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UNIVERSITY OF DURHAM

A THESIS

ENTITLED

APPROACHES TO NEW FLUORIDE ION SOURCES

Submitted by

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(GRADUATE SOCIETY)

A candidate for the degree of Master of Science

Department of Chemistry

1988



17 JUL 1989

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Finally I would like to thank Dr. S. Korn, my industrial supervisor, and I.C.I. for providing my maintainance grant.

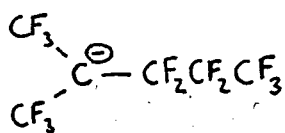
MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1987 and October 1988. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

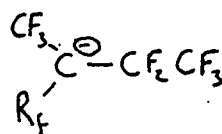
ABSTRACT

Fluoride ion sources have been surveyed and perfluoroalkyl anions and hindered amine/HF adducts prepared and investigated as reagents.

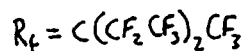
The perfluoroalkyl anions (I) and (II) have been used in an attempt to fluorinate various organic compounds such as alkyl halides, alkyl tosylates, aryl halides and acetyl chloride.



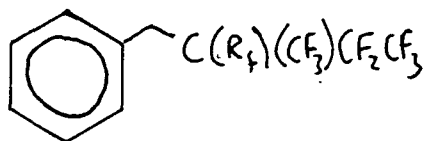
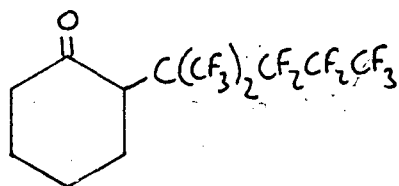
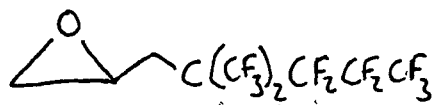
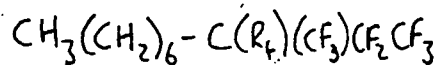
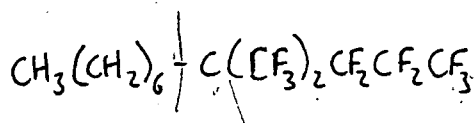
I



II



The following new compounds have been synthesised and identified by glc-mass spec and, where possible, ^{19}F nmr.



These arose from reaction of the substrate with the perfluoroalkyl anion rather than with F^- .

Preliminary work on hindered amine bases, particularly proton sponge and tri-n-octylamine, with HF was undertaken, these being studied as possible soluble fluoride ion sources. Solid adducts were obtained in most cases from ether solutions and they were shown to behave as fluoride ion sources under various conditions.

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CHAPTER ONE

1 GENERAL INTRODUCTION

It has only been since the last World War that extensive research has been carried out on the formation of organofluorine compounds. These compounds do not occur naturally but have found a wide range of applications due to the unusual properties they acquire on the introduction of fluorine ^{1,2,3}.

Table 1 summarises a number of the applications of highly fluorinated compounds and gives an example of each.

All the compounds in this category have high thermal and chemical stability and, importantly, low toxicity.

Table 2 summarises the low fluorinated compounds. These, in contrast to the highly fluorinated compounds show pronounced biological activity due, in part, to the fact ^{that} the compounds bear a certain similarity to natural products (e.g. nucleobases, steroids and amino acids).

Table 1 Highly fluorinated compounds

APPLICATION	COMPOUND
Refrigerants	Chlorofluorocarbons
Aerosol propellants	e.g. CF_2Cl_2
Fire Extinguishers	Bromofluoroalkanes e.g. CF_3Br



APPLICATION	COMPOUND
Inhalation Anaesthetics	CF ₃ CHClBr (halothane)
Surfactants	F ₁₅ C ₇ SO ₃ H
Polymers (e.g. lubricants)	Polytetrafluoroethylene P.T.F.E.
Blood substitutes	Perfluorinated cycloalkanes

Table 2 Low fluorinated compounds

APPLICATION	COMPOUND
Pharmaceuticals	$ \begin{array}{c} \text{CH}_2\text{F} \\ \\ \text{H}_2\text{N}-\text{C}-\text{D} \\ \\ \text{COOH} \end{array} $ 'DFA' a cell wall active antibiotic
Plant protection	$ \begin{array}{c} \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{F}_3\text{C} \quad \text{S} \quad \text{N}-\text{CONHCH}_3 \\ \\ \text{CH}_3 \end{array} $ Thiazafluron herbicide

Because of this wide range of applications, the use of the most readily available source of fluorine, the fluoride ion, is a very attractive (opportunity)

possibility

CHAPTER TWO

2 A SURVEY OF FLUORIDE ION SOURCES

2.1 Introduction

In this chapter it is intended to survey sources of fluoride ion currently employed and give examples of both their advantages and disadvantages in particular reactions. There are a number of major books and reviews covering aspects of fluoride ion chemistry⁴⁻⁶. It is first useful to look at the characteristics of the fluoride ion and its modes of reaction before looking at specific sources.

a) The Fluoride Ion

A look at the physical data of the series of halide ions (Table 1) shows the uniqueness of the fluoride ion.

Table 1

Halide	Ionic radius Å	Heat of hydration kJ mol ⁻¹	Polarizability Å ³
F ⁻	1.36	517	0.86
Cl ⁻	1.81	374	3.05
Br ⁻	1.96	340	4.17
I ⁻	2.16	302	6.28

It can be seen that the volume-charge density of fluorine is significantly larger than for the other halide ions. A direct consequence of this is that the fluoride ion forms stronger hydrogen bonds than the other ions (reflected also in the high heat of hydration). This has important consequences when it comes to the type of reaction in which the fluoride ion can be used but it leads to difficulties such as poor nucleophilicity, and it is these which have provided the driving force behind the search for newer and better sources of fluoride ion.

The fluoride ion has been observed to react in a number of ways. These can be divided into three categories:

1. C-F bond formation (e.g. halogen exchange)
2. As a base (e.g. Michael addition)
3. C-C bond formation (e.g. oligomerisation of fluorinated alkenes)

The categories will be discussed in more detail in the relevant sections but there are some general observations that have a bearing on the way fluoride ion can be used.

b) Bond energies

Both the carbon-fluorine and hydrogen-fluorine bond strengths are much larger than the corresponding bonds to other halides:

Bond energies/ kJ mol^{-1}

	F	Cl	Br	I	O	N
C-X	536	328	285	218	358*	305*
H-X	569	432	366	299	428	314

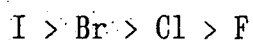
* single bonds

It can be seen that the strength of the relevant fluorine bond is advantageous in both its reactions as a nucleophile (with the higher energy of the C-F bond providing a driving force) and as a base.

c) Solvent

The strength of the H-F bond and the heat of hydration of the fluoride ion means that their use in water or other protic material diminishes the reactivity of the ion.

The nucleophilic strength of halide ions in aqueous solution run in the order:



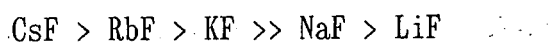
This is due mainly to the hydration sphere around the smaller fluoride ion.

In base reactions the same problem applies with water masking the fluoride ion (but not reacting with it as with other bases) and so reducing reactivity.

The solution to the problem of solvation of the fluoride ion is to use a polar aprotic solvent such as MeCN, DMF, diglyme, sulfolane, etc. However the solubility of the alkali metal fluorides, which are the most easily accessible fluoride ion source, is extremely low. It is the search for both new soluble fluoride ion sources, and ways of improving the solubility of existing sources, that has provided the stimulus for much of the research reported here.

2.2 ALKALI METAL FLUORIDES

Alkali metal fluorides are still the most commonly used source of fluoride ion and as such have found a wide application in organic synthesis. This is due to the fact they have the advantages of being easily dried, easy to handle and they have high thermal stability. However, they have the drawbacks of being very insoluble in all but a few protic solvents and are hygroscopic, thus necessitating rigorously anhydrous reaction conditions. Potassium fluoride has found the widest application because it is both less expensive and less hygroscopic than the more reactive caesium fluoride. The activity of the alkali metal fluorides is generally accepted to be:



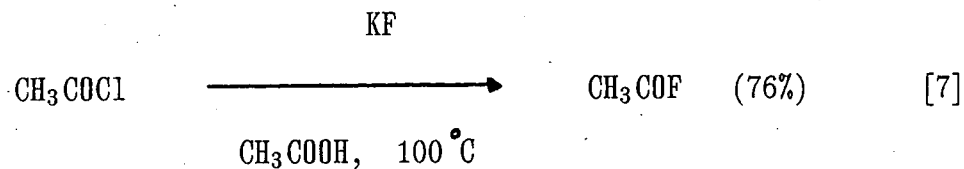
But a balance must be drawn between reactivity and cost. A closer look at some of the reactions shows the areas in which alkali metal fluorides are particularly useful and where improvements have necessitated the search for better fluoride ion sources.

a) Halogen Exchange

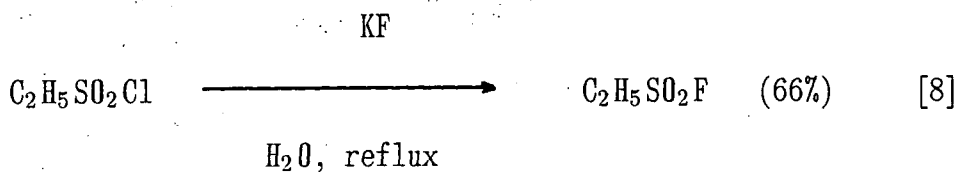
This area is covered in depth in a number of major books and reviews ^{4,6}. Potassium fluoride has proved the most useful reagent for substituting fluorine for a halogen or oxygen-bonded function. It has been found that potassium fluoride substitutes

fluorine for halogen in the following classes of compound:

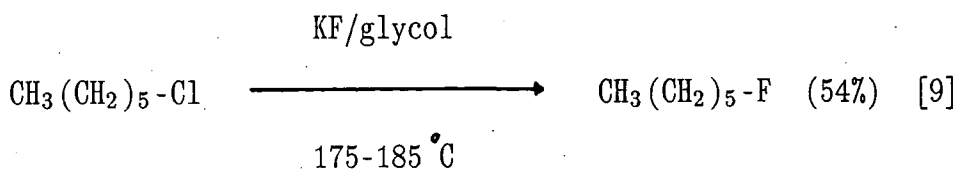
1. Carboxylic acid halides



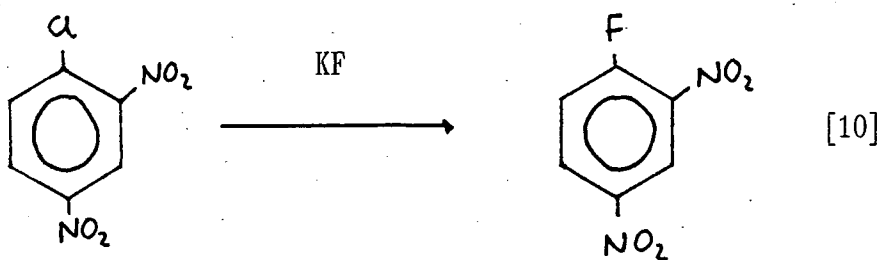
2. Aryl- and alkyl-sulfonyl halides.



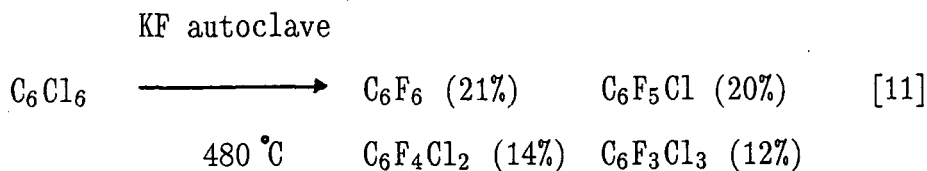
3. Primary alkyl halides



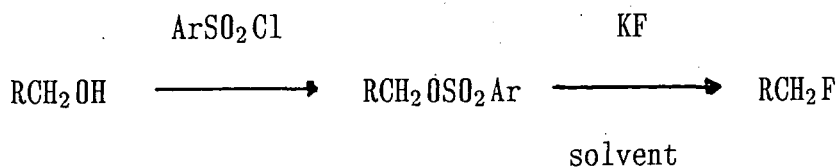
4. Aromatic halides substituted in ortho or para positions by an electron-withdrawing group, especially nitro.



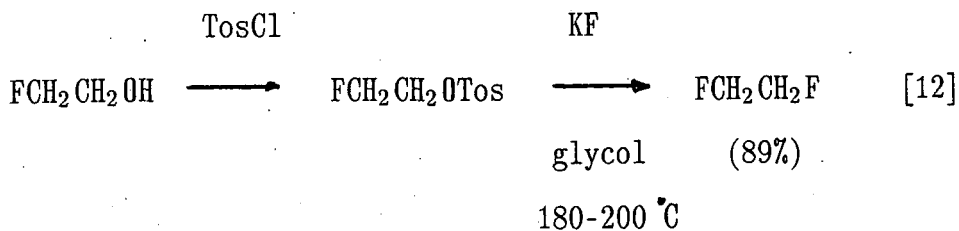
5. Perchlorinated aromatic compounds, especially hexachlorobenzene.



Lower temperatures have been achieved using suitable aprotic, dipolar solvents, however the reactions are probably not simple solution reactions but rely on the presence of the surface of the excess solid. In conjunction with the lower temperatures obtainable the use of *p*-toluenesulfonate and methylsulfonate ester groups have been used in the sequence:



This avoids the relatively vigorous conditions required for the direct preparation of fluorides. For example:



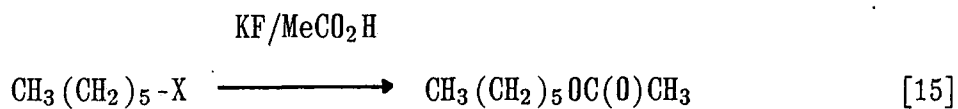
This use of the alkali metal fluorides as fluorinating agents has been matched by their use as bases.

b) Base Reactions

The first examples of fluoride ion being used as a base¹³ utilised potassium fluoride and until about 1970 this was almost entirely the only source. The strong hydrogen bonding of the fluoride ion and the hygroscopicity of potassium fluoride have led to it being especially useful in certain classes of base reaction. An excellent review⁵ covers this aspect of fluoride ion chemistry in detail.

(i) Esterification

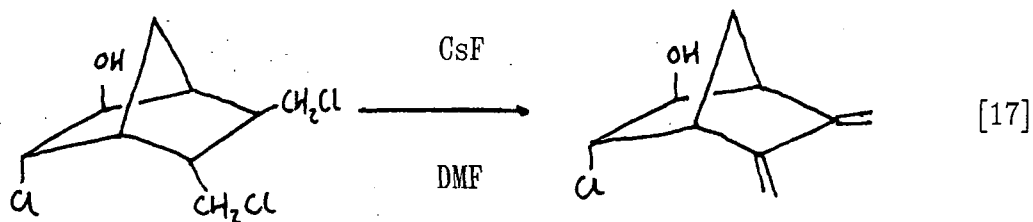
The form of esterification particularly promoted by alkali metal fluorides is that of carboxylic acids with alkyl halides. This relies on the fact potassium fluoride (as well as CsF and RbF) are very soluble in liquid carboxylic acids¹⁴, so that reactions may be carried out using the reactant acid as bulk solvent. The employment of KF in these reactions lead to good yields of esters, free from by-products^{15,16}.



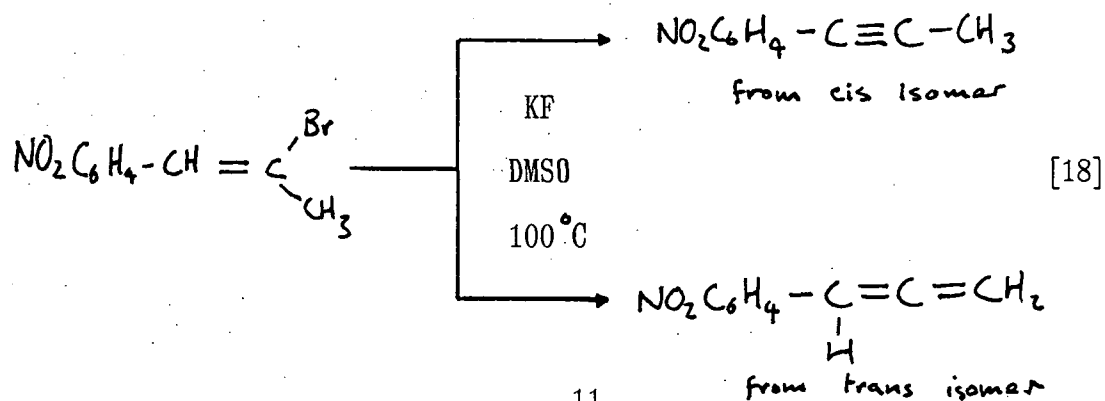
X=	Cl	Br	I
%	85	100	67

(ii) Dehydrohalogenation

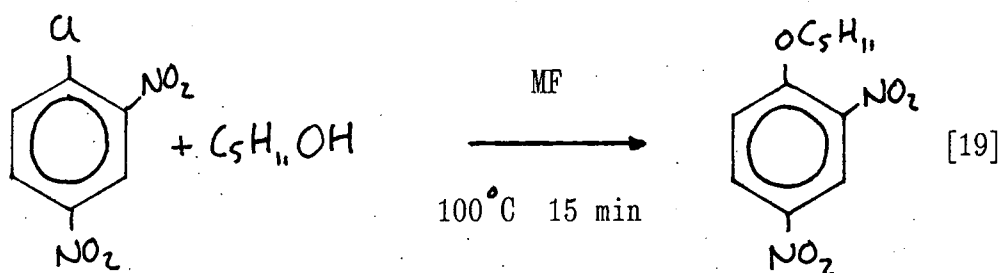
The majority of research published reports a tetraalkylammonium fluoride (section 2.4) as the elimination-promoting base. There is also a steady number of reported examples using alkali metal fluorides:



Also a more straight forward application of solid KF in aprotic solvent involves the cis and trans isomers of (I):



An interesting reaction involving the formation of ethers revealed the relative reactivities of the alkali metal fluorides:



M	Cs	Rb	K
%	85	68	4

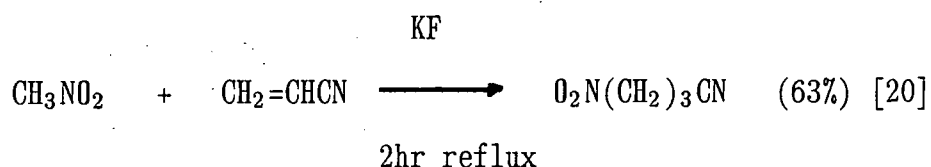
(iii) Michael and Knoevanagel

The use of fluorides in these reactions have a number of advantages:

1. Special preparation of a strong base is not required;
2. Separation of the catalyst is easy;
3. Reactions can be accomplished when other strong bases are inert.

Again potassium fluoride has received the most attention as a source. However, recently the use of tetraalkylammonium

fluorides (section 2.4) has increased. In the reaction below it can be seen that there is a balance to be drawn between reactivity and solubility:



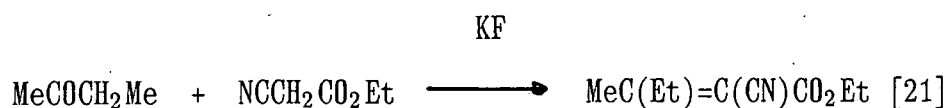
The effectiveness of various solvents was shown to be:

95% EtOH > 50% aqueous EtOH > Me₂CHOH > Me₃COH > dioxane-water.

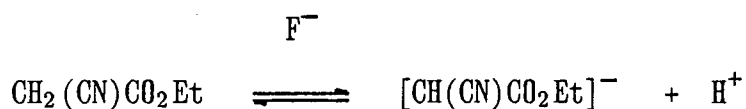
Pure dioxane gave no reaction. The problem of insolubility of the alkali metal fluorides can be solved in this reaction but only by a loss in reactivity. The search for new soluble sources, or better solvating agents is dealt with later.

The Knoevanagel reaction, in which water is eliminated from the intermediate aldol product has proved susceptible to catalysis by the ionic fluorides, aided by their high affinity for water.

Aoyama, Sakuri and co-workers have demonstrated the use of KF as catalyst (in ethanol or di-ethyl ether) for the reaction:



Rand and co-workers have reported a kinetic study on the reaction of cyclohexanone with ethyl cyanoacetate in ethanol²². They suggested a mechanism in which the fluoride ion promotes the dissociation of the methylene compound.



The order for the alkali metal fluorides was found to be CsF > RbF > KF and a hydrogen bonded intermediate was postulated. A further example of the basic strength of the fluorides has been the condensation of acetonitrile with cyclic alkanones in the presence of sodium octyl oxide or magnesium neophentyl glycolate to produce nitriles useful as pharmaceuticals ²³.

c) Carbon-carbon bond formation

A number of fluoride ion sources have been used in the attempt to produce oligomers of simple perfluorinated alkenes ²⁴. However caesium fluoride has provided most examples of this type of reaction (Table 1).

As CsF is easier to manipulate than crown ethers (as well as less toxic) it has proved to be the reagent of choice in most of these type of reactions.

Co-oligomerisation also provides a source of complex perfluorinated compounds. An example of this is:

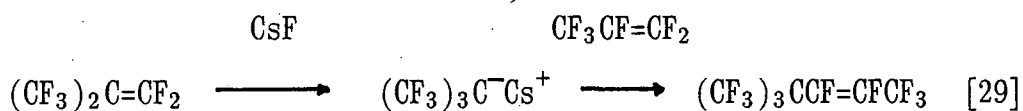
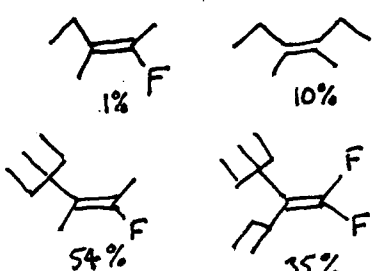
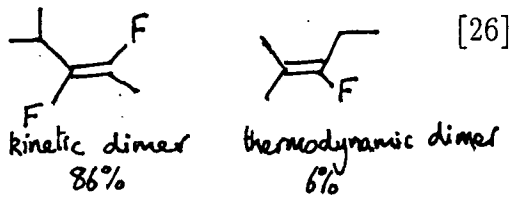

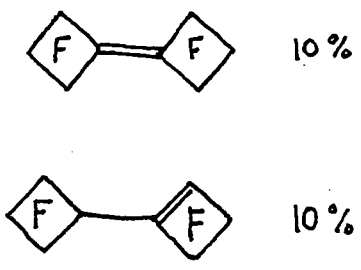
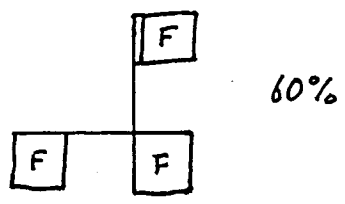

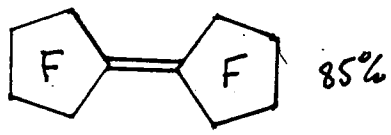


Table 1 *

Alkene	Conditions	Oligomers	Ref
$\text{CF}_2=\text{CF}_2$	CsF/diglyme 100°C/ 20psi	 1% 10%	[25]
$\text{CF}_3\text{CF}=\text{CF}_2$	KF/ CH_3CN room temp	 kinetic dimer 86% thermodynamic dimer 6%	[26]
$\text{CF}_3\text{CF}=\text{CF}_2$	KF/18-C-6 CH_3CN	thermodynamic dimer 89% trimers 7%	
	CsF/DMF Ni tube	 10% 10%	[27]
		 60%	
	CsF/sulfolane 125°C	 85%	[28]

* All unmarked bonds to fluorine

d) Procedures for modifying reactivity - general considerations

It can be seen that the alkali metal fluorides have found a number of applications, and are particularly suited to reactions when higher temperatures or anhydrous conditions are required.

It is the limitations of insolubility and hygroscopicity, however, that have led to the continued search for better fluoride ion sources, both to increase the effectiveness of the alkali metal fluorides and in the search for new fluorinated compounds.

The attempts to improve the reactivity of the alkali metal fluorides have taken two forms

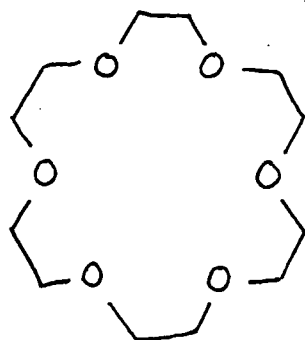
1. Those designed to improve solubility
2. Those aimed at an increased surface area

2.3 Improving the reactivity of alkali metal fluorides

a) Crown-ethers

The use of crown ethers to solubilise alkali metal salts in organic solvents to enhance the reactivity of the anion has been a major area of research since the late 1960's. Among this research has been the study of the alkali metal fluorides, which are particularly limited by their low solubility in non-aqueous solvents.

Liotta and Harris³⁰ were the first to report a solution of the complex of KF and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) (A) in acetonitrile and benzene and coined the term 'naked fluoride' to describe the state of the anion.



