84)**.



(96) **(84)**

In order to ascertain which mechanism is in operation, a small amount of radical inhibitor was added to the reaction mixture in order to try to inhibit radical reaction.

$$\textbf{(96)} + NBu_4I \xrightarrow[-CF_3I]{i} \textbf{(87)}$$

i. CH_3CN, reflux, 48 hr

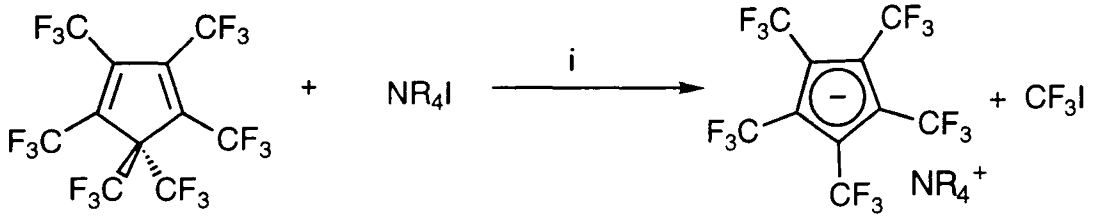
a. α-pinene 40% y.

b. *meta*-dinitrobenzene 60% y.

This significant inhibition, and the related result that the reaction rate is increased when it is performed under ultraviolet irradiation, points to a radical mechanism.

IV.3.D. Reaction of Cyclic Diene (96) with Other Tetraalkylammonium Iodides

Diene **(96)** also reacts with tetraethylammonium iodide and tetrapropylammonium iodide under similar conditions to give the corresponding tetraethylammonium **(100)** and tetrapropylammonium **(101)** pentakis(trifluoromethyl)cyclopentadienide salts.



(96) i. CH_3CN, reflux, 48 hr

R = Et **(100)** 75% y.
Pr **(101)** 73% y.

Crystals of both salts were grown using a similar procedure to that described for the tetrabutylammonium salt and full was analysis obtained. There are some interesting variations in physical properties between the salts. Whereas, the tetraethylammonium salt **(100)** crystallises as sharp needles, the tetabutylammonium salt **(87)** forms crystals which are cuboidal in nature. The melting points of the salts are also revealing, with

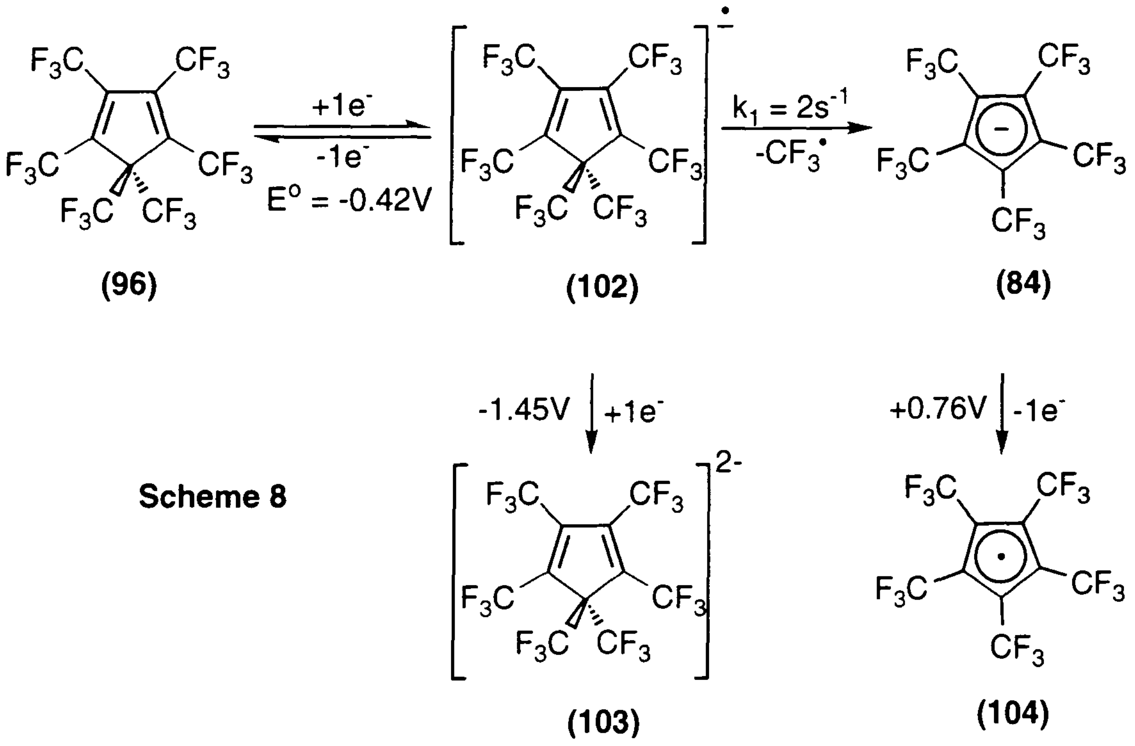
(100) having a boiling point 100°C higher than that of **(87)**. One possible reason for both these observations is that the tetrabutylammonium salt has a greater degree of distortion within the crystal, making efficient packing more difficult. Crystallographic data tends to confirm this, and will be discussed in **Chapter Five**.

IV.3.E. Electrochemical Reduction of Cyclic Diene (96) (With Dr. M. Médebielle, Universite Denis Diderot, Paris)

Formation of **(84)** can be observed upon reduction of cyclic diene **(96)** in an electrochemical cell.

The ease of electron-transfer to **(96)** is dramatically illustrated by the low reduction potential of -0.42 V (carbon electrode) under standard conditions (see experimental section). The rate constant of the decay of the radical anion **(102)** (**Scheme 8**) has been calculated as $k_1=2\ s^{-1}$ on the basis of an electrochemical mechanism. The formation of the unstable dianion **(103)** from **(102)** at -1.45 V was also observed and further illustrates the remarkable stabilising properties of trifluoromethyl groups on anionic sites.

Anion **(84)** can be oxidised to give the corresponding radical **(104)** by a potential of +0.76 V.



Scheme 8

For comparison with the reduction potentials of other fluorinated diene systems, **Table 3**, it has been established that **(96)** has a peak potential of -0.67 V using a platinum electrode.

Table 3. Reduction potentials of some perfluorinated dienes[224]

Diene	Epc (V vs SCE)*
(14)	-2.35
(99)	-2.25
(12)	-2.03
(96)	-0.67

* See experimental section

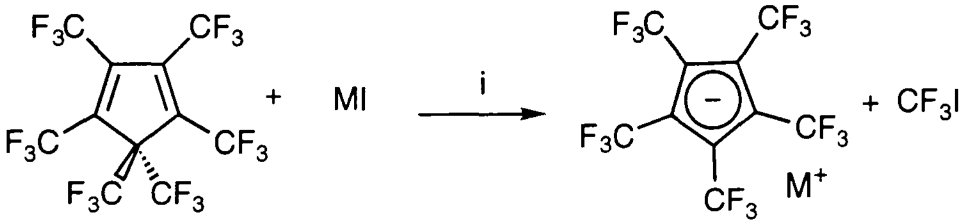
Irreversible oxidation of the cyclopentadienide **(84)** was observed at +0.76 V under standard conditions with a second irreversible oxidation step at a potential close to +0.90V. The rather high first oxidation step of **(84)** is consistent with the fact that it is a very poor nucleophile.

These result provides firm proof that chemical reduction of **(96)** to **(84)** can be achieved by single electron transfer.

IV.3.F. Reaction of (96) with Alkali Metal Iodides

As discussed in **Section IV.1.A.4.**, recent work in Durham has allowed the isolation of cesium pentakis(trifluoromethyl)cyclopentadienide, although it had been previously reported.[184, 205]

A range of alkali metal iodides will react with **(96)** to give the corresponding alkali metal cyclopentadienide salts.



(96) **(84)**

i. CH_3CN, reflux

Where $M^+ = Li^+, Na^+, K^+, Cs^+$

Table 4. Yield (^{19}F NMR) of alkali metal salts of **(84)**

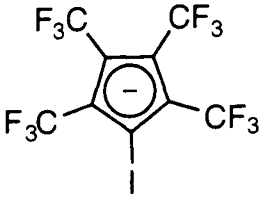
Metal Iodide	Duration of reaction (hr)	Crude yield (%)	Isolated yield (%)
LiI	36	95	17
NaI	48	95	22
KI	4 days	75	42
CsI	7 days	65	26

All salts revealed the characteristic single resonance at δ_F -49ppm (s) in their ^{19}F NMR spectra, indicating the presence of the anion **(84)**, and gave strong peaks for all cations and anions upon FAB-MS analysis. Isolation of alkali metal cyclopentadienide salts bearing electron withdrawing substituents is notoriously difficult.[203] The alkali metal salts of **(84)** are no exception. This is due to their solubility in a large range of both polar and apolar solvents. Isolation of the lithium and sodium salts was particularly difficult, possibly due to their intrinsic instability caused by the large difference in size between the cation and the anion. It is possible that the cations may even be solvated in both cases. All four alkali metal salts were isolated, however, by a combination of filtration, low temperature precipitation and column chromatography, although isolated yield were very low, in the cases of the lithium and sodium salts presenting just enough material for elemental analysis. Due to these difficulties further study of these salts was not considered viable.

It is interesting to note that as the atomic radius of the cation increases, so the rate of reaction decreases. This is simply a consequence of lattice energy.

CsI < KI < NaI < LiI
Reactivity

When cesium iodide or potassium iodide are used as the reducing agents, the ^{19}F NMR spectrum of the crude reaction mixture revealed formation of a second trifluoromethylated compound **(105)** in *ca.* 15% yield with peaks at δ_F -50.4ppm and δ_F -51.1ppm. By comparison of ^{19}F NMR data with that of other similar compounds,[227] **(105)** is thought to have the structure shown below.

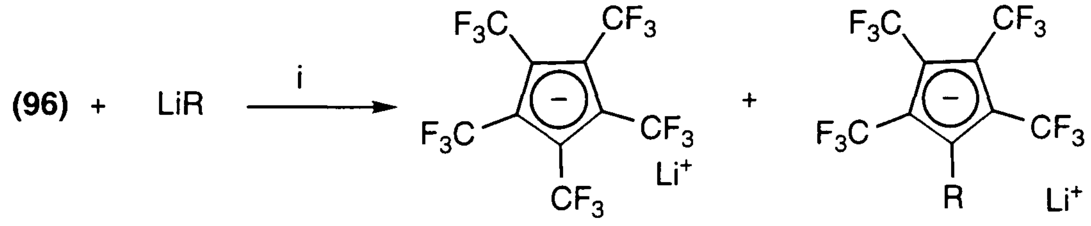


(105)

Attempts to isolate **(105)** were unsuccessful. Compound **(105)** is almost certainly formed via attack of atomic iodine on **(84)**.

IV.3.G. Reaction of Diene (96) with Alkyl and Aryl Lithium Compounds

Diene **(96)** appears to be an effective agent for transfer of the trifluoromethyl moiety. If **(96)** could transfer such a species to common organic systems, such as simple aromatics and aliphatics it could act as a model for the production of other trifluoromethylating reagents. Under dry nitrogen, a sealable round bottomed flask was charged with **(96)** and an excess of phenyl lithium and the mixture stirred for 4 hours at room temperature. ^{19}F NMR revealed formation of the pentakis(trifluoromethyl)cyclopentadienide anion **(84)** and a second product with two ^{19}F NMR peaks at δ_F -51.8ppm and δ_F -52.4ppm which are thought to correspond to structure **(106)**.



i. CH_3CN, r.t., 4 hr

(84) ca. 80% y.

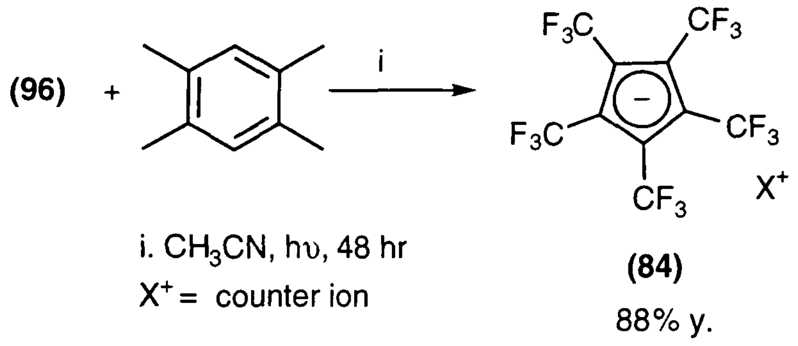
(106)

R = *t*-Bu, no formation of **(106)**
R = Ph, **(106)** formed in ca. 15% y.

The reaction was repeated using tertiary butyl lithium and pentakis(trifluoromethyl) cyclopentadienide was formed with no trace of the tertiary butyl analogue of **(106)**. This would tend to point to compound **(106)** as the product in the reaction with phenyl lithium, since the hindered tetrabutyl group will be unable to attack the pentakis(trifluoromethyl) cyclopentadienide anion.

IV.3.H. Reaction of (96) with Electron Rich Aromatics

Cyclic diene **(96)** should react with electron rich aromatics to give either the cyclopentadienide anion **(84)** or some simple derivative of it. Under ultraviolet irradiation, **(96)** reacts with durene, but none of the lower alkyl aromatics such as mesitylene.


(96) + → (84)

i. CH_3CN, hν, 48 hr

X^+ = counter ion

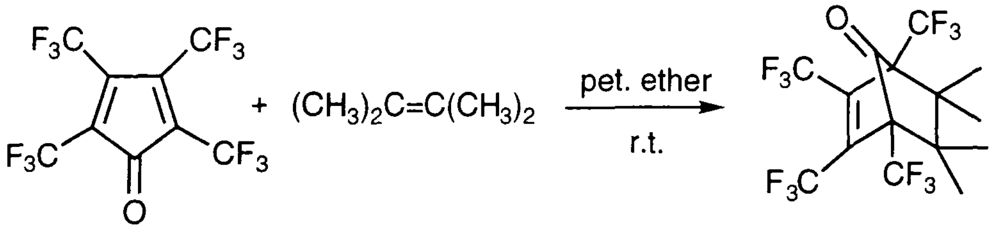
(84) 88% y.

The anion **(84)** could be clearly seen in the ^{19}F NMR spectrum (δ_F -49ppm), although the nature of the cation was not clear. Isolation was not possible.

Diene **(96)** does not react with the functionalised aromatics phenol and thiophenol. The failure of **(96)** to react with thiophenol is surprising and can only be due to the steric bulk of the trifluoromethyl groups.

IV.3.I. Attempted Cyclo-addition Reactions of Diene (96)

Tetrakis(trifluoromethyl)cyclopentadienone **(76)** readily reacts with electron rich alkenes, such as tetramethylethylene and cyclohexene, to give 'inverse electron demand'[228] [4+2] cycloadducts.[229]

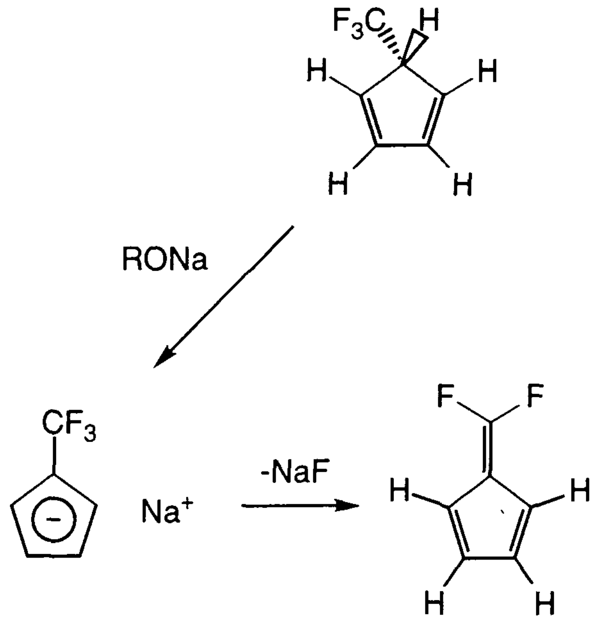

(76)

Diene **(96)**, despite being structurally similar to **(76)**, will not undergo such pericyclic reactions, even at elevated temperatures and with non-sterically demanding dienophiles, including ethylene, tetrafluoroethylene and cyclopentadiene. The reason for this must lie in the steric bulk of the geminal trifluoromethyl groups hindering attack.[223]

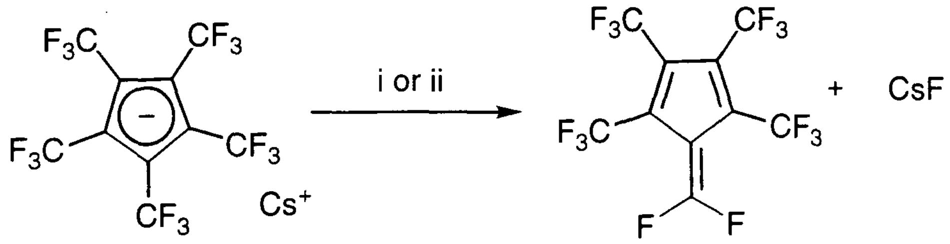
IV.4. Reactions of pentakis(trifluoromethyl)cyclopentadienide (84)

IV.4.A. Attempted Formation of Fulvene Derivative (107)

In 1986 Gassman and Winter reported the synthesis of difluorofulvene from sodium trifluoromethylcyclopentadienide.



Heating the cesium salt (**86**) under high vacuum failed to yield (**107**) by an analogous defluorination process. Similarly, addition of borontrifluoride etherate to (**86**) was also unsuccessful.



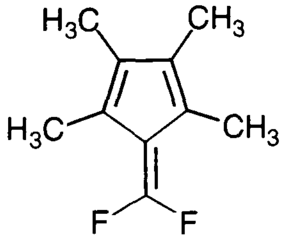
(86)

i. Δ, high vacuum
ii. BF_3-EtO_2

(107)

not formed

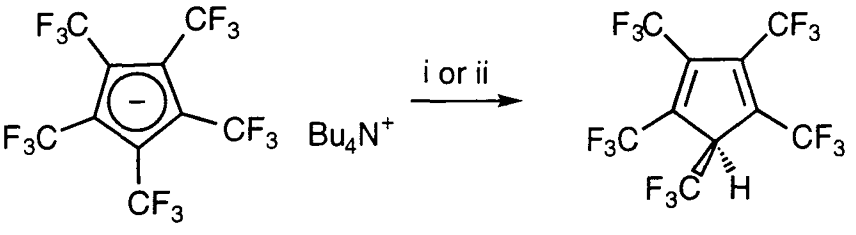
Further investigation by Gassman and co-workers[230] in 1996 on other fluorinated fulvenes, including the tetramethyltrifluoromethylcyclopentadienide derivative (**108**), led to the formulation of an additivity scheme for fluoride ion affinities in trifluoromethylated cyclopentadienides. It was concluded, on the basis of both experimental observations and theoretical study that as the number of trifluoromethyl substituents increases so the stability of the anion increases and its propensity to eliminate fluoride ion decreases, these predictions are consistent with our results.



(108)

IV.4.B. Formation of Pentakis(trifluoromethyl)cyclopentadiene (109)

A consequence of the intrinsic stability of pentakis(trifluoromethyl)cyclopentadienide is that exceedingly strong acids such as concentrated sulphuric acid or hydrogen fluoride are required for protonation to give carbon acid (**109**). Addition of 98% sulphuric acid to the tetrabutylammonium salt (**87**) gave (**109**) as a volatile liquid in 86% yield. Diene (**109**) is not stable and decomposes on standing, with vigorous etching of glass. Addition of hydrogen fluoride to (**87**), under vacuum, also gave (**109**).

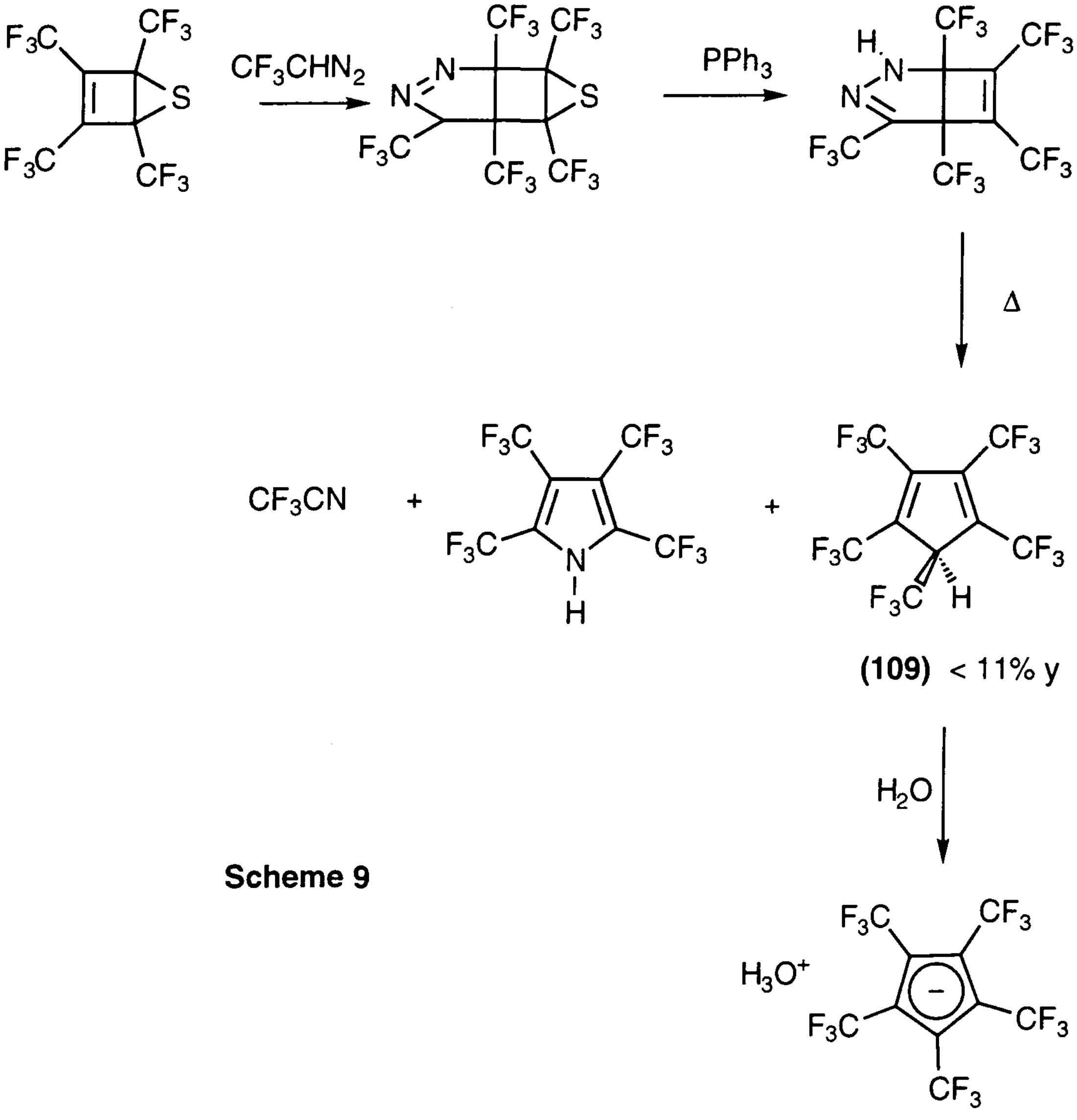


(87) i. Conc. H_2SO_4, vacuum
ii. HF

(109) ca. 86% y.

The product can be clearly identified by its ^{19}F NMR spectrum which shows three peaks in a 2:1:2 ratio at δ_F -56.0, δ_F -59.1 and δ_F -60.2 respectively. The molecular ion [M^+ 406] can also be seen upon GLC-MS analysis. Acid (**109**) is exceptionally strong, its pK_a has been estimated at -2[231] (cf. nitric acid, pK_a -1.2). It has also been claimed that in the gas state it is even stronger than triflic acid (Ho -14.1; 110 times stronger than concentrated sulphuric acid).[230]

A previous synthesis of (**109**) by Laganis and Lemal[231] was via the much more complicated route shown in **Scheme 9.**



(109) < 11% y

(84)

Scheme 9

IV.4.C. Reaction of (84) with Electrophiles

As discussed previously, cyclopentadienide **(84)** is an exceedingly poor nucleophile and as a consequence does not react with common electrophiles such as ethanoyl chloride, methyl iodide or acetyl bromide.

IV.5. Conclusion

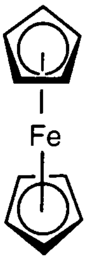
An efficient synthesis of hexakis(trifluoromethyl)cyclopentadiene **(96)** has been reported and a range of tetraalkylammonium and alkali metal salts of pentakis(trifluoromethyl)cyclopentadienide **(84)** prepared from it. It has been established that **(84)** can be formed from **(96)** by single electron transfer and that **(96)** is a potent electron acceptor. Consequently anion **(84)** is a very poor nucleophile and reacts only with exceptionally strong acids to give a direct route to pentakis(trifluoromethyl)cyclopentadiene **(109)**.

CHAPTER FIVE

Pentakis(trifluoromethyl)cyclopentadienyl Transition Metal Complexes

V.1. Introduction

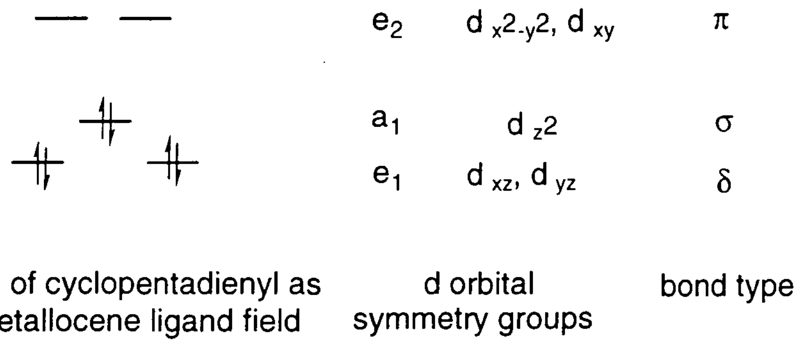
The birth of cyclopentadienyl transition metal chemistry occurred in 1951 when Pauson and Kealy[232] discovered complex **(110)**, later characterised as bis(η^5-cyclopentadienyl)iron, or ferrocene.



(110)

The introduction of substituents into the cyclopentadienyl backbone is well known to dramatically affect the reactivity of transition metals bearing these ligands.[1, 200, 233] Whilst complexes of electron rich derivatives, such as pentamethylcyclopentadienyls, have been extensively studied metal centres that contain cyclopentadienyl groups bearing electron withdrawing substituents remain relatively unexplored.

One reason for this is that cyclopentadienyl complexes which are completely substituted with electron withdrawing groups are generally unstable and synthesis of such systems is notoriously difficult. This is due to several important factors.[234, 235]



Scheme 1

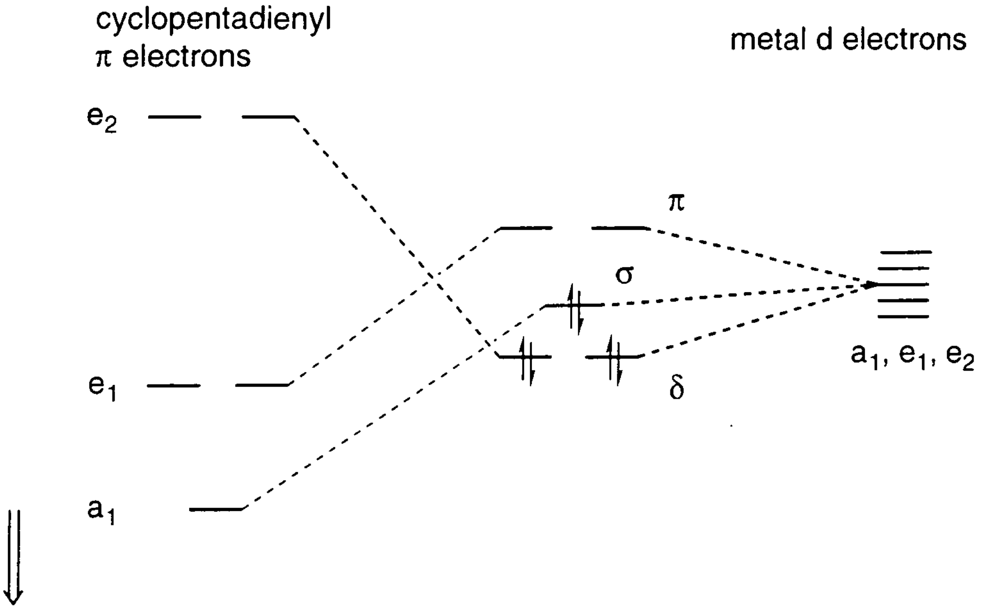
A pentahapto (covalent) bond between a cyclopentadienyl ring and a transition metal has several components, refer to **Scheme 1**:-

i. a σ bond resulting in donation of an electron pair from the filled cyclopentadienyl ring a_1 orbitals with no nodes to an empty metal orbital with appropriate symmetry;

ii. two orthogonal π bonds resulting in donation of electron pairs from the two filled orthogonal cyclopentadienyl ring e_1 orbitals into an empty metal orbital with appropriate symmetry; and

iii. up to two orthogonal δ bond resulting in back donation of electrons from metal orbital with appropriate symmetry into the two cyclopentadienyl ring e_2 orthogonal orbitals.

Complete substitution of cyclopentadienyl hydrogens with electron withdrawing groups, such as cyano, alkoxy carbonyl and perfluoroalkyl should lead to removal of electron density from the filled ring a_1 and e_1 orbitals lowering them in energy to the extent that stable pentahapto ring-metal bonds are no longer possible, see **Scheme 2**.



With electron withdrawing substituents the energy level of the a_1 ligand orbital is dramatically lowered in energy so as to make covalent bonding difficult .

Scheme 2. Simplified molecular orbital diagram for ferrocene (only metal d orbitals are shown).

This appears to be the case. Reaction between pentacyanocyclopentadienide and ferrous chloride gives an ionic iron (II) pentacyanocyclopentadienide salt rather than decacyanoferrocene[209] and later studies of the reactions of pentakis(methoxycarbonyl)cyclopentadiene gave similar results.[211, 236]

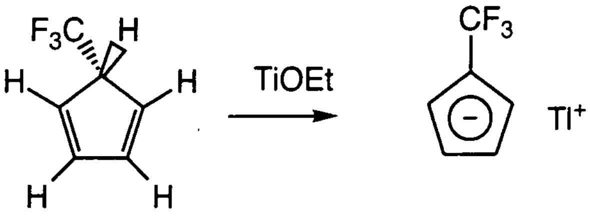
However, the formation of decachloroferrocene and some covalent complexes of pentakis(methoxycarbonyl)cyclopentadienyl (see **Section V.1.A.2.**) in recent years suggests that failure to produce such species may have been a consequence of the low nucleophilicity of the precursor cyclopentadienide salts rather than the intrinsic instability of the ring-metal bond.

Previous syntheses of electron deficient cyclopentadienyl complexes are reviewed below.

V.1.A. Electron Deficient Cyclopentadienyl Complexes

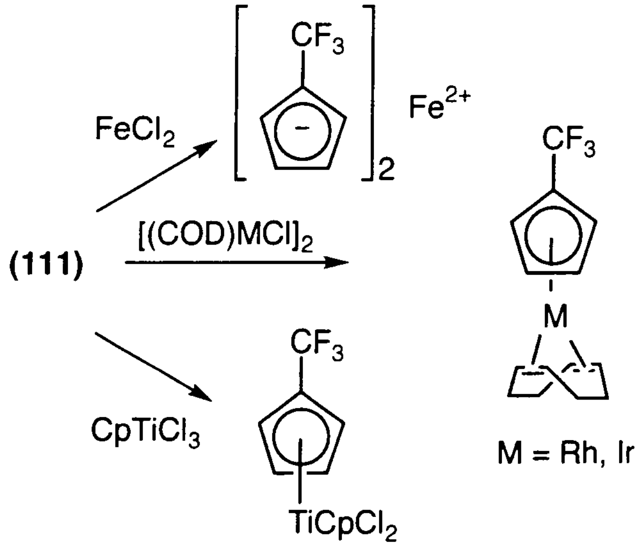
V.1.A.1. Trifluoromethylated Cyclopentadienyl Complexes

In 1986 Gassman and Winter[237] first synthesised thallium trifluoromethylcyclopentadienyl (**111**).

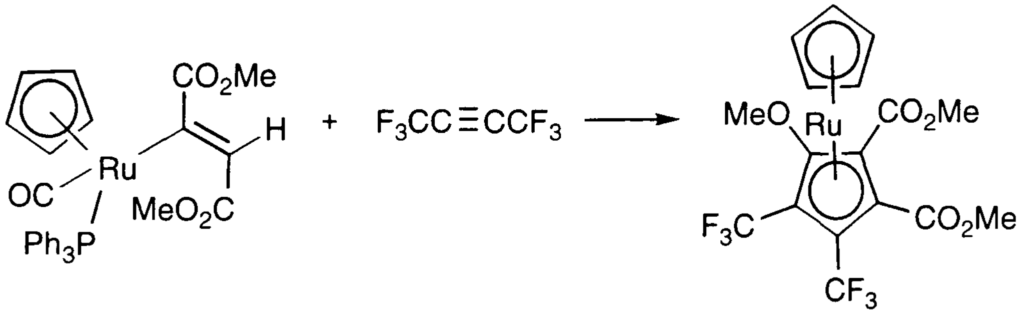


(111)

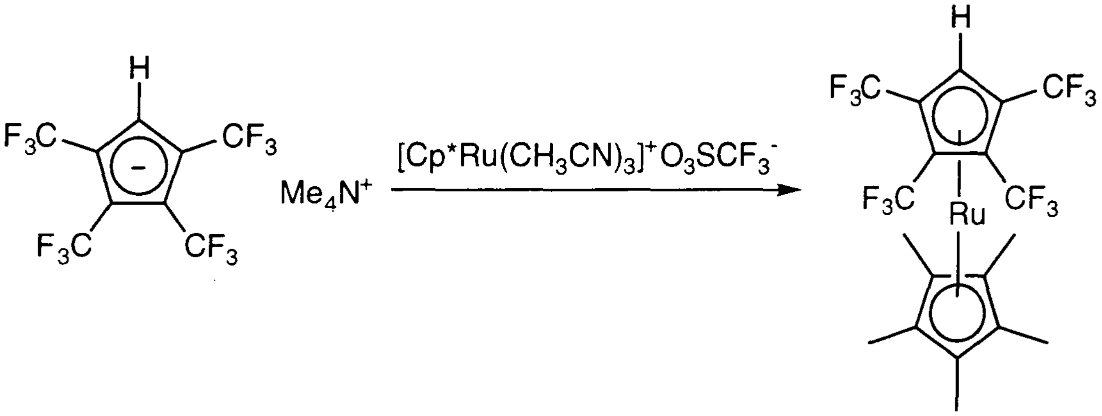
Basola and Cheong[238] have used (**111**) as a synthon for a variety of transition metal complexes. The thallium salt is used in preference to more conventional metal salts, such as the alkali metals, because of the *pseudo*-covalent nature of the cation-anion interaction.



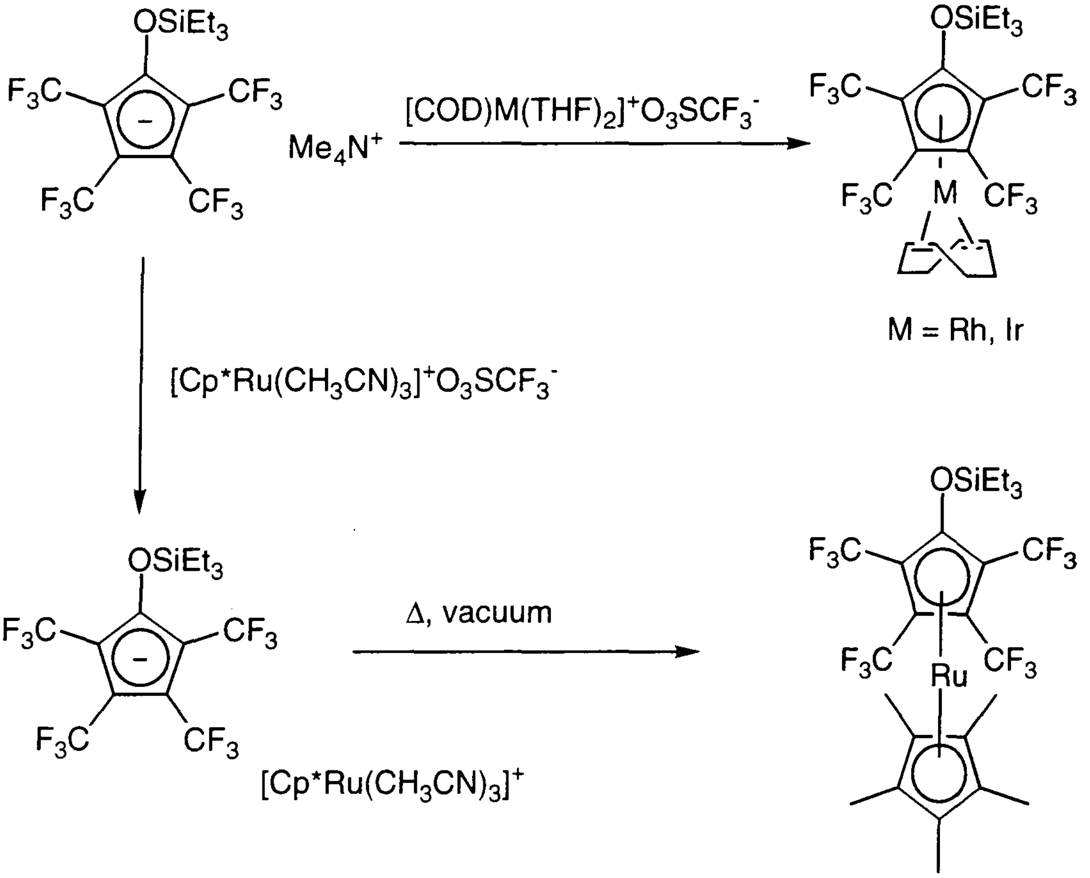
Bruce and co-workers[239] reported the only example of a cyclopentadienyl ligand bearing two trifluoromethyl groups when they achieved the remarkable ligand cyclisation shown below.



The only other reported use of a trifluoromethylated cyclopentadiene derivative as a transition metal ligand was by Burk and co-workers[240] who used the tetrakis(trifluoromethyl)cyclopentadienyl group as a ligand for ruthenium by displacement of acetonitrile. Because of the poor nucleophilicity of the ligand use of electrophilic, highly solvated metal cations is important in such reactions and attempts to displace halides from transition metals by reaction with the anion were ineffective. However, replacement of weakly bound solvent ligands was more successful.



Triethylsiloxytetrakis(trifluoromethyl)cyclopentadiene can also form a number of transition metal complexes in a similar manner, as shown in **Scheme 3**. The use of, highly electrophilic, solvated metal cations in these reactions is again important, due to the instability of the products.



Scheme 3

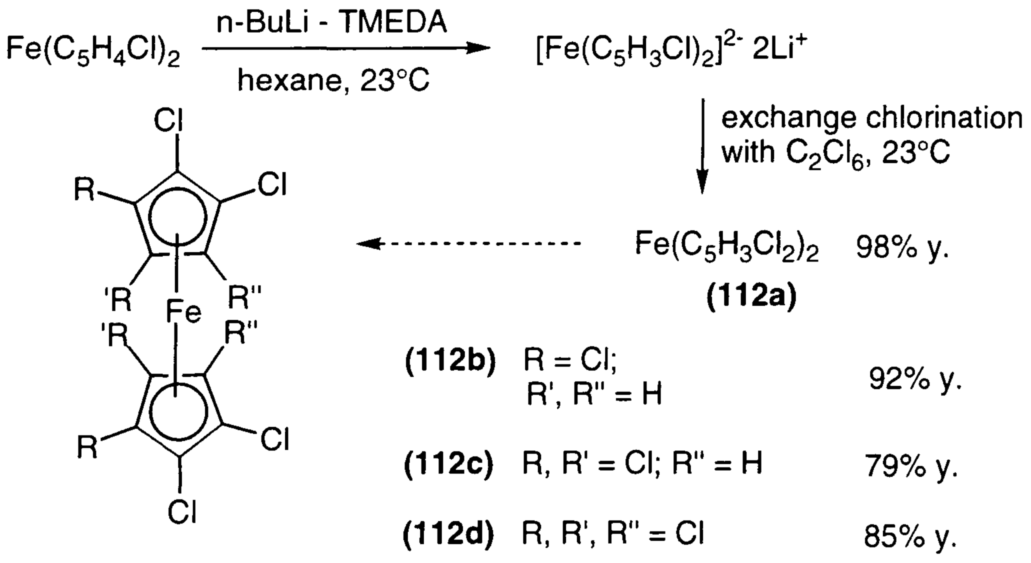
Ligand substitution studies[240] indicate that the Cp*Ru($C_9F_{12}OSiEt_3$) complex is stable to attack by CH_3CN, CO and $P(CH_3)_3$ and is resilient to heating up to 80°C. This is thought to be due to the steric bulk around the Ru centre rather than inherent ligand-metal bond strength since reaction of the less hindered (COD)M($C_9F_{12}OSiEt_3$) systems with two equivalents of PPh_3 led to a clean displacement of the five membered ring.

The electrochemical oxidation potential of Cp*Ru($C_9F_{12}OSiEt_3$) was measured at 1.58eV.[240] This is 1.03eV more positive than that recorded for decamethylruthenocene and indicates the strong electron withdrawing power of the ligand. Interestingly, Cp*Ru($C_9F_{12}OSiEt_3$) is also fluorocarbon soluble to the extent of 12mg/ml in perfluorohexane; the non-fluorinated analogue decamethylruthenocene is essentially insoluble in this solvent. These attributes may be important in constructing transition metal catalysts which are both resistant to oxidation and fluorocarbon soluble.

In many of the examples shown above the capacity of large metal cations, such as ruthenium, to bind to these inherently weak ligand should be noted. This phenomenon may be due to the inherent 'softness' of the metal providing an adequate surface for the ligand to bind, allied to a greater willingness to form covalent bonds.[1]

V.1.A.2. Polychlorinated Cyclopentadienyl Complexes

Interest in these compounds was first fuelled by attempts to produce oxidation resistant metallocenes. Pioneering work by Hedberg[241] led to the synthesis of the chlorinated ferrocenes shown in **Scheme 4**.

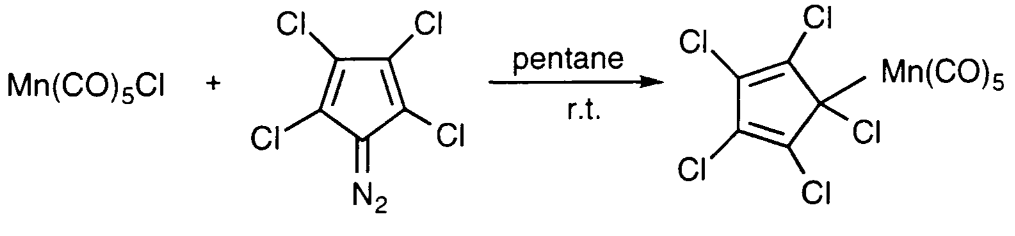


Scheme 4

The anticipated increase in stability towards oxidation in the higher polychlorinated ferrocenes was apparent, with **(112c)** and **(112d)** being unaffected on heating to 100°C in concentrated nitric or sulphuric acid.

The corresponding ruthenocene derivatives were also synthesised by an analogous route and a crystal structure of decachlororuthenocene obtained.[242]

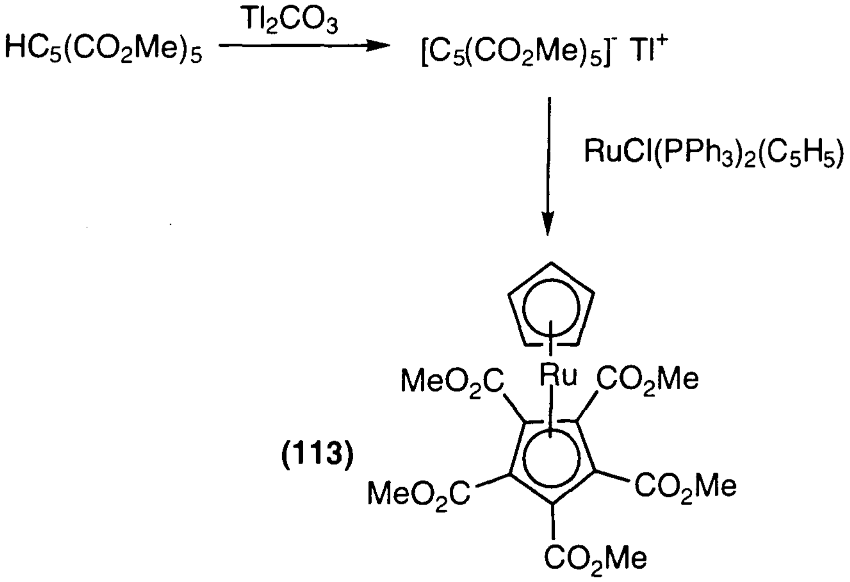
The novel σ bonded, air stable, η^1-complex $(C_5Cl_5)(CO)_5Mn$ has been reported and its crystal structure solved.[243]



A related η^5- complex $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$ has also been synthesised by Wrighton.[244]

V.1.A.3. Pentakis(methoxycarbonyl)cyclopentadienyl Complexes

Preparation of some ruthenium and rhodium based covalently bonded complexes has been accomplished.[245, 246]

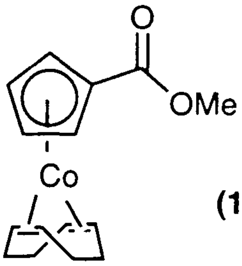


(113)

The corresponding rhodium complex was obtained using the same methodology. The formation of **(113)**, which was confirmed by crystal structure, tends to indicate that, contrary to accepted understanding, cyclopentadienyl complexes which are fully substituted with electron withdrawing groups can be made. However, the inherent instability of such systems is implied by the ready loss of the ligand from **(113)** on contact with triphenylphosphine.

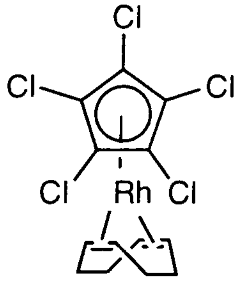
V.1.B. Uses of Cyclopentadienyl Complexes Bearing Electron Withdrawing Substituents

In 1985 Bonnemann[247] catalysed the cyclo-trimerisation of two acetylenes and a nitrile to give a variety of pyridine derivatives using transition metal cyclopentadienyl systems. It was demonstrated that an electron poor cyclopentadienyl moiety, such as that in **(114)**, enhanced catalytic performance.



(114)

Booth and co-workers[248] also found that rhodium catalysts bearing electron deficient cyclopentadienyl ligands, such as **(115)**, gave the fastest rates for hex-3-yne cyclo-trimerisation.

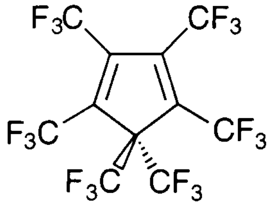


(115)

V.2. Reaction of Hexakis(trifluoromethyl)cyclopentadiene (96) with Transition Metals

V.2.A. Introduction

As discussed in **Chapter Four** hexakis(trifluoromethyl)cyclopentadiene (**96**) has a reduction potential of -0.42eV and is therefore susceptible to electron capture from oxidising agents, such as iodide ion. This chapter will be concerned with reduction of (**96**) by transition metal species, to give some interesting pentakis(trifluoromethyl)cyclopentadienide species.

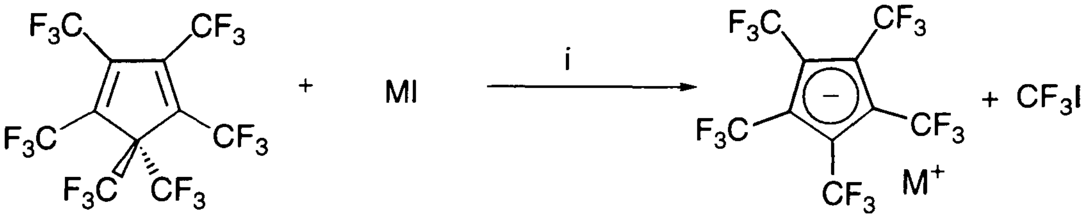


(96)

V.2.B. Reaction of Cyclic Diene (96) with Copper (I) Iodide and Silver (I) Iodide

In general, copper (I) compounds have more covalent character than their group 1 counterparts.[1] It was therefore hoped that a copper (I) pentakis(trifluoromethyl)cyclopentadienide complex would display a degree of pentahapto bonding.

Extension of the methodology used in **Chapter Four** led to the observation that whilst copper (I) iodide and silver (I) iodide are not strong enough reducing agents to effect conversion of (**96**) to pentakis(trifluoromethyl)cyclopentadienide (**84**) thermally, ultraviolet irradiation under a medium pressure mercury lamp, in acetonitrile, gave copper and silver salts of (**84**) in good yield.



(96) i. CH_3CN, uv light, 48 hr

M = Cu **(116)**; 88% y.
Ag **(117)**; 85% y.

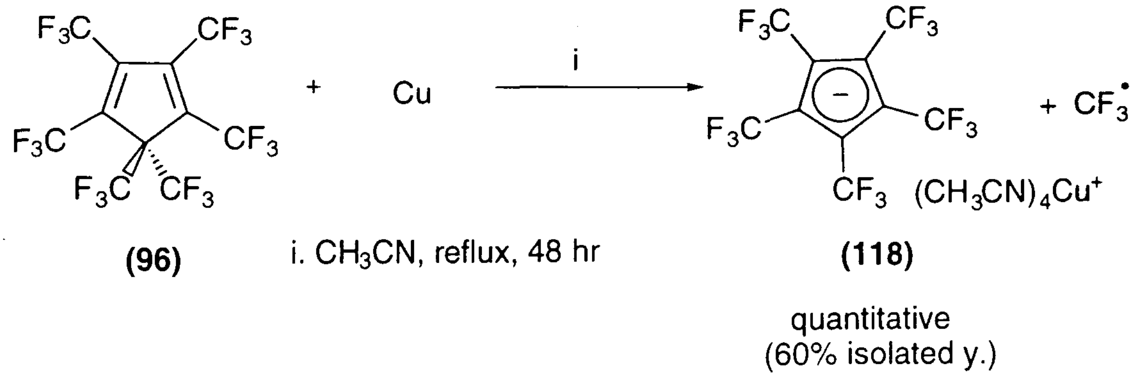
Although the salts **(116)** and **(117)** were observed in high yield, by ^{19}F NMR integration, both showing the characteristic pentakis(trifluoromethyl)cyclopentadienide anion resonance at *ca.* δ_F -49ppm (s), they could not be fully characterised due to the difficulty of isolation. In order to try to isolate these potentially significant transition metal salts another method of preparation was required.

V.2.C. Reaction of Cyclic Diene (96) with Copper Powder

Copper metal has a single electron outside the filled 4d shell, but cannot be classed in group 1 of the periodic table, since it has little in common with the alkalis except formal stoichiometries in the +1 oxidation state. The filled d shell is much less effective than is a noble gas shell at shielding the s electron from nuclear charge, so that the first ionisation enthalpy of copper is much higher than those of the alkalis.[1]

metal cation	reduction potential
Na^+	-2.698
K^+	-2.925
Cs^+	-2.952
Cu^+	+0.521

Addition of powdered copper metal to a refluxing solution of cyclic diene **(96)** in acetonitrile gives the solvated copper salt **(118)** in quantitative yield.



(96) i. CH_3CN, reflux, 48 hr **(118)**

quantitative
(60% isolated y.)

The trifluoromethyl radical produced as a by-product of the reaction attacks acetonitrile to give a number of species, detectable by ^{19}F NMR, one of which was identified as trifluoromethane (δ_F -78.3ppm, d, *J* 80Hz). Compound **(118)** was isolated by filtration of unreacted copper and, after removal of solvent, recrystalisation from dichloromethane gave the stable product. The FAB-MS spectrum of the cation in **(118)**, shown in **Figure 1**, was extreme revealing and intuitively provided the exact structure of the salt.

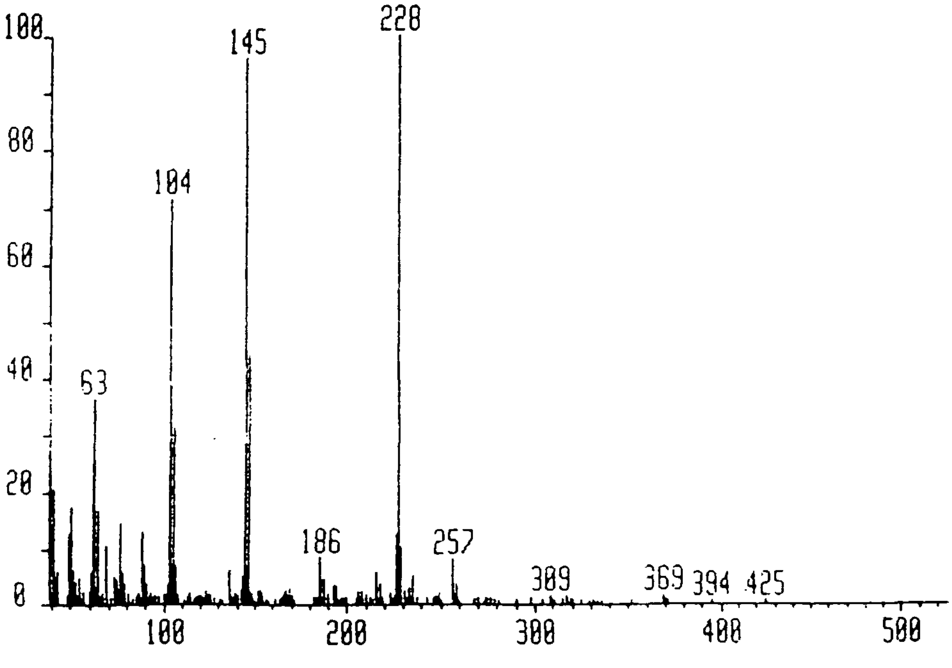


Figure 1. FAB-MS of salt **(118)**

Not only can the copper atom be clearly seen, but peaks pertaining to the $Cu^+(CH_3CN)$ *(104)*, $Cu^+(CH_3CN)_2$ *(145)*, $Cu^+(CH_3CN)_3$ *(186)* and $Cu^+(CH_3CN)_4$ *(228)* fragments are also evident. The ^{19}F NMR spectrum of **(118)** revealed the characteristic pentakis(trifluoromethyl)cyclopentadienide anion peak at δ_F -49ppm (s) and both ^{13}C

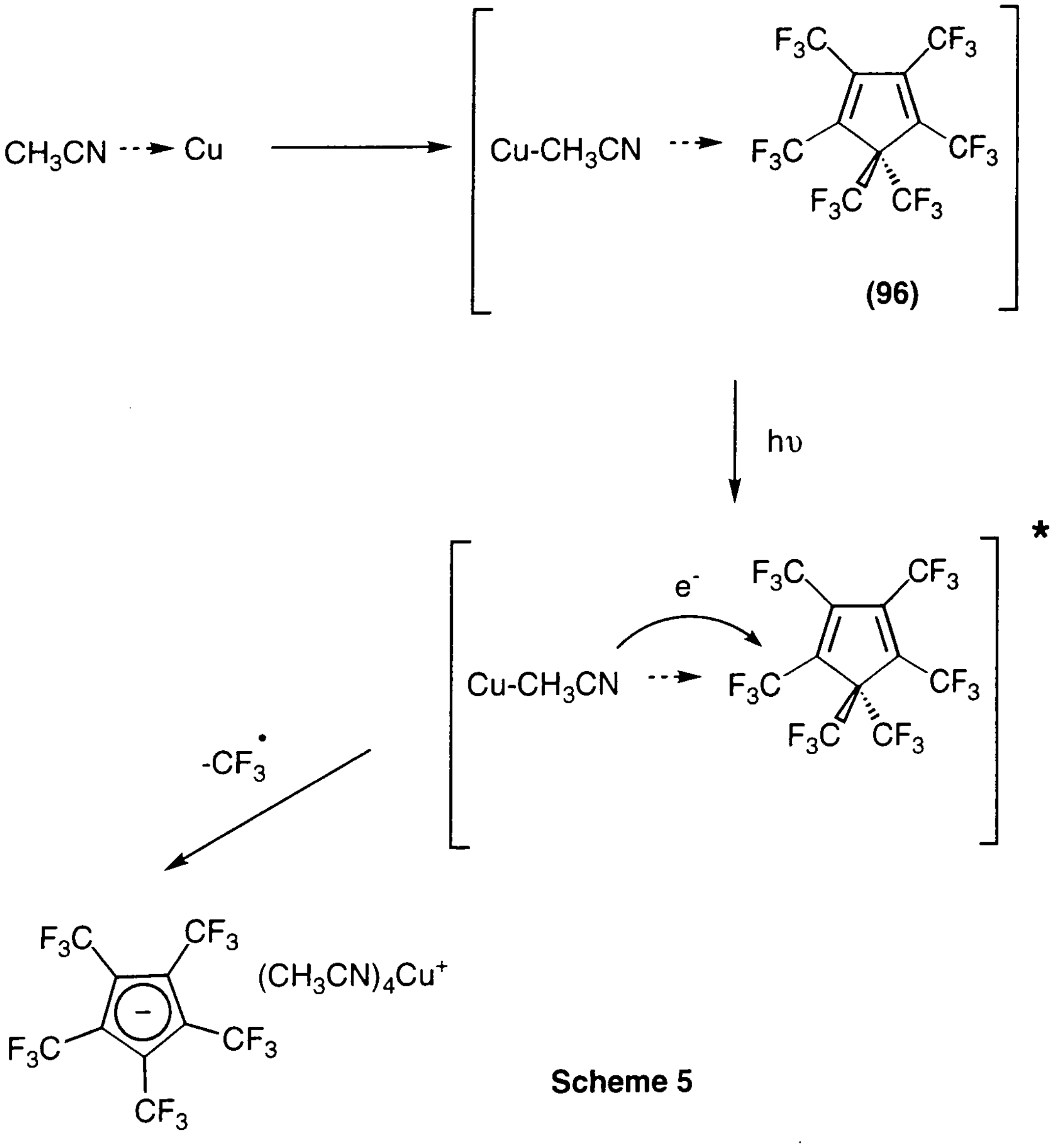
and ^{1}H spectra, as well as micro-analysis, were consistent with the tetra-solvated structure shown. The crystal structure of **(118)** will be discussed in **Section V.2.E**.

The use of acetonitrile as the solvent in the reaction appears to be crucial since in other media, such as tetrahydrofuran, diethyl ether, hexane, benzonitrile and nitromethane no reaction was observed. In ammonia attack of the solvent upon **(96)** led to various ill-defined products, including anion **(84)**. These findings are surprising since acetonitrile solvates **(96)** only sparingly.

The role of acetonitrile can be explained in terms of the known ability of nitrogen donor solvents, especially acetonitrile, to stabilise copper (I) species. Copper halides have exceedingly high solubility in acetonitrile (*e.g.* CuI 35g per Kg CH_3CN) and the tetrahedral ion $Cu^+(CH_3CN)_4$ has previously been isolated in salts with large anions (e.g. ClO_4^-, and PF_6^-).[1, 249]

It is therefore concluded that the reaction mechanism must involve complexation of **(96)** with the surface of the metal, which is sufficiently stabilised by acetonitrile to allow excitation and subsequent electron transfer.

The full mechanism is given in **Scheme 5**.

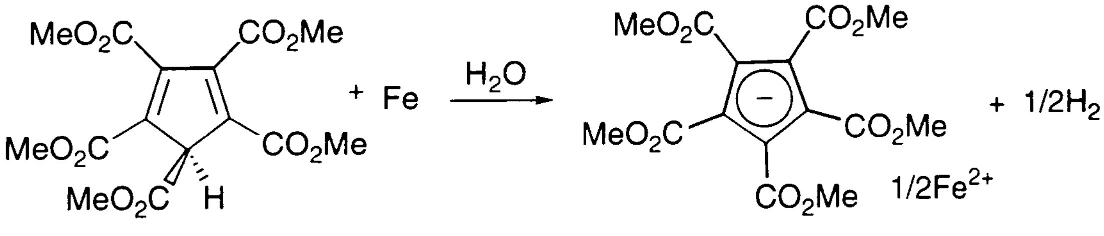


(96)

(118)

Scheme 5

The only other literature example of a transition metal effecting the reduction of a cyclopentadiene is the reaction of iron with pentakis(methoxycarbonyl)cyclopentadiene (**93**) to give the corresponding cyclopentadienide (**95**).



(93) **(95)**

The product was ill-characterised, however, and described as a ferrous salt rather than ferrocene.

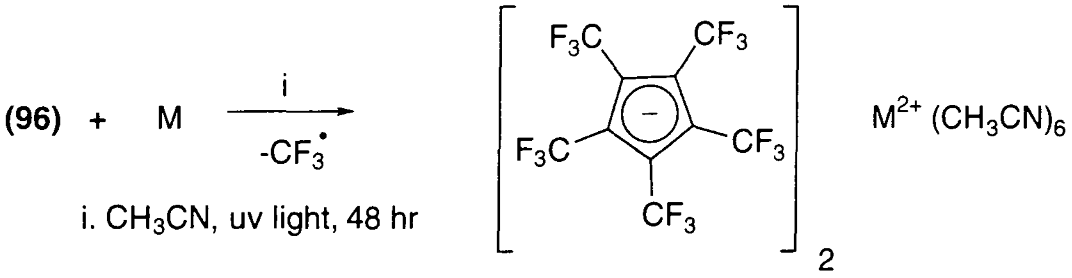
V.2.D. Reaction of Cyclic Diene (96) with Other Transition Metal Powders

Other first row transition metals are generally more easily oxidised than copper, and should therefore react with **(96)** in a similar manner, as shown in **Table 1**.

Table 1. Electronic configuration of some transition metals

Metal	Electronic structure	Most stable cation	Reduction potential
Fe	$3d^6, 4s^2$	Fe^{2+}	-0.440
Co	$3d^7, 4s^2$	Co^{2+}	-0.28
Ni	$3d^8, 4s^2$	Ni^{2+}	-0.23
Cu	$3d^{10}, 4s^1$	Cu^+	+5.21

Surprisingly, however, copper appears to be unique in reacting with **(96)** thermally, because ultraviolet irradiation is required to generate hexa-solvated iron (II), cobalt (II) and nickel (II) salts of the pentakis(trifluoromethyl)cyclopentadienide anion **(84)** in acetonitrile.

