Functional fluorocarbons via free radical additions to hexafluoropropene

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U N I V E R S I T Y O F D U R H A M

A THESIS
entitled

FUNCTIONAL FLUOROCARBONS VIA FREE RADICAL ADDITIONS TO HEXAFLUOROPROPENE

Submitted by

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A candidate for the degree of Doctor of Philosophy

1987

To
my parents for their
continuing support during my
university career and my
wife, Carol, without whose
support this thesis would
not have seen the light of
day

ACKNOWLEDGEMENTS

Thanks to Dr R. Matthews, Dr M. Jones, and Mrs M. Cocks for their help with numerous spectra and analyses. Thanks to Mr T. Holmes and members of lab. 117 for their help and companionship. And special thanks to Mr J. Parkinson and Mr D. Hunter for help with equipment and to Mr R. Hart and Mr G. Haswell for making vast amounts of glassware. And thanks to all the other technical and academic staff too numerous to mention and the people of Durham for making my university career so pleasant.

Thanks to Professor R.D. Chambers for his continued helpful advice and for many useful theoretical discussions. Also to Dr. R.L. Powell (ICI, Mond) and Dr. F. Drakesmith (Electricity Council Research Council) for their interest and for their co-operation with the Science and Engineering Research Council in providing a CASE award for the support of this work.

MEMORANDUM

The work described in this thesis was carried out at the University of Durham between October 1982 and October 1985. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

NOMENCLATURE

A capital F in a ring denotes that the ring and all unmarked substituents are fully fluorinated.

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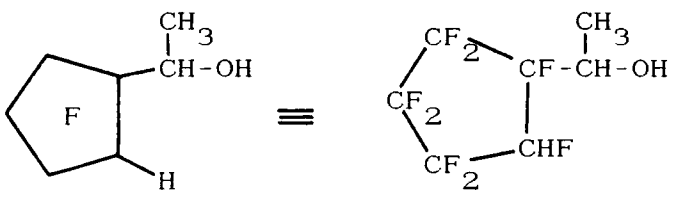


ABSTRACT

The effect of substituents on the carbon-hydrogen bond reactivity in free radical additions to hexafluoropropene has been investegated. Ethers, amines, amides, isocyanates and silanes all give free radical adducts. The order of reactivity has been compiled. The reactivity of cyclic ethers, amines and amides is discussed in terms of the stereoelectronic effect. The reactivity of tetrahydrofuran and N-methylpyrrolidine towards hexafluoropropene under uninitiated conditions has also been demonstrated.

The ease of hydrogen abstraction from the substrates was estimated using a method based on the thermal decomposition of ditertiarybutylperoxide. A correlation between the ease of hydrogen abstraction and free radical reactivity is demonstrated, although the reactivity of aldehydes is not simply explained.

The adducts of ethers and amines can be dehydrofluorinated to give a variety of alkenes. Further reactions of aldehyde and isocyanate adducts has given good synthetic routes to other functionally substituted fluorocarbons. The amide adducts are also a useful source of fluorinated amines which cannot be obtained directly.

An amine 1:1 adduct has been fully fluorinated over cobalt trifluoride at 440°C in good yield, although higher adducts give lower yields. Remarkably high yields of perfluorinated alkanes are produced by successive reaction with sulphur tetrafluoride and cobalt trifluoride.

CONTENTS

INTRODUCTION

CHAPTER 1

EFFECT OF ADJACENT FUNCTIONAL GROUPS ON THE FORMATION AND REACTIVITY OF FREE RADICALS

A INTRODUCTION

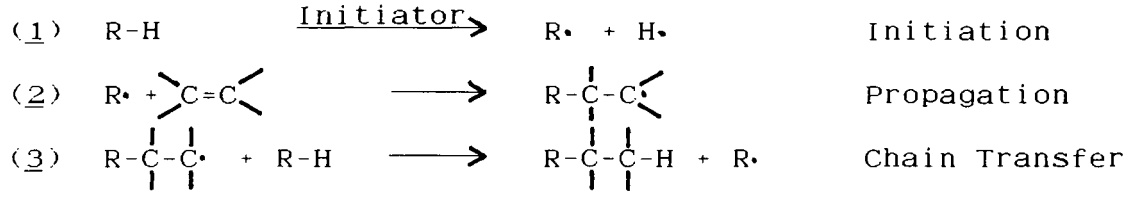
The introduction of fluorine can have a profound effect on the properties of organic compounds, whether the molecule contains a single fluorine atom or is fully fluorinated. Also the similar steric requirement of fluorine and hydrogen atoms are such that, in principle, a range of fluorocarbon compounds could be synthesised that is analagous to the huge range of known hydrocarbon compounds. As there are only very few naturally occurring compounds containing fluorine, the chemistry which has evolved is entirely synthetic. A wide range of methods has been developed over the years and a number of books have been published on the subject[1-5]. The special properties of fluorinated compounds have led to their use in a wide variety of applications despite their intrinsic high cost. Thus their thermal and chemical stability, their unususal biological activity, and their extreme water and oil repellancy have found applications such as in plastics, refrigerants, aerosol propellants, blood substitutes, anaesthetics, pesticides and surfactants.

The free radical addition of carbon centred radicals to alkenes have been known since the late 1940's and is the subject of early reviews[6-10], however the use of these reactions in synthetic chemistry has attracted little

attention. Free radical additions to fluorinated alkenes is a potential route to new functional fluorocarbon compounds[11,12] and will be discussed in detail.

B FREE RADICAL CHAIN MECHANISM

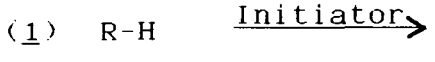
The free radical addition reaction occurs via three important steps, though in some cases alternative competing reactions may also occur simultaneously, such as telomerisation. The important steps are:-



In order to form a rapid and long chain reaction, steps (2) and (3) must be of low activation energy, and neither must be too endothermic. It is the aim of this discussion to show the importance of substitution of both the radical and the alkene in order to meet these requirements.

1 The Effect of Substitution on the Formation of Radicals

The initiation step in a free radical addition reaction involves the breaking of a bond to form a radical pair (1). The reaction is influenced by many factors and



has been recently reviewed[13,14]. In this section the factors

influencing the breaking of the carbon-hydrogen bond will be discussed.

(a) Bond Dissociation

The initiation step in a free radical addition involves the breaking of a bond to form a radical pair. The energy required to do this is the bond dissociation energy (B.D.E.):-

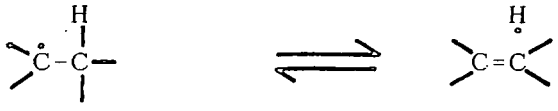
(1) R-H $\xrightarrow{\text{Initiator}}$ R$\cdot$ + H$\cdot$ $\quad\Delta H$ = B.D.E. (R-H)

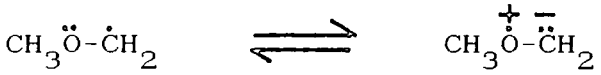
If the initiator and the type of bond being broken remains constant then other factors such as stereochemistry will be small. In this thesis the bond being broken is a carbon-hydrogen bond and a series of B.D.E.'s for different environments is shown[15,16] (table 1). Any substitution of

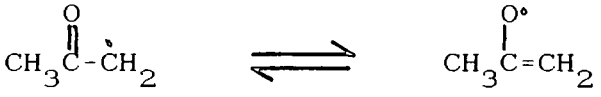
Table 1 Bond Dissociation Energies for C-H

R-H	KJ mol^{-1}	R-H	KJ mol^{-1}
H_3C-H	434	CH_2=$CHCH_2$-H	356
Cl_3C-H	402	CH_3COCH_2-H	385
F_3C-H	434	$HOCH_2$-H	389
Et-H	410	HOCH(Me)-H	389
^{i}Pr-H	395	CH_3OCH_2-H	385
^{t}Bu-H	380	HOCO-H	376
Ph-H	431	HCO-H	368
$PhCH_2$-H	356	CH_3CO-H	366
Ph_3C-H	313	PhCO-H	310

a methyl group leads to stabilisation. Simple hydrocarbons are able to stabilise a radical via hyperconjugation (4). Substitution with groups containing non-bonded p electrons (5) or π electrons (6) are stabilised by delocalisation of the unpaired radical[17].

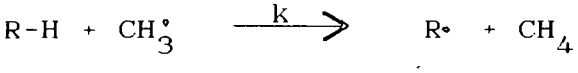
(4) 

(5) 

(6) 

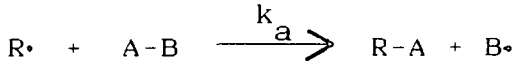
(b) Hydrogen Atom Abstraction Rates

The stability of a radical can also be demonstrated by the rates of hydrogen abstraction (7). If the abstracting radical remains constant then the rate will depend on the B.D.E. and the stability of the radical produced. A series

(7) 

of rate constants is shown[18] (table 2). These rate constants show the same trends as the B.D.E.'s. Thus it is clear that radicals can be produced more easily in substituted compounds.

The rate constant for a radical-molecule reaction:-



is defined by the relationship:-

$$-\frac{d[AB]}{dt} = \frac{d[RA]}{dt} = k_a[R\bullet][AB]$$

Table 2 Rate Constants for Hydrogen Abstraction

$$R\text{-}H + CH_3^\bullet \longrightarrow R\bullet + CH_4$$

R-H	log k_2($cm^3 mol^{-1} s^{-1}$)	R-H	log k_2($cm^3 mol^{-1} s^{-1}$)
CH_3-H	4.6	CH_3COCH_2-H	6.6
CF_3-H	4.7	$HOCH_2$-H	6.2
Et-H	5.9	HOCH(Me)-H	6.8
^{i}Pr-H	6.8	CH_3OCH_2-H	6.5
^{t}Bu-H	7.4	HCO_2CH_2-H	5.6
Ph-H	6.2	$CH_3CO_2CH_2$-H	7.6
$PhCH_2$-H	6.8	HCO-H	9.0
Me_2NCH_2-H	7.4	CH_3CO-H	7.8
Me_3SiCH_2-H	6.4		

In order to determine rate constants it is necessary to know the rate of reaction and also the concentration of the radical. Since most radicals are extremely reactive, the measured rates will often be close to the diffusion-controlled limit and the radical concentrations will be very low. Thus absolute rate constant measurement may be difficult. There are three main methods used for these absolute rate constant measurements. The rotating sector method[19] can be used for photo-initiated reactions. The beam of light used for the initiation is passed through a disc which has a sector cut out. The variation of overall reaction rate with variation of rotation speed of the disc

can be used to calculate the rate constant. The photochemical aftereffect method relies on being able to observe some physical property after initiation has ceased. Laser flash photolysis[20-22] and pulsed radiolysis are special cases of this method. Steady-state E.S.R.[23] can be used if a high concentration of radicals can be achieved and usually requires a very high rate of initiation.

The above physical techniques, while being accurate are not very convenient for the synthetic organic chemist who simply wants to know approximate rates of a new reaction without spending a lot of time and money finding it. The alternative is to use two competing reactions where the rate of one is known and then the rate of the other can be found. The competing reaction of known rate may be a rearrangement or an alternative radical-molecule reaction.

One of the most widely used radical clocks is that using the β-scission of the tertiarybutoxy radical which has been used for over thirty years[24]. This easily produced radical will undergo a rearrangement to acetone and methyl radical with a known rate (k_b). Thus the rate of abstraction of a hydrogen atom from a substrate (k_a) can be

$$^{t}BuO\bullet + A\text{-}H \xrightarrow{k_a} {}^{t}BuOH + A\bullet$$

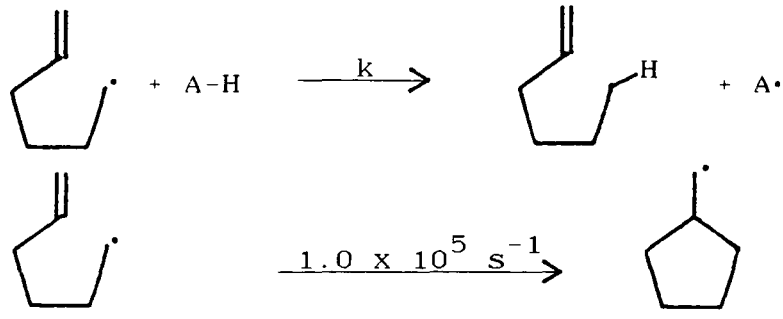
$$^{t}BuO\bullet \xrightarrow{k_b} CH_3COCH_3 + CH_3\bullet$$

found from measuring the tertiary butanol and acetone produced in the reaction. If the substrate is present in excess:-

$$\frac{k_a}{k_b} = \frac{[^tBuOH]}{[AH][Me_2CO]}$$

It is usual to repeat this method with a substrate whose rate of hydrogen abstraction is known, or is to be used as a standard for comparison.

There are now a large number of radical clocks whose rate of rearrangement have been accurately measured. One which has been given a lot of attention in the cyclisation of the 5-hexenyl radical system[25]:-



and has been used in a wide variety of mechanistic studies[26].

The simplicity of apparatus used and the relative ease of product analysis will ensure that radical clock techniques will be widely used by organic chemists in the future.

(c) Polar Effects

Polar Effects can be demonstrated by free radical halogenation reactions. The two important propagation steps are reactions (8) and (9). The enthalpies of reaction are shown for bromine and chlorine[8]. Halogenation of a hydrocarbon compound gives a mixture of all possible halides from

				ΔH/KJ mol^{-1}	Cl	Br
(8)	X• + R-H	⟶	R• + HX		-20	+46
(9)	R• + X_2	⟶	R-X + X•		-97	-92

abstraction of the various hydrogen atoms in the molecule. The relative reactivity of the different hydrogen atoms can be expressed as their relative selectivities:-

$$\text{Relative Selectivity, } RS_x^y = \frac{k_y}{k_x} \times \frac{x}{y}$$

k_x, k_y are rate constants for hydrogen abstraction at positions x and y.

x, y are the number of hydrogen atoms at positions x and y.

The position of halogenation will be determined by the position of hydrogen abstraction (8). For chlorination this reaction is exothermic , thus according to the Hammond Postulate[27], the transition state will occur early on the reaction coordinate. Little bond making or breaking will have occurred and so polar effects will become important (10).

(10) X-C-H ←+ ····· +→ •Cl X= Electron withdrawing group

Relative selectivities for chlorination of a series of substituted butanes is shown[8] (table 3). The substitution pattern shows that the high reactivity of the chlorine atom leads to low selectivity. Substitution of the 1-position with an electron withdrawing group leads to induction of two opposing dipoles in the transition state (10) and causes

Table 3 Relative Selectivities for Chlorination of Substituted Butanes

X	CH_2X ——	CH_2 ——	CH_2 ——	CH_3
H	1	3.6	3.6	1
F	0.9	1.7	3.7	1
Cl	0.8	2.1	3.7	1
CF_3	0.04	1.2	4.3	1

deactivation. A small effect is also seen for the 2-position while the 3- and 4- positions are unaffected.

For bromination the hydrogen abstraction reaction is endothermic, thus according to the Hammond Postulate[27], the transition state will occur late on the reaction co-ordinate. Carbon-bromine bond formation will be advanced and the carbon-hydrogen bond almost fully dissociated (11) and so the B.D.E. of the two bonds will be the dominant

(11) Br —— H ····· ·C 

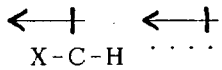
factor. Relative selectivities for bromination of a series of substituted butanes is shown[8] (table 4). The lower reactivity of the bromine atom leads to higher selectivities. At the 1-position, substitution lowers the carbon-hydrogen B.D.E. and is activated. Polar effects, however, will be important at the 2-position and is thus deactivating.

Polar effects are also important in hydrogen abstraction by methyl radicals. In the transition state however the dipole formed by the hydrogen atom and the

Table 4 Relative Selectivities for Bromination of Substituted Butanes

X	CH_2X	—	CH_2	—	CH_2	—	CH_3
H	1		80		80		1
F	9		7		90		1
Cl	34		32		80		1
CF_3	1		7		80		1

attacking radical is reversed (12). Relative selectivities for hydrogen abstraction by methyl radicals from a series of

(12)  X = electron withdrawing group

substituted butanes are shown[14] (table 5). The substitution of an electron withdrawing group activates the 1-position by the favourable dipoles produced in the transition state. Thus it can be seen that the methyl radical is nucleophilic while the chlorine atom is electrophilic.

Table 5 Relative Selectivities for Hydrogen Abstraction by Methyl Radicals

X	CH_2X	—	CH_2	—	CH_2	—	CH_3
F	8		10		10		1
CF_3	1.3		3		10		1

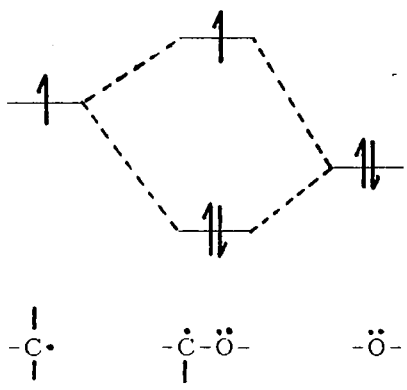
(d) Stereoelectronic Effect

The interaction of a lone pair of electrons or π-bonded electrons adjacent to a radical leads to

stabilisation. This can be shown, for example for an ether, by simple valence bond theory (13) or frontier orbital theory[28] (14).

(13) $CH_3\ddot{O}\text{-}\dot{C}H_2 \longleftrightarrow CH_3\overset{+}{\dot{O}}\text{-}\overset{-}{\ddot{C}}H_2$

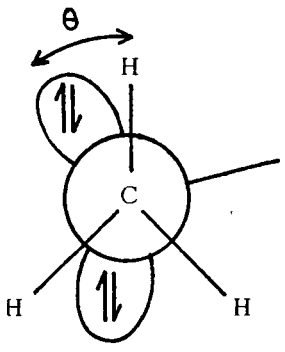
(14)



For maximum stabilisation of a radical by an adjacent lone pair of electrons, the two atomic orbitals involved must be co-planar[29,30]. A theoretical rationalisation has been based on the concept of conjugative delocalisation[31] between the adjacent non-bonded electron pair and the radical orbital.

The lone pairs on an oxygen can be considered to be sp^3 hybridized or one having more p character and the other more s character[32]. For this discussion it will be assumed that they are equivalent sp^3 orbitals.

The extent of the delocalisation becomes a function of the dihedral angle (θ) between the C-H bond being broken and the orbital of the heteroatom. Many rate constants for hydrogen abstraction have been measured and some are shown[33] (table 6) to demonstrate the stereoelectronic effect. The reactivity of cyclic ethers varies with



View down C-O bond

different ring size and decreases in the order:-

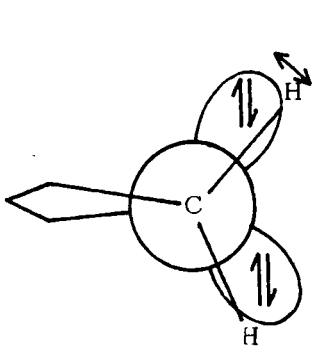
$$5 > 7 > 4 > \text{acyclic} > 6$$

Table 6 Rates of H Abstraction by $^{t}BuO\cdot$ at 27°C

Ether	$M^{-1}s^{-1}$
oxacyclobutane	4.0×10^{6}
tetrahydrofuran	8.25×10^{6}
tetrahydropyran	2.7×10^{6}
oxacycloheptane	4.4×10^{6}
diethylether	3.9×10^{6}

This can be explained simply by looking at the conformation of the ethers. For a five membered ring (15) the ring will be nearly planar and the resulting value for θ will be close to 0°. For a six membered ring, in a chair

(15)

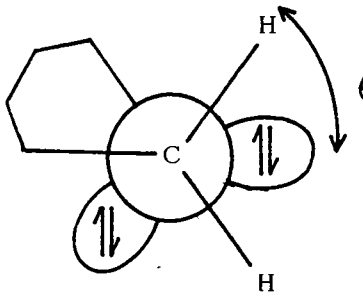


View down C-O bond

conformation (16), the value for θ will be nearer 60° and so the stabilisation effect will be very small. By considering all of the rings, the order found is explained by the stereoelectronic effect.

A similar result would be obtained if the carbon-hydrogen bond were required to be co-planar with the oxygen lone pair for abstraction to occur. The extra strain energy

(16)

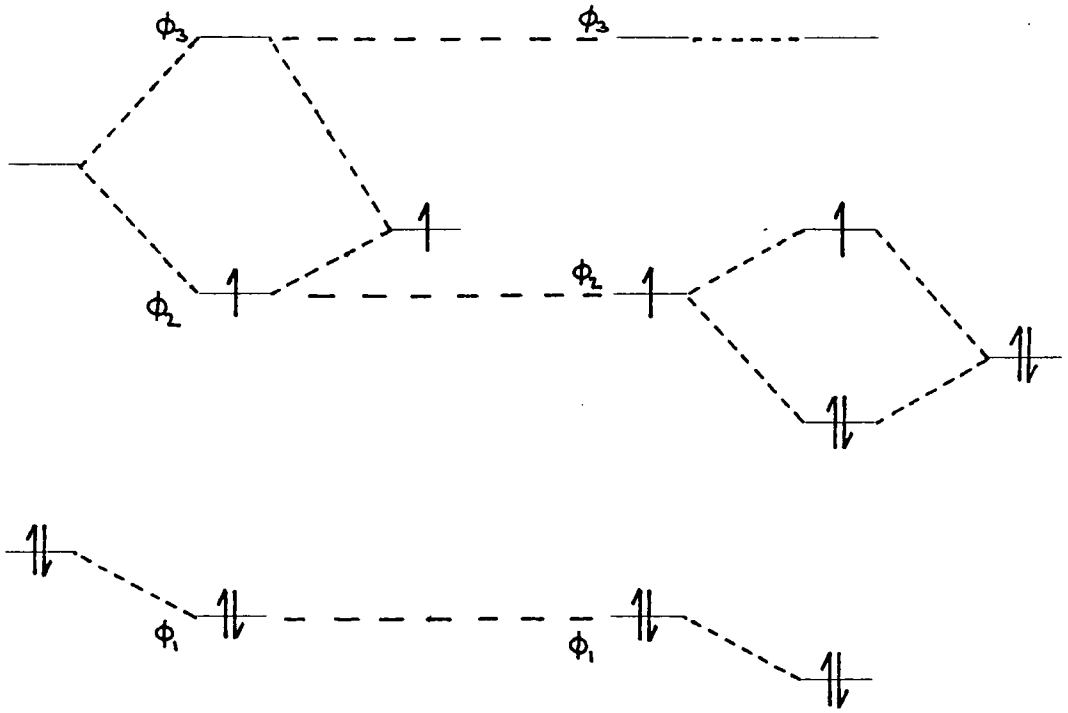


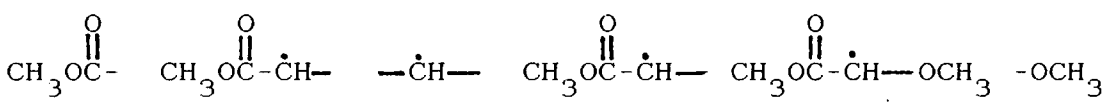
View down C-O bond

required to flatten the rings would destabilise the process. The six membered ring would again be expected to be the least reactive as this would require the largest amount of energy to make the ring planar.

(e) Captodative Effect

It has been seen that substitution of a radical by either an electron withdrawing or electron donating group leads to stabilisation. The substitution of a radical by both types of group simultaneously can act synergetically and lead to very stable radicals. The concept of merostabilisation[34] or captodative stabilisation[35,36] has led to a new range of radical reactions and stable radicals. The stabilisation can be rationalised by frontier orbital theory, for example in $CH_3OCH_2CO_2CH_3$.





2 The Effect of Radical Substitution on Reactivity

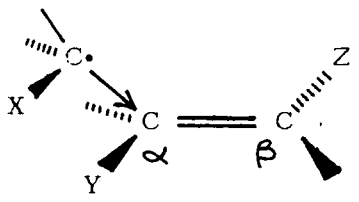
The propagation step in a free radical addition (2) will be affected by the character of both the radical and the alkene. The factors affecting this reaction have recently been reviewed[37,38] and in this section the effect of radical substitution is discussed.

(2) 

(a) Molecular Orbital Theory and Polar Effects

The propagation step in the addition reaction involves the formation of a σ bond and the breaking of a π bond and so will in general be exothermic[7]. Thus according to the Hammond postulate[27] the transition state will occur early on

the reaction coordinate, so that the σ bond making and π bond breaking are not far advanced. Calculations favour an unsymmetrical transition state (17) in which the distances

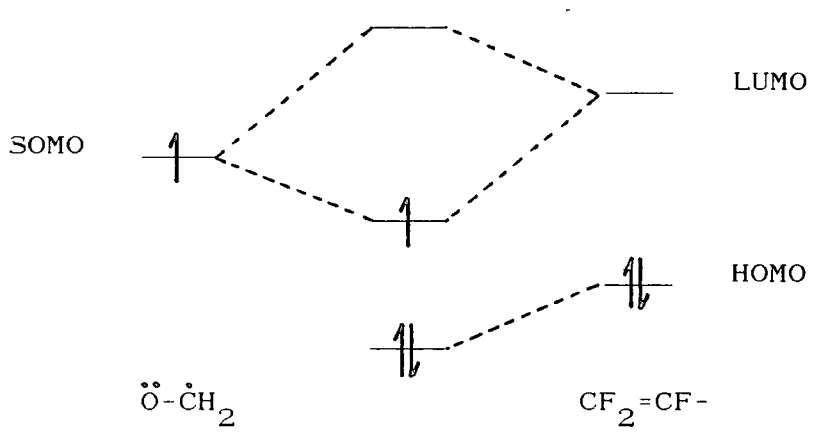
(17) 

between the radical and the two vinylic carbon atoms are unequal[39,40]. If the α-steric effects are small (i.e. Y is small), then the existence of an early transition state allows us to predict polar effects in the free radical addition by the use of frontier orbital theory.

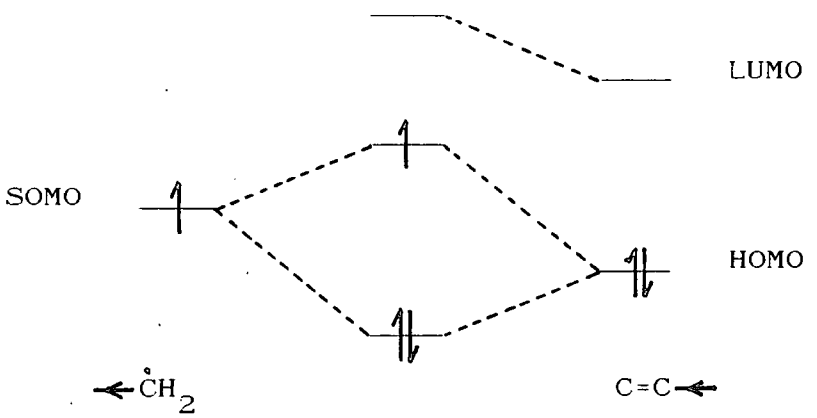
To a first approximation, the theory states that the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecualr orbital (LUMO) of the reactants will determine the rate variations[28]. The smaller the energy difference between these two frontier orbitals, the larger will be the stabilising effect. The frontier orbital of the radical will be the singly occupied molecular orbital (SOMO) and the interaction of this with the HOMO and LUMO of the alkene should allow us to predict the polar effects. The interaction of the orbitals depends on whether the SOMO of the radical is closer in energy to the HOMO or LUMO of the alkene.

If we have a radical with electron donating substituents then the energy of its SOMO will be increased, the energy difference between the SOMO and the LUMO of the

alkene will be reduced and will lead to an increased rate of addition. Furthermore if electron withdrawing substituents are now incorporated into the alkene the LUMO energy will be decreased and again the LUMO-SOMO energy difference will be reduced and lead to a further increase in rate of addition. For example in the case of addition of dimethylether to hexafluoropropene:-



For radicals with electron withdrawing substituents the energy of its SOMO will be decreased and the interaction of the SOMO with the HOMO of the alkene will become dominant:-



To sum up the theory, the greater the power of electron withdrawing substituents on the radical, the greater will be

its reactivity towards electron rich double bonds. While, the greater the power of electron donating substituents, the greater will be its reactivity towards electron deficient double bonds. This can be demonstrated by comparing the relative reactivity of a range of methyl radicals towards ethene and a range of fluorinated alkenes[37] (table 7). As the methyl radical becomes more electrophilic with increased fluorine substitution the reactivity towards the electron deficient fluorinated alkenes becomes lower. As the alkenes become more electron deficient the reactivity of the nucleophilic methyl radical increases while the reactivity of the electrophilic trifluoromethyl radical decreases.

Table 7 Ratios of Rate of Addition

$k(alkene)/k(CH_2=CH_2)$

	$CH_2=CHF$	$CH_2=CF_2$	$CHF=CF_2$	$CF_2=CF_2$
$\bullet CH_3$	1.1	-	5.8	9.5
$\bullet CH_2F$	0.4	-	-	3.4
$\bullet CHF_2$	0.4	0.1	0.3	1.1
$\bullet CF_3$	0.5	0.2	0.05	0.1

(b) Steric Effects

Steric effects can have a major influence on free radical reactions. Thus in the addition of substituted methyl radicals[13] (table 8) to ethene it can be seen that as the bulk of the radical is increased the rate of addition is decreased, showing steric effects to be important. If the substituent groups are large enough the radicals may

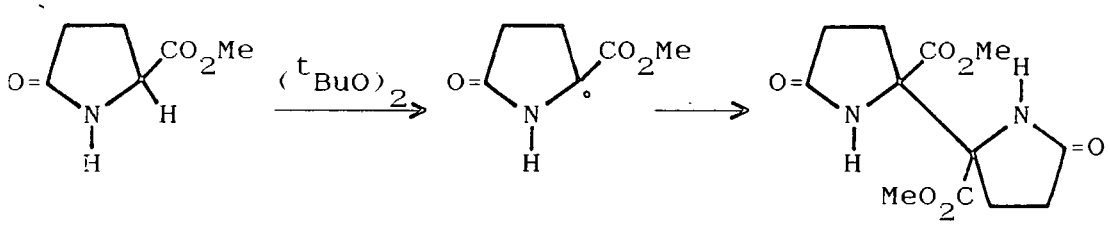
Table 8 Relative Rates of Addition to Ethene

Radical:-	$CH_3^{\bullet}$	$CH_3CH_2^{\bullet}$	$(CH_3)_2CH^{\bullet}$	$(CH_3)_3C^{\bullet}$
k_{rel}	1.0	0.8	0.5	0.2

become persistent and the reactivity reduced to zero, for example in the radicals $R_3C^{\bullet}$ where R is ^{i}Pr[41], ^{t}Bu[42], Me_3Si[42] and $(CF_3)_2CF$[43].

(c) Captodative Effects

The stability of captodative radicals prevents their reaction with alkenes due to the large loss of stabilisation energy in the addition step. Thus they normally undergo dimerisation or react with other radicals. The dehydro-dimerisation of captodatively substituted compounds can be achieved very easily, for example[36]:-



3 The Effect of Alkene Substitution on Reactivity

The effect of substitution of the alkene on the reactivity towards radicals (2) will be discussed in this section and has been the subject of recent reviews[37,38].

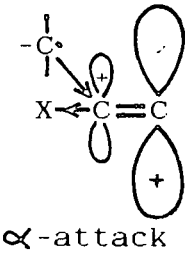
(2) $R^{\bullet} + >C=C< \longrightarrow R-\overset{|}{C}-\overset{|}{C}^{\bullet}$

(a) Molecular Orbital Theory and Polar Effects

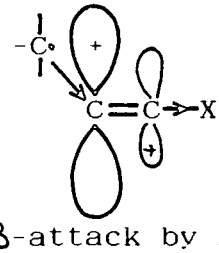
In the previous section, frontier orbital theory has predicted an increase in reactivity of a radical by either

electron donating or electron withdrawing substitution. It also predicts a further increase in reactivity if the alkene is substituted with a group of opposite polarity to that of the radical substituents. The theory further predicts the relative effects of α and β substitution of the alkene by considering the effects on the atomic orbital coefficients. This is because the rate of a reaction involving bond formation increases with the orbital coefficients of the two atoms involved. Frontier orbital theory has previously been used to predict ease of nucleophilic attack on fluorinated alkenes[44] and can also be applied to nucleophilic radical additions.

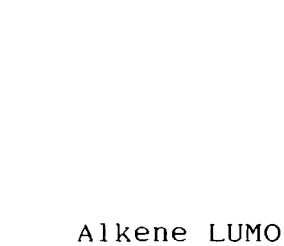
If an alkene is substituted with an electron withdrawing group then, for the LUMO of the alkene, the orbital coefficient on the substituted carbon atom will be decreased and the coefficent on the non-substituted carbon atom will be increased. Thus for attack by a nucleophilic radical at



α-attack by R



β-attack by R



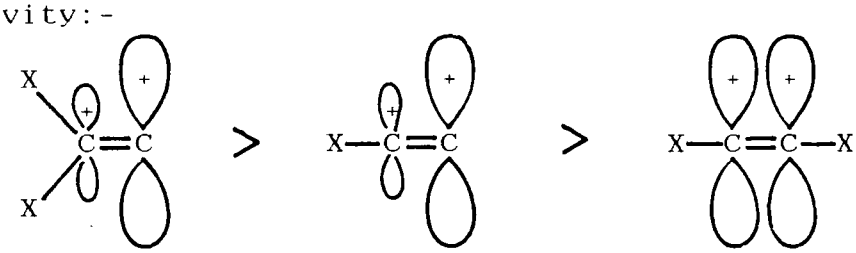
Alkene LUMO

the β-position an electron withdrawing substituent will increase the rate of reaction by both lowering the alkene LUMO energy and increasing the orbital coefficient on the β-carbon. However, for α-attack, the increase in the rate due to the lower alkene LUMO energy will be opposed by a decrease in orbital coefficient on the α-carbon atom. Thus the effect of substituents will be much greater for radical

attack at the β-position.

If a second electron withdrawing group is added the reactivity will again depend on both the orbital coefficients and the LUMO energy. The coefficients will depend on the substitution pattern, however the LUMO energy will simply be decreased. If the two substituents are at the same end of the alkene then the orbital coefficient on the

Reactivity:-



substituted carbon atom will be further deacreased and the coefficient on the non-substituted carbon atom further increased. Thus the reactivity will be increased. If the substituents are at opposite ends of the alkene then the effect of the two groups will be opposed and the coefficients will be equal. Thus the activating effect of the first substituent will be opposed by the second substituent.

Perfluoroisobutene[45] reacts readily with tetrahydrofuran whereas perfluoro-2-butene[12] is less reactive than hexafluoropropene towards cyclic ethers. Thus additions to fluorinated alkenes can be rationalised by frontier orbital theory.

(b) Steric Effects

The steric requirements of an alkene can have a large effect on radical addition. For substituted alkenes[13]

(table 9) it can be seen that the regiospecificity of addition is high and that steric factors far outweigh the polar effects of the different groups. However the overall rate of reaction is that which would have been predicted from polar effects.

Table 9 $CF_3^\circ + \overset{\alpha}{C}H_2=\overset{\beta}{C}HX$ k_e = Rate of Addition to Ethene

X	Regiospecificity (α:β)	k_α/k_e
CH_3	1 : 0.1	2.3
CF_3	1 : 0.02	0.4
F	1 : 0.09	0.5
$CH=CH_2$	1 : 0.01	20

(c) Electron Delocalisation in the Adduct Radical

The addition of a radical to an alkene is in general exothermic and so from the Hammond postulate[27] it would be predicted that there is an early transition state. The effect of the product radical stabilisation would therefore be small. This is demonstrated in table 10 where the rate

Table 10 Arrhenius Parameters for $CF_3^\circ + \overset{\alpha}{C}H_2=\overset{\beta}{C}HX$

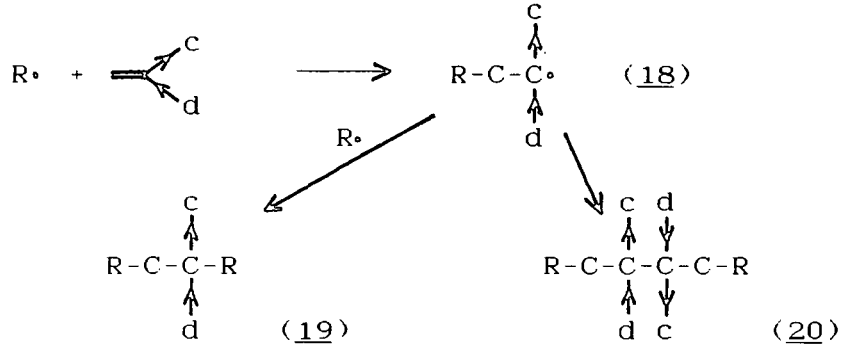
k_e = Rate of Addition to Ethene

X	k_α/k_e	log A	E_A
H	1	8.0	2.9
F	0.5	7.9	3.3
Cl	1.3	7.8	2.3
Br	1.2	7.8	2.2
CN	0.7	7.4	2.1
$COCH_3$	2.1	7.9	1.3

of reaction is little affected by the possibility of resonance in the adduct radical.

(d) Captodative Alkenes

If one end of an alkene is simultaneously substituted with an electron withdrawing group and an electron donating group it becomes extremely reactive towards both nucleophilic and electrophilic radicals. This is because the addition reaction becomes very exothermic due to the high stability of the captodative adduct radical (18) formed.

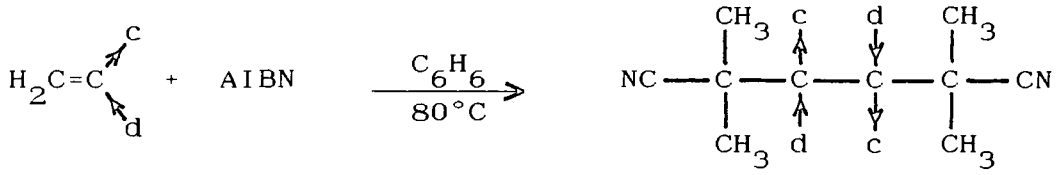


The adduct radical will usually be too stable to abstract a hydrogen atom from the substrate and will either react with another radical (19) or dimerise[35] (20) (table 11).

C SYNTHESIS VIA FREE RADICAL ADDITION REACTIONS

The formation of carbon-carbon bonds via polar processes has received a major share of attention and new methods are continually being developed[46]. Non-polar methods have also been developed and in particular pericyclic reactions which have become widely used[47]. In contrast the use of free radical addition reactions has

Table 11 Formation of Bisadducts from Captodative Alkenes



c	d	yield %	c	d	yield %
CO_2Me	MeO	49	CN	MeS	18
CO_2Me	MeS	35	CN	^tBuS	88
CO_2Me	^tBuS	76	CN	Me_2N	38
CO_2Me	Et_2N	37	CN	Morpholino	68
$CONMe_2$	Me_2N	40	CN	Me_3SiO	33

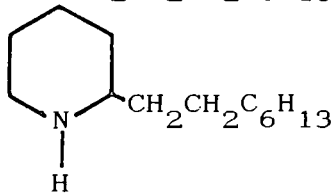
received comparatively little attention, although recently workers have begun to recognise the potential of these reactions[48].

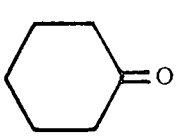
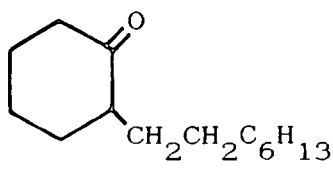
Table 12 Free Radical Additions to 1-octene

$CHCl_3$ + $CH_2{=}CHC_6H_{13}$-n $\xrightarrow{Bz_2O_2}$ $CCl_3CH_2CH_2C_6H_{13}$ (51) 22%

CH_3CHO + $CH_2{=}CHC_6H_{13}$-n $\xrightarrow{\text{Peroxide}}$ $CH_3COCH_2CH_2C_6H_{13}$ (52) 36%

MeOH + $CH_2{=}CHC_6H_{13}$-n $\xrightarrow{DTBP}$ $HOCH_2CH_2CH_2C_6H_{13}$ (53) 16%

Piperidine + $CH_2{=}CHC_6H_{13}$-n $\xrightarrow[hv]{\text{Peroxide}}$  (54) 70%

 + $CH_2{=}CHC_6H_{13}$-n $\xrightarrow{hv}$  (55) 25%

1 Intermolecular Addition Reactions

Many free radical addition reactions have been known since the 1940's and additions of alkyl, aryl, acyl, ∝-halo, ∝-oxy, ∝-amino, and ∝-carbonyl radicals to hydrocarbon alkenes are well established[49,50] and examples are given (table 12). Despite the simplicity and synthetic potential of these reactions they are seldom used.

Addition to fluorinated alkenes has been known since 1948[56]. A potential complication with many fluorinated alkenes and especially tetrafluoroethene is the appearance of telomers as side products.

$$R\bullet + CF_2{=}CF_2 \longrightarrow R\text{-}CF_2\text{-}CF_2\bullet$$

Addition

$$R\text{-}(CF_2\text{-}CF_2)_n\bullet + CF_2{=}CF_2 \longrightarrow R\text{-}(CF_2\text{-}CF_2)_{n+1}\bullet$$

Telomerisation

$$R\text{-}(CF_2\text{-}CF_2)_n\bullet + R\text{-}H \longrightarrow R\bullet + R\text{-}(CF_2\text{-}CF_2)_n H$$

Chain Transfer

As the most common radical systems involve nucleophilic radicals, electron deficient fluorinated alkenes are ideally suited to addition reactions and their use has been reviewed[11]. The use of hexafluoropropene which gives no telomeric products is ideal for a systematic study of the synthesis of functional fluorocarbons and will be discussed in later chapters.

The use of electrophilic radical systems has received very little attention but one example is in the synthesis of ∝-alkyl mono- and di-carboxylic acids[57] (21).

$$ROOC(CH_2)_nCOOR + CH_2{=}CHR' \xrightarrow{DTBP} ROOCCH(CH_2)_{n-1}COOR \quad (21)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2CH_2R'$$

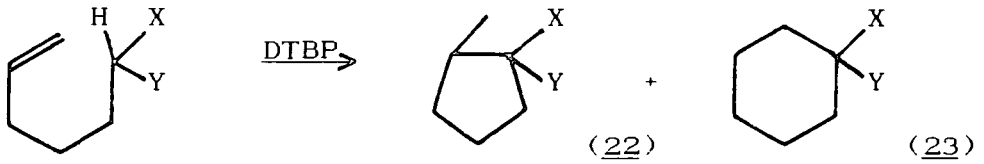
R = H, CH_3, Et n = 1, 2, 4, 7, 8.

R' = Alkyl

2 Intramolecular Cyclisation Reactions

Radical addition to carbon-carbon double bonds can also occur in intramolecular reactions. Such reactions lead to cyclisation products and are of interest both in synthesis and for the mechanistic problems they pose. A common system is the 5-hexenyl system which can cyclise to either a 5- or 6-membered ring. The size of ring formed is controlled by both kinetic and thermodynamic factors and a knowledge of these is required in order to select conditions to favour the required ring size. The formation of a 6-membered ring involves addition at the unsubstituted end of the double bond and would also lead to a more stable secondary radical. The variability of ring size formed can be demonstrated by the cyclisation of a series of stabilized 5-hexenyl radicals[58] (table 13). This shows an increasing preference for the 6-membered ring product with increasing stabilisation and thus lower reactivity of the radicals. The reaction has also been shown to be reversible by the pyrolysis of substituted peresters[58] (24) and (25) (table 14). The results show that the reaction for (24a) and (25a) are completely reversible and for (24b) and (25b) only partly so. These results show that for highly reactive, unstabilised radicals the 5-membered ring is formed under kinetic control. As the stability of the radical is

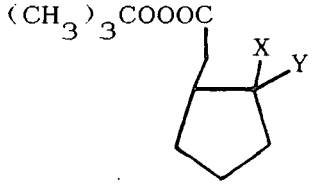
Table 13 Cyclisation of Substituted 5-hexenyl Radicals with DTBP

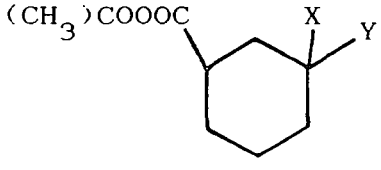


(22) (23)

X	Y	% (22)	% (23)	X	Y	% (22)	% (23)
H	H	100	0	CO_2Et	CO_2Et	70	30
H	CN	100	0	$COCH_3$	CO_2Et	50	50
H	$COCH_3$	72	28	CN	CO_2Et	16	84
H	CO_2Et	56	44	=O		0	100

Table 14 Pyrolysis of Peresters



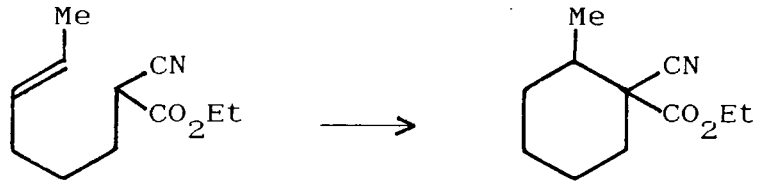


(24a) X = CN, Y = CO_2Et (25a) X = CN, Y = CO_2Et

(24b) XY = =O (25b) XY = =O

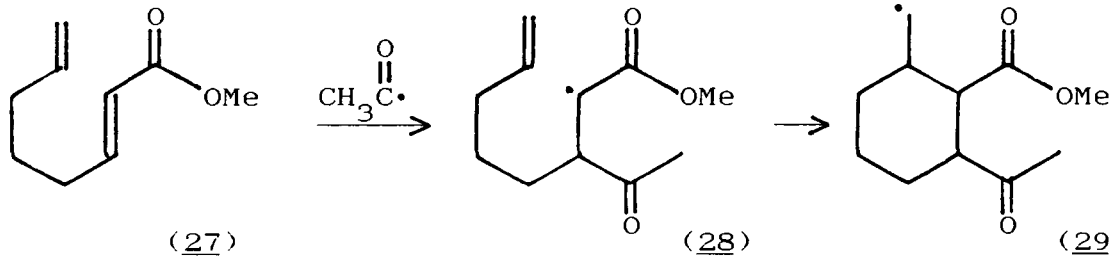
Precursor	Yield %	(22)	(23)
24a		20	80
25a		15	85
Cyclisation		16	84
24b		30	70
25b		0	100
Cyclisation		0	100

increased the reaction becomes reversible and the more stable 6-membered ring product is formed. If the double bond is substituted then the addition will tend to occur at the least substituted end if the group is large, however a terminal methyl group can lead to only the 6-membered ring product (26). Thus the rules of cyclisation have to an extent been rationalised[59]. The cyclisation can also be



(26)

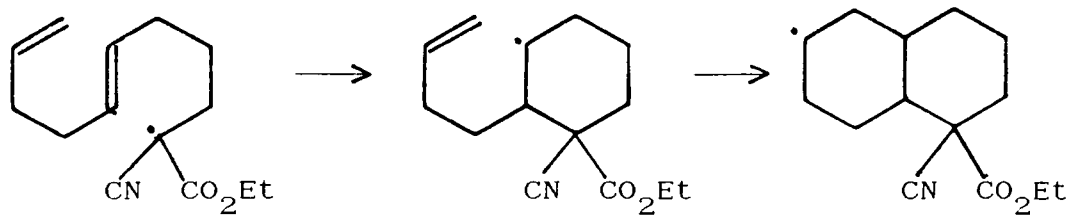
made to occur by the addition of a radical to a suitable diene. Thus in the reaction of acetaldehyde with ester[60] (27), the nucleophilic acyl radical first attacks the most electron deficient double bond to form the radical (28) which then cyclises to give the expected 6-membered ring (29).



(27) (28) (29)

The intramolecular addition reactions are not confined to the formation of monocyclic compounds. The use of suitable dienes (30) can lead to bicyclic products[58]. The intermediate radical (31) is unsubstituted and might be expected to give the more favourable 5-membered ring. However the sterochemistry of the cyclohexene ring already

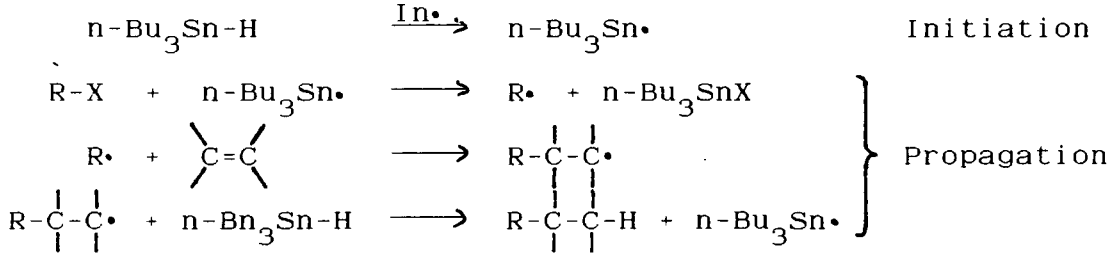
formed makes this less favourable and a second 6-membered ring is formed (32).



(30) (31) (32)

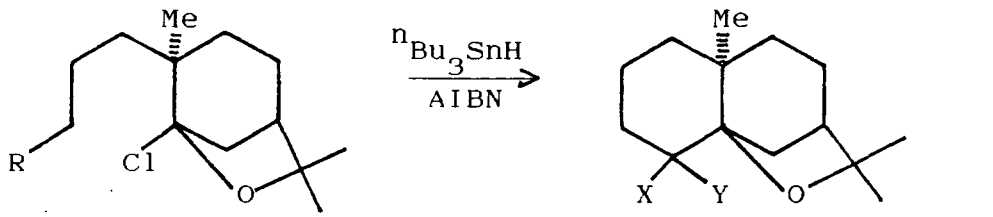
3 Tin Hydride Mediated Reactions

The synthesis of radicals from substituted alkyl halides with tin hydrides has been used by many workers. The mediation of tin hydride is convenient for the type of reactions already described but can also be used for less easily produced radicals.



This method has been used recently for cyclisation of many ethers and amides of which many are of synthetic interest to the natural product chemist. However there is the problem of the lack of stereospecificity of radical additions although in many cases this has proved to be less of a problem than expected. The attempted synthesis of dihydro-β-agarofuran[61] from the α-chloroether (33a) gave a mixture of the possible isomers (34a). If however the silyl alkynyl derivative is used the cyclisation leads to a single

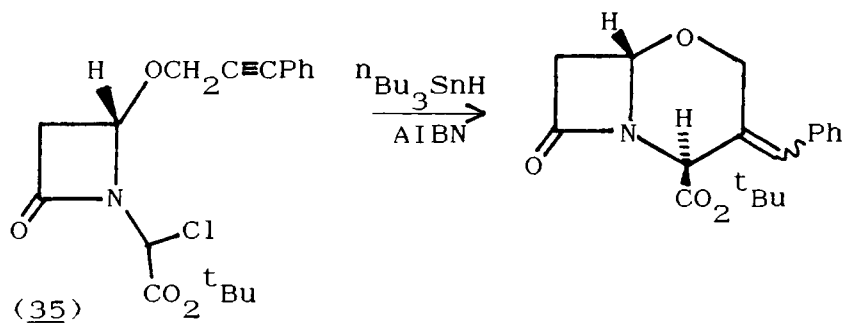
product (34b) which can be dehydrosilylated using stereo-specific methods to give the required isomer.



(33a) R = $-CH=CH_2$ (34a) X = H, Y = Me

(33b) R = $-C\equiv CSiMe_3$ (34b) XY = $=CH-SiMe_3$

Much attention has been focussed on the cyclisation of α-acylamino compounds for alkaloid synthesis and for example β-lactams have been used[62] (35).



(35)

DISCUSSION

CHAPTER 2

FREE RADICAL ADDITIONS OF NITROGEN FUNCTION SUBSTRATES TO FLUOROALKENES

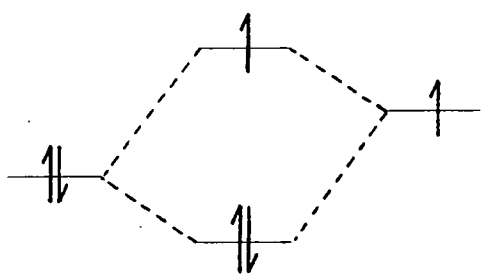
A INTRODUCTION

The free radical addition of amines to fluorocarbon alkenes is potentially a direct route to fluorocarbon amines. There is some indication from the literature that amine additions will work but they are mainly photochemical reactions (tables 16, 21 and 22). Thus an investigation into the γ-ray initiated addition of amines was undertaken.

The stabilisation of a radical by the lone pairs of electrons on an adjacent oxygen atom is well known. Also the availability of the lone pair of electrons on nitrogen is demonstrated by the basicity of amines. Thus the possibility of strong stabilisation of an α-amino radical and the reactivity of such a radical towards alkenes is therefore good.

$$R_2\ddot{N}-\dot{C}H-R' \longleftrightarrow R_2\overset{+}{\dot{N}}-\ddot{C}H-R'$$

The lone pair of a nitrogen will interact in an analagous way to oxygen and should result in a nucleophilic radical which would be ideal for reaction with electron



$-\ddot{N}-$ $\quad$ $-\ddot{N}-\dot{C}-$ $\quad$ $-\dot{C}-$

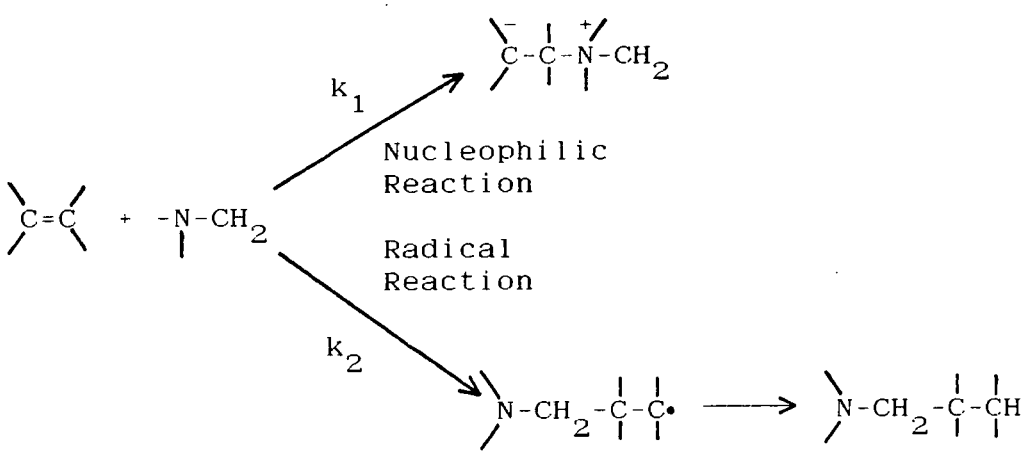
deficient fluoriated alkenes. This stabilisation of an ∝-amino radical is shown in the rate of hydrogen abstraction by a methyl radical from trimethylamine[18] (table 15). The rate is higher than that of dimethylether and so the ∝-amino radical is thus easier to produce than the ∝-oxy radical. Preliminary results have also indicated that stereoelectronic effects are important[21] in the abstraction of a hydrogen atom from amines.

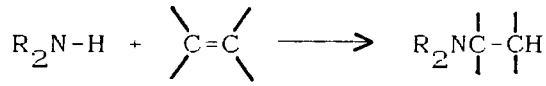
Table 15 Rate Constants for the Reactions:-

$$R\text{-}H + CH_3^{\bullet} \longrightarrow R^{\bullet} + CH_4$$

R-H	Rate / log k ($cm^3\ mol^{-1}\ s^{-1}$)
CH_3-H	4.6
CH_3OCH_2-H	6.5
$(CH_3)_2NCH_2$-H	7.4

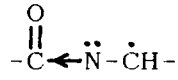
There is however the problem of competing nucleophilic reactions[3]. The success of the radical reaction will thus depend on the rate of the radical reaction (k_2) being higher than the rate of nucleophilic reaction (k_1). Primary and secondary amines react readily with fluorocarbon alkenes by addition and free radical reaction is unlikely to compete.





B ADDITION OF AMIDES TO FLUOROALKENES

The basicity of amides is much lower than that of amines and the possibility of competing nucleophilic reaction is reduced. The lower basicity will be accompanied by lower availability of the lone pair of electrons for stabilisation of the radical. The electron withdrawing group will also make the radical less nucleophilic.



1 Addition of Tertiary Amides to Hexafluoropropene

Some examples of amide additions are known from the literature (table 16). The reactions of N,N-dimethyl-acetamide, tetramethyl urea, N-methylpyrrolidine, N-acetyl-piperidine and N-acetylmorpholine to hexafluoropropene have also been carried out previously in this laboratory[12] using γ-ray initiation.

A series of cyclic amides were studied for comparison with esters and for possible stereoelectronic effects (table 17). The reactions all give adducts in high yield which

Table 16a Addition of Amides to Tetrafluoroethene

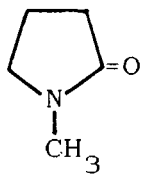
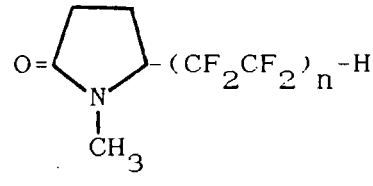
Amide	Initiation	Products	Reference
	$(^{t}BuO)_2$		[63]

Table 16b Addition of Amides to Chlorotrifluoroethene

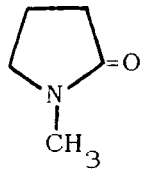
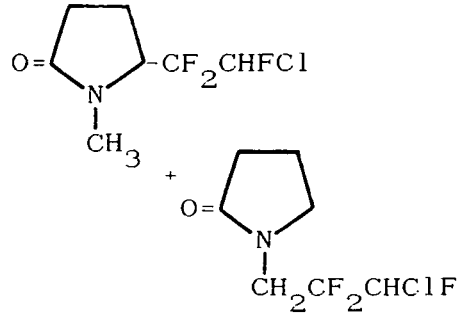
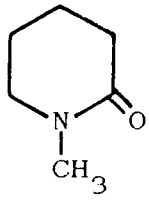
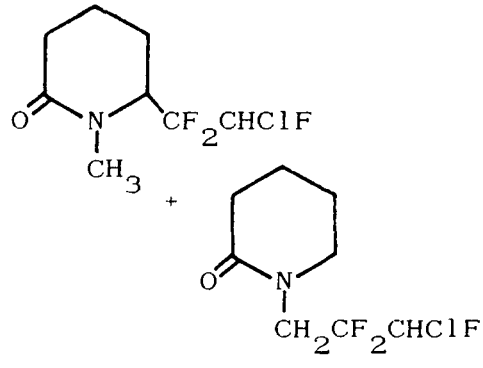
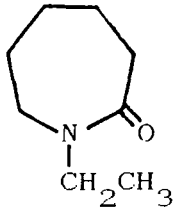
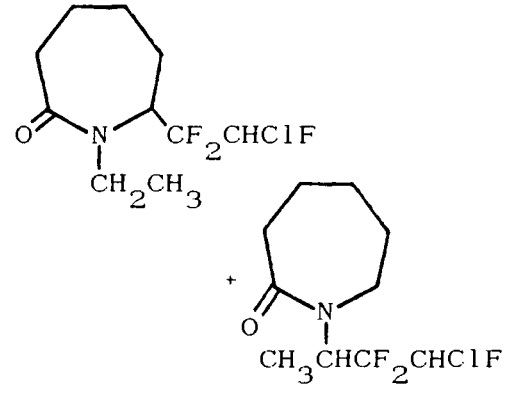
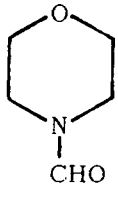
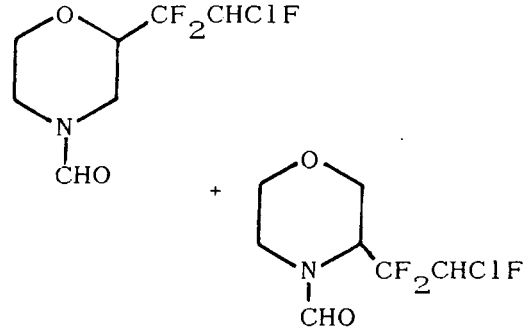
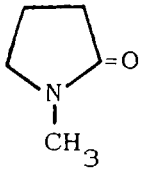
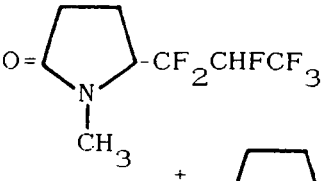
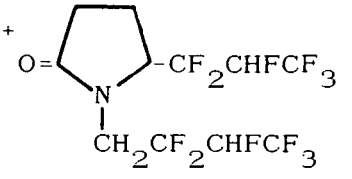
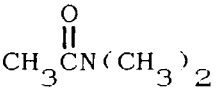
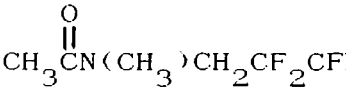
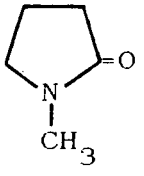
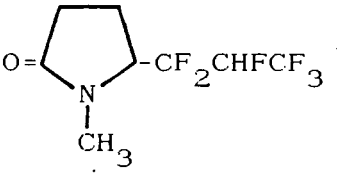
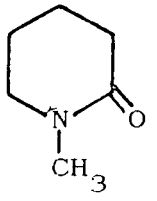
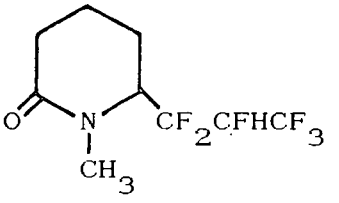
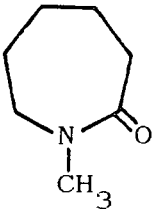
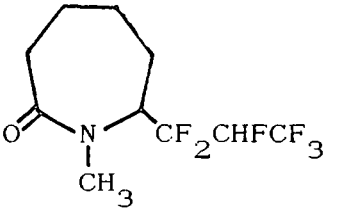
Amide	Initiation	Products	Reference
	UV, acetone		[64]
	UV, acetone		[64]
	UV, acetone		[64]
	UV, acetone		[64]

Table 16c Addition of Amides to Hexafluoropropene

Amide	Initiation	Products	Reference
	$(^tBuO)_2$	 + 	[63]

contrasts with the behaviour of esters, which give only low yields or only react at higher temperatures[12]. Thus nitrogen is more efficient at stabilising a radical than oxygen.

Table 17 Addition of Cyclic Amides to Hexafluoropropene with γ-ray Initiation

Amide	Product		% Conversion[a]
		(36)	98
		(37)	98
		(38)	84
		(39)	60

a - based on unreacted hexafluoropropene recovered

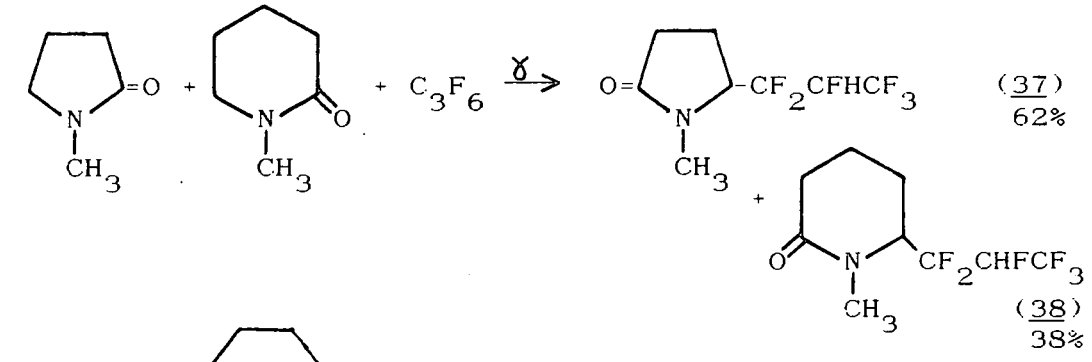
In the study of stereoelectronic effects in ethers it has been shown that different size rings have differing reactivities in the order[12,33]:-

$$5 > 7 > 6$$

Thus a series of cyclic amides containing the carbonyl group in the ring were reacted with hexafluoropropene with γ-ray initiation (table 17). The yields obtained show that the effect of a carbonyl group of an amide does not prevent reaction. Thus the nitrogen atom is highly effective at stabilising a radical centre. In contrast to amines the amides form only 1:1 adducts, thus the combined electron withdrawal of a carbonyl group and a hexafluoropropyl group prevent further reaction. In all cases reaction occurs exclusively at the ring CH_2 group, the methyl group being less reactive. The reactivity order with change in ring size is:-

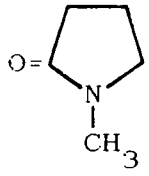
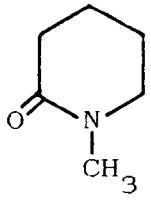
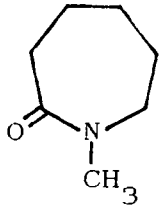
$$5 > 6 > 7$$

which does not agree with the order found for cyclic ethers.



The order is confirmed by competition reactions and the relative reactivity (table 18) can be found from the product mixture. The competition between N-methylpiperidone and N-methylcaprolactam was unsuccessful as the product mixture could not be separated by gas chromatography.

Table 18 Relative Reactivity of Amides in Competition Reactions

Amide	Reactivity	Acetone / ^{t}BuOH Ratio
	1.00	0.21
	0.60	0.25
	0.39	0.27

Thus the sp^2 hybridised carbon atom of the carbonyl group may have an effect on the conformation of the ring which alters the expected reactivity order.

If the carbonyl group is placed outside the ring then reaction only occurs in the ring position (table 19). The acetyl group is not reactive and so reaction only takes place at the ring carbon atoms adjacent to the nitrogen atom. As all the ring carbon atoms are sp^3 hybridised the reactivity due to stereoelectronic effect would be expected

to parallel the reactivity of the ethers. The five and six membered ring amides both gave very high conversions and so stereoelectronic effects could not be detected.

If the nitrogen is substituted with a formyl group the possibility of alternative reaction at this group may be expected. This is found with N.N-dimethylformamide giving

Table 19 Addition of N-acetyl Amides to Hexafluoropropene

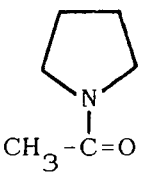
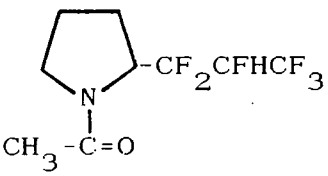
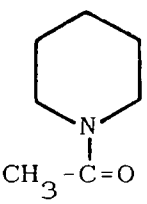
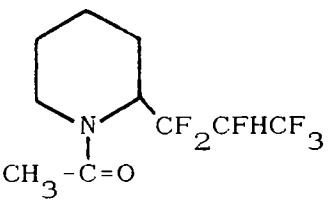
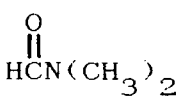
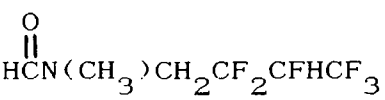
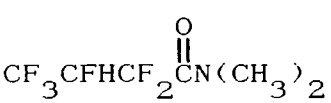
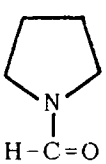
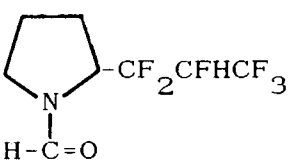
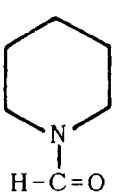
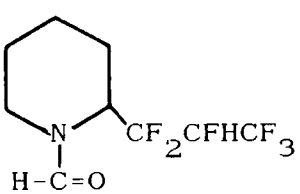
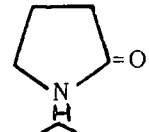
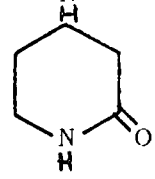
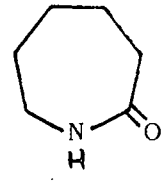
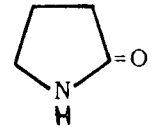
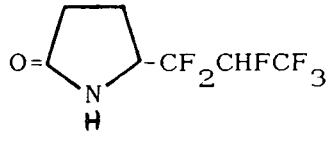
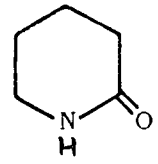
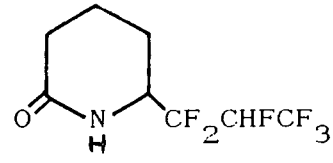
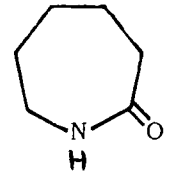
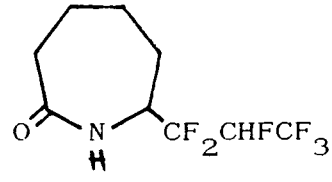
Amide	Product		% Conversion
		(40)	98
		(41)	98

Table 20 Reaction of Formamides with Hexafluoropropene

Amide	Product		% Conversion
		(42)	47
		(43)	22
		(44)	98
		(45)	46

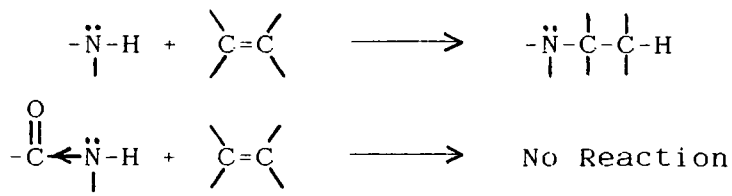
47% methyl substitution and 22% formyl substitution. In the reaction of two cyclic formamides (table 20) reaction only occurs at the ring position. Thus the secondary radical of the ring is much favoured over a formyl radical. The stereoelectronic effect is shown by the greater reactivity of the five membered ring.

Table 21 Additions to Secondary Amides

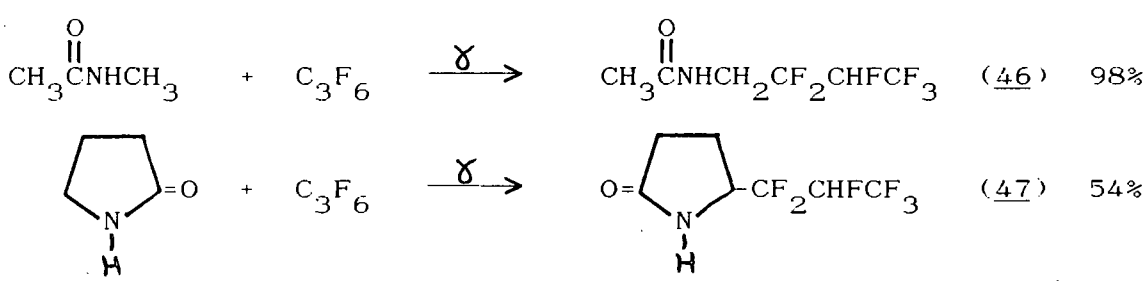
Alkene	Amide	Initiation	Products	Ref.
$CF_2=CF_2$		$(^tBuO)_2$	Mixture of Telomers	(63)
		$(^tBuO)_2$	Mixture of Telomers	(63)
		$(^tBuO)_2$	Mixture of Telomers	(63)
$CF_3CF=CF_2$		$(^tBuO)_2$		(63)
		$(^tBuO)_2$		(63)
		$(^tBuO)_2$		(63)
$CFCl=CF_2$	H_2NCHO	UV, acetone	$H_2NC(=O)CF_2CHFCF_3$	(64)
	$Me_2CHNHCHO$	UV, acetone	$Me_2CHNHC(=O)CF_2CHFCF_3$	(64)

2 Addition of Secondary Amides to Hexafluoropropene

Amines containing an N-H bond readily undergo addition to fluorinated alkenes via nucleophilic attack. Amides with N-H bonds are less basic and nucleophilic additions to



fluorinated alkenes do not occur. Some examples of free radical additions are known (table 21). A preliminary study of reactivity of secondary amides on the addition to hexafluoropropene using γ-ray initiation was undertaken. It was found that N-methylacetamide and 2-pyrrolidone reacted to give good yields to 1:1 adducts.



c ADDITION OF AMINES TO FLUOROALKENES

Although the base strengths of amines are high and nucleophilic attack on fluoroalkene is often the preferred reaction some examples of free radical additions are known from the literature (table 22). Preliminary studies in this laboratory[12] have indicated that only low yields of adduct are obtained with addition of N-methylpiperidine and N-methylmorpholine with hexafluoropropene. In this study the addition of various cyclic amines to hexafluoropropene

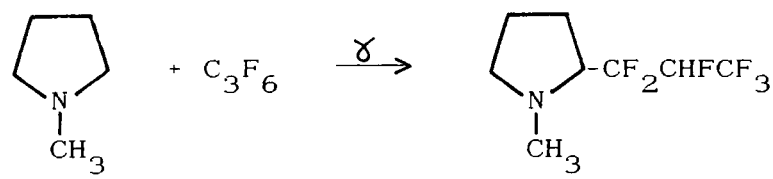
and of N-methylpyrrolidine to various fluorinated alkenes have been examined.

Table 22 Addition of Amines to Chlorotrifluoroethene

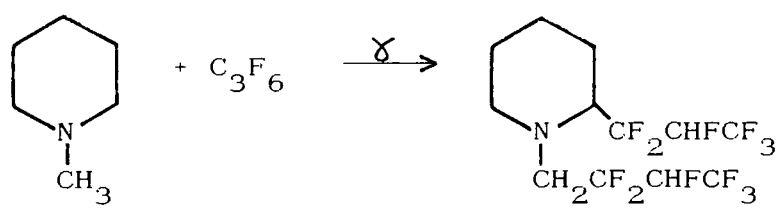
Amine	Initiation	Products	Reference
Me_3N	γ	Telomer adducts + $ClCHFCONMe_2$	[65]
Et_3N	γ	Many Products	[65]

1 Additions to Hexafluoropropene

The addition of N-methylpyrrolidine and N-methylpiperidine to hexafluoropropene give very high yields of

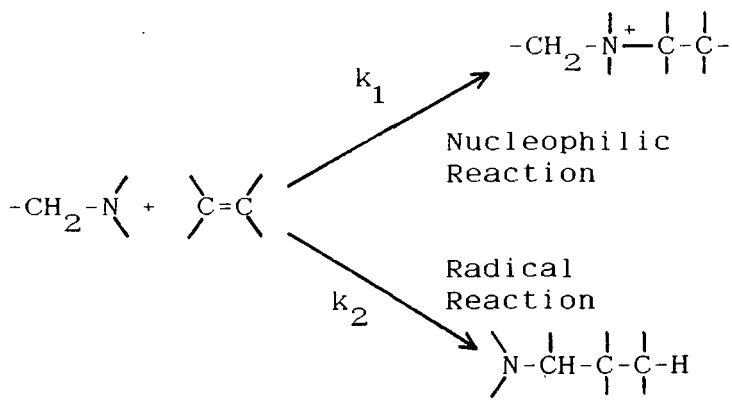


(48) 95%



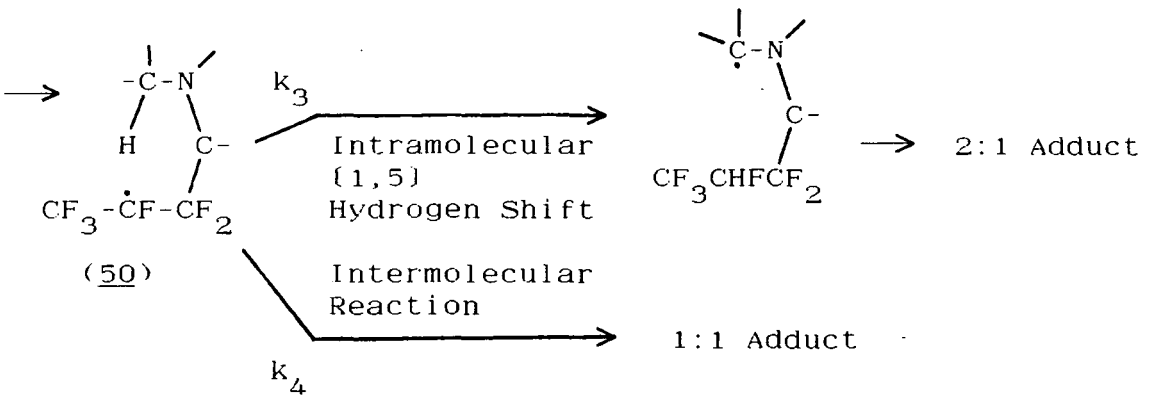
(49) 81%

adducts. The reaction will be a competition between radical reaction (k_2) and nucleophilic reaction (k_1). It is clear that the radical reaction has a much higher rate than any



competing nucleophilic reaction. The main product with N-methylpiperidine is the 2:1 adduct. This reaction proceeds via an intramolecular [1,5] hydrogen shift. In any

amine the ratio of 1:1 and 2:1 adducts produced will be related to the rates of the intermolecular hydrogen abstraction reactions (k_4) and the intramolecular (1,5) hydrogen shift (k_3). The rate of the (1,5) shift will vary

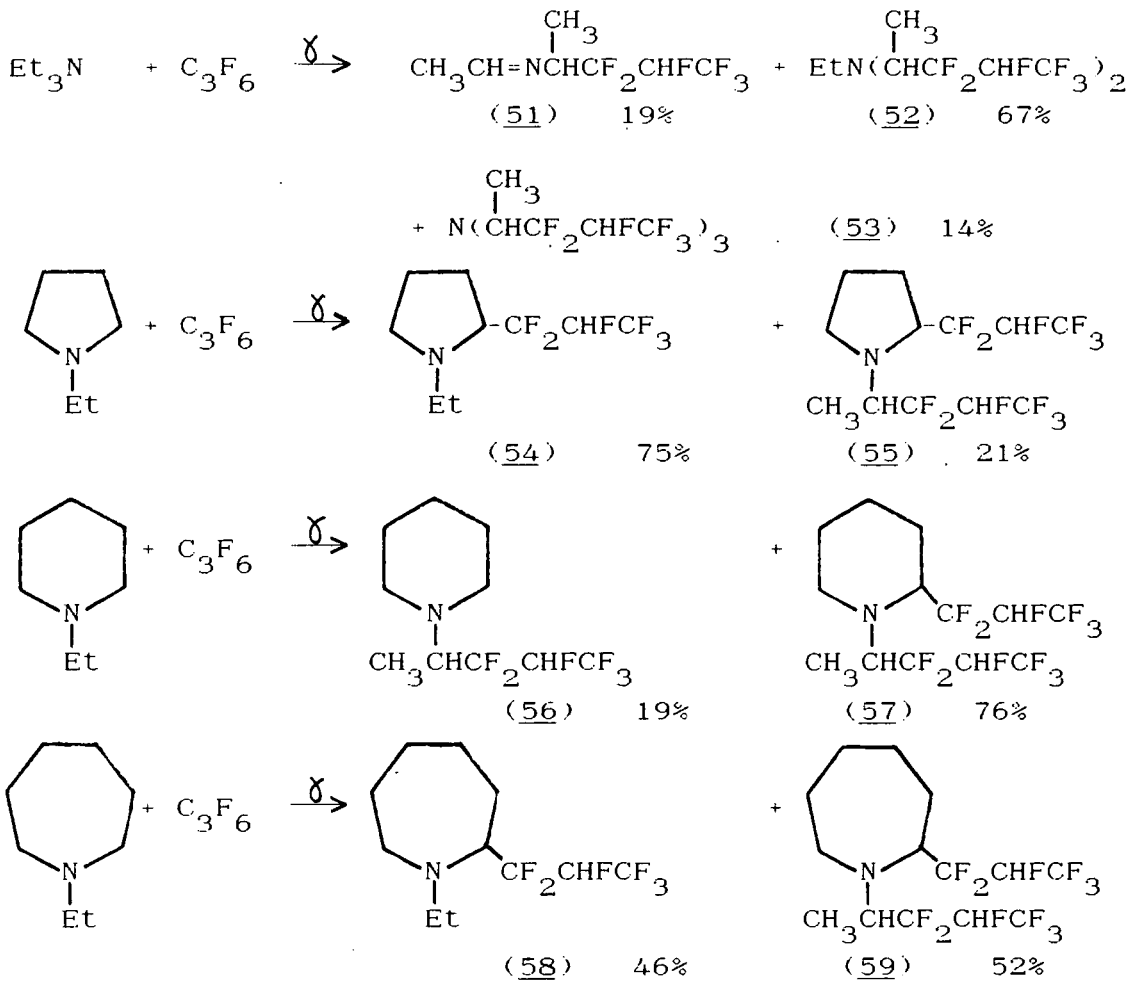


little with change in amine unless the hydrogen involved is sterically hindered as the steric requirement of the hexafluoropropyl group will be large itself. Thus the ratio of products will be mainly influenced by the ease of hydrogen abstraction from the substrate by the adduct radical (50). With N-methylpyrrolidine the steric effect results in very easy abstraction of a hydrogen atom and so this could account for the fact that the 1:1 adduct is the major product. For N-methylpiperidine the slow abstraction from the six membered ring would therefore lead to the 2:1 adduct being the major product.

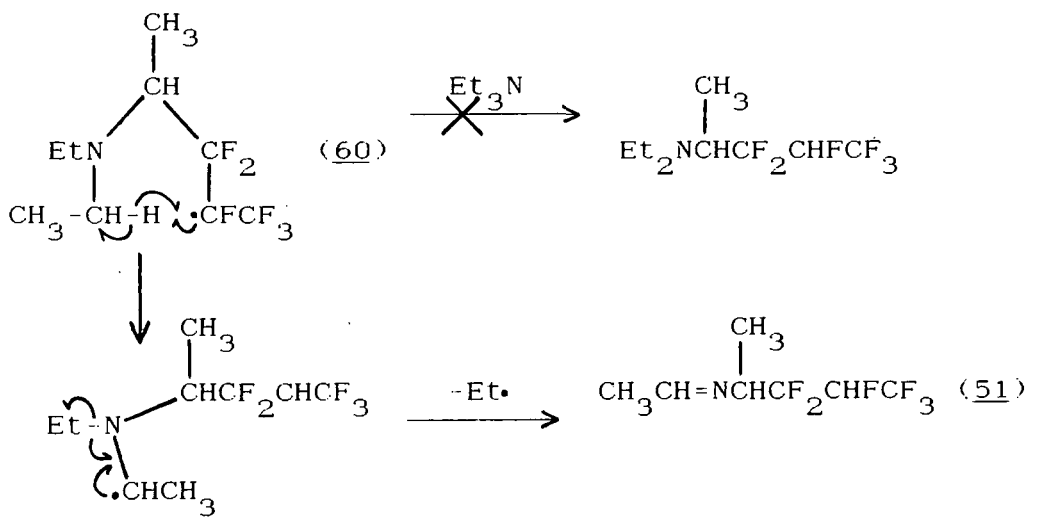
In order to investigate this effect a series of N-ethyl amines were investigated. The CH_2 group of the side chain being comparable with the CH_2 group in the ring as they are both secondary sites. The order of amount of 1:1 adduct produced with ring size is:-

$$5 > 7 > 6 = \text{Acyclic}$$

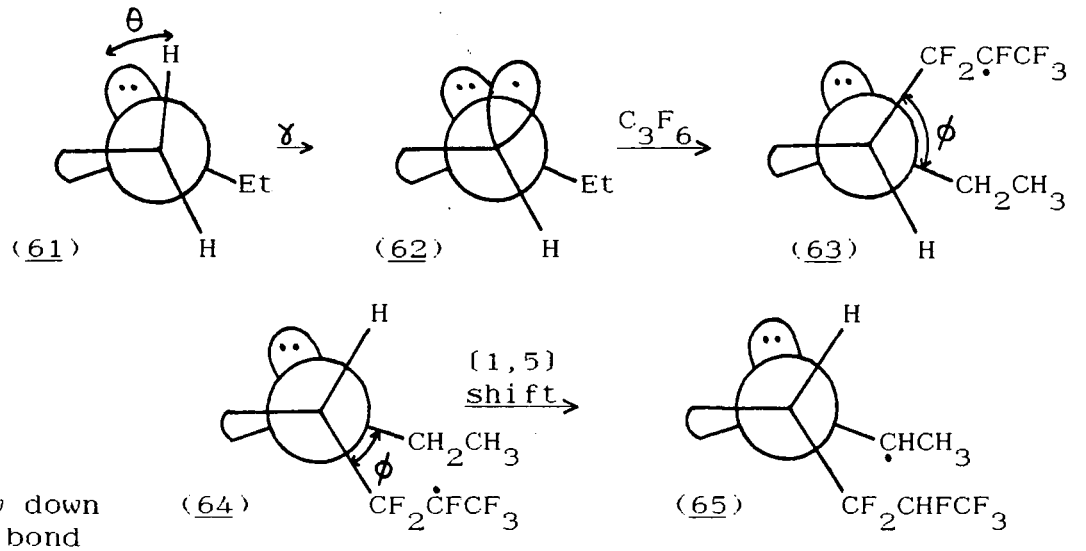
As stated above this order will reflect the ease of



hydrogen abstraction from the amine and corresponds with a stereoelectronic effect. In the reaction with triethyl amine the expected 1:1 adduct is not formed, the initial adduct radical (60) undergoes a [1,5] hydrogen atom shift followed by loss of an ethyl radical to give the imine (51).



Triethylamine also gives a moderate yield of 3:1 adduct (53). This is due to greater ease of [1,5] hydrogen shift in the intermediate radicals, resulting from free rotation of all C-N bonds. In the cyclic amines (61) the hydrogen atom abstracted will be that where θ is smallest. If inversion in the radical (62) does not occur then the adduct radical (63) formed will have the hexafluoropropyl group and the



view down C-N bond

ethyl group at a large distance apart (ϕ). Thus a [1,5] hydrogen shift will be disfavoured. However if inversion does occur then the angle ϕ (64) will be much smaller and the [1,5] shift will be more favourable. In the case of triethylamine no such restraints occur and so free rotation will allow the [1,5] shift to proceed more easily.

2 Additions to Tetrafluoroethene

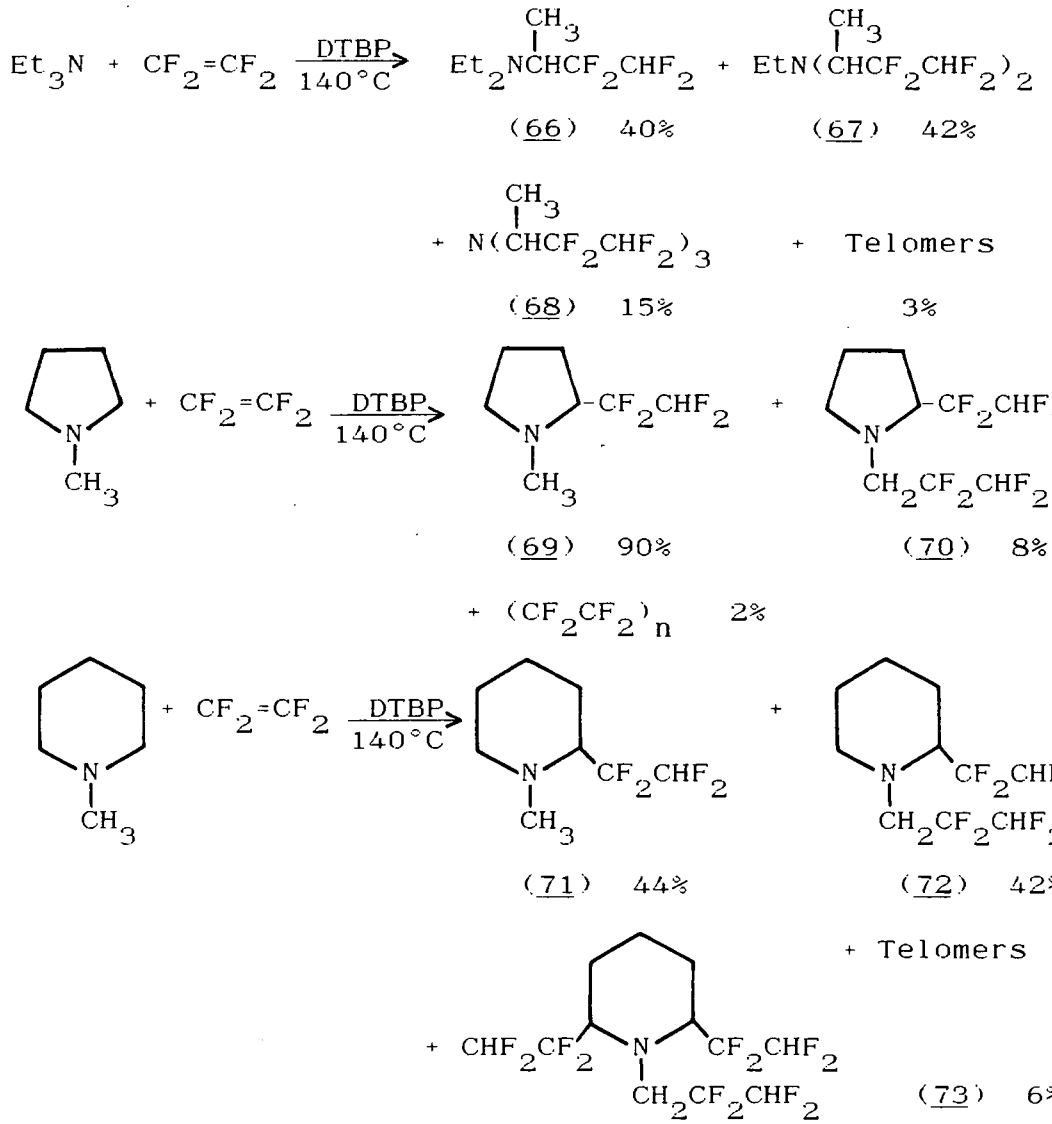
In the addition of a substrate to tetrafluoroethene the products normally contain telomers. The initial adduct radical can undergo two reactions, either chain transfer or telomerisation. In the case of tetrafluoroethene, which is

easily polymerised the telomerisation step competes favourably with chain transfer and so gives rise to telomeric products. The product distribution will depend on the relative rates of these two processes. If the rate of hydrogen abstraction from the substrate is very high then the main product will be simple 1:1 adducts. If the abstraction rate is reduced then the yield of telomer adducts will increase and the chain length of the telomer adducts will also increase.

$$R\text{-}CF_2\text{-}CF_2^{\bullet} + R\text{-}H \longrightarrow R\text{-}CF_2\text{-}CF_2H \quad \text{Chain Transfer}$$

$$R(CF_2\text{-}CF_2)_n^{\bullet} + CF_2{=}CF_2 \longrightarrow R(CF_2\text{-}CF_2)_{n+1}^{\bullet} \quad \text{Telomerisation}$$

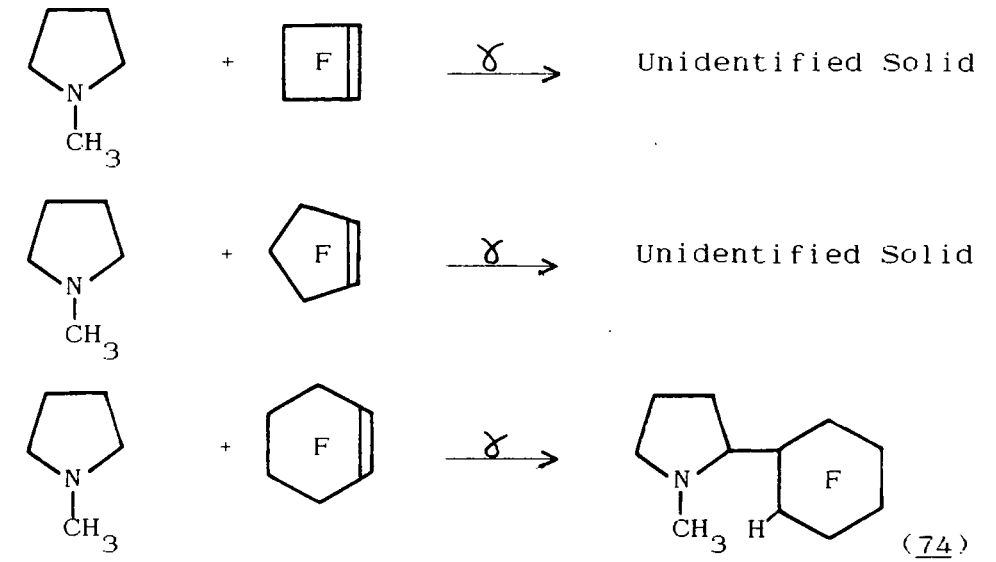
In the addition of amines to tetrafluoroethene it has been found in this study that the main products are simple 1:1 and 2:1 adducts. In the addition of triethylamine and N-methylpiperidine to excess tetrafluoroethene only small amounts of telomeric products are formed. The yield of 1:1 adducts is much higher than in additions to hexafluoropropene, thus the (1,5) hydrogen atom shift in the adduct radical does not compete as successfully with intermolecular hydrogen abstraction. Thus the primary adduct radical will have a lower steric requirement in both the inter- and intramolecular reactions, making them faster. The effect on the intermolecular is much greater and this leads to a greater yield of 1:1 adducts. In the addition of N-methylpyrrolidine to tetrafluroethene the 1:1 adduct is formed in high yield, comparable to that obtained in the addition to hexafluoropropene, and a small amount of



tetrafluoroethene oligomers.

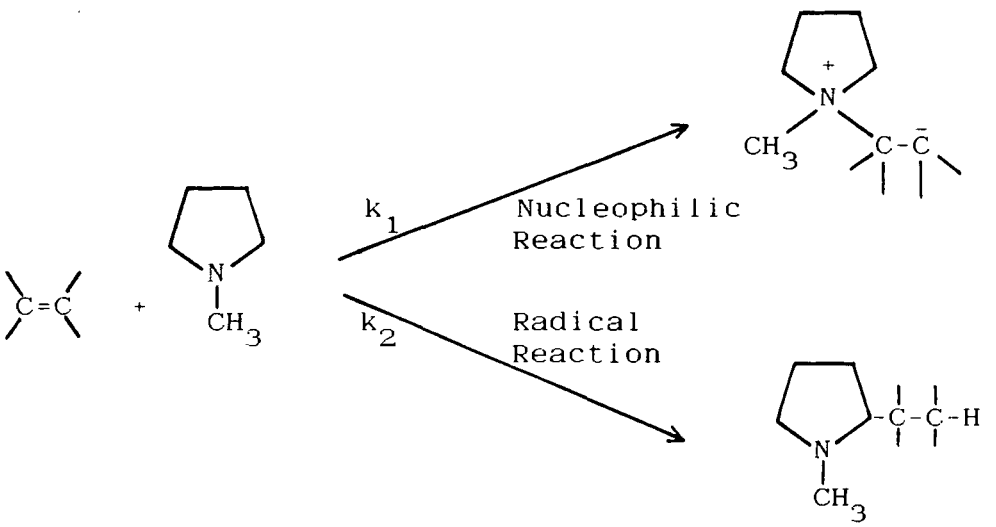
3 Additions to Cyclic Fluoroalkenes

It has been shown that tertiary amines can react with cyclic fluoroalkenes nucleophilically to form ylides[66]. The addition of N-methylpyrrolidine to perfluorocyclobutene and perfluorocyclopentene was attempted and gave unidentified solids which rapidly hydrolysed in air. In contrast the addition of N-Methylpyrrolidine to perfluorocyclohexene gave only the 1:1 adduct (74) in good yield.



(74) 57%

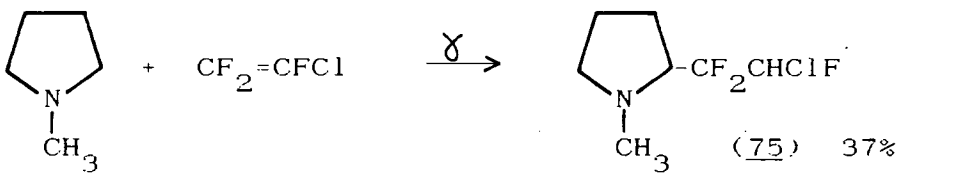
In these reactions there is a competition between nucleophilic attack and radical reactions. For the addition to perfluorocyclobutene and perfluorocyclopentene the rate of nucleophilic reaction (k_1) is much higher than that of the radical reaction (k_2). The driving force for the nucleophilic attack on these alkenes is the relief of strain



energy due to eclipsing of the fluorine atoms. In perfluorocyclohexene the ring can take up a conformation which reduces this strain energy to a minimum, thus reducing the rate of the nucleophilic reaction (k_1) and allowing the free radical reaction to compete.

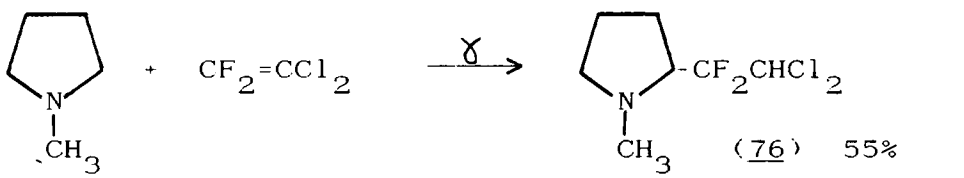
4 Additions to Chlorofluoroalkenes

The additions of N-methylpyrrolidine to chlorotrifluoroethene and 1,1-dichlorodifluoroethene gives modest yields of the 1:1 adducts along with unidentified nucleophilic products. Addition is found to occur exclusively at the CF_2 end of the alkene. Thus the large steric requirement of the chlorine atoms prevents addition at the end of the alkene so substituted and reaction occurs at the less hindered CF_2 group.