(A)

This discovery enabled milder conditions to be utilised for a number of reactions (Table 3).

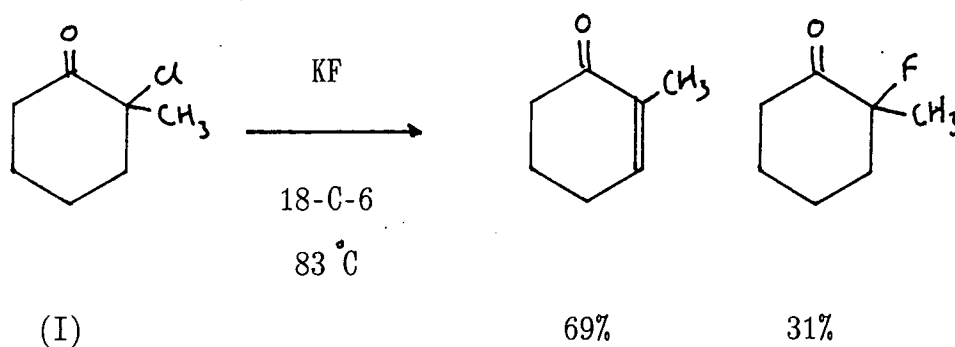
Table 3 Reactions using KF / 18-crown-6 in MeCN

Substrate	Product	Temp/°C	t _{1/2} /hrs*
PhCH ₂ Br	PhCH ₂ F	83	11.5
1-bromooctane	1-fluorooctane	83	11.5
	1-octene (8%)		
CH ₃ COCl	CH ₃ COF	25	5.5

*Time for half the substrate to react.

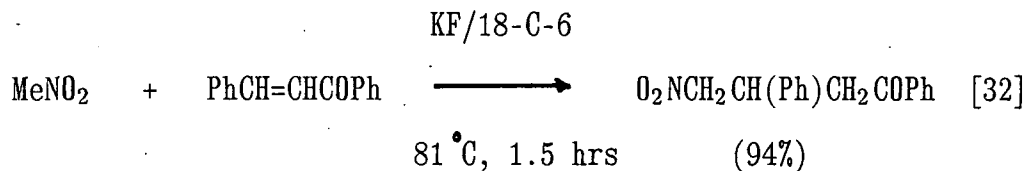
Less than 5% reaction takes place in the absence of the crown ether under identical conditions.

An interesting reaction illustrating the competition between displacement (nucleophilic) and elimination (basic) processes was that with 2-chloro-2-methylcyclohexanone (I):

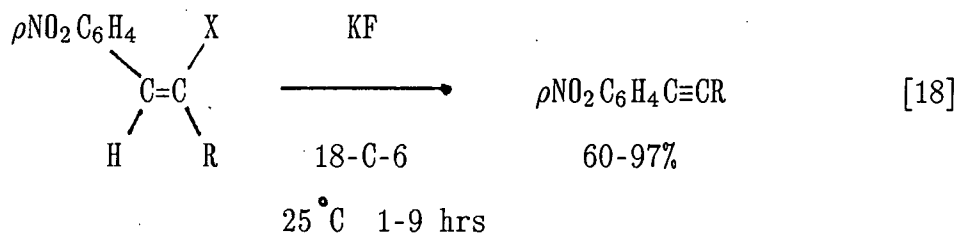


This use as a base has been exploited and shown to be an improvement over existing methods^{18,31}. It has proved especially effective as a base catalyst in Michael reactions. Belsky describes a Michael addition, using KF-crown ether, of

nitromethane to chalcone and acrylonitrile:



The effect of crown ether catalysis is dependent on the nature of the solvent. For instance it is quite dramatic in MeCN but much less important in DMF for the reaction:



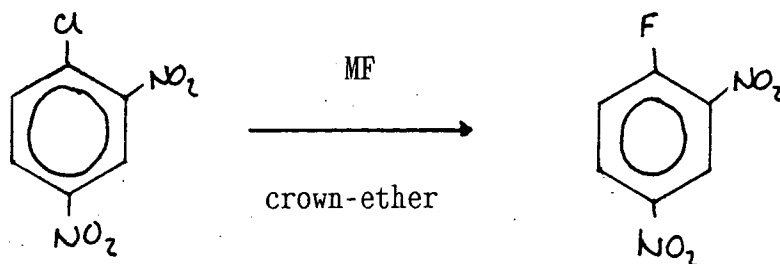
[X = Br, Cl R = H, Me]

KF in MeCN alone after 1 hour at 80 C gave 0% but KF-crown ether under the same conditions gave 53%.

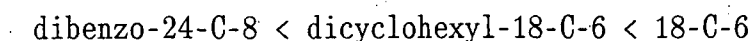
More recent Russian studies have looked systematically at the effect of solvent on the complexes and also when these are immobilised on appropriate support ³³.

Crown ethers have also proved effective in the replacement of chlorine in chloroaromatic compounds ³⁴.

The model reaction:



revealed the effectiveness of the crown ethers in the order:



Thus it can be seen that the crown ethers can be used to improve the rate and efficiency of KF promoted reactions. However the drawbacks are their high toxicity and expense. Nor is their mode of operation clear. The concept of 'naked' fluoride has been called into question by n.m.r. evidence ³⁵ which revealed tight ion pairs in KF-crown ether, leading to a degree of fluoride masking. Nevertheless crown-ethers have been particularly useful in systems in which these milder conditions are necessary (i.e. with steroids ³⁶ and nucleosides ³⁷).

b) Spray-dried KF

Another attempt at increasing the surface area (and hence the reactivity) and at the same time reducing the hygroscopicity of potassium fluoride has been claimed by Ishikawa and co-workers ³⁸.

They prepared spray-dried KF and normal calcine-dried KF which were then exposed to the atmosphere for 1 hour. Whereas the calcine-dried KF had increased its weight by 26% the spray-dried showed only a 3% increase. The physical properties of the two samples showed how they differed:

	particle size (μm)	surface area (m^2/g)
spray-dried	10-50	1.3
calcine-dried	200-300	0.1

The fluorination of organohalogen compounds using the spray-dried sample in acetonitrile showed an increase in reactivity.

Substrate	Temp/ $^{\circ}\text{C}$	Time/hrs	Product	Yield/%
PhCH_2Br	83	10	PhCH_2F	68
2,4-DNCB *	83	10	2,4-DNFB *	58
CH_3COCl	20	3	CH_3COF	83

* 2,4-DNCB is 2,4-dinitrochlorobenzene

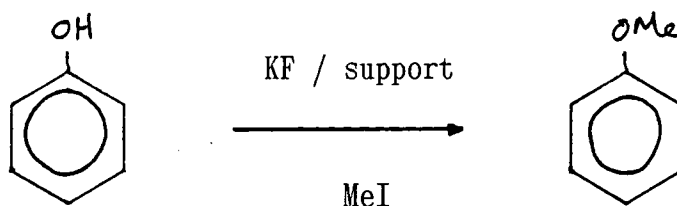
2,4-DNFB is 2,4-dinitrofluorobenzene.

The physical properties suggest that the decreased particle size and hence increased surface area are the main contribution to the increased reactivity. However this does not explain the lack of hygroscopicity and this has yet to be researched and explained.

c) Supported alkali metal fluorides

An alternative to solid alkali metal fluoride is to use inorganic solids to support them. This has been done particularly with KF. The advantage of reactions on solid supports is the possibility of an enhanced reactivity and/or increased selectivity of the reagents as well as manipulative convenience.

Ando and Yamawaki studied hydrogen-bond assisted alkylations to determine the most reactive solid support for KF³⁹. The supports tried included Celite 454 (which they had previously studied⁴⁰), various molecular sieves, alumina and silica gel. The reaction chosen to compare these various supports was:



The results showed that KF-alumina was the reagent of choice, yielding 96% product after 4 hours. Following their conclusions KF on an alumina support has been by far the most used of this kind of reagent.

(i) MF-Alumina

Alumina as an insoluble inorganic support has seen a considerable growth over the last few years ^{41,42}. It has been particularly utilised as a solid base in a variety of reactions such as substitutions, eliminations, additions and condensations. Clark and co-workers have found that a combination of low MF loadings and highly efficient drying procedures give the best reagent for catalytic reactions. For non-catalytic reactions somewhat higher loadings and more moderate drying conditions give the best reagents ⁴³.

The mechanism for the high reactivity of KF-alumina as heterogeneous base for catalytic as well as non-catalytic reactions is still unclear. Weinstock et.al ⁴⁴ have noted the presence of K_3AlF_6 in unspecified samples of KF- Al_2O_3 and suggest that fluoride ion has little or no direct role in the enhanced reactivity claiming this is due to potassium hydroxide and/or aluminates:



Clark and co-workers have shown ⁴¹ by titrimetric analyses that KF-alumina does not owe its basic activity solely to the formation of these compounds. They have proposed three possible mechanisms:

- 1 Dispersion and increased surface area of KF giving co-ordinatively unsaturated F⁻.
- 2 Liberation of strong base during preparation
- 3 Cooperative action of F⁻ and the hydrated alumina surface

(ii) Newer supports

#

More recent attempts at providing support for the alkali metal fluorides include the CaF₂-MF system, where M is K or Cs ^{45,46}. The attempt was made to alleviate the problem associated with KF-alumina, namely the low reactivity as a source of nucleophilic fluorine (due as seen to the surface OH...F⁻ hydrogen bonds). Calcium fluoride provides a surface which is not hydroxylated, yet has a high surface area required for an inert support material. Comparisons with other sources of alkali metal fluoride show this ⁴⁵:

Reagent	surface area (m ² /g)
CaF ₂ -MF	10
Alumina-KF	100-200
normal KF	0.1
spray-dried KF	1.3

The system has been shown to be effective with a range of substrates in fluorination:

Substrate	Reagent	Product	Temp/ °C	Time/h	Yield %
PhCH ₂ Br	KF-CaF ₂	PhCH ₂ F	80	16	68
"	CsF-CaF ₂	"	80	2	97
1-BrC ₁₂ H ₂₅	KF-CaF ₂	1-FC ₁₂ H ₂₅	160	5	84
		dodec-1-ene			16
CH ₃ COCl	KF-CaF ₂	CH ₃ COF	30	0.2	74

This reactivity enhancement can be explained as with the spray-dried KF as being due to the high surface area of the support material. The reactivity can be shown by direct comparison to other systems, using fluorination of PhCH₂Br as the model reaction ⁴⁶:

Fluoride	Yield (%)
KF	0.6
CaF ₂	0.3
KF-CaF ₂	89 *
spray dried KF	68
KF/18-C-6	50

Conditions: reflux for 10 hours in MeCN

* Ref 45 reports this as 68 % however

Another reported support for the alkali metal fluorides is graphite ⁴⁷. The system was used in the attempted fluorination of pentachloropyridine. Although some improvement is observed with KF there is very little with CsF.

The use of solid supports can be seen as a growing area, especially in its applications to base catalysed reactions. The problems still arise however of the balance of loss of reactivity with reduced hygroscopicity and this has kept alive the search for newer sources of fluoride.

d) Phase Transfer Catalysis

The constant problem of the alkali metal fluorides is that of solubility and a number of attempts have been made to improve this. Phase transfer catalysis (PTC) has provided a particularly fruitful area of research and there are many books and patents on the subject ⁴⁸.

There are two areas of PTC, the liquid/solid of which the KF-crown ethers have provided the bulk of information (see earlier); and liquid/liquid PTC in which complex organic cations continuously transfer anionic reagents from an aqueous to a water insoluble organic phase. The anions are then particularly reactive in this phase due to both the poor solvation and the low energy of interaction of the complex cation.

With PTC there is still competition between nucleophilic and basic processes, and catalysts have been found for both applications.

The majority of work on the liquid/liquid systems has been the study of the reaction:



where RX is usually an alkyl or aryl halide.

The catalysis takes place in the presence of quaternary ammonium or phosphonium salts functioning as liquid anion exchangers which transport the reacting anions across the interphase.

The reaction above suffers from several difficulties ⁴⁹:

1. The extraction coefficient ⁵⁰ of the fluoride anion by lipophilic quaternary cations is extremely low. Consequently the selectivity constants ⁵¹ (K_{sel}) of the relevant anion pairs $\text{Cl}^{\text{-}}/\text{F}^{\text{-}}$ or $\text{Br}^{\text{-}}/\text{F}^{\text{-}}$ are also very small. Hence a very large excess of fluoride salt is required to obtain reasonable rates.

2. The high basicity of extracted fluoride ion results in several undesired side reactions ^{5,52}.

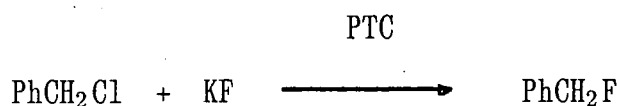
3. Utilisation of polar solvents to improve extractability result in a lower nucleophilicity of the extracted fluoride anion due to solvation and co-extraction of water molecules with the fluoride ion pair ⁵³⁻⁵⁵.

Recent work ⁵⁶ has optimised the ratio of KF to water to provide the most efficient extraction at lower temperatures.

Montanari and co-workers ⁴⁹ stirred primary and secondary allyl

bromides, chlorides or mesylates at 100-160°C with saturated KF solution and catalytic amounts of tributylhexadecylphosphonium bromide $[C_{16}H_{33}P(C_4H_9)_3]^+Br^-$ for 7-16 hours. Primary and benzylic compounds gave fluoride yields of 70-90%. Cyclohexyl chloride and 2-bromooctane gave olefins and alcohols only. 2-octomesylates, however, gave 54% fluoride.

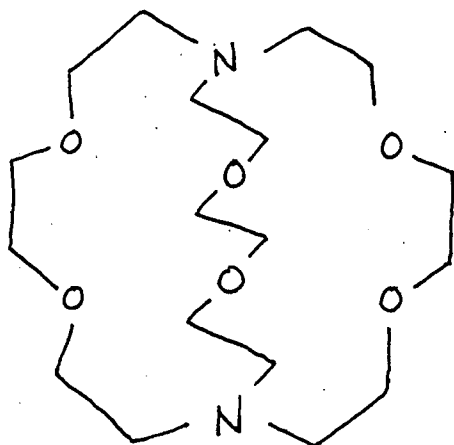
Deliberate attempts to use the PTC system as a base have led to tetra-n-butylammonium chloride-KF-H₂O being used in the Michael addition of nitromethane to chalcone⁵⁷. The reported efficiency of the method (94% recovery after 0.5 hr at 25°C) is excellent. The use of tertiary onium salts has primarily been concerned with liquid/liquid PTC. However they can also be used in the liquid/solid PTC where crown ethers are added as catalysts. Zwan et.al. have discovered that the catalytic capacity of tertiary ammonium salts in aprotic dipolar solvents is equal to or greater than that of crown ethers in comparisons of the properties of PTC in liquid/solid two phase reactions⁵⁸.



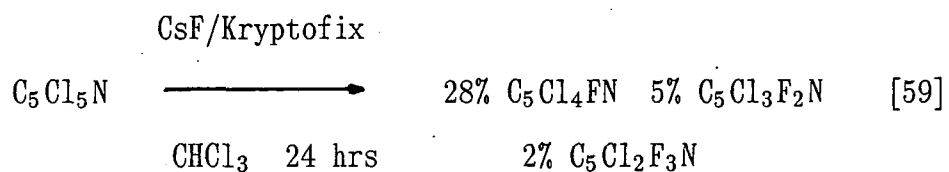
PTC	$t_{1/2}/hrs$ *
Aliquat 336	42
18-crown-6	147
Me ₂ NCH ₂ CH ₂ NMe ₂	107

* Time to react half the PhCH₂Cl

The more recent work in this area has utilised cryptates, such as Kryptofix[2.2.2.]:



This compound has been used with both KF and CsF. An example of the reaction of this reagent at room temperature is:



This area of research has produced new catalysts, the aim being to improve both the extraction of the fluoride ion and enhance the stability of the catalysts.

2.4 Tetraalkylammonium fluorides

Tetraalkylammonium fluorides, of which tetrabutylammonium fluoride (TBAF), tetraethylammonium fluoride (TEAF), butyltrimethylammonium fluoride (BTMAF) and, to a lesser extent, tetramethylammonium fluoride (TMAF) have received the most attention. They are soluble in polar aprotic solvents. However their hygroscopicity is such that, on dissolution, the fluoride will almost certainly be accompanied by varying amounts of water or some other protic material ⁶⁰.

The efficient removal of water from the fluoride is the key to the reactivity and usually requires drying at 30-40 °C for 24 hours under high vacuum. At temperatures over 80 °C, decomposition occurs. Work in this laboratory ⁶¹ has also found a significant loss of material at the more moderate drying conditions, but the fluoride ion strength remains. The tetraalkylammonium fluorides have been used in the full range of fluoride ion reactions.

a) Halogen Exchange

Tetraalkylammonium fluorides have been used in both alkyl ⁶² and aromatic substitutions ⁶³. With these reagents fluorination occurs at room temperature (Table 4).

Table 4 Reactions using TBAF

Substrate	Time/hrs	Product	Yield %
$\text{CH}_2=\text{CHCH}_2\text{Br}$	0.1	$\text{CH}_2=\text{CHCH}_2\text{F}$	85
$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	8	$\text{C}_6\text{H}_5\text{CH}_2\text{F}$	100
$\text{CH}_3(\text{CH}_2)_7\text{Br}$	<1	$\text{CH}_3(\text{CH}_2)_7\text{F}$,	48
		$\text{CH}_2=\text{CH}(\text{CH}_2)_5\text{CH}_3$,	12
		$\text{CH}_3(\text{CH}_2)_7\text{OH}$	40
$\text{CH}_3(\text{CH}_2)_7\text{OTs}$	<1	$\text{CH}_3(\text{CH}_2)_7\text{F}$	98
$\text{C}_6\text{H}_5\text{COCl}$	<1	$\text{C}_6\text{H}_5\text{COF}$	81

As can be seen from the case of 1-bromooctane there are problems of the reactivity of the fluoride ion as a base and also significant reaction to form the alcohol due to traces of water.

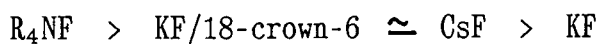
b) Base Reactions

Tetraalkylammonium fluorides have proved particularly useful in base reactions due to their reactivity and solubility, subject to the removal of protic material.

(i) Dehydrohalogenations

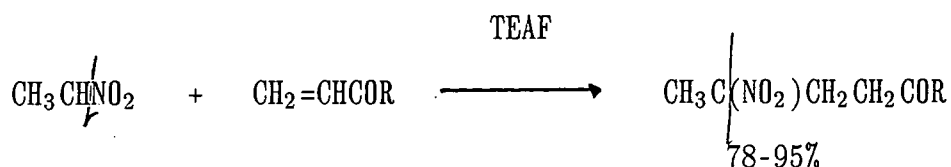
In these reactions the most utilised sources of fluoride ion are the tetraalkylammonium fluorides. Bartsch, in his studies on eliminations from 2-halobutanes, demonstrated TBAF in DMF as an effective reagent for the dehydrohalogenation of 2-bromobutane

and 2-iodobutane under mild conditions ⁶⁴. Ono and co-workers have studied in detail the TEAF-promoted dehydrohalogenations ⁶⁵. The most important result was the effect of bases in promoting the E2 reaction of 2-chloroethylbenzene, where they concluded that TEAF is about 800 times as effective as sodium ethoxide. The evidence available suggests the order of reactivity:



(ii) Michael and Knoevenagel

In this form of reaction, although KF itself has received the most attention, there are examples using tetraalkylammonium fluorides and these provide some of the most impressive fluoride catalysed Michael additions involving nitroalkanes ⁶⁶:



[R= CH₃, OCH₃, OCH₂CH₃]

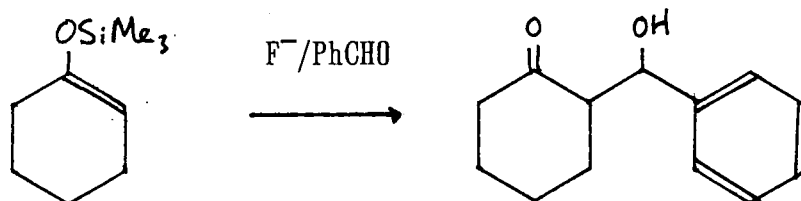
Here TEAF is clearly superior to resins, phosphine or hydrides. Again, the factor in Michael reaction catalysation is the solvation of the catalyst ²⁰ which leads to the higher reactivity of the tetraalkylammonium fluorides and which also allied to their high affinity for water.

c) Carbon-carbon bond formation

With TBAF as the fluoride ion source in the oligomerisation of perfluoroalkenes⁶¹ the problem of decomposition of the fluoride was encountered. However TBAF shows high fluoride ion activity in the oligomerisation of hexafluoropropene.

d) Supported TBAF

As with the alkali metal fluorides there has been an attempt to produce a stable, non-hygroscopic fluoride ion source by carrying TBAF on silica gel⁶⁷. It is easily prepared and is less hygroscopic and more thermally stable than TBAF alone. However it has a lower reactivity than TBAF and a large amount of reagent is required especially where the reaction is non-catalytic. A recent study⁶⁸ of the fluoride catalysed aldol condensation gives an idea of the relative reactivities of some fluoride ion sources:



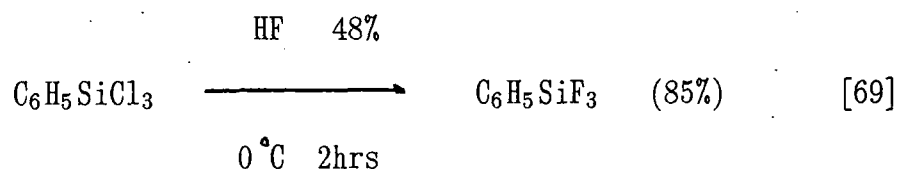
Fluoride	Solvent	Temp/°C	Time/hrs	Yield %
TBAF	THF	-78	3.5	84
CsF	THF/CH ₃ CN	60	45	20
KF	CH ₃ CN	60	18	41
KF/18-C-6	C ₆ H ₆	23	16	50

Summary

Tetraalkylammonium fluorides are generally speaking the most active fluoride ion sources and can usually be used at room temperature. Their low thermal stability precludes their use at temperatures above 80°C.

2.5 Hydrogen Fluoride

Hydrogen fluoride is the most extensively used industrial fluorinating agent, and is the basic chemical of the fluorochemical industry. Fluorination is achieved via addition of HF to double and triple carbon-carbon bonds and as such is not a source of fluoride ions. However there are examples of substitution of halogen by fluorine using HF. The most easily replaceable halogens are those attached to silicon, phosphorus and arsenic atoms:



Only the most reactive organic halides, such as acyclic or benzylic, can be fluorinated using anhydrous hydrogen fluoride alone.



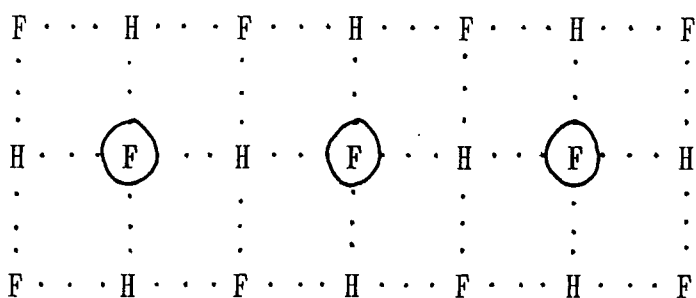
R :	C ₂ H ₅	C ₃ H ₇	C ₄ H ₉
% :	89	91	92

The problems with hydrogen fluoride are its low boiling point (19.6°C), its highly corrosive nature and the need for careful

handling, and the high pressures needed to overcome its lack of reactivity.

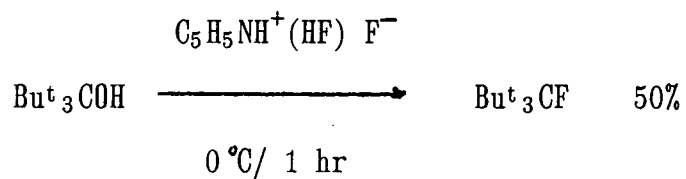
The most important development in the field of hydrogen fluoride as a fluorinating agent has been the use of various N-donor bases to form less volatile complexes of HF. The first reported application of such a reagent was in 1955 by Hirschman ⁷¹. Subsequently, stable solutions of HF have been formed with amines ⁷², amides ⁷³ and alcohols ⁷⁴. However it has been the work of Olah and colleagues ⁷⁵ using a pyridine-hydrogen fluoride system that has proved most effective. Pyridinium hydrogen fluoride is difficult to prepare, as bi- and poly- hydrogen fluoride form preferentially. However the use of the remarkably stable pyridinium poly (hydrogen fluoride) (30% pyridine-70% hydrogen fluoride), known as Olah's reagent, has proved a convenient general purpose fluorinating agent. It remains stable to 55 C and ¹⁹F nmr suggests a poly hydrogen fluoride species to be present in which each fluorine atom is surrounded by four hydrogen atoms:

55°



It has proved extremely useful at atmospheric pressures as a

general purpose fluorinating agent for various additions to alkenes and alkynes. It will also fluorinate tertiary and secondary alcohols at low temperatures, e.g.:



However the relative weakness of the polymeric $\text{F}(\text{HF})^-$ ion as compared to the monomeric fluoride is such that its most extensive use is as a reagent for HF addition.