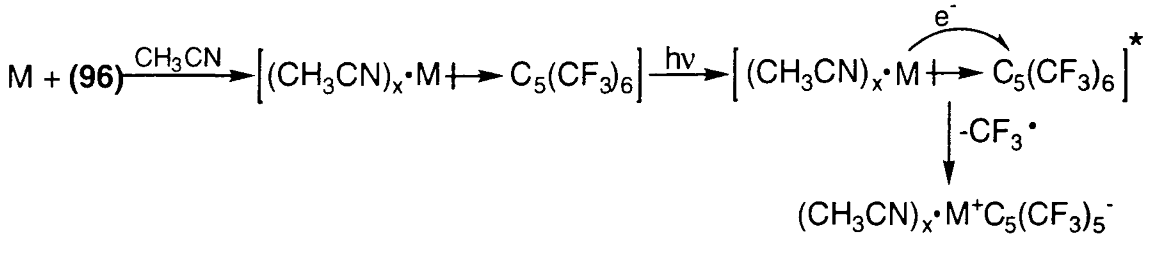


i. CH_3CN, uv light, 48 hr

Metal (M)	Salt	Yield
Ni	$(CH_3CN)_6Ni^{2+}[C_5(CF_3)_5]_2$ **(119)**	62%
Co	$(CH_3CN)_6Co^{2+}[C_5(CF_3)_5]_2$ **(120)**	76%
Fe	$(CH_3CN)_6Fe^{2+}[C_5(CF_3)_5]_2$ **(121)**	74%

The products were isolated by canular filtration of unreacted metal, under dry nitrogen, and pipetting off of unreacted **(96)** as a lower layer. Subsequent removal of solvent under reduced pressure gave the pure compound, as a powder, in good yield. The iron (II) pentakis(trifluoromethyl)cyclopentadienide salt **(121)** and the cobalt (II) pentakis(trifluoromethyl)cyclopentadienide salt **(120)** were very unstable, decomposing in air after a few hours. The nickel (II) pentakis(trifluoromethyl)cyclopentadienide salt **(119)** showed greater stability, however, and could be stored for up to two days without significant decomposition. The hexa-solvated cation structures shown are consistent with the known preferred co-ordination spheres of the dications of all three metals[1, 235] and was confirmed by microanalysis. The visible appearance of the salts was also revealing, with all showing the familiar colouring of their hexa-co-ordinated metal dications; cobalt (pale blue), nickel (pink) and iron (white).[1]

Once again acetonitrile is important in the formation of these compounds, with no reaction of **(96)** in a wide range of both co-ordinating and non co-ordinating solvents under the same conditions. The reactions proceed via an analogous mechanism to that shown in **Scheme 5** for the formation of **(118)**.



$$M + \mathbf{(96)} \xrightarrow{CH_3CN} \left[(CH_3CN)_x{\cdot}M \rightarrow C_5(CF_3)_6\right] \xrightarrow{h\nu} \left[(CH_3CN)_x{\cdot}\overset{e^-}{M \rightarrow} C_5(CF_3)_6\right]^* \xrightarrow{-CF_3\cdot} (CH_3CN)_x{\cdot}M^+C_5(CF_3)_5^-$$

The key to the unique, and unexpected, reactivity of copper metal in this series of reactions appears to lie in the initial formation of a stable charge transfer complex between the solvated metal and the diene, and this complex appears to assist electron transfer. Evidence for this is provided by the observation that reaction of copper with **(96)** occurs in tandem with the development of a characteristic lime green precipitate in the solution. This precipitate was insoluble in common organic media and powder x-ray analysis revealed it to be amorphous. It is, however, almost certainly formed as a result of initial interaction between the solvent and the metal. Formation of such complexes by copper has been noted previously.[1]

Unstable silver **(122)**, zinc **(123)** and cadmium **(124)** salts of **(96)** were produced under ultraviolet light using the same methodology, but could not be fully characterised before decomposition occurred. The silver salt **(122)** was stable in solution for four days but attempts to isolate it under vacuum were unsuccessful. This appears to be further proof of the extraordinary ability of acetonitrile to stabilise transition metal cations.

Other authors (see **Section V.1.A**) have used larger transition metals such as ruthenium in order to form covalent transition metal complexes with electron deficient cyclopentadienide rings. It was hoped that if ruthenium metal could be brought into contact with **(96)** under ultraviolet light that a covalent, rather than an ionic, complex may form. Powdered ruthenium metal and diene **(96)** were sealed in a quart Carius tube *in vacuo* and irradiated with broad band ultraviolet light for two days. Examination by ^{19}F NMR of the brown material obtained from the reaction upon filtration of excess ruthenium and removal of both solvent and unreacted diene revealed the characteristic pentakis(trifluoromethyl)cyclopentadienide resonance at δ_F -49ppm. However, although the anion could be clearly seen by FAB-MS no trace of a ruthenium cation could be found and this extremely unstable material appeared to decompose to give a viscous oil before further analysis could be obtained. Repetition of the reaction failed to reveal the identity of the compound.

V.2.E. Crystallographic Study of Copper Salt (118)

Single crystals of the stable copper salt (**118**) were grown from dichloromethane over 3 days at -15°C and an x-ray crystal structure obtained; **Figure 2**.

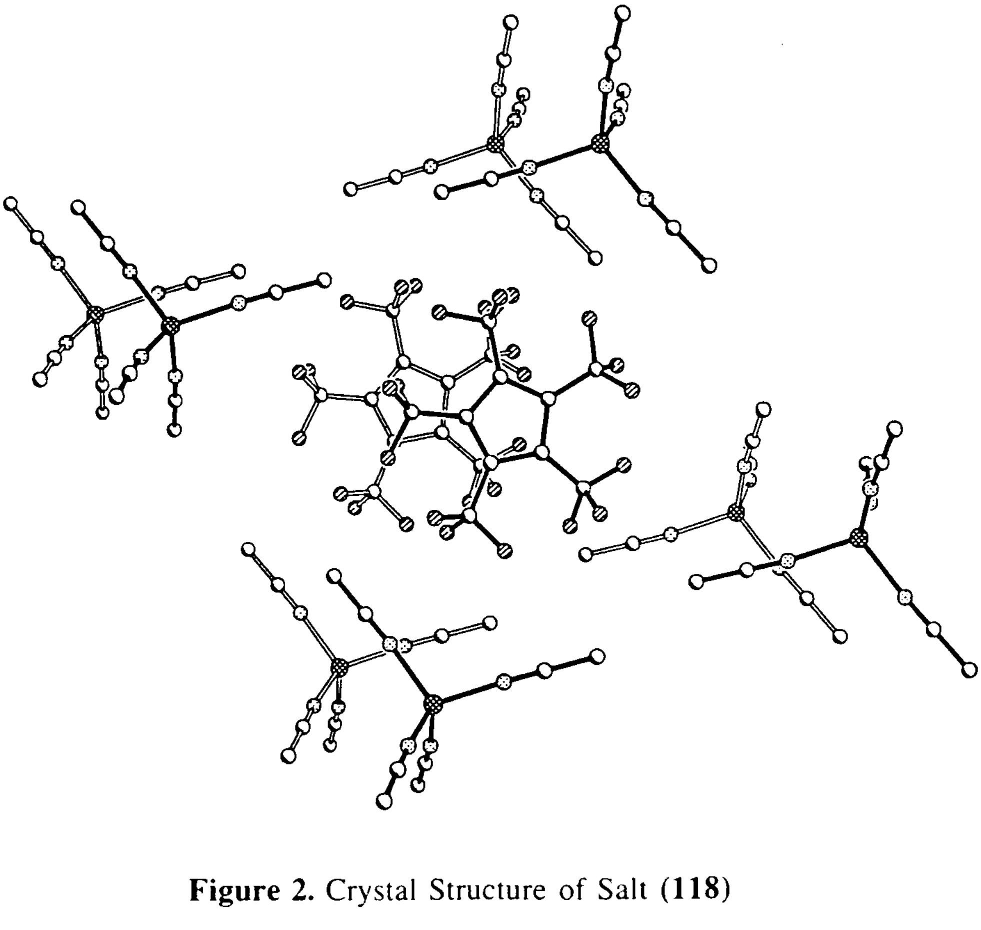


Figure 2. Crystal Structure of Salt (**118**)

Compound **(118)** is clearly ionic with no significant electronic interaction between anions and cations and no evidence for hydrogen bonding between the fluorine atoms of the cyclopentadienide ring and the hydrogen atoms of acetonitrile. The shortest F...H contacts (2.40-2.53Å) are roughly the sum of the Van der Waals radii (2.47Å).

The trifluoromethyl groups are freely rotating in the crystal and do not appear to hinder the movement of one another. Low temperature crystal analysis revealed their motion to be a rocking one, although the reason for this is not yet clear. The ring itself is non planar as shown in **Figure 3** and this slight puckering, and the rapid exchange between the various conformational states, together with concerted out of plane bending and rotation of the CF_3 groups, made solution of its structure very difficult.

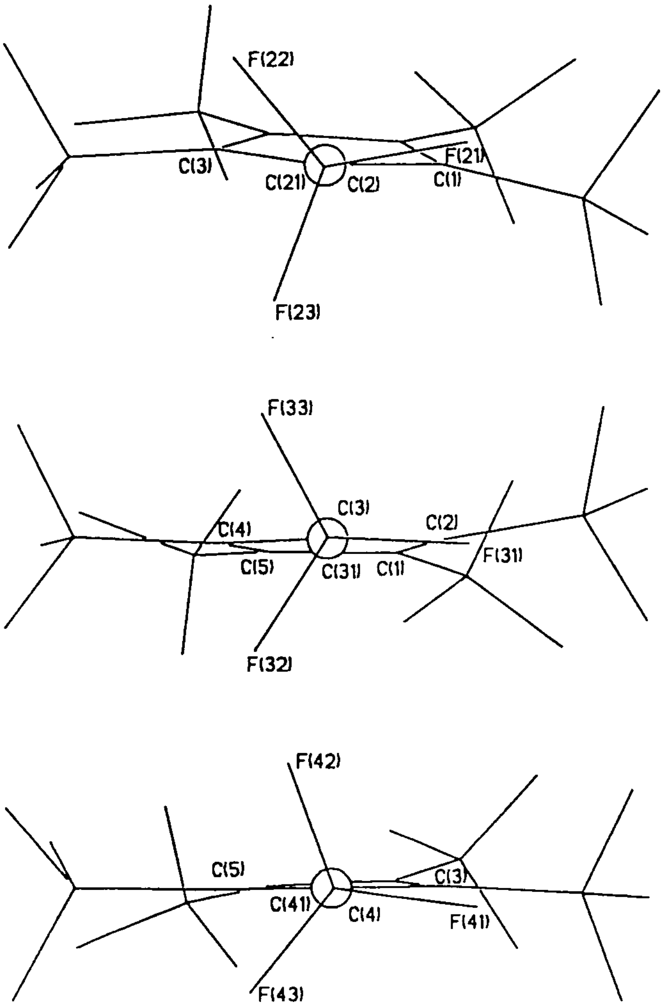


Figure 3. Conformations of the cyclopentadienide ring

This is the first time the x-ray crystal structure of a polytrifluoromethylated aromatic ring has been solved.

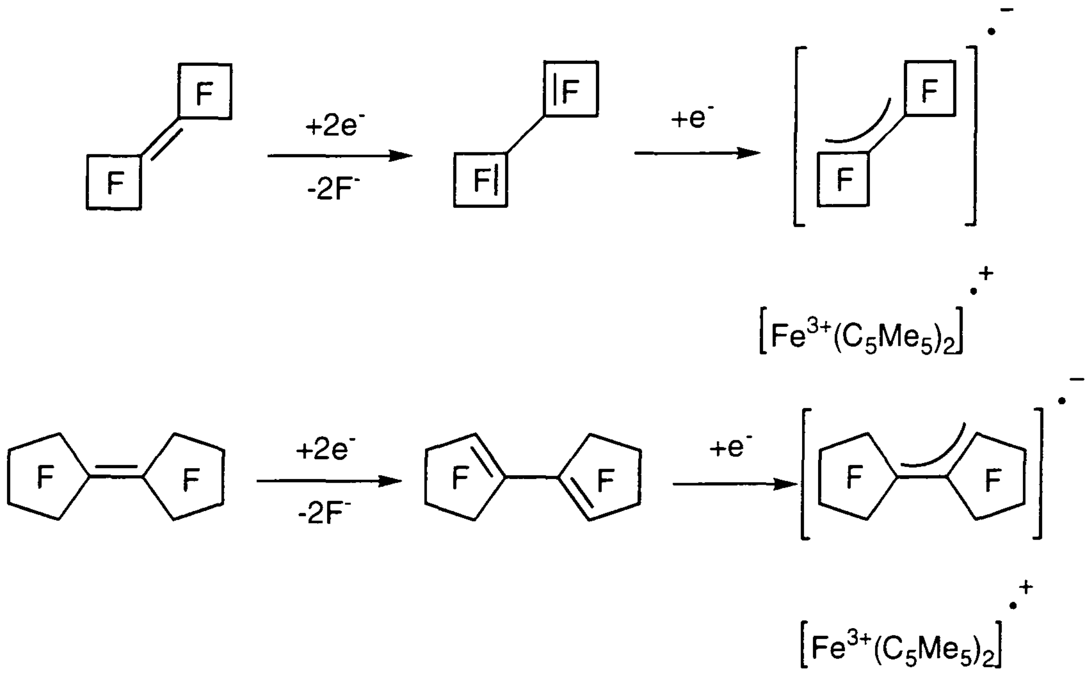
V.2.F. Solid State ^{19}F NMR of Copper Salt (118)

The twisted nature of the anion (**84**) in the solid is further revealed by the solid state ^{19}F NMR of (**118**) which has a relatively sharp peak, with a width at half height of 8 kHz, indicating free rotation of the trifluoromethyl groups within the lattice.

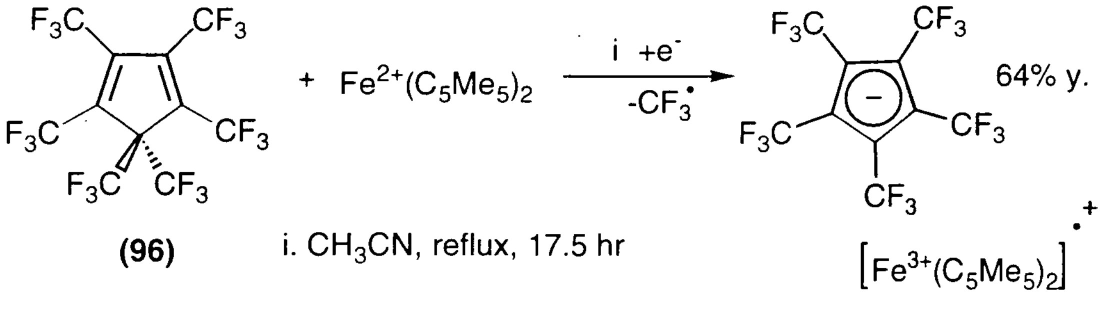
V.2.G. Reaction of (96) with Decamethylferrocene (With Dr. J. F. S. Vaughan)

in 1987 Miller[250] described the first example of an organic magnet when he reacted tetracyanoethene with decamethylferrocene and obtained the crystalline charge transfer salt $[Fe(C_5Me_5)^+$ $[TCNE]^-$

Work by Briscoe and Mullins[180, 184, 191] in these laboratories has produced metallocene charge transfer complexes with fluorocarbon acceptor molecules. Fluorinated alkenes were reacted with decamethylferrocene, under mild conditions, to give green charge transfer complexes, derived from a three electron reduction of the molecule.



Decamethylferrocene has an electrode potential of -0.1V,[237] which indicates the ease with which it is oxidised. Diene (**96**) is readily reduced by decamethylferrocene under reflux to give decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienide in good yield.



(96) i. CH_3CN, reflux, 17.5 hr

(125)

Dark green crystals of **(125)** were grown, as for the copper salt **(118)**, and a crystal structure obtained; **Figure 4**.

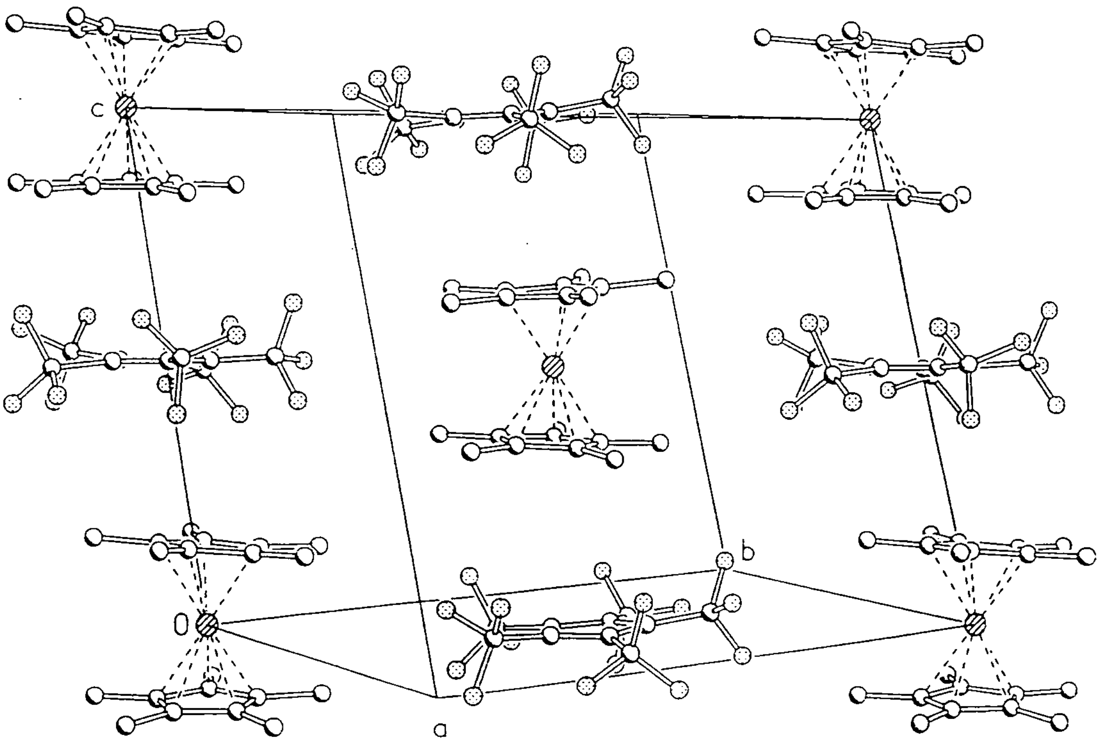
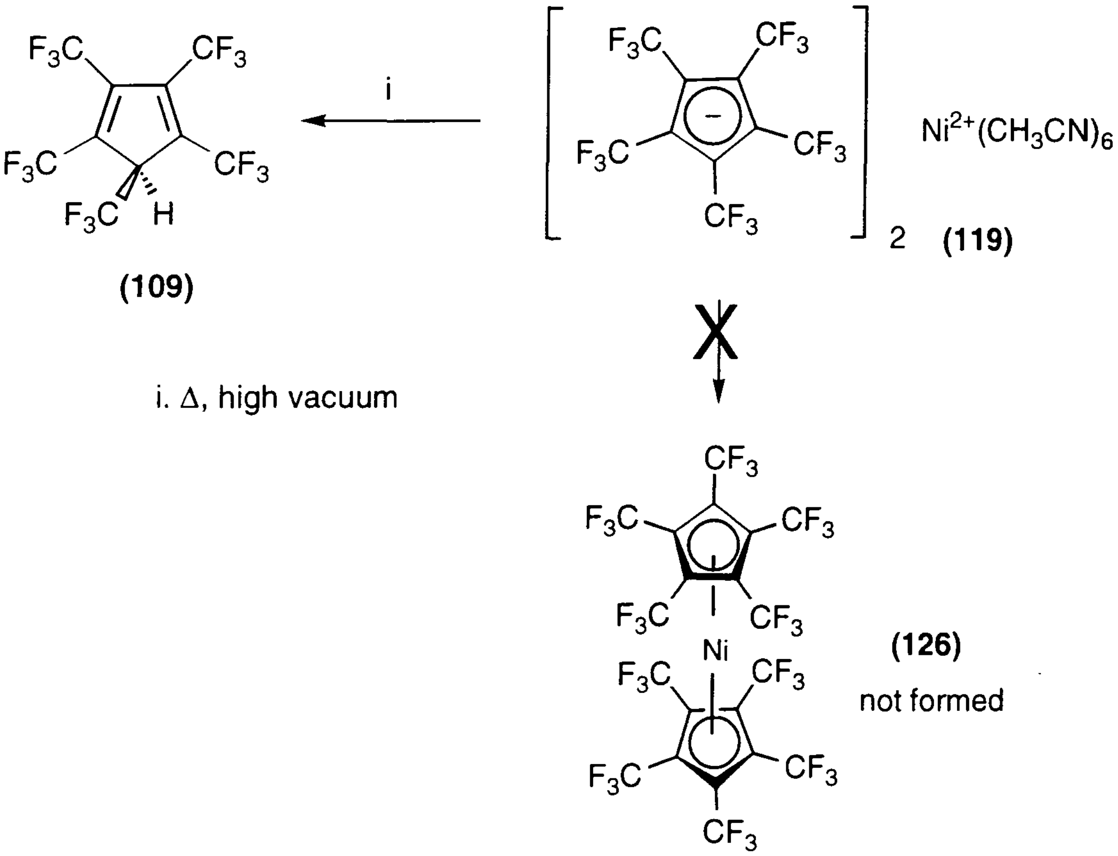


Figure 4. Crystal Structure of Salt **(125)**

V.2.H. Attempted Formation of Covalent Cyclopentadienyl Complexes from Nickel Salt (119)

Salt (**119**) was the most stable of the divalent transition metal salts of (**84**) and attempt was made to see if the acetonitrile ligands around the metal could be removed and a covalent complex, such as (**126**), formed. Progressively heating (**119**) under high vacuum led to loss of the pentakis(trifluoromethyl)cyclopentadienide moiety from the salt and subsequent decomposition. Volatile material produced in the decomposition process were held in a liquid air trap, and upon analysis shown by ^{19}F NMR to contain the anion (**84**). The only plausible explanation for this is that the pentakis(trifluoromethyl)cyclopentadienide anion accepts a proton from acetonitrile upon thermolysis, to give acid (**109**), and subsequent trapping regenerated the anion, possibly as the H_3O^+ salt.

Elemental analysis of the involatile decomposition product was unreliable upon repetition and failed to reveal its identity although it still contained carbon, nitrogen, fluorine and hydrogen, suggesting that only partial loss of either acetonitrile or the anion moiety had occurred.



(109)

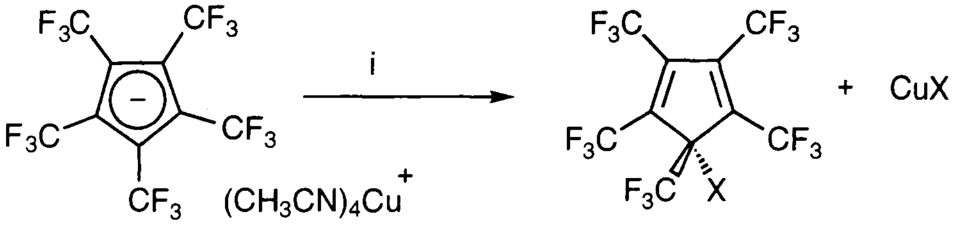
(119)

i. Δ, high vacuum

(126)
not formed

V.3. Reaction of (118) with Halogens

As we have shown the pentakis(trifluoromethyl)cyclopentadienide anion (**84**) is exceedingly stable and, as such resistant to oxidation. The elemental halogens are known to be highly reactive, with diatomic fluorine the most reactive of all elements, and as such should be good candidates for the oxidation of (**84**). Copper salt (**118**) will react with fluorine, chlorine and bromine to give the corresponding fluoro-, chloro- and bromo-pentakis(trifluoromethyl)cyclopentadienes (**127**), (**128**) and (**129**) respectively.



(118)

X = F **(127)** , Cl **(128)**, Br **(129)**

i. X_2, r.t.

Product	Conditions	Yield
(**127**)	Bubble F_2 through (**118**) in acetonitrile at a rate of 5ml min^{-1} for 30 min.	21%
(**128**)	Bubble Cl_2 through (**118**) in acetonitrile at a rate of 5ml min^{-1} for 30 min.	14%
(**129**)	Stir Br_2 with (**118**) in dichloromethane for 24 hours.	8%

None of these halo-dienes appears to be particularly stable and attempts to isolate the products were unsuccessful. All three products were characterised by ^{19}F NMR, with only the fluoro-diene (**127**) being stable enough to give a molecular ion in its mass spectrum [M^+ 424]. Comparison of the chemical shifts of compounds (**127**), (**128**) and (**129**) with the structurally analogous carbon acid (**109**), see **Table 2**, illustrates the effect of an electron withdrawing group upon the chemical shift of surrounding atoms.

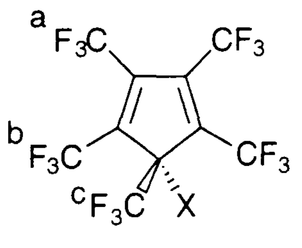
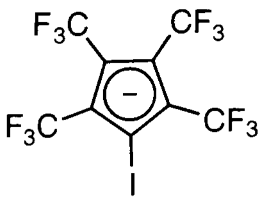


Table 2. Chemical shifts of substituted cyclopentadienes.

Compound	Chemical Shift of atoms **a** (ppm)	Chemical Shift of atoms **b** (ppm)	Chemical Shift of atoms **c** (ppm)
(127) (X = F)	-61.0	-57.3	-69.7
(128) (X = Cl)	-63.8	-55.0	-69.6
(129) (X = Br)	-60.3	-55.7	-64.5
(109) (X = H)	-60.2	-56.0	-59.1

The chemical shifts of the fluorines attached to atoms **a** and **b** remain remarkably similar, irrespective of the nature of atom X. The shift of the fluorines on atom **c**, however, move steadily downfield as the electronegativity of X decreases, indicating a strong interaction between X and the vicinal fluorines.

Stirring iodine with **(118)** for 24 hours gave compound **(105)** in low yield, the nature of the counter ion is not clear.



12% y.

(105)

Surprisingly when the reactions were repeated using the tetrabutylammonium salt **(87)** only with bromine and iodine did reaction occur to give the expected product. Clearly, the stability of the copper containing by-products is of major importance in these reactions.

The surprisingly low yield in these halogenation reactions was at first a mystery, since the initial ^{19}F NMR spectrum revealed only the peaks corresponding to the products. Upon standing for a few hours, however, the anion peak was observed and the true yield became apparent. One explanation for this unusual phenomenon is the formation of an insoluble, transient copper (II) cyclopentadienide species upon initial reaction with the halogen. Yet again, the incredibly stability of the anion is apparent.

V.4. Metal Vapour Synthesis (with Prof. F. G. N. Cloke, University of Sussex, Brighton)

Metal vapour synthesis (MVS) is historically one of the more important synthetic developments in the field of organometallic chemistry.[251] The process was developed by Timms[252, 253] in the late 1960's, when he succeeded in producing $[Cr(\eta^6\text{-}C_6H_6)_2]$ in high yield by co-condensing chromium atoms with benzene. The method was elaborated with great effect by Cloke, Green and their co-workers.[254]

The MVS technique involves the low temperature co-condensation of thermally generated metal atoms with molecules of a suitable ligand in an evacuated reaction chamber. The procedure is attractive since atomic metal is far more reactive than bulk metal, as there is considerably greater surface area for collisions and lattice forces are absent. If one considers **Figure 5**, the activation energy for the gas phase reaction, ΔG_g^*, is much lower than that for the standard state reaction, ΔG_S^*. Thus kinetically, MVS has an important advantage over conventional syntheses.

MVS also has thermodynamic advantages. For a favourable process, ΔG, the change in Gibbs' free energy on going from reactants to products, must be negative. From the diagram, the value of ΔG_g for the gas phase reaction will obviously be larger than ΔG_S for the standard state reaction and the possibility also occurs that for certain processes, ΔG_S will actually be positive. In this situation, the reaction will only proceed in the gas phase.

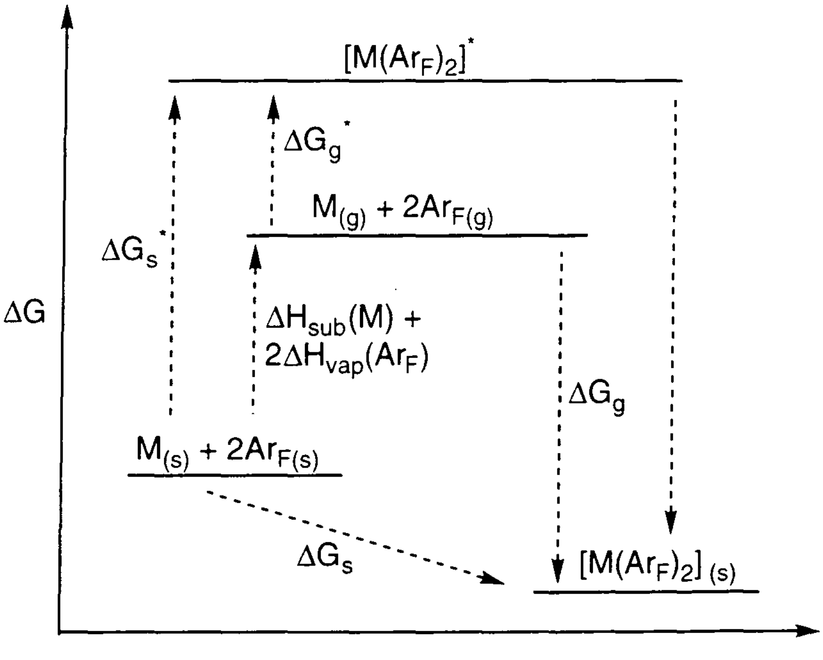


Figure 5

V.4.A. The MVS Apparatus

The study described in this section was carried out in collaboration with Prof. F.G.N. Cloke at the University of Sussex on apparatus based on a machine built at Oxford by Green and Cloke.[255] A schematic representation is given in **Figure 6**. Timms' apparatus[256] employed an alumina crucible wound with tungsten wire which was resistively heated. This method only has a useful range up to the melting point of the crucible, (*ca* 1700°C). The reduction by certain metals, *e.g.* the lanthanides, of the crucible at such elevated temperatures is also a problem. Refinements made by Cloke and Green included the development of an electron beam furnace. This consists of a resistively heated tungsten filament which encircles a water-cooled copper hearth. The metal sample is located on the hearth. Originally,[257] a 1.4 kW power source was used, with the hearth at earth potential. As the filament is heated, it becomes a thermionic emitter and the beam of electrons is focused onto the metal sample by a stainless steel shield. The metal surface is heated by transfer of kinetic energy, resulting in the production of metal atoms. However, this original design was found to be unable to vaporise certain metals (*e.g.* zirconium, tungsten) and at high potentials, stray electrons were suspected to be the cause of decomposition of ligand and products. Cloke and Green[255] modified the apparatus to employ a hearth at positive potential, in which much higher energies could be employed (3.5 kW), enabling vaporisation of even zirconium and tungsten with little risk of stray electrons.

One of the major criteria for efficient MVS is a high vacuum. In earlier apparatus, a cryogenic pumping system was used, but this was replaced in the Sussex machine by a more efficient system using a two-stage rotary pump and a turbo-molecular pump. This enables an ultimate pressure of 1×10^{-7} mbar to be achieved and a pressure of *ca.* 1×10^{-5} mbar to be maintained during the course of the co-condensation.

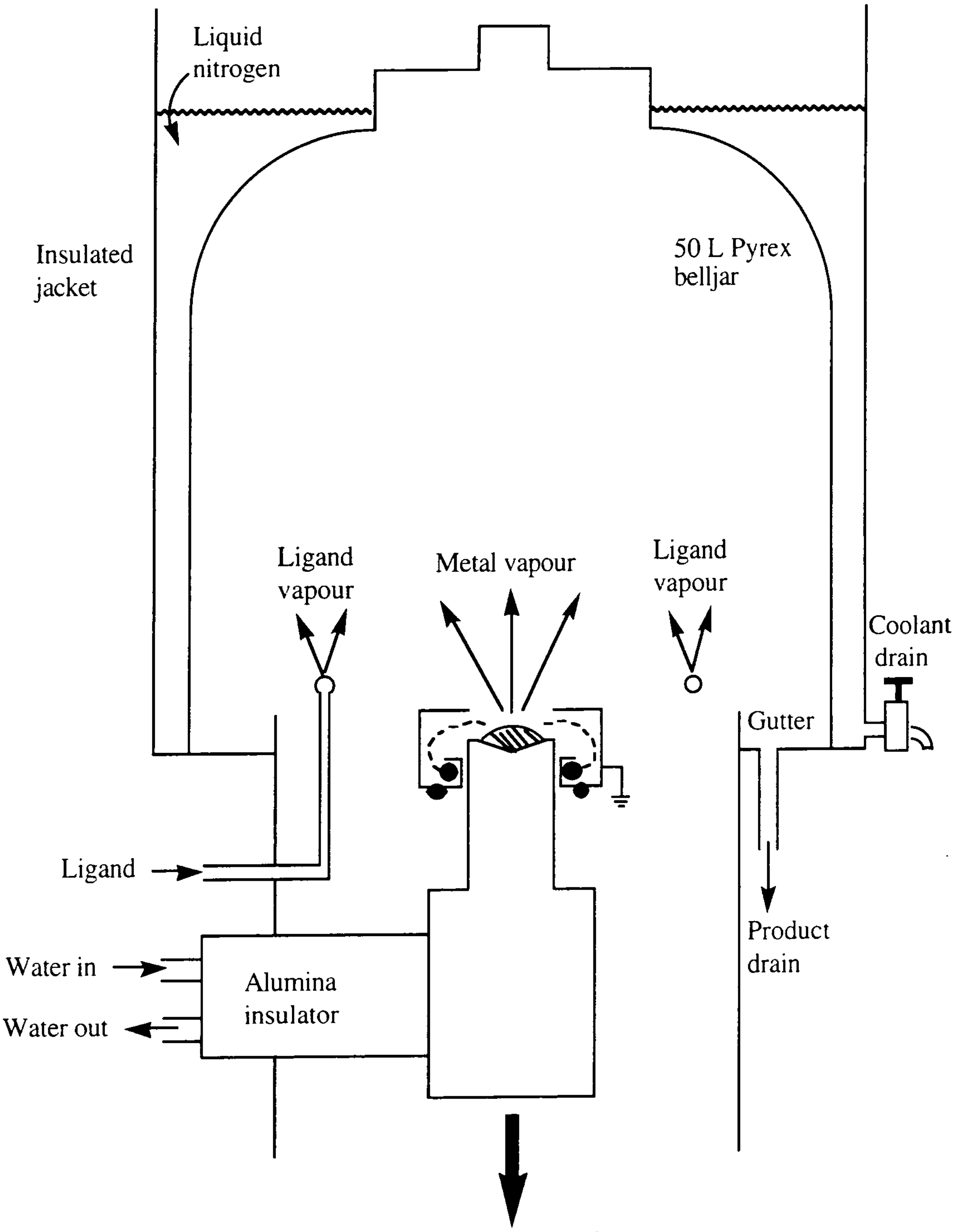


Figure 6. MVS apparatus used at Sussex

The reaction vessel is a Pyrex belljar of either 5 or 50 litres capacity, depending on the desired scale. The base of the belljar is fitted with a viton 'O' ring, which acts as a vacuum seal. The bottom of the belljar is also fitted with a heating coil to prevent freezing of the 'O' ring, as it is in close proximity to the cooling jacket. The insulated jacket surrounds the belljar to a level *ca.* 3 cms. from the base and is filled with liquid nitrogen during the course of the reaction.

V.4.B. Description of the MVS Technique

Although the actual MVS apparatus has evolved considerably over the years, the basic technique remains the same. The reactants must be vaporised into an evacuated chamber, where they co-condense onto the walls, which are cooled to 77K by liquid nitrogen. The low temperature and high vacuum in the chamber serve a number of purposes:-

i. the cooled surface provides a co-condensation and reaction site;

ii. the high vacuum aids vaporisation of the metal and provides a long mean-free path to discourage gas phase reactions;

iii. the low temperature keeps the vapour pressure of the ligand to a minimum within the chamber, thus maintaining the high vacuum.

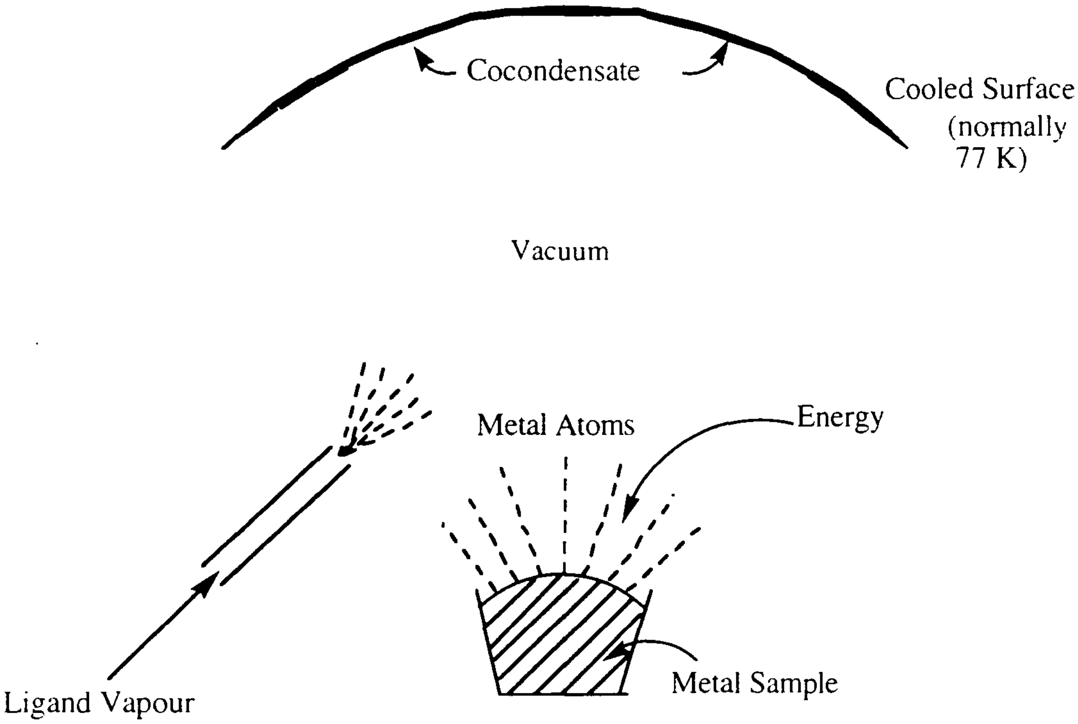
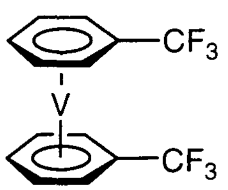


Figure 7. Basics of the MVS Technique

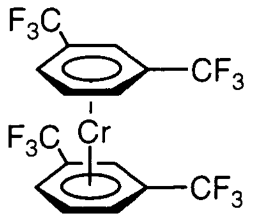
The walls of the reaction bell jar are initially coated with a thin layer of the ligand, onto which the metal atoms and further ligand are subsequently vaporised. This ensures that each metal atom is surrounded by an excess of ligand molecules, increasing the likelihood of reaction and lowering the possibility of metal atom recombinations. To this end, the normal ligand-metal excess is approximately tenfold. The coating of ligand on the bell jar also assists in the product removal step since a layer of metal is very difficult to remove with solvent. Thereafter, both metal and ligand are simultaneously vaporised at a rate sufficient to maintain a vacuum of *ca.* 1x10^{-5} mbar. After the required quantity of ligand has been vaporised, evaporation of the metal is halted and the coolant is removed from the insulated jacket. The reaction chamber is isolated from the pumping system and filled with nitrogen or argon. A mercury bubbler fitted to the apparatus allows for the expansion of the gas on warming to ambient temperature. The products are subsequently washed from the chamber using a suitable solvent, usually 40-60° petroleum ether or toluene. The resulting solution is filtered to remove colloidal metal, which can lead to product degradation. The solvent / ligand is removed under reduced pressure, or relatively involatile excess ligands may be removed by *in vacuo* sublimation onto a glass finger cooled to 77K.

V.4.C. Previous Syntheses of Fluorinated Transition Metal Complexes Using MVS

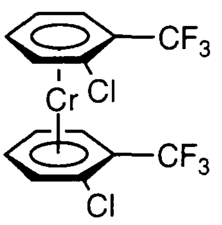
Although MVS has never been used successfully to produce fluorinated cyclopentadienyl transition metal complexes a range of trifluoromethylated benzene sandwich species have been synthesised. In 1975 Klabunde[258] condensed vapours of both vanadium and chromium with mono- and bis(trifluoromethyl)benzenes to give the zero valent η^6-complexes shown in **Figure 8**.



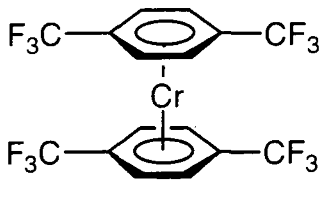
(130)



(131)



(132)

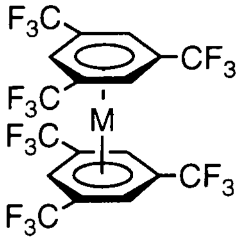


(133)

Figure 8

It was noted that the presence of two strongly electron withdrawing substituents significantly disfavoured complex formation, relative to their parent bis-benzene derivatives. Indeed, infra red studies of complex **(133)** indicated a weaker ring-metal bond than in bis(benzene)chromium (0).[259] Conversely, however, all of the complexes showed a surprisingly high degree of air and temperature stability, with **(131)** only decomposing slowly in air at 200°C. It has been postulated that this is a kinetic effect and that the presence of electron withdrawing substituents makes the metal centre resistant to facile one electron oxidation, the first step in the decomposition process.

Probably the most interesting recent study of these systems was carried out at the University of Sussex in 1995.[260] Vanadium, chromium and niobium complexes of 1,3,5-tris(trifluoromethyl)benzene were synthesised by the MVS technique.



M = V, Cr, Nb

The chromium complex was described as air stable, whereas the 17 electron niobium and chromium species were found to decompose rapidly.

V.4.D. Co-condensation of Ruthenium Metal and Diene (96) by MVS

For reasons described in other parts of this chapter ruthenium is an excellent candidate for the formation of covalently bonded transition metal complexes with electron deficient five membered rings. In the reaction described below perfluoromethylcyclohexane was used as a solvent for two reasons:-

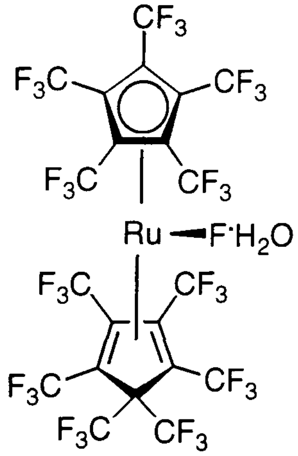
i. it is a non-co-ordinating solvent (*i.e.* it does not co-ordinate transition metals in the way solvents such as acetonitrile do) and is therefore more likely to give covalent compounds rather than salts;

ii. it is an exceptionally good solvent for diene **(96)** and is also liable to solvate any covalently bonded species produced in the reaction.

Using the methodology described above ruthenium metal was co-condensed with diene **(96)** and perfluoromethylcyclohexane in the MVS apparatus for two hours at 77K with the gradual formation of a pink matrix. The condensed material was extracted into perfluoromethylcyclohexane to give a yellow solution. Removal of solvent, and any unreacted diene present, by flash distillation left an air stable brown/yellow oil in very low yield.

The EI mass spectrum of the material revealed it to have a molecular ion of [M^+ 1018]. The isotope pattern of this peak, and other significant peaks at [M^+-F 999], [M^+-CF_3 949], [M^+-C_5F_{13} 711] and [M^+-C_7F_{16} 630] was distinctively that of ruthenium. The material was also studied under chemical ionisation and FAB-MS, both revealing the molecular ion [M^+ 1018] and showing a similar fragmentation pattern (see **Appendix Two**). The fact that the major component of the material has a molecular mass or 1018 is surprising, since a compound of this mass cannot contain only ruthenium carbon and fluorine. The molecular weight of decakis(trifluoromethyl)ruthenocene is 912. The ^{19}F NMR spectrum of the material is also confusing, although it does suggest that there is one major component. Resonances that can be assigned to both the pentakis(trifluoromethyl)cyclopentadienide anion and the hexakis(trifluoromethyl)cyclopentadiene were present, along with smaller peaks at δ_F -69.2ppm, δ_F -77.7ppm, δ_F -120.3ppm and δ_F -148.5ppm. The scarcity of material made resolution and accurate integration of the spectrum difficult.

Attempts to further characterise the material were unsuccessful, firstly due to the low yield obtained and also due to its large molecular mass, making accurate mass measurement unreliable. On the basis of the information available **(134)** is postulated as the most likely structure of the major component.

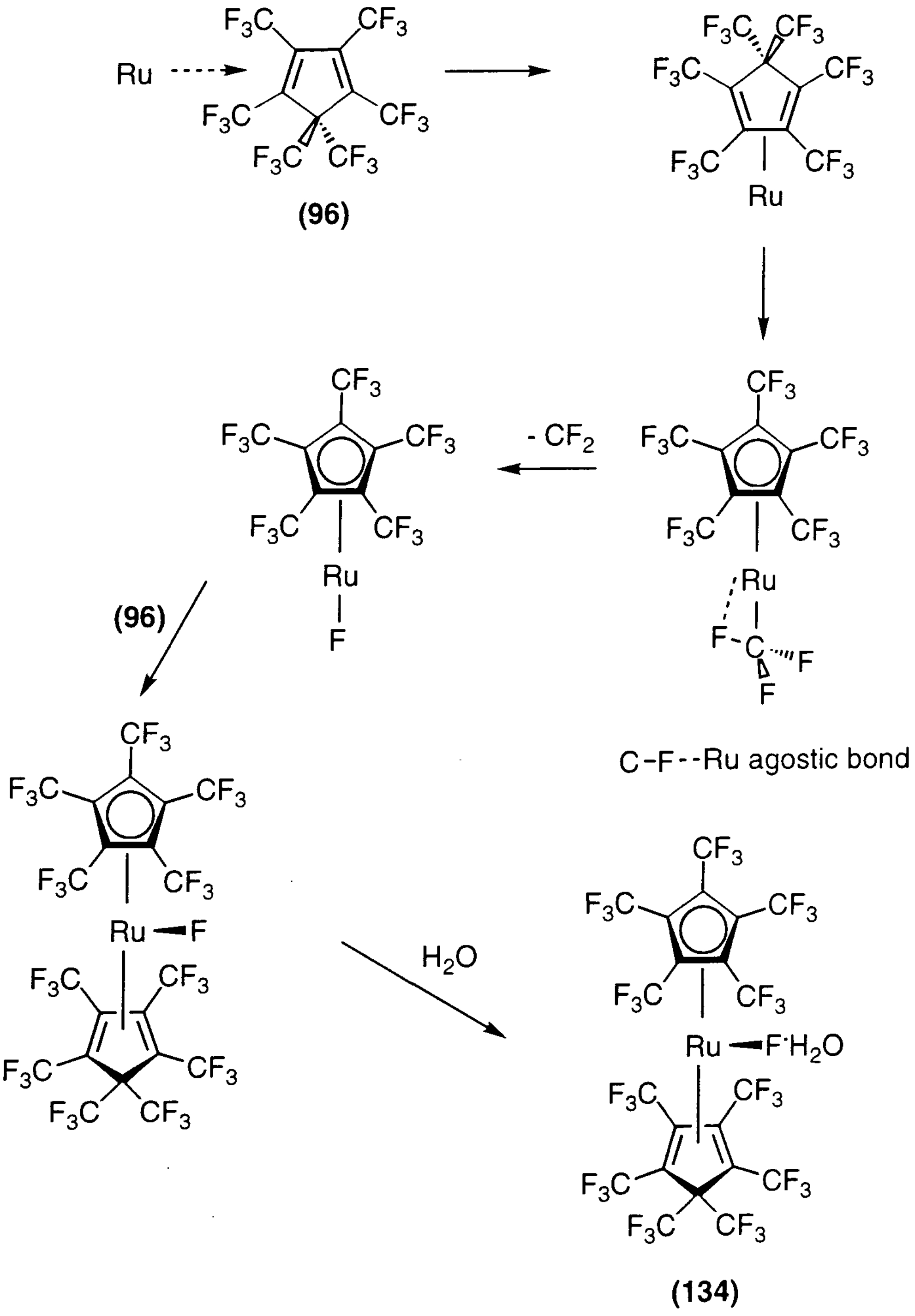


(134)

The exact position of the water molecule, where it comes from and its role in stabilising the system is not clear. One of the unassigned peaks in the ^{19}F NMR spectrum corresponds to the fluorine atom of the Ru-F bond. The others may belong to a minor impurity. This is the first example of a pentakis(trifluoromethyl)cyclopentadienyl complex.

Compound **(134)** may appear to be a rather surprising product of such a process. Indeed the presence of water in the structure suggests a degree of carelessness in preparation. The reaction was repeated in order to obtain a more comprehensive analysis and, although the yield was again too low to allow further analysis, the same material was obtained.

A possible mechanism for the production of **(134)** as a stable compound in the reaction is given in **Scheme 6**.



Scheme 6

The kinetics of such a mechanism are not yet fully understood, and there is a scarcity of literature on such species, reiterating the unique nature of such a system. Agostic C-F-Ru interactions have been previously described, however,[261] and this does seem a likely route to formation of the Ru-F bond. Compound **(134)** obeys the 18 electron rule, if the cyclopentadiene ring is assumed to be η^4-bound and the cyclopentadienide ring η^5-bound, and as such should be reasonably stable. One possible hindrance to the formation of decakis(trifluoromethyl)ruthenocene could be the initial formation of a relatively strong Ru-F bond. Further analysis of this compound, as well as attempts to synthesise other similar systems by MVS will be carried out.

V.5. Conclusions

Solvated transition metal salts of the pentakis(trifluoromethyl)cyclopentadienide anion **(84)** can be formed by reaction of the powdered metal with hexakis(trifluoromethyl)cyclopentadiene **(96)**. Use of acetonitrile to solvate and stabilise the positively charged metal centre appears to be very important. The tetrakis(acetonitrile) copper salt **(118)** is surprisingly stable and a crystal structure was obtained. Salt **(118)** reacts with elemental fluorine, chlorine and bromine to yield the corresponding mono-halo pentakis(trifluoromethyl)cyclopentadiene.

The use of Metal Vapour Synthesis to obtain the first examples of pentakis(trifluoromethyl)cyclopentadienide complexes show a great deal of potential and merits further study.

Instrumentation and Reagents

Gas Liquid Chromatographic Analysis

Analyses were performed on a Fisons Trio 1000 spectrometer linked to a Hewlett Packard 5890 Series II gas liquid chromatograph equipped with a 20m cross-linked methyl silicone capillary column. All GLC-MS mass spectra were generated by electron impact.

Preparative scale GC was performed on a Varian Aerograph Model 920 (catharometer detector) gas chromatograph, fitted with a 3m 10% SE30 packed column.

Elemental Analysis

Carbon, hydrogen, and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba Strumentazione 1106 Elemental Analyser.

NMR Spectra

^{1}H NMR spectra were recorded on a Bruker AC250 spectrometer operating at 250.13 MHz, a Varian Gemini VXR200 spectrometer operating at 199.98 MHz, or a Varian VXR400S spectrometer operating at 399.96 MHz. ^{19}F NMR spectra were recorded on the Bruker AC250 spectrometer operating at 235.34 MHz or on the Varian VXR400S spectrometer operating at 376.29 MHz. ^{13}C spectra were recorded on the Varian VXR400S spectrometer operating at 100.58 MHz, or the Varian Gemini VXR200 spectrometer operating at 50.29 MHz. All spectra were recorded with TMS and fluorotrichloromethane as internal references. *J* Values are given in Hz.

FT-IR Spectra

Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer using KBr discs (solid samples) or thin films between two KBr plates (liquid samples), or volatile compounds were run in a sealed gas cell fitted with KBr plates.

Mass Spectra

Mass spectra of solid samples were recorded on a VG7070E spectrometer. Fast atom bombardment (FAB) mass spectrometry were performed on the same machine, with glycerol or glycerol/H_2O as a solvent.

Distillation

Fractional distillation of product mixtures was carried out using a Fischer Spahltroh MMS255 small concentric tube apparatus. Boiling points were recorded during the distillation.

Melting Points

Melting points were carried out at atmospheric pressure, using a Gallenkamp apparatus, and are uncorrected.

Reagents and Solvents

Unless otherwise stated, chemicals were used as received from suppliers (Aldrich, Fluorochem, Fluka, Jansen, BDH). Solvents were dried by standard methods and stored over a molecular sieve (type 4A). A current of dry nitrogen was maintained for removal of the solvent with a syringe.

Caution: The unsaturated fluorocarbons described in this thesis should be assumed to be toxic.

CHAPTER SIX

Experimental to Chapter Two

VI.1. Defluorination of Perfluoro-3,4-dimethylhex-3-ene (13) with TDAE (8)

A solution of TDAE (**8**) (5.00g, 2.50mmol, 5.80cm^3) in dichloromethane (5cm^3), was added dropwise under dry nitrogen, to a stirred mixture of *Z*- and *E*- isomers of (**13**) (11.00g, 27.50mmol) in dichloromethane (10cm^3) at 0°C (ice bath), with the development of a deep red colour and a fine precipitate. Cooling was discontinued after 30 minutes, and the mixture was stirred at room temperature for a further 30 minutes. A lower clear layer was then isolated by syringe, and found to contain one component by GLC, which was identified as *Z,Z*- and *E,Z*-perfluoro-3,4-dimethylhexa-2,4-diene (**14**)[136] (*Z,Z*- isomer predominant) (8.90g, 24.58mmol, 88%); b.p. 73-74°C; (Found: C, 26.3; F, 72.8. Calc. for C_8F_{14}: C, 26.5; F, 73.5%); NMR spectra 6 and 7, Mass Spectrum 1, IR spectrum 1.

The precipitate was then filtered off, under a blanket of dry nitrogen, and washed with dichloromethane (5x5cm^3) to afford a white powdery solid which was identified as octamethyloxamidium difluoride (**10**) (4.50g, 18.91mmol, 68.6%, based on TDAE); NMR spectrum 11, Mass Spectrum 3. The solid was extremely hygroscopic, causing accurate micro-analysis to be difficult.

VI.2. Reactions of $TDAE^{2+}2F^-$ (10)

VI.2.A. Halogen Exchange Reactions using $TDAE^{2+}2F^-$

VI.2.A.1. With Benzoyl Chloride

Benzoyl chloride (0.28g, 2.00mmol) was added to a solution of $TDAE^{2+}2F^-$ (**10**) (0.50g, 2.10mmol) in sulfolane (10cm^3) under dry nitrogen. The mixture was stirred vigorously for 72h at 80°C in a sealable round bottomed flask. Fluorobenzene (0.20g, 2.10mmol) was added as a marker and the products analysed by ^{19}F NMR which revealed an essentially quantitative yield of benzoyl fluoride (0.25g, 2.00mmol estimated); δ_F (235 MHz, $CFCl_3$) +17.3 ppm (1F, s, PhCOF): as compared to literature data (δ_F +17.1 ppm).[262] A peak at δ_F -166 ppm (s) was observed for the chlorofluoro salt. The reaction was repeated using cesium fluoride as the fluoride ion source and a yield of 90% obtained under the same conditions.

VI.2.A.2. With Benzyl Bromide

Benzyl bromide (0.34g, 2.00mmol) was added to a solution of $TDAE^{2+}2F^-$ (**10**) (0.50g, 2.10mmol) in sulfolane (10cm^3) under dry nitrogen. The mixture was stirred vigorously for 72h at 80°C in a sealable round bottomed flask. Fluorobenzene (0.20g, 2.10mmol) was added as a marker and the products analysed by ^{19}F NMR which revealed a 54% yield of benzyl fluoride (0.12g, 1.08mmol estimated); δ_F (235 MHz, $CFCl_3$) -205.8 ppm (1F, t, *J* 47Hz, $PhCH_2F$); as compared to literature data (δ_F -207 ppm).[262] A peak at δ_F -165 ppm (s) was observed for the bromofluoro salt. The reaction was repeated using cesium fluoride as the fluoride ion source and a yield of 66% obtained under the same conditions.

VI.2.A.3. With Allyl Bromide

Allyl bromide (0.24g, 2.00mmol) was added to a solution of $TDAE^{2+}2F^-$ **(10)** (0.50g, 2.10mmol) in sulfolane (10cm^3) under dry nitrogen. The mixture was stirred vigorously for 72h at 80°C in a sealable round bottomed flask. Fluorobenzene (0.20g, 2.10mmol) was added as a marker and the products analysed by ^{19}F NMR which revealed a 16% yield of allyl fluoride (0.02g, 0.32mmol estimated); δ_F (235 MHz, $CFCl_3$) -214.2 ppm (1F, t, *J* 49Hz, $CH_2{=}CHCH_2F$); as compared to literature data (δ_F -216 ppm).[262] A peak at δ_F -165 ppm (s) was observed for the bromofluoro salt. The reaction was repeated using cesium fluoride as the fluoride ion source and a yield of 21% obtained under the same conditions.

VI.2.A.4. With Octyl Iodide

Octyl Iodide (0.48g, 2.00mmol) was added to a solution of $TDAE^{2+}2F^-$ **(10)** (0.50g, 2.10mmol) in sulfolane (10cm^3) under dry nitrogen. The mixture was stirred vigorously for 72h at 80°C in a sealable round bottomed flask. Fluorobenzene (0.20g, 2.10mmol) was added as a marker and the products analysed by ^{19}F NMR which revealed a 12% yield of octyl fluoride (0.03g, 0.24mmol estimated); δ_F (235 MHz, $CFCl_3$) -216.6 ppm (1F, t, *J* 49Hz, $CH_3(CH_2)_7F$); as compared to literature data (δ_F -219 ppm).[262] A peak at δ_F -166 ppm (s) was observed for the iodofluoro salt. The reaction was repeated using cesium fluoride as the fluoride ion source and a yield of 25% obtained under the same conditions.

VI.2.A.5. With *p*-Toluene Sulphonyl Chloride

p-Toluene sulphonyl chloride (0.38g, 2.00mmol) was added to a solution of $TDAE^{2+}2F^-$ **(10)** (0.50g, 2.10mmol) in sulfolane (10cm^3) under dry nitrogen. The mixture was stirred vigorously for 72h at 80°C in a sealable round bottomed flask. Fluorobenzene (0.20g, 2.10mmol) was added as a marker and the products analysed by ^{19}F NMR which revealed a 66% yield of *p*-toluene sulphonyl fluoride (0.23g, 1.32mmol estimated); δ_F (235 MHz, $CFCl_3$) +66.7 ppm (1F, s, CH_3PhSO_2F); as compared to literature data for similar systems (δ_F +65 ppm, $PhSO_2F$).[263] A peak at δ_F -168 ppm (s) was observed for the chlorofluoro salt. The reaction was repeated using cesium fluoride as the fluoride ion source and a yield of 53% obtained under the same conditions.

VI.2.A.6. With Heptanol Tosylate Ester

Heptanol tosylate ester (prepared by literature procedures[264]) (0.54g, 2.00mmol) was added to a solution of $TDAE^{2+}2F^-$ **(10)** (0.50g, 2.10mmol) in sulfolane (10cm^3) under dry nitrogen. The mixture was stirred vigorously for 72h at 80°C in a sealable round bottomed flask. Fluorobenzene (0.20g, 2.10mmol) was added as a marker and the products analysed by ^{19}F NMR which revealed a 47% yield of heptyl fluoride (0.11g, 0.94mmol estimated); δ_F (235 MHz, $CFCl_3$) -217.4 ppm (1F, t, *J* 45Hz, $CH_3(CH_2)_6F$); as compared to literature data (δ_F -219 ppm).[263] A peak at δ_F -166 ppm (s) was observed for a fluoro salt. The reaction was repeated using cesium fluoride as the fluoride ion source and a yield of 51% obtained under the same conditions.

VI.2.B. Attempted Fluorination of 2,4-Dinitrochlorobenzene

2,4-Dinitrochlorobenzene (1.50g, 7.42mmol) and $TDAE^{2+}F^-$ **(10)** (2.00g, 8.40mmol) in sulpholane (10cm^3) were stirred for 48 h, in a sealable round bottomed flask at 80°C, under dry nitrogen. After this time a sample of the solution was studied by ^{19}F NMR, which revealed no evidence for the formation of 2,4-Dinitrofluorobenzene, or any other fluoro-aromatic.

VI.2.C. Attempted Formation of an Observable Anion from (6)

Perfluoro-2-methylpent-2-ene **(6)** (2.00g, 6.67mmol) and $TDAE^{2+}F^-$ **(10)** (2.00g, 8.40mmol) in acetonitrile (20cm^3) were stirred for 4 days at room temperature, in a round bottomed flask, sealed with a 'suba seal' and under dry nitrogen. After this time a sample of the upper solvent layer was studied by ^{19}F NMR, which revealed no evidence for the formation of the perfluoro-2-methyl pentaneyl anion **(15)**. The reaction was repeated at 60°C over the same time period, and in a range of solvents (tetraglyme, DMSO, sulpholane, DMF), but again the anion was not formed.

VI.2.D. Dimerisation of Hexafluoropropene (1)

A Carius tube was charged with $TDAE^{2+}2F^-$ **(10)** (0.20g, 0.84mmol), hexafluoropropene **(1)** (2.00g, 13.33mmol) and acetonitrile (10cm^3), was sealed *in vacuo* and agitated for 24 h on a rotating arm at room temperature. After this time the tube was opened and a lower layer isolated. After distillation (atmospheric pressure) the product was shown to contain one major fluorinated compound, which was identified by reference to an authentic sample as perfluoro-4-methylpent-2-ene **(5)**; (1.55g, 5.15mmol, 77%); NMR spectrum 12, Mass Spectrum 4.

VI.2.E. Formation of Cyclohexanone by Reaction of Cyclohexene-1-ol trimethylsilylether with $TDAE^{2+}2F^-$ in Acetonitrile

A sealable round bottomed flask was charged with cyclohexene-1-ol trimethylsilylether (0.96g, 5.65mmol), $TDAE^{2+}2F^-$ **(10)** (3.00g, 12.60mmol) and acetonitrile (20cm^3). The flask was sealed under nitrogen and stirred at 0°C for 48 h. After this time the solvent was removed under reduced pressure and organic material extracted into ether and filtered. Solvent was again removed and GLC and GLC-MS of the remaining material revealed it to be a mixture of two components; cyclohexene-1-ol trimethylsilylether (7%) and cyclohexanone (93%). The experiment was repeated with an excess of iodomethane in the reaction vessel and a similar work up procedure followed by distillation yielded; cyclohexanone (61%) m/z (EI$^+$) 98 (M$^+$ 34%); δ_H (400 MHz, $CDCl_3$); 1.59 (2H, q m J 5.6 Hz, 4-CH_2), 1.72 (4H, quin. m J 5.6 Hz, 3-CH_2), 2.19 (4H, t m J 6.8 Hz, 2-CH_2) and 2-methylcyclohexanone (30%) m/z (EI+) 112 (M+ 63%); δ_H (400 MHz, $CDCl_3$); 0.87 (3H, d J 6.8 Hz, 2'-CH_3) and 6 other resonances between δ_H 1.2 and δ_H 2.3 integrating as 9H.

VI.3. Reaction of TDAE (8) with Elemental Fluorine

A Teflon flask was charged with TDAE (**8**) (2.00g, 10.00mmol) and anhydrous acetonitrile (10cm^3) under a flow of dry nitrogen. 10% elemental fluorine was bubbled through the vessel at a rate of 5ml min^{-1} until an equivalence had been used. The solution turned deep red in colour and a white precipitate was observed in the bottom of the vessel. The precipitate was filtered off, under a blanket of dry nitrogen, and washed with dichloromethane (as above) to afford a white powdery solid which was identified as octamethyloxamidium difluoride (**10**) (1.94g, 8.15mmol, 81.5%, based on TDAE); NMR spectrum 11, Mass Spectrum 3.

VI.4. TDAE (8) Catalysed Reactions

VI.4.A. Dimerisation of Hexafluoropropene (1) at Room Temperature

A Carius tube (60cm^3), charged with TDAE (**8**) (0.10g, 0.50mmol) and hexafluoropropene (**1**) (6.00g, 40.00mmol), was sealed *in vacuo* and agitated for 24 h on a rotating arm at room temperature. After this time the tube was opened and volatile material (5.70g) transferred to a cold trap under reduced pressure. After distillation (atmospheric pressure) the product was shown to contain one major fluorinated compound, which was identified by reference to an authentic sample[123] as perfluoro-4-methylpent-2-ene (**5**); (5.28g, 17.65mmol, 88%); NMR spectrum 12, Mass Spectrum 4.