(75) 37%

+ Unidentified Solid

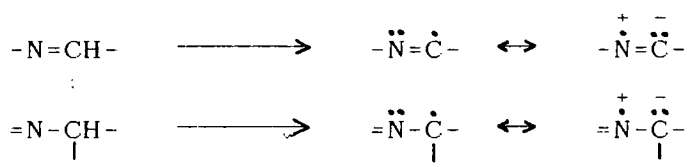


(76) 55%

+ Unidentified Solid

D ADDITION OF DOUBLE BONDED SUBSTRATES

If a nitrogen atom is double bonded it retains its lone pair of electrons which can take part in stabilisation of an adjacent radical site. The carbon atom of the radical



site can have either a single or double bond to the nitrogen. It is found that a simple imine such as ethylidine ethylimine gives only nucleophilic products, thus

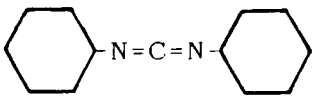
the nitrogen is too basic to allow radical reactions to

$$CH_3CH{=}NCH_2CH_3 + C_3F_6 \xrightarrow{\gamma} \text{Nucleophilic products}$$

compete. An investigation of compounds of the type R-N=C=X in which =C=X group is electron withdrawing was undertaken. The addition of ethylisocyanate to hexafluoropropene gives only a moderate yield of adduct with no nucleophilic reaction being detected. When X is a sulphur or nitrogen no reaction was detected.

$$CH_3CH_2NCO + C_3F_6 \xrightarrow{\gamma} CF_3CHFCF_2\underset{\displaystyle CH_3}{\underset{|}{C}}HNCO \quad (\underline{77})\ 25\%$$

$$CH_3CH_2NCS + C_3F_6 \xrightarrow{\gamma} \text{No Reaction}$$



$$+ C_3F_6 \xrightarrow{\gamma} \text{No Reaction}$$

CHAPTER 3

FREE-RADICAL ADDITIONS OF SILICON COMPOUNDS TO HEXAFLUOROPROPENE

A INTRODUCTION

The use of organic silicon compounds in chemistry has received much attention and is the subject of early reviews[67,68]. Silicon compounds are now being used increasingly in organic synthesis[69-71] and a range of applications has been found[72,73]. Thus the unusual properties of silicon to stabilise α-carbanions and β-carbocations, undergo nucleophilic substitution and it s electropositive nature has led to it s extensive use in synthesis and also as a versatile protecting group. The ability of silicones to form oils, rubbers, and resins and their unusual characteristics of water repellency, wide temperature range, and good electrical insulation has led to their use in industrial applications[74]. Silicones however suffer two main drawbacks: their poor solvent resistance and the difficulty of modification of their structure by chemical methods. These problems have been overcome to a certain extent by copolymerisation[75]. More recently, polymers made from polysilanes and polysilazanes have been studied and may introduce new uses for silicon containing polymers[75].

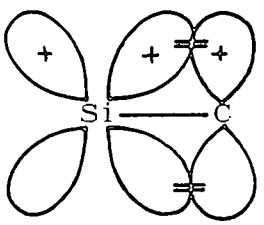
The chemistry of silyl radicals has received much attention and has been reviewed[11,76], but silicon substituted carbon centred radicals have received less

attention and have only recently been the subject of a review[77]. ∝-Silyl radicals can be produced by hydrogen abstraction with acyl radicals, giving high enough concentrations to be detected by esr[78]. A series of compounds was studied (table 23), radicals being formed ∝ to the silicon atom unless an alkoxy group is present, then an

Table 23 Hydrogen Abstraction by $CH_3\overset{O}{\overset{\|}{C}}\cdot$

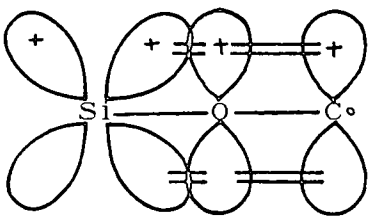
Substrate	Product detected by esr
Me_4Si	$Me_3SiCH_2^{\cdot}$
Et_4Si	$Et_3SiCHCH_3^{\cdot}$
$Me_3SiSiMe_3$	$Me_3SiSi(Me_2)CH_2^{\cdot}$
$Me_3SiOSiMe_3$	$Me_3SiOSi(Me_2)CH_2^{\cdot}$
Me_3SiOCH_3	$Me_3SiOCH_2^{\cdot}$
$(MeO)_4Si$	$(MeO)_3SiOCH_2^{\cdot}$
$Me_2Si(OMe)_2$	$Me_2(MeO)SiOCH_2^{\cdot}$

∝-oxy radical is formed. For similar compounds where the silicon is replaced by a carbon atom, no radicals were detected by esr. Thus a silicon atom is capable of stabilising an ∝-radical. This is due to the possible interaction of the radical p orbital with an empty d orbital of the silicon atom. The exclusive abstraction at a methoxy site shows that this stabilisation effect is not as



p_π-d_π overlap in ∝-silyl radical

effective as with an ∝-oxy group. The esr of the substituted methoxy radicals show a restricted Si-O bond rotation indicating that there is some bonding between the silicon and oxygen atoms.



A comparison of the rates of hydrogen abstraction from dimethylether (table 24), trimethylamine (table 25) and

Table 24 Hydrogen Abstraction from Dimethylether

Radical	EA	log A	Radical Source
CH_3	41.4	11.62	CH_3COCH_3
CF_3	28.3	11.71	CF_3COCF_3
CF_2Cl	17.5	11.30	$CF_2ClCOCF_2Cl$

Table 25 Hydrogen Abstraction from Trimethylamine

Radical	EA	log A	Radical Source
CH_3	37.2	11.90	CH_3COCH_3
CF_3	18.8	11.82	CF_3COCF_3
CF_2Cl	15.9	10.60	$CF_2ClCOCF_2Cl$

Table 26 Hydrogen Abstraction from Tetramethylsilane

Radical	EA	log A	Radical Source
CH_3	46.0	12.60	CH_3NNCH_3
CF_3	30.2	11.88	CF_3COCF_3
CF_2Cl	20.3	11.95	$CF_2ClCOCF_2Cl$

tetramethylsilane (table 26) has been carried out[79]. The formation of the nucleophilic α-oxy or α-amino radicals has a lower activation energy for the more electrophilic attacking radicals. This trend is also found in the formation of the α-silyl radical, thus the polar effects for the α-silyl radicals are similar to those of the α-oxy and α-amino radicals.

The stability of α-silyl radicals has also been demonstrated by the lack of rearrangement when compared to carbon analogues. Thus the well known rearrangement of the 2,2,2-triphenylethyl radical has been compared with the triphenylsilylmethyl radical[80]. The phenyldimethylsilyl-methyl and trimethylsilylmethyl radicals have also been studied[81] and shown not to rearrange. The conclusion drawn

$$Ph_3CCH_2CHO \xrightarrow{DTBP} Ph_3C\dot{C}H_2 \longrightarrow Ph_2\dot{C}CH_2Ph \longrightarrow Ph_2CHCH_2Ph$$

$$Ph_3SiCH_2CHO \xrightarrow{DTBP} Ph_3Si\dot{C}H_2 \not\longrightarrow Ph_2\dot{S}iCH_2Ph$$

$$\downarrow$$

$$Ph_3SiCH_3$$

is that this must be due to the stabilisation effect of an α-silyl group by d_π-p_π bonding and that while energetic, steric and polar effects may operate, these are only minor effects.

The reduction of an alkyl halide by tributyltin hydride is a useful reaction. The mechanism is via a

$$RX + Bu_3SnH \xrightarrow{AIBN} RH + Bu_3SnX$$

free-radical abstraction of the halogen atom, thus the stability of the radical produced will have a great effect on the reaction. It has been found that the reduction of α-chlorosilane can also be accomplished in this way. When a compound containing both a chloroalkyl and an α-chlorosilyl group is used, reaction occurs exclusively at the

$$Me_3SiCH_2Cl \xrightarrow{Bu_3SnH} Me_3SiCH_3$$

$$ClCH_2C(CH_3)_2CH_2CH_2Si(CH_3)_2CH_2Cl \xrightarrow{Bu_3SnH} ClCH_2C(CH_3)_2CH_2CH_2Si(CH_3)_3$$

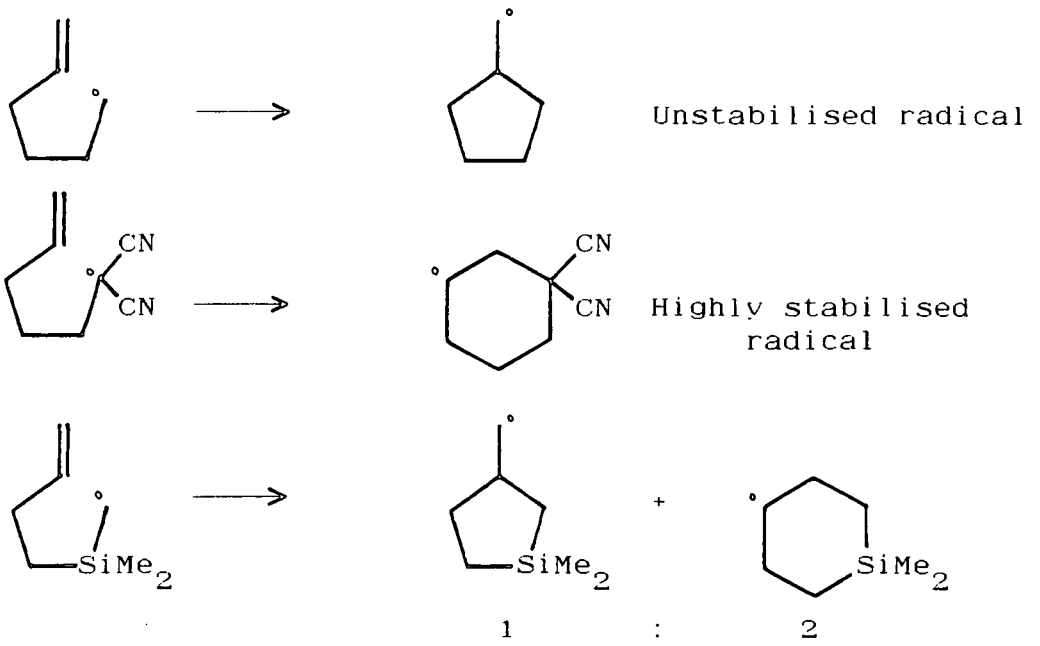
α-chlorosilyl group[82]. The relative rates of these reductions have also been measured for a range of silicon compounds[83] and have been shown to be two orders of magnitude faster for silicon compounds relative to analogous

$$Me_3SiCH_2Cl \xrightarrow{Bu_3SnH} Me_4Si \qquad k_{rel} = 1.0$$

$$Me_3CCH_2Cl \xrightarrow{Bu_3SnH} Me_4C \qquad k_{rel} < 0.01$$

carbon compounds. This can only be accounted for by the stabilisation of the radical produced by interaction with silicon d-orbitals.

The cyclisation of 5-hexenyl radicals has been discussed in the introduction chapter. Normally this gives a five membered ring product, unless the intermediate radical is stabilised, in which case the six membered ring becomes the dominant product. If a silicon atom is incorporated into



the ring in the 2-position it is found that a mixture of both ring sizes are formed with the 6 membered ring being the major product[84]. This suggests that the radical centre is stabilised by the presence of the ∝-silyl group.

B ADDITIONS OF SILANES TO HEXAFLUOROPROPENE

1 Acetone/t-Butanol Ratios

While ∝-silyl radicals are intermediates in some reactions, in order to add to fluorinated alkenes they must be easily formed and must be nucleophilic in character. The ease of hydrogen abstraction can be shown by reaction with tertiarybutoxy radicals as described in the introduction chapter. This radical rearranges to acetone and methyl radical with a constant rate (k_b). The rate of hydrogen

$$t\text{-BuO}\circ + RH \xrightarrow{k_a} R\circ + t\text{-BuOH}$$

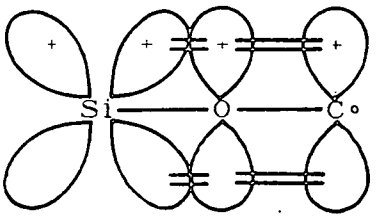
$$t\text{-BuO}\circ \xrightarrow{k_b} CH_3COCH_3 + CH_3^\circ$$

abstraction can therefore be found by comparing the rate (k_a) with that of rearrangement, which in turn can be followed by detection of the side products, tertiarybutanol and acetone. The ratio of acetone to butanol will be lower the more easily the hydrogen atom is abstracted. The ratio does not give any information on the reactivity of the radical formed, although it has been shown previously[12] that values lower than unity may indicate that the substrate will react with hexafluoropropene. The acetone/t-butanol ratios have been measured for a variety of silanes (table 27). The value for tetramethylsilane is just

Table 27 Acetone/t-Butanol Ratios

Substrates	Ratio
Me_4Si	0.92
$Me_3SiOSiMe_3$	0.03
$(Me_2SiO)_4$	1.73
$Me_2Si(OEt)_2$	0.25

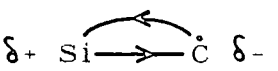
below unity and indicates that the hydrogen abstraction is slow and reaction with hexafluoropropene may be unpredictable. The ratio for dimethyldiethoxysilane is much lower than that of tetramethylsilane but is higher than that of diethylether[12] (Et_2O = 0.08). Thus the presence of a silicon atom reduces the availability of the oxygen lone pair for radical stabilisation by the overlap of the oxygen p-orbital and the silicon d-orbital. This overlap also gives rise to an increase in the ability of the silicon atom to stabilise an adjacent radical and is demonstrated by the low



acetone/butanol ratio of hexamethyldisiloxane. The ratio for octamethylcyclotetrasiloxane is very high and is an expression of the stereoelectronic effect. Thus the ring conformation is that in which orbital overlap is minimised and so the stabilisation is small.

2 Silanes and Siloxanes

The nucleophilic character of an α-silyl radical will depend on the balance between electron donation along the Si-C σ-bond by the electropositive silicon and electron



withdrawal due to d_{π}-p_{π} back bonding. Addition of dimethylpolysiloxanes to hexafluoropropene[85], chlorotrifluoroethene[86] and other perfluoroalkenes[87] has previously been achieved using peroxide initiaters at 130-140°C showing the radicals to be nucleophilic. For tetramethylsilane the acetone/t-butanol ratio is near unity and so hydrogen abstraction is slow and addition to hexafluoropropene is unpredictable. The yield of adduct (78) from tetramethylsilane and hexafluoropropene using γ-rays is low, however using peroxide initiation, a high yield of the 1:1 adduct (78) is obtained along with some 2:1 adduct (79). Thus

$SiMe_4 + C_3F_6 \longrightarrow Me_3SiCH_2CF_2CHFCF_3 + Me_2Si(CH_2CF_2CHFCF_3)_2$

(78) (79)

γ	14%	-
DTBP	89%	11%

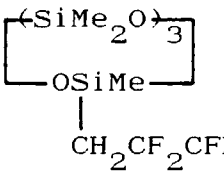
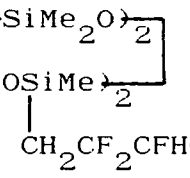
while the formation of the α-silyl radical is slow, the ability to add to hexafluoropropene indicates that the radical is nucleophilic in character.

The yields of adducts for siloxanes are higher and are consistent with the lower acetone/t-butanol ratios. Thus the introduction of a fluorinated side chain into the siloxanes can be achieved and these compounds may be useful precursors for the synthesis of new silicon oils and rubbers. The introduction of a fluorinated group directly into a silicon oil has also been achieved. The addition of hexafluoropropene gives a 49% convertion into an oil with a fluorinated side chain substituted at about every fifth silicon atom (83).

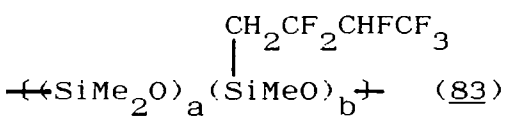
$(Me_3Si)_2O + C_3F_6 \longrightarrow Me_3SiOSiMe_2CH_2CF_2CFHCF_3$ + 2:1 adducts

(80)

γ	52%	-
DTBP	76%	24%

$(SiMe_2O)_4 + C_3F_6 \longrightarrow$  (81) +  (82)

γ	33%	-
DTBP	84%	16%

$(SiMe_2O)_n + C_3F_6 \xrightarrow{\gamma}$  (83)

silicon oil 49% a/b = 4.8

3 Alkoxy- and Alkylaminosilanes

The preference for formation of a radical ∝ to the oxygen atom has been discussed in the introduction to this chapter. The addition of methoxytrimethylsilane to octene[88,89] and hexafluoropropene[11] has also been shown to occur preferentially via the ∝-oxy radical. The addition of

$$Me_3SiOMe + CH_2{=}CHC_6H_{13} \xrightarrow{DTBP} Me_3SiOC_9H_{19} \quad 80\%$$
$$+ Me_2(MeO)SiC_9H_{19} \quad 12\%$$

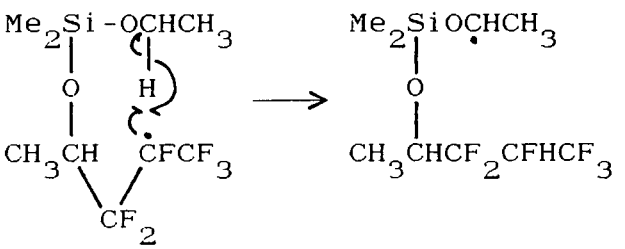
$$Me_3SiOMe + C_3F_6 \xrightarrow{\gamma} Me_3SiOCH_2CF_2CFHCF_3 \quad 62\%$$

dimethyldiethoxysilane to hexafluoropropene proceeds with a high conversion to give 1:1 adduct (84), and 2:1 adduct (85). Substitution occurs exclusively ∝ to the oxygen. The

$$Me_2Si(OEt)_2 + C_3F_6 \xrightarrow{\gamma} \underset{\substack{|\\EtO}}{Me_2Si}\underset{\substack{|\\CH_3}}{OCHCF_2CFHCF_3} + Me_2Si(\underset{\substack{|\\CH_3}}{OCHCF_2CFHCF_3})_2$$
(84) 30% (85) 69%

high yield of 2:1 adduct (85) suggests that a [1,7] hydrogen atom shift occurs in the intermediate adduct radical although this is not proven.

The acetone/t-butanol ratios for bisdialkylamino-silanes could not be measured as no acetone or t-butanol



could be detected in the reaction with ditertiarybutyl-peroxide. The addition of bisdimethylaminodimethylsilane gave a high yield of 1:1 adduct (86) along with some 2:1 adducts. As with the alkoxysilane, reaction occurred exclusively at the position α to the nitrogen atom.

$$Me_2Si(NMe_2)_2 + C_3F_6 \xrightarrow{\gamma} \underset{\underset{Me_2N\ \ Me}{|\ \ |}}{Me_2SiNCH_2CF_2CFHCF_3} + \text{2:1 adducts}$$

(86)

87% 13%

Thus it appears that both alkoxy- and alkylamino-silanes react as ethers and amines, the silicon being unable to compete in stabilisation of an α radical.

C REACTIONS OF SILANE ADDUCTS

The reactions of haloalkyl silanes have been reviewed[90-92] and in general it has been shown that silanes containing a halogen β to the silicon atom are less stable and undergo facile β-elimination. The thermal stability of a range of fluoroalkyl silanes has also been determined (table 28) and again show that substitution in the β position leads to a lower stability than for α or γ substitution. The thermal stability of the adduct of tetramethylsilane and

Table 28 Thermal stability of Fluoroalkyl Silanes

Silane	Temp/°C	Order	ln Rate(s^{-1})	Mechanism	
$F_3SiCF_2CHF_2$	452	1	-6.50	Carbene	[93]
$F_3SiCH_2CHF_2$	201	1	-6.51	Concerted	[94]
$F_3SiCH_2CH_2CF_3$	551	1.5	-1.90	Radical Chain	[95]

hexafluoropropene (78) was investigated by heating in a sealed tube. At 100°C no reaction occurred but at 200°C elimination of hydrogen fluoride occurred.

$$Me_3SiCH_2CF_2CFHCF_3 \xrightarrow{200°C} Me_3SiCH{=}CFCFHCF_3 \qquad (87)$$

The use of tetrabutylammomium fluoride (TBAF)[96] for the desilylation of silyl ethers[97] and alkyl silanes[98] and for β-eiminations of functional alkyl silanes[99] has become a general procedure. When the adduct (78) was refluxed with

$$Me_3SiCH_2CF_2CFHCF_3 \xrightarrow{TBAF} CH_2{=}CFCFHCF_3 \ 30\% \qquad (88)$$

tetrabutylammonium fluoride in tetrahydrofuran, elimination of trimethylsilylfluoride occurred to give an alkene (88).

D ATTEMPTED ADDITION OF STANNANES TO HEXAFLUOROPROPENE

It has been shown that a radical can be formed α to a tin atom by hydrogen abstraction by acyl radicals, giving concentrations high enough for detection by esr[78]. A series of compounds was studied (table 29) where radicals were formed α to the tin atom, except where an alkoxy group is present. These results are similar to those of silicon compounds.

Table 29 Hydrogen Abstraction by Acyl Radicals

Substrate	Product detected by esr
Me_4Sn	$Me_3Sn\dot{C}H_2$
Et_4Sn	$Et_3Sn\dot{C}HCH_3$
$n\text{-}Bu_3SnOMe$	$n\text{-}Bu_3Sn\dot{O}CH_2$

The attempted addition of tetramethyltin to hexafluoropropene gave an unidentified solid mixture with a conversion of 64%. No reaction occured in the absence of gamma ray initiation, thus suggesting that a radical mechanism is involved.

$$Me_4Sn + C_3F_6 \xrightarrow{\gamma} \text{Unidentified Solid} \quad 64\%$$

CHAPTER 4

FREE RADICAL ADDITION OF OXYGEN FUNCTION SUBSTRATES TO FLUOROALKENES

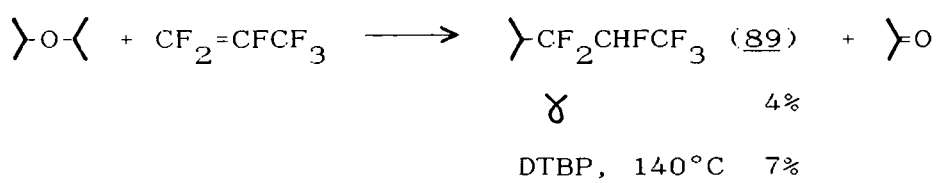
A INTRODUCTION

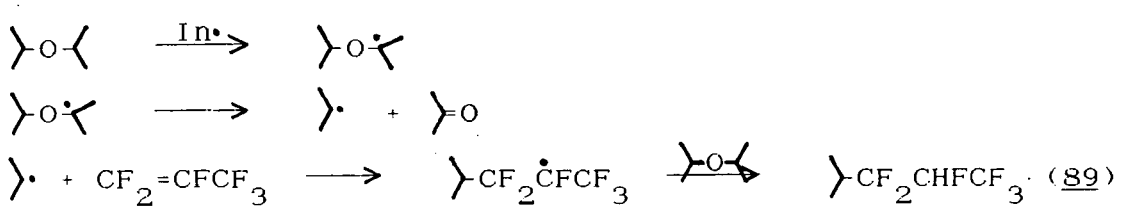
This chapter contains miscellaneous reactions which are meant to complete work which has gone before in this laboratory[11,12]. There are also reactions for which the products were required for further synthesis or for comparison with compounds synthesised by different routes. Mechanistic aspects of these additions will be discussed in the next chapter.

B ADDITIONS OF HEXAFLUOROPROPENE α-TO OXYGEN

1 Diisopropylether

Previously additions of n-alkylethers to hexafluoropropene have been studied[12] and the yields found to be high. The reaction of diisopropylether however gave only a very small yield of an unidentified product. This reaction has been repeated and the products shown to be acetone and 1,1,1,2,3,3-hexafluoro-4-methylpentane (89), which is



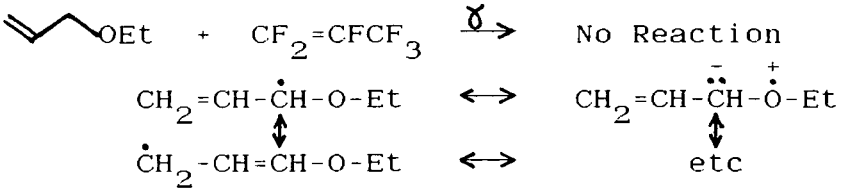


derived from an intermediate isopropyl radical. Thus the bulky diisopropylether radical does not undergo addition but rearranges to acetone and an isopropyl radical which can then itself add to the hexafluoropene to give the product obtained.

2 Allyl Ethers

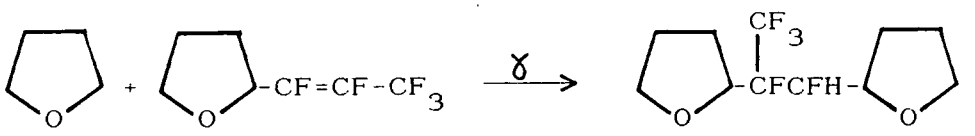
In the attempted addition of unsaturated ethers, it has been found that vinyl ethers copolymerise with hexafluoropropene under free radical conditions[12].

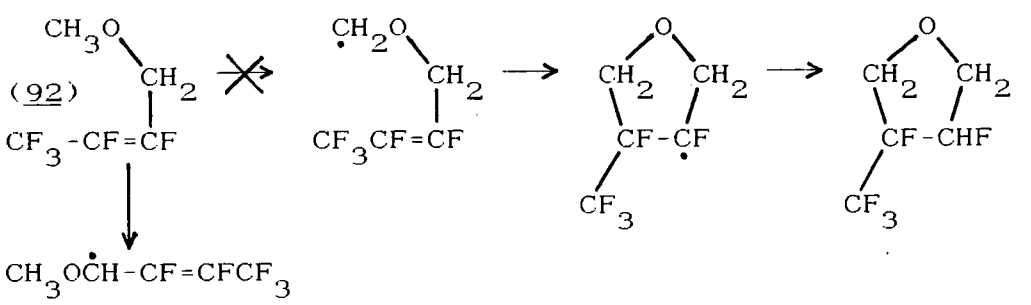
The addition of an allylic ether was attempted but no reaction occurred. The radical is formed at the allylic



position and is extensively stabilised by interaction with electrons in the oxygen lone pair and the double bond, therefore rendering it too stable to undergo addition.

Addition to the double bond of an allylic ether is

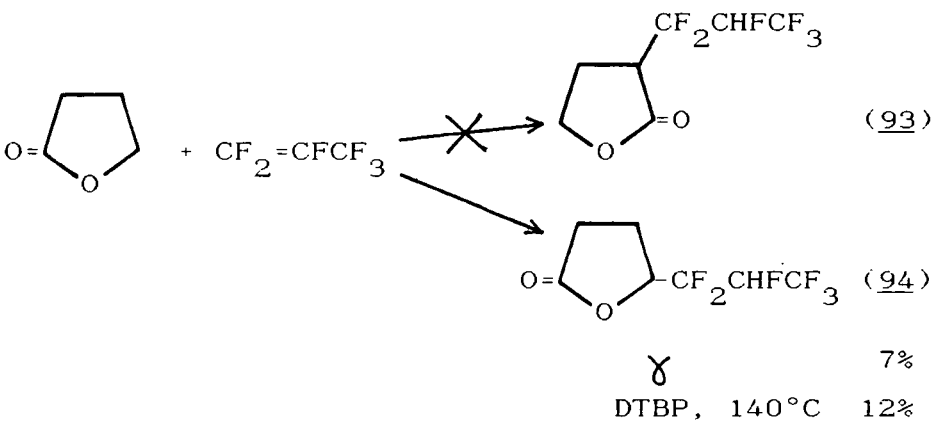




also possible. Thus in the addition of tetrahydrofuran to the fluorinated allylic ether (90) a small yield of adduct (91) is formed. An attempt was made to cyclise an allyl ether (92) by an intramolecular addition. The lack of reaction is again due to the formation of a highly stabilised allylic radical.

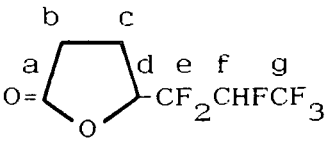
3' Lactones

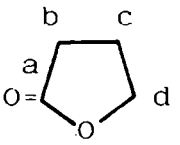
It had previously been reported that γ-butyrolactone reacts with hexafluoropropene to give 3-(2H-hexafluoropropyl)butyrolactone (93)[11]. The reaction has been repeated



and the product identified as 5-(2H-hexafluoropropyl)butyrolactone (94) by ^{13}C nmr (table 30). The chemical shifts of the carbon atoms at the 2,3, and 4-position (a,b and c) are comparable with those of the starting material[100]. That for the 5-position (d) is found at a higher shift due to the substitution of the electron withdrawing hexafluoropropyl group. The shifts for the side chain carbons are readily assigned from the carbon-fluorine couplings.

Table 30 ^{13}C nmr (^{1}H decoupled)

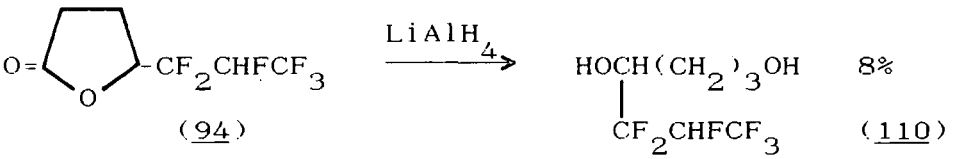




[100]

a/	176ppm	S	177.9ppm
b/	27ppm	S	27.7ppm
c/	20ppm	S	22.2ppm
d/	75ppm	D of D } diastereoisomers	68.6ppm
	76ppm	D of D } diastereoisomers	
e/	117ppm	T of T	
f/	85ppm	D of M	
g/	121ppm	Q of T	

Further evidence for the structure of the adduct (94) is obtained by it s reduction with lithium aluminium hydride

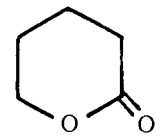


(94) (110)

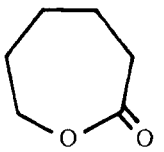
to give 1,1,1,2,3,3-hexafluoroheptane-4,7-diol (110). The structure of this diol is confirmed by comparison with an authentic sample obtained by the addition of butane-1,4-diol to hexafluoropropene (section IV.E.2). Reduction of the previously reported lactone adduct (93) would give 1,1,1,2,3,3-hexafluoro-4-hydroxymethylhexan-6-ol which is not obtained.

(93)

In the attempted addition of δ-valerolactone and ε-caprolactam only the dimers (95) and (96) were recovered along with the hexafluoropropene.



+ $CF_2=CFCF_3$ $\xrightarrow{\gamma}$ $+(CH_2)_4CO_2+_2$ (95)

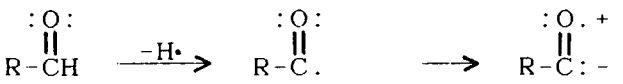


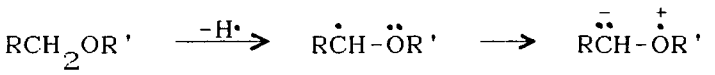
+ $CF_2=CFCF_3$ $\xrightarrow{\gamma}$ $+(CH_2)_5CO_2+_2$ (96)

C ADDITION OF CARBONYL COMPOUNDS TO HEXAFLUOROPROPENE

1 Aldehydes

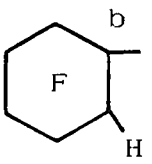
A radical may be produced by abstraction of a hydrogen atom from an aldehyde. The reactivity is accounted for by stabilisation, involving the adjacent oxygen lone pair of





electrons in an analogous manner to that with ethers. To test this rationale a study of the effect of substitution in the aldehyde on the reactivity towards hexafluoropropene was undertaken in an attempt to compare the effect with those found previously with ethers. Previous results[12] (table 31) show that ethers substituted with aromatic or haloalkyl groups do not react with hexafluoropropene while ethers substituted with alkyl groups or groups containing oxygen atoms react readily with hexafluoropropene.

Table 31 Ethers

Activating	Deactivating
H-[a]	Cl_3C-[a]
Alkyl-[a]	Ph-[a]
CH_3OCH_2-[b]	
$HOCH_2$-[b]	

a/ $R\text{-}CH_2OCH_2R$

b/ $R\text{-}CH_2OCH_3$

It is found that acetaldehyde reacts with hexafluoropropene to give the adduct (97) in high yield. Chloral,

$$CH_3\overset{O}{\overset{\|}{C}}\text{-}H + CF_2{=}CFCF_3 \xrightarrow{\gamma} CH_3\overset{O}{\overset{\|}{C}}CF_2CHFCF_3 \quad (97) \quad 94\%$$

crotonaldehyde, benzaldehyde, and p-methoxybenzaldehyde do not react and only starting materials are recovered with γ-ray or ditertiarybutylperoxide initiation. A more detailed discussion of these effects (table 32) is made in the next chapter.

Table 32 Aldehydes R-CHO

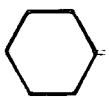
Activating	Deactivating
CH_3O-[12]	Cl_3C-
$(CH_3)_2N$-[12]	$CH_3CH{=}CH$-
CH_3-	Ph-
	p-$MeOC_6H_4$-

If the oxygen atom of an aldehyde is replaced by a nitrogen atom then a similar radical stabilisation is expected. However in the attempted additions of ethylidine

ethylimine and ethyidine t-butylimine to hexafluoropropene the imines were too basic and only nucleophilic reaction occurred.

2 Ketones

It has been shown previously that cyclohexanone can be added to tetrafluoroethene[101] to give telomeric products. In the attempted addition of acetone and cyclopentanone to hexafluoropropene only starting materials were recovered, however the reaction with cyclohexanone gave a small yield of an unidentified product.



$$+ CF_2{=}CFCF_3 \xrightarrow{\delta} \text{Unidentified Product} \quad 10\%$$

A comparison of oxygen and nitrogen was made by the attempted addition of acetonitrile to hexafluoropropene. As with the ketones only starting materials were recovered.

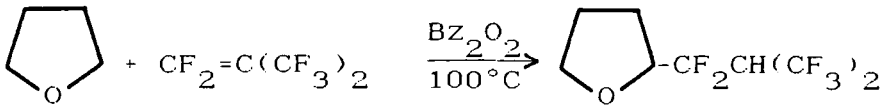
$$CH_3CN + CF_2{=}CFCF_3 \xrightarrow{\delta} \text{No Reaction}$$

D COMPARISON OF ADDITIONS TO CHLORINATED AND FLUORINATED ALKENES

The addition to chlorinated alkenes was attempted in order to compare the effects of chlorine and fluorine substitution on the reactivity of an alkene. While the electron withdrawing ability of a chlorine atom is similar to that of fluorine, the steric bulk is much larger and is more comparible to that of a CF_3 group.

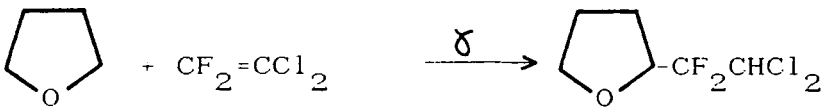
1 Additions to 1,1-Dichlorodifluoroethene

The addition of tetrahydrofuran to perfluoroisobutene has been reported to give a good yield of adduct (98)[45]. This may be compared with additions to 1,1-dichlorodifluoroethene in which the CF_3 groups have been replaced by chlorine atoms. For tetrahydrofuran the yield of adduct with



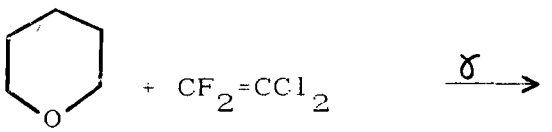
(98) [45]

48%



(98)

36%

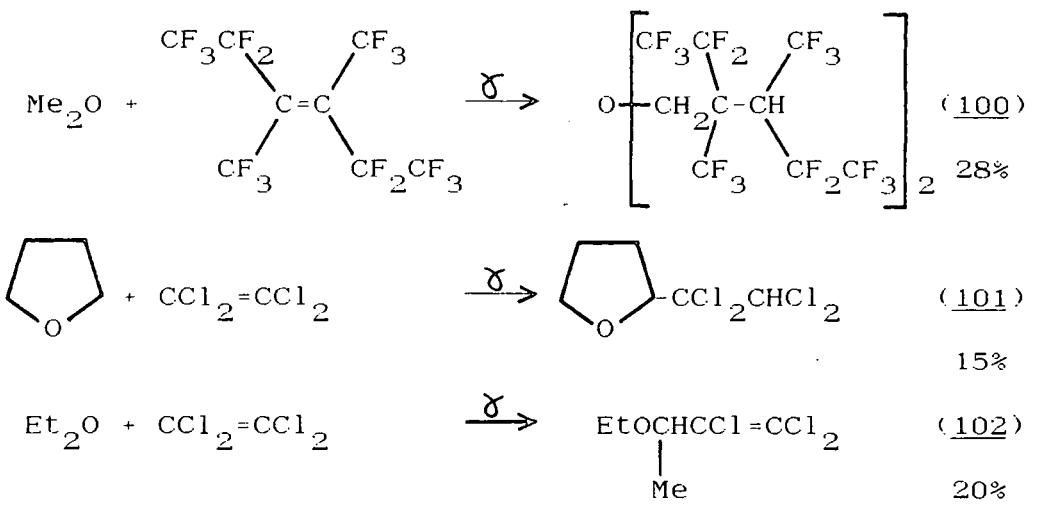


the dichloroethene is similar to that reported for perfluoroisobutene. Thus the chlorine substitution has little effect on the reactivity of the alkene with respect to trifluoromethyl substitution. The lack of reaction with tetrahydropyran is explained by the large steric bulk of the intermediate $-\dot{C}Cl_2$ radical reducing it's reactivity and making the propagation step slow.

2 Additions to Tetrachloroethene

Reactivity of chlorine and fluoroalkyl substituted alkenes may also be studied by the comparison of additions to tetrachloroethene and perfluoro-3,4-dimethyl-3-hexene. The addition of dimethyl ether to perfluoro-3,4-dimethyl-3-hexene gives a moderate yield of the 2:1 adduct (100)[11].

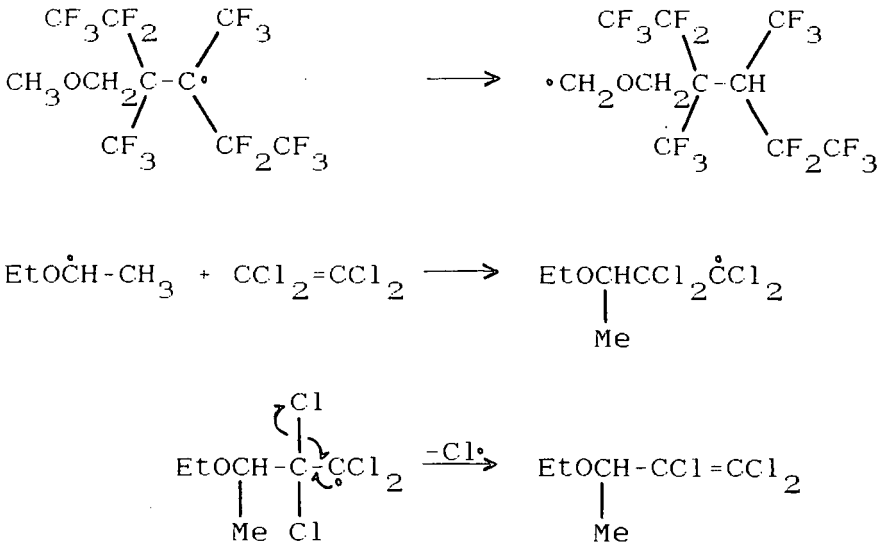
Tetrahydrofuran adds to tetrachloroethene to give a low yield of 1:1 adduct (101), whereas diethylether gives an unsaturated product (102). These results are explained by



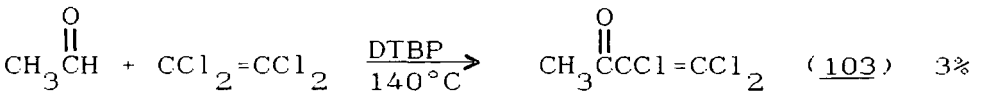
the steric bulk of the intermediate adduct radical, which reduces the rate of the propagation step and allows alternative reactions to compete. In the addition to the fluorinated alkene a (1,5) occurs, leading to the formation of the 2:1 adduct (100). In the addition of diethylether to tetrachloroethene, elimination of a chlorine atom occurs to give the unsaturated product obtained (102). For the addition of tetrahydrofuran, the high reactivity of this ether allows the propagation step to proceed at a competitive rate giving the simple adduct (101).

For the addition of methanol and acetaldehyde to tetrachloroethene no adducts were formed with gamma ray initiation. At 140°C using peroxide initiation unsaturated products are formed via loss of a chlorine atom.

Thus, in additions the steric effect of a chlorine atom and a fluoroalkyl group are similar, however in

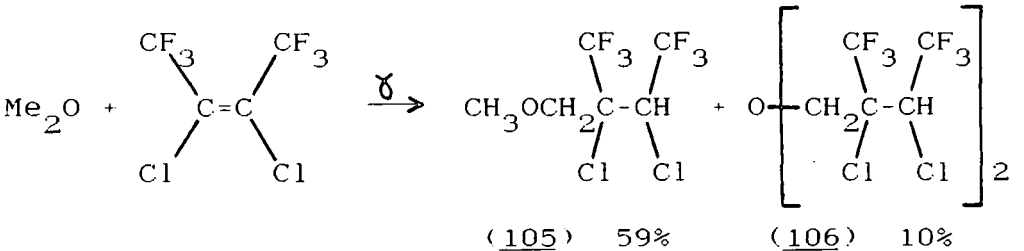


chlorinated alkenes the steric effects in the propagation step can be relieved by the elimination of a chlorine atom.



3 Additions to 2,3-Dichlorohexafluorobut-2-ene

A further comparison of a chlorine atom and a fluoroalkyl group can be made in the addition to 2,3-dichlorohexafluorobut-2-ene. Dimethylether adds in high yield to give both 1:1 (105) and 2:1 (106) adducts. Thus the steric hindrance in this alkene is less than for perfluoro-



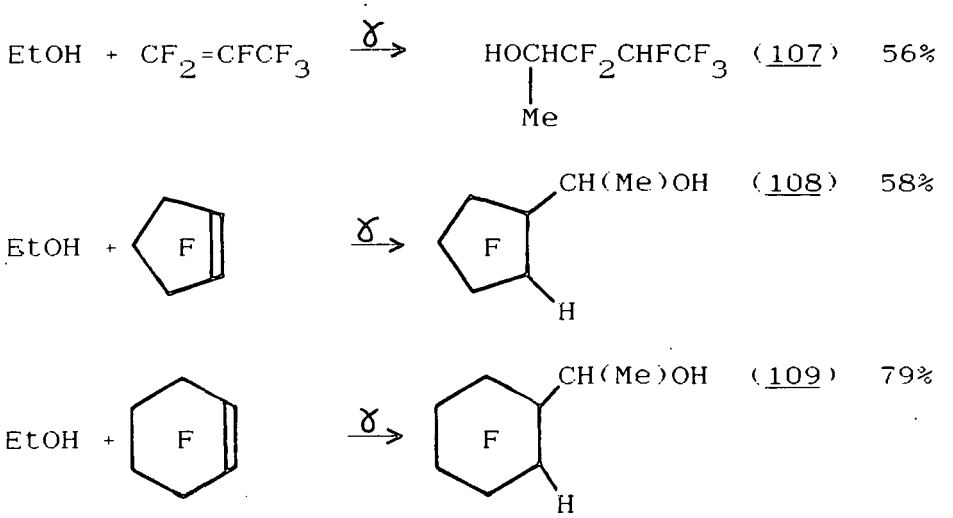
3,4-dimethyl-3-hexene (see above), as shown by the higher overall yields and the large proportion of 1:1 adduct (105) formed.

E Additions of Alcohols

1 Additions of Ethanol

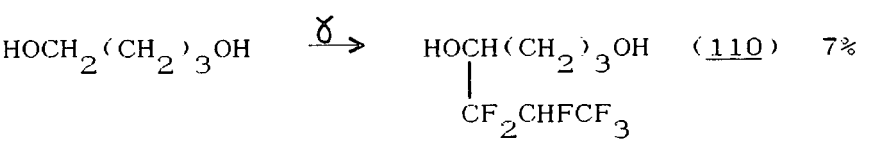
The additions of alcohols to fluorinated alkenes has previously been studied in this laboratorary[11]. The additions of ethanol were attempted for the possible use of the adducts obtained in further synthesis.

Ethanol adds to hexafluoropropene, perfluorocyclopentene and perfluorocyclohexene in high yields.



2 Addition of Butane-1,4-diol

The addition of butane-1,4-diol to hexafluoropropene gives a low yield of simple 1:1 adduct (110), which was used for comparison elsewhere (section IV.B.3).

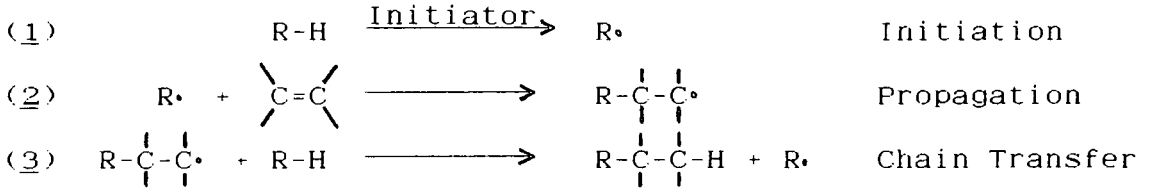


CHAPTER 5

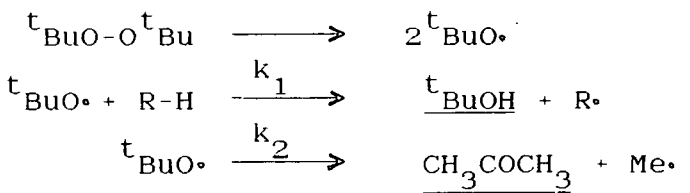
CONFORMATION AND SUBTITUENT EFFECTS IN FREE RADICAL ADDITION REACTIONS

A INTRODUCTION

A large number of preparative experiments have been discussed in the previous three chapters. Many of these have been designed to investigate the effects of both substitution and conformation on the reactivity of radicals towards fluorocarbon alkenes. The overall reactivity can be measured by the yield of the products obtained. However, as



the reaction is a three step chain reaction the yields cannot tell us why, if a reaction has failed. The initiation step can easily be probed using ditertiarybutyl-peroxide as the initiator. The tertiarybutoxy radical undergoes a β-scission reaction to give acetone and a methyl



radical with a constant rate (k_2). The abstraction rate (k_1) of a hydrogen atom from the substrate will vary with

the ease of production of a radical from the substrate, tertiarybutanol being produced as a side product. Thus the relative rates of the two reactions can be found from the ratio of acetone and tertiarybutanol formed in the reaction.

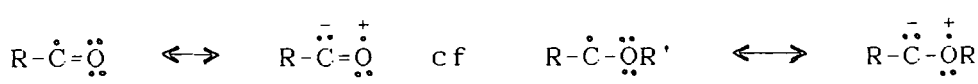
$$\frac{k_2}{k_1} \propto \frac{[CH_3COCH_3]}{[{}^tBuOH]}$$

B SUBSTITUTION EFFECTS

Substitution of a radical may affect any of the three steps of the reaction. The ease of radical production can be measured by the ratio of acetone and tertiarybutanol obtained by reacting the substrate with ditertiarybutyl-peroxide. It has been suggested[12] that for ethers a ratio of less than 0.4 indicates that the substrate will react in high yield with hexafluoropropene and that a ratio above unity indicates that the substrate will be unreactive. This however assumes that only the initiation step is important for the success of the reaction.

1 Aldehydes

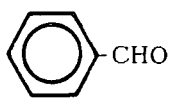
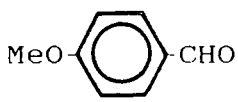
The stabilisation of an acyl radical can be compared to an α-oxy radical of an ether. A series of reactions of aldehydes with hexafluoropropene and acetone/tertiary-butanol ratios of the aldehydes is shown (table 33) along with a series of ethers for comparison. The effect of

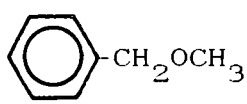


acyl radical α-oxy radical

substitution has a very similar effect on both acyl and α-oxy radicals as expected. However the yields and the acetone/tertiarybutanol ratios are not fully in agreement. Acetaldehyde and diethylether both give a high yield of

Table 33 Comparison of Aldehydes and Ether Reactivity

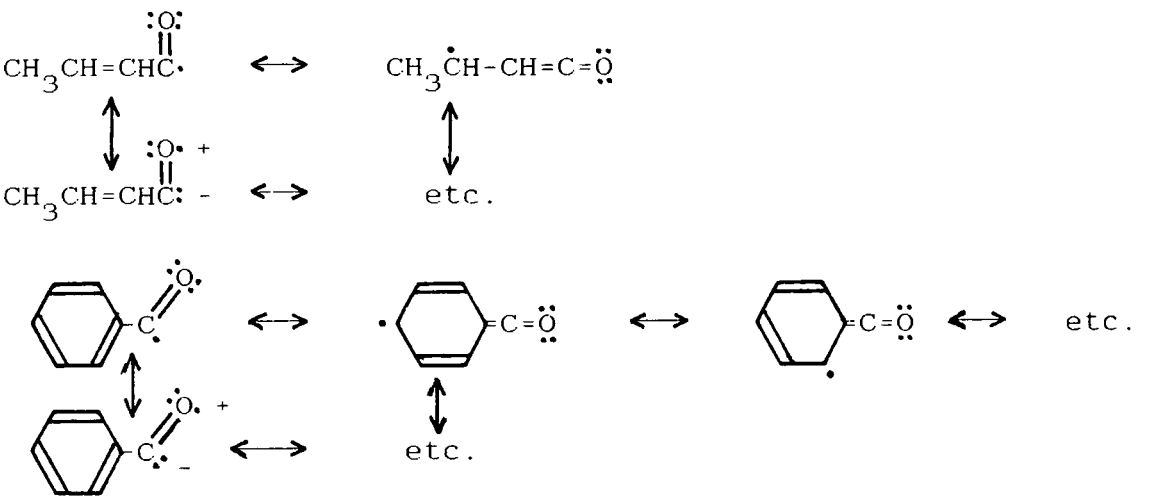
Aldehyde	% Conversion[a] with C_3F_6	Acetone ^tBuOH
CH_3CHO	94	0.13
CCl_3CHO	0	2.12
$CH_3CH{=}CHCHO$	0	0.15
	0	0.11
	0	0.08
CH_3OCHO	0[12]	-
$(CH_3)_2NCHO$	69	0.09[12]

Ether	% Conversion[a] with C_3F_6	Acetone ^tBuOH
Et_2O	98	0.08[12]
$(ClCH_2CH_2)_2O$	0[12]	1.59[12]
$CH_2{=}CHCH_2OEt$	0	0.09
	0[11]	-
$CH_3OCH_2OCH_3$	80[11,b]	0.21[12]

a - Based on Hexafluoropropene Recovered

b - Reaction occurs at the CH_3O group

adduct and have a very low acetone/tertiarybutanol ratio. If R is a chloro methyl group then it is found that no reaction occurs. The acetone/tertiarybutanol ratio which is increased to greater than unity shows that this is due to the radical being difficult to produce. If an unsaturated group is substituted then reaction is again stopped, however the acetone/tertiarybutanol ratio suggests that radicals are being produced in the system. The radicals produced will be stabilised both by the oxygen atom and also by delocalisation of the radical into the unsaturated group. This extra delocalisation involves no charge separation and so will be highly stabilising. This will therefore make the addition step less exothermic due to loss of this extra stabilisation energy and so preventing reaction. The results of substitution with a second heteroatom are less clear. Methylformate is unreactive while N,N-dimethylformamide gives a high yield of adducts.



2 Nitrogen Compounds

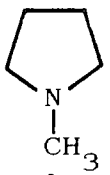
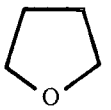
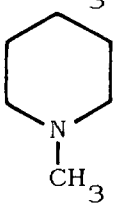
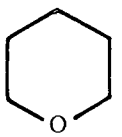
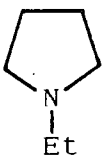
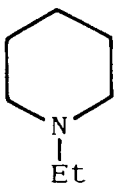
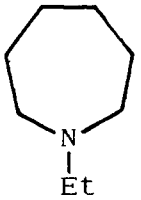
The substitution effects in oxygen systems have received much attention[11,12]. In this section the relative

ability of oxygen and nitrogen to stabilise a radical and the effects of substitution in nitrogen compounds is considered.

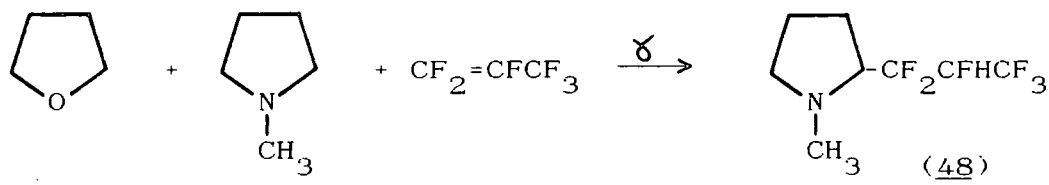
(a) Comparison of α-amino and α-oxy Radicals

The stabilisation of a radical by the lone pair of electrons on nitrogen or oxygen will depend on their availability. The increased basicity of amines over ethers would suggest that the lone pair on nitrogen is more readily

Table 34 Comparison of α-amino and α-oxy Radicals

Amine	% Conversion with C_3F_6	Acetone ^tBuOH	Ether	% Conversion with C_3F_6	Acetone ^tBuOH
	95	0		98	0.07[12]
	81	0		98	0.08[12]
Et_3N	98	0.01	Et_2O	98	0.08[12]
	96	-			
	95	-			
	95	-			

available than on oxygen and so α-amino radicals will be highly stabilised. The acetone/tertiarybutanol ratios for ethers is extremely low, while for some amines acetone is not detected, thus the α-amino radicals are more easily produced than α-oxy radicals. It is found that ethers give almost quantitative yields of adducts with hexafluoropropene and so no conclusions can be made from the comparison of the similar quantitative yields from amines (table 34). However the greater reactivity of the amines can be demonstrated by a competition reaction. Thus if an equimolar mixture of tetrahydrofuran and N-methylpyrrolidine are reacted with a deficiency of hexafluoropropene only the amine adduct (48) is formed.



(48)

(b) Amides

The substitution of a carbonyl group next to a nitrogen will reduce the availability of the nitrogen lone pair of electrons for stabilisation of a radical. This is apparent from the increase in the acetone/tertiarybutanol ratio of the amides, however the values are below 0.4 and so the high reactivity towards hexafluoropropene is expected. By comparison of the reactivity of amides and esters (table 35) it can be seen that the nitrogen is more effective at stabilisation of a radical than oxygen.

Table 35 Effect of Carbonyl Substitution

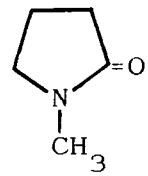
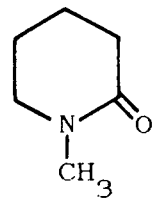
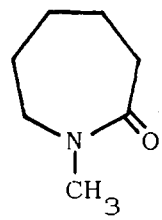
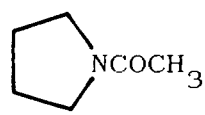
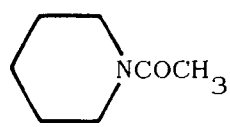
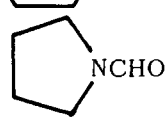
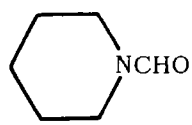
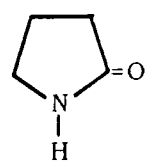
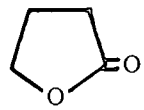
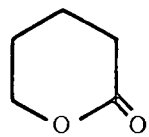
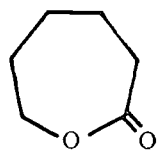
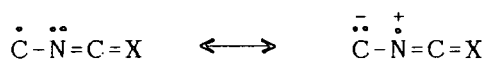
Amide	% Conversion with C_3F_6	Acetone ^tBuOH
$MeCONMe_2$	98	0.42
	98	0.21
	84	0.25
	60	0.27
	98	-
	57[12]	0.35
	98	0.34
	98	0.34
	54	1.24
$CH_3CONHCH_3$	98	-

Table 35 Continued...

Ester	% Conversion with C_3F_6	Acetone ^tBuOH
$CH_3CO_2CH_3$	0	-
	23	2.37
	0	-
	0	0.81

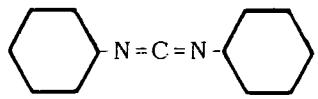
(c) Double Bonded Nitrogen Substrates

The effect of a double bonded nitrogen should be very similar to that where the nitrogen is only singly bonded, as



the lone pair is unaffected. If we consider compounds of the type R-N=C=X (table 36) then there is the possibility of further delocalisation of the radical and also the effect of variation of X. It is found that, when X is oxygen, radicals are formed and addition to hexafluoropropene takes place. However when X is sulphur, although radicals are formed, the addition is prevented. When X is nitrogen the addition is also prevented.

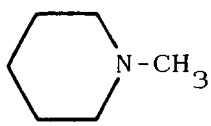
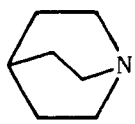
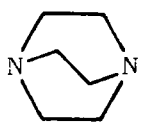
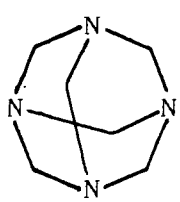
Table 36 Comparison of R-N=C=X

Substrate	% Conversion with C_3F_6	Acetone t_{BuOH}
EtNCO	28	0.10
EtNCS	0	0.36
	0	-

C CONFORMATION EFFECTS

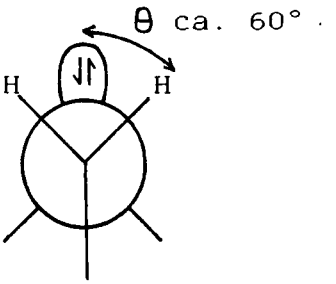
The effects of confomation in ring systems has been discussed in detail in the introduction and elsewhere[102,103] for ethers. Some initial studies have been done on the

Table 37 Hydrogen Abstraction Rates for Tertiary Amines

Amine	$\frac{t\text{-BuO}}{M^{-1}s^{-1}}$[104]	$\frac{CO_3^-}{M^{-1}s^{-1}}$[105]
Et_3N	1.8×10^8	6.4×10^8
		2.6×10^6
 (Quinuclidine)	6.0×10^6	
 (DABCO)	2.8×10^7	$(1.7 \times 10^7)^a$
 (HMT)		1.7×10^4

a - see discussion

hydrogen abstraction from amines with butoxy radicals[104] and carbonate radicals[105] (table 37). In the reaction with carbonate radicals the possibility of an alternative one electron transfer reaction has been suggested and an intermediate radical cation is detected in the case of 1,4-diazabicyclo[2,2,2]octane (DABCO) which may account for the increased rate for this compound. The low reactivity, for both abstracting radicals, of the bicyclic and tricyclic compounds can be rationalised by a stereoelectronic effect. In these three compounds the conformations of the molecules are fixed so that the nitrogen lone pair and the radical orbit are about 60° apart (θ). Therefore the stabilisation of the radical by the lone pair will be small due to the limited overlap of the two orbitals.

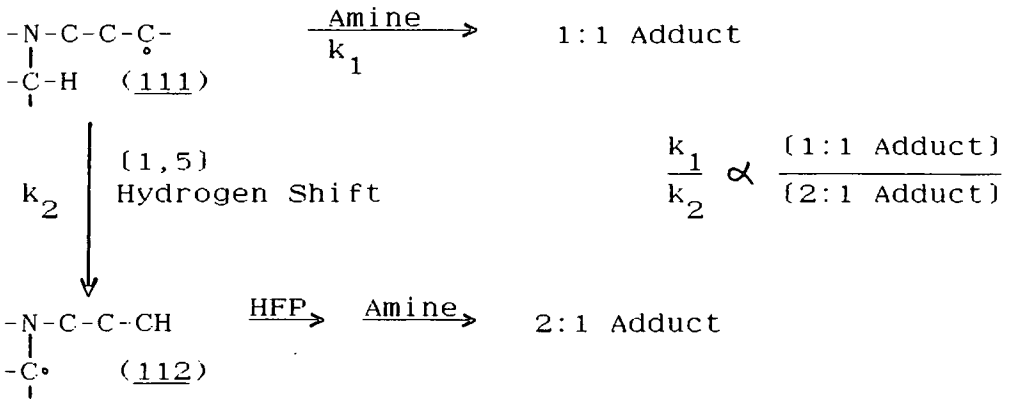


View down C-N bond for DABCO, Quinuclidine and HMT.

1 Amines

For ethers the order of the reactivity of cyclic systems was investigated by competition reactions[12], however this is more difficult for amines due to the appearance of 2:1 adducts making product analysis more difficult. In chapter two it was shown that the order of reactivity can be derived from the proportions of 1:1 and 2:1 adduct formed in a single reaction. The intermediate radical (111) can react with the amine (k_1) to give 1:1 adduct or undergo a [1,5]

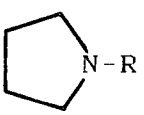
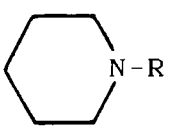
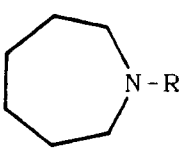
hydrogen shift (k_2) to lead to 2:1 adduct. The rate of the (1,5) shift however will vary little with amine structure, whereas the chain transfer (k_1) will depend on the ease of



hydrogen abstraction from the amine. Thus the ease of abstraction can be found. In a series of additions of cyclic amines to fluorinated alkenes (table 38) it is found that the proportion of 1:1 adduct and therefore the reactivity of the amine follows the same order as found for ethers for varying ring size:-

$$5 > 7 > 6$$

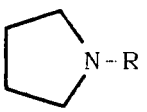
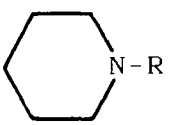
Table 38 Proportion of 1:1 Adduct Formed in Amine Additions

	C_3F_6, R=CH_3	C_3F_6, R=CH_2CH_3	C_2F_4, R=CH_3
	95%	75%	90%
	10%	19%	44%
		46%	

2 Amides

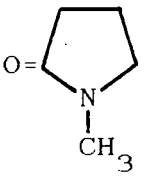
For cyclic amides the carbonyl group may be either incorporated into or outside the ring. For compounds with the carbonyl group outside the ring, the conformations of the rings will be little affected and so the normal reactivity order with change of ring size should be unaffected. Additions to amides of this type have only been carried out on the five and six membered ring compounds (table 39) and so the results are inconclusive. If the

Table 39 % Conversion for Cyclic Amide Additions to Hexafluoropropene

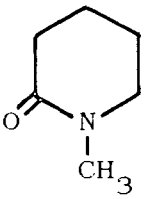
	R=CHO	$R=COCH_3$
	98	98
	98	57[12]

carbonyl group is in the ring this may effect the conformation and so alter the stability of the amide radicals. In the addition of a series of cyclic amides to hexafluoropropene (table 40) it is found that the order of reactivity (5 > 6 > 7) is not as expected, and so the carbonyl group must be affecting the ring conformations. For a five membered ring, an amine will have eclipsing interactions between all of the hydrogens and the lone pair of electrons and the substituted group on the nitrogen. Replacing a

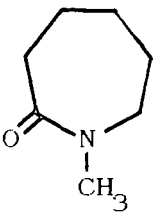
Table 40 % Conversion for Cyclic Amide Additions to Hexafluoropropene



98



84



60

CH_2 group next to the nitrogen with a carbonyl group will remove these eclipsing interactions on either side. The planar conformation of the ring will be more stable and so the stereoelectronic effect will be unchanged. For the six membered ring an amine will have no eclipsing interactions in the chair conformation. However introduction of a carbonyl group will now cause eclipsing between itself and both the adjacent CH_2 group and the nitrogen substituents. This will cause the chair conformation to twist and so reduce the angle between the nitrogen lone pair and the adjacent hydrogen atom. This will cause the intermediate radical to be more stabilised and therefore increase the reactivity of the six membered ring. For a seven membered ring the flexibility will be little changed, so an average conformation will be similar to that of the amine and the stereoelectronic effect will be unchanged. Thus the order of

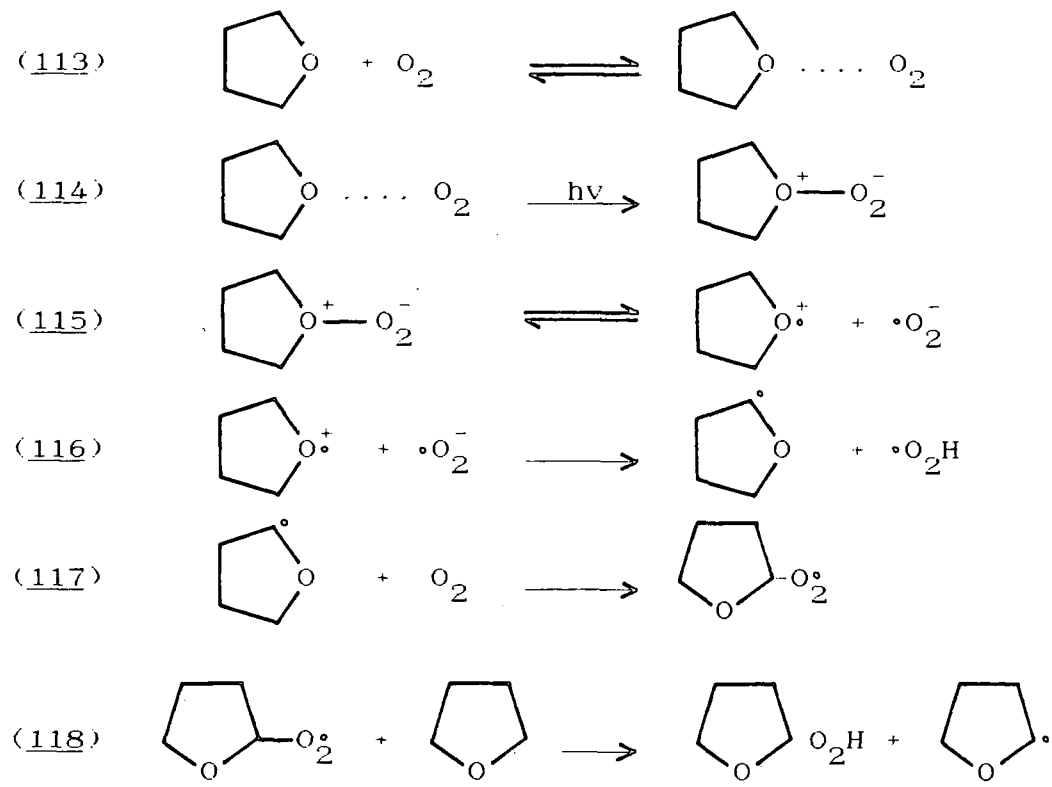
reactivity found is mainly due to an increase in reactivity of the six membered ring, while the five and seven membered rings are largely unaffected.

D UNINITIATED REACTIONS

It has been identified[106] that there are three types of intermolecular processes in which radicals can be produced from the interaction of closed shell molecules. These are: molecule assisted homolysis[107] or homosolvolysis[108], in which acceleration of a single bond homolysis is caused by the interaction of one molecule with another; interaction of two π systems leading to diradicals; and one electron transfer reactions[109] in which a donor and an acceptor exchange an electron to produce two radicals or radical ions. The mechanisms of many such processes are not fully established.

One of the most important spontaneous radical reactions is the autoxidation of ethers[110]. The reaction is essentially a free radical chain mechanism (117) and (118), however the initiation of the reaction is more complex. It has been shown[111] that an initial charge transfer comples is formed between the ether and oxygen (113). This complex is excited by light (114) and dissociates to form a radical ion pair (115). The peroxy radical anion then abstracts a proton from the ether radical cation to give the α-oxy radical (116) which can enter into the remaining chain reaction.

The unininitiated addition of ethers to alkenes has also been found to occur by several workers and are



summarised (table 41). Most of these reactions have been shown to be free radical reactions by addition of radical inhibitors which prevents reaction or by comparison of product mixtures with those obtained when radical inhibitors are used. The initiation of these reactions may be similar to the autoxidation reaction[112]. It has been shown that ethers can form charge transfer complexes with electron deficient alkenes and that these require irradiation with only low energy light to promote a one electron transfer, which can be detected by esr[116]. A proton transfer to the alkene radical anion will then give the ∝-oxy radical which can promote a chain reaction. Alternatively, the radical pair produced could combine in the cage to give the final product without a chain mechanism occurring.

Table 41a Uninitiated Reactions of Ethers and $MeO_2CC{\equiv}CCO_2Me$[112]

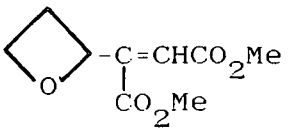
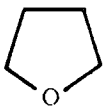
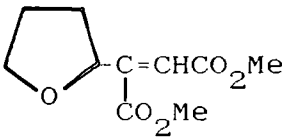
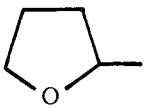
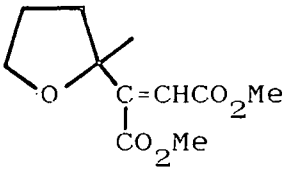
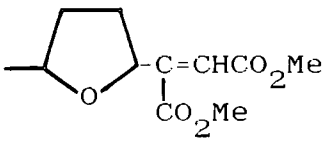
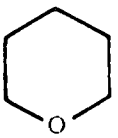
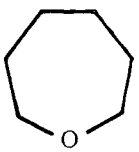
Ether	Conditions	Product	
	20°C		20%
	20°C		30%
	20°C		70%
			20%
	20°C	No Reaction	
	20°C	No Reaction	

Table 41b Uninitiated Reactions of Ethers and $NCCH{=}CHCN$[113]

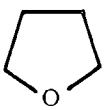
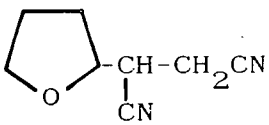
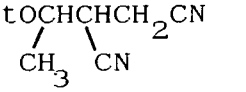
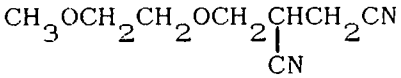
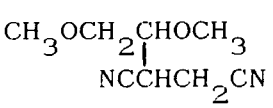
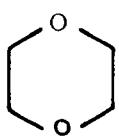
Ether	Conditions	Product	
	Reflux		37%
Et_2O	Reflux		41%
$CH_3OCH_2CH_2OCH_3$	Reflux		6%
		+ 	6%
	Reflux	No Reaction	

Table 41c Uninitiated Reactions of Tetrahydrofuran to Fluorinated Alkenes[114]

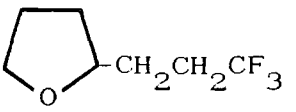
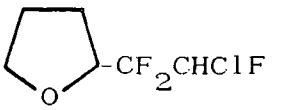
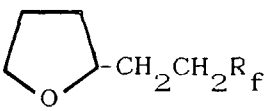
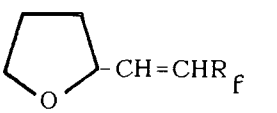
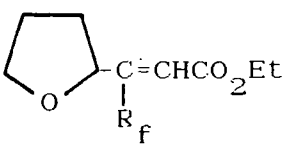
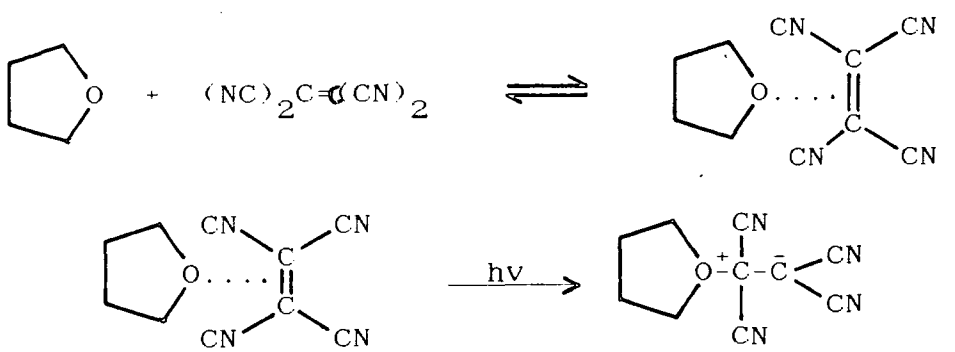
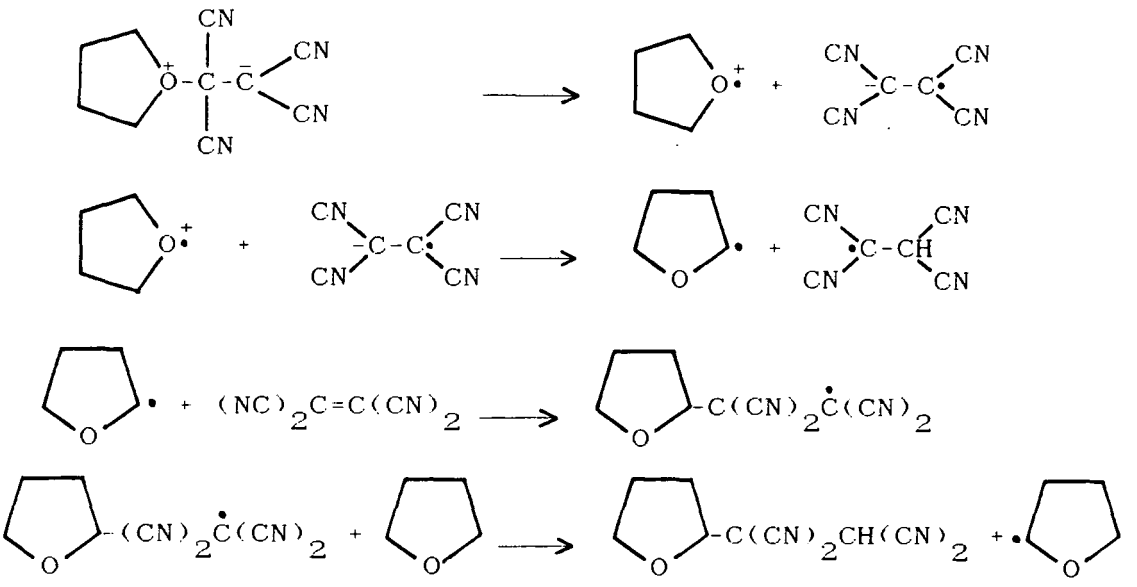
Alkene	Conditions	Product	
$CF_3CH=CH_2$	RT		8%
		+ higher adducts	
$ClCF=CF_2$	RT		20%

Table 41d Uninitiated Reactions of Tetrahydrofuran to Fluoroalkyl, Alkenes and Alkynes[115]

Alkene	Conditions	Product	
$R_fCH=CH_2$[a]	Reflux		100%
$R_fC\equiv CH$[a]	Reflux		100%
$R_fC\equiv CCO_2Et$[a]	Reflux		100%

a - R_f = C_4F_9, C_6F_{13}, C_8F_{17}





1 Additions To Hexafluoropropene

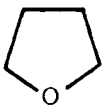
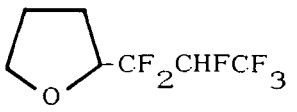
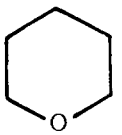
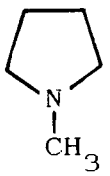
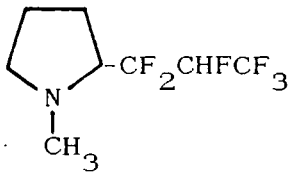
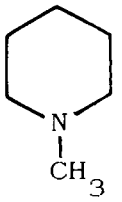
Uninitiated addition of tetrahydrofuran to hexafluoropropene has previously been observed[117] in the presence of potassium fluoride. Also while studying the free radical additions of amines to hexafluoropropene it was found that addition occurred with N-methylpyrrolidine in an uninitiated control experiment. Uninitiated additions of several ethers and amines were attempted (table 42) but only N-methylpyrrolidine and tetrahydrofuran were successful.

This observation can be explained by the high stability of the radicals in the five membered ring, making the electron transfer from an initial complex favourable.

2 Additions to Other Alkenes

Uninitiated additions of tetrahydrofuran, tetrahydropyran, N-methylpyrrolidine, and N-methylpiperidine were also attempted with chlorotrifluoroethene and 1,1-dichlorodifluoroethene, however none were successful at temperatures in the range 20 to 140°C.

Table 42 Uninitiated Additions to Hexafluoropropene at 20°C

Substrate	Product	Yield (%)
		72
	No Reaction	
Et_2O	No Reaction	
		98
	No Reaction	
Et_3N	No Reaction	

CHAPTER 6

REACTIONS OF FREE RADICAL ADDUCTS

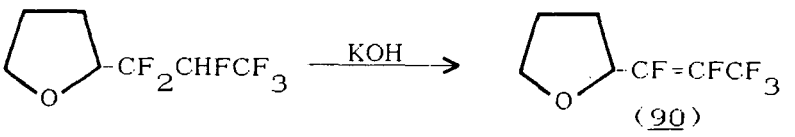
A INTRODUCTION

There are many fluorocarbon compounds which have been prepared by free radical addition, but there are very few reports of further reactions of the adducts. It is the aim of this work to show that a much wider range of compounds, not available by direct addition, can be synthesised by simple reactions. This chapter contains results for the introduction of new functional groups, while chapter 7 contains results for synthesis of highly fluorinated inert fluids.

B SYNTHESIS OF ALKENES

(a) Ethers

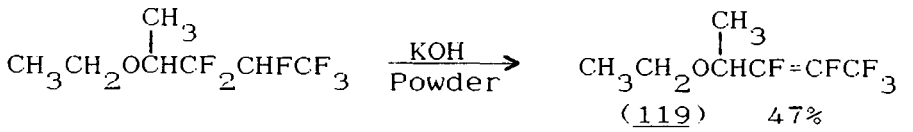
It has been reported that the dehydrofluorination of 2-(2H-hexafluoropropyl)oxolane and 1,1,1,2,3,3-hexafluoro-4-ethoxypentane can be achieved by reaction with potassium hydroxide in diglyme at 120°C[118]. This reaction was repeated and a moderate yield of alkene (90) was produced, but this was difficult to separate from the unreacted starting material. The reaction was repeated by refluxing the starting material over powdered potassium hydroxide. This gave the alkene in high purity along with some polymeric material. The reaction was repeated with diethyl and dimethyl ether adducts. The yield decreasing as the boiling point of the adduct decreases.



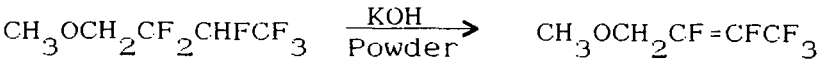
(90)

Diglyme 36%

Powdered KOH 75%



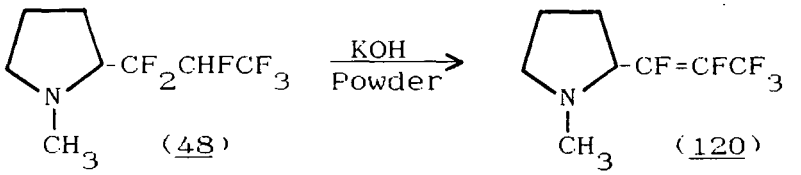
(119) 47%



(92) 24%

(b) Amines

The N-methylpyrrolidine adduct (48) was reacted with powdered potassium hydroxide and dehydrofluorination occurred giving a good yield, which is comparable with the ethers. Thus the amine function does not interfere with the reaction.

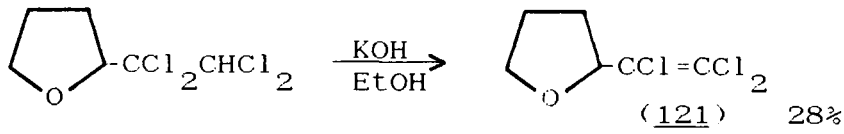


(48) (120) 66%

2 Chloroalkene Adducts

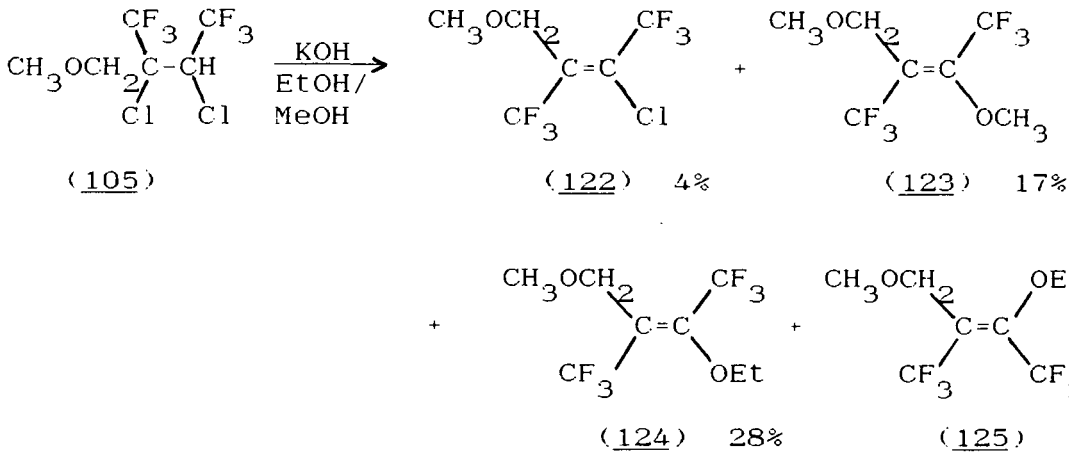
(a) Dehydrochlorination

In some addition reactions the dehydrochlorinated adduct is the major product, this is due to the loss of a chlorine atom from the adduct radical. This process can occur with tetrachloroethene additions as described in chapter 4. In other cases where the saturated adduct is formed, these can be readily dehydrochlorinated. Thus the adduct of tetrahydrofuran and tetrachloroethene (101) was dehydrochlorinated with ethanolic potassium hydroxide at



(121) 28%

room temperature. Attempted dehydrochlorination of the adduct of dimethylether and 2,3-dichlorohexafluorobut-2-ene



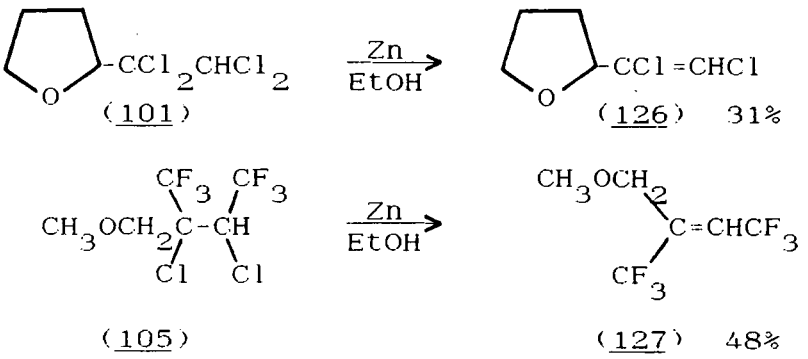
(105) (122) 4% (123) 17%

(124) 28% (125) 13%

(105) in a methylated spirit solution gave mainly substituted products. Thus the CF_3 groups in the initial product (122) makes substitution of the remaining chlorine atom very facile.

(b) Dechlorination

Adducts with vicinal chlorine atoms can be converted into alkenes by dechlorination with zinc. Thus the adduct of tetrahydrofuran and tetrachloroethene (101) dechlorinates to give the alkene (126), further dechlorination not occurring. The adduct of dimethylether and 2,3-dichlorohexafluorobut-2-ene (105) also gives a good yield of the dechlorinated product (127).



(101) (126) 31%

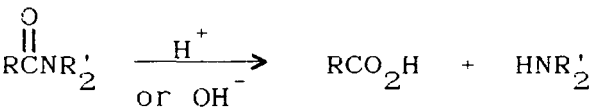
(105) (127) 48%

C AMIDES

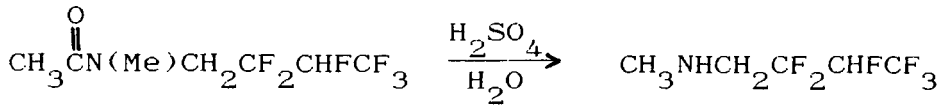
The presence of the reactive amide group in the adduct allows the synthesis of a range of primary, secondary, and tertiary amines by either hydrolysis or reduction. Many of these would not be available by simple addition reactions.

1 Synthesis of Amines by Hydrolysis

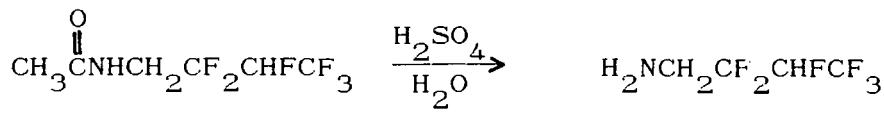
Amides can be hydrolysed by acid or base catalysis. However the presence of a hexafluoropropyl group may complicate the reaction by dehydrofluorination if base is



used. Thus the hexafluoropropene adducts of N-methylacetamide (46) and N,N-dimethylacetamide (36) were hydrolysed in 10% aqueous sulphuric acid to give 2,2,3,4,4,4-hexafluorobutylamine (129) and methyl-2,2,3,4,4,4-hexafluorobutylamine (128). This represents a very simple two step synthesis of primary and secondary fluorinated amines.



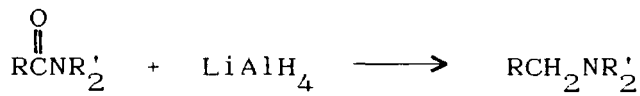
(36) (128) 26%



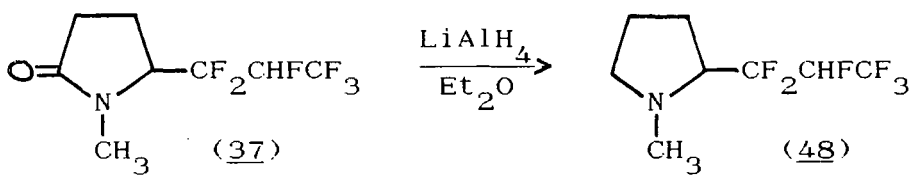
(46) (129) 26%

2 Synthesis of Amines by Reduction

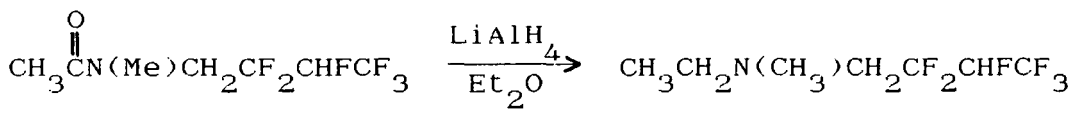
Reduction of amides using lithium aluminium hydride gives the corresponding amine. The reduction of the



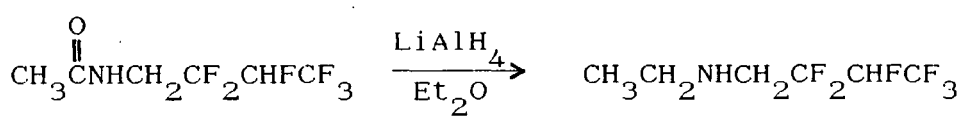
N-methylpyrrolidone adduct (37) gives the N-methyl-pyrrolidine derivative (48), the hexafluoropropyl group is unaffected. The reaction can be used to synthesise tertiary and secondary amines by reduction of acetamide adducts. The N-methylacetamide adduct (36) gives methylethyl-(1H,1H,3H-hexafluorobutyl)amine (130) and the N-methylacetamide adduct (46) gives ethyl-(1H,1H,3H-hexafluorobutyl)amine (131).



(37) (48) 55%



(36) (130) 26%



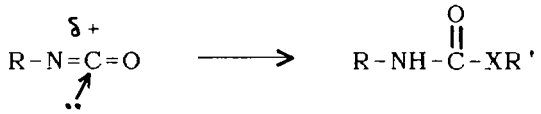
(46) (131) 47%

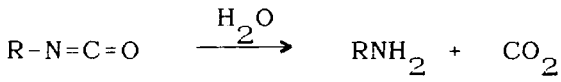
D ISOCYANATES

The isocyanate group is a very reactive group and can be used in further synthesis.

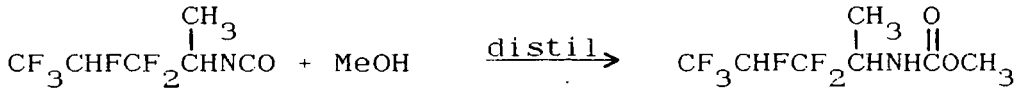
1 Addition Reactions

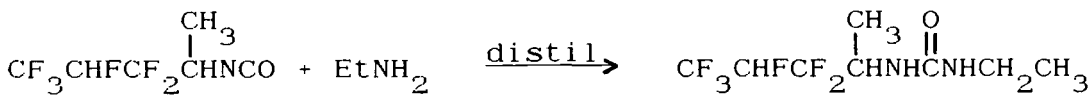
The isocyanate group is very susceptible to nucleophilic attack, undergoing addition to alcohols and amines. These type of reactions are very important in polyurethane manufacture.





In an addition the fluorinated group may be contained in either the isocyanate compound or the nucleophile. The adduct of ethylisocyanate and hexafluoropropene (77) reacts with methanol and ethylamine to give a good yield of urethane (132) and urea (133) derivatives respectively. The





electron withdrawing ability of the hexafluoropropyl group makes the carbon of the isocyanate group more electron

deficient and so nucleophilic attack will be more favourable. If the fluorinated group is in the alcohol or amine, their nucleophilicity will be reduced. The addition of

$$CF_3CHFCF_2CH_2OH + CH_3NCO \xrightarrow{\text{distil}} CF_3CHFCF_2CH_2O\overset{\overset{O}{\|}}{C}NHCH_3$$

(134) 43%

$$CF_3CHFCF_2CH_2NH_2 + CH_3NCO \xrightarrow{\text{distil}} CF_3CHFCF_2CH_2N\overset{\overset{O}{\|}}{C}NHCH_3$$

(128) (135) 68%

hexafluorobutanol and hexafluorobutylamine (128) to methylisocyanate, however, proceeds without problem to give the urethane (134) and the urea (135) derivatives respectively. The addition also occurs if fluorinated groups are incorperated in both the alcohol and the isocyanate to give the urethane (136).

$$CF_3CHFCF_2CH_2OH + OCN\overset{\overset{CH_3}{|}}{C}HCF_2CHFCF_3 \xrightarrow{\text{distil}}$$

(77)

$$CF_3CHFCF_2CH_2O\overset{\overset{O}{\|}}{C}NH\overset{\overset{CH_3}{|}}{C}HCF_2CHFCF_3$$

(136) 62%

2 Photolysis

The photolysis of isocyanates can give nitrenes via loss of carbon monoxide. Nitrenes can be used in many

$$R-\ddot{N}=C=O \xrightarrow{h\nu} R-\ddot{\underset{\cdot\cdot}{N}}: + CO$$

synthetic reactions by addition to double bonds and insertion into single bonds. The ultra violet spectra

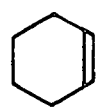
(table 43) shows that the addition of the hexafluoropropyl group has a large effect on the isocyanate group. The band

Table 43 UV Spectra of Isocyanates

Compound	Wavelength	Extinction Coefficient $M\,cm^{-1}$
CH_3CH_2NCO	261nm	7.8
	229nm	13.5
$CF_3CHFCF_2\overset{CH_3}{\underset{\vert}{C}}HNCO$	322nm	0.8
	226nm	24.9

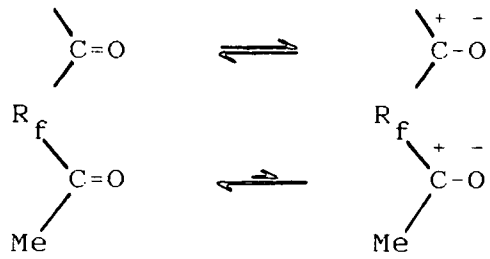
at 229nm becomes stronger, but the band at 261nm becomes very weak and is moved to a much longer wavelength. The absorbance at 254nm is much reduced. The photolysis of the adduct with cyclohexane and cyclohexene gives no reaction, thus the nitrene is not produced.

$CF_3CHFCF_2\overset{CH_3}{\underset{\vert}{C}}HNCO$ +  $\xrightarrow{254nm}$ No Reaction

$CF_3CHFCF_2\overset{CH_3}{\underset{\vert}{C}}HNCO$ +  $\xrightarrow{254nm}$ No Reaction

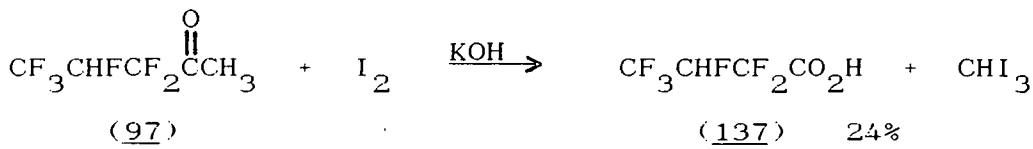
E METHYLKETONES

The carbonyl group is extremely versatile in organic synthesis and has been used for a large number of reactions. The presence of a fluoroalkyl group will effect the normal polarity of the group. The presence of an electron withdrawing group will oppose the normal polarity of the group, the carbon will therefore be more electron deficient.



1 Haloform Reaction

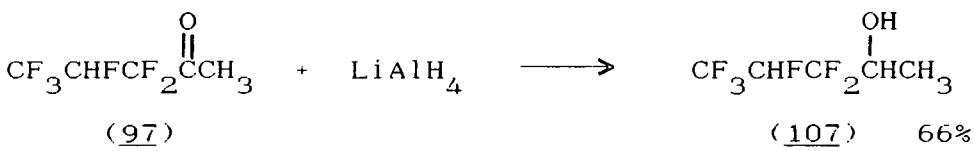
The methyl ketone (97) reacts at room temperature with iodine and base to give iodoform and the fluorinated acid (137). This represents a much easier route to this compound than the oxidation of 2,2,3,4,4,4-hexafluorobutanol[119].



(97) (137) 24%

2 Reduction

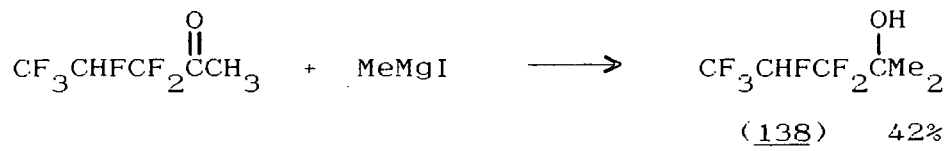
The methyl ketone reacts normally with lithium aluminium hydride to form the secondary alcohol (107). This product however can be made by direct addition of ethanol to hexafluoropropene (section IV.E.1).



(97) (107) 66%

3 Grignard Reagents

The methyl ketone reacts readily with methyl magnesium iodide to give the tertiary alcohol (138), which cannot be synthesised directly from isopropanol and hexafluoropropene. This reaction would allow the introduction of a large variety of groups into the fluorinated ketone, giving alcohols which may not be easily synthesised directly.

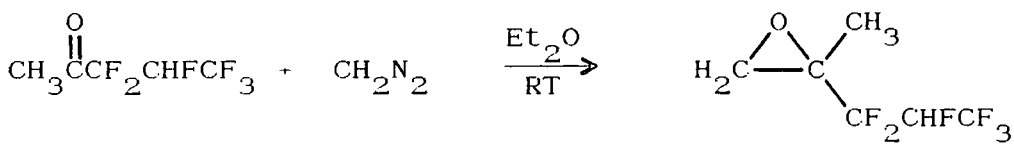


(138) 42%

4 Diazomethane

The reaction of diazomethane and methyl ketones may give either insertion of a methylene group, if the

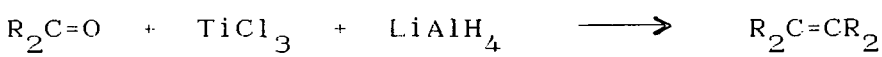
substituent can undergo a (1,2) shift, or give the epoxide. Neither the methyl nor the hexafluoropropyl group of the ketone (97) undergo a shift and so the epoxide (139) is produced.



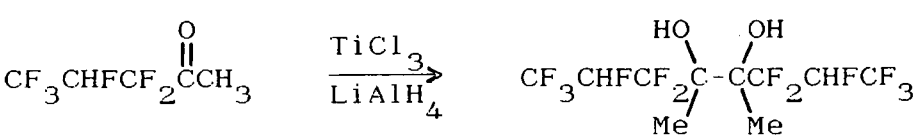
(139) 23%

5 McMurry Reaction

It has been shown by McMurry[120,121] that a ketone will react with reduced titanium species to give an alkene.



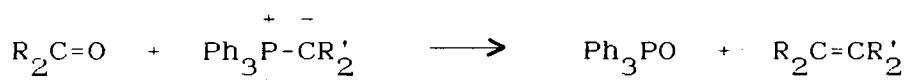
The reaction of the methyl ketone (97) with reduced titanium trichloride gave only the pinacol (140) in a small yield.



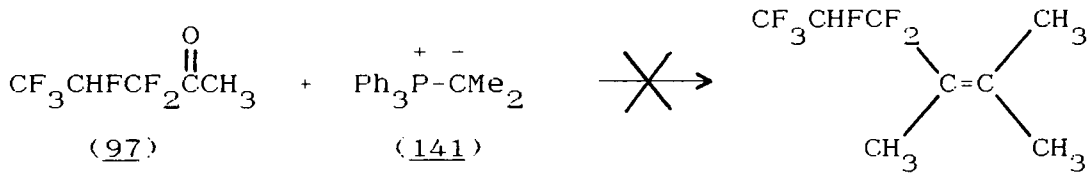
(140) 9%

6 Wittig Reaction

Double bonds can also be synthesised by the Wittig



reaction from ketones. When the ketone (97) was reacted with the phosphorous ylid (141) no reaction occurred.