2.6 Recent developments

a) Ion-exchange Resins

The concept of bonding a reagent to the surface of a solid carrier, and of using it in synthesis reactions, is a major trend in organic synthesis. As we have seen (section 2.3) this has already been utilised in the case of the ionic fluorides. A variation is the conversion of commercial basic ion-exchange resin to the fluoride form. With such resins fluoride displacement reactions are reported to proceed under more moderate conditions than with liquid/liquid or liquid/solid PTC ⁷⁶⁻⁷⁸.

The most commonly used resins are the microreticular Amberlite IRA 900 and Amberlyst A-26 and A-27 (Fig 1), and the macroporous Dowex MSA-1.

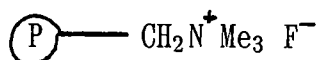


Fig 1

These ion-exchange resins have been utilised in both halogen exchange reactions ⁷⁶ with Amberlyst A-26 and Amberlite IRA 900 (Table 5).

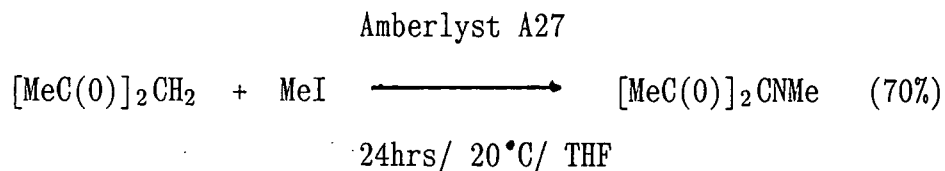
Table 5 Fluorination with resin-F⁻



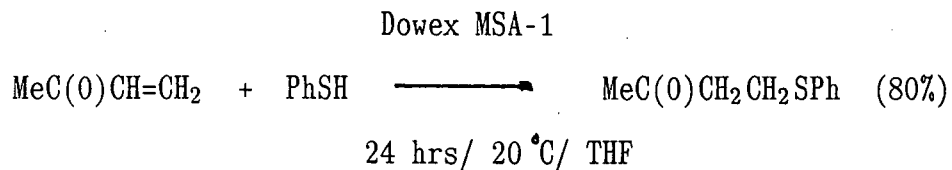
X	Time/hrs	Yield %
-OSO ₂ CH ₃	28	74
-I	28	74
-Br	68	70
-Cl	28	17

The ion-exchanger F-resins have also been used in basic reactions such as C and O alkylations (in which the microreticular are effective) and Michael additions (in which the macroporous Dowex MSA-1 is effective) ⁷⁹, e.g. :

C-alkylation



Michael addition



The advantages of these resins are their ease of preparation, being able to perform the reaction on solid phase, and the fact

they are inexpensive. They do however have low thermal stability and problems arise ensuring complete extraction of the product.

b) Tetraphenylphosphonium Hydrogendifluoride

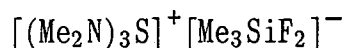
In the course of investigation into phosphorane salts Clark and co-workers came across a new source of fluoride ion⁸⁰. Normally alkali metal hydrogen difluorides only behave as fluoride ion sources to highly activated electrophiles such as 2,4,6,-trinitrochlorobenzene. In the case of tetraphenylphosphonium hydrogendifluoride (Ph_4PHF_2), however, spectroscopic evidence suggests some $\text{P}^+\cdots\text{F}^-$ interaction distorting the normally unreactive HF_2^- and makes fluorination possible:

Substrate	Temp/°C	Time/hrs	Product	Yield/ %
PhCH_2Br	52	2.5	PhCH_2F	100
$\text{CF}_3\text{CF}=\text{CF}_2$	25	ca.0	C_6F_{12}	
$\text{PhCH}=\text{CHCOPh}$	25	1	$\text{CH(Ph)CH}_2\text{COPh}$	100
+ EtNO_2			$\text{CH(NO}_2\text{)Me}$	

The reagent is very soluble in polar aprotic solvents such as acetonitrile and dimethyl sulfoxide. It is easily prepared and dried, and picks up only limited quantities of water from the atmosphere over long periods of time. It also has good thermal stability.

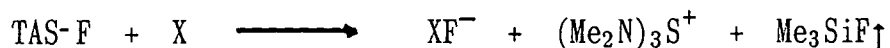
c) Trisdimethylaminosulfonium trimethylsilyldifluoride (TAS-F)

The family of tris(substituted amino) sulfonium salts, including the title compound, were reported in 1976 ⁸¹.



TAS-F has been employed in halogen exchange reactions ⁸², as a catalyst in the group transfer (living) polymerisation of acrylate monomers ⁸³, as a reagent for desilylation reactions ⁸⁴, and recently with unsaturated polyfluoro-compounds ^{61,84}.

The mode of action of TAS-F with a fluoride-receptor molecule (X) is shown below:



The volatile trimethylfluorosilane fragment appears to act as a fluoride ion carrier and is ejected on fluoride donation, and this is thought to account for the increased reactivity of the fluoride ion source by making the reaction effectively irreversible.

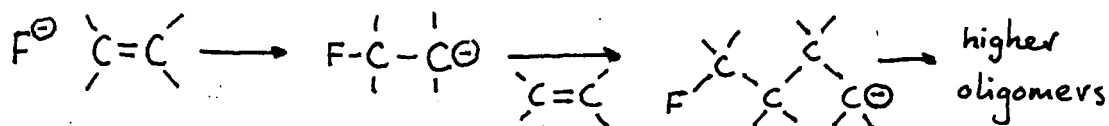
CHAPTER THREE

3 FLUOROCARBANIONS AS SOLUBLE FLUORIDE ION SOURCES

3.1 INTRODUCTION



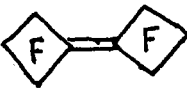
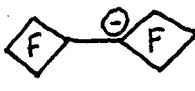
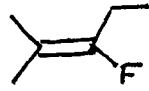

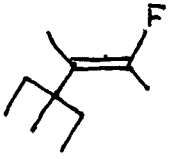

Generation of fluorocarbanions

A number of methods have been employed to produce fluorocarbanions. These include decarboxylations⁸⁵⁻⁸⁷, base induced deprotonations^{88,89} and the use of a nucleophile with a perfluorinated alkene (for example cyanide, azide⁹⁰ and others⁹¹). In this last category it is the fluoride ion which has provided by far the most convenient and popular method for the generation of fluorocarbanions. In particular it is the generation of perfluoroalkyl anions, using fluoride ion sources in reactions of fluorinated alkenes that has produced the most interest⁹². However these are rarely long-lived since they promote oligomerisation of the corresponding alkene :



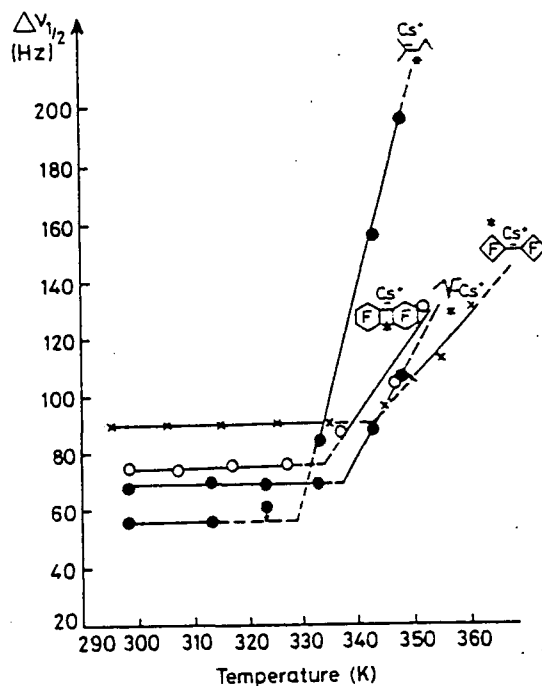
Work in this laboratory has identified a number of stable carbanions, observable on the nmr timescale (Table 1).

Table 1 *

	Alkene	Carbanion	Ref
1			[89]
2			[85]
3			[93]
4			[2A]

By careful monitoring of the line broadening of the ^{19}F nmr signal of fluorine adjacent to the negative carbon centre the temperature at which fluoride ion exchange occurs can be followed (Fig 1).

Figure 1



* All unmarked bonds to fluorine.

As figure 1 shows, at a temperature above 70°C the line broadening of the fluorine increases dramatically indicating rapid exchange occurring on the nmr timescale. It was this property of the carbanion that suggested a possible soluble source of fluoride ion.

Reactions of the fluorocarbanions

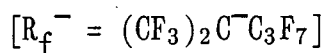
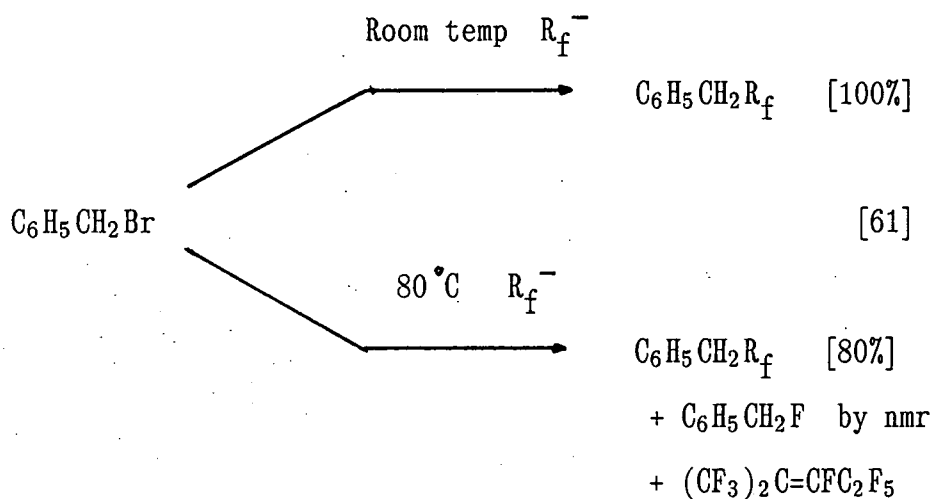
The majority of fluorocarbanions do not have significant lifetimes and therefore must be reacted in the presence of their substrate^{89,94}. However it is the work with the long-lived fluorocarbanions that has provided the stimulus for this research.

The trapping of the carbanions can be achieved by a number of electrophiles using the scheme below:

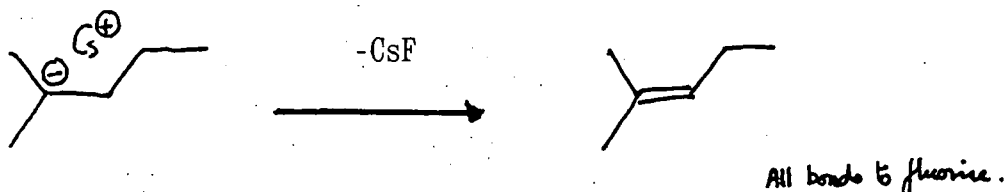


where E is, for example, halogens; alkyl, benzyl and allyl halides.

In the course of the trapping reactions using perfluoro-2-methylpent-2-yl anion (3a) it was observed that both increase in temperature and the hardness of the site of nucleophilic attack influenced the mode of reaction.



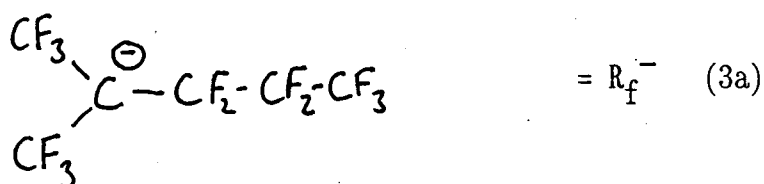
However, repeating these reactions showed only very small amounts of benzyl fluoride and there appears to be no correlation between the amount of dimer recovered and the yield of benzyl fluoride. The reason for this may be the elimination of CsF from the carbanion leaving behind the perfluoroalkene:



With acetyl chloride as the electrophile there was detected acetyl fluoride (this time at room temperature). The suggested reason for this result was the hardness of the electrophilic carbon centre in acetyl chloride. The work reported in this chapter has attempted to improve the reaction of the carbanions as fluoride ion sources. For this reason attempts were made to vary both the leaving group and the temperature of the reaction in order to achieve this.

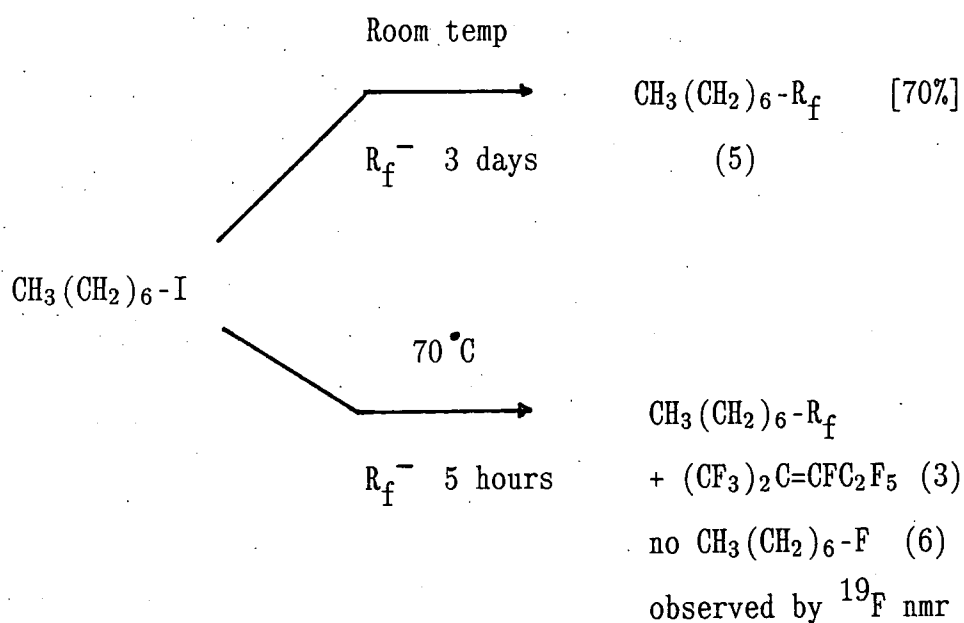
3.2 Investigation into possible reactions of perfluorocarbanions as fluoride ion sources

Perfluoro-2-methylpent-2-yl anion

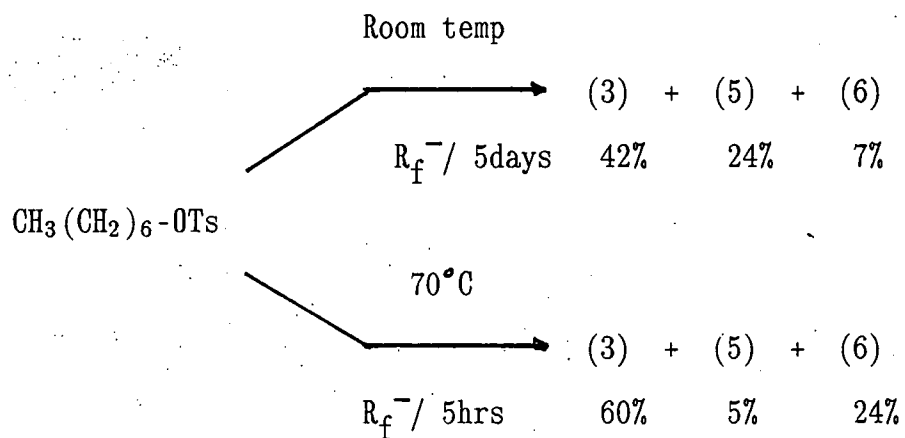


This investigation has attempted to explore further the viability of both (3a) and (4a) as fluoride ion sources.

The attempt to improve the leaving group, and so the hardness of the electrophilic centre was combined with an increase in temperature. This is shown in the following reaction scheme which produced a good yield of 2-heptylperfluoro-2-methylpentane (5) a new fluorinated derivative in which half of the molecule is fluorinated:



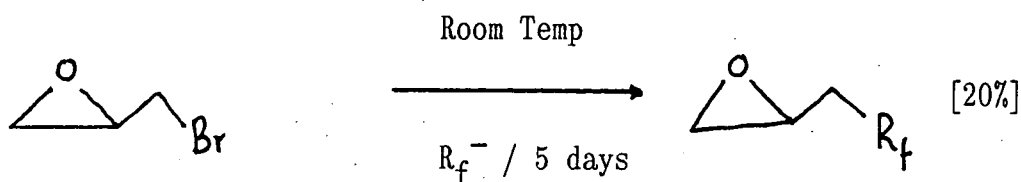
The use of 1-tosylheptane showed a marked improvement in the carbanions ability to act as a fluorinating agent, with 1-fluoroheptane (6) being observed in the volatile materials:



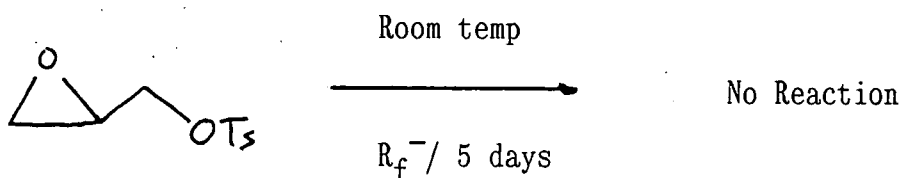
It can be seen that the change in leaving group has produced a small yield of the fluorinated product. The ratio of alkylated to fluorinated product in the tosylate method increases:

Temp/ °C	(5)	:	(6)
20	3.4	:	1
70	1	:	4.8

This approach was also attempted in an effort to synthesise an epoxide derivative but with only partial success:

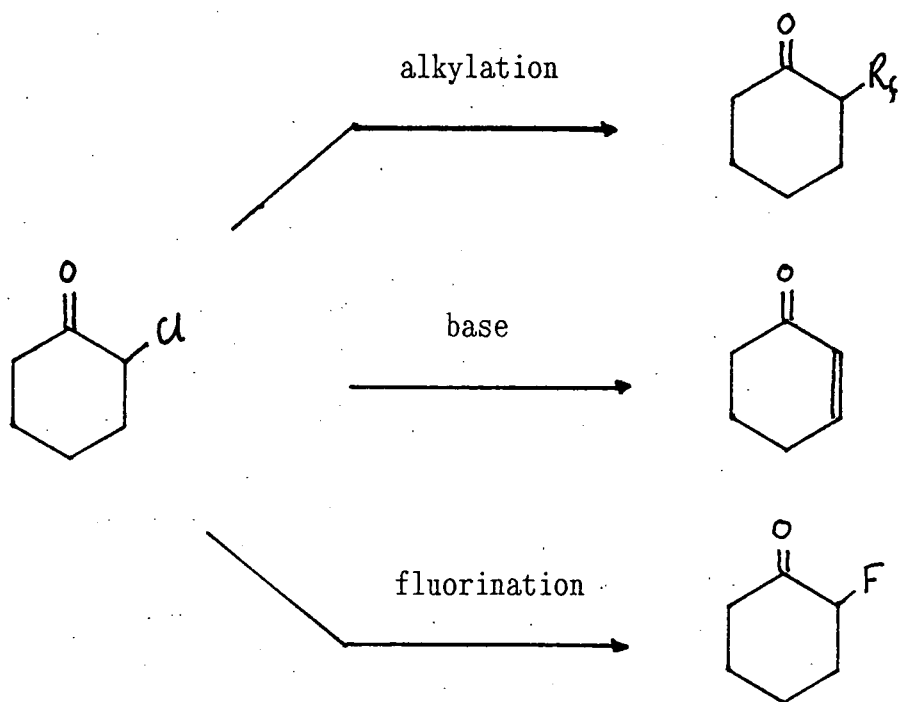


The low yield of the perfluoroalkylated product indicates the weakness of the electrophile compared to benzyl bromide (see previous). However the following reaction surprisingly gave no product:



This suggests that this is an even weaker nucleophile.

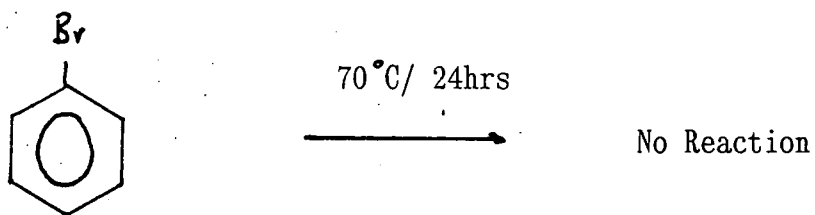
The use of 2-chlorocyclohexanone (7) was tried in order to determine the most likely mode of reaction of the carbanion (3a):

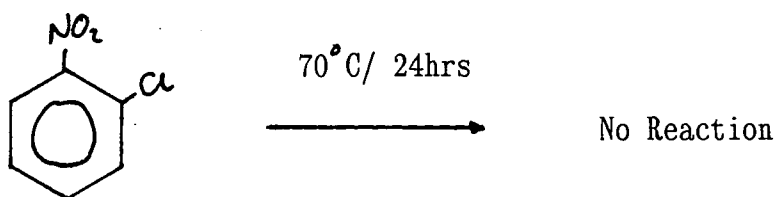


This was attempted at both room temperature and 70°C. At room temperature no reaction occurred. At 70°C there were many side products, but of the volatile material recovered 50% (by glc-mass spec) was the new derivative

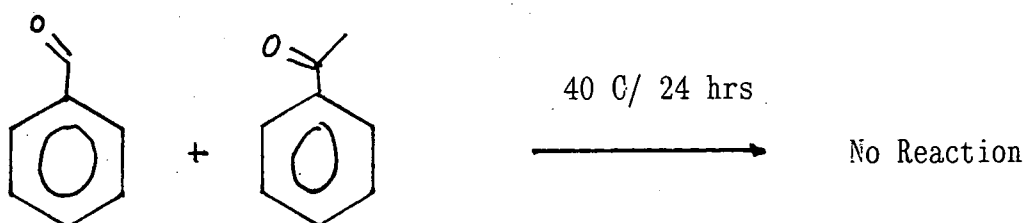
2-perfluoro-2-methylpentylcyclohexanone.

However for bromobenzene and 2-chloronitrobenzene no reaction occurred under the following conditions:

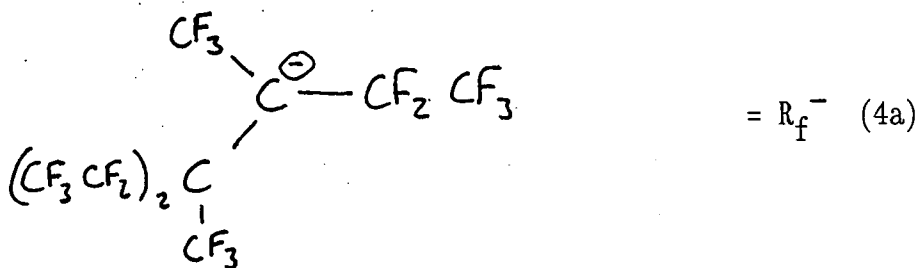




Using the carbanion as a base was considered with acetophenone as the compound to be deprotonated in an aldol condensation reaction with benzaldehyde. However despite several attempts no product was obtained:

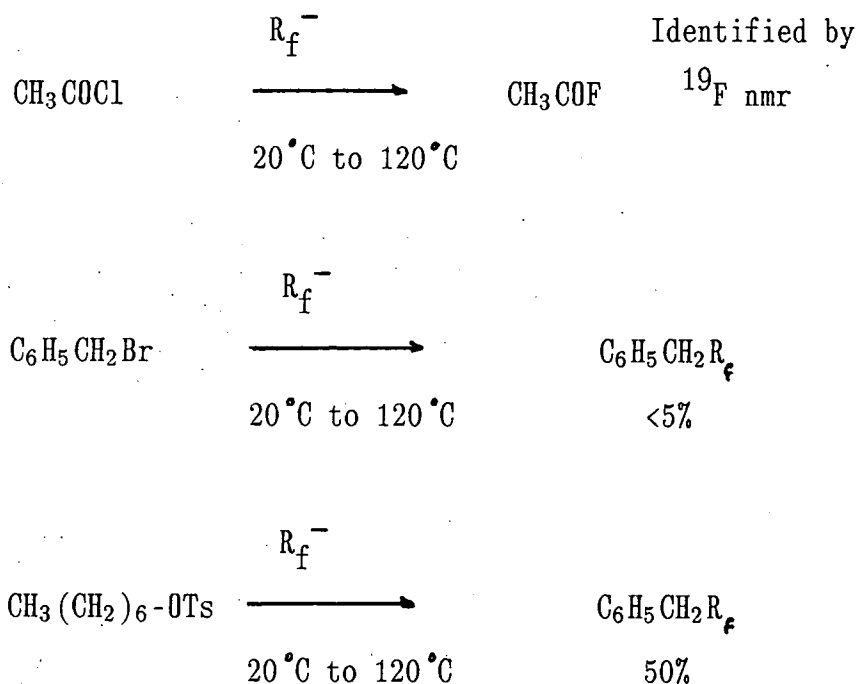


Perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion



In view of the prevalence of alkylation in the reaction of perfluoro-2-methylpent-2-yl anion it was decided to use the more stable (and more difficultly formed) perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion (4a). It was hoped that the more bulky carbanion would prove to be a poor alkylating

agent and instead act as a fluoride ion donor. Previous work in this area had attempted trapping of this anion with several electrophiles⁶¹ without success. This earlier work had been done at room temperature. However using higher temperatures it has now been possible to react the anion and obtain perfluoroalkyl substituted products. The carbanion was heated in the presence of the electrophiles to about the exchange temperature (for this carbanion 120°C). The results show that only in the case of acetyl chloride could any fluorination be detected. Again dissociation of CsF and the alkene predominated with alkylation also occurring.