VI.4.B. Dimerisation of Hexafluoropropene (1) at 60°C

A Carius tube (60cm^3), charged with TDAE (**8**) (0.10g, 0.50mmol) and hexafluoropropene (**1**) (6.00g, 40.00mmol), was sealed *in vacuo* and heated to 60°C in a protective metal tube for 24 h. After this time the tube was opened and volatile material (5.45g) transferred to a cold trap under reduced pressure. After distillation (atmospheric pressure) the product was shown to contain one major fluorinated compound, which was identified by reference to an authentic sample[123] as perfluoro-2-methylpent-2-ene (**6**) (4.90g, 16.33mmol, 82%); NMR spectrum 13, Mass Spectrum 5.

VI.4.C. Formation of an Observable Anion from (6)

A Carius tube (60cm^3), charged with hexafluoropropene **(1)** (5.25g, 35.00mmol) and a significantly larger quantity of TDAE **(8)** than used in the reaction above (2.00g, 10.00mmol) in acetonitrile (10cm^3), was sealed *in vacuo* and agitated for 24 h on a rotating arm at room temperature. After this time the tube was opened and volatile material (0.60g) was isolated by transfer to a cold trap under reduced pressure and identified as perfluoro-4-methylpent-2-ene **(5)** (0.50g,1.67mmol, 10%). Examination of the residual solid by ^{19}F NMR revealed the perfluoro-2-methyl pentaneyl anion **(15)**.[36] The nature of the counter cation could not be ascertained, and this made accurate calculation of yield difficult; NMR spectrum 14.

VI.4.D. Dimerisation of Octafluorocyclopentene (17)

A Carius tube was charged with, TDAE **(8)** (0.30g, 1.50mmol) and octafluorocyclopentene **(17)** (1.00g, 4.72mmol) in acetonitrile (10cm^3), was sealed *in vacuo* and agitated for 48 h on a rotating arm at room temperature. The tube was opened and the contents examined by ^{19}F NMR which revealed the salt **(20)** to be the only component in solution in a yield of approximately 28% (by ^{19}F NMR integration); NMR spectrum 15. An excess of BF_3 etherate (0.50g, 3.52mmol) was added to the solution and perfluoro-1,1'-bicyclopent-1-enyl **(12)** was formed from **(20)**; (0.20g, 0.51mmol, 22%; based on **(17)** consumed) identified by comparison of spectra with that of an authentic sample; NMR spectrum 9, IR spectrum 2. The reaction vessel also contained a large amount of black insoluble material which could not be identified. Repitition of the reaction with varying ratios of TDAE to substrate failed to provide any definite information as to the nature of the material.

VI.4.E. Attempted Dimerisation of Hexafluorocyclobutene (19)

A Carius tube was charged with, TDAE **(8)** (0.30g, 1.50mmol) and hexafluorocyclobutene **(19)** (1.00g, 6.17mmol) in acetonitrile (10cm^3), was sealed *in vacuo* and agitated for 48 h on a rotating arm at room temperature. The tube was opened and shown to contain only a black insoluble material which could not be identified by either mass spectroscopy or micro-analysis.

VI.4.F. Co-dimerisation of Hexafluoropropene (1) and Octafluorocyclopentene (17)

A Carius tube was charged with, TDAE **(8)** (0.10g, 0.50mmol), hexafluoropropene **(1)** (5.00g, 33.33mmol) and octafluorocyclopentene **(17)** (2.35g, 11.08mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, fluorobenzene added as a marker and volatile materials (6.98g) were transferred to a cold trap under reduced pressure and analysed by GLC-MS and ^{19}F NMR. There were four main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[28] perfluoro-1-isopropylcyclopentene **(21)** (61% by ^{19}F

NMR integration); *m/z* (EI$^+$) 362 (M$^+$ 3%); NMR spectrum 16, Mass Spectrum 6; perfluoro-1,2-di-isopropylcyclopentene **(22)** (26% by ^{19}F NMR integration); *m/z* (EI$^+$) 493 (M$^+$-F 2%); NMR spectrum 17, Mass Spectrum 7; the previously unrecorded perfluoro-1-(1',1'-dimethyl)butylcyclopentene **(23)** (8% by ^{19}F NMR integration) a sample of which was isolated for characterisation by preparative scale GLC; b.p. 125°C; R_F 0.3 (Found C, 26.8; F, 75.2%; M$^+$-F, 492.970, $C_{11}F_{19}$ requires C, 26.8; F, 75.2%; M$^+$-F, 492.969); *m/z* (EI$^+$) 493 (M$^+$-F 68%); NMR spectrum 18, Mass Spectrum 8, IR spectrum 3; and hexafluoropropene dimer **(6)**.

VI.4.G. Perfluoroalkylation of Pentafluoropyridine (24) with Hexafluoropropene (1)

A Carius tube (60cm^3), charged with, TDAE **(8)** (0.10g, 0.50mmol), hexafluoropropene **(1)** (4.12g, 27.47mmol) and pentafluoropyridine **(24)** (1.50g, 8.88mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, volatile materials (5.65g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were five main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[160] perfluoro-4-isopropylpyridine **(25)** (21% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI$^+$) 319 (M$^+$ 21%); NMR spectrum 19, Mass Spectrum 9; perfluoro-2,4-di-isopropylpyridine **(26)** (10% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI$^+$) 469 (M$^+$ 14%); NMR spectrum 20, Mass Spectrum 10; perfluoro-2,4,5-tri-isopropylpyridine **(27)** (7% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI$^+$) 619 (M$^+$ 14%); NMR spectrum 21, Mass Spectrum 11; perfluoro-2,4,6-tri-isopropylpyridine **(28)** (35% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI$^+$) 619 (M$^+$ 14%); NMR spectrum 22, Mass Spectrum 12; and hexafluoropropene dimer **(6)**.

VI.4.H. Perfluoroalkylation of Pentafluoropyridine (24) with Hexafluoropropene Dimer (5)

A Carius tube (60cm^3), charged with, TDAE **(8)** (0.10g, 0.50mmol), hexafluoropropene dimer **(5)** (8.25g, 27.50mmol) and pentafluoropyridine **(24)** (1.51g, 8.88mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, volatile materials (7.63g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were two main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[160] perfluoro-4-isopropylpyridine **(25)** (5% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 319 (M^+ 21%); NMR spectrum 19, Mass Spectrum 9; and hexafluoropropene dimer (**6**).

VI.4.I. Perfluoroalkylation of Tetrafluoropyrimidine (29) with Hexafluoropropene (1)

A Carius tube ($60cm^3$), charged with, TDAE (**8**) (0.10g, 0.50mmol), hexafluoropropene (**1**) (6.00g, 40.00mmol) and tetrafluoropyrimidine (**29**) (2.00g, 13.16mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, volatile materials (7.76g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were six main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[158] perfluoro-4-isopropylpyrimidine (**30**) (2% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 302 (M^+ 29%); NMR spectrum 23, Mass Spectrum 13; perfluoro-4,6-di-isopropylpyrimidine (**31**) (41% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 452 (M^+ 21%); NMR spectrum 24, Mass Spectrum 14; perfluoro-2,4,6-tri-isopropylpyrimidine (**32**) (40% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 602 (M^+ 14%); NMR spectrum 25, Mass Spectrum 15; perfluoro-2,4,5,6-tetraisopropylpyrimidine (**34**) (2% by ^{19}F NMR integration of tertiary fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 752 (M^+ 1%); NMR spectrum 27, Mass Spectrum 17; the previously uncharacterised *perfluoro-4-(1',1'-dimethyl)butylpyrimidine* (**33**) (8% by ^{19}F NMR integration) a sample of which was isolated by preparative scale GLC; (Found: C, 26.5; F, 67.3; N, 6.19%. M^+, 451.981, $C_{10}F_{16}N_2$ requires C, 26.5; F, 67.3; N, 6.19%. M^+, 451.981); *m/z* (EI^+) 452 (M^+ 16%); NMR spectrum 26, Mass Spectrum 16, IR spectrum 4; and hexafluoropropene dimer (**6**).

VI.4.J. Formation of Perfluoro-2,4,5,6-tetraisopropylpyrimidine (34) Exclusively by Perfluoroalkylation of (29)

To an evacuated round bottomed flask (50ml) containing (**29**) (2.00g, 13.16mmol) and TDAE (**8**) (0.20g, 1.00mmol) in acetonitrile ($10cm^3$) was attached an expandable gas bladder (2 litre), fitted with a tap, and charged with hexafluoropropene (**1**) (9.00g, 60.00mmol). The bladder was opened to the flask and the hexafluoropropene allowed to diffuse into the sealed system. The flask was agitated, using a magnetic stirrer, for 48 h at room temperature. After this time the lower fluorocarbon layer was isolated and the products distilled (atmospheric pressure) to give perfluoro-2,4,5,6-tetraisopropylpyrimidine (**34**) (6.14g, 8.16mmol, 62% isolated yield) and hexafluoropropene dimer (**5**).

VI.4.K. Perfluoroalkylation of Tetrafluoropyrimidine (29) with Hexafluoropropene Dimer (5)

A Carius tube ($60cm^3$), charged with, TDAE (**8**) (0.10g, 0.50mmol), hexafluoropropene dimer (**5**) (12.00g, 40.00mmol) and tetrafluoropyrimidine (**29**) (2.00g, 13.16mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, volatile materials (9.06g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were four main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[158] perfluoro-4-isopropylpyrimidine (**30**) (9% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 302 (M^+ 29%); NMR spectrum 23, Mass Spectrum 13; perfluoro-4-(1',1'-dimethyl)butylpyrimidine (**33**) (41% by ^{19}F NMR integration of ring fluorine resonances against those of fluorobenzene); *m/z* (EI^+) 452 (M^+ 16%); NMR spectrum 26, Mass Spectrum 16, IR spectrum 4; perfluoro-6-isopropyl-4-(1',1'-dimethyl)butylpyrimidine (**35**) (11% by ^{19}F NMR integration of ring fluorine resonances against those of fluorobenzene); *m/z* (EI^+) 602 (M^+ 48%); Mass Spectrum 18; perfluoro-2,6-di-isopropyl-4-(1',1'-dimethyl)butylpyrimidine (**36**) (19% by ^{19}F NMR integration of ring fluorine resonances against those of fluorobenzene); *m/z* (EI^+) 752 (M^+ 11%); NMR spectrum 28, Mass Spectrum 19; and hexafluoropropene dimer (**6**).

VI.4.L. Perfluoroalkylation of 2,4-Dinitrofluorobenzene (38) with Hexafluoropropene (1)

To an evacuated round bottomed flask (50ml) containing 2,4-dinitrofluorobenzene (**38**) (2.00g, 16.13mmol) and TDAE (**8**) (0.20g, 1.00mmol) in acetonitrile ($10cm^3$) was attached an expandable gas bladder (2 litre), fitted with a tap, and charged with hexafluoropropene (**1**) (9.00g, 60.00mmol). The bladder was opened to the flask and the hexafluoropropene allowed to diffuse into the sealed system. The flask was agitated, using a magnetic stirrer, for 3 days at 60°C. After this time solvent was removed under reduced pressure and the residue shown to contain *2,4-dinitroheptafluoroisopropylbenzene* (**39**) (85% by GLC integration) and 2,4-dinitrofluorobenzene. A sample of (**39**) was isolated by preparative scale GLC (0.60g, 1.79mmol); (Found: C, 32.0; H, 0.8; N, 8.3%. $C_9H_3F_7N_2O_4$ requires C, 32.1; H, 0.9; N, 8.3%); *m/z* (EI^+) 336 (M^+ 13%); NMR spectrum 29, Mass Spectrum 20, IR spectrum 5.

VI.4.M. Attempted Perfluoroalkylation of *p*-Nitrofluorobenzene with Hexafluoropropene (1)

To an evacuated round bottomed flask (50ml) containing *p*-nitrofluorobenzene (2.00g, 14.18mmol) and TDAE (**8**) (0.20g, 1.00mmol) in acetonitrile ($10cm^3$) was attached an expandable gas bladder (2 litre), fitted with a tap, and charged with hexafluoropropene (**1**) (9.00g, 60.00mmol). The bladder was opened to the flask and the hexafluoropropene allowed to diffuse into the sealed system. The flask was agitated, using a magnetic stirrer, for 3 days at 60°C. After this time solvent was removed under reduced pressure and the residue shown to contain only *p*-nitrofluorobenzene.

VI.5. Trialkylamine Catalysed Reactions

VI.5.A. Dimerisation of Hexafluoropropene (1) at Room Temperature with Trimethylamine

A Carius tube (60cm^3), charged with trimethylamine (0.10g, 1.69mmol) and hexafluoropropene (**1**) (3.00g, 20.00mmol), was sealed *in vacuo* and agitated for 24 h on a rotating arm at room temperature. After this time the tube was opened and volatile material (1.88g) transferred to a cold trap under reduced pressure. After distillation (atmospheric pressure) the product was shown to contain one major fluorinated compound, which was identified by reference to an authentic sample (see above) as perfluoro-4-methylpent-2-ene (**5**); (1.80g, 6.00mmol, 60%).

VI.5.B. Dimerisation of Hexafluoropropene (1) at Room Temperature with Tributylamine

A Carius tube (60cm^3), charged with tributylamine (0.10g, 1.69mmol) and hexafluoropropene (**1**) (3.00g, 20.00mmol), was sealed *in vacuo* and agitated for 24 h on a rotating arm at room temperature. After this time the tube was opened and volatile material (1.58g) transferred to a cold trap under reduced pressure. After distillation (atmospheric pressure) the product was shown to contain one major fluorinated compound, which was identified by reference to an authentic sample (see above) as perfluoro-4-methylpent-2-ene (**5**); (1.50g, 5.00mmol, 50%).

VI.5.C. Oligomerisation of Tetrafluoroethylene (2)

A Carius tube (60cm^3), charged with, trimethylamine (0.10g, 1.69mmol) and tetrafluoroethene (**2**) (3.00g, 30.00mmol) in dimethylformamide (10cm^3), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. After this time the tube was opened and volatile materials (2.78g) isolated by distillation under reduced pressure at 70°C. The isolated material was shown to contain five major fluorinated compounds, which were identified by reference to authentic samples;[40] dimer (6% by GLC); trimer (8% by GLC); tetramer (11% by GLC); pentamer (58% by GLC); and hexamer (12% by GLC). Reference compounds kindly supplied by Dr R. L. Powell (ICI Ltd.).

VI.5.D. Co-dimerisation of Hexafluoropropene (1) and Octafluorocyclopentene (17)

A Carius tube was charged with, trimethylamine (0.10g, 1.69mmol), hexafluoropropene **(1)** (5.00g, 33.33mmol) and octafluorocyclopentene **(17)** (2.40g, 11.32mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, fluorobenzene added as a marker and volatile materials (4.32g) were transferred to a cold trap under reduced pressure and analysed by GLC-MS and ^{19}F NMR. There were four main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[28] perfluoro-1-isopropylcyclopentene **(21)** (55% by ^{19}F NMR integration); *m/z* (EI$^+$) 362 (M$^+$ 3%); NMR spectrum 16, Mass Spectrum 6; perfluoro-1,2-di-isopropylcyclopentene **(22)** (21% by ^{19}F NMR integration); *m/z* (EI$^+$) 493 (M$^+$-F 2%); NMR spectrum 17, Mass Spectrum 7; the previously unrecorded perfluoro-1-(1',1'-dimethyl)butylcyclopentene **(23)** (4% by ^{19}F NMR integration) a sample of which was isolated for characterisation by preparative scale GLC (0.71g, 1.37mmol); b.p. 125°C; R_F 0.3 (Found C, 26.8; F, 75.2%; M$^+$-F, 492.970, $C_{11}F_{19}$ requires C, 26.8; F, 75.2%; M$^+$-F, 492.969); *m/z* (EI$^+$) 493 (M$^+$-F 68%); NMR spectrum 18, Mass Spectrum 8, IR spectrum 3; and hexafluoropropene dimer **(6)**.

VI.5.E. Co-dimerisation of Hexafluoropropene (1) and Hexafluorocyclobutene (19)

A Carius tube was charged with, trimethylamine (0.10g, 1.69mmol), hexafluoropropene **(1)** (5.00g, 33.33mmol) and hexafluorocyclobutene **(19)** (2.00g, 12.35mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, fluorobenzene added as a marker and volatile materials (4.32g) were transferred to a cold trap under reduced pressure and analysed by GLC-MS and ^{19}F NMR. There were five main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[28] perfluoroisopropylidenecyclobutane **(40)** (16% by ^{19}F NMR integration); *m/z* (EI$^+$) 312 (M$^+$ 3%); NMR spectrum 30, Mass Spectrum 21; perfluoro-2-cyclobut-1-en-1yl-2,3-dimethylbutane **(41)** (32% by ^{19}F NMR integration); *m/z* (EI$^+$) 462 (M$^+$ 11%); NMR spectrum 31, Mass Spectrum 22; perfluoro-2-cyclobut-1-en-1-yl-2-cyclobutylpropane **(42)** (17% by ^{19}F NMR integration); *m/z* (EI$^+$) 474 (M$^+$ 22%); NMR spectrum 32, Mass Spectrum 23; perfluoro-1-(1',1',2',2',3'-pentamethyl)butylcyclobutene **(43)** (1% by ^{19}F NMR integration); *m/z* (EI$^+$) 593 (M$^+$-F 10%); Mass Spectrum 24; and hexafluoropropene dimer **(6)**.

VI.5.F. Perfluoroalkylation of Pentafluoropyridine (24) with Hexafluoropropene (1)

A Carius tube (60cm^3), charged with, trimethylamine (0.10g, 1.69mmol), hexafluoropropene **(1)** (4.20g, 24.85mmol) and pentafluoropyridine **(24)** (1.50g, 8.88mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h.

The tube was opened, volatile materials (5.25g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were three main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[160] perfluoro-4-isopropylpyridine **(25)** (20% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 319 (M^+ 21%); NMR spectrum 19, Mass Spectrum 9; perfluoro-2,4-di-isopropylpyridine **(26)** (8% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 469 (M^+ 14%); NMR spectrum 20, Mass Spectrum 10; and hexafluoropropene dimer **(6)**.

VI.5.G. Perfluoroalkylation of Pentafluoropyridine (24) with Tetrafluoroethene (2)

A Carius tube ($60cm^3$), charged with, trimethylamine (0.10g, 1.69mmol), tetrafluoroethene **(2)** (2.80g, 28.00mmol) and pentafluoropyridine **(24)** (1.50g, 8.88mmol) in dimethylformamide ($10cm^3$), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, volatile materials (4.15g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were three main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[164] perfluoro-4-ethylpyridine **(44)** (60% by ^{19}F NMR integration); *m/z* (EI^+) 269 (M^+ 16%); NMR spectrum 33, Mass Spectrum 25; perfluoro-2,4-diethylpyridine **(45)** (10% by ^{19}F NMR integration); *m/z* (EI^+) 369 (M^+ 6%); NMR spectrum 34, Mass Spectrum 26; perfluoro-2,4,5-triethylpyridine **(46)** (25% by ^{19}F NMR integration); *m/z* (EI^+) 469 (M^+ 10%); NMR spectrum 35, Mass Spectrum 27.

VI.5.H. Perfluoroalkylation of Tetrafluoropyrimidine (29) with Hexafluoropropene (1)

A Carius tube ($60cm^3$), charged with, trimethylamine (0.10g, 1.69mmol), hexafluoropropene **(1)** (6.00g, 40.00mmol) and tetrafluoropyrimidine **(29)** (2.00g, 13.16mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, volatile materials (7.51g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were four main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[158] perfluoro-4,6-di-isopropylpyrimidine **(31)** (42% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 452 (M^+ 21%); NMR spectrum 24, Mass Spectrum 14; perfluoro-2,4,6-tri-isopropylpyrimidine **(32)** (44% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 602 (M^+ 14%); NMR spectrum 25, Mass Spectrum 15; perfluoro-2,4,5,6-tetraisopropylpyrimidine **(34)** (2% by ^{19}F NMR integration of tertiary fluorine resonances against that of fluorobenzene); *m/z* (EI^+) 752 (M^+ 1%); NMR spectrum 27, Mass Spectrum 17; and hexafluoropropene dimer **(6)**.

VI.5.I. Perfluoroalkylation of Tetrafluoropyrimidine (29) with Hexafluoropropene Dimer (5)

A Carius tube (60cm^3), charged with, trimethylamine (0.10g, 1.69mmol), hexafluoropropene dimer **(5)** (12.00g, 40.00mmol) and tetrafluoropyrimidine **(29)** (2.00g, 13.16mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, volatile materials (8.44g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were two main components in the mixture which could be characterised by comparison of spectra with those obtained previously (see above); perfluoro-4-(1',1'-dimethyl)butylpyrimidine **(33)** (48% by ^{19}F NMR integration) a sample of which was isolated by preparative scale GLC; (Found: C, 26.5; F, 67.3; N, 6.19%. M^+, 451.981, $C_{10}F_{16}N_2$ requires C, 26.5; F, 67.3; N, 6.19%. M^+, 451.981), *m/z* (EI^+) 452 (M^+ 16%); NMR spectrum 26, Mass Spectrum 16, IR spectrum 4; and hexafluoropropene dimer **(6)**.

VI.5.J. Perfluoroalkylation of Trifluoro-s-triazine (37) with Hexafluoropropene (1)

A Carius tube (60cm^3), charged with, trimethylamine (0.10g, 1.69mmol), hexafluoropropene **(1)** (3.60g, 24.00mmol) and trifluoro-s-triazine **(37)** (1.00g, 7.40mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, volatile materials (4.23g) transferred to a cold trap under reduced pressure, and products analysed by GLC-MS and ^{19}F NMR. There were two main components in the mixture which were separated by distillation (atmospheric pressure); perfluoro-2,4,6-tri-isopropyl-s-triazine **(47)** (4.11g, 7.03mmol, 95%); m.p. 47°C, b.p.138°C; *m/z* (EI^+) 585 (M^+ 10%); NMR spectrum 36, Mass Spectrum 28, IR spectrum 6; and hexafluoropropene dimer **(6)**.

VI.5.K. Perfluoroalkylation of Trifluoro-s-triazine (37) with Hexafluoropropene Dimer (5)

A Carius tube (60cm^3), charged with, trimethylamine (0.10g, 1.69mmol), hexafluoropropene dimer **(5)** (7.00g, 23.33mmol) and trifluoro-s-triazine **(37)** (1.00g, 7.40mmol), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, volatile materials (7.05g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were two main components in the mixture which were separated by distillation (atmospheric pressure); perfluoro-4-(1',1'-dimethyl)butyl-s-triazine **(48)**

(0.13g, 0.29mmol, 4%); *m/z* (EI+) 435 (M+ 13%); and hexafluoropropene dimer **(6)**. Due to the low yield of **(48)** it could not be fully characterised.

VI.5.L. Perfluoroalkylation of Trifluoro-s-triazine (37) with Hexafluoropropene (1) in a Solvent

A Carius tube (60cm^3), charged with, trimethylamine (0.20g, 3.38mmol), hexafluoropropene **(1)** (3.00g, 22.22mmol), trifluoro-s-triazine **(37)** (1.00g, 7.40mmol) and acetonitrile (10cm^3), was sealed *in vacuo* and heated in a protective metal tube at 60°C for 48 h. The tube was opened, the clear lower layer isolated, volatile materials (1.30g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were three main components in the mixture which could be characterised by comparison of spectra with those obtained previously;[39] perfluoro-2-isopropyl-s-triazine **(49)** (11% by ^{19}F NMR integration); *m/z* (EI+) 285 (M+ 24%); NMR spectrum 37, Mass Spectrum 29; perfluoro-2,4-di-isopropyl-s-triazine **(50)** (16% by ^{19}F NMR integration); *m/z* (EI+) 435 (M+ 14%); NMR spectrum 38, Mass Spectrum 30; and hexafluoropropene dimer **(6)**. The orange upper layer was also examined by ^{19}F NMR, after addition of a marker, and shown by comparison of spectra with those obtained previously to contain two fluorinated components; perfluoro-2-isopropyl-s-triazine σ-complex **(51)** (29% by ^{19}F NMR integration); NMR spectrum 39; perfluoro-2,4-isopropyl-s-triazine σ-complex **(52)** (40% by ^{19}F NMR integration); NMR spectrum 40. The nature of the counter ion to these σ-complexes could not be ascertained.

VI.6. Halogen Exchange Reactions with TDAE and Fluoro-organic Species

VI.6.A. Fluorination with TDAE (8) and Hexafluoropropene (1)

To an evacuated round bottomed flask containing benzoyl chloride (1.40g, 10.00mmol) and TDAE **(8)** (1.80g, 9.00mmol), in acetonitrile (20cm^3), was attached an expandable gas bladder (2 litre), fitted with a tap, and charged with hexafluoropropene **(1)** (2.25g, 15.00mmol). The bladder was opened to the flask and the mixture stirred for 48 hours at 80°C. A lower layer of dimer **(6)** (1.54g, 5.13mmol) was pipetted off, fluorobenzene added as a marker, and the upper organic layer shown to contain, by ^{19}F NMR, benzoyl fluoride in 49% yield (see **Section VI.2**). The ^{19}F NMR spectrum also revealed a number of other peaks between δ_F -40ppm and δ_F -150ppm, which may be part of the fluoride ion salt.

The reaction was repeated with benzyl bromide as the substrate and benzyl fluoride obtained, as above, in a yield of 36%.

VI.6.B. Fluorination with TDAE (8) and Benzoyl Fluoride

An evacuated round bottomed flask was charged with benzyl chloride (1.70g, 10.00mmol), TDAE (**8**) (1.80g, 9.00mmol) and benzoyl fluoride (1.20g, 9.68mmol) in acetonitrile (20cm^3) and the mixture stirred for 48 hours at 80°C. Fluorobenzene was then added as a marker and the solution shown to contain, by ^{19}F NMR, benzyl fluoride in 30% yield (see **Section VI.2**).

The reaction was repeated with allyl bromide and octyl iodide as substrates and the corresponding fluorides obtained, as above, in yields of 16% and 17% respectively.

The yield of the reaction with benzyl bromide was studied over a longer time period, but the reaction yield did not increase significantly.

CHAPTER SEVEN

Experimental to Chapter Three

VII.1. Reaction of Perfluoro-3,4-dimethylhexa-2,4-diene (14) with Catechol

Dried cesium fluoride (2.00g, 13.16mmol) was added to a sample of freshly sublimed catechol (0.36g, 3.31mmol) in acetonitrile (30cm^3) and stirred in a sealable round bottomed flask for 5 minutes. Diene **(4)** (1.00g, 2.76mmol) was then added under dry nitrogen and the mixture stirred for 7 days at room temperature. After this time recovered cesium fluoride, and other insoluble material, was filtered off to leave a clear yellow solution, which upon addition of a small amount of water (4cm^3) gave an involatile clear lower layer. The lower layer was isolated and, after removal of residual solvent under a continuous vacuum, found to be; tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin **(54)** (1.07g, 2.49mmol, 90%); b.p. 97°C; (Found: C, 38.7; F, 0.9. Calc. for $C_{14}H_4O_2F_{12}$: C, 38.9; H, 0.9%); $\lambda_{max}(CH_2Cl_2)$/nm 229 (ε/dm^3 mol^{-1} cm^{-1} 25,425), 273 (ε/dm^3 mol^{-1} cm^{-1} 12,075); NMR spectrum 41, Mass Spectrum 31, IR spectrum 7. Compounds **(55)** and **(56)** were also formed in low yield and characterised by reference to previous work.[180]

VII.2. Photochemical Electrocyclisation of Benzodioxocin Derivative (54)

A quarts Carius tube (60cm^3) was charged with **(54)** (3.00g, 6.94mmol) and acetonitrile (10cm^3), sealed *in vacuo*, and agitated on a rotating arm under ultraviolet irradiation (broad band) for 24 h. The tube was opened and the material refrigerated (-15°C) for 48 h, after which time a gel-like solid had fallen from solution. The material was isolated, residual solvent removed under a continuous vacuum, and identified as; *tetrakis(1,6,7,8-trifluoromethyl)-3,4-benzo-2,5-dioxabicyclo[4.2.0]octa-3,7-diene* **(58)** (2.82g, 6.52mmol, 94%); b.p. 109°C; (Found: C, 38.5; F, 0.9. Calc. for $C_{14}H_4O_2F_{12}$: C, 38.9; H, 0.9%); $\lambda_{max}(CH_2Cl_2)$/nm 265 (ε/dm^3 mol^{-1} cm^{-1} 2627); NMR spectrum 42, Mass Spectrum 32, IR spectrum 8.

VII.3. Attempted Thermal Electrocyclisation of Benzodioxocin Derivative (54)

A sample of **(54)** (0.25g, 0.58mmol) in acetonitrile (1cm^3) in a quartz NMR tube was heated gradually up to 180°C over a period of 7 days. Repeated ^{19}F NMR analysis showed that no formation of **(58)** had occured and apparent decomposition of **(54)** in the upper temperature range.

VII.4. Reaction of Diene (14) with Phenol

Diene **(14)** (1.00g, 2.76mmol) was added to dried cesium fluoride (2.00g, 13.16mmol) and freshly sublimed phenol (0.65g, 7.00mmol) in acetonitrile (10cm^3) under dry nitrogen. The mixture was stirred for 48 h in a sealable round bottomed flask at room temperature. After this time unreacted cesium fluoride, and other insoluble material, was filtered off to leave a clear pink solution which, upon addition of a small amount of water

($4cm^3$) gave an involatile clear lower layer. The lower layer was isolated and, after removing residual solvent under a continuous vacuum, revealed by comparison of its ^{19}F NMR spectrum with previous work,[180] to be tetrakis(1,2,3,4-trifluoromethyl)-1,4-diphenoxybuta-1,3-diene (mixture of isomers with Z,Z- predominating) **(59)** (1.01g, 1.99mmol, 72%); NMR spectrum 43. A small amount of mono-addition products were also formed but easily removed by distillation and not characterised.

VII.5. Attempted Photochemical Electrocyclisation of Diphenoxy Derivative (59)

A quarts NMR tube was charged with **(59)** (0.20g, 0.39mmol) and acetonitrile ($1cm^3$), sealed *in vacuo*, and agitated on a rotating arm under ultraviolet irradiation (broad band) for 24 h. The tube was opened and revealed by ^{19}F NMR and GLC-MS to contain only starting material.

VII.6. Attempted Thermal Electrocyclisation of Diphenoxy Derivative (59)

A sample of **(59)** (0.18g, 0.38mmol) in acetonitrile ($1cm^3$) in a quartz NMR tube was heated gradually up to 80°C over a period of 48 h. ^{19}F NMR and GLC-MS revealed only starting material in the solution, with some evidence of decomposition.

VII.7. Reaction of (54) with Nitric Acid

Benzodioxocin derivative **(54)** (2.00g, 4.63mmol), concentrated nitric acid (0.80g, 12.70mmol) and acetonitrile ($10cm^3$) were stirred in a round bottomed flask for 3 days at room temperature. After neutralising the solution and removing solvent GLC-MS revealed formation of a dinitro-adduct **(60)**, which due to its low yield (*ca.* 5%) could not be fully characterised. Several repetitions of the reaction in dimethylformamide, using first concentrated and then fuming sulphuric acid at various temperatures failed to improve the yield significantly; Mass Spectrum 33.

VII.8. Reaction of (54) with Bromine

Benzodioxocin **(54)** (3.00g, 6.94mmol), bromine (2.50g, 15.62mmol) and dichloromethane ($10cm^3$) were stirred in a round bottomed flask for 3 days at room temperature. After washing with a saturated aqueous solution of sodium metabisulphite ($10cm^3$ water), to remove unreacted bromine, and removing solvent GLC-MS revealed formation of a monobromo-adduct **(61a)** and a dibromo-adduct **(61b)**, which due to their low yield (*ca.* 8%) could not be fully characterised. Several repetitions of the reaction in other solvents (acetonitrile, diethyl ether) and at different temperatures failed to improve the yield significantly; Mass Spectra 34 and 35.

VII.9. Reaction of Benzodioxocin Derivative (54) with Methoxide

A freshly prepared solution of sodium methoxide in methanol was stirred in an ice bath whilst **(54)** (2.00g, 4.63mmol) added dropwise with the formation of a light blue colour. Stirring was continued for 5 minutes and after this time diethyl ether and water added to give an upper organic layer which was pipetted off, washed with magnesium sulphate and pumped on *in vacuo* to remove solvent. GLC revealed the remaining organic material to be composed of two main components (2:1 ratio), and numerous minor ones, which could not be separated by preparative scale GLC or column chromatography. The largest component in the mixture is thought to correspond to; *tris(1,2,4-trifluoromethyl)-3-difluoromethoxymethyl-4-methoxy-1-(2-hydroxy)phenoxybuta-1,3-diene.* **(62)**; NMR spectrum 44, Mass Spectrum 36. The other major product appears to be an isomer of **(62)**.

VII.10. Epoxidation of Benzodioxocin Derivative (54)

Benzodioxocin **(54)** (3.00g, 6.94mmol), calcium hypochlorite (2.20g, 15.38mmol) and acetonitrile (10cm^3) were stirred in a round bottomed flask for 4 days at 80°C. After filtration of unreacted calcium hypochlorite and other insoluble material, solvent was removed under reduced pressure to leave a mixture of the monoepoxide **(67)** (30% yield by GLC); NMR spectrum 45, Mass Spectrum 37; and diepoxide **(66)** (68% yield by GLC).

The reaction was repeated under similar conditions, but stirred for 7 days to give diepoxide **(66)** almost exclusively. Filtration and solvent removal were as above and the residue (2.58g) was dissolved up in a small amount of diethyl ether (5cm^3) and refrigerated (-15°C) for 2 days. A white precipitate formed and was isolated and residual solvent removed under reduced pressure to give; *2,4-diepoxytetrakis(2,3,4,5-trifluoromethyl)benzodioxocin* **(66)** (2.31g, 4.99mmol, 72%); b.p. 62°C; (Found: C, 36.2; F, 0.7. Calc. for $C_{14}H_4O_4F_{12}$: C, 36.2; H, 0.9%); NMR spectrum 46, Mass Spectrum 38, IR spectrum 9.

VII.11. Epoxidation of (58)

Tetrakis(1,6,7,8-trifluoromethyl)-3,4-benzo-2,5-dioxabicyclo[4.2.0]octa-3,7-diene **(58)** (3.00g, 6.94mmol), calcium hypochlorite (1.20g, 8.39mmol) and acetonitrile (10cm^3) were stirred in a round bottomed flask for 4 days at room temperature. After filtration of unreacted calcium hypochlorite and other insoluble material, solvent was removed under reduced pressure to leave; *tetrakis(1,6,7,8-trifluoromethyl)-3,4-benzo-2,5-dioxabicyclo[4.2.0]octa-3,7-diene-epoxide* **(69)** (2.55g, 5.69mmol, 82%); m.p. 69°C; (Found: C, 37.1; F, 0.7. Calc. for $C_{14}H_4O_3F_{12}$: C, 37.5; H, 0.9%); NMR spectrum 47, Mass Spectrum 39, IR spectrum 10.

VII.12. Attempted Thermal Ring Opening of Diepoxide (66)

Diepoxide **(66)** (0.25g, 0.54mmol) in a solvating amount of diethyl ether (1cm^3), was sealed in a quartz NMR tube *in vacuo*, and heated to 100°C in a furnace for 24 h. By ^{19}F NMR there was no evidence for ring opening. The reaction was repeated at 150°C, 200°C, 250°C, 300°C and 350°C. At 300°C the starting material appeared to be decomposing, as the intensity of the ^{19}F NMR spectrum reduced, and after heating at 350°C almost complete decomposition had occurred.

VII.13. Co-dimerisation of Hexafluoropropene (1) and Perfluoro-3,4-dimethylhexa-2,4-diene (14)

VII.13.A. Cesium Fluoride Catalysis

A Carius tube was charged with diene **(14)** (2.00g, 5.52mmol), hexafluoropropene **(1)** (3.30g, 22.00mmol) and cesium fluoride (1.00g, 6.66mmol) in acetonitrile (10cm^3). The tube was sealed *in vacuo* and stirred for 48 h at 60°C in a rotating oil bath. The tube was opened and a lower layer (6.45g) isolated and analysed by GLC-MS and ^{19}F NMR. There were two main components in the mixture which were separated by preparative scale GLC; *perfluoro-2,3,4,5-tetramethylhepta-2,4-diene* **(75)** (84% by GLC integration based on **(14)** consumed); b.p. 84-86°C (Found C, 25.5. Calc. for $C_{11}F_{20}$: C, 25.8%); $\lambda_{max}(CH_2Cl_2)$/nm 253 (ε/dm^3 mol^{-1} cm^{-1} 500); υ_{max}/cm^{-1} 1650s, 1600s,1550s, 1350-1180br; *m/z* (EI$^+$) 493 (M$^+$-F 1%); NMR spectrum 48, Mass Spectrum 40, IR spectrum 11; and hexafluoropropene dimer **(6)**.

VII.13.B. TDAE (8) Catalysis

A Carius tube, charged with, TDAE **(8)** (0.80g, 4.00mmol), hexafluoropropene **(1)** (5.00g, 33.33mmol) and diene **(14)** (4.00g, 11.04mmol), was sealed *in vacuo* and agitated for 48 h in a rotating oil bath at 60°C. The tube was opened, volatile material transferred to a cold trap and studied by GLC-MS, which did not show any evidence for formation of a mono- or di-adduct or any product of reductive defluorination.

VII.13.C. Trimethylamine Catalysis

Diene **(14)** (4.00g, 11.04mmol) and trimethylamine (0.10g, 1.69mmol) in acetonitrile (10cm^3) were added to a 2-neck round bottomed flask which was attached to an expandable gas bladder (2 litre), fitted with a tap, and charged with hexafluoropropene **(1)** (9.00g, 60.00mmol). The bladder was opened to the flask and the hexafluoropropene allowed to diffuse into the sealed system. The contents of the flask were agitated, using a magnetic stirrer, for 48 h at 60°C. Examination of the lower layer by GLC-MS revealed it to contain hexafluoropropene dimer **(6)**, diene **(14)** and a small amount of a mono-adduct **(75)** (8% by GLC) (see above for analysis).

CHAPTER EIGHT

Experimental to Chapter Four

VIII.1. Synthesis of Hexakis(trifluoromethyl)cyclopentadiene (96)

Samples of 1,1,3,3,3-pentafluoropropene **(97)** (2.20g, 16.67mmol), perfluoro-3,4-dimethylhexa-2,4-diene **(14)** (3.00g, 8.29mmol) and anhydrous acetonitrile (5 cm^3) were transferred *in vacuo* into a Carius tube (60 cm^3) containing freshly dried cesium fluoride (5.00g, 32.90mmol), which was then sealed *in vacuo* and rotated, using a mechanical arm, at ambient temperature for 48 h. The tube was opened, volatile material was then removed by vacuum transfer, and the lower layer contained one component (by GLC) which was identified as hexakis(trifluoromethyl)cyclopentadiene **(96)** (2.90g, 6.12mmol, 74%), b.p. 109°C (Found: C, 27.6; F, 72.3. Calc. for $C_{11}F_{18}$ C, 27.8; F, 72.2%); ν_{max}/cm^{-1} 1730m (C=C), 1200s-1280s (C-F); $\lambda_{max}(CH_2Cl_2)$/nm 253 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 1674); *m/z* 474 (M^+ 10%) and 455 (40); NMR spectrum 49, Mass Spectrum 41, IR spectrum 12.

Distilled water (10 cm^3) was then added to the involatile material and a lower layer formed (1.76g) which contained two resolved components by GLC (*ca.* 1:2), both with *m/z*=586 as the highest value. The ^{19}F NMR spectrum showed ca. eleven CF_3 resonances (54-80 ppm), and several which could be attributed to a CF_2 group (98-108 ppm). Preparative scale gas chromatography was attempted to separate these components, with only limited success, and no further investigation was made.

VIII.2. Reactions of Diene (96) with Alkali Metal Fluorides

VIII.2.A. Cesium Fluoride

Cesium fluoride (0.50g, 3.29mmol), diene **(96)** (1.00g, 2.11mmol) and anhydrous acetonitrile (10cm^3) were refluxed at 80°C for 24 h. After this time the reaction mixture was studied by ^{19}F NMR and FAB-MS and found to contain *cesium pentakis(trifluoromethyl)cyclopentadienide* **(86)** (48% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker); *m/z* FAB- 405 (M^+, 100%) and FAB+ 133 (M^+, 100%), 225 (Cs+glycerol, 6%); NMR spectrum 53, Mass Spectrum 45. Attempts to isolate the reaction product were unsuccessful.

VIII.2.B. Potassium Fluoride

Potassium fluoride (0.20g, 3.45mmol), diene **(96)** (1.00g, 2.11mmol) and anhydrous acetonitrile (10cm^3) were refluxed at 80°C for 24 h. After this time the reaction mixture was studied by ^{19}F NMR and FAB-MS and found to contain *potassium pentakis(trifluoromethyl)cyclopentadienide* (39% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker); *m/z* FAB- 405 (M^+, 100%) and FAB+ 39 (M^+, 42%), 131 (K+glycerol, 2%); NMR spectrum 54, Mass Spectrum 46. Attempts to isolate the reaction product were unsuccessful.

VIII.3. Reactions of Diene (96) with Tetra-alkylammonium Iodides

VIII.3.A. Tetrabutylammonium Iodide

Tetrabutylammonium iodide (0.70g, 1.90mmol) was added to anhydrous acetonitrile (10cm^3), which was refluxed at 80°C, and diene **(96)** (1.00g, 2.11mmol) was then added slowly, with the formation of a red colour, and the mixture was refluxed for 48 h, after which time the solution was cooled and filtered. Solvent was then removed under reduced pressure and the residue redissolved in dichloromethane (10cm^3), which was then washed with a saturated solution of sodium metabisulphite (10cm^3 of water), in order to remove any iodine which was present. The lower layer was then isolated, hexane (10cm^3) was added and the mixture was cooled (-15°C) for two days. Colourless cuboidal crystals were isolated and identified as *tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienide* **(87)** (0.95g, 1.47mmol, 70%), m.p. 118-119°C (Found: C, 48.2; H, 5.4; N, 2.2. $C_{26}H_{36}F_{15}N$ requires C, 48.2; H, 5.6; N, 2.2%); ν_{max}/cm^{-1} 2880w-3000m (C-H), 1495m (aromatic C=C), 1180s-1300s (C-F); *m/z* FAB- 405 (M^+, 100%) and FAB+ 242 (M^+, 23); NMR spectrum 50, Mass Spectrum 42, IR spectrum 13.

VIII.3.B. Tetraethylammonium Iodide

Tetraethylammonium iodide (0.49g, 1.91mmol) was added to anhydrous acetonitrile (10cm^3), and heated under reflux at 80°C. Diene **(96)** (1.00g, 2.11mmol) was then added slowly, with the formation of a red colour, and the mixture was refluxed for 48 h, after which time the solution was cooled and filtered. Solvent was then removed under reduced pressure and the residue redissolved in dichloromethane (10cm^3), which was then washed with a saturated solution of sodium metabisulphite (10cm^3 of water), in order to remove any iodine which was present. The lower layer was then isolated, hexane (10cm^3) was added and the mixture was cooled (-15°C) for two days. Colourless crystals formed, which were identified as *tetraethylammonium pentakis(trifluoromethyl)cyclopentadienide* **(100)** (0.85g, 1.59mmol, 75%), m.p. 241°C (dec) (Found: C, 40.2; H, 3.8; N, 2.5. $C_{18}H_{20}F_{15}N$ requires C, 40.4; H, 3.7; N, 2.6%); ν_{max}/cm^{-1} 2780w and 2990w (C-H), 1495m (aromatic C=C), 1180s-1240s (C-F); *m/z* FAB- 405 (M^+, 100%) and FAB+ 130 (M^+, 25); NMR spectrum 52, Mass Spectrum 44, IR spectrum 15.

VIII.3.C. Tetrapropylammonium Iodide

Tetrapropylammonium iodide (0.59g, 1.89mmol) was added to anhydrous acetonitrile (10cm^3), which was refluxed at 80°C, and diene **(96)** (1.00g, 2.11mmol) was then added slowly, with the formation of a red colour, and the mixture was refluxed for 48 h, after which time the solution was cooled and filtered. Solvent was then removed under reduced pressure and the residue redissolved in dichloromethane (10cm^3), which was then washed with a saturated solution of sodium metabisulphite (10cm^3 of water), in order to remove any iodine which was present. The lower layer was then isolated, hexane (10cm^3) was added and the mixture was cooled (-15°C) for two days. Colourless crystals were isolated and identified as *tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienide* **(101)** (0.90g, 1.47mmol, 73%), m.p. 141-142°C (Found: C, 44.7; H, 4.8; N, 2.5. $C_{22}H_{28}F_{15}N$ requires C, 44.9; H, 4.8; N, 2.4%); ν_{max}/cm^{-1} 2900w-3000w (C-H), 1400s (aromatic C=C), 1170s-1250s (C-F); *m/z* FAB- 405 (M^+, 100%) and FAB+ 186 (M^+, 100); NMR spectrum 51, Mass Spectrum 43, IR spectrum 14.

VIII.3.D. Tetrabutylammonium Iodide under Ultraviolet Irradiation

A quartz Carius tube ($30cm^3$) containing a small magnetic stirrer bar was charged with tetrabutylammonium iodide (0.70g, 1.90mmol), diene **(96)** (1.00g, 2.11mmol) and anhydrous acetonitrile ($10cm^3$). The tube was sealed *in vacuo* and irradiated with a medium pressure mercury lamp (1kW) for 24 h with continuous stirring. After this time a sample of the neat mixture was analysed by ^{19}F NMR and shown to contain Iodotrifluoromethane and tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienide **(87)**, after comparison with the data from authentic samples; see above.

VIII.3.E. Tetrabutylammonium Iodide in the presence of *m*-Dinitrobenzene

Tetrabutylammonium iodide (0.70g, 1.90mmol), *meta*-dinitrobenzene (0.20g, 1.21mmol) and diene **(96)** (1.00g, 2.11mmol) were added to anhydrous acetonitrile ($10cm^3$) and the mixture was refluxed, for 48 h, with the development of a red colour. After this time a sample was analysed by ^{19}F NMR and shown to contain diene **(96)** and tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienide **(87)** (50% yield by integration), after comparison with the data from authentic samples; see above.

VIII.3.F. Tetrabutylammonium Iodide in the presence of α-Pinene

Tetrabutylammonium iodide (0.70g, 1.90mmol), α-Pinene (0.20g, 0.46mmol) and diene **(96)** (1.00g, 2.11mmol) were added to anhydrous acetonitrile ($10cm^3$) and the mixture was refluxed, for 48 h, with the development of a red colour. After this time a sample was analysed by ^{19}F NMR and shown to contain diene **(96)** and tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienide **(87)** (40% yield by integration), after comparison with the data from authentic samples; see above.

VIII.4. Reactions of Diene (96) with Alkali Metal Iodides

VIII.4.A. Cesium Iodide

Cesium iodide (0.70g, 2.69mmol), diene **(96)** (1.00g, 2.11mmol) and anhydrous acetonitrile ($10cm^3$) were refluxed at 80°C for 7 days, with the formation of a red colour, and the mixture was refluxed for 48 h, after which time the solution was cooled and filtered. Solvent was then removed under reduced pressure and the residue redissolved in dichloromethane (10cm^3), which was then washed with a saturated solution of sodium metabisulphite (10cm^3 of water), in order to remove any iodine which was present. The lower layer was then isolated, hexane (10cm^3) was added and the mixture was cooled (-15°C) for two days. *Cesium pentakis(trifluoromethyl)cyclopentadienide* **(86)** was isolated (65% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker, 0.30g, 0.56mmol, 26% isolated), m.p. >300°C (Found: C, 22.5. $C_{10}F_{15}Cs$ requires C, 22.3%); ν_{max}/cm^{-1} 1110s-1250s (C-F), 1505m (C=C); *m/z* FAB- 405 (M$^+$, 100%) and FAB+ 133 (M$^+$, 100%), 225 (Cs+glycerol, 6%); NMR spectrum 53, Mass Spectrum 45, IR spectrum 16.

VIII.4.B. Potassium Iodide

Potassium iodide (0.44g, 2.70mmol), diene **(96)** (1.00g, 2.11mmol) and anhydrous acetonitrile (10cm^3) were refluxed at 80°C for 4 days. Using the procedure described for cesium iodide, *potassium pentakis(trifluoromethyl)cyclopentadienide* was isolated (75% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker, 0.40g, 0.90mmol, 42% isolated), m.p. >300°C (Found: C, 27.3. $C_{10}F_{15}K$ requires C, 27.0%); ν_{max}/cm^{-1} 1150s-1260s (C-F), 1510m (aromatic C=C); *m/z* FAB- 405 (M$^+$, 100%) and FAB+ 39 (M$^+$, 42%), 131 (K$^+$+glycerol, 2%); NMR spectrum 54, Mass Spectrum 46, IR spectrum 17.

VIII.4.C. Sodium Iodide

Sodium iodide (0.40g, 2.70mmol), diene **(96)** (1.00g, 2.11mmol) and anhydrous acetonitrile (10cm^3) were refluxed at 80°C for 48 h. Using the procedure described for cesium iodide, *sodium pentakis(trifluoromethyl)cyclopentadienide* was isolated (95% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker, 0.20g, 0.47mmol, 22% isolated), m.p. >300°C (Found: C, 28.1. $C_{10}F_{15}Na$ requires C, 28.0%); ν_{max}/cm^{-1} 1100s-1230s (C-F); *m/z* FAB- 405 (M$^+$, 100%) and FAB+ 23 (M$^+$, 42%), 115 (Na$^+$+glycerol, 100%); NMR spectrum 54, Mass Spectrum 47, IR spectrum 18.

VIII.4.D. Lithium Iodide

Lithium iodide (0.37g, 2.76mmol), diene **(96)** (1.00g, 2.11mmol) and anhydrous acetonitrile (10cm^3) were refluxed at 80°C for 36 h. Using the procedure described for cesium iodide, *lithium pentakis(trifluoromethyl)cyclopentadienide* was isolated (95% yield by ^{19}F NMR integration of the crude mixture against trifluorotoluene as a marker, 0.15g, 17% isolated), m.p. >300°C (Found: C, 28.8. $C_{10}F_{15}Li$ requires C, 29.1%); ν_{max}/cm^{-1} 1100s-1230s (C-F); *m/z* FAB- 405 (M$^+$, 100%) and FAB+ 99 (Li$^+$+glycerol, 100%), 191 (Li$^+$+2glycerol); NMR spectrum 54, Mass Spectrum 48, IR spectrum 19.

VIII.5. Reaction of Diene (96) with Alkyl and Aryl Lithium Species

VIII.5.A. Reaction of Diene (96) with Phenyl Lithium

A round bottomed flask, fitted with a rubber 'Suba seal' septum under a dynamic nitrogen atmosphere was charged with 1.8M phenyl lithium in cyclohexane/ether (1.10ml, 1.98mmol) and dry acetonitrile (5cm^3) and stirred at room temperature. Diene **(96)** (0.50g, 1.06mmol) was then slowly added with the formation of a dark brown colour. The mixture was stirred at room temperature for 6 h, after which time a neat sample was taken and shown by ^{19}F NMR to contain lithium pentakis(trifluoromethyl)cyclopentadienide (80% yield by ^{19}F NMR integration); NMR spectrum 54, Mass Spectrum 48, IR spectrum 19. ^{19}F NMR also revealed a compound (15% yield by ^{19}F NMR integration) with peaks at δ_F (235MHz, $CDCl_3$) -51.8ppm (s) and -52.4ppm (s) which was thought to be lithium tetrakis(trifluoromethyl)phenylcyclopentadienide **(106)**. The compound could not be isolated; NMR spectrum 56.

VIII.5.B. Reaction of Diene (96) with *t*-Butyl Lithium

A round bottomed flask, fitted with a rubber 'Suba seal' septum under a dynamic nitrogen atmosphere was charged with 1.8M *t*-butyl lithium in cyclohexane/ether (1.20ml, 2.16mmol) and dry acetonitrile (5cm^3) and stirred at room temperature. Diene **(96)** (0.50g, 1.06mmol) was then slowly added with the formation of a dark brown colour. The mixture was stirred at room temperature for 6 h, after which time a neat sample was taken and shown by ^{19}F NMR to contain lithium pentakis(trifluoromethyl)cyclopentadienide (80% yield by ^{19}F NMR integration); NMR spectrum 54, Mass Spectrum 48, IR spectrum 19. ^{19}F NMR also revealed no trace of the *t*-butyl analogue of compound **(106)**.

VIII.6. Reaction of Diene (96) with 1,2,4,5-Tetramethylbenzene (Durene) under Ultraviolet Irradiation

A quartz Carius tube (30cm^3) containing a small magnetic stirrer bar was charged with 1,2,4,5-Tetramethylbenzene (2.94g, 2.2mmol), diene **(96)** (1.00g, 2.11mmol) and dry acetonitrile (10cm^3). The tube was sealed *in vacuo* and irradiated with ultraviolet light (254 nm) for 48 h with continuous stirring. After this time a sample of the neat mixture was analysed by ^{19}F NMR and shown to contain the pentakis(trifluoromethyl)cyclopentadienide anion **(84)** (88% yield by integration); δ_F (235MHz, $CDCl_3$) -49.8 ppm (s). FAB-MS failed to reveal the nature of the counter ion.

VIII.7. Attempted Reaction of Diene (96) with Phenol

A round bottomed flask was charged with phenol (6.00g, 63.82mmol) and diene **(96)** (0.50g, 1.06mmol) and the mixture refluxed at 80°C for 48 h, after this time a neat sample was taken and shown by ^{19}F NMR to contain only starting material.

VIII.8. Attempted Reaction of Diene (96) with Thiophenol

A round bottomed flask was charged with thiophenol (6.00g, 54.54mmol) and diene **(96)** (0.50g, 1.06mmol) and the mixture refluxed at 80°C for 48 h, after this time a neat sample was taken and shown by ^{19}F NMR to contain only starting material.

VIII.9. Attempted Reaction of Diene (96) with 2,3-Dimethylbut-2-ene

A quartz Carius tube (30cm^3) was charged with furan (2.50g, 29.76mmol) and diene **(96)** (1.00g, 2.11mmol) sealed *in vacuo* and heated to 120°C in a furnace for 3 days. After this time the tube was opened and the crude contents shown by ^{19}F NMR and GLC-MS to be only starting material. The reaction was repeated at elevated temperature up to 300°C, which resulted in decomposition of **(96)**.

VIII.10. Attempted Reaction of Diene (96) with Ethene

A quartz Carius tube (30cm^3) was charged with ethene (0.50g, 17.86mmol) and diene **(96)** (1.00g, 2.11mmol) sealed *in vacuo* and heated to 120°C in a furnace for 3 days. After this time the tube was opened and the crude contents shown by ^{19}F NMR and GLC-MS to be only starting material. The reaction was repeated at elevated temperature up to 300°C, which resulted in decomposition of **(96)**.

VIII.11. Attempted Reaction of Diene (96) with Tetrafluoroethene (2)

A quartz Carius tube (30cm^3) was charged with **(2)** (2.00g, 20.00mmol) and diene **(96)** (1.00g, 2.11mmol) sealed *in vacuo* and heated to 120°C in a furnace for 3 days. After this time the tube was opened and the crude contents shown by ^{19}F NMR and GLC-MS to be only starting material.

VIII.12. Attempted Reaction of Diene (96) with Cyclopentadiene

A quartz Carius tube (30cm^3) was charged with cyclopentadiene (2.00g, 30.30mmol) and diene **(96)** (1.00g, 2.11mmol) sealed *in vacuo* and heated to 120°C in a furnace for 3 days. After this time the tube was opened and the crude contents shown by ^{19}F NMR and GLC-MS to be only starting material.

VIII.13. Attempted Formation of Fulvene Derivative (107) Under Reduced Pressure

A sample of cesium salt **(86)** (0.98g, 1.82mmol) was placed in a round bottomed flask and heated steadily to 240°C under a dynamic vacuum. Any volatile material produced was collected in one of two cold traps (liquid air). After heating for 3 h no volatile material had been collected and heating was discontinued.

VIII.14. Attempted Formation of Fulvene Derivative (107) with Boron Trifluoride

To a stirred solution of cesium salt **(86)** (0.65g, 1.21mmol) in acetonitrile (5cm^3) under dry nitrogen was added an equivalence of boron trifluoride etherate (0.18g, 1.27mmol). The mixture was stirred for 2 h at room temperature and after this time ^{19}F NMR revealed only the anion **(84)** in solution, with no evidence for defluorination.

VIII.15. Formation of Carbon Acid (109) by Reaction of (87) with Concentrated Sulphuric Acid

Concentrated sulphuric acid (20cm^3) was slowly added to tetrabutylammonium salt **(87)** (0.30g, 0.46mmol). The system was under reduced pressure and any volatile material produced collected on a cold finger. The material so collected was identified as *5H-perfluoropentamethylcyclopentadiene* **(109)** (0.12g, 0.29mmol, 64%); NMR spectrum 57, Mass Spectrum 49, IR spectrum 20.

VIII.16. Formation of Carbon Acid (109) by Reaction of (87) with Hydrogen Fluoride

An equivalence of hydrogen fluoride was slowly added through a teflon manifold to an acetonitrile solution of tetrabutylammonium salt **(87)** (0.20g, 0.31mmol) in a teflon NMR tube. The tube was sealed with a soldering iron and ^{19}F NMR revealed only *5H-perfluoropentamethylcyclopentadiene* **(109)** in solution by comparison of the spectrum with that obtained above; NMR spectrum 57, Mass Spectrum 49, IR spectrum 20.

CHAPTER NINE

Experimental to Chapter Five

IX.1. Reactions of Diene (96) with Transition Metal Iodides

IX.1.A. Copper Iodide under Ultraviolet Irradiation

A quartz Carius tube (20cm^3) charged with diene **(96)** (1.00g, 2.11mmol), copper iodide (0.45g, 2.37mmol) and anhydrous acetonitrile (5cm^3), was sealed *in vacuo* and agitated for 48h on a rotating arm, whilst irradiating with a medium pressure mercury lamp (1kW). After this time the tube was opened and the insoluble material filtered off to leave a brown solution. Solvent was removed under reduced pressure and the residue (1.05g) was then dissolved in dichloromethane and refridgerated at -15°C for 3 days. Small needle shaped crystals were formed and two subsequent recrystalisations (dichloromethane/hexane; 1:1) yielded *tetrakis(acetonitrile)copper (I) pentakis(trifluoromethyl)cyclopentadienide* **(118)** (0.55g, 0.87mmol, 41% isolated yield), m.p. 100°C (dec) (Found: C, 33.9; N, 8.7; H, 1.8. $C_{18}H_{12}N_4F_{15}Cu$ requires C, 34.2; N, 8.9; H, 1.9%); ν_{max}/cm^{-1} 2750w and 2950w (C-H), 2325 (CN), 1530m (aromatic C=C), 1215s and 1120s (C-F); $\lambda_{max}(CH_3CN)/nm$ 208 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 70,000); *m/z* FAB- 405 (M^+, 100%) and FAB+ 227 ($Cu^+ + 4CH_3CN$, 13%), 186 ($Cu^+ + 3CH_3CN$, 8%), 145 ($Cu^+ + 2CH_3CN$, 100%), 104 ($Cu^+ + CH_3CN$, 77%), 63 (Cu^+, 36%); NMR spectrum 58, Mass Spectrum 50, IR spectrum 118.

IX.I.B. Silver Iodide under Ultraviolet Irradiation

A quartz Carius tube (20cm^3) was charged with diene **(96)** (1.00g, 2.11mmol), silver iodide (0.60g, 2.55mmol) and anhydrous acetonitrile (5cm^3). Using the procedure described for **(118)**, *tetrakis(acetonitrile)silver (I) pentakis(trifluoromethyl)cyclopentadienide* **(122)** was isolated (85% yield by ^{19}F NMR integration against trifluorotoluene as a marker, 0.40g, 28% isolated), m.p. >300°C (dec) (Found: C, 31.9; N, 6.0; H, 1.8. $C_{18}H_{12}N_4F_{15}Ag$ requires C, 31.9; N, 8.2; H, 1.8%); ν_{max}/cm^{-1} 2750w and 2950w (C-H), 2325 (CN), 1496m (aromatic C=C), 1215s and 1120s (C-F); *m/z* FAB- 405 (M^+, 100%) and FAB+ 108 (Ag^+, 100%); NMR spectrum 59, Mass Spectrum 51, IR spectrum 122.

IX.2. Reactions of Diene (96) with Transition Metal Powders

IX.2.A. Thermal Reaction with Copper Powder

Copper powder (0.25g, 3.94mmol) was added to anhydrous acetonitrile (10cm^3) which was refluxed at 80°C. Diene **(96)** (1.00g, 2.11mmol) was then slowly added and the solution was refluxed for 48 h, with the formation of a dark green colour. After this time the solution was cooled and filtered to leave a brown solution. The crude solution was studied by ^{19}F NMR which revealed a large peak at δ_F -49.8 ppm (rel. int. 5) and a range of smaller peaks between δ_F -56 and δ_F -78 ppm (rel. int. 1). Solvent and volatile products were removed under reduced pressure and the residue (1.24g) was then dissolved in dichloromethane and refrigerated (-15°C) for 3 days. Small needle shaped crystals were formed and two subsequent recrystalisations (dichloromethane/hexane; 1:1) yielded *tetrakis(acetonitrile)copper (I) pentakis(trifluoromethyl)cyclopentadienide* **(118)** (0.80g, 1.27mmol, 60% isolated yield), which was identified by comparison with data from an authentic sample; see above.

IX.2.B. Copper Powder with Ultraviolet Irradiation

A quartz Carius tube (20cm^3) was charged with diene **(96)** (1.00g, 2.11mmol), copper powder (0.20g, 3.17mmol) and anhydrous acetonitrile (5cm^3), was sealed *in vacuo* and agitated for 48h on a rotating arm, whilst irradiating with a medium pressure mercury lamp (1kW). After this time the tube was opened in a glove box under an atmosphere of dry nitrogen and insoluble material was filtered off to leave a dark brown solution. Solvent and volatile products were removed under reduced pressure and the residue (1.14g) was then dissolved in dichloromethane and refrigerated (-15°C) for 3 days. Small needle shaped crystals were formed and two subsequent recrystalisations (dichloromethane/hexane; 1:1) yielded; *tetrakis(acetonitrile)copper (I) pentakis(trifluoromethyl)cyclopentadienide* **(118)** (0.85g, 1.35mmol, 64% isolated yield) by comparison with data from an authentic sample; see above.

IX.2.C. Nickel Powder with Ultraviolet Irradiation

A quartz Carius tube (20cm^3) charged with diene **(96)** (1.00g, 2.11mmol), nickel powder (0.20g, 3.38mmol) and anhydrous acetonitrile (5cm^3), was sealed *in vacuo* and agitated for 48h on a rotating arm, whilst irradiating with a medium pressure mercury lamp (1kW). After this time the tube was opened in a glove box under an atmosphere of dry nitrogen and insoluble material was filtered off to leave a pale blue upper layer and a lower clear layer of unreacted diene (0.55g, 1.16mmol). The upper layer was isolated and solvent removed under reduced pressure, the residue (0.50g) was then washed with dichloromethane to give a fine white powder (0.40g, 0.36mmol) which was shown to be *hexakis(acetonitrile)nickel (II) dipentakis(trifluoromethyl)cyclopentadienide* **(119)** (76% isolated yield based on reacted diene), m.p. >300°C (dec) (Found: C, 34.1; N, 7.2; H, 1.5. $C_{32}H_{18}N_6F_{30}Ni$ requires C, 34.4; N, 7.5; H, 1.6%); ν_{max}/cm^{-1} 2753w and 2950w (C-H), 2320 (CN), 1505m (aromatic C=C), 1210s and 1125s (C-F); *m/z* FAB- 405 (M^+, 100%) and FAB+ 58 (Ni^{2+}, 16%); NMR spectrum 60, Mass Spectrum 52, IR spectrum 23.