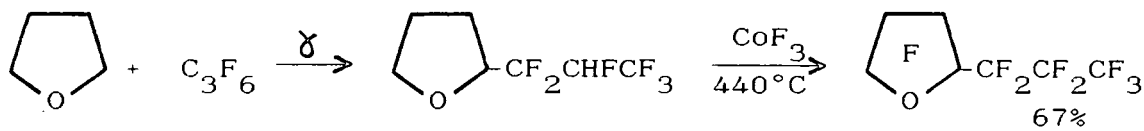


CHAPTER 7

INERT FLUIDS

A INTRODUCTION

Funding for the work in this thesis was originally given for the development of inert fluids. Previous work in this laboratory focussed on the use of cobalt trifluoride fluorination techniques to fully fluorinate the adducts of ethers and fluorinated alkenes[12]. Thus, for example, the adduct of tetrahydrofuran and hexafluoropropene can be converted to perfluoro-2-propyloxolane in high yield by



passing over cobalt trifluoride at 440°C. This method gives much better yields of fully fluorinated compounds with far less breakdown than electrochemical fluorination techniques. This chapter discusses the fluorination of a much wider range of free-radical adducts to give inert fluids.

B PERFLUORINATED AMINES

Industrially, perfluorinated tertiary amines are important in the electronics and other fields[122]. At present, the only commercial route to these compounds is via electrochemical fluorination[130], this method has been widely used and examples are given (table 44). The yields are often low and many products may be formed making purification difficult and expensive.

Table 44 Electrochemical Fluorination of Amines

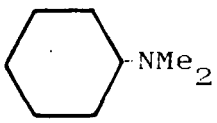
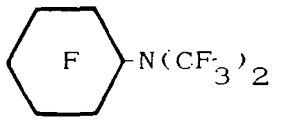
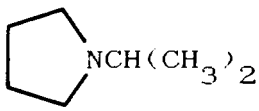
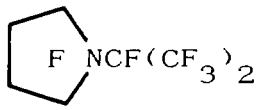
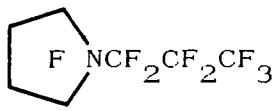
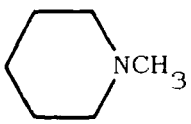
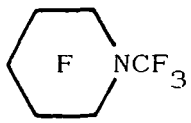
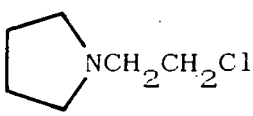
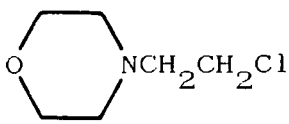
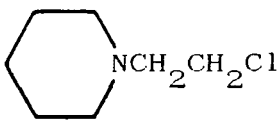
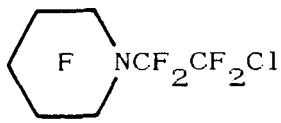
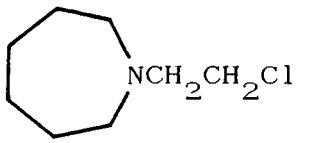
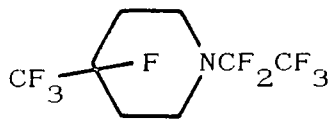
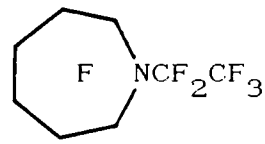
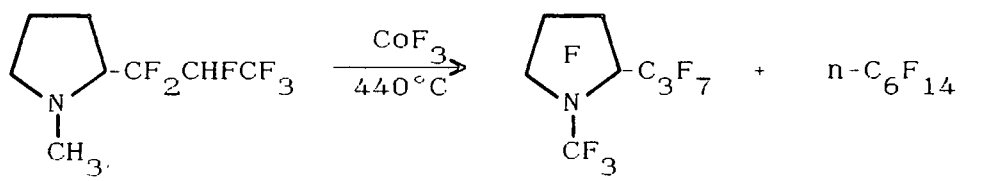
Starting Material	Products		Reference
Me_3N	$(CF_3)_3N$	11%	[123]
	$CHF_2N(CF_3)_2$	2%	
$EtNMe_2$	$CF_3CF_2N(CF_3)_2$	41%	[123]
	$(CF_3)_3N$	5%	
		23%	[124]
		27%	[125]
		9%	
		39%	[126]
$Et_2NCH_2CH_2Cl$	$(C_2F_5)_2NCF_2CF_2Cl$	12%	[127]
		19%	[127]
		5%	[127]
		5%	[128]
		31%	

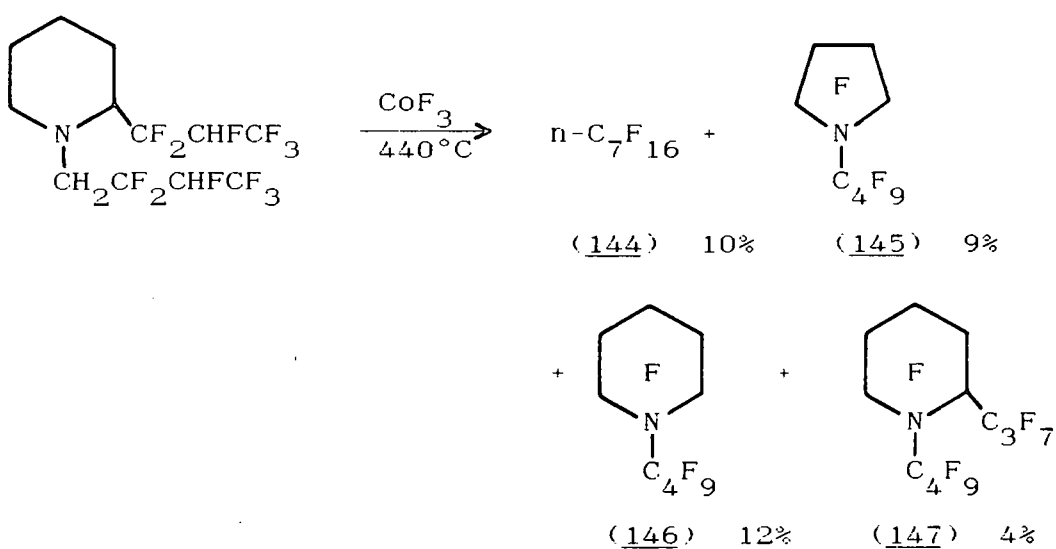
Table 44 continued...

Starting Material	Products		Reference
		28%	(129)
		21%	

The use of cobalt trifluoride was investigated, thus the fluorination of N-methyl-2-hexafluoropropylpyrrolidine (48) gives perfluoro-N-methyl-2-pyrrolidine (142) in good yield and some perfluorohexane (143). This reaction is therefore comparable to the cobalt trifluoride fluorination of ethers. With 2:1 and 3:1 adducts the yields and purities were not as good. With the 2:1 adduct of N-methylpiperidine

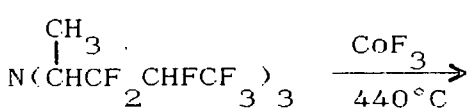


(48) (142) 60% (143) 30%



(144) 10% (145) 9%

(146) 12% (147) 4%



Many Products

and hexafluoropropene (49), reaction with cobalt trifluoride gives about fifty products although four major products were separated and identified. The 3:1 adduct of triethylamine and hexafluoropropene (53) however gives many unidentified products. This method is therefore only suitable for simple 1:1 adducts.

C PERFLUORINATED ALKANES AND ETHERS

The use of sulphur tetrafluoride has become widespread for the selective introduction of small numbers of fluorine atoms into molecules. In general the conditions used are mild and selectivity is very high. Sulphur tetrafluoride replaces oxygen atoms of a range of functional groups (table 45) with fluorine atoms and it s use has been reviewed elsewhere[12,131]. Alcohols and acids react readily with sulphur tetrafluoride whereas esters, anhydrides and ketones are often catalysed with hydrogen fluoride or lewis acids such as boron trifluoride. With starting materials which are easily hydrolysed some breakdown may occur, though this is minimised by using Lewis acid catalysts.

Table 45 General Reactions of SF_4

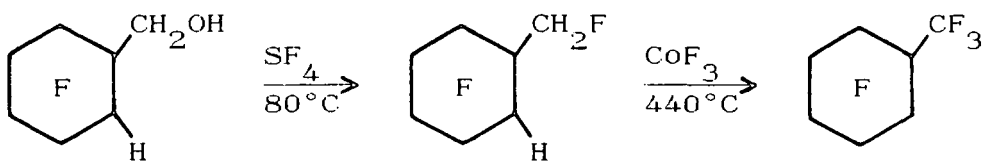
Starting Material	Products
ROH	RF
R_2CO	R_2CF_2
RCO_2H	RCOF (low temperature)
RCO_2H	RCF_3 (high temperature)
$(RCO)_2O$	$(RCF_2)_2O$
RCO_2R'	RCF_2OR'

1 Alcohols

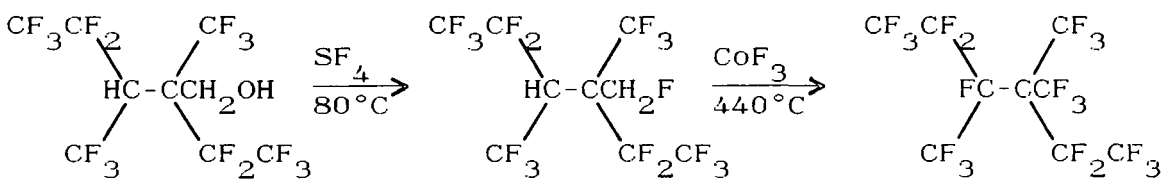
The adducts of alcohols cannot be directly fluorinated with cobalt trifluoride. However if the hydroxyl group is first fluorinated with sulphur tetrafluoride the product may

$$ROH \xrightarrow{SF_4} RF \xrightarrow{CoF_3} R_fF \qquad R_f = \text{perfluoroalkyl group}$$

then be converted to a fully fluorinated alkane. The alcohol adducts react with sulphur tetrafluoride at 80-100°C replacing the hydroxyl group in good yield. The fluoroalkanes are then fully fluorinated over cobalt trifluoride at 440°C. The yields are good except for the highly branched perfluoro-3,3,4-trimethylhexane (151).



(148) 67% (149) 59%



(150) 67% (151) 17%

$$H(CF_2CF_2)_5CH_2OH \xrightarrow[100°C]{SF_4} H(CF_2CF_2)_5CH_2F \xrightarrow[440°C]{CoF_3} n\text{-}C_{11}F_{24}$$

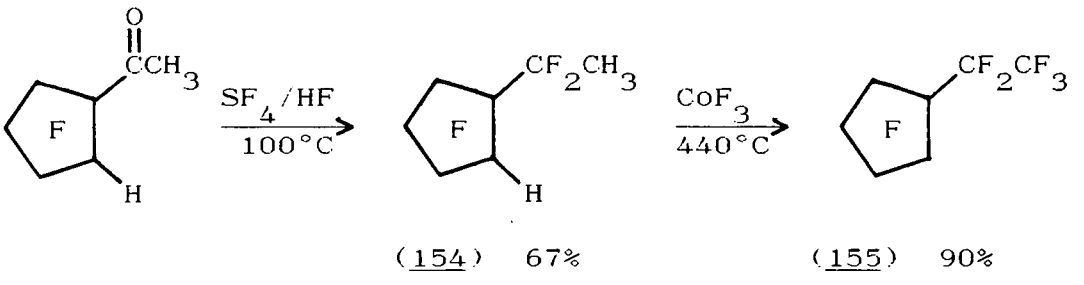
(152) 48% (153) 78%

2 Ketones

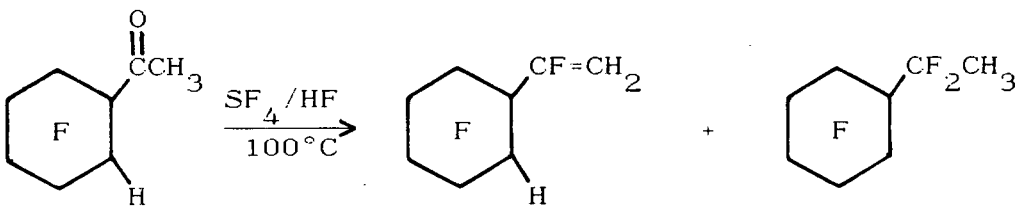
The free radical adducts of acetaldehyde can be reacted with sulphur tetrafluoride to replace the carbonyl

$$RCOCH_3 \xrightarrow[HF]{SF_4} RCF_2CH_3 \xrightarrow[440°C]{CoF_3} R_fCF_2CF_3$$

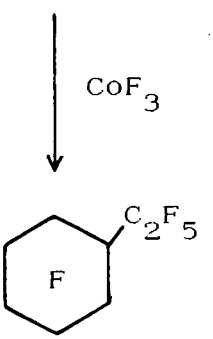
group with a CF_2 group. This compound can then be fully fluorinated using cobalt trifluoride. The ketones are less reactive than the alcohols and a hydrogen fluoride catalyst is required. The reaction proceeds in good yield except with the perfluoro-3,4-dimethylhexene adduct where no reaction

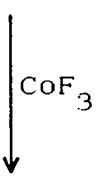


(154) 67% (155) 90%



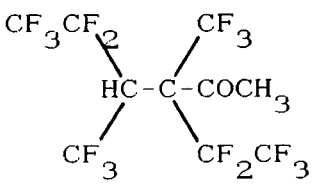
(156) 46% (157) 41%





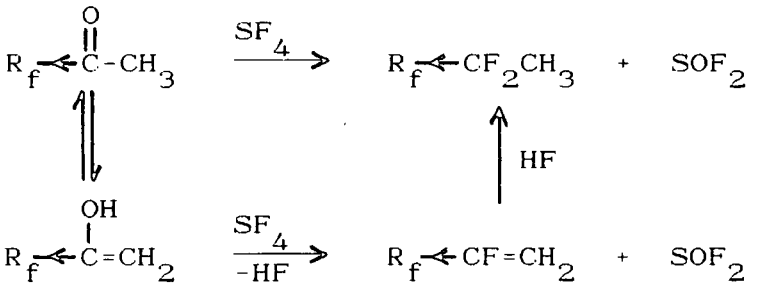
(158) 54%

(158) 35%



$\xrightarrow[100°C]{SF_4/HF}$ No Reaction

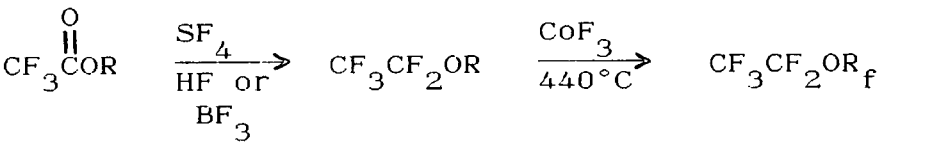
occurred. This is due to the steric hindrance of the very bulky fluoroalkyl group preventing attack by the sulphur tetrafluoride. The appearance of unsaturated products (156) are derived from reaction with the enol form of the ketone. The fluoroalkyl group will be highly electron withdrawing, this will tend to make the carbonyl carbon atom extremely electron deficient and thus destabilise the group. The enol



form will not be destabilised in this manner and so the equilibrium will favour the enol form[132]. The enol will react readily with sulphur tetrafluoride to replace the hydroxyl group. The hydrogen fluoride eliminated in this reaction may then add to the double bond under pressure giving the expected product.

3 Esters

Sulphur tetrafluoride reacts with esters to replace the carbonyl group by CF_2. A catalyst is required and hydrogen fluoride is usually used, however if the ester is prone to hydrolysis a lewis acid catalyst, such as boron trifluoride, is necessary. The adduct of methanol and hexa-



fluoropropene can be readily esterified with trifluoroacetic anhydride. When the ester (159) is reacted with sulphur tetrafluoride using a hydrogen fluoride catalyst only a

$$(CF_3CO)_2O + HOCH_2CF_2CHFCF_3 \longrightarrow CF_3\overset{O}{\overset{\|}{C}}CH_2CF_2CHFCF_3$$

(159)

$$CF_3\overset{O}{\overset{\|}{C}}OCH_2CF_2CHFCF_3 \xrightarrow[175°C]{SF_4/HF} CF_3CF_2OCH_2CF_2CHFCF_3 \text{ (160) } 36\%$$

(159)

$$+ FCH_2CF_2CHFCF_3 + \text{(159)}$$

(161) 41% 23%

moderate yield was obtained and accompanied with breakdown. When the reaction was repeated with a boron trifluoride catalyst, the yield of the required product (160) is increased and the breakdown reduced to a low level. The ether (160) was then fluorinated over cobalt trifluoride to give the fully fluorinated ether (162) in moderate yield.

$$CF_3\overset{O}{\overset{\|}{C}}OCH_2CF_2CHFCF_3 \xrightarrow[175°C]{SF_4/BF_3} \text{(160) } 45\% + \text{(161) } 5\% + \text{(159) } 50\%$$

$$CF_3CF_2OCH_2CF_2CHFCF_3 \xrightarrow[440°C]{CoF_3} CF_3CF_2OCF_2CF_2CF_2CF_3$$

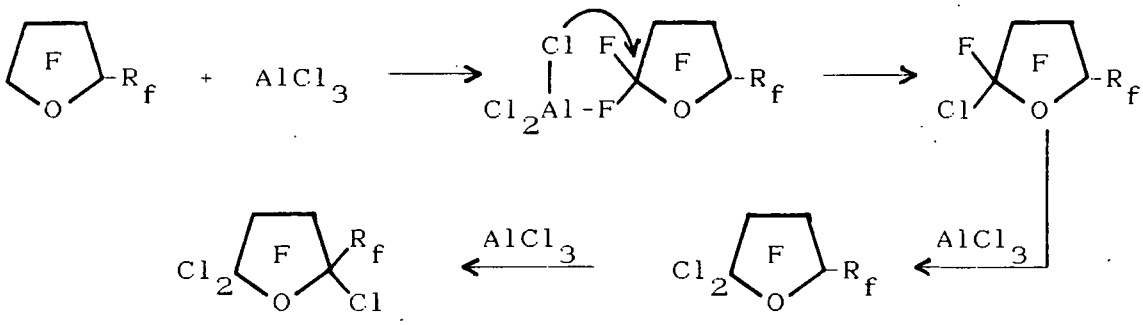
(160) (162) 34%

D REACTIONS OF FLUOROCARBON ETHERS

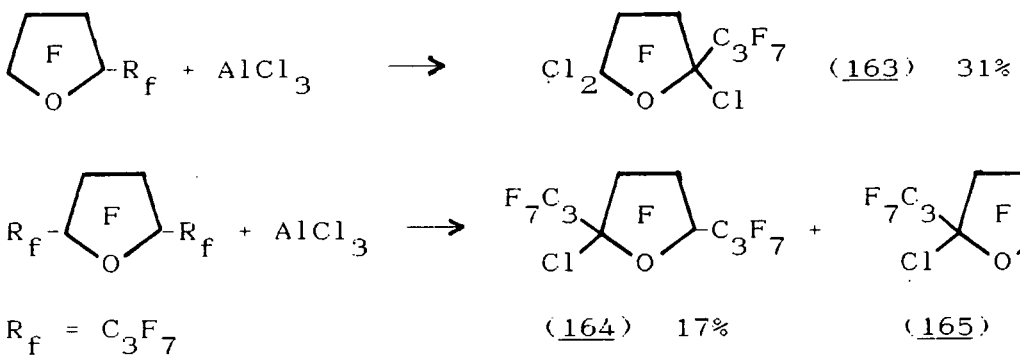
Fully fluorinated compounds are extremely inert and only react under very harsh conditions. The defluorination over iron and chlorination with aluminium trichloride are two reactions which can be achieved under reasonable conditions.

1 Reaction with Aluminium Trichloride

Fluorocarbon ethers are extremely resistant to chemical reagents, however halogen exchange can be achieved by reaction with strong lewis acids such as aluminium trichloride[133,134]. The reaction proceeds with the aluminium trichloride complexing with a fluorine atom and thus a slight positive charge develops on the carbon atom adjacent



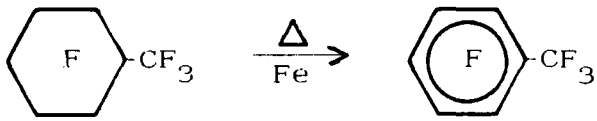
to oxygen in the intermediate. If the position is substituted with an electron withdrawing group then the charge will be destabilised and so reaction would be less favourable. Perfluoro-2-propyloxolane reacts with aluminium trichloride in a heterogeneous system to give a moderate yield of the trichloro compound (163). The reaction of the disubstituted perfluoro-2,5-dipropyloxolane gives mono (164) and dichloro (165) products, thus the first substitution reduces the reactivity.



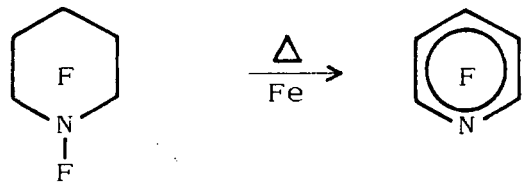
$R_f = C_3F_7$

2 Pyrolysis Over Iron

Fluorocarbon compounds can be defluorinated by passing over iron at high temperatures. The reaction can be used to produce fluorinated aromatics[135] and pyridines[136]. An

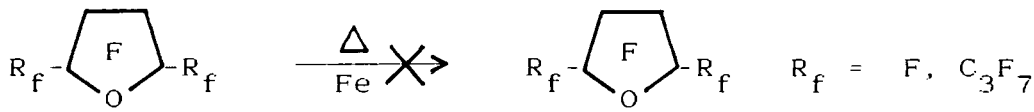


25% [135]



8% [136]

attempt to defluorinate oxolane derivatives to form fluorinated furans was made. The pyrolysis yielded only gaseous products at higher temperatures. The carbon-fluorine



bonds appear to be less susceptible to cleavage than the carbon-carbon bonds. The pyrolysis was therefore repeated with 2,5,5-trichloroperfluoro-2-propyloxolane (163) which contains the weaker carbon-chlorine bonds, however this compound broke down at a lower temperature (table 46). An acyclic fluorocarbon ether was also pyrolysed over iron. The recovery of starting material (table 47) decreased with increasing temperature, as with the cyclic ethers, but a small yield of perfluoro-2-pentene was also recovered.

Table 46 Pyrolysis of Oxolane Derivatives

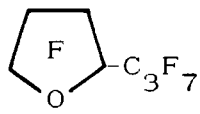
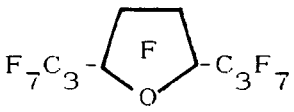
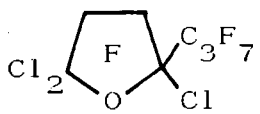
Oxolane	Temperature	Starting Material Recovered
	450°C	93%
	500°C	83%
	550°C	26%
	600°C	0%
	450°C	78%
	500°C	76%
	550°C	0%
	400°C	0%

Table 47 Pyrolysis of $(i\text{-}C_5F_{11})_2O$

$$(i\text{-}C_5F_{11})_2O \xrightarrow{\Delta} CF_3CF{=}CFCF_2CF_3 \quad (166)$$

Temperature	Recovery	(166)
500°C	85%	3%
550°C	40%	8%

EXPERIMENTAL

INSTRUMENTATION

Quantitative gas liquid chromatography (GLC) analysis was carried out on a Varian Aerograph Model 920 equipped with a gas density balance detector, using columns packed with Krytox fluid on chromosorb P (Column K) or 20% diisodecylphthalate on chomosorb P (Column A). Preparative scale GLC was carried out on a Varian Aerograph 920.

Fractional distillation of product mixtures was carried out using Fischer-Spaltrohr HMS500 and MS200, large and small concentric tube systems.

Melting points and boiling points were determined at atmospheric pressure, unless otherwise stated and are uncorrected. Boiling points were recorded by the Siwoloboff method or during fractional distillation.

Carbon, hydrogen, and nitrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analysis for halogens was performed by the literature method[137].

Ultra violet spectra were recorded using a Unicam SP8-100 spectrophotometer and using Spectrosol grade solvents.

Infra red spectra were recorded on a Perkin-Elmer 457 Grating Spectrophotometer using convensional techniques.

Proton and fluorine nuclear magnetic resonance spectra (NMR) were recorded on a Varian EL360M spectrometer operating at 60MHz and 56.46MHz respectively. Chemical shifts are quoted in p.p.m. relative to internal tetramethylsilane (TMS) and trichlorofluoromethane, upfield

shifts positive. Carbon NMR spectra were recorded on a Bruker WH-360 spectrometer operating at 90.6MHz and chemical shifts are quoted in p.p.m. relative to internal TMS in deuterochloroform solvent.

Mass spectra were recorded on a V.G. Micromass 12B spectrometer fitted with a Pye 104 gas chromatograph or on a VG7070E spectrometer.

CHAPTER 8

EXPERIMENTAL TO CHAPTER 2

A GENERAL PROCEDURE

1 Purification of Reagents

In general all chemicals were used as recieved from suppliers. N-Methylpyrrolidine was dried by distillation onto molecular sieve (4A). N-Ethylpyrrolidine, N-ethyl-piperidine, and N-ethylhexamethyleneimine were synthesised by the reaction of the cyclic amine with ethyliodide, then distilled after neutralisation with sodium carbonate. Perfluorocyclobutene and perfluorocyclopentene were prepared by technical staff.

2 Gamma Ray Initiation

The free radical additions were carried out using sealed pyrex Carius tubes (ca. 100ml). The liquid reagents were added to the tube and thoroughly degassed and then any gaseous reagents transferred into the tube using normal vacuum line techniques. The tube being sealed with the reagents frozen (liquid air) and under vacuum. The tube was irradiated with gamma rays in a purpose built ^{60}Co gamma ray facility to a total dose of ca. 16Mrad at a temperature of 18°C. The tube was opened while the contents were frozen (liquid air) and the gaseous compounds transferred under vacuum. Unless stated the remainder of the product is unreacted starting materials.

3 Tetrafluoroethene Additions

Additions to tetrafluoroethene were carried out at the ICI high pressure laboratories at Winnington, Cheshire. The amine and ditertiarybutylperoxide (DTBP, ca. 5% w/w) were placed in a steel autoclave (ca. 200ml) fitted with a mechanical stirrer. The autoclave was pressurised with tetrafluoroethene (10 bar) and then heated to 140°C. As reaction proceeded the pressure of tetrafluoroethene was maintained at 20 bar. When the reaction ceased the autoclave was cooled, excess tetrafluoroethene vented and the liquid contents removed. Unless stated the remainder of the product is unreacted starting material.

B ADDITION OF AMIDES TO FLUOROALKENES

In the addition of amides and amines to hexafluoropropene, difficulty has been found in obtaining satisfactory elemental analyses.

1 ADDITION OF TERTIARY AMIDES TO HEXAFLUOROPROPENE

(a) N,N-Dimethylacetamide

A mixture of N,N-dimethylacetamide (22.0g, 253mmol) and hexafluoropropene (26.3g, 175mmol) was irradiated with gamma rays. The product was distilled to give N-(1H,1H,3H-hexafluorobutyl)-N-methylacetamide (36), (29.4g, 71%), b.p. 93°C (5mmHg) (identified by comparison of spectra with those of an authentic sample[12]).

(b) N-Methyl-2-pyrrolidone

A mixture of N-methyl-2-pyrrolidone (11.6g, 117mmol) and hexafluoropropene (5.1g, 34mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (0.1g) and a liquid (15.8g). The liquid was distilled to give 5-(2H-hexafluoropropyl)-N-methyl-2-pyrrolidone (37), (6.6g, 78%), b.p. 59°C (0.03mmHg) (identified by comparison of spectra with those of an authentic sample[12]).

(c) N-Methyl-2-piperidone

A mixture of N-methyl-2-piperidone (10.0g, 88mmol) and hexafluoropropene (5.1g, 34mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (0.8g) and a liquid (13.5g). The liquid was distilled to give 6-(2H-hexafluoropropyl)-N-methyl-2-piperidone (38), (2.8g, 32%), b.p. 45°C (0.02mmHg); IR spectrum 1; NMR spectrum 1; mass spectrum 1, m/z 263 (M+, 4%), 262 (M-1, 27), 112 (M-151, 99).

(d) N-Methylcaprolactam

A mixture of N-methylcaprolactam (10.0g, 79mmol) and hexafluoropropene (5.1g, 34mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (2.1g) and a liquid (12.4g). The liquid was distilled to give 7-(2H-hexafluoropropyl)-N-methylcaprolactam (39), (2.4g, 55%), b.p. 73°C (0.005mmHg) (Found: C, 43.6; H, 4.5; N, 5.5; F, 41.7. $C_{10}H_{13}F_6NO$ requires C, 43.3; H, 4.7; N, 5.1; F, 41.2%); IR spectrum 2; NMR spectrum 2; mass spectrum 2, m/z 277 (M+, 6%).

(e) N-Acetylpyrrolidine

A mixture of N-acetylpyrrolidine (5.1g, 45mmol) and hexafluoropropene (2.5g, 17mmol) was irradiated with gamma rays. The product was distilled to give N-acetyl-2-(2H-hexafluoropropyl)pyrrolidine (40), (1.4g, 31%), b.p. 66°C (2mmHg); IR spectrum 3; NMR spectrum 3; mass spectrum 3, chemical ionisation, m/z 264 (M+1, 100%).

(f) N-Acetylpiperidine

A mixture of N-acetylpiperidine (5.2g, 41mmol) and hexafluoropropene (2.4g, 16mmol) was irradiated with gamma rays. The product was distilled to give N-acetyl-2-(2H-hexafluoropropyl)piperidine (41), (0.8g, 19%), b.p. 51°C (0.005mmHg) (identified by comparison of spectra with those of an authentic sample[12]).

(g) N,N-Dimethylformamide

A mixture of N,N-dimethylformamide (14.8g, 203mmol) and hexafluoropropene (15.5g, 104mmol) was irradiated with gamma rays to give a liquid (28.8g) composed of N-(1H,1H,3H-hexafluorobutyl)-N-methylformamide (42), (47% by GLC, column K, 150°C) and 3H-hexafluoro-N,N-dimethyl-butanamide (43), (22% by GLC) (identified by comparison of mass spectrum/GLC with those of authentic samples[12]).

(h) N-Formylpyrrolidine

A mixture of N-formylpyrrolidine (10.0g, 101mmol) and hexafluoropropene (5.0g, 33mmol) was irradiated with gamma rays. The product was distilled to give N-formyl-

2-(2H-hexafluoropropyl)pyrrolidine (44), (1.5g, 18%), b.p. 65°C (0.01 mmHg) (Found: C, 37.9; H, 3.8; N, 5.3; F, 46.2. $C_8H_9F_6NO$ requires C, 38.5; H, 3.6; N, 5.6; F, 45.8%); IR spectrum 4; NMR spectrum 4; mass spectrum 4, chemical ionisation, m/z 250 (M+1, 60%).

(i) N-Formylpiperidine

A mixture of N-formylpiperidine (10.0g, 88mmol) and hexafluoropropene (5.0g, 34mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (2.7g) and a liquid (11.7g). The liquid was distilled to give N-formyl-2-(2H-hexafluoropropyl)piperidine (45), (1.0g, 11%), b.p. 46°C (0.1mmHg) (Found: C, 39.3; H, 3.0; N, 5.5; F, 43.8. $C_9H_{11}F_6NO$ requires C, 41.1; H, 4.2; N, 5.3; F, 43.3%); IR spectrum 5; NMR spectrum 5; mass spectrum 5, chemical ionisation, m/z 264 (M+1, 99%).

C ADDITIONS OF SECONDARY AMIDES TO HEXAFLUOROPROPENE

1 N-Methylacetamide

A mixture of N-methylacetamide (24.0g, 329mmol) and hexafluoropropene (26.6g, 177mmol) was irradiated with gamma rays. The product mixture was poored into water (250ml) and the solid product filtered to give N-(1H,1H,3H-hexafluorobutyl)acetamide (46), (20.4g, 51%), m.p. 48°C (Found: C, 31.9; H, 2.8; N, 6.0; F, 51.0. $C_6H_7F_6NO$ requires C, 32.3; H, 3.1; N, 6.3; F, 51.1%); IR spectrum 6; NMR spectrum 6; mass spectrum 6.

2 2-Pyrrolidone

A mixture of 2-pyrrolidone (17.0g, 240mmol) and hexafluoropropene (11.1g, 74mmol) was irradiated with gamma rays. The product was transferred under vacuum to give alkene (5.1g) and a liquid (23.0g). The liquid was distilled to give 5-(2H-hexafluoropropyl)-2-pyrrolidone (47), (4.8g, 28%), b.p. 96°C (0.01mmHg) (Found: C, 36.0; H, 3.3; N, 6.4; F, 47.5. $C_7H_7F_6NO$ requires C, 35.7; H, 3.0; N, 6.0; F, 48.5%); IR spectrum 7; NMR spectrum 7; mass spectrum 7, chemical ionisation, m/z 236 (M+1, 97%).

D ADDITIONS OF AMINES TO HEXAFLUOROPROPENE

1 N-Methylpyrrolidine

A mixture of N-methylpyrrolidine (10.1g, 119mmol) and hexafluoropropene (8.5g, 56mmol) was irradiated with gamma rays. The product mixture was transferred under vacuum to give a gas (0.4g) and a liquid (15.1g). The liquid was distilled to give 2-(2H-hexafluoropropyl)-N-methylpyrrolidine (48), (6.2g, 47%), b.p. 149-150°C (Found: C, 40.9; H, 4.6; N, 6.3; F, 48.6. $C_8H_{11}F_6N$ requires C, 40.9; H, 4.7; N, 6.0; F, 48.5%); IR spectrum 8; NMR spectrum 8; mass spectrum 8.

2 N-Methylpiperidine

A mixture of N-methylpiperidine (9.9g, 117mmol) and hexafluoropropene (5.4g, 36mmol) was irradiated with gamma rays. The product mixture was transferred under vacuum to give a gas (0.13g) and a liquid (15.5g). The liquid was shown to contain N-(1H,1H,3H-hexafluorobutyl)piperidine,

(4%), 2-(2H-hexafluoropropyl)-N-methylpiperidine, (4%), and N-(1H,1H,3H-hexafluorobutyl)-2-(2H-hexafluoropropyl)-piperidine (49), (15%) (identified by comparison of GLC/mass spectra of authentic samples[12]).

3 Triethylamine

A mixture of triethylamine (14.8g, 147mmol) and hexafluoropropene (7.6g, 51mmol) was irradiated with gamma rays. The product was distilled to give ethylidine-3,3,4,5,5,5-hexafluoro-2-pentylimine (51), (2.1g, 19%), b.p. 132°C; IR spectrum 9; NMR spectrum 9; mass spectrum 9, chemical ionisation, m/z 222 (M+1, 100%): ethylbis-(3,3,4,5,5,5-hexafluoro-2-pentyl)amine (52), (13.7g, 67%), b.p. 216°C (Found: C, 36.3; H, 4.1; N, 3.5; F, 56.7. $C_{12}H_{15}F_{12}N$ requires C, 35.9; H, 3.7; N, 3.5; F, 56.9%); IR spectrum 10; NMR spectrum 10; mass spectrum 10, chemical ionisation, m/z 402 (M+1, 100%): tris-(3,3,4,5,5,5-hexafluoro-2-pentyl)amine (53), (3.9g, 14%), b.p. 92°C (2mmHg); IR spectrum 11; NMR spectrum 11; mass spectrum 11, m/z 550 (M-1, 1%), 400 (M-151, 79%).

4 N-Ethylpyrrolidine

A mixture of N-ethylpyrrolidine (5.6g, 56mmol) and hexafluoropropene (3.1g, 21mmol) was irradiated with gamma rays. The product liquid (8.3g) was distilled to give N-ethyl-2-(2H-hexafluoropropyl)pyrrolidine (54), (3.9g, 75%), b.p. 77°C (50mmHg); IR spectrum 12; NMR spectrum 12; mass spectrum 12, chemical ionisation, m/z 250, (M+1, 47%): N-(3,3,4,5,5,5-hexafluoro-2-pentyl)-2-(2H-hexafluoropropyl)-

pyrrolidine (55), (1.8g, 21%), b.p. 61°C (1mmHg); IR spectrum 13; NMR spectrum 13; mass spectrum 13, chemical ionisation, m/z 400 (M+1, 73%).

5 N-Ethylpiperidine

A mixture of N-ethylpiperidine (5.5g, 48mmol) and hexafluoropropene (3.7g, 25mmol) was irradiated with gamma rays. The product was distilled to give N-(3,3,4,5,5,5-hexafluoro-2-pentyl)piperidine (56), (1.2g, 19%), b.p. 50°C (2mmHg) (Found: C, 45.2; H, 6.1; N, 5.4; F, 44.0. $C_{10}H_{15}F_6N$ requires C, 45.6; H, 5.7; N, 5.3; F, 43.4%); IR spectrum 14; NMR spectrum 14; mass spectrum 14, chemical ionisation, m/z 264 (M+1, 27%): N-(3,3,4,5,5,5-hexafluoro-2-pentyl)-2-(2H-hexafluoropropyl)piperidine (57), (7.8g, 76%), b.p. 66°C (0.5mmHg); IR spectrum 15; NMR spectrum 15; mass spectrum 15, chemical ionisation, m/z 414 (M+1, 30%).

6 N-Ethylhexamethyleneimine

A mixture of N-ethylhexamethyleneimine (10.3g, 81mmol) and hexafluoropropene (4.9g, 33mmol) was irradiated with gamma rays. The liquid product (14.8g) was distilled to give N-ethyl-2-(2H-hexafluoropropyl)hexamethyleneimine (58), (4.2g, 46%), b.p. 63°C (5mmHg); IR spectrum 16; NMR spectrum 16; mass spectrum 16, chemical ionisation, m/z 278 (M+1, 61%): N-(3,3,4,5,5,5-hexafluoro-2-pentyl)-2-(2H-hexafluoro-propyl)hexamethyleneimine (59), (7.3g, 52%), b.p. 62°C (0.02mmHg); IR spectrum 17; NMR spectrum 17; mass spectrum 17, chemical ionisation, m/z 428 (M+1, 9%).

E ADDITIONS OF AMINES TO TETRAFLUOROETHENE

1 Triethylamine

A mixture of triethylamine (15.5g, 153mmol) and di-tertiarybutylperoxide (0.5g) were reacted with tetrafluoroethene at 140°C. The product mixture was distilled to give diethyl(3,3,4,4-tetrafluoro-2-butyl)amine (66), (12.3g, 40%), b.p. 89°C (100mmHg); IR spectrum 18; NMR spectrum 18; mass spectrum 18, chemical ionisation, m/z 202 (M+1, 26%): ethylbis-(3,3,4,4-hexafluoro-2-butyl)amine (67), (19.3g, 67%), b.p. 93°C (10mmHg) (Found: C, 40.1; H, 5.3; N, 4.9; F, 50.8. $C_{10}H_{15}F_8N$ requires C, 39.9; H, 5.0; N, 4.7; F, 50.5%); IR spectrum 19; NMR spectrum 19; mass spectrum 19, chemical ionisation, m/z 302 (M+1, 25%): tris-(3,3,4,4-hexafluoro-2-butyl)amine (68), (9.2g, 15%), b.p. 85°C (2mmHg) (Found: C, 35.7; H, 3.5; N, 3.6; F, 57.4. $C_{12}H_{15}F_{12}N$ requires C, 35.9; H, 3.7; N, 3.5; F, 56.9%); IR spectrum 20; NMR spectrum 20; mass spectrum 20, chemical ionisation, m/z 402 (M+1, 8%).

2 N-Methylpyrrolidine

A mixture of N-methylpyrrolidine (16.0g, 188mmol) and ditertiarybutylperoxide (0.5g) was reacted with tetrafluoroethene at 140°C. The product liquid (28.1g) was distilled to give N-methyl-2-(2H-tetrafluoroethyl)pyrrolidine (69), (31.3g, 90%), b.p. 82°C (100mmHg); IR spectrum 21; NMR spectrum 21; mass spectrum 21, chemical ionisation, m/z 186 (M+1, 100%): N-(3,3,4,4-hexafluoro-2-butyl)-2-(2H-tetrafluoroethyl)pyrrolidine (70), (3.0g, 8%), b.p. 85°C (10mmHg); IR spectrum 22; NMR spectrum 22; mass spectrum 22, chemical ionisation, m/z 286 (M+1, 47%).

3 N-Methylpiperidine

A mixture of N-methylpiperidine (16.5g, 167mmol) and ditertiarybutylperoxide (0.5g) was reacted with tetrafluoroethene at 140°C. The product liquid (37.8g) was distilled to give N-methyl-2-(2H-tetrafluoroethyl)piperidine (71), (14.6g, 44%), b.p. 166°C (Found: C, 48.7; H, 6.6; N, 7.1; F, 38.5. $C_8H_{13}F_4N$ requires C, 48.2; H, 6.5; N, 7.0; F, 38.2%); IR spectrum 23; NMR spectrum 23; mass spectrum 23, chemical ionisation, m/z 200 (M+1, 64%): N-(3,3,4,4-hexafluoro-2-butyl)-2-(2H-hexafluoroethyl)piperidine (72), (21.0g, 42%), b.p. 97°C (10mmHg); IR spectrum 24; NMR spectrum 24; mass spectrum 24, chemical ionisation, m/z 300 (M+1, 97%): N-(3,3,4,4-tetrafluoro-2-butyl)-2,6-bis-(2H-tetrafluoroethyl)piperidine (73), (4.0g, 6%); IR spectrum 25; NMR spectrum 25; mass spectrum 25, chemical ionisation, m/z 400 (M+1, 67%).

F ADDITIONS OF N-METHYLPYRROLIDINE TO CYCLIC FLUOROALKENES

1 Addition to perfluorocyclobutene

A mixture of N-methylpyrrolidine (0.4g, 4.7mmol) and perfluorocyclobutene (0.4g, 2.3mmol) was irradiated with gamma rays. The product consisted of a tar and was not investigated further.

2 Addition to perfluorocyclopentene

A mixture of N-methylpyrrolidine (0.3g, 3.8mmol) and perfluorocyclopentene (0.5g, 2.3mmol) was irradiated with gamma rays. The product consisted of a tar and was not investigated further.

3 Addition to perfluorocyclohexene

A mixture of N-methylpyrrolidine (4.7g, 56mmol) and perfluorocyclohexene (5.0g, 19mmol) was irradiated with gamma rays. The product liquid (9.5g) was washed with water (2x10ml) and distilled to give 2-(2H-perfluorocyclohexyl)-N-methylpyrrolidine (74), (3.8g, 57%), b.p. 94°C (20mmHg) (Found: C, 37.8; H, 2.8; N, 4.3; F, 55.3. $C_{11}H_{11}F_{10}N$ requires C, 38.0; H, 3.2; N, 4.0; F, 54.8%); IR spectrum 26; NMR spectrum 26; mass spectrum 26, chemical ionisation, m/z 348 (M+1, 71%).

G ADDITIONS OF N-METHYLPYRROLIDINE TO CHLOROFLUOROALKENES

1 Addition to Chlorotrifluoroethene

A mixture of N-methylpyrrolidine (5.15g, 61mmol) and chlorotrifluoroethene (2.7g, 23mmol) was irradiated with gamma rays. The product liquid (7.1g) was distilled to give N-methyl-2-(2H-2-chlorotrifluoroethyl)pyrrolidine (75), (1.7g, 37%), b.p. 95°C (50mmHg); IR spectrum 27; NMR spectrum 27; mass spectrum 27, chemical ionisation, m/z 202 (M+1, 54%), 204 (M+3, 18).

2 Addition to 1,1-dichlorodifluoroethene

A mixture of N-methylpyrrolidine (5.0g, 59mmol) and 1,1-dichlorodifluoroethene (2.8g, 21mmol) was irradiated with gamma rays. The product liquid (4.4g) was transferred under vacuum to leave an unidentified solid (2.5g). The liquid was distilled to give N-methyl-2-(2H-2,2-dichlorodifluoroethyl)pyrrolidine (76), (2.5g, 55%), b.p. 95° (10mmHg) (Found: C, 37.8; H, 5.4; N, 6.0; Cl, 32.2; F, 17.5.

$C_7H_{11}Cl_2F_2N$ requires C, 38.5; H, 5.1; N, 6.4; Cl, 32.6; F, 17.4%); IR spectrum 28; NMR spectrum 28; mass spectrum 28, chemical ionisation, m/z 218 (M+1, 46%), 220 (M+3, 27).

H ADDITION TO DOUBLE BONDED NITROGEN SUBSTRATES

1 Addition of Ethylisocyanate to Hexafluoropropene

A mixture of ethylisocyanate (5.1g, 72mmol) and hexafluoropropene (3.4g, 22mmol) was irradiated with gamma rays. The products were transferred under vacuum to give a gas (2.4g) and a liquid (5.2g). The liquid was distilled to give 3,3,4,5,5,5-hexafluoro-2-pentylisocyanate (77), (1.2g, 25%), b.p. 128-129°C; IR spectrum 29; NMR spectrum 29; mass spectrum 29, chemical ionisation, m/z 222 (M+1, 51%).

2 Attempted Addition of Ethylisothiocyanate

A mixture of ethylisothiocyanate (11.8g, 135mmol) and hexafluoropropene (6.8g, 46mmol) was irradiated with gamma rays. The product mixture was transferred under vacuum to give unreacted hexafluoropropene (5.6g) and a liquid (11.8g) which contained only starting materials.

3 Attempted Addition of Cyclohexylcarbodiimine

A mixture of cyclohexylcarbodiimine (5.0g, 24mmol) and hexafluoropropene (1.5g, 10mmol) was irradiated with gamma rays. The product mixture was transferred under vacuum to give unreacted hexafluoropropene (1.1g) and a liquid which contained only starting materials.

CHAPTER 9

EXPERIMENTAL TO CHAPTER 3

A GENERAL PROCEDURE

1 Purification of Reagents

All chemicals were used as received from suppliers.

2 Acetone/t-Butanol Ratios

A mixture of the substrate and ditertiarybutylperoxide (DTBP, ca. 0.1g, 10%(mol)) was placed in a Carius tube (ca. 25ml) and thoroughly degassed. The tube was sealed with the contents frozen (liquid air) and under vacuum, then heated at 140°C for 24hrs. The tube was opened while the contents were frozen (liquid air) and after warming to room temperature, analysed by GLC (column A, 100°C) for acetone and t-butanol.

3 Gamma Ray Initiation

Reactions with gamma ray initiation were carried out using the method of chapter 8.

4 Ditertiarybutylperoxide Initiation

Reactions with peroxide initiation were carried out using the method of chapter 8.

B ADDITIONS OF SILANES TO HEXAFLUOROPROPENE

1 Acetone/t-Butanol Ratios

(a) Tetramethylsilane

A mixture of tetramethylsilane (0.61g, 6.9mmol) and DTBP (0.10g, 0.68mmol) was heated at 140°C. The product mixture was analysed and the acetone/t-butanol ratio shown to be 0.92.

(b) Hexamethyldisiloxane

A mixture of hexamethyldisiloxane (1.12g, 6.9mmol) and DTBP (0.10g, 0.68mmol) was heated at 140°C. The product mixture was analysed and the acetone/t-butanol ratio shown to be 0.03.

(c) Octamethylcyclotetrasiloxane

A mixture of octamethylcyclotetrasiloxane (2.11g, 7.1mmol) and DTBP (0.11g, 0.75mmol) was heated at 140°C. The product mixture was analysed and the acetone/t-butanol ratio shown to be 1.73.

(d) Diethoxydimethylsilane

A mixture of diethoxydimethylsilane (1.01g, 6.8mmol) and DTBP (0.13g, 0.89mmol) was heated at 140°C. The product mixture was analysed and the acetone/t-butanol ratio shown to be 0.24.

2 Silanes and Siloxanes

(a) Tetramethylsilane

i/ Gamma Ray Initiation

A mixture of tetramethylsilane (1.7g, 19mmol) and hexafluoropropene (1.5g, 10mmol) was irradiated with gamma rays. The product was distilled to give 1H,1H,3H-hexafluorobutyltrimethylsilane (78), (0.3g, 7%), b.p. 116°C (Found: C, 35.6; H, 5.2; F, 47.4. $C_7H_{12}F_6Si$ requires C, 35.3; H, 5.0; F, 47.9%); IR spectrum 30; NMR spectrum 30; mass spectrum 30.

ii/ Peroxide Initiation

A mixture of tetramethylsilane (1.7g, 19mmol), hexafluoropropene (1.5g, 10mmol) and DTBP (0.12g) was heated at 140°C for 24hrs. The liquid obtained was distilled to give 1H,1H,3H-hexafluorobutyltrimethylsilane (78), (0.6g, 27%) and bis-(1H,1H,3H-hexafluorobutyl)dimethylsilane (79), (0.1g, 3%), b.p. 130°C (100mmHg); IR spectrum 31; NMR spectrum 31; mass spectrum 31.

(b) Hexamethyldisiloxane

i/ Gamma Ray Initiation

A mixture of hexamethyldisiloxane (6.6g, 41mmol) and hexafluoropropene (2.6g, 17mmol) was irradiated with gamma rays. The liquid obtained (7.4g) was distilled to give 1H,1H,3H-hexafluorobutylpentamethyldisiloxane (80), (0.5g, 9%), b.p. 97°C (100mmHg) (Found: C, 34.9; H, 6.2; F, 36.4. $C_9H_{18}F_6OSi_2$ requires C, 34.6; H, 5.8; F, 36.5%); IR spectrum

32; NMR spectrum 32; mass spectrum 32, chemical ionisation, m/z 313 (M+1, 4%).

ii/ Peroxide Initiation

A mixture of hexamethyldisiloxane (3.1g, 19mmol), hexafluoropropene (1.7g, 11mmol) and DTBP (0.12g) was heated at 140°C for 24hrs. The liquid was examined by gas chromatography (column K, 150°C), showing it to contain 1:1 adduct (80), (76%) and a partially resolved mixture of 2:1 adducts (24%).

(c) Octamethylcyclotetrasiloxane

i/ Gamma Ray Initiation

A mixture of octamethylcyclotetrasiloxane (40.1g, 135mmol) and hexafluoropropene (17.2g, 114mmol) was irradiated with gamma rays. Unreacted hexafluoropropene (11.4g) was removed under vacuum (50mmHg) and the liquid obtained analysed by GLC (column K, 150°C) showing it to contain 1:1 adduct (81), (11%).

ii/ Peroxide Initiation

The liquid product obtained in i/ was mixed with octamethylcyclotetrasiloxane (10.1g, 34mmol), hexafluoropropene (12.7g, 85mmol), and DTBP (0.97g), then heated at 140°C for 24hrs. The liquid obtained was distilled to give 1H,1H,3H-hexafluorobutylheptamethylcyclotetrasiloxane (81), (28.8g, 76%), b.p. 102°C (10mmHg) (Found: C, 29.5; H, 5.6; F, 26.0. $C_{11}H_{24}F_6O_4Si_4$ requires C, 29.6; H, 5.4; F, 25.6%); IR spectrum 33; NMR spectrum 33; mass spectrum 33, chemical

ionisation, m/z 447 (M+1, 3%) and bis-(1H,1H,3H-hexafluorobutyl)hexamethylcyclotetrasiloxane (82), (12.2g, 24%), b.p. 94°C (1mmHg) (Found: C, 27.6; H, 4.0; F, 38.7. $C_{14}H_{24}F_{12}O_4Si_4$ requires C, 28.2; H, 4.0; F, 38.3%); IR spectrum 34; NMR spectrum 34; mass spectrum 34, chemical ionisation, m/z 597 (M+1, 1%).

(d) Dimethylpolysiloxane (Silicone Oil)

A mixture of silicone oil (9.1g) and hexafluoropropene (7.9g, 52mmol) was irradiated with gamma rays to a dose of 80Mrad. Unreacted hexafluoropropene (4.0g) was removed under vacuum (0.1mmHg) to give a liquid (83), (11.9g), (Found: F, 21.3. $(C_2H_6OSi)_{5.2}C_3F_6$ requires F, 21.3%); IR spectrum 35, ^{19}F NMR spectrum 35.

3 Alkoxy- and Alkylaminosilanes

(a) Methoxytrimethylsilane

A mixture of methoxytrimethylsilane (5.1g, 49mmol) and hexafluoropropene (3.4g, 23mmol) was irradiated with gamma rays. Unreacted hexafluoropropene (0.04g) was removed under vacuum (100mmHg) and the liquid obtained distilled to give 1H,1H,3H-hexafluorobutoxytrimethylsilane, (3.6g, 62%) (identified by comparison of spectra with those of an authentic sample[11]).

(b) Diethoxydimethylsilane

A mixture of diethoxydimethylsilane (10.0g, 68mmol) and hexafluoropropene (5.8g, 39mmol) was irradiated with gamma rays. The liquid obtained was distilled to give

ethoxy(3,3,4,5,5,5-hexafluoro-2-pentyloxy)dimethylsilane (84), (3.5g, 30%), b.p. 78°C (50mmHg); IR spectrum 36; NMR spectrum 36; mass spectrum 35, chemical ionisation, m/z 299 (M+1, 44%) and bis-(3,3,4,5,5,5-hexafluoro-2-propyloxy)-dimethylsilane (85), (12.1g, 69%), b.p. 93°C (10mmHg); IR spectrum 37; NMR spectrum 37; mass spectrum 36, chemical ionisation, m/z 449 (M+1, 6%).

(c) Bisdimethylaminodimethylsilane

A mixture of bisdimethylaminodimethylsilane (5.4g, 37mmol) and hexafluoropropene (3.0g, 20mmol) was irradiated with gamma rays. The liquid obtained was distilled to give (1H,1H,3H-hexafluorobutylmethylamino)dimethylaminodimethyl-silane (86), (5.2g, 87%), b.p. 93°C (50mmHg); IR spectrum 38; NMR spectrum 38; mass spectrum 37, chemical ionisation, m/z 297 (M+1, 55%).

C REACTIONS OF SILANES

1 Pyrolysis of 1H,1H,3H-Hexafluorobutyltrimethylsilane

1H,1H,3H-hexafluorobutyltrimethylsilane (78) (ca. 0.5g) was placed in an NMR tube which was then sealed. No change in the NMR spectrum was observed after heating at 100°C for 24hrs. Heating at 200°C for 24hrs gave 1H,3H-pentafluoro-1-trimethylsilylbutene (87); IR spectrum 39, 1670cm^{-1} (C=C); NMR spectrum 39.

2 1H,1H,3H-Hexafluorobutyltrimethylsilane and Tetrabutylammonium Fluoride (TBAF)

To a mixture of 1H,1H,3H-hexafluorobutyltrimethylsilane (78) (5.0g, 21mmol), iodine (8.0g, 31mmol) and ether (10ml) was added a solution of TBAF (1.2M, 20ml) in tetrahydrofuran. The mixture was refluxed for 1hr, gaseous products being trapped at liquid air temperature in a stream of nitrogen. The contents of the trap were transferred under vacuum to give 1,1,1,2,3-pentafluoro-3-butene (88), (0.9g, 30%); IR spectrum 40, 1770cm^{-1} (C=C).

D ATTEMPTED ADDITION OF STANNANES TO HEXAFLUOROPROPENE

A mixture of tetramethyltin (2.2g, 18mmol) and hexafluoropropene (1.3g, 9mmol) was irradiated with gamma rays. Unreacted hexafluoropropene (0.5g) was removed under vacuum (100mmHg) and the solid obtained (0.1g) sublimed (0.1mmHg) to give an unidentified mixture.

CHAPTER 10

EXPERIMENTAL TO CHAPTER 4

A GENERAL PROCEDURE

1 Purification of Reagents

All chemicals were used as received from suppliers, except perfluorocyclobutene and perfluorocyclopentene which were prepared by technical staff.

2 Gamma Ray Initiation

Reactions with gamma ray initiation were carried out using the method of chapter 8.

3 Ditertiarybutylperoxide Initiation

Reactions with peroxide initiation were carried out using the method of chapter 8.

B ADDITIONS OF HEXAFLUOROPROPENE TO OXYGEN

1 Diisopropylether

(a) Gamma Ray Initiation

A mixture of diisopropylether (10.1g, 99mmol) and hexafluoropropene (4.6g, 30mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (3.4g) and a liquid (10.5g) which contained acetone (2%), diisopropylether (94%), and 1,1,1,2,3,3-hexafluoro-4-methylpentane (89), (4%) (identified by comparison of mass spectrum/GLC with those obtained in (b)).

(b) Peroxide Initiation

A mixture of diisopropylether (5.0g, 49mmol), DTBP (0.2g), and hexafluoropropene (2.9g, 19mmol) was heated at 140°C for 24hrs. The products were transferred under vacuum to give alkene (1.6g) and a liquid (5.5g). The liquid mixture was separated by preparative scale GLC to give acetone (0.3g, 10%) and 1,1,1,2,3,3-hexafluoro-4-methyl-pentane (89), (0.7g, 7%), (Found: C, 36.8; H, 4.5. $C_6H_8F_6O$ requires C, 37.1; H, 4.1%); IR spectrum 41; NMR spectrum 40; mass spectrum 38.

2 Allylethylether

(a) Gamma Ray Initiation

A mixture of allylethylether (5.2g, 61mmol) and hexafluoropropene (2.9g, 19mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (1.8g) and a liquid containing only starting materials.

(a) Peroxide Initiation

A mixture of allylethylether (2.1g, 24mmol), DTBP (0.11g), and hexafluoropropene (1.9g, 13mmol) was heated at 140°C for 24hrs. The products were transferred under vacuum to give alkene (1.3g) and a liquid containing only starting materials.

3 Tetrahydrofuran to Pentafluoropropenyloxolane (90)

(a) Gamma Ray Initiation

A mixture of tetrahydrofuran (5.3g, 73mmol) and pentafluoropropenyloxolane (90), (5.0g, 25mmol) was irradiated

with gamma rays. The liquid product contained 1,2-bis-tetrahydrofuryl-1H-pentafluoropropane (91), (6%) (identified by comparison of mass spectrum/GLC with those obtained in (b)).

(b) Peroxide Initiation

A mixture of tetrahydrofuran (2.0g, 28mmol), DTBP (0.11g), and pentafluoropropenyloxolane (90), (2.0g, 10mmol) was heated at 140°C for 24hrs. The liquid product (4.0g) was distilled to give 1,2-bistetrahydrofuryl-1H-pentafluoro-propane (91), (0.16g, 6%), b.p. 132°C (0.5mmHg) (Found: C, 48.2; H, 6.0; F, 34.2. $C_{11}H_{15}F_5O_2$ requires C, 48.2; H, 5.5; F, 34.7%); IR spectrum 42; NMR spectrum 41; mass spectrum 39, chemical ionisation, m/z 275 (M+1, 45%).

4 Attempted Cyclisation of 1-Methoxy-2,3,4,4,4-pentafluoro-2-butene (92)

(a) Gamma Ray Initiation

1-Methoxy-2,3,4,4,4-pentafluoro-2-butene (92), (2.0g, 11mmol) was irradiated with gamma rays. The liquid product was shown to contain only starting material by GLC (column k, 100°C).

(b) Peroxide Initiation

A mixture of 1-methoxy-2,3,4,4,4-pentafluoro-2-butene (92), (2.0g, 11mmol) and DTBP (0.1g) was heated at 140°C for 24hrs. The liquid product was shown to contain only starting material by GLC (column k, 100°C).

5 γ-Butyrolactone

(a) Gamma Ray Initiation

A mixture of γ-butyrolactone (10.0g, 116mmol) and hexafluoropropene (6.6g, 44mmol) was irradiated with gamma rays. Unreacted alkene (5.0g) was removed under vacuum (0.1mmHg), the liquid product (11.5g) poored into water (50ml) and the lower organic layer separated and purified by molecular distillation (0.1mmHg) to give 5-(2H-hexafluoropropyl)butyrolactone (94), (0.7g, 7%) (identified by ^{13}C NMR, see text).

(b) Peroxide Initiation

A mixture of γ-butyrolactone (6.1g, 71mmol), hexafluoropropene (3.9g, 26mmol) and DTBP (0.5g) was heated at 140°C for 24hrs. Unreacted alkene (2.7g) was removed under vacuum (0.1mmHg), the liquid product (7.1g) poored into water (50ml) and the lower organic layer separated and purified by molecular distillation to give 5-(2H-hexafluoropropyl)butyrolactone (94), (0.7g, 12%).

6 Reduction of 5-(2H-hexafluoropropyl)butyrolactone (94)

A solution of 5-(2H-hexafluoropropyl)butyrolactone (94), (1.5g, 6mmol) in diethylether (10ml) was added dropwise to a mixture of aluminium lithium hydride (1.0g, 27mmol) and diethylether (10ml) and then refluxed for 30min. To this was added water (5ml) and sulphuric acid (50ml, 20%) and then continuously extracted with ether (50ml) to give 1,1,1,2,3,3-heptane-4,7-diol (110), (0.1g, 8%) (identified by comparison of spectra with those of an authentic sample).

7 δ-Valerolactone

A mixture of δ-valerolactone (7.0g, 70mmol), hexafluoropropene (5.6g, 37mmol) and DTBP (0.5g) was heated at 140°C for 24hrs. Unreacted alkene (2.2g) was removed under vacuum (0.1mmHg) and the solid product (8.9g) recrystalised from ethanol to give valerolactone dimer (95), (0.5g, 6%), m.p. 50-51°C; IR spectrum 43; NMR spectrum 42; mass spectrum 40.

8 ε-Caprolactone

A mixture of ε-caprolactone (8.0g, 70mmol), hexafluoropropene (3.9g, 26mmol) and DTBP (0.5g) was heated at 140°C for 24hrs. Unreacted alkene (4.0g) was removed under vacuum (0.1mmHg) and the solid product (8.4g) recrystalised from ethanol to give caprolactone dimer (96), (2.5g, 31%), m.p. 44-45°C; IR spectrum 44; NMR spectrum 43; mass spectrum 41.

C ADDITION OF CARBONYL COMPOUNDS TO HEXAFLUOROPROPENE

1 Aldehydes

(a) Acetaldehyde

A mixture of acetaldehyde (9.8g, 222mmol) and hexafluoropropene (11.1g, 74mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (0.6g) and a liquid (19.7g). The liquid was distilled to give 1,1,1,2,3,3-hexafluoro-4-pentanone (97), (8.8g, 61%), b.p. 76-77°C (Found: C, 30.7; H, 2.4; F, 58.5. $C_5H_4F_6O$ requires C, 30.9; H, 2.1; F, 58.8%); IR spectrum 45; NMR spectrum 44; mass spectrum 42.

(b) Chloral

i/ Gamma Ray Initiation

A mixture of chloral (6.7g, 45mmol) and hexafluoropropene (2.5g, 17mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (2.6g) and a liquid (3.0g) which contained only starting materials.

ii/ Peroxide Initiation

A mixture of chloral (3.1g, 21mmol), hexafluoropropene (0.9g, 6mmol), and DTBP (0.14g) was heated at 140°C for 24hrs. The products were transferred under vacuum to give alkene (0.9g) and a liquid (2.0g) which contained only starting materials.

(c) Crotonaldehyde

i/ Gamma Ray Initiation

A mixture of crotonaldehyde (8.7g, 125mmol) and hexafluoropropene (6.4g, 43mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (7.2g) and a liquid (5.9g) which contained only starting materials.

ii/ Peroxide Initiation

A mixture of crotonaldehyde (1.4g, 20mmol), hexafluoropropene (1.1g, 7mmol), and DTBP (0.10g) was heated at 140°C for 24hrs. The products were transferred under vacuum to give alkene (1.2g) and a liquid (1.2g) which contained only starting materials.

(d) Benzaldehyde

i/ Gamma Ray Initiation

A mixture of benzaldehyde (8.7g, 82mmol) and hexafluoropropene (5.1g, 34mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (5.1g) and a liquid (6.0g) which contained only starting materials.

ii/ Peroxide Initiation

A mixture of benzaldehyde (2.0g, 19mmol), hexafluoropropene (1.0g, 7mmol), and DTBP (0.11g) was heated at 140°C for 24hrs. The products were transferred under vacuum to give alkene (1.2g) and a liquid (0.8g) which contained only starting materials.

(e) p-Methoxybenzaldehyde

i/ Gamma Ray Initiation

A mixture of p-methoxybenzaldehyde (15.9g, 117mmol) and hexafluoropropene (5.8g, 39mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (5.6g) and a liquid (15.6g) which contained only starting materials.

ii/ Peroxide Initiation

A mixture of p-methoxybenzaldehyde (2.2g, 16mmol), hexafluoropropene (0.8g, 5mmol), and DTBP (0.10g) was heated at 140°C for 24hrs. The products were transferred under vacuum to give alkene (0.7g) and a liquid (1.8g) which contained only starting materials.

2 Ketones

(a) Acetone

i/ Gamma Ray Initiation

A mixture of acetone (6.0g, 103mmol) and hexafluoropropene (5.5g, 37mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (4.8g) and a liquid (5.7g) which contained only starting materials.

ii/ Peroxide Initiation

A mixture of acetone (1.8g, 31mmol), hexafluoropropene (1.8g, 12mmol), and DTBP (0.11g) was heated at 140°C for 24hrs. The products were transferred under vacuum to give alkene (1.4g) and a liquid which contained only starting materials.

(b) Cyclopentanone

i/ Gamma Ray Initiation

A mixture of cyclopentanone (5.0g, 60mmol) and hexafluoropropene (3.8g, 25mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (3.4g) and a liquid (4.4g) which contained only starting materials.

ii/ Peroxide Initiation

A mixture of cyclopentanone (2.6g, 31mmol), hexafluoropropene (2.0g, 14mmol), and DTBP (0.10g) was heated at 140°C for 24hrs. The products were transferred under vacuum to give alkene (1.8g) and a liquid which contained only starting materials.

(c) Cyclohexanone

i/ Gamma Ray Initiation

A mixture of cyclohexanone (10.1g, 103mmol) and hexafluoropropene (4.4g, 30mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (3.4g) and a liquid (10.3g) which was distilled to give an unidentified liquid (0.69g), b.p. 87°C (1mmHg).

ii/ Peroxide Initiation

A mixture of cyclohexanone (3.0g, 31mmol), hexafluoropropene (2.4g, 16mmol), and DTBP (0.11g) was heated at 140°C for 24hrs. The products were transferred under vacuum to give alkene (2.2g) and a liquid (3.2g) which was distilled to give an unidentified liquid (0.20g), b.p. 87°C (1mmHg).

(d) Acetylacetone

A mixture of acetylacetone (6.6g, 66mmol) and hexafluoropropene (4.4g, 29mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (4.2g) and a liquid (6.4g) which contained only starting materials.

(e) Acetonitrile

A mixture of acetonitrile (5.3g, 128mmol) and hexafluoropropene (5.9g, 39mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (4.8g) and a liquid (5.4g) which contained only starting materials.

D COMPARISON OF ADDITIONS TO CHLORINATED AND FLUORINATED ALKENES

1 Additions to 1,1-Dichlorodifluoroethene

(a) Tetrahydrofuran

A mixture of tetrahydrofuran (5.1g, 70mmol) and 1,1-dichlorodifluoroethene (3.4g, 26mmol) was irradiated with gamma rays. The product liquid (7.7g) was distilled to give 2-(2,2-dichlorodifluoroethyl)oxolane (99), (1.9g, 36%), b.p. 88°C (20mmHg) (Found: C, 35.5; H, 4.2; Cl, 34.5; F, 17.5. $C_6H_8Cl_2F_2$ requires C, 35.1; H, 3.9; Cl, 34.6; F, 18.5%); IR spectrum 50; NMR spectrum 49; mass spectrum 47, chemical ionisation, m/z 205 (M+1, 62%), 207 (M+3, 38), 209 (M+5, 6).

(b) Tetrahydropyran

A mixture of tetrahydropyran (5.1g, 59mmol) and 1,1-dichlorodifluoroethene (4.1g, 31mmol) was irradiated with gamma rays. The product liquid (7.9g) was shown to contain only starting material by GLC (column K, 140°C).

2 Additions to Tetrachloroethene

(a) Tetrahydrofuran

A mixture of tetrahydrofuran (7.1g, 98mmol) and tetrachloroethene (5.4g, 33mmol) was irradiated with gamma rays. The product liquid was distilled to give 2-(2H-tetrachloroethyl)oxolane (101), (3.7g, 48%); IR spectrum 46; NMR spectrum 45; mass spectrum 43, m/z 71 ($M-CCl_2CHCl_2$, 100%).

(b) Diethylether

A mixture of diethylether (7.1g, 95mmol) and tetrachloroethene (5.1g, 31mmol) was irradiated with gamma rays. The product liquid was distilled to give 1,1,2-trichloro-3-ethoxybutene (102), (1.5g, 20%); IR spectrum 47; NMR spectrum 46; mass spectrum 44, m/z 202 (M+, 4%), 204 (M+2, 4).

(c) Acetaldehyde

A mixture of acetaldehyde (1.3g, 30mmol), tetrachloroethene (1.7g, 10mmol) and DTBP (0.16g) was heated at 140°C for 24hrs. The product liquid was distilled to give 1,1,2-trichlorobuten-3-one (103), (0.05g, 3%); IR spectrum 48; NMR spectrum 47; mass spectrum 45, m/z 172 (M+, 38%), 174 (M+2, 37), 176 (M+4, 12).

(d) Methanol

A mixture of methanol (1.3g, 42mmol), tetrachloroethene (2.1g, 13mmol) and DTBP (0.13g) was heated at 140°C for 24hrs. The product liquid was distilled to give 1,1,2-trichloro-3-hydroxypropene (104), (1.2g, 56%); IR spectrum 49; NMR spectrum 48; mass spectrum 46, m/z 160 (M+, 18%), 162 (M+2, 17), 164 (M+4, 6).

3 Additions to 2,3-Dichlorohexafluorobut-2-ene

(a) Dimethylether

A mixture of dimethylether (13.4g, 290mmol) and 2,3-dichlorohexafluorobut-2-ene (14.5g, 62mmol) was irradiated with gamma rays. The products were transferred

under vacuum to give dimethylether (10.5g) and a liquid (16.6g). The liquid was distilled to give 2,3-dichloro-4,4,4-trifluoro-1-methoxy-2-trifluoromethylbutane (105), (10.2g, 59%), b.p. 82-83°C (100mmHg); IR spectrum 51; NMR spectrum 50; mass spectrum 48, m/z 277 (M-1, 8%): bis-(2,3-dichloro-4,4,4-trifluoro-2-trifluoromethylbutyl)-ether (106), (3.0g, 10%), b.p. 62-65°C (0.7mmHg); IR spectrum 52; NMR spectrum 51; mass spectrum 49, m/z 247 (27%), 249 (17).

E ADDITIONS OF ALCOHOLS

1 Additions of Ethanol

(a) Hexafluoropropene

A mixture of ethanol (6.6g, 143mmol) and hexafluoropropene (7.9g, 53mmol) was irradiated with gamma rays. The product liquid was distilled to give 3,3,4,5,5,5-hexafluoro-2-pentanol (107), (5.8g, 56%), b.p. 116-117°C; IR spectrum 53; NMR spectrum 52; mass spectrum 50, chemical ionisation, m/z 197 (M+1, 50%).

(b) Perfluorocyclopentene

A mixture of ethanol (6.2g, 134mmol) and perfluorocyclopentene (9.9g, 47mmol) was irradiated with gamma rays. The product liquid was distilled to give 1-(2H-octafluorocyclopentyl)ethanol (108), (7.0g, 58%), b.p. 153°C (Found: C, 32.7; H, 2.5; F, 59.5. $C_7H_6F_8O$ requires C, 32.6; H, 2.3; F, 58.9%); IR spectrum 54; NMR spectrum 53; mass spectrum 51, chemical ionisation, m/z 259 (M+1, 28%).

(c) Perfluorocyclohexene

A mixture of ethanol (7.9g, 172mmol) and perfluorocyclohexene (15.1g, 58mmol) was irradiated with gamma rays. The product liquid was distilled to give 1-(2H-decafluorocyclohexyl)ethanol (109), (14.0g, 79%) b.p. 76-78°C (25mmHg) (Found: C, 31.5; H, 1.9; F, 61.1. $C_8H_6F_{10}O$ requires C, 31.2; H, 2.0; F, 61.7%); IR spectrum 55; NMR spectrum 54; mass spectrum 52.

2 Addition of Butane-1,4-diol

A mixture of butane-1,4-diol (10.1g, 112mmol) and hexafluoropropene (7.8g, 52mmol) was irradiated with gamma rays. The products were transferred under vacuum to give alkene (6.0g) and a liquid. The liquid was distilled to give 1,1,1,2,3,3-hexafluoroheptane-4,7-diol (110), (0.8g, 7%), b.p. 109°C (6mmHg); IR spectrum 56; NMR spectrum 55; mass spectrum 53, chemical ionisation, m/z 241 (M+1, 7%).

CHAPTER 11

EXPERIMENTAL TO CHAPTER 5

A GENERAL PROCEDURE

1 Purification of Reagents

All chemicals were used as received from suppliers.

2 Acetone/t-Butanol Ratios

Acetone/t-butanol ratios were measured using the method of chapter 9.

3 Uninitiated Additions

Uninitiated additions were carried out in sealed pyrex Carius tubes (ca. 100ml) or sealed NMR tubes (5mm). The liquid and solid reagents were added to the tube, thoroughly degassed and then any gaseous reagents transferred into the tube using normal vacuum line techniques. The tube being sealed with the reagents frozen (liquid air) and under vacuum. The tube was then kept in the dark at 20°C for 72hrs. The tube was opened with the contents frozen (liquid air) and the gaseous products transferred under vacuum after warming to room temperature. Unless stated the remainder of the product is unreacted starting materials.

B Substitution Effects

1 Aldehydes

Acetone/t-butanol ratios were measured using the general procedure.

Substrate			DTBP		Acetone/
	/g	/mmol	/g	/mmol	t-butanol
CH_3CHO	0.32	7.2	0.10	0.68	0.13
CCl_3CHO	1.23	8.3	0.12	0.82	2.12
$CH_3CH=CHCHO$	0.51	7.3	0.11	0.75	0.15
PhCHO	0.89	8.4	0.12	0.82	0.11
p-MeO-C_6H_4CHO	1.03	7.6	0.11	0.75	0.08
$CH_2=CHCH_2OEt$	0.60	7.0	0.09	0.62	0.09

2 Nitrogen Compounds

(a) Comparison of α-Amino and α-Oxy Radicals

i/ Acetone/t-Butanol Ratios

Acetone/t-butanol ratios were measured using the general procedure.

Substrate			DTBP		Acetone/
	/g	/mmol	/g	/mmol	t-butanol
N-Methylpyrrolidine	0.61	7.2	0.10	0.68	0.01
N-Methylpiperidine	0.71	7.2	0.10	0.68	0.01
Triethylamine	0.74	7.3	0.11	0.75	0.01

ii/ Competition Between N-Methylpyrrolidine and Tetrahydrofuran

N-Methylpyrrolidine (2.0g, 24mmol) and tetrahydrofuran (2.0g, 28mmol) were placed in a Carius tube (ca. 25ml) and thoroughly degassed. To this was added under vacuum hexafluoropropene (1.9g, 13mmol). The tube was sealed frozen and under vacuum, then irradiated with gamma rays to a dose of 16Mrad. The tube was opened and the liquid product mixture

analysed by GLC (column K, 100°C) and shown to contain N-methyl-2-(2H-hexafluoropropyl)pyrrolidine (48) and starting materials only.

(b) Amides

Acetone/t-butanol ratios were measured using the general procedure.

Substrate			DTBP		Acetone/
	/g	/mmol	/g	/mmol	t-butanol
N,N-Dimethylacetamide	0.62	7.1	0.11	0.75	0.42
N-Methylpyrrolidone	0.60	6.1	0.10	0.68	0.21
N-Methylpiperidone	0.72	6.4	0.11	0.75	0.25
N-Methylcaprolactam	0.83	6.5	0.12	0.82	0.27
N-Acetylpiperidine	0.89	7.0	0.11	0.75	0.35
N-Formylpyrrolidine	0.72	7.3	0.11	0.75	0.34
N-Formylpiperidine	0.83	7.3	0.10	0.68	0.34
2-Pyrrolidone	0.65	7.6	0.11	0.75	1.24
γ-Butyrolactone	0.60	7.0	0.11	0.75	2.37
ϵ-Caprolactone	0.78	6.8	0.10	0.68	0.81

(c) Double Bonded Nitrogen Substrates

Acetone/t-butanol ratios were measured using the general procedure.

Substrate			DTBP		Acetone/
	/g	/mmol	/g	/mmol	t-butanol
EtNCO	0.60	8.5	0.09	0.62	0.10
EtNCS	0.61	7.0	0.10	0.68	0.36

C Uninitiated Reactions

1 Additions to Hexafluoropropene

(a) Tetrahydrofuran

A mixture of tetrahydrofuran (5.1g, 71mmol) and hexafluoropropene (3.2g, 22mmol) was kept in the dark at room temperature for 72hrs. The products were transferred under vacuum to give alkene (0.9g) and a liquid (6.8g). The liquid was distilled to give 2-(2H-hexafluoropropyl)oxolane (3.2g, 66%), b.p. 138°C (identified by comparison of spectra with those of an authentic sample[12]).

(b) N-Methylpyrrolidine

A mixture of N-methylpyrrolidine (9.9g, 117mmol) and hexafluoropropene (5.4g, 36mmol) was kept in the dark at room temperature for 72hrs. The products were transferred under vacuum to give alkene (0.1g) and a liquid (14.4g). The liquid was distilled to give N-methyl-2-(2H-hexafluoropropyl)pyrrolidine (48), (6.6g, 78%), b.p. 87°C (10mmHg) (identified by comparison of spectra with those of an authentic sample)

(c) Other Substrates

Other substrates were reacted using the general procedure. The product liquids were analysed by GLC (column K, 100-140°C), showing them to contain only starting materials.

Substrate			Hexafluoropropene	
	/g	/mmol	/g	/mmol
Tetrahydropyran	2.2	23	2.2	15
Diethylether	5.0	68	3.6	24
N-Methylpiperidine	9.8	99	5.3	36
Triethylamine	4.7	46	2.5	16

2 Other Alkenes

(a) Chlorotrifluoroethene

The substrates were reacted with chlorotrifluoroethene in a sealed NMR tube using the general procedure. The products were analysed by ^{19}F NMR showing only the presence of starting materials. The reactions were repeated at 50°C, 100°C, and 140°C with no change in the NMR spectrum.

Substrate			Hexafluoropropene	
	/g	/mmol	/g	/mmol
Tetrahydrofuran	0.35	4.9	0.58	5.0
Tetrahydropyran	0.53	6.2	0.88	7.6
N-Methylpyrrolidine	0.42	4.9	0.62	5.3
N-Methylpiperidine	0.48	4.8	0.58	5.0

(b) 1,1-Dichlorodifluoroethene

The substrates were reacted using the same procedure as used for the chlorotrifluoroethene reactions.

Substrate			Hexafluoropropene	
	/g	/mmol	/g	/mmol
Tetrahydrofuran	0.51	7.1	0.55	4.1
Tetrahydropyran	0.55	6.4	0.46	3.5
N-Methylpyrrolidine	0.39	4.6	0.60	4.5
N-Methylpiperidine	0.54	5.5	0.40	3.0

CHAPTER 12

EXPERIMENTAL TO CHAPTER 6

A SYNTHESIS OF ALKENES

1 Dehydrofluorination of Hexafluoropropene Adducts

(a) Ethers

i/ Tetrahydrofuran Adduct in Dyglyme

A mixture of 2-(2H-hexafluoropropyl)oxolane (20g, 90mmol), potassium hydroxide (15g, 268mmol), and diglyme (50ml) was heated at 115°C for 8hrs. The mixture was distilled (110°C-140°C) and the product washed with water (20ml), the lower organic layer separated and distilled to give 2-(pentafluoropropenyl)oxolane (90), (6.6g, 36%), b.p. 128-135°C (identified by comparison of spectra with those obtained in ii/).

ii/ Tetrahydrofuran Adduct with Solid Potassium Hydroxide

2-(2H-hexafluoropropyl)oxolane (50g, 226mmol) was refluxed over powdered potassium hydroxide (50g, 896mmol) for 2hrs. The product was distilled to give 2-(pentafluoropropenyl)oxolane (90), (34g, 75%), b.p. 136°C (Found: C, 41.9; H, 3.8; F, 47.5. $C_7H_7F_5O$ requires C, 41.6; H, 3.5; F, 47.0%); IR spectrum 57; NMR spectrum 56; mass spectrum 54.

iii/ Diethylether Adduct

1,1,1,2,3,3-hexafluoro-4-ethoxypentane (7.2g, 32mmol) was refluxed over powdered potassium hydroxide (7.2g, 127mmol) for 2hrs. The product was distilled to give

1,1,1,2,3-pentafluoro-4-ethoxy-2-pentene (119), (3.1g, 47%), b.p. 104°C (Found: C, 41.5; H, 4.8; F, 46.2. $C_7H_9F_5O$ requires C, 41.2; H, 4.4; F, 46.6%); IR spectrum 58; NMR spectrum 57; mass spectrum 55.

iv/ Dimethylether Adduct

1,1,1,2,3,3-hexafluoro-4-methoxybutane (26.8g, 137 mmol) was refluxed over powdered potassium hydroxide (25.0g, 380mmol) for 3hrs. The product was distilled to give 1,1,1,2,3-pentafluoro-4-methoxy-2-butene (92), (5.7g, 24%), b.p. 76°C (Found: C, 34.4; H, 2.6; F, 54.5. $C_5H_5F_5O$ requires C, 34.1; H, 2.8; F, 54.0%); IR spectrum 59; NMR spectrum 58; mass spectrum 56, chemical ionisation, m/z 177 (M+1, 9%).

(b) N-Methylpyrrolidine Adduct (48)

N-Methyl-2-(2H-hexafluoropropyl)pyrrolidine (48), (3.8g, 16mmol) was refluxed over powdered potassium hydroxide (4.1g, 62mmol) for 2hrs. The product was distilled to give N-methyl-2-(pentafluoropropenyl)pyrrolidine (120), (2.3g, 67%), b.p. 135°C; IR spectrum 60; NMR spectrum 59; mass spectrum 57, chemical ionisation, m/z 216 (M+1, 68%).

2 Chloroalkene Adducts

(a) Dehydrochlorination

i/ 2-(2H-tetrachloroethyl)oxolane (101)

A solution of potassium hydroxide (1.6g, 28mmol) in ethanol was added dropwise to a solution of 2-(2H-tetrachloroethyl)oxolane (101), (5.4g, 23mmol) and then kept at 20°C for 30min. The mixture was washed with water (15ml),

the organic layer separated, dried ($MgSO_4$) and distilled to give 2-(trichloroethenyl)oxolane (121), (1.3g, 28%), b.p. 71°C (10mmHg) (Found: C, 35.6; H, 3.4; Cl, 53.3. $C_7H_7Cl_3O$ requires C, 35.7; H, 3.5; Cl, 52.9%); IR spectrum 61; NMR spectrum 60; mass spectrum 58.

ii/ 2,3-Dichloro-4,4,4-trifluoro-1-methoxy-2-trifluoromethylbutane (105)

A mixture of the adduct (105), (5.5g, 20mmol), potassium hydroxide (2.5g, 45mmol) and methylated spirit (25ml) was refluxed for 2.5hrs. The mixture was filtered, the filtrate washed with water (50ml) and the organic layer separated, dried ($MgSO_4$) and the mixture obtained separated by preparative GLC to give 2-chloro-1,1,1,4,4,4-hexafluoro-3-methoxymethyl-2-butene (122), (0.2g, 4%); IR spectrum 62; NMR spectrum 61; mass spectrum 59, m/z 207 (M-Cl, 6%): trans-1,1,1,4,4,4-hexafluoro-2-methoxy-3-methoxymethyl-2-butene (123), (0.8g, 17%), b.p. 120-121°C (Found: C, 35.5; H, 3.4; F, 47.5. $C_7H_8F_6O_2$ requires C, 35.3; H, 3.4; F, 47.9%); IR spectrum 63; NMR spectrum 62; mass spectrum 60: trans-1,1,1,4,4,4-hexafluoro-2-ethoxy-3-methoxymethyl-2-butene (124), (1.4g, 28%), b.p. 137-138°C; IR spectrum 64; NMR spectrum 63; mass spectrum 61, m/z 223 (M-Et, 11%): cis-1,1,1,4,4,4-hexafluoro-2-ethoxy-3-methoxymethyl-2-butene (125), (0.6g, 13%), b.p. 148-149°C; IR spectrum 65; NMR spectrum 64; mass spectrum 62, m/z 223 (M-Et, 8%).

(b) Dechlorination

i/ 2-(2H-tetrachloroethyl)oxolane (101)

2-(2H-tetrachloroethyl)oxolane (101), (5.1g, 22mmol) was added dropwise to a mixture of zinc dust (2.0g, 30mmol) and ethanol (15ml) which was refluxed for 2.5hrs with stirring. The solution was filtered and the filtrate washed with hydrochloric acid (50ml, 2M). The lower organic layer was separated, dried ($MgSO_4$) and distilled to give 2-(1,2-dichloroethenyl)oxolane (126), (1.1g, 31%), b.p. 50°C (50mmHg); IR spectrum 66; NMR spectrum 65; mass spectrum 63, m/z 166 (M+, 3%), 165 (M-1, 3), 133 (M-33, 31), 131 (M-35, 92).

ii/ 2,3-Dichloro-4,4,4-trifluoro-1-methoxy-2-trifluoromethylbutane (105)

A solution of adduct (105), (5.0g, 18mmol) in ethanol (10ml) was added dropwise to a mixture of zinc dust (2.4g, 37mmol) and ethanol (15ml) and then refluxed for 2.5hrs. The mixture was filtered and the filtrate washed with water (50ml). The lower organic layer separated, dried ($MgSO_4$) and distilled to give 1,1,1,4,4,4-hexafluoro-2-methoxymethyl-2-butene (127), (1.8g, 48%), b.p. 99°C; IR spectrum 67; NMR spectrum 66; mass spectrum 64, m/z 207 (M-1, 3%), 139 ($M-CF_3$, 79%).

B AMIDES

1 Synthesis of Amines by Hydrolysis

(a) N-Methyl-N-(1H,1H,3H-hexafluorobutyl)acetamide (36)

A mixture of adduct (36), (5.1g, 23mmol) and sulphuric acid (50ml, 1.7M) was refluxed for 2.5hrs. To this was then added potassium hydroxide (200ml, 1M). The lower organic layer separated, dried ($MgSO_4$) and distilled to give methyl-(1H,1H,3H-hexafluorobutyl)amine (128), (3.6g, 81%), b.p. 102°C (Found: C, 30.6; H, 3.9; N, 6.9; F, 57.9. $C_5H_7F_6N$ requires C, 30.8; H, 3.6; N, 7.2; F, 58.5%); IR spectrum 69; NMR spectrum 68; mass spectrum 66, chemical ionisation, m/z 196 (M+1, 50%).

(b) N-(1H,1H,3H-Hexafluorobutyl)acetamide (46)

A mixture of the adduct (46), (5.3g, 24mmol) and sulphuric acid (50ml, 1M) was refluxed for 2.5hrs. To this was added potassium hydroxide (150ml, 3M). The lower organic layer separated, dried ($MgSO_4$) and distilled to give 1H,1H,3H-hexafluorobutylamine (129), (0.9g, 21%), b.p. 97-98°C; IR spectrum 68; NMR spectrum 67; mass spectrum 65, chemical ionisation, m/z 210 (M+1, 64%).

2 Synthesis of Amines by Reduction

(a) N-Methyl-5-(2H-hexafluoropropyl)-2-pyrrolidone (37)

A solution of adduct (37), (1.7g, 7mmol) in ether (10ml) was added dropwise to a mixture of lithium aluminium hydride (0.57g, 15mmol) and ether (10ml) and refluxed for 30min. To this was added ethylacetate (2g) and then sodium hydroxide (3ml, 10M). The mixture was filtered, the filtrate

washed with water (10ml) and the lower organic layer separated to give N-methyl-2-(2H-hexafluoropropyl)-pyrrolidine (48), (0.8g, 50%) (identified by comparison of spectra with those of an authentic sample).

(b) N-Methyl-N-(1H,1H,3H-hexafluorobutyl)acetamide (36)

A solution of adduct (36), (5.1g, 21mmol) in ether (25ml) was added dropwise to a mixture of lithium aluminium hydride (3.1g, 81mmol) and ether (40ml) and refluxed for 1hr. To this was then added potassium hydroxide (20ml, 8M), the lower organic layer separated, dried ($MgSO_4$) and distilled to give ethylmethyl(1H,1H,3H-hexafluorobutyl)amine (130), (1.1g, 23%), b.p. 110°C (Found: C, 38.0; H, 5.3; N, 6.0; F, 50.6. $C_7H_{11}F_6N$ requires C, 37.7; H, 4.9; N, 6.3; F, 51.1%); IR spectrum 71; NMR spectrum 70; mass spectrum 68, chemical ionisation, m/z 224 (M+1, 100%).

(c) N-(1H,1H,3H-Hexafluorobutyl)acetamide (46)

A solution of adduct (46), (5.1g, 23mmol) in ether (25ml) was added dropwise to a mixture of lithium aluminium hydride (3.5g, 91mmol) and ether (40ml) and refluxed for 1hr. To this was added potassium hydroxide (20ml, 8M), the lower organic layer separated, dried ($MgSO_4$) and distilled to give ethyl(1H,1H,3H-hexafluorobutyl)amine (131), (1.9g, 40%), b.p. 105°C; IR spectrum 70, NMR spectrum 69, mass spectrum 67, chemical ionisation, m/z 210 (M+1, 64%).

C ISOCYANATES

1 Addition Reactions

(a) 1,1,1,2,3,3-Hexafluoro-4-pentylisocyanate (77) and Methanol

A mixture of adduct (77), (5.0g, 23mmol) and methanol (1.5g, 47mmol) was kept at 20°C for 1hr and then distilled to give methyl-N-(1,1,1,2,3,3-hexafluoro-4-pentyl)carbamate (132), (3.0g, 51%), b.p. 121°C (50mmHg); IR spectrum 72; NMR spectrum 71; mass spectrum 69, chemical ionisation, m/z 254 (M+1, 85%).

(b) 1,1,1,2,3,3-Hexafluoro-4-pentylisocyanate (77) and Ethylamine

A mixture of adduct (77), (4.9g, 22mmol) and ethylamine (10ml) were kept at 20°C for 1hr and then distilled to give N-ethyl-N'-(1,1,1,2,3,3-hexafluoro-4-pentyl)urea (133), (3.8g, 64%), b.p. 171°C (2mmHg), m.p. 54°C; IR spectrum 73; NMR spectrum 72; mass spectrum 70, chemical ionisation, m/z 267 (M+1, 81%).

(c) 2,2,3,4,4,4-Hexafluorobutanol and Methylisocyanate

A mixture of 2,2,3,4,4,4-hexafluorobutanol (3.7g, 20mmol) and methylisocyanate (10ml) was refluxed for 8hrs. The mixture was then distilled to give 2,2,3,4,4,4-hexafluorobutyl-N-methylcarbamate (134), (2.1g, 43%), b.p. 100-101°C (10mmHg); IR spectrum 74; NMR spectrum 73; mass spectrum 71, chemical ionisation, m/z 240 (M+1, 96%).

(d) 2,2,3,4,4,4-Hexafluorobutylamine (128) and Methylisocyanate

A mixture of amine (128), (3.5g, 19mmol) and methylisocyanate (10ml) was kept at 20°C for 1hr and then distilled to give N-methyl-N'-(2,2,3,4,4,4-hexafluorobutyl)-urea (135), (3.1g, 68%), b.p. 125-126°C (0.1mmHg); IR spectrum 75, NMR spectrum 74; mass spectrum 72, chemical ionisation, m/z 239 (M+1, 32%).

(e) 2,2,3,4,4,4-Hexafluorobutanol and 1,1,1,2,3,3-Hexafluoro-4-pentylisocyanate (77)

A mixture of 2,2,3,4,4,4-hexafluorobutanol (5.0g, 28mmol) and adduct (77), (5.0g, 23mmol) was kept at 20°C for 1hr and then distilled to give 2,2,3,4,4,4-hexafluorobutyl-N-(1,1,1,2,3,3-hexafluoro-4-pentyl)carbamate (136), (5.8g, 62%), b.p. 84°C (1mmHg) (Found: C, 30.0; H, 2.2; N, 3.3; F, 56.1. $C_{10}H_9F_{12}NO_2$ requires C, 29.8; H, 2.2; N, 3.5; F, 56.6%); IR spectrum 76; NMR spectrum 75; mass spectrum 73, chemical ionisation, m/z 404 (M+1, 59%).

2 Photolysis

(a) 1,1,1,2,3,3-Hexafluoro-4-pentylisocyanate (77) and Cyclohexane

Cyclohexane (2.0g, 24mmol) and adduct (77), (3.1g, 14mmol) were placed in a quartz Carius tube (ca. 100ml) and degassed. The tube was sealed and irradiated with uv (254nm) in a '208' type reactor for 60hrs. On opening the liquid obtained was shown to contain only starting materials by GLC (column K, 150°C).

(b) 1,1,1,2,3,3-Hexafluoro-4-pentylisocyanate (77) and Cyclohexene

Cyclohexene (2.1g, 25mmol) and adduct (77), (3.0g, 14mmol) were placed in a quartz Carius tube (ca. 100ml) and degassed. The tube was sealed and irradiated with uv (254nm) in a '208' type reactor for 60hrs. On opening the liquid obtained was shown to contain only starting materials by GLC (column K, 150°C).

D REACTIONS OF 3,3,4,5,5,5-HEXAFLUORO-2-PENTANONE (97)

1 Haloform Reaction

A mixture of ketone (97), (10.1g, 52mmol), iodine (38.5g, 151mmol) and potassium hydroxide (50ml, 8M) was heated at 60°C for 30min. The mixture was filtered, the filtrate neutralised with sulphuric acid (conc.) and then continuously extracted (Soxhlet) with ether (100ml). The solution obtained was dried ($MgSO_4$) and evaporated to give 2,2,3,4,4,4-hexafluorobutanoic acid (137), (2.5g, 24%) (identified by comparison of spectra with those of an authentic sample[138]).

2 Reduction

A mixture of lithium aluminium hydride (3.0g, 80mmol) and ether was stirred for 10min. To this was added dropwise ketone (97), (5.1g, 26mmol) and refluxed for 1hr. The mixture was poored into ice (50g) and to this added sulphuric acid (100ml, 2M). The organic layer was separated, dried and distilled to give 3,3,4,5,5,5-hexafluoro-2-

pentanol (107), (3.4g, 66%) (identified by comparison of spectra with those of an authentic sample).

3 Addition of Methylmagnesium Iodide

To a mixture of magnesium turnings (0.85g, 35mmol) and ether (20ml) was added dropwise a solution of methyl iodide (3.8g, 27mmol) in ether (20ml) with stirring and the mixture then refluxed for 30min. After cooling a solution of ketone (97), (5.0g, 26mmol) in ether (10ml) was added dropwise and then refluxed for 30min. To this was added water (25ml) and then extracted with ether (3X25ml). The extracts were dried ($MgSO_4$), evaporated and the residue distilled to give 2-methyl-3,3,4,5,5,5-hexafluoro-2-pentanol (138), (2.3g, 42%), b.p. 61°C, IR spectrum 77; NMR spectrum 76.

4 Reaction with Diazomethane

(a) Diazomethane[139]

A solution of potassium hydroxide (6.1g, 92mmol), water (10ml), digol (35ml) and ether (10ml) was brought to reflux. To this was added dropwise a solution of Diazald[140] (21.5g, 100mmol) in ether (125ml) followed by ether (50ml), maintaining a steady distillation. The solution of diazomethane was collected in a receiver cooled in ice and used immediately.

(b) Reaction with Diazomethane

The solution of diazomethane obtained above was added to a solution of ketone (97), (10.0g, 52mmol) in ether (25ml) and refluxed for 12hrs. The mixture was distilled to

give 2-methyl-3,3,4,5,5,5-hexafluoro-1,2-epoxypentane (139), (2.5g, 23%), b.p. 108°C (Found: C, 34.9; H, 2.9; F, 54.1. $C_6H_6F_6O$ requires C, 34.6; H, 2.9; F, 54.8%); IR spectrum 78; NMR spectrum 77; mass spectrum 74, chemical ionisation, m/z 209 (M+1, 32%).

5 Attempted McMurray Reaction

A 1:2 mixture of titanium trichloride and lithium aluminium hydride[140] (7.4g, 32mmol ($TiCl_3$)) was added to tetrahydrofuran (50ml). After the initial exothermic reaction the mixture was refluxed for 5min. To this was then added a solution of ketone (97), (5.6g, 29mmol) in tetrahydrofuran (10ml) and then refluxed for 5hrs. To this was added water (50ml) and the lower organic layer (1.7g) separated and purified by preparative GLC (column K, 150°C) to give 2H,7H-4,5-dimethyl-4,5-dihydroxyperfluorooctane (140), (0.9g, 8%), mass spectrum 75, m/z 373 (M-OH, 2%), 195 (M/2, 40).

6 Attempted Wittig Reactions

(a) 2-Propyltriphenylphosphonium Iodide

A mixture of triphenylphosphine (20.1g, 77mmol), 2-iodopropane (15.1g, 89mmol) and toluene (45ml) was heated at 100°C for 24hrs. After cooling the product was filtered and washed with 60/80 petroleum ether to give 2-propyl-triphenylphosphonium iodide (8.1g, 23%).