3.3 Conclusion

The use of these stable perfluoroalkyl anions as sources of soluble fluoride ion appears to be limited in scale. The competing reaction of the carbanion as nucleophile competes with the reaction as fluoride ion donor. Even at temperatures close to the fluoride ion exchange temperature for the carbanion the amount of products from fluorination is small, with the dissociation of CsF and the alkene predominating and many side products being formed.

3.4. EXPERIMENTAL

a) Dimerisation of hexafluoropropene, with agitation, giving thermodynamic dimer

A carius tube was charged with caesium fluoride (2.4g, 16mmol) and acetonitrile (40 ml), and hexafluoropropene (31g, 207mmol) was transfered *in vacuo* to the tube which was cooled in liquid air. The mixture was then agitated on a rotating arm for 24hrs giving an 85% yield of the thermodynamic dimer with only minor impurities. ^{19}F nmr ($N^{\circ}.1$) mass spec ($N^{\circ}.1$).

b) Generation of caesium perfluorocarbanion salts

The alkenes 3 and 4 were stirred vigorously in tetraglyme with well dried caesium fluoride in the proportions, and for the time, shown below. The orange upper layer was removed under nitrogen and transfered to a dry, well sealed flask. This solution of carbanion could then be used as a stock solution and used as required in reactions.

No	ALKENE		CsF		solvent	time
	g	mmol	g	mmol		
3	6.0	20	4	26.3	20	4
4	4.5	9	1.7	11.2	5	11

c) Reactions of perfluoro-2-methylpent-2-yl anion.

General procedure for reactions at room temperature

To a homogeneous solution containing the perfluorocarbanion (obtained as above) an excess of the electrophile was added and the resulting mixture stirred for a period dependent upon the amount present in the lower liquid layer (not more than 5 days). A ^{19}F nmr spectra of the upper tetraglyme layer was then run to determine whether any fluorine containing material was still present. Volatile products were then transferred *in vacuo* to a cold trap and the transferred products run on a G.C. capillary column and a ^{19}F nmr spectra taken.

i) Benzyl bromide

The general procedure was followed using 14 mmol of carbanion and 2.5g (14.7 mmol) of benzyl bromide. The tetraglyme layer showed no fluorine present. Volatile material (90% recovery) showed 2-benzylperfluoro-2-methylpentane by comparison with literature data⁹³ and excess benzyl bromide (by comparison to the glc peak of pure reactant).

ii) Acetyl chloride

The general procedure was followed using 6.5 mmol of carbanion and 0.6 g (7.6 mmol) of acetyl chloride. The tetraglyme layer showed a peak at σ_{F} 49 consistent with the literature value for acetyl fluoride⁹⁵.

iii) 1-Iodoheptane

The general procedure was followed using 6 mmol of carbanion and 1.5g (6.6 mmol) of 1-iodoheptane. The tetraglyme layer showed no fluorine present. The volatile material (1.7g) was the new derivative 2-heptylperfluoro-2-methylpentane which was identified by mass spec (N^o.3) and confirmed by ¹⁹F nmr spectroscopy (N^o5).

iv) 1-Tosylheptane

The general procedure was followed using 9 mmol of carbanion and 2.5g (9.3 mmol) of 1-tosylheptane. The tetraglyme layer showed some carbanion remained after 5 days, with other unidentified peaks. The volatile materials (0.8g) showed a complex glc with many side products among which was again identified 2-heptylperfluoro-2-methylpentane (by ¹⁹F nmr (N^o.5) and mass spec (N^o.3)) plus perfluoro-2-methylpent-2-ene (3) ¹⁹F nmr (N^o.1) mass spec (N^o.1), and 1-fluoroheptane mass spec (N^o.4).

v) Bromoepoxide

The general procedure was followed using 6 mmol of carbanion and 0.9g (6.5 mmol) of bromoepoxide. The tetraglyme layer showed a small amount of carbanion as the only fluorine present. Volatile materials (0.8g) showed the new derivative 2-epoxideperfluoro-2-methylpentane characterised by ¹⁹F nmr (N^o.6) and mass spec (N^o.5). Also present was perfluoro-2-methylpent-2-ene (3) ¹⁹F nmr (N^o.1) mass spec (N^o.1).

vi) Tosylepoxide

The general procedure was followed using 7 mmol of carbanion and 1.68g (7.4 mmol) of tosylepoxide. There was no visible reaction. The tetraglyme layer showed carbanion remained after 5 days.

vii) 2-Chlorocyclohexanone

The general procedure was followed using 9.4 mmol of carbanion and 1.3g (9.8 mmol) of 2-chlorocyclohexanone. There was no visible reaction. The tetraglyme layer showed carbanion only.

General procedure for reactions at 70°C

A flask was charged with an excess of the appropriate reactant in tetraglyme and heated with stirring to 70°C. A solution of the formed perfluorocarbanion was slowly added and the solution was stirred for a further period. A sample of the tetraglyme layer was then removed for ^{19}F nmr. The volatile materials were then transferred under vacuum to a cold trap and, where possible, analysed by g.l.c., ^{19}F nmr and G.C-mass spec.

i) Benzyl bromide

The general procedure was followed using 14 mmol of carbanion and 2.5g (14.5 mmol) of benzyl bromide. The tetraglyme layer was found to contain a trace of benzyl fluoride $\sigma_{\text{F}} -207$ by comparison of ^{19}F nmr with literature data⁹⁶. The volatile material (2g) contained 2-benzylperfluoro-2-methylpentane by comparison of the

literature data ⁹⁵ and perfluoro-2-methylpent-2-ene (3) by ¹⁹F nmr (N^o.1) and mass spec (N^o.1).

ii) 1-Iodoheptane

The general procedure was followed using 6 mmol of carbanion and 1.5g (6.6 mmol) of 1-iodoheptane. The tetraglyme layer showed no trace of 1-fluoroheptane. Volatile materials showed 2-heptylperfluoro-2-methylpentane by ¹⁹F nmr (N^o.5) and mass spec (N^o.3) and perfluoro-2-methylpent-2-ene (3) by ¹⁹F nmr (N^o.1) and mass spec (N^o.1).

iii) 1-Tosylheptane

The general procedure was followed using 9 mmol of carbanion and 2.53g (9.4 mmol) of 1-tosylheptane. The tetraglyme layer showed a complex fluorine spectrum after 2 hours. The volatile materials (1.5g) showed many side products. Observable by mass spec were 1-fluoroheptane (N^o.4) , 2-heptylperfluoro-2-methylpentane (N^o.3) and perfluoro-2-methylpent-2-ene (N^o.1).

iv) 1-Chlorocyclohexanone

The general procedure was followed using 9 mmol of carbanion and 1.3g (9.8 mmol) of 1-chlorocyclohexanone. The tetraglyme layer showed a complex fluorine spectrum including carbanion. The volatile materials (0.68g) showed many side products including the new derivative 2-perfluoro-2-methylpentylcyclohexanone mass spec (N^o.6).

v) 2-Chloronitrobenzene

The general procedure was followed using 7 mmol of carbanion and 1.1g (7.1 mmol) of 2-chloronitrobenzene. There was no visible reaction, with the tetraglyme layer showing carbanion only.

vi) Bromobenzene

The general procedure was followed using 8 mmol of carbanion and 1.3g (8.2 mmol) of bromobenzene. There was no visible reaction with the tetraglyme layer showing carbanion only.

Aldol condensation

The attempt was made to use the carbanion as a base. A typical reaction was 7 mmol of carbanion stirred with 0.74g (5 mmol) of acetophenone at 40°C. To this reaction mixture was added 0.75g (5 mmol) of benzaldehyde. The stirring continued for 2 days. However the carbanion remained (observed by ^{19}F nmr).

d) Reactions of Perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion (4a)

The general procedure was followed as for the reaction of (3a) at room temperature for the electrophiles acetyl chloride, benzyl bromide and 1-tosylheptane. No reaction was observed at room temperature, only the anion appearing in the ^{19}F nmr. These reactions were transferred to small carius tubes which were then sealed, placed in a metal sleeve and heated in an oven to 120 °C

for 24 hrs. The reactions were then treated as previously described.

i) Acetyl chloride

The general procedure was followed using 2 mmol of carbanion and 0.2g (3 mmol) of acetyl chloride. The tetraglyme layer showed the characteristic peak of acetyl fluoride at σ_F 49. The volatile materials showed only (4) by ^{19}F nmr (N^o.3) and mass spec (N^o.2).

ii) Benzyl bromide

The general procedure was followed using 2 mmol of carbanion and 0.38g (2.2 mmol) of benzyl bromide. No fluorinated material was observed in the tetraglyme layer. The volatile materials yielded mainly pentamer (90%), the other 10% being unidentified side products among which was observed the new derivative 3-benzylperfluoro-3,4-dimethyl-4-ethylhexane by mass spec (N^o.7).

iii) 1-Tosylheptane

The general procedure was followed using 2 mmol of carbanion and 0.51g (2.1 mmol) of 1-tosylheptane. The tetraglyme layer showed no fluorinated material. Volatile material was found to contain 50% of the new derivative 3-heptylperfluoro-3,4-dimethyl-4-ethylhexane, identified by mass spec (N^o.8), the alkene (4) and many side products.

CHAPTER FOUR

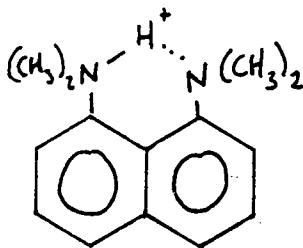
4 Investigation into strong amine base/HF as a source of fluoride ion

4.1 Introduction

As discussed in chapter 2 pyridinium poly(hydrogen fluoride), Olah's reagent, has been used in several reactions in which it has behaved as a fluorinating agent (i.e. secondary alcohols) or in HF addition (i.e. alkenes and alkynes). The structure of this reagent was discussed previously.

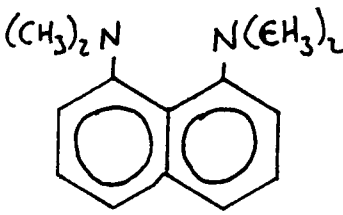
The idea of the present work is to use hindered, strong amine bases as systems where the H^+ is effectively buried as listed in Table 1.

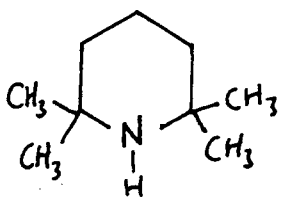
This present work has particularly concentrated on proton sponge. As first noted by Alder et.al.⁹⁷ it has an unusually high basicity which has been attributed to steric strain. This is partly relieved on protonation:

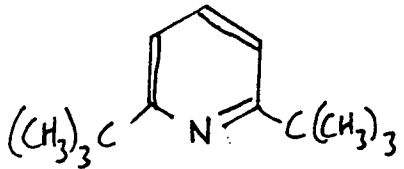


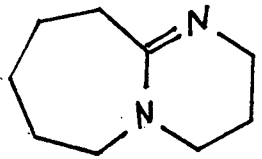
Here the added proton links the two nitrogen atoms by strong hydrogen bonding⁹⁸.

Table 1

1.  Proton Sponge

2.  2,2,6,6-Tetramethylpiperidine

3.  2,6-Di-tert-butylpyridine

4.  DBU

5. $[N(CH_2(CH_2)_6CH_3)_3]$ Trioctylamine

a) Generation of amine/HF adducts

After investigating the various methods for producing the adducts the best solution to the problem proved to be the use of an ether/HF solution of known weight of HF per cm³ of ether. This enables the reagent to be measured and transferred by volume. To a solution of the amine of known mass, dissolved in ether, was added the correct volume of ether/HF mixture. The ether was then removed under vacuum leaving a solid adduct, except in the case of tri-n-octylamine which was a liquid. The benefit of this system was that a large amount of the adduct was prepared and could be stored for further use under anhydrous conditions.

b) Physical properties of amine/HF systems

The solubility of the adducts and also their ¹⁹F nmr data was determined (Table 2). The data in Table 2 does not provide a reliable guide to reactivity.

Table 2

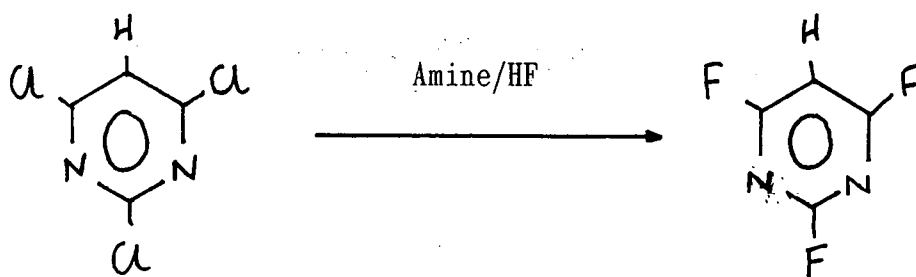
Base	adduct	solubility			σ ppm*
		tetraglyme	sulfolane	CH ₃ CN	
1	solid	×	✓	✓	-165.6
2	not formed	—	—	—	—
3	solid	✓	✓	✓	-172.2
4	solid	✓	✓	✓	-153.4
5	liquid	—	—	—	-168.9
no base	—				-182.8

* solutions in sulfolane; the chemical shift of the HF signal is known to be variable under these conditions⁹⁹.

c) Comparison of amine/HF systems as halogen exchange reagents

The reaction of figure 1 in which 2,4,6-trifluoropyrimidine is formed from 2,4,6-trichloropyrimidine was chosen as a basis for comparison of the various amine/HF systems as fluorinating agents with acetonitrile as the solvent.

Figure 1



The results (Table 3) showed some correlation with the observed ^{19}F nmr shifts in that proton sponge (1) and DBU (4) showed most reactivity.

Table 3

Base	Yield (%) *
1	73
3	24
4	64
5	30

* Derived from ^{19}F nmr integrations.

4.2 Proton sponge/HF

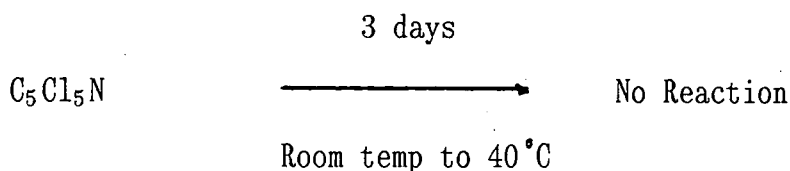
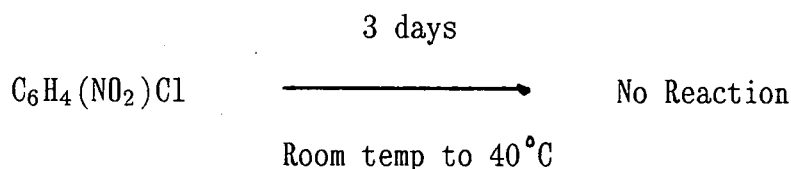
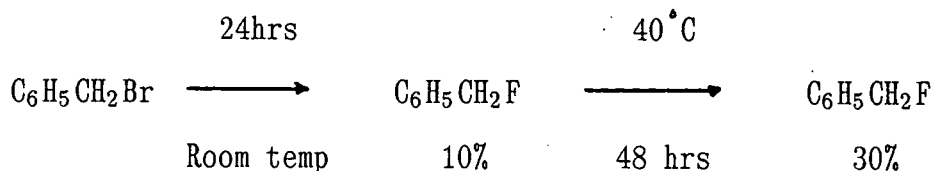
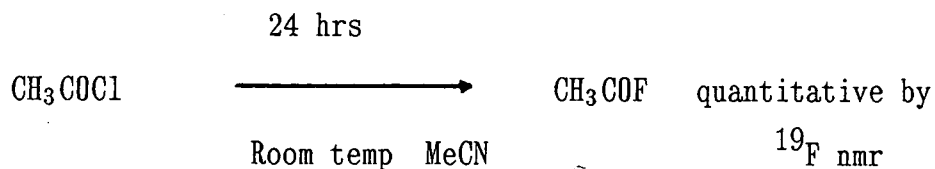
A series of reactions was chosen to explore the range of fluoride ion applications using mainly proton sponge/HF as the reagent, since this proved to be the most effective system. The reactions were (i) halogen exchange, (ii) attempted formation of perfluoro-2-methylpent-2-yl anion and (iii) dimerisation of perfluoroalkenes.

a) Halogen Exchange

The reaction used as a standard in the comparison reaction (fig 1) was shown to go to completion after 48 hours in acetonitrile. Solid crystals formed continuously and were assumed to be the HCl adduct (as both the HF adduct and proton sponge are soluble in

CH₃CN). The reaction was also attempted in sulfolane, but this reaction was slower, taking 3 days and requiring heating to 40°C to go to completion.

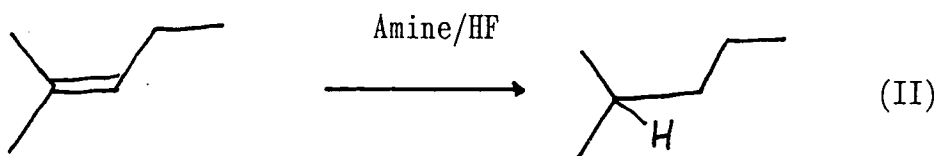
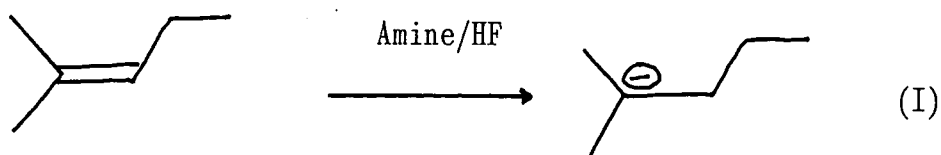
The proton sponge/HF/CH₃CN system was also attempted on the following reactions:



b) Attempted formation of perfluoro-2-methylpent-2-yl anion

It was originally hoped that the reaction to produce the carbanion (I) could be used to gauge all the adducts as fluoride

ion donors. However all the adducts (except DBU which reacted with the perfluoroalkene) produced the addition product (II):



All unmarked bonds to fluorine.

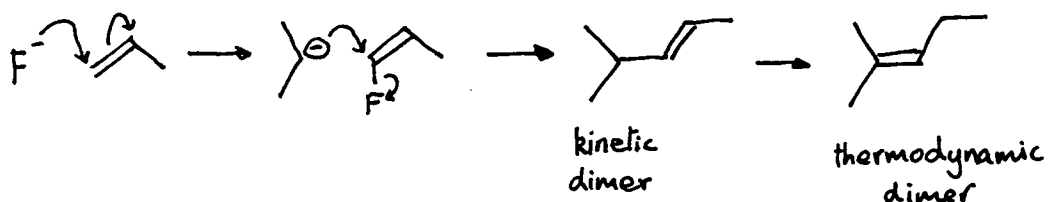
The reaction was attempted in tetraglyme because of the known sensitivity of (I) to solvent ⁶¹. In the case of the proton sponge which is insoluble in tetraglyme, addition of the perfluoroalkene led to immediate disappearance of the adduct. Unsuccessful attempts were made to trap out any possible intermediate by having MeI present in the reaction mixture from the start, but no such trapped products were observed.

c) Attempted dimerisation

The use of caesium fluoride as a catalyst in the reaction (fig 2) prompted the attempt to use proton sponge/HF system in a similar

manner.

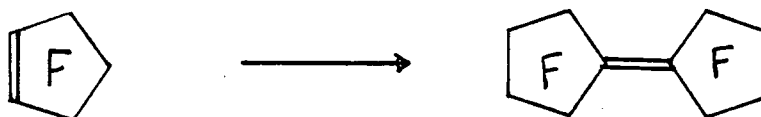
Figure 2



(all unmarked bonds to F)

The reaction was initially tried with tetraglyme using proton sponge/HF and a small amount of dimerisation was observed. However which form of HF addition product had been produced was impossible to determine due to the poor yield. A much more impressive result was obtained using acetonitrile as the solvent in the reaction. In this case 0.1 molar equivalent of proton sponge/HF was used and a good yield of dimeric products was obtained. From glc-mass spec data this was determined to be a mixture of (I) and (II).

The proton sponge/HF system in acetonitrile was also tried on the less reactive perfluorocyclopentene dimerisation. However several attempts were all unsuccessful including one at 125 °C, the temperature at which CsF causes dimerisation:



4.3 Tri-n-octylamine/HF

This system, unlike proton sponge/HF, was a liquid and it was hoped it could be used without solvent dilution. The same reactions were tried as with proton sponge/HF.

a) Halogen exchange

Tri-n-octylamine was investigated in the 2,4,6-trichloropyrimidine reaction (figure 1) due to the fact it was the only liquid adduct. However the formation of a gel preventing stirring was observed and the addition of pentane was used to free the solution. This gel was again attributed to the formation of the HCl adduct. The reaction went to completion after 4 days with heating to 40°C required.

b) Attempted formation of perfluoro-2-methylpent-2-yl anion

As described earlier the anion could not be observed by ^{19}F nmr spectroscopy using the amine/HF as a fluoride ion source. Instead the HF addition product (II) was again formed.

c) Attempted dimerisation

The dimerisation of hexafluoropropene was attempted using tri-n-octylamine with both an absence of solvent and MeCN as solvent. On neither occasion was dimer observed.

4.4 Conclusion

This preliminary work on the preparation and reactions of amine/HF adducts has shown their potential as fluoride ion sources. Proton sponge/HF in particular reacts as both a fluoride ion catalyst (in the dimerisation of hexafluoropropene) and as a halogen exchange reagent (in the reaction with acetyl chloride and trichloropyrimidine). In this respect it can be said that proton sponge/HF in acetonitrile is a soluble source of fluoride ion.

4.5 Experimental

a) Initial attempts to form amine/HF adducts

Initial attempts were made to produce amine/HF adducts in both tetraglyme and sulfolane. Methods used to achieve this include the transfer of a known mass of HF (1g) into a Nickel tube containing a volume (10 cm^3) of the appropriate solvent. This proved a difficult and potentially hazardous procedure due to the increased amount of HF transfer required. The best solution proved to be the bubbling of HF through a known volume of the solvent. This system was adopted for the easiest preparation of amine/HF adduct (see below).

b) Formation of ether/HF solution

HF was bubbled through ether in an ice-cooled FEP bottle. To determine the concentration of HF in the ether this was titrated against a standard solution of 0.1M NaOH using methyl red as the indicator. This concentration was expressed as $\text{g}_{\text{HF}}/\text{cm}^3 \text{ Et}_2\text{O}$ and enabled the correct volume to be added to the amine thus avoiding unnecessary manipulation of the mixture.

c) Formation of amine/HF adduct

General procedure - To a known mass of amine (dissolved in a minimum volume of ether) in a round-bottomed flask was pipetted

the required volume of ether/HF solution. This flask was then attached to a vacuum line and the ether carefully removed leaving the solid amine/HF adduct (a liquid in the case of tri-n-octylamine). This could then be used as an easily manipulated reagent with the precautions afforded to caesium fluoride (i.e minimum exposure to the atmosphere).

d) Comparison reaction

To a clean nmr tube was added an equal molar concentration (3.3 mmol) of each amine/HF adduct in acetonitrile (1cm³).