IX.2.D. Cobalt Powder with Ultraviolet Irradiation

A quartz Carius tube (20cm^3) was charged with diene **(96)** (1.00g, 2.11mmol), cobalt powder (0.20g, 3.38mmol) and anhydrous acetonitrile (5cm^3). Using the procedure described for **(119)** (recovered diene; 0.45g, 0.95mmol), a fine white powder (0.40g, 0.36mmol) was identified as *hexakis(acetonitrile)cobalt (II) dipentakis(trifluoromethyl)cyclopentadienide* **(120)** (62% isolated yield based on reacted diene), m.p. >300°C (dec) (Found: C, 34.1; N, 7.0; H, 1.5. $C_{32}H_{18}N_6F_{30}Co$ requires

C, 34.4; N, 7.5; H, 1.6%); ν_{max}/cm^{-1} 2753w and 2947w (C-H), 2330 (CN), 1497m (aromatic C=C), 1215s and 1127s (C-F); *m/z* FAB- 405 (M^+, 100%) and FAB+ 59 (Co^{2+}, 21%); NMR spectrum 61, Mass Spectrum 53, IR spectrum 24.

IX.2.E. Iron Powder with Ultraviolet Irradiation

A quartz Carius tube (20cm^3) was charged with diene **(96)** (1.00g, 2.11mmol), iron powder (0.20g, 3.63mmol) and anhydrous acetonitrile (5cm^3). Using the procedure described for **(119)** (recovered diene; 0.48g, 1.01mmol), a fine white powder (0.45g, 0.40mmol) was identified as *hexakis(acetonitrile)iron (II) dipentakis(trifluoromethyl)cyclopentadienide* **(121)** (74% isolated yield based on reacted diene), m.p. >300°C (dec) (Found: C, 34.5; N, 7.2; H, 1.6. $C_{32}H_{18}N_6F_{30}Fe$ requires C, 34.5; N, 7.5; H, 1.6%); ν_{max}/cm^{-1} 2750w and 2954w (C-H), 2325 (CN), 1500m (aromatic C=C), 1210s and 1117s (C-F); *m/z* FAB- 405 (M^+, 100%) and FAB+ 56 (Fe^{2+}, 21%); NMR spectrum 62, Mass Spectrum 54, IR spectrum 25.

IX.2.F. Ruthenium Powder with Ultraviolet Irradiation

A quartz Carius tube (20cm^3) was charged with diene **(96)** (1.00g, 2.11mmol) and ruthenium powder (0.35g, 3.43mmol), was sealed *in vacuo* and agitated for 48h on a rotating arm, whilst irradiating with a medium pressure mercury lamp (1kW). After this time the tube was opened in a glove box under an atmosphere of dry nitrogen and insoluble material was filtered off to leave a brown solid with a peak in its FAB-MS corresponding to the pentakis(trifluoromethyl)cyclopentadiene anion **(84)** [M^+ 405]. ^{19}F NMR also revealed the anion **(84)** to be present, with a peak at δ_F -49.8ppm. The solid decomposed rapidly and full analysis was could not be obtained.

IX.3. Reaction of Diene (96) With Decamethylferrocene

A mixture containing decamethylferrocene (0.60g, 1.84mmol) and dry acetonitrile (70 cm^3) was heated under reflux at 85°C. Diene **(96)** (1.00g, 2.10mmol) was then slowly added, and a dark green colour immediately formed. The mixture was refluxed for 17.5 h, after which the solvent was evaporated to half its volume and the solution cooled to -30°C for 6 h, using a cryostat. No crystalline material was observed, so the solvent was removed and the resultant residue recrystallised from a minimum of dry acetonitrile to give small, dark green crystals (0.86g, 1.17mmol, 64%), identified as *decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienide* **(125)**, m.p. >330°C (Found C, 49.2; H, 4.2; Fe, 8.2. $C_{30}H_{30}F_{15}Fe$ requires C, 49.3; H, 4.10; Fe, 7.7); ν_{max}/cm^{-1} 2905w and 2985w (C-H), 1505s (aromatic C=C), 1200s and 1120s (C-F); *m/z* FAB- 405 (M^+, 100%) and FAB+ 326 ($(C_{10}H_{15})_2Fe$, 31%); NMR spectrum 63, Mass Spectrum 55, IR spectrum 26.

IX.4. Reaction of Nickel Salt (119) under Heat

A sample of nickel salt **(119)** (0.36g, 0.32mmol) was placed in a round bottomed flask and heated steadily to 300°C under a dynamic vacuum. Any volatile material produced was collected in one of two cold traps (liquid air). After heating for 4 h some volatile material had been collected and was identified by ^{19}F NMR as a salt of the pentakis(trifluoromethyl)cyclopentadienide anion **(84)**. Examination of the involatile material by microanalysis revealed it to still contain carbon, nitrogen, hydrogen and fluorine, but in different ratios to the starting material. Repetition of the experiment gave a different ratio of elements and it was concluded that the involatile material was a mixture of ill-defined salts.

IX.5. Reaction of Copper Salt (118) with Halogens

IX.5.A. Fluorine

A Teflon flask was charged with copper salt **(118)** (3.00g, 4.75mmol) and anhydrous acetonitrile (10cm^3) under a flow of dry nitrogen. 10% elemental fluorine was bubbled through the vessel at a rate of 5ml min^{-1} until a slight excess had been used. The solution turned red in colour and ^{19}F NMR and GLC-MS analysis revealed formation of *perfluoropentamethylcyclopentadiene* **(127)** (21% by ^{19}F NMR integration); NMR spectrum 64, Mass Spectrum 56. Attempts to isolate the compound by flash distillation were unsuccessful due to its unstable nature.

IX.5.B. Chlorine

A Teflon flask was charged with copper salt **(118)** (3.00g, 4.75mmol) and anhydrous acetonitrile (10cm^3) under a flow of dry nitrogen. Chlorine was bubbled through the vessel at a rate of 5ml min^{-1} until a slight excess had been used. The solution turned yellow in colour and after standing for 30 minutes ^{19}F NMR analysis revealed formation of *5-chloropentakis(trifluoromethyl)cyclopentadiene* **(128)** (14% by ^{19}F NMR integration); NMR spectrum 65. Attempts to isolate the compound by flash distillation were unsuccessful due to its unstable nature and the molecular ion could not be found by Mass Spectroscopy.

IX.5.C. Bromine

A round bottomed flask was charged with copper salt **(118)** (3.00g, 4.75mmol) and anhydrous dichloromethane (10cm^3) under a flow of dry nitrogen. Bromine (0.80g, 5.06mmol) was added to the solution and the mixture stirred for 24 h at room temperature. After standing for 30 minutes ^{19}F NMR analysis revealed formation of *5-bromopentakis(trifluoromethyl)cyclopentadiene* **(129)** (8% by ^{19}F NMR integration); NMR spectrum 66. Attempts to isolate the compound by flash distillation were unsuccessful due to its unstable nature and the molecular ion could not be found by Mass Spectroscopy.

IX.5.D. Iodine

A round bottomed flask was charged with copper salt **(118)** (2.00g, 3.16mmol) and anhydrous dichloromethane (10cm^3) under a flow of dry nitrogen. Iodine (1.00g, 3.94mmol) was added to the solution and the mixture stirred for 24 h at room temperature. After standing for 30 minutes ^{19}F NMR analysis revealed formation of the *iodotetrakis(trifluoromethyl)cyclopentadienide anion* **(105)** (12% by ^{19}F NMR integration); NMR spectrum 55. Attempts to isolate the compound were unsuccessful.

IX.6. Reaction of Tetrabutylammonium Salt (87) with Halogens

IX.6.A. Fluorine

A Teflon flask was charged with salt **(87)** (1.00g, 1.54mmol) and anhydrous acetonitrile (10cm^3) under a flow of dry nitrogen. 10% elemental fluorine was bubbled through the vessel at a rate of 5ml min^{-1} until a slight excess had been used. ^{19}F NMR analysis revealed only starting to be present in the solution.

IX.6.B. Chlorine

A Teflon flask was charged with salt **(87)** (1.00g, 1.54mmol) and anhydrous acetonitrile (10cm^3) under a flow of dry nitrogen. Chlorine was bubbled through the vessel at a rate of 5ml min^{-1} until a slight excess had been used. The solution turned yellow in colour and after standing for 30 minutes ^{19}F NMR analysis revealed only starting material to be present in the mixture.

IX.7. Synthesis of Ruthenium Compex (134) using MVS

The pre-melted and pre-weighed ruthenium ingot (3.42g) was placed on an Al_2O_3 crucible on the copper hearth and the apparatus assembled as described in **Chapter Five**. The ligand **(96)** (7.50g, 15.82mmol) and perfluoromethylcyclohexane (30.00g, 85.71mmol) were placed in a thick-walled ampoule and degassed. The ampoule was connected to the ligand inlet system. The entire apparatus was subsequently evacuated to 5 x 10^{-7} mbar for approximately 12 hours before the start of the reaction.

The insulated jacket was filled with liquid nitrogen and the flange heater switched on. The ligand mantle and delivery line were also heated to a 115°C, a slightly higher temperature than the boiling point of the ligand. The ligand manifold was then opened to the reaction chamber, allowing a thin layer of the solvated ligand to condense onto the walls of the bell-jar. A voltage of between 5.2kV and 6.4kV was then applied to heat resistively the tungsten wire around the crucible, causing the metal to evaporate. The rates of metal evaporation and ligand sublimation were regulated to maintain a vacuum of 1 x 10^{-5} mbar.

Co-condensation of ruthenium (0.74g, 7.25mmols) and solvated ligand was continued for 2 hours, until all the ligand had been sublimed. A gradual build up of a pink matrix was observed.

At the end of the experiment, all heating systems were switched off (except the vacuum seal flange) and the liquid nitrogen drained from the jacket. The pumps were then shut off, the reaction chamber filled with nitrogen and the apparatus allowed to achieve ambient temperature (a mercury bubbler fitted to the apparatus allows for the expansion of the gas). The product was washed from the walls of the reaction chamber with dry, degassed perfluoromethylcyclohexane (ca. 500 ml), to yield a yellow solution. The perfluoromethylcyclohexane and excess ligand were subsequently removed *in vacuo*, leaving a yellow-brown viscous liquid (0.21g, 0.21mmol, 1.33% yield; based on ligand condensed). Due to the low yield the material could not be fully characterised. On the basis of EI-MS, CI-MS, FAB-MS and ^{19}F NMR compound **(134)** was tentatively suggested as a major component; NMR spectrum 57, Mass Spectrum 67.

IX.8. Electrochemistry

IX.8.A. General Apparatus

Cyclic voltammetry was performed using a 'home-made' potentiostat[265] with a positive feedback ohmic drop compensation and a Tacussel GSTP4 signal generator. The working electrode was a glassy-carbon (Tokai Corp.) disk (3mm diameter) and the reference electrode a saturated calomel electrode (SCE). Calculations were made with a Digisim 2.0, Cyclic Voltammetric Simulator (Bioanalytical Systems, Inc.) on a Pentium 90 computer. The supporting electrolyte was tetraethylammonium tetrafluoroborate (Et_4NBF_4; Fluka puriss) and acetonitrile was used as a solvent, without purification.

IX.8.B. Electrolysis of Diene (96)

A solution of hexakis(trifluoromethyl)cyclopentadiene **(96)** (0.24g, 0.51mmol) and Et_4NBF_4 (2.17g, 10.00mmol) in acetonitrile (80 cm^3) was reduced at -0.45 V (vs SCE), in a three compartment cell, until all the starting material was consumed (0.7 F/mole as checked by cyclic voltammetry). A circular carbon felt (5cm x 5cm) was used as the cathode, and was separated from the anolyte (carbon felt) with a glass frit of porosity 4. The solution was then evaporated to dryness, using a water aspirator (bath temperature below 40°C), to give a white residue as crude material. The presence of pentakis(trifluoromethyl)cyclopentadienide ion **(84)** was confirmed by ^{19}F NMR spectroscopy; δ_F (376 MHz; CD_3CN) -51.2 (s) ppm). Two other resonances were observed (δ_F -75.9 and -83.7 ppm; rel. int. 1), which integrated to approximately 9:1.

IX.9. X-ray Crystallography

Single-crystal X-ray diffraction experiments were carried out at T=150 K on a Siemens 3-circle diffractometer with a CCD area detector or Rigaku AFC6S 4-circle diffractometer, both using graphite-monochromated Mo-K_α radiation (l=0.71073 Å) and Cryostream open-flow N_2 gas cryostats. SHELXTL-PLUS software[266] was used for structure solutions and refinement, the latter was performed against F^2 of all data with Chebyshev weighting scheme. Of the discrepancy factors given below, ωR and goodness-of-fit S refer to F^2 of all data, R to F of observed data, with $I \geq 2\sigma(I)$. Atomic co-ordinates and thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic data Centre, see Notice to Authors, Issue No.1, 1996.

Molecular Dynamics Calculations for the pentakis(trifluoromethyl)cyclopentadienide anion were performed using Chem-X software.[267] A molecular dynamics run was extended over 50 ps at 150 K with 0.5 fc steps. The observed energy range was 0.0 to 18.7 kcal mol^{-1}. Twenty-three conformations with lowest energies (≤2.0 kcal mol^{-1}) were sampled from this run and their structural parameters (torsion angles, distortions of the ring planarity, *etc.*) were determined. A run for T=300 K was performed in the same manner, giving energy variations from 0 to 20.0 kcal mol^{-1}; twenty-nine conformations with the energy below 2.5 kcal mol^{-1} were sampled for geometrical analysis.

IX.9.A. Tetrakis(acetonitrile)copper (I) pentakis(trifluoromethyl)cyclopentadienide (118)

$C_8H_{12}N_4Cu^+C_{10}F_{15}^-$ **(118)**, M=632.9, orthorhombic, T=150 K, *a*=21.100(2), *b*=43.273(4), *c*=5.216(1) Å, V=4763(1)Å^3 from 399 reflections with 12<θ<23°, space group Pmmn (No. 59), Z=8, D_c=1.765 g cm^{-3}, F(000)=2496, μ=10.5 cm^{-1}, colourless crystal of 0.3x0.2x0.1 mm size. Data collection on a Siemens 3-circle diffractometer with a CCD area detector graphite-monochromated Mo-K_α radiation (λ=0.71073 Å), ω scan mode, 2θ≤51.5°, 19425 total, 4390 unique and 2907 observed data. Substantial overlap of reflections along *b** axis resulted in rather high R_{int} of 0.136 and irreducible final R. The structure was solved by a combination of Patterson and direct methods. All non-H atoms were refined by full-matrix least squares with anisotopic displacement parameters and all methyl groups as rigid bodies with refined U_{iso} (all of them, except $C(32)H_3$, were treated as disordered over two symmetrically-related orientations). The refinement of 390 variables against 3827 non-negative data converged at wR=0.229, R=0.082, S=1.08, max. final shift/e.s.d. ratio of 0.13 (Me-group rotation). Three largest residual peaks of electron density (0.7-1.1 eÅ^{-3}) were located in the vicinity of Cu atoms and some smaller ones (0.4-0.6 eÅ^{-3}) between CF_3 groups of the anion. The latter peaks could be interpreted as a small (10-15%) contribution of another orientation of the anion, staggered with respect to the major one, but refinement of this model gave no meaningful improvement.

IX.9.B. Decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienide (125)

$C_{20}H_{30}Fe^{+}C_{10}F_{15}^{-}$ **(125)**, M=731.4, monoclinic, T=150 K, *a*=9.089(2), *b*=14.956 (2), *c*=11.976(2) Å, β=110.73(1)°, V=1522.5(5) $Å^3$, from 25 reflections with 16<θ<25°, space group $P2_1/n$ (No. 14), Z=2, D_c=1.595 g cm^{-3}, F(000)=742, μ=6.1 cm^{-1}, ω/2θ scan mode, 2θ≤56°, 3124 total, 2959 unique (R_{int}=0.060) and 1663 observed data, green crystal of 0.5x0.25x0.1 mm size. Data collection on a Rigaku AFC6S 4-circle diffractometer with a CCD area detector graphite-monochromated Mo-K_α radiation (λ=0.71073 Å). Empirical absorption correction (TEXSAN software[268]) was insignificant (T_{min}=0.96, T_{max}=1.00). Structure solution by direct methods proved impossible, while the position of Fe atom at inversion centre (clear from the Patterson map) rendered it useless for phase determination. In the event, the first coordination sphere of the Fe atom was determined from Patterson vectors. Subsequent Fourier expansion revealed the entire cation, but a rather shapeless cloud of electron density at the anion position. The latter was rationalised essentially by a trial-and-error fitting of a rigid-body pentamethylcyclopentadienide skeleton. All fluorine positions were then located from Fourier map. With the anion disordered over two inversion-related positions and the C_5Me_5 ring over two symmetrically independent positions with essentially equal occupancies (proved by refinement of occupancy factors), actually every atom in the structure was refined with a 50% occupancy. Final refinement was performed by full-matrix least squares with no geometrical restraints for non-H atoms. Ring carbon atoms were refined in isotropic approximation, other non-H atoms with anisotropic displacement parameters, methyl groups were refined as rigid bodies with refined isotropic U for each three hydrogens. The refinement of 357 variables converged at R=0.042, wR=0.108, S=1.03, residual $\Delta\rho_{max}$=0.28, $\Delta\rho_{min}$=-0.26 $eÅ^{-3}$, max. final shift/e.s.d. ratio of 0.002. Our attempts to refine the structure in space groups $P2_1$ and P*n*, or as a twinned crystal, did not lead to any meaningful improvement. At room temperature, the lattice is monoclinic I, *a*=9.308(2), *b*=15.023(4), *c*=12.164(3) Å, β=110.34(2)°, V=1594.9(7) $Å^3$.

Appendices

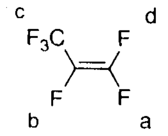
Appendix One

NMR Data

1. Hexafluoropropene (**1**)
2. Octafluorocyclopentene (**17**)
3. Hexafluorocyclobutene (**19**)
4. *E*-Perfluoro-3,4-dimethylhex-3-ene (**13a**)
5. *Z*-Perfluoro-3,4-dimethylhex-3-ene (**13b**)
6. *Z,Z*-Perfluoro-3,4-dimethylhexa-2,4-diene (**14a**)
7. *Z,E*-Perfluoro-3,4-dimethylhexa-2,4-diene (**14b**)
8. Perfluorobicyclopentylidene (**11**)
9. Perfluoro-1,1'-bicyclo-1-pentenyl (**12**)
10. Tetrakis(dimethylamino)ethene (**8**)
11. Octamethyloxamidium difluoride (**10**)
12. Perfluoro-4-methylpent-2-ene (**5**)
13. Perfluoro-2-methylpent-2-ene (**6**)
14. Perfluoro-4-methylpentanyl (**15**)
15. Perfluoro-1-bicyclo-1-pentenide anion (**20**)
16. Perfluoro-1-isopropylcyclopentene (**21**)
17. Perfluoro-1,2-di-isopropylcyclopentene (**22**)
18. Perfluoro-1-(1',1'-dimethyl)butylcyclopentene (**23**)
19. Perfluoro-4-isopropylpyridine (**25**)
20. Perfluoro-2,4-di-isopropylpyridine (**26**)
21. Perfluoro-2,4,5-tri-isopropylpyridine (**27**)
22. Perfluoro-2,4,6-tri-isopropylpyridine (**28**)
23. Perfluoro-4-isopropylpyrimidine (**30**)
24. Perfluoro-4,6-di-isopropylpyrimidine (**31**)
25. Perfluoro-2,4,6-tri-isopropylpyrimidine (**32**)
26. Perfluoro-4-(1',1'-dimethyl)butylpyrimidine (**33**)
27. Perfluoro-2,4,5,6-tetra-isopropylpyrimidine (**34**)
28. Perfluoro-2,6-di-isopropyl-4-(1',1'-dimethyl)butylpyrimidine (**36**)
29. 2,4-Dinitroheptafluoroisopropylbenzene (**39**)
30. Perfluoroisopropylidenecyclobutane (**40**)
31. Perfluoro-2-cyclobut-1-en-1-yl-2,3-dimethylbutane (**41**)
32. Perfluoro-2-cyclobut-1-en-1-yl-2-cyclobutylpropane (**42**)
33. Perfluoro-4-ethylpyridine (**44**)
34. Perfluoro-2,4-diethylpyridine (**45**)
35. Perfluoro-2,4,5-triethylpyridine (**46**)
36. Perfluoro-2,4,6-tri-isopropyl-s-triazine (**47**)

37. Perfluoro-2-isopropyl-s-triazine (**49**)
38. Perfluoro-2,4-di-isopropyl-s-triazine (**50**)
39. Perfluoro-2-isopropyl-s-triazine σ-complex (**51**)
40. Perfluoro-2,4-di-isopropyl-s-triazine σ-complex (**52**)
41. Tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin (**54**)
42. Tetrakis(1,6,7,8-trifluoromethyl)-3,4-benzo-2,5-dioxabicyclo[4.2.0]octa-3,7-diene (**58**)
43. *Z,Z*-Tetrakis(1,2,3,4-trifluoromethyl)-1,4-diphenoxybuta-1,3-diene (**59**)
44. Tris(1,2,4-trifluoromethyl)-3-difluoromethoxymethyl-4-methoxy-1-(2-hydroxy)phenoxybuta-1,3-diene. (**62**)
45. 2-Epoxytetrakis(2,3,4,5-trifluoromethyl)benzodioxocin (**67**)
46. 2,4-Diepoxytetrakis(2,3,4,5-trifluoromethyl)benzodioxocin (**66**)
47. Tetrakis(1,6,7,8-trifluoromethyl)-3,4-benzo-2,5-dioxabicyclo[4.2.0]octa-3,7-diene-epoxide (**69**)
48. Perfluoro-2,3,4,5-tetramethylhepta-2,4-diene (**75**)
49. Hexakis(trifluoromethyl)cyclopentadiene (**96**)
50. Tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienide (**87**)
51. Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienide (**101**)
52. Tetraethylammonium pentakis(trifluoromethyl)cyclopentadienide (**100**)
53. Cesium pentakis(trifluoromethyl)cyclopentadienide (**86**)
54. Pentakis(trifluoromethyl)cyclopentadienide (**84**); with potassium, sodium and lithium counter ions
55. Lithium tetrakis(trifluoromethyl)iodocyclopentadienide (**105**)
56. Lithium tetrakis(trifluoromethyl)phenylcyclopentadienide (**106**)
57. 5H-Perfluoropentamethylcyclopentadiene (**109**)
58. Tetrakis(acetonitrile)copper (I) pentakis(trifluoromethyl)cyclopentadienide (**118**) (including ^{19}F NMR solid state spectrum)
59. Tetrakis(acetonitrile)silver (I) pentakis(trifluoromethyl)cyclopentadienide (**122**)
60. Hexakis(acetonitrile)nickel(II)dipentakis(trifluoromethyl)cyclopentadienide (**119**)
61. Hexakis(acetonitrile)cobalt(II)dipentakis(trifluoromethyl)cyclopentadienide (**120**)
62. Hexakis(acetonitrile)iron (II) dipentakis(trifluoromethyl)cyclopentadienide (**121**)
63. Decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienide (**125**)
64. Perfluoropentamethylcyclopentadiene (**127**)
65. 5-Chloropentakis(trifluoromethyl)cyclopentadiene (**128**)
66. 5-Bromopentakis(trifluoromethyl)cyclopentadiene (**129**)
67. Ruthenium Complex (**134**)

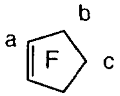
Spectrum No. 1



(1)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-69.4	ddd	J_{cd} 21.2, J_{cb} 12.7, J_{ca} 8.5	3	c
	-94.1	ddq	J_{ad} 58.1, J_{ab} 39.8, J_{ac} 8.5	1	a
	-107.6	ddq	J_{db} 117.7, J_{da} 58.1, J_{dc} 21.2	1	d
	-193.1	dqd	J_{bd} 117.7, J_{bc} 12.7, J_{ba} 39.8	1	b

Spectrum No. 2



(17)

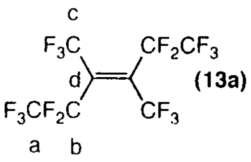
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-121.3	dd	J_{ba} 11.4, J_{bc} 11.3	2	b
	-133.2	s	-	1	c
	-153.5	tt	J_{ab} 11.5, $J_{ab'}$ 11.7	1	a

Spectrum No. 3

(19)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-125.1	m	-	2	b
	-136.3	m	-	1	a

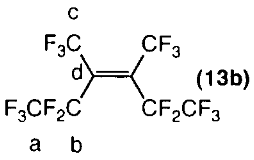
Spectrum No. 4



(13a)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-57.7	tq	J_{cb} 21.8, J_{ca} 3.4	3	c
	-74.1	psuedo septet	$J_{a,b+b'}$ 3.4	3	a
	-99.3	br.s	-	2	b
^{13}C	110.5	t	J_{CF} 43.9	-	b
	112.9	q	J_{CF} 265.4		c
	117.9	qt	J_{dc} 289.2, J_{db} 34.3	-	d
	118.9	q	J_{CF} 278.5	-	a

Spectrum No. 5

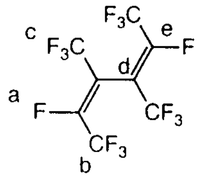


(13b)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-57.1	qt	$J_{cc'}$ 20.3, J_{bc} 6.8	3	c
	-74.0	psuedo septet	$J_{a,c+c'}$ 6.4	3	a
	-99.3	br.s	-	2	b

^{13}C Spectrum was coincidental with E-isomer.

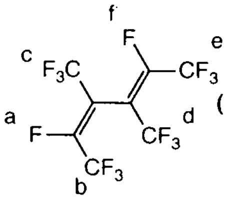
Spectrum No. 6



(14a)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-60.5	d pseudo-septets	J_{ca} 19.2, $J_{c,b+c'}$ 1.5	3	c
	-68.2	d pseudo-septets	J_{ba} 8.3, $J_{b,c+c'}$ 1.7	3	b
	-100.9	qq	J_{ac} 19.3, J_{ab} 7.5	1	a
^{13}C	107.3	qdd	J_{CF} 38.8, J_{da} 17.5, $J_{da'}$ 5.8	-	d
	116.9	qd	J_{CF} 276.6, J_{ca} 38.1	-	c
	119.9	qd	J_{CF} 277.3, J_{ba} 12.6	-	b
	152.7	dq	J_{ea} 291.2, J_{CF} 40.4	-	e

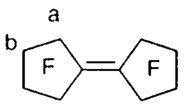
Spectrum No. 7



(14b)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-56.6	overlapping dqq	$J_{d,e+f+c}$ 1.9	3	d
	-60.3	dqq	J_{ca} 18.8, J_{cd}2.3, J_{cb} 1.1	3	c
	-67.9	qd	J_{ed} 10.5, J_{ef} 7.5	3	e
	-68.8	dq	J_{ba} 7.1, J_{bc} 2.3	3	b
	-97.4	qq	J_{fd} 14.1, J_{fe} 3.8	1	a
	-102.2	qq	J_{ac} 19.2, J_{ab} 6.8	1	f

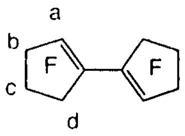
Spectrum No. 8



(11)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-110.0	s	-	1	a
	-135.6	s	-	1	b

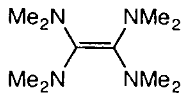
Spectrum No. 9



(12)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-107.2	t	J_{dc} 17.2	2	d
	-109.1	tt	J_{ab} 44.0, $J_{a,c\text{ or }d}$ 14.7	1	a
	-119.1	d	J_{ba} 14.7	2	b
	-129.8	s	-	2	c

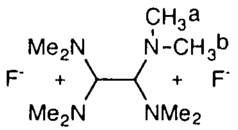
Spectrum No. 10



(8)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{1}H	2.45	br.s	-	-	

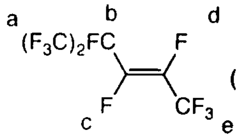
Spectrum No. 11



(10)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-106.0	s	-	-	
^{1}H	3.2	s	-	1	a or b
	3.6	s	-	1	a or b

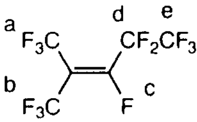
Spectrum No. 12



(5)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-71.7	dd	J_{ed} 20.9, J_{ec} 9.0	3	e
	-76.0	m	-	6	a
	-158.0	d	J_{dc} 139.8	1	d
	-161.1	dd	J_{cd} 45.8, J_{cb} 139.8	1	c
	-189.8	d	J_{bc} 45.8	1	b

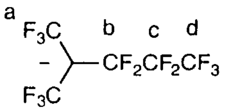
Spectrum No. 13



(6)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-60.3	m	-	3	a
	-63.0	dq	J_{bc} 33.2, J_{ba} 9.1	3	b
	-86.4	m	-	3	e
	-100.4	br.s	-	1	c
	-119.5	qd	J_{de} 20.3 J_{dc} 4.7	2	d

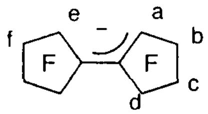
Spectrum No. 14



(15)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-42.2	tt	J_{ab} 19.8, J_{ac} 6.4	6	a
	-81.4	t	J_{dc} 10.0	3	d
	-91.6	m	-	2	b
	-126,7	m	-	2	c

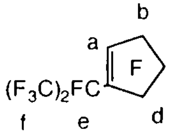
Spectrum No. 15



(20)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-80.5	d	J_{ea} 29	4	e
	-107.7	br.s	-	2	d
	-110.5	br.s	-	2	b
	-129.2	br.s	-	2	c
	-129.7	br.s	-	4	f
	-157.1	br.s	-	1	a

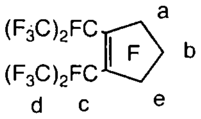
Spectrum No. 16



(21)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-74.4	overlapping dq	-	6	f
	-107.6	br.m	-	2	d
	-111.4	br.m	-	1	a
	-122.1	d	J_{ba} 15	2	b
	-132.0	m	-	2	c
	-189.2	sept.	J_{ef} 9	1	e

Spectrum No. 17

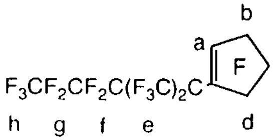


(22)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-71.9	d	J_{dc} 47.4	12	d
	-109.6	d	J_{ac} 47.0	2	a
	-111.5	d	J_{ec} 47.0	2	e
	-136.7	m	-	2	b
	-169.9	sept.	J_{cd} 47.1	2	c

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-71.9	d	J_{dc} 47.4	12	d
	-110.6	m	-	4	a and e
	-136.7	m	-	2	b
	-175.5	sept.m	J_{cd} 46.6	2	c

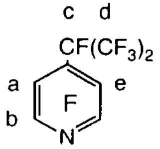
Spectrum No. 18



(23)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-60.0	d	J_{ea} 20.2 J_{ef} 10.5	6	e
	-81.1	t	J_{hf} 12.2	3	h
	-89.5	t	J_{ab} 2.6	1	a
	-105.3	m	-	2	b or d
	-105.9	m	-	2	b or d
	-122.1	dd	J_{fa} 12.8, J 4.5	2	f
	-122.6	m	-	2	g
	-133.0	m	-	2	c

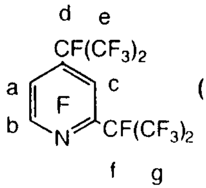
Spectrum No. 19



(25)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-74.3	d	J_{dc} 6.0	6	d
	-86.7	dd	J_{ba} 21.0, J_{be} 29.4	2	b
	-135.2	d	J_{ac} 85.1	1	a
	-136.4	d	J_{ec} 85.0	1	e
	-180.3	dq	J_{ca} 21.3, J_{cd} 6.0	1	c

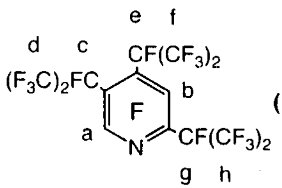
Spectrum No. 20



(26)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-74.0	m	-	6	e
	-74.1 ? see paper	m	-	6	g
	-82.3	m	-	1	b
	-119.0	dd	J_{ca} 20.3, J_{cb} 30.3	1	c
	-121.3	d	J_{ab} 23.4	1	a
	-177.3	dm	J_{dc} 85.0	1	d
	-181.4	dm	J_{fc} 60.0	1	f

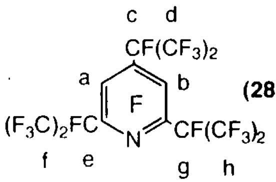
Spectrum No. 21



(27)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-50.5	m	-	1	a
	-72.6	m	-	12	d and f
	-74.4	m	-	6	h
	-110.5	ddsept.	J_{be} 58.2, J_{ba} 30.0, J_{bh} 3.0	1	b
	-166.6	dm	J_{ca} 32.2	2	c and e
	-184.2	dm	J_{gb} 58.0	1	g

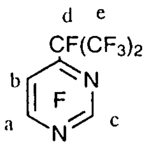
Spectrum No. 22



(28)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-74.1	d	J_{fa} 3.0	12	f and h
	-74.8	m	-	6	d
	-106.4	ddsept.	J_{ae} 57.3, J_{ad} 19.2, J_{af} 3.0	1	a
	-107.5	ddsept.	J_{bc} 92.2, J_{bg} 58.3, J_{bh} 3.0	1	b
	-179.3	dm	J_{ca} 6.0	1	c
	-185.2	dm	J_{eh} 6.0	2	e and g

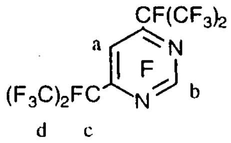
Spectrum No. 23



(30)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-47.7	d	J_{cb} 27.8	1	c
	-69.9	d	J_{ab} 21.8	1	a
	-74.8	d	J_{ed} 6.2	6	e
	-151.7	m	-	1	b
	-186.2	dm	J_{db} 53.0	1	d

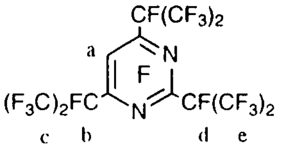
Spectrum No. 24



(31)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-48.6	d	J_{ba} 27.8	1	b
	-74.5	m	-	12	d
	-134.1	dd	J_{ab} 30.4, $J_{ac'}$ 5.0	1	a
	-185.7	dsept.	J_{ca} 53.0, J_{cd} 6.8	2	c

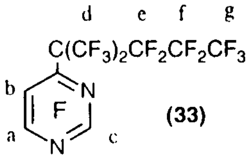
Spectrum No. 25



(32)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-74.2	m	-	12	c
	-74.9	m	-	6	e
	-122.7	t	$J_{a,b+b'}$ 51.1	1	a
	-181.1	sept.	J_{dc} 6.0	1	d
	-185.5	sept	J_{bc} 6.0	2	b

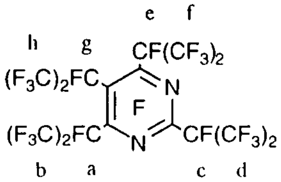
Spectrum No. 26



(33)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-47.4	s	-	1	c
	-59.1	m	-	6	d
	-67.6	d	J_{ab} 21.1	1	a
	-81.2	m	-	3	g
	-104.5	m	-	2	e
	-122.6	m	-	2	f
	142.8	m	-	1	b

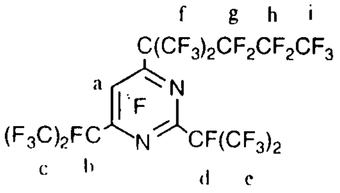
Spectrum No. 27



(34)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-70.0	m	-	6	h
	-71.9	dd	J_{fe} 30.0, J_{fg} 18.4	6	f
	-72.8	m	-	6	b
	-74.7	d	J_{dc} 7.5	6	d
	-150.7	dsept.sept.	J_{ge} 125.9, J_{gh} 17.3, J_{gf} 3.0	1	g
	-176.5	dm	J_{ag} 126.3	1	a
	-181.4	sept.m	J_{ef} 43.6	1	e
	-183.3	sept	J_{cd} 6.8	1	c

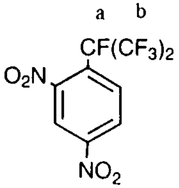
Spectrum No. 28



(36)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-60.7	s	-	6	
	-74.2	br.s	-	12	
	-80.6	br.s	-	3	
	-105.0	br.s	-	2	
?	-123.6	m	-	2	
?	-123.6	m	-	1	
	-185.5	br.s	-	2	

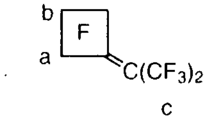
Spectrum No. 29



(39)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-74.2	br.s	-	6	b
	-182.9	m	-	1	a

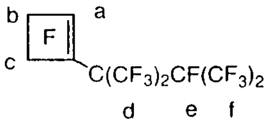
Spectrum No. 30



(40)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-65.3	overlapping dq	-	6	c
	-116.9	br.m	-	4	a
	-132.5	br.m	-	2	b

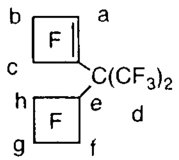
Spectrum No. 31



(41)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-63.3	m	-	6	d
	-71.8	d	J_{fe} 47.0	6	f
	-95.5	m	-	1	a
	-116.4	m	-	2	b or c
	-124.6	m	-	2	b or c
	-172.8	m	-	1	e

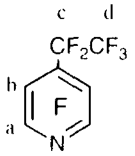
Spectrum No. 32



(42)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-65.6	overlapping qd	J 13.2, J_{da} 5.0	6	d
	-91.4	m	-	1	a
	-114.1	m	-	2	b or c
	-124.0	m	-	2	b or c
	-130.3	br.s	-	2	f or h
	-130.5	br.s	-	2	f or h
	-134.2	br. s	-	2	g
	-179.1	m	-	1	e

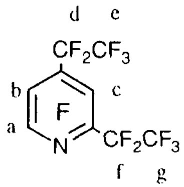
Spectrum No. 33



(44)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-86.0	t	J_{dc} 6.4	3	d
	-89.7	dd	J_{ab} 13.7, $J_{ab'}$ 8.3	2	a
	-113.6	t	J_{cb} 28.6	2	c
	-141.1	br.m	-	2	b

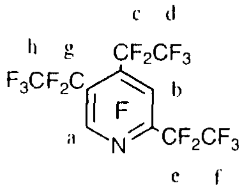
Spectrum No. 34



(45)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-83.8	m	-	1	a
	-84.9	m	-	3	e
	-86.6	m	-	3	g
	-113.2	t	$J_{d,b+c}$ 30.0	2	d
	-116.9	t	$J_{f,a+c}$ 31.1	2	f
	-118.5	br.m	-	1	c
	-126.4	br.m	-	1	b

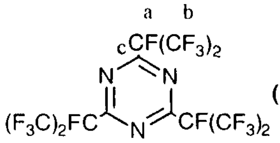
Spectrum No. 35



(46)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-55.5	m	-	1	a
	-81.4	m	-	6	d and h
	-83.2	m	-	3	f
	-103.2	br.m	-	4	c and g
	-115.8	s	-	1	b
	-116.0	m	-	2	e

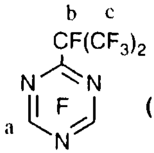
Spectrum No. 36



(47)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-75.5	d	J_{ba} 7.5	18	b
	-186.4	sept.	J_{ab} 7.5	3	a
^{13}C	88.6	dsept.	J_{CF} 215.3, J_{ab} 33.4	3	a
	118.3	qd	J_{CF} 286.4, J_{ba} 26.5	6	b
	166.6	d	J_{ca} 22.0	3	c

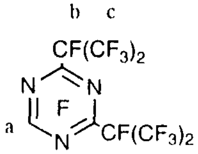
Spectrum No. 37



(49)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-30.4	s	-	2	a
	-74.4	d	J_{cb} 7.5	6	c
	-188.8	sept.	J_{bc} 7.5	1	b

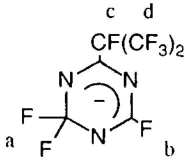
Spectrum No. 38



(50)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-30.0	s	-	1	a
	-75.7	d	J_{cb} 7.5	12	c
	-186.4	sept.	J_{bc} 7.5	2	b

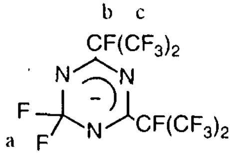
Spectrum No. 39



(51)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-2.3	br.s	-	2	a
	-50.4	s	-	1	b
	-74.2	d	J_{dc} 7.5	6	d
	-183.4	sept.	J_{cd} 7.5	1	c

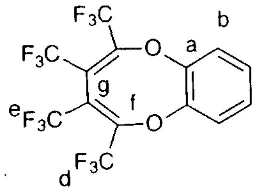
Spectrum No. 40



(52)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-1.5	br.s	-	2	a
	-74.3	d	J_{db} 7.5	12	c
	-183.8	sept.	Jbd 7.5	2	b

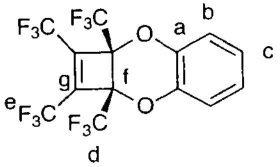
Spectrum No. 41



(54)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-56.4	q	J_{de} 12.0	1	d
	-65.0	q	J_{ed} 12.0	1	e
^{13}C	107.5	dq	J_{CF} 76.2, $J_{CF(e)}$ 27.0	-	g
	117.0	q	$J_{CF(e)}$ 276.9	-	e
	119.0	q	$J_{CF(d)}$ 273.5	-	d
	121.2	s	-	-	b
	126.1	s	-	-	c
	141.6	s	-	-	a
	144.4	q	$J_{CF(d)}$ 41.4	-	f
^{1}H	7.15	s	-	1	b
	7.16	s	-	1	c

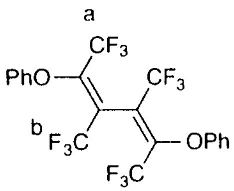
Spectrum No. 42



(58)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-63.9	t	J_{ed} 2.0	1	e
	-73.4	t	J_{de} 2.0	1	d
^{13}C	115.6	q	$J_{CF(e)}$ 272.3	-	e
	116.1	s	-	-	g
	118.1	s	-	-	b
	118.5	q	$J_{CF(d)}$ 287.5	-	d
	126.3	s	-	-	c
	138.7	s	-	-	a
^{1}H	6.93	AA'BB'	including splittings of J 6.0 and 3.6	1	b
	7.01	AA'BB'	including splittings of J 6.0 and 3.6	1	c

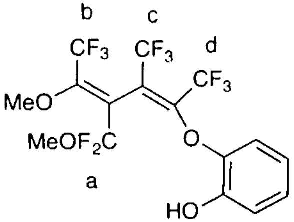
Spectrum No. 43



(59)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-60.2	q	J_{ab} 2.3	1	b
	-73.4	q	J_{ab} 2.0	1	a

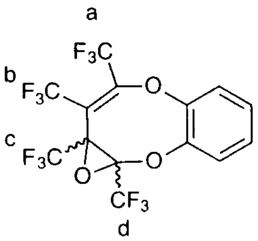
Spectrum No. 44



(62)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-57.2	s	-	3	c
	-64.2	m	-	3	b of d
	-64.3	m	-	3	b or d
	-65.0	m	-	2	a

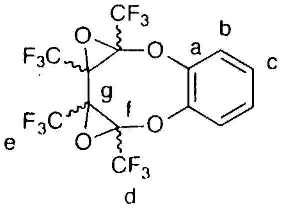
Spectrum No. 45



(67)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-56.7	br.s	-	1	a
	-65.1	br.s	-	1	b
	-65.7	br.s	-	1	d
	-70.7	br.s	-	1	c

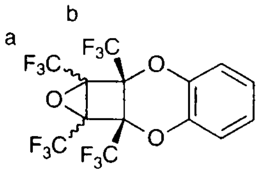
Spectrum No. 46



(66)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-65.3	qt	J_{de} 11.3, J 1.1	1	d
	-69.1	q	J_{ed} 11.3	1	e
^{13}C	63.7	q	$J_{CF(e)}$ 40.9	-	g
	82.8	q	$J_{CF(d)}$ 43.2	-	f
	120.3	q	$J_{CF(e)}$ 282.5	-	e
	120.5	q	$J_{CF(d)}$ 279.9	-	d
	123.9	s	-	-	b
	129.7	s	-	-	c
	143.5	s	-	-	a
^{1}H	7.51	s	-	1	b
	7.53	s	-	1	c

Spectrum No. 47



(69)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-65.9	br.s	-	1	a
	-72.0	br.s	-	1	b

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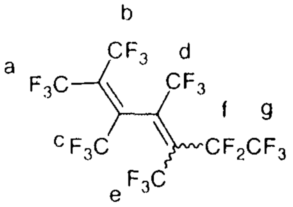
Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-66.3	br.s	-	1	a
	-71.1	br.s	-	1	b

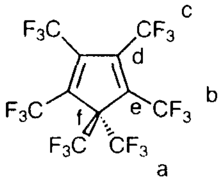
Spectrum No. 48



(75)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-56.2	br.s	-	3	c or d
	-56.7	br.s	-	3	c or d
	-57.5	d	J_{FF} 9.4	3	e
	-59.3	d	J_{FF} 10.4	3	a or b
	-59.6	br.s	-	3	a or b
	-79.0	t	J_{fg} 7.5	3	g
	-106.8	br.m	-	2	f

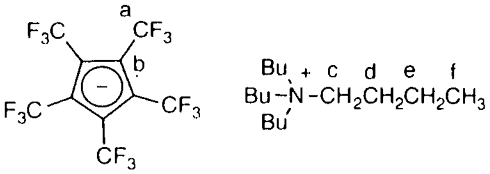
Spectrum No. 49



(96)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-55.6	m	containing J_{FF} 10.5	1	b
	-59.4	psuedo septet	cotaining J_{FF} 10.9	1	c
	-59.7	m	containing J_{FF} 12.4	1	a
^{13}C	66.5	s	-	-	a
	117.8	q	J_{CF} 276.5	-	b or c or f
	118.8	q	J_{CF} 274.5	-	b or c or f
	120.2	q	J_{CF} 288.5	-	b or c or f
	137.7	q	J_{CF} 40.7	-	e or d

Spectrum No. 50

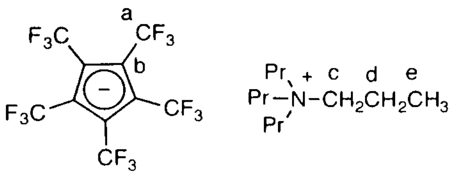


$[C_5(CF_3)_5]^- \; Bu_3N^+CH_2CH_2CH_2CH_3$

(87)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^1H	0.96	t	J_{dc} 7.2	3	f
	1.35	sextet	$J_{e,f+d}$ 7.6	2	e
	1.60	quintet	$J_{d,e+c}$ 8.4	2	d
	3.08	m	-	2	c
^{19}F	-50.51	s	-	-	a
$^{13}C(^1H)$	13.13	s	-	-	f
	19.22	s	-	-	e
	23.43	s	-	-	d
	58.46	s	-	-	c
	123.57	q	J_{CF} 269.0	-	a
	109.62	q	J_{CF} 13.4	-	b

Spectrum No. 51

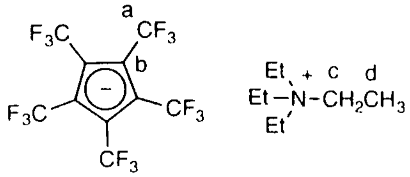


$[C_5(CF_3)_5]^- \; Pr_3N^+CH_2CH_2CH_3$

(101)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^1H	0.94	t	J_{dc} 7.2	3	e
	1.65	sextet	$J_{c,f+d}$ 7.6	2	d
	3.04	m	-	2	c
^{19}F	-51.0	s	-	-	a
$^{13}C(^1H)$	15.3	s	-	-	e
	30.9	s	-	-	d
	55.2	s	-	-	c
	123.3	q	J_{CF} 269.7	-	a

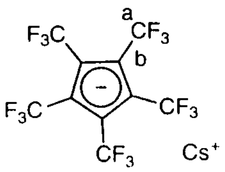
Spectrum No. 52



(100)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{1}H	1.20	tt	J_{dc} 7.2, $J_{H(c)N}$ 1.6	3	d
	3.15	q	J_{cd} 7.2	2	c
^{19}F	-51.0	s	-	-	a
$^{13}C(^{1}H)$	15.7	s	-	-	d
	53.0	t	$J_{C(c)N}$ 2.6	-	c
	124.6	q	J_{CF} 270.9	-	a

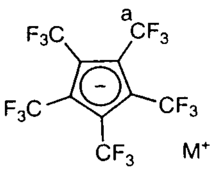
Spectrum No. 53



(86)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-49.74	s	-	-	a
^{13}C	110.67	q	J_{CF} 19.2	-	b
	124.67	q	J_{CF} 270.6	-	a

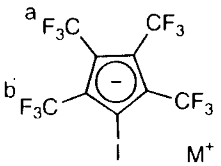
Spectrum No. 54



(84)

Metal (M)	Chemical Shift (ppm)	Assignment
K	-49.8	a
Na	-49.6	a
Li	-49.9	a

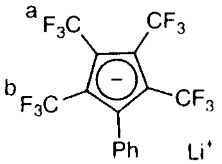
Spectrum No. 55



(105)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-51.7	s	-	1	a or b
	-54.1	s	-	1	a or b

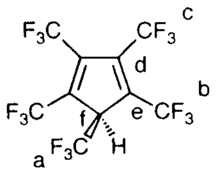
Spectrum No. 56



(106)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{19}F	-51.8	s	-	1	a or b
	-52.4	s	-	1	a or b

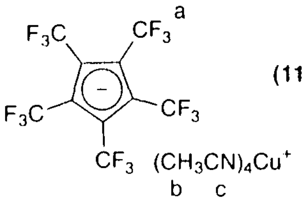
Spectrum No. 57



(109)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{1}H	4.82	q	$J_{HF(a)}$ 5.7	-	f
^{19}F	-56.0	md	$J_{F(b)H}$ 3.4	2	b
	-59.1	m	-	1	a
	-60.2	m	-	2	c
$^{13}C(^{1}H)$	58.4	q	J_{CF} 32.2	-	f
	119.2	q	J_{CF} 272.7	-	b or c
	120.2	q	J_{CF} 272.4	-	b or c
	122.5	q	J_{CF} 284.2	-	a
	139.6	q	J_{CF} 40.0	-	d or e
	139.8	q	J_{CF} 40.3	-	d or e

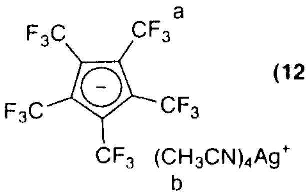
Spectrum No. 58



(118)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{1}H	2.0	s	-	-	b
^{19}F	49.7	s	-	-	a
$^{13}C(^{1}H)$	1.0	s	-	4	b
	118.1	s	-	4	c
	123.4	q	J_{CF} 269.3	5	a

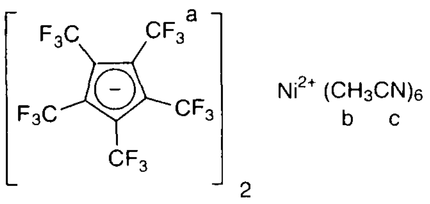
Spectrum No. 59



(122)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{1}H	2.0	s	-	-	b
^{19}F	-49.7	s	-	-	a

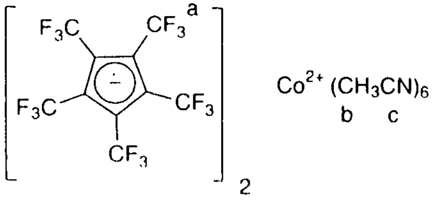
Spectrum No. 60



(119)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{1}H	2.0	s	-	-	b
^{19}F	-49.8	s	-	-	a
$^{13}C(^{1}H)$	1.0	s	-	3	b
	118.1	s	-	3	c
	121.0	br.s	-	5	a

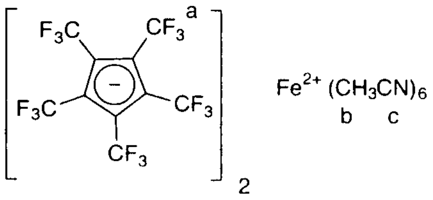
Spectrum No. 61



(120)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{1}H	2.0	s	-	-	b
^{19}F	-49.8	s	-	-	a
^{13}C(^{1}H)	1.0	s	-	3	b
	118.1	s	-	3	c
	121.0	br.s	-	5	a

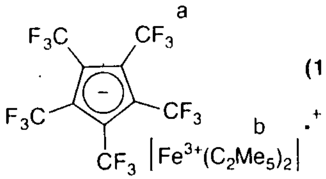
Spectrum No. 62



(121)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{1}H	2.0	s	-	-	b
^{19}F	-49.9	s	-	-	a
^{13}C(^{1}H)	1.0	s	-	3	b
	118.1	s	-	3	c
	121.0	br.s	-	5	a

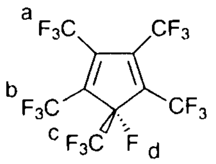
Spectrum No. 63



(125)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Integral	Assignment
^{1}H	5.45	s	-	-	b
^{19}F	49.7	s	-	-	a
$^{13}C(^{1}H)$	55.4	s	-	-	b
	124.7	q	J_{CF} 270.7	-	a

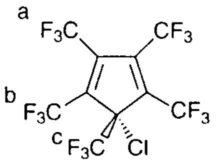
Spectrum No. 64



(127)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-57.3	br.s	-	6	b
	-61.0	br.s	-	6	a
	69.7	br.s	-	3	c
	-195.4	br.s	-	1	d

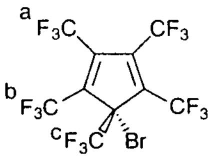
Spectrum No. 65



(128)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-55.0	br.s	-	2	b
	-63.8	br.s	-	2	a
	-69.6	br.s	-	1	c

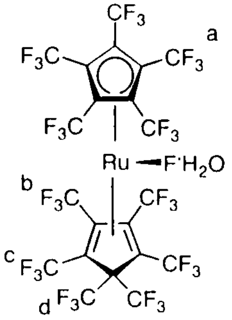
Spectrum No. 66



(129)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-55.7	br.s	-	2	b
	-60.3	br.s	-	2	a
	-64.5	br.s	-	1	c

Spectrum No. 67



(134)

Nucleus	Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{19}F	-49.8	br.s	-	-	a
	-58.0	br.s	-	-	c
	-58.3	br.s	-	-	b
	-59.0	br.s	-	-	d

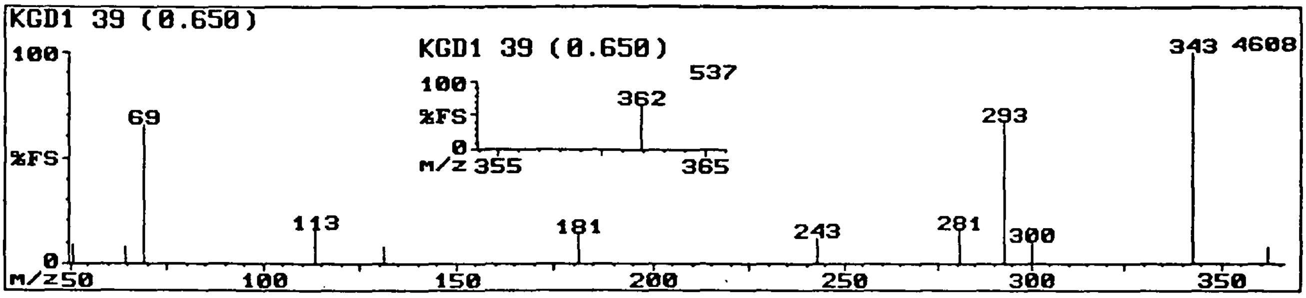
Appendix Two

Mass Spectra (EI unless otherwise stated)

1. Perfluoro-3,4-dimethylhexa-2,4-diene (**14**)
2. Perfluoro-1,1'-bicyclo-1-pentenyl (**12**)
3. Octamethyloxamidium difluoride (**10**)
4. Perfluoro-4-methylpent-2-ene (**5**)
5. Perfluoro-2-methylpent-2-ene (**6**)
6. Perfluoro-1-isopropylcyclopentene (**21**)
7. Perfluoro-1,2-di-isopropylcyclopentene (**22**)
8. Perfluoro-1-(1',1'-dimethyl)butylcyclopentene (**23**)
9. Perfluoro-4-isopropylpyridine (**25**)
10. Perfluoro-2,4-di-isopropylpyridine (**26**)
11. Perfluoro-2,4,5-tri-isopropylpyridine (**27**)
12. Perfluoro-2,4,6-tri-isopropylpyridine (**28**)
13. Perfluoro-4-isopropylpyrimidine (**30**)
14. Perfluoro-4,6-di-isopropylpyrimidine (**31**)
15. Perfluoro-2,4,6-tri-isopropylpyrimidine (**32**)
16. Perfluoro-4-(1',1'-dimethyl)butylpyrimidine (**33**)
17. Perfluoro-2,4,5,6-tetra-isopropylpyrimidine (**34**)
18. perfluoro-6-isopropyl-4-(1',1'-dimethyl)butylpyrimidine (**35**)
19. Perfluoro-2,6-di-isopropyl-4-(1',1'-dimethyl)butylpyrimidine (**36**)
20. 2,4-Dinitroheptafluoroisopropylbenzene (**39**)
21. Perfluoroisopropylidenecyclobutane (**40**)
22. Perfluoro-2-cyclobut-1-en-1-yl-2,3-dimethylbutane (**41**)
23. Perfluoro-2-cyclobut-1-en-1-yl-2-cyclobutylpropane (**42**)
24. perfluoro-1-(1',1',2',2',3'-pentamethyl)butylcyclobutene (**43**)
25. Perfluoro-4-ethylpyridine (**44**)
26. Perfluoro-2,4-diethylpyridine (**45**)
27. Perfluoro-2,4,5-triethylpyridine (**46**)
28. Perfluoro-2,4,6-tri-isopropyl-s-triazine (**47**)
29. Perfluoro-2-isopropyl-s-triazine (**49**)
30. Perfluoro-2,4-di-isopropyl-s-triazine (**50**)
31. Tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin (**54**)
32. Tetrakis(1,6,7,8-trifluoromethyl)-3,4-benzo-2,5-dioxabicyclo[4.2.0]octa-3,7-diene (**58**)
33. Tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin di-nitro adduct (**60**)
34. Tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin mono-bromo adduct (**61a**)

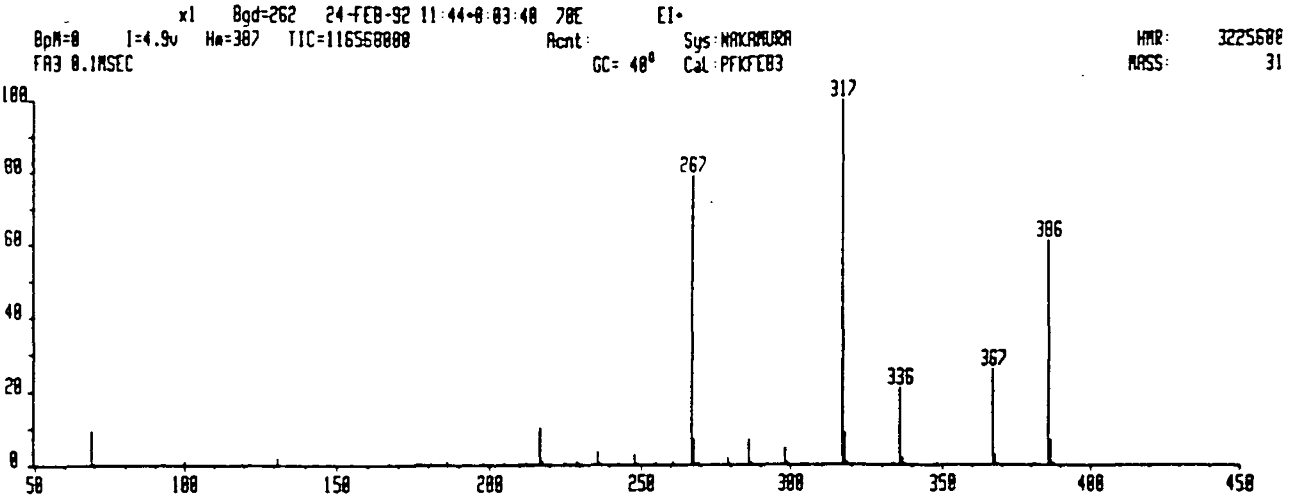
35. Tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin di-bromo adduct (**61b**)
36. Tris(1,2,4-trifluoromethyl)-3-difluoromethoxymethyl-4-methoxy-1-(2-hydroxy)phenoxybuta-1,3-diene. (**62**)
37. 2-Epoxytetrakis(2,3,4,5-trifluoromethyl)benzodioxocin (**67**)
38. 2,4-Diepoxytetrakis(2,3,4,5-trifluoromethyl)benzodioxocin (**66**)
39. Tetrakis(1,6,7,8-trifluoromethyl)-3,4-benzo-2,5-dioxabicyclo[4.2.0]octa-3,7-diene-epoxide (**69**)
40. Perfluoro-2,3,4,5-tetramethylhepta-2,4-diene (**75**)
41. Hexakis(trifluoromethyl)cyclopentadiene (**96**)
42. Tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienide (**87**) *FAB*
43. Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienide (**101**) *FAB*
44. Tetraethylammonium pentakis(trifluoromethyl)cyclopentadienide (**100**) *FAB*
45. Cesium pentakis(trifluoromethyl)cyclopentadienide (**86**) *FAB*
46. Pentakis(trifluoromethyl)cyclopentadienide (**84**); with potassium counter ion *FAB*
47. Pentakis(trifluoromethyl)cyclopentadienide (**84**); with sodium counter ion *FAB*
48. Pentakis(trifluoromethyl)cyclopentadienide (**84**); with lithium counter ion *FAB*
49. 5H-Perfluoropentamethylcyclopentadiene (**109**)
50. Tetrakis(acetonitrile)copper (I) pentakis(trifluoromethyl)cyclopentadienide (**118**) *FAB*
51. Tetrakis(acetonitrile)silver (I) pentakis(trifluoromethyl)cyclopentadienide (**122**) *FAB*
52. Hexakis(acetonitrile)nickel(II)dipentakis(trifluoromethyl)cyclopentadienide (**119**) *FAB*
53. Hexakis(acetonitrile)cobalt(II)dipentakis(trifluoromethyl)cyclopentadienide (**120**) *FAB*
54. Hexakis(acetonitrile)iron (II) dipentakis(trifluoromethyl)cyclopentadienide (**121**) *FAB*
55. Decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienide (**125**) *FAB*
56. Perfluoropentamethylcyclopentadiene (**127**)
57. Ruthenium Complex (**134**) *EI, CI and FAB*

Spectrum No. 1



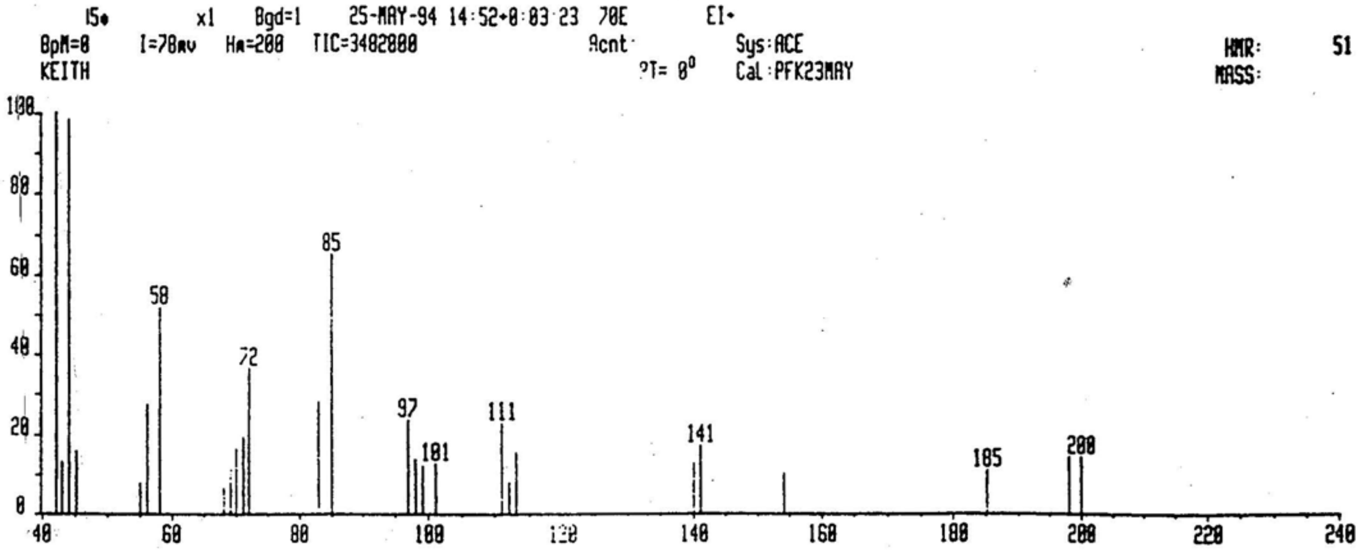
```
 -------------------------------------------------------------------------------
KGD1 39 (0.650)                                                            37632
--------------------+-------------------+-------------------+--------------------
Mass    Rel Int    | Mass    Rel Int    | Mass    Rel Int   | Mass    Rel Int
--------------------+-------------------+-------------------+--------------------
  51       1.03    |  113       1.96    |  243       1.48   |  300       1.22
  64       0.98    |  131       0.92    |  281       1.95   |  343      12.24
  69       7.95    |  181       1.61    |  293       8.16   |  362       0.92
--------------------+-------------------+-------------------+--------------------
```