(b) Addition

n-Butyllithium (1.55M, 20ml) was added to a solution of 2-propyltriphenylphosphonium iodide (13.4g, 31mmol) in ether (100ml) and stirred for 4hrs. To this was then added dropwise ketone (97), (6.1g, 31mmol) and refluxed for 3hrs. The mixture was diluted with water (100ml) and extracted with ether (3x50ml). After evaporation an unidentified residue (0.29g) was obtained.

CHAPTER 13

EXPERIMENTAL TO CHAPTER 7

A GENERAL PROCEDURE

1 Cobalt Trifluoride Fluorination

Cobalt trifluoride fluorinations were carried out in a purpose built reactor[12]. The reactor was first recharged by heating to 300°C and passing fluorine through (ca. 7g/hr) until detected at the outlet using moist starch/iodide paper. The reactor was then heated to 440°C, nitrogen (50cm^3 min^{-1}) passed through and a trap cooled to -176°C connected to the outlet. The starting material was added dropwise (ca. 1 drop/sec) to the inlet and then allowed to react for a further 30min. The trap was then disconnected and warmed to room temperature. The product was washed with saturated aqueous sodium bicarbonate and transferred under vacuum before further purification.

2 Sulphur Tetrafluoride Fluorination

Substrate and water (if HF catalyst used) were placed in a nickel autoclave (ca. 100ml), SF_4 and BF_3 (if used) were then added by vacuum transfer and the autoclave sealed. The autoclave was heated to the required temperature with rocking. After reaction the excess SF_4 was vented to the atmosphere, the product mixture washed with saturated aqueous sodium bicarbonate and then transferred under vacuum before further purification.

3 Pyrolysis over Iron

Pyrolyses were carried out by passing the reactant through a heated quartz tube (ca 30cm x 3cm dia) in a stream of nitrogen. The tube was heated to the required temperature, nitrogen ($50cm^3\ min^{-1}$) passed through and a trap, cooled to -176°C, connected to the outlet. The reactant was placed in a flask connected to the inlet such that the nitrogen bubbled through it and the reaction continued until the reactant had evaporated. The trap was then disconnected, warmed to room temperature and the product analysed by GLC (column A) before further purification.

B PERFLUORINATED AMINES

1 N-Methyl-2-(2H-hexafluoropropyl)pyrrolidine (48)

N-Methyl-2-(2H-hexafluoropropyl)pyrrolidine (48), (4.0g, 17mmol) was passed over CoF_3 at 440°C following the general procedure. The product mixture was separated by preparative scale GLC (column A, 20°C) to give perfluorohexane (143), (1.0g, 18%) and perfluoro-N-methyl-2-propylpyrrolidine (142), (2.5g, 34%), b.p. 106°C (Found: C, 22.1; N, 3.6; F, 74.1. $C_8F_{17}N$ requires C, 22.2; N, 3.3; F, 74.6%); IR spectrum 79; NMR spectrum 78; mass spectrum 76.

2 N-(1H,1H,3H-hexafluorobutyl)-2-(2H-hexafluoropropyl)-piperidine (49)

The adduct (49), (4.1g, 10.3mmol) was passed over CoF_3 at 440°C following the general procedure. The four major products were separated by preparative scale GLC (column A,

20°C) to give perfluoroheptane (144), (0.4g, 10%): perfluoro-N-butylpyrrolidine (145), (0.4g, 9%); NMR spectrum 79; mass spectrum 77, chemical ionisation, m/z 414 (M-F, 54%): perfluoro-N-butylpiperidine (146), (0.6g, 12%); IR spectrum 80; NMR spectrum 80; mass spectrum 78: perfluoro-N-butyl-2-propylpiperidine (147), (0.2g, 4%), b.p. 177°C; NMR spectrum 81; mass spectrum 79

3 Tris(1,1,1,2,3,3-hexafluoro-4-pentyl)amine (53)

The adduct (53), (4.3g, 8mmol) was passed over CoF_3 at 440°C following the general procedure. The product was shown to contain a large number of components and separation was not attempted.

C PERFLUORINATED ALKANES AND ETHERS

1 Alcohols

(a) Perfluoromethylcyclohexane (149)

i/ (2H-decafluorocyclohexyl)methanol and sulphur tetrafluoride

(2H-Decafluorocyclohexyl)methanol[11] (20.1g, 68mmol) and sulphur tetrafluoride (32.0g, 296mmol) were reacted using the general procedure at 80°C for 10hrs. The product was distilled to give (2H-decafluorocyclohexyl)fluoromethane (148), (13.6g, 67%), b.p. 109°C (Found: C, 28.7; H, 1.1; F, 71.0. $C_7H_3F_{11}$ requires C, 28.4; H, 1.0; F, 70.6%); IR spectrum 81; NMR spectrum 82; mass spectrum 80.

ii/ (2H-Decafluorocyclohexyl)fluoromethane (148) and Cobalt Trifluoride

(2H-Decafluorocyclohexyl)fluoromethane (148) was passed over cobalt trifluoride at 440°C using the general procedure. The product was purified by preparative scale GLC (column A, 50°C) to give perfluoromethylcyclohexane (149), (3.7g, 59%), b.p. 76°C (Found: C, 24.3; F, 76.2. C_7F_{14} requires C, 24.0; F, 76.0%); IR spectrum 82; NMR spectrum 83; mass spectrum 81.

(b) Perfluoro-3,3,4-trimethylhexane (151)

i/ 3-Hydroxymethylperfluoro-4H-3,4-dimethylhexane and Sulphur Tetrafluoride

3-Hydroxymethylperfluoro-4H-3,4-dimethylhexane[11] (15.0g, 35mmol) and sulphur tetrafluoride (12.4g, 115mmol) were reacted using the general procedure at 100°C for 19hrs. The product was distilled to give 3-fluoromethylperfluoro-4H-3,4-dimethylhexane (150), (4.9g, 32%), b.p. 134°C (Found: C, 24.7; H, 0.5; F, 74.9. $C_9H_3F_{17}$ requires C, 24.9; H, 0.7; F, 74.4%); IR spectrum 83, NMR spectrum 84; mass spectrum 82.

ii/ 3-Fluoromethylperfluoro-4H-3,4-dimethylhexane (150) and Cobalt Trifluoride

3-Fluoromethylperfluoro-4H-3,4-dimethylhexane (150), (5.3g, 12mmol) was passed over cobalt trifluoride at 440°C using the general procedure. The product was distilled to give perfluoro-3,3,4-trimethylhexane (151), (1.0g, 17%), IR spectrum 84; NMR spectrum 85; mass spectrum 83.

(c) Perfluoroundecane (153)

i/ Perfluoro-1H,1H,11H-Undecanol and Sulphur Tetrafluoride

Perfluoro-1H,1H,11H-Undecanol (26.0g, 49mmol) and sulphur tetrafluoride (21.0g, 194mmol) were reacted using the general procedure at 100°C for 10hrs. The product was recrystalised from ethanol to give perfluoro-1H,1H,11H-undecane (152), (12.6g, 48%), m.p. 64-65°C (Found: C, 24.6; H, 0.3; F, 75.2. $C_{11}H_3F_{21}$ requires C, 24.7; H, 0.6; F, 74.7%); IR spectrum 85; NMR spectrum 86; mass spectrum 84.

ii/ Perfluoro-1H,1H,11H-undecane (152) and Cobalt Trifluoride

Perfluoro-1H,1H,11H-undecane (152), (4.9g, 9mmol) was passed over cobalt trifluoride at 440°C using the general procedure. The product was sublimed to give perfluoro-undecane (153), (4.2g, 78%), m.p. 53-55°C (Found: C, 22.2; F, 77.1. $C_{11}F_{24}$ requires C, 22.5; F, 77.6%); IR spectrum 86; NMR spectrum 87; mass spectrum 85.

2 Ketones

(a) Perfluoroethylcyclopentane (155)

i/ (2H-Octafluorocyclopentyl)ethanone and Sulphur Tetrafluoride

(2H-Octafluorocyclopentyl)ethanone[11] (10.1g, 40mmol), water (0.26g, 14mmol) and sulphur tetrafluoride (14.7g, 136mmol) were reacted using the general procedure at 100°C for 20hrs. The product was distilled to give (2H-octafluorocyclopentyl)-1,1-difluoroethane (154), (6.7g,

60%), b.p. 98-99°C (Found: C, 30.5; H, 1.1; F, 67.8. $C_7H_4F_{10}$ requires C, 30.2; H, 1.4; F, 68.4%); IR spectrum 87; NMR spectrum 88; mass spectrum 86.

ii/ (2H-Octafluorocyclopentyl)-1,1-difluoroethane (154) and Cobalt Trifluoride

(2H-Octafluorocyclopentyl)-1,1-difluoroethane (154), (5.2g, 19mmol) was passed over cobalt trifluoride at 440°C using the general procedure. The product was distilled to give perfluoroethylcyclopentane (155), (5.9g, 89%), b.p. 74°C (Found: C, 24.3; F, 75.7. C_7F_{14} requires C, 24.0; F, 76.0%); IR spectrum 88; NMR spectrum 89; mass spectrum 87.

(b) Perfluoroethylcyclohexane (158)

i/ (2H-Decafluorocyclohexyl)ethanone and Sulphur Tetrafluoride

(2H-Decafluorocyclohexyl)ethanone[11] (20.0g, 65mmol), water (0.25g, 14mmol) and sulphur tetrafluoride (23.0g, 213mmol) were reacted using the general procedure at 95°C for 16hrs. The product mixture was distilled to give 1-(2H-decafluorocyclohexyl)-1-fluoroethene (156), (9.2g, 46%), b.p. 80°C (Found: C, 30.9; H, 1.0; F, 67.3. $C_8H_4F_{12}$ requires C, 31.2; H, 1.0; F, 67.9%); IR spectrum 89; NMR spectrum 90; mass spectrum 88 and 1-(2H-hexafluorocyclohexyl)-1,1-difluoroethane (157), (8.7g, 41%), b.p. 87°C; IR spectrum 90; NMR spectrum 91; mass spectrum 89.

ii/ 1-(2H-Decafluorocyclohexyl)-1-fluoroethene (156) and Cobalt Trifluoride

1-(2H-Decafluorocyclohexyl)-1-fluoroethene (156), (5.1g, 17mmol) was passed over cobalt trifluoride at 440°C using the general procedure. The product was purified by preparative GLC (column A, 45°C) to give perfluoroethylcyclohexane (158), (3.6g, 54%), b.p. 98°C; IR spectrum 91; NMR spectrum 92; mass spectrum 90.

iii/ 1-(2H-Decafluorocyclohexyl)-1,1-difluoroethane (157) and Cobalt Trifluoride

1-(2H-Decafluorocyclohexyl)-1,1-difluoroethane (157), (3.0g, 9mmol) was passed over cobalt trifluoride at 440°C using the general procedure. The product was purified by preparative GLC (column A, 45°C) to give perfluoroethylcyclohexane (158), (1.3g, 35%), b.p. 98°C (identified by comparison of spectra with those of an authentic sample).

(c) Attempted Reaction of 3-Acetylperfluoro-4H-3,4-dimethylhexane and Sulphur Tetrafluoride

3-Acetylperfluoro-4H-3,4-dimethylhexane[11] (15.0g, 34mmol), water (0.27g, 15mmol) and sulphur tetrafluoride (14.0g, 130mmol) were reacted using the general procedure at 100°C for 20hrs. The product obtained was shown to contain only starting material by GLC.

3 ESTERS

(a) Perfluoro-1-ethoxy-1H,1H,3H-butane (160)

i/ Fluorination with Sulphur Tetrafluoride and Hydrogen Fluoride catalyst

A mixture of trifluoroacetic anhydride (23.5g, 112mmol) and 2,2,3,4,4,4-hexafluorobutanol[11] (16.2g, 89mmol) was refluxed for 30min. The mixture obtained (17.2g) and sulphur tetrafluoride (20.0g, 185mmol) were reacted using the general procedure at 175°C for 6hrs. The product mixture obtained (6.5g) was analysed by GLC (column K, 75°C) and shown to contain perfluoro-1H,1H,3H-butane (161), (41%), perfluoro-1-ethoxy-1H,1H,3H-butane (160), (36%) and ester (159), (23%) (identified by comparison of GLC/mass spectra with those obtained in ii/).

ii/ Fluorination with Sulphur Tetrafluoride and Boron Trifluoride catalyst

2,2,3,4,4,4-Hexafluorobutanol[11] (17.0g, 93mmol) and trifluoroacetic anhydride (21.2g, 101mmol) were mixed and distilled to give 2,2,3,4,4,4-hexafluorobutyltrifluoroacetate (159), (22.3g, 86%), b.p. 105°C (Found: C, 26.2; H, 1.3; F, 61.1. $C_6H_3F_9O_2$ requires C, 25.9; H, 1.1; F, 61.5%); IR spectrum 92; NMR spectrum 93; mass spectrum 91. The ester (159), (22.3g, 80mmol), boron trifluoride (1.7g, 25mmol) and sulphur tetrafluoride (14.8g, 137mmol) were reacted using the general procedure at 175°C for 6hrs. The liquid obtained (15.3g) was further reacted with boron trifluoride (1.8g, 26mmol) and sulphur tetrafluoride (12.3g, 114mmol) using the general procedure at 175°C for 24hrs. The liquid obtained

(9.7g) was analysed by GLC and shown to contain perfluoro-1H,1H,3H-butane (161), (5%), perfluoro-1-ethoxy-1H,1H,3H-butane (160), (45%) and ester (159), (50%). The mixture was distilled to give perfluoro-1-ethoxy-1H,1H,3H-butane (160), (5.0g, 18%), b.p. 96°C (Found: C, 23.8; H, 0.8; F, 69.9. $C_6H_3F_{11}O$ requires C, 24.0; H, 1.0; F, 69.7%); IR spectrum 93; NMR spectrum 94; mass spectrum 92.

(b) Perfluoroethoxybutane (162)

Ether (160), (5.0g, 17mmol) was passed over cobalt trifluoride at 440°C using the general procedure. The product obtained was purified by preparative scale GLC (column A, 20°C) to give perfluoroethoxybutane (162), (0.69g, 6%), b.p. 56-57°C; IR spectrum 94; NMR spectrum 95; mass spectrum 93.

D REACTIONS WITH FLUOROCARBON ETHERS

(a) Reaction with Aluminium Trichloride

i/ Perfluoro-2-propyloxolane

A mixture of perfluoro-2-propyloxolane (1.8g, 5mmol) and sublimed aluminium trichloride (1.4g, 10mmol) was heated at 250°C for 24hrs in a nickel autoclave (ca. 200ml). The liquid obtained (1.3g) was purified by preparative GLC (column K, 150°C) to give 2,5,5-trichloroperfluoro-2-propyl-oxolane (163), (0.63g, 31%), b.p. 152°C; IR spectrum 95; NMR spectrum 96; mass spectrum 94.

ii/ Perfluoro-2,5-dipropyloxolane

A mixture of perfluoro-2,5-dipropyloxolane (2.3g, 4mmol) and sublimed aluminium trichloride (1.8g, 13mmol) was heated at 250°C for 42hrs in a nickel autoclave (ca. 200ml). The liquid obtained was purified by preparative GLC (column K, 150°C) to give 2-chloroperfluoro-2,5-dipropyloxolane (164), (0.37g, 17%); mass spectrum 95 and 2,5-dichloro-perfluoro-2,5-dipropyloxolane (165), (0.22g, 10%); mass spectrum 96.

2 Pyrolysis over Iron

(a) Perfluoro-2-propyloxolane

Perfluoro-2-propyloxolane was pyrolysed over iron using the general procedure at several temperatures.

Temperature	Substrate/g	% Substrate Recovered
450°C	4.33	93
500°C	3.59	83
550°C	2.58	26
600°C	3.06	0

(b) Perfluoro-2,5-dipropyloxolane

Perfluoro-2,5-dipropyloxolane was pyrolysed over iron using the general procedure at several temperatures.

Temperature	Substrate/g	% Substrate Recovered
450°C	2.17	78
500°C	1.52	76
550°C	0.99	0

(c) Perfluoro-2,5,5-trichloro-2-propyloxolane

Perfluoro-2,5,5-trichloro-2-propyloxolane was pyrolysed over iron using the general procedure at 400°C.

Temperature	Substrate/g	% Substrate Recovered
400°C	0.80	0

(d) Perfluoroisopentylether

Perfluoroisopentylether was pyrolysed over iron using the general procedure. The product liquid was analysed by GLC showing it to contain substrate and perfluoro-2-pentene, mass spectrum 97.

Temperature	Substrate/g	% Substrate Recovered	% perfluoro-2-pentene
500°C	2.42	85	3
550°C	1.49	40	8

APPENDICES

APPENDIX I

NMR SPECTRA

1 N-Methyl-6-(2H-hexafluoropropyl)-2-piperidone (38).

2 N-Methyl-7-(2H-hexafluoropropyl)-ϵ-caprolactam (39).

3 N-Acetyl-2-(2H-hexafluoropropyl)pyrrolidine (40).

4 N-Formyl-2-(2H-hexafluoropropyl)pyrrolidine (44).

5 N-Formyl-2-(2H-hexafluoropropyl)piperidine (45).

6 N-(1H,1H,3H-hexafluorobutyl)acetamide (46).

7 5-(2H-Hexafluoropropyl)-2-pyrrolidone (47).

8 N-Methyl-2-(2H-hexafluoropropyl)pyrrolidine (48).

9 Ethylidine-1,1,1,2,3,3-hexafluoro-4-pentylimine (51).

10 Bis-(1,1,1,2,3,3-hexafluoro-4-pentyl)ethylamine (52).

11 Tris-(1,1,1,2,3,3-hexafluoro-4-pentyl)amine (53).

12 N-Ethyl-2-(2H-hexafluoropropyl)pyrrolidine (54).

13 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)-2-
(2H-hexafluoropropyl)pyrrolidine (55).

14 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)piperidine (56).

15 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)-2-
(2H-hexafluoropropyl)piperidine (57).

16 N-Ethyl-2-(2H-hexafluoropropyl)hexamethyleneimine (58).

17 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)-2-
(2H-hexafluoropropyl)hexamethyleneimine (59).

18 (1,1,2,2-Tetrafluoro-3-butyl)diethylamine (66).

19 Bis-(1,1,2,2-tetrafluoro-3-butyl)ethylamine (67).

20 Tris-(1,1,2,2-tetrafluoro-3-butyl)amine (68).

21 N-Methyl-2-(2H-tetrafluoroethyl)pyrrolidine (69).

22 N-(2,2,3,3-tetrafluoropropyl)-2-(2H-tetrafluoroethyl)pyrrolidine (70).

23 N-Methyl-2-(2H-tetrafluoroethyl)piperidine (71).

24 N-(2,2,3,3-tetrafluoropropyl)-2-(2H-tetrafluoroethyl)piperidine (72).

25 N-(2,2,3,3-tetrafluoropropyl)-2,6-bis-(2H-tetrafluoroethyl)piperidine (73).

26 N-Methyl-2-(2H-perfluorocyclohexyl)pyrrolidine (74).

27 N-Methyl-2-(2H,2-chlorotrifluoroethyl)pyrrolidine (75).

28 N-Methyl-2-(2H,2,2-dichlorodifluoroethyl)pyrrolidine (76).

29 (1,1,1,2,3,3-hexafluoro-4-pentyl)isocyanate (77).

30 (1H,1H,3H-Hexafluorobutyl)trimethylsilane (78).

31 Bis-(1H,1H,3H-Hexafluorobutyl)dimethylsilane (79).

32 (1H,1H,3H-Hexafluorobutyl)pentamethyldisiloxane (80).

33 (1H,1H,3H-Hexafluorobutyl)heptamethylcyclotetrasiloxane (81).

34 Bis-(1H,1H,3H-Hexafluorobutyl)hexamethylcyclotetrasiloxane (82).

35 Fluorinated Silicon Oil (83).

36 (1,1,1,2,3,3-Hexafluoro-4-pentyloxy)ethoxydimethylsilane (84).

37 Bis-(1,1,1,2,3,3-Hexafluoro-4-pentyloxy)dimethylsilane (85).

38 (1H,1H,3H-Hexafluorobutylmethylamino)dimethylaminodimethylsilane (86).

39 1H,3H-Pentafluorobutenyltrimethylsilane (87).

40 1,1,1,2,3,3-Hexafluoro-4-methylpentane (89).

41 1,2-Bis-(2-tetrahydrofuryl)-1H-pentafluoropropane (91).

42 δ-Valerolactone Dimer (95).

43 ϵ-Caprolactone Dimer (96).

44 1,1,1,2,3,3-Hexafluoro-4-pentanone (97).

45 2-(2H-Tetrachloroethyl)oxolane (101).

46 1,1,2-Trichloro-3-ethoxybutene (102).

47 1,1,2-Trichlorobuten-3-one (103).

48 1,1,2-Trichlorobuten-3-ol (104).

49 2-(2H,2,2-Dichlorodifluoroethyl)oxolane (99).

50 2,3-Dichloro-1,1,1,4,4,4-hexafluoro-3-methoxymethyl-butane (105).

51 Bis-(2,3-dichloro-4,4,4-trifluoro-2-trifluoromethyl-butyl)ether (106).

52 1,1,1,2,3,3-Hexafluoro-4-pentanol (107).

53 1-(2H-Octafluorocyclopentyl)ethanol (108).

54 1-(2H-Decafluorocyclohexyl)ethanol (109).

55 1,1,1,2,3,3-Hexafluoroheptane-4,7-diol (110).

56 2-(Pentafluoropropenyl)oxolane (90).

57 1,1,1,2,3-Pentafluoro-4-ethoxy-2-pentene (119).

58 1,1,1,2,3-Pentafluoro-4-methoxy-2-butene (92).

59 N-Methyl-2-(Pentafluoropropenyl)pyrrolidine (120).

60 2-(Trichloroethenyl)oxolane (121).

61 Trans-2-Chloro-1,1,1,4,4,4-hexafluoro-3-methoxymethyl-2-butene (122).

62 Trans-1,1,1,4,4,4-hexafluoro-2-methoxy-3-methoxymethyl-2-butene (123).

63 Trans-1,1,1,4,4,4-hexafluoro-2-ethoxy-3-methoxymethyl-2-butene (124).

64 Cis-1,1,1,4,4,4-hexafluoro-2-ethoxy-3-methoxymethyl-2-butene (125).

65 2-(1,2-Dichloroethenyl)oxolane (126).

66 1,1,1,4,4,4-Hexafluoro-2-methoxymethyl-2-butene (127).

67 2,2,3,4,4,4-Hexafluorobutylamine (129).

68 (2,2,3,4,4,4-Hexafluorobutyl)methylamine (128).

69 (2,2,3,4,4,4-Hexafluorobutyl)ethylamine (131).

70 (2,2,3,4,4,4-Hexafluorobutyl)ethylmethylamine (130).

71 Methyl-N-(1,1,1,2,3,3-Hexafluoro-4-pentyl)carbamate (132).

72 N-Ethyl-N'-(1,1,1,2,3,3-hexafluoro-4-pentyl)urea (133).

73 (1H,1H,3H-Hexafluorobutyl)-N-methylcarbamate (134).

74 N-Methyl-N'-(1H,1H,3H-hexafluorobutyl)urea (135).

75 (1H,1H,3H-Hexafluorobutyl)-N-(1,1,1,2,3,3-hexafluoro-4-pentyl)carbamate (136).

76 1,1,1,2,3,3-Hexafluoro-4-methyl-4-pentanol (138).

77 1,1,1,2,3,3-Hexafluoro-4-methyl-4,5-epoxypentane (139).

78 Perfluoro-N-methyl-2-propylpyrrolidine (142).

79 Perfluoro-N-butylpyrrolidine (145).

80 Perfluoro-N-butylpiperidine (146).

81 Perfluoro-N-butyl-2-propylpiperidine (147).

82 (2H-Decafluorocyclohexyl)fluoromethane (148).

83 Perfluoromethylcyclohexane (149).

84 3-Fluoromethylperfluoro-4H,3,4-dimethylhexane (150).

85 Perfluoro-3,3,4-trimethylhexane (151).

86 Perfluoro-1H,1H,11H-undecane (152).

87 Perfluoroundecane (153).

88 1-(2H-Octafluorocyclopentyl)-1,1-difluoroethane (154).

89 Perfluoroethylcyclopentane (155).

90 1-(2H-Decafluorocyclohexyl)-1-fluoroethene (156).

91 1-(2H-Decafluorocyclohexyl)-1,1-difluoroethane (157).

92 Perfluoroethylcyclohexane (158).

93 1H,1H,3H-Hexafluorobutyltrifluoroacetate (159).

94 Perfluoro-1-ethoxy-1H,1H,3H-butane (160).

95 Perfluoroethoxybutane (162).

96 2,5,5-Trichloroperfluoro-2-propyloxolane (163).

97 Perfluoro-2-pentene.

ABBREVIATIONS

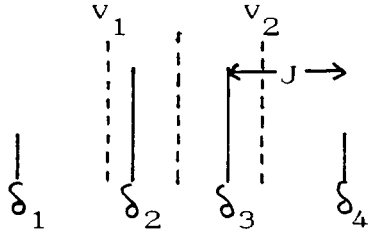
The following abbreviations are used for the splitting patterns of the NMR resonances:-

S	Singlet
D	Doublet
T	Triplet
Q	Quartet
P	Pentet
SEXT	Sextet
SEPT	Septet

AB:-

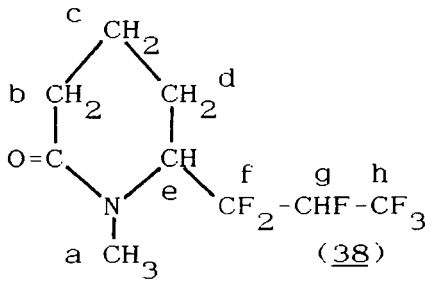
Chemical shifts quoted as 'centre of gravity' or $\pm\Delta\nu/2$ from the mid point of the pattern, calculated from:-

$$(\delta_1 - \delta_3) = (\delta_2 - \delta_4) = \sqrt{(\Delta\nu)^2 + J^2}$$



No.1 N-METHYL-6-(2H-HEXAFLUOROPROPYL)-2-PIPERIDONE (38)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.90	S		2	c
2.10	S		2	d
2.42	S		2	b
3.07	S		3	a
3.46	S		1	e
5.28	D of M	J_{HF}= 43Hz	1	g
^{19}F:-				
74.5	S		3	h
113.7	S			
112.7	AB	J_{AB}=263Hz	2	f
119.2				
212.1	D	J_{HF}= 45HZ	1	g



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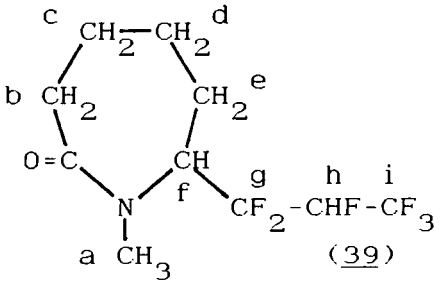


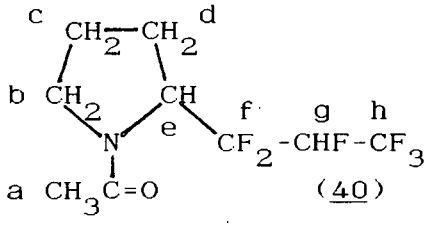
(39)

No.2 N-METHYL-7-(2H-HEXAFLUOROPROPYL)-ε-CAPROLACTAM (39)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.73	S		4	c,d
1.98	S		2	e
2.62	S		2	b
2.97	S		3	a
3.43	S		1	f
5.12	D of M	J_{HF}= 43Hz	1	h
^{19}F:-				
75.0	S		3	i
117.2	S			
112.2	AB	J_{AB}=301Hz	2	g
119.2				
211.7	D	J_{HF}= 45Hz	1	h

No.3 N-ACETYL-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (40)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.80	S		3	a
1.90	S		4	c,d
3.40	S		2	b
4.32	S		1	e
4.70	S			
5.40	D	J_{HF}= 42Hz	1	g
^{19}F:-				
76.0	S		3	h
116.7	AB	J_{AB}=263Hz	2	f
125.7				
119.2	AB	J_{AB}=263Hz		
127.4				
212.3	D	J_{HF}= 36HZ	1	g
214.1	D	J_{HF}= 36HZ		



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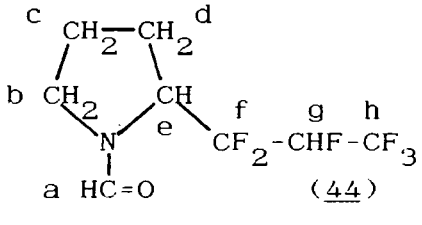

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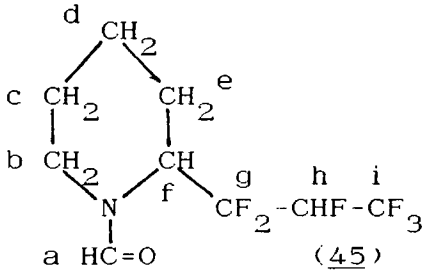
No.4 N-FORMYL-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (44)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.94	S		4	c,d
3.38	S		2	b
3.54	S		1	e
5.30	D of M	J_{HF}= 43Hz	1	g
8.28	S		1	a
^{19}F:-				
74.8	S		3	h
114.3	AB	J_{AB}=282Hz	2	f
123.0				
119.7	AB	J_{AB}=282Hz		
128.0				
213.5	D	J_{HF}= 42Hz	1	g

No.5 N-FORMYL-2-(2H-HEXAFLUOROPROPYL)PIPERIDINE (45)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.70	S		6	c,d,e
3.40	S		3	b,f
5.20	D of M	J_{HF}= 43Hz	1	h
8.15	S		1	a
^{19}F:-				
74.7	S		3	i
110.1, 118.9	AB	J_{AB}=282Hz	2	g
111.4, 117.8	AB	J_{AB}=273Hz		
211.4	D	J_{HF}= 42HZ	1	h
212.5	D	J_{HF}= 42HZ		



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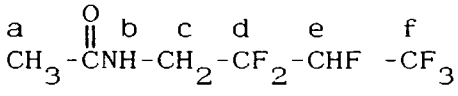

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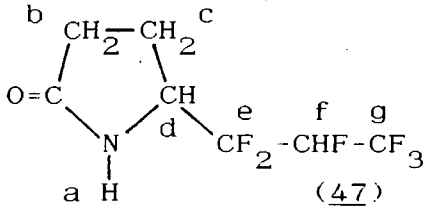
No.6 N-(1H,1H,3H-HEXAFLUOROBUTYL)ACETAMIDE (46)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
2.10	S		3	a
3.90	D of T	J_D = 6Hz, J_T = 15Hz	2	c
4.95	D of P	J_{HF}= 42Hz, J_P = 6Hz	1	e
7.30	S		1	b
^{19}F:-				
75.1	D of Q	J_D = 6Hz, J_Q = 10Hz	3	f
113.4, 119.5	AB	J_{AB}=282Hz	2	d
212.6	D of Q	J_{HF}= 42Hz, J_Q = 10Hz	1	e

No.7 5-(2H-HEXAFLUOROPROPYL)-2-PYRROLIDONE (47)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
2.38	S		4	b,c
4.13	S		1	d
5.23	D	J_{HF} = 42Hz	1	f
8.40	S		1	a
8.60	S			
^{19}F:-				
75.2	S		3	g
122.2	SEXT	J = 11Hz	2	e
126.5	SEXT	J = 11Hz		
213.4	D of Q	J_{HF} = 42HZ, J_Q = 9HZ	1	f
215.9	D of Q	J_{HF} = 42HZ, J_Q = 10HZ		



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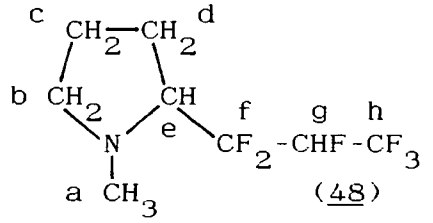


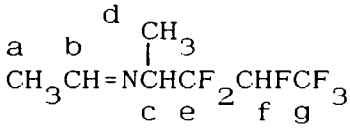
(48)

No.8 N-METHYL-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (48)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.90	S		4	c,d
2.48	S		3	a
3.10	S		3	b,e
5.17	D of M	J_{HF} = 43Hz	1	g
^{19}F:-				
74.4	Q of D	J_Q = 11Hz, J_D = 6Hz	3	h
111.3	AB	J_{AB}=282Hz	2	f
119.4				
120.3	AB	J_{AB}=263Hz		
128.9				
211.0	D of Q	J_{HF} = 41Hz, J_Q = 9Hz	1	g
213.3	D	J_{HF} = 41Hz		

No.9 ETHYLIDINE-1,1,1,2,3,3-HEXAFLUORO-4-PENTYLIMINE (51)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
0.83	S		3	d
1.58	S		3	a
3.05	S		1	c
4.70	D	J_{HF}= 40Hz	1	f
7.38	S		1	b
^{19}F:-				
76.7	S		3	g
114.3, 122.0	AB	J_{AB}=263Hz	2	e
124.4, 130.2	AB	J_{AB}=263Hz		
217.1	D	J_{HF}= 40HZ	1	f



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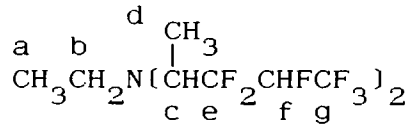


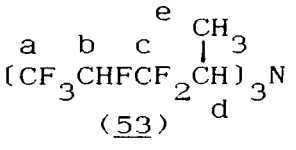
(52)

No.10 BIS-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)ETHYLAMINE (52)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.10	S		6	a,d
2.60	S		2	b
3.30	S		1	c
4.90	D of M	J_{HF}= 43Hz	1	f
^{19}F:-				
76.6	S		3	g
117.8, 124.8	AB	J_{AB}=301Hz	2	e
212.3	D	J_{HF}= 43Hz	1	f
213.2	D	J_{HF}= 43Hz		

No.11 TRIS-(1,1,1,2,3,3-HEXAFLUOROPROPYL-4-PENTYL)AMINE (53)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.35	S		3	e
3.58	S		1	d
3.97	S			
4.60	D of M	J_{HF}= 39Hz	1	b
^{19}F:-				
75.2	S		3	a
109.0 - 126.0	Unassigned		2	c
211.0	D	J_{HF}= 47HZ	1	b



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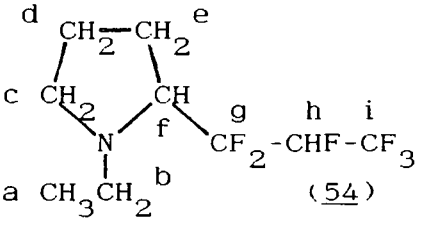


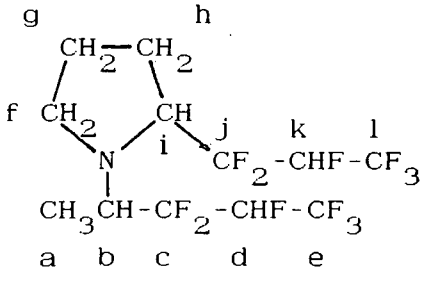
(54)

No.12 N-ETHYL-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (54)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.10	T	J = 7Hz	3	a
1.90	S		4	d,e
2.60	S		4	b,c
3.10	M		1	f
5.30	D of M	J_{HF}= 44Hz	1	h
^{19}F:-				
81.3	S		3	i
109.9	AB	J_{AB}=282Hz	2	g
120.1				
121.3	AB	J_{AB}=282Hz		
130.0				
211.5	D of M	J_{HF}= 41Hz	1	h
213.9	D of M	J_{HF}= 41Hz		

No.13 N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (55)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
1.15	D J = 6HZ	3	a
1.80	S	4	g,h
2.80 - 3.50	Unassigned	4	b,f,i
4.95	D of M J_{HF}= 44Hz	2	d,k
^{19}F:-			
76.3	S	6	e,l
119.5	S		
119.5, 126.9	AB J_{AB}=282Hz	4	c,j
213.8	M	2	d,k



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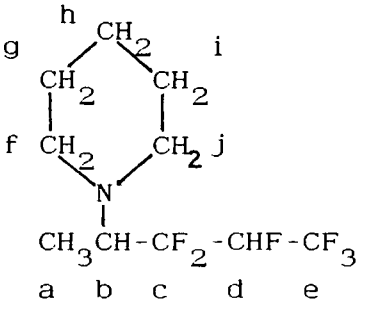


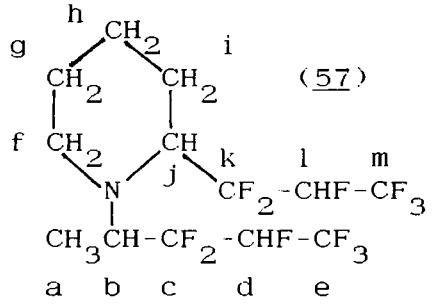
(56)

No.14 N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)PIPERIDINE (56)

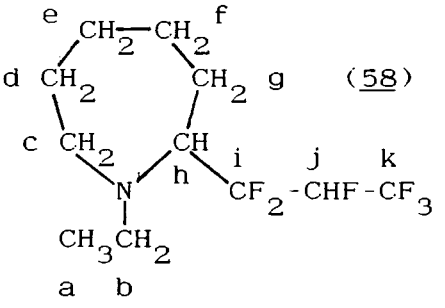
SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
0.92	D J = 7Hz	3	a
1.30	S	6	g,h,i
2.30	S	4	f,j
2.80	S	1	b
5.05	D J_{HF}= 46Hz	1	d
^{19}F:-			
76.4	Q of D J_Q = 12Hz, J_D = 7Hz	3	e
118.9	M		
121.3, 127.9	AB J_{AB}=269Hz	2	c
214.4	D J_{HF}= 41Hz	1	d
221.8	D J_{HF}= 43Hz		

No.15 N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)-2-(2H-HEXAFLUOROPROPYL)PIPERIDINE (57)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
1.23	S	3	a
1.46	S	6	g,h,i
2.80	S	2	f
3.08	S	1	b
3.38	S	1	j
4.76	D J_{HF}= 41Hz	2	d,l
^{19}F:-			
76.6	S	6	e,m
117.3	S		
119.3 }	AB J_{AB}=267Hz	4	c,k
125.1 }			
213.2	D J_{HF}= 43Hz		
215.2	D J_{HF}= 43Hz	2	d,l



(57)



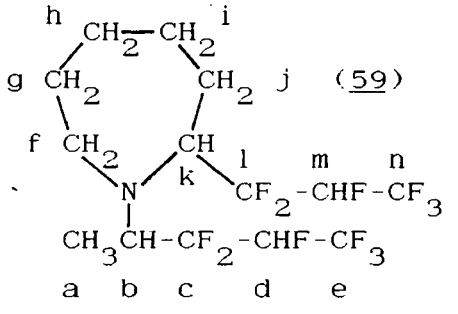
(58)

No.16 N-ETHYL-2-(2H-HEXAFLUOROPROPYL)HEXAMETHYLENEIMINE (58)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
0.90	T J = 7Hz	3	a
1.50	S	8	d,e,f,g
2.44	S	4	b,c
2.82	S	1	h
5.12	D of M J_{HF}= 45Hz	1	j
^{19}F:-			
75.7	S	3	k
116.0 }	AB J_{AB}=273Hz		
123.1 }		2	i
122.1 }	AB J_{AB}=282Hz		
130.5 }			
213.3	D J_{HF}= 44Hz		
215.6	D J_{HF}= 44Hz	1	j

No.17 N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)-2-(2H-HEXAFLUOROPROPYL)HEXAMETHYLENEIMINE (59)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
1.40	D, J = 7Hz	3	a
1.65	S	8	g,h,i,j
3.00	S	2	f
3.50	S	2	b,k
4.88	D, J_{HF}= 42Hz	2	d,m
^{19}F:-			
74.8	S	6	e,n
120.6	S		
115.1, 122.1	AB, J_{AB}=282Hz	4	c,l
119.2, 128.9	AB, J_{AB}=282Hz		
211.2	D, J_{HF}= 41Hz	2	d,m
212.9	D, J_{HF}= 47Hz		



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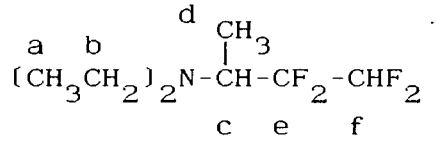


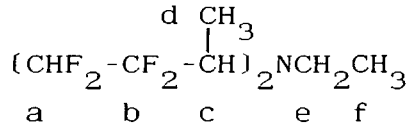
(66)

No.18 (1,1,2,2-TETRAFLUORO-3-BUTYL)DIETHYLAMINE (66)

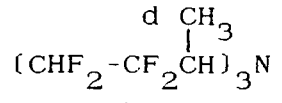
SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
1.05	T, J_{ab}= 7Hz	6	a
1.20	D, J_{cd}= 7Hz	3	d
2.53	Q, J_{ab}= 6Hz	4	b
3.47	M	1	c
6.27	T of D, J_{HF}= 54Hz, J_{D}= 9Hz	1	f
^{19}F:-			
125.9, 131.7	AB, J_{AB}=280Hz	2	e
136.6, 147.9	AB of D, J_{AB}=286Hz, J_{HF}= 53Hz	2	f

No.19 BIS-(1,1,2,2-TETRAFLUORO-3-BUTYL)ETHYLAMINE (67)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.20	T	J_{fg} = 6Hz	3	f
2.25	D	J_{cd} = 6Hz	3	d
2.65	M		2	e
3.35	M		1	c
5.93	T	J_{HF} = 54Hz	1	a
^{19}F:-				
126.3	S		2	b
135.3 } 143.6 }	AB of D	J_{AB} = 301Hz, J_{HF} = 53Hz	2	a



(67)



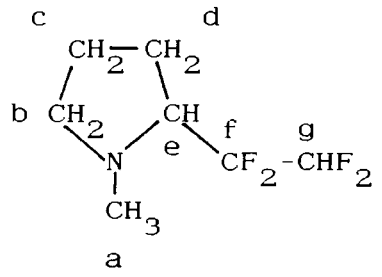
(68)

No.20 TRIS-(1,1,2,2-TETRAFLUORO-3-BUTYL)AMINE (68)

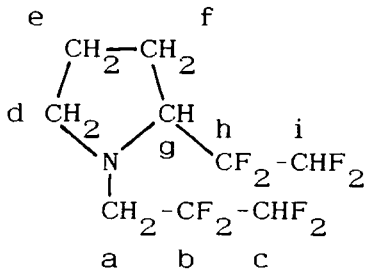
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.30	D	J_{cd} = 10Hz	3	d
3.45	Q	J_{cd} = 8Hz	1	c
3.90	Q			
5.65	T of D	J_{HF} = 54Hz, J_{ab} = 11Hz, J_{HF} = 54Hz	1	a
5.80	D			
^{19}F:-				
111.0 - 141.0	Unassigned			

No.21 N-METHYL-2-(2H-TETRAFLUOROETHYL)PYRROLIDINE (69)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.60	S		4	c,d
2.17	S		3	a
2.72	S		3	b,e
5.77	T of T	J_{HF}= 55Hz J_{fg}= 10Hz	1	g
^{19}F:-				
123.1 131.3	AB	J_{AB}=263Hz	2	f
141.4	D	J_{HF}= 51Hz	2	g



(69)



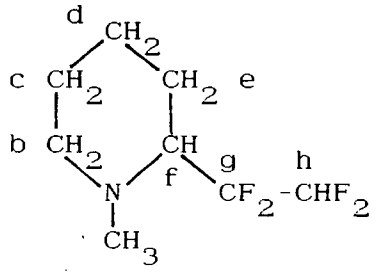
(70)

No.22 N-(2,2,3,3-TETRAFLUOROPROPYL)-2-(2H-TETRAFLUOROETHYL)PYRROLIDINE (70)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.80	M		4	e,f
3.00	M		5	a,d,g
5.70	T	J_{HF}= 54Hz	2	c,i
^{19}F:-				
120.9	S			
122.7	M		4	b,h
127.1	M			
139.0	D			
140.5	D	J_{HF}= 51Hz	4	c,i
141.3	D			

No.23 N-METHYL-2-(2H-TETRAFLUOROETHYL)PIPERIDINE (71)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.40	S		6	c,d,e
2.22	S		3	a
2.60	S		2	b
2.80	S		1	f
5.80	T of T	J_{HF}= 54Hz J_{gh}= 6Hz	1	h
^{19}F:-				
118.3 125.0	AB	J_{AB}=271Hz	2	g
140.7 141.0 141.1 142.5	D D D D	J_{HF}= 51Hz	2	h



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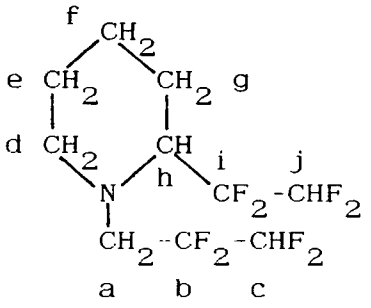


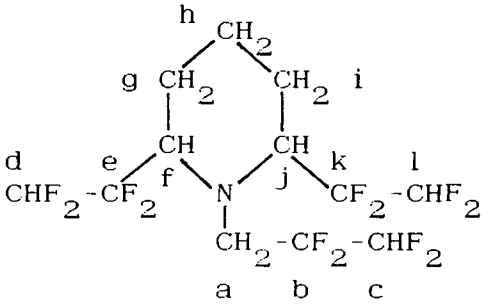
(72)

No.24 N-(2,2,3,3-TETRAFLUOROPROPYL)-2-(2H-TETRAFLUOROETHYL)PIPERIDINE (72)

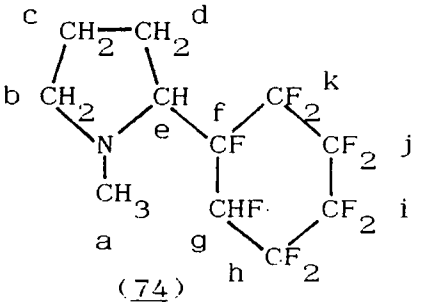
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.67	S		6	e,f,g
2.83	S		2	d
3.08	S		2	a
3.30	S		1	h
5.80	T	J_{HF}= 54Hz	2	c,j
^{19}F:-				
122.1 124.6 125.8	S S S		4	b,i
139.0 - 144.0			4	c,j

No.25 N-(2,2,3,3-TETRAFLUOROPROPYL-2,6-BIS-(2H-TETRAFLUOROETHYL)PIPERIDINE (73)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
1.12	S	6	g,h,i
3.38	M	2	a
3.60	M	2	f,j
5.13	T J_{HF}= 54Hz	3	c,d,l
^{19}F:-			
112.0 - 133.0	M	6	b,e,k
137.0 - 143.0	M	6	c,d,l



(73)



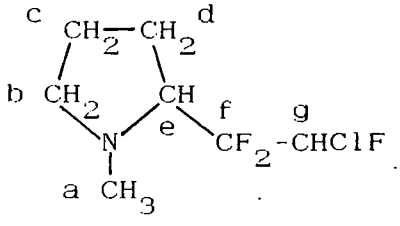
(74)

No.26 N-METHYL-2-(2H-PERFLUOROCYCLOHEXYL)PYRROLIDINE (74)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
1.80	S	4	c,d
2.47	S	3	a
3.00	M	3	b,e
5.45	D J_{HF}= 43Hz	1	g
^{19}F:-			
115.5 - 149.8		8	h,i,j,k
177.6			
188.5			
196.3		2	f,g
207.9			
212.7			
229.8			

No.27 N-METHYL-2-(2H,2-CHLOROTRIFLUOROETHYL)PYRROLIDINE (75)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.92	S		4	c,d
2.50	S		3	a
3.07	S		3	b,e
6.43	D	J_{HF}= 48Hz	1	g
^{19}F:-				
114.3, 123.9	AB	J_{AB}=269Hz	2	f
121.0, 126.1	AB	J_{AB}=263Hz		
152.0	D of T	J_{HF}= 47Hz, J_{fg}= 12Hz	1	g
155.7	D of T	J_{HF}= 47Hz, J_{fg}= 12Hz		



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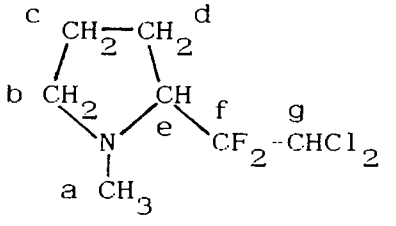


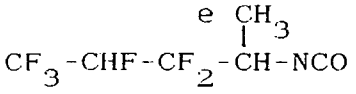
(76)

No.28 N-METHYL-2-(2H,2,2-DICHLORODIFLUOROETHYL)PYRROLIDINE (76)

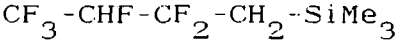
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.95	M		4	c,d
2.50	S		3	a
3.10	M		3	b,e
6.10	T	J_{fg}= 9Hz	1	g
^{19}F:-				
117.7	D of D	J_{ef}= 13Hz, J_{fg}= 9Hz	2	f

No.29 (1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)ISOCYANATE (77)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.18	D	J_{de} = 6Hz	3	e
3.72	M		1	d
4.74	D of M	J_{HF} = 43Hz	1	b
^{19}F:-				
77.3	S		3	a
123.7	M			
125.7 }	AB	J_{AB}=273Hz	2	c
131.6 }				
215.2	D	J_{HF} = 42Hz	1	b
216.8	D	J_{HF} = 45Hz		



(77)



(78)

No.30 (1H,1H,3H-HEXAFLUOROBUTYL)TRIMETHYLSILANE (78)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
0.20	S		9	e
1.16 }	AB	J_{AB} = 18Hz	2	d
1.66 }				
4.57	D of M	J_{HF} = 45Hz	1	b
^{19}F:-				
76.1	S		3	a
93.6 }	AB	J_{AB}=263Hz	2	c
100.2 }				
209.0	D of Q	J_{HF} = 43Hz J_{ab} = 10Hz	1	b

No.31 BIS-(1H,1H,3H-HEXAFLUOROBUTYL)DIMETHYLSILANE (79)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
0.32	S		6	e
0.52	S			
1.47	AB	J_{AB}= 16Hz	2	d
1.99				
4.71	D of Q	J_{HF}= 45Hz J_{ab}= 7Hz	1	b
^{19}F:-				
76.2	S		3	a
93.4	AB	J_{AB}=263Hz	2	c
100.4				
209.4	D of Q	J_{HF}= 42Hz J_{ab}= 10Hz	1	b

$[CF_3-CHF-CF_2-CH_2]_2SiMe_2$ (79)

a b c d e

$CF_3-CHF-CF_2-CH_2-SiMe_2OSiMe_3$ (80)

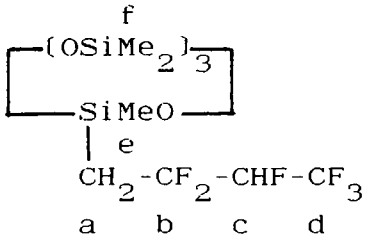
a b c d e f

No.32 (1H,1H,3H-HEXAFLUOROBUTYL)PENTAMETHYLDISILOXANE (80)

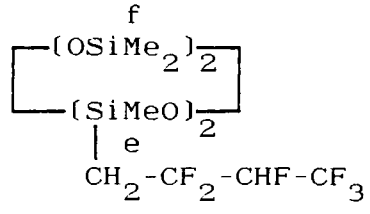
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
-0.18	S		9	f
-0.07	S		6	e
0.63	AB	J_{AB}= 21Hz	2	d
1.35				
4.29	D	J_{HF}= 44Hz	1	b
^{19}F:-				
76.3	S		3	a
97.4	M		2	c
209.9	D of Q	J_{HF}= 42Hz J_{ab}= 10Hz	1	b

No.33 (1H,1H,3H-HEXAFLUOROBUTYL)HEPTAMETHYLCYCLOTETRASILOXANE (81)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
0.25	S		18	f
0.40	S		3	e
1.42, 2.13	AB	J_{AB} = 21Hz	2	a
5.20	D of M	J_{HF} = 44Hz	1	c
^{19}F:-				
75.3	Q of D	J_Q = 11Hz, J_D = 6Hz	3	d
96.9	M		2	b
209.3	D of Q	J_{HF} = 44Hz, J_{cd} = 10Hz	1	c



(81)



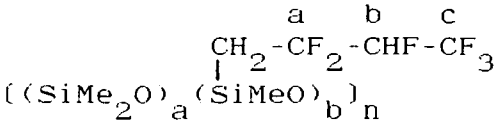
(82)

No.34 BIS-(1H,1H,3H-HEXAFLUOROBUTYL)HEXAMETHYLCYCLOTETRASILOXANE (82)

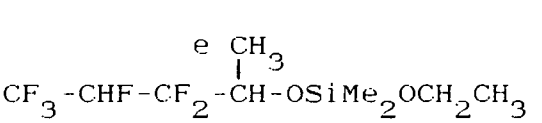
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
0.03	S		12	f
0.17	S		6	e
1.21, 1.58	AB	J_{AB} = 20Hz	2	a
4.52	D of M	J_{HF} = 44Hz	1	c
^{19}F:-				
78.4	M		3	d
100.0	M		2	b
209.3	D of M	J_{HF} = 44Hz	1	c

No.35 FLUORINATED SILICONE OIL (83)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
75.2	S	3	c
122.1	M	2	a
125.3	M		
213.5	M	1	b



(83)



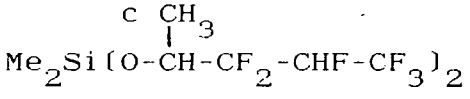
(84)

No.36 (1,1,1,2,3,3-HEXAFLUORO-4-PENTYLOXY)ETHOXYDIMETHYL SILANE (84)

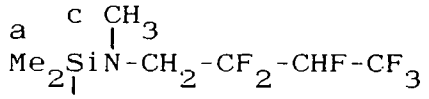
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
0.05	S		6	f
1.13	T	J_{gh}= 7Hz	3	h
1.30	D	J_{de}= 7Hz	3	e
3.69	Q	J_{gh}= 7Hz	2	g
4.20	M		1	d
5.10	D of M	J_{HF}= 44Hz	1	b
^{19}F:-				
75.0	M		3	a
118.8	AB	J_{AB}=263Hz	2	c
127.1				
125.8	AB	J_{AB}=263Hz		
132.8				
214.7	M		1	b

No.37 BIS-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYLOXY)DIMETHYL SILANE (85)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
0.18	S		6	a
1.30	D	J_{bc}= 6Hz	6	c
4.20	M		2	b
4.88	D of M	J_{HF}= 44Hz	2	e
^{19}F:-				
75.3	M		6	f
119.2, 127.1	AB	J_{AB}=273Hz	4	d
125.9, 132.6	AB	J_{AB}=263Hz		
214.9	D	J_{HF}= 41Hz	2	e



(85)



(86)

No.38 (1H,1H,3H-HEXAFLUOROBUTYLMETHYLAMINO)DIMETHYLAMINO-DIMETHYLSILANE (86)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
-0.03	S		6	a
2.33	S		6	b
2.39	S		3	c
3.00	M		2	d
4.63	D of M	J_{HF}= 42Hz	1	f
^{19}F:-				
75.2	M		3	g
111.6, 118.2	AB	J_{AB}=263Hz	2	e
211.8	D of M	J_{HF}= 41Hz	1	f

No.39 1H,3H-PENTAFLUOROBUTENYLTRIMETHYLSILANE (87)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
0.12	S		9	e
4.75	D of D	J_{cd} = 42Hz J_{bd} = 4Hz	1	d
4.93	D of M	J_{HF} = 43Hz	1	b
^{19}F:-				
79.7	P	J = 7Hz	3	a
115.0	M		1	c
203.8	D of D of Q	J_{HF} = 42Hz J_{bc} = 23Hz J_{ab} = 13Hz	1	b

CF_3-CHF-CF=CH-$SiMe_3$

a b c d e

(87)

a CH_3

CH_3-CH-CF_2-CHF-CF_3

b c d e f

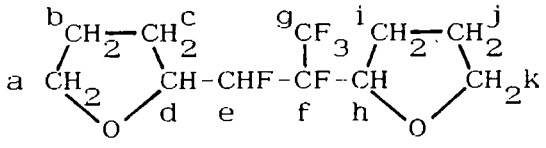
(89)

No.40 1,1,1,2,3,3-HEXAFLUORO-4-METHYLPENTANE (89)

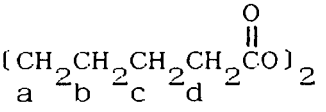
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
0.73	D	J = 7Hz	6	a,b
1.87	M		1	c
4.43	D of M	J_{HF} = 44Hz	1	e
^{19}F:-				
77.0	M		3	f
118.6 124.4	AB	J_{AB}=268Hz	2	d
213.3	D of M	J_{HF} = 42Hz	1	e

No.41 1,2-BIS-(2-TETRAHYDROFURYL)-1H-PENTAFLUOROPROPANE (91)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^1H:-			
1.90	S	8	b,c,i,j
3.80	S	4	a,k
4.30	M	2	d,h
4.70	D of M	1	e
^{19}F:-			
73.4	M	3	g
189.9	M	1	f
207.4	D of M	1	e



(91)



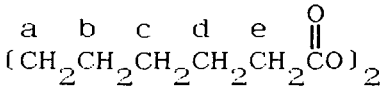
(95)

No.42 δ-VALEROLACTONE DIMER (95)

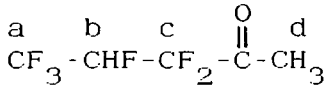
SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^1H:-			
1.72	M	4	b,c
2.36	M	2	d
4.09	M	2	a

No.43 ε-CAPROLACTONE DIMER (96)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
1.50	M	6	b,c,d
2.33	M	2	e
4.02	M	2	a



(96)



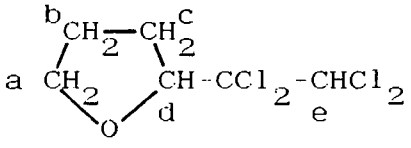
(97)

No.44 1,1,1,2,3,3-HEXAFLUORO-4-PENTANONE (97)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
2.45	S	3	d
3.28	D of M J_{HF}= 44Hz	1	b
^{19}F:-			
74.9	M	3	a
115.8, 123.9	AB J_{AB}=292Hz	2	c
216.8	D of M J_{HF}= 41Hz	1	b

No.45 2-(2H-TETRACHLOROETHYL)OXOLANE (101)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
2.27	M		4	b,c
4.11	T	J_{ab}= 6Hz	2	a
4.77	T	J_{cd}= 6Hz	1	d
6.43	S		1	e



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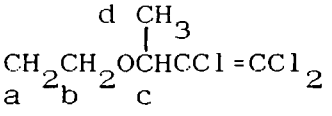


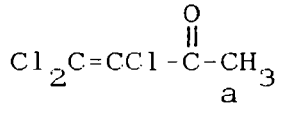
(102)

No.46 1,1,2-TRICHLORO-3-ETHOXYBUTENE (102)

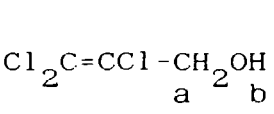
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.22	T	J_{ab}= 7Hz	3	a
1.33	D	J_{cd}= 7Hz	3	d
3.39	Q	J_{ab}= 7Hz	2	b
4.71	Q	J_{cd}= 6Hz	1	c

No.47 1,1,2-TRICHLOROBUTEN-3-ONE (103)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
2.44	S	3	a



(103)



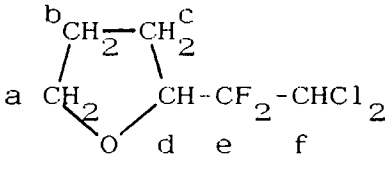
(104)

No.48 1,1,2-TRICHLOROBUTEN-3-OL (104)

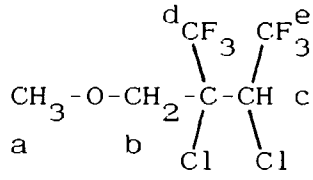
SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
5.03	S	2	a
5.66	S	1	b

No.49 2-(2H,2,2-DICHLORODIFLUOROETHYL)OXOLANE (99)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
2.10	M		4	b,c
3.88	T	J_{ab} = 6Hz	2	a
4.45	D of D of T	J_{de} = 20Hz J_{de} = 6Hz J_{cd} = 5Hz	1	d
6.08	D of D	J_{de} = 16Hz J_{ef} = 4Hz	1	f
^{19}F:-				
119.8 125.9	AB of D of D	J_{AB} = 250Hz J_{de} = 15Hz J_{de} = 5Hz	2	e



(99)



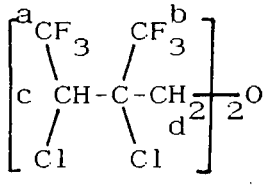
(105)

No.50 2,3-DICHLORO-1,1,1,4,4,4-HEXAFLUORO-3-METHOXYMETHYL-BUTANE (105)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
3.25	S		3	a
3.65	S		2	b
4.65 4.75	Q Q	J_{ce} = 6Hz	1	c
^{19}F:-				
69.0 72.0	D of Q D of Q	J_{ce} = 6Hz J_{de} = 3Hz	3	e
69.4 70.6	Q Q	J_{de} = 11Hz	3	d

No.51 BIS-(2,3-DICHLORO-4,4,4-TRIFLUORO-2-TRIFLUOROMETHYL-BUTYL)ETHER (106)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
4.10	S		2	d
4.82	S		1	c
^{19}F:-				
68.4	S	Unassigned		
70.1	S			
71.5	S			



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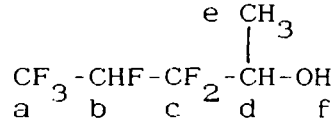


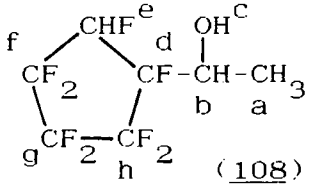
(107)

No.52 1,1,1,2,3,3-HEXAFLUORO-4-PENTANOL (107)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.18	D	J_{de}= 7Hz	3	e
3.42	Q	J_{de}= 6Hz	1	d
3.78	Q			
3.95	S		1	f
4.82	D of M	J_{HF}= 44Hz	1	b
^{19}F:-				
77.1	M		3	a
123.2	AB	J_{AB}=263Hz	2	c
128.9				
126.9	AB	J_{AB}=273Hz		
134.3				
215.6	D of M	J_{HF}= 43Hz	1	b
217.4	D of M			

No.53 1-(2H-OCTAFLUOROCYCLOPENTYL)ETHANOL (108)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.50	S		3	a
3.40	S		1	c
4.30	M		1	b
5.00	M		1	e
^{19}F:-				
114.5 - 137.1	Unassigned		6	f,g,h
192.0	M			
196.0	M		1	d
197.8	M			
199.4	M			
209.4	D			
211.8	D			
221.2	D	J_{HF}= 47Hz	1	e
226.5	D			



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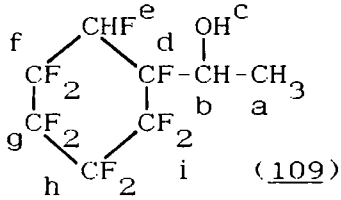


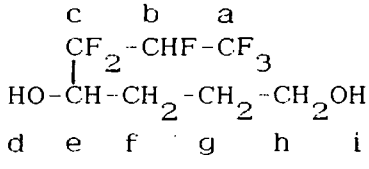
(109)

No.54 1-(2H-DECAFLUOROCYCLOHEXYL)ETHANOL (109)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.53	S		3	a
3.36	S		1	c
4.50	M		1	b
5.10	D of M	J_{HF}= 42Hz	1	e
^{19}F:-				
115.0 - 149.0	Unassigned		8	f,g,h,i
193.7	M		1	d
200.0	M			
210.4	D			
230.9	D	J_{HF}= 44Hz	1	e
233.4	D			

No.55 1,1,1,2,3,3-HEXAFLUOROHEPTANE-4,7-DIOL (110)

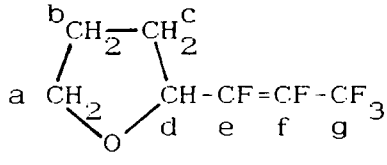
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.63	M		2	g
1.73	M		2	f
3.60	M		3	e,h
4.90	S		2	d,i
5.40	D of M	J_{HF}= 44Hz	1	b
^{19}F:-				
75.2	M		3	a
119.6 }	AB	J_{AB}=263Hz }	2	c
126.1 }		}		
124.8 }	AB	J_{AB}=263Hz }		
131.1 }		}		
213.8	D	J_{HF}= 39Hz	1	b
215.9	D	J_{HF}= 40Hz		



(110)

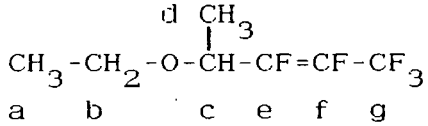
No.56 2-(PENTAFLUOROPROPENYL)OXOLANE (90)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
2.10	M		2	b
2.17	M		2	c
3.89	T	J_{ab} = 6Hz	2	a
4.78	D	J_{de} = 29Hz	1	d
^{19}F:- 141				
CIS Isomer		CIS/TRANS = 1.86		
66.5	D of D	J_{fg} = 11Hz	3	g
		J_{eg} = 9Hz		
141.0	D of Q	J_{de} = 28Hz	1	e
		J_{eg} = 9Hz		
156.8	Q	J_{fg} = 11HZ	1	f
TRANS Isomer				
69.0	D of D	J_{eg} = 23Hz	3	g
		J_{fg} = 10Hz		
156.8	D of D	J_{ef} = 132Hz	1	e
	of Q	J_{de} = 26Hz		
		J_{eg} = 21Hz		
174.4	D of Q	J_{ef} = 132HZ	1	f
	of D	J_{fg} = 11Hz		
		J_{df} = 5Hz		



No.57 1,1,1,2,3,3-PENTAFLUORO-4-ETHOXY-2-PENTENE (119)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
0.80	T	J_{ab}= 7Hz	3	a
1.00	D	J_{cd}= 7Hz	3	d
3.04	Q	J_{ab}= 7Hz	2	b
3.92	D of Q	J_{ce}= 27Hz J_{cd}= 7Hz	1	c
^{19}F:-				
CIS Isomer		CIS/TRANS = 9.0		
69.4	D of D	J_{fg}= 11Hz J_{eg}= 9Hz	3	g
143.2	D of Q	J_{ce}= 26Hz J_{eg}= 8Hz	1	e
159.7	Q	J_{fg}= 12HZ	1	f
TRANS Isomer				
72.0	D of D	J_{eg}= 23Hz J_{fg}= 11Hz	3	g



(119)

No.58 1,1,1,2,3,3-PENTAFLUORO-4-METHOXY-2-BUTENE (92)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
3.42	S		3	a
4.18	D	J_{bc} = 23Hz	2	b
^{19}F:-				
CIS Isomer		CIS/TRANS = 3.9		
68.1	D of D	J_{de} = 10Hz	3	e
		J_{ce} = 10Hz		
127.5	M		1	c
155.0	Q	J_{de} = 10HZ	1	d
TRANS Isomer				
69.9	D of D	J_{de} = 21Hz	3	e
		J_{ce} = 10Hz		
146.3	D of Q	J_{cd} = 134Hz	1	c
		J_{ce} = 22Hz		
171.7	D	J_{cd} = 134Hz	1	d

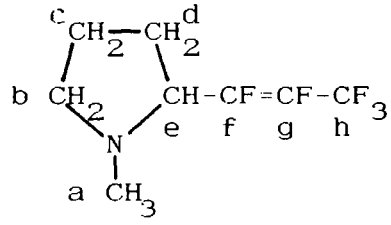
CH_3-O-CH_2-CF=CF-CF_3

a b c d e

(92)

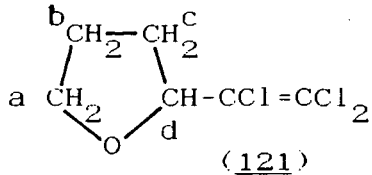
No.59 N-METHYL-2-(PENTAFLUOROPROPENYL)PYRROLIDINE (120)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.98	M		4	c,d
2.37	S		3	a
3.12	M		2	b
3.37	D	J_{ef}= 23Hz	1	e
^{19}F:-				
CIS Isomer		CIS/TRANS = 5.1		
65.7	D of D	J_{gh}= 10Hz	3	h
		J_{fh}= 10Hz		
137.2	D of Q	J_{ef}= 28Hz	1	f
		J_{fh}= 8Hz		
156.6	Q	J_{gh}= 11HZ	1	g
TRANS Isomer				
68.9	D of D	J_{gh}= 22Hz	3	h
		J_{fh}= 10Hz		
154.2	D of M	J_{fg}=132Hz	1	f
176.3	D	J_{fg}=132HZ	1	g

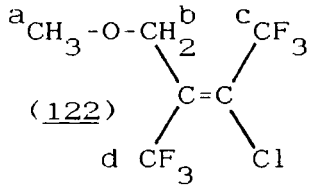


No.60 2-(TRICHLOROETHENYL)OXOLANE (121)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
2.10	M	4	b,c
3.90	M	2	a
5.10	M	1	d



(121)



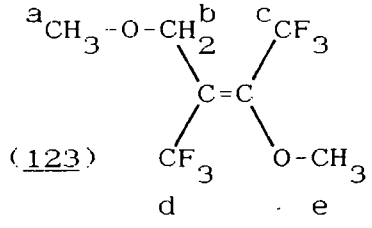
(122)

No.61 TRANS-2-CHLORO-1,1,1,4,4,4-HEXAFLUORO-3-METHOXYMETHYL-2-BUTENE (122)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
3.09	S	3	a
3.98	S	2	b
^{19}F:-			
62.5	S	3	c,d
65.5	S	3	

No.62 TRANS-1,1,1,4,4,4-HEXAFLUORO-2-METHOXY-3-METHOXY-METHYL-2-BUTENE (123)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^1H:-			
2.87	S	3	a
3.35	S	3	e
3.66	S	2	b
^{19}F:-			
63.0	S	6	c,d



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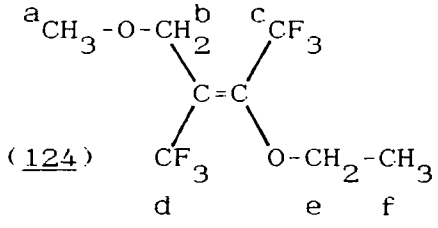


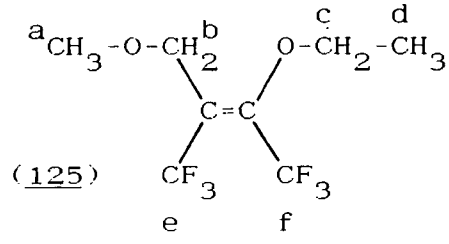
(124)

No.63 TRANS-1,1,1,4,4,4-HEXAFLUORO-2-ETHOXY-3-METHOXY-METHYL-2-BUTENE (124)

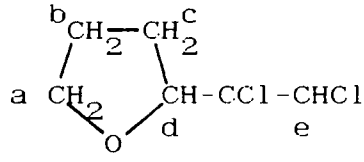
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
0.79	T	J_{ef}= 7Hz	3	f
2.93	S		3	a
3.49	Q	J_{ef}= 7Hz	2	e
3.72	M		2	b
^{19}F:-				
63.3	S		3	c,d
63.8	S		3	c,d

No.64 CIS-1,1,1,4,4,4-HEXAFLUORO-2-ETHOXY-3-METHOXY-METHYL-2-BUTENE (125)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
0.99	T	J_{cd}= 7Hz	3	d
2.97	S		3	a
3.66	Q	J_{cd}= 7Hz	2	c
3.82	S		2	b
^{19}F:-				
60.5	Q	J_{ef}= 13Hz	6	e,f
66.2	Q			



(125)



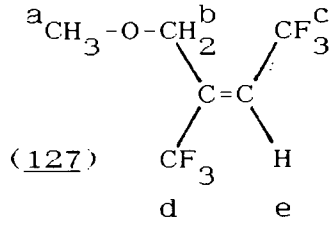
(126)

No.65 2-(1,2-DICHLOROETHENYL)OXOLANE (126)

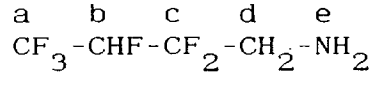
SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^1H:-			
2.00	M	4	b,c
3.90	M	2	a
4.50	M	1	d
6.60	S	1	e

No.66 1,1,1,4,4,4-HEXAFLUORO-2-METHOXYMETHYL-2-BUTENE (127)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
2.82	S	cis/trans	3	a
2.90	S			
3.56	S	cis/trans	2	b
3.72	S			
5.73	Q	J_{ce}= 8Hz	1	e
^{19}F:-				
CIS ISOMER		CIS/TRANS = 1.3		
60.8	Q of D	J_{cd}= 11Hz	3	c
		J_{ce}= 8Hz		
65.5	Q	J_{cd}= 11Hz	3	d
TRANS ISOMER				
61.3	D	J_{ce}= 8Hz	3	c
70.6	S		3	d



(127)



(129)

No.67 2,2,3,4,4,4-HEXAFLUOROBUTYLAMINE (129)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.16	S		2	e
2.92	T	J_{cd}= 15Hz	2	d
5.00	D of M	J_{HF}= 44Hz	1	b
^{19}F:-				
77.2	M		3	a
121.2	M		2	c
217.1	D of M	J_{HF}= 41Hz	1	b

No.68 (2,2,3,4,4,4-HEXAFLUOROBUTYL)METHYLAMINE (128)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.04	S		1	e
2.13	S		3	f
2.65	T	J_{cd} = 13Hz	2	d
4.82	D of M	J_{HF} = 43Hz	1	b
^{19}F:-				
77.9	M		3	a
119.9	M		2	c
217.6	D of M	J_{HF} = 45Hz	1	b

a b c d e f
CF_3-CHF-CF_2-CH_2-NH-CH_3

(128)

a b c d e f g
CF_3-CHF-CF_2-CH_2-NH-CH_2-CH_3

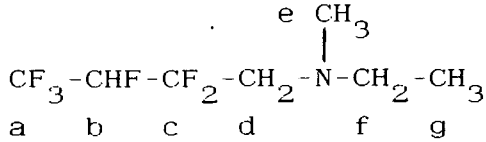
(131)

No.69 (2,2,3,4,4,4-HEXAFLUOROBUTYL)ETHYLAMINE (131)

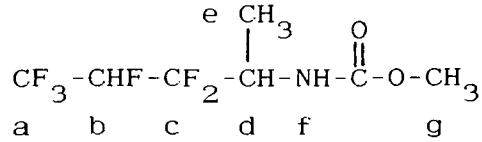
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
0.75	T	J_{fg} = 7Hz	3	g
1.92	M		1	e
2.30	Q	J_{fg} = 7Hz	2	f
3.15	M		2	d
5.29	D of M	J_{HF} = 41Hz	1	b
^{19}F:-				
76.7	M		3	a
119.5	M		2	c
216.4	M		1	b

No.70 (2,2,3,4,4,4-HEXAFLUOROBUTYL)ETHYLMETHYLAMINE (130)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
0.70	T	J_{fg}= 7Hz	3	g
2.00	S		3	e
2.22	Q	J_{fg}= 7Hz	2	f
2.67	M		2	d
4.85	D of M	J_{HF}= 43Hz	1	b
^{19}F:-				
76.4	M		3	a
118.1	M		2	c
215.6	D of M	J_{HF}= 41Hz	1	b



(130)



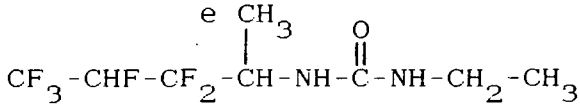
(132)

No.71 METHYL-N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)CARBAMATE (132)

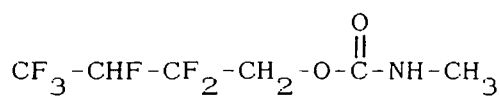
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.33	D	J_{de}= 7Hz	3	e
3.68	S		3	g
4.40	M		1	d
4.95	D of M	J_{HF}= 44Hz	1	b
5.58	M		1	f
^{19}F:-				
75.3	M		3	a
118.7, 125.6	AB	J_{AB}=277Hz	2	c
122.0, 128.8	AB	J_{AB}=273Hz		
212.3	D of M	J_{HF}= 42Hz	1	b
213.3	D of M	J_{HF}= 42Hz		

No.72 N-ETHYL-N'-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)UREA (133)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
1.18	T	J_{hi} = 7Hz	3	i
1.28	D	J_{de} = 7Hz	3	e
3.13	M		2	h
4.43	M		1	d
4.90	D of M		1	b
6.16	S		2	f,g
^{19}F:-				
75.3	M		3	a
118.7, 124.9	AB	J_{AB}=263Hz	2	c
122.2, 129.7	AB	J_{AB}=272Hz		
211.5	D of M	J_{HF}= .38Hz	1	b
213.5	D of M	J_{HF}= 41Hz		



(133)



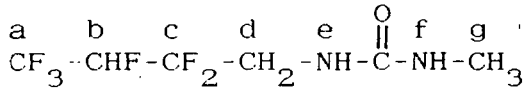
(134)

No.73 (1H,1H,3H-HEXAFLUOROBUTYL)-N-METHYLCARBAMATE (134)

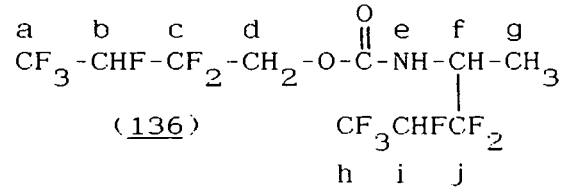
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^1H:-				
2.88	D	J_{ef} = 6Hz	3	f
4.53	T	J_{cd} = 15Hz	2	d
5.12	D of M	J_{HF} = 44Hz	1	b
5.83	M		1	e
^{19}F:-				
75.0	M		3	a
116.1, 122.7	AB	J_{AB}=282Hz	2	c
214.2	D of M	J_{HF}= 42Hz	1	b

No.74 N-METHYL-N'-(1H,1H,3H-HEXAFLUOROBUTYL)UREA (135)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
2.69	D	J_{fg}= 4Hz	3	g
3.72	M		2	d
4.87	D of M		1	b
5.95, 6.32	M, M		2	e,f
^{19}F:-				
75.3	M		3	a
116.1, 119.6	AB	J_{AB}=263Hz	2	c
114.9, 120.7	AB	J_{AB}=263Hz		
213.0	D of M	J_{HF}= 42Hz	1	b



(135)



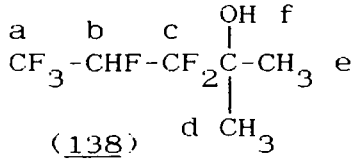
(136)

No.75 (1H,1H,3H-HEXAFLUOROBUTYL)-N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)CARBAMATE (136)

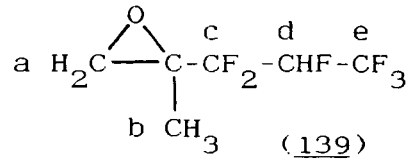
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.38	D	J_{fg}= 7Hz	3	g
4.50	M		1	f
4.52	T	J_{cd}= 12Hz	2	d
4.93	D of M		2	b,i
5.62, 5.80	S		1	e
^{19}F:-				
75.3	M		6	a,h
115.8, 122.2	AB		4	c,j
119.1, 124.9	AB			
121.5, 127.6	AB			
212.2	D of M	J_{HF}= 43Hz	2	b,i
213.9	D of M	J_{HF}= 43Hz		

No.76 1,1,1,2,3,3-HEXAFLUORO-4-METHYL-4-PENTANOL (138)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.10	S		6	d,e
3.19	S		1	f
4.83	D of M	J_{HF}= 44Hz	1	b
^{19}F:-				
76.5	M		3	a
123.6 }	AB	J_{AB}=282Hz	2	c
130.0 }				
209.3	D of M	J_{HF}= 43Hz	1	b



(138)



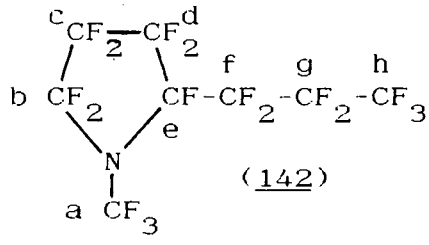
(139)

No.77 1,1,1,2,3,3-HEXAFLUORO-4-METHYL-4,5-EPOXYPENTANE (139)

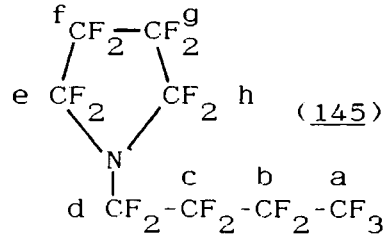
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
1.55	S		3	b
2.65 }	AB	J_{AB}= 5Hz	2	a
3.08 }				
4.97	D of M	J_{HF}= 44Hz	1	d
^{19}F:-				
75.1	M		3	e
116.3 }	AB	J_{AB}=282Hz	2	c
122.8 }				
118.6 }	AB	J_{AB}=282Hz		
126.1 }				
211.5	D of M	J_{HF}= 42Hz	1	d
212.1	D of M	J_{HF}= 42Hz		

No.78 PERFLUORO-N-METHYL-2-PROPYLPYRROLIDINE (142)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
54.1	M	3	a
82.7	T J_{gh}= 12Hz	3	h
88.6, 93.5	AB J_{AB}=179Hz	2	b
114.7 - 138.4		9	c,d,e,f,g



(142)



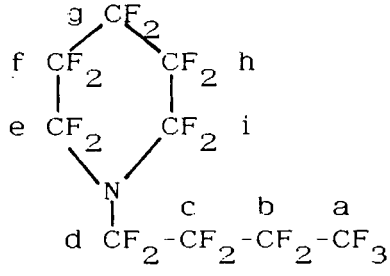
(145)

No.79 PERFLUORO-N-BUTYLPYRROLIDINE (145)

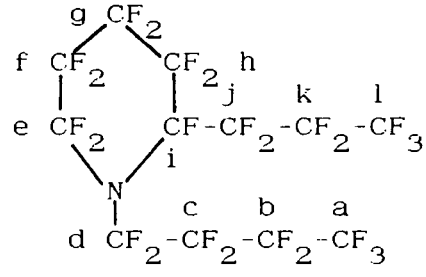
SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
84.2	T J_{ab}= 11Hz	3	a
93.2	T J_{ef}= 12Hz	4	e,h
94.7	M	2	d
125.8	M	2	c
129.2	M	2	b
136.2	S	4	f,g

No.80 PERFLUORO-N-BUTYLPIPERIDINE (146)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
84.1	T	J_{ab} = 11Hz 3	a
91.4	M	2	d
93.1	M	4	e,i
126.2	M	2	c
129.3	M	2	b
134.9	M	4	f,h
137.3	M	2	g



(146)



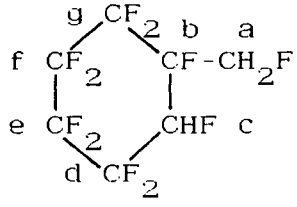
(147)

No.81 PERFLUORO-N-BUTYL-2-PROPYLPIPERIDINE (147)

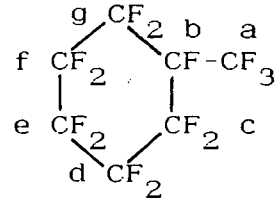
SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
73.0 - 77.0	Unassigned		
84.0	M	6	a,l
125.0	M	2	c
128.0	M	2	j
129.3	M	4	b,k
136.0 - 153.0	Unassigned		

No.82 (2H-DECAFLUOROCYCLOHEXYL)FLUOROMETHANE (148)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
5.50	D J_{HF}= 45Hz	2	a
5.80	D J_{HF}= 43Hz	1	c
^{19}F:-			
CIS ISOMER			
117.3 - 149.5		10	Unassigned
199.4	S	1	b
235.3	D J_{HF}= 37Hz	1	c
237.3	T J_{HF}= 45Hz	1	a
TRANS ISOMER			
117.3 - 149.5		10	Unassigned
189.3	S	1	b
211.9	D J_{HF}= 37Hz	1	c
252.5	T J_{HF}= 43Hz	1	a



(148)



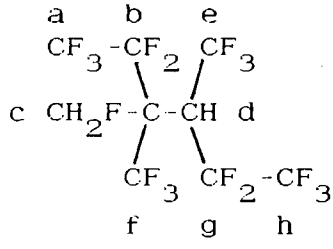
(149)

No.83 PERFLUOROMETHYLCYCLOHEXANE (149)

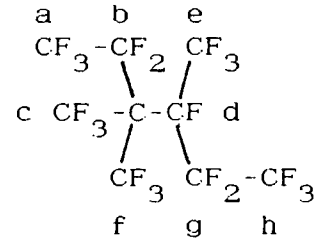
SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
72.1	M	3	a
119.3 - 148.0		10	Unassigned
191.3	M	1	b

No.84 3-FLUOROMETHYLPERFLUORO-4H,3,4-DIMETHYLHEXANE (150)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
4.04	Broad M	1	d
4.84	D J_{HF}= 44Hz	2	c
^{19}F:-			
58.7	M	3	e,f
63.1	M	3	
81.7	M	3	a,h
85.7	M	3	
109.6	M	2	b,g
111.2	M	2	
230.0	M	1	c



(150)



(151)

No.85 PERFLUORO-3,3,4-TRIMETHYLHEXANE (151)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
76.3	M	9	c,e,f
84.7	M	6	a,h
120.2	M	2	b,g
122.5	M	2	
187.9	M	1	d
189.8	M		

No.86 PERFLUORO-1H,1H,11H-UNDECANE (152)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
4.88	D of T	J_{HF} = 44Hz J^{ef} = 12Hz	2	f
6.56	T of T	J^{HF} = 52Hz J_{ab} = 5Hz	1	a
^{19}F:-				
121.7	S		12	c
123.1	S		4	b,d
129.4	S		2	e
138.2	D	J_{HF} = 51Hz	2	a
243.2	T	J_{HF} = 45Hz	1	f

a b c d e f
$HCF_2-CF_2-(CF_2)_6-CF_2-CF_2-CH_2F$

(152)

a b c d e f g
$CF_3-CF_2-CF_2-(CF_2)_5-CF_2-CF_2-CF_3$

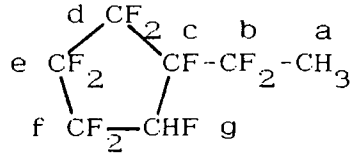
(153)

No.87 PERFLUOROUNDECANE (153)

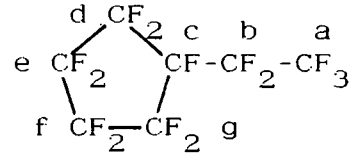
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-				
118.2	T	J_{ab} = 9Hz	6	a,g
122.2	S		10	d
123.0	S		4	c,e
126.7	S		4	b,f

No.88 1-(2H-OCTAFLUOROCYCLOPENTYL)-1,1-DIFLUOROETHANE (154)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
1.60	T	J_{HF}= 20Hz 3	a
5.00	Broad	1	g
^{19}F:-			
103.6	M	2	b
118.0 - 137.5		6	d,e,f
195.3	M	1	c
227.2	D	J_{HF}= 42Hz 1	g



(154)



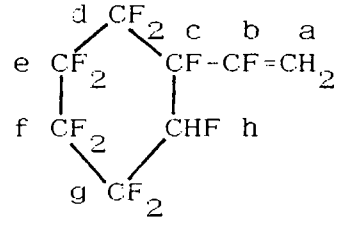
(155)

No.89 PERFLUOROETHYLCYCLOPENTANE (155)

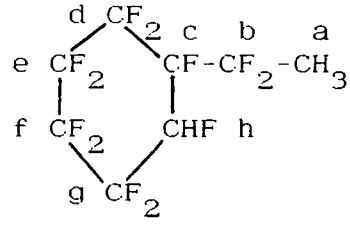
SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
85.0	M	3	a
122.8 - 138.3		6	b,d,e,f,g
189.3	M	1	c

No.90 1-(2H-DECAFLUOROCYCLOHEXYL)-1-FLUOROETHENE (156)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
5.13	D of T	J_{ab}= 8Hz, J_{aa}= 4Hz	2	a
5.64	D of T	J_{ab}= 23Hz, J_{aa}= 4Hz		
5.30	Broad M		1	h
^{19}F:-				
116.3 - 150.8			9	b,d,e,f,g
191.4	M		1	c
233.3	D	J_{HF}= 41Hz	1	h



(156)



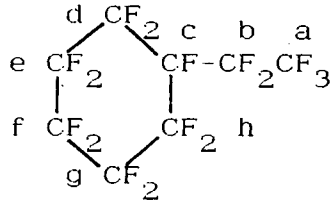
(157)

No.91 1-(2H-DECAFLUOROCYCLOHEXYL)-1,1-DIFLUOROETHANE (157)

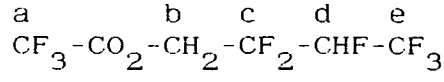
SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
2.12	T	J_{ab}= 20Hz	3	a
5.50	D of M	J_{HF}= 43Hz	1	h
^{19}F:-				
100.9	M		2	b
123.7 - 152.0			8	b,c,d,e
198.0	M		1	c
223.7	D	J_{HF}= 38Hz	1	h

No.92 PERFLUOROETHYLCYCLOHEXANE (158)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
85.2	Q	J_{ab} = 16Hz 3	a
120.0	M	2	b
119.7 - 149.0		8	d,e,f,g
189.5	M	1	c



(158)



(159)

No.93 1H,1H,3H-HEXAFLUOROBUTYLTRIFLUOROACETATE (159)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-			
4.68	T	J_{bc} = 12Hz 2	b
4.94	D of M	J_{HF} = 43Hz 1	d
^{19}F:-			
74.6	M	3	e
75.2	S	3	a
113.5 } 120.9 }	AB	J_{AB}=282Hz 2	c
212.9	D of M	J_{HF} = 42Hz 1	d

No.94 PERFLUOROETHOXY-1H,1H,3H-BUTANE (160)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{1}H:-				
4.29	T	J_{cd}= 10Hz	2	c
4.87	M		1	e
^{19}F:-				
75.3	M		3	f
87.0	S		3	a
92.9	S		2	b
116.1 }	AB	J_{AB}=282Hz	2	d
123.6 }				
214.3	M		1	e

a b c d e f
CF_3-CF_2-O-CH_2-CF_2-CHF-CF_3

(160)

a b c d e f
CF_3-CF_2-O-CF_2-CF_2-CF_2-CF_3

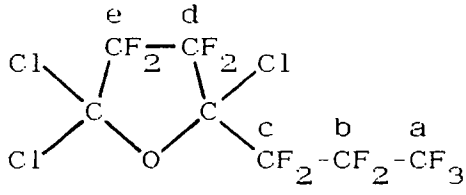
(162)

No.95 PERFLUOROETHOXYBUTANE (162)

SHIFT (PPM)	FINE STRUCTURE		RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-				
85.5	M }		6	a,f
91.2	M }			
87.1	M }		4	b,c
92.2	M }			
130.2	M		4	d,e

No.96 2,5,5-TRICHLOROPERFLUORO-2-PROPYLOXOLANE (163)

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
83.0	T	J_{ab}= 11Hz 3	a
109.0 124.5	AB	J_{AB}=245Hz 2	e
112.7 121.7	AB	J_{AB}=230Hz 2	d
116.3	D	J_{bc}= 14Hz 2	c
122.3	M	2	b



(163)

a b c d e
CF_3-CF=CF-CF_2-CF_3

No.97 PERFLUORO-2-PENTENE

SHIFT (PPM)	FINE STRUCTURE	RELATIVE INTENSITY	ASSIGNMENT
^{19}F:-			
72.9	M	3	a
88.4	M	3	e
125.0	M	2	d
161.1	M	2	b,c

APPENDIX II

INFRA-RED SPECTRA

1 N-Methyl-6-(2H-hexafluoropropyl)-2-piperidone (38).

2 N-Methyl-7-(2H-hexafluoropropyl)-ϵ-caprolactam (39).

3 N-Acetyl-2-(2H-hexafluoropropyl)pyrrolidine (40).

4 N-Formyl-2-(2H-hexafluoropropyl)pyrrolidine (44).

5 N-Formyl-2-(2H-hexafluoropropyl)piperidine (45).

6 N-(1H,1H,3H-hexafluorobutyl)acetamide (46).

7 5-(2H-Hexafluoropropyl)-2-pyrrolidone (47).

8 N-Methyl-2-(2H-hexafluoropropyl)pyrrolidine (48).

9 Ethylidine-1,1,1,2,3,3-hexafluoro-4-pentylimine (51).

10 Bis-(1,1,1,2,3,3-hexafluoro-4-pentyl)ethylamine (52).

11 Tris-(1,1,1,2,3,3-hexafluoro-4-pentyl)amine (53).

12 N-Ethyl-2-(2H-hexafluoropropyl)pyrrolidine (54).

13 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)-2-
(2H-hexafluoropropyl)pyrrolidine (55).

14 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)piperidine (56).

15 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)-2-
(2H-hexafluoropropyl)piperidine (57).

16 N-Ethyl-2-(2H-hexafluoropropyl)hexamethyleneimine (58).

17 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)-2-
(2H-hexafluoropropyl)hexamethyleneimine (59).

18 (1,1,2,2-Tetrafluoro-3-butyl)diethylamine (66).

19 Bis-(1,1,2,2-tetrafluoro-3-butyl)ethylamine (67).

20 Tris-(1,1,2,2-tetrafluoro-3-butyl)amine (68).

21 N-Methyl-2-(2H-tetrafluoroethyl)pyrrolidine (69).

22 N-(2,2,3,3-tetrafluoropropyl)-2-(2H-tetrafluoroethyl)pyrrolidine (70).

23 N-Methyl-2-(2H-tetrafluoroethyl)piperidine (71).

24 N-(2,2,3,3-tetrafluoropropyl)-2-(2H-tetrafluoroethyl)piperidine (72).

25 N-(2,2,3,3-tetrafluoropropyl)-2,6-bis-(2H-tetrafluoroethyl)piperidine (73).

26 N-Methyl-2-(2H-perfluorocyclohexyl)pyrrolidine (74).

27 N-Methyl-2-(2H,2-chlorotrifluoroethyl)pyrrolidine (75).

28 N-Methyl-2-(2H,2,2-dichlorodifluoroethyl)pyrrolidine (76).

29 (1,1,1,2,3,3-hexafluoro-4-pentyl)isocyanate (77).

30 (1H,1H,3H-Hexafluorobutyl)trimethylsilane (78).

31 Bis-(1H,1H,3H-Hexafluorobutyl)dimethylsilane (79).

32 (1H,1H,3H-Hexafluorobutyl)pentamethyldisiloxane (80).

33 (1H,1H,3H-Hexafluorobutyl)heptamethylcyclotetrasiloxane (81).

34 Bis-(1H,1H,3H-Hexafluorobutyl)hexamethylcyclotetrasiloxane (82).

35 Fluorinated Silicon Oil.

36 (1,1,1,2,3,3-Hexafluoro-4-pentyloxy)ethoxydimethylsilane (84).

37 Bis-(1,1,1,2,3,3-Hexafluoro-4-pentyloxy)dimethylsilane (85).

38 (1H,1H,3H-Hexafluorobutylmethylamino)dimethylaminodimethylsilane (86).

39 1H,3H-Pentafluorobutenyltrimethylsilane (87).

40 2,3,4,4,4-Pentafluorobutene (88).

41 1,1,1,2,3,3-Hexafluoro-4-methylpentane (89).

42 1,2-Bis-(2-tetrahydrofuryl)-1H-pentafluoropropane (91).

43 δ-Valerolactone Dimer (95).

44 ε-Caprolactone Dimer (96).

45 1,1,1,2,3,3-Hexafluoro-4-pentanone (97).

46 2-(2H-Tetrachloroethyl)oxolane (101).

47 1,1,2-Trichloro-3-ethoxybutene (102).

48 1,1,2-Trichlorobuten-3-one (103).

49 1,1,2-Trichlorobuten-3-ol (104).

50 2-(2H,2,2-Dichlorodifluoroethyl)oxolane (99).

51 2,3-Dichloro-1,1,1,4,4,4-hexafluoro-3-methoxymethyl-butane (105).

52 Bis-(2,3-dichloro-4,4,4-trifluoro-2-trifluoromethyl-butyl)ether (106).

53 1,1,1,2,3,3-Hexafluoro-4-pentanol (107).

54 1-(2H-Octafluorocyclopentyl)ethanol (108).

55 1-(2H-Decafluorocyclohexyl)ethanol (109).

56 1,1,1,2,3,3-Hexafluoroheptane-4,7-diol (110).

57 2-(Pentafluoropropenyl)oxolane (90).

58 1,1,1,2,3-Pentafluoro-4-ethoxy-2-pentene (119).

59 1,1,1,2,3-Pentafluoro-4-methoxy-2-butene (92).

60 N-Methyl-2-(Pentafluoropropenyl)pyrrolidine (120).

61 2-(Trichloroethenyl)oxolane (121).

62 Trans-2-Chloro-1,1,1,4,4,4-hexafluoro-3-methoxymethyl-2-butene (122).

63 Trans-1,1,1,4,4,4-hexafluoro-2-methoxy-3-methoxymethyl-2-butene (123).

64 Trans-1,1,1,4,4,4-hexafluoro-2-ethoxy-3-methoxymethyl-2-butene (124).

65 Cis-1,1,1,4,4,4-hexafluoro-2-ethoxy-3-methoxymethyl-2-butene (125).

66 2-(1,2-Dichloroethenyl)oxolane (126).

67 1,1,1,4,4,4-Hexafluoro-2-methoxymethyl-2-butene (127).

68 2,2,3,4,4,4-Hexafluorobutylamine (129).

69 (2,2,3,4,4,4-Hexafluorobutyl)methylamine (128).

70 (2,2,3,4,4,4-Hexafluorobutyl)ethylamine (131).

71 (2,2,3,4,4,4-Hexafluorobutyl)ethylmethylamine (130).