- i) Proton sponge/HF 0.71g
- ii) 2,6-Di-tert-butylpyridine/HF 0.64g
- iii) DBU/HF 0.5g
- iv) Tri-n-octylamine/HF 1.6g

To this was then added 0.2g (1.1 mmol) of 2,4,6-trichloropyrimidine. The course of the reaction was followed by ¹⁹F nmr spectroscopy and by integration the conversion of the HF to fluoropyrimidine could be followed giving the yield of the product with the appropriate amine/HF.

e) Proton sponge/HF adduct reactions

Halogen exchange

General procedure - To a stirred solution of the amine/HF adduct in the appropriate solvent was added an excess of the reactant (a 0.3 molar equivalent in the case of the chloropyrimidine). At

intervals a sample was removed and analysed by ^{19}F nmr spectroscopy. The integration yielded the extent to which the reaction had proceeded.

i) Acetyl chloride

The general procedure was followed using 1.1g (4.7 mmol) of proton sponge/HF adduct in 10 cm^3 of acetonitrile. To this was added 0.5g (6.3 mmol) of acetyl chloride. The reaction proceeded to completion after 24 hours at room temperature by following the appearance of the acetyl fluoride peak at $\sigma_{\text{F}}+49$.

ii) Benzyl bromide

The reaction was conducted following the general procedure using 0.54g (2.3 mmol) of proton sponge/HF adduct in 10 cm^3 of acetonitrile. To this was added 0.5g (2.9 mmol) of benzyl bromide. After 24 hours at room temperature the reaction had produced 10% benzyl fluoride (peak at $\sigma_{\text{F}}-207$ as compared to the literature data ⁹⁶). This mixture was then heated on a hot-plate, with continuous stirring, to 40°C for 48 hours. After this period the reaction showed 30% benzyl fluoride (by integration of the ^{19}F nmr peaks).

iii) 2-chloronitrobenzene

The general procedure was followed using 0.54g (2.3 mmol) of proton sponge/HF adduct in 10 cm^3 of acetonitrile. To this was added 0.4g (2.5 mmol) of 2-chloronitrobenzene. The reaction

mixture showed no evidence of 2-fluoronitrobenzene by ^{19}F nmr after 24 hours. The temperature was raised to 40°C for 48 hours but there was still no evidence of reaction.

iv) Pentachloropyridine

The general procedure was followed using 1.58g (6.8 mmol) of proton sponge/HF in 10 cm^3 of acetonitrile. To this was added 0.3g (1.2 mmol) of pentachloropyridine. No evidence of fluorinated product was observed, even after heating at 40°C for 48 hours.

v) 2,4,6-trichloropyrimidine

The general procedure was followed using both sulfolane and acetonitrile as solvents. In both cases 1.5g (6.4 mmol) of proton sponge/HF adduct in 10 cm^3 of the solvent was used. To this was added 0.4g (2.1 mmol) of the pyrimidine. The formation of the fluorinated product was followed using peaks in the range $\sigma_{\text{F}}-40$ to -55 representing various isomers of the intermediate products. The final peaks showed at $\sigma_{\text{F}}-44$ and -52 . In the case of the acetonitrile reaction this was completed in 48 hours with no heating required. The sulfolane reaction was incomplete after 48 hours and upon heating at 40°C for 24 hours also went to completion.

Attempted formation of perfluoro-2-methylpent-2-yl anion

General procedure - To a stirred solution of the appropriate amine/HF adduct in tetraglyme was added a molar equivalent of

perfluoro-2-methylpent-2-ene. This was stirred for 24 hours and a sample of the tetraglyme layer removed for ^{19}F nmr and showed no fluorine present. The lower layer was removed by pipette and analysed by both ^{19}F nmr and G.C mass spectroscopy. This showed in each case (except for that of DBU which reacted with the dimer giving a complex ^{19}F nmr spectrum) the presence of 2-hydroperfluoro-2-methylpentane ^{19}F nmr (δ 7) mass spec (δ 9).

The amines used in this reaction were:

- i) Proton sponge
- ii) DBU
- iii) Di-tert-butylpyridine
- iv) Tri-n-octylamine

Attempted trapping using MeI

The general procedure outlined above was followed with the modification that MeI was present in solution before the alkene was added. By G.C.-mass spec it was found that no trapping product was present.

Attempted dimerisation

General procedure - A carius tube was charged with the amine/HF adduct and solvent. The alkene to be dimerised was introduced by vacuum transfer and the tube sealed. This was then treated as described below. To analyse the products they were transferred in vacuo to a cold trap and then to ^{19}F nmr and G.C.-mass spec as appropriate.

i) Hexafluoropropene

Tetraglyme as solvent

The general procedure was followed using 0.6g (2.6 mmol) of solid proton sponge/HF in 10 cm³ of tetraglyme. To this was introduced 3.9g (26 mmol) of hexafluoropropene. This was then rotated for 24 hours. Upon transfer of the products it was obvious that they consisted mainly of gas. These were transferred to a sealed silica nmr tube and upon analysis proved to be a mixture of hexafluoropropene ¹⁹F nmr (N^o.8) and 2-hydroperfluoropropane ¹H nmr (N^o.1) in the approximate ratio 10:1 by integration of the ¹⁹F nmr peaks.

The small amount of liquid product (<5%) proved to be a mixture of dimer and HF addition product.

Acetonitrile as solvent

The general procedure was followed using 0.52g (2 mmol) of proton sponge/HF in 5 cm³ of acetonitrile. To this was introduced 3.35g (22 mmol) of hexafluoropropene and as with the caesium fluoride there was an initial exotherm. The carius tube was rotated for 24 hours and then the volatile products were analysed. This time 50% of the recovered material proved to be mainly the thermodynamic dimer, with a small amount (<5%) of the HF addition product and higher oligomers of hexafluoropropene by glc-mass spec.

ii) Perfluorocyclopentene

The general procedure was followed using the proton sponge/HF adduct (1.7g, 7.3 mmol) in 10 cm³ of acetonitrile. To this was added 3.5g of perfluorocyclopentene. The reaction was carried out using a number of temperatures (20°C, 40°C, 80°C, 125°C) but on each occasion the only product that could be identified was the starting material (by glc and ¹⁹F nmr (N^o.9)).

f) Tri-n-octylamine/HF adduct reactions

i) 2,4,6-trichloropyrimidine

The general procedure, as described for the proton sponge/HF adduct, was followed using 5.3g (15 mmol) of tri-n-octylamine/HF to which was added 0.93 (5 mmol) of trichloropyrimidine with no solvent initially. After the first sample was taken the gelling of the reaction mixture was observed and this was dissolved using pentane. The reaction proceeded to completion after heating to 40°C for 4 days. The end point was again determined by monitoring the fluoropyrimidine peaks.

ii) Hexafluoropropene

The general procedure was carried out as with the proton sponge/HF adduct. Tri-n-octylamine/HF (1.2g, 3.3 mmol) was used in 10:1 molar ratio with the alkene (5g, 33.3 mmol). In this case none of the volatile material proved to be liquid and ¹⁹F nmr revealed only the presence of hexafluoropropene (N^o.8).

APPENDIX I - NMR SPECTRA

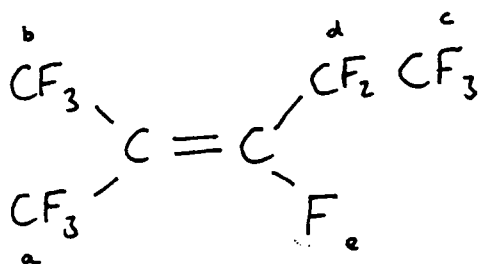
¹⁹F NMR

1. Perfluoro-2-methylpent-2-ene (3)
2. Perfluoro-2-methylpent-2-yl anion (3a)
3. Perfluoro-3,4-dimethyl-4-ethylhex-3-ene (4)
4. Perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion (4a)
5. 2-Heptylperfluoro-2-methylpentane
6. 2-Epoxyperfluoro-2-methylpentane
7. 2-Hydroperfluoro-2-methylpentane
8. Hexafluoropropene
9. Perfluorocyclopentene

¹H NMR

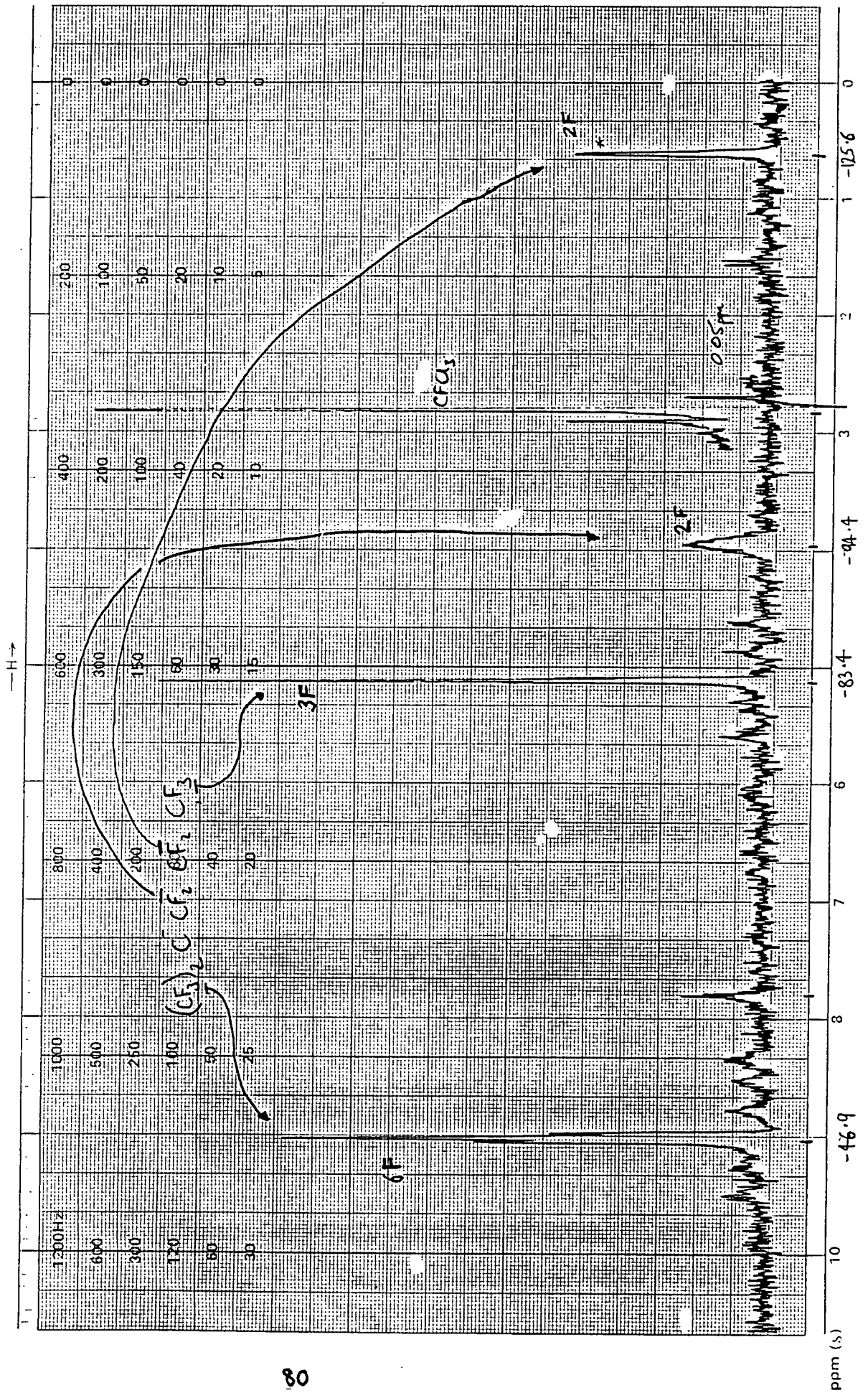
1. 2-Hydroperfluoropropane

1. Perfluoro -2- methyl pent-2-ene

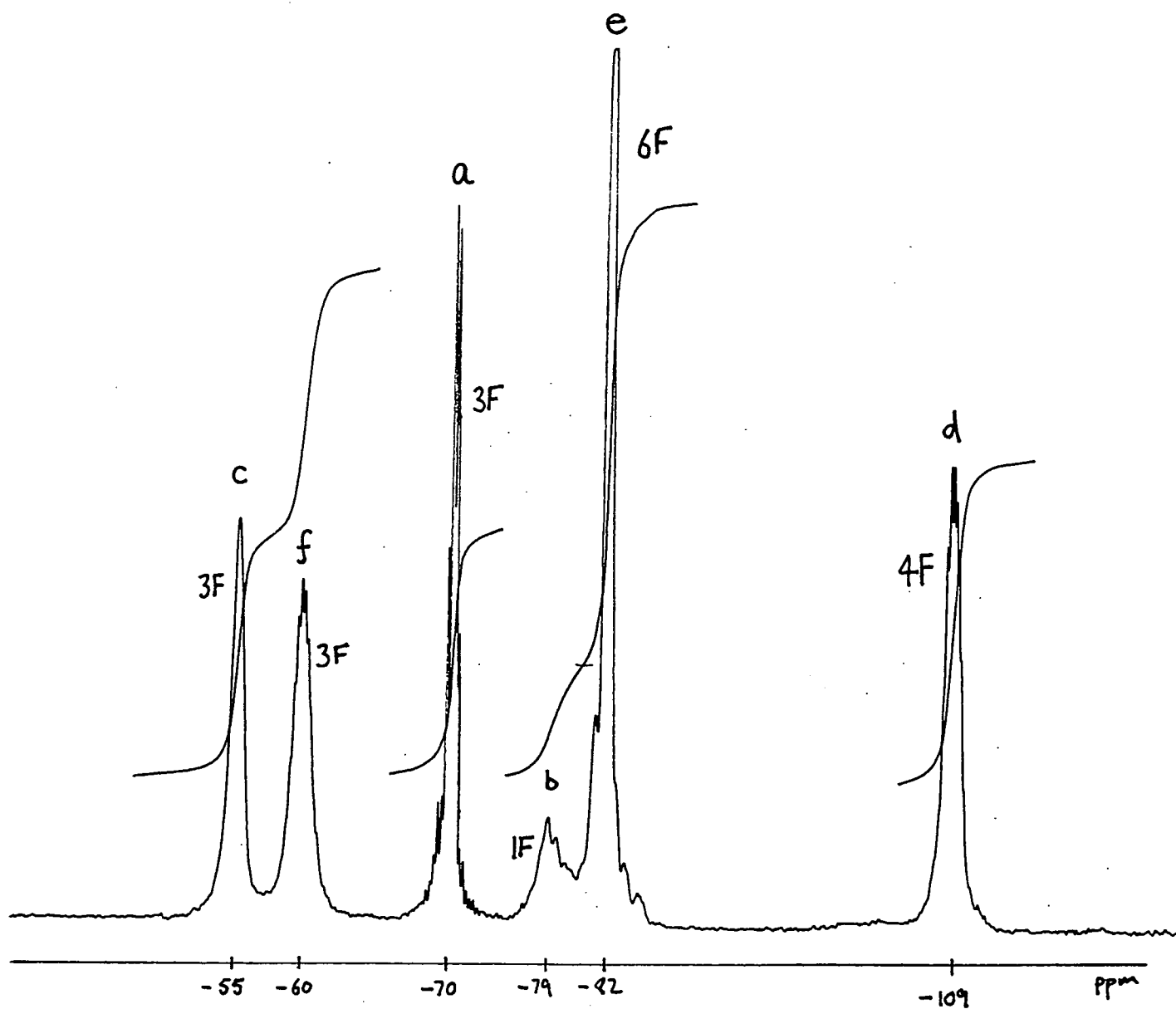
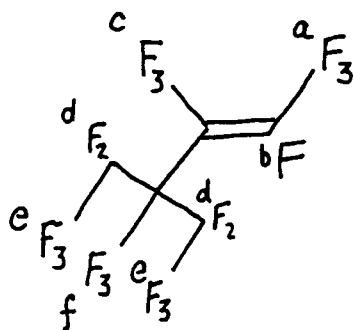


Assignment	Integral	Shift /ppm
a	3F	-62.8
b	3F	-60.2
c	3F	-86.4
d	2F	-119.6
e	1F	-100.5

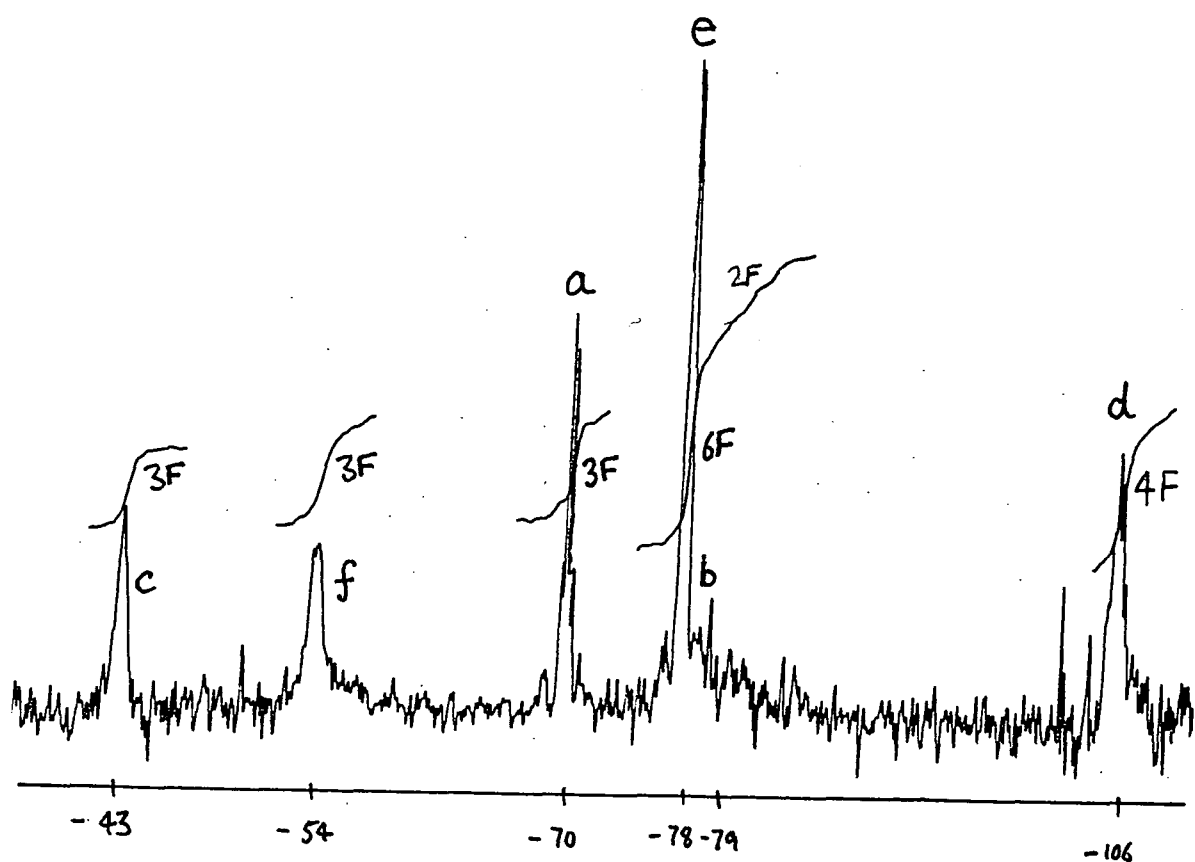
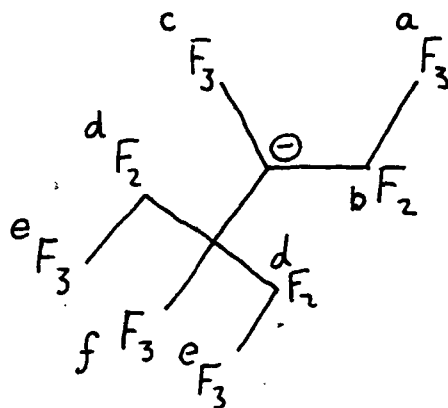
2. Perfluoro-2-methylpent-2-yl anion



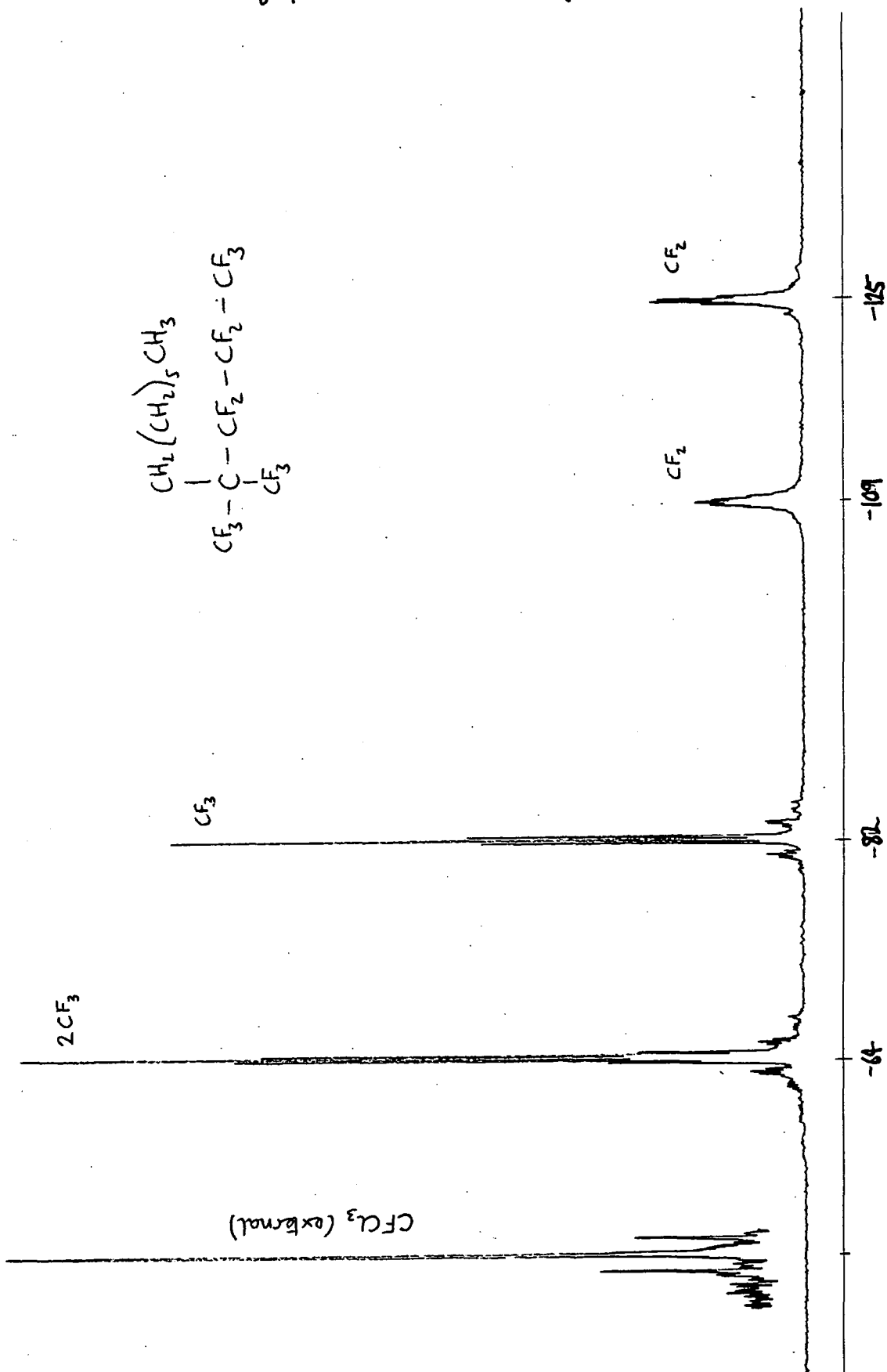
3. Perfluoro-3,4-dimethyl-4-ethylhex-3-ene



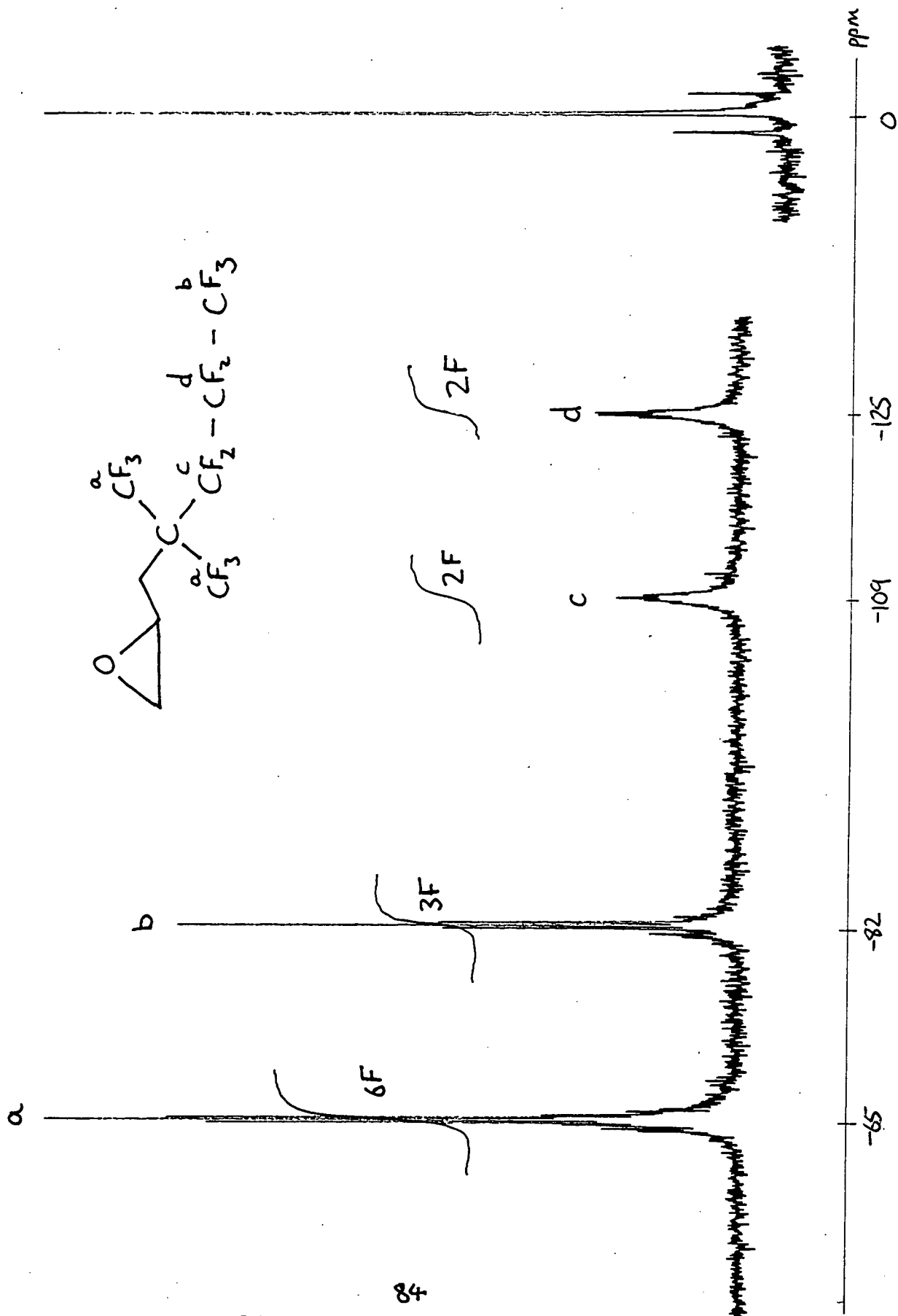
4. Perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion



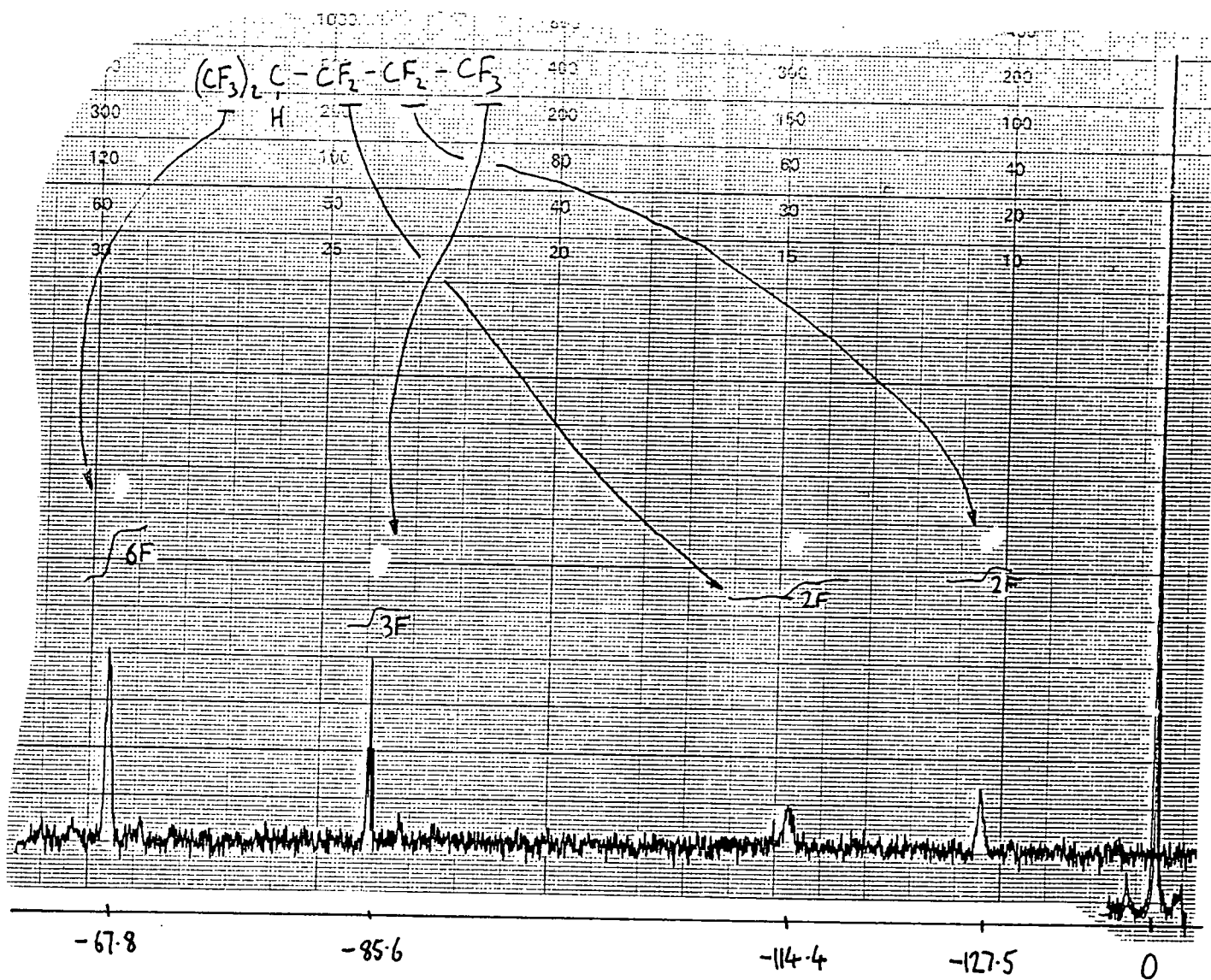
5. 2-Heptylperfluoro-2-methylpentane



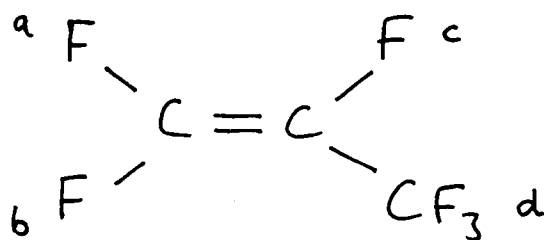
6. 2-Epoxyperfluoro-2-methylpentane



7. 2-Hydroperfluoro-2-methylpentane

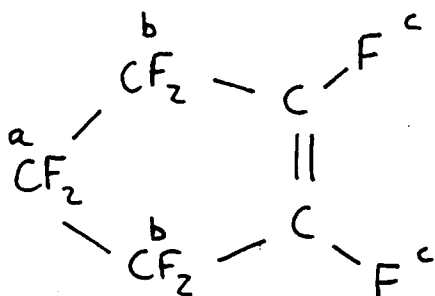


8. Hexafluoropropene



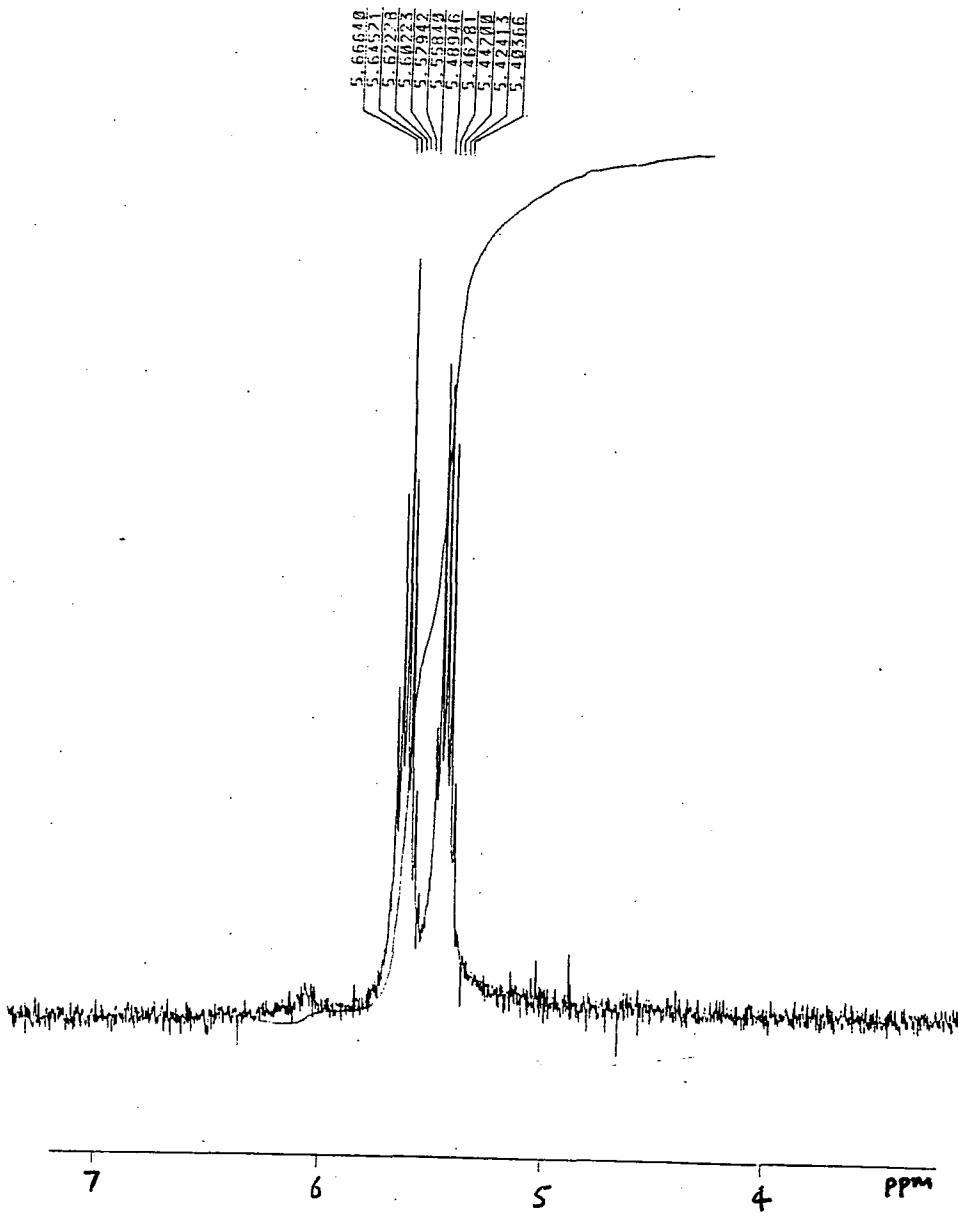
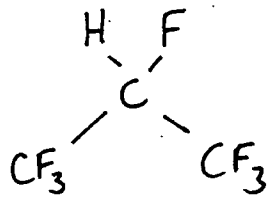
Assignment	Integral	Shift /ppm
a	1F	-93
b	1F	-192
c	1F	-107
d	3F	-72

9. Perfluorocyclopentene



Assignment	Integral	Shift /ppm
a	2F	-133.2
b	4F	-121.3
c	2F	-153.5

¹H NMR spectrum of 2-Hydroperfluoropropane



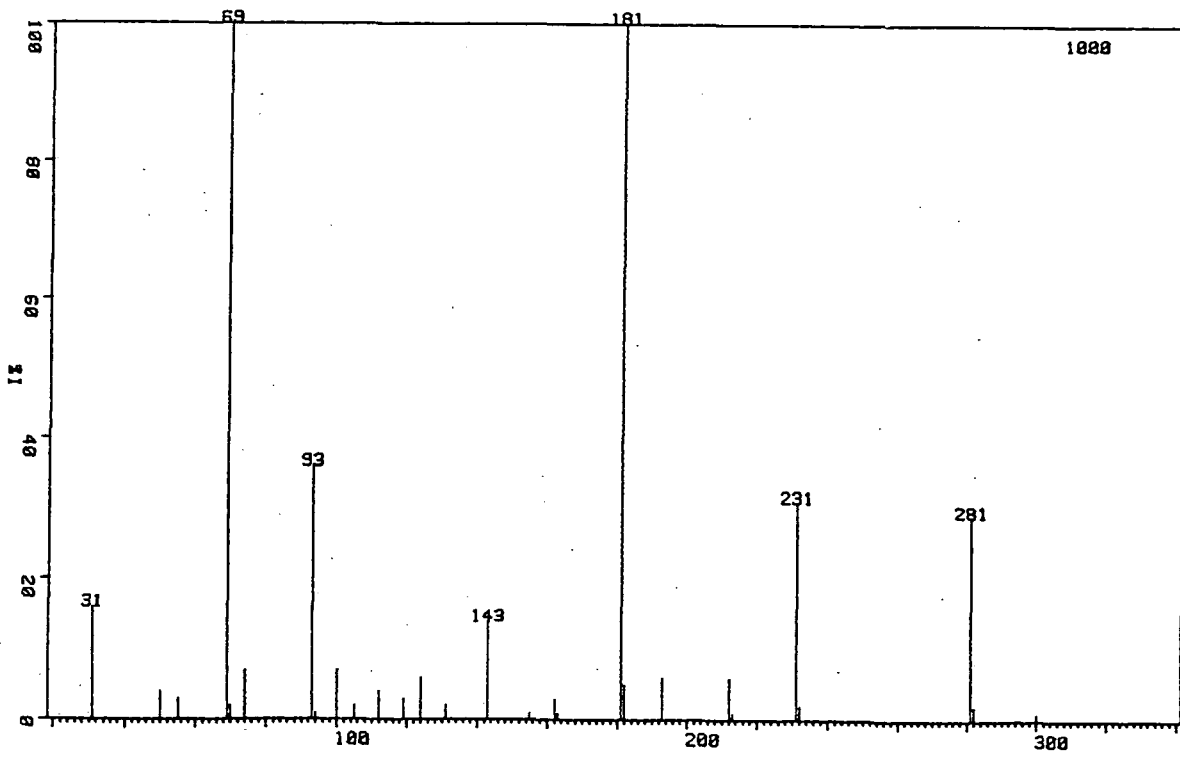
APPENDIX II - MASS SPECTRA

1. Perfluoro-2-methylpent-2-ene (3)
2. Perfluoro-3,4-dimethyl-4-ethylhex-3-ene (4)
3. 2-Heptylperfluoro-2-methylpentane
4. 1-Fluoroheptane
5. 2-Epoxideperfluoro-2-methylpentane
6. 2-Perfluoro-2-methylpentylcyclohexanone
7. 3-Benzylperfluoro-3,4-dimethyl-4-ethylhexane (EI⁺)
- 7a. 3-Benzylperfluoro-3,4-dimethyl-4-ethylhexane (CI⁻)
8. 3-Heptylperfluoro-3,4-dimethyl-4-ethylhexane (EI⁺)
- 8a. 3-Heptylperfluoro-3,4-dimethyl-4-ethylhexane (CI⁻)
9. 2-Hydroperfluoro-2-methylpentane

1. Perfluoro-2-methylpent-2-ene

x1 Bgd=75 17-FEB-88 09:0+0:01:22 70E EI+ 2.1
I=10v Hm=300 TIC=257214000 Acnt: Sys: EMSL
GC= 52 Cal: PFK162

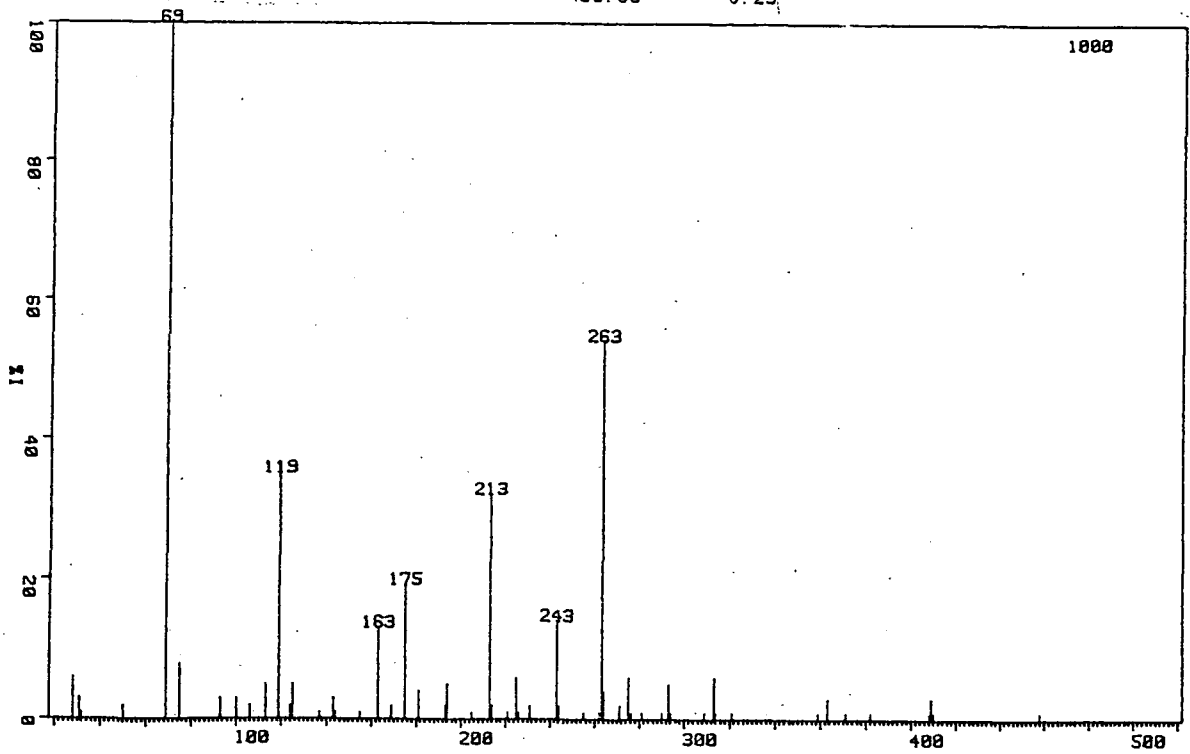
Mass	% Base
31.03	15.66
50.05	3.79
55.06	2.32
69.05	100.00 0
70.06	1.68
74.06	6.96
93.07	35.72
94.08	1.00
100.07	7.14
105.08	1.69
112.08	3.86
119.08	2.61
124.09	5.42
131.09	2.11
143.09	13.35
150.09	0.24
155.10	0.42
162.10	2.72
163.11	0.42
169.10	0.06
174.10	0.04
181.09	100.00 0
182.10	4.48
193.11	5.76
194.12	0.22
212.11	5.94
213.12	0.39
231.12	30.77
232.13	1.73
281.13	28.52
282.14	1.90
300.14	0.32



2. Perfluoro - 3,4 - dimethyl - 4 - ethylhex - 3 - ene

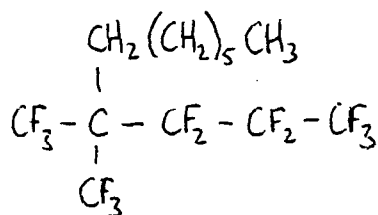
JJE318#95* x1 Bgd=92 8-JUL-88 16:2+0:01:41 70E EI+ 2
 BpM=0 I=3.3v Hm=458 TIC=86432000 Acnt: Sys:EMSL
 GC= 45 Cal:PFK265

Mass	% Base	Mass	% Base
27.56	5.32	231.07	1.72
30.58	2.93	232.07	0.20
31.59	1.18	242.82	0.16
50.86	1.74	243.05	13.27
69.08	100.00	244.05	2.16
75.26	7.70	245.09	0.16
93.25	2.36	255.05	1.18
100.18	2.49	261.91	0.11
106.16	1.60	262.04	0.21
113.11	4.94	262.23	0.18
119.09	34.38	262.46	0.18
124.09	1.78	262.53	0.18
125.10	5.15	262.76	0.48
137.10	1.19	263.05	53.67
143.08	2.51	263.28	0.15
144.09	1.04	264.05	3.40
155.08	1.05	271.03	1.30
163.09	12.51	271.99	0.16
169.08	2.01	272.04	0.18
175.09	18.84	275.05	5.84
181.08	3.80	275.41	0.16
193.06	1.74	276.05	0.53
194.07	4.34	281.05	0.36
205.06	0.67	290.01	0.37
212.08	0.14	293.02	4.87
212.10	0.10	294.03	0.76
212.85	0.33	308.99	0.85
213.07	32.15	313.01	5.81
214.08	1.87	314.02	0.33
215.06	0.14	321.00	0.77
221.07	0.81	330.98	0.11
224.05	0.18	342.99	9.24
224.23	0.26	343.99	0.77
224.56	0.30	358.96	0.75
224.86	0.22	362.98	3.06
225.08	6.19	363.98	0.25
225.42	0.14	370.97	0.74
225.47	0.14	371.96	0.19
225.54	0.11	381.98	0.89
226.08	0.33	408.94	3.08
		409.95	0.33
		458.86	0.25

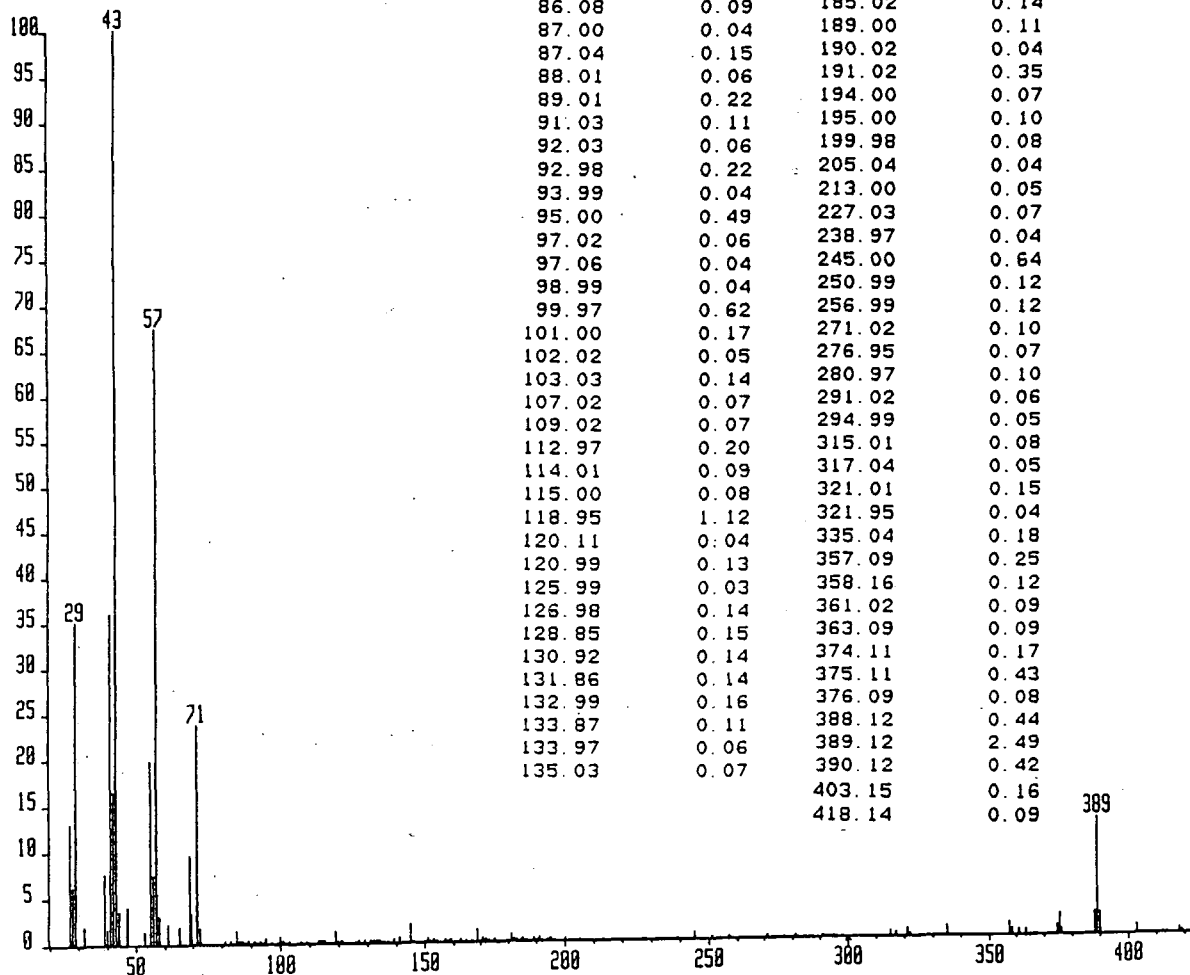


3. Mass spectrum of 2-heptylperfluoro-2-methylpentane

JJE521#436 x1 Bgd=432 25-MAR-88 12:2+0:07:46 70E EI+ I.
 BpM=0 I=8.2v Hm=918 TIC=217845000 Acnt: Sys:EMSL
 GC= 116 Cal:PFK243F