Spectrum No. 2



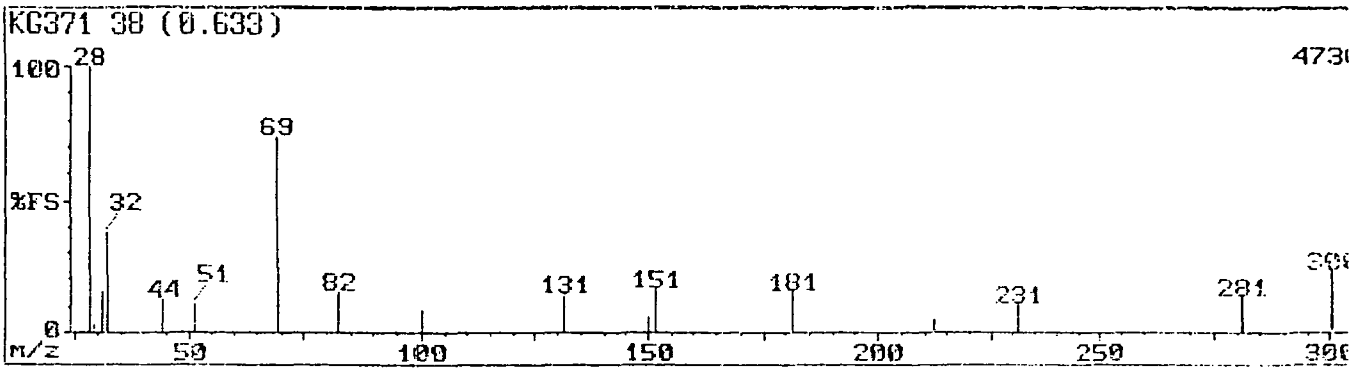
Mass	% Base	
69.01	8.91	
100.01	0.69	
131.01	1.88	
186.01	0.79	
205.01	0.49	
217.01	9.52	
218.02	0.79	
229.00	0.79	
236.00	3.17	
248.00	2.38	
261.00	0.79	
266.98	79.37	F
267.99	6.35	F
278.99	1.73	
286.00	6.35	
286.99	0.47	
298.00	4.05	
299.02	0.33	
316.99	100.00	F
317.98	8.29	F
318.99	0.33	
335.97	20.63	F
336.99	1.75	F
348.00	0.32	
366.96	25.60	F
367.98	2.51	F
385.97	61.16	F
386.98	6.35	F

Spectrum No. 3



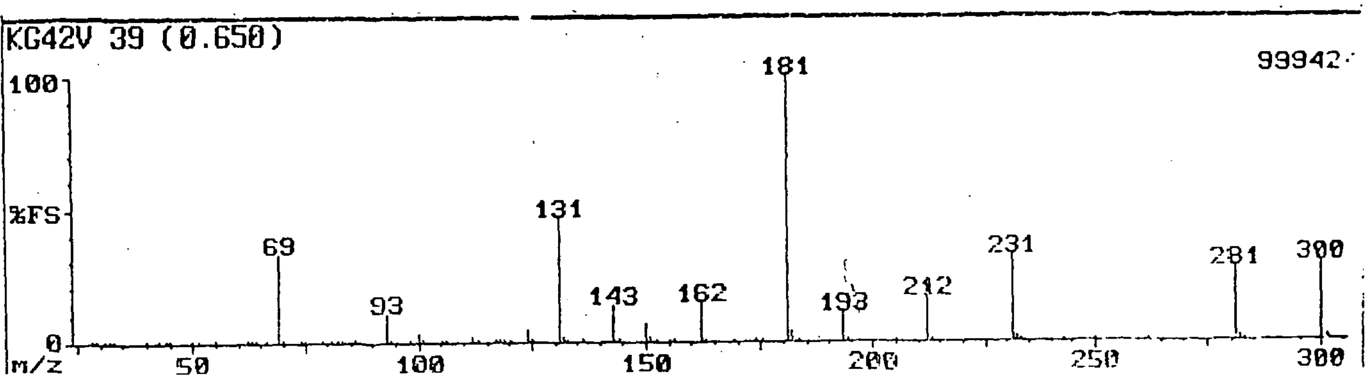
Mass	% Base
42.10	100.00
43.11	12.62
44.11	97.86
45.12	15.53
55.07	7.57
56.08	27.18
58.09	51.46
68.04	6.21
69.03	10.87
70.05	16.12
71.05	18.83
72.03	35.92
83.04	27.77
85.05	64.66
97.06	23.30
98.06	13.40
99.07	11.65
101.09	12.43
111.06	22.52
112.07	7.38
113.09	14.95
140.08	12.23
141.09	16.89
154.10	9.90
185.15	10.68
198.16	13.98
200.16	14.17

Spectrum No. 4



```
KG371  38  (0.633)                                                          4736
---------------------+--------------------+--------------------+---------------------
 Mass     Rel  Int   | Mass     Rel  Int  | Mass     Rel  Int  | Mass     Rel  Int
---------------------+--------------------+--------------------+---------------------
   28     100.00     |   51       10.81   |  150        6.17   |  281      13.68
   29       3.00     |   69       73.31   |  151       16.47   |  300      22.97
   31      15.79     |   82       15.88   |  181       15.12   |
   32      37.84     |  100        8.70   |  212        4.90   |
   44      12.33     |  131       14.36   |  231       10.73   |
---------------------+--------------------+--------------------+---------------------
```

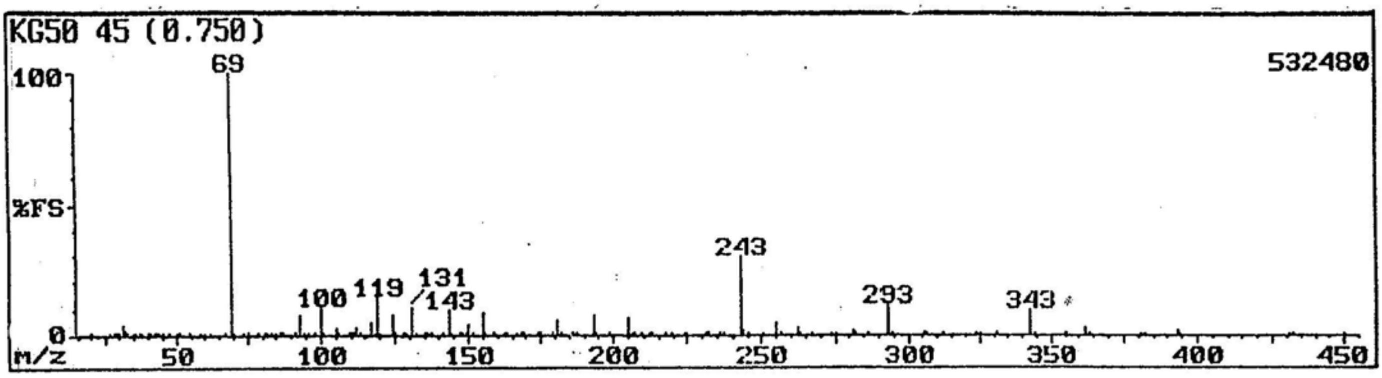
Spectrum No. 5



KG42V 39 (0.650) 999424

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.40	75	0.06	124	4.53	182	4.12
29	0.02	79	0.03	125	0.22	183	0.11
31	0.77	81	0.35	131	46.31	193	10.96
32	0.20	82	1.16	132	1.66	194	0.60
33	0.04	83	0.04	133	0.21	205	0.03
40	0.01	86	0.22	136	0.14	212	16.39
43	0.03	93	10.55	143	13.93	213	0.92
44	0.15	94	0.39	144	0.65	231	32.38
45	0.05	98	0.06	150	6.76	232	1.66
50	0.31	100	2.69	151	1.77	233	0.05
51	0.71	101	0.20	152	0.06	243	0.08
55	0.16	105	0.98	155	0.72	250	0.03
62	0.15	106	0.09	156	0.05	262	0.09
63	0.08	112	2.15	162	14.86	281	27.05
64	0.21	113	0.24	163	0.81	282	1.64
66	0.02	117	0.44	169	0.04	283	0.06
69	32.79	118	0.03	174	0.33	300	29.51
70	0.46	119	0.63	175	0.03		
74	1.10	120	0.02	181	100.00		

Spectrum No. 6



```
------------------------------------------------------------------------------------------------------
KG50 45 (0.750)                                                                            532480
--------------------+-----------------------+-----------------------+--------------------------------
Mass   Rel Int      | Mass    Rel Int       | Mass    Rel Int       | Mass    Rel Int
--------------------+-----------------------+-----------------------+--------------------------------
  20      0.09      |   86      0.55        |  150      4.28        |  244      1.95
  27      0.08      |   87      0.05        |  151      0.11        |  245      0.07
  28      1.32      |   91      0.18        |  155      8.51        |  250      0.05
  29      0.95      |   93      7.45        |  156      0.47        |  255      4.66
  30      0.18      |   94      0.42        |  159      0.08        |  256      0.36
  31      4.28      |   96      0.18        |  162      0.45        |  262      2.78
  32      1.68      |   98      0.50        |  163      0.05        |  263      0.20
  33      0.07      |  100     10.67        |  167      0.83        |  267      0.05
  35      0.10      |  101      0.28        |  168      0.07        |  274      0.54
  36      0.42      |  105      2.44        |  169      1.07        |  275      0.07
  37      0.03      |  106      0.14        |  174      1.17        |  281      2.19
  38      0.15      |  109      0.05        |  175      0.07        |  282      0.16
  40      0.08      |  110      0.04        |  179      0.10        |  286      0.05
  41      0.06      |  111      0.32           181      6.01        |  293     11.68
  42      0.09      |  112      2.45           182      0.26        |  294      0.85
  43      0.08      |  113      0.17        |  186      1.35        |  305      0.93
  44      0.22      |  117      5.05        |  187      0.11        |  306      0.08
  45      0.03      |  118      0.27        |  193      7.60        |  312      0.05
  47      0.08      |  119     15.00        |  194      0.40        |  324      1.42
  50      1.03      |  120      0.35        |  198      0.07        |  325      0.14
  51      0.05      |  124      7.45        |  205      6.97        |  331      0.25
  55      0.39      |  125      0.35        |  206      0.47        |  343      9.71
  58      0.04      |  128      0.10        |  207      0.15        |  344      0.83
  60      0.05      |  129      0.17        |  209      0.10        |  355      0.11
  62      0.13      |  131     10.24        |  212      0.85        |  362      3.06
  67      0.06      |  132      0.35        |  213      0.07        |
  69    100.00      |  135      0.09        |  217      0.46        |
  70      1.24      |  136      1.25        |  219      0.11        |
  74      1.41      |  137      0.13        |  224      0.32        |
  75      0.07      |  141      0.08        |  225      0.05        |
  79      0.29      |  143      9.28        |  231      1.26        |
  81      0.50      |  144      0.39        |  232      0.08        |
  82      0.06      |  147      0.32        |  236      0.59        |
  83      0.13      |  148      0.44        |  237      0.05        |
  85      0.11      |  149      0.10        |  243     30.00        |
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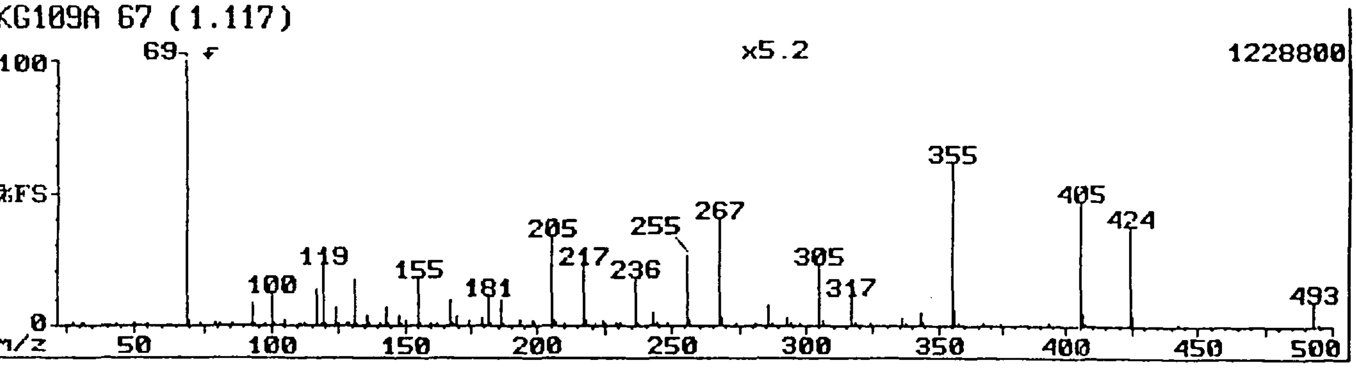
Spectrum No. 7

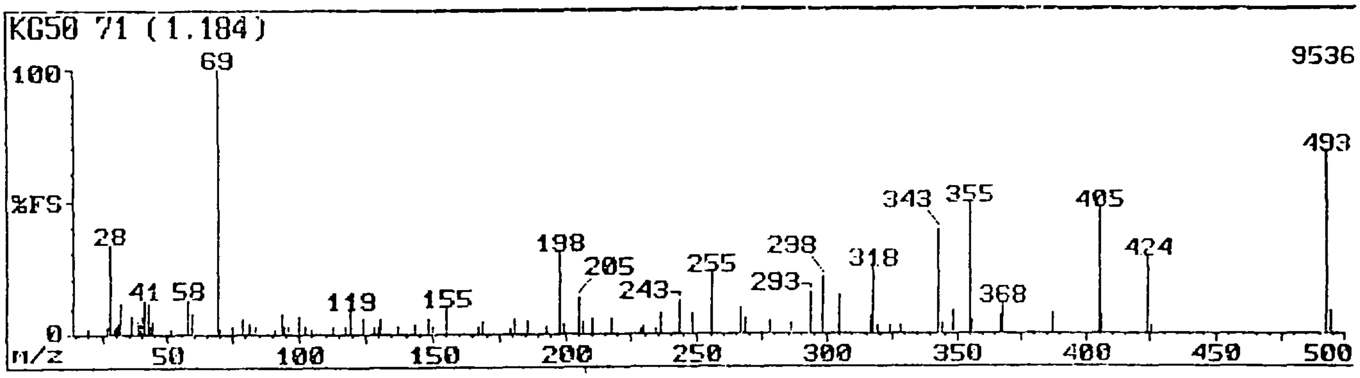


KG109A 67 (1.117)

1228800

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.40	93	1.75	124	1.40	149	0.04	182	0.09	224	0.39	268	0.66	324	0.08	406	0.98
31	0.57	94	0.06	125	0.06	150	0.45	186	1.81	225	0.03	274	0.11	336	0.48	407	0.05
32	0.18	98	0.20	128	0.04	155	3.44	187	0.12	229	0.20	281	0.03	337	0.05	424	7.25
44	0.05	100	2.25	129	0.21	156	0.19	193	0.45	231	0.12	286	1.58	343	1.00	425	0.77
50	0.51	101	0.06	131	3.35	160	0.07	198	0.38	236	3.40	287	0.15	344	0.09	443	0.14
55	0.05	105	0.42	132	0.12	162	0.09	199	0.03	237	0.27	293	0.56	355	11.83	493	1.75
69	100.00	110	0.04	136	0.72	167	1.96	205	6.50	243	0.96	294	0.04	356	1.09	494	0.22
70	1.48	112	0.22	137	0.06	168	0.14	206	0.43	244	0.06	298	0.03	357	0.05		
74	0.17	117	2.58	141	0.11	169	0.81	207	0.04	248	0.24	305	4.42	367	0.02		
79	0.07	118	0.14	143	1.29	174	0.43	210	0.07	255	5.10	306	0.35	374	0.17		
81	0.11	119	4.27	144	0.05	179	0.59	217	4.25	256	0.38	317	2.15	393	0.11		
86	0.12	120	0.11	148	0.68	181	2.00	218	0.32	267	7.75	318	0.21	405	9.08		

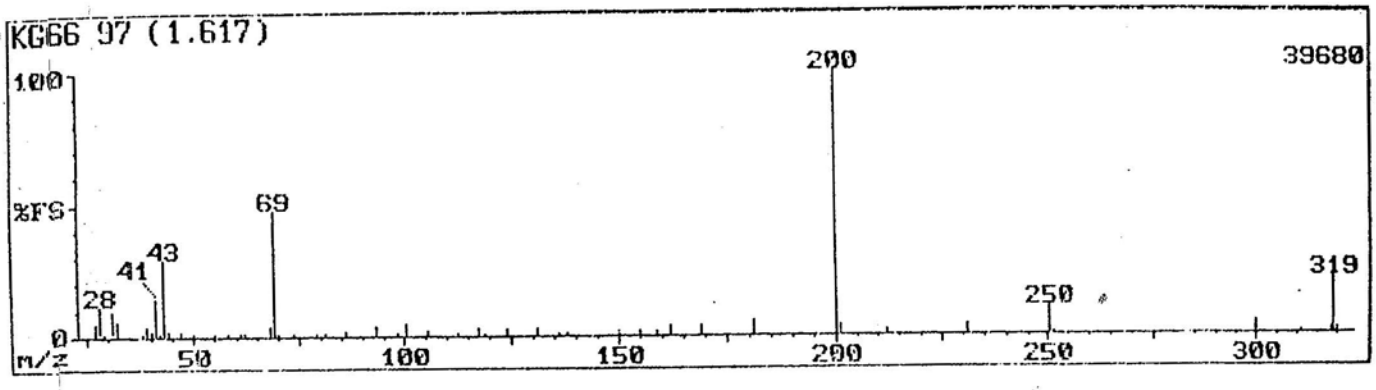
Spectrum No. 8



KG50 71 (1.184) 9536

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	2.39	81	4.07	169	4.99	293	15.44
27	2.98	84	2.68	179	2.34	298	21.14
28	32.72	91	2.25	181	5.66	305	14.26
29	2.16	93	7.55	186	4.78	317	6.71
30	3.27	94	2.81	193	3.31	318	24.50
31	3.65	96	2.46	198	29.87	319	2.98
32	11.74	100	7.21	199	3.73	324	3.06
36	7.26	102	2.85	205	13.93	328	2.63
38	4.45	105	2.36	207	4.66	343	39.09
39	3.65	113	2.81	210	5.58	344	4.19
40	7.01	117	3.40	217	6.25	348	9.02
41	12.92	119	9.19	228	2.00	355	48.32
42	11.41	124	6.29	229	2.57	356	4.95
43	2.85	128	2.50	234	1.59	367	7.01
44	4.40	130	2.58	236	7.72	368	10.44
51	1.92	131	6.25	243	13.09	387	7.42
58	12.25	137	3.23	248	7.76	405	46.98
59	7.38	143	4.15	255	22.32	406	6.59
69	100.00	148	5.75	267	9.56	424	28.52
70	2.40	150	3.27	268	5.45	425	3.27
75	2.81	155	9.27	278	4.45	493	67.79
79	5.83	167	3.15	286	3.48		

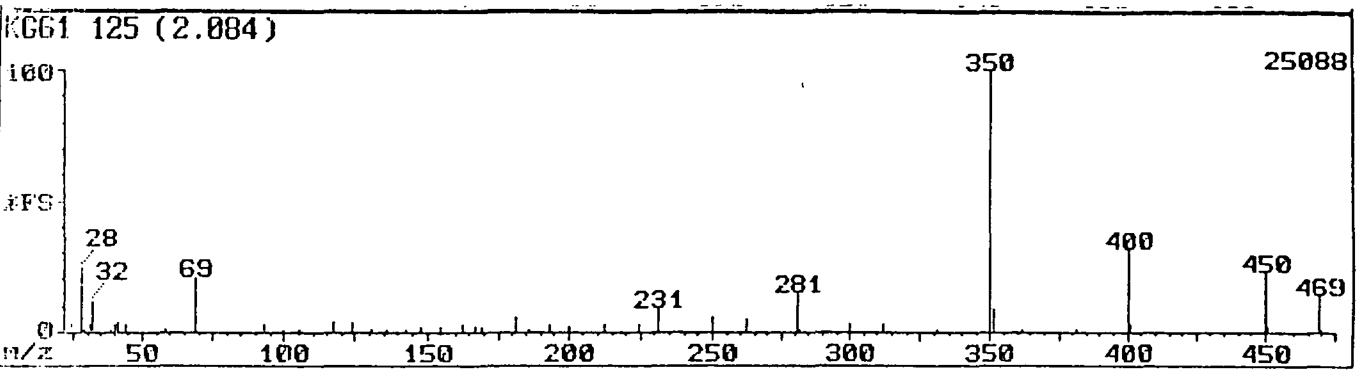
Spectrum No. 9



KG66 97 (1.617) 39680

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
27	4.52	55	1.19	105	1.76	200	100.00
28	11.77	58	0.87	112	1.01	201	4.23
29	0.50	61	0.96	117	2.90	212	2.37
31	9.72	62	0.98	119	0.65	231	3.55
32	6.05	68	3.63	124	2.48	250	10.48
38	0.75	69	47.74	131	2.52	251	0.89
39	3.63	70	0.67	136	1.31	300	4.88
40	1.90	74	0.98	138	0.76	311	0.60
41	14.19	79	0.85	150	2.25	318	1.58
42	1.02	81	1.07	155	1.46	319	21.13
43	29.52	86	1.46	159	1.72		
44	1.53	93	3.67	162	3.99		
47	2.32	98	0.80	169	3.47		
50	1.20	100	4.72	181	5.65		

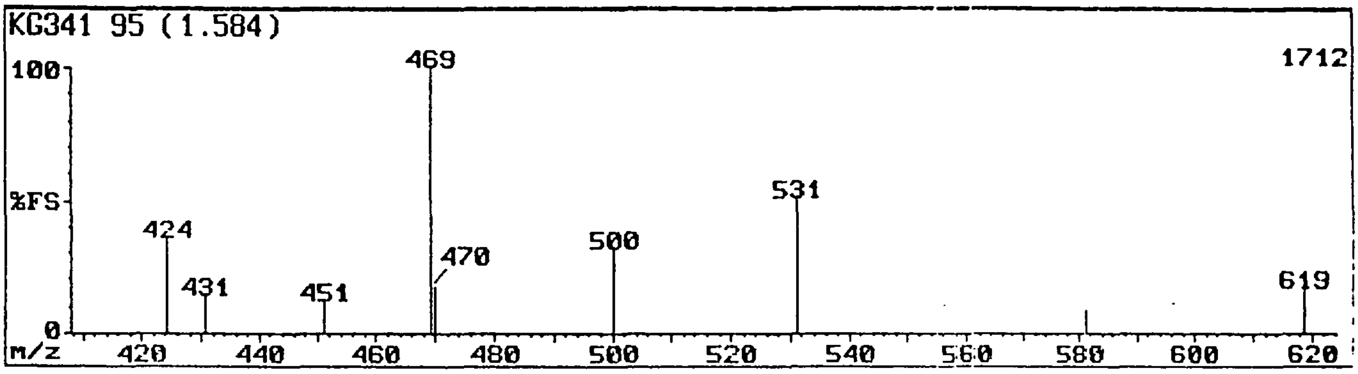
Spectrum No. 10



KG61 125 (2.084) 25088

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	23.98	105	1.12	186	1.02	331	1.32
29	0.76	117	3.87	193	2.46	350	100.00
31	2.73	124	3.57	200	1.98	351	8.42
32	11.67	131	1.43	212	3.27	362	1.15
39	0.88	136	0.60	224	3.17	381	0.61
40	3.11	143	1.02	231	9.18	400	30.87
41	3.87	148	1.79	250	5.87	401	3.24
44	2.49	155	1.80	262	5.10	450	22.45
58	1.02	162	2.90	281	14.22	451	2.01
69	20.15	167	1.75	282	1.24	469	14.03
93	2.52	169	1.79	300	2.95		
100	1.23	181	5.42	312	2.65		

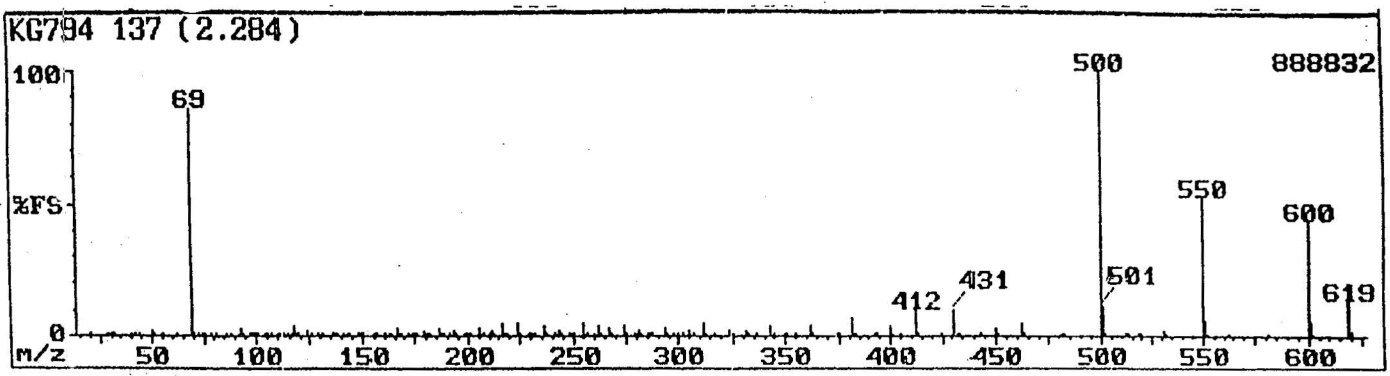
Spectrum No. 11



KG341 95 (1.584) 688128

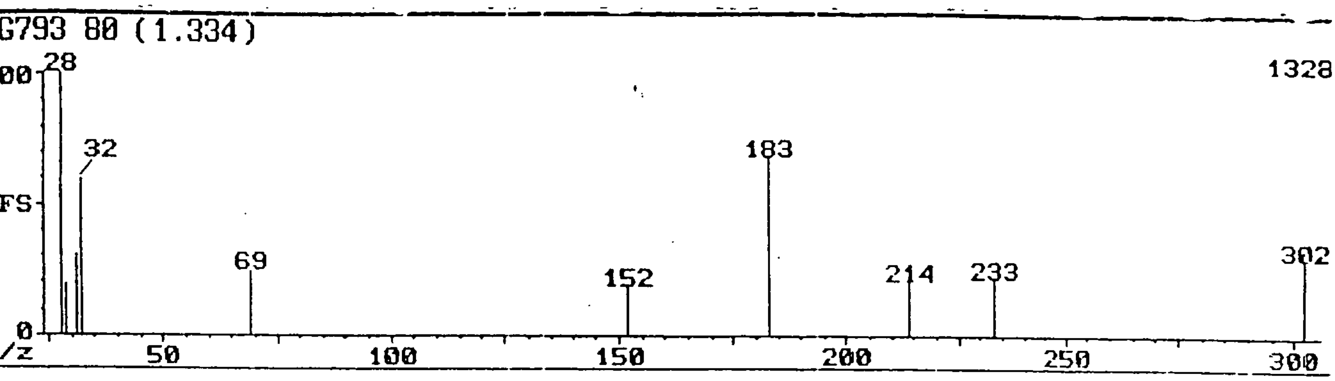
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.06	77	0.03	138	0.97	219	0.29
24	0.07	79	0.50	139	0.04	220	0.03
25	0.08	80	0.07	143	0.94	224	0.07
26	1.15	81	1.13	144	0.28	231	6.44
27	0.20	82	0.35	145	0.06	232	0.69
28	2.64	83	0.04	148	0.78	233	0.04
29	0.16	85	0.04	150	11.01	236	0.23
31	14.73	86	1.79	151	1.00	243	0.05
32	0.63	87	0.25	152	0.06	250	5.43
33	0.05	88	0.16	155	6.85	251	0.65
34	0.03	93	5.58	156	0.40	252	0.03
35	0.18	94	0.29	162	13.39	262	1.40
36	0.15	95	0.08	163	1.10	263	0.15
37	0.20	98	1.13	164	0.08	269	0.04
38	0.24	99	0.21	167	0.88	281	1.61
39	0.09	100	9.23	168	0.10	282	0.19
40	0.02	101	0.49	169	3.79	299	0.10
41	0.03	102	0.02	170	0.15	300	4.06
42	0.07	105	3.20	174	0.24	301	0.35
43	0.20	106	0.28	175	0.06	319	14.14
44	0.33	107	0.14	176	0.06	320	0.87
45	0.12	110	0.08	178	0.05	321	0.07
46	0.05	112	1.80	179	0.03	350	0.17
47	0.50	113	0.38	181	23.81	351	0.04
48	0.07	114	0.37	182	3.13	370	0.03
50	4.35	116	0.02	183	0.20	374	0.04
51	0.59	117	10.27	186	2.49	381	0.03
52	0.05	118	0.66	187	0.17	388	3.01
55	0.86	119	0.49	188	0.09	389	0.32
56	0.16	120	0.08	193	1.37	393	0.03
57	0.16	124	3.16	194	0.16	400	0.05
60	0.03	125	0.19	197	0.05	405	0.02
62	0.99	126	0.14	198	0.03	424	0.09
63	0.18	127	0.13	200	100.00	431	0.04
64	0.03	129	0.09	201	6.70	451	0.03
66	0.06	130	0.06	202	0.17	469	0.25
67	0.14	131	8.07	205	1.28	470	0.04
69	76.79	132	0.74	206	0.06	500	0.08
70	0.99	133	0.06	211	0.03	531	0.13
74	1.29	135	0.03	212	2.94	581	0.02
75	0.34	136	3.24	213	0.40	619	0.04
76	0.44	137	0.26	217	0.07		

Spectrum No. 12



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	131	0.89	230	0.07	355	0.26
28	0.55	136	1.08	231	1.30	362	3.40
29	0.03	137	0.06	232	0.12	363	0.34
31	1.20	138	0.31	236	3.69	374	1.02
32	0.26	141	0.20	237	0.26	375	0.10
40	0.03	143	0.99	241	0.10	381	6.62
42	0.04	144	0.05	243	1.62	382	0.63
44	0.08	148	1.43	244	0.15	383	0.03
50	1.50	149	0.10	248	0.54	393	1.09
51	0.05	150	0.28	249	0.05	394	0.11
55	0.07	155	1.45	250	0.63	400	3.92
62	0.04	156	0.09	254	0.17	401	0.35
69	85.25	160	0.10	255	4.84	405	0.04
70	0.91	162	1.10	256	0.41	412	10.02
72	0.03	163	0.07	260	0.03	413	0.99
74	0.13	167	3.37	261	0.20	424	0.19
75	0.04	168	0.21	262	4.23	431	9.79
76	0.23	169	0.11	263	0.35	432	1.01
79	0.14	172	0.04	267	2.45	433	0.05
81	0.14	174	0.60	268	0.19	443	0.20
85	0.02	175	0.05	274	3.57	450	3.05
86	0.10	176	0.07	275	0.32	451	0.30
88	0.04	179	1.68	279	0.11	462	5.13
92	0.19	180	0.06	280	0.06	463	0.52
93	2.56	181	0.67	281	1.53	481	1.25
94	0.10	182	0.04	282	0.14	482	0.14
97	0.03	186	3.08	285	0.07	500	100.00
98	0.12	187	0.20	286	1.35	501	11.64
99	0.11	188	0.02	287	0.06	502	0.66
100	1.17	191	0.09	293	2.85	512	1.27
101	0.04	193	1.93	294	0.28	513	0.15
104	0.03	194	0.07	298	0.08	519	0.34
105	0.30	198	1.26	300	0.41	520	0.03
107	0.08	199	0.05	301	0.03	531	2.30
110	0.09	200	0.44	305	2.04	532	0.34
111	0.03	201	0.03	306	0.10	550	52.53
112	0.28	205	3.02	312	4.67	551	5.96
114	0.12	206	0.12	313	0.39	552	0.36
116	0.32	207	0.03	317	0.19	562	0.05
117	3.83	210	0.16	324	1.74	581	0.03
118	0.26	212	2.28	325	0.17	600	42.33
119	0.55	213	0.17	331	1.47	601	5.41
123	0.12	217	5.30	332	0.14	602	0.33
124	1.47	218	0.37	336	0.11	619	13.94
125	0.10	219	0.07	343	3.77		
126	0.02	224	5.24	344	0.36		
129	0.42	225	0.41	350	1.45		
130	0.09	229	0.63	351	0.12		

Spectrum No. 13



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KG793 80 (1.334)                                                                    1328
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Mass    Rel Int   | Mass    Rel Int   | Mass    Rel Int   | Mass    Rel Int
------------------+-------------------+-------------------+-----------------------
 28     100.00    |  32      59.34    | 183      68.37    | 302      29.22
 29      19.20    |  69      24.70    | 214      20.48    |
 31      30.12    | 152      18.83    | 233      21.39    |
------------------+-------------------+-------------------+-----------------------
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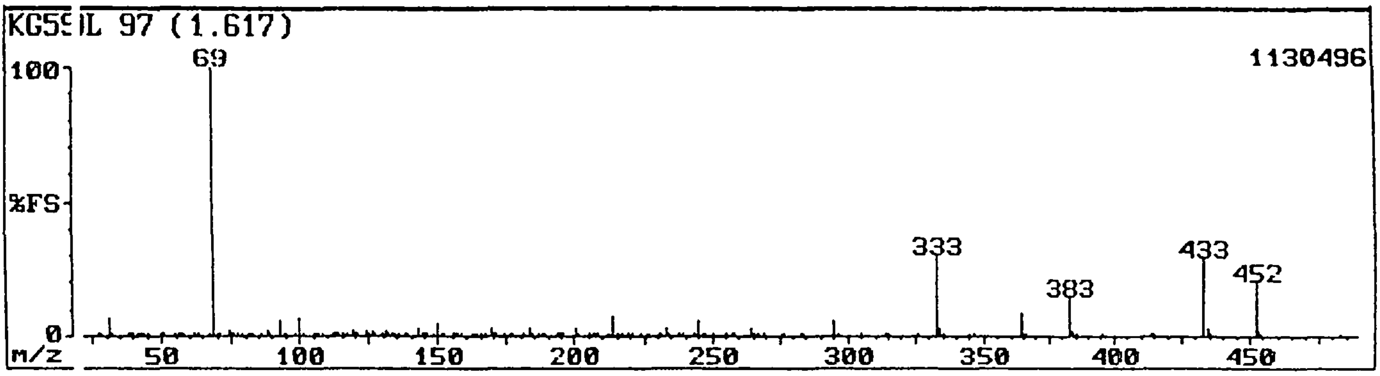
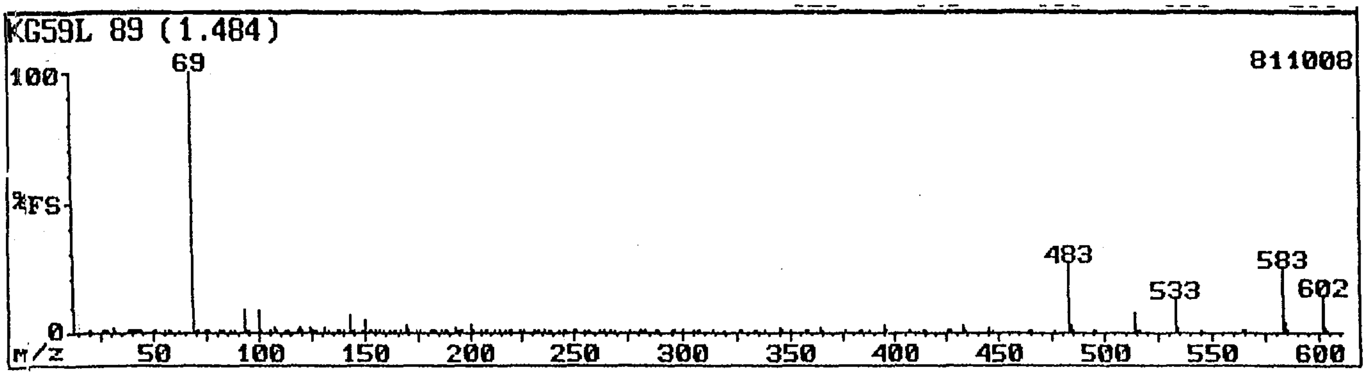
Spectrum No. 14



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
27	0.02	101	0.30	165	0.09	247	0.03
28	0.40	105	0.78	167	0.15	250	0.42
31	6.34	106	0.04	169	2.65	255	0.03
32	0.23	107	0.54	170	0.16	257	0.36
38	0.07	108	0.02	171	0.05	258	0.03
39	0.02	112	1.35	174	0.18	264	3.17
40	0.05	113	0.07	176	1.04	265	0.33
41	0.07	114	0.91	177	0.06	267	0.05
42	0.02	115	0.03	181	0.40	269	0.04
43	0.03	117	0.50	183	2.90	276	1.45
44	0.07	119	2.02	184	0.18	277	0.12
45	0.09	120	0.09	186	0.13	283	0.76
50	1.10	121	0.11	188	0.85	284	0.05
51	0.07	124	2.36	189	0.06	295	5.80
55	0.30	125	0.11	193	1.29	296	0.54
56	0.02	126	1.56	194	0.08	305	0.04
57	0.20	127	0.07	195	0.96	314	0.68
58	0.03	129	0.03	196	0.11	315	0.21
62	0.26	131	1.59	200	2.79	326	0.05
63	0.02	132	0.09	201	0.20	333	30.43
67	0.02	133	0.83	205	0.20	334	2.83
69	100.00	134	0.05	207	1.08	335	0.14
70	1.40	136	0.12	208	0.09	345	0.50
71	0.10	138	1.19	212	0.17	346	0.06
74	2.36	139	0.07	214	8.24	364	8.97
75	0.12	143	2.90	215	0.64	365	0.97
76	0.69	144	0.14	217	0.04	366	0.05
77	0.02	145	0.69	219	0.22	383	14.22
79	0.02	146	0.06	221	0.08	384	1.54
81	0.71	148	0.09	224	0.09	385	0.08
82	0.04	150	5.00	226	0.93	395	0.07
83	0.17	151	0.29	227	0.08	414	0.11
86	0.20	152	0.06	231	0.38	415	0.03
88	1.49	155	0.58	233	2.83	433	28.99
89	0.04	156	0.04	234	0.12	434	3.17
93	5.89	157	0.79	238	0.40	435	0.18
94	0.23	158	0.05	239	0.03	452	20.65
95	0.38	162	1.42	243	0.07		
98	0.04	163	0.08	245	6.16		
100	6.61	164	0.83	246	0.52		

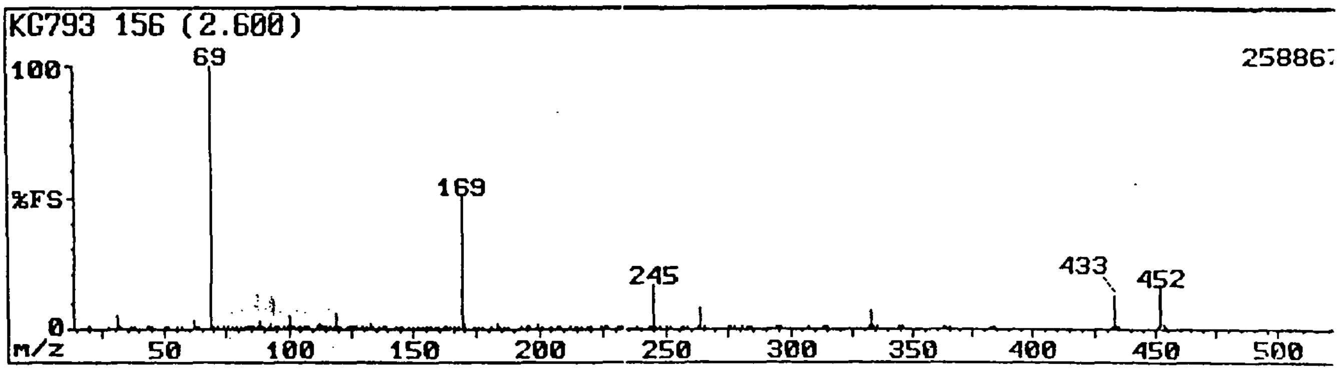
Spectrum No. 15



KG59L 89 (1.484) 811008

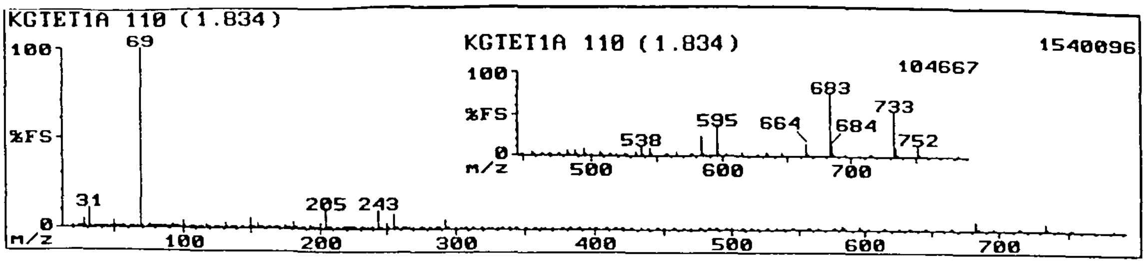
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	124	2.24	212	0.33	357	0.34
26	0.02	125	0.11	214	0.26	358	0.04
27	0.04	126	1.43	217	0.06	364	1.88
28	0.70	127	0.07	219	0.54	365	0.21
31	2.21	131	1.76	220	0.05	376	0.18
32	0.32	132	0.06	224	0.08	383	0.69
38	0.04	133	0.25	226	0.20	384	0.07
39	0.04	136	0.07	231	0.29	388	0.05
40	0.10	138	1.37	233	0.32	395	3.16
41	0.16	139	0.05	236	0.05	396	0.35
42	0.03	143	6.82	238	1.02	407	0.06
43	0.03	144	0.31	239	0.08	414	1.30
44	0.11	145	0.42	243	0.12	415	0.19
50	0.76	148	0.05	245	0.97	426	0.63
51	0.06	150	4.67	246	0.09	427	0.06
55	0.15	151	0.23	250	1.16	433	2.84
57	0.08	152	0.03	251	0.10	434	0.32
58	0.06	155	0.69	255	0.06	445	2.15
62	0.05	156	0.04	257	0.41	446	0.26
69	100.00	157	0.65	262	0.08	464	0.37
70	1.33	158	0.04	264	0.20	465	0.17
71	0.08	162	1.06	267	0.07	476	0.06
74	1.23	163	0.07	269	0.23	483	25.88
75	0.08	164	0.11	276	0.67	484	3.13
76	1.04	167	0.19	281	0.10	485	0.16
81	0.43	169	3.31	283	0.36	495	0.53
82	0.04	170	0.18	288	1.29	496	0.05
83	0.04	174	0.26	289	0.10	514	8.08
86	0.11	176	0.41	295	0.88	515	1.17
88	0.30	181	0.53	296	0.09	516	0.06
93	8.46	182	0.04	300	0.20	533	12.25
94	0.30	183	0.54	305	0.06	534	1.70
95	0.05	186	0.19	307	0.75	545	0.07
100	8.46	188	0.84	308	0.06	564	0.09
101	0.37	189	0.06	314	0.09	565	0.04
105	0.61	193	1.72	319	0.12	583	24.49
107	2.05	194	0.11	326	0.61	584	3.69
108	0.09	195	0.63	327	0.06	585	0.26
112	1.06	196	0.05	333	1.14	602	13.76
113	0.06	200	2.43	334	0.10		
114	0.39	201	0.16	338	0.28		
117	0.19	205	0.35	345	1.89		
119	1.63	207	0.57	346	0.19		
120	0.07	208	0.05	350	0.07		

Spectrum No. 16



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.02	101	0.15	163	0.02	256	0.01
28	0.20	102	0.03	164	0.13	257	0.45
31	5.10	104	0.03	165	0.03	258	0.04
32	0.14	105	0.70	167	0.03	263	0.27
36	0.01	106	0.07	169	50.63	264	7.63
38	0.20	107	0.82	170	1.48	265	0.59
43	0.03	108	0.04	174	0.22	275	0.03
44	0.04	111	0.07	176	0.64	276	0.79
45	0.12	112	1.50	177	0.05	277	0.07
50	1.14	113	0.08	181	1.38	281	0.02
51	0.03	114	0.50	183	2.16	282	0.01
52	0.01	115	0.02	184	0.11	283	0.26
55	0.18	116	0.02	186	0.03	284	0.04
57	0.26	117	0.44	188	0.10	294	0.05
62	3.24	118	0.27	193	0.28	295	1.22
63	0.08	119	6.01	195	1.33	296	0.10
64	0.07	120	0.09	196	0.12	307	0.02
69	100.00	121	0.04	200	1.81	313	0.02
70	1.20	123	0.05	201	0.10	314	0.32
71	0.13	124	1.04	205	0.14	315	0.03
74	0.61	125	0.09	207	0.74	332	0.27
76	0.89	126	1.34	208	0.06	333	6.65
77	0.03	127	0.04	212	0.03	334	0.58
79	0.03	129	0.01	214	1.32	335	0.03
81	1.22	131	1.37	215	0.10	344	0.04
82	0.07	133	2.21	217	0.02	345	1.01
83	0.93	134	0.10	219	0.16	346	0.09
84	0.05	136	0.14	220	0.01	363	0.02
85	0.02	138	0.37	224	0.01	364	0.24
86	0.23	139	0.02	226	0.21	365	0.03
87	0.09	143	0.58	227	0.01	382	0.02
88	2.43	145	0.79	231	0.15	383	0.39
89	0.10	146	0.04	232	0.01	384	0.03
90	0.02	148	0.01	233	0.05	432	0.92
92	0.07	150	0.92	238	0.03	433	12.66
93	1.95	152	1.01	243	0.03	434	1.39
94	0.07	153	0.02	244	0.40	435	0.07
95	0.22	155	0.63	245	16.61	451	1.18
96	0.01	157	0.37	246	1.30	452	15.51
98	0.06	158	0.01	247	0.04		
99	0.23	159	0.02	250	0.10		
100	5.06	162	0.41	252	0.02		

Spectrum No. 17

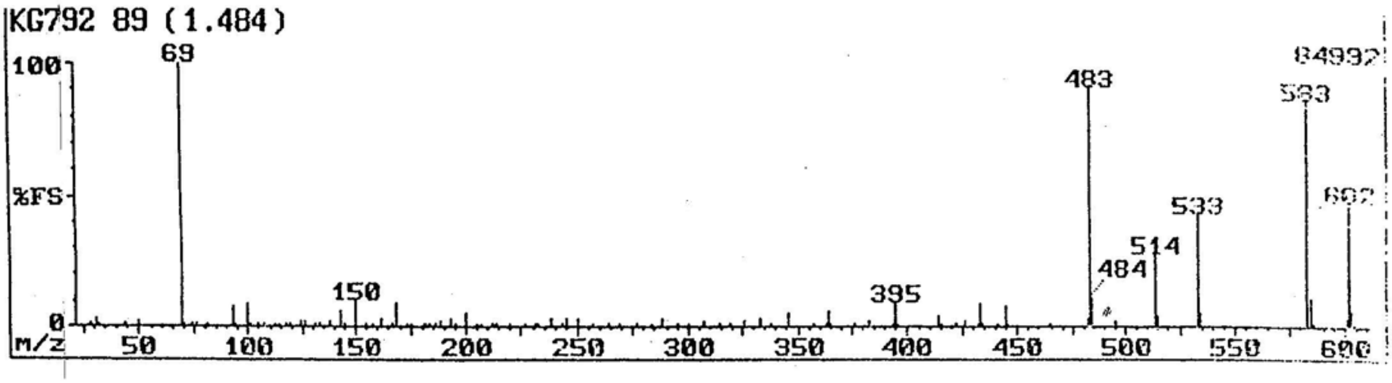


KGTET1A 110 (1.834)

1540096

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.65	90	0.03	176	0.86	270	0.03
24	0.07	91	0.02	177	0.08	274	0.99
25	0.03	93	2.06	179	0.05	275	0.09
26	0.59	94	0.09	181	3.71	276	0.12
27	0.30	95	0.07	182	0.18	277	0.03
28	5.05	96	0.03	183	0.28	281	0.28
29	0.20	98	0.20	186	0.82	282	0.04
31	10.31	100	4.26	187	0.09	283	0.05
32	0.42	101	0.14	188	0.28	286	0.03
33	0.20	105	0.51	189	0.03	288	0.31
35	0.04	106	0.07	193	2.33	289	0.04
36	0.09	107	1.10	194	0.14	293	4.65
37	0.05	108	0.07	195	0.10	294	0.35
38	0.75	109	0.02	196	0.08	295	0.24
39	0.32	112	0.58	198	0.05	296	0.04
40	0.14	113	0.10	200	2.61	300	0.96
41	0.18	114	0.31	201	0.19	301	0.09
42	0.04	117	1.85	205	9.51	305	0.12
43	0.25	118	0.12	206	0.59	307	0.22
44	0.90	119	1.10	207	0.34	308	0.03
45	0.11	120	0.05	208	0.04	312	0.21
47	1.20	124	1.06	212	0.96	313	0.03
48	0.10	125	0.08	213	0.07	314	0.02
50	3.67	126	0.49	214	0.02	319	0.23
51	0.37	127	0.16	217	0.31	320	0.03
52	0.06	129	0.05	219	0.26	324	0.10
54	0.03	131	2.48	220	0.04	326	0.11
55	0.28	132	0.12	221	0.51	327	0.02
56	0.06	133	0.05	222	0.03	331	0.11
57	0.58	136	0.53	224	1.41	333	0.37
58	0.06	137	0.08	225	0.14	334	0.04
62	0.48	138	0.61	226	0.20	338	0.32
63	0.09	139	0.04	227	0.04	339	0.04
64	0.04	143	0.91	231	0.55	343	0.79
66	0.25	144	0.06	232	0.07	344	0.07
67	0.10	145	0.08	233	0.09	345	0.18
69	100.00	148	0.14	236	0.29	350	0.38
70	1.18	150	5.45	238	0.53	351	0.05
71	0.12	151	0.24	239	0.06	357	0.26
74	0.42	152	0.04	243	9.91	358	0.03
75	0.13	155	2.96	244	0.63	362	0.04
76	1.53	156	0.17	245	0.36	364	0.04
77	0.09	157	0.51	246	0.04	369	0.16
78	0.02	158	0.06	250	2.81	370	0.02
79	0.14	159	0.07	251	0.22	376	0.09
80	0.08	162	1.20	255	7.38	377	0.02
81	0.98	163	0.10	256	0.54	381	0.02
82	0.16	164	0.11	257	0.29	383	0.07
407	0.30	476	0.12	545	0.64	645	0.36
408	0.04	477	0.04	546	0.09	646	0.06
414	0.08	483	0.48	557	0.11	664	0.96
415	0.03	484	0.07	558	0.02	665	0.15
419	0.08	488	0.40	564	0.26	666	0.02
420	0.02	489	0.06	565	0.06	683	5.05
426	0.08	495	0.60	576	0.07	684	0.90
427	0.02	496	0.08	577	0.02	685	0.06
433	0.10	500	0.02	583	1.63	695	0.05
438	0.12	507	0.26	584	0.25	714	0.07
439	0.02	508	0.04	585	0.02	715	0.02
445	0.67	514	0.14	595	2.33	733	3.66
446	0.09	515	0.04	596	0.36	734	0.66
450	0.13	519	0.05	597	0.03	735	0.06
457	0.22	526	0.10	602	0.01	752	0.89
458	0.03	527	0.03	614	0.26		
[illegible]	0.07	533	[illegible]	615	0.06		

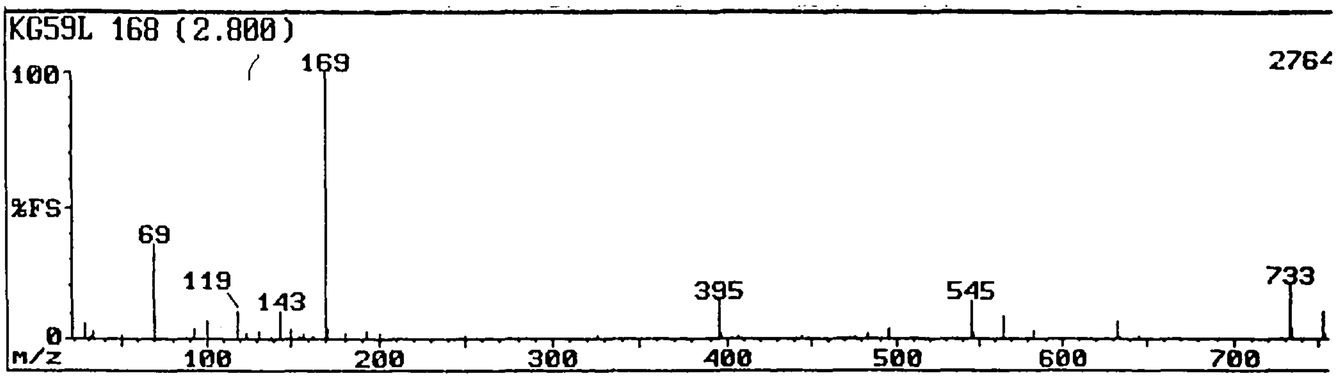
Spectrum No. 18



KG792 89 (1.484) 84992

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	1.22	150	9.56	257	1.08	426	1.52
31	2.58	155	1.06	264	0.33	432	0.29
32	0.86	157	0.58	269	0.30	433	8.96
44	0.36	162	2.43	276	1.07	434	1.02
50	1.66	167	0.56	283	0.56	441	0.78
69	100.00	169	8.81	288	3.29	445	7.30
70	1.24	174	0.27	295	1.36	446	0.92
74	1.26	176	0.64	300	0.56	464	1.37
76	1.09	181	1.45	307	1.90	482	2.88
81	0.51	183	0.89	314	0.35	483	91.57
93	7.83	186	0.58	319	0.39	484	11.14
94	0.34	188	1.49	326	1.64	495	1.64
100	8.58	193	2.56	333	2.94	513	1.13
101	0.43	195	1.12	338	0.77	514	26.81
105	0.48	200	4.57	345	5.05	515	3.60
107	1.01	205	1.03	357	1.00	533	42.47
112	0.57	207	1.34	363	0.20	534	5.20
114	0.37	212	0.97	364	5.35	583	86.75
117	0.53	214	0.80	365	0.51	584	10.32
119	0.95	219	0.93	376	0.61	585	0.74
124	1.56	226	0.51	383	2.13	601	2.58
126	2.15	231	0.91	394	0.24	602	47.59
131	1.36	233	0.75	395	9.19		
133	0.47	238	2.84	396	1.01		
138	1.64	243	0.38	414	4.18		
143	6.17	245	2.75	415	0.47		
145	0.89	250	3.11	422	0.48		

Spectrum No. 19



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KG59L  168  (2.800)                                                                  27648
-----------------------+------------------------+------------------------+-----------------
Mass     Rel  Int      | Mass     Rel  Int      | Mass     Rel  Int      | Mass     Rel  Int
-----------------------+------------------------+------------------------+-----------------
  28        5.96       |  143       10.53       |  326        1.00       |  565        1.45
  31        0.90       |  150        3.70       |  395       14.29       |  583        2.45
  32        2.86       |  155        0.65       |  396        1.71       |  633        6.37
  50        0.63       |  157        1.95       |  407        0.84       |  634        1.03
  69       36.34       |  162        0.88       |  445        1.14       |  645        1.20
  93        4.22       |  169      100.00       |  476        0.91       |  733       19.91
 100        6.89       |  170        3.49       |  483        1.77       |  734        3.70
 119       10.36       |  181        1.95       |  495        3.56       |  752       10.65
 124        1.90       |  193        2.55       |  545       15.05       |
 131        2.81       |  200        2.31       |  546        2.36       |
 138        1.22       |  250        1.13       |  564        8.97       |
-----------------------+------------------------+------------------------+-----------------
```
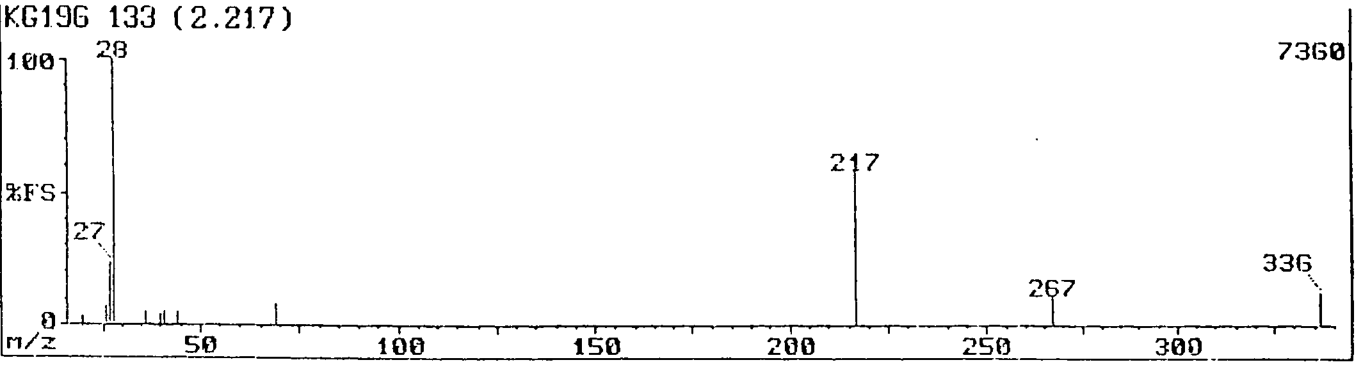