72 Methyl-N-(1,1,1,2,3,3-Hexafluoro-4-pentyl)carbamate (132).

73 N-Ethyl-N'-(1,1,1,2,3,3-hexafluoro-4-pentyl)urea (133).

74 (1H,1H,3H-Hexafluorobutyl)-N-methylcarbamate (134).

75 N-Methyl-N'-(1H,1H,3H-hexafluorobutyl)urea (135).

76 (1H,1H,3H-Hexafluorobutyl)-N-(1,1,1,2,3,3-hexafluoro-4-pentyl)carbamate (136).

77 1,1,1,2,3,3-Hexafluoro-4-methyl-4-pentanol (138).

78 1,1,1,2,3,3-Hexafluoro-4-methyl-4,5-epoxypentane (139).

79 Perfluoro-N-methyl-2-propylpyrrolidine (142).

80 Perfluoro-N-butylpiperidine (146).

81 (2H-Decafluorocyclohexyl)fluoromethane (148).

82 Perfluoromethylcyclohexane (149).

83 3-Fluoromethylperfluoro-4H,3,4-dimethylhexane (150).

84 Perfluoro-3,3,4-trimethylhexane (151).

85 Perfluoro-1H,1H,11H-undecane (152).

86 Perfluoroundecane (153).

87 1-(2H-Octafluorocyclopentyl)-1,1-difluoroethane (154).

88 Perfluoroethylcyclopentane (155).

89 1-(2H-Decafluorocyclohexyl)-1-fluoroethene (156).

90 1-(2H-Decafluorocyclohexyl)-1,1-difluoroethane (157).

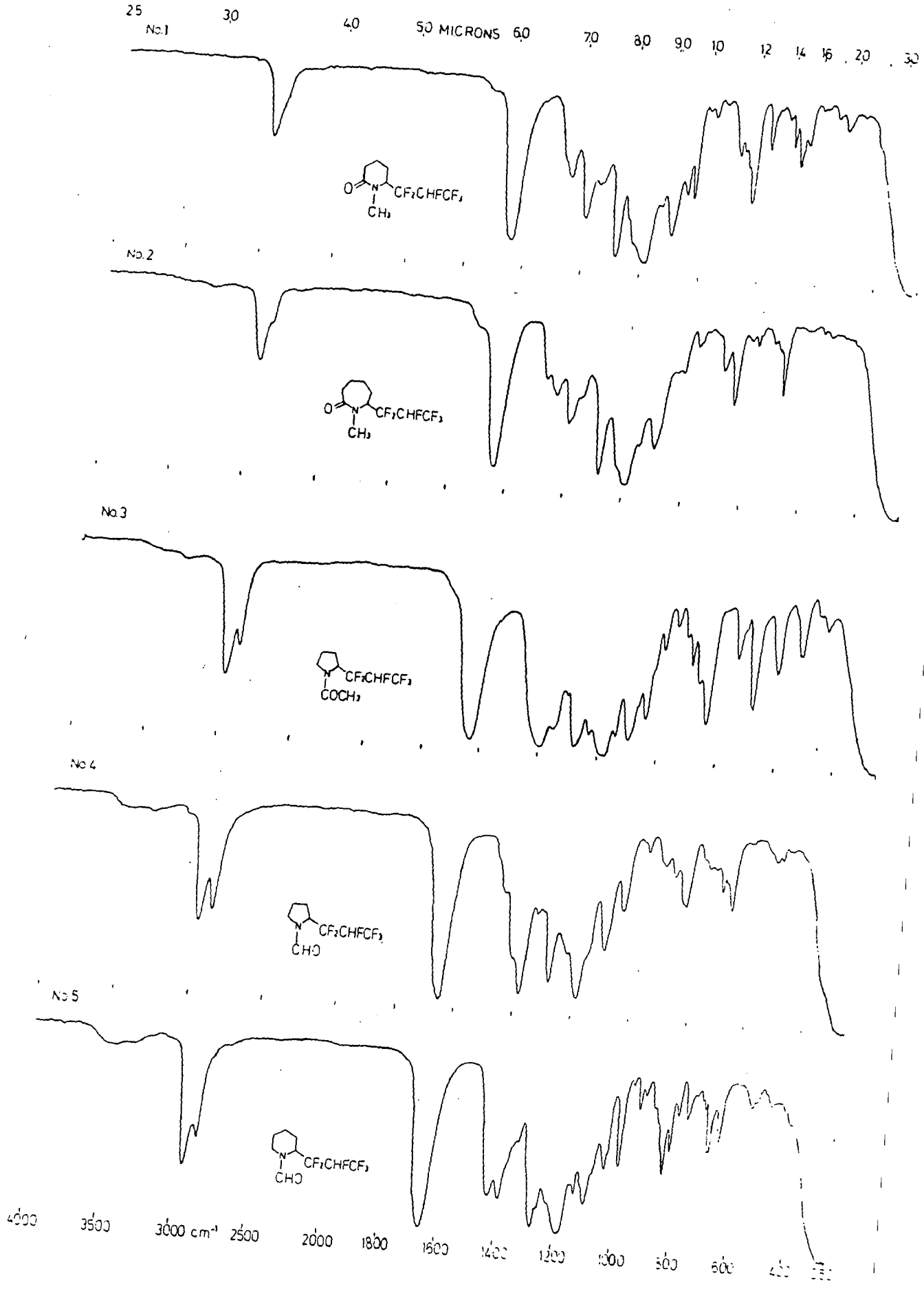
91 Perfluoroethylcyclohexane (158).

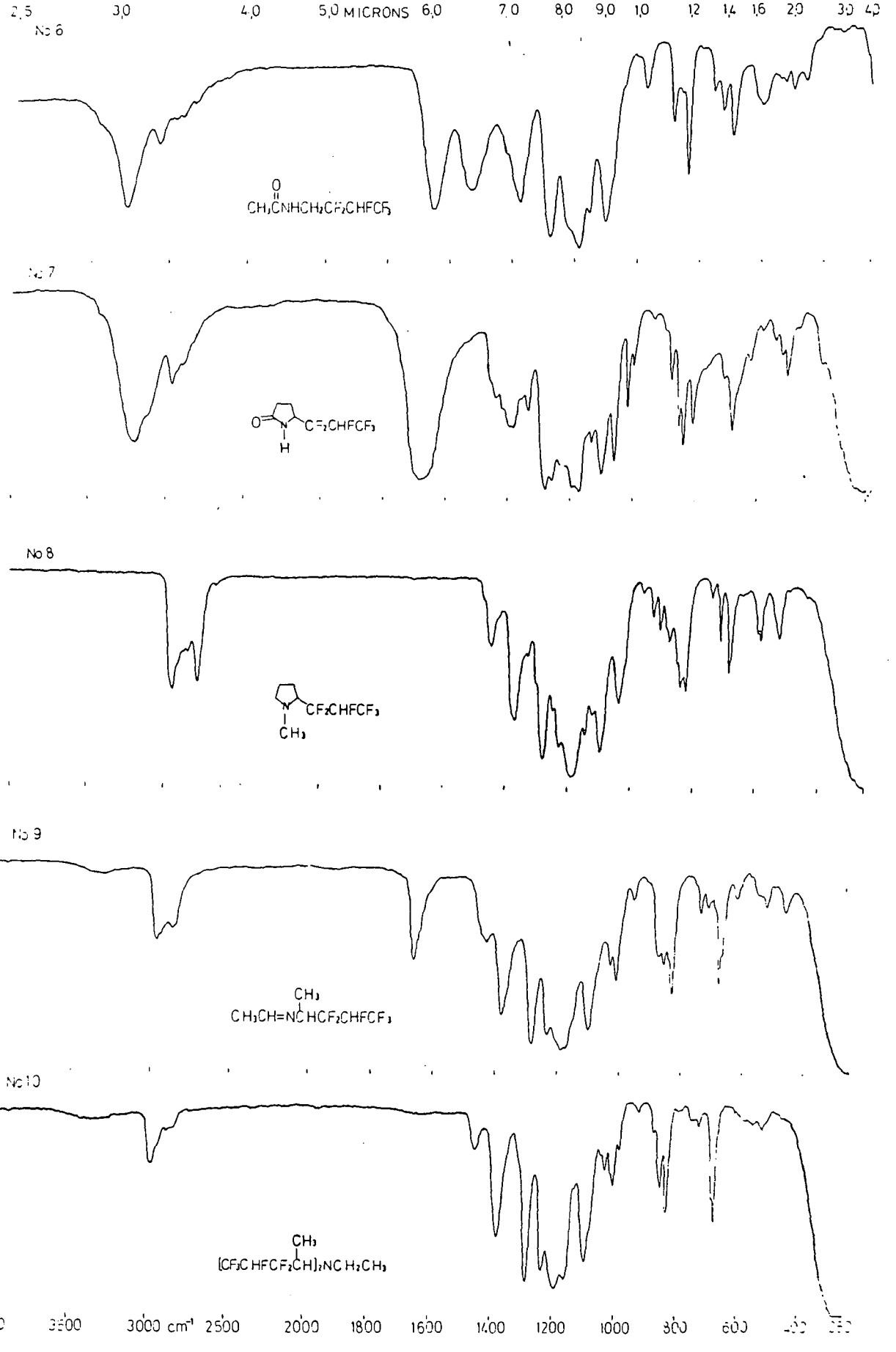
92 1H,1H,3H-Hexafluorobutyltrifluoroacetate (159).

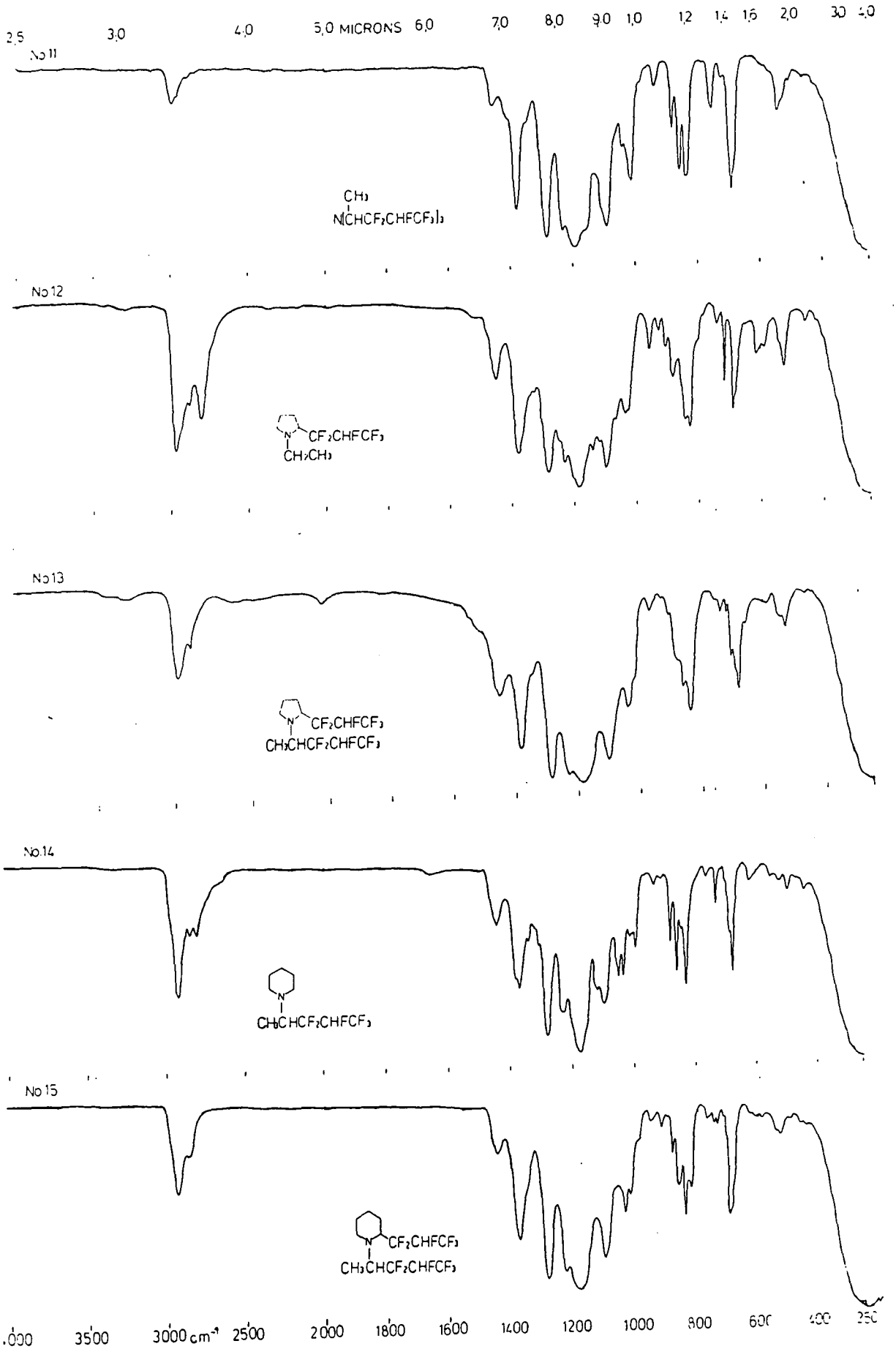
93 Perfluoro-1-ethoxy-1H,1H,3H-butane (160).

94 Perfluoroethoxybutane (162).

95 2,5,5-Trichloroperfluoro-2-propyloxolane (163).


25
No.1
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
20
30
O
N
CH₃
CF₂CHFCF₃
No.2
No.3
COCH₃
No.4
CHO
No.5
4000
3500
3000 cm⁻¹
2500
2000
1800
1600
1400
1200
1000
800
600


2,5
3,0
4,0
5,0 MICRONS
6,0
7,0
8,0
9,0
1,0
1,2
1,4
1,6
2,0
3,0
4,0
No 6
O
CH3CNHCH2CF2CHFCF3
No 7
O
N
H
CF2CHFCF3
No 8
N
CH3
CF2CHFCF3
No 9
CH3
CH3CH=NCHCF2CHFCF3
No 10
CH3
[CF3CHFCF2CH]2NCH2CH3
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600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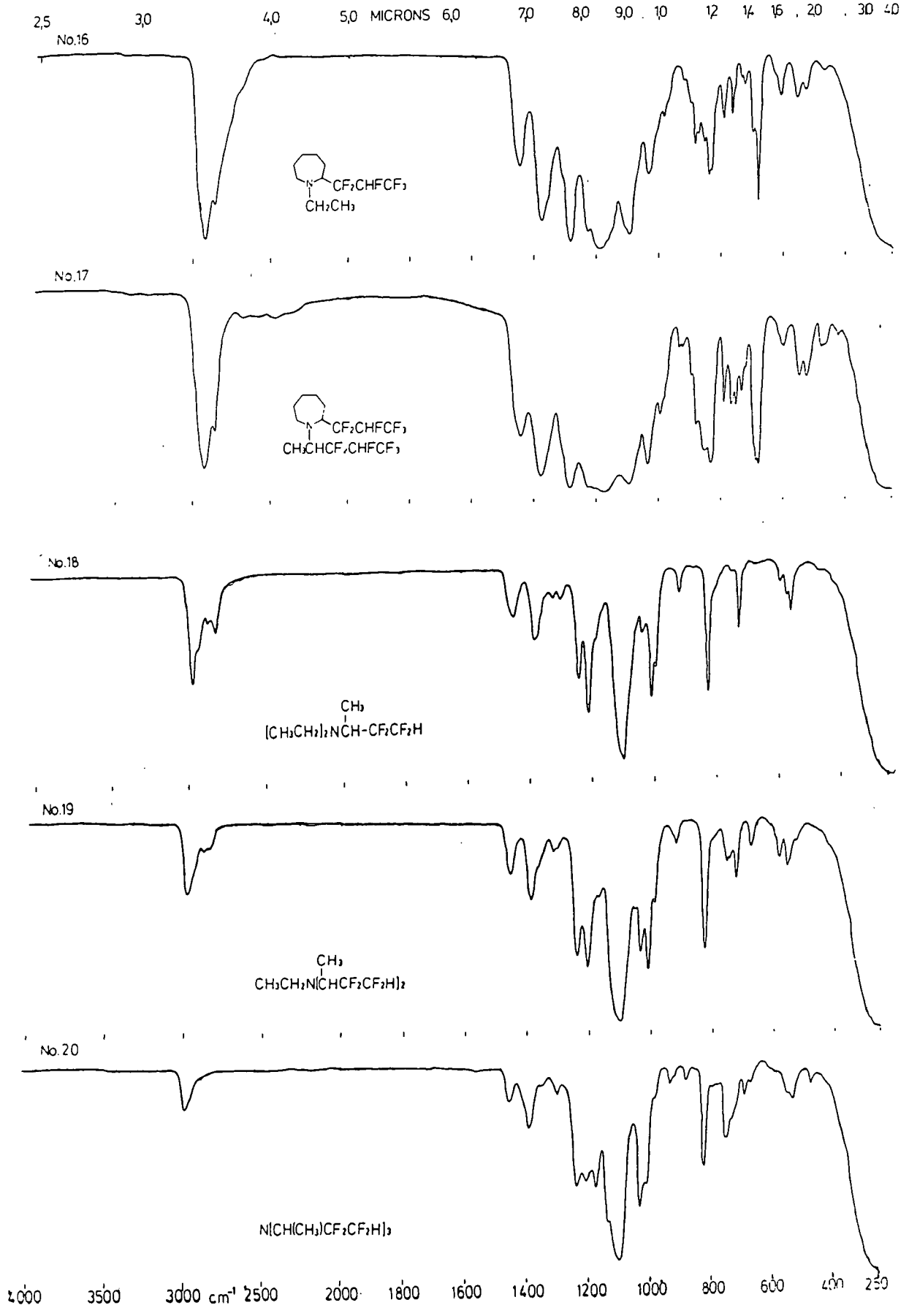
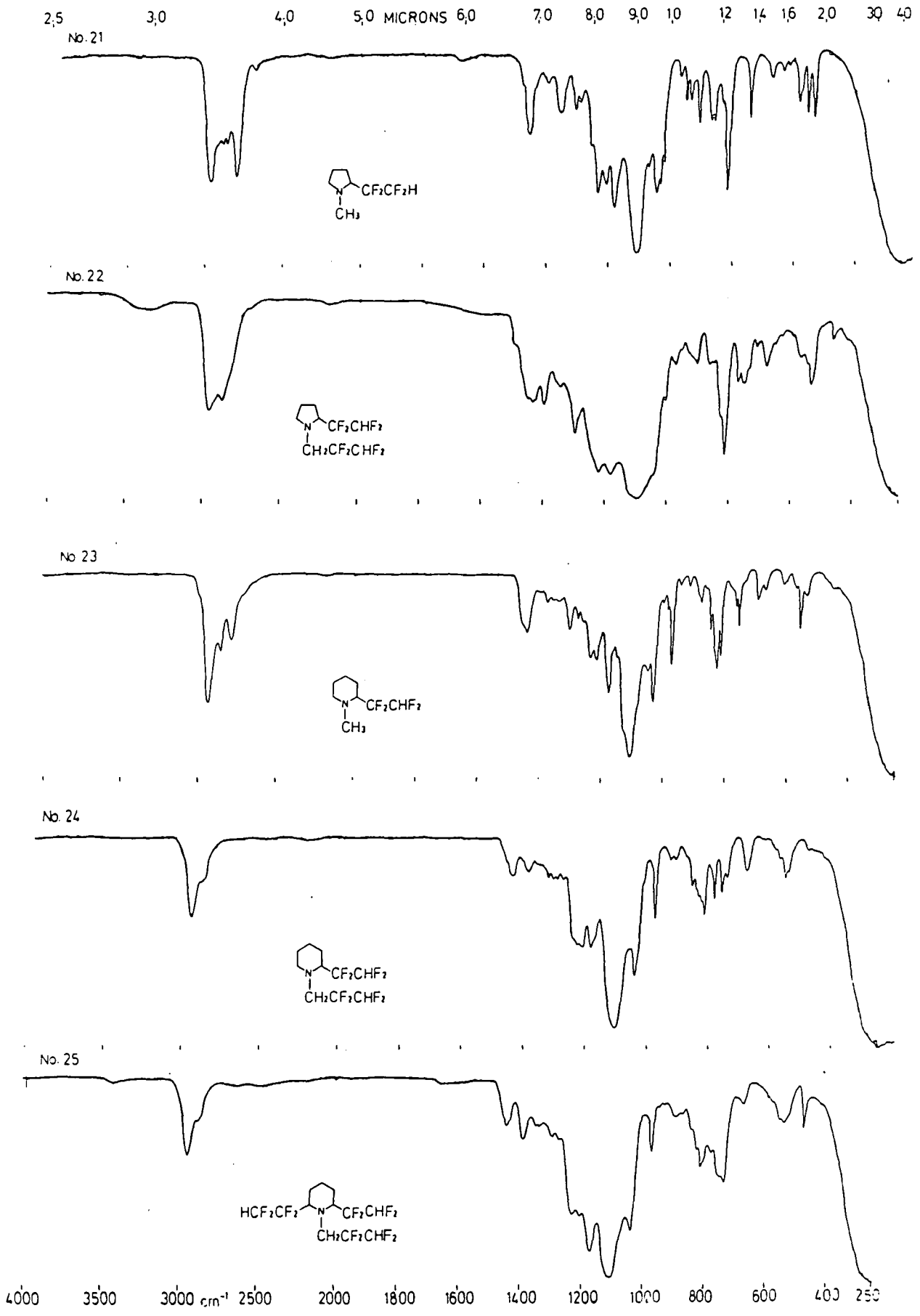
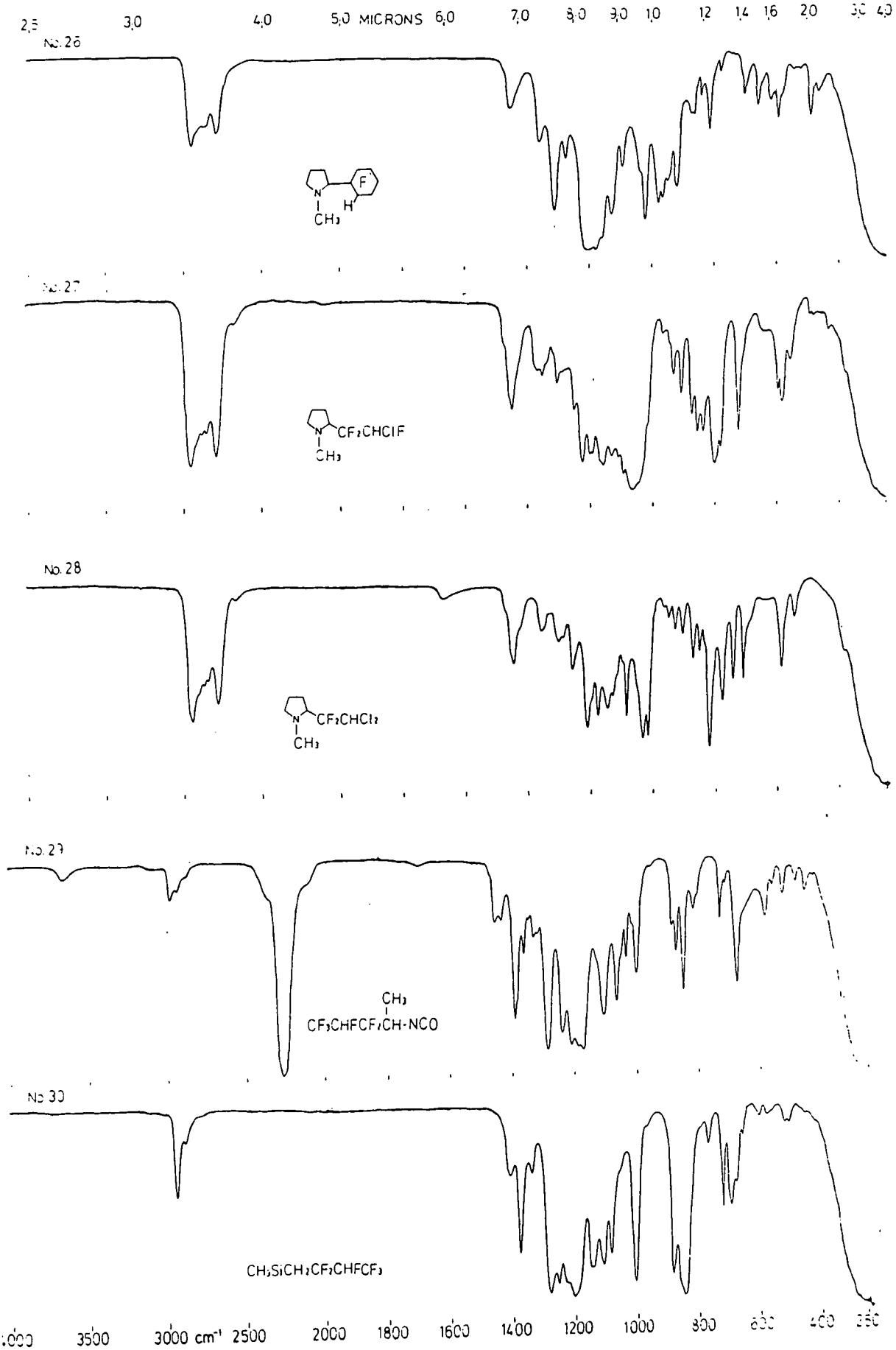
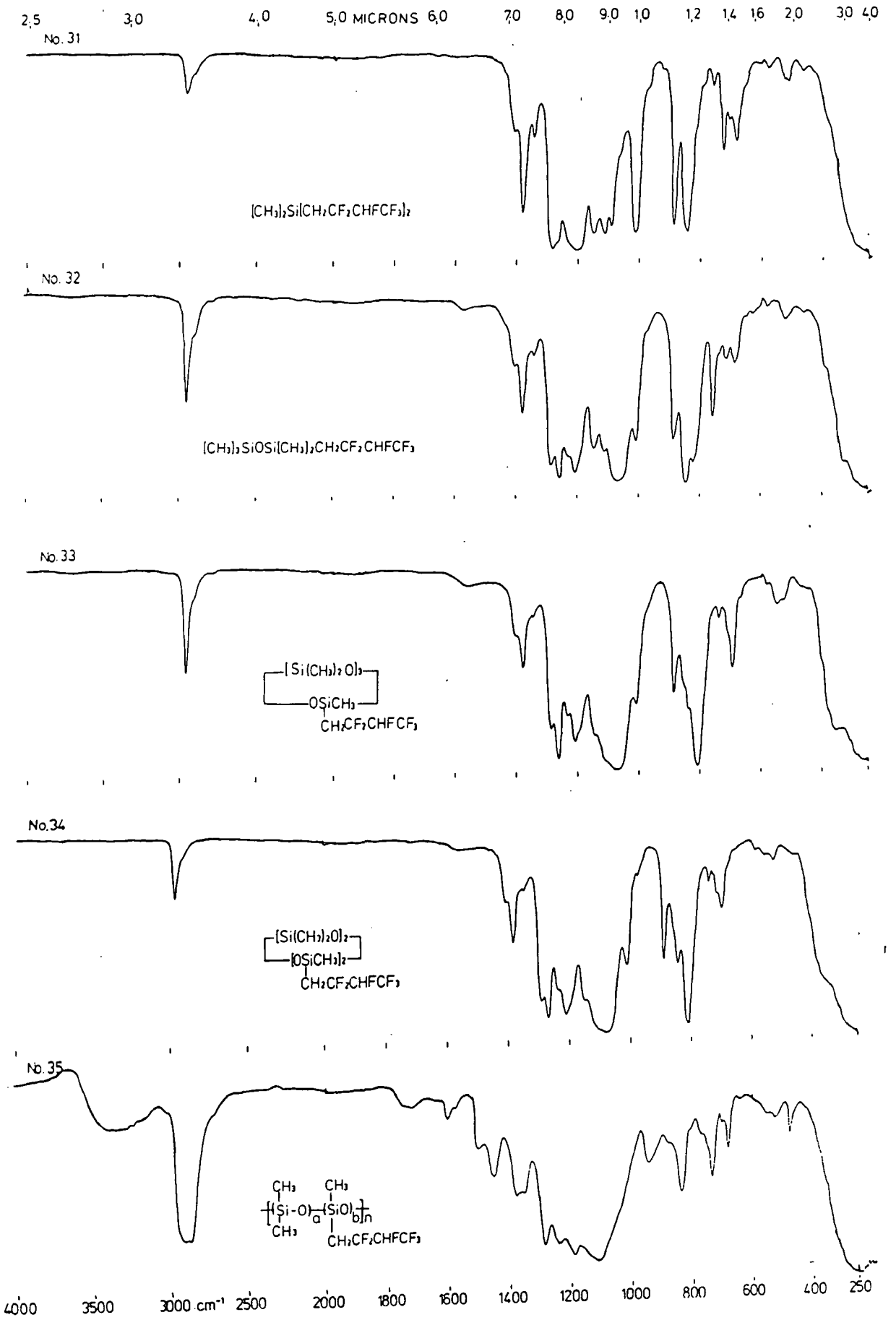
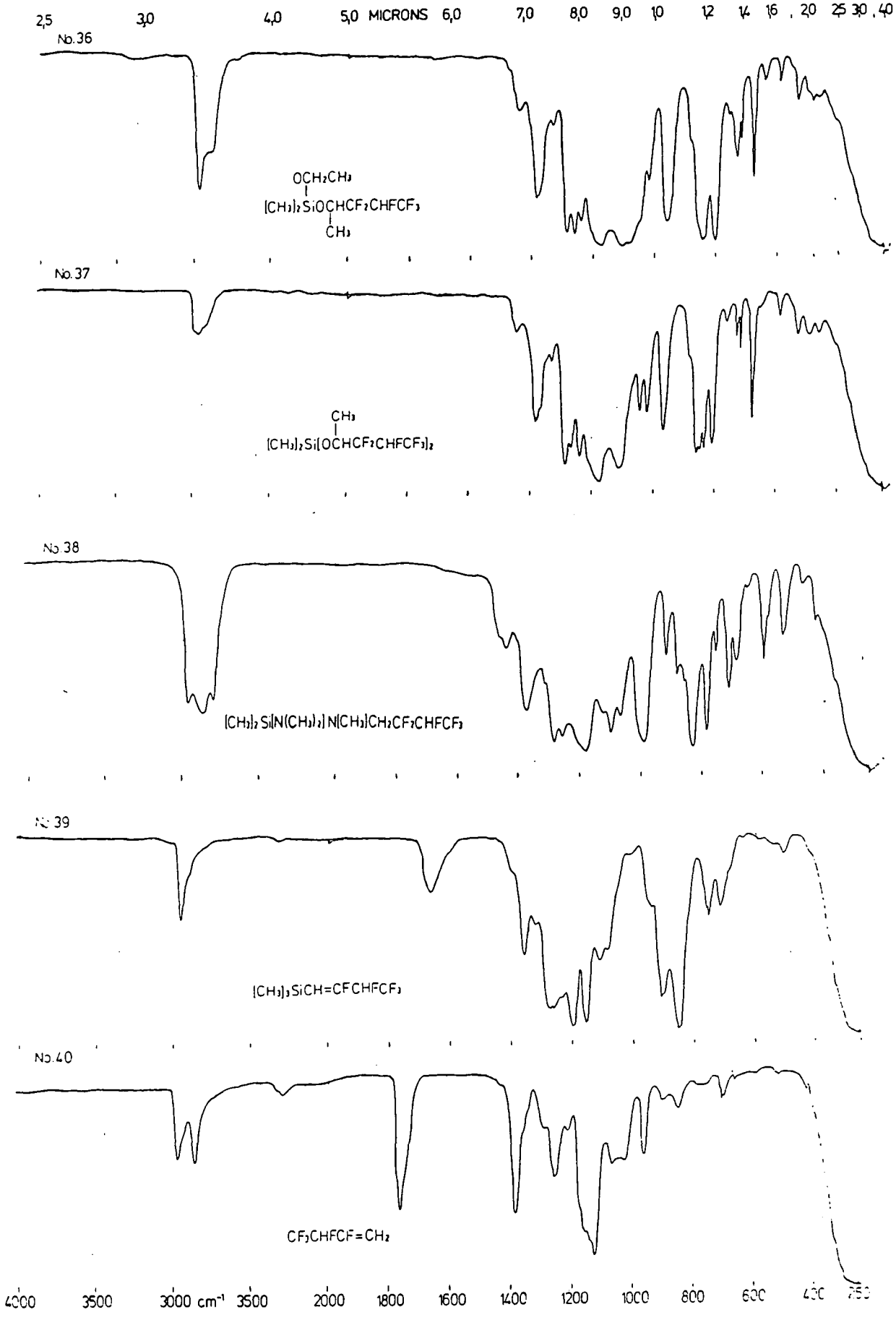
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
1.0
1.2
1.4
1.6
2.0
3.0
4.0
No 11
N[CHCF2CHFCF3]3
No 12
CF2CHFCF3
CH2CH3
No 13
CF2CHFCF3
CH3CHCF2CHFCF3
No 14
CH3CHCF2CHFCF3
No 15
CF2CHFCF3
CH3CHCF2CHFCF3
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

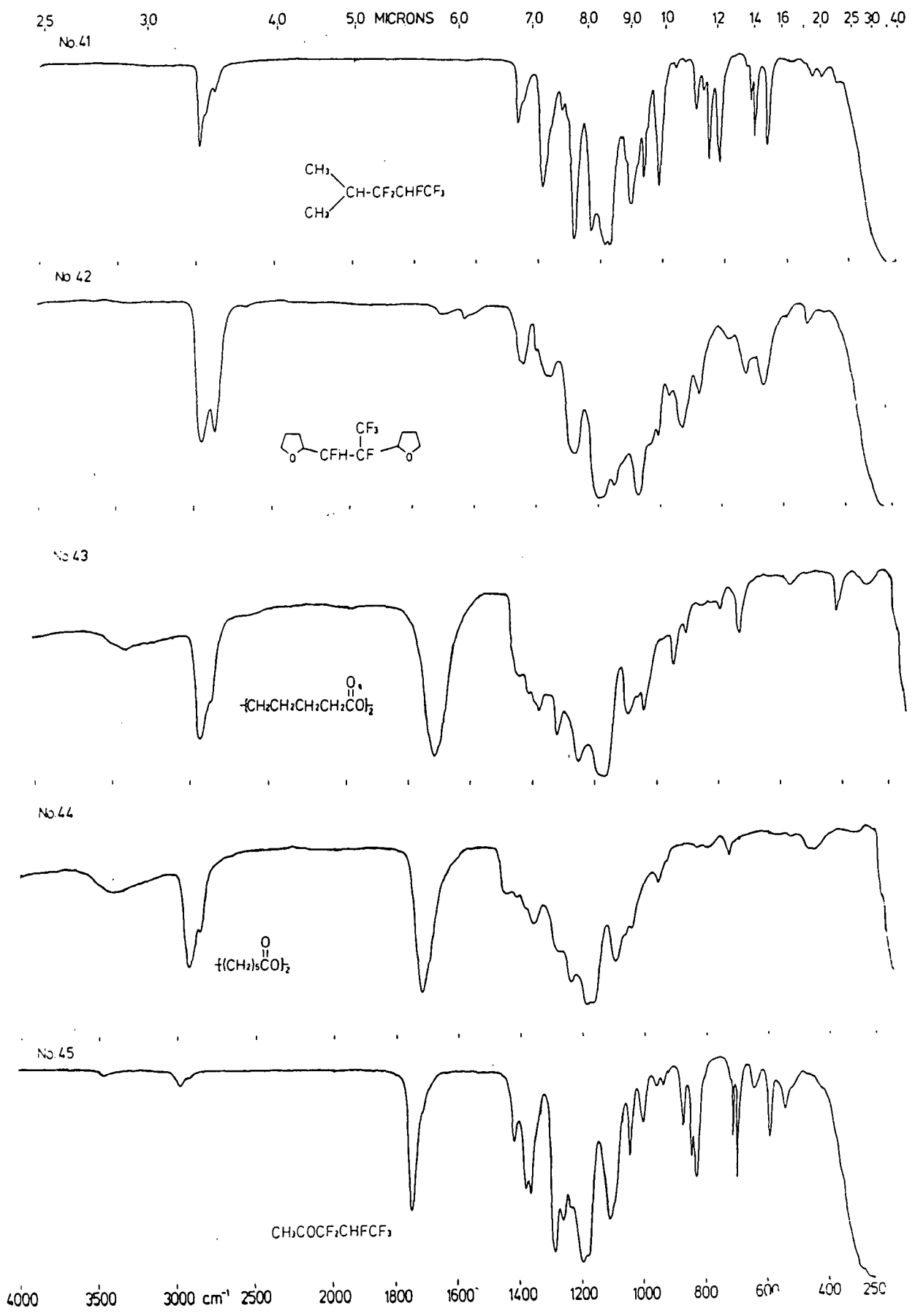

2,5
3,0
4,0
5,0 MICRONS 6,0
7,0
8,0
9,0
10
12
14
16
20
30
40
No.16
CF₂CHFCF₃
CH₂CH₃
No.17
CF₂CHFCF₃
CH₃CHCF₂CHFCF₃
No.18
CH₃
[CH₃CH₂]₂NCH-CF₂CF₂H
No.19
CH₃
CH₃CH₂N[CHCF₂CF₂H]₂
No.20
N[CH(CH₃)CF₂CF₂H]₃
4000
3500
3000 cm⁻¹
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

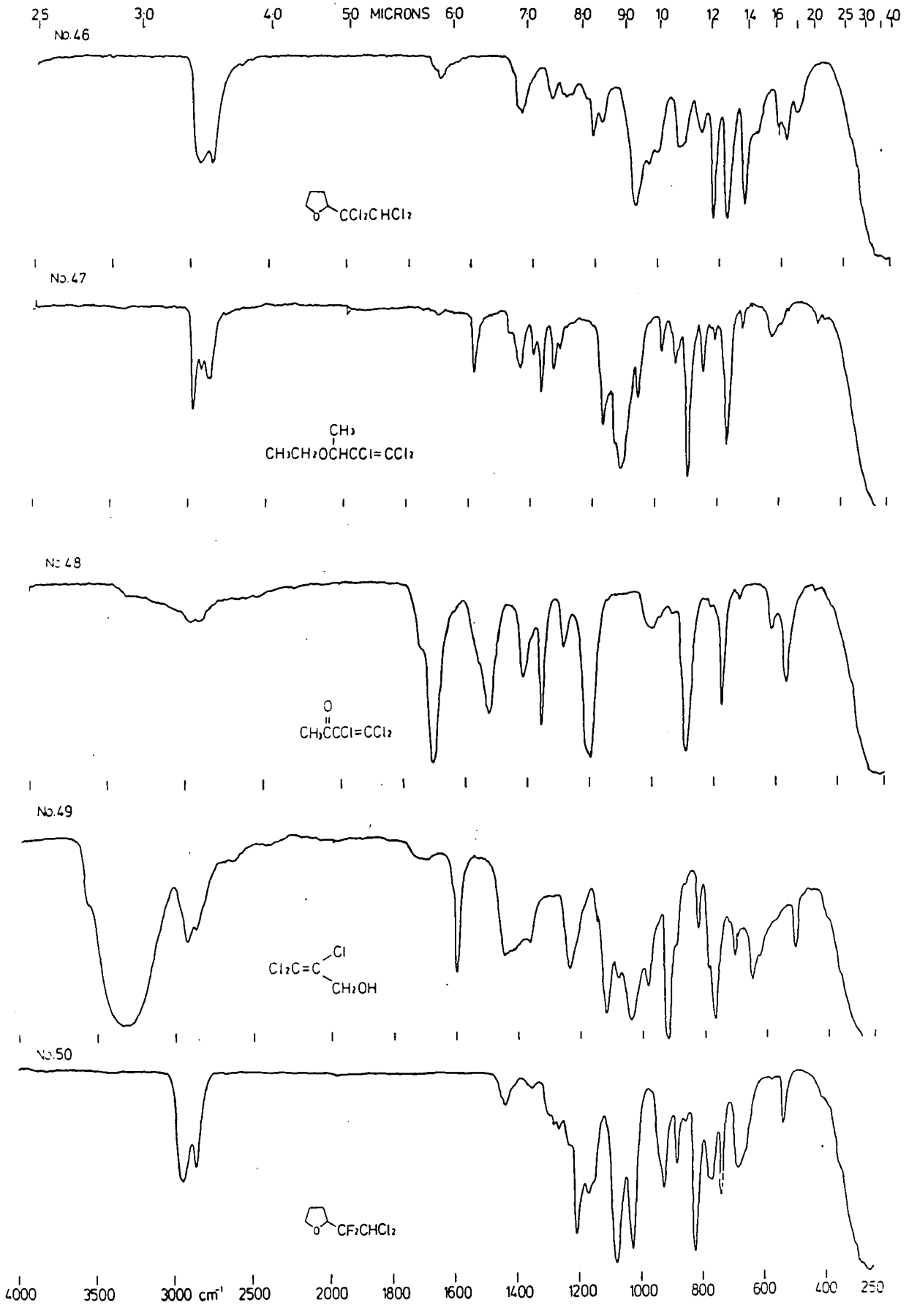

2.5
3.0
4.0
5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
16
20
30
40
No. 21
CF2CF2H
CH3
No. 22
CF2CHF2
CH2CF2CHF2
No. 23
CF2CHF2
CH3
No. 24
CF2CHF2
CH2CF2CHF2
No. 25
HCF2CF2
CF2CHF2
CH2CF2CHF2
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

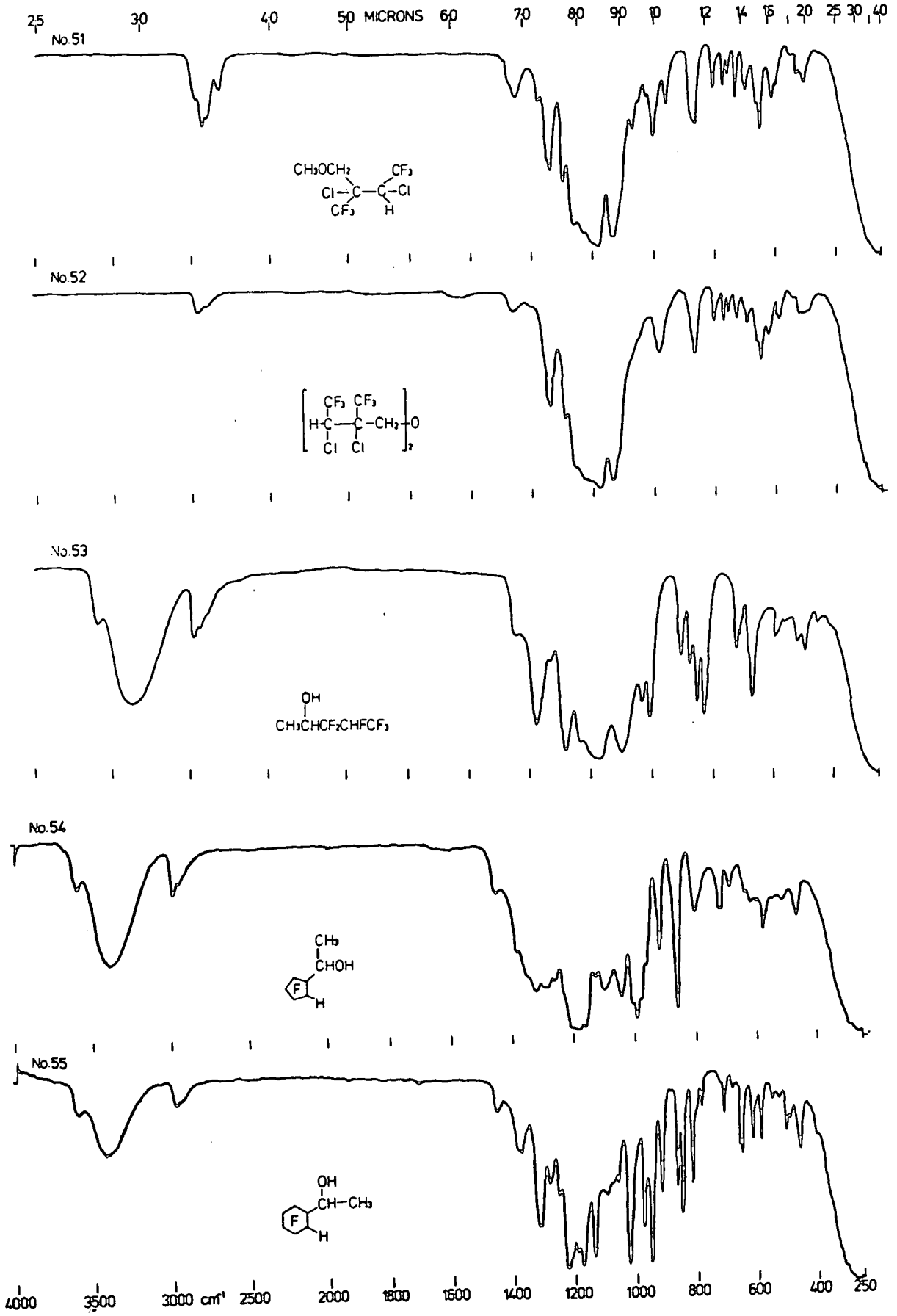

2.5
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
20
30
40
No. 26
F
H
N
CH3
No. 27
CF2CHClF
No. 28
CF2CHCl2
No. 29
CH3
CF3CHFCF2CH·NCO
No. 30
CH3SiCH2CF2CHFCF3
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

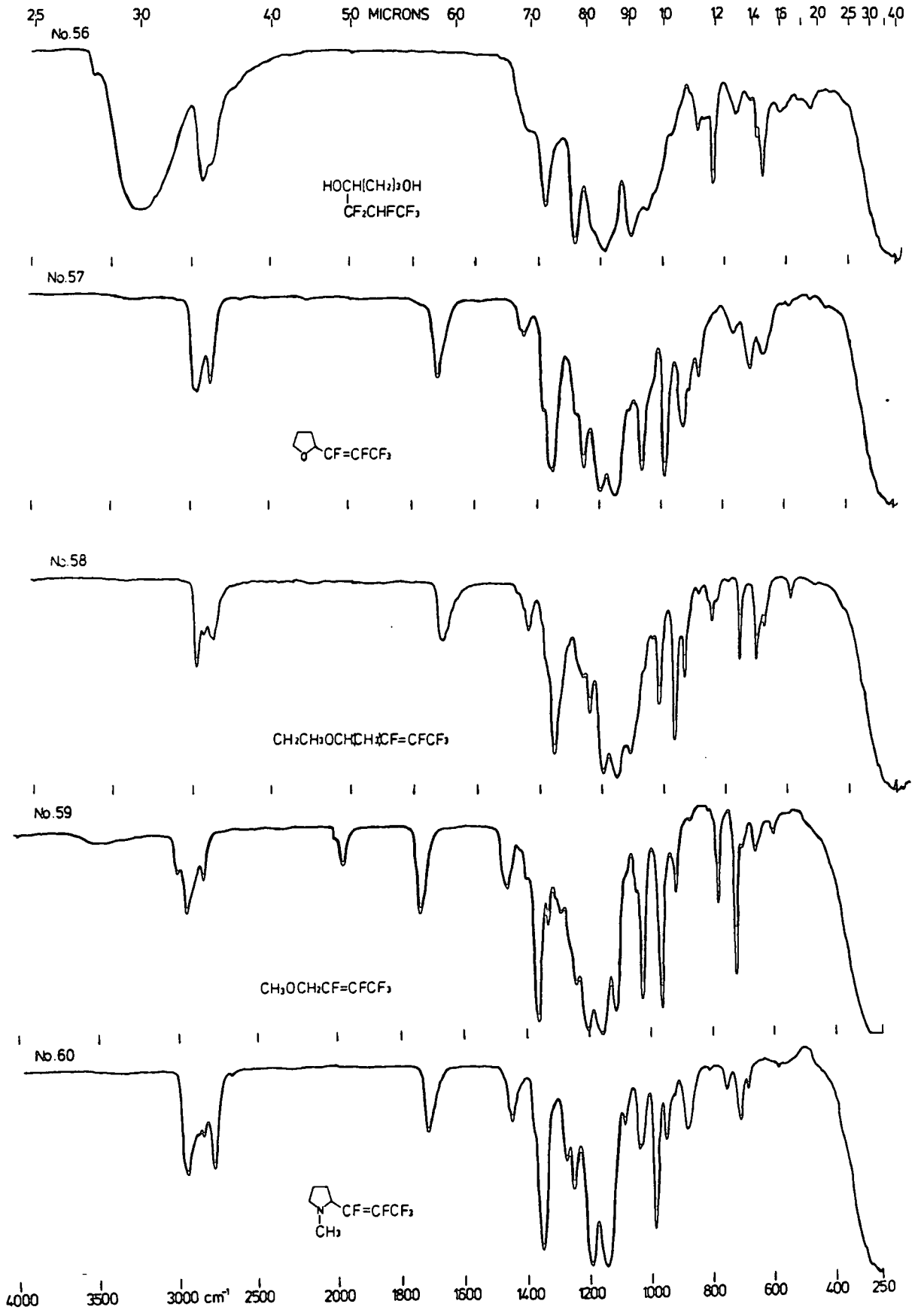

2.5
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
1.0
1.2
1.4
1.6
2.0
3.0
4.0
No. 31
[CH3]2Si[CH2CF2CHFCF3]2
No. 32
[CH3]3SiOSi[CH3]2CH2CF2CHFCF3
No. 33
[Si(CH3)2O]3
OSiCH3
CH2CF2CHFCF3
No. 34
[Si(CH3)2O]2
[OSiCH3]2
CH2CF2CHFCF3
No. 35
CH3
CH3
Si-O
Si-O
a
b
n
CH3
CH2CF2CHFCF3
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

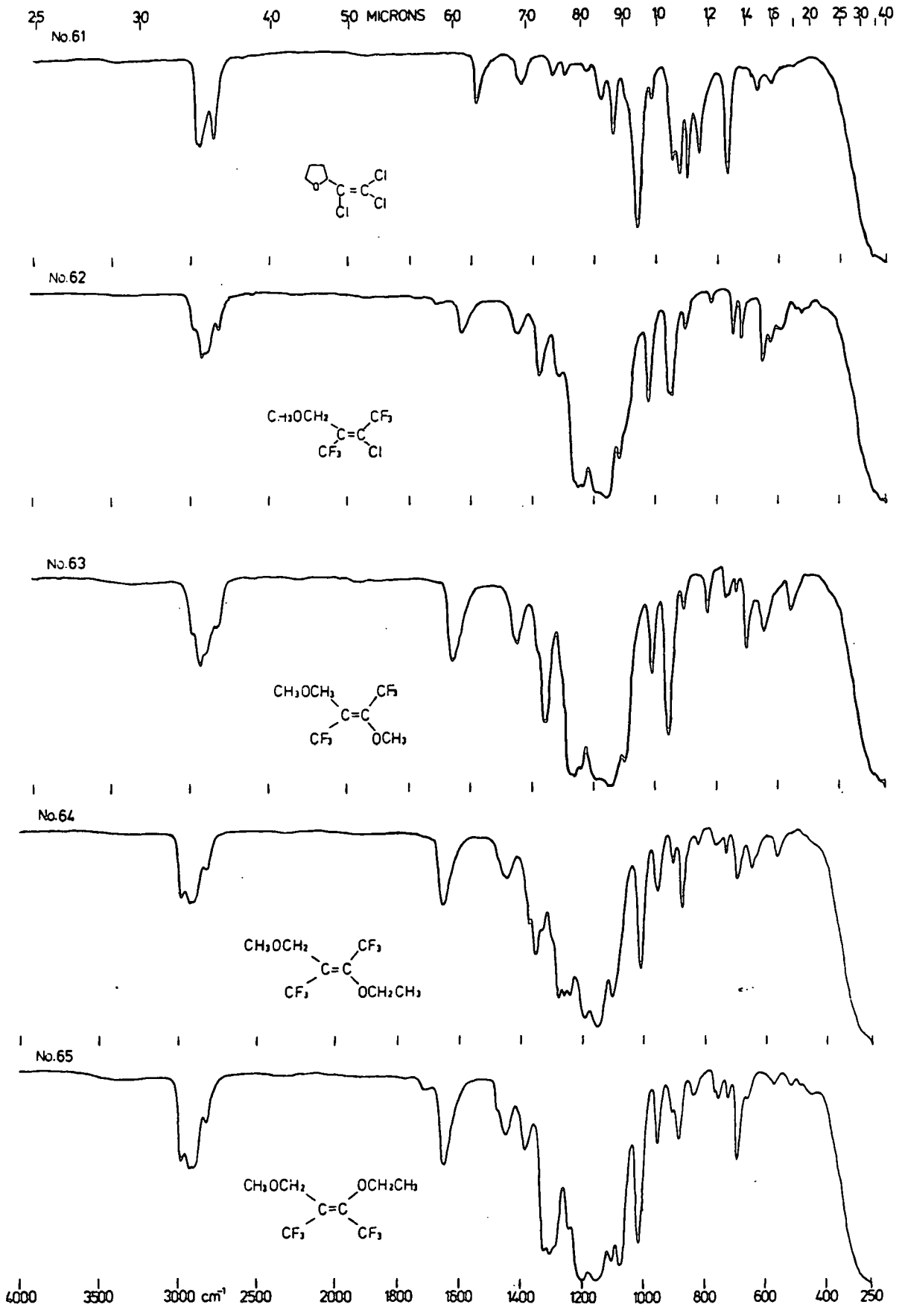

2,5
3,0
4,0
5,0 MICRONS
6,0
7,0
8,0
9,0
10
12
14
16
20
25
30
40
No. 36
OCH2CH3
[CH3]2SiOCHCF2CHFCF3
CH3
No. 37
CH3
[CH3]2Si[OCHCF2CHFCF3]2
No. 38
[CH3]2Si[N(CH3)2]N[CH3]CH2CF2CHFCF3
No. 39
[CH3]3SiCH=CFCHFCF3
No. 40
CF3CHFCF=CH2
4000
3500
3000 cm-1
3500
2000
1800
1600
1400
1200
1000
800
600
400
250

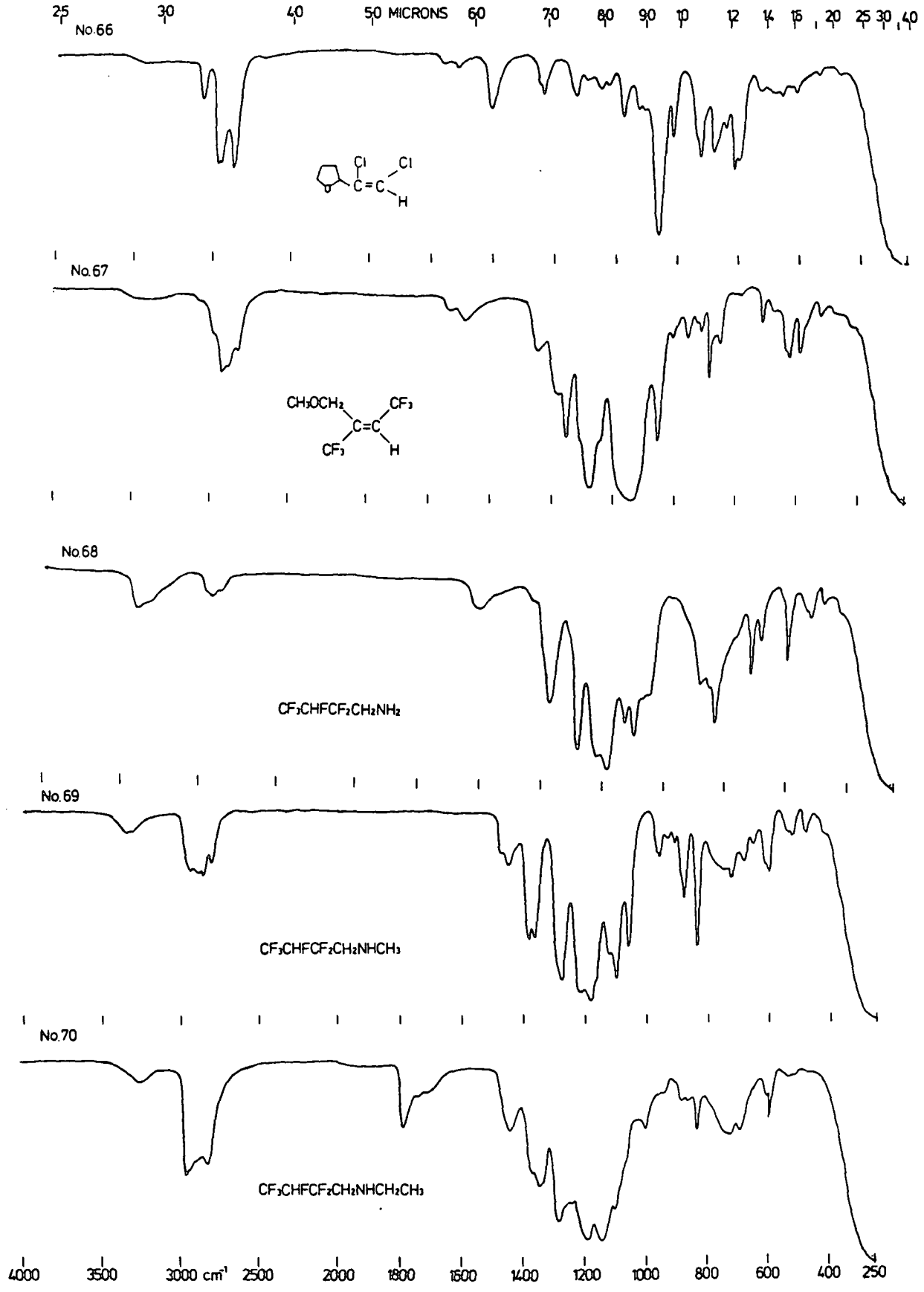

2.5 3.0 4.0 5.0 MICRONS 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
No.41
CH3
CH-CF2CHFCF3
CH3
No.42
CF3
CFH-CF
No.43
O
-(CH2CH2CH2CH2CO)2
No.44
O
-(CH2)5CO)2
No.45
CH3COCF2CHFCF3
4000 3500 3000 cm-1 2500 2000 1800 1600 1400 1200 1000 800 600 400 250

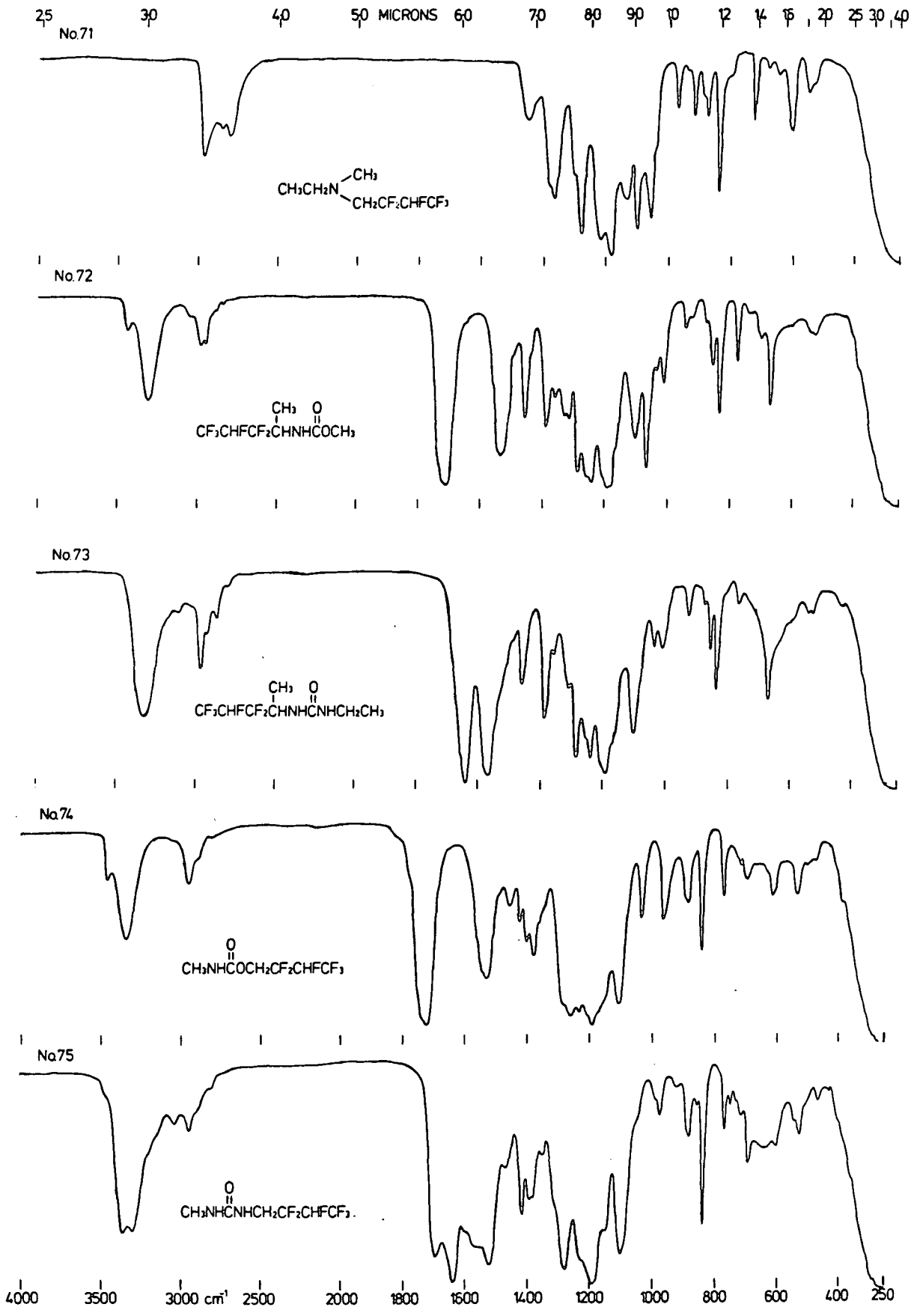

2.5
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
No.46
CCl2CHCl2
No.47
CH3
CH3CH2OCHCCl=CCl2
No.48
O
CH3CCCl=CCl2
No.49
Cl
Cl2C=C
CH2OH
No.50
CF2CHCl2
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

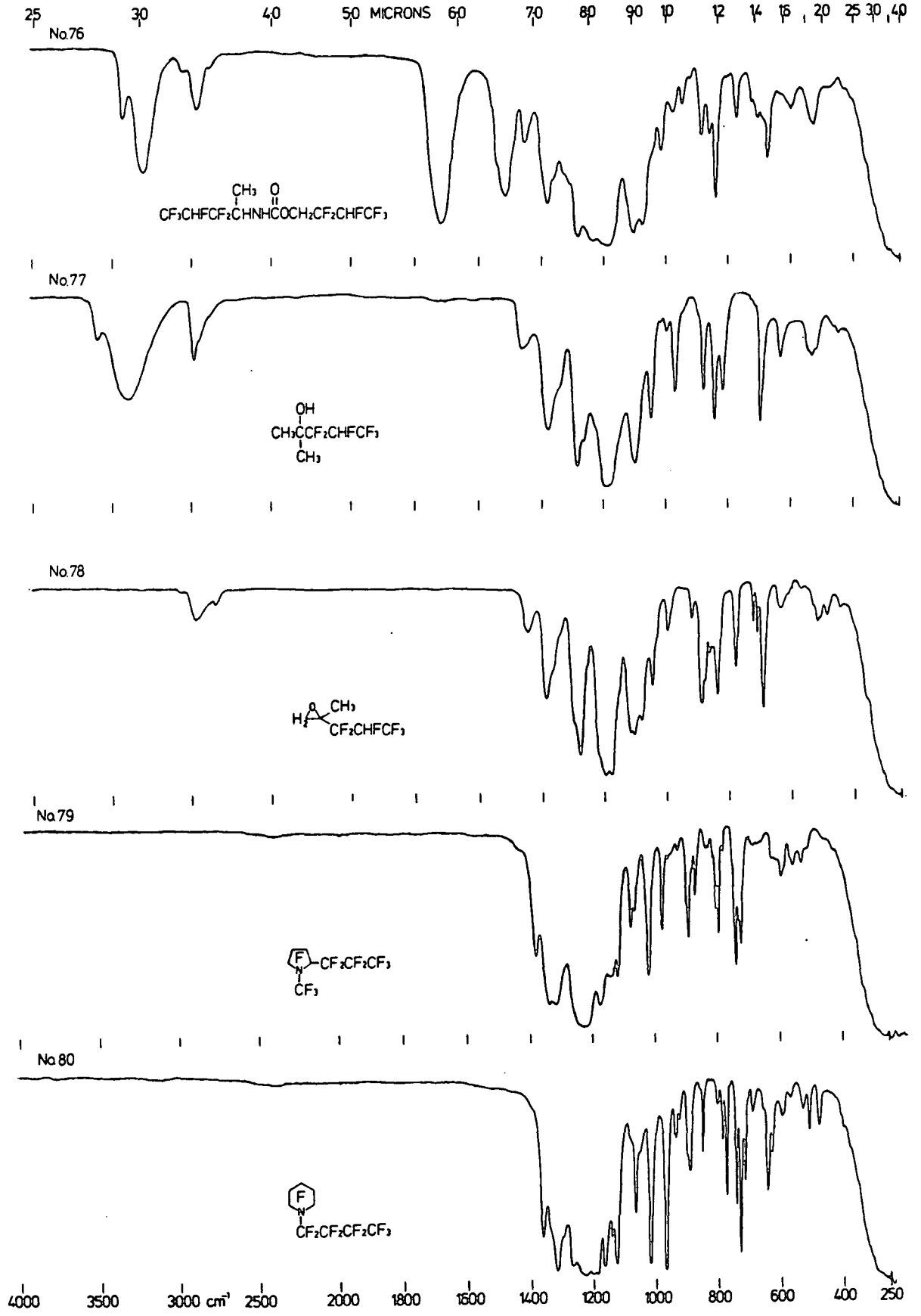

25 30 40 50 MICRONS 60 70 80 90 10 12 14 16 20 25 30 40
No.51
No.52
No.53
No.54
No.55
4000 3500 3000 cm⁻¹ 2500 2000 1800 1600 1400 1200 1000 800 600 400 250

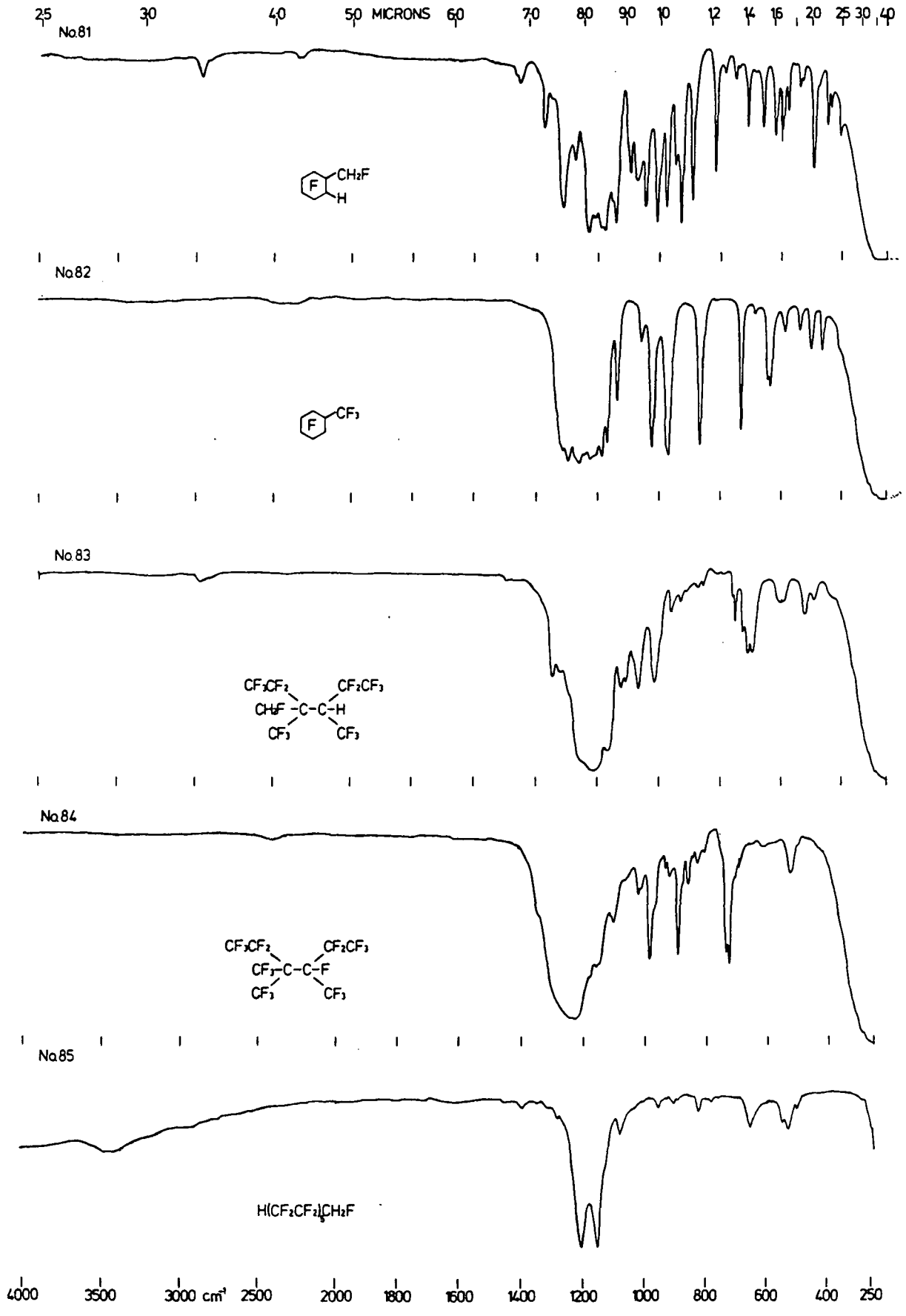

2.5
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
No.56
HOCH(CH2)3OH
CF2CHFCF3
No.57
CF=CFCF3
No.58
CH2CH3OCH(CH3)CF=CFCF3
No.59
CH3OCH2CF=CFCF3
No.60
CF=CFCF3
CH3
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

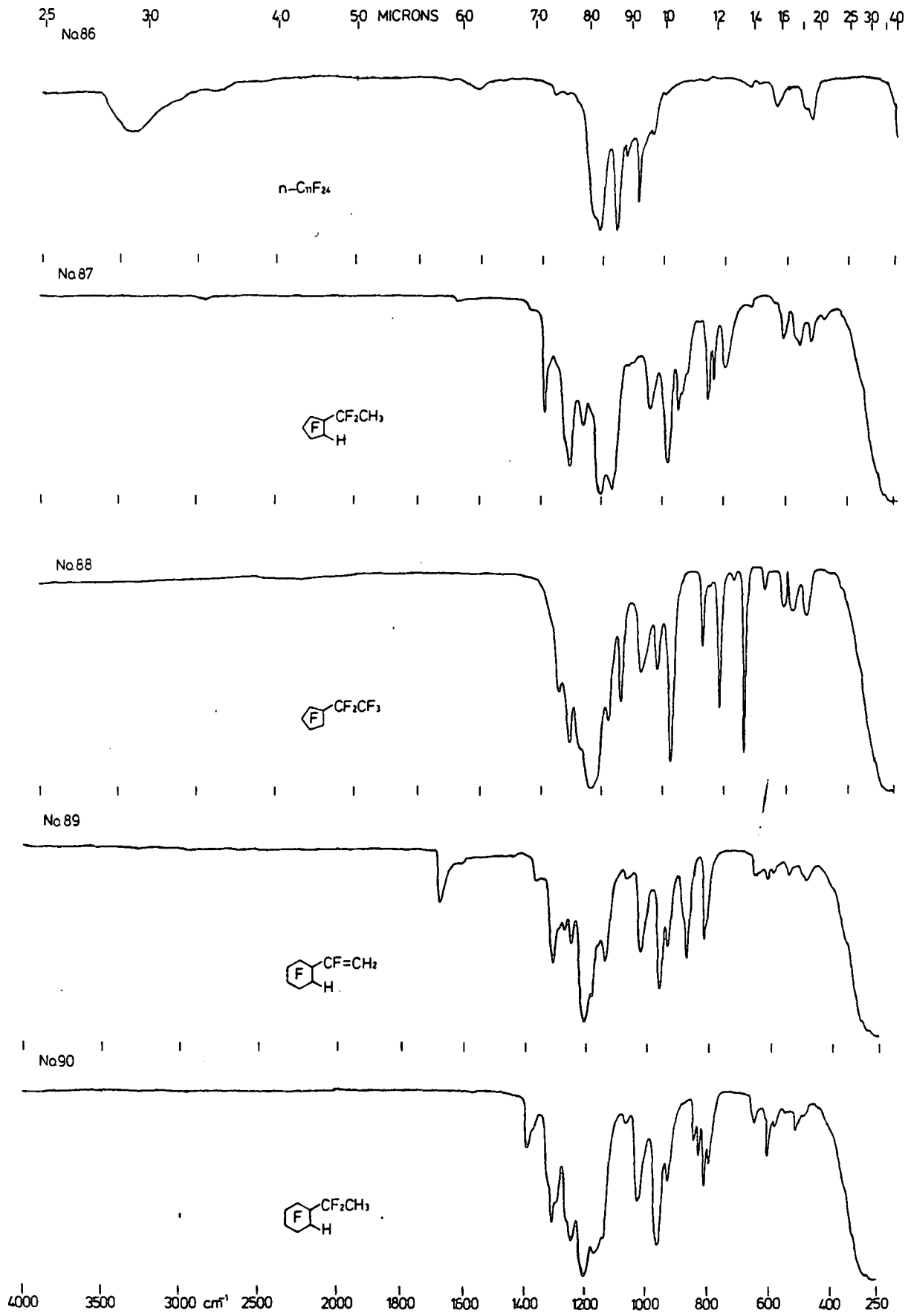

2.5
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
No.61
No.62
No.63
No.64
No.65
4000
3500
3000 cm⁻¹
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

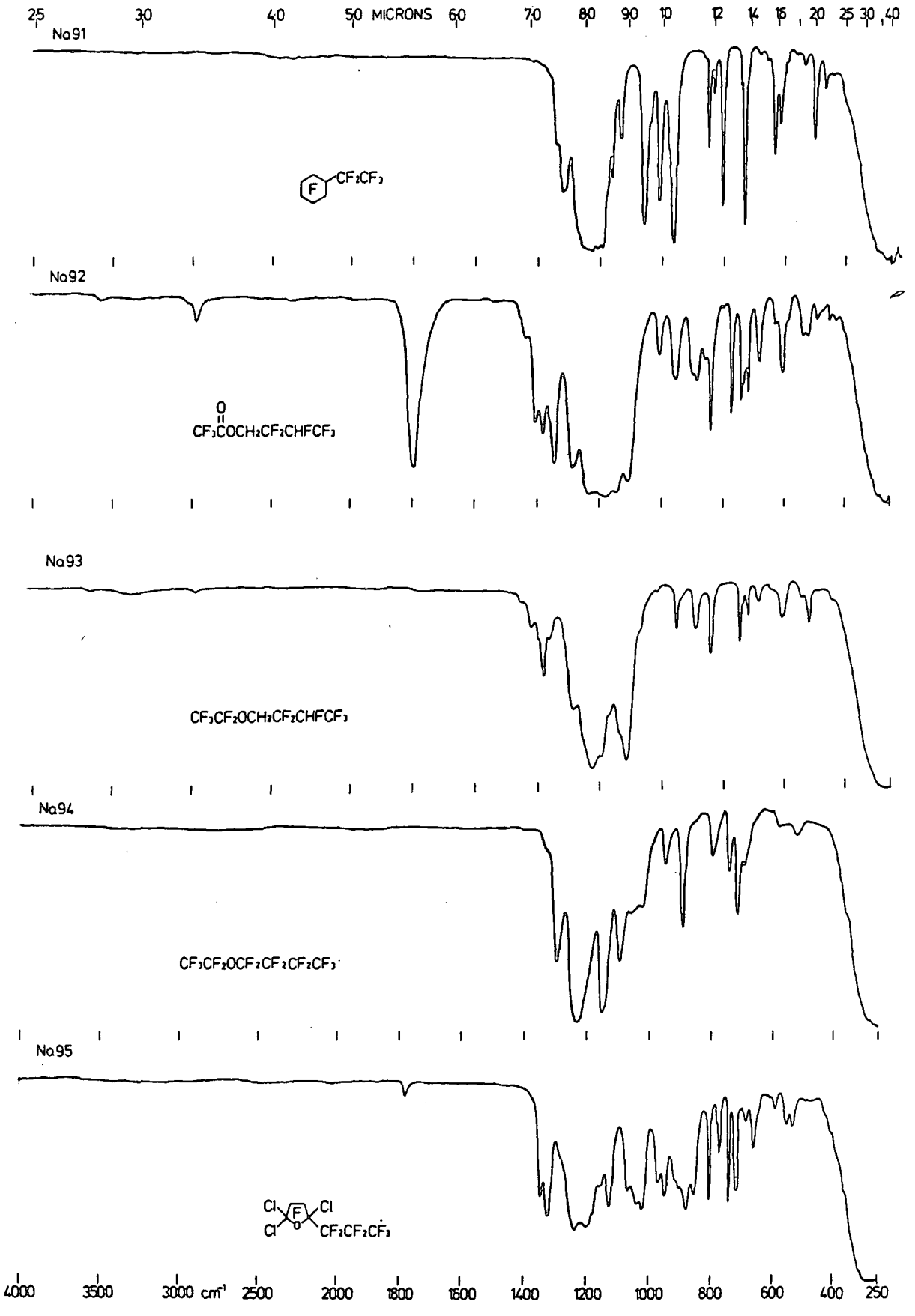

25 30 40 50 MICRONS 60 70 80 90 10 12 14 16 20 25 30 40
No.66
Cl
Cl
C=C
H
No.67
CH3OCH2
CF3
C=C
CF3
H
No.68
CF3CHFCF2CH2NH2
No.69
CF3CHFCF2CH2NHCH3
No.70
CF3CHFCF2CH2NHCH2CH3
4000 3500 3000 cm-1 2500 2000 1800 1600 1400 1200 1000 800 600 400 250


2.5
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
No.71
CH3CH2N(CH3)CH2CF2CHFCF3
No.72
CF3CHFCF2CH(CH3)NHCOCH3
No.73
CF3CHFCF2CH(CH3)NHCONHCH2CH3
No.74
CH3NHCOCH2CF2CHFCF3
No.75
CH3NHCONHCH2CF2CHFCF3
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600
400
250


25 30 40 50 MICRONS 60 70 80 90 10 12 14 16 20 25 30 40
No.76
CH3 O
CF3CHFCF2CHNHCOCH2CF2CHFCF3
No.77
OH
CH3CCF2CHFCF3
CH3
No.78
CH3
CF2CHFCF3
No.79
CF2CF2CF3
CF3
No.80
CF2CF2CF2CF3
4000 3500 3000 cm-1 2500 2000 1800 1600 1400 1200 1000 800 600 400 250


25 30 40 50 MICRONS 60 70 80 90 10 12 14 16 20 25 30 40
No.81
CH₂F
F
H
No.82
CF₃
F
No.83
CF₃CF₂ CF₂CF₃
CH₂F C C H
CF₃ CF₃
No.84
CF₃CF₂ CF₂CF₃
CF₃ C C F
CF₃ CF₃
No.85
H(CF₂CF₂)₅CH₂F
4000 3500 3000 cm⁻¹ 2500 2000 1800 1600 1400 1200 1000 800 600 400 250


2.5
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
No 86
n-C11F24
No 87
F
CF2CH3
H
No 88
F
CF2CF3
No 89
F
CF=CH2
H
No 90
F
CF2CH3
H
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600
400
250


2.5
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
Na91
F
CF2CF3
Na92
O
CF3COCH2CF2CHFCF3
Na93
CF3CF2OCH2CF2CHFCF3
Na94
CF3CF2OCF2CF2CF2CF3
Na95
Cl
Cl
F
O
Cl
Cl
CF2CF2CF3
4000
3500
3000 cm-1
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

APPENDIX III

MASS SPECTRA

1 N-Methyl-6-(2H-hexafluoropropyl)-2-piperidone (38).

2 N-Methyl-7-(2H-hexafluoropropyl)-ϵ-caprolactam (39).

3 N-Acetyl-2-(2H-hexafluoropropyl)pyrrolidine (40).

4 N-Formyl-2-(2H-hexafluoropropyl)pyrrolidine (44).

5 N-Formyl-2-(2H-hexafluoropropyl)piperidine (45).

6 N-(1H,1H,3H-hexafluorobutyl)acetamide (46).

7 5-(2H-Hexafluoropropyl)-2-pyrrolidone (47).

8 N-Methyl-2-(2H-hexafluoropropyl)pyrrolidine (48).

9 Ethylidine-1,1,1,2,3,3-hexafluoro-4-pentylimine (51).

10 Bis-(1,1,1,2,3,3-hexafluoro-4-pentyl)ethylamine (52).

11 Tris-(1,1,1,2,3,3-hexafluoro-4-pentyl)amine (53).

12 N-Ethyl-2-(2H-hexafluoropropyl)pyrrolidine (54).

13 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)-2-
(2H-hexafluoropropyl)pyrrolidine (55).

14 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)piperidine (56).

15 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)-2-
(2H-hexafluoropropyl)piperidine (57).

16 N-Ethyl-2-(2H-hexafluoropropyl)hexamethyleneimine (58).

17 N-(1,1,1,2,3,3-hexafluoro-4-pentyl)-2-
(2H-hexafluoropropyl)hexamethyleneimine (59).

18 (1,1,2,2-Tetrafluoro-3-butyl)diethylamine (66).

19 Bis-(1,1,2,2-tetrafluoro-3-butyl)ethylamine (67).

20 Tris-(1,1,2,2-tetrafluoro-3-butyl)amine (68).

21 N-Methyl-2-(2H-tetrafluoroethyl)pyrrolidine (69).

22 N-(2,2,3,3-tetrafluoropropyl)-2-(2H-tetrafluoroethyl)pyrrolidine (70).

23 N-Methyl-2-(2H-tetrafluoroethyl)piperidine (71).

24 N-(2,2,3,3-tetrafluoropropyl)-2-(2H-tetrafluoroethyl)piperidine (72).

25 N-(2,2,3,3-tetrafluoropropyl)-2,6-bis-(2H-tetrafluoroethyl)piperidine (73).

26 N-Methyl-2-(2H-perfluorocyclohexyl)pyrrolidine (74).

27 N-Methyl-2-(2H,2-chlorotrifluoroethyl)pyrrolidine (75).

28 N-Methyl-2-(2H,2,2-dichlorodifluoroethyl)pyrrolidine (76).

29 (1,1,1,2,3,3-hexafluoro-4-pentyl)isocyanate (77).

30 (1H,1H,3H-Hexafluorobutyl)trimethylsilane (78).

31 Bis-(1H,1H,3H-Hexafluorobutyl)dimethylsilane (79).

32 (1H,1H,3H-Hexafluorobutyl)pentamethyldisiloxane (80).

33 (1H,1H,3H-Hexafluorobutyl)heptamethylcyclotetrasiloxane (81).

34 Bis-(1H,1H,3H-Hexafluorobutyl)hexamethylcyclotetrasiloxane (82).

35 (1,1,1,2,3,3-Hexafluoro-4-pentyloxy)ethoxydimethylsilane (84).

36 Bis-(1,1,1,2,3,3-Hexafluoro-4-pentyloxy)dimethylsilane (85).

37 (1H,1H,3H-Hexafluorobutylmethylamino)dimethylaminodimethylsilane (86).

38 1,1,1,2,3,3-Hexafluoro-4-methylpentane (89).

39 1,2-Bis-(2-tetrahydrofuryl)-1H-pentafluoropropane (91).

40 δ-Valerolactone Dimer (95).

41 ε-Caprolactone Dimer (96).

42 1,1,1,2,3,3-Hexafluoro-4-pentanone (97).

43 2-(2H-Tetrachloroethyl)oxolane (101).

44 1,1,2-Trichloro-3-ethoxybutene (102).

45 1,1,2-Trichlorobuten-3-one (103).

46 1,1,2-Trichlorobuten-3-ol (104).

47 2-(2H,2,2-Dichlorodifluoroethyl)oxolane (99).

48 2,3-Dichloro-1,1,1,4,4,4-hexafluoro-3-methoxymethyl-butane (105).

49 Bis-(2,3-dichloro-4,4,4-trifluoro-2-trifluoromethyl-butyl)ether (106).

50 1,1,1,2,3,3-Hexafluoro-4-pentanol (107).

51 1-(2H-Octafluorocyclopentyl)ethanol (108).

52 1-(2H-Decafluorocyclohexyl)ethanol (109).

53 1,1,1,2,3,3-Hexafluoroheptane-4,7-diol (110).

54 2-(Pentafluoropropenyl)oxolane (90).

55 1,1,1,2,3-Pentafluoro-4-ethoxy-2-pentene (119).

56 1,1,1,2,3-Pentafluoro-4-methoxy-2-butene (92).

57 N-Methyl-2-(Pentafluoropropenyl)pyrrolidine (120).

58 2-(Trichloroethenyl)oxolane (121).

59 Trans-2-Chloro-1,1,1,4,4,4-hexafluoro-3-methoxymethyl-2-butene (122).

60 Trans-1,1,1,4,4,4-hexafluoro-2-methoxy-3-methoxymethyl-2-butene (123).

61 Trans-1,1,1,4,4,4-hexafluoro-2-ethoxy-3-methoxymethyl-2-butene (124).

62 Cis-1,1,1,4,4,4-hexafluoro-2-ethoxy-3-methoxymethyl-2-butene (125).

63 2-(1,2-Dichloroethenyl)oxolane (126).

64 1,1,1,4,4,4-Hexafluoro-2-methoxymethyl-2-butene (127).

65 2,2,3,4,4,4-Hexafluorobutylamine (129).

66 (2,2,3,4,4,4-Hexafluorobutyl)methylamine (128).

67 (2,2,3,4,4,4-Hexafluorobutyl)ethylamine (131).

68 (2,2,3,4,4,4-Hexafluorobutyl)ethylmethylamine (130).

69 Methyl-N-(1,1,1,2,3,3-Hexafluoro-4-pentyl)carbamate (132).

70 N-Ethyl-N'-(1,1,1,2,3,3-hexafluoro-4-pentyl)urea (133).

71 (1H,1H,3H-Hexafluorobutyl)-N-methylcarbamate (134).

72 N-Methyl-N'-(1H,1H,3H-hexafluorobutyl)urea (135).

73 (1H,1H,3H-Hexafluorobutyl)-N-(1,1,1,2,3,3-hexafluoro-4-pentyl)carbamate (136).

74 1,1,1,2,3,3-Hexafluoro-4-methyl-4,5-epoxypentane (139).

75 2H,7H,4,5-Dihydroxy-4,5-dimethylperfluorooctane (140).

76 Perfluoro-N-methyl-2-propylpyrrolidine (142).

77 Perfluoro-N-butylpyrrolidine (145).

78 Perfluoro-N-butylpiperidine (146).

79 Perfluoro-N-butyl-2-propylpiperidine (147).

80 (2H-Decafluorocyclohexyl)fluoromethane (148).

81 Perfluoromethylcyclohexane (149).

82 3-Fluoromethylperfluoro-4H,3,4-dimethylhexane (150).

83 Perfluoro-3,3,4-trimethylhexane (151).

84 Perfluoro-1H,1H,11H-undecane (152).

85 Perfluoroundecane (153).

86 1-(2H-Octafluorocyclopentyl)-1,1-difluoroethane (154).

87 Perfluoroethylcyclopentane (155).

88 1-(2H-Decafluorocyclohexyl)-1-fluoroethene (156).

89 1-(2H-Decafluorocyclohexyl)-1,1-difluoroethane (157).

90 Perfluoroethylcyclohexane (158).

91 1H,1H,3H-Hexafluorobutyltrifluoroacetate (159).

92 Perfluoro-1-ethoxy-1H,1H,3H-butane (160).

93 Perfluoroethoxybutane (162).

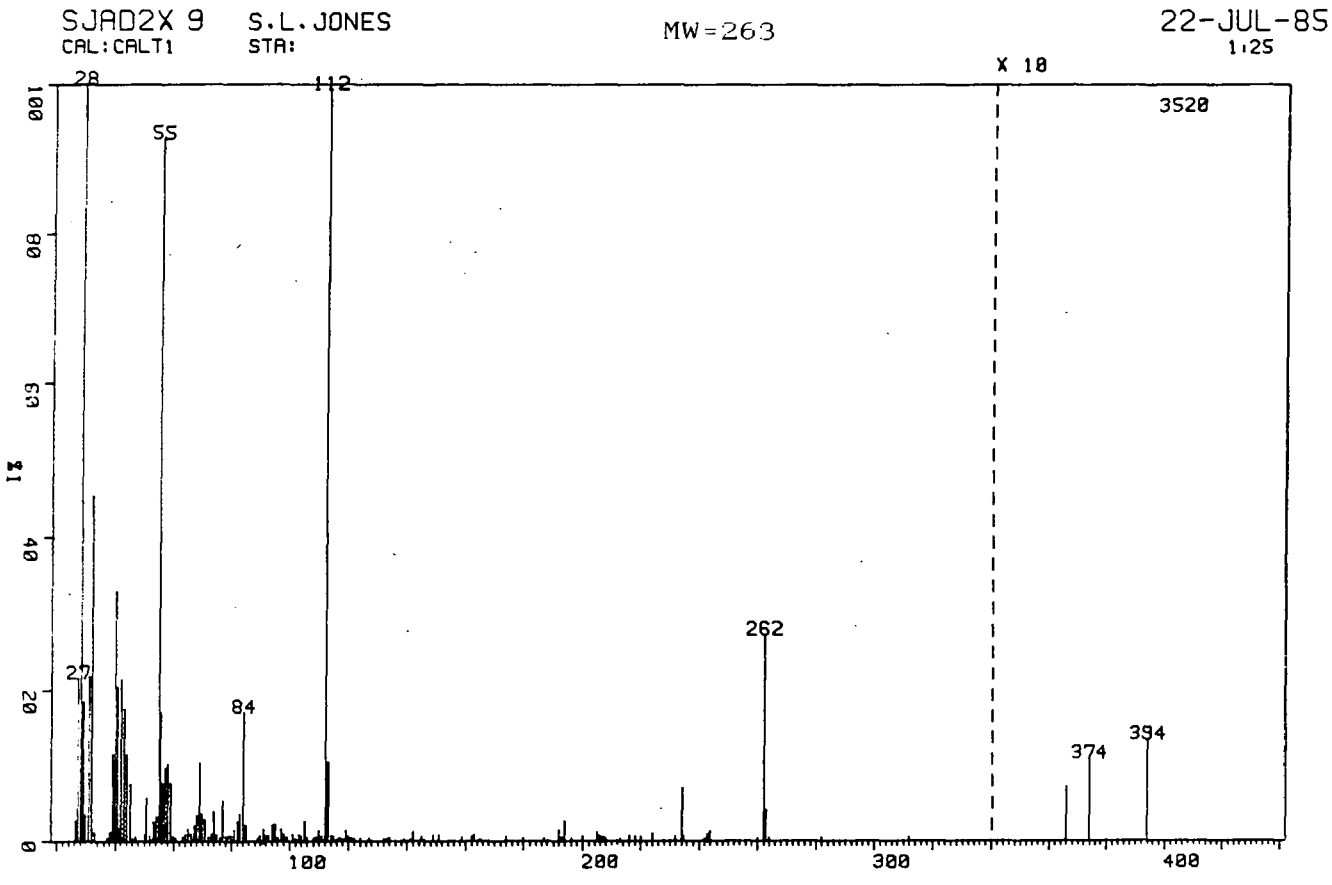
94 2,5,5-Trichloroperfluoro-2-propyloxolane (163).

95 2-Chloroperfluoro-2,5-dipropyloxolane (164).

96 2,5-Dichloroperfluoro-2,5-dipropyloxolane (165).

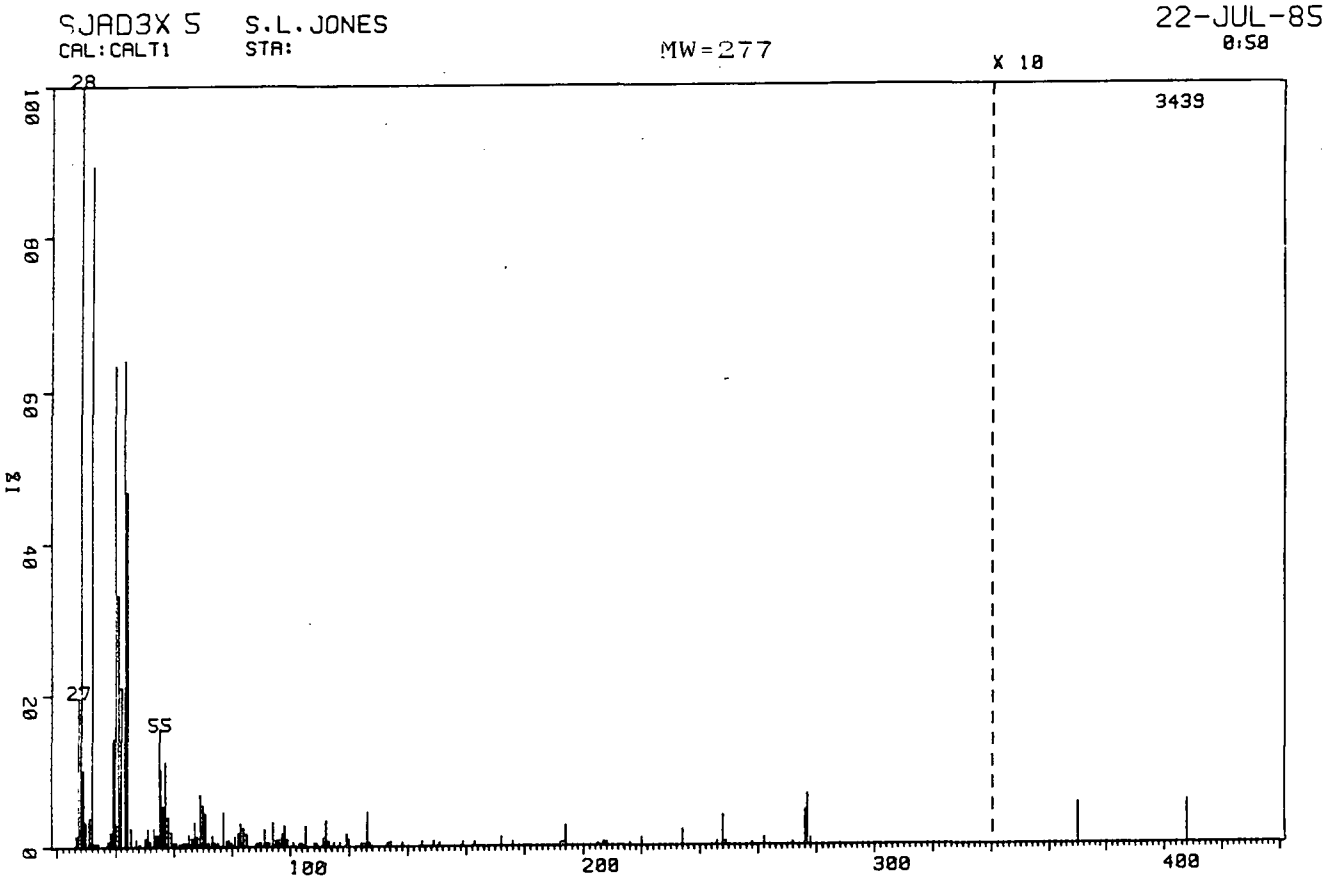
97 Perfluoro-2-pentene.