Mass	% Base	Mass	% Base
27.01	12.92	135.86	0.04
27.99	6.12 F	136.99	0.04
28.02	4.45 F	138.99	0.25
29.03	35.02	141.00	0.39
31.98	1.86	144.99	1.87
39.01	7.36	146.01	0.05
40.02	1.45	149.97	0.06
41.02	35.90	151.00	0.30
42.03	16.39	151.99	0.06
43.04	100.00	153.01	0.08
44.04	3.34	154.01	0.05
47.01	3.85	156.98	0.19
53.02	1.18	158.00	0.06
55.04	19.69	159.00	0.15
56.05	7.21	162.97	0.20
57.06	67.21	164.99	0.04
58.06	2.83	166.99	0.04
61.04	2.04	168.95	1.20
65.01	1.62	170.00	0.06
68.98	9.43 F	170.99	0.29
69.06	3.02 F	172.00	0.16
71.08	23.63	172.98	0.07
72.08	1.47	174.95	0.12
81.05	0.10	180.95	0.55
83.03	0.15	181.97	0.09
85.09	1.21	182.96	0.03
86.08	0.09	185.02	0.14
87.00	0.04	189.00	0.11
87.04	0.15	190.02	0.04
88.01	0.06	191.02	0.35
89.01	0.22	194.00	0.07
91.03	0.11	195.00	0.10
92.03	0.06	199.98	0.08
92.98	0.22	205.04	0.04
93.99	0.04	213.00	0.05
95.00	0.49	227.03	0.07
97.02	0.06	238.97	0.04
97.06	0.04	245.00	0.64
98.99	0.04	250.99	0.12
99.97	0.62	256.99	0.12
101.00	0.17	271.02	0.10
102.02	0.05	276.95	0.07
103.03	0.14	280.97	0.10
107.02	0.07	291.02	0.06
109.02	0.07	294.99	0.05
112.97	0.20	315.01	0.08
114.01	0.09	317.04	0.05
115.00	0.08	321.01	0.15
118.95	1.12	321.95	0.04
120.11	0.04	335.04	0.18
120.99	0.13	357.09	0.25
125.99	0.03	358.16	0.12
126.98	0.14	361.02	0.09
128.85	0.15	363.09	0.09
130.92	0.14	374.11	0.17
131.86	0.14	375.11	0.43
132.99	0.16	376.09	0.08
133.87	0.11	388.12	0.44
133.97	0.06	389.12	2.49
135.03	0.07	390.12	0.42
		403.15	0.16
		418.14	0.09
			389

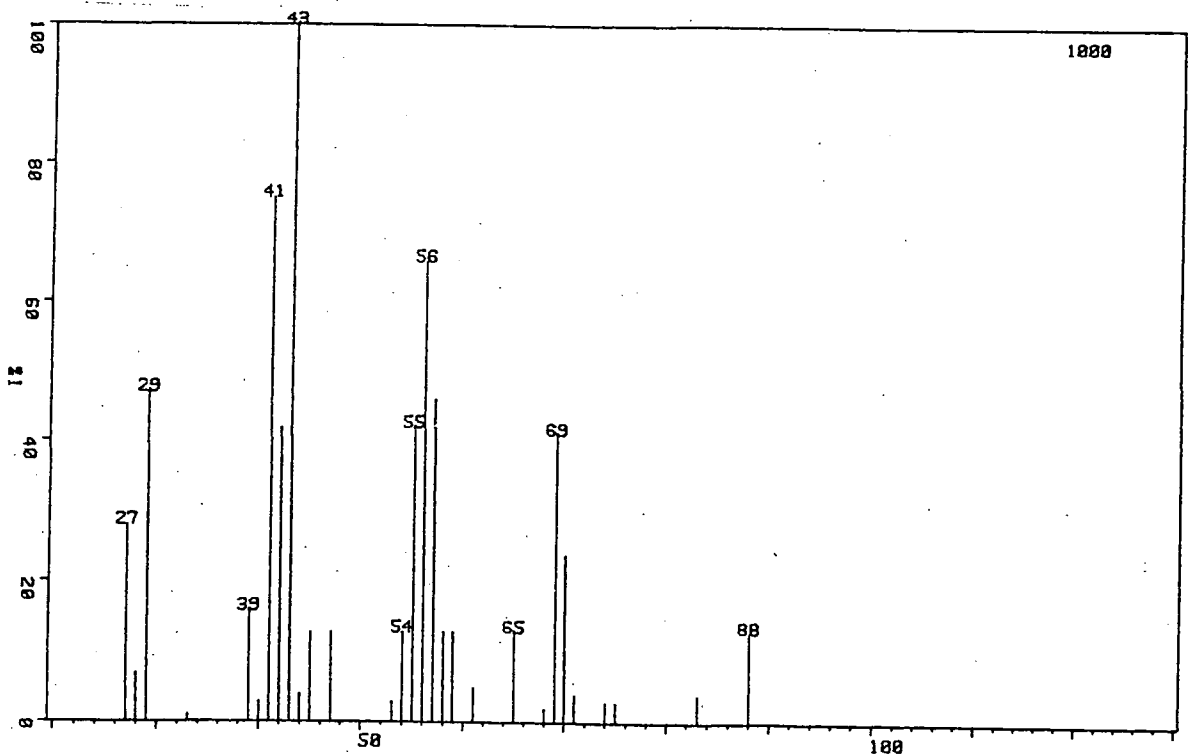


JJE521#436 x1 Bgd=432 25-MAR-88 12:2+0:07:46 70E EI+
 BpM=0 I=8.2v Hm=918 TIC=217845000 Acnt: Sys:EMSL
 GC= 116 Cal:PFK243F
 *XS=0

4. 1-Fluorheptane

JJE11A#247* x1 Bgd=243 29-APR-88 10:1+0:04:24 70E EI+ 13
BpM=0 I=2.1v Hm=145 TIC=118286000 Acnt: Sys: EMSL
GC= 83 Cal: PFK284

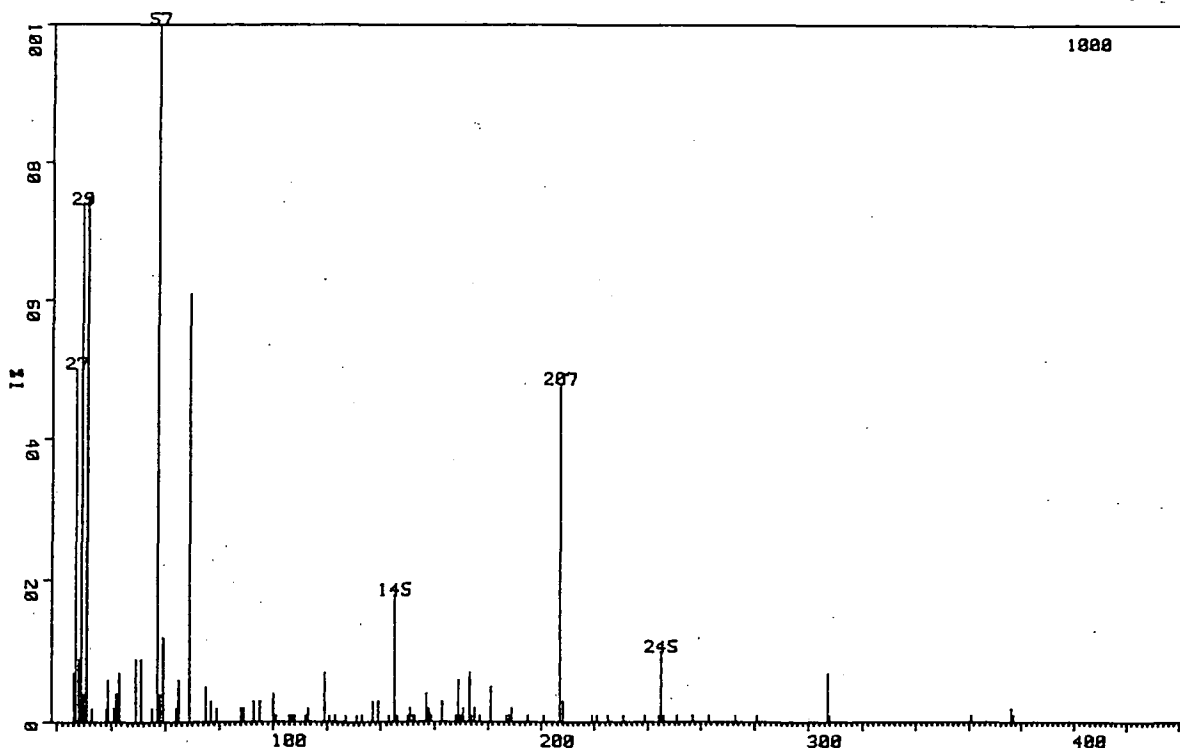
Mass	% Base
27.01	27.77 F
27.02	28.03 F
28.02	6.69
29.03	46.41 F
29.05	23.63 F
33.02	12.73
39.04	15.30
40.05	2.74
41.06	74.91 F
41.07	25.45 F
42.07	41.82
43.08	100.00
44.08	3.27
45.05	12.73
47.05	12.83 F
47.07	12.73 F
53.07	2.91
54.08	12.73
55.08	27.17 F
55.10	41.82 F
56.10	65.96
57.11	46.12
58.11	12.73
59.07	12.73
61.09	4.28
65.09	12.73
68.10	2.20
69.10	41.82 F
69.13	23.29 F
70.10	21.83 F
70.13	23.99 F
71.13	3.87
74.10	2.61
75.10	2.52
83.14	3.73
88.14	12.73



5. 2-Epoxyperfluoro-2-methylpentane

118267* 11 Bgd=252 11-MAR-88 14:5+0:04:45 70E EI+
 0 I=10v Hm=377 TIC=462205000 Acnt: GC= 76 Sys: EMSL
 Cal: PFK43

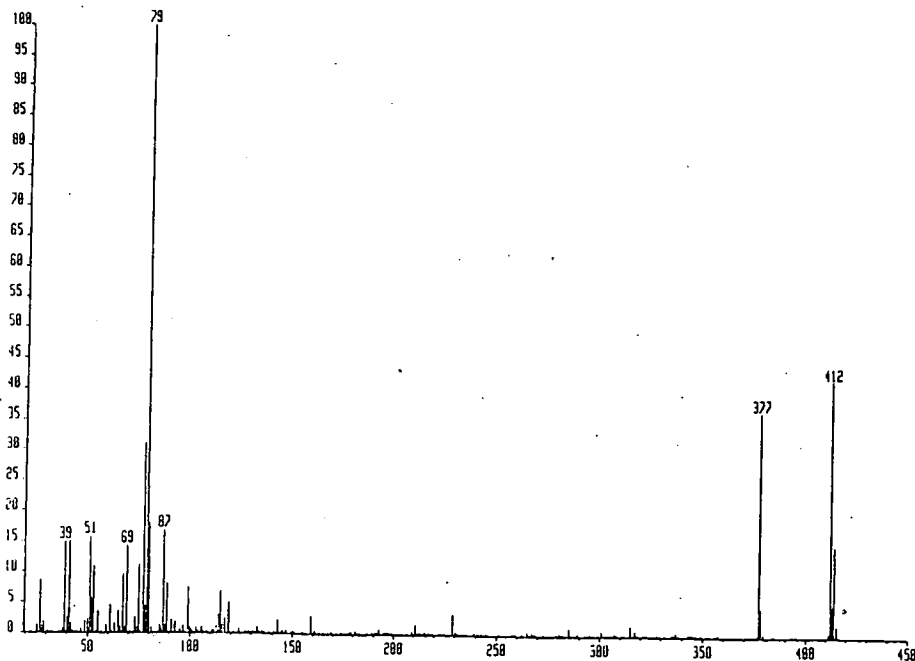
Mass	Z Base	Mass	Z Base	Mass	Z Base
26.03	7.27	137.07	2.57	223.09	0.04
27.04	49.54	138.08	0.20	225.09	0.91
28.05	9.26	139.09	2.60	227.12	0.19
29.02	73.86 F	140.10	0.13	231.09	0.38
29.06	49.62 F	141.11	0.05	237.11	0.09
30.03	3.90 F	143.06	0.45	239.12	0.41
31.04	74.58	144.07	0.10	243.10	0.10
33.04	2.05	144.47	0.05	245.11	10.14
38.04	1.54	144.64	0.04	246.12	0.65
39.05	5.91	144.77	0.07	251.11	0.51
41.06	1.34	145.07	17.42	257.12	0.53
42.03	3.92	146.08	0.73	259.11	0.13
43.04	7.06	147.06	0.17	263.11	0.48
46.05	8.75	149.08	0.13	269.12	0.24
47.06	5.02	150.07	0.39	271.13	1.13
51.03	8.86	151.08	1.40	273.12	0.04
55.05	1.57	152.10	0.54	274.11	0.04
57.07	100.00 0	153.07	0.62	275.11	0.19
58.07	3.95	154.07	0.08	281.10	0.82
59.07	11.84	155.07	0.08	289.14	0.14
64.05	2.21	156.08	0.08	307.14	7.15
65.06	5.96	157.08	3.42	308.15	0.58
69.04	61.13	158.08	1.31	354.19	0.07
75.05	4.71	159.09	0.57	361.14	0.42
77.06	2.49	162.04	0.06	375.17	1.67
79.08	1.45	162.06	0.04	377.18	0.28
88.06	1.41	163.07	2.26		
89.07	1.85	164.08	0.07		
92.98	2.48 F	167.07	0.08		
93.04	2.26 F	168.08	0.38		
94.98	2.20 F	169.05	6.17		
95.06	3.37 F	170.07	0.31		
100.05	4.11	171.08	1.88		
101.07	0.99	172.07	0.22		
102.08	0.20	173.08	6.94		
103.09	0.11	174.07	0.36		
103.98	0.11	175.08	1.31		
104.99	0.51	176.08	0.25		
106.01	0.99	177.10	0.90		
107.04	0.92	181.07	5.20		
108.00	0.89 F	182.08	0.24		
108.08	0.53 F	183.10	0.07		
109.05	0.18	185.09	0.05		
112.05	0.91	187.08	0.34		
113.06	2.14	188.11	1.15		
114.07	0.10	189.10	1.43		
115.07	0.18	190.11	0.07		
117.07	0.11	191.10	0.10		
119.06	6.57	193.07	0.11		
120.07	0.22	195.09	1.19		
121.09	0.77	199.10	0.05		
122.10	0.04	200.09	0.10		
123.07	0.51	201.11	0.89		
124.06	0.17	202.10	0.06		
125.07	0.44	207.11	47.58		
126.08	0.27	208.12	2.96		
127.08	0.76	209.12	0.24		
131.06	1.00	213.09	0.27		
132.08	0.16	219.10	0.30		
133.08	0.30	221.13	0.30		



6. 2-Perfluoro-2-methylpentylcyclohexanone

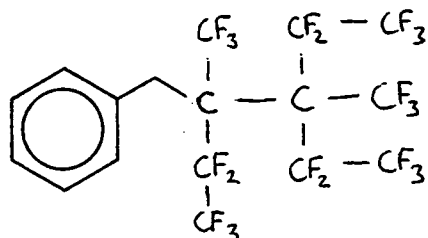
JUE12B#538+ r1 Bgd=526 13-MAY-88 02:30:09:34 70E EI+ 14
 Dpm=0 I=6.1v Hm=416 TIC=213013000 Acnt: Sys:EMSL
 GC= 134 Cal:PFK284

Mass	Z Base	Mass	Z Base	Mass	Z Base	Mass	Z Base
27.01	8.53	134.09	0.28	231.09	0.10	376.79	0.30
39.04	14.85	135.07	0.34	237.13	0.10	377.16	36.38
40.03	2.52	135.98	0.09	238.14	0.12	378.16	4.39
41.06	14.77	139.09	0.09	239.08	0.27	378.72	0.07
50.04	2.49	141.11	0.31	242.06	0.09	379.16	0.45
51.05	13.68	142.01	0.04	245.06	0.33	384.13	0.11
52.06	5.84	143.05	2.11	246.06	0.05	393.14	0.17
53.07	10.93	144.07	0.11	247.05	0.41	395.15	0.11
55.05	3.50	145.07	0.50	248.07	0.09	403.18	0.05
61.02	4.58	146.07	0.05	249.07	0.10	410.11	0.12
65.07	3.62	147.03	0.39	272.73	0.08	410.60	0.07
67.09	9.63	149.06	3.13	279.12	0.25	411.36	0.69
69.03	14.23	150.06	0.31	280.11	0.45	412.14	41.73
73.02	2.55	151.07	0.12	281.10	0.14	412.57	0.09
75.05	11.12	155.06	0.16	281.78	0.08	412.75	0.13
77.03	2.87 F	159.05	2.83	282.05	0.09	413.14	5.23
77.08	31.07 F	160.07	0.07	283.08	1.19	413.56	0.10
78.08	4.66	161.09	0.37	285.24	0.07	413.76	0.15
79.09	100.00	163.06	0.20	286.07	0.17	414.14	14.81
80.10	17.86	165.10	0.14	287.11	0.10	414.61	0.09
87.05	16.71	167.10	0.07	289.09	0.23	415.14	1.76
89.05	8.19	169.08	0.32	293.09	0.07	416.14	0.13
91.05	2.01	174.08	0.09	295.06	0.10		
99.12	7.56	177.11	0.12	299.10	0.09		
100.09	0.88	178.03	0.20	301.06	0.71		
101.08	0.55	179.07	0.41	303.09	0.14		
102.06	0.44	181.06	0.40	307.13	0.14		
103.09	0.74	183.08	0.14	308.14	0.21		
104.06	0.23	187.09	0.10	311.10	0.18		
105.08	0.20	189.09	0.36	315.07	1.59		
106.05	0.85	190.09	0.07	316.13	0.17		
107.06	0.12	191.10	0.33	317.09	0.75		
108.05	0.51	192.05	0.09	318.09	0.13		
109.10	0.10	193.04	0.72	321.11	0.09		
111.05	0.43	195.08	0.12	322.12	0.06		
112.06	0.49	196.05	0.28	323.10	0.07		
113.06	1.12	196.58	0.13	328.15	0.10		
114.08	3.29	197.06	0.13	329.11	0.06		
115.09	7.00	198.05	0.22	333.13	0.25		
116.07	1.48	199.08	0.09	336.12	0.07		
117.08	2.32	201.07	0.13	337.13	0.52		
118.08	0.23	204.06	0.07	338.14	0.06		
118.86	0.07	207.07	0.11	342.22	0.05		
118.91	0.07	209.09	0.43	342.64	0.09		
119.04	3.00	211.11	1.52	342.88	0.08		
120.05	0.21	212.07	0.19	343.10	0.20		
120.09	0.05	213.04	0.13	343.39	0.12		
121.09	0.12	213.12	0.08	343.75	0.10		
124.05	0.74	217.07	0.13	344.19	0.22		
127.09	0.27	219.10	0.21	345.08	0.33		
129.10	0.09	223.09	0.14	346.64	0.16		
129.14	0.09	225.08	0.12	346.89	0.10		
129.95	0.10	229.13	3.23	349.12	0.21		
129.08	0.35	230.12	0.49	350.12	0.05		
130.07	0.13	231.10	0.11	353.11	0.09		
130.97	0.09	239.12	0.25	356.17	0.35		
131.07	0.29	241.14	0.08	357.15	0.37		
131.96	0.13	243.06	0.14	375.14	0.13		
132.08	0.16	245.09	0.16	375.14	0.13		
133.08	0.99	248.10	0.07	375.14	0.13		

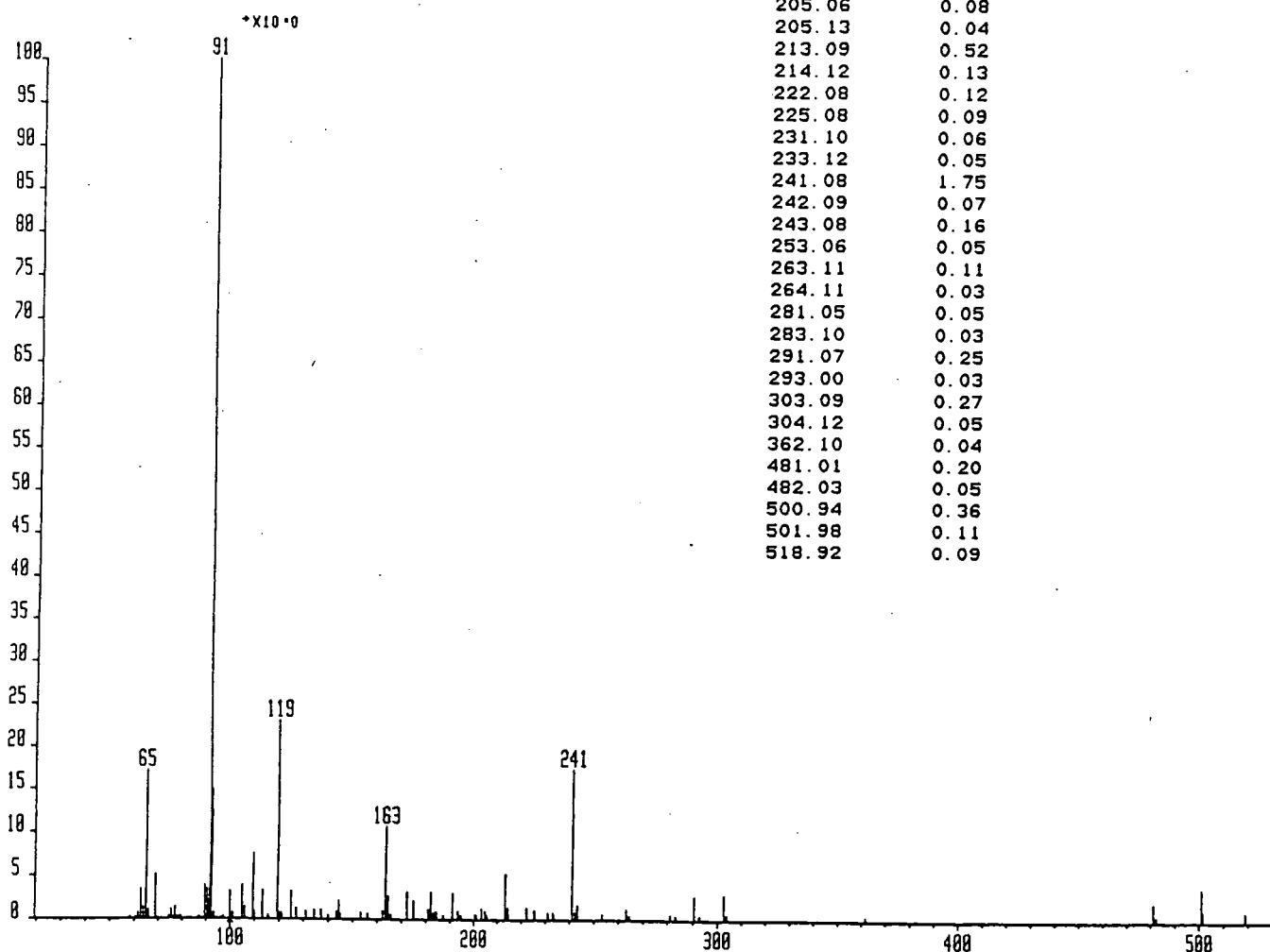


7. Mass spectrum of 3-benzylperfluoro-3,4-dimethyl-4-ethylhexane

31A#643* x1 Bgd=636 8-JUL-88 15:5+0:11:26 70E EI+ 7.
 I=10v Hm=519 TIC=123816000 Acnt: Sys:EMSL
 GC= 143 Cal:PFK265



Mass	% Base
62.71	3.34
63.79	1.14
64.88	17.14
69.09	5.05
77.42	1.26
89.35	3.74
90.35	3.32 F
91.25	1.66 F
91.34	100.00 0
92.33	14.83
119.10	2.30
163.11	1.06
200.13	0.04
201.12	0.03
203.10	0.10
205.06	0.08
205.13	0.04
213.09	0.52
214.12	0.13
222.08	0.12
225.08	0.09
231.10	0.06
233.12	0.05
241.08	1.75
242.09	0.07
243.08	0.16
253.06	0.05
263.11	0.11
264.11	0.03
281.05	0.05
283.10	0.03
291.07	0.25
293.00	0.03
303.09	0.27
304.12	0.05
362.10	0.04
481.01	0.20
482.03	0.05
500.94	0.36
501.98	0.11
518.92	0.09