Spectrum No. 20



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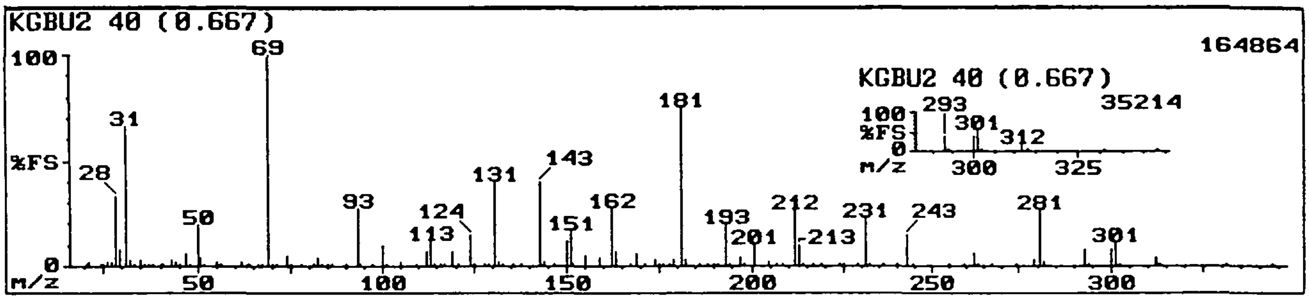
K6196 133 (2.217)                                                                                                           7360
--------------+---------------+---------------+---------------+---------------+---------------+---------------+---------------+--------------
Mass  Rel Int | Mass  Rel Int | Mass  Rel Int | Mass  Rel Int | Mass  Rel Int | Mass  Rel Int | Mass  Rel Int | Mass  Rel Int | Mass  Rel Int
--------------+---------------+---------------+---------------+---------------+---------------+---------------+---------------+--------------
 20     2.87  |  27    23.04  |  36      4.40 |  41      4.57 |  69      7.61 | 267     10.87 |               |               |
 26     6.50  |  28   100.00  |  40      4.13 |  44      4.73 | 217     50.26 | 336     12.50 |               |               |
--------------+---------------+---------------+---------------+---------------+---------------+---------------+---------------+--------------
```

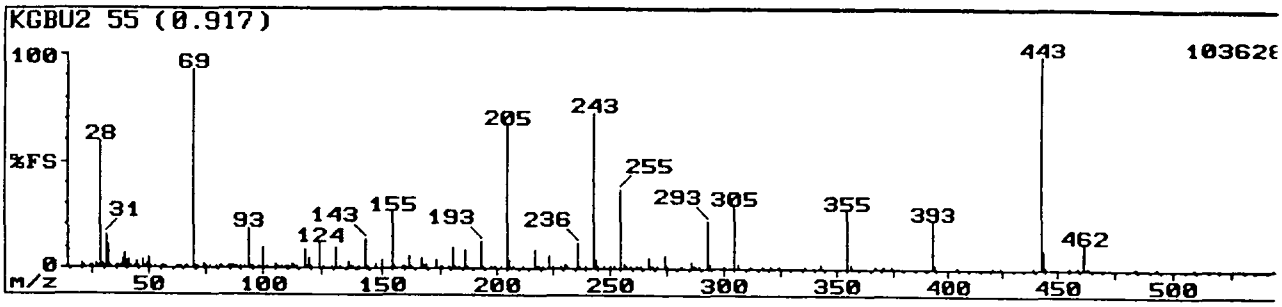
Spectrum No. 21



KGBU2 40 (0.667) 164864

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.66	70	1.05	138	0.22	212	25.93
21	2.14	71	0.45	143	39.44	213	9.39
24	0.68	74	5.09	144	2.38	214	0.96
25	0.59	75	1.03	147	0.19	217	0.32
26	1.63	78	0.16	150	11.49	219	0.23
27	1.51	81	1.16	151	16.93	224	0.81
28	33.23	82	3.92	152	0.38	225	0.23
29	7.45	83	0.13	155	4.54	229	0.22
31	66.46	85	0.25	159	3.84	231	22.52
32	3.30	86	0.43	162	27.33	232	0.91
33	0.34	90	0.17	163	6.83	236	0.24
35	2.48	93	26.71	167	0.21	240	0.28
36	0.67	94	1.16	169	5.94	243	14.13
37	0.93	97	0.18	171	0.20	244	0.62
38	0.21	100	10.09	174	2.68	255	0.51
40	0.28	101	0.48	175	0.32	259	0.97
41	0.16	105	1.64	176	0.29	262	5.43
43	3.03	109	0.32	178	0.45	263	0.53
44	2.07	112	6.41	179	2.56	267	0.18
45	0.58	113	11.65	181	74.53	274	0.31
47	5.90	114	0.64	182	2.76	279	3.30
48	0.39	116	0.84	186	0.34	281	25.78
50	19.10	117	0.96	188	0.20	282	1.70
51	4.23	119	7.18	190	0.34	293	8.07
52	0.20	121	0.17	191	0.39	294	0.39
55	2.26	124	14.75	193	19.25	300	7.53
56	0.41	125	0.87	194	0.62	301	10.71
62	1.83	128	0.34	197	3.96	302	0.59
63	0.54	129	1.27	198	0.14	312	3.49
64	0.19	131	39.75	201	9.90		
66	0.30	132	2.22	205	1.52		
67	0.23	133	0.36	207	0.25		
69	100.00	136	0.30	209	0.65		

Spectrum No. 22



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            ----------------------------------------------------------------
   KGBU2 55 (0.917)                                                  1036288
 -------------------+--------------------+--------------------+-------------------
   Mass    Rel Int  | Mass    Rel Int    | Mass    Rel Int    | Mass    Rel Int
 -------------------+--------------------+--------------------+-------------------
     20      1.80   |   82      0.12     |  167      5.01     |  267      4.47
     21      0.04   |   84      0.56     |  168      0.23     |  268      0.32
     24      0.14   |   85      0.80     |  169      1.98     |  269      0.03
     25      0.16   |   86      1.14     |  174      4.03     |  271      0.07
     26      1.93   |   87      0.11     |  175      0.37     |  274      6.05
     27      1.44   |   88      0.09     |  176      0.05     |  275      0.69
     28     59.68   |   90      0.03     |  179      0.38     |  281      0.19
     29      1.61   |   91      0.02     |  181      9.29     |  286      2.54
     30      0.36   |   93     18.68     |  182      0.22     |  287      0.23
     31     16.01   |   94      0.66     |  183      0.07     |  288      0.02
     32     10.28   |   95      0.14     |  186      8.40     |  290      0.04
     33      0.13   |   98      0.79     |  187      0.52     |  293     22.63
     35      1.33   |  100      9.78     |  193     12.35     |  294      1.63
     36      0.35   |  101      0.25     |  194      0.34     |  300      0.04
     37      0.48   |  105      2.37     |  198      0.38     |  305     28.85
     38      3.51   |  106      0.18     |  200      0.08     |  306      2.12
     39      6.62   |  107      0.03     |  202      0.05     |  312      0.11
     40      2.84   |  109      0.06     |  205     67.19     |  317      0.06
     41      3.71   |  110      0.05     |  206      3.73     |  321      0.02
     42      0.39   |  112      2.32     |  207      0.09     |  324      0.73
     43      0.50   |  113      0.21     |  212      0.98     |  336      0.08
     44      2.74   |  114      0.16     |  217      8.60     |  343      1.88
     45      0.28   |  117      9.09     |  218      0.61     |  355     26.88
     47      3.83   |  118      0.59     |  219      0.14     |  356      1.95
     48      0.49   |  119      5.24     |  221      0.07     |  367      0.07
     49      1.83   |  120      0.13     |  224      5.98     |  371      0.03
     50      4.84   |  124     11.86     |  225      0.53     |  374      1.25
     51      0.62   |  125      0.56     |  229      0.04     |  393     22.23
     52      0.08   |  129      0.29     |  231      2.17     |  394      1.83
     55      0.70   |  131     10.08     |  232      0.06     |  405      0.04
     56      0.05   |  132      0.25     |  236     11.76     |  421      0.08
     57      0.05   |  136      3.06     |  237      0.80     |  424      0.03
     62      0.36   |  137      0.45     |  240      0.08     |  440      0.03
     63      0.04   |  138      0.07     |  243     72.73     |  443    100.00
     64      0.05   |  141      0.06     |  244      4.00     |  444      8.79
     66      0.44   |  143     13.34     |  245      0.16     |  445      0.39
     67      0.11   |  144      0.52     |  248      0.10     |  455      0.13
     69     93.68   |  148      1.56     |  250      0.07     |  459      0.06
     70      1.15   |  150      4.30     |  252      0.06     |  462     11.36
     71      0.13   |  155     26.09     |  255     36.76     |
     74      1.88   |  156      1.35     |  256      2.32     |
     75      0.17   |  159      0.09     |  257      0.07     |
     76      0.07   |  160      0.05     |  259      0.04     |
     79      0.28   |  162      5.58     |  262      0.37     |
     81      1.13   |  163      0.22     |  264      0.05     |
 -------------------+--------------------+--------------------+-------------------
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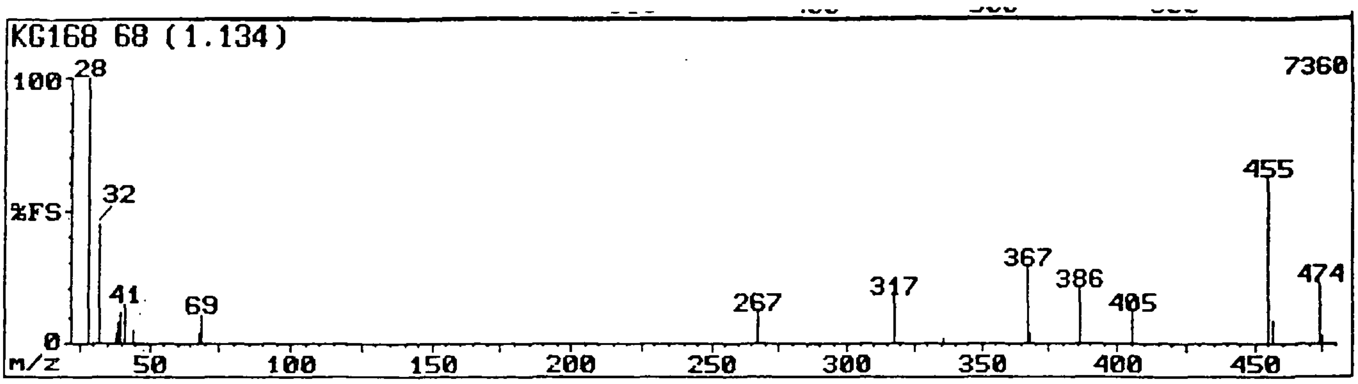
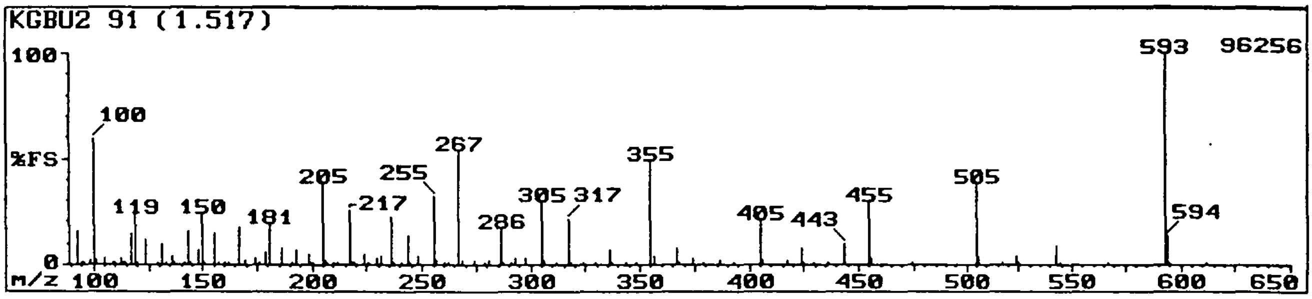
Spectrum No. 23



KG168 68 (1.134) 7360

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	100.00	39	7.83	44	4.73	267	11.96	367	27.83	405	11.36	474	22.39				
32	44.78	40	11.47	68	4.35	317	17.61	368	3.91	455	62.61						
38	3.42	41	14.57	69	10.38	336	2.27	386	20.43	456	9.13						

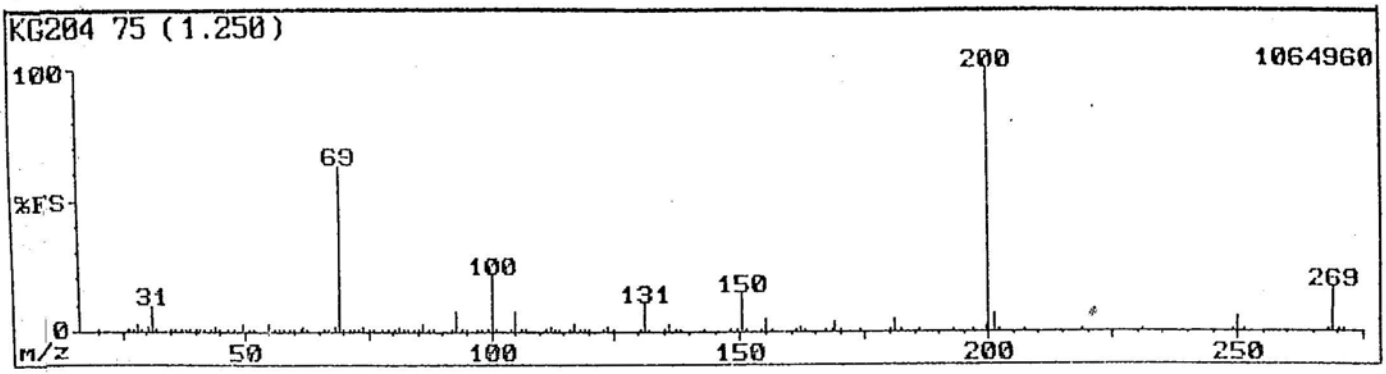
Spectrum No. 24



KGBU2 91 (1.517) 950272

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
93	1.58	162	0.06	248	0.43	374	0.31
94	0.04	167	1.72	255	3.26	379	0.04
95	0.05	169	0.25	256	0.23	386	0.17
98	0.20	174	0.28	260	0.04	393	0.08
100	6.01	176	0.05	262	0.05	405	2.05
101	0.15	179	0.56	267	5.36	406	0.19
105	0.25	181	1.86	268	0.24	417	0.24
109	0.05	186	0.79	274	0.23	424	0.77
110	0.05	191	0.02	279	0.12	425	0.12
112	0.25	193	0.64	281	0.16	429	0.04
113	0.05	198	0.48	286	1.69	436	0.14
114	0.10	199	0.06	287	0.09	443	0.94
117	1.50	200	0.06	291	0.03	455	2.94
119	2.32	205	3.85	293	0.30	456	0.34
120	0.06	206	0.24	298	0.26	474	0.03
124	1.14	207	0.06	305	2.99	505	3.85
129	0.13	210	0.04	306	0.23	506	0.44
131	1.02	212	0.09	312	0.04	517	0.03
133	0.03	217	2.56	317	2.18	524	0.36
136	0.36	218	0.14	318	0.13	525	0.04
137	0.03	219	0.09	324	0.07	543	0.88
141	0.09	224	0.44	329	0.08	544	0.11
143	1.62	225	0.04	336	0.66	567	0.05
144	0.06	229	0.34	337	0.06	593	10.13
148	0.65	231	0.44	343	0.04	594	1.34
150	2.37	236	2.24	348	0.09	595	0.08
151	0.11	237	0.13	355	4.88	612	0.07
155	1.49	241	0.05	356	0.42		
157	0.02	243	1.41	367	0.84		
160	0.10	244	0.08	368	0.13		

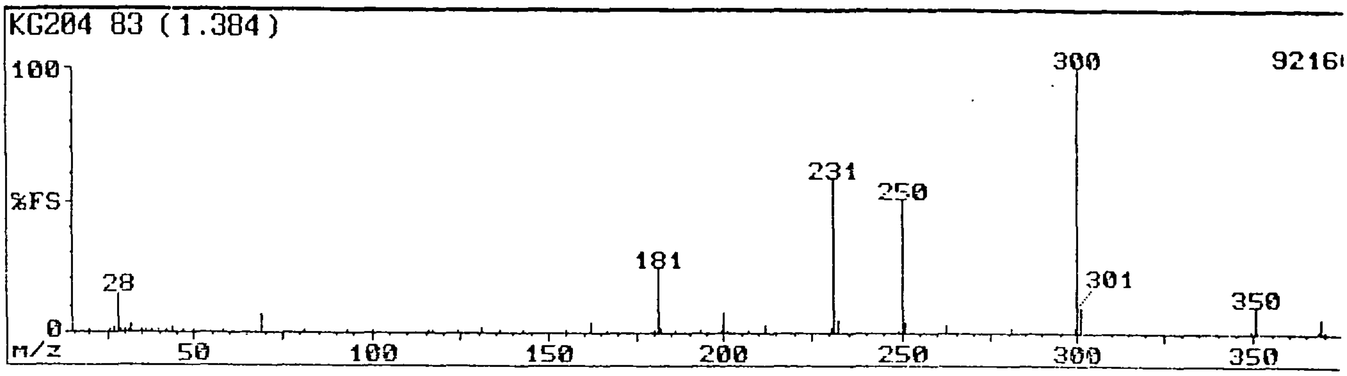
Spectrum No. 25



KG204 75 (1.250) 1064960

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.10	40	0.12	58	0.10	74	1.97	92	0.20	112	1.56	135	0.03	163	0.09	201	6.35
26	0.20	41	0.33	59	0.07	75	0.15	93	7.79	113	0.14	136	2.88	167	0.04	202	0.22
26	0.04	42	0.53	60	0.16	76	0.76	94	0.31	114	0.21	137	0.15	168	0.07	207	0.08
27	0.87	43	0.27	61	0.05	78	0.21	95	0.05	116	0.06	138	0.23	169	3.61	219	0.24
28	2.69	44	1.78	62	1.61	79	0.36	97	0.02	117	3.32	143	0.37	170	0.20	231	0.37
29	0.16	45	0.14	63	0.21	80	0.09	98	0.53	118	0.18	148	0.08	174	0.03	249	0.11
30	1.83	47	1.13	66	0.23	81	1.90	99	0.40	119	1.21	149	0.23	180	0.10	250	5.89
31	9.90	48	0.20	67	0.12	82	0.52	100	21.06	120	0.05	150	14.13	181	5.31	251	0.47
32	0.61	50	2.60	68	2.12	83	0.16	101	1.00	123	0.04	151	1.00	182	0.47	268	0.27
35	0.17	51	0.21	69	62.69	84	0.03	104	0.12	124	2.38	154	0.09	186	0.31	269	16.25
36	0.26	52	0.05	70	0.76	85	0.20	105	7.60	125	0.18	155	4.69	193	0.06		
37	0.17	55	2.48	71	0.06	86	2.60	106	0.37	130	0.14	156	0.24	197	0.06		
38	0.29	56	0.19	72	0.12	87	0.21	107	0.12	131	10.58	161	0.04	199	1.83		
39	0.34	57	0.17	73	0.07	88	0.18	111	0.03	132	0.62	162	1.80	200	100.00		

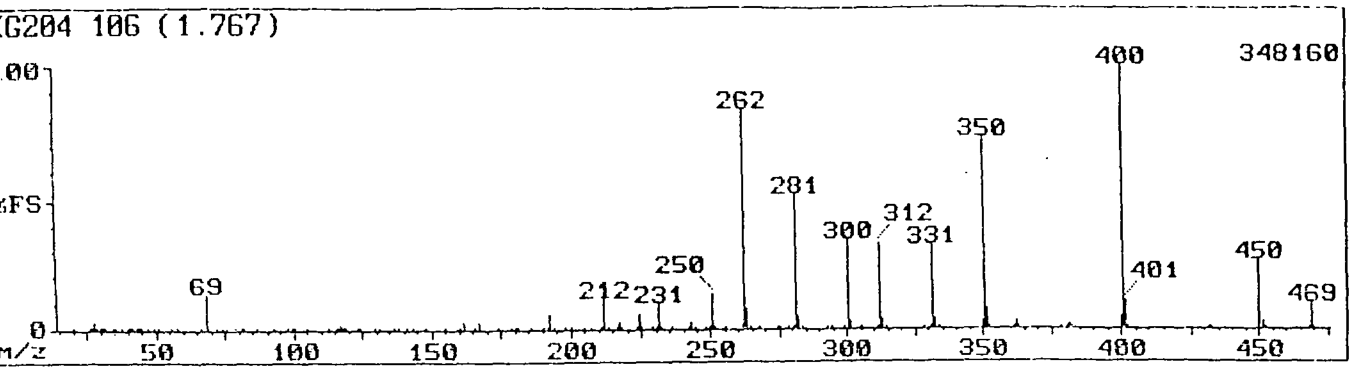
Spectrum No. 26



KG204 83 (1.384) 921

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.03	32	3.23	47	1.06	116	0.32	162	4.25	199	0.21	232	4.79	300	100.00		
26	0.51	35	0.98	50	0.83	117	1.13	167	0.65	200	7.71	249	1.15	301	9.24		
27	1.77	36	1.00	58	0.62	124	0.87	180	0.41	201	0.52	250	50.83	349	0.56		
28	15.00	38	0.46	69	6.81	131	2.20	181	24.17	207	0.46	251	4.01	350	9.86		
29	0.72	40	0.63	81	0.72	136	1.44	182	1.84	212	3.14	262	2.76	351	1.09		
30	0.49	42	0.88	93	0.64	143	0.89	186	1.11	230	1.63	281	2.19	368	0.37		
31	1.30	44	1.74	100	0.76	155	0.66	193	0.82	231	58.33	299	2.10	369	6.11		

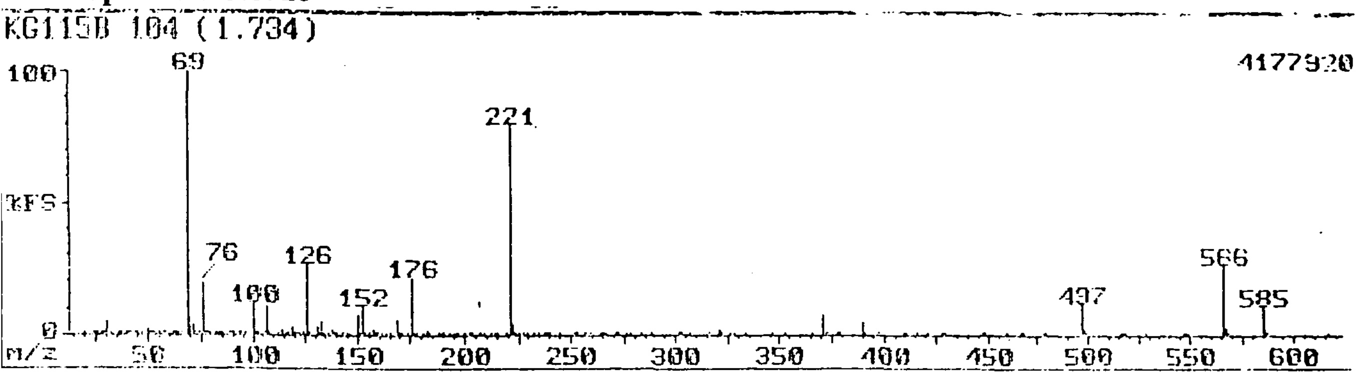
Spectrum No. 27



KG204 106 (1.767) 348160

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.27	45	0.21	93	0.66	138	0.21	193	5.37	230	0.22	267	0.45	313	3.53	381	1.84
26	0.14	47	0.43	98	0.21	141	0.16	194	0.45	231	9.26	274	1.14	314	0.17	382	0.55
27	0.61	50	0.44	99	0.07	143	0.47	198	0.87	232	0.93	275	0.14	328	0.21	399	5.22
28	3.33	51	0.59	100	1.01	148	1.38	200	1.21	236	0.40	278	0.16	330	1.13	400	100.00
29	0.22	56	0.20	105	0.15	155	1.21	205	0.80	242	0.08	280	0.97	331	32.35	401	10.96
30	0.28	58	0.27	112	0.11	160	0.14	207	0.21	243	2.56	281	51.47	332	3.55	402	0.54
31	0.65	66	0.12	116	0.07	162	3.07	211	0.24	244	0.51	282	5.15	333	0.18	431	0.17
32	0.73	69	13.75	116	0.09	166	0.21	212	11.47	248	0.24	283	0.24	349	3.03	432	0.11
35	0.18	72	0.81	117	1.65	167	2.74	213	1.08	249	0.24	293	1.40	350	72.94	449	2.02
36	0.27	74	0.23	118	0.10	174	0.58	216	0.07	250	13.82	294	0.27	351	7.35	450	25.89
38	0.16	76	0.22	119	0.68	179	0.91	217	2.67	251	1.07	299	0.78	352	0.39	451	3.13
40	0.29	79	0.16	123	0.18	180	0.05	218	0.17	255	0.51	300	34.41	361	0.21	452	0.18
41	0.26	81	0.19	124	1.43	181	1.27	223	0.13	261	2.08	301	3.22	362	3.13	468	0.78
42	1.29	82	0.21	129	0.19	186	0.95	224	5.81	262	83.53	305	0.15	363	0.38	469	10.07
43	0.41	86	0.19	131	0.70	190	0.28	225	0.57	263	7.57	311	0.78	378	0.12		
44	1.31	92	0.05	136	0.27	192	0.10	229	0.15	264	0.36	312	32.94	380	0.15		

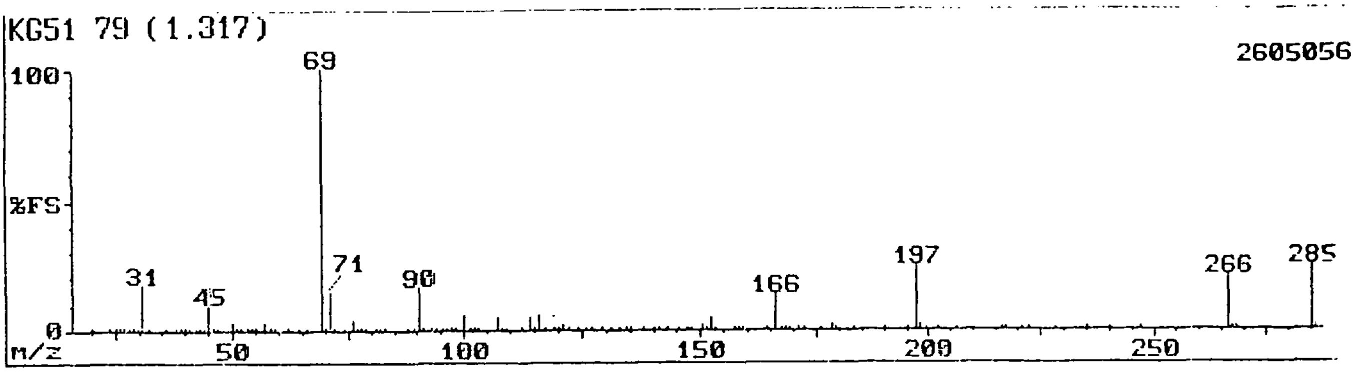
Spectrum No. 28



KG115B 104 (1.734) 4177920

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.03	55	0.04	89	0.05	122	0.02	159	0.01	202	0.75	257	0.02	366	0.02	497	11.18
24	0.01	57	0.94	90	0.02	124	0.04	162	0.16	203	0.05	259	0.01	371	7.65	498	1.46
25	0.01	58	0.08	93	0.79	126	26.27	164	0.18	207	0.05	264	0.91	372	0.58	499	0.08
26	0.04	62	0.13	94	0.02	127	0.04	165	0.01	209	0.01	265	0.05	373	0.03	516	0.21
27	0.01	63	0.01	95	0.39	131	2.67	166	0.01	212	0.05	266	0.01	378	0.00	517	0.10
28	0.15	64	0.01	96	0.03	132	0.05	169	6.27	214	0.10	271	0.14	379	0.01	518	0.01
29	0.00	66	0.02	97	0.02	133	5.02	170	0.17	215	0.01	272	0.02	390	4.98	528	0.06
31	5.17	69	100.00	100	11.67	134	0.22	171	0.29	219	0.04	276	0.06	391	0.38	547	0.06
32	0.10	70	3.16	101	0.31	136	0.01	174	0.01	221	79.61	278	0.09	397	0.02	548	0.04
36	0.01	71	3.48	102	0.35	138	1.62	176	21.08	222	3.77	283	0.47	403	0.17	549	0.01
38	0.19	72	0.11	103	0.02	139	0.07	177	0.80	223	0.09	288	0.06	410	0.02	566	26.27
39	0.01	74	0.17	105	0.03	140	0.02	178	0.17	226	0.10	302	1.29	416	0.06	567	3.31
40	0.01	76	19.12	107	10.69	143	0.21	181	0.31	228	0.56	303	0.12	421	0.01	568	0.17
41	0.00	77	0.50	108	0.46	145	0.27	183	2.35	229	0.03	307	0.02	428	0.07	585	10.29
43	0.03	78	0.38	112	1.07	146	0.01	184	0.11	233	0.38	316	0.02	429	0.05		
44	0.05	79	0.01	114	2.28	150	7.45	188	0.24	234	0.03	321	1.46	447	0.04		
45	0.01	81	1.32	115	0.05	151	0.13	190	0.01	238	0.18	322	0.12	448	0.03		
47	0.03	82	0.08	116	0.03	152	10.78	193	0.06	239	0.01	326	0.01	459	0.01		
50	2.40	83	0.21	117	0.01	153	0.55	195	1.31	240	0.02	328	0.01	466	0.46		
51	0.14	84	0.03	119	2.62	155	0.01	196	0.06	245	0.16	333	0.04	467	0.06		
52	0.10	85	0.02	120	0.04	157	1.91	197	0.02	252	0.09	347	0.02	478	0.40		
53	0.04	88	1.23	121	0.25	158	0.09	200	0.13	253	0.03	352	0.02	479	0.05		

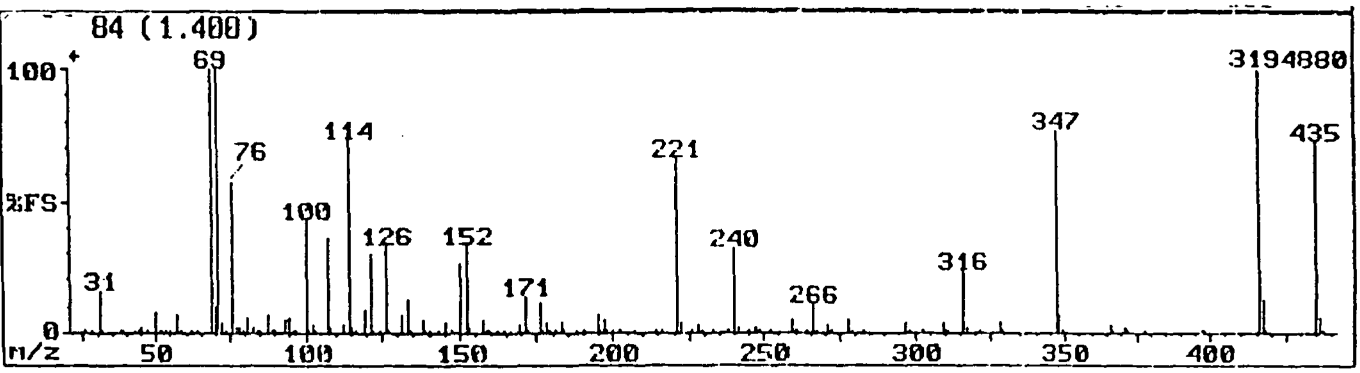
Spectrum No. 29



KG51 79 (1.317) 2605056

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	66	0.02	115	0.07	168	0.02
24	0.08	69	100.00	116	5.90	169	0.09
25	0.01	70	1.12	117	0.28	171	0.33
26	0.14	71	14.47	119	0.97	172	0.02
27	0.08	72	0.47	120	0.02	176	0.12
28	0.51	74	0.18	121	1.54	178	2.16
29	0.03	76	3.69	122	0.06	179	0.14
30	0.03	77	0.11	124	0.03	183	0.05
31	17.61	78	0.19	126	0.92	190	0.02
32	0.32	79	0.03	127	0.04	195	0.08
36	0.04	81	0.58	129	0.02	197	24.37
38	0.62	82	0.03	131	0.57	198	1.48
39	0.08	83	0.16	133	1.24	199	0.05
40	0.20	88	1.00	134	0.07	202	0.02
41	0.28	89	0.02	135	0.07	206	0.01
42	0.07	90	16.35	138	0.28	216	0.65
43	0.28	91	0.51	140	0.30	217	0.08
44	0.26	93	0.74	141	0.01	221	0.85
45	10.06	94	0.03	143	0.02	222	0.05
46	0.17	95	0.91	145	0.29	228	0.13
47	0.04	96	0.04	147	0.10	235	0.01
50	2.71	97	0.37	148	0.04	240	0.04
51	0.09	98	0.03	150	1.88	247	0.16
52	0.67	100	5.90	151	0.05	266	20.13
53	0.03	101	0.08	152	4.56	267	1.33
54	0.03	102	0.56	153	0.22	268	0.04
55	0.12	103	0.03	157	0.38	285	24.37
57	2.75	107	4.83	158	0.01		
58	0.14	108	0.18	159	0.11		
59	0.04	109	0.03	164	0.03		
62	0.28	112	0.19	166	13.99		
64	0.07	114	4.40	167	0.74		

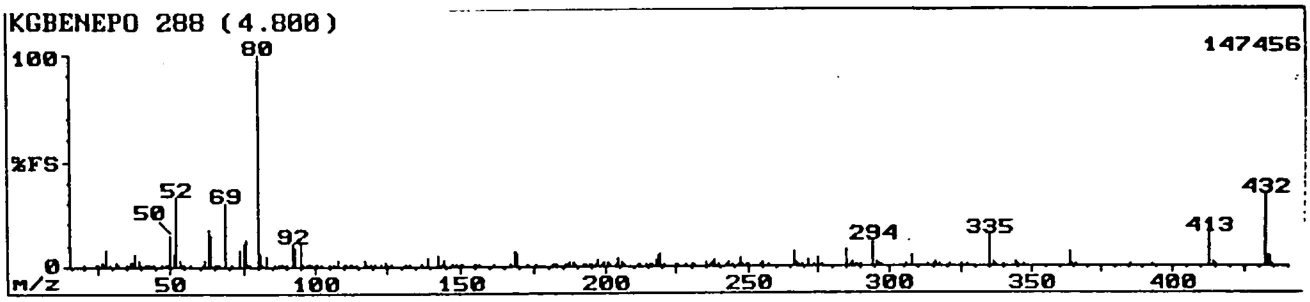
Spectrum No. 30



84 (1.400) 3194880

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.01	58	0.09	88	1.34	116	0.04	150	5.19	181	0.07	226	0.07	271	0.51	347	15.38
28	0.05	62	0.14	89	0.07	119	1.71	152	6.60	183	0.70	228	0.66	272	0.04	348	1.40
31	3.11	64	0.06	90	0.15	121	6.06	153	0.34	184	0.04	229	0.07	278	0.91	349	0.07
32	0.06	69	100.00	93	1.04	122	0.24	157	0.99	188	0.04	233	0.14	279	0.12	366	0.54
38	0.13	70	1.88	95	1.13	124	0.03	158	0.03	190	0.14	238	0.05	283	0.11	367	0.12
39	0.01	71	23.21	96	0.04	126	6.60	159	0.04	195	1.41	240	6.35	297	0.76	371	0.45
43	0.04	72	0.78	97	0.20	127	0.24	162	0.09	196	0.05	241	0.35	298	0.09	372	0.04
44	0.02	74	0.23	100	8.59	131	1.37	164	0.26	197	0.93	245	0.05	302	0.10	378	0.04
45	0.43	76	11.54	101	0.25	133	2.47	166	0.19	198	0.06	247	0.48	309	0.77	397	0.06
47	0.02	77	0.31	102	0.55	134	0.12	169	0.55	200	0.03	248	0.05	310	0.06	398	0.02
50	1.59	78	0.29	103	0.08	138	0.91	171	2.69	202	0.20	252	0.05	311	0.03	416	29.10
51	0.08	79	0.05	107	7.28	139	0.05	172	0.14	207	0.02	259	1.06	316	4.74	417	2.60
52	0.17	81	1.07	108	0.30	140	0.05	176	2.37	214	0.11	260	0.09	317	0.38	418	0.11
53	0.01	83	0.34	112	0.53	143	0.05	177	0.03	216	0.11	264	0.19	321	0.12	435	14.43
55	0.05	84	0.03	114	14.43	145	0.83	178	0.72	221	13.21	265	2.21	328	0.72		
57	1.36	85	0.02	115	0.38	147	0.11	179	0.05	222	0.76	267	0.16	329	0.08		

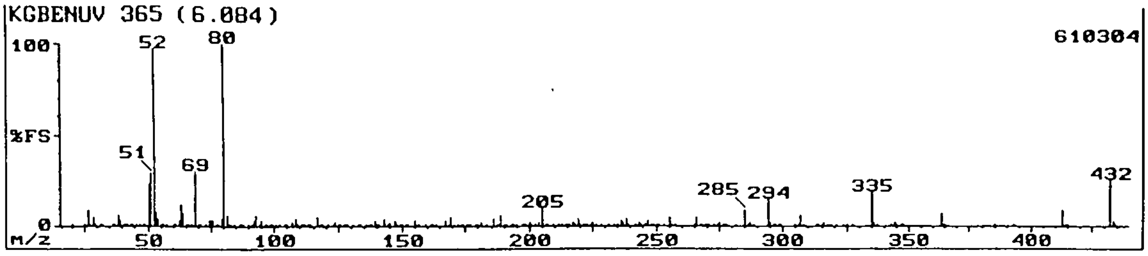
Spectrum No. 31



KGBENEPO 288 (4.800) 14

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.18	88	0.38	181	0.72	254	0.97
24	0.19	89	0.37	182	0.35	255	1.70
25	0.27	90	0.25	183	0.54	257	0.32
26	1.71	92	10.94	185	0.36	266	6.42
27	0.80	93	9.11	186	1.04	267	1.95
28	7.90	95	10.29	187	1.66	268	0.64
29	0.34	96	0.68	188	1.63	269	0.38
31	2.20	97	0.55	189	1.19	271	2.76
32	0.93	98	0.95	192	0.52	273	0.32
35	1.02	99	1.45	193	1.26	275	3.65
36	1.65	100	0.58	195	0.12	276	0.43
37	1.48	101	0.22	195	0.37	285	7.38
38	5.64	102	0.21	196	1.42	286	1.00
39	3.39	105	1.16	197	2.47	287	1.88
40	0.53	107	0.77	198	0.72	288	0.34
41	0.75	108	3.17	199	1.53	290	0.24
42	0.40	110	0.11	200	1.92	294	11.28
43	0.59	111	0.50	201	0.24	295	1.52
44	1.19	112	0.53	203	0.94	296	0.27
47	0.24	113	0.24	204	3.43	297	0.71
48	0.26	114	0.56	205	1.71	305	0.53
49	0.54	117	2.86	206	0.43	307	4.51
50	14.58	118	0.26	211	0.17	313	0.55
51	6.29	119	0.63	212	0.18	315	0.71
52	33.16	121	0.66	214	0.19	316	1.75
53	2.78	123	0.44	215	0.67	317	0.22
54	0.84	124	1.68	216	1.36	321	1.17
55	0.69	125	0.47	217	2.45	325	0.37
57	0.79	126	0.38	218	4.43	327	0.09
61	0.37	131	0.93	219	5.73	335	14.58
62	2.60	133	0.43	220	0.54	336	1.83
63	17.71	137	0.33	224	0.63	337	0.13
64	14.58	139	3.82	225	1.18	340	0.11
65	1.14	143	4.64	228	0.23	344	2.00
66	0.34	144	0.19	231	0.23	345	0.41
67	0.45	145	3.39	231	0.31	347	0.97
69	30.21	147	0.92	235	1.96	363	6.68
71	0.56	148	0.27	236	1.43	364	1.31
74	7.81	149	0.94	238	1.87	365	0.29
75	10.29	150	0.69	238	3.04	385	0.33
76	12.50	151	0.76	239	0.44	393	0.23
77	1.19	155	1.20	242	1.02	413	15.28
78	0.16	156	0.26	243	1.83	414	2.34
80	100.00	161	0.33	244	0.36	415	0.23
81	5.64	167	0.52	246	1.38	432	33.85
82	0.37	169	6.81	247	4.08		
83	5.34	169	6.29	248	0.48		
86	0.82	173	0.30	249	0.98		
87	0.33	176	0.31	250	0.48		

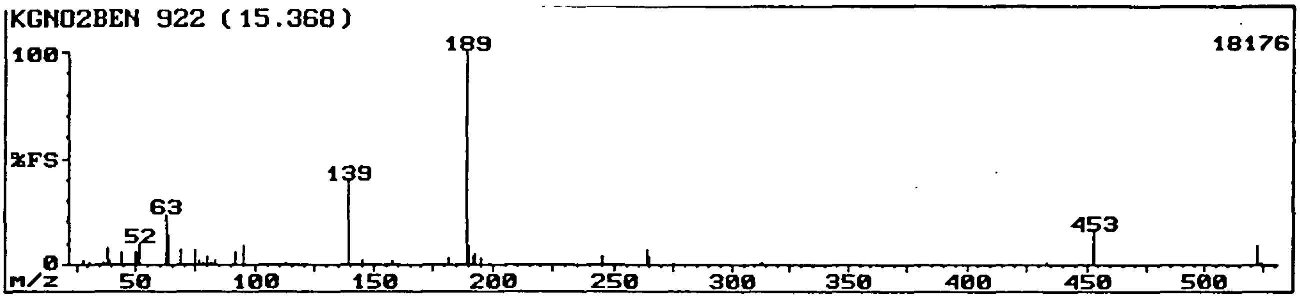
Spectrum No. 32



KGBENUV 365 (6.084)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.09	88	0.09	159	0.18	231	0.24
25	0.22	90	0.17	161	0.15	233	0.06
26	8.60	91	0.20	162	0.38	235	0.57
27	0.92	92	2.60	163	0.16	236	2.58
28	4.78	93	6.25	167	3.36	237	1.53
29	0.30	94	0.26	168	0.39	238	3.82
31	0.84	95	3.36	169	4.82	239	0.37
32	1.10	96	0.22	170	0.43	242	0.79
36	0.09	97	0.52	172	0.28	243	1.54
37	1.38	98	0.64	173	0.86	244	0.29
38	5.66	99	0.60	174	0.41	245	0.11
39	3.27	100	0.28	175	0.08	246	0.19
40	0.52	102	0.08	176	0.14	247	2.49
41	0.27	104	0.27	177	0.09	248	0.27
42	0.17	105	0.66	179	0.06	249	0.68
43	0.09	107	1.48	180	0.07	250	0.50
44	0.86	108	4.28	181	1.94	251	0.11
45	0.09	109	0.41	183	0.77	253	0.06
47	0.10	110	0.11	186	3.48	255	4.61
48	0.08	111	0.25	187	1.02	256	0.41
49	1.22	112	0.41	188	0.33	257	0.33
50	23.32	113	0.15	189	5.41	265	0.37
51	29.03	114	0.22	190	0.42	266	4.87
52	96.64	117	5.16	191	0.18	267	0.78
53	7.80	118	0.30	193	1.13	268	0.25
54	3.90	119	0.29	194	0.07	269	0.65
55	1.18	121	0.49	195	0.39	270	0.53
56	0.12	123	0.70	197	1.43	271	0.47
57	0.42	124	1.54	198	0.18	273	0.60
60	0.04	125	0.41	199	0.17	274	0.15
61	0.81	126	0.23	200	1.88	275	1.93
62	2.58	127	0.07	201	0.59	276	0.22
63	11.58	128	0.15	202	0.10	277	0.15
64	6.84	129	0.24	204	2.16	278	0.11
65	0.67	131	0.62	205	9.82	281	0.09
66	0.25	133	0.33	206	0.71	285	9.14
67	1.07	134	0.11	207	0.78	286	0.99
69	30.54	136	0.85	209	0.18	287	2.37
70	0.35	137	0.28	211	0.06	288	0.33
71	0.37	138	0.16	213	0.13	294	14.93
73	0.36	139	2.58	214	0.29	295	1.71
74	3.02	140	0.18	215	0.05	296	0.20
75	2.55	141	0.06	216	0.55	297	0.61
76	3.06	143	3.78	217	1.89	298	0.06
77	0.57	144	0.18	218	1.41	299	0.21
78	0.22	145	2.17	219	3.48	305	0.43
79	4.11	147	2.54	220	0.35	306	0.31
80	100.00	148	1.41	221	0.19	307	6.17
81	5.54	149	0.47	222	0.06	308	0.61
82	0.41	150	0.45	223	0.23	313	0.57
83	0.59	151	0.42	224	0.29	314	0.07
85	0.11	152	0.09	225	1.49	315	0.62
86	0.27	155	3.31	226	0.16	316	1.47
319	0.10	336	2.10	348	0.10	413	8.81
321	0.34	337	0.20	363	6.96	414	1.06
324	0.07	343	0.23	364	0.81	415	0.10
325	0.30	344	1.96	365	0.17	432	25.17
327	0.24	345	0.17	385	0.18		
335	18.46	347	0.77	393	0.13		

Spectrum No. 33



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                 ----------------------------------------------------------------
   KGNO2BEN 922 (15.368)
------------------+------------------+------------------+----------------
   Mass   Rel Int | Mass    Rel Int  | Mass    Rel Int  | Mass    Rel Int
------------------+------------------+------------------+----------------
     28      2.22 |   64      14.00  |  113       1.08  |  245       4.16
     31      0.84 |   69       7.22  |  139      38.73  |  264       6.34
     37      0.90 |   75       7.04  |  145       1.63  |  264       4.27
     38      8.10 |   76       1.91  |  157       1.80  |  313       0.72
     39      2.09 |   78       1.40  |  182       3.19  |  433       1.04
     44      5.57 |   80       4.14  |  189     100.00  |  453      15.23
     50      6.07 |   81       1.05  |  190       8.54  |  522       8.80
     51      5.24 |   83       2.31  |  192       3.43  |
     52      9.42 |   91       6.16  |  192       4.91  |
     63     23.24 |   95       8.98  |  195       2.64  |
------------------+------------------+------------------+----------------
```
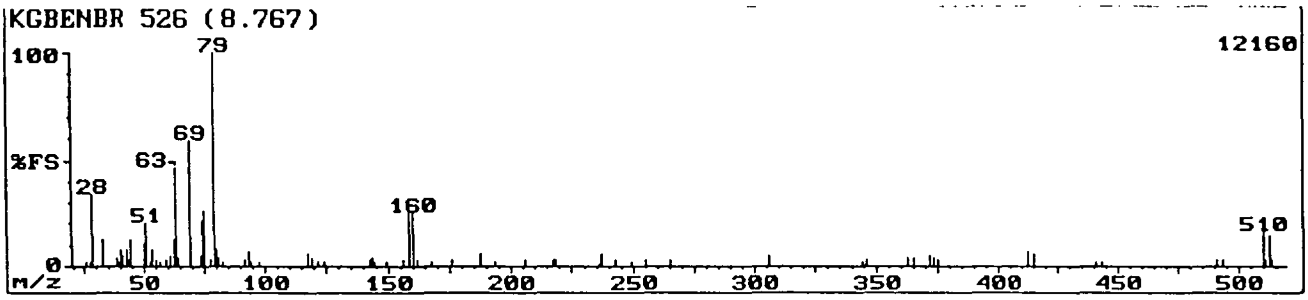
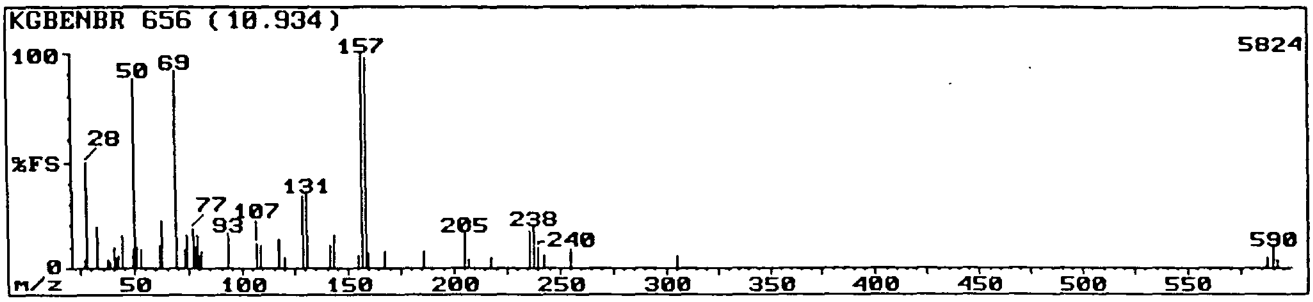

Spectrum No. 34



KGBENBR 526 (8.767)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	1.85	63	46.84	143	3.95	306	5.07
27	1.57	64	3.59	144	1.88	344	2.04
28	33.68	69	59.47	149	1.86	346	3.29
32	12.76	73	4.93	155	2.93	363	3.88
38	3.42	74	21.84	158	25.39	365	3.78
39	2.40	75	25.79	160	25.53	372	5.30
40	8.03	77	2.73	161	3.09	374	3.88
41	5.23	79	100.00	167	2.06	375	2.70
42	7.86	80	8.19	175	2.60	413	6.32
43	2.60	81	4.01	187	5.92	415	5.69
44	13.03	82	2.30	193	2.20	441	2.24
50	10.26	91	2.73	205	2.86	443	1.78
51	20.26	93	7.07	217	2.96	491	3.03
52	2.40	94	2.24	218	3.36	493	3.06
53	7.57	97	1.95	236	1.41	510	16.71
55	2.57	117	5.72	237	5.79	511	2.70
56	1.63	119	3.49	243	3.09	512	14.87
59	2.89	121	1.79	249	1.64	513	2.83
61	4.80	124	2.10	255	3.22		
62	12.76	142	3.29	265	2.76		

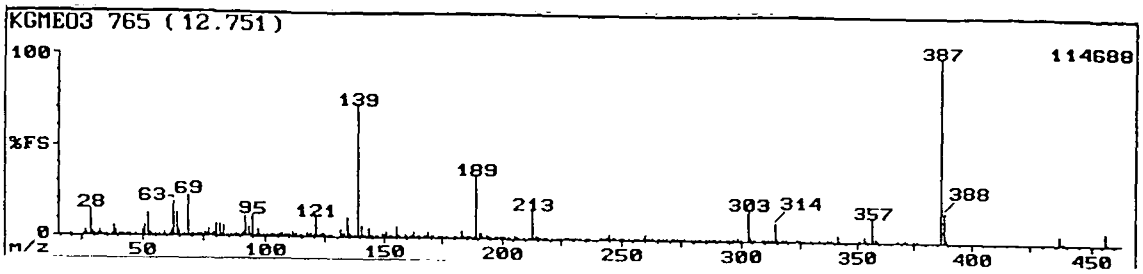
Spectrum No. 35



KGBENBR 656 (10.934)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
27	3.76	61	10.44	117	13.32	207	3.55
28	49.73	62	22.53	120	4.74	217	4.53
32	19.51	69	92.31	129	34.34	236	17.58
37	3.64	73	9.00	131	34.62	238	19.51
38	2.87	74	15.80	141	10.30	240	9.89
40	9.41	77	18.68	143	16.00	243	5.36
41	5.15	78	9.48	155	5.56	255	8.38
42	5.70	79	15.73	157	100.00	305	5.77
44	15.93	80	5.63	159	97.80	588	5.08
49	8.72	81	7.55	160	6.52	590	9.34
50	87.91	93	16.90	167	7.90	592	3.85
51	9.75	107	11.81	186	8.17		
53	8.79	109	10.92	205	16.90		

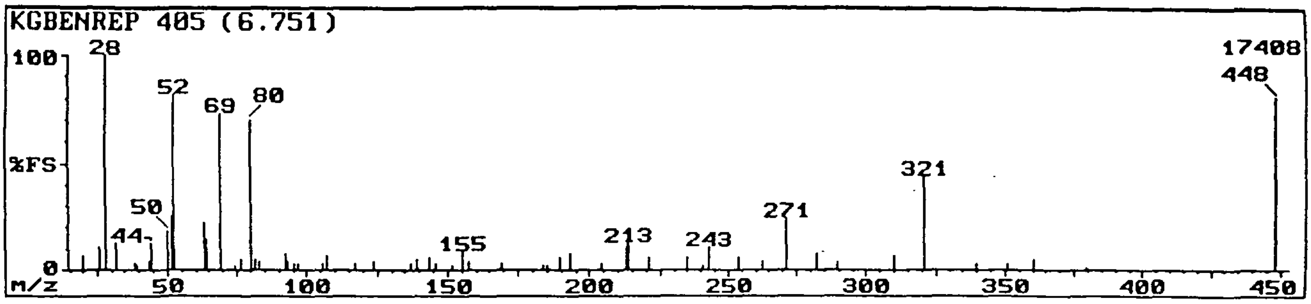
Spectrum No. 36



KGMEO3 765 (12.751)

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel
20	0.22	88	0.24	149	2.12	215	0.56
25	0.14	89	0.73	150	0.57	216	0.50
26	2.65	90	0.27	151	2.68	217	1.12
27	0.91	91	2.05	152	0.67	218	0.22
28	14.73	92	10.94	153	0.47	219	0.62
29	2.13	93	4.74	155	5.52	221	1.00
30	0.43	94	0.57	156	0.65	223	0.33
31	0.89	95	11.44	157	1.12	225	0.89
32	3.11	96	0.98	159	2.08	226	0.21
33	0.80	97	4.35	160	0.53	227	1.07
35	0.47	98	0.29	161	0.72	228	1.02
37	1.02	99	0.70	162	0.28	229	0.27
38	5.75	101	0.64	163	2.79	231	0.59
39	2.87	102	0.36	164	0.47	232	0.72
40	0.40	103	0.26	165	0.34	233	1.07
41	0.81	104	0.38	167	1.00	235	0.65
42	0.42	105	1.42	168	0.43	236	0.19
43	1.03	106	0.51	169	2.65	237	0.67
44	0.81	107	1.94	170	0.84	241	1.19
45	0.51	108	0.63	171	0.41	242	0.18
47	0.91	109	0.79	173	0.34	243	0.47
50	2.87	110	0.18	174	0.83	244	0.52
51	5.64	111	2.83	175	1.00	245	2.80
52	12.72	112	0.43	176	0.52	246	0.36
53	2.26	113	1.63	177	0.32	247	0.73
54	0.70	114	0.54	180	0.56	249	1.27
55	0.48	115	0.27	181	0.95	250	0.23
57	0.65	117	1.63	183	3.91	251	0.21
59	1.58	119	1.48	184	0.74	253	0.63
61	0.59	120	0.66	185	0.77	255	0.89
62	3.04	121	10.88	186	0.25	257	0.29
63	18.75	122	0.91	187	1.26	259	0.21
64	12.44	123	0.84	188	0.38	260	3.36
65	2.59	124	1.81	189	34.15	261	1.24
66	0.48	125	1.03	190	3.13	263	1.13
67	0.35	126	0.50	191	2.99	265	0.33
69	22.54	127	0.65	192	0.35	266	0.28
70	0.46	128	0.40	193	2.30	267	0.58
71	1.34	131	4.24	194	0.54	269	0.24
72	0.17	132	0.50	195	0.88	271	0.54
73	0.23	133	1.76	197	0.64	272	0.47
74	0.52	134	10.32	198	0.17	273	0.61
75	1.70	135	2.15	199	0.49	275	1.12
76	1.13	136	0.82	200	0.46	276	0.18
77	3.47	137	1.35	201	0.29	279	0.31
78	0.86	139	72.32	202	0.75	281	0.32
79	2.25	140	5.80	203	0.52	282	0.18
80	6.58	141	0.55	205	2.27	283	0.71
81	6.42	142	1.30	206	0.30	285	0.33
82	0.26	143	4.69	207	0.88	287	0.79
83	5.64	144	0.70	209	0.44	288	0.99
84	0.36	145	1.38	211	0.39	289	0.14
86	0.27	146	0.22	213	15.40	291	0.40
87	0.40	147	0.68	214	1.81	294	0.23
295	1.19	313	0.98	337	0.21	371	0.16
296	0.24	314	9.77	338	0.75	372	0.30
297	0.32	315	1.38	341	4.02	375	0.95
299	2.22	317	0.88	342	0.65	376	0.18
300	0.30	319	0.22	351	0.22	387	100.00
303	16.96	323	0.20	353	3.18	388	16.52
304	2.26	324	0.31	354	0.52	389	2.11
305	0.51	325	1.44	357	12.33	437	4.69

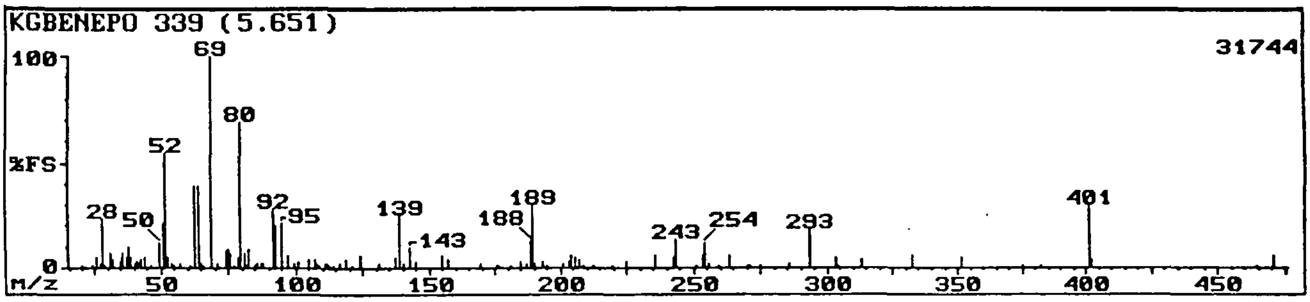
Spectrum No. 37



KGBENREP 405 (6.751) 17408

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	6.53	76	5.28	145	2.92	243	10.20
26	10.75	80	70.22	151	1.95	254	5.49
28	100.00	81	4.46	155	9.19	263	3.79
32	12.50	83	3.54	157	3.52	271	24.26
38	3.33	92	8.00	169	3.06	282	7.54
39	1.82	93	3.75	183	2.27	290	4.09
44	3.91	95	3.35	185	2.09	310	6.34
44	12.68	97	2.60	189	5.42	321	43.38
50	18.01	105	2.53	193	7.63	340	2.85
51	25.37	107	6.89	204	2.92	351	3.31
52	81.62	117	2.87	213	11.03	360	4.48
63	22.06	124	4.34	213	13.05	379	1.17
64	14.98	137	2.69	221	5.88	448	80.88
69	72.79	139	4.57	235	5.97		
74	2.41	143	5.38	241	1.75		

Spectrum No. 38



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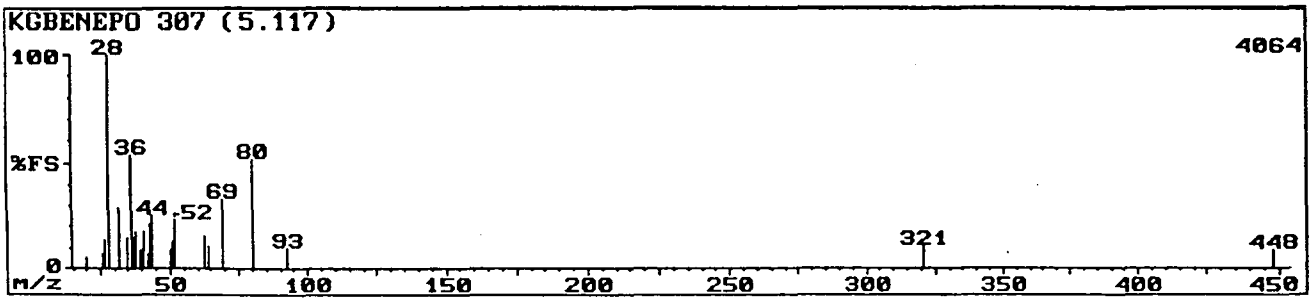
 KGBENEPO 339 (5.651)                                                                 3
-----------------+------------------+------------------+------------------
 Mass   Rel Int  | Mass   Rel Int   | Mass   Rel Int   | Mass   Rel Int
-----------------+------------------+------------------+------------------
   20     0.79   |   66     1.13    |  117     1.99    |  212     1.22
   24     0.37   |   69   100.00    |  119     3.93    |  219     1.03
   26     5.14   |   71     1.92    |  121     1.40    |  225     3.38
   27     1.85   |   74     7.61    |  124     5.80    |  235     5.95
   28    23.39   |   75     8.82    |  131     2.24    |  243     4.59
   29     1.12   |   76     7.21    |  137     4.69    |  243    13.31
   31     7.16   |   77     1.40    |  139    25.00    |  251     1.16
   32     4.28   |   79     5.04    |  140     1.63    |  253     5.65
   35     2.71   |   80    69.35    |  143     9.58    |  254    11.59
   36     6.35   |   81     6.50    |  145     2.80    |  255     1.81
   37     4.64   |   82     1.37    |  155     5.90    |  259     0.89
   38     9.38   |   83     8.77    |  157     3.78    |  263     5.85
   39     5.09   |   85     0.55    |  169     1.56    |  270     1.08
   40     1.79   |   86     2.33    |  175     0.93    |  271     0.81
   41     3.16   |   87     1.86    |  176     1.27    |  275     1.35
   42     1.79   |   88     1.90    |  181     1.23    |  285     1.55
   43     4.28   |   92    27.82    |  184     1.42    |  293    18.55
   44     5.14   |   93    20.77    |  185     2.71    |  303     5.14
   47     1.32   |   95    20.97    |  187     1.61    |  304     0.76
   50    11.69   |   97     5.34    |  188    12.15    |  313     4.08
   51    21.57   |  100     2.21    |  189    29.64    |  332     6.20
   52    54.03   |  101     3.09    |  190     2.39    |  351     4.54
   53     4.89   |  105     3.43    |  193     2.67    |  375     0.92
   54     2.32   |  107     4.28    |  194     0.78    |  382     0.79
   55     1.41   |  108     1.84    |  201     2.38    |  401    30.44
   57     1.63   |  109     0.79    |  203     3.28    |  402     3.93
   61     1.31   |  111     1.55    |  204     6.05    |  464     1.35
   63    38.51   |  112     1.71    |  205     5.09    |
   64    39.31   |  113     0.82    |  207     3.48    |
   65     2.32   |  114     0.67    |  209     1.36    |
-----------------+------------------+------------------+------------------
```

Spectrum No. 39



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-----------------------------------------------------------------
KGBENEPO 307 (5.117)
-----------------+------------------+------------------+-------------
 Mass   Rel Int  | Mass   Rel Int   | Mass   Rel Int   | Mass   Rel Int
-----------------+------------------+------------------+-------------
   20     5.29   |   37     14.96   |   44     25.20   |   80     51.57
   26     6.69   |   38     17.03   |   50      8.96   |   93      9.35
   27    13.39   |   39      9.15   |   51     12.20   |  321     10.63
   28   100.00   |   40      9.15   |   52     22.83   |  448      9.15
   32    29.13   |   41     17.03   |   63     15.06   |
   35    14.27   |   42      6.69   |   64     11.02   |
   36    53.54   |   43     21.46   |   69     33.46   |
-----------------+------------------+------------------+-------------
```
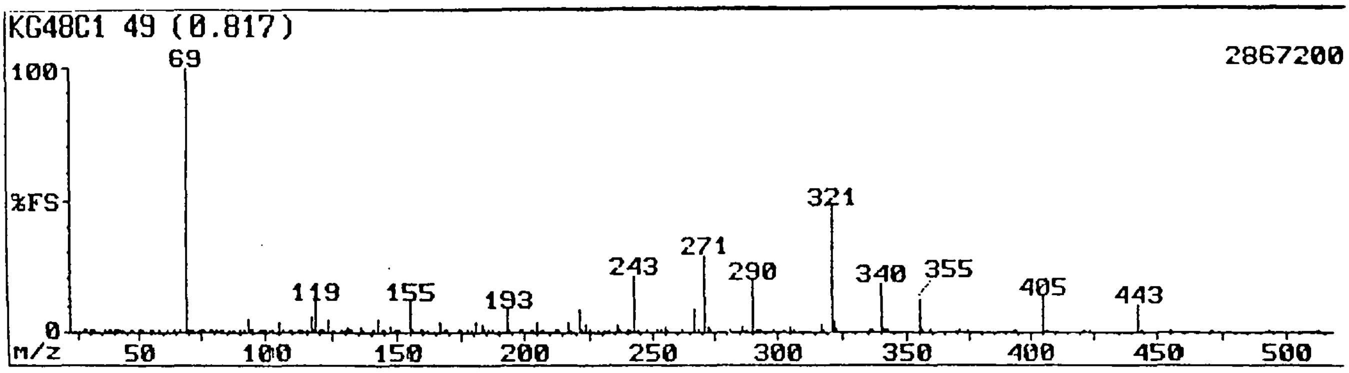
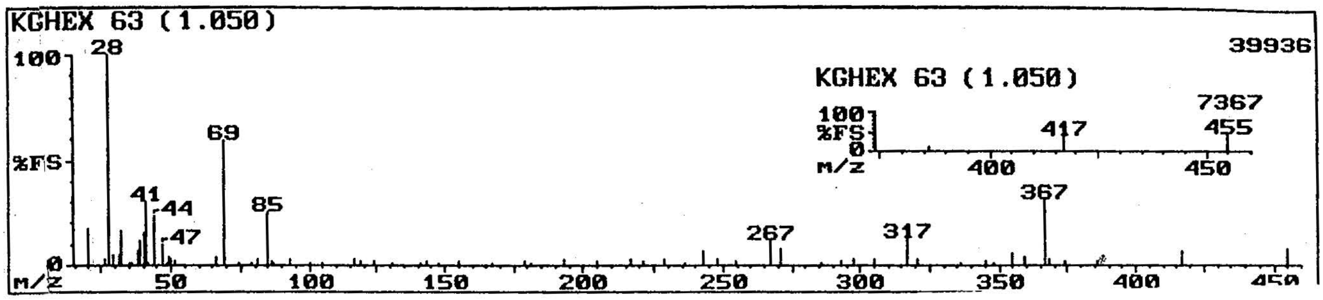

Spectrum No. 40



KG48C1 49 (0.817) 2867200

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.08	98	0.63	169	0.10	268	0.63
29	0.08	99	0.04	174	1.21	271	29.00
30	0.02	100	0.67	175	0.09	272	1.78
31	0.89	101	0.14	177	0.01	273	0.12
32	0.20	102	0.02	179	0.65	281	0.02
36	0.04	105	3.61	181	3.46	286	2.32
38	0.07	106	0.15	183	3.00	287	0.18
39	0.11	109	0.04	184	0.16	290	19.71
40	0.27	110	0.07	186	0.71	291	1.15
41	0.52	112	0.39	187	0.05	292	0.03
42	0.03	113	0.03	190	0.02	293	0.26
43	0.11	114	0.30	193	9.04	298	0.02
44	0.03	115	0.02	194	0.40	302	0.07
47	0.09	117	6.25	198	0.49	305	2.32
48	0.03	118	0.25	199	0.04	306	0.17
50	1.00	119	11.43	202	0.38	317	2.64
51	0.04	120	0.24	203	0.04	318	0.22
52	0.01	121	0.12	205	4.36	321	47.43
55	0.45	122	0.02	206	0.24	322	3.43
56	0.01	124	4.89	207	0.02	323	0.23
58	0.03	125	0.19	212	0.58	336	1.25
62	0.10	126	0.46	213	0.03	337	0.11
64	0.01	129	0.47	217	3.79	340	18.00
67	0.16	130	0.02	218	0.24	341	1.27
69	100.00	131	2.36	221	8.93	342	0.08
70	1.36	132	0.07	222	0.47	343	0.11
71	0.58	133	0.08	224	3.36	355	12.86
72	0.04	136	2.29	225	0.18	356	1.00
74	0.94	137	0.12	229	0.17	359	0.03
75	0.04	141	0.14	231	0.39	371	0.02
76	0.01	143	5.21	233	0.31	374	0.03
78	0.14	144	0.20	236	3.18	393	1.19
79	0.29	145	0.02	237	0.20	394	0.09
81	0.17	148	1.53	240	0.84	405	13.29
82	0.07	149	0.09	241	0.05	406	1.13
83	0.02	150	0.04	243	21.14	421	0.03
86	1.04	151	0.10	244	1.15	424	0.05
87	0.06	155	11.29	248	0.21	443	10.29
90	0.98	156	0.52	252	0.10	444	0.82
91	0.05	159	0.11	253	0.03	455	0.01
93	4.50	160	0.15	255	2.21	471	0.02
94	0.13	162	0.08	256	0.13	493	0.76
95	0.24	167	3.54	262	0.46	512	0.02
97	0.20	168	0.21	267	9.14		