No. 1 N-METHYL-6-(2H-HEXAFLUOROPROPYL)-2-PIPERIDONE (38)



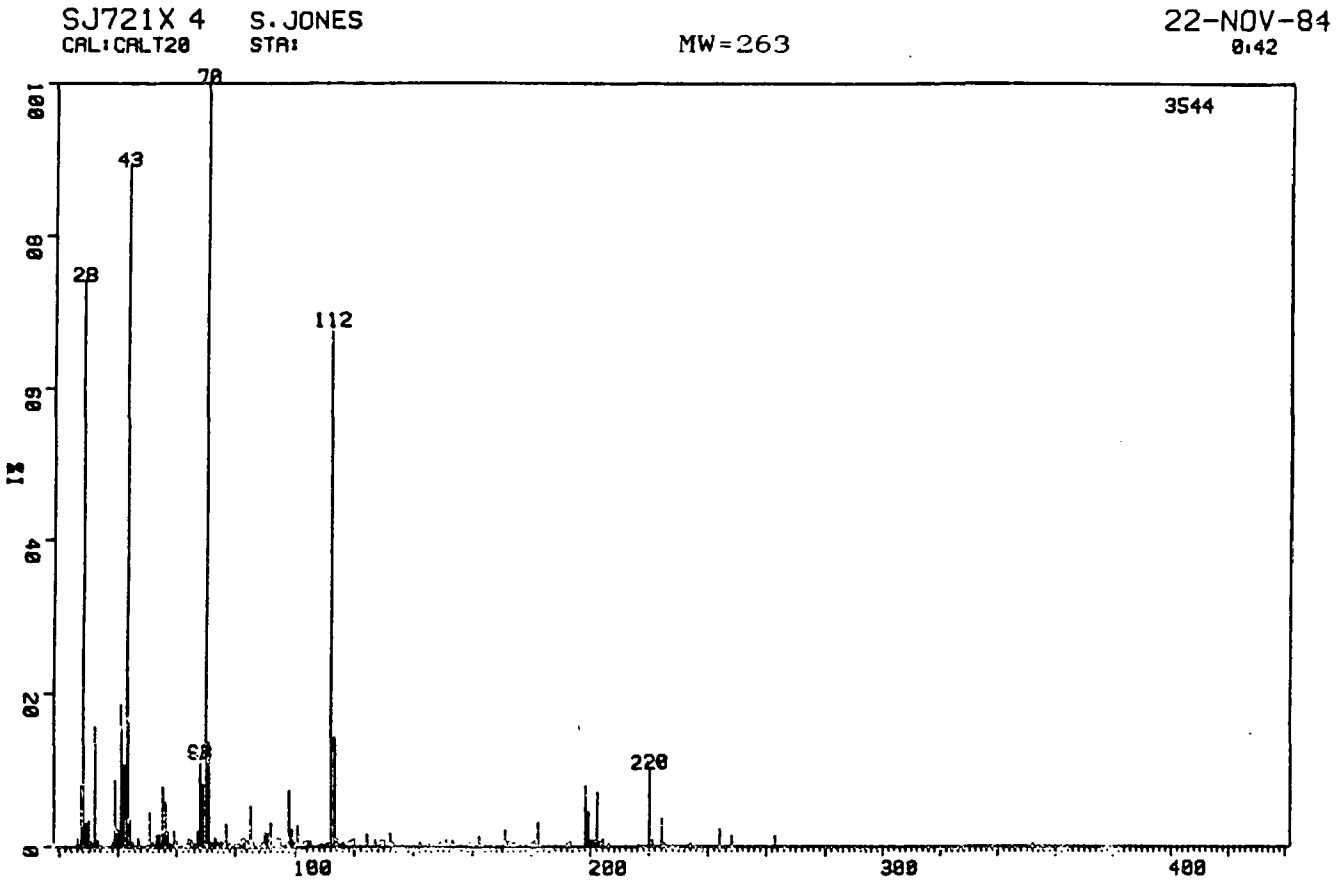
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.37	2.70	23	53.09	2.64	45	85.09	2.07
2	27.30	21.68	24	54.12	3.24	46	90.98	1.59
3	28.17	100.00	25	55.11	92.73	47	94.06	2.19
4	28.18	9.43	26	55.14	16.93	48	95.06	2.30
5	29.02	3.78	27	56.12	7.64	49	97.07	1.62
6	29.05	18.44	28	57.11	9.57	50	105.05	2.67
7	29.88	3.49	29	58.07	10.20	51	109.92	1.45
8	30.95	21.90	30	59.00	7.70	52	112.01	99.32
9	32.03	45.45	31	65.10	1.59	53	113.02	10.43
10	33.13	1.11	32	66.11	1.05	54	118.97	1.45
11	38.07	1.25	33	67.06	2.13	55	141.94	1.28
12	38.99	11.48	34	68.03	3.49	56	191.92	1.48
13	39.82	33.07	35	68.95	10.31	57	193.98	2.70
14	39.88	2.53	36	69.92	3.64	58	204.94	1.19
15	40.97	20.45	37	70.99	2.93	59	223.98	1.02
16	41.51	1.68	38	73.05	1.05	60	233.97	6.90
17	42.02	12.02	39	74.10	3.89	61	243.95	1.34
18	42.05	21.45	40	77.04	5.26	62	261.93	27.41
19	43.12	17.50	41	80.98	1.56	63	262.94	4.09
20	44.15	11.36	42	82.02	2.61	64	373.86	1.08
21	45.15	7.56	43	83.07	3.61	65	393.91	1.34
22	50.94	5.71	44	84.11	17.05			

No.2 N-METHYL-7-(2H-HEXAFLUOROPROPYL)-ε-CAPROLACTAM (39)



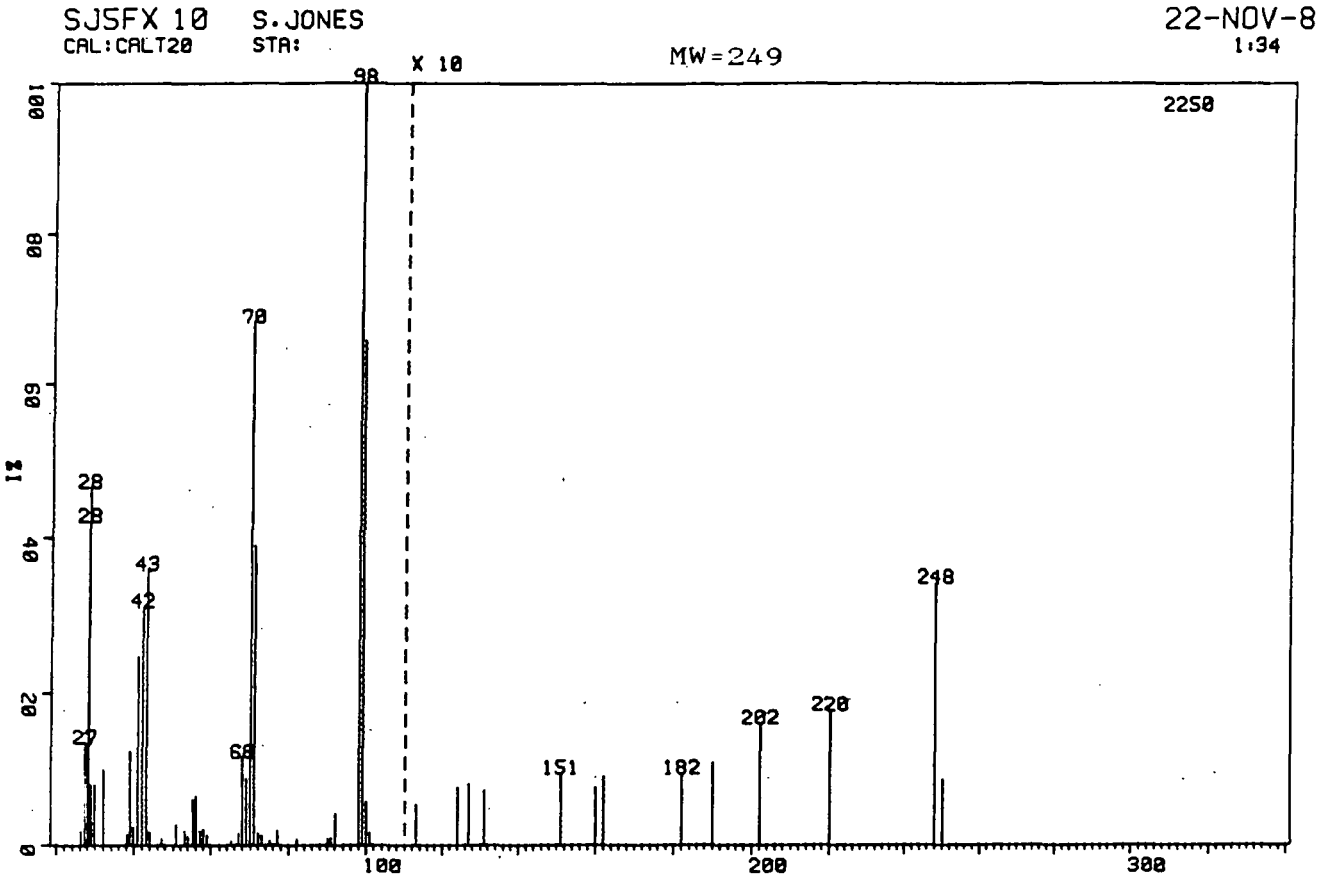
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.37	1.45	23	55.12	15.27	45	94.06	3.08
2	27.30	19.66	24	55.15	9.97	46	95.07	0.90
3	28.17	100.00	25	56.14	5.15	47	96.09	0.93
4	29.02	4.19	26	57.13	10.99	48	97.09	1.69
5	29.05	9.92	27	58.07	3.84	49	98.06	2.65
6	29.88	3.17	28	59.01	1.89	50	99.01	0.99
7	30.95	3.78	29	65.12	1.63	51	105.07	2.70
8	32.03	89.33	30	66.09	1.10	52	111.05	1.08
9	38.08	1.86	31	67.08	3.20	53	112.04	3.29
10	38.99	14.10	32	68.04	1.34	54	118.98	1.63
11	39.83	63.27	33	68.97	6.69	55	119.95	0.96
12	39.89	2.85	34	69.94	5.32	56	126.05	4.36
13	40.98	33.24	35	71.01	4.22	57	171.95	1.16
14	42.06	21.02	36	73.06	1.48	58	193.98	2.59
15	43.13	63.94	37	77.05	4.36	59	219.90	1.02
16	44.16	47.11	38	79.00	0.90	60	233.98	2.06
17	45.17	2.41	39	81.02	1.34	61	247.96	3.87
18	47.11	0.99	40	82.04	1.74	62	261.95	1.02
19	49.89	1.13	41	83.08	2.94	63	275.96	4.48
20	50.96	2.30	42	84.11	2.41	64	276.96	6.57
21	53.10	2.30	43	85.10	1.69	65	277.96	0.87
22	54.13	1.54	44	90.97	2.24			

No.3 N-ACETYL-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (40)



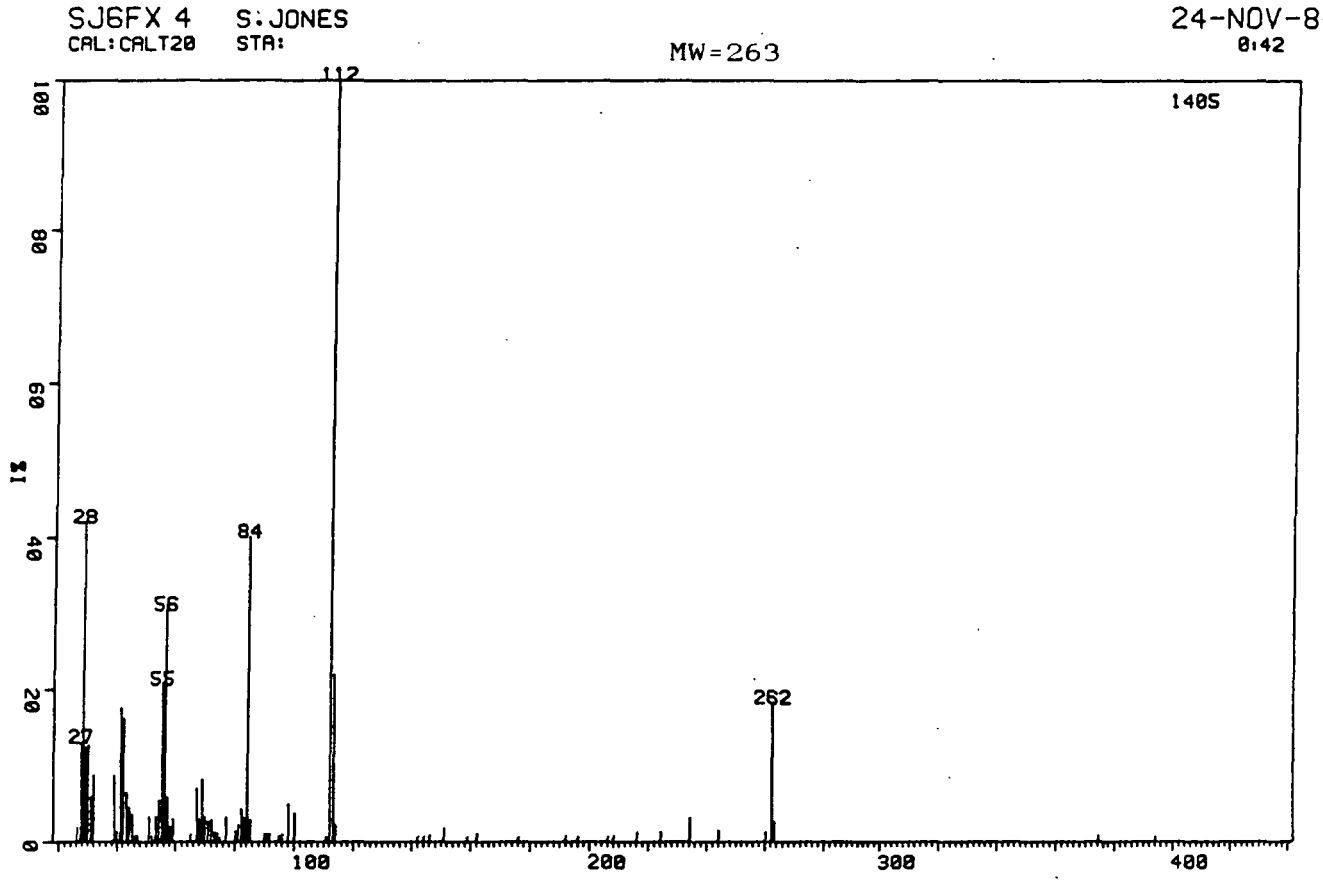
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.29	0.53	23	57.15	0.93	45	113.11	7.40
2	27.23	4.01	24	59.01	0.93	46	114.10	0.48
3	28.11	36.19	25	64.11	0.48	47	120.00	0.45
4	28.96	0.64	26	67.13	1.07	48	124.03	0.70
5	29.00	1.51	27	68.06	6.14	49	132.07	0.87
6	29.83	1.79	28	68.99	4.21	50	162.10	0.70
7	31.97	8.77	29	69.97	100.00	51	171.03	1.04
8	38.04	0.42	30	71.03	6.53	52	182.08	1.49
9	38.96	4.40	31	73.09	0.53	53	198.10	3.95
10	39.80	0.56	32	77.07	1.37	54	199.09	2.16
11	39.86	1.07	33	82.02	0.53	55	202.12	3.70
12	40.94	9.22	34	83.13	0.64	56	204.10	0.48
13	42.03	5.35	35	85.01	1.49	57	220.05	5.05
14	43.08	45.11	36	85.09	2.66	58	224.13	1.74
15	43.11	11.24	37	89.93	0.84	59	244.12	1.09
16	44.14	1.57	38	90.99	0.76	60	248.05	0.64
17	47.11	0.50	39	92.02	1.43	61	263.11	0.67
18	50.95	2.21	40	98.06	3.81			
19	53.10	0.70	41	99.03	1.12			
20	54.14	0.73	42	100.98	1.37			
21	55.16	3.90	43	104.08	0.48			
22	56.13	3.11	44	112.09	33.31			

No.4 N-FORMYL-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (44)



PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.28	1.87	23	56.10	6.40	45	100.00	5.64
2	27.22	13.47	24	56.14	1.16	46	101.04	1.60
3	28.09	42.18	25	57.13	1.91	47	113.04	0.53
4	28.11	46.58	26	58.05	2.09	48	124.06	0.76
5	28.96	7.87	27	59.00	1.33	49	127.06	0.80
6	28.98	2.98	28	65.11	0.53	50	130.99	0.71
7	29.82	7.91	29	67.08	1.51	51	151.00	0.93
8	31.95	9.82	30	68.05	11.47	52	160.02	0.76
9	38.03	1.47	31	68.95	8.67	53	162.10	0.89
10	38.95	12.22	32	69.01	3.42	54	182.10	0.93
11	39.79	0.67	33	69.95	68.27	55	190.04	1.07
12	39.85	2.40	34	70.98	38.93	56	202.11	1.60
13	40.93	24.84	35	72.03	1.56	57	220.05	1.78
14	42.02	31.29	36	73.07	1.24	58	248.09	3.42
15	43.09	35.96	37	75.06	0.58	59	250.09	0.84
16	44.10	1.16	38	77.05	1.87			
17	44.13	1.69	39	81.99	0.84			
18	47.09	0.89	40	89.93	0.89			
19	50.93	2.67	41	91.00	0.93			
20	53.09	1.91	42	92.03	4.04			
21	54.11	1.20	43	98.07	100.00			
22	55.14	6.00	44	99.04	65.60			

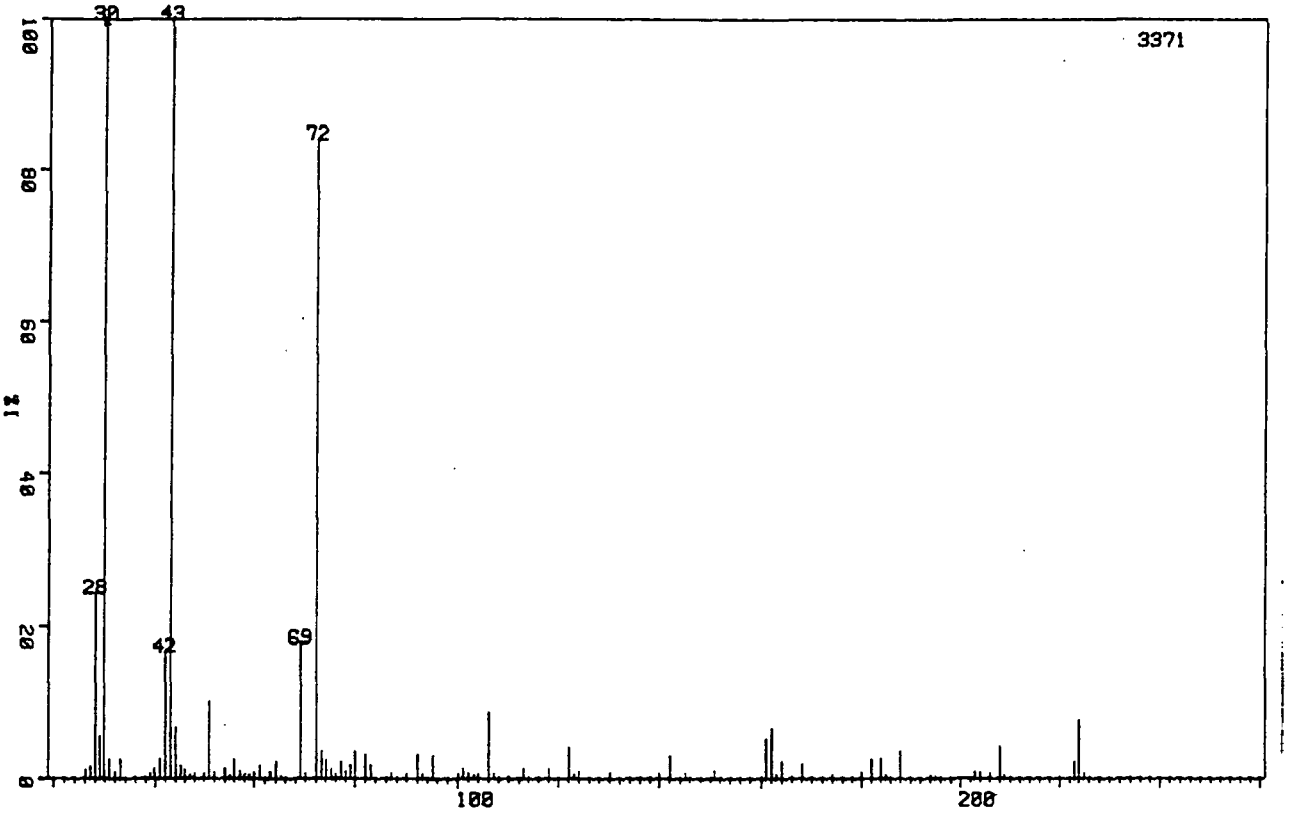
No.5 N-FORMYL-2-(2H-HEXAFLUOROPROPYL)PIPERIDINE (45)



PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.29	1.99	23	59.03	3.06	45	98.02	5.05
2	27.22	13.02	24	65.14	1.07	46	99.96	3.77
3	28.11	42.06	25	67.10	7.05	47	112.05	100.00
4	28.98	12.38	26	68.04	2.99	48	113.07	22.06
5	29.82	12.67	27	68.95	8.26	49	114.10	2.21
6	30.88	5.91	28	69.94	3.35	50	146.10	0.93
7	31.96	8.75	29	70.98	2.78	51	150.93	1.85
8	38.96	8.75	30	72.03	3.06	52	162.08	1.14
9	39.86	1.35	31	73.06	1.35	53	192.04	0.85
10	40.94	17.58	32	74.11	1.21	54	208.03	0.85
11	42.03	16.16	33	77.01	3.27	55	216.13	1.35
12	43.10	6.55	34	79.92	1.42	56	224.11	1.35
13	44.14	4.56	35	80.91	2.28	57	234.08	3.20
14	45.14	3.63	36	80.98	1.00	58	244.11	1.57
15	47.10	0.93	37	82.02	4.34	59	260.04	1.35
16	50.95	3.35	38	83.06	3.20	60	262.09	18.15
17	53.10	3.42	39	84.09	40.14	61	263.11	2.70
18	54.14	5.48	40	85.09	2.99			
19	55.16	20.78	41	89.91	1.14			
20	56.15	30.68	42	90.97	1.07			
21	57.13	5.91	43	92.01	1.07			
22	58.08	2.06	44	96.10	1.07			

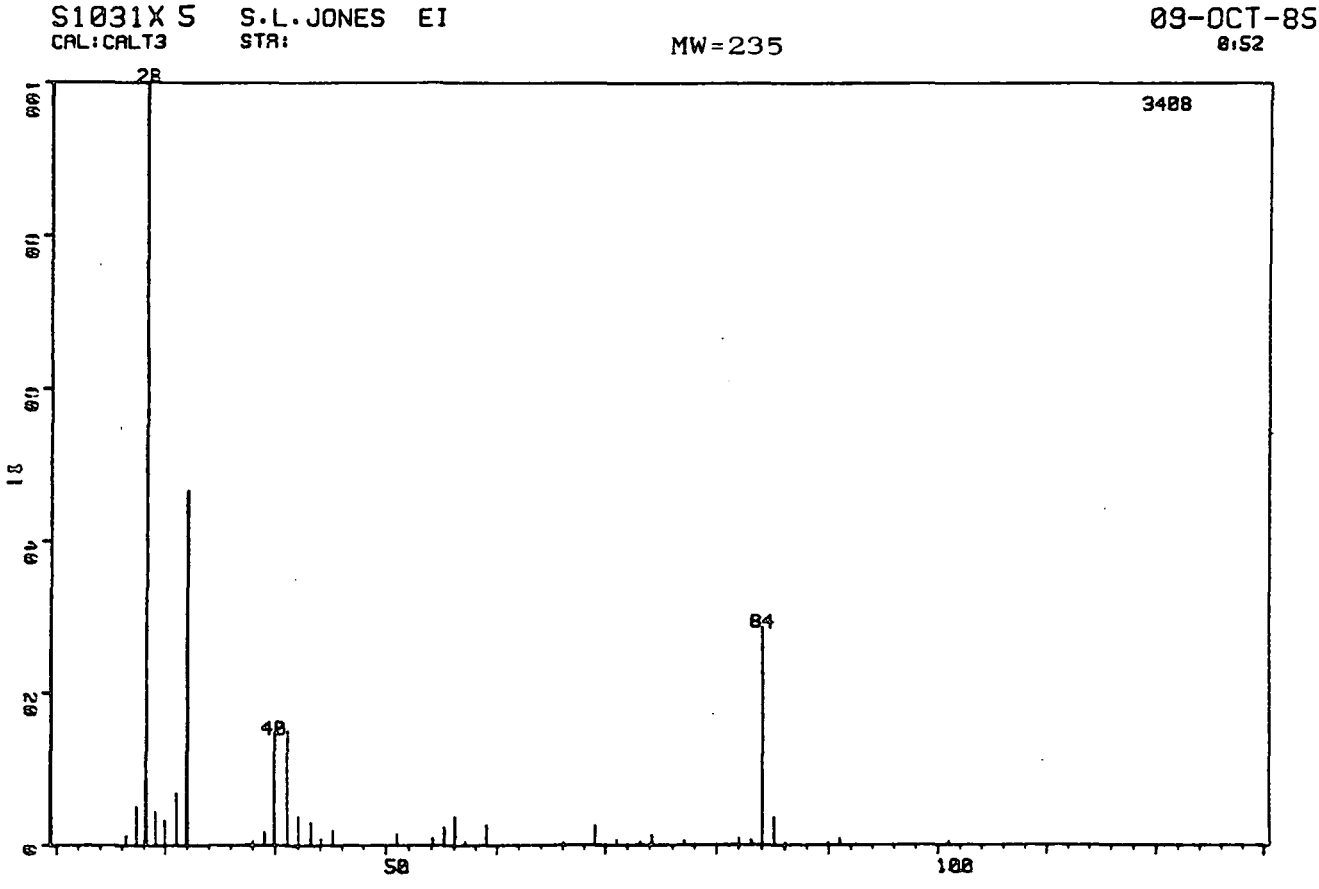
No.6 N-(1H,1H,3H-HEXAFLUOROBUTYL)-ACETAMIDE (46)

SJ661X 7 S.L.JONES 24-OCT-84
CAL:CALTS STA: MW=223 1:6



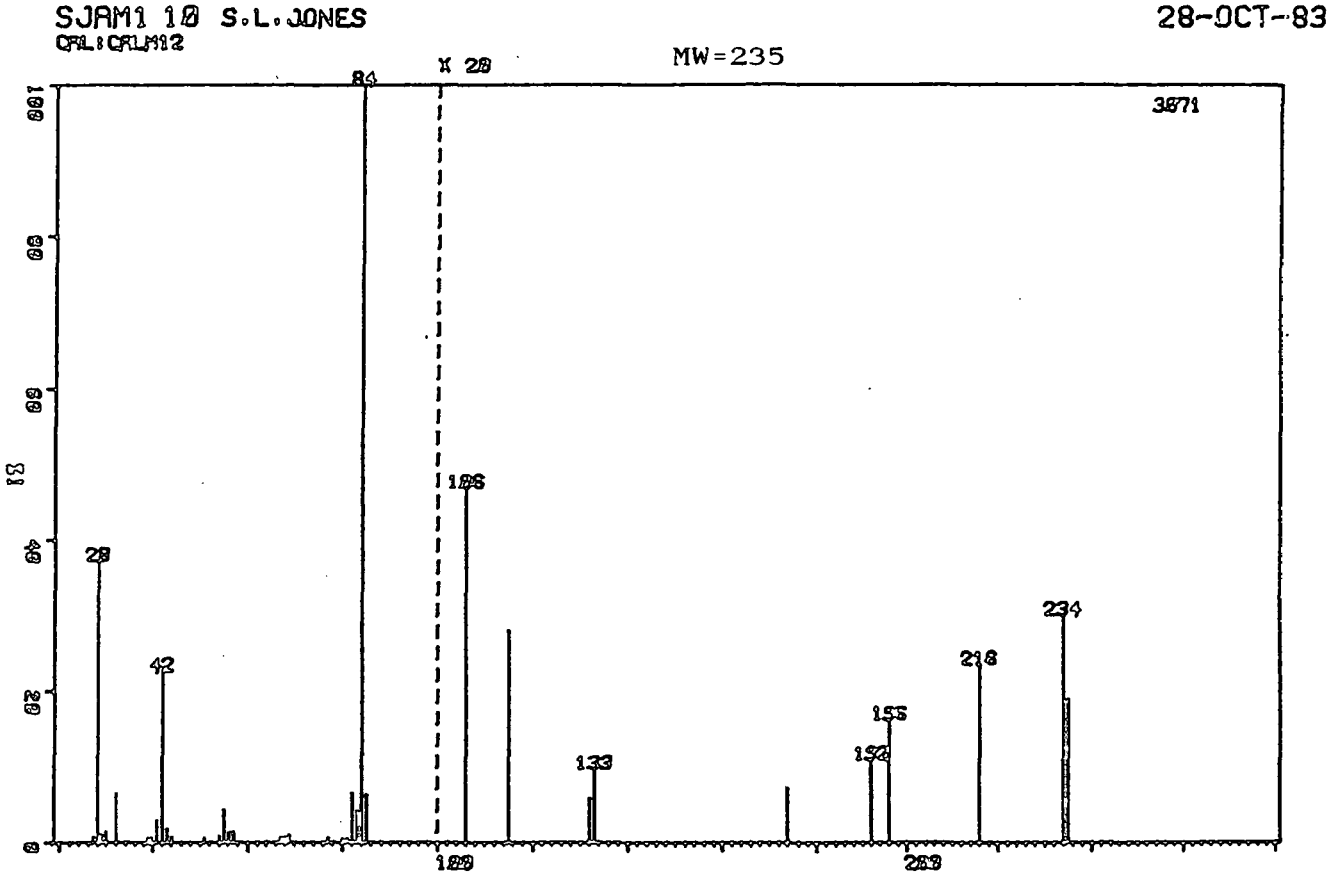
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.20	1.04	23	60.92	1.63	45	124.00	0.82
2	27.14	1.44	24	63.01	0.82	46	129.95	0.76
3	28.03	23.17	25	64.04	2.11	47	141.97	2.67
4	28.90	5.26	26	68.93	16.95	48	144.99	0.73
5	29.75	100.00	27	72.05	79.70	49	150.92	0.99
6	30.75	2.34	28	73.08	3.38	50	160.94	4.93
7	30.80	2.22	29	74.07	2.28	51	161.98	6.28
8	31.87	0.79	30	75.07	1.13	52	163.99	2.11
9	32.97	2.31	31	77.06	2.11	53	167.95	1.80
10	39.77	1.15	32	78.02	0.82	54	179.91	0.84
11	40.83	2.34	33	78.98	1.60	55	181.96	2.39
12	41.91	15.85	34	79.94	3.35	56	183.98	2.48
13	42.98	94.90	35	81.99	2.96	57	187.93	3.41
14	44.02	6.31	36	83.03	1.60	58	202.94	0.82
15	45.04	1.46	37	87.03	0.70	59	203.96	0.84
16	46.03	1.07	38	92.00	2.96	60	207.91	3.97
17	50.85	9.54	39	95.04	2.67	61	222.94	1.97
18	51.94	0.76	40	100.95	1.21	62	223.94	7.38
19	54.04	1.24	41	106.02	8.33	63	224.95	0.70
20	56.04	2.34	42	112.99	1.21			
21	57.02	0.90	43	117.98	1.18			
22	59.86	0.76	44	122.00	3.86			

No. 7 5-(2H-HEXAFLUOROPROPYL)-2-PYRROLIDONE (47)



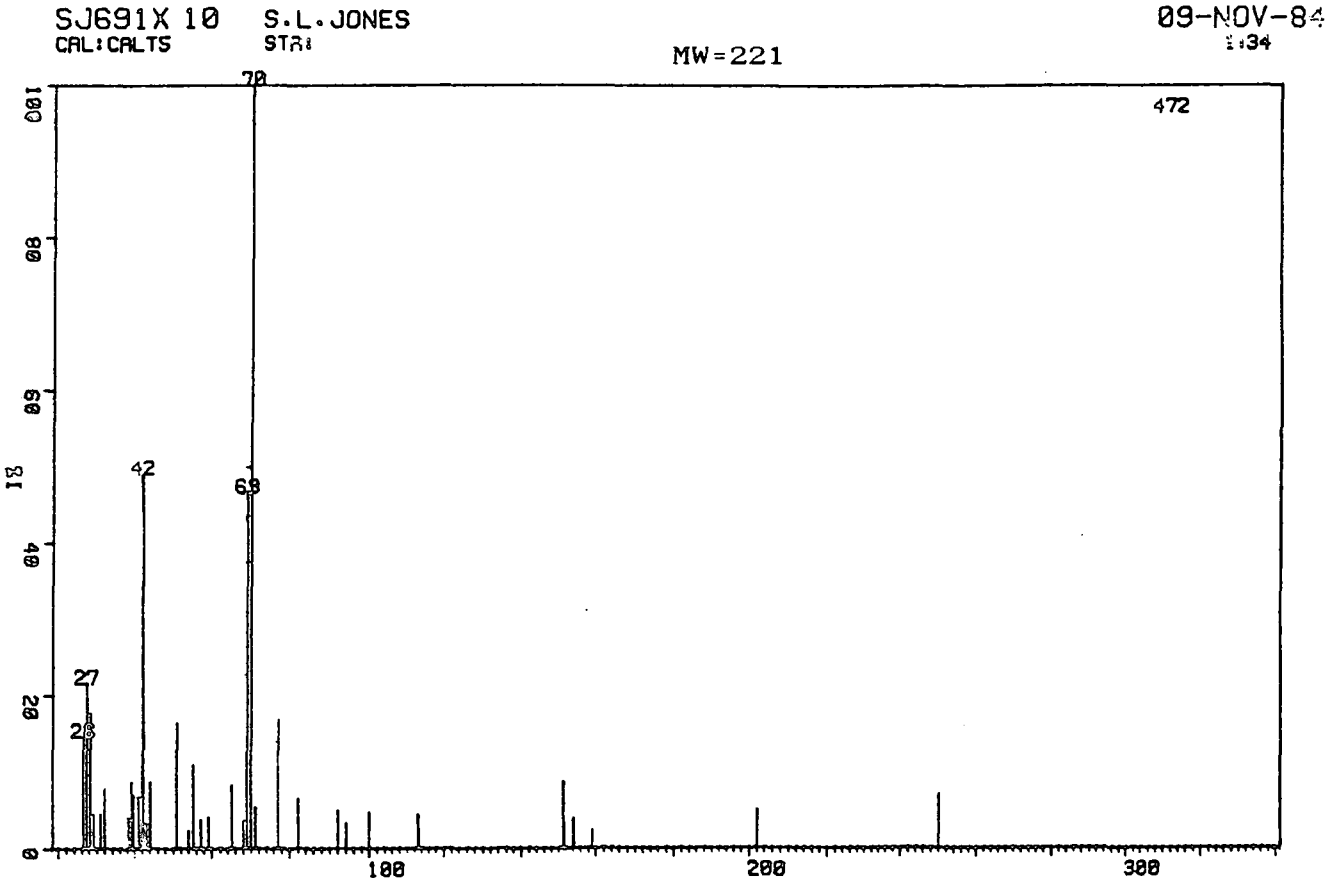
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.36	1.26	23	56.14	3.79
2	27.29	5.05	24	57.09	0.26
3	28.17	100.00	25	57.14	0.53
4	29.02	2.49	26	59.02	2.64
5	29.05	4.43	27	66.13	0.32
6	29.88	3.26	28	68.99	2.52
7	30.95	6.84	29	71.01	0.70
8	32.03	46.68	30	73.13	0.50
9	38.08	0.50	31	74.17	1.32
10	39.00	1.76	32	77.06	0.59
11	39.83	14.52	33	82.01	0.97
12	39.89	0.73	34	83.07	0.67
13	40.98	14.94	35	84.11	28.84
14	42.07	3.73	36	85.09	3.67
15	43.10	0.91	37	86.08	0.32
16	43.14	2.99	38	89.92	0.32
17	44.12	0.91	39	90.99	0.88
18	45.13	0.67	40	100.96	0.50
19	45.16	1.94			
20	50.96	1.50			
21	54.13	0.97			
22	55.13	2.41			

No.8 N-METHYL-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (48)



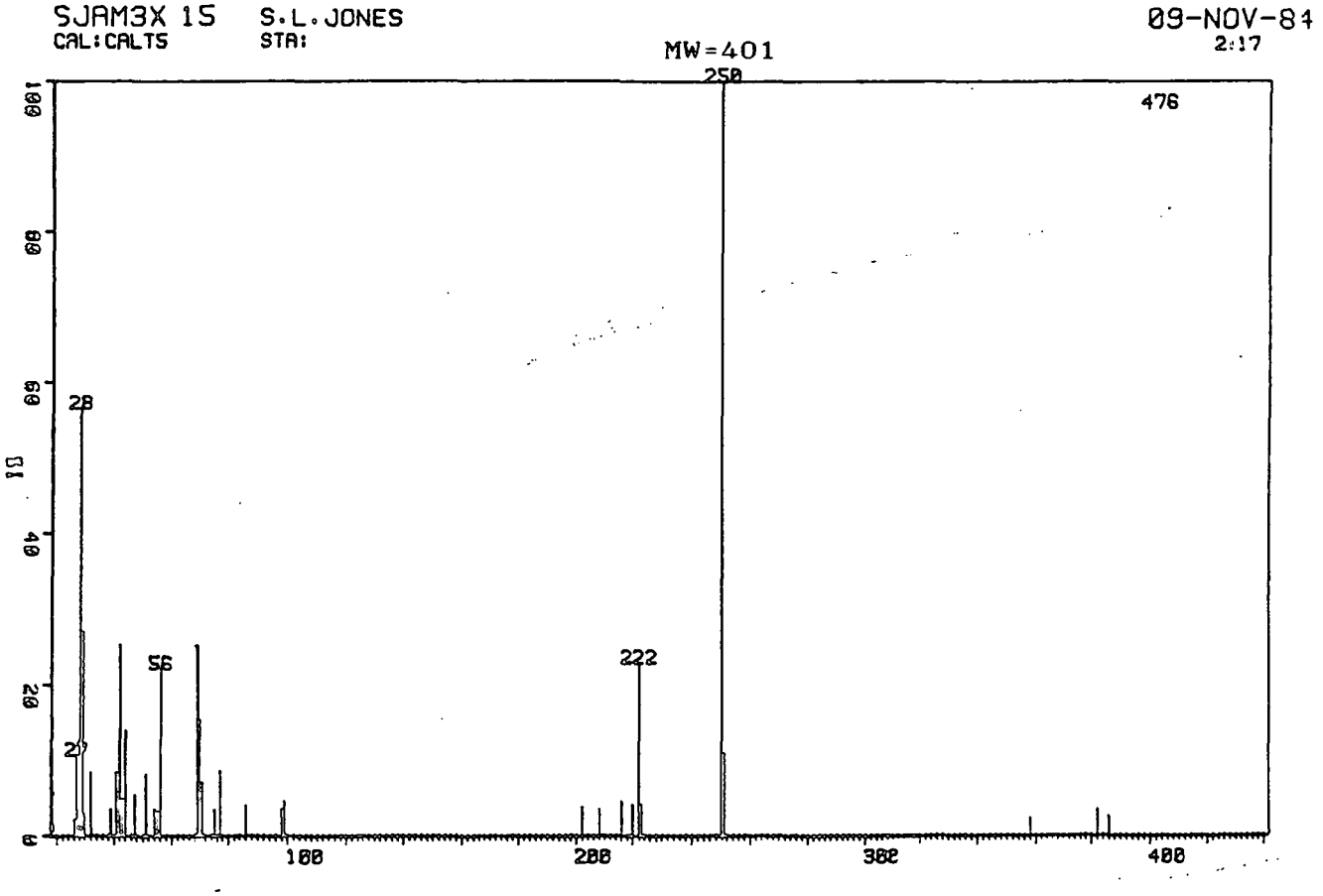
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.18	0.85	23	82.04	6.55
2	28.06	37.35	24	83.08	4.17
3	28.96	1.04	25	84.10	100.00
4	29.80	1.37	26	85.10	6.22
5	31.94	6.55	27	106.01	2.34
6	38.96	0.62	28	115.04	1.40
7	39.80	0.62	29	131.97	0.29
8	40.94	3.00	30	132.99	0.49
9	42.03	22.73	31	173.91	0.36
10	43.10	1.79	32	191.91	0.55
11	44.15	0.68	33	195.96	0.81
12	50.93	0.52	34	215.95	1.17
13	54.12	0.85	35	233.90	1.50
14	55.14	4.43	36	234.93	0.94
15	56.13	1.30			
16	57.11	1.40			
17	67.10	0.55			
18	68.06	0.55			
19	68.98	0.94			
20	77.05	0.55			
21	79.96	0.36			
22	81.01	0.49			

No.9 ETHYLIDINE-1,1,1,2,3,3-HEXAFLUORO-4-PENTYLIMINE (51)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.37	14.62	23	69.96	100.00
2	27.29	21.61	24	71.02	5.30
3	28.17	17.58	25	77.07	16.74
4	29.05	4.45	26	82.02	6.57
5	30.94	4.45	27	92.06	4.87
6	32.03	7.84	28	94.14	3.18
7	38.07	4.03	29	100.05	4.66
8	38.99	8.69	30	113.03	4.45
9	39.82	6.99	31	150.99	8.69
10	39.88	4.66	32	154.08	3.81
11	40.97	6.78	33	159.05	2.33
12	42.05	49.15	34	202.18	4.87
13	43.15	3.18	35	250.08	6.99
14	44.17	8.69			
15	50.95	16.31			
16	54.15	2.33			
17	55.14	10.81			
18	57.10	3.60			
19	59.03	4.03			
20	65.12	8.26			
21	68.08	3.60			
22	68.96	46.61			

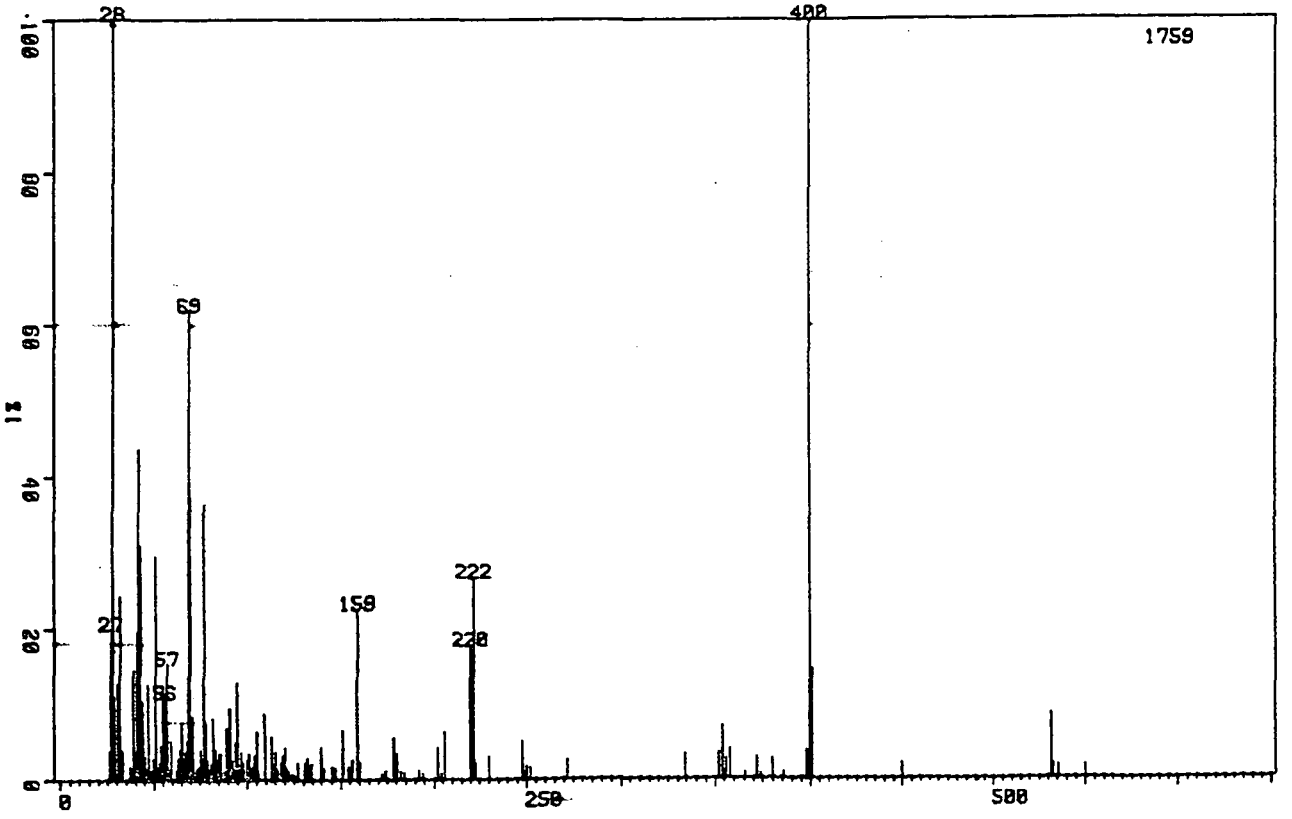
No.10 BIS-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)ETHYLAMINE (52)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.37	2.10	23	98.11	3.57
2	27.30	10.71	24	99.07	4.62
3	28.17	56.51	25	202.11	3.78
4	29.06	26.89	26	208.05	3.57
5	29.89	2.94	27	216.15	4.62
6	32.04	8.40	28	220.01	4.20
7	39.00	3.57	29	222.00	22.90
8	40.98	8.40	30	223.10	4.20
9	42.06	25.21	31	249.98	100.00
10	43.14	4.83	32	251.04	10.92
11	44.17	13.87			
12	47.13	5.46			
13	50.97	8.19			
14	54.15	3.57			
15	55.17	3.15			
16	56.15	22.06			
17	69.01	25.21			
18	70.00	15.34			
19	71.08	7.14			
20	75.14	3.36			
21	77.08	8.61			
22	86.14	3.99			

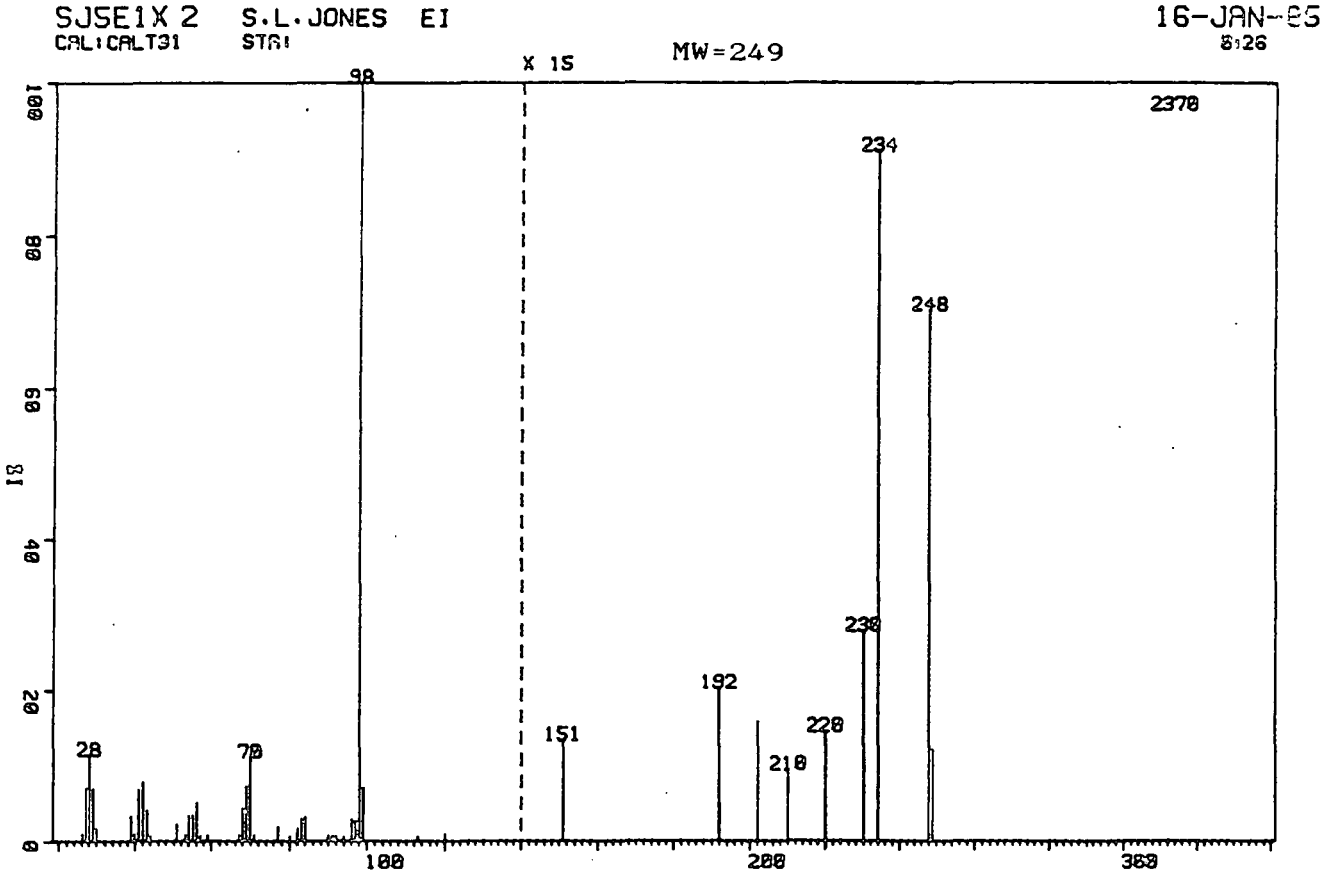
No.11 TRIS-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)AMINE (53)

SJ693X 6 S.L.JONES 24-OCT-84
CAL:CALTS STA: MW=551 8:57



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.21	2.92	23	67.06	2.83	45	112.98	4.50
2	27.15	15.74	24	68.03	4.05	46	115.00	2.88
3	28.03	100.00	25	68.94	48.90	47	119.97	3.33
4	28.89	3.19	26	69.00	9.45	48	138.94	3.42
5	28.93	8.82	27	69.94	29.46	49	150.92	5.17
6	30.76	10.03	28	71.00	6.66	50	158.95	17.81
7	31.87	19.21	29	75.05	3.01	51	177.95	4.41
8	32.98	3.06	30	77.03	28.74	52	179.96	2.65
9	38.89	11.52	31	78.01	5.85	53	202.00	3.28
10	40.86	15.52	32	81.97	6.43	54	205.97	4.90
11	41.95	34.50	33	83.09	3.15	55	219.94	14.04
12	43.03	24.43	34	85.10	2.70	56	221.98	21.05
13	44.07	8.23	35	86.03	2.65	57	247.97	3.96
14	47.04	10.03	36	88.92	5.40	58	333.91	2.52
15	50.88	23.30	37	89.88	3.37	59	351.90	2.61
16	54.06	3.55	38	90.97	7.47	60	353.90	5.49
17	55.10	9.94	39	94.05	3.82	61	357.88	3.06
18	56.10	8.64	40	95.03	10.21	62	397.93	2.92
19	57.09	12.19	41	97.02	2.83	63	399.92	79.13
20	58.96	4.05	42	100.96	2.65	64	400.93	11.47
21	64.06	3.15	43	105.07	4.99	65	531.82	6.70
22	65.09	5.98	44	108.96	6.97			

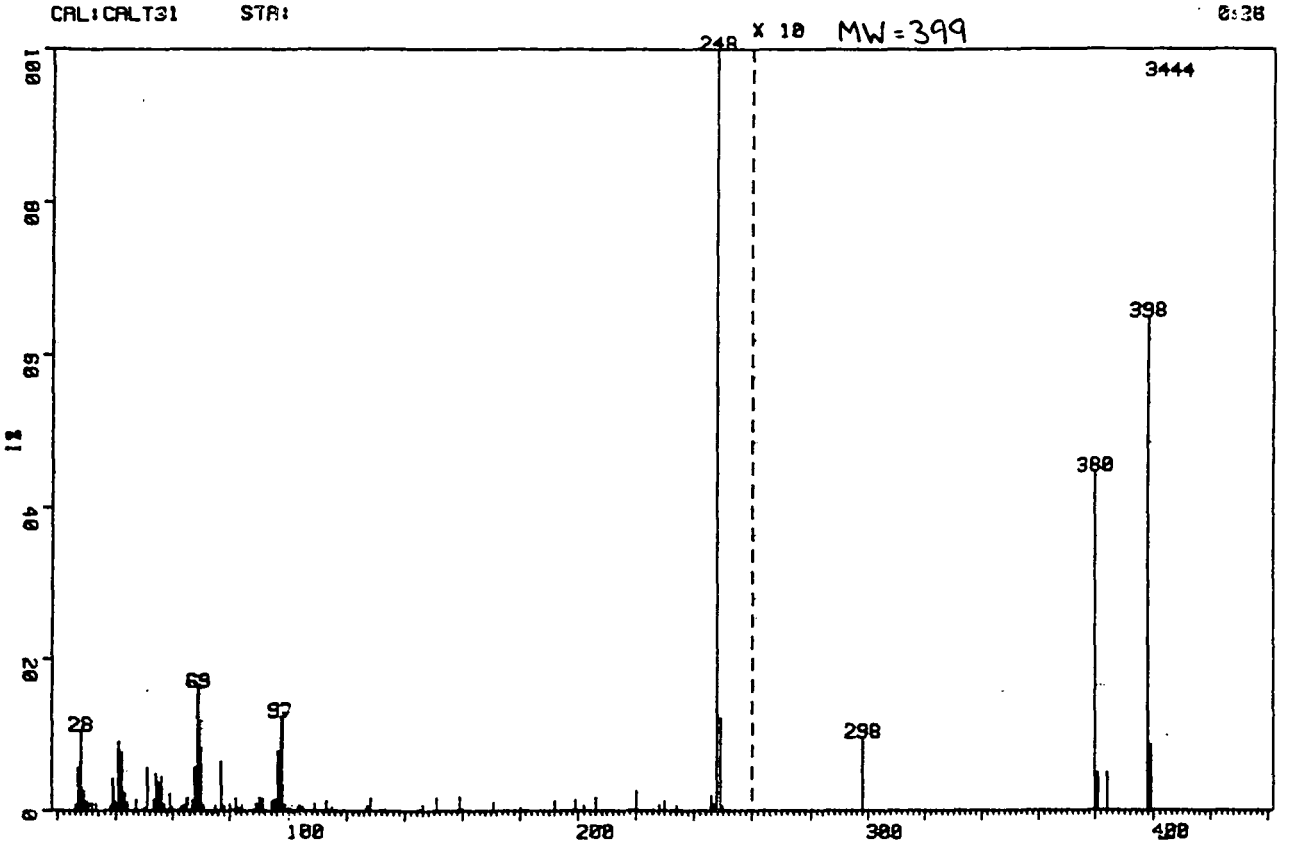
No. 12 N-ETHYL-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (54)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	0.97	23	70.99	0.80	45	219.90	0.97
2	27.22	7.00	24	77.02	1.98	46	229.96	1.86
3	28.11	11.39	25	79.90	0.68	47	233.98	6.08
4	28.99	6.92	26	81.94	1.10	48	247.93	4.68
5	29.81	1.65	27	82.01	1.60	49	248.92	0.80
6	38.94	3.33	28	83.05	2.87			
7	39.83	0.89	29	84.07	3.21			
8	40.91	6.75	30	89.87	0.80			
9	42.00	7.85	31	90.95	0.59			
10	43.08	4.01	32	91.99	0.63			
11	44.11	0.68	33	94.06	0.46			
12	50.90	2.24	34	96.09	2.83			
13	53.06	0.93	35	97.08	2.57			
14	54.08	3.25	36	98.06	100.00			
15	55.10	3.25	37	99.03	7.00			
16	56.10	5.02	38	112.98	0.59			
17	57.08	0.59	39	119.95	0.97			
18	58.96	0.80	40	150.90	0.89			
19	67.06	0.89	41	191.87	1.35			
20	68.03	4.35	42	191.98	0.34			
21	68.95	7.22	43	201.94	1.05			
22	69.93	11.10	44	209.91	0.63			

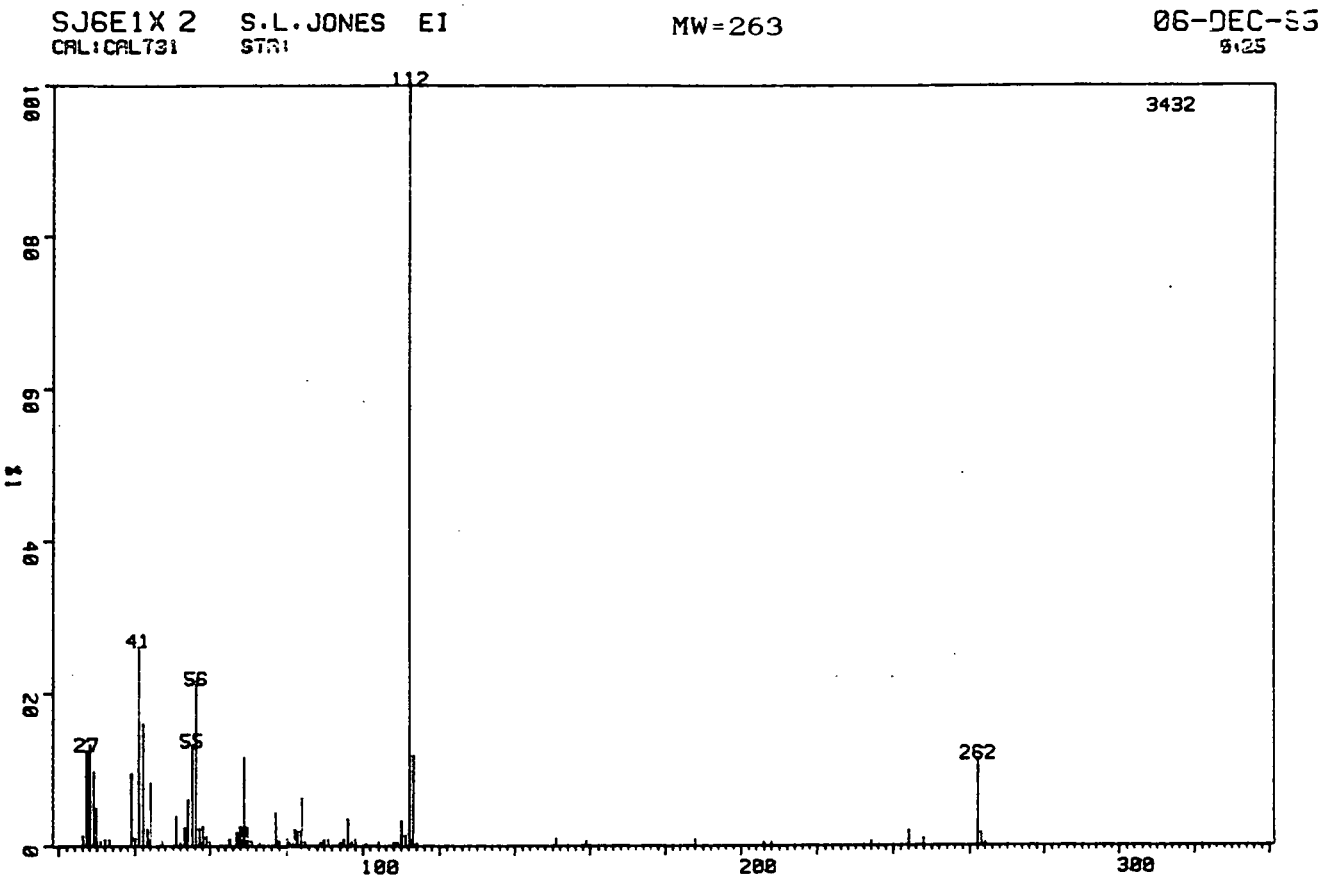
No. 13 N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)-2-(2H-HEXAFLUOROPROPYL)PYRROLIDINE (55)

SJSE2X 2 S.L.JONES EI 16-JAN-85
CAL:CALT31 STA: 0:38



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	0.84	23	58.96	2.15	45	100.94	0.90
2	27.22	5.63	24	64.05	0.81	46	104.03	0.81
3	28.11	10.57	25	65.07	1.71	47	108.96	0.96
4	28.99	2.61	26	67.06	1.36	48	113.00	1.31
5	29.81	1.34	27	68.03	5.75	49	128.03	1.68
6	30.84	0.90	28	68.93	16.35	50	146.03	0.84
7	31.95	1.02	29	68.98	12.31	51	150.91	1.74
8	33.06	0.93	30	69.93	8.28	52	158.91	1.89
9	38.94	4.09	31	70.95	0.81	53	170.91	1.07
10	39.83	1.07	32	77.02	6.48	54	191.89	1.34
11	40.92	8.94	33	79.90	0.96	55	198.93	1.42
12	42.00	7.64	34	81.96	1.68	56	205.94	1.66
13	43.07	2.41	35	84.06	0.84	57	219.90	2.58
14	44.11	1.10	36	88.92	0.90	58	229.96	1.22
15	47.06	1.45	37	89.87	1.83	59	245.93	1.95
16	50.90	5.69	38	90.95	1.60	60	246.94	0.84
17	53.05	1.45	39	94.07	1.31	61	247.93	100.00
18	54.08	4.88	40	95.02	1.51	62	248.94	12.05
19	55.10	3.75	41	96.09	7.75	63	297.91	0.96
20	56.06	1.16	42	97.08	12.49	64	379.82	4.47
21	56.10	4.38	43	98.06	13.07	65	397.89	6.50
22	57.08	0.96	44	99.01	0.81	66	398.90	0.87

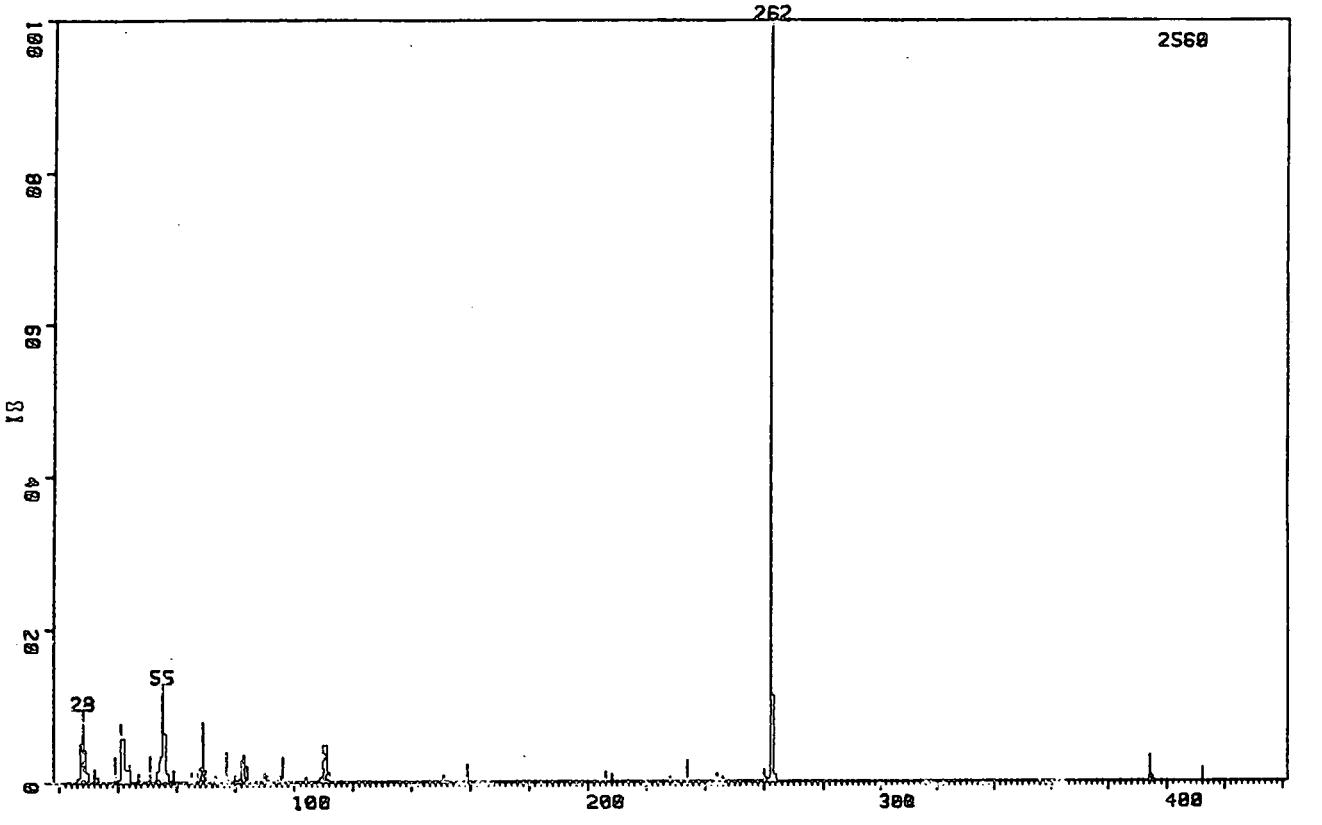
No. 14 N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)PIPERIDINE (56)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	1.37	23	57.11	2.30	45	95.04	0.90
2	27.22	12.56	24	58.09	2.71	46	96.11	3.61
3	28.11	13.29	25	59.00	1.31	47	98.06	0.90
4	28.12	6.26	26	59.92	0.61	48	104.04	0.50
5	28.99	9.79	27	65.11	0.96	49	108.06	0.50
6	29.82	5.01	28	67.09	1.84	50	108.98	0.50
7	30.85	0.55	29	68.05	2.62	51	110.01	3.29
8	31.96	0.90	30	68.95	11.68	52	111.06	1.49
9	33.07	0.87	31	69.02	10.11	53	112.10	100.00
10	38.95	9.53	32	69.96	2.51	54	113.00	0.87
11	39.85	1.02	33	70.98	0.58	55	113.13	11.86
12	40.94	26.17	34	71.03	0.73	56	150.96	1.02
13	42.02	16.05	35	77.05	4.40	57	158.98	0.67
14	43.09	2.27	36	78.02	0.67	58	188.04	0.90
15	44.13	8.30	37	79.94	1.02	59	208.06	0.52
16	47.09	0.67	38	81.99	1.37	60	234.10	0.70
17	50.93	3.90	39	82.05	2.24	61	244.14	2.01
18	52.02	0.50	40	83.09	1.98	62	248.05	1.05
19	53.09	2.42	41	84.12	6.35	63	262.08	11.42
20	54.11	6.09	42	85.09	0.55	64	263.10	1.78
21	55.14	13.05	43	89.89	0.79			
22	56.14	21.18	44	90.98	0.79			

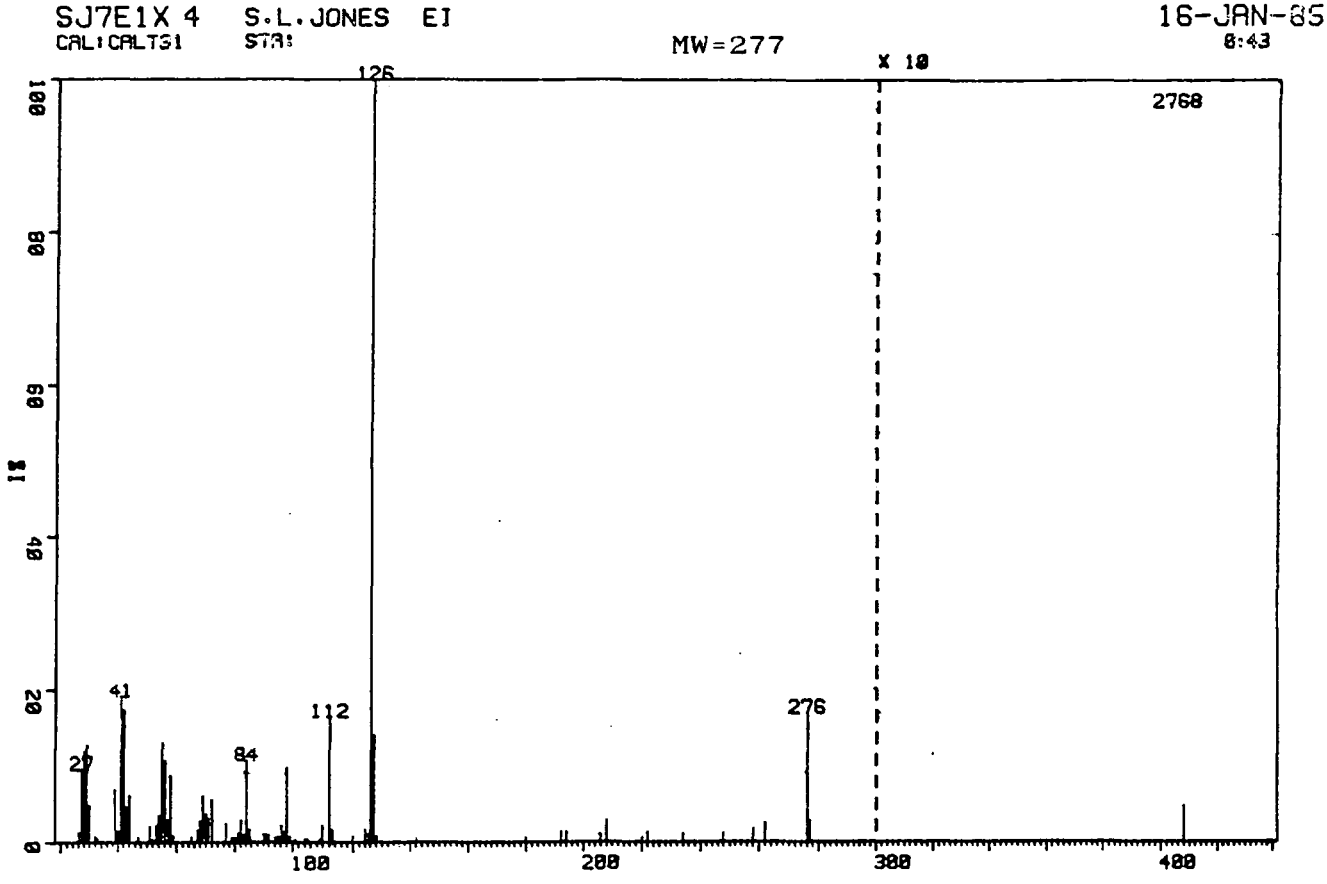
No. 15 N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)-2-(2H-HEXAFLUOROPROPYL)PIPERIDINE (57)

SJ6E2X 3 S.L.JONES EI 06-DEC-85
CAL:CALT31 STR: 8:33



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	0.51	23	67.10	1.52	45	150.96	0.90
2	27.22	5.08	24	68.05	1.99	46	158.98	2.34
3	28.11	9.61	25	68.94	7.97	47	206.03	1.37
4	28.99	4.26	26	69.00	1.76	48	208.02	1.02
5	29.82	1.25	27	69.95	1.60	49	228.08	0.59
6	31.96	1.76	28	73.06	0.82	50	234.05	2.81
7	33.06	0.66	29	77.04	3.87	51	244.09	1.13
8	38.95	3.36	30	78.01	0.39	52	246.06	0.59
9	39.79	0.51	31	79.93	0.90	53	260.03	1.60
10	40.93	7.70	32	80.99	0.51	54	261.07	0.47
11	42.02	5.74	33	82.03	2.81	55	262.06	100.00
12	43.10	1.68	34	83.08	3.55	56	263.08	11.25
13	44.13	2.30	35	84.10	2.11	57	264.09	0.86
14	47.09	1.13	36	89.87	1.21	58	394.14	3.48
15	50.93	3.48	37	90.96	0.82	59	395.13	0.70
16	53.08	1.48	38	95.03	0.74	60	412.07	1.87
17	54.11	3.44	39	96.10	3.24			
18	55.13	13.01	40	104.06	0.59			
19	56.13	6.41	41	108.99	0.70			
20	57.11	1.21	42	110.01	4.84			
21	58.98	1.64	43	111.06	4.80			
22	65.10	1.33	44	112.10	1.25			

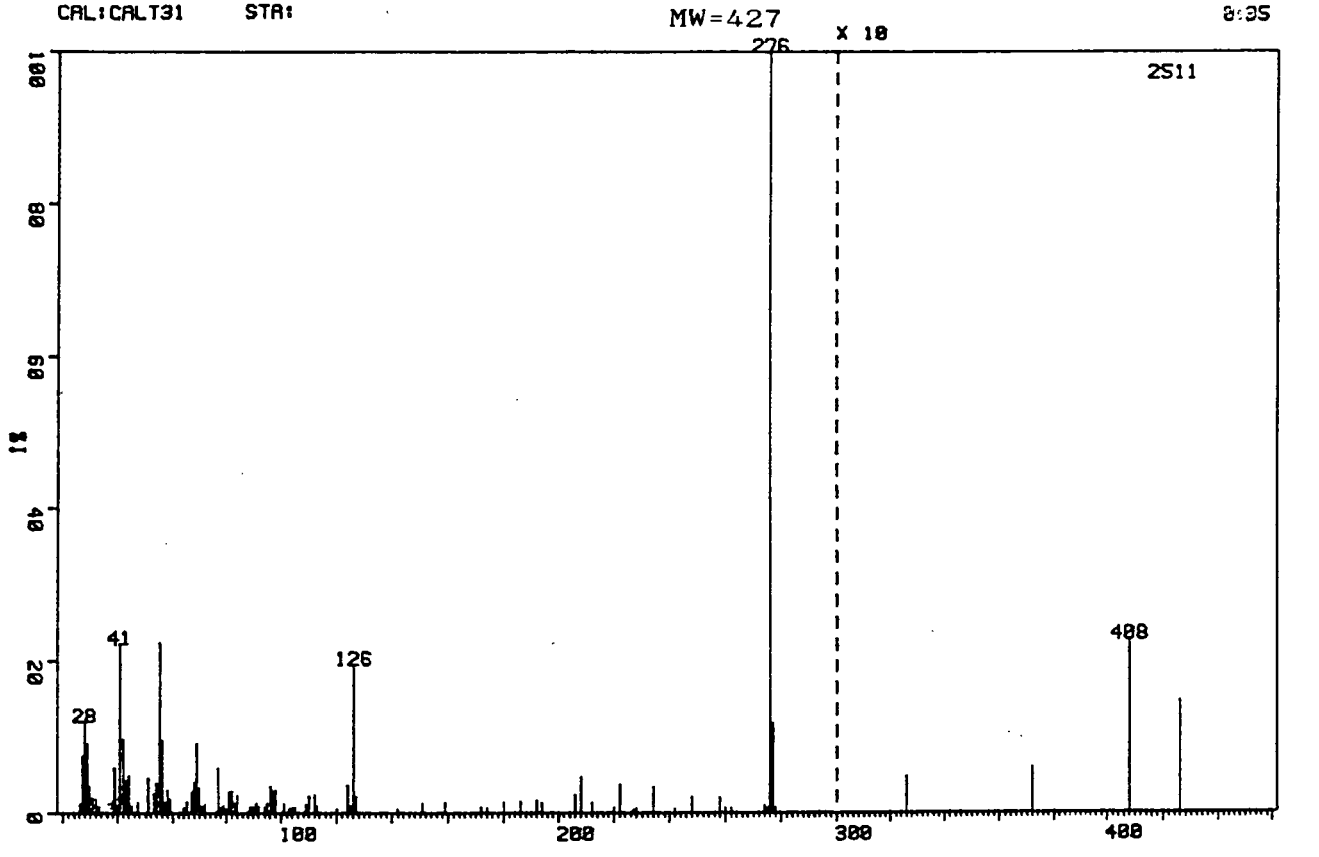
No. 16 N-ETHYL-2-(2H-HEXAFLUOROPROPYL)HEXAMETHYLENEIMINE (58)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.28	1.34	23	68.06	2.85	45	112.08	16.47
2	27.22	9.54	24	68.98	6.11	46	113.11	1.59
3	28.11	11.92	25	69.96	3.68	47	119.94	0.79
4	28.98	12.72	26	71.03	3.11	48	124.10	1.70
5	29.81	4.73	27	72.08	5.53	49	125.09	1.12
6	31.95	0.76	28	77.05	2.46	50	126.11	100.00
7	38.95	6.90	29	81.00	1.26	51	127.08	14.02
8	39.84	1.45	30	81.97	0.83	52	128.05	0.83
9	40.92	19.08	31	82.05	3.00	53	191.94	1.41
10	42.01	17.23	32	83.08	0.98	54	193.99	1.34
11	43.08	4.52	33	84.10	10.73	55	205.97	1.01
12	44.12	6.11	34	85.09	1.63	56	207.96	2.82
13	50.92	2.10	35	89.87	1.12	57	222.01	1.30
14	53.07	2.17	36	90.96	0.94	58	234.01	1.08
15	54.10	3.50	37	92.01	0.94	59	247.98	1.19
16	55.13	13.04	38	94.08	0.65	60	258.04	1.73
17	56.12	10.69	39	95.03	0.69	61	262.04	2.53
18	57.10	3.00	40	96.11	2.17	62	276.03	16.91
19	58.06	8.74	41	97.06	1.34	63	277.03	2.75
20	58.97	0.90	42	98.05	9.75			
21	65.09	0.69	43	99.01	0.69			
22	67.09	1.63	44	109.99	2.28			

No. 17 N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)-2-(2H-HEXAFLUOROPROPYL)HEXAMETHYLENEIMINE (59)

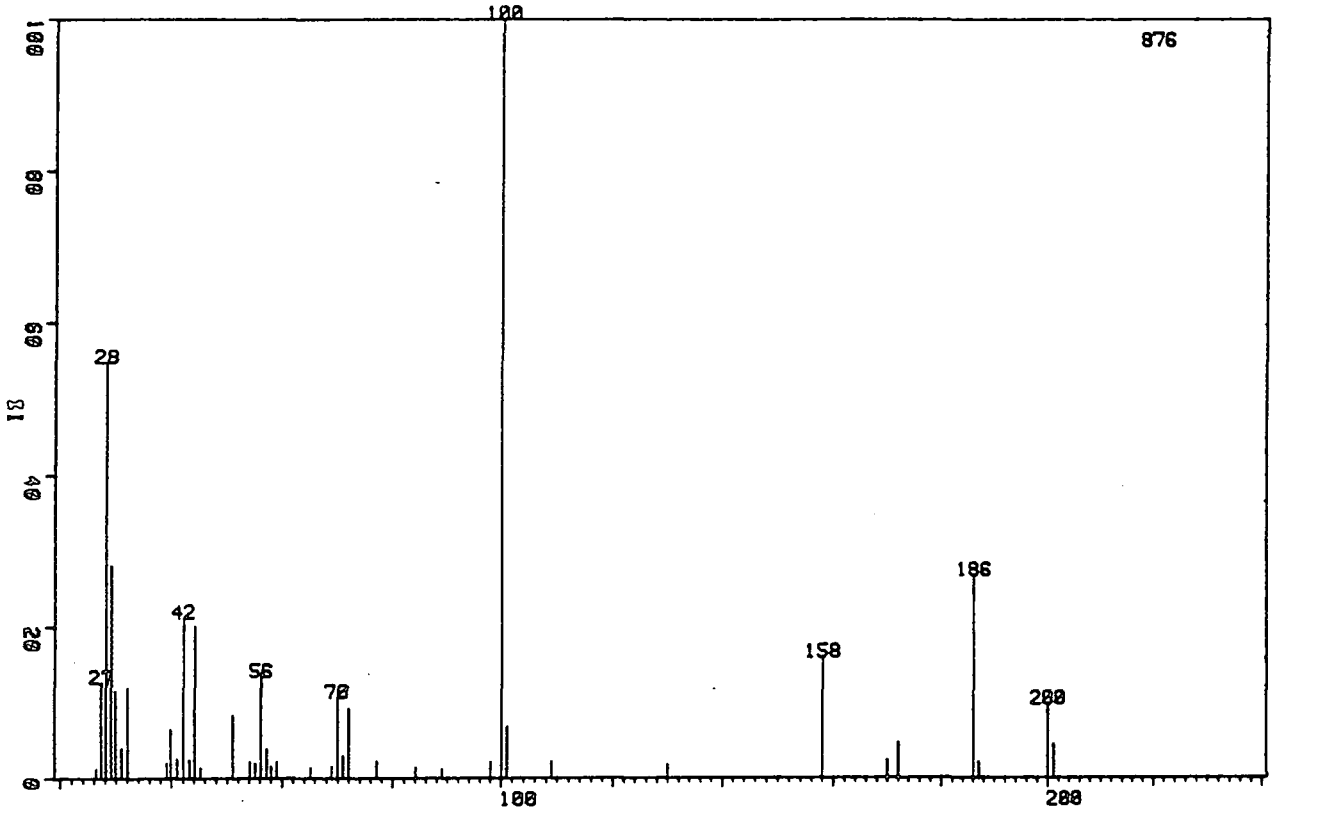
SJ7E2X 3 S.L.JONES EI 16-JAN-85
CAL:CALT31 STA: 8:35



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	1.19	23	65.10	1.47	45	124.12	3.62
2	27.22	7.41	24	67.09	2.75	46	126.10	19.55
3	28.11	11.99	25	68.06	4.02	47	127.07	2.15
4	28.99	9.04	26	68.99	9.16	48	150.89	1.35
5	29.82	3.46	27	69.97	3.31	49	158.94	1.39
6	30.87	2.03	28	72.09	1.19	50	179.89	1.43
7	31.96	1.91	29	77.05	5.93	51	186.01	1.51
8	38.95	5.93	30	79.00	1.04	52	191.96	1.63
9	39.85	1.04	31	81.02	2.75	53	193.99	1.27
10	40.93	22.26	32	81.99	1.08	54	205.99	2.35
11	42.02	9.68	33	82.06	2.91	55	208.00	4.70
12	43.09	4.22	34	83.08	1.27	56	212.00	1.31
13	44.13	4.98	35	84.11	2.31	57	222.02	3.78
14	47.08	1.43	36	90.97	1.31	58	234.03	3.42
15	50.93	4.58	37	95.06	1.23	59	247.98	2.11
16	53.08	2.55	38	96.11	3.54	60	258.06	2.07
17	54.11	3.90	39	97.08	2.83	61	274.02	1.04
18	55.14	22.42	40	98.05	3.07	62	276.05	100.00
19	56.12	9.48	41	100.92	1.27	63	277.05	11.79
20	57.11	1.47	42	108.97	1.08	64	408.08	2.27
21	58.07	3.03	43	109.99	2.23	65	426.09	1.47
22	58.99	1.87	44	112.07	2.47			

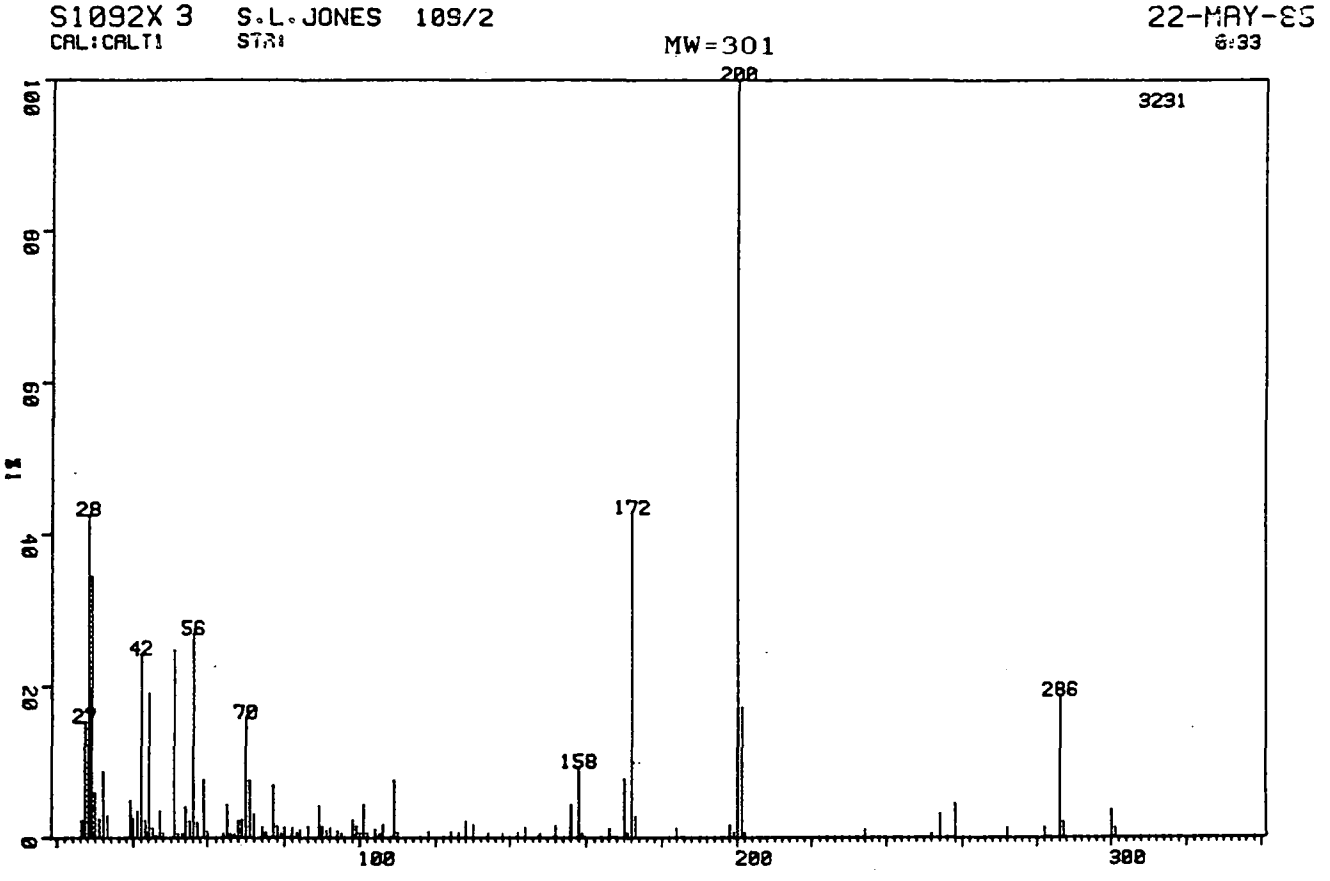
No. 18 (1,1,2,2-TETRAFLUORO-3-BUTYL)DIETHYLAMINE (66)

S1091X 6 S.L.JONES 22-MAY-85
CAL:CALT1 STR: MW=201 3:53



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.36	1.26	23	69.01	1.60
2	27.29	12.67	24	69.95	10.73
3	28.17	54.79	25	71.02	2.97
4	29.05	28.08	26	72.08	9.25
5	29.88	11.53	27	77.06	2.28
6	30.95	4.00	28	84.15	1.48
7	32.03	11.99	29	88.96	1.26
8	38.99	2.05	30	98.09	2.17
9	39.83	6.51	31	100.03	100.00
10	40.97	2.63	32	100.95	1.26
11	42.06	21.23	33	101.08	6.85
12	43.13	2.40	34	108.98	2.28
13	44.17	20.09	35	129.93	1.83
14	45.16	1.37	36	158.05	15.98
15	50.95	8.33	37	170.00	2.40
16	54.13	2.17	38	172.06	4.68
17	55.15	1.94	39	186.09	26.83
18	56.14	13.47	40	187.10	2.17
19	57.13	3.88	41	200.05	9.82
20	58.09	1.60	42	201.08	4.45
21	59.01	2.17			
22	65.11	1.48			

No.19 BIS-(1,1,2,2-TETRAFLUORO-3-BUTYL)ETHYLAMINE (67)

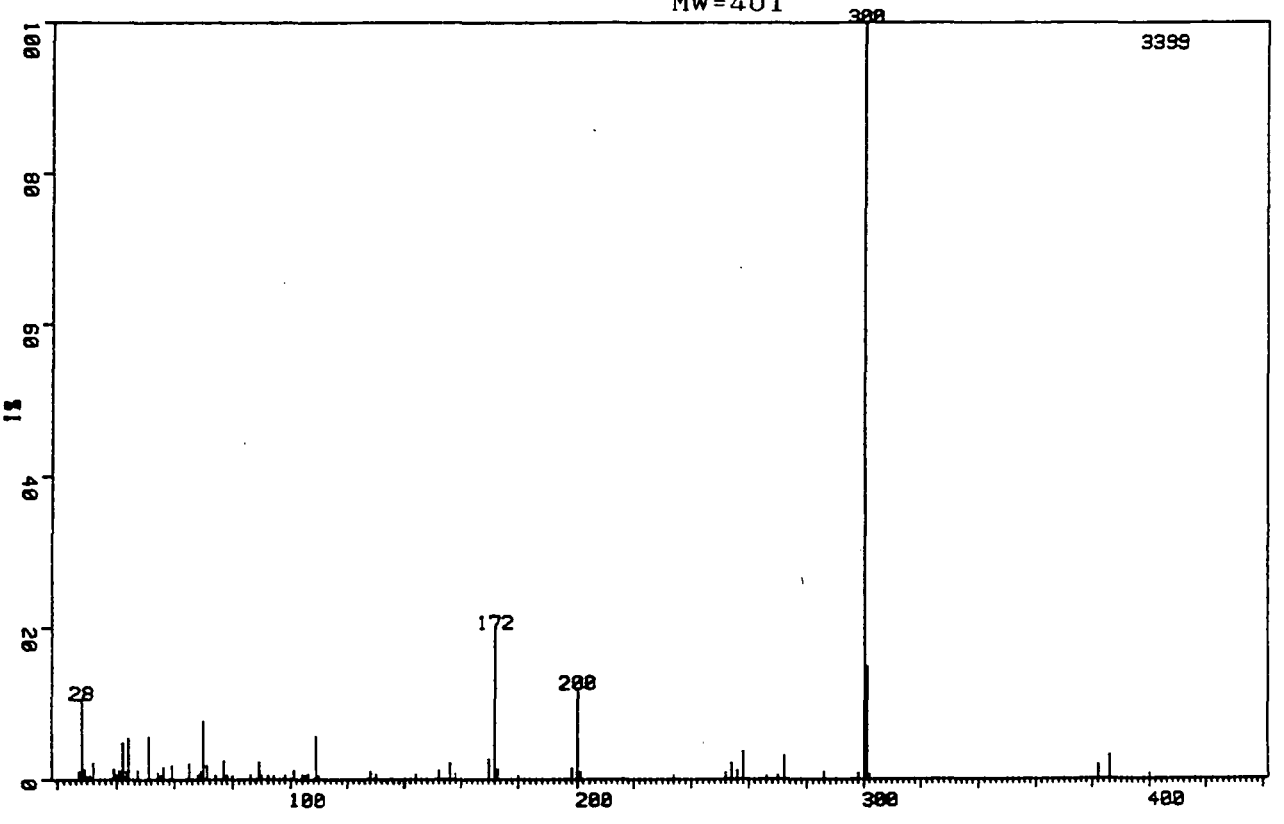


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.37	2.26	23	57.10	1.55	45	108.99	7.58
2	27.30	15.35	24	57.14	2.01	46	128.00	2.20
3	28.17	42.59	25	59.02	7.68	47	129.96	1.76
4	28.18	19.78	26	65.13	4.36	48	144.05	1.39
5	29.05	34.42	27	68.07	2.23	49	152.07	1.58
6	29.88	5.97	28	69.02	2.38	50	156.07	4.30
7	30.93	1.55	29	69.97	15.82	51	158.05	9.32
8	30.95	2.45	30	71.04	7.61	52	169.99	7.77
9	32.03	8.79	31	72.09	3.19	53	172.05	42.80
10	33.13	2.94	32	74.11	1.45	54	173.08	2.82
11	39.00	4.89	33	77.02	6.96	55	198.09	1.70
12	39.84	2.54	34	78.00	1.52	56	200.07	100.00
13	40.98	3.56	35	79.91	1.39	57	201.10	17.18
14	42.07	24.26	36	81.98	1.30	58	254.14	3.10
15	43.14	2.32	37	86.04	1.55	59	258.05	4.55
16	44.17	19.03	38	88.94	4.24	60	272.09	1.33
17	45.17	1.33	39	89.89	1.52	61	282.14	1.39
18	47.13	3.53	40	92.02	1.36	62	286.10	18.66
19	50.96	24.73	41	98.09	2.32	63	287.11	2.07
20	54.14	4.09	42	99.06	1.55	64	300.08	3.65
21	55.16	2.23	43	100.97	4.39	65	301.07	1.33
22	56.16	26.90	44	106.08	1.76			

No.20 TRIS-(1,1,2,2-TETRAFLUORO-3-BUTYL)AMINE (68)

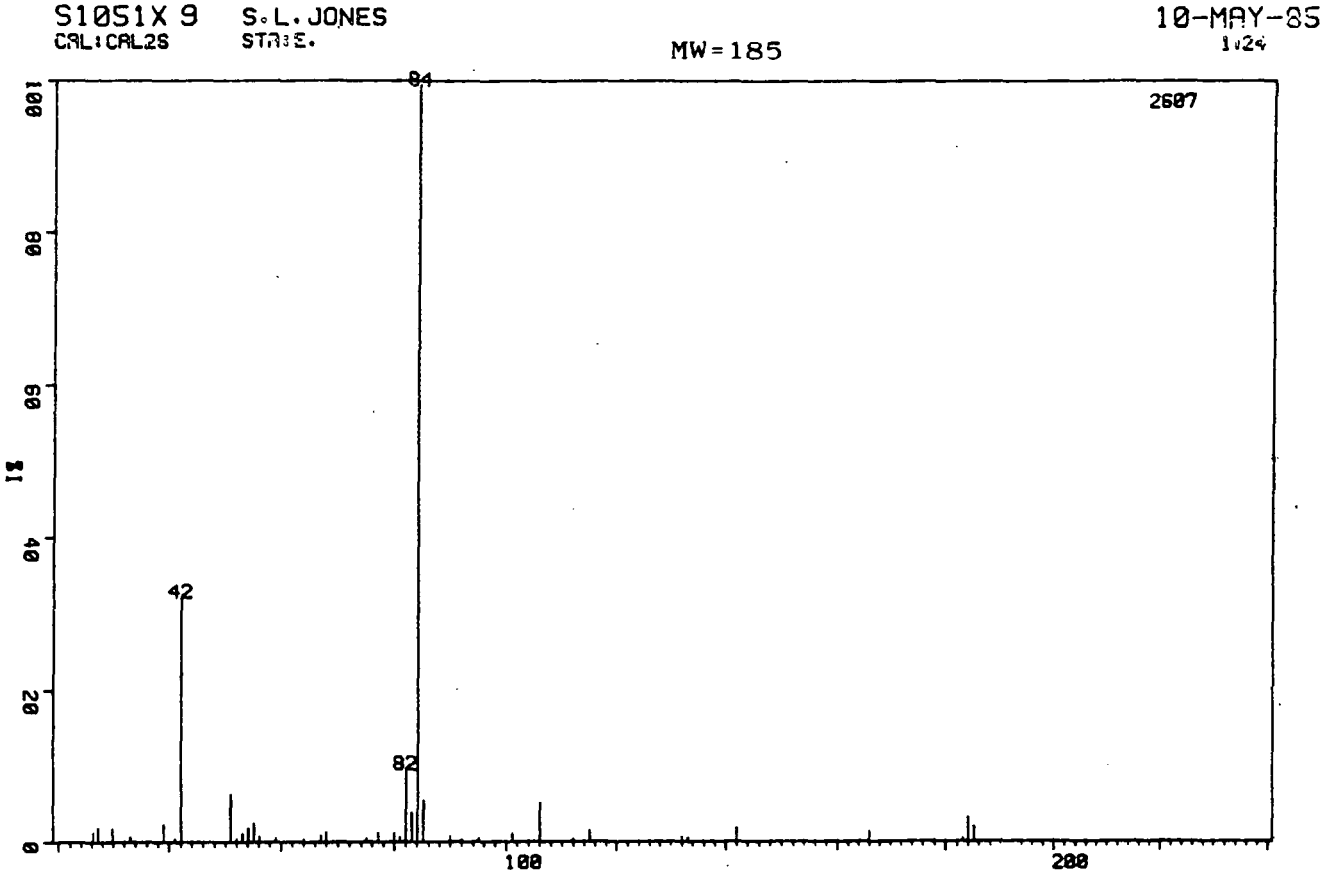
S1093X 5 S.L.JONES 109/3 22-MAY-85
CAL:CALT1 STA: 0:50

MW=401



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.29	1.00	23	69.98	7.74	45	170.06	2.71
2	28.17	10.62	24	71.05	1.91	46	172.13	19.98
3	28.19	0.44	25	74.12	0.56	47	173.11	1.41
4	29.05	1.32	26	77.06	2.47	48	180.07	0.53
5	30.95	0.44	27	78.04	0.62	49	198.12	1.47
6	32.03	2.15	28	79.96	0.44	50	200.07	11.97
7	39.00	1.38	29	86.12	0.62	51	201.10	1.06
8	39.84	0.62	30	88.99	2.35	52	234.13	0.56
9	40.99	1.21	31	89.94	0.53	53	252.10	0.94
10	42.07	4.80	32	92.04	0.56	54	254.14	2.18
11	43.15	1.03	33	98.12	0.44	55	256.06	1.15
12	44.18	5.47	34	100.99	1.21	56	258.07	3.74
13	47.13	1.21	35	104.10	0.62	57	270.06	0.50
14	50.97	5.71	36	106.12	0.74	58	272.12	3.12
15	54.15	0.91	37	109.00	5.77	59	286.14	1.06
16	55.18	0.44	38	109.96	0.53	60	298.10	0.85
17	56.17	1.62	39	128.02	1.06	61	300.10	100.00
18	59.03	1.88	40	129.98	0.68	62	301.12	14.86
19	65.14	2.09	41	144.12	0.68	63	302.08	0.74
20	68.07	0.62	42	152.09	1.15	64	382.23	1.91
21	68.97	0.53	43	156.10	2.21	65	386.14	3.21
22	69.04	1.06	44	158.09	0.79	66	400.15	0.76

No.21 N-METHYL-2-(2H-TETRAFLUOROETHYL)PYRROLIDINE (69)