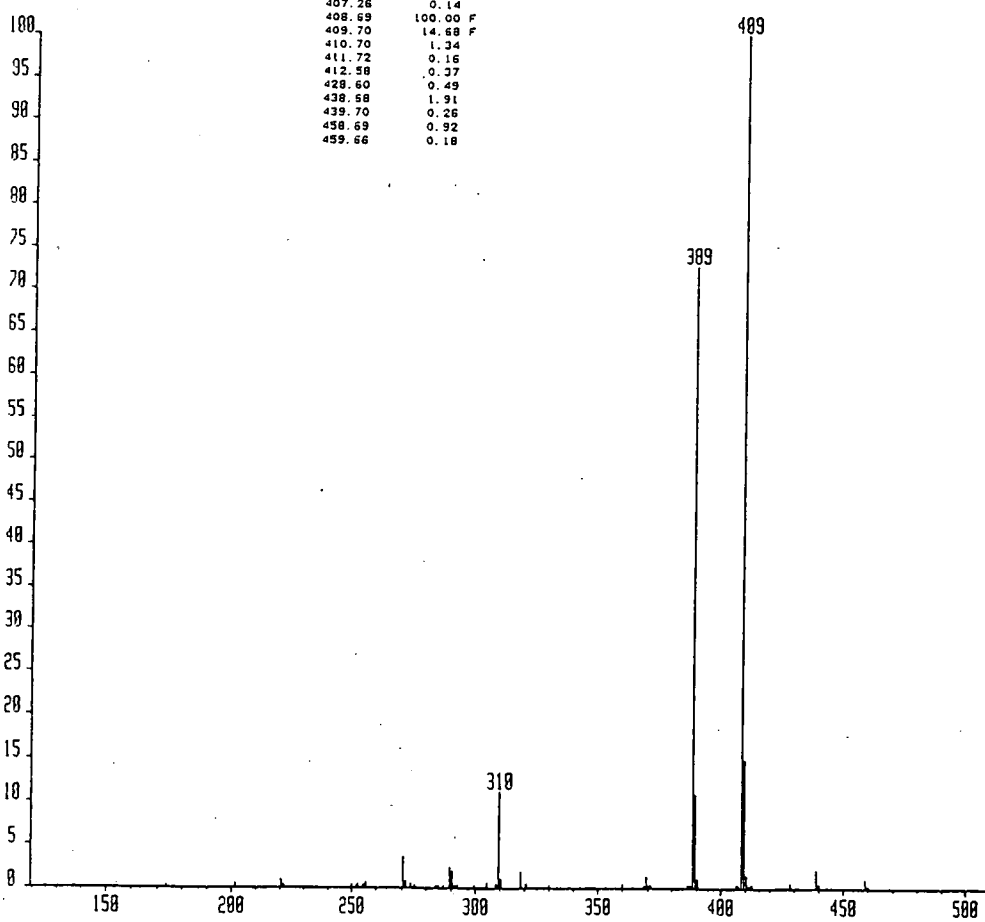


JJE31A#643* x1 Bgd=636 8-JUL-88 15:5+0:11:26 70E EI+
 BpM=91 I=10v Hm=519 TIC=123816000 Acnt: Sys:EMSL
 GC= 143° Cal:PFK265

7a. 3-Benzylperfluoro-3,4-dimethyl-4-ethylhexane

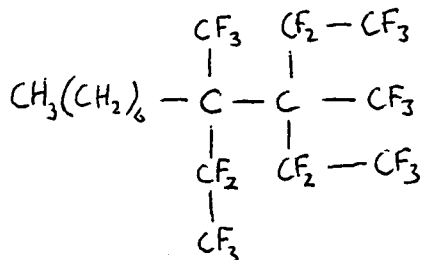
JJE318N1617* x1 Bgd=607 13-OCT-88 12:1+0:10:58 70E CI-
 BpM=0 I=3.2v H#-459 TIC=48940000 Acnt: Sys:OPEN
 GC= 138° Cal:PFK

Mass	% Base
251.71	0.22
252.71	0.24
254.73	0.22
255.71	0.41
270.70	3.41
271.71	0.57
273.72	0.34
275.73	0.13
283.70	0.11
284.66	0.16
286.82	0.14
289.87	2.19
290.65	1.77
291.54	3.15
291.73	0.15
292.56	0.19
292.73	0.18
299.71	0.11
304.68	0.39
308.67	0.24
309.35	0.20
309.66	10.89
309.88	0.11
310.66	0.95
318.65	1.64
320.65	0.26
329.76	0.11
359.63	0.26
368.67	0.15
368.79	0.14
369.73	1.22
370.98	0.20
371.10	0.12
371.18	0.13
386.27	0.11
386.54	0.11
386.70	0.23
387.03	0.12
387.54	0.14
388.68	72.77 F
389.70	10.68 F
390.71	0.87
406.60	0.26
407.11	0.12
407.21	0.17
407.26	0.14
408.69	100.00 F
409.70	14.68 F
410.70	1.34
411.72	0.16
412.58	0.37
428.60	0.49
438.58	1.91
439.70	0.26
458.69	0.92
459.66	0.18

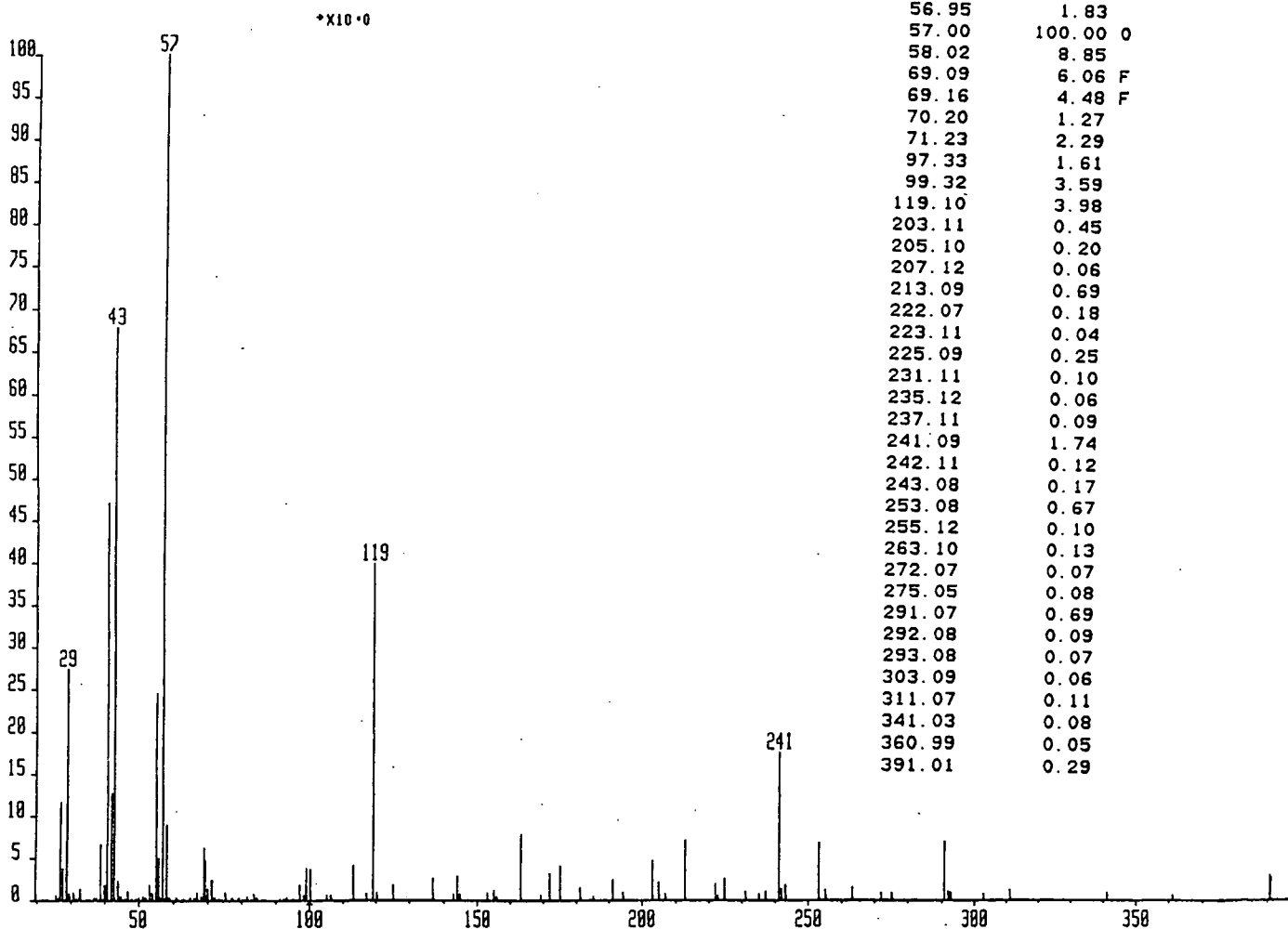


8. Mass spectrum of 3-heptylperfluoro-3,4-dimethyl-4-ethylhexane

JJE318#627* x1 Bgd=608 8-JUL-88 16:2+0:11:08 70E EI+
 BpM=0 I=10v Hm=391 TIC=245361000 Acnt:
 GC= 140°



Mass	% Base
26.57	11.49
27.59	3.70 F
28.61	27.34
32.62	1.25
38.72	6.49
39.74	1.60
40.76	46.93
41.78	12.57
42.80	67.71
43.82	2.10
52.93	1.61
54.96	24.35
55.98	4.87
56.95	1.83
57.00	100.00 O
58.02	8.85
69.09	6.06 F
69.16	4.48 F
70.20	1.27
71.23	2.29
97.33	1.61
99.32	3.59
119.10	3.98
203.11	0.45
205.10	0.20
207.12	0.06
213.09	0.69
222.07	0.18
223.11	0.04
225.09	0.25
231.11	0.10
235.12	0.06
237.11	0.09
241.09	1.74
242.11	0.12
243.08	0.17
253.08	0.67
255.12	0.10
263.10	0.13
272.07	0.07
275.05	0.08
291.07	0.69
292.08	0.09
293.08	0.07
303.09	0.06
311.07	0.11
341.03	0.08
360.99	0.05
391.01	0.29

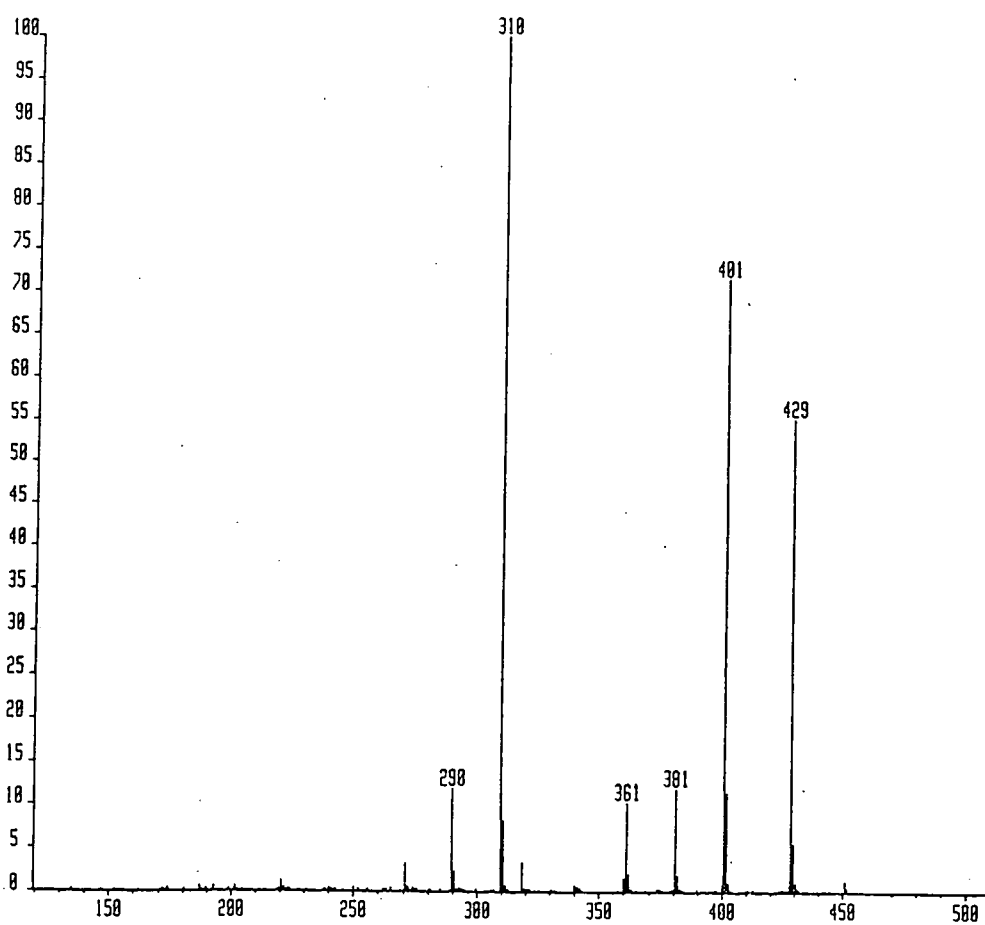


JJE318#627* x1 Bgd=608 8-JUL-88 16:2+0:11:08 70E EI+
 BpM=0 I=10v Hm=391 TIC=245361000 Acnt: Sys:EMSL
 GC= 140° Cal:PFK265

8a. 3-Heptylperfluoro-3,4-dimethyl-4-ethylhexane

JJE31AN1634* x1 Bgd=628 13-OCT-98 11:30-11:17 78E C1-
 8pt=8 I=10v Hw=718 TIC=211388888 Acnt:COI Sys:OPEN
 GC=141^o Cal:PFK

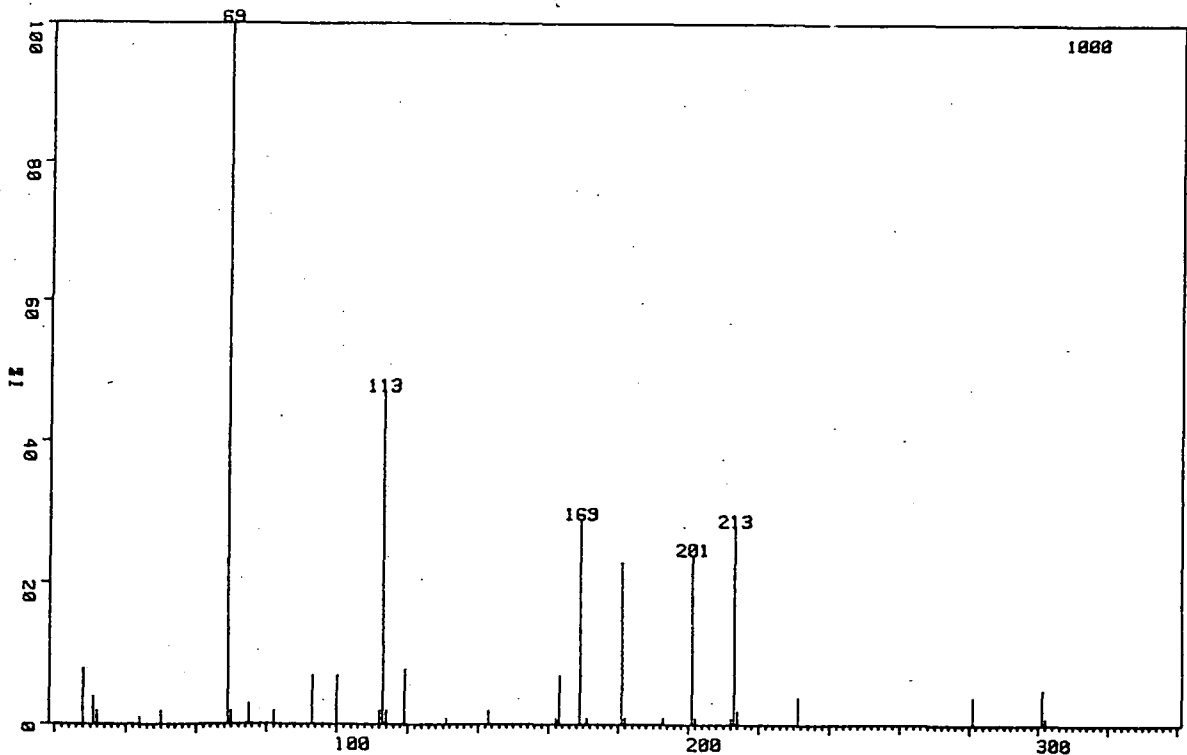
Mass	Z Base	Mass	Z Base	Mass	Z Base
220.74	1.10	321.73	0.10	405.74	0.06
251.56	0.05	323.77	0.05	408.51	0.04
251.74	0.18	325.08	0.07	409.63	0.03
255.74	0.17	325.69	0.03	410.65	0.13
261.73	0.11	330.71	0.08	411.62	0.07
262.63	0.03	331.79	0.05	412.60	0.15
262.75	0.14	331.83	0.02	418.64	0.06
264.80	0.32	339.66	0.59	422.33	0.03
268.78	0.03	340.69	0.50	423.57	0.06
270.17	0.03	340.94	0.05	424.15	0.03
270.39	0.03	341.74	0.23	424.96	0.08
270.75	3.04	342.62	0.06	425.14	0.05
271.38	0.07	357.72	0.05	425.28	0.05
271.74	0.41	359.67	1.43	425.32	0.06
272.50	0.05	359.99	0.08	425.49	0.06
272.78	0.07	360.70	10.24	425.70	0.05
273.74	0.24	361.72	1.39	425.77	0.05
274.74	0.08	362.69	0.19	425.95	0.06
275.71	0.08	364.93	0.04	426.11	0.05
280.70	0.09	365.02	0.04	426.23	0.05
284.67	0.08	368.46	0.05	426.38	0.06
288.56	0.03	373.63	0.09	426.68	0.07
289.02	0.05	374.44	0.03	427.32	0.64 F
289.10	0.06	374.65	0.10	427.92	55.09 F
289.24	0.05	375.65	0.02	429.63	5.52
289.69	11.80	378.68	0.05	430.06	0.06
290.40	0.03	379.26	0.05	430.22	0.06
290.70	2.25	379.66	0.08	430.55	0.85
290.96	0.04	379.79	0.03	430.96	0.05
291.72	0.19	380.29	0.17	431.39	0.04
292.71	0.32	380.68	11.96	431.65	0.13
293.70	0.10	381.02	0.03	450.65	0.39
294.71	0.03	381.11	0.08	451.63	0.03
299.69	0.15	381.35	0.06	454.94	0.03
303.93	0.07	381.69	1.79	561.61	0.06
304.67	0.05	382.72	0.18		
304.75	0.05	383.49	0.06		
304.94	0.05	383.62	0.05		
305.34	0.05	383.78	0.05		
305.63	0.05	389.62	0.17		
305.71	0.04	391.69	0.07		
305.90	0.05	391.81	0.05		
306.26	0.05	392.66	0.06		
306.29	0.05	395.00	0.03		
306.49	0.06	395.49	0.05		
306.62	0.07	395.76	0.05		
306.70	0.05	395.82	0.03		
306.74	0.06	396.11	0.03		
306.92	0.08	396.33	0.05		
309.70	100.00 F0	396.61	0.04		
310.68	3.13 F	396.69	0.06		
311.22	0.04	396.81	0.05		
311.38	0.07	396.99	0.07		
311.68	0.60	397.29	0.09		
312.69	0.14	397.73	0.07		
318.40	0.05	400.29	0.78 F		
318.68	3.23	400.67	71.50 F		
319.68	0.24	401.68	11.41 F		
320.67	0.19	402.67	0.36		
321.26	0.06	403.19	0.06		



9. 2-Fluoropentane-2-methyl

JJE31#80* x1 Bgd=75 17-FEB-88 09:0+0:01:25 70E EI+ 3
BpM=0 I=10v Hm=302 TIC=216654000 Acnt: Sys:EMSL
GC= 53 Cal:PFK16E

Mass	% Base
28.04	7.47
31.03	3.61
32.02	1.60
44.03	1.25
50.04	1.44
69.05	100.00
70.05	2.09
75.06	2.44
82.06	1.39
93.06	6.83
100.06	6.66
112.07	1.32
113.07	46.28
114.08	1.34
119.06	7.94
131.07	1.05
143.07	1.79
150.07	0.23
155.07	0.05
159.07	0.10
162.06	0.37
163.07	7.10
164.08	0.24
169.08	28.31
170.08	0.86
181.08	22.30
182.08	0.91
193.09	0.86
194.12	0.05
201.09	23.91
202.10	1.06
212.09	0.60
213.09	27.77
214.09	1.46
231.09	3.78
232.10	0.23
251.10	0.17
281.10	3.98
282.11	0.23
301.11	4.51
302.12	0.22



COLLOQUIA AND CONFERENCES

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

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

b) all research conferences attended and papers presented by the author during the period in which the research for the thesis was carried out;

c) details of the postgraduate induction course.

a) COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS

1st AUGUST 1987 to 31st JULY 1988

1987

- 15th October * WINTER, Dr. M.J. (University of Sheffield)
Pyrotechnics (Demonstration Lecture)
- 22nd October * GRAY, Prof. G.W (University of Hull)
Liquid Crystals
- 29th October * van ROSE, Mrs. S. (Geological Museum)
Chemistry of Volcanoes
- 4th November MAPLETOFT, Mrs. M. (Durham Teachers' Centre)
Salters' Chemistry
- 5th November * BUTLER, Dr. A.R. (University of St Andrews)
Chinese Alchemy
- 12th November * SEEBACH, Prof. D. (E.T.H. Zurich)
From Synthetic Methods to Mechanistic Insight



- 19th November DAVIDSON, Dr. J. (Herriot-Watt University)
Metal Promoted Oligomerisation Reactions
- 26th November WILLIAMS, Dr. D.H. (University of Cambridge)
* Molecular Recognition
- 3rd December HOWARD, Dr. J. (I.C.I. Wilton)
* Chemistry of Non-Equilibrium Processes
- 10th December LUDMAN, Dr. C.J. (Durham University)
* Explosives
- 16th December SWART, Mr. R.M. (I.C.I.)
* The Interaction of Chemicals with Bilayers
- 19th December SAMMES, Prof. P.G. (Smith, Kline and French)
* Chemical Aspects of Drug Development

1988

- 21st January PALMER, Dr. F. (University of Nottingham)
* Luminescence (Demonstration Lecture)
- 28th January CAIRNS-SMITH, Dr. A. (Glasgow University)
* Clay Minerals and the Origins of Life
- 9th February LACEY, Mr. (Durham Chemistry Teachers' Centre)
Double Award Science
- 11th February TURNER, Prof. J.J. (University of Nottingham)
Catching Organometallic Intermediates
- 18th February BORER, Dr. K. (Industrial Research Laboratories)
* The Brighton Bomb - A Forensic Science View
- 25th February UNDERHILL, Prof. A. (University of Bangor)
* Molecular Electronics
- 3rd March GRAHAM, Prof. W.A.G. (University of Alberta)
Rhodium and Iridium Complexes in the
Activation of Carbon-Hydrogen Bonds
- 7th March KOCH, Prof. H.F. (Ithaca College, U.S.A.)
* Does the E2 Mechanism Occur in Solution?
- 16th March BOSSONS, L. (Durham Chemistry Teachers' Centre)
GCSE Practical Assessment
- 7th April HARTSHORN, Prof. M.P. (Canterbury University)
Aspects of Ipso-Nitration

- 13th April ROBERTS, Mrs. E. (SATRO Officer for Sunderland)
Links Between School and Industry
- 18th April NIETO DE CASTRO, Prof. C.A. (University of
Lisbon and Imperial College)
Transport Properties of Non-Polar Fluids
- 25th April BIRCHALL, Prof. D. (I.C.I. Advanced Materials)
* Environmental Chemistry of Aluminium
- 27th April RICHARDSON, Dr. R. (University of Bristol)
X-Ray Diffraction from Spread Monolayers
- 27th April ROBINSON, Dr. J.A. (University of Southampton)
* Aspects of Antibiotic Synthesis
- 28th April PINES, Prof. A. (University of California)
* Some Magnetic Moments
- 11th May SODEAU, Dr. J. (University of East Anglia)
Spray Cans, Smog and Society
- 11th May MCDONALD, Dr. W.A. (I.C.I. Wilton)
* Liquid Crystal Polymers
- 8th June MAJORAL, Prof. J.-P. (Universite Paul Sabatier)
Stabilisation by Complexation of Short-Lived
Phosphorous Species
- 29th June OLAH, Prof. G.A. (University of Southern
* California)
New Aspects of Hydrocarbon Chemistry
- 29th June JONES, Dr. M.E. (Durham Teachers' Centre)
GCSE Chemistry Post-Mortem
- 6th July JONES, Dr. M.E. (Durham Teachers' Centre)
GCE Chemistry A Level Post-Mortem

Lectures attended are starred.

b) RESEARCH CONFERENCES ATTENDED

21st Sheffield Symposium on 'Heterocycles', Sheffield,
Decemeber, 1987.

Graduate Symposium, Durham, April, 1988.

c) POSTGRADUATE INDUCTION COURSE

In each part of the course, the uses and limitations of the various services available were explained.

Departmental Organisation:- Dr. E.J.F. Ross.

Safety Matters:- Dr. M.R. Crampton.

Electrical Appliances:- Mr. B.T. Barker and Dr. A. Royston

Chromatography and Micro Analysis:- Mr. T.H.F. Holmes.

Atomic Adsorption Spectrometry and Inorganic Analysis:-
Mr R. Coult.

Library Facilities:- Mr. R.B. Woodward.

Mass Spectrometry:- Dr. M. Jones.

Nuclear Magnetic Resonance Spectroscopy:- Dr. R.S. Matthews.

Glassblowing Techniques:- Mr. R. Hart and Mr. G. Haswell.

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5. J.H. Clark, Chem. Rev., **80**, 429 (1980).
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