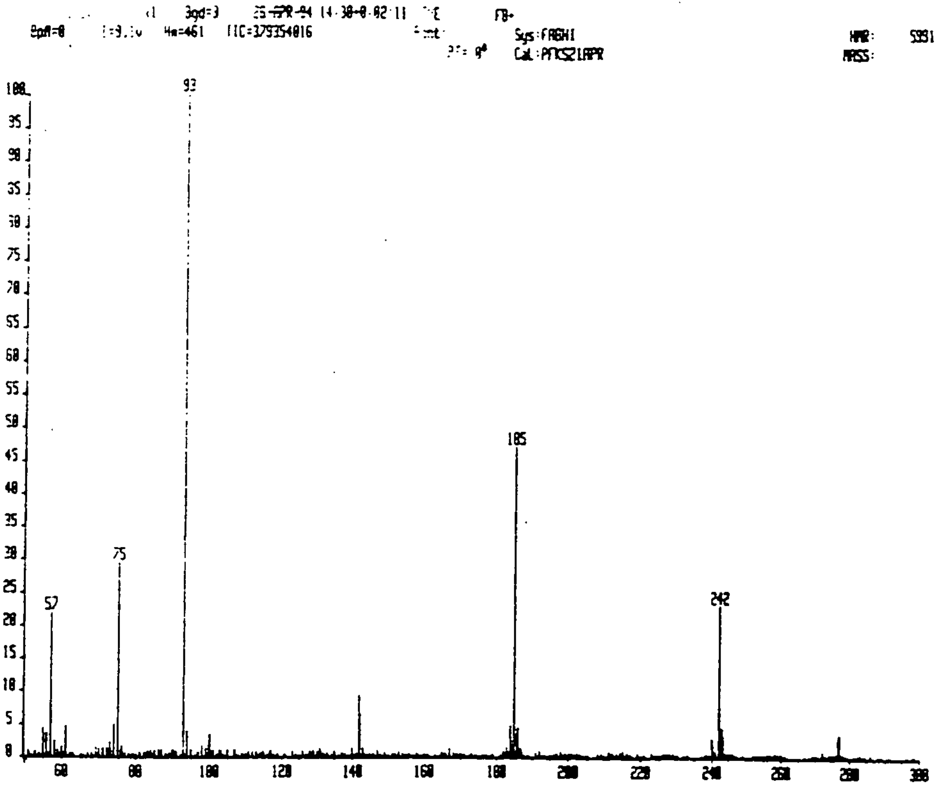
Spectrum No. 41

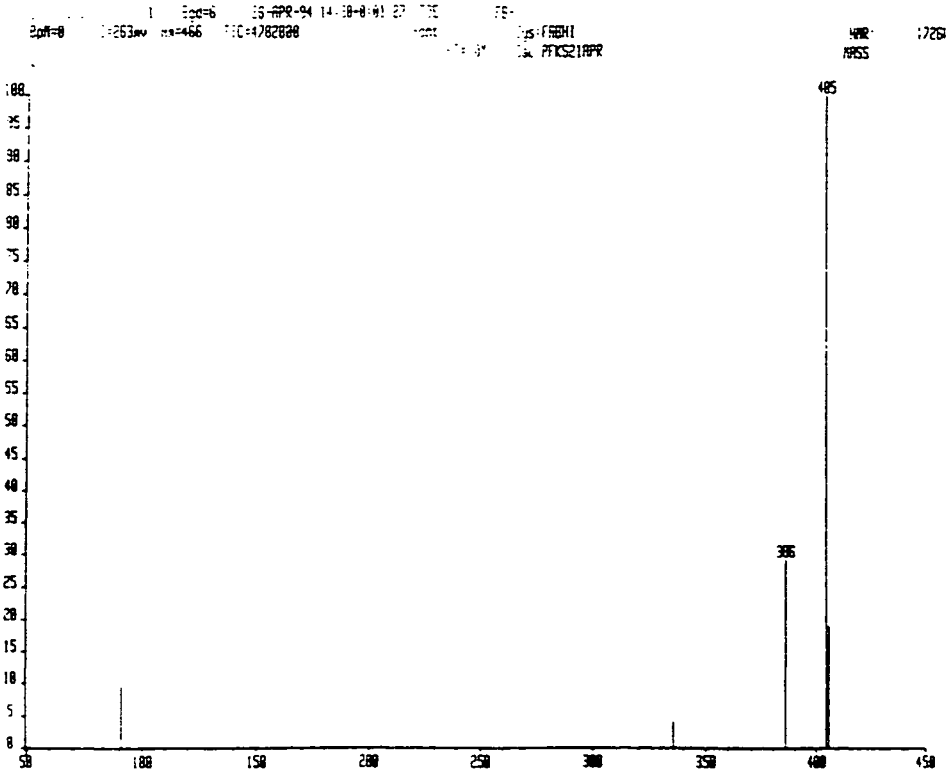


KGHEX 63 (1.050) 39936

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	17.15	51	1.52	148	0.93	298	2.92
26	2.60	66	3.73	155	2.00	305	2.84
28	100.00	69	59.62	167	1.19	317	12.98
29	4.81	74	1.12	179	1.46	321	2.56
31	4.45	79	1.12	181	0.67	336	1.45
32	16.19	81	2.84	193	3.13	345	2.35
35	0.97	85	25.32	205	1.59	348	1.21
36	1.06	86	2.15	217	2.96	355	5.81
38	6.45	87	0.91	221	1.80	359	3.41
39	11.54	93	3.13	229	2.60	367	31.41
40	15.71	100	0.97	236	1.36	368	3.00
41	29.97	105	1.02	243	6.81	374	1.65
42	1.38	117	2.49	248	2.60	386	1.48
44	23.72	119	1.89	255	1.90	417	7.25
47	10.10	124	1.80	267	12.02	455	7.37
48	1.16	131	1.05	271	7.69		
49	4.09	141	0.84	286	1.42		
50	2.68	143	2.28	293	2.00		

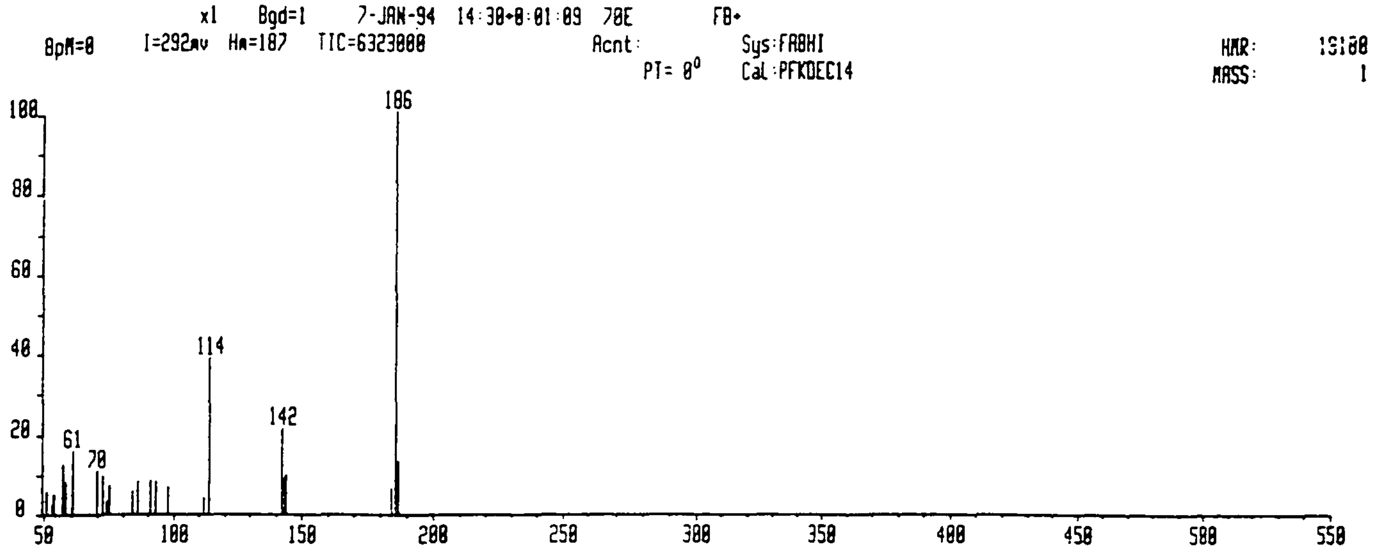
Spectrum No. 42

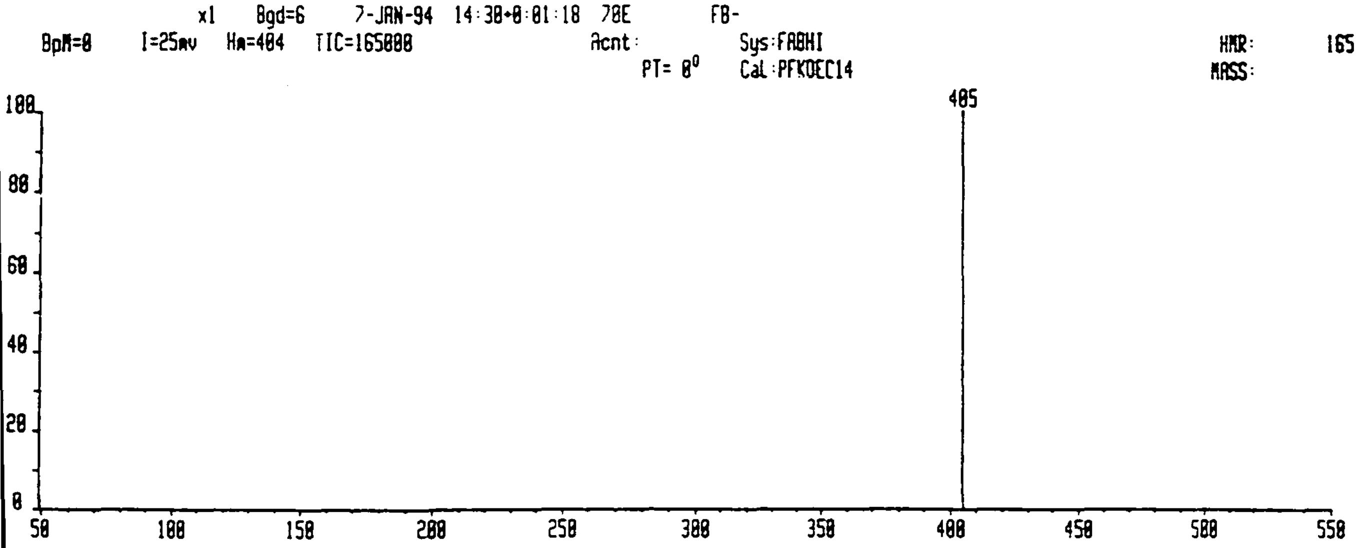




Mass	% Base	Mass	% Base
241.17	0.85	404.53	11.30
242.22	23.12	404.76	100.00 F
243.06	2.30 F	404.90	88.99 F
		405.83	18.71

Spectrum No. 43

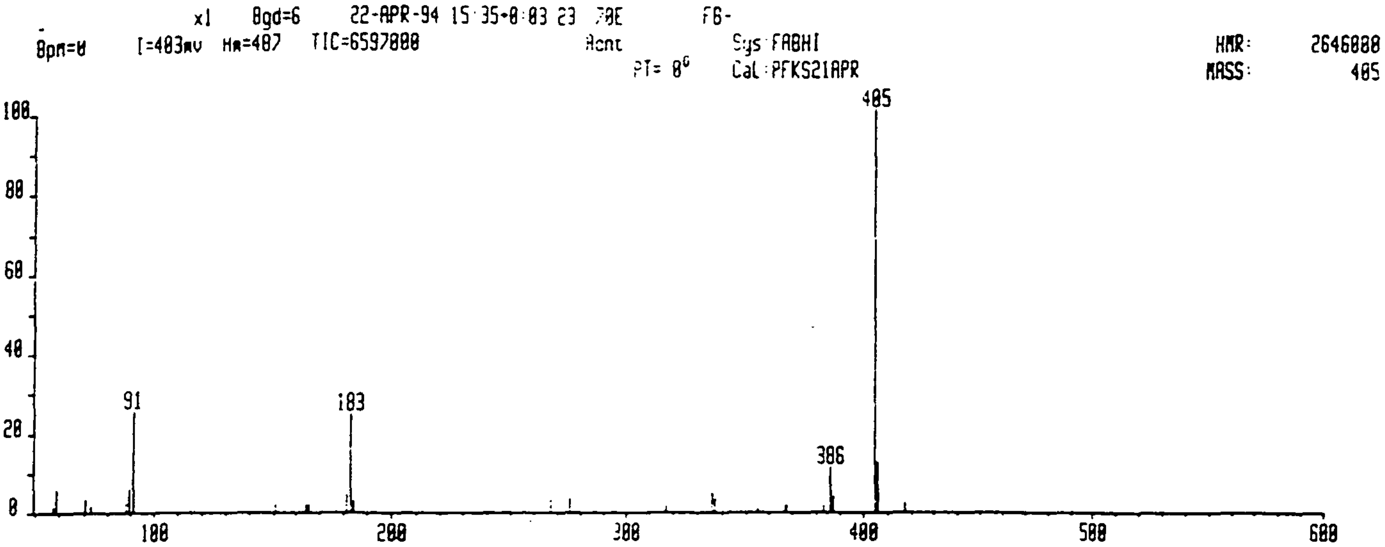


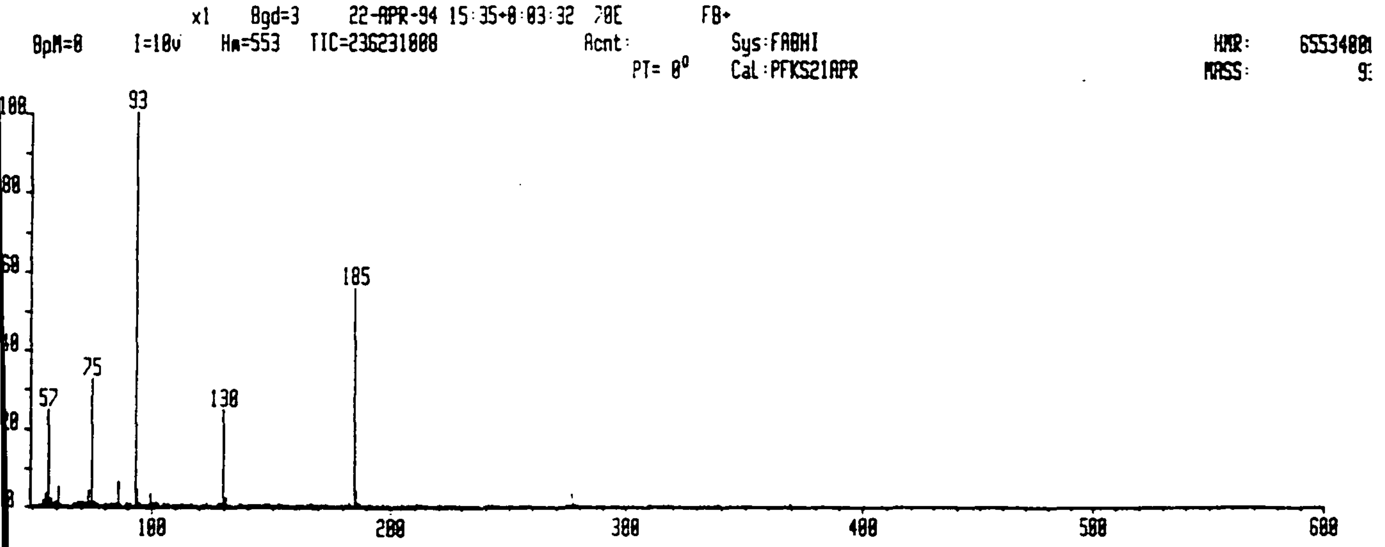


Mass	% Base
51.01	5.58
53.02	2.50
54.02	4.64
57.01	12.25
58.04	7.98
61.00	15.80
70.02	7.51
70.04	10.74
72.04	9.33
73.98	3.02
75.00	6.78
84.04	5.53
86.05	7.97
91.01	8.34
93.01	7.98
98.04	6.57
112.05	3.02
112.08	3.75
114.07	38.53
142.08	21.06
143.09	9.02
144.10	9.59
184.11	6.31
184.14	3.08
186.13	100.00
187.13	12.88

Mass	% Base
404.73	100.00

Spectrum No. 44

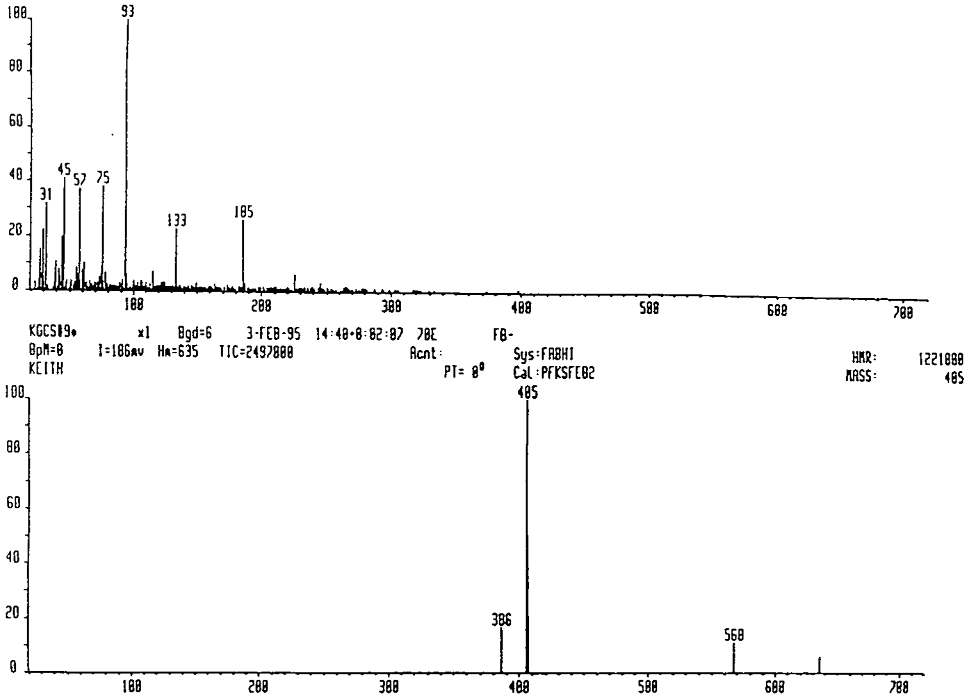




Mass	% Base
58.00	1.06
59.00	5.52
71.00	3.10
73.02	1.28
88.01	2.04
88 04	1 59
89.02	5.44
91.03	25.17
151.05	1.70
151.09	1.10
164.09	1.63
165 05	1.70
165.11	1.55
181.08	4 27
183 11	24.23
184 10	2 49
267 04	1 76
275 15	3 33
317 06	1 55
336 04	1 57
337 05	3 21
354 99	1 72
367 02	0 98
367.12	1 44
367 24	1 44
382.92	1 44
383.03	1 28
386.04	11.11
387.03	3.85
405.04	100.00
406 05	12.24

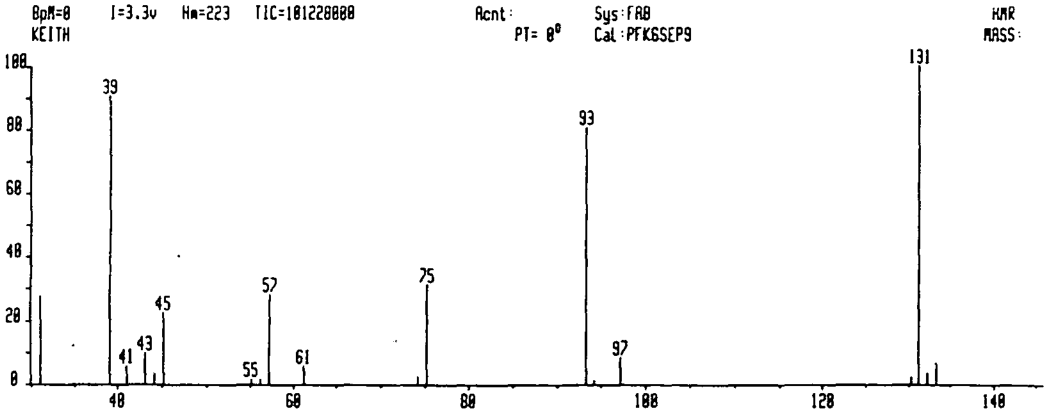
Mass	% Base
129.04	0.79
130.00	5.30 F
130.11	24.82 F
131.09	2.36

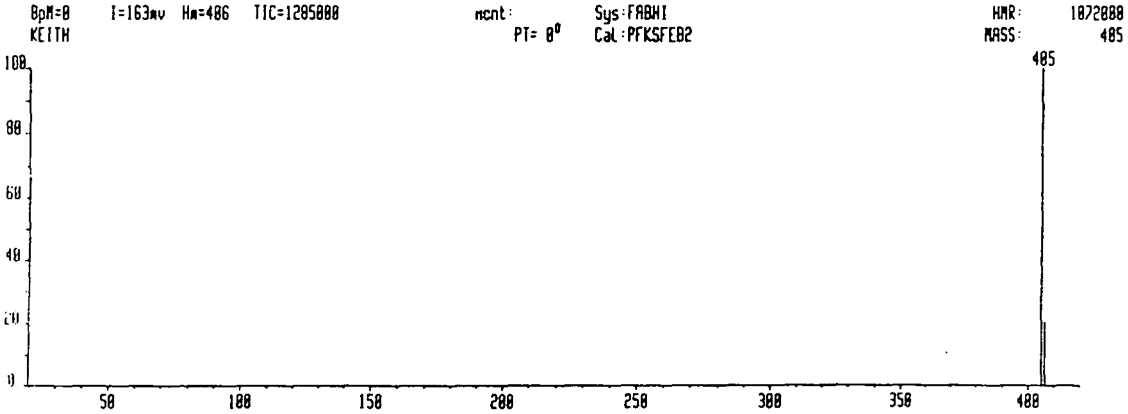
Spectrum No. 45



Mass	% Base	
40.14	1.36	
41.11	1.14	
41.14	7.70	
42.12	4.76	
43.12	19.15	F
43.15	3.44	F
43.39	0.53	
44.12	5.73	F
44.14	3.20	F
45.13	40.73	
46.14	1.84	
47.11	3.47	
47.15	1.61	
49.12	0.73	
50.11	2.36	
51.11	3.31	
52.12	1.67	
53.12	3.09	
54.10	0.73	
54.14	0.44	
55.10	8.23	F
55.13	3.37	F
56.10	5.52	F
56.13	2.98	F
57.11	37.15	
58.12	3.36	
59.09	7.16	F
59.13	2.67	F
60.08	2.89	F
60.10	3.21	F
60.15	0.51	
61.09	10.03	
62.09	2.39	
63.09	2.81	
64.08	0.94	
65.09	2.93	
66.10	0.80	
67.06	0.86	
67.11	2.05	
68.09	1.41	
69.04	2.89	F
69.08	2.87	F
70.10	2.40	
71.08	2.87	
72.08	1.65	
73.08	4.64	
74.08	5.73	
75.08	38.05	
76 08	3.00	
77 08	6.38	
78.09	1 89	
79.09	2.28	
80.09	1.32	
81.07	1.89	F
81.10	1.92	F
82.09	1.84	
83 10	1.87	
84.09	1.00	
84.13	1.19	
85.08	1 87	
86.07	0.72	
86.14	1.41	
87.08	1.21	
88.10	0.61	
89.09	2.63	
90.09	1.99	
91.10	3.73	F
91.13	2.72	F
92.11	1.02	
93.11	100.00	
94.12	5.75	
95.11	2.32	
96.13	0.68	
97.09	0.86	
97.14	1.26	
98.10	0.68	
99.10	1.55	
100.15	3.33	
101.12	1.55	
102.12	1.66	
103.10	2.75	
104.11	1.35	
105.11	2.65	
106.13	3.52	
107.13	2.87	
108.13	1.24	
109.12	1.43	
110.14	2.57	
111.12	1.18	
113.11	2.56	
114.14	0.52	
115.11	6.86	
116.11	1.29	
117.12	1.35	
118.13	1.72	
119.12	1.71	
120.15	1.74	
121.14	1.72	
122.14	2.59	
123.14	2.88	
124.15	2.92	
125.13	1.71	
126.14	1.25	
127.14	1.40	
128.14	1.38	
129.13	1.33	
130.15	1.46	
131.13	1.71	
132.14	1.44	
132.98	22.46	F
133.13	2.56	F
134.15	1.58	
135.16	1.46	
136.16	1.96	
137.15	1.42	
138.13	0 71	
139.14	1.45	
140.15	1.30	
141.14	1.09	
142.16	0.88	
386.36	16.38	
405.38	100.00	F
405.51	50.29	F
406.43	21.05	
567.57	11.06	
635.56	5.73	

Spectrum No. 46





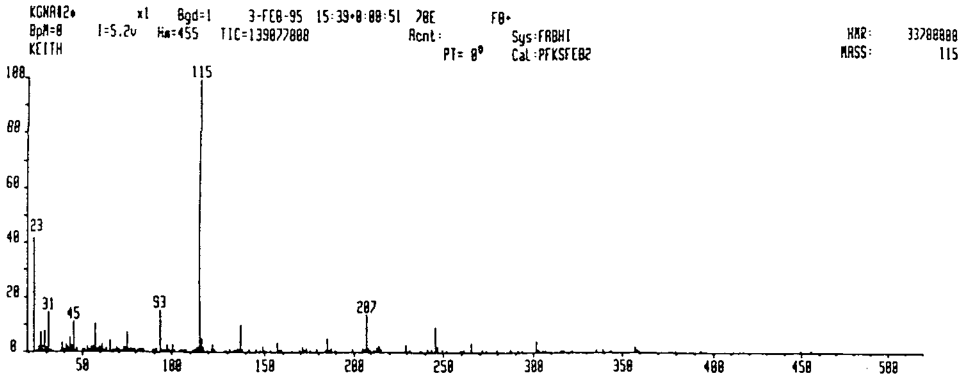
KEITH

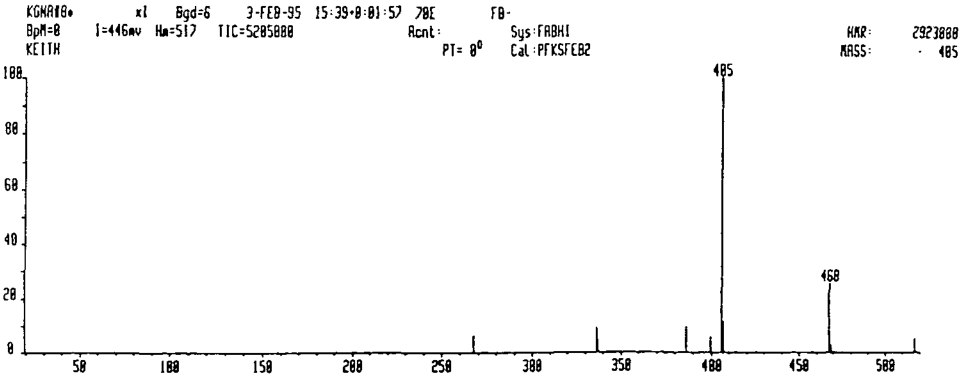
Mass	% Base
31.06	27.34
39.03	90.48 F
45.13	22.18
57.16	28.17
75.21	31.28
93.26	80.95
131.29	100.00

KEITH

Mass	% Base
405.46	100.00
406.45	19.87

Spectrum No. 47



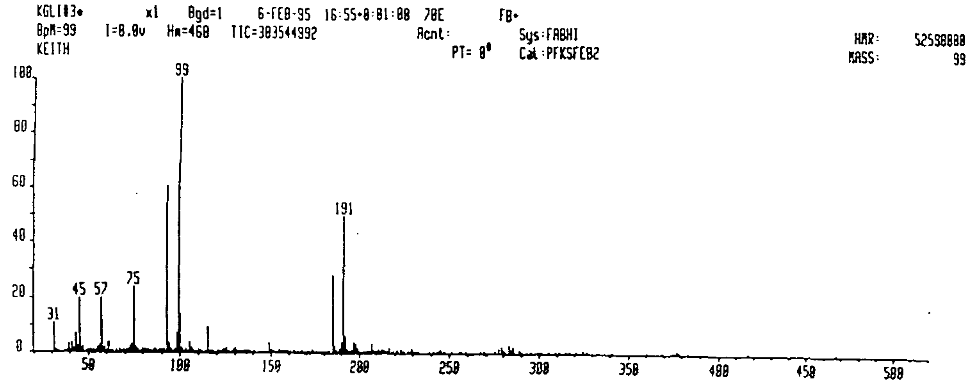


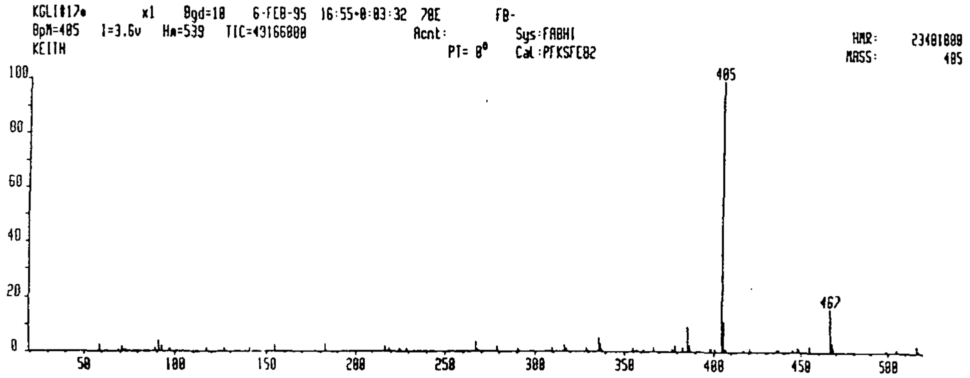
Mass	% Base	
40.14	0.79	
41.12	0.77	
41.15	2.45	
42.12	1.78	F
42.15	1.39	F
43.13	4.70	F
43.17	1.01	F
44.14	2.05	
45.14	10.67	
47.09	0.50	
47.12	1.05	
50.12	0.70	
51.13	0.68	
53.11	1.63	
54.11	0.33	
54.14	0.65	
55.12	1.70	F
55.15	1.64	F
56.13	1.82	
57.13	9.78	F
57.17	2.73	F
58.14	1.00	
59.13	1.58	
60.11	1.38	
61.11	2.24	
62.11	0.36	
63.06	0.86	
65.05	3.78	
65.11	0.43	
67.09	0.84	
67.14	0.37	
68.11	0.47	
69.07	1.39	
69.10	0.67	
69.13	0.34	
70.13	0.69	
72.09	0.32	
73.10	1.20	
74.10	1.52	
75.11	6.94	
76.12	0.67	
77.11	1.03	
78.11	0.53	
79.12	0.75	
81.09	0.73	
82.12	0.52	
83.08	0.80	
84.09	0.63	
89.10	0.72	
90.12	0.74	
91.07	0.41	
91.13	1.01	
93.14	15.16	
94.14	0.83	
95.12	0.35	
95.16	0.38	
96.12	0.36	
97.12	2.33	
98.13	0.74	
99.16	0.38	

Mass	% Base	
100.17	2.49	
101.18	0.41	
105.10	0.70	
107.06	0.45	
107.15	0.52	
111.12	0.38	
112.14	0.65	
113.12	1.52	
114.13	1.84	
115.14	100.00	
116.14	4.44	
117.14	1.46	
119.12	0.41	
121.17	0.56	
122.17	2.36	
123.17	0.67	
129.17	0.46	
131.14	0.59	
133.16	0.31	
134.12	0.34	
135.18	0.88	
137.14	9.59	
138.16	0.78	
141.18	0.65	
145.18	0.54	
149.17	1.77	
150.17	0.44	
157.15	3.01	
159.17	0.59	
169.23	0.36	
171.21	1.52	
172.19	0.46	
173.04	1.14	
173.22	0.54	
175.20	0.36	
179.16	0.76	
185.25	4.37	
186.26	0.36	
187.24	1.07	
189.22	0.46	
199.24	0.83	
205.24	0.97	
206.24	0.63	
207.25	13.32	
208.25	1.00	
209.25	0.47	
213.29	0.99	
214.22	1.27	F
214.30	1.56	F
215.29	0.83	
229.25	2.19	
241.32	0.66	
243.32	0.75	
245.35	8.82	
246.34	1.55	
249.27	0.78	
261.34	0.75	
265.15	3.19	
271.26	0.67	
273.28	0.46	

Mass	% Base
267.33	6.02
336.39	9.00
337.41	4.52
386.47	9.31
399.46	5.51
405.49	100.00
406.49	11.15
467.55	25.21
468.55	2.43
517.55	4.93

Spectrum No. 48



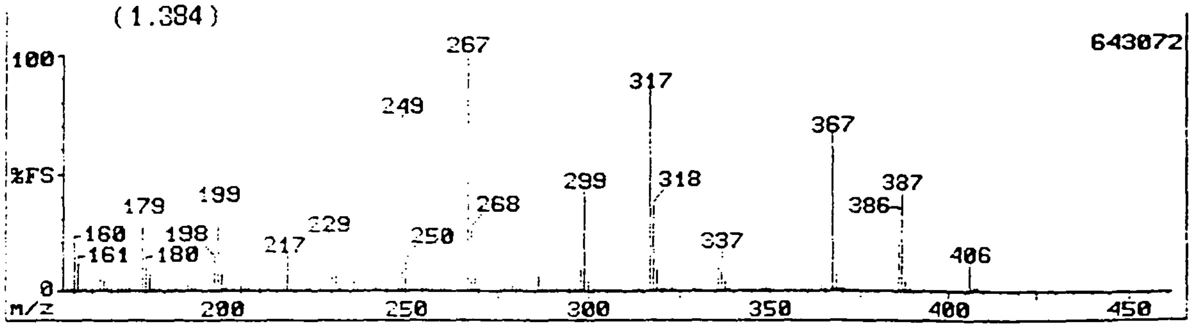


Mass	% Base
40.20	0.47
41.20	3.06
42.16	1.27 F
42.19	0.97 F
43.16	6.55 F
43.18	1.61 F
43.20	1.42 F
43.54	0.37
44.15	1.95 F
44.16	2.21 F
44.19	0.93 F
45.16	19.28
46.16	0.97
47.13	1.79
49.12	0.49
50.11	0.37
51.11	0.57
51.44	0.34
51.48	0.30
52.11	0.30
53.10	0.55
54.11	0.60
55.08	1.81 F
55.12	1.17 F
56.08	2.41 F
56.11	1.40 F
57.08	19.55 F
57.13	2.59 F
58.09	1.60 F
58.11	0.92 F
59.09	1.67
60.06	0.80
61.06	3.40
62.06	0.50
63.06	0.47
65.06	0.60
67.05	0.97
68.06	0.49
69.04	0.57
70.07	0.62
71.06	0.53
72.04	0.96
73.03	2.02
74.03	2.82
74.09	0.31
75.04	23.12
76.04	1.55
77.04	1.08
78.04	0.35
79.05	0.42
80.04	0.92
81.04	1.05
82.05	0.59
83.05	0.58
84.06	0.47
85.01	0.41
86.08	0.93
87.04	0.54
89.03	0.58
90 03	0.63

Mass	% Base
91.05	1.02
93.05	59.88
94.05	2.99
95.06	0.97
96.05	0.41
97.05	0.97
98.06	6.76
99.06	100.00
100.07	13.79
101.08	1.46
102.14	0.48
103.06	1.04
104.06	0.49
105.06	3.31
106.07	1.52
107.06	0.68
108.07	0.47
110.07	1.19
111.06	0.56
113.07	0.51
114.06	0.47
115.03	9.26
116.04	0.61
117.06	0.57
119.06	0.51
120.06	0.53
121.05	0.71
122.06	0.42
123.06	1.02
124.07	1.01
125.07	1.75
127.08	0.49
128.09	0.30
129.07	0.99
130.13	1.69 F
130.18	1.04 F
131.06	0.65
132.07	0.33
132.90	0.33
133.07	0.30
135.07	0.57
136.07	0.53
137.06	0.77
138.05	0.55
139.09	0.48
141.05	0.58
143.08	0.47
145.10	0.48
146.08	0.30
147.06	0.38
148.07	0.35
149.03	3.44
150.04	0.97
151.07	0.71
152.06	0.50
153.08	0.31
154.06	0.52
155.07	1.02
156.08	0.35
157.09	0.53

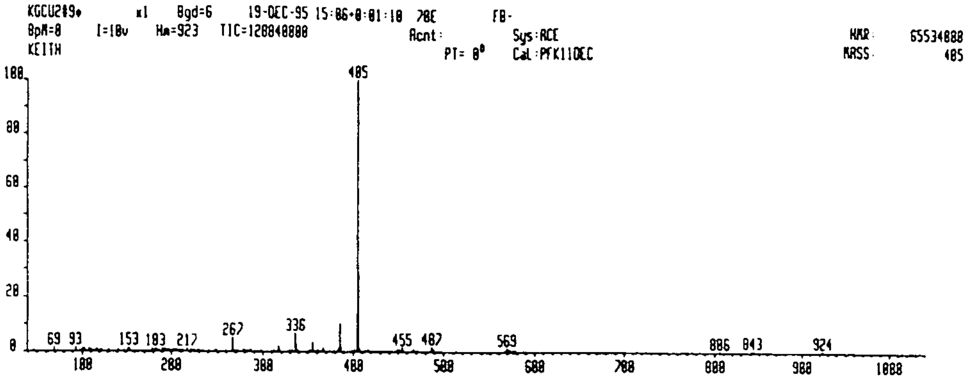
Mass	% Base
59.03	1.94
68.97	0.38
70.98	1.26
72.97	0.33
88.98	0.73
90.99	3.31
92.95	1.88
97.01	0.74
116.94	1.04
126.84	0.93
140.98	0.87
154.93	1.90
183.01	2.40 F
183.09	1.41 F
216.91	1.49
218.86	0.71
224.89	0.60
228.88	0.66
266.89	3.22
267.90	0.50
278.90	1.42
290.92	0.62
309.89	1.12
316.77	1.95 F
316.90	1.93 F
317.82	0.66
328.83	0.95
335.83	4.42
336.78	2.36 F
336.92	2.44 F
337.83	0.48
354.88	1.09
356.93	0.49
360.92	0.46
366.86	1.24
376.91	0.83
378.88	2.20
382.83	1.28
385.84	8.99
386.84	2.01
397.87	0.90
398.88	1.09
400.85	0.77
404.82	100.00
405.83	10.95
406.85	0.72
417.00	0.48
420.83	1.14
435.82	0.30
436.91	0.60
444.81	0.53
447.85	1.23
448.83	0.92
454.79	1.90
466.79	15.59
467.76	3.13 F
467.97	1.24 F
498.98	0.34
504.85	0.67
516.94	2.25

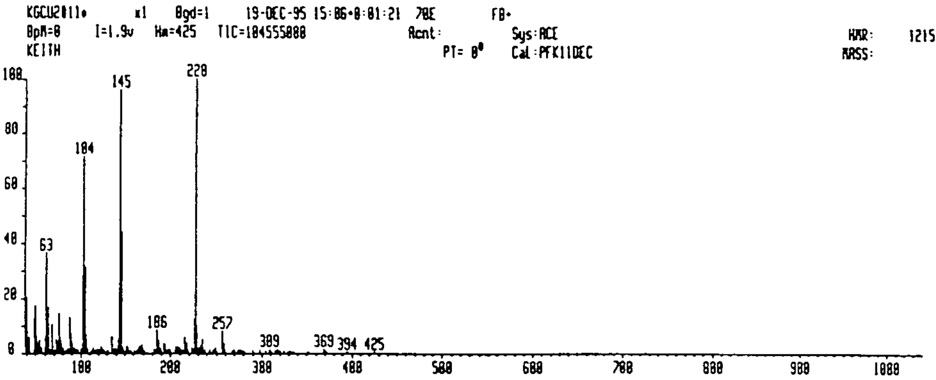
Spectrum No. 49



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
157	0.03	200	1.72	250	2.89	319	2.14
159	0.02	201	0.10	251	0.18	320	0.16
160	4.88	203	0.01	255	0.02	321	0.01
161	2.93	205	0.36	256	0.00	323	0.01
162	0.28	206	0.03	260	0.05	329	0.01
163	0.04	207	0.03	261	0.03	336	2.49
165	0.01	210	0.56	267	24.53	337	4.38
167	1.27	211	0.27	268	6.29	338	0.88
168	1.03	212	0.03	269	1.16	339	0.07
169	0.11	217	3.87	270	0.08	345	0.81
170	0.01	218	3.75	276	0.01	346	0.09
172	0.18	219	0.31	277	0.02	348	0.19
173	0.02	220	0.02	279	0.68	349	0.19
174	0.16	223	0.02	280	0.21	350	0.02
175	0.04	224	0.02	281	0.03	364	0.43
179	7.93	227	0.01	286	1.97	365	0.05
180	2.77	229	6.05	287	0.30	367	16.09
181	1.66	230	1.51	288	0.03	368	1.82
182	0.11	231	1.63	291	0.01	369	0.12
184	0.22	232	0.13	295	0.21	370	0.01
186	0.15	236	1.04	296	0.03	386	7.77
187	0.18	237	0.20	298	2.21	387	10.31
188	0.01	241	0.14	299	10.47	388	1.05
191	0.36	242	0.01	300	0.92	389	0.05
192	0.10	243	0.01	301	0.04	406	2.85
193	0.10	245	0.06	314	0.04		
198	3.09	248	4.57	317	20.78		
199	8.95	249	18.13	318	8.79		

Spectrum No. 50





Mass	% Base	
40.98	20.35	
41.98	4.41	
43.00	5.71	
48.95	1.28	
49.95	12.39	
50 96	17.05	
51.97	5.72	
52.97	3.85	
53.98	1.20	
54.98	4.32	
55.96	0.77	
56.00	0.51	
56.99	2.16	
60.95	2.18	
61.95	5.52	
62.86	36.36	F
62 96	11.30	F
63.96	2.24	
64.85	16.39	F
64.97	4.30	F
65.97	1.04	
66.98	1.66	
68.92	10.19	
71.00	0.91	
72.96	1.51	
73.92	4.81	
74.92	4.28	
75.93	2.52	
76.94	14.55	
77.95	5.36	
78.95	3.41	
80.95	1.57	
82.96	0.62	
84.98	0.96	
85.91	0.58	
86.91	1.70	
87.92	0.55	
88.93	12.62	
89.92	6.96	
90.93	3.50	
91.89	1.04	
92.88	1.82	
93.92	0.68	
94.95	1.25	
97.00	1.04	
100.85	1.44	
102.86	2.92	
103.83	71.20	
104.87	6.03	
105.84	31.16	
106.89	6.66	
107.91	1.31	
112.82	0.87	
114.87	1.83	
116 84	0.63	
117.89	0.54	
118 87	1.04	
119 91	1 20	

F

Mass	% Base
122.83	2.21
123.86	1.31
124.82	1.44
127.90	0.68
130.79	0.76
135.86	5.69
136.84	1.01
137.89	1.12
138.82	1.80
140.84	1.29
142.71	2.39
143.81	4.81
144.80	95.88
145.81	6.14
146.80	43.71
147.80	2.12
148.80	1.55
151.74	1.97
152.78	1.87
153.78	2.39
154.80	1.74
156.79	0.70
160.81	0.75
163.81	0.69
164.70	0.95
165.72	1.84
166.75	0.94
167.71	2.23
168.75	1.44
169.73	2.78
170.80	1.30
171.75	0.60
182.69	1.04
183.68	1.04
184.72	1.04
185.68	8.11
186.72	0.76
187.68	4.62
189.68	1.67
192.66	3.58
193.69	0.82
194.66	2.95
196.64	0.56
197.74	1.04
198.77	0.58
199.70	1.04
204.66	0.70
206.65	2.17
207.68	0.88
208.66	2.00
210.67	1.59
212.68	0.90
213.72	0.63
215.68	5.45
216.70	0.66
217 65	3.40
218.70	0.96

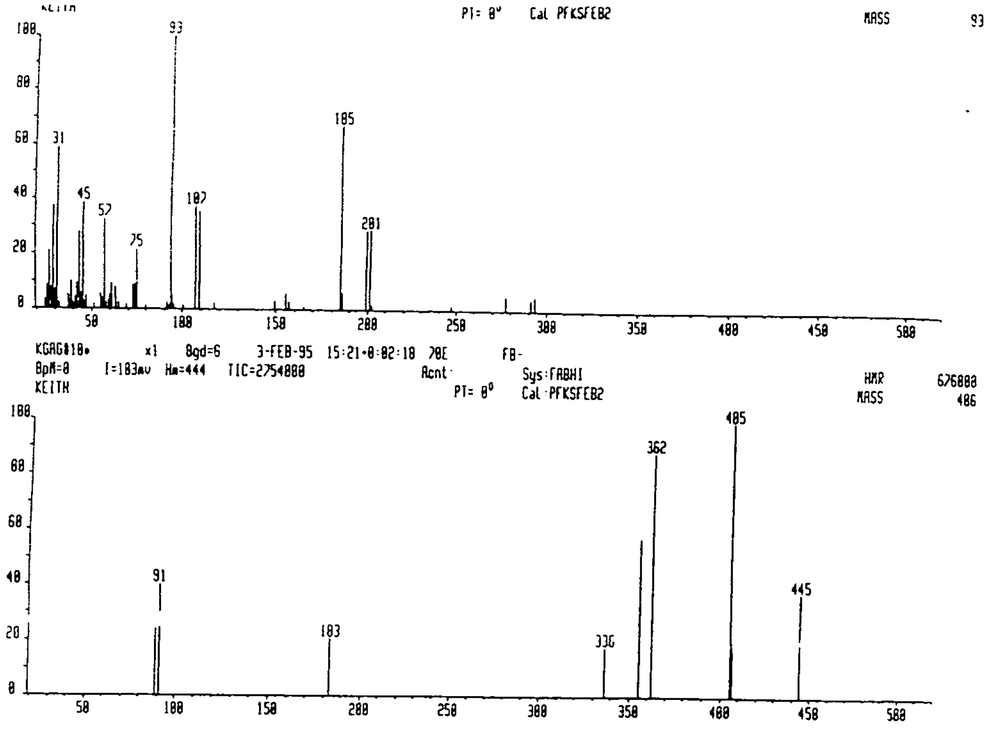
KEITH

Mass	% Base	
68 95	0 91	
92.93	1.06	
100.87	0.63	
102.85	0.53	
107.87	0.68	
116.91	0.64	
152.93	0.92	
154.87	0.72	
178.83	0.53	
182.71	0.84	
189.79	0.67	
191.76	0.66	
216.86	0.57	
266.84	4.82	
278.83	0.58	
285.83	0.68	
316.79	1.75	
335.80	6.60	
336.79	2.32	
354.80	3.12	
366.79	0.97	
382.77	1.07	
385.74	10.09	
386.75	1.63	
404.68	100.00	FO
405.73	27.87	F
406.73	1.19	F
454.74	0.98	
486.63	1.36	
488.62	0.80	
568.78	0.91	
570.59	0.78	

KEITH

Mass	% Base
226.65	12.17
228.15	100.00
228.62	9.83
230.66	2.06
231.54	0 53
233.63	2.61
234.58	0.85
235.61	4.82
237.63	1.04
242.58	1.04
246.56	0.72
247.57	1.04
248.64	0.91
249.58	1.72
256.67	7.92
257.66	1.31
258.67	3.47
267.53	0.77
269.53	1.04
274.49	1.04
276.51	1.04
278.53	0.53
290.54	0.76
297.53	0.88
304.56	0.81
308.52	1.44
309.49	0.66
315.49	0.77
317.46	1.31
319.46	0.69
320.52	0.54
324.47	0.66
331.46	0.71
368.52	1.31
370.43	0.72

Spectrum No. 51



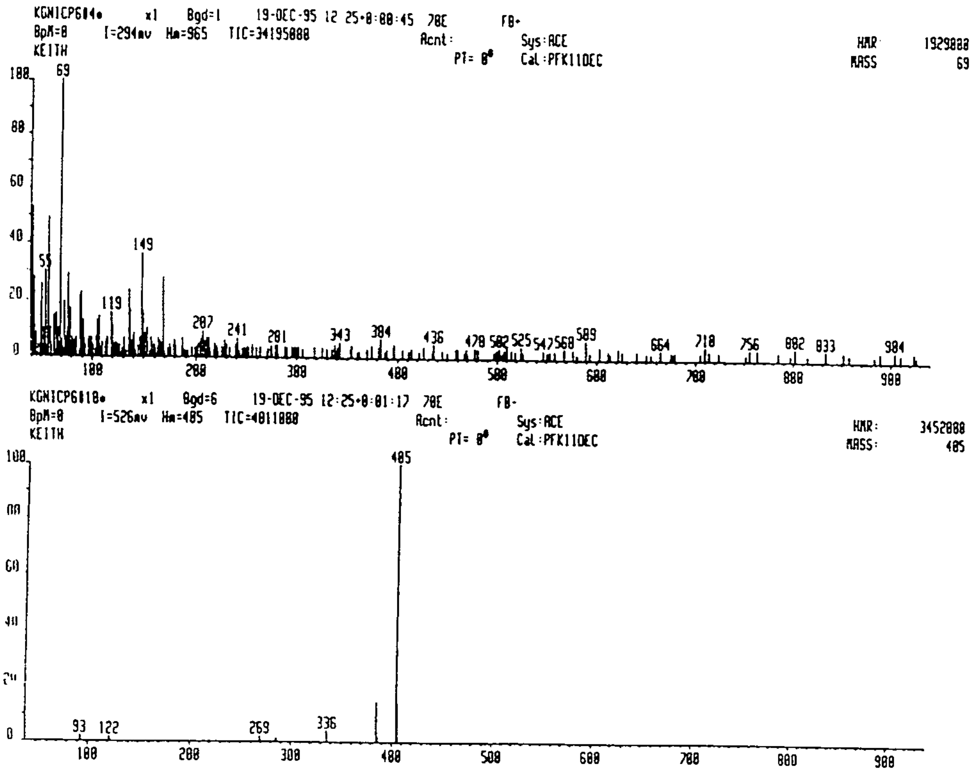
BpM=0 I=952mv Hm=293 TIC
KEITH

Mass	% Base	
40.15	2.19	
41.16	4.23	
42.13	8.95	
43.13	27.70	F
43.15	5.54	F
44.14	5.59	
45.15	38.33	
46.15	2.27	
47.12	4.29	
51.13	1.46	
55.12	5.27	
55.16	1.84	
56.13	3.92	
57.12	30.74	F
57.14	32.12	F
58.13	1.89	
59.11	2.79	
60.12	4.85	
61.12	8.89	
63.02	7.49	
65.01	2.10	
69.07	1.39	
73.10	8.20	
74.10	8.42	
75.10	16.30	F
75.14	21.22	F
80.13	0.86	
91.12	1.97	
93.02	1.22	
93.14	100.00	
94.15	4.42	
95.16	1.46	
100.18	0.86	
107.02	36.89	
109.02	35.32	
117.16	2.00	
149.21	2.88	
155 13	5.57	
157.11	2.47	
165.24	0.62	
185.26	67.41	
186.28	5.70	
199.13	28.39	
201.14	28.61	
202.15	1.35	
247.25	1.41	
277.37	5.14	
291.23	3.84	
293.26	4.93	

KEITH

Mass	% Base
89.13	27.22
91.15	39.79
183.33	20.27
336.43	17.46
355.54	57.25
362.48	87.87
405.51	100.00
406.50	20.12
444.51	37.43

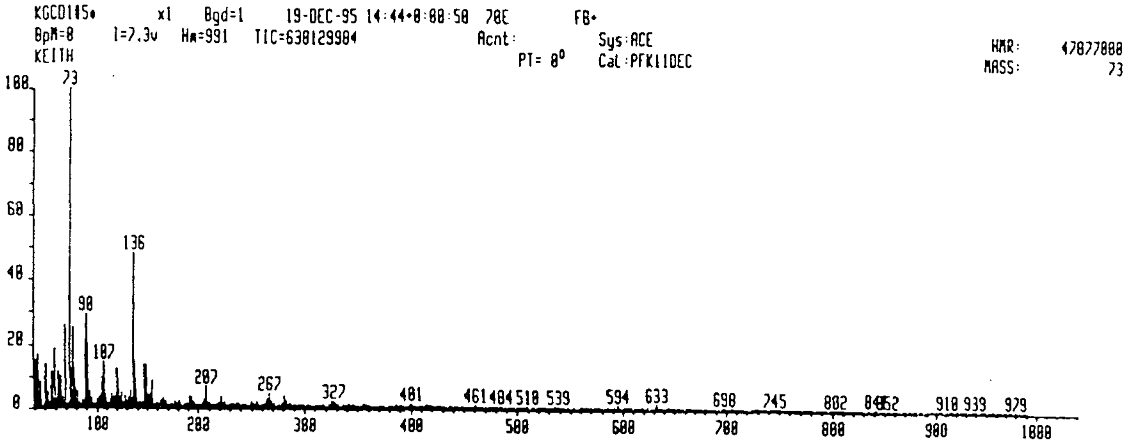
Spectrum No. 52

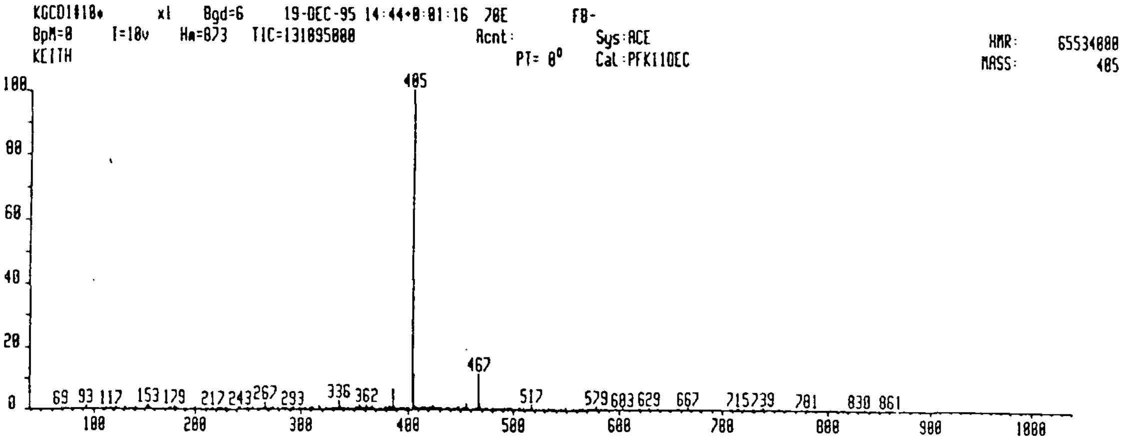


Mass	% Base
40.68	2.28
41.00	52.72
41.64	1.92
42.00	18.87
43.00	27.58
43.99	4.82
44.99	8.24
45.06	1.81
45.19	1.97
46.95	5.08
48.35	3.99
49.49	2.02
49.96	18.46
50.38	1.97
50.98	25.25
51.73	2.07
51.98	3.42
52.51	2.80
52.98	9.90
53.99	4.87
54.56	2.02
54.99	29.86
55.38	3.11
55.86	1.56
56.02	9.43
56.20	2.70
57.02	48.89
57.55	2.28
57.89	2.90
58.98	9.80
59.28	2.02
59.99	3.73
61.97	13.06
62.96	14.31
63.47	1.81
63.86	1.50
64.42	1.45
64.99	14.93
65.40	1.87
65.61	2.23
66.00	6.58
66.99	9.90
68.00	4.51
68.93	100.00 F
69.02	17.63 F
70.03	5.39
70.49	1.92
71.04	6.58
71.55	2.59
71.99	2.28
72.99	19.03
73.74	2.28
73.95	6.58
74.96	6.58
75.32	3.27
75.98	8.24
76.96	29.03
77.99	8.24
78.98	16.90
[illegible]	4.37
80.71	2.80
80.97	6.58
81.96	4.82
82.98	5.44
83.21	2.59
84.47	2.80
85.00	6.58
87.61	1.87
88.96	21.51
89.97	22.50
90.98	12.75
91.69	2.02
91.96	6.07
92.96	3.63
95.97	5.39
96.93	6.58
97.45	2.38
98.94	6.58
99.93	4.10
101.11	3.32
102.65	2.13
103.56	2.23
103.92	6.48
104.23	2.18
104.92	12.60
105.84	2.70
105.94	9.07
106.97	14.00
107.97	3.27
109.80	2.85
109.92	4.87
112.50	1.87
112.87	3.99
113.91	5.60
114.95	6.58
118.91	15.34
119.96	10.99
120.36	1.87
120.94	4.41
121.90	2.02
122.99	4.46
123.90	4.72
124.91	4.15
126.89	4.04
128.78	1.45
129.60	2.75
130.86	6.58
132.81	2.07
133.65	1.45
134.87	3.32
135.90	23.64
136.94	16.43
137.86	5.44
138.90	3.37
139.93	5.75
140.42	2.02
140.87	8.24
142.11	1.97
143.02	1.81
145.25	3.73

Mass	% Base
92.95	1.88
121.93	1.45
268.93	1.71
285.84	1.13
335.89	3.68
385.83	14.28
386.72	1.59
404.80	100.00
405.89	13.64

Spectrum No. 53

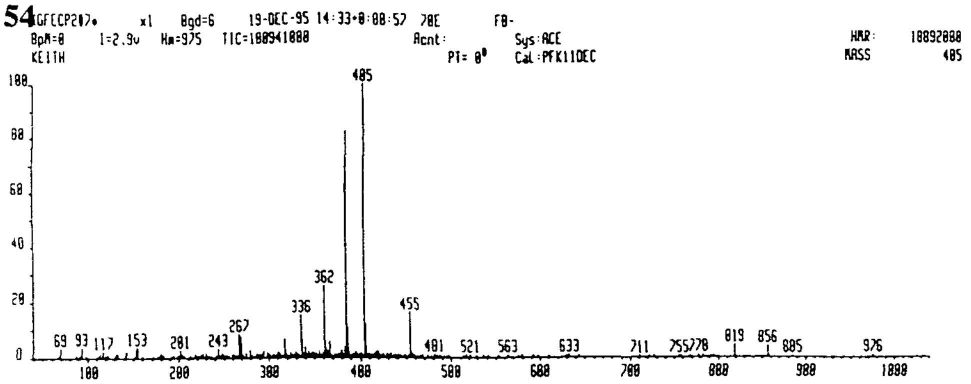


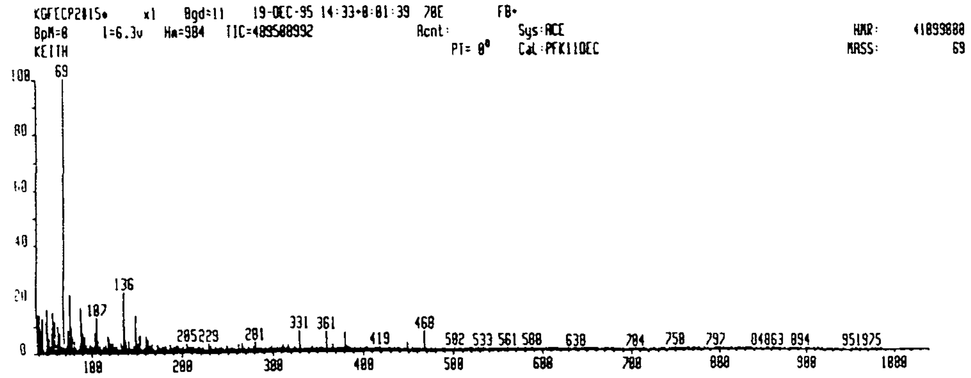


Mass	% Base
41.00	15.24
41.99	10.28
42.98	16.86
43.98	2.97
44.97	8.13
45.98	1.01
46.95	2.83
48.97	1.25
49.97	9.61
50.98	13.80
51.99	5.13
52.98	5.29
53.99	1.99
55.00	6.89
56.00	11.36
57.01	11.42
57.99	2.90
58.98	18.56
59.98	1.87
60.97	2.91
61.97	4.12
62.97	11.38
63.98	3.31
64.99	9.98
65.99	3.26
66.99	3.54
67.98	1.71
68.95	25.76
69.98	1.31
70.99	1.38
71.99	1.94
72.99	100.00
73.98	9.50
74.97	12.76
75.97	5.21
76.97	24.86
77.98	12.45
78.98	6.18
79.98	2.04
80.96	5.17
81.97	1.38
82.97	2.54
83.97	0.87
84.98	2.73
85.96	2.19
86.97	2.84
87.96	2.93
88.97	20.74
89.98	29.04
90.98	20.17
91.97	4.10
92.96	4.97

Mass	% Base	
92.94	0.68	
116.92	0.50	
151.93	0.58	
152.92	0.96	
154.88	0.59	
178.85	0.56	
266.76	1.97	
316.74	0.98	
335.84	2.90	
336.82	1.36	
351.87	0.58	
354.84	1.41	
355.89	0.53	
361.83	1.47	
366.81	1.03	
378.84	0.68	
382.81	0.87	
385.81	6.49	
386.85	0.75	
397.82	0.50	
404.78	100.00	FO
405.81	11.10	F
406.80	0.68	
423.81	0.91	
447.84	0.59	
454.82	1.74	
466.78	11.22	
467.82	1.33	
516.81	1.28	
578.69	0.83	

Spectrum No. 54



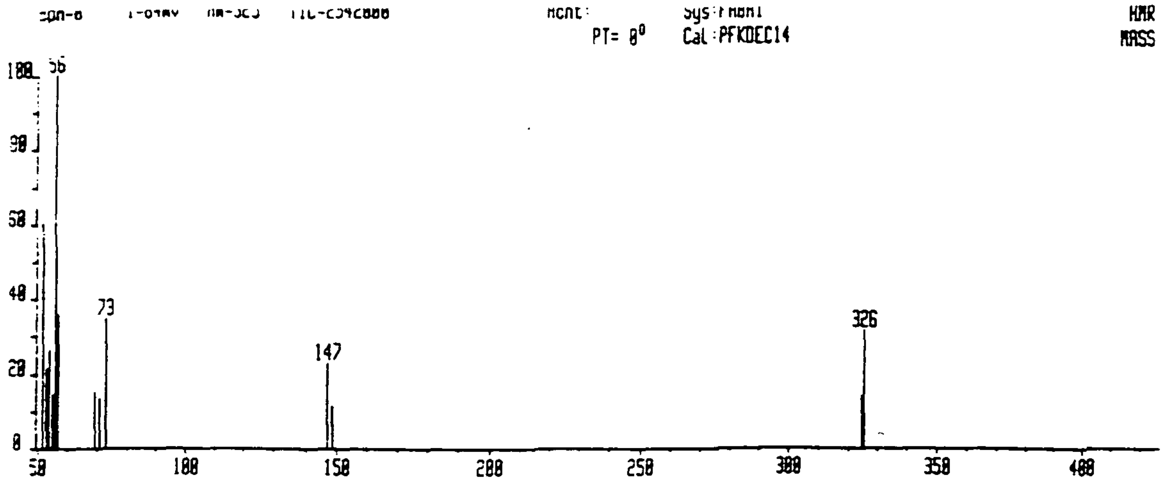


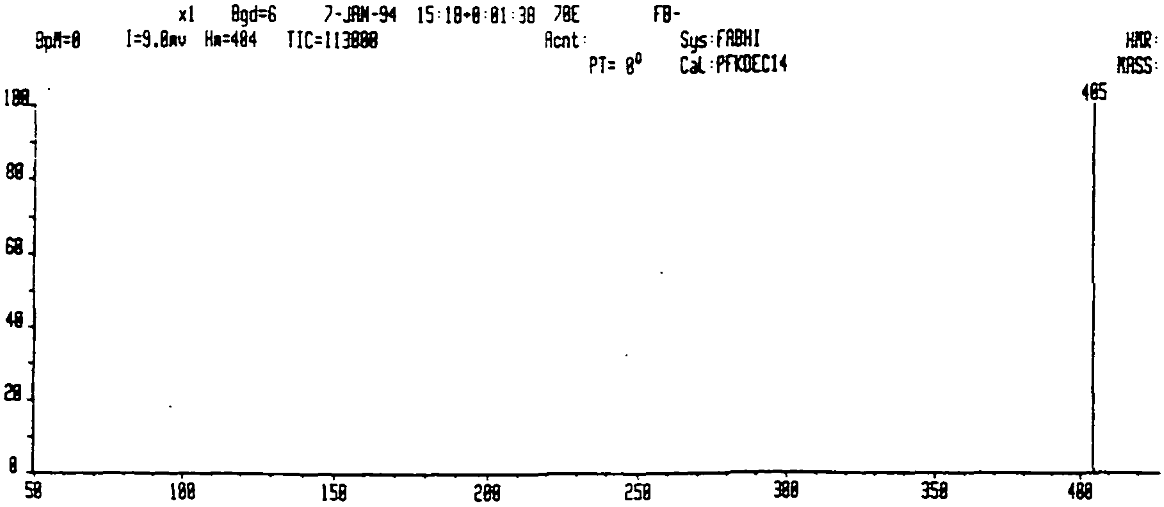
Mass	% Base
40 99	13.97
41 98	13.78
42 98	9.02
43.99	7 32
44 98	12.57
45.98	0.49
46.95	1.21
47.98	0.37
48.96	1 64
49 96	11.20
50 95	16.12
51 97	4.98
52 97	5.34
53.98	2.36
54.97	7.02
55 88	2.82 F
55 98	9.27 F
57.00	14.81
57.98	4.44
58.96	11.14
59.96	1.15
60.95	3.03
61 95	4.72
62.96	9.74
63.97	3.14
64.97	7.27
65.97	2.16
66.98	2.88
67.97	2.10
68.93	100.00
69.95	1.81
70.98	2.58
71.97	2.74
72.96	6.58
73.95	5.92
74.94	8.10
75.95	5.16
76.96	21.29
77.96	9.22
78.96	5.31
79.96	1.63
80 94	4.24
81.95	1.55
82 95	2.74
83.96	1.09
84 95	1.31
85.94	2.57
86.95	3.29
87 95	2 56
88 95	16.56
89.95	10.47
90.96	6.98
91.95	3.31
92.93	5.89
93.95	1.79
94.95	2.95
95 95	1.22
96 96	2.04
97 94	2.33
98 92	2.99