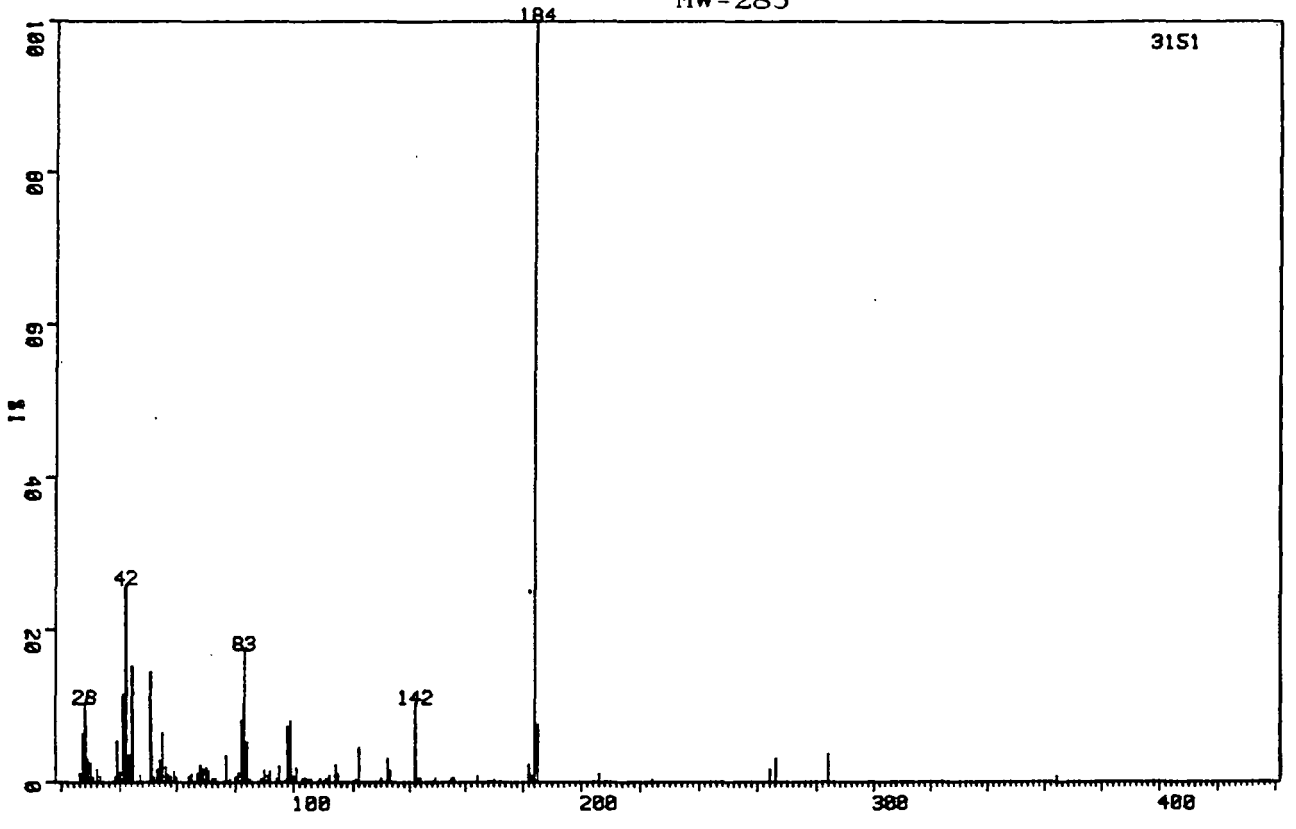
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.27	1.23	23	82.03	9.59
2	27.20	1.92	24	83.07	3.80
3	29.80	1.73	25	84.10	99.46
4	33.05	0.69	26	85.12	5.45
5	38.95	2.34	27	89.91	0.73
6	40.92	0.38	28	92.01	0.35
7	42.01	32.18	29	95.05	0.38
8	44.12	0.12	30	100.98	1.11
9	50.93	6.33	31	106.08	5.14
10	52.01	0.42	32	112.06	0.42
11	53.08	1.11	33	115.12	1.46
12	54.11	1.80	34	132.04	0.65
13	55.13	2.45	35	133.07	0.46
14	56.13	0.73	36	142.01	1.84
15	59.00	0.50	37	166.09	1.27
16	64.07	0.42	38	183.09	0.46
17	67.08	0.88	39	184.08	3.18
18	68.04	1.30	40	185.10	1.96
19	75.02	0.42			
20	77.00	1.19			
21	79.89	1.19			
22	80.97	0.58			

No.22 N-(2,2,3,3-TETRAFLUOROPROPYL)-2-(2H-TETRAFLUOROETHYL)PYRROLIDINE (70)

S1052X 2 S.L.JONES EI 10-DEC-85

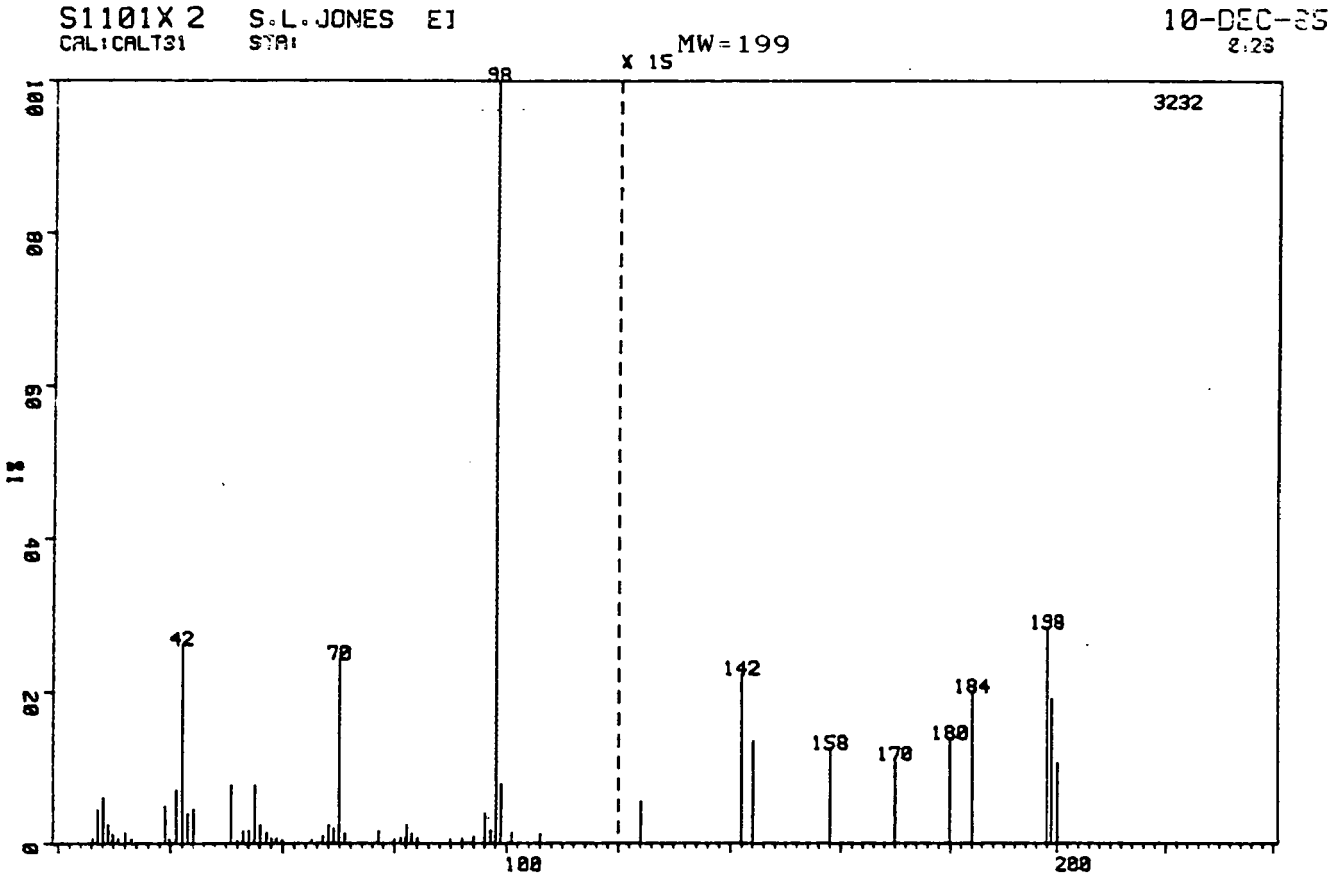
CAL:CALT31 STR: 8:26

MW=285



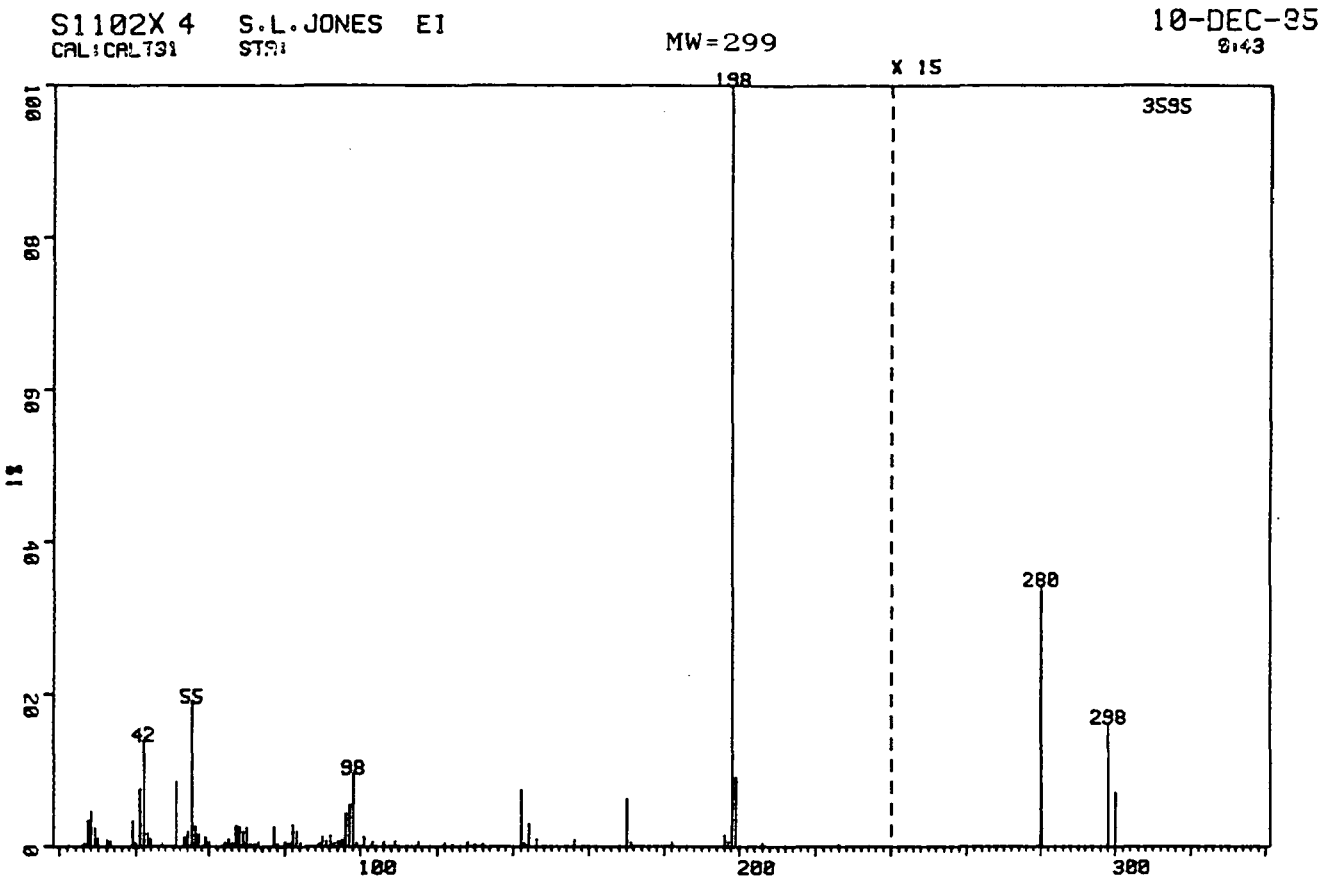
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.30	1.14	23	57.13	0.83	45	99.98	0.79
2	27.23	6.35	24	58.06	0.73	46	100.96	1.90
3	28.11	10.41	25	59.00	1.36	47	112.06	0.89
4	28.12	7.43	26	64.10	0.76	48	114.11	2.32
5	29.00	3.01	27	65.09	1.05	49	115.04	1.11
6	29.83	2.54	28	67.09	1.21	50	122.02	4.54
7	31.97	1.78	29	68.06	2.22	51	132.05	3.08
8	33.08	0.79	30	68.96	1.36	52	133.07	1.52
9	38.96	5.43	31	69.02	1.78	53	142.02	10.38
10	39.80	0.73	32	69.96	2.00	54	164.09	0.83
11	39.86	1.33	33	70.99	1.52	55	182.05	2.35
12	40.94	11.52	34	77.05	3.52	56	183.07	0.92
13	42.03	26.02	35	81.00	1.17	57	184.08	100.00
14	43.10	3.52	36	82.05	8.03	58	185.08	7.52
15	44.14	15.30	37	83.09	17.49	59	206.04	1.11
16	47.10	0.95	38	84.11	5.33	60	264.06	1.71
17	50.94	14.54	39	89.89	1.62	61	266.09	3.11
18	53.09	1.62	40	90.98	0.89	62	284.07	3.65
19	54.12	2.73	41	92.01	1.49	63	364.14	0.76
20	55.14	6.41	42	95.05	2.13			
21	56.12	1.97	43	98.05	7.24			
22	57.08	0.98	44	99.02	8.12			

No.23 N-METHYL-2-(2H-TETRAFLUOROETHYL)PIPERIDINE (71)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	0.71	23	58.97	0.68	45	99.03	7.83
2	27.22	4.36	24	59.90	0.40	46	100.93	1.39
3	28.11	6.03	25	65.09	0.37	47	106.05	1.24
4	28.99	2.38	26	67.09	1.02	48	124.04	0.37
5	29.82	1.21	27	68.05	2.38	49	141.99	1.49
6	30.85	0.56	28	68.95	0.40	50	144.04	0.90
7	31.95	1.39	29	69.02	1.95	51	158.02	0.84
8	33.06	0.56	30	69.95	24.23	52	169.97	0.74
9	38.95	4.92	31	71.02	1.33	53	179.98	0.93
10	39.84	0.56	32	77.04	1.58	54	184.03	1.33
11	40.92	7.05	33	79.92	0.56	55	198.01	1.89
12	42.01	26.21	34	80.99	0.77	56	199.00	1.27
13	43.08	3.87	35	81.97	0.84	57	199.98	0.71
14	44.12	4.52	36	82.03	2.38			
15	50.92	7.67	37	83.08	1.27			
16	52.00	0.34	38	84.09	0.77			
17	53.07	1.64	39	89.90	0.53			
18	54.10	1.70	40	91.99	0.71			
19	55.12	7.67	41	94.06	0.90			
20	56.11	2.38	42	96.08	3.96			
21	57.10	1.42	43	97.07	1.70			
22	58.06	0.65	44	98.05	100.00			

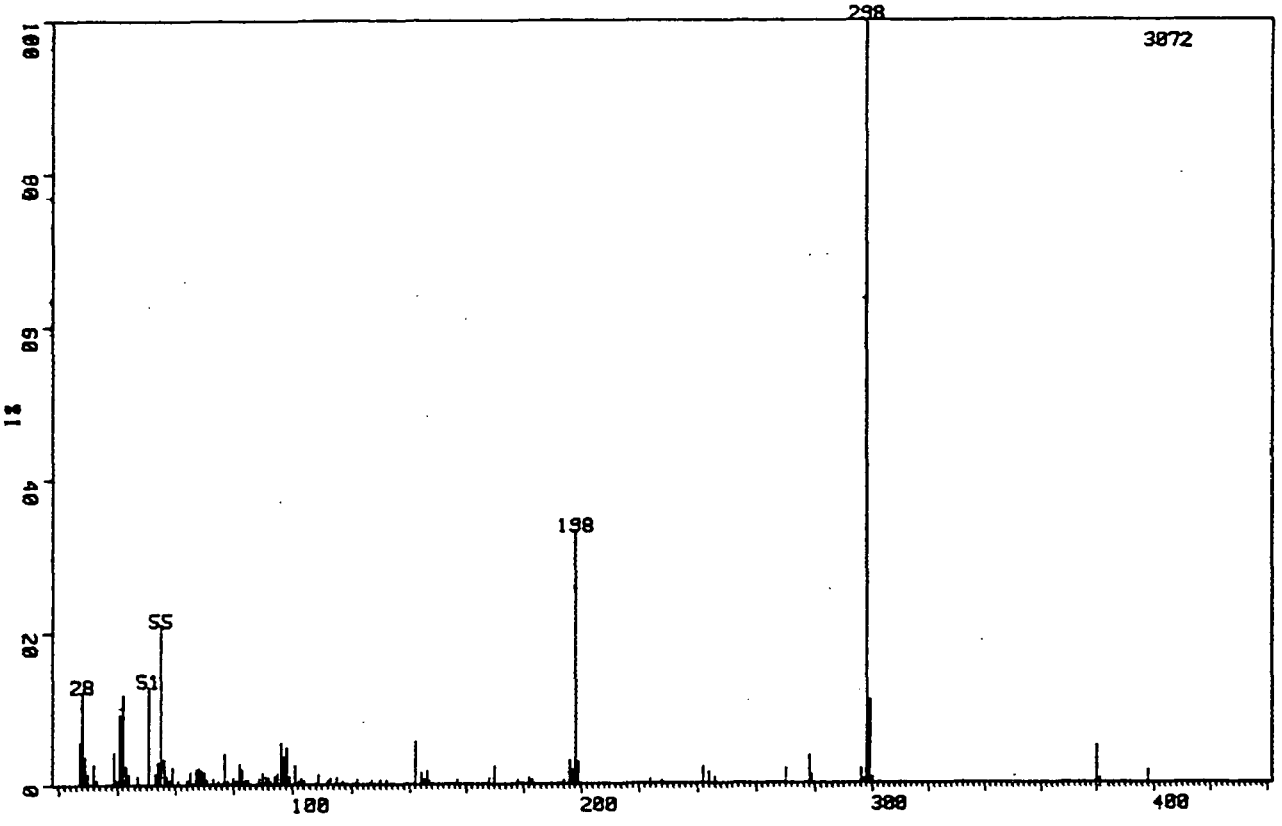
No.24 N-(2,2,3,3-TETRAFLUOROPROPYL)-2-(2H-TETRAFLUOROETHYL)PIPERIDINE (72)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.22	3.48	23	65.10	1.03	45	103.04	0.53
2	28.11	4.65	24	67.08	2.73	46	106.07	0.64
3	28.99	2.48	25	68.04	2.64	47	108.98	0.70
4	29.82	1.11	26	68.94	0.72	48	115.04	0.67
5	31.95	0.92	27	69.01	1.95	49	128.08	0.53
6	33.06	0.78	28	69.95	2.53	50	142.02	7.37
7	38.95	3.39	29	73.06	0.70	51	144.07	3.03
8	39.79	0.50	30	77.03	2.64	52	146.10	0.97
9	40.93	7.57	31	79.92	0.64	53	156.06	0.86
10	42.01	13.99	32	81.98	0.53	54	170.00	6.26
11	43.09	1.75	33	82.04	2.87	55	171.03	0.58
12	44.13	1.08	34	83.06	2.06	56	196.09	1.45
13	50.93	8.51	35	89.90	1.34	57	197.08	0.58
14	53.08	1.22	36	90.98	0.75	58	198.07	100.00
15	54.11	1.95	37	92.03	1.45	59	199.05	9.10
16	55.14	18.97	38	94.09	0.72	60	280.05	2.28
17	56.13	2.67	39	95.05	0.89	61	298.11	1.08
18	57.07	0.50	40	96.11	4.37			
19	57.11	1.59	41	97.08	5.48			
20	58.98	1.28	42	98.06	9.62			
21	59.91	0.64	43	99.03	0.53			
22	64.08	0.53	44	100.93	1.34			

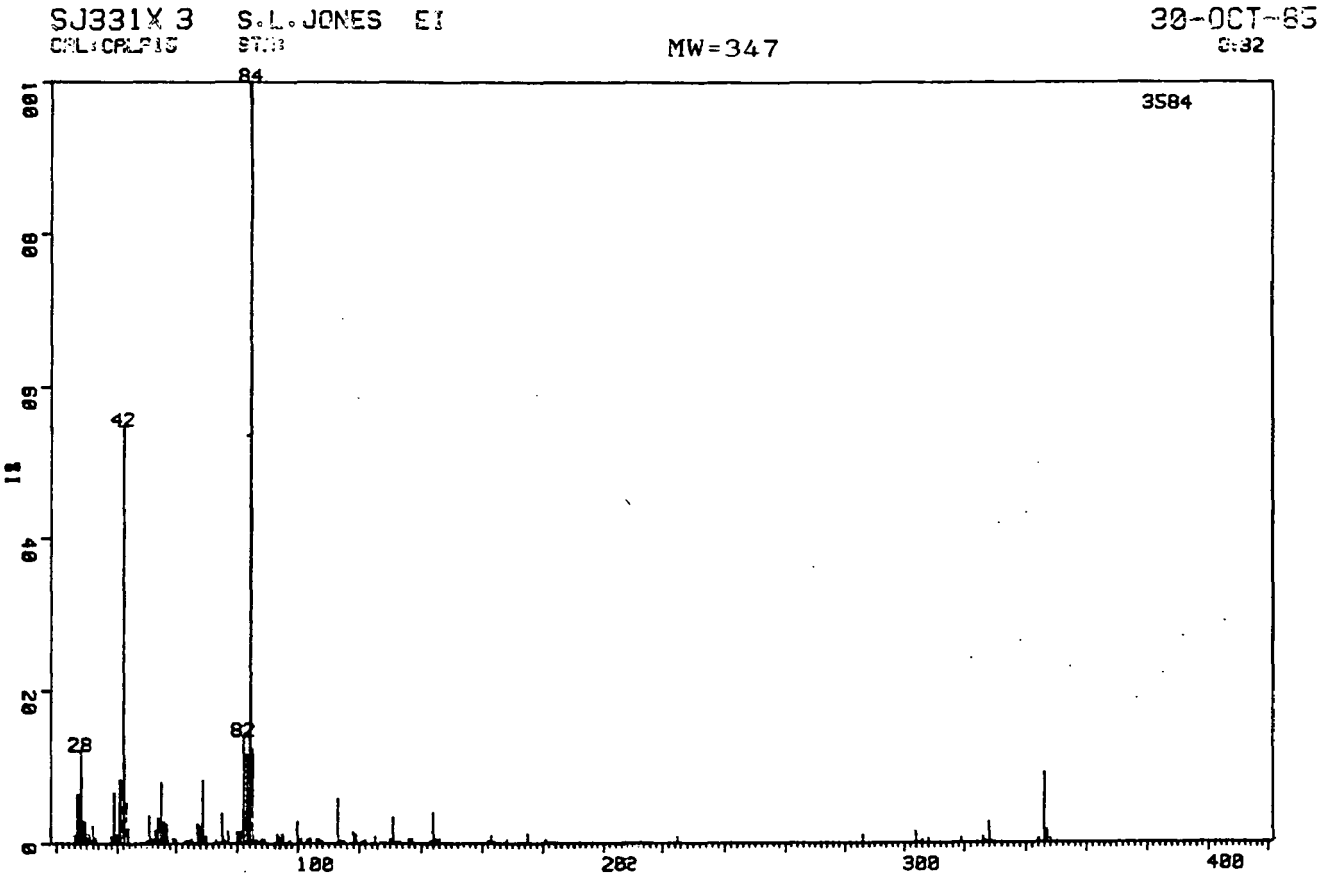
No.25 N-(2,2,3,3-TETRAFLUOROPROPYL)-2,5-BIS-(2H-TETRAFLUOROETHYL)PIPERIDINE (73)

S1103X 10 S.L.JONES EI 10-DEC-85
CRL:CRLT31 STR1 MW=399



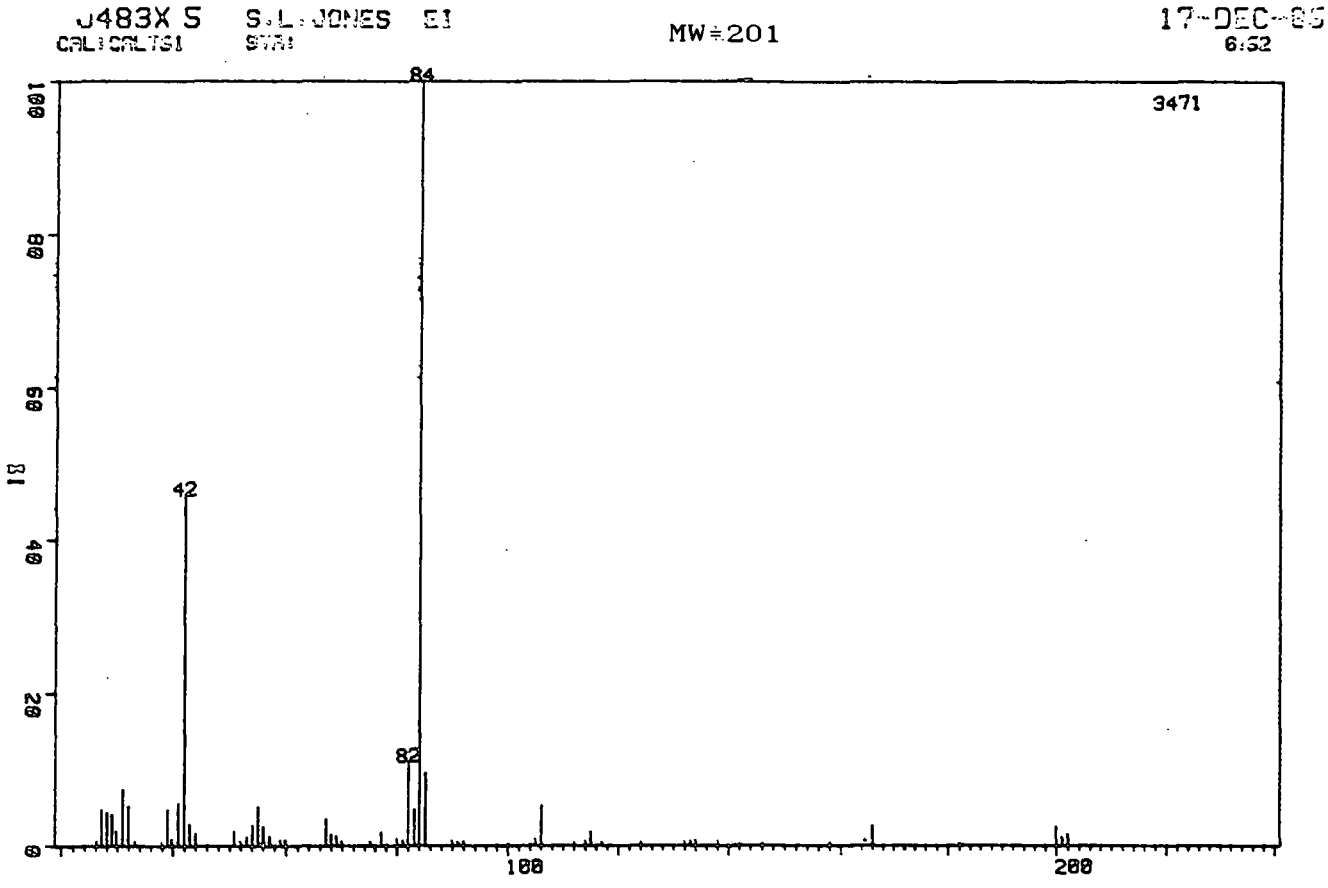
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.22	5.44	23	69.01	1.40	45	182.03	0.81
2	28.11	12.14	24	69.95	1.56	46	196.06	3.09
3	28.99	3.58	25	77.04	4.07	47	197.06	1.82
4	29.82	1.37	26	79.93	0.91	48	198.05	33.07
5	31.96	2.57	27	82.04	2.60	49	199.05	2.90
6	38.96	4.17	28	83.08	1.92	50	241.99	2.18
7	40.94	9.21	29	89.88	1.50	51	244.01	1.46
8	42.02	11.72	30	90.97	0.94	52	246.05	0.75
9	43.10	2.41	31	92.00	0.91	53	270.00	1.99
10	44.13	1.30	32	94.09	1.07	54	278.05	3.61
11	47.09	1.07	33	95.04	1.46	55	279.02	1.11
12	50.93	12.83	34	96.09	5.40	56	296.07	1.92
13	53.08	1.46	35	97.09	3.61	57	298.05	100.00
14	54.11	2.86	36	98.07	4.85	58	299.07	10.90
15	55.14	20.83	37	99.05	1.14	59	300.06	0.78
16	56.14	3.29	38	100.95	2.44	60	380.13	4.82
17	57.11	1.11	39	108.99	1.27	61	398.07	1.66
18	58.99	2.25	40	115.07	0.81			
19	65.11	1.60	41	142.04	5.50			
20	67.08	1.95	42	144.09	1.53			
21	68.04	2.08	43	146.12	1.69			
22	68.95	1.86	44	169.98	2.34			

No.26 N-METHYL-2-(2H-PERFLUOROCYCLOHEXYL)PYRROLIDINE (74)



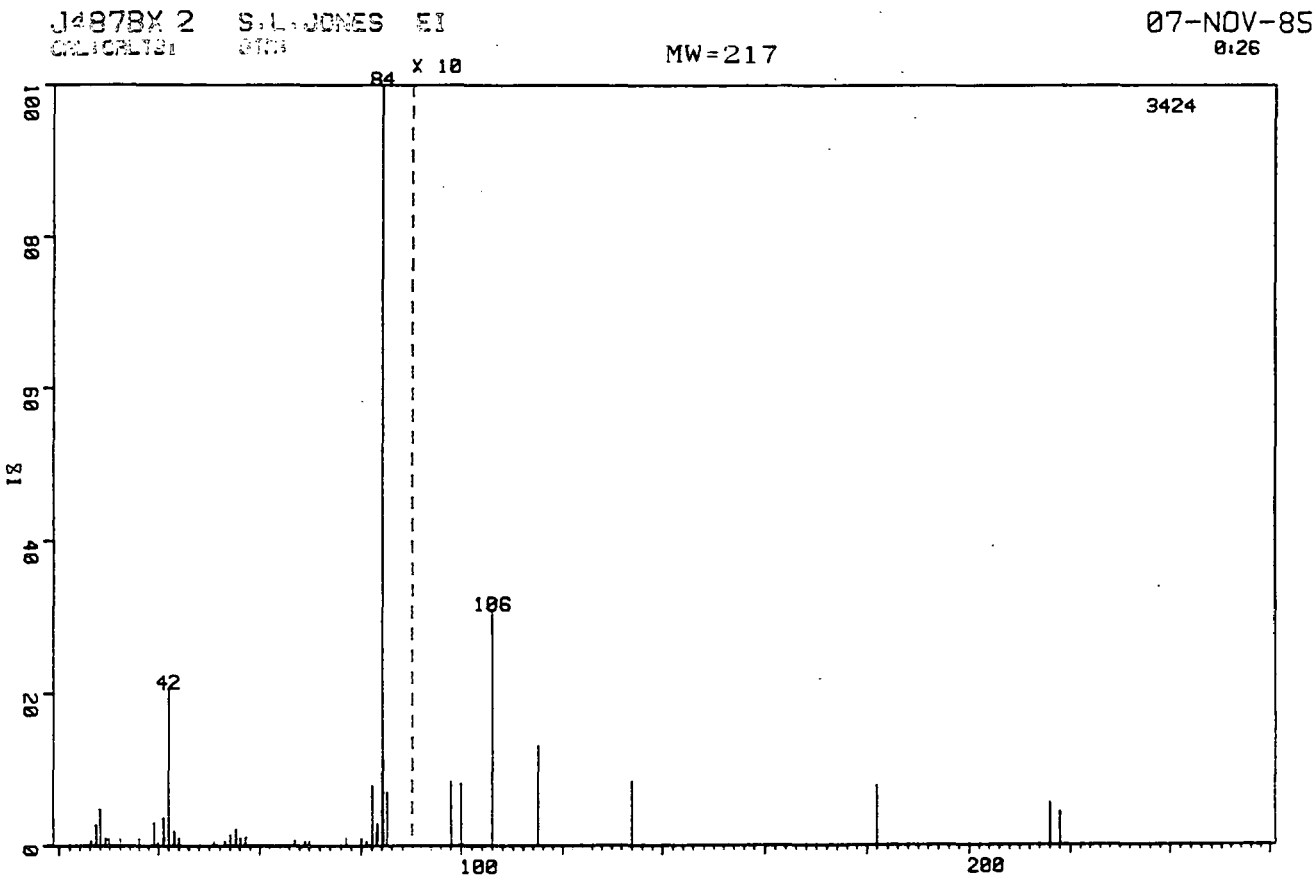
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.28	1.03	23	55.13	8.01	45	99.87	2.87
2	27.22	6.45	24	56.13	2.82	46	100.96	0.70
3	28.10	12.19	25	57.07	1.37	47	104.06	0.75
4	28.11	8.62	26	57.11	2.57	48	113.00	5.92
5	28.98	2.93	27	58.99	0.70	49	118.02	1.62
6	29.82	2.85	28	59.91	0.64	50	118.94	1.26
7	30.85	1.23	29	67.08	2.54	51	125.01	0.95
8	31.96	2.29	30	68.05	2.26	52	130.93	3.49
9	33.06	0.75	31	68.95	8.34	53	137.01	0.64
10	38.03	0.86	32	69.01	1.53	54	143.98	4.02
11	38.96	6.70	33	69.95	1.00	55	162.95	1.00
12	39.80	0.70	34	75.06	3.93	56	174.94	1.28
13	39.85	1.14	35	77.06	1.59	57	224.91	0.86
14	40.94	8.34	36	79.95	1.48	58	285.90	1.09
15	42.02	54.88	37	80.99	1.62	59	303.88	1.56
16	43.09	5.33	38	82.06	14.12	60	318.92	0.70
17	44.07	0.98	39	83.09	11.69	61	325.93	0.84
18	44.14	1.95	40	84.12	100.00	62	327.95	2.76
19	50.94	3.63	41	85.09	12.36	63	345.91	9.21
20	52.02	0.61	42	92.97	1.20	64	346.93	1.65
21	53.08	1.65	43	94.00	0.81			
22	54.11	3.29	44	95.01	1.28			

No.27 N-METHYL-2-(2H,2-CHLOROTRIFLUOROÉTHYL)PYRROLIDINE (75)



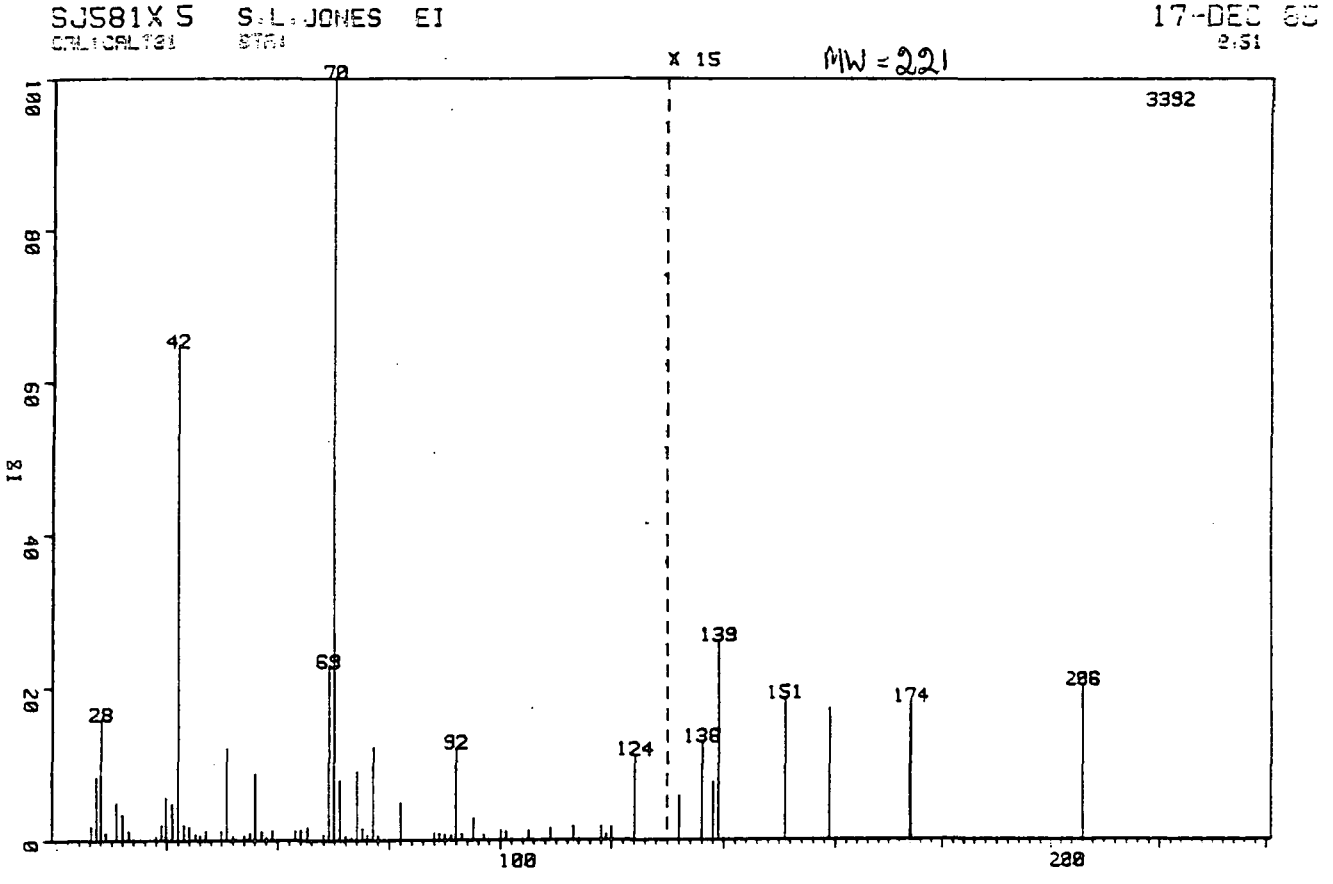
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	0.69	23	54.11	2.68	45	90.96	0.43
2	27.22	4.78	24	55.13	5.10	46	92.00	0.43
3	28.11	4.38	25	56.13	2.51	47	99.96	0.32
4	28.96	4.09	26	57.07	0.84	48	105.07	0.89
5	28.99	1.70	27	57.11	1.24	49	106.07	5.33
6	29.80	0.61	28	58.98	0.72	50	112.05	0.37
7	29.82	1.96	29	59.91	0.72	51	114.10	0.63
8	30.87	7.46	30	67.03	3.51	52	115.11	1.82
9	31.95	0.86	31	67.09	1.53	53	116.96	0.49
10	32.00	5.21	32	68.07	1.44	54	124.04	0.43
11	33.06	0.61	33	68.95	1.30	55	132.04	0.61
12	38.03	0.49	34	69.03	1.07	56	133.06	0.66
13	38.95	4.78	35	69.97	0.52	57	134.08	0.78
14	39.79	0.49	36	75.07	0.55	58	138.04	0.66
15	39.85	0.89	37	77.06	1.79	59	146.08	0.35
16	40.93	5.59	38	79.95	0.95	60	157.97	0.49
17	42.01	45.98	39	81.01	0.72	61	166.08	2.68
18	43.09	2.85	40	82.06	11.12	62	182.03	0.35
19	44.13	1.64	41	83.09	4.72	63	199.97	2.56
20	50.93	1.87	42	84.12	100.00	64	200.99	1.18
21	52.01	0.37	43	85.10	9.51	65	202.02	1.47
22	53.08	1.15	44	89.88	0.66			

No.28 N-METHYL-2-(2H,2,2-DICHLORODIFLUOROETHYL)PYRROLIDINE (76)



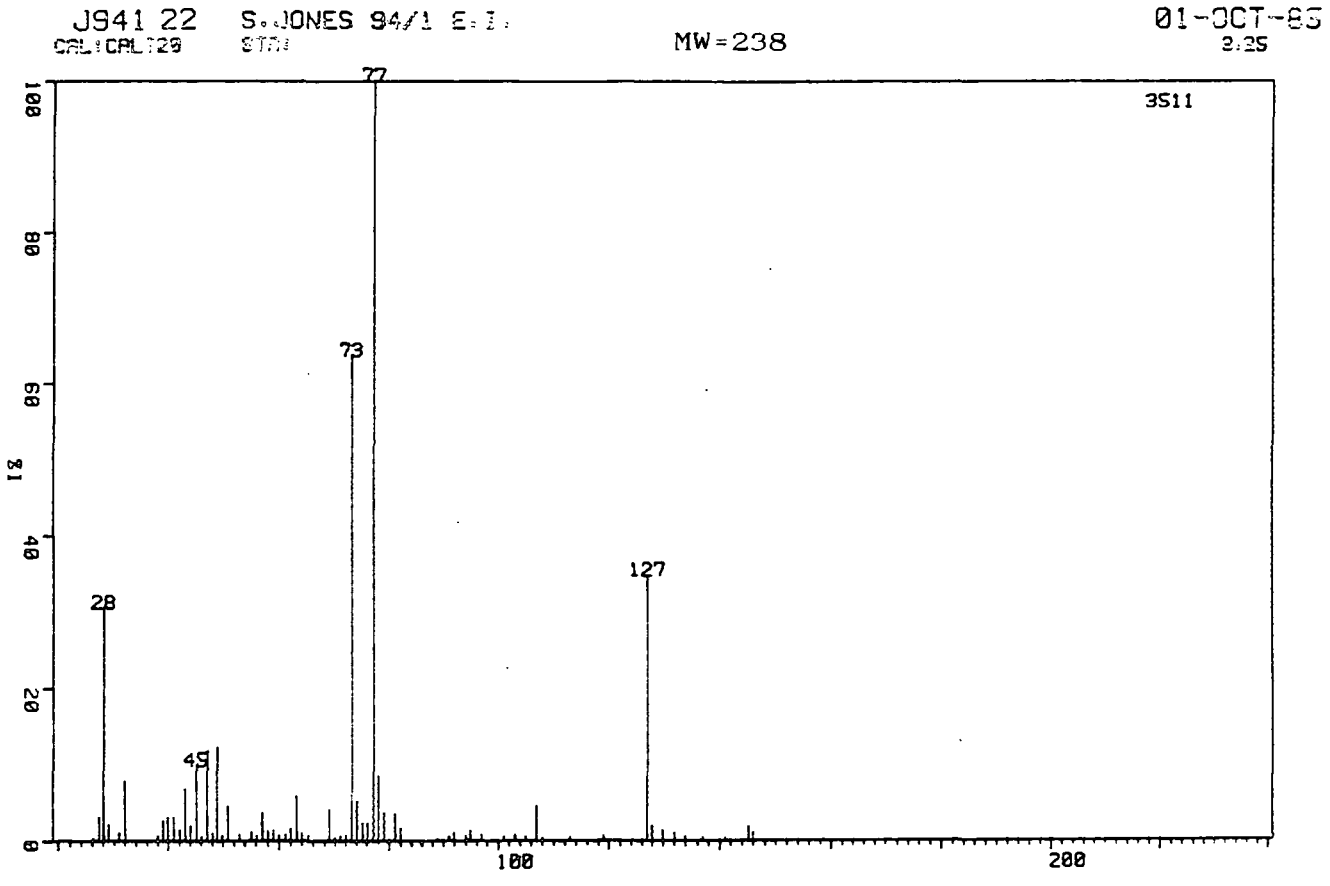
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	0.61	23	69.95	0.58
2	27.22	2.69	24	77.05	1.02
3	28.11	4.76	25	79.94	0.96
4	28.99	1.05	26	81.00	0.53
5	29.82	0.91	27	82.06	7.91
6	31.96	0.88	28	82.97	1.72
7	36.09	0.96	29	83.09	2.89
8	38.95	3.01	30	84.11	100.00
9	39.85	0.44	31	84.12	11.24
10	40.93	3.65	32	84.93	0.85
11	42.01	20.77	33	85.06	7.01
12	43.09	1.87	34	97.91	0.85
13	44.13	0.93	35	99.90	0.82
14	50.92	0.41	36	106.02	3.10
15	53.08	0.55	37	115.07	1.31
16	54.11	1.37	38	134.06	0.85
17	55.13	2.19	39	181.99	0.79
18	56.12	1.05	40	215.97	0.55
19	57.07	0.41	41	217.97	0.44
20	57.11	1.20			
21	67.09	0.76			
22	69.02	0.64			

No.29 (1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)ISOCYANATE (77)



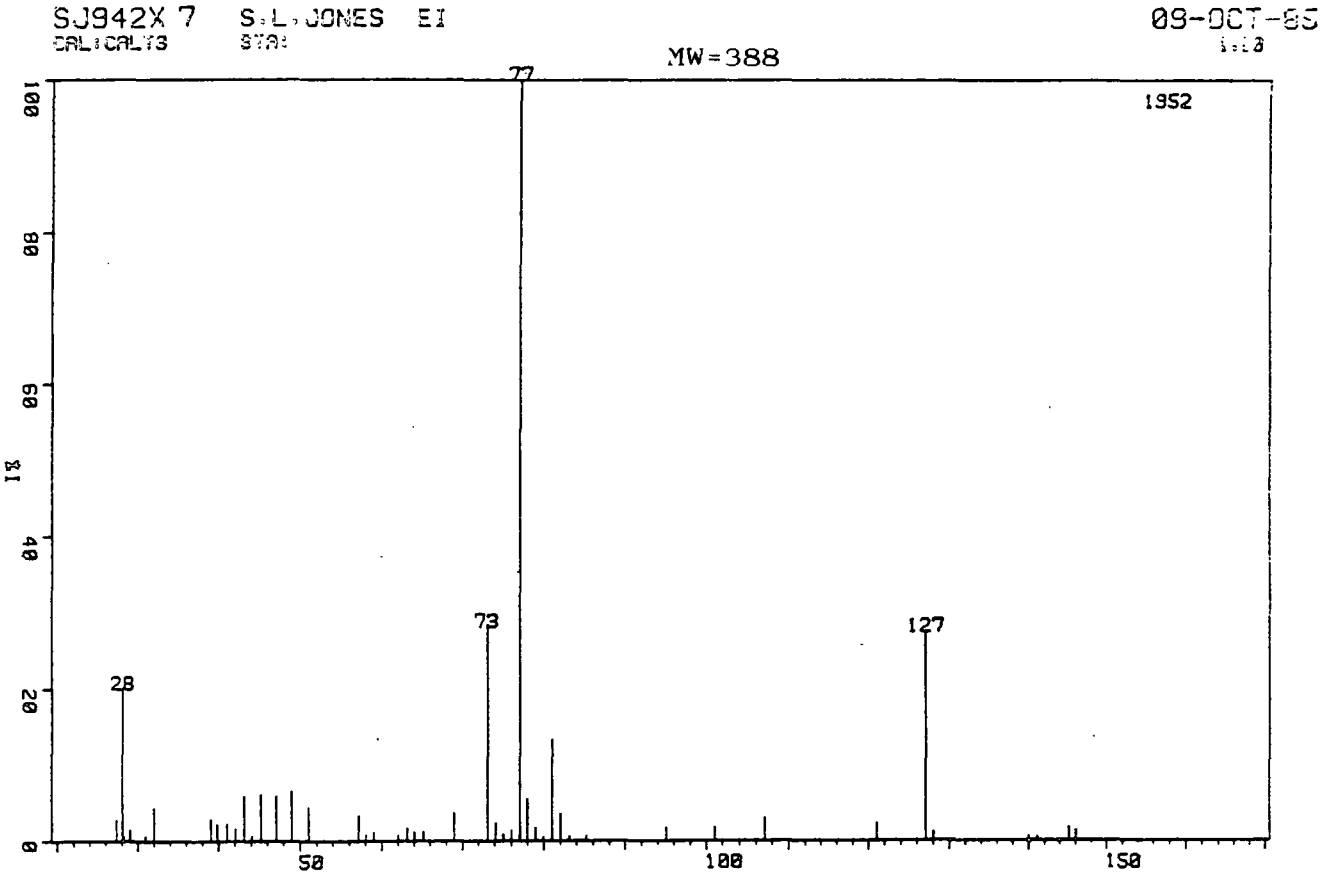
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	1.86	23	55.10	0.94	45	93.01	0.91
2	27.22	8.34	24	56.10	8.70	46	95.05	2.89
3	28.11	15.77	25	57.08	1.21	47	97.05	0.74
4	28.96	1.03	26	59.00	1.33	48	99.93	1.27
5	28.99	0.74	27	63.06	1.27	49	100.97	1.09
6	30.86	4.92	28	64.10	1.33	50	105.04	1.27
7	31.96	3.36	29	65.11	1.74	51	109.00	1.50
8	31.98	0.62	30	68.02	0.85	52	113.03	1.80
9	33.07	1.27	31	68.95	22.76	53	118.03	1.83
10	38.95	2.00	32	69.92	100.00	54	119.00	0.77
11	39.85	5.57	33	70.98	7.87	55	119.97	1.65
12	40.93	4.83	34	74.05	8.93	56	124.04	11.08
13	42.02	64.62	35	75.06	1.56	57	136.05	0.85
14	43.08	2.06	36	76.05	0.68	58	139.02	1.74
15	44.09	1.74	37	77.05	12.18	59	151.01	1.24
16	44.14	1.15	38	78.01	0.62	60	159.03	1.15
17	45.12	0.83	39	81.99	4.89	61	174.05	1.21
18	46.11	0.65	40	88.01	0.97	62	206.07	1.36
19	47.06	1.33	41	88.97	0.85			
20	47.09	1.15	42	89.91	0.77			
21	49.87	1.27	43	90.98	0.68			
22	50.93	12.03	44	91.97	12.03			

No.30 (1H,1H,3H-HEXAFLUOROBUTYL)TRIMETHYLSILANE (78)



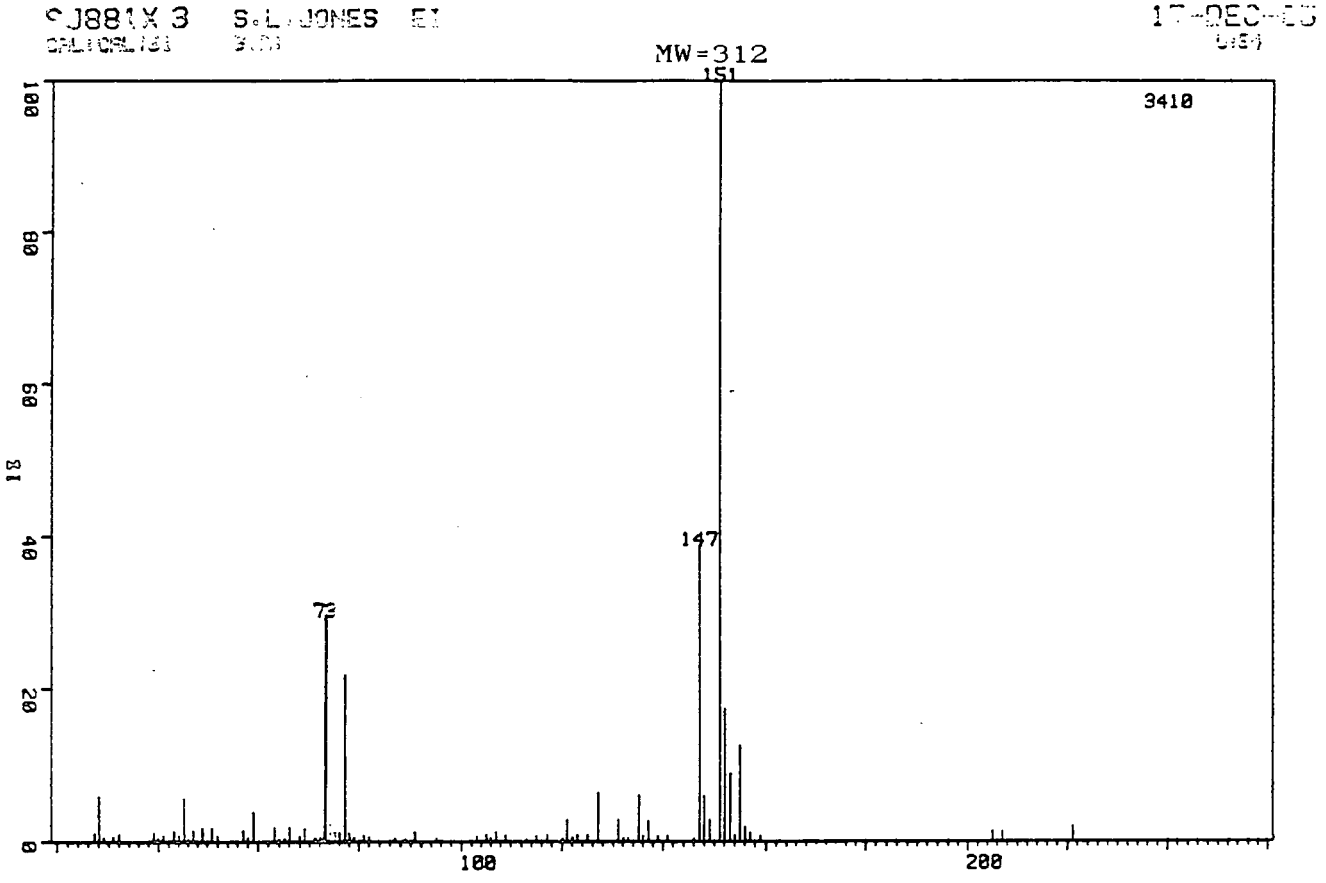
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	3.13	23	50.91	4.56	45	76.03	2.22
2	28.08	0.83	24	53.01	0.85	46	77.01	100.00
3	28.11	30.53	25	55.07	1.20	47	77.99	8.49
4	28.13	0.66	26	55.12	1.05	48	78.94	3.70
5	28.95	2.08	27	56.12	0.66	49	80.90	3.56
6	28.99	1.22	28	57.05	3.65	50	81.95	1.62
7	30.86	1.03	29	57.10	1.54	51	91.98	1.03
8	31.96	7.83	30	58.02	1.34	52	94.93	1.34
9	38.03	0.60	31	58.97	1.40	53	95.00	0.77
10	38.95	2.59	32	59.85	0.68	54	96.90	0.80
11	39.79	3.13	33	60.91	0.83	55	103.00	0.83
12	40.93	3.10	34	61.98	1.59	56	106.97	4.53
13	41.97	1.40	35	63.02	5.90	57	118.99	0.68
14	42.02	1.45	36	64.05	1.05	58	126.95	34.80
15	43.03	6.72	37	65.07	0.66	59	127.94	1.97
16	43.09	5.70	38	68.93	4.10	60	129.77	1.40
17	44.08	1.94	39	69.00	1.03	61	131.87	1.14
18	45.10	9.88	40	71.00	0.66	62	145.09	1.91
19	47.02	11.85	41	72.00	0.77	63	146.02	1.08
20	47.98	0.94	42	73.04	63.77			
21	48.93	12.28	43	74.07	5.21			
22	49.84	0.68	44	75.06	2.34			

No.31 BIS-(1H,1H,3H-HEXAFLUOROBUTYL)DIMETHYLSILANE (79)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.30	2.72	23	62.05	0.77	45	127.07	27.56
2	28.17	19.98	24	63.10	1.69	46	128.05	1.18
3	28.19	0.56	25	64.10	1.18	47	140.05	0.67
4	29.01	0.56	26	65.10	1.28	48	141.09	0.56
5	29.05	1.54	27	68.97	3.69	49	145.12	1.79
6	30.93	0.72	28	73.11	28.07	50	146.09	1.38
7	30.96	0.56	29	74.11	2.36			
8	32.04	4.35	30	75.04	0.92			
9	39.01	2.82	31	75.08	0.87			
10	39.84	2.15	32	76.05	1.38			
11	40.99	2.36	33	77.04	100.00			
12	42.08	1.59	34	78.01	5.48			
13	43.10	1.54	35	78.96	1.69			
14	43.15	5.89	36	79.88	0.56			
15	44.14	0.67	37	80.98	13.32			
16	45.16	6.10	38	82.02	3.53			
17	47.08	5.89	39	83.05	0.61			
18	48.98	6.51	40	85.13	0.67			
19	50.97	4.41	41	95.07	1.74			
20	57.11	3.33	42	101.00	1.79			
21	58.08	0.87	43	107.06	2.97			
22	59.03	1.18	44	121.02	2.31			

No.32 (1H,1H,3H-HEXAFLUOROBUTYL)PENTAMETHYLDISILOXANE (80)

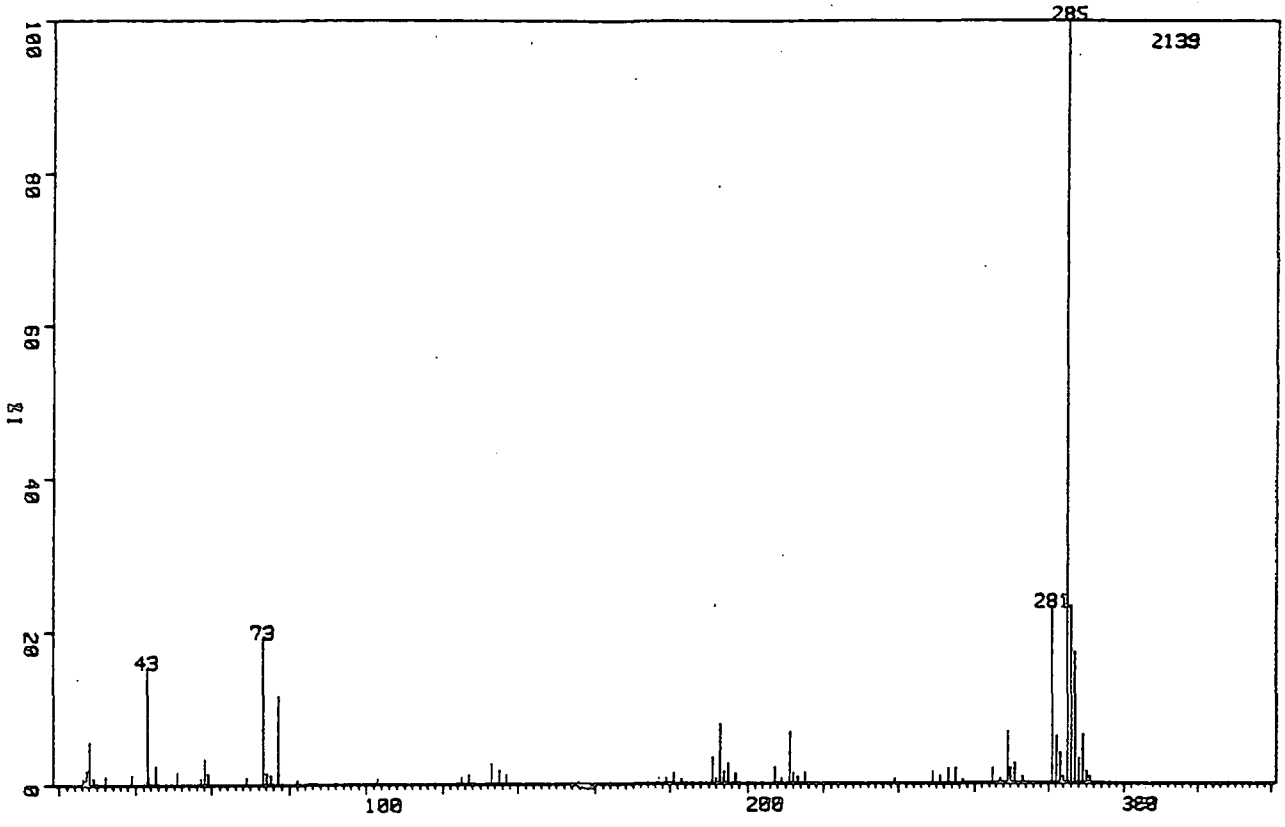


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	1.11	23	72.06	0.56	45	127.05	6.30
2	28.11	5.92	24	73.09	29.53	46	131.01	2.82
3	28.95	0.50	25	74.12	2.29	47	133.05	0.50
4	30.86	0.59	26	75.07	1.35	48	135.05	6.13
5	31.97	1.06	27	76.05	1.23	49	136.06	0.73
6	38.96	1.14	28	77.03	21.88	50	137.05	2.70
7	40.94	0.82	29	78.01	1.09	51	138.98	0.76
8	43.05	1.41	30	78.95	0.56	52	140.99	0.73
9	43.10	1.03	31	80.92	0.85	53	147.09	38.91
10	44.09	0.85	32	81.97	0.59	54	148.07	5.95
11	45.11	5.60	33	90.87	1.26	55	149.05	2.84
12	47.05	1.44	34	103.04	0.70	56	151.02	100.00
13	48.94	1.85	35	105.05	0.97	57	152.06	17.36
14	50.93	1.79	36	106.02	0.50	58	153.06	8.89
15	52.00	0.73	37	107.02	1.35	59	154.07	0.85
16	57.07	1.44	38	108.97	0.85	60	155.05	12.52
17	58.04	0.53	39	115.05	0.76	61	156.05	1.88
18	58.99	3.84	40	117.05	0.91	62	157.04	1.11
19	63.06	1.91	41	120.97	2.82	63	158.97	0.70
20	66.10	1.91	42	122.02	0.53	64	205.03	1.38
21	68.03	0.65	43	123.03	0.91	65	207.03	1.29
22	68.97	1.73	44	125.02	0.91	66	221.04	1.99

No.33 (1H,1H,3H-HEXAFLUOROBUTYL)HEPTAMETHYLCYCLOTETRA-SILOXANE (81)

SJ111X 4 S.L.JONES 111/1 EI 19-DEC-85

MW=446

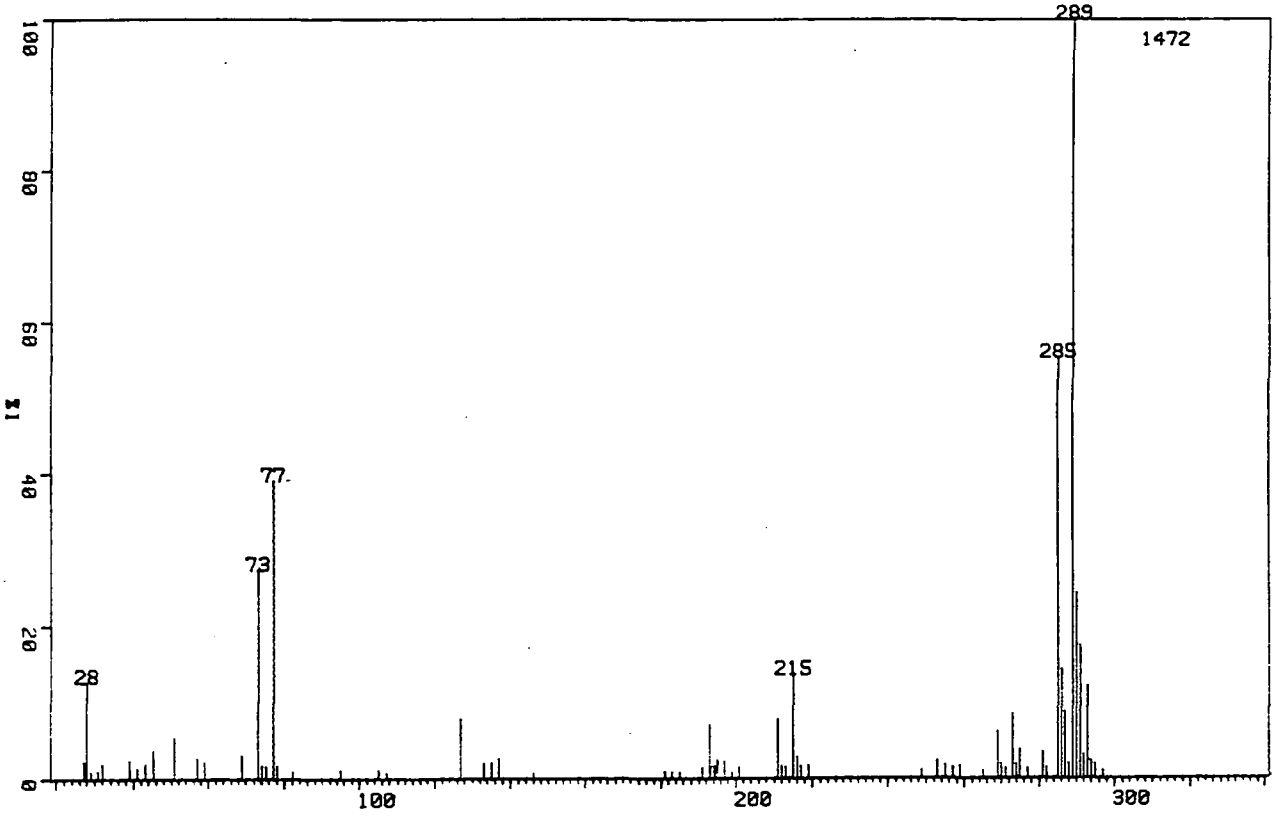


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.30	0.89	23	133.04	2.76	45	253.01	2.06
2	27.23	1.87	24	135.04	1.82	46	255.02	2.10
3	28.11	5.66	25	137.02	1.26	47	257.00	0.42
4	29.00	0.89	26	177.01	0.84	48	265.07	2.06
5	31.97	1.17	27	178.97	0.75	49	267.08	0.65
6	38.96	1.36	28	180.96	1.40	50	269.03	6.87
7	43.07	15.29	29	183.01	0.61	51	270.00	2.06
8	43.11	1.03	30	191.00	3.46	52	271.02	2.66
9	45.12	2.43	31	192.03	0.65	53	273.02	0.98
10	50.94	1.64	32	193.00	7.85	54	281.06	23.00
11	57.09	0.79	33	194.02	1.59	55	282.10	6.17
12	58.07	3.41	34	195.01	2.62	56	283.06	4.07
13	59.01	1.50	35	197.02	1.31	57	284.10	0.89
14	68.99	0.94	36	207.07	2.20	58	285.05	100.00
15	73.11	19.26	37	209.00	0.75	59	286.04	23.19
16	74.10	1.54	38	211.02	6.83	60	287.05	17.16
17	75.07	1.22	39	212.04	1.40	61	288.03	3.32
18	77.03	11.78	40	213.05	0.89	62	289.02	6.40
19	81.98	0.61	41	215.04	1.45	63	290.00	1.64
20	102.97	0.75	42	238.98	0.65	64	291.02	0.89
21	125.04	0.98	43	248.98	1.59			
22	127.04	1.31	44	251.00	1.03			

No.34 BIS-(1H,1H,3H-HEXAFLUOROBUTYL)HEXAMETHYLCYCLOTETRA-SILOXANE (82)

S1112X 6 S.L.JONES 16-JAN-86

CRL:CRLY81 MW=596

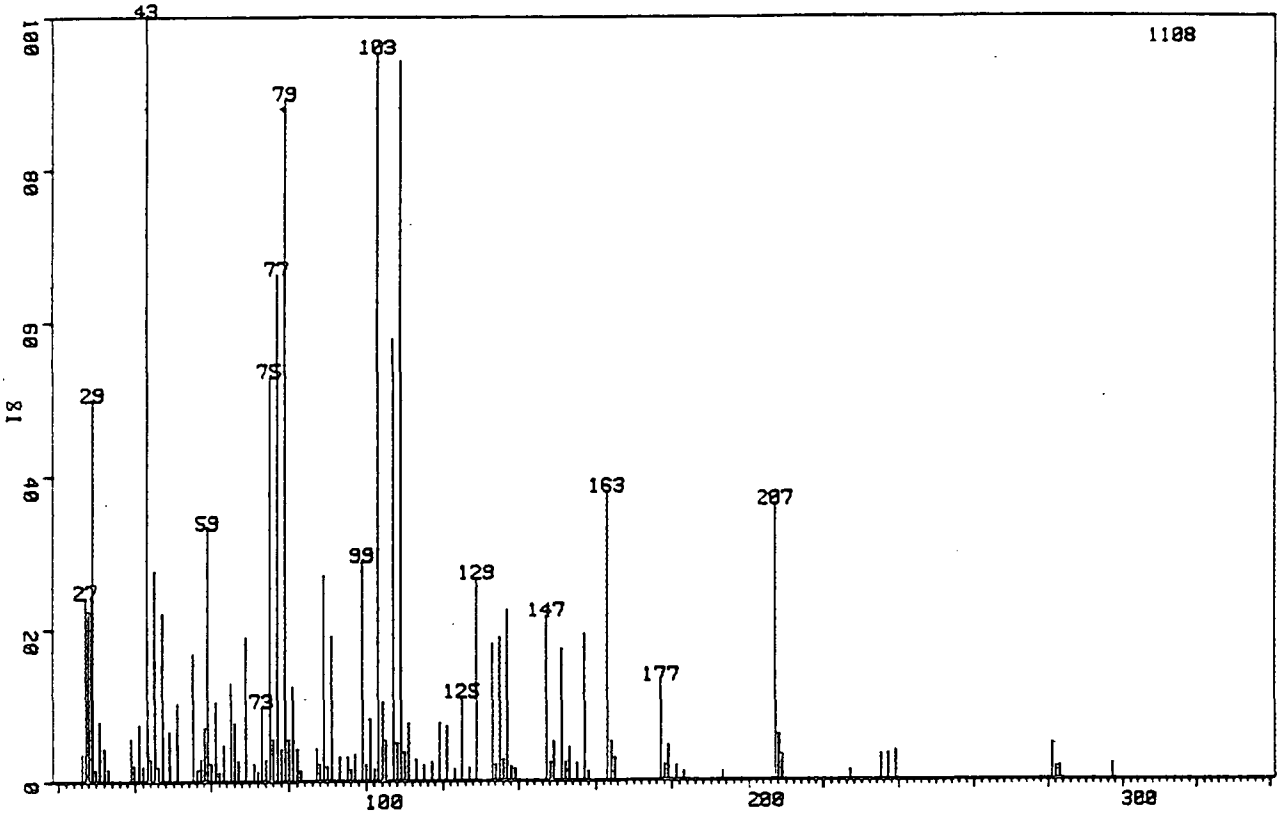


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	2.24	23	135.04	2.11	45	269.95	1.97
2	28.11	12.77	24	137.02	2.65	46	270.95	1.22
3	30.86	1.02	25	190.97	1.49	47	272.95	8.42
4	31.97	1.97	26	192.97	7.13	48	273.95	1.90
5	38.96	2.45	27	193.99	1.63	49	274.95	3.74
6	40.95	1.22	28	194.98	2.51	50	276.92	1.22
7	43.11	1.97	29	196.95	2.24	51	280.98	3.46
8	45.12	3.74	30	200.92	1.56	52	281.99	1.36
9	50.94	5.37	31	210.97	7.81	53	285.00	55.37
10	57.08	2.79	32	212.00	1.70	54	286.01	14.27
11	59.00	2.24	33	213.00	1.56	55	286.99	8.70
12	68.98	3.12	34	214.98	13.65	56	288.01	1.97
13	73.11	27.45	35	215.98	2.85	57	288.96	100.00
14	74.10	1.83	36	216.99	1.63	58	289.94	24.25
15	75.08	1.70	37	218.94	1.77	59	290.96	17.39
16	77.05	39.13	38	248.94	1.09	60	291.98	3.12
17	78.02	1.83	39	252.94	2.24	61	292.94	12.02
18	81.99	1.02	40	254.97	1.83	62	293.96	2.31
19	95.04	1.15	41	256.93	1.49	63	294.94	1.90
20	105.04	1.15	42	258.92	1.70	64	296.95	1.02
21	127.04	7.95	43	265.00	1.02			
22	133.03	2.04	44	268.96	6.18			

No.35 (1,1,1,2,3,3-HEXAFLUORO-4-PENTYLOXY)ETHOXYDIMETHYL-SILANE (84)

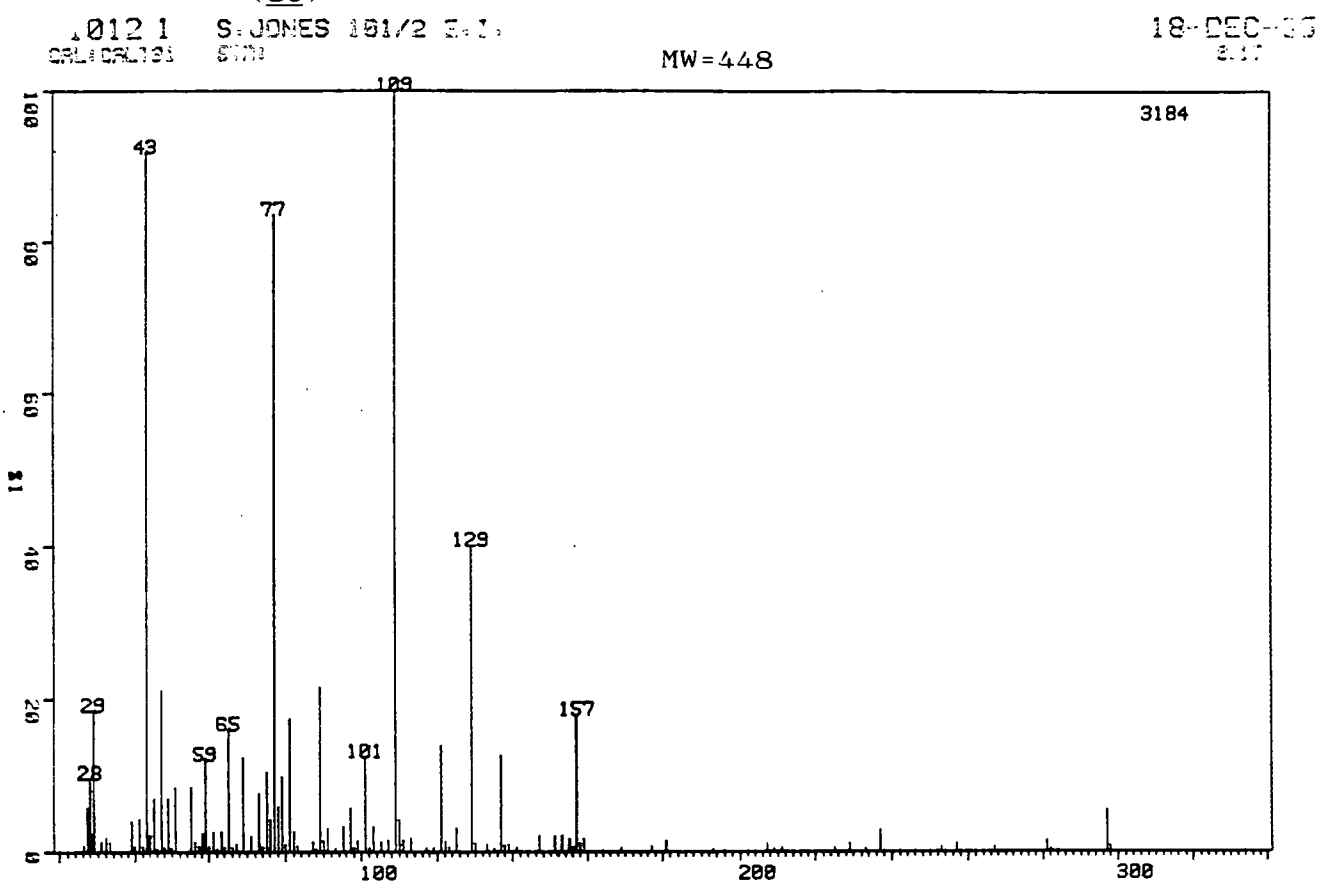
J1011X 5 S. JONES EI 18-DEC-85

MW=298



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	24.19	23	75.09	52.89	45	125.07	11.01
2	28.11	22.47	24	76.08	5.51	46	129.00	26.62
3	28.13	6.86	25	77.06	66.25	47	133.08	18.14
4	28.96	24.10	26	78.02	4.24	48	135.08	18.86
5	29.00	49.82	27	78.96	89.17	49	137.07	22.47
6	30.88	7.85	28	79.91	5.51	50	147.12	21.66
7	38.96	5.60	29	80.96	12.55	51	149.03	5.14
8	40.95	7.49	30	82.01	4.24	52	151.00	17.42
9	43.07	100.00	31	87.06	4.33	53	153.04	4.42
10	45.09	27.62	32	88.99	27.08	54	157.04	19.31
11	45.14	15.79	33	90.99	19.04	55	163.08	37.82
12	47.08	22.11	34	98.98	28.88	56	164.08	5.14
13	48.95	6.59	35	100.99	8.21	57	177.09	13.09
14	50.95	10.29	36	103.09	95.22	58	179.05	4.60
15	55.12	16.79	37	104.11	10.56	59	207.11	36.10
16	58.06	7.13	38	105.06	5.32	60	208.07	6.05
17	59.00	33.21	39	107.05	57.85	61	281.06	4.87
18	60.98	10.47	40	108.03	5.05	62	297.14	2.17
19	65.12	13.00	41	108.99	94.22			
20	66.10	7.67	42	110.97	7.58			
21	68.96	18.95	43	119.00	7.67			
22	73.08	9.84	44	121.02	7.22			

No.36 BIS-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYLOXY)DIMETHYLSILANE (85)

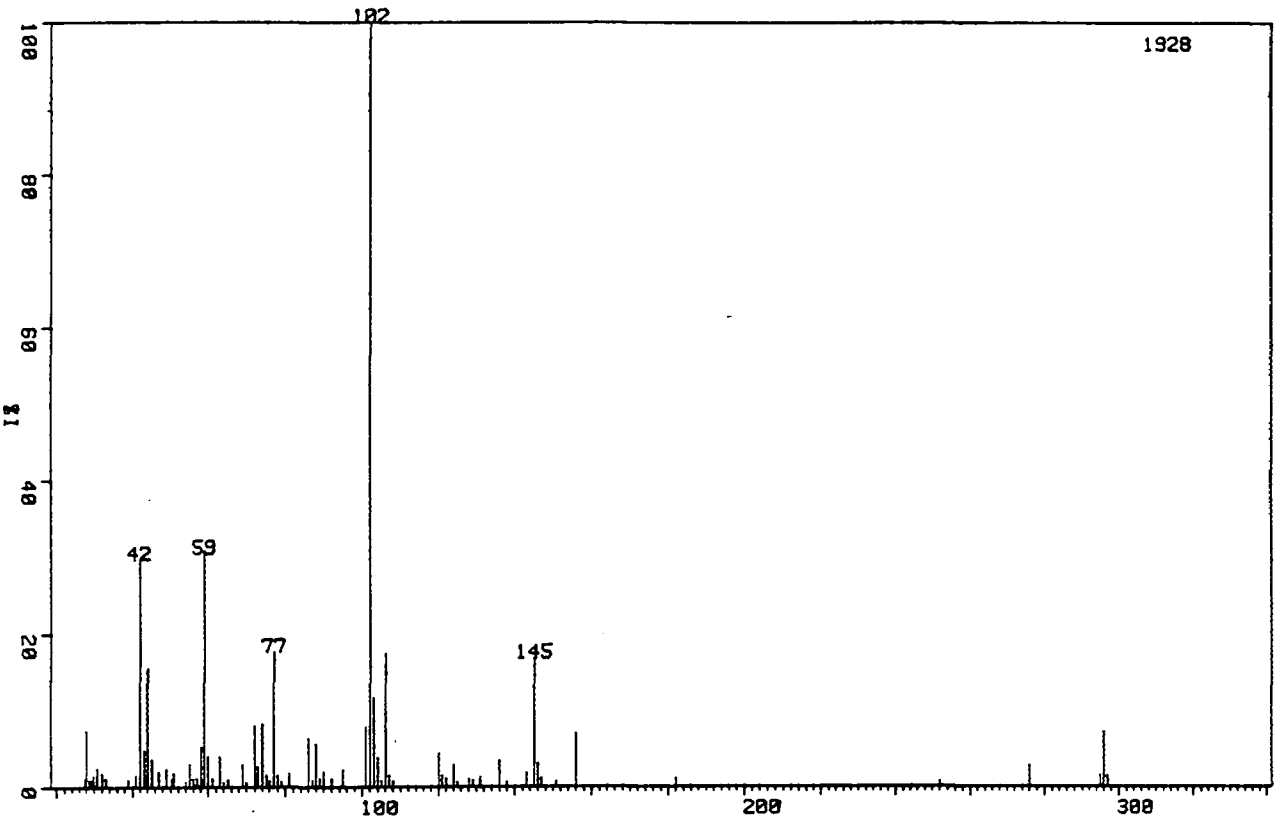


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	5.78	23	68.94	12.41	45	125.09	3.11
2	28.11	9.61	24	70.96	2.01	46	129.02	40.20
3	28.13	2.36	25	73.06	7.66	47	137.06	12.66
4	28.97	18.44	26	75.06	10.55	48	147.04	2.14
5	29.00	4.77	27	76.05	4.27	49	151.03	2.07
6	31.97	1.85	28	77.03	83.67	50	153.07	2.20
7	38.96	4.05	29	78.00	5.94	51	155.07	1.76
8	40.95	4.33	30	78.94	9.92	52	157.08	18.00
9	43.07	91.93	31	80.96	17.43	53	159.04	1.73
10	43.11	2.10	32	82.00	2.67	54	237.05	2.80
11	44.11	2.20	33	88.98	21.61	55	281.08	1.57
12	45.09	5.72	34	90.99	3.11	56	297.13	5.50
13	45.14	7.00	35	95.06	3.33			
14	47.08	21.11	36	97.06	5.75			
15	48.95	7.00	37	100.98	12.47			
16	50.95	8.39	38	103.09	3.23			
17	55.12	8.51	39	107.07	1.57			
18	58.05	2.39	40	109.02	100.00			
19	59.00	12.06	41	109.98	4.21			
20	60.97	2.64	42	111.01	1.57			
21	63.07	2.67	43	113.05	1.82			
22	65.10	16.05	44	121.06	13.88			

No.37 (1H,1H,3H-HEXAFLUOROBUTYLMETHYLAMINO)DIMETHYLAMINO-DIMETHYLSILANE (86)

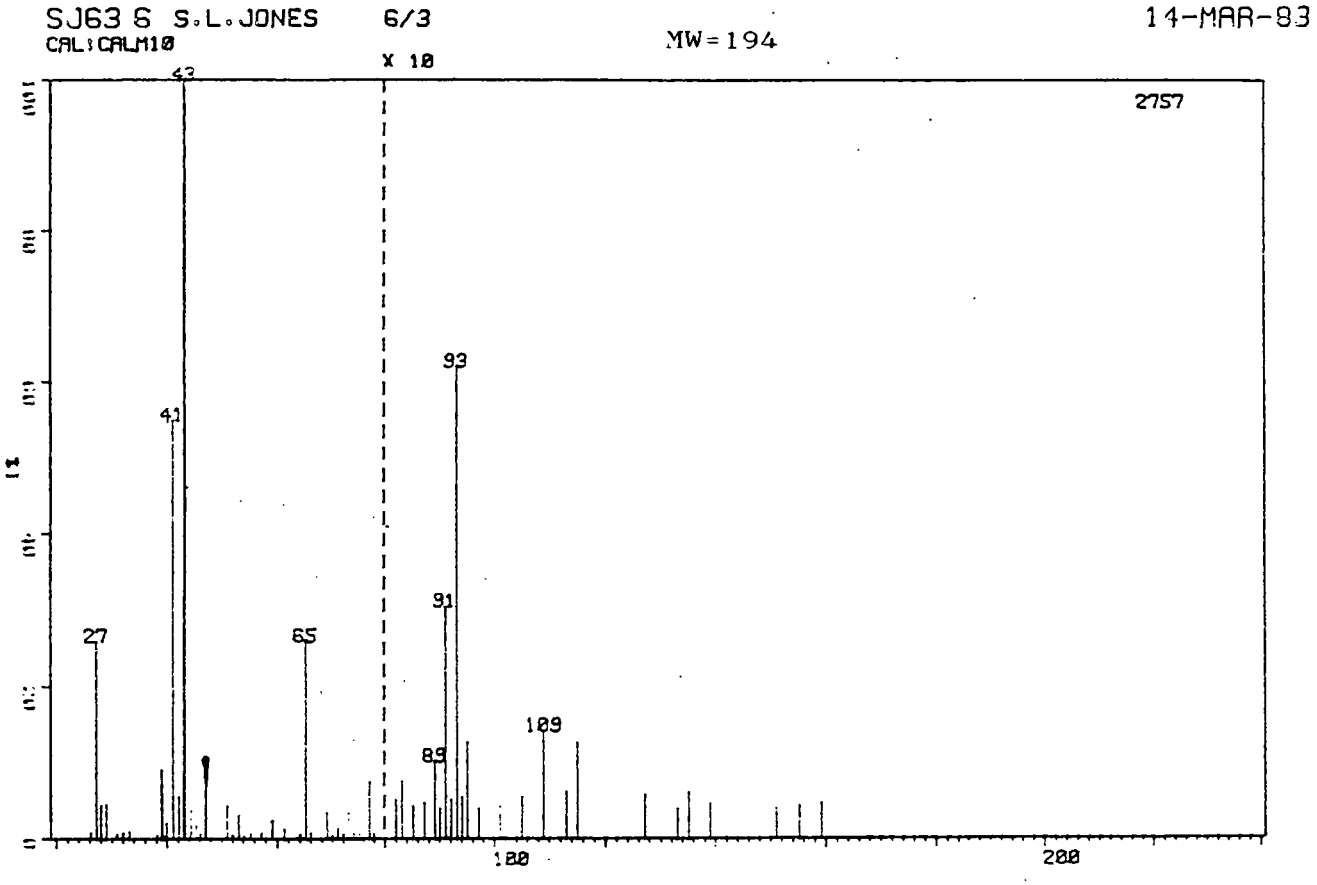
SJ891X 4 S.L.JONES EI 18-DEC-1

MW=296



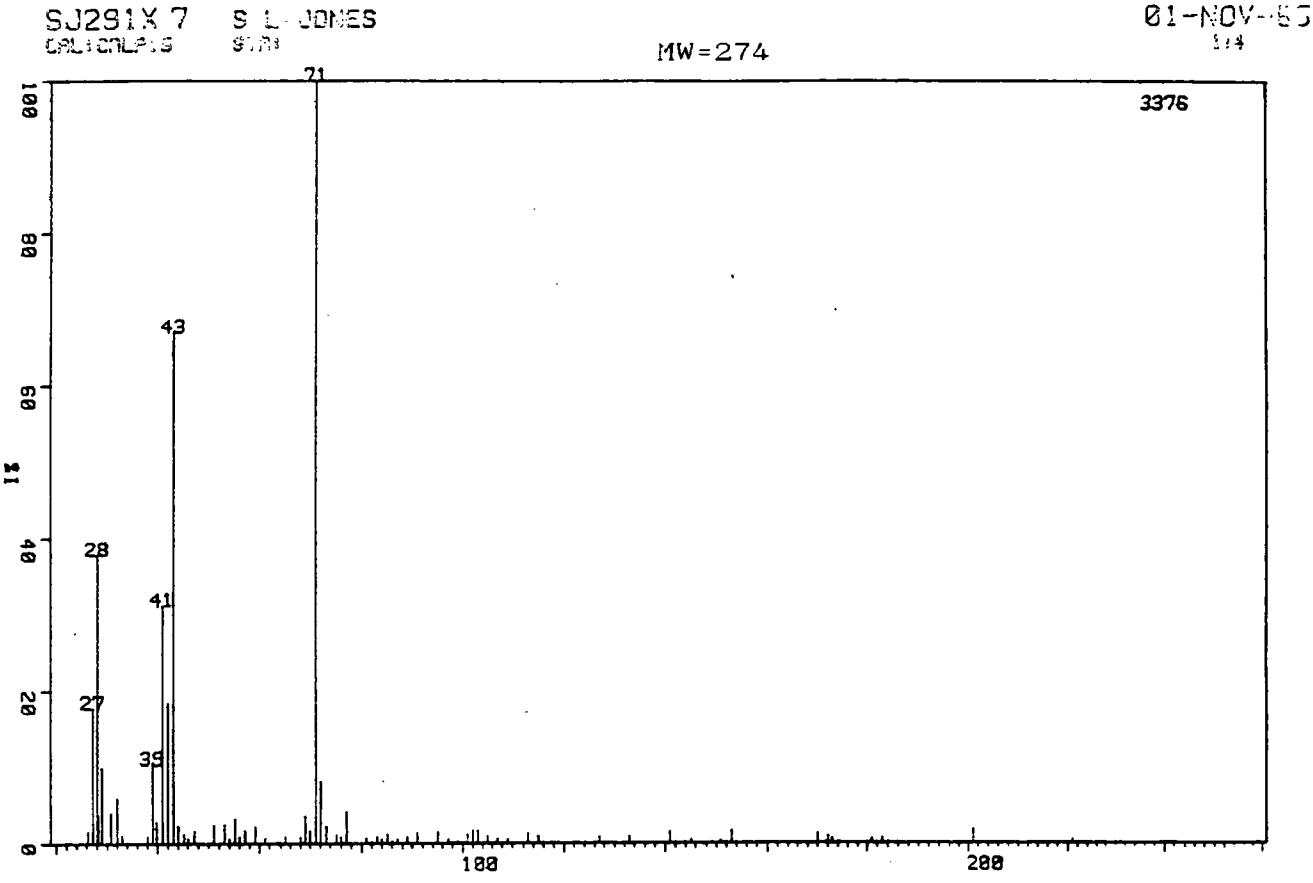
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	1.09	23	59.91	3.99	45	106.07	17.53
2	28.11	7.37	24	60.97	1.14	46	107.06	1.50
3	29.82	1.56	25	63.05	3.99	47	119.99	4.41
4	30.86	2.44	26	68.94	2.96	48	121.03	1.50
5	31.96	1.82	27	72.05	8.04	49	122.07	1.09
6	33.07	1.09	28	72.58	1.71	50	124.06	2.90
7	40.93	1.50	29	73.07	2.65	51	128.00	1.09
8	42.02	29.72	30	74.09	8.35	52	131.07	1.30
9	43.04	4.82	31	75.10	1.56	53	136.05	3.48
10	43.09	2.13	32	77.05	17.74	54	143.10	1.87
11	44.13	15.56	33	78.02	1.50	55	145.13	16.96
12	45.11	3.63	34	80.94	1.82	56	146.09	3.11
13	45.15	1.09	35	86.08	6.43	57	147.09	1.09
14	47.04	2.02	36	88.04	5.65	58	156.01	7.00
15	48.93	2.39	37	88.98	1.14	59	182.00	1.09
16	50.41	1.04	38	89.92	2.02	60	275.99	2.85
17	50.93	1.82	39	92.01	1.14	61	294.99	1.50
18	55.13	3.06	40	95.04	2.28	62	296.01	7.26
19	56.07	1.14	41	101.01	7.88	63	297.00	1.40
20	57.07	1.14	42	102.05	100.00			
21	58.06	5.34	43	103.07	11.67			
22	58.98	30.55	44	104.08	3.79			

No.38 1,1,1,2,3,3-HEXAFLUORO-4-METHYLPENTANE (89)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.30	0.80	23	53.22	3.12	45	89.03	1.02
2	27.24	25.79	24	54.28	0.33	46	90.00	0.40
3	28.13	4.39	25	55.30	0.58	47	91.07	3.05
4	29.02	4.53	26	57.23	0.65	48	92.15	0.51
5	30.93	0.47	27	59.14	2.39	49	93.14	6.20
6	32.03	0.76	28	61.18	1.23	50	94.11	0.54
7	33.15	0.91	29	64.24	0.54	51	95.05	1.27
8	38.15	0.40	30	65.19	25.86	52	97.09	0.40
9	39.03	9.10	31	66.15	0.73	53	101.01	0.44
10	39.13	7.15	32	68.97	3.41	54	105.16	0.54
11	39.34	0.40	33	69.94	0.44	55	109.03	1.41
12	39.94	2.07	34	71.02	1.34	56	113.09	0.62
13	41.05	54.95	35	72.09	0.51	57	115.12	1.27
14	42.15	5.55	36	73.13	3.37	58	127.20	0.58
15	43.22	100.00	37	74.12	0.62	59	133.13	0.40
16	44.26	3.77	38	75.05	0.62	60	135.16	0.62
17	45.24	1.78	39	77.04	7.47	61	139.08	0.47
18	46.24	0.58	40	78.02	0.69	62	151.15	0.40
19	47.20	10.85	41	82.04	0.51	63	155.28	0.44
20	48.15	0.51	42	83.10	0.76	64	159.23	0.47
21	51.05	4.32	43	85.10	0.44			
22	52.13	0.36	44	87.15	0.47			

No.39 1,2-BIS-(2-TETRAHYDROFURYL)-1H-PENTAFLUOROPROPANE (91)

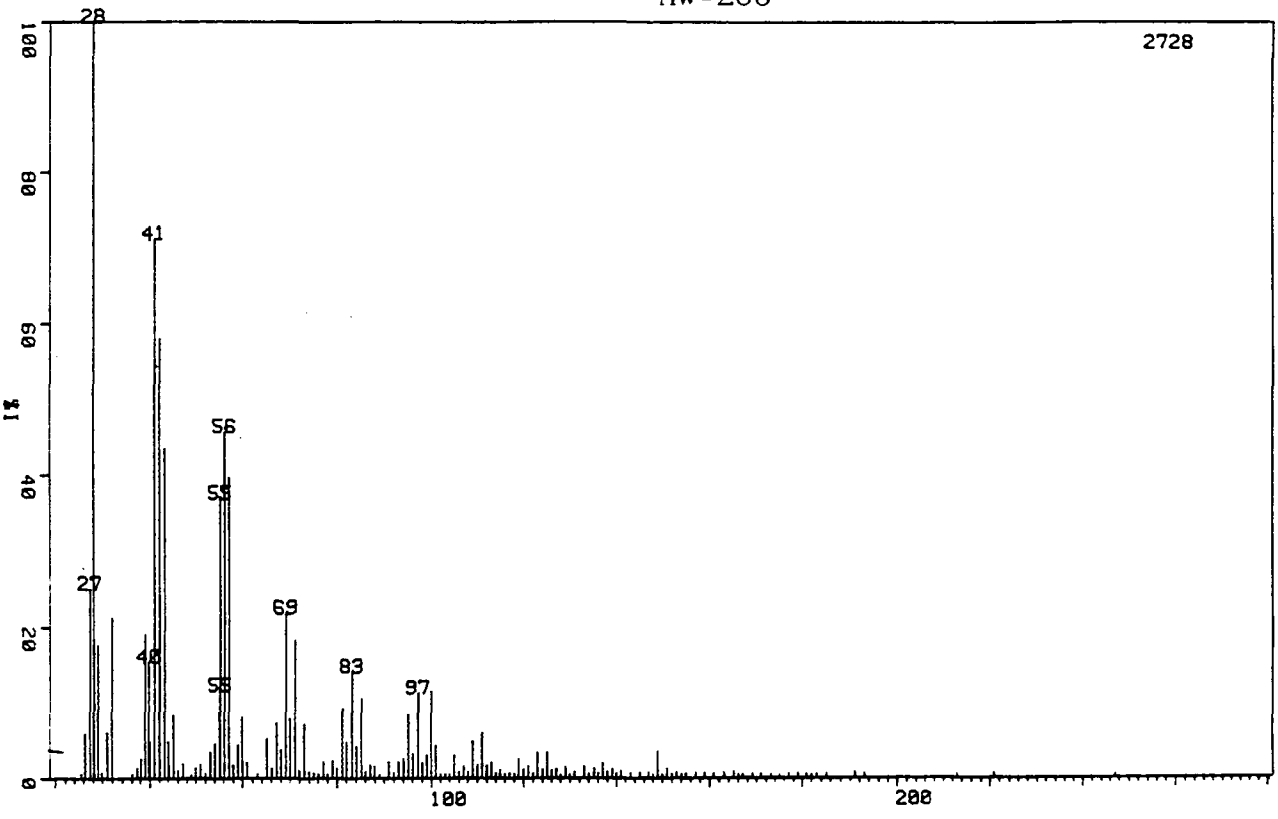


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.28	1.63	23	50.95	2.43	45	140.94	1.57
2	27.22	17.74	24	53.09	2.52	46	153.07	1.69
3	28.10	37.91	25	55.11	1.66	47	169.96	1.33
4	28.12	3.70	26	55.15	3.23	48	200.96	1.84
5	28.96	9.92	27	57.09	1.78			
6	28.99	4.38	28	57.13	1.07			
7	30.87	4.06	29	59.00	2.22			
8	31.96	5.98	30	68.94	3.58			
9	33.06	1.10	31	68.97	3.44			
10	38.96	10.43	32	69.92	1.69			
11	39.80	2.01	33	70.98	100.00			
12	39.86	2.84	34	72.03	8.15			
13	40.95	31.28	35	73.06	2.34			
14	42.00	2.99	36	75.06	1.16			
15	42.04	18.45	37	77.04	4.15			
16	43.07	4.30	38	85.08	1.27			
17	43.11	67.03	39	90.98	1.36			
18	44.08	2.31	40	95.04	1.57			
19	44.12	1.42	41	100.96	1.16			
20	44.15	2.16	42	102.02	1.78			
21	45.14	1.27	43	103.04	1.75			
22	47.10	1.78	44	113.01	1.30			

No.40 δ-VALEROLACTONE DIMER (95)