Mass	% Base
99.94	1.06
100.92	1.77
101.94	2.29
102.94	1.77
103.94	2.78
104.92	7.04
105.93	6.84
106.94	12.54
107.93	4.28
108.93	1.77
109.94	2.90
110.92	1.55
111.93	1.15
112.90	2.16
113.93	1.52
114.93	2.42
115.94	1.81
116.89	2.97
117.92	1.73
118.90	6.05
119.92	5.14
120.93	3.41
121.92	2.67
122.92	3.09
123.91	3.37
124.91	2.13
125.92	2.15
126.92	2.17
127.93	1.55
128.90	2.46
129.92	1.31
130.91	1.48
131.91	1.10
132.90	3.90
133.91	2.82
134.90	2.18
135.90	22.18
136.90	9.27
137.90	4.05
138.90	3.01
139.91	1.48
140.88	4.05
141.90	1.20
142.89	2.18
143.89	1.09
144.86	1.96
145.86	1.05
146.88	2.80
147.88	1.68
148.88	13.79
149.88	4.82
150.89	3.08
151.91	3.66
152.89	6.13
153.89	6.14
154.87	2.56
155.87	1.24
156.88	0.93
157.90	0.89
158.90	1.83

373.86	0.67
374.88	0.67
375.80	1.01
376.77	1.07
377.73	0.66
378.79	2 06
379.80	2.28
380 65	0.83
381 75	1 17
382.70	3.41
383 75	0.67
385 68	82.66 F
386 73	10.30 F
387.79	1.62
388.83	0.67
389.63	0.50
390.82	0.66
391.76	1.01
392.72	0.50
393.77	1.20
394.75	2.20
395.76	0.95
396.74	0.62
397.73	0.66
398.78	1.01
399.76	0.86
400.78	1.20
401.78	0.60
402.82	0.56
404.70	100.00
405.71	11.71
406.78	0.83
407.81	0.57
408.80	0 89

Spectrum No. 55

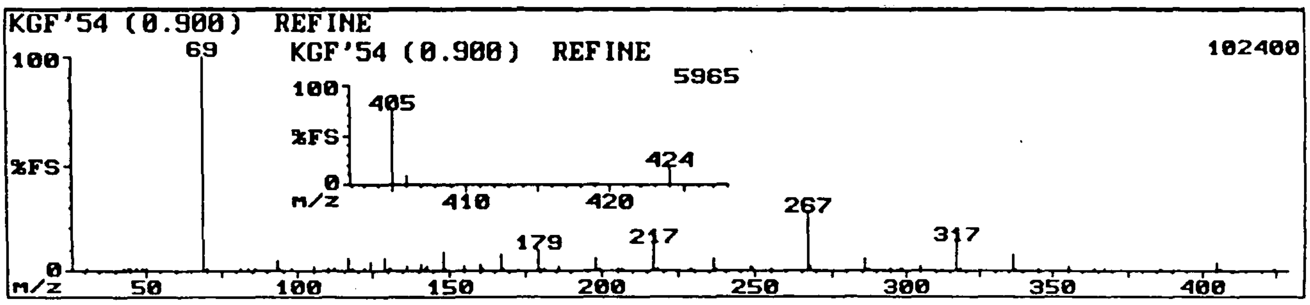




Mass	% Base
51.91	60.00
52.90	10.09
52.91	21.08
52.92	9.55
53.91	11.53
53.92	25.95
54.98	14.41
55.90	100.00
56.91	35.68
56.99	29.01
68.89	14.77
70.90	13.15
72.89	34.41
146.88	22.52
148.89	10.99
324.92	13.69
325.94	31.17

Mass	% Base
404.56	91.53
404.66	100.00

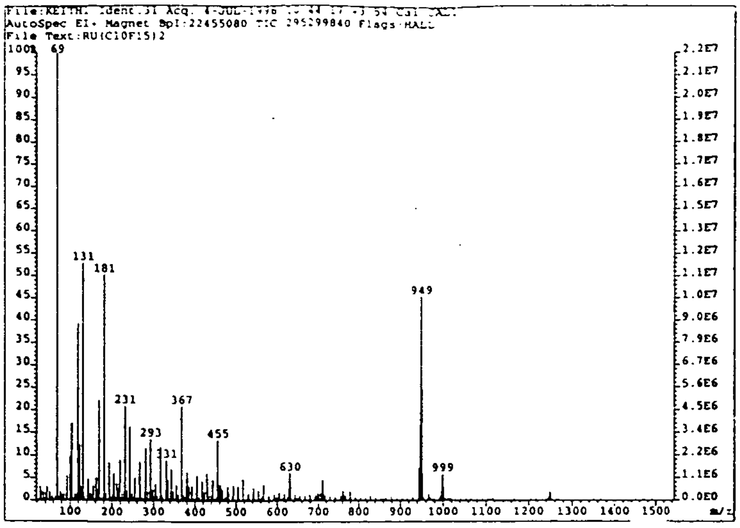
Spectrum No. 56

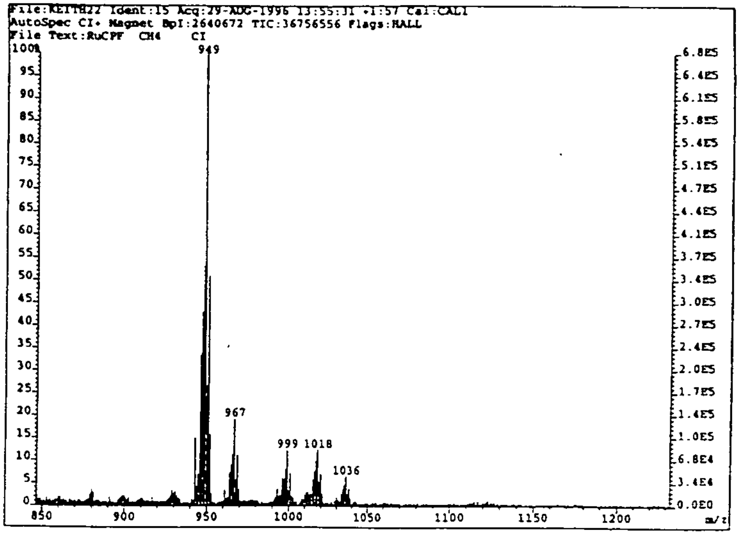


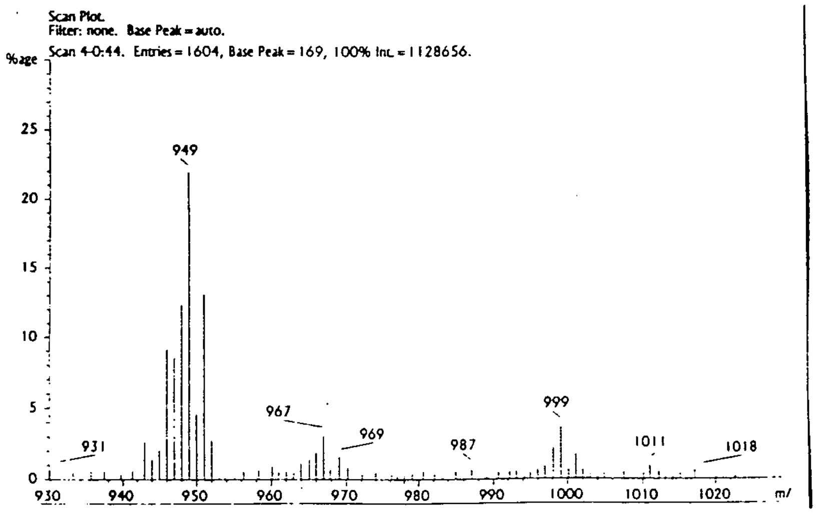
KGF 54 (0.900) 102400

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.27	70	1.45	143	2.00	255	0.71
24	0.31	74	0.37	148	8.31	267	27.25
25	0.71	79	1.08	149	0.72	268	2.30
26	1.38	80	0.29	155	2.08	286	5.75
27	1.27	81	0.37	160	3.06	287	0.51
28	8.75	84	1.28	161	0.38	295	0.35
29	0.46	86	1.22	167	7.69	298	0.25
31	1.42	93	4.69	168	0.57	299	0.26
32	3.17	94	0.25	179	9.50	305	0.25
38	9.94	98	1.25	180	0.79	317	13.13
39	17.00	105	1.50	181	0.15	318	1.28
40	43.00	110	1.03	186	1.89	336	7.63
41	80.00	112	0.38	198	6.00	337	0.83
42	2.63	117	5.50	199	0.71	345	0.93
43	0.31	118	0.34	205	0.93	355	0.60
44	2.03	122	0.52	207	0.16	364	0.58
45	0.46	124	3.48	217	12.56	367	0.45
47	0.30	129	5.69	218	1.03	386	0.24
49	0.93	130	0.42	229	1.42	405	4.31
50	0.96	131	0.52	236	5.56	406	0.46
51	0.34	136	1.86	237	0.47	424	0.97
65	1.19	141	3.34	248	2.09		
69	100.00	142	0.29	249	0.62		

Spectrum No. 57





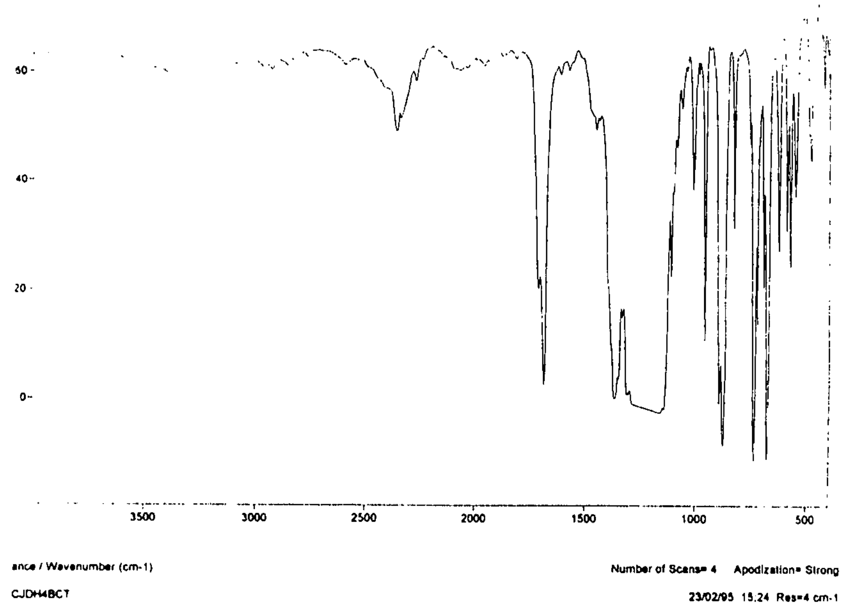


Appendix Three

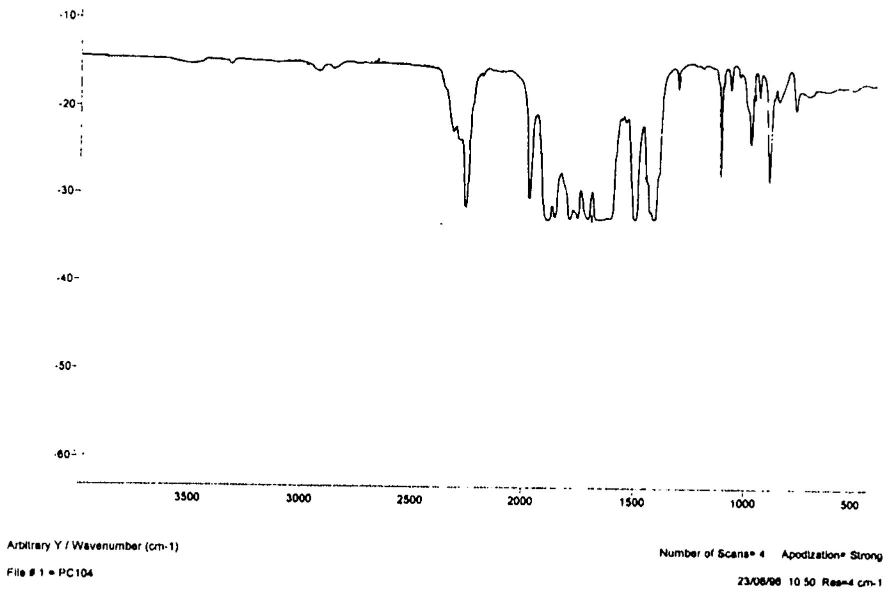
Infra Red Spectra

1. Perfluoro-3,4-dimethylhexa-2,4-diene **(14)**
2. Perfluoro-1,1'-bicyclo-1-pentenyl **(12)**
3. Perfluoro-1-(1',1'-dimethyl)butylcyclopentene **(23)**
4. Perfluoro-4-(1',1'-dimethyl)butylpyrimidine **(33)**
5. 2,4-Dinitroheptafluoroisopropylbenzene **(39)**
6. Perfluoro-2,4,6-tri-isopropyl-s-triazine **(47)**
7. Tetrakis(2,3,4,5-trifluoromethyl)benzodioxocin **(54)**
8. Tetrakis(1,6,7,8-trifluoromethyl)-3,4-benzo-2,5-dioxabicyclo[4.2.0]octa-3,7-diene **(58)**
9. 2,4-Diepoxytetrakis(2,3,4,5-trifluoromethyl)benzodioxocin **(66)**
10. Tetrakis(1,6,7,8-trifluoromethyl)-3,4-benzo-2,5-dioxabicyclo[4.2.0]octa-3,7-diene-epoxide **(69)**
11. Perfluoro-2,3,4,5-tetramethylhepta-2,4-diene **(75)**
12. Hexakis(trifluoromethyl)cyclopentadiene **(96)**
13. Tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienide **(87)**
14. Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienide **(101)**
15. Tetraethylammonium pentakis(trifluoromethyl)cyclopentadienide **(100)**
16. Cesium pentakis(trifluoromethyl)cyclopentadienide **(86)**
17. Pentakis(trifluoromethyl)cyclopentadienide **(84)**; with potassium counter ion
18. Pentakis(trifluoromethyl)cyclopentadienide **(84)**; with sodium counter ion
19. Pentakis(trifluoromethyl)cyclopentadienide **(84)**; with lithium counter ion
20. 5H-Perfluoropentamethylcyclopentadiene **(109)**
21. Tetrakis(acetonitrile)copper (I) pentakis(trifluoromethyl)cyclopentadienide **(118)**
22. Tetrakis(acetonitrile)silver (I) pentakis(trifluoromethyl)cyclopentadienide **(122)**
23. Hexakis(acetonitrile)nickel(II)dipentakis(trifluoromethyl)cyclopentadienide **(119)**
24. Hexakis(acetonitrile)cobalt(II)dipentakis(trifluoromethyl)cyclopentadienide **(120)**
25. Hexakis(acetonitrile)iron (II) dipentakis(trifluoromethyl)cyclopentadienide **(121)**
26. Decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienide **(125)**

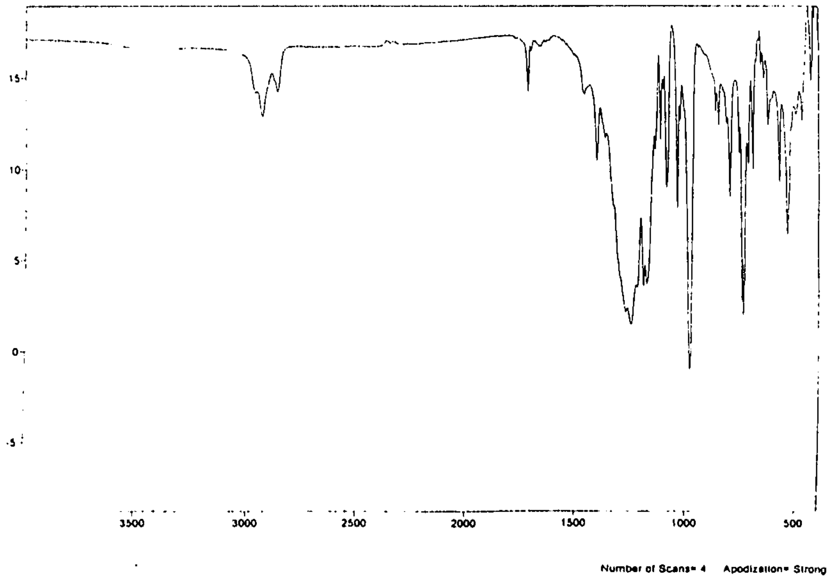
Spectrum No. 1



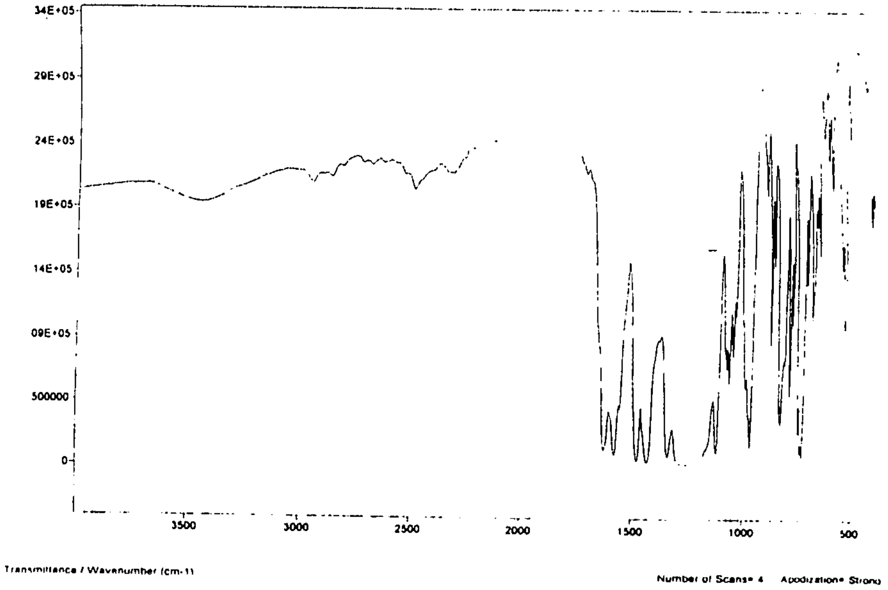
Spectrum No. 2



Spectrum No. 3



Spectrum No. 4



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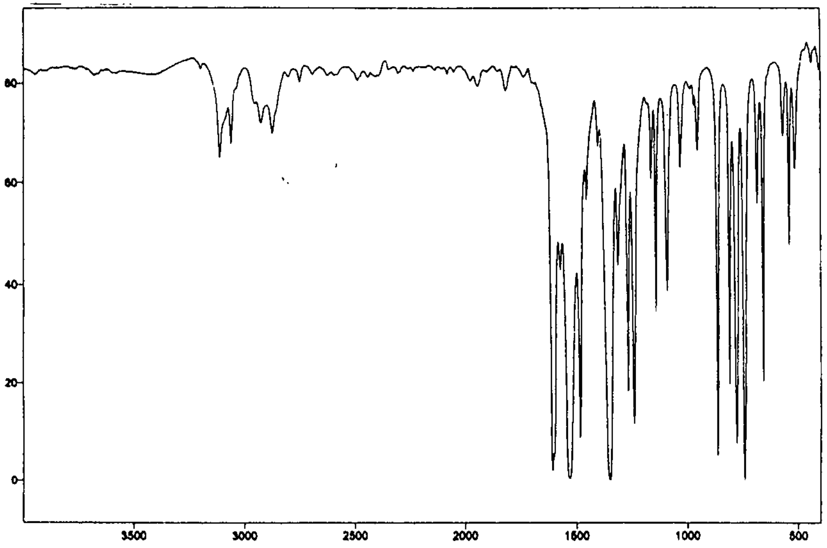
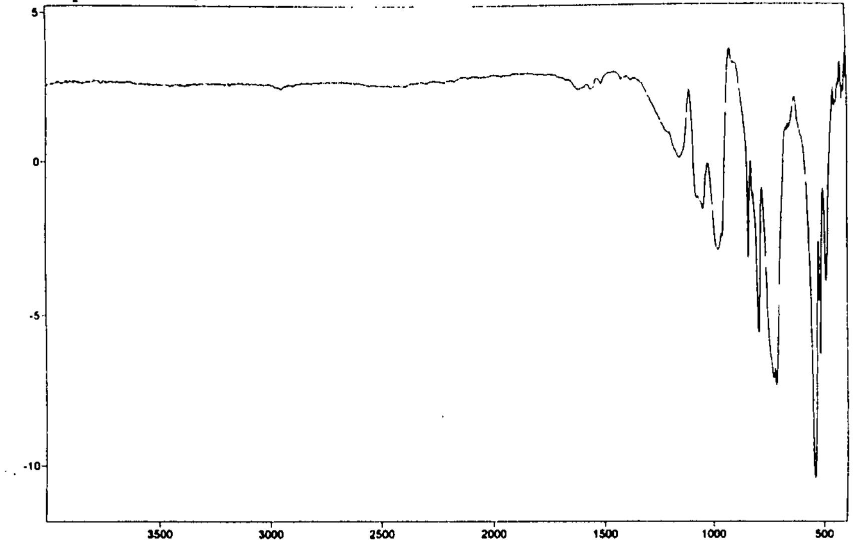


smittance / Wavenumber (cm-1)
1 : KG
dinitro product

Number of Scans= 4 Apodization= Strong
23/08/96 11:40 Res=4 cm-1

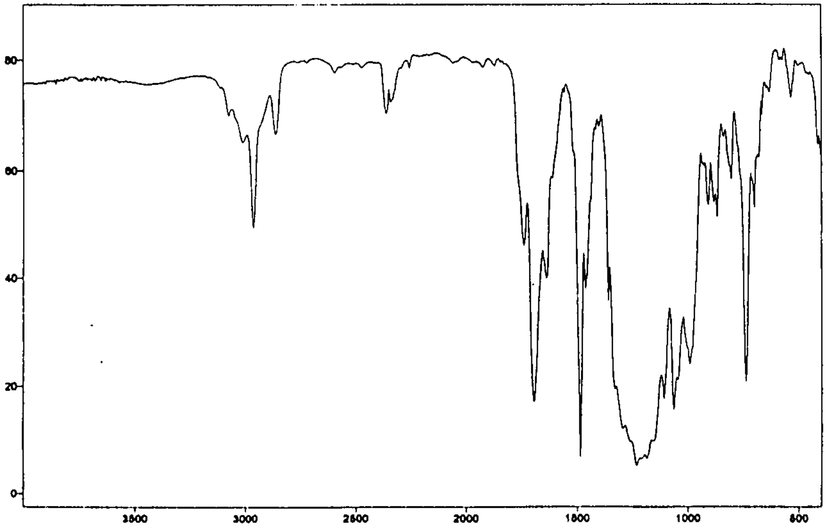
Spectrum No. 6



Transmittance / Wavenumber (cm-1)
File # 1 : RJPB0
kgtri3

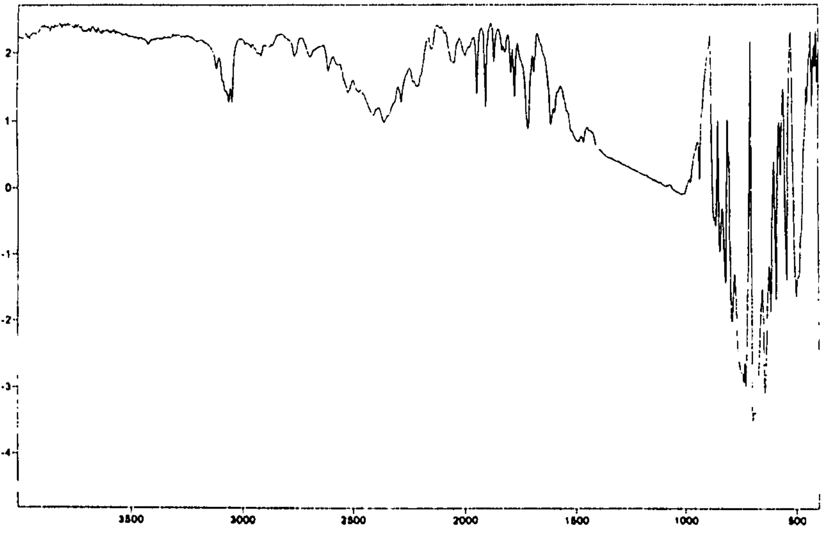
Number of Scans= 4 Apodization= Strong
19/01/95 13:10 Res=4 cm-1

Spectrum No. 7



Number of Scans= 8 Apodization= Strong

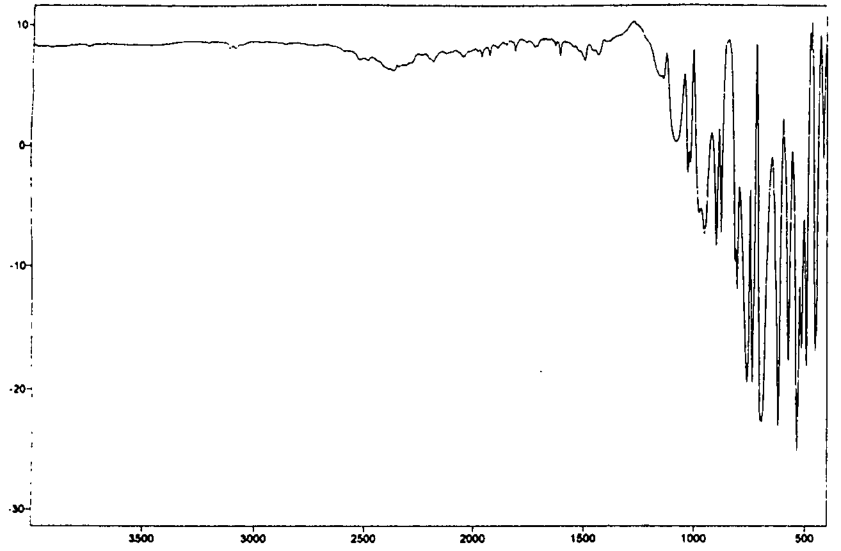
Spectrum No. 8



Transmittance / Wavenumber (cm-1)

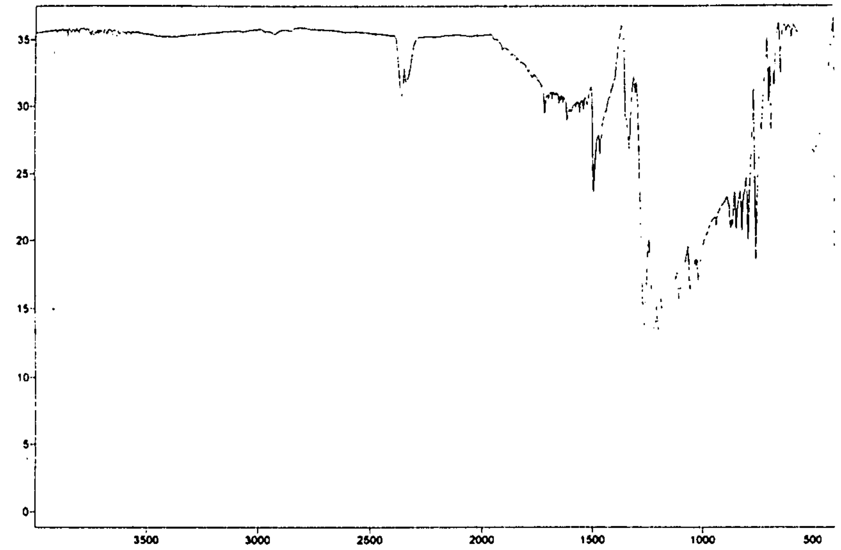
Number of Scans= 8 Apodization= Strong

Spectrum No. 9



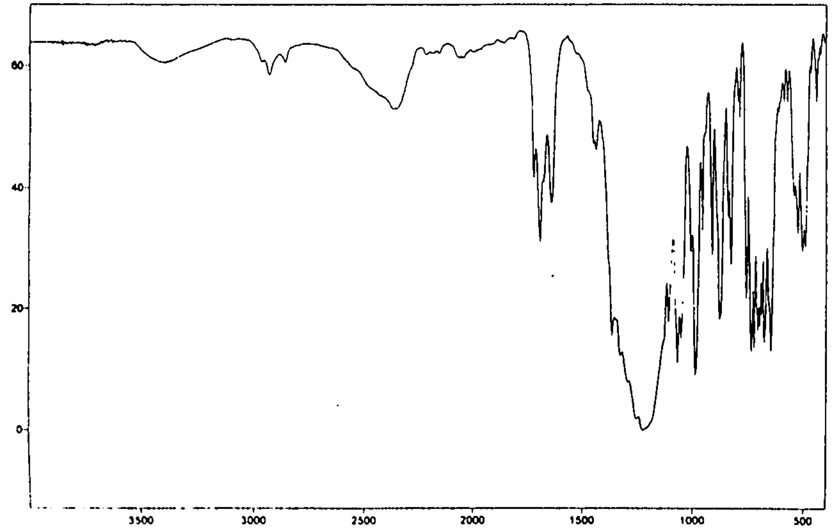
ttance / Wavenumber (cm-1) Number of Scans= 4 Apodization= Strong
PC81 28/08/98 10:17 Res=4 cm-1
diepoxide

Spectrum No. 10

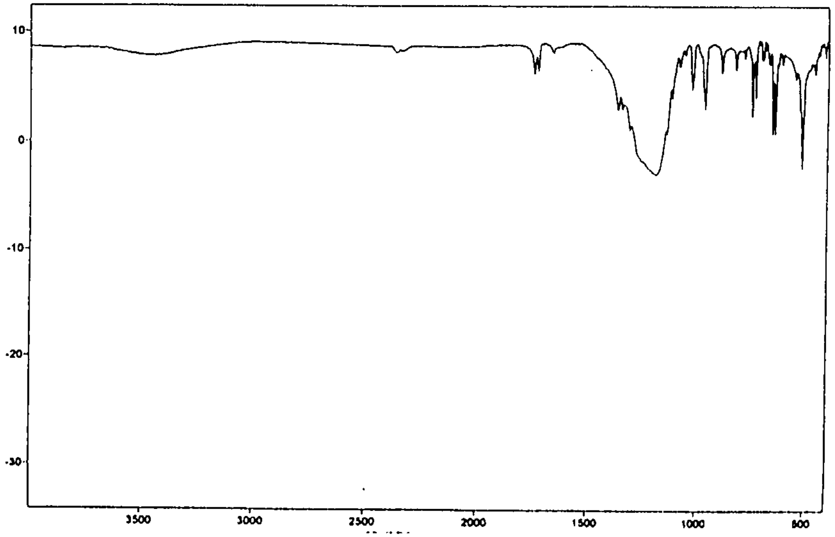


Transmittance / Wavenumber (cm-1) Number of Scans= 4 Apodization= Strong
File # 2 : . 20/03/98 11:47 Res=4 cm-1
K Gray Benzo. cyclisation

Spectrum No. 11



Spectrum No. 12



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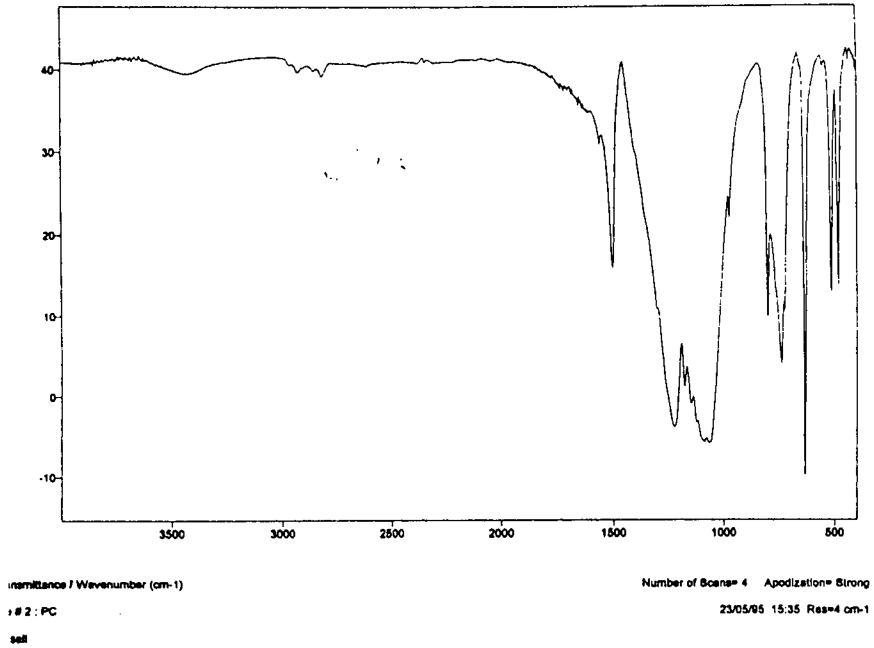
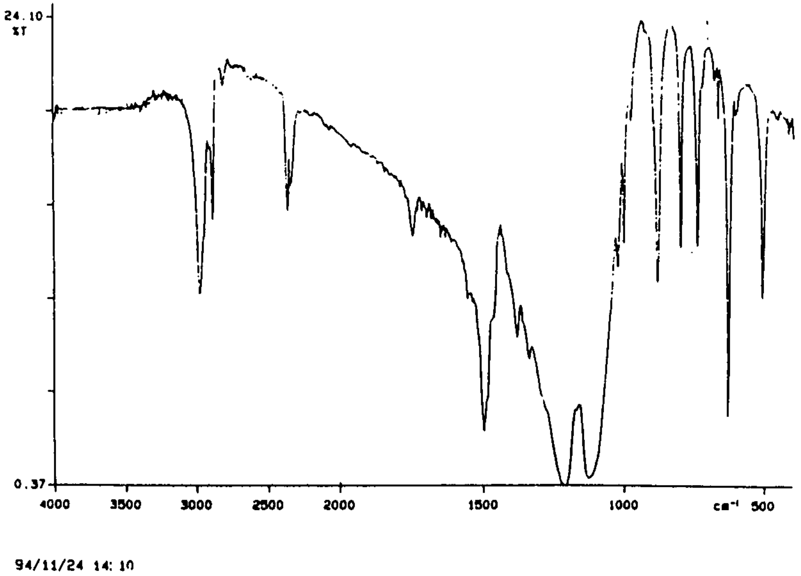
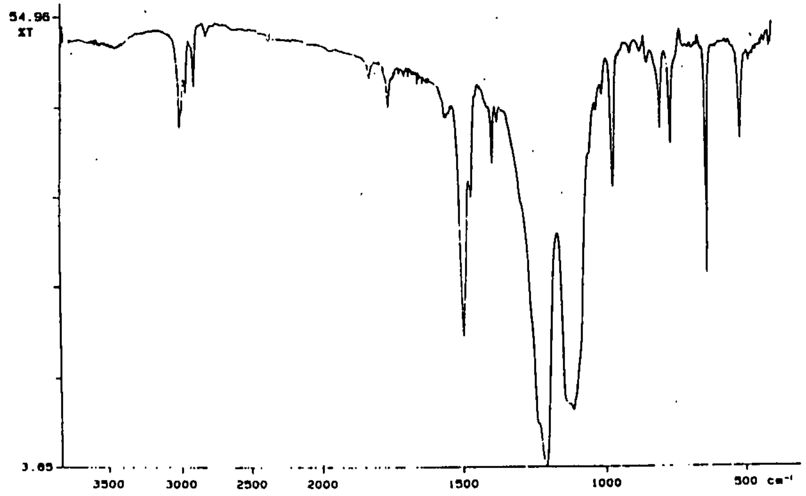


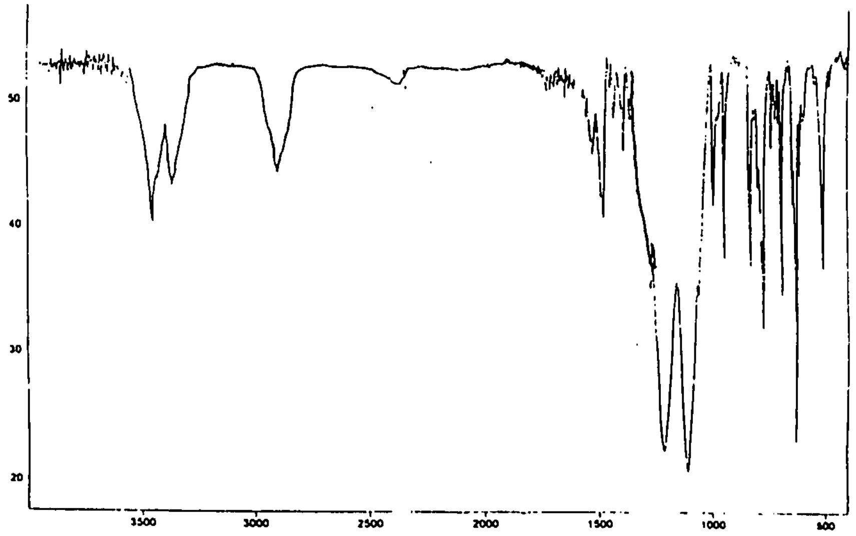
Spectrum No. 14



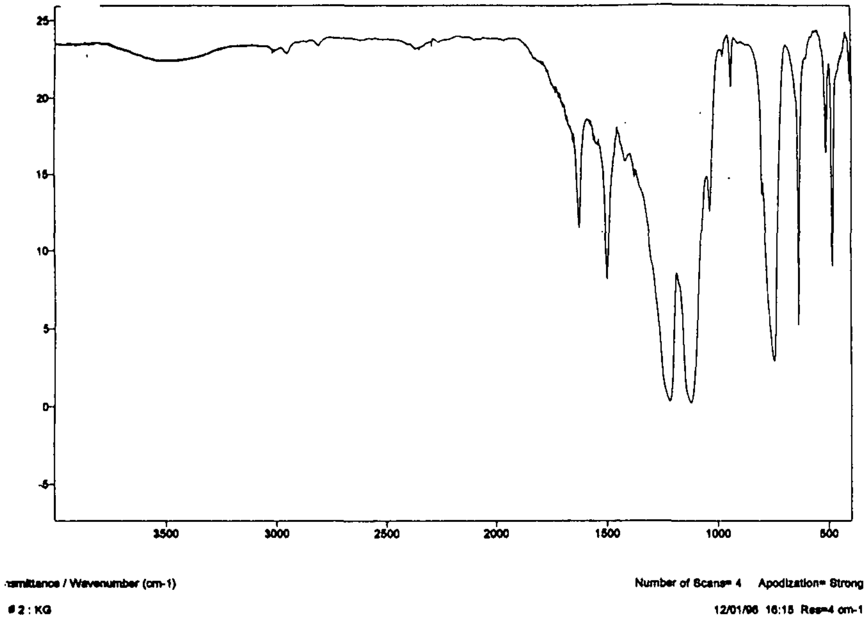
Spectrum No. 15



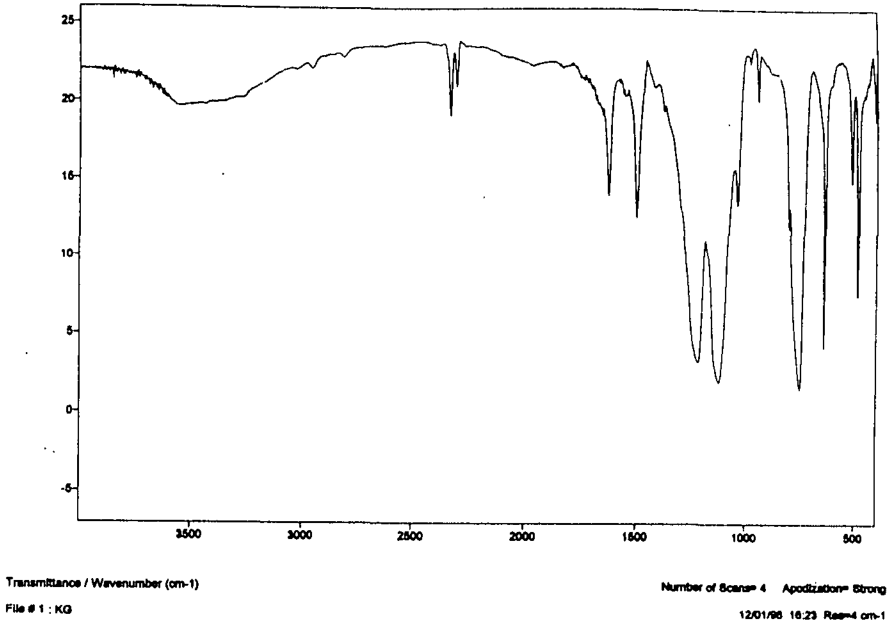
Spectrum No. 16



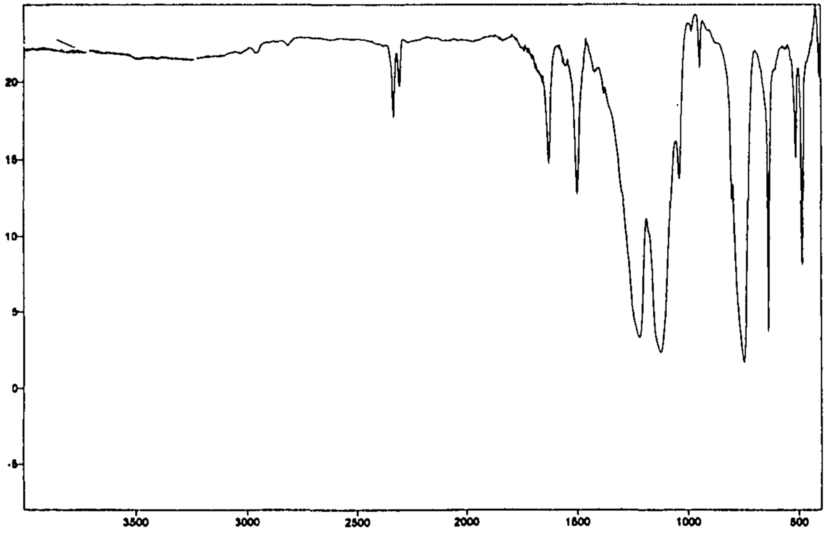
Spectrum No. 17



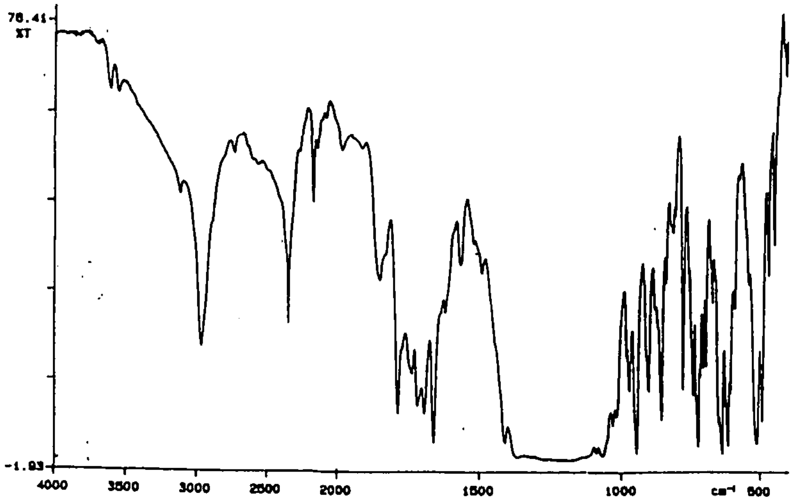
Spectrum No. 18



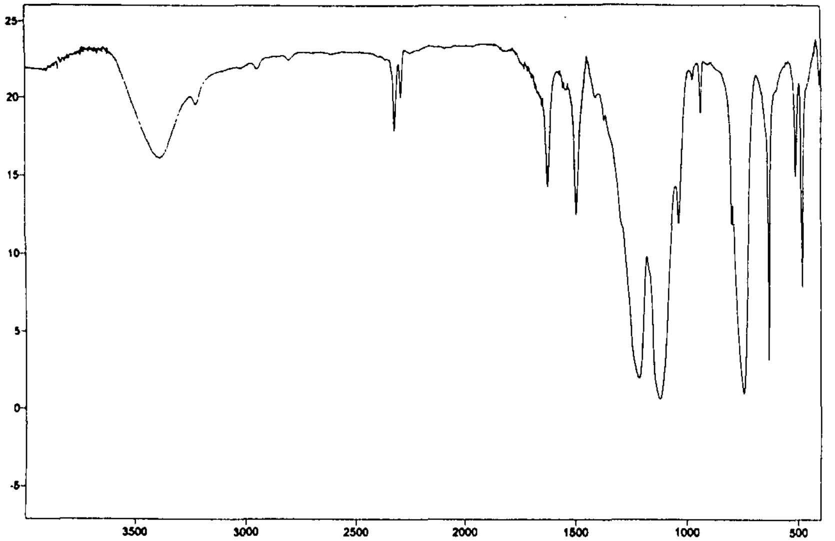
Spectrum No. 19



Spectrum No. 20



Spectrum No. 21

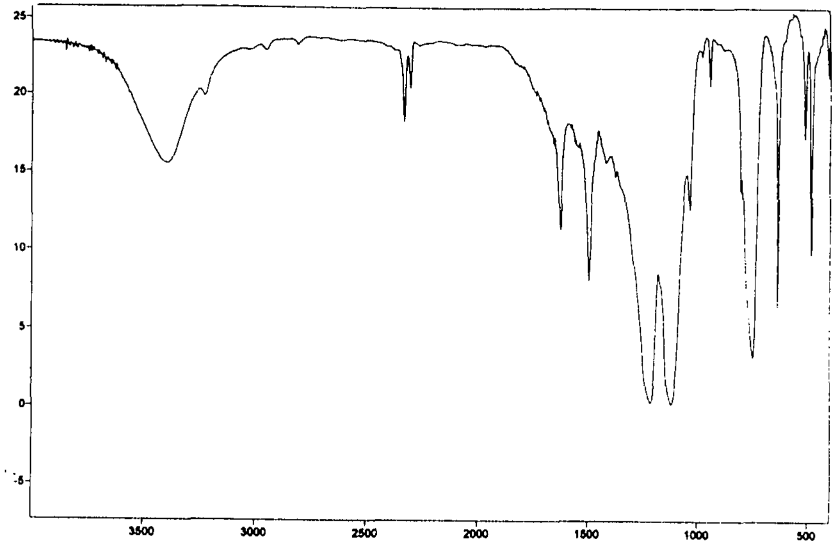


mittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

1 : KG
12/01/96 16:17 Res=4 cm-1

u

Spectrum No. 22

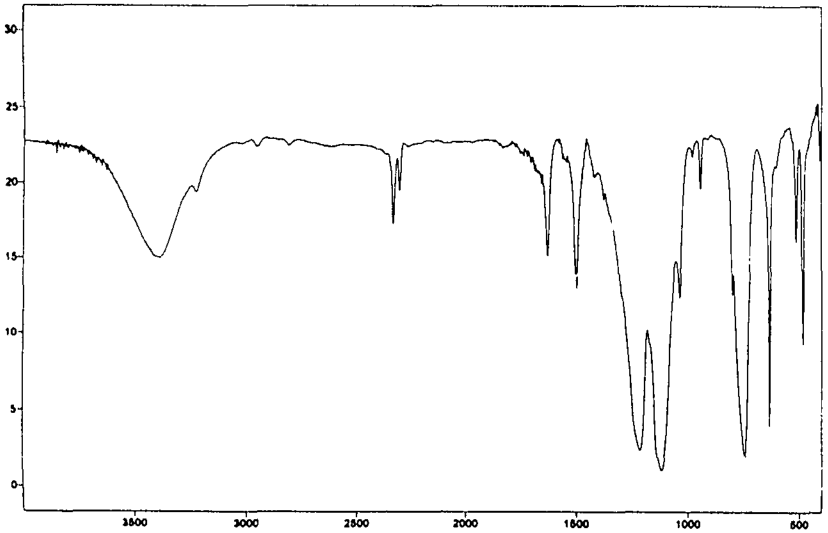


Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

File # 3 : KG
12/01/96 16:19 Res=4 cm-1

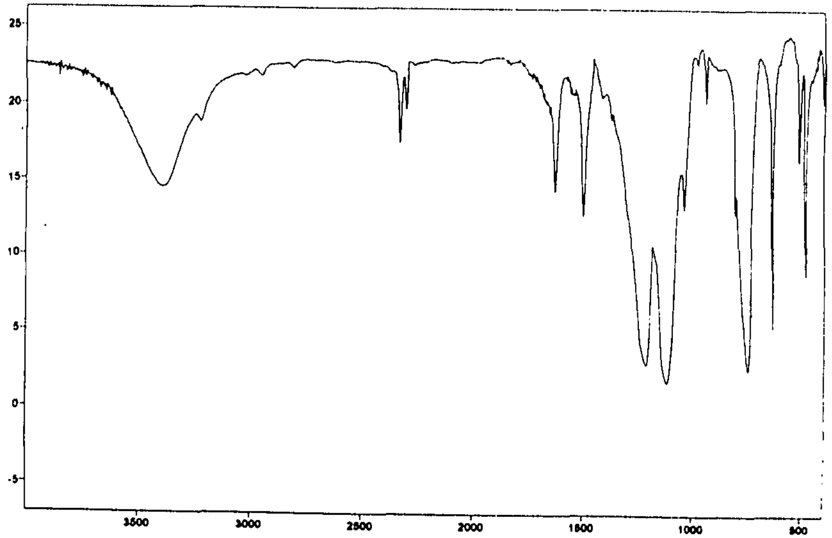
KG Ag

Spectrum No. 23



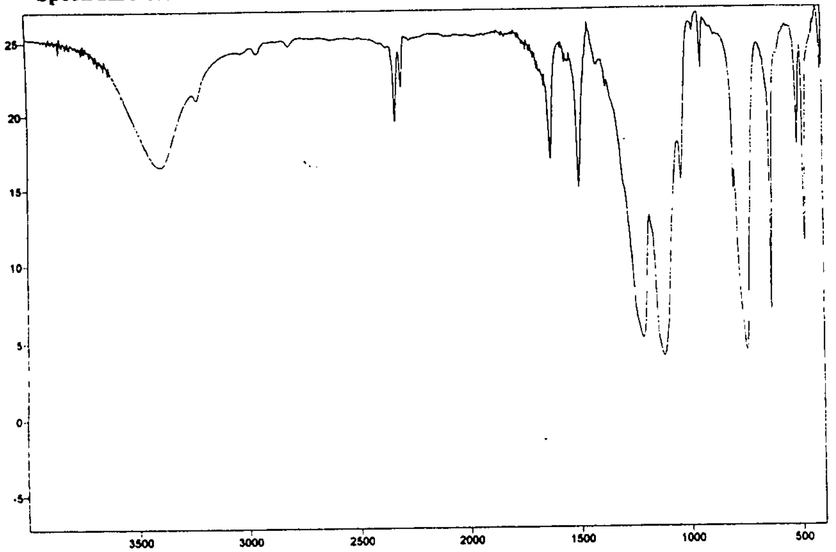
mittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

Spectrum No. 24



Transmittance / Wavenumber (cm-1)
Number of Scans= 4 Apodization= Strong

Spectrum No. 25



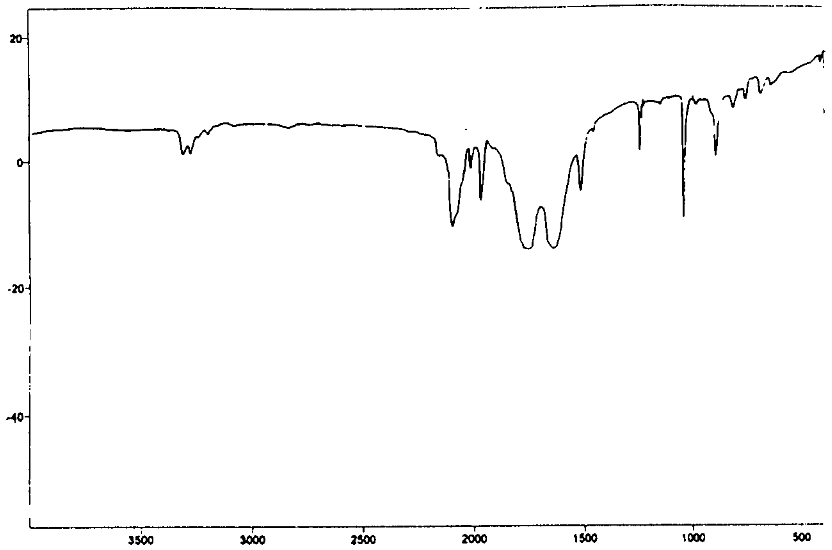
nittance / Wavenumber (cm-1)

2 : KG

Number of Scans= 4 Apodization= Strong

12/01/96 15:38 Res=4 cm-1

Spectrum No. 26



Arbitrary Y / Wavenumber (cm-1)

File # 1 : PC104

Number of Scans= 4 Apodization= Strong

23/08/96 10:11 Res=4 cm-1

Appendix Four

Requirements for the Board of Studies

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

i. all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

ii. lectures organised by Durham University Chemical Society;

iii. details of the postgraduate induction course; and

iv. all research conferences attended and papers presented by the author during the period when research for the thesis was carried out.

Colloquia, Lectures and Seminars From Invited Speakers

1993-1996

September 13 Prof. Dr. A. D. Schlüter, Freie Universität Berlin, Germany*
Synthesis and Characterisation of Molecular Rods and Ribbons.

September 13 Prof. K. J. Wynne, Office of Naval Research, Washington, U.S.A.
Polymer Surface Design for Minimal Adhesion

September 14 Prof. J. M. DeSimone, University of North Carolina, Chapel Hill, U.S.A.
Homogeneous and Heterogeneous Polymerisations in Enviromentally Responsible Carbon Dioxide.

September 28 Prof. H. Ila., North Eastern University, India*
Synthetic Strategies for Cyclopentanoids via OxoKetene Dithiacetals.

October 4 Prof. F. J. Feher†, University of California at Irvine
Bridging the Gap between Surfaces and Solution with Sessilquioxanes.

October 14 Dr. P. Hubberstey, University of Nottingham*
Alkali Metals: Alchemist's Nightmare, Biochemist's Puzzle and Technologist's Dream.

October 20 Dr. P. Quayle†, Unversity of Manchester*
Aspects of Aqueous Romp Chemistry.

October 23 Prof. R. Adams†, University of S. Carolina*
The Chemistry of Metal Carbonyl Cluster Complexes Containing Platinum and Iron, Ruthenium or Osmium and the Development of a Cluster Based Alkyne Hydrogenating Catalyst.

October 27 Dr. R. A. L. Jones†, Cavendish Laboratory*
'Perambulating Polymers'.

November 10 Prof. M. N. R. Ashfold†, University of Bristol
High-Resolution Photofragment Translational Spectroscopy: A New Way to Watch Photodissociation.

November 17	Dr. A. Parker†, Laser Support Facility *Applications of Time Resolved Resonance Raman Spectroscopy to Chemical and Biochemical Problems.*
November 24	Dr. P. G. Bruce†, University of St. Andrews* *Synthesis and Applications of Inorganic Materials.*
December 1	Prof. M. A. McKervey†, Queens University, Belfast* *Functionlised Calixerenes.*
December 8	Prof. O. Meth-Cohen, Sunderland University* *Friedel's Folly Revisited.*
December 16	Prof. R. F. Hudson, University of Kent *Close Encounters of the Second Kind.*

1994

January 26	Prof. J. Evans†, University of Southhampton* *Shining Light on Catalysts.*
February 2	Dr. A. Masters†, University of Manchester* *Modelling Water Without Using Pair Potentials.*
February 9	Prof. D. Young†, University of Sussex *Chemical and Biological Studies on the Coenzyme Tetrahydrofolic Acid.*
February 16	Prof. K. H. Theopold, University of Delaware, U.S.A *Paramagnetic Chromium Alkyls: Synthesis and Reactivity.*
February 23	Prof. P. M. Maitlis†, University of Sheffield* *Why Rodium in Homogenous Catalysis.*
March 2	Dr. C. Hunter†, University of Sheffield *Non Covalent Interactions between Aromatic Molecules.*
March 9	Prof. F. Wilkinson, Loughborough University of Technology *Nanosecond and Picosecond Laser Flash Photolysis.*

March 10	Prof. S.V. Ley, University of Cambridge* *New Methods for Organic Synthesis.*
March 25	Dr. J. Dilworth, University of Essex *Technetium and Rhenium Compounds with Applications as Imaging Agents.*
April 28	Prof. R. J. Gillespie, McMaster University, Canada* *The Molecular Structure of some Metal Fluorides and OxoFluorides: Apparent Exceptions to the VSEPR Model.*
May 12	Prof. D. A. Humphreys, McMaster University, Canada *Bringing Knowledge to Life*
October 5	Prof. N. L. Owen, Brigham Young University, Utah, USA *Determining Molecular Structure - the INADEQUATE NMR way*
October 19	Prof. N. Bartlett, University of California* *Some Aspects of Ag(II) and Ag(III) Chemistry*
November 2	Dr P. G. Edwards, University of Wales, Cardiff* *The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands*
November 3	Prof. B. F. G. Johnson, Edinburgh University* *Arene - Metal Clusters - DUCS Lecture*
November 9	Dr J. P. S. Badyal, University of Durham* *Chemistry at Surfaces, A Demonstration Lecture*
November 9	Dr G. Hogarth, University College, London *New Vistas in Metal Imido Chemistry*
November 10	Dr M. Block, Zeneca Pharmaceuticals, Macclesfield* *Large Scale Manufacture of the Thromboxane Antagonist Synthase Inhibitor ZD 1542*
November 16	Prof. M. Page, University of Huddersfield* *Four Membered Rings and b-Lactamase*

November 23	Dr J. M. J. Williams, University of Loughborough* *New Approaches to Asymmetric Catalysis*
December 7	Prof. D. Briggs, ICI and University of Durham *Surface Mass Spectrometry*

1995

January 11	Prof. P. Parsons, University of Reading* *Applications of Tandem Reactions in Organic Synthesis*
January 18	Dr G. Rumbles, Imperial College, London *Real or Imaginary 3rd Order non-Linear Optical Materials*
January 25	Dr D. A. Roberts, Zeneca Pharmaceuticals* *The Design and Synthesis of Inhibitors of the Renin-Angiotensin System*
February 1	Dr T. Cosgrove, Bristol University *Polymers do it at Interfaces*
February 8	Dr D. O'Hare, Oxford University* *Synthesis and Solid State Properties of Poly-, Oligo- and Multidecker Metallocenes*
February 22	Prof. E. Schaumann, University of Clausthal* *Silicon and Sulphur Mediated Ring-opening Reactions of Epoxide*
March 1	Dr M. Rosseinsky, Oxford University* *Fullerene Intercalation Chemistry*
October 11	Prof. P. Lugar, Frei Univ Berlin, FRG* *Low Temperature Crystallography*
October 13	Prof. R. Schmultzer, Univ Braunschweig, FRG* *Calixarene-Phosphorus Chemistry: A New Dimension in Phosphorus Chemistry*

October 18 Prof. A. Alexakis, Univ. Pierre et Marie Curie, Paris*
Synthetic and Analytical Uses of Chiral Diamines

October 25 Dr.D.Martin Davies, University of Northumbria*
Chemical reactions in organised systems.

November 1 Prof. W. Motherwell, UCL London*
New Reactions for Organic Synthesis

November 3 Dr B. Langlois, University Claude Bernard-Lyon*
Radical Anionic and Psuedo Cationic Trifluoromethylation

November 8 Dr. D. Craig, Imperial College, London*
New Stategies for the Assembly of Heterocyclic Systems

November 15 Dr Andrea Sella, UCL, London
Chemistry of Lanthanides with Polypyrazoylborate Ligands

November 17 Prof. David Bergbreiter, Texas A&M, USA
Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers

November 22 Prof. I Soutar, Lancaster University
A Water of Glass? Luminescence Studies of Water-Soluble Polymers.

November 29 Prof. Dennis Tuck, University of Windsor, Ontario, Canada*
New Indium Coordination Chemistry

December 8 Professor M.T. Reetz, Max Planck Institut, Mulheim
Perkin Regional Meeting

1996

January 10 Dr Bill Henderson, Waikato University, NZ*
Electrospray Mass Spectrometry - a new sporting technique

January 17 Prof. J. W. Emsley , Southampton University
Liquid Crystals: More than Meets the Eye

January 24	Dr Alan Armstrong, Nottingham Univesity *Alkene Oxidation and Natural Product Synthesis*
January 31	Dr J. Penfold, Rutherford Appleton Laboratory, *Soft Soap and Surfaces*
February 7	Dr R.B. Moody, Exeter University* *Nitrosations, Nitrations and Oxidations with Nitrous Acid*
February 12	Dr Paul Pringle, University of Bristol *Catalytic Self-Replication of Phosphines on Platinum(O)*
February 14	Dr J. Rohr, Univ Gottingen, FRG* *Goals and Aspects of Biosynthetic Studies on Low Molecular Weight Natural Products*
February 21	Dr C R Pulham , Univ. Edinburgh *Heavy Metal Hydrides - an exploration of the chemistry of stannanes and plumbanes*
February 28	Prof. E. W. Randall, Queen Mary & Westfield College *New Perspectives in NMR Imaging*
March 6	Dr Richard Whitby, Univ of Southampton *New approaches to chiral catalysts: Induction of planar and metal centred asymmetry*
March 7	Dr D.S. Wright, University of Cambridge* *Synthetic Applications of* Me_2N*-p-Block Metal Reagents*
March 12	RSC Endowed Lecture - Prof. V. Balzani, Univ of Bologna *Supramolecular Photochemistry*
March 13	Prof. Dave Garner, Manchester University* *Mushrooming in Chemistry*
April 30	Dr L.D.Pettit, Chairman, IUPAC Commission of Equilibrium Data *pH-metric studies using very small quantities of uncertain purity*

† Invited specially for the graduate training programme.

* Those attended,

First Year Induction Courses

This course consists of a series of one hour lectures on the services available in the department.

Departmental Organisation - Dr. E.J.F. Ross
Safety Matters - Dr. G.M. Brooke
Electrical Appliances - Mr. B.T. Barker
Chromatography and Microanalysis - Mr. T.F. Holmes
Absorptiometry and Inorganic Analysis - Mr. R. Coult
Library Facilities - Mr. R.B. Woodward
Mass Spectroscopy - Dr. M. Jones
Nuclear Magnetic Resonance Spectroscopy - Dr. R.S. Matthews
Glass-blowing Techniques - Mr. R. Hart and Mr. G. Haswell

Research Conferences Attended

September 1995	11th European Symposium on Fluorine Chemistry Bled, Slovenia.
November 1995	Irvine Review Lectures University of St. Andrews.

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