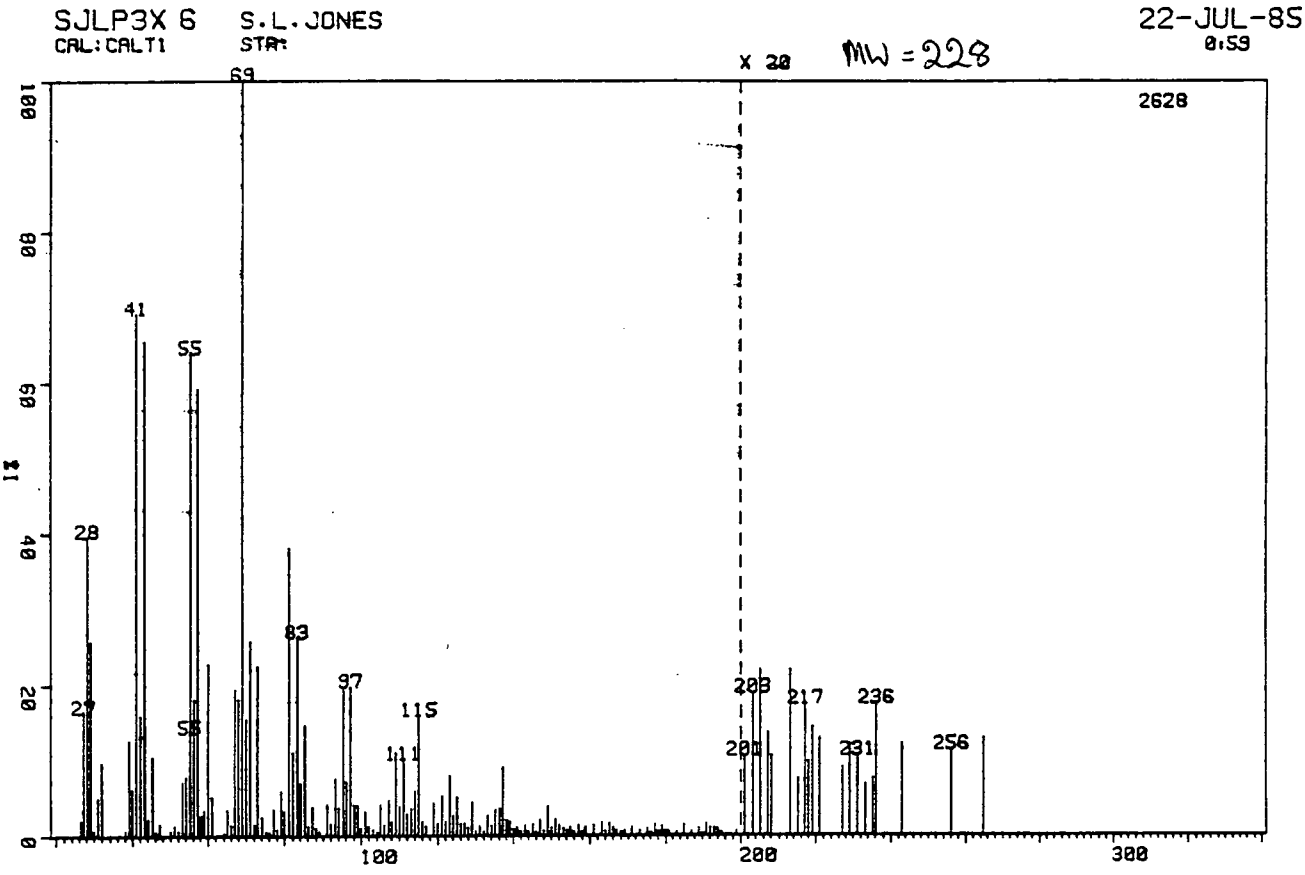
SJLP2X 12 S.L.JONES 22-JUL-80

MW=200



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.37	5.87	23	55.10	11.62	45	93.03	2.16
2	27.30	25.00	24	55.14	36.91	46	94.03	2.60
3	28.17	100.00	25	56.14	45.71	47	95.07	8.47
4	28.19	18.29	26	57.12	39.66	48	96.07	3.26
5	29.02	8.69	27	59.00	4.36	49	97.06	11.25
6	29.05	17.60	28	59.90	8.14	50	98.03	2.05
7	30.95	6.05	29	60.97	2.02	51	98.99	3.04
8	32.03	21.19	30	65.09	5.28	52	99.92	11.55
9	38.07	2.53	31	67.09	7.29	53	100.96	4.22
10	38.99	19.02	32	68.05	3.78	54	105.04	3.04
11	39.82	15.36	33	69.01	21.81	55	108.99	4.91
12	39.89	4.84	34	69.94	7.88	56	110.99	6.01
13	40.97	71.15	35	71.02	18.18	57	113.03	2.13
14	42.02	58.03	36	73.06	7.15	58	118.95	2.57
15	42.06	24.19	37	77.06	2.16	59	123.01	3.41
16	43.09	12.79	38	79.01	2.35	60	125.04	3.45
17	43.12	43.55	39	81.02	9.16	61	137.03	2.02
18	44.12	4.84	40	82.06	4.73	62	148.88	3.56
19	45.12	2.68	41	83.11	14.08			
20	45.15	8.39	42	84.10	4.18			
21	53.09	3.48	43	85.11	10.52			
22	54.12	4.55	44	90.94	2.20			

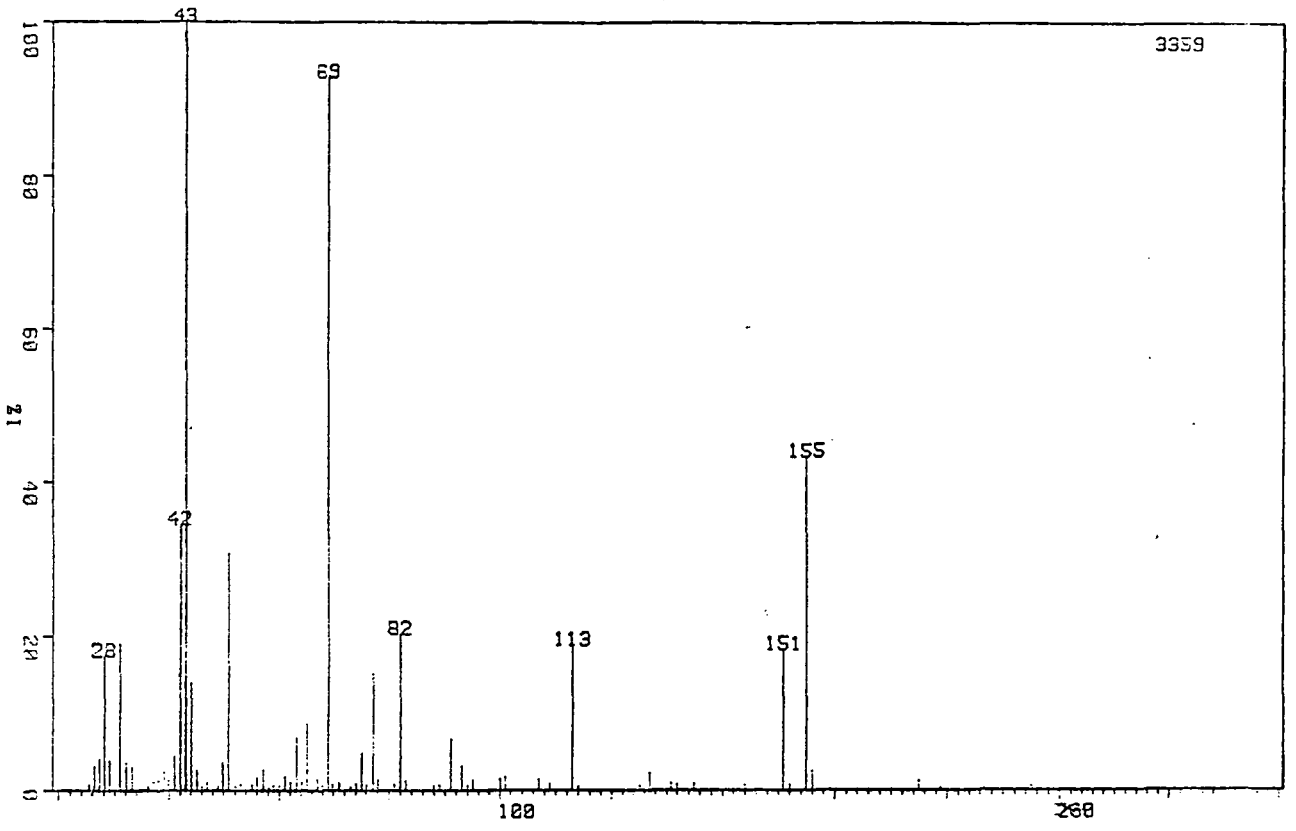
No.41 ε-CAPROLACTONE DIMER (96)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.30	16.40	23	60.98	5.18	45	108.99	11.03
2	28.17	39.69	24	67.08	19.44	46	111.00	10.20
3	28.19	6.01	25	68.05	18.19	47	114.02	5.94
4	29.02	4.22	26	69.00	100.00	48	115.03	15.98
5	29.05	25.72	27	69.95	15.45	49	118.96	4.30
6	30.95	5.06	28	71.01	25.84	50	120.96	5.33
7	32.03	9.67	29	73.05	22.56	51	123.03	7.99
8	38.99	12.67	30	79.00	5.97	52	125.05	5.14
9	39.83	6.16	31	81.02	38.17	53	128.96	4.45
10	40.98	69.10	32	82.07	11.07	54	137.04	9.09
11	42.03	4.15	33	83.10	26.29			
12	42.07	15.94	34	84.08	6.89			
13	43.09	14.50	35	85.10	14.69			
14	43.13	65.45	36	90.95	4.15			
15	45.16	10.54	37	93.03	7.57			
16	53.10	7.15	38	95.07	19.44			
17	54.13	7.88	39	96.06	7.19			
18	55.11	13.66	40	97.06	19.82			
19	55.14	63.93	41	98.03	4.11			
20	56.14	18.07	42	99.00	4.03			
21	57.13	59.17	43	105.04	4.11			
22	59.91	22.83	44	107.04	4.76			

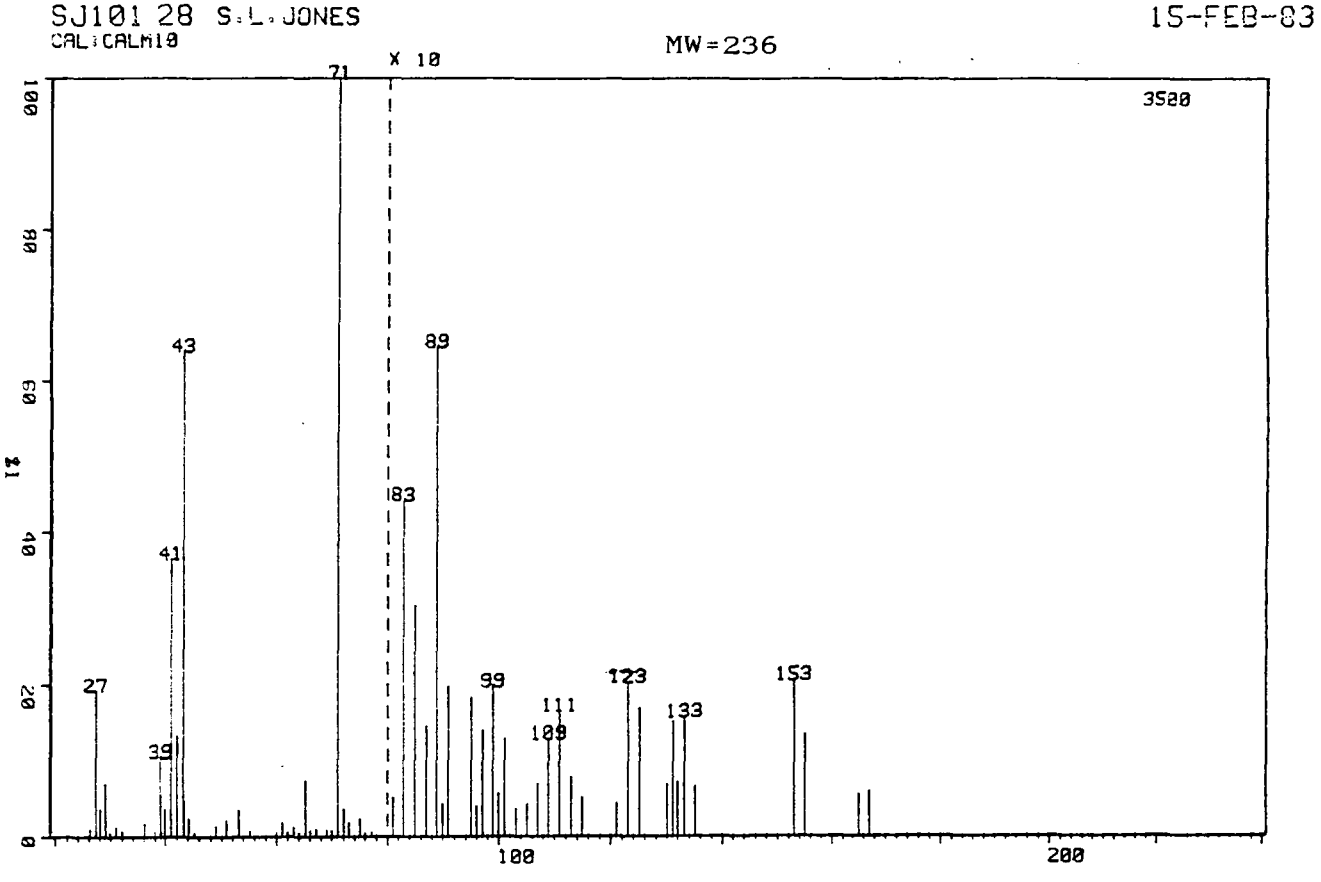
No.42 1,1,1,2,3,3-HEXAFLUORO-4-PENTANONE (97)

SJ201X 12 S.JONES 20/1 04-JUL-85
CAL:CAL:1 SIG: MW=194 1:50



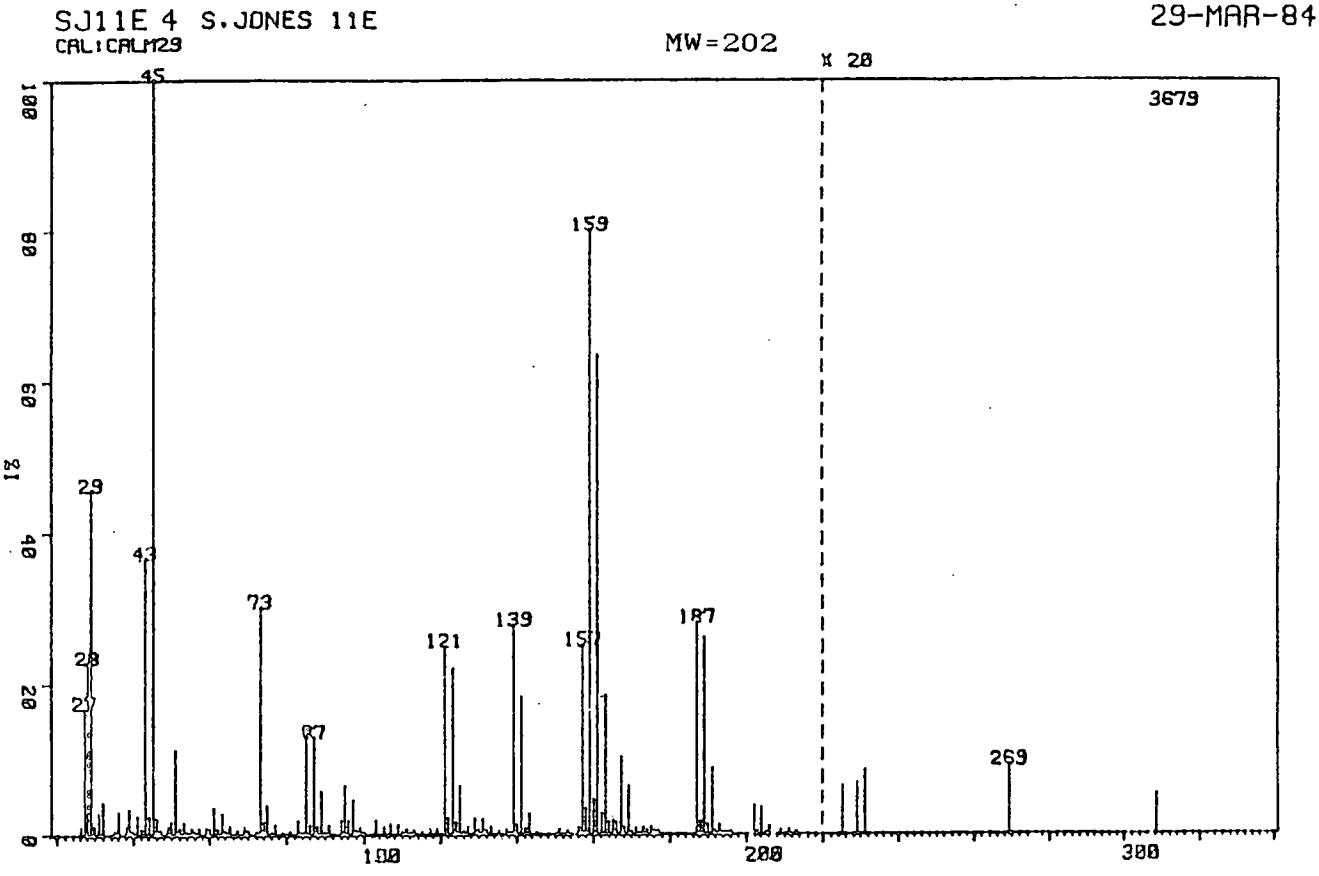
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	25.41	0.74	23	50.93	30.78	45	88.98	0.77
2	26.37	3.10	24	53.04	0.80	46	90.96	6.73
3	27.30	4.08	25	55.08	0.77	47	93.02	3.16
4	28.17	17.45	26	56.07	1.70	48	95.05	1.40
5	29.02	3.81	27	57.06	2.65	49	99.92	1.49
6	29.05	0.74	28	60.93	1.88	50	100.96	1.82
7	30.93	19.02	29	61.98	1.07	51	107.02	1.46
8	32.03	3.60	30	63.02	6.88	52	108.96	0.89
9	33.13	3.07	31	64.06	1.10	53	112.98	18.90
10	37.13	1.13	32	65.07	8.75	54	126.97	2.35
11	38.07	1.28	33	67.02	1.43	55	130.88	1.01
12	38.99	2.41	34	68.93	92.85	56	131.95	0.80
13	39.82	1.22	35	69.88	0.80	57	134.99	0.92
14	40.93	4.44	36	70.95	0.98	58	143.99	0.74
15	40.97	1.04	37	74.06	0.92	59	150.90	18.34
16	42.02	34.53	38	75.07	4.82	60	151.96	0.74
17	43.08	100.00	39	76.07	0.77	61	154.99	43.35
18	43.12	2.05	40	77.07	15.18	62	155.99	2.50
19	44.12	14.05	41	78.02	1.40	63	174.97	1.22
20	45.13	2.59	42	80.96	0.80			
21	47.07	1.07	43	82.01	20.33			
22	49.87	3.66	44	83.04	1.22			

No.43 2-(2H-TETRACHLOROETHYL)OXOLANE (101)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.30	1.06	23	60.91	1.91	45	98.93	1.97
2	27.24	19.26	24	61.99	0.54	46	99.90	0.57
3	28.13	3.63	25	63.02	1.29	47	100.94	1.29
4	28.99	7.06	26	64.06	0.54	48	106.94	0.69
5	30.92	1.26	27	65.10	7.40	49	108.89	1.29
6	32.00	0.71	28	66.06	0.77	50	110.89	1.66
7	36.14	1.69	29	67.04	1.06	51	113.00	0.77
8	38.06	0.60	30	68.94	0.89	52	115.01	0.51
9	38.99	10.49	31	69.89	0.74	53	123.01	2.03
10	39.02	5.46	32	70.98	100.00	54	125.01	1.69
11	39.34	0.51	33	72.02	3.63	55	129.89	0.69
12	39.89	3.60	34	72.99	1.86	56	131.04	1.51
13	40.97	36.54	35	75.02	2.37	57	131.96	0.71
14	42.07	13.29	36	76.98	0.57	58	133.03	1.57
15	43.13	63.97	37	80.91	0.51	59	135.07	0.66
16	43.23	4.69	38	82.89	4.43	60	152.98	2.06
17	44.17	2.43	39	84.95	3.03	61	155.00	1.34
18	48.94	1.40	40	86.99	1.46	62	165.00	0.54
19	50.94	2.11	41	88.90	6.46	63	167.03	0.60
20	53.07	3.57	42	90.91	1.97			
21	55.10	0.74	43	94.97	1.83			
22	59.86	0.51	44	96.95	1.40			

No.44 1,1,2-TRICHLORO-3-ETHOXYBUTENE (102)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.19	16.77	23	121.00	24.98	45	167.16	10.41
2	28.07	22.72	24	122.04	2.34	46	168.04	1.01
3	28.96	45.64	25	123.05	22.10	47	169.08	6.61
4	30.87	2.91	26	125.08	6.63	48	171.13	0.92
5	31.96	4.46	27	128.97	2.26	49	173.09	1.03
6	36.12	3.18	28	131.01	2.15	50	174.12	0.63
7	38.99	3.56	29	139.04	27.72	51	175.07	1.03
8	40.98	2.56	30	141.05	18.29	52	187.08	28.05
9	43.11	36.61	31	143.12	2.91	53	188.08	1.79
10	44.16	2.56	32	151.11	0.68	54	189.05	26.09
11	45.19	100.00	33	153.16	0.57	55	190.08	1.39
12	46.18	2.17	34	156.03	0.95	56	191.07	8.86
13	51.02	11.36	35	157.05	25.14	57	193.12	1.30
14	61.02	3.78	36	158.03	3.56	58	202.14	3.94
15	63.13	2.83	37	159.00	80.16	59	204.13	3.70
16	73.12	30.12	38	159.99	4.81	60	206.12	1.14
17	75.02	3.94	39	161.00	63.60	61	209.05	0.63
18	85.01	14.62	40	162.06	2.83	62	211.11	0.68
19	87.01	13.02	41	163.04	18.43			
20	88.94	6.06	42	164.05	1.77			
21	95.03	6.66	43	165.06	1.93			
22	97.02	4.73	44	166.04	1.69			

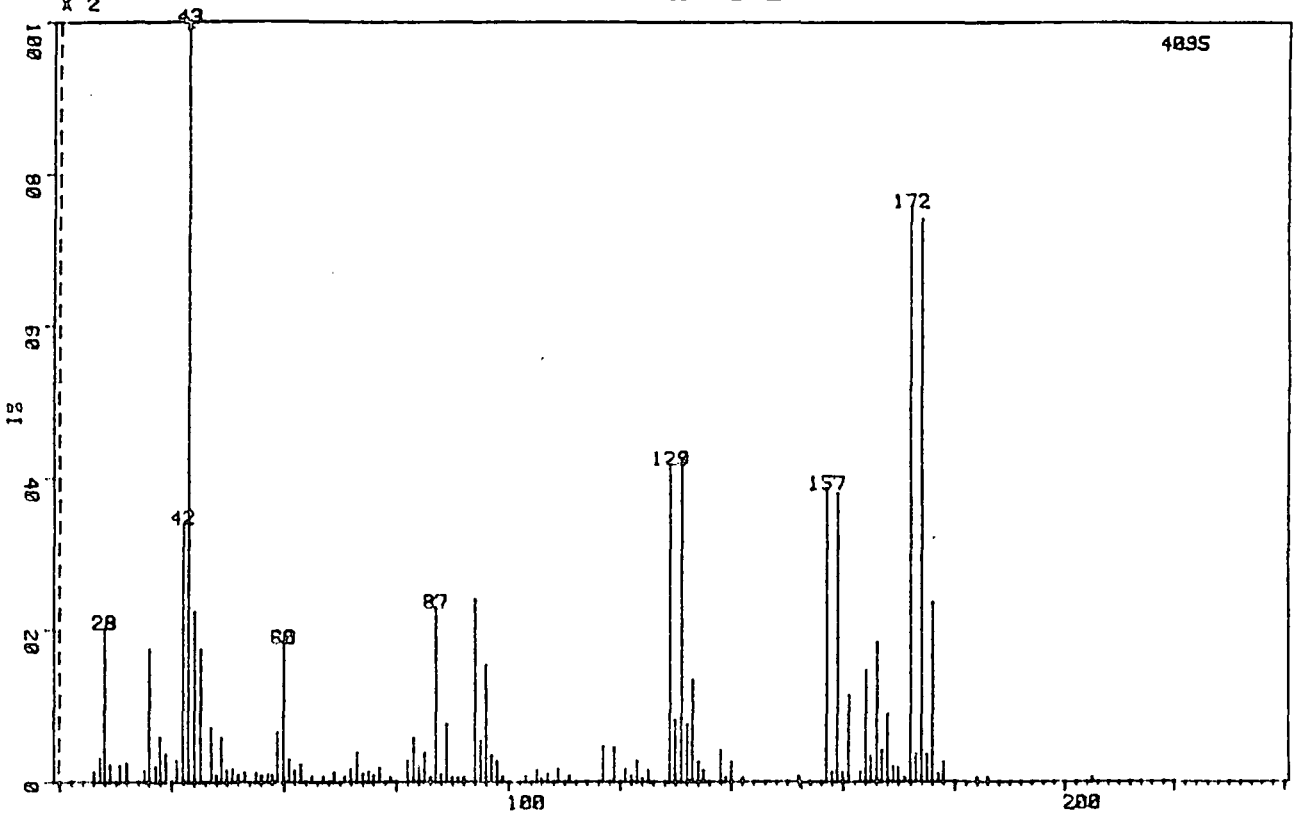
No.45 1,1,2-TRICHLOROBUTEN-3-ONE (103)

SJ11A 2 S.L.JONES 23-MAR-84

CAL:CCC

X 2

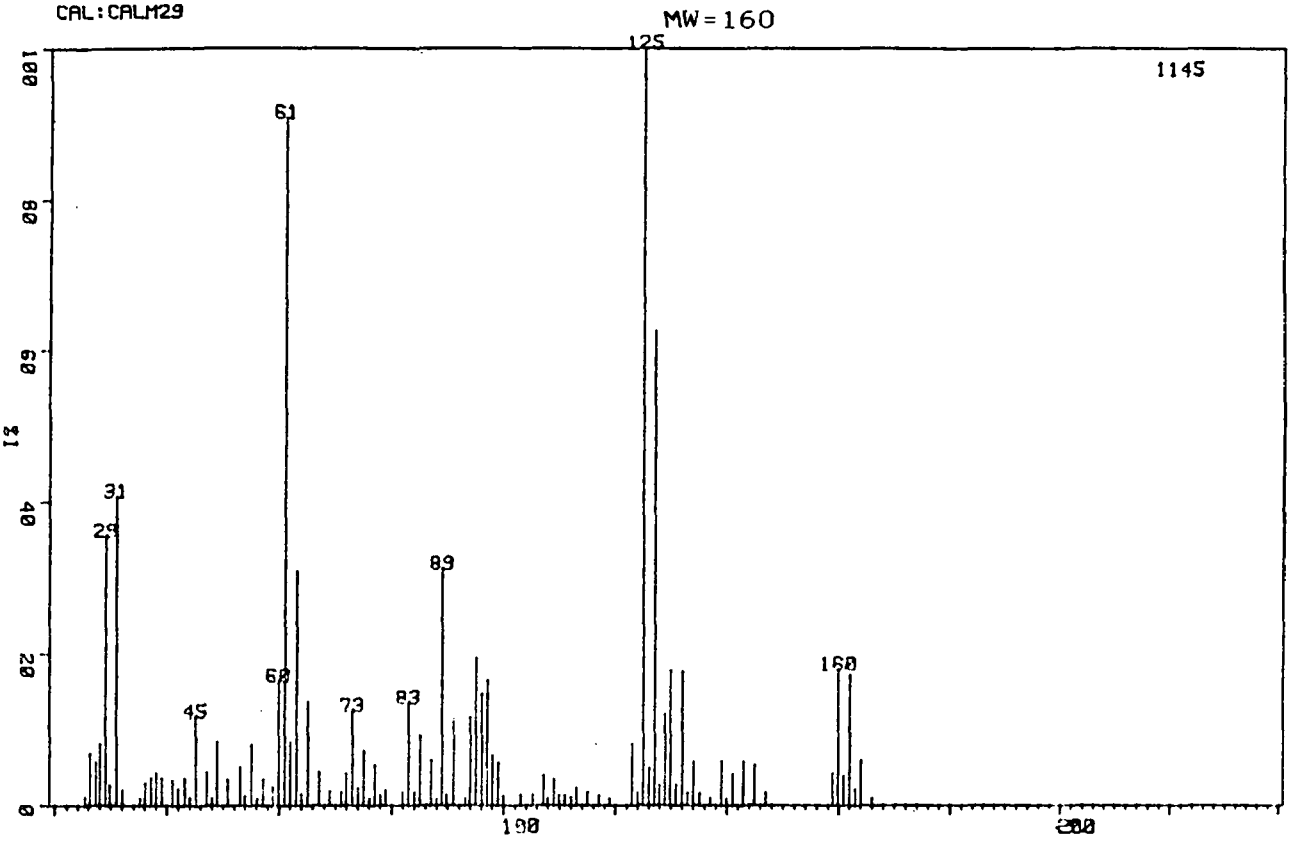
MW=172



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.18	1.59	23	82.96	2.91	45	158.90	19.00
2	28.06	10.09	24	83.97	1.05	46	160.92	5.69
3	28.95	1.12	25	84.99	1.93	47	163.96	7.37
4	30.85	1.10	26	86.98	11.45	48	164.96	1.68
5	31.95	1.22	27	88.90	3.76	49	165.94	9.16
6	36.09	8.82	28	93.94	11.99	50	166.97	2.08
7	37.08	1.05	29	94.98	2.71	51	167.91	4.47
8	38.01	2.98	30	95.95	7.69	52	168.91	1.03
9	38.96	1.88	31	96.94	1.78	53	172.01	37.83
10	40.93	1.47	32	97.91	1.37	54	173.02	1.83
11	42.00	17.02	33	116.92	2.34	55	174.02	37.05
12	43.07	100.00	34	118.90	2.27	56	175.03	1.83
13	44.11	11.21	35	123.01	1.37	57	176.03	11.82
14	45.11	8.74	36	128.90	20.88	58	178.02	1.29
15	47.04	3.59	37	129.89	4.08	59	236.05	1.05
16	48.93	2.91	38	130.93	21.25			
17	58.94	3.30	39	131.97	3.79			
18	59.89	9.11	40	132.97	6.69			
19	60.91	1.51	41	134.04	1.29			
20	63.01	1.15	42	138.02	2.08			
21	73.02	1.93	43	139.95	1.29			
22	81.91	1.39	44	156.94	19.32			

No.46 1,1,2-TRICHLOROBUTEN-3-OL (104)

SJ11M 4 S.L.JONES 29-FEB-84
CAL:CALM29

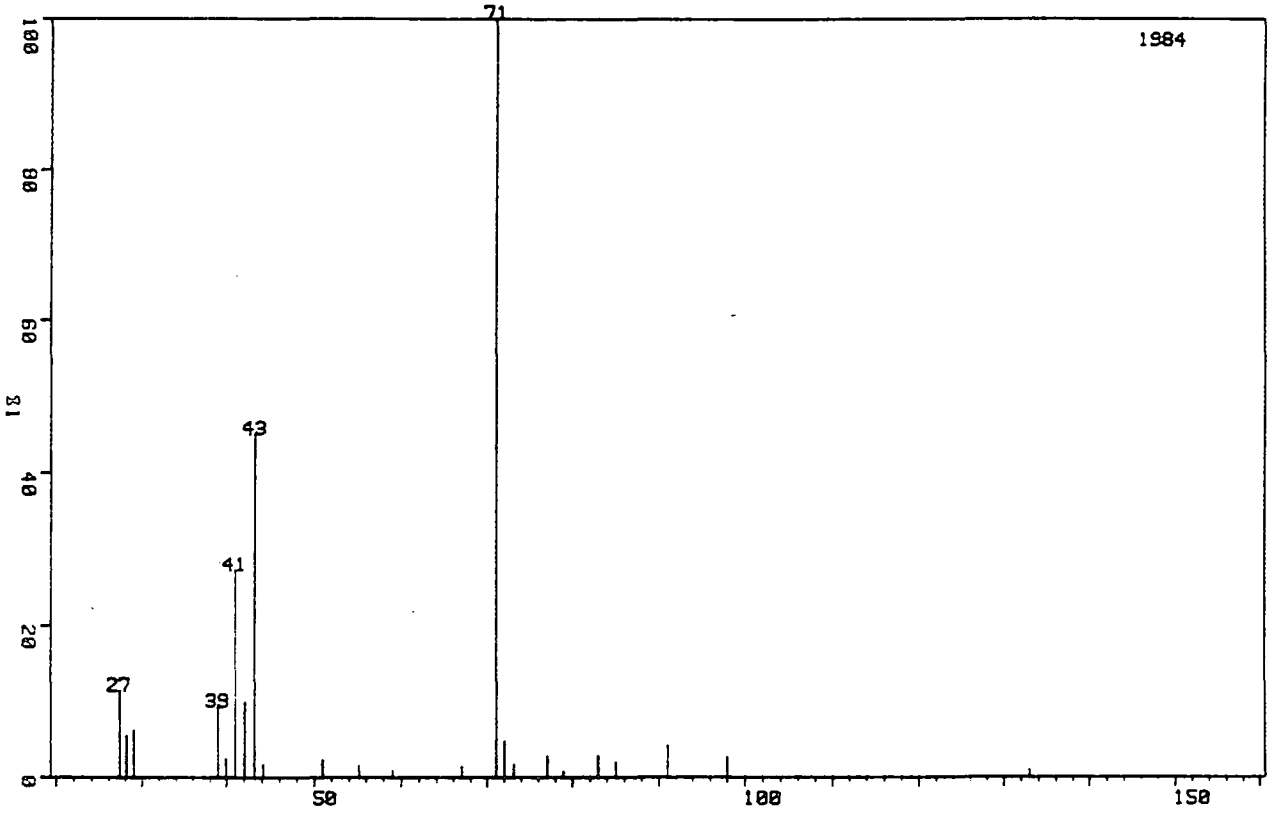


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.31	6.90	23	63.02	30.92	45	125.96	4.89
2	27.25	5.68	24	65.05	13.71	46	126.93	62.53
3	28.13	8.12	25	67.02	4.45	47	127.91	2.71
4	28.99	35.55	26	71.95	4.28	48	128.88	12.05
5	29.83	2.71	27	73.00	12.49	49	129.84	17.73
6	30.92	40.70	28	75.03	7.25	50	130.91	2.71
7	36.14	2.97	29	76.99	5.24	51	131.93	17.64
8	37.13	3.67	30	82.95	13.54	52	133.96	5.68
9	38.07	4.28	31	84.98	9.17	53	138.97	5.85
10	38.99	3.67	32	86.96	5.94	54	140.96	4.10
11	40.97	3.32	33	88.91	31.18	55	142.94	5.68
12	43.11	3.58	34	90.94	11.35	56	144.95	5.33
13	45.16	11.70	35	93.98	11.70	57	158.85	4.28
14	47.05	4.54	36	94.99	19.48	58	159.88	17.99
15	48.94	8.47	37	96.00	14.76	59	160.93	3.93
16	50.91	3.41	38	96.99	16.51	60	161.96	17.29
17	53.06	5.07	39	97.97	6.55	61	163.97	5.85
18	55.10	7.95	40	98.94	5.50			
19	57.12	3.49	41	107.00	3.93			
20	59.86	16.42	42	108.95	3.41			
21	60.92	90.92	43	122.92	8.12			
22	61.97	8.38	44	124.95	100.00			

No.47 2-(2H,2,2-DICHLORODIFLUOROETHYL)OXOLANE (99)

SJ485X S S.L. JONES 01-NOV-85
CHLOROFORM 5.07M 2.37

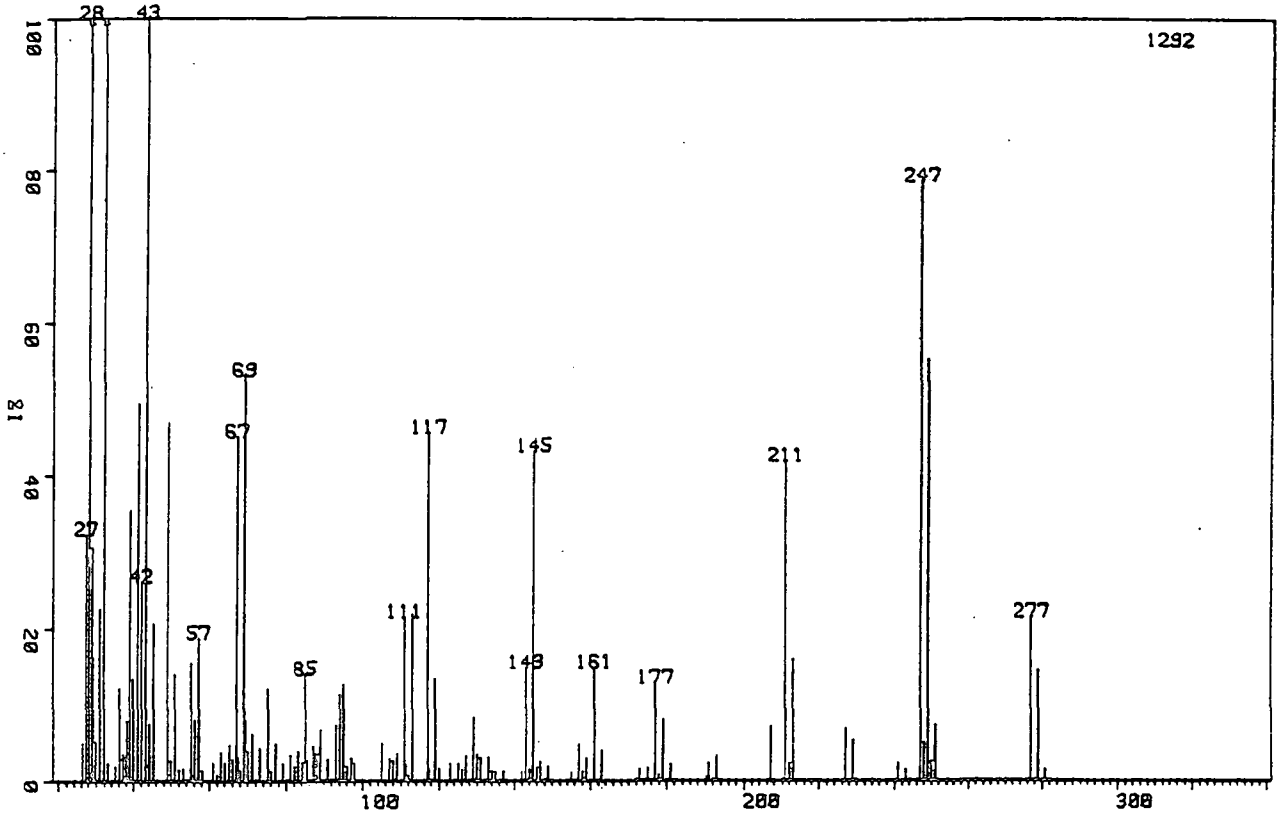
MW=204



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.22	11.44	23	78.94	0.81
2	28.10	5.49	24	82.97	2.92
3	28.12	0.96	25	83.05	1.31
4	28.96	6.25	26	84.99	2.02
5	28.99	1.01	27	90.99	4.28
6	38.96	9.37	28	97.96	2.67
7	39.86	2.47	29	132.93	1.06
8	40.94	27.37			
9	41.99	1.97			
10	42.03	9.93			
11	43.07	1.86			
12	43.10	45.11			
13	44.15	1.66			
14	50.94	2.32			
15	50.95	1.76			
16	55.14	1.56			
17	58.99	0.96			
18	67.02	1.46			
19	71.00	100.00			
20	72.05	4.74			
21	73.07	1.66			
22	77.06	2.82			

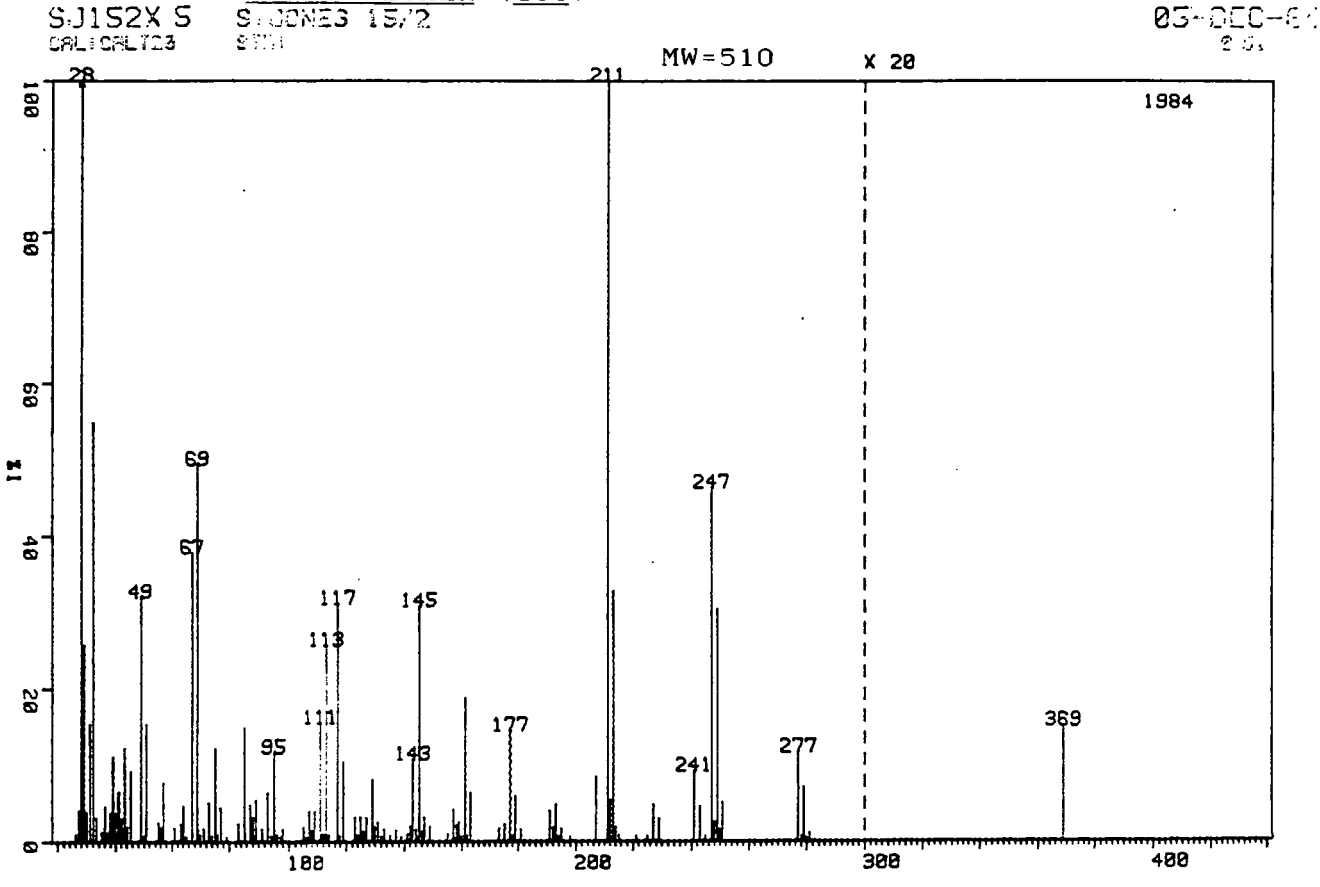
No.48 2,3-DICHLORO-1,1,1,4,4,4-HEXAFLUORO-3-METHOXYMETHYL-BUTANE (105)

SJ151X 6 S.L.JONES 15/1 06-DEC-84
CAL:CALT20 STA: MW=278 0:59



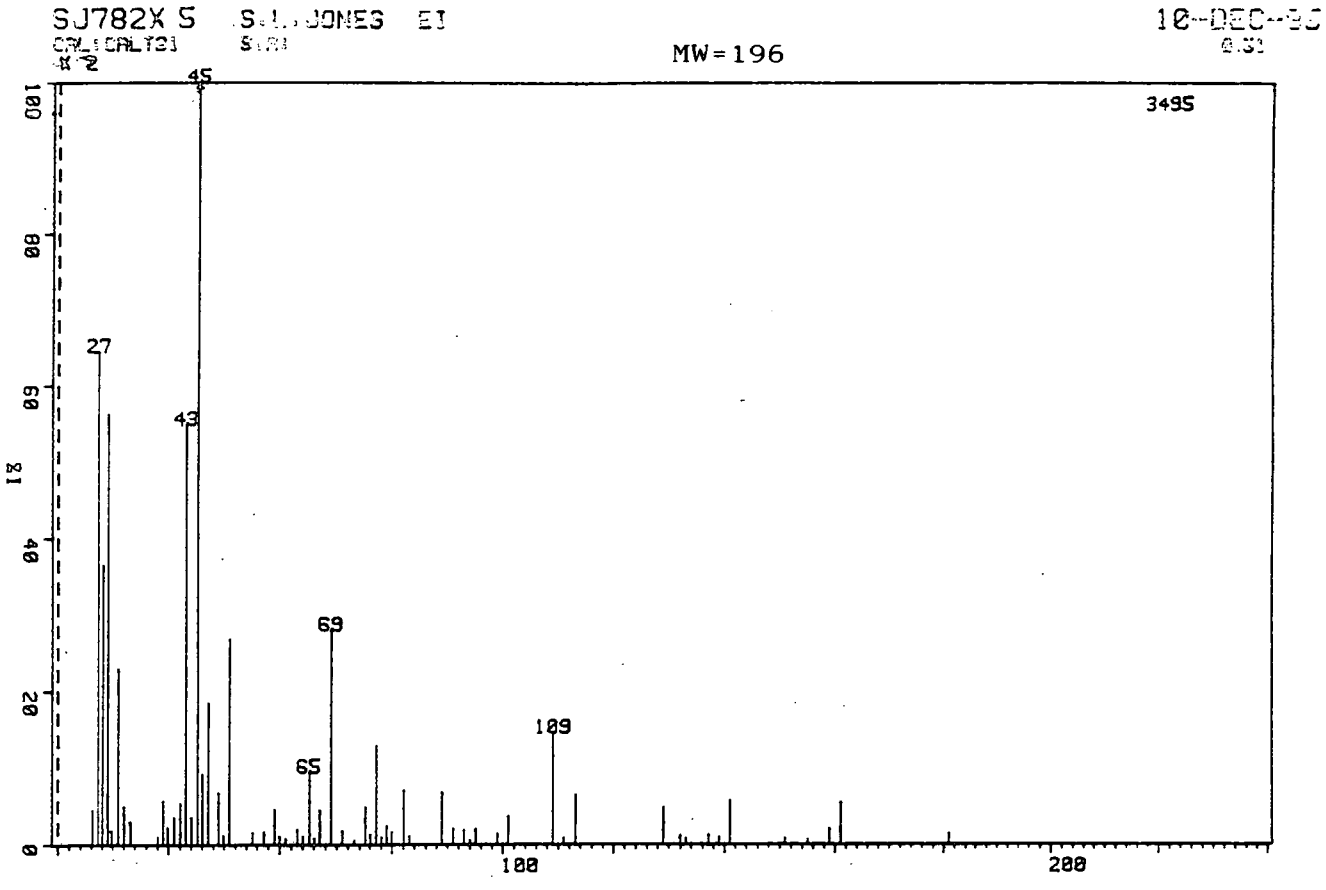
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	12.59	23	57.13	7.29	45	210.89	16.35
2	28.11	100.00	24	67.00	17.59	46	212.94	6.23
3	28.96	11.89	25	68.93	20.69	47	226.92	2.65
4	29.00	6.29	26	69.00	3.07	48	228.89	2.08
5	29.80	2.02	27	71.02	2.38	49	246.94	30.68
6	30.88	8.79	28	75.04	4.70	50	248.91	21.59
7	31.96	84.28	29	84.95	5.45	51	250.94	2.86
8	36.10	4.73	30	88.92	2.59	52	276.94	8.37
9	38.04	3.07	31	92.98	2.83	53	278.91	5.69
10	38.96	13.82	32	94.05	4.40			
11	39.80	5.21	33	95.02	4.94			
12	39.86	2.62	34	110.91	8.37			
13	40.94	19.27	35	112.98	8.52			
14	42.03	10.18	36	116.96	17.77			
15	43.11	38.90	37	118.91	5.21			
16	44.07	2.89	38	128.92	3.22			
17	45.13	8.04	39	142.96	5.78			
18	48.94	18.31	40	144.98	16.83			
19	50.92	5.45	41	160.90	5.78			
20	55.14	6.05	42	176.95	5.00			
21	56.14	3.13	43	178.88	3.10			
22	57.07	2.32	44	206.98	2.80			

No.49 BIS-(2,3-DICHLORO-4,4,4-TRIFLUORO-2-TRIFLUOROMETHYL-PROPYL)ETHER (106)



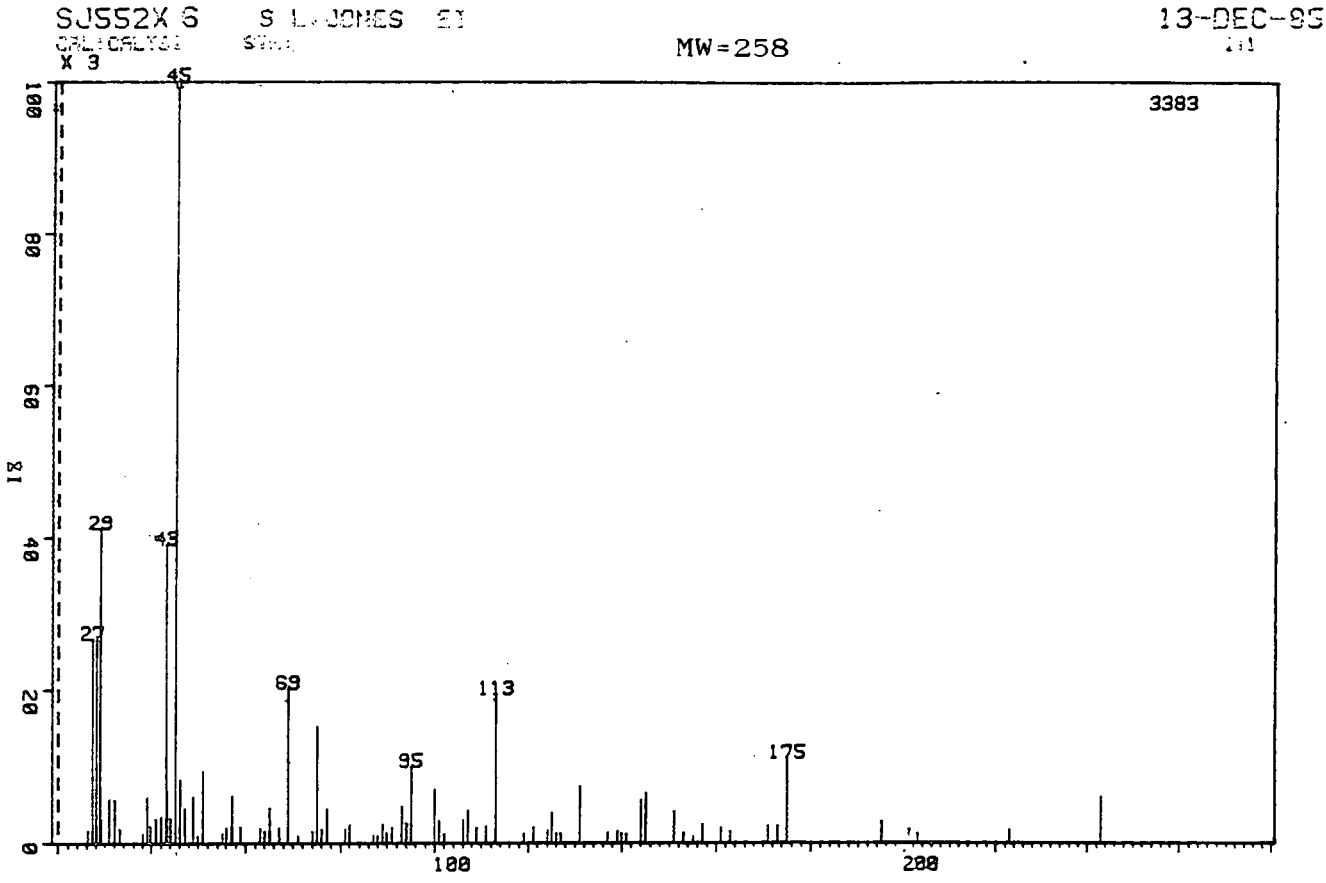
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	2.34	23	77.08	2.55	45	207.01	4.86
2	28.11	100.00	24	85.03	8.56	46	210.92	57.41
3	28.97	14.79	25	86.98	2.78	47	211.96	3.10
4	29.81	2.20	26	88.96	3.15	48	212.94	18.81
5	30.88	8.80	27	92.99	3.67	49	226.93	2.75
6	31.97	31.45	28	95.03	6.68	50	240.94	5.30
7	36.10	2.66	29	107.01	2.31	51	242.98	2.63
8	38.04	2.17	30	108.92	2.26	52	246.95	26.59
9	38.96	6.37	31	110.91	8.94	53	248.92	17.45
10	39.80	2.14	32	112.99	14.79	54	250.91	2.92
11	40.94	3.73	33	116.98	17.94	55	276.94	6.74
12	43.11	7.03	34	118.93	6.02	56	278.90	4.08
13	45.14	5.30	35	128.93	4.66			
14	48.94	18.40	36	142.98	6.19			
15	50.93	8.83	37	145.01	17.74			
16	57.08	4.46	38	157.00	2.43			
17	57.14	2.92	39	160.93	10.82			
18	64.10	2.69	40	162.98	3.67			
19	67.04	21.76	41	177.01	8.36			
20	68.97	28.36	42	178.93	3.41			
21	73.03	2.95	43	190.93	2.26			
22	75.08	7.00	44	192.98	2.78			

No.50 1,1,1,2,3,3-HEXAFLUORO-4-PENTANOL (107)



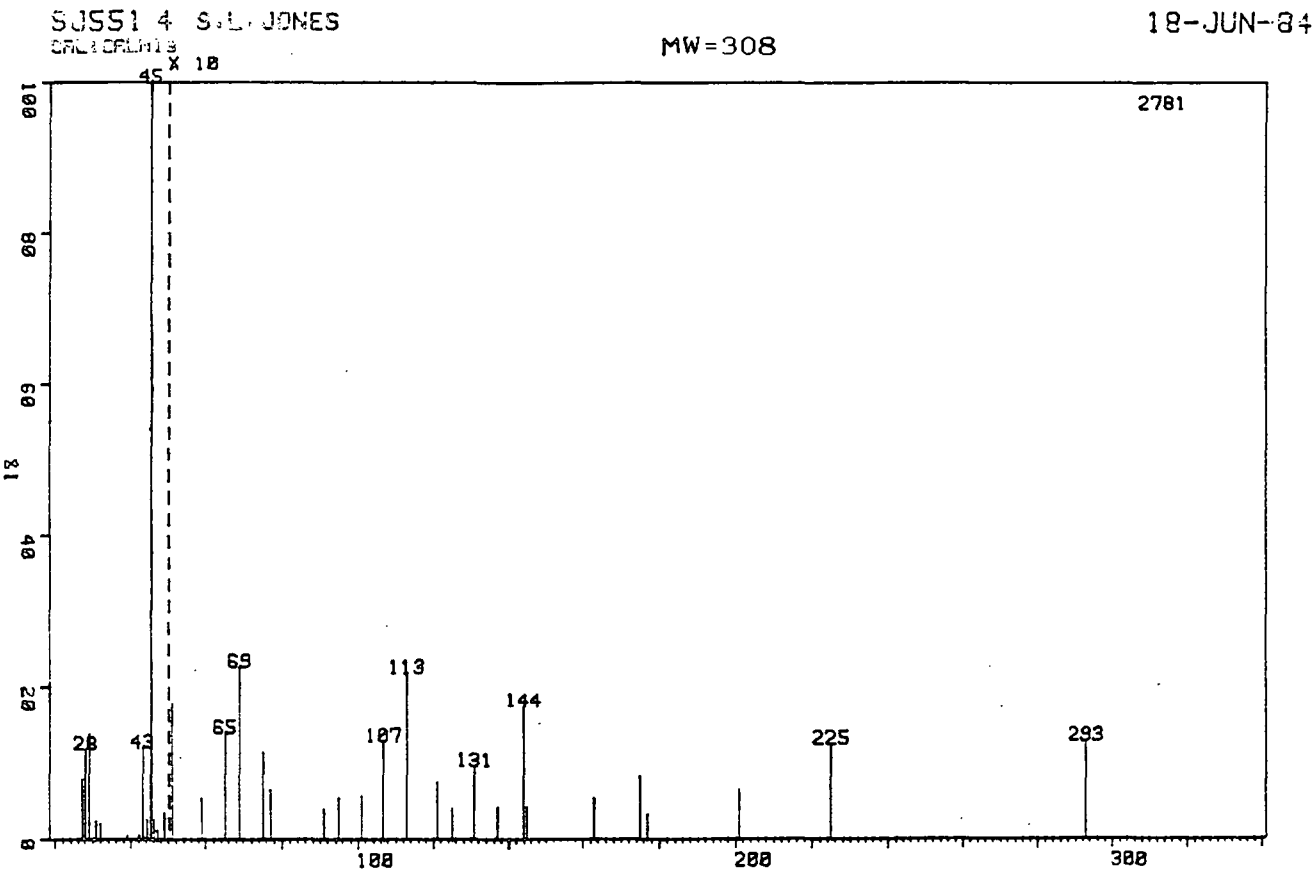
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.30	2.29	23	49.87	0.63	45	81.99	3.61
2	27.23	32.27	24	50.94	13.45	46	83.02	0.54
3	28.11	18.31	25	55.11	0.80	47	88.97	3.46
4	28.96	28.21	26	55.15	0.49	48	90.96	1.06
5	29.00	3.35	27	57.08	0.77	49	93.02	0.97
6	29.80	0.94	28	57.14	0.89	50	95.05	1.03
7	30.88	11.53	29	59.00	2.35	51	98.96	0.72
8	31.96	2.52	30	59.91	0.54	52	100.95	1.86
9	33.07	1.52	31	63.07	1.00	53	109.00	7.30
10	38.04	0.54	32	64.10	0.54	54	110.98	0.43
11	38.96	2.86	33	65.11	4.72	55	113.03	3.26
12	39.80	1.17	34	66.10	0.43	56	128.99	2.46
13	40.90	0.43	35	67.04	2.26	57	132.02	0.63
14	40.94	1.80	36	68.95	14.02	58	137.06	0.66
15	42.00	2.72	37	70.98	0.94	59	139.02	0.52
16	42.04	0.77	38	75.07	2.49	60	141.00	2.89
17	43.07	27.47	39	76.07	0.69	61	150.99	0.43
18	44.11	1.80	40	77.05	6.47	62	159.03	1.06
19	45.13	100.00	41	78.02	0.49	63	161.01	2.78
20	46.13	4.58	42	78.95	1.23	64	181.02	0.72
21	47.09	9.27	43	78.99	0.49			
22	48.96	3.38	44	79.90	0.83			

No.51 1-(2H-OCTAFLUOROCYCLOPENTYL)ETHANOL (108)



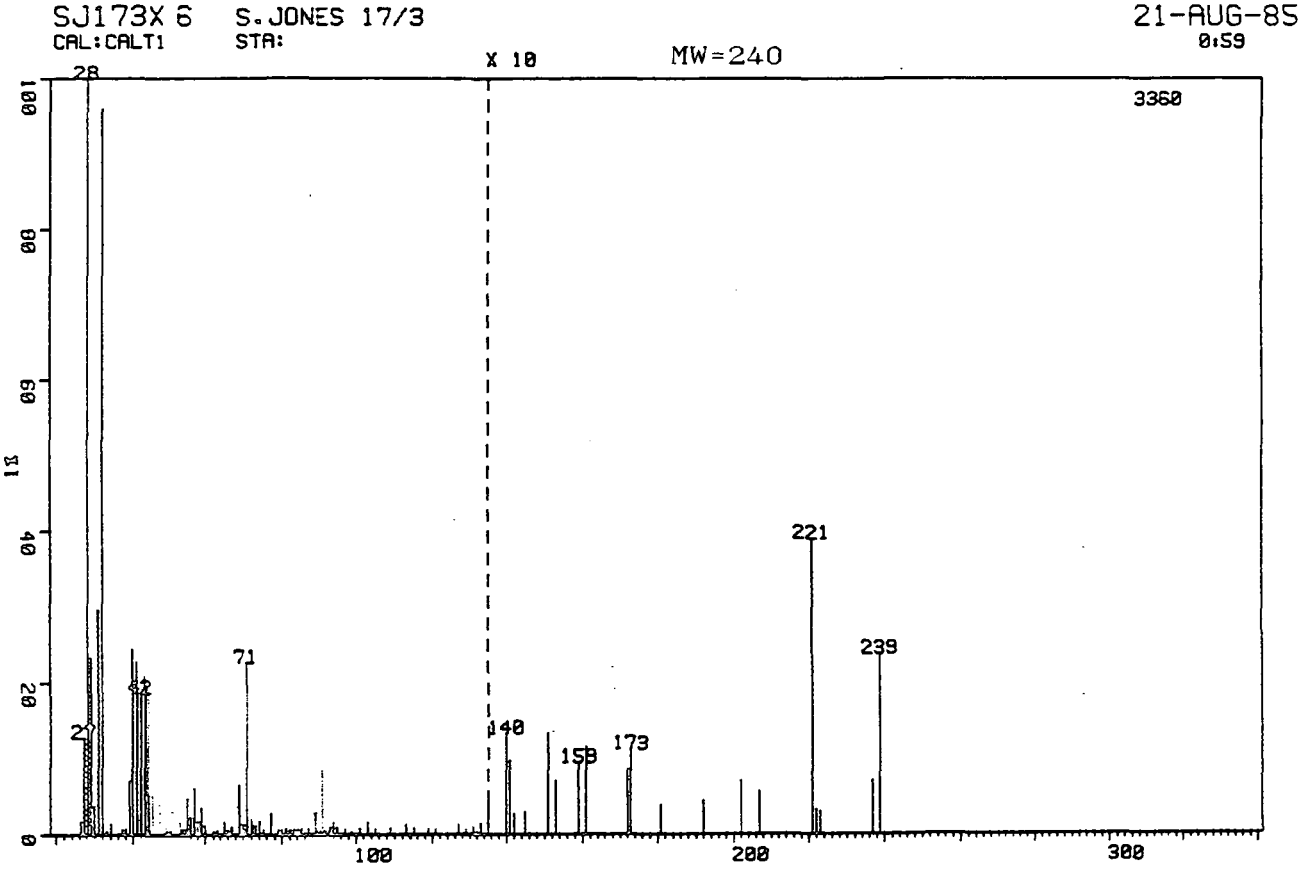
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	8.90	23	59.00	0.71	45	121.01	0.71
2	28.11	9.05	24	63.06	0.65	46	125.06	1.33
3	28.13	0.77	25	65.10	1.54	47	130.98	2.45
4	28.96	13.75	26	67.03	0.68	48	144.04	1.86
5	29.00	1.03	27	68.95	6.74	49	145.05	2.19
6	30.87	1.92	28	75.05	5.11	50	151.00	1.39
7	31.97	1.89	29	76.06	0.62	51	157.04	0.83
8	33.07	0.62	30	77.03	1.48	52	160.99	0.68
9	38.96	1.98	31	80.93	0.62	53	171.01	0.77
10	39.80	0.74	32	81.97	0.80	54	173.04	0.74
11	40.94	1.06	33	88.95	0.83	55	175.03	3.69
12	42.00	1.15	34	90.95	0.68	56	195.03	0.95
13	43.06	13.07	35	92.99	1.60	57	200.99	0.62
14	43.10	2.28	36	94.01	0.86	58	242.98	2.04
15	44.11	1.09	37	95.03	3.34			
16	45.13	100.00	38	99.89	2.34			
17	46.13	2.78	39	100.98	0.98			
18	47.09	1.51	40	106.04	1.03			
19	48.96	2.04	41	107.05	1.45			
20	50.93	3.13	42	109.00	0.68			
21	56.09	0.68	43	110.98	0.74			
22	57.07	2.07	44	113.03	6.50			

No.52 1-(2H-DECAFLUOROCYCLOHEXYL)ETHANOL (109)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.24	7.80	23	106.69	1.29
2	28.12	11.79	24	112.97	2.19
3	28.99	13.92	25	120.96	0.76
4	30.92	2.37	26	125.00	0.40
5	32.00	2.01	27	130.93	0.97
6	39.00	0.40	28	136.98	0.43
7	42.05	0.43	29	143.98	1.76
8	43.10	12.12	30	145.01	0.43
9	44.14	2.52	31	162.98	0.54
10	45.17	100.00	32	175.00	0.83
11	46.16	2.59	33	176.98	0.32
12	47.12	1.26	34	200.94	0.65
13	48.97	3.56	35	224.95	1.26
14	50.94	1.80	36	292.94	1.29
15	59.02	0.54			
16	65.12	1.40			
17	68.94	2.27			
18	75.04	1.15			
19	77.03	0.65			
20	90.94	0.40			
21	95.02	0.54			
22	100.96	0.58			

No.53 1,1,1,2,3,3-HEXAFLUOROHEPTANE-4,7-DIOL (110)

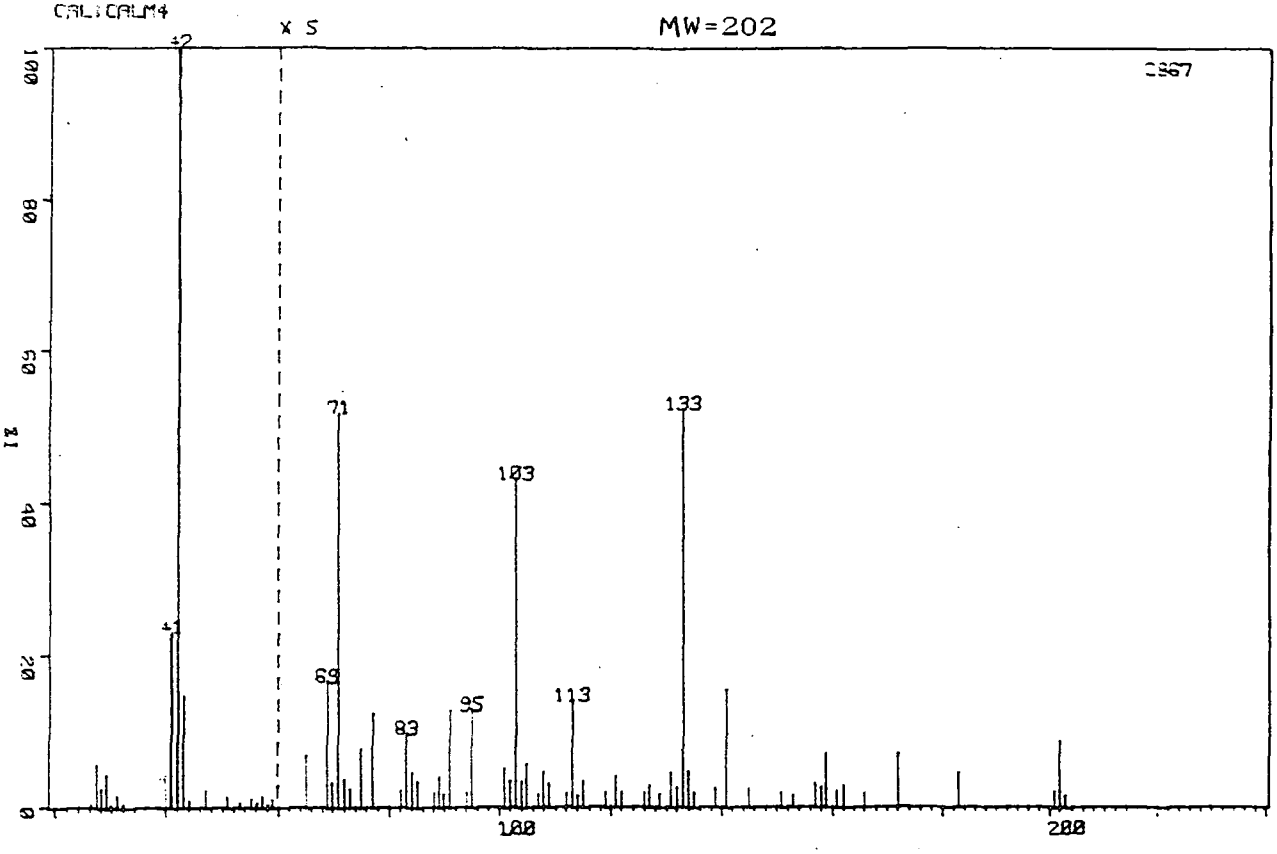


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.37	1.73	23	53.10	1.64	45	112.94	1.31
2	27.30	12.86	24	55.12	1.58	46	126.96	1.34
3	28.17	100.00	25	55.15	4.85	47	132.99	1.46
4	29.03	23.30	26	56.15	2.29	48	139.91	1.34
5	29.06	8.07	27	57.11	6.19	49	150.92	1.34
6	29.86	3.72	28	58.06	1.76	50	160.91	1.16
7	30.95	29.58	29	59.00	3.51	51	172.96	1.13
8	32.03	95.95	30	59.94	1.22	52	220.91	3.90
9	34.16	1.46	31	65.10	1.67	53	238.89	2.38
10	38.99	7.14	32	67.08	1.01			
11	39.83	24.49	33	68.96	6.64			
12	39.89	2.38	34	69.95	1.40			
13	40.98	22.86	35	70.98	22.77			
14	42.03	1.93	36	72.04	2.14			
15	42.07	18.75	37	73.06	1.28			
16	43.10	6.40	38	74.11	1.82			
17	43.14	20.92	39	77.02	2.86			
18	44.10	7.89	40	88.96	2.92			
19	44.14	19.29	41	90.93	8.57			
20	45.16	5.21	42	92.99	1.07			
21	47.11	4.02	43	94.02	1.64			
22	50.95	3.07	44	103.00	1.58			

No.54 2-(PENTAFLUOROPROPENYL)OXOLANE (90)

SJ231 S S.L.JONES 23/1 04-NOV-83

CAL:CALM4

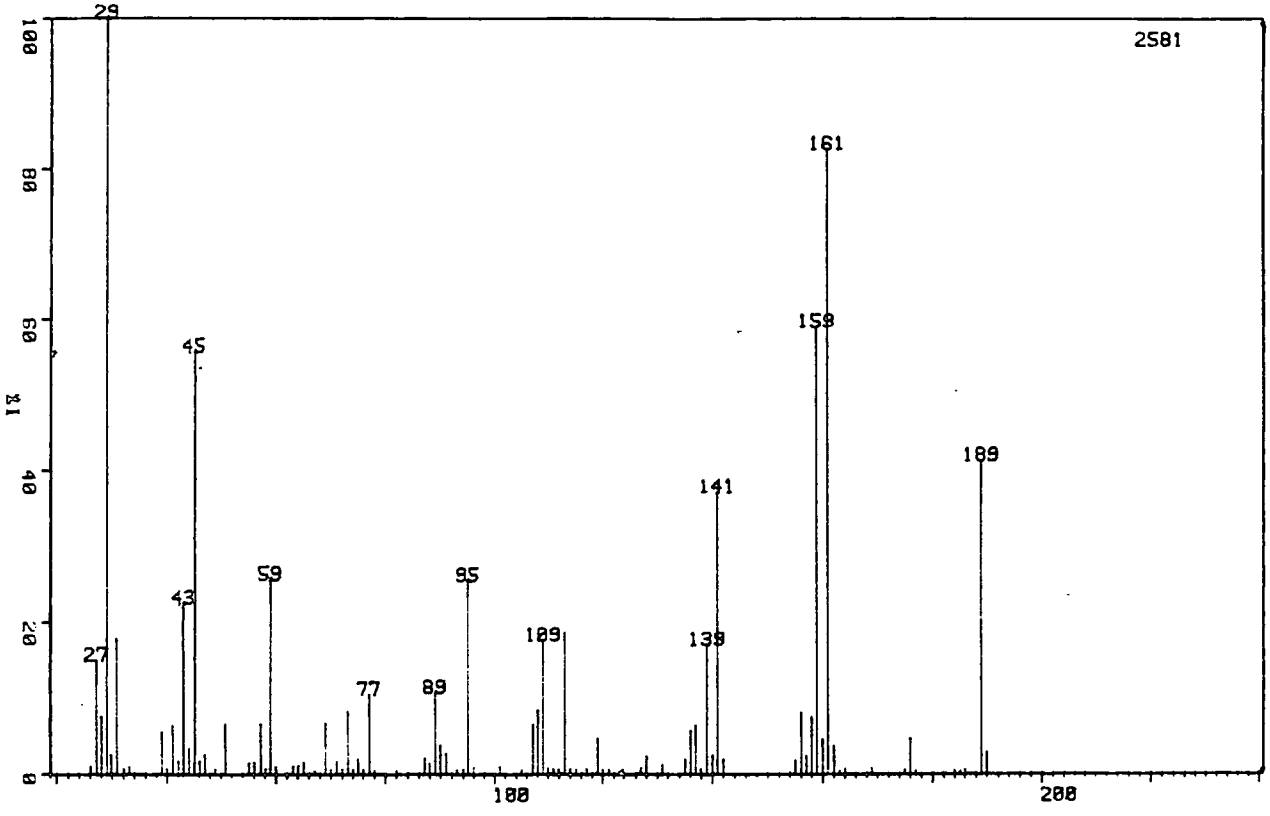


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.24	5.62	23	75.03	1.53	45	134.01	0.94
2	28.13	2.48	24	77.02	2.48	46	140.88	3.10
3	28.99	4.29	25	82.99	1.92	47	156.98	0.63
4	30.92	1.53	26	84.04	0.91	48	157.99	0.52
5	38.99	3.80	27	85.04	0.66	49	158.93	1.40
6	39.88	4.22	28	88.93	0.80	50	162.01	0.56
7	40.97	23.06	29	90.91	2.55	51	171.98	1.43
8	42.06	100.00	30	95.00	2.55	52	183.02	0.91
9	43.12	14.65	31	100.92	1.01	53	201.93	1.74
10	44.14	0.84	32	101.96	0.70			
11	47.11	2.27	33	102.97	8.62			
12	50.93	1.33	34	104.01	0.66			
13	53.10	0.59	35	104.97	1.15			
14	55.12	1.08	36	107.92	0.94			
15	56.13	0.56	37	108.88	0.63			
16	57.09	1.43	38	112.95	2.79			
17	58.99	1.01	39	115.03	0.66			
18	65.11	1.36	40	120.95	0.80			
19	68.95	3.31	41	127.00	0.56			
20	69.92	0.66	42	130.91	0.91			
21	70.97	10.36	43	131.95	0.52			
22	72.03	0.73	44	133.00	10.46			

No.55 1,1,1,2,3-PENTAFLUORO-4-ETHOXY-2-PENTENE (119)

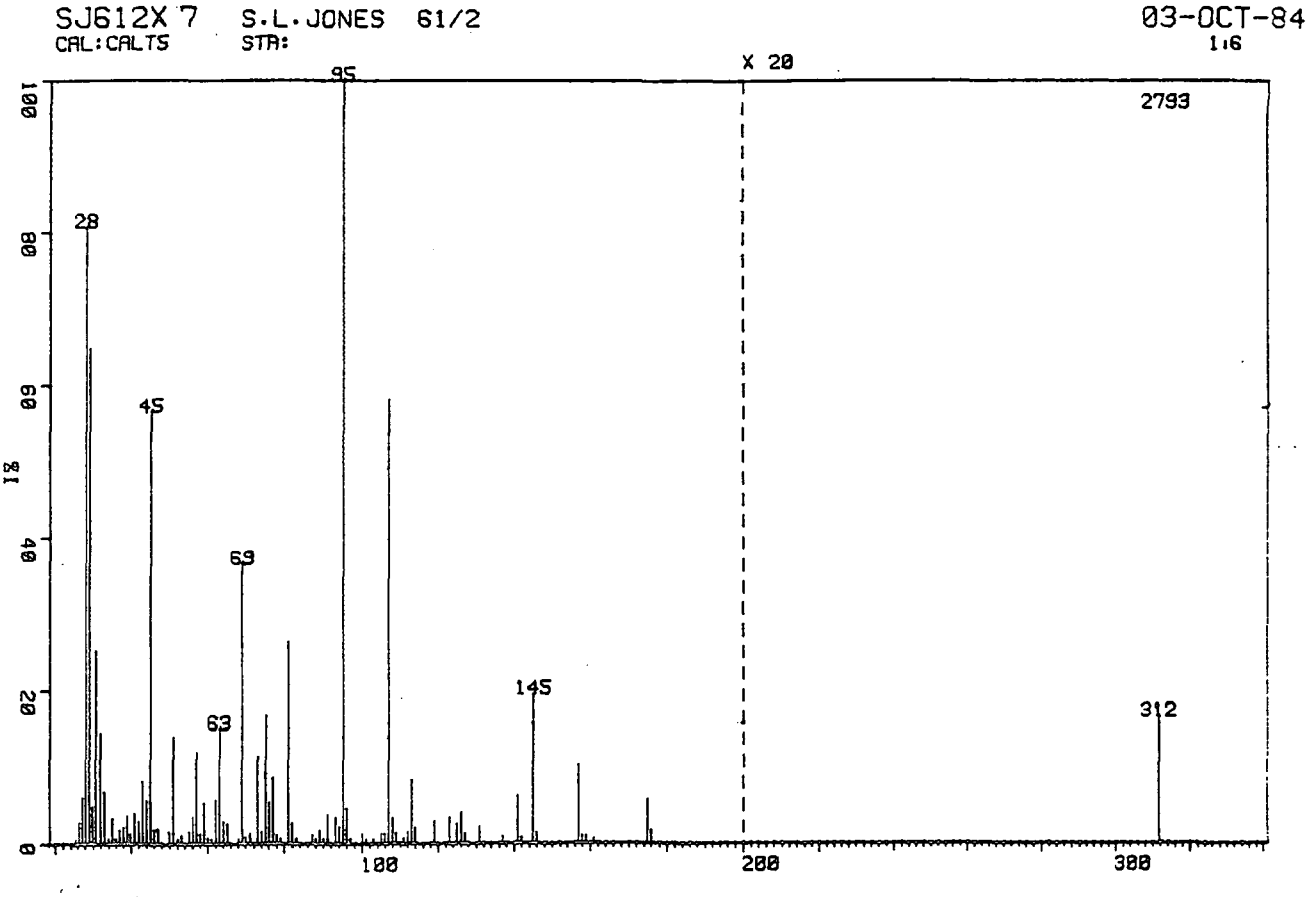
SJ232 S S.L. JONES 05-DEC-83
CAL:CALM23 STA: 1:0

MW=204



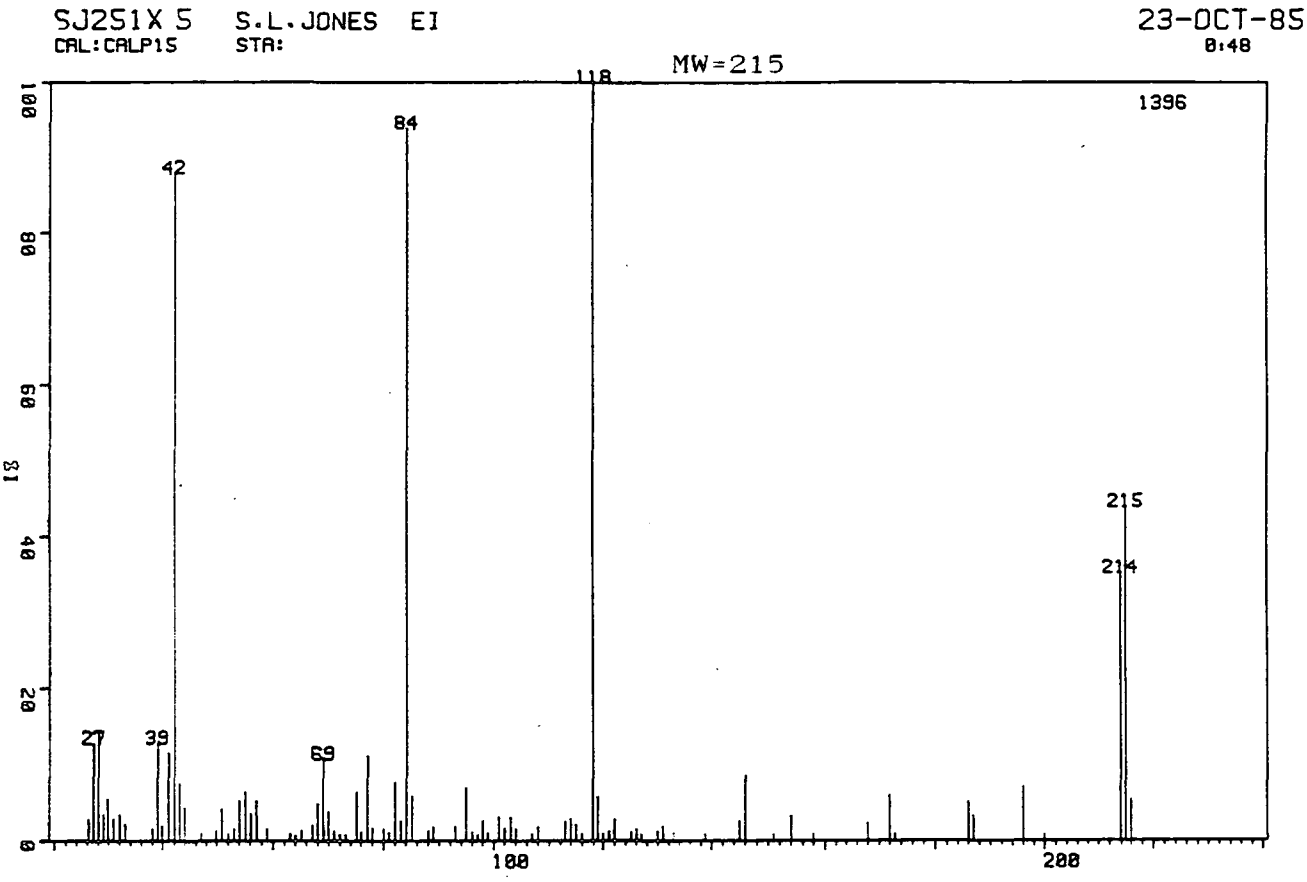
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.22	1.05	23	65.08	1.51	45	138.95	17.13
2	27.17	14.99	24	68.95	6.74	46	139.91	2.44
3	28.06	7.59	25	70.96	1.67	47	140.90	37.31
4	28.95	100.00	26	73.08	8.29	48	141.96	1.94
5	29.79	2.56	27	75.03	1.98	49	154.98	1.82
6	30.83	17.78	28	77.02	10.54	50	156.00	8.21
7	38.95	5.54	29	87.01	2.13	51	157.00	2.36
8	40.93	6.35	30	87.96	1.43	52	157.96	7.48
9	41.99	1.74	31	88.93	10.73	53	158.93	59.20
10	43.05	22.55	32	89.89	3.80	54	159.92	4.61
11	44.10	3.37	33	90.95	2.67	55	160.92	82.84
12	45.12	55.75	34	95.03	25.53	56	161.95	3.68
13	46.12	1.67	35	107.02	6.55	57	176.01	4.77
14	47.09	2.52	36	107.97	8.49	58	188.94	41.38
15	50.91	6.55	37	108.96	17.63	59	189.94	2.94
16	55.11	1.43	38	112.98	18.60			
17	56.11	1.63	39	118.97	4.65			
18	57.08	6.59	40	127.98	2.32			
19	58.98	25.69	41	130.93	1.36			
20	59.91	1.05	42	135.07	1.98			
21	63.05	1.01	43	136.00	5.77			
22	64.06	1.08	44	137.00	6.47			

No.56 1,1,1,2,3-PENTAFLUORO-4-METHOXY-2-BUTENE (92)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.22	2.72	23	56.01	3.54	45	107.99	3.26
2	27.15	6.12	24	57.00	11.89	46	112.96	8.34
3	28.03	80.74	25	58.92	5.30	47	113.98	2.04
4	28.90	64.73	26	61.97	5.69	48	118.90	2.79
5	29.74	4.80	27	63.02	14.93	49	122.95	3.29
6	30.77	25.17	28	64.04	2.86	50	124.97	2.54
7	31.88	14.36	29	65.06	2.51	51	125.97	3.94
8	32.98	6.80	30	68.94	36.63	52	130.88	2.18
9	35.07	3.26	31	73.06	11.42	53	140.88	6.19
10	37.01	1.83	32	74.08	1.61	54	144.97	19.48
11	37.96	2.08	33	75.07	16.68	55	156.95	10.35
12	38.88	3.65	34	76.07	5.41	56	174.93	5.76
13	40.85	3.94	35	77.05	8.63	57	175.92	1.61
14	41.93	2.97	36	80.95	26.39			
15	43.00	8.20	37	81.98	2.61			
16	44.01	5.59	38	88.96	1.75			
17	45.05	56.57	39	90.92	3.76			
18	46.04	1.90	40	92.97	3.47			
19	47.00	1.93	41	93.99	2.22			
20	49.79	1.61	42	95.01	100.00			
21	50.84	13.89	43	96.01	4.58			
22	55.03	1.54	44	107.02	58.07			

No.57 N-METHYL-2-(PENTAFLUOROPROPENYL)PYRROLIDINE (120)



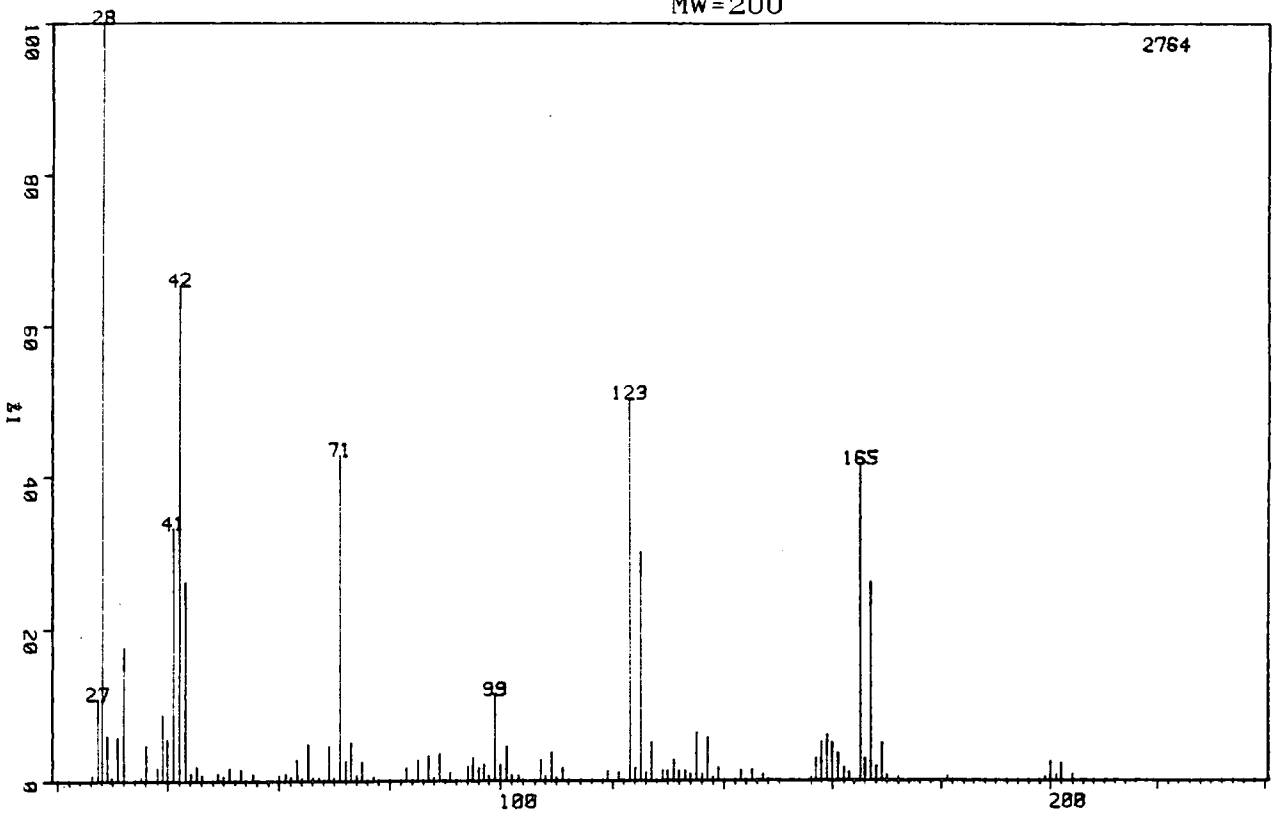
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.28	2.79	23	58.96	1.50	45	107.96	1.79
2	27.21	12.75	24	67.07	1.93	46	112.96	2.51
3	28.10	14.11	25	68.03	4.87	47	114.03	2.87
4	28.98	3.37	26	68.94	10.67	48	115.00	2.08
5	29.81	5.44	27	68.99	1.65	49	117.97	100.00
6	30.84	2.87	28	69.96	3.80	50	118.94	5.73
7	31.95	3.37	29	75.07	6.38	51	121.97	2.79
8	33.05	2.15	30	77.05	11.17	52	126.05	1.50
9	38.02	1.50	31	78.04	1.65	53	130.92	1.86
10	38.95	12.75	32	79.96	1.50	54	145.00	2.51
11	39.84	1.93	33	82.06	7.66	55	146.04	8.52
12	40.92	11.53	34	83.07	2.58	56	153.98	3.22
13	42.01	87.89	35	84.12	93.91	57	167.96	2.29
14	43.08	7.52	36	85.09	5.87	58	171.92	5.95
15	44.12	4.30	37	88.95	1.79	59	185.95	5.09
16	50.93	4.15	38	92.97	1.86	60	186.94	3.22
17	53.07	1.50	39	95.00	6.95	61	195.98	7.09
18	54.09	5.23	40	97.99	2.58	62	213.96	35.17
19	55.11	6.38	41	100.92	3.08	63	214.98	43.91
20	56.11	3.51	42	101.96	1.58	64	215.99	5.37
21	57.05	5.23	43	102.99	3.08			
22	57.09	3.01	44	104.01	1.50			

No.58 2-(TRICHLOROETHENYL)OXOLANE (121)

SJ108 2 S.L.JONES 12-AUG-83

CAL:CALH27

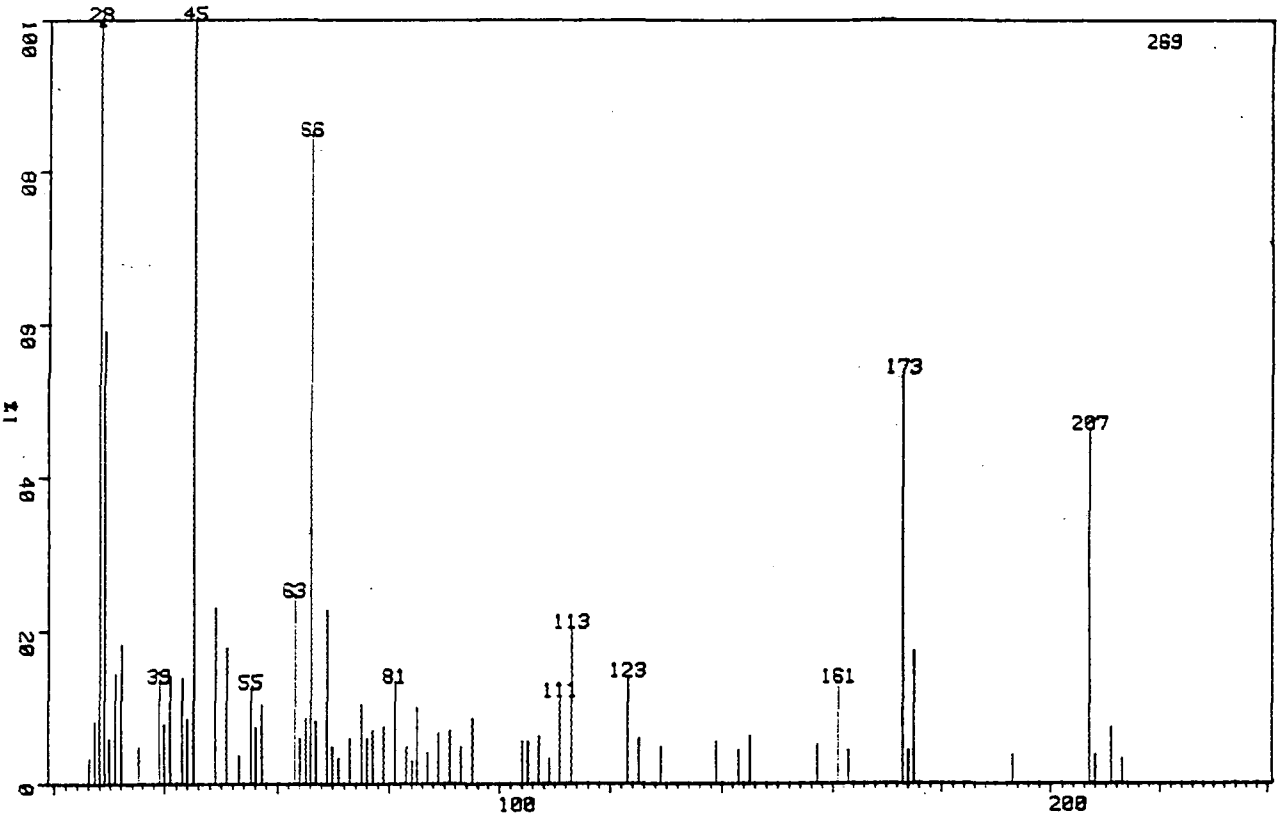
MW=200



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.25	10.78	23	85.00	2.68	45	157.97	5.14
2	28.13	100.00	24	86.98	3.26	46	158.97	6.04
3	29.00	6.04	25	88.93	3.51	47	159.94	4.96
4	30.93	5.75	26	93.99	1.88	48	160.97	3.51
5	32.02	17.55	27	94.99	2.97	49	162.01	1.66
6	36.15	4.59	28	96.00	1.63	50	165.11	41.68
7	38.06	1.63	29	97.00	2.13	51	166.09	2.79
8	39.01	8.68	30	98.98	11.25	52	167.06	26.05
9	39.89	5.39	31	99.96	2.03	53	168.07	1.88
10	40.99	33.29	32	101.00	4.45	54	169.05	4.96
11	42.09	65.38	33	107.01	2.71	55	200.02	2.50
12	43.16	26.19	34	108.95	3.76	56	202.06	2.28
13	45.19	1.92	35	110.94	1.63			
14	50.98	1.70	36	123.02	50.33			
15	63.10	2.75	37	124.05	1.70			
16	65.14	4.81	38	125.02	30.07			
17	68.94	4.63	39	127.03	5.07			
18	70.99	42.87	40	131.05	2.71			
19	72.01	2.57	41	135.10	6.22			
20	73.01	5.03	42	137.08	5.57			
21	75.03	2.46	43	139.03	1.70			
22	82.95	1.70	44	157.01	2.93			

No.59 TRANS-2-CHLORO-1,1,1,4,4,4-HEXAFLUORO-3-METHOXYMETHYL-2-BUTENE (122)

SJ154X 44 S.L.JONES 15/4 10-DEC-84
CAL:CALM30 STA: MW=242 6:26

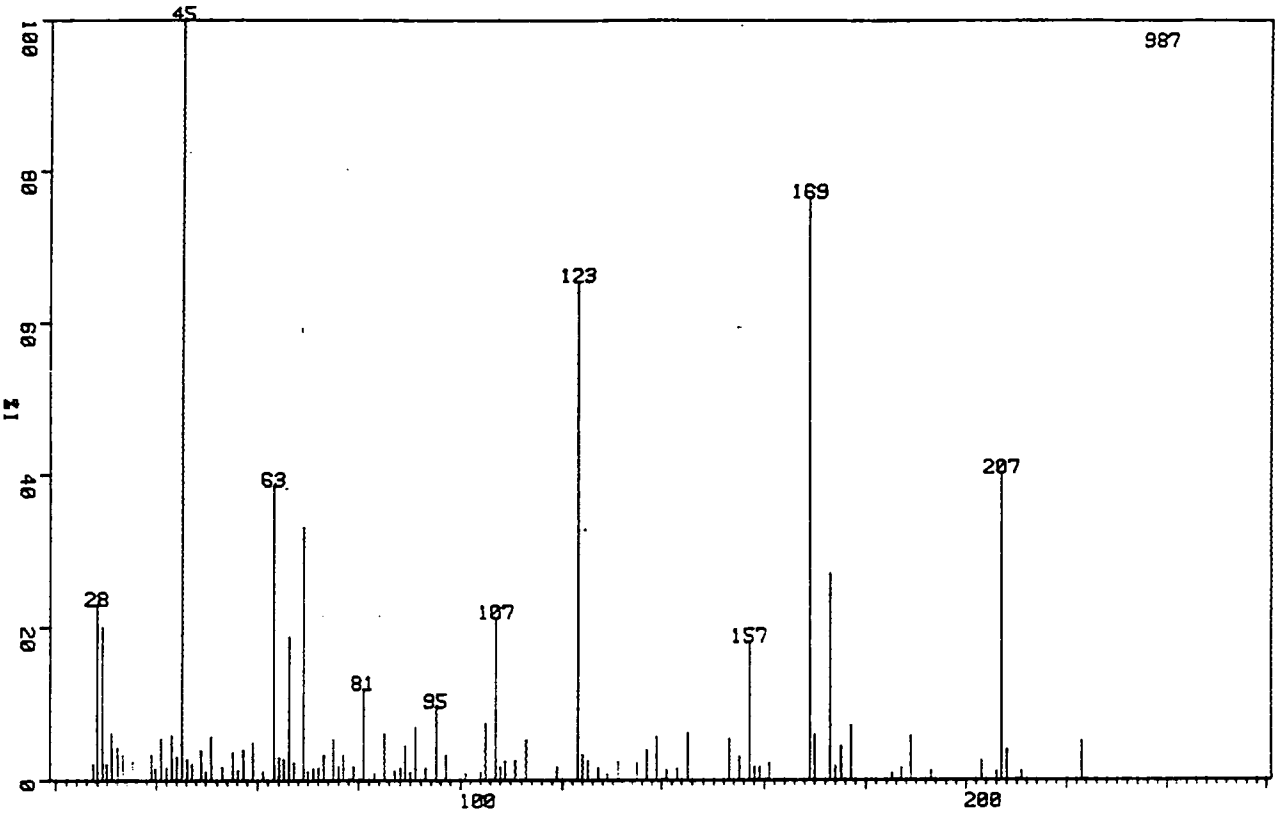


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.23	0.46	23	65.11	1.19	45	107.01	0.88
2	27.18	1.14	24	66.09	11.77	46	108.92	0.46
3	28.07	17.19	25	67.06	1.14	47	110.91	1.60
4	28.94	8.21	26	68.96	3.15	48	112.98	2.84
5	29.78	0.83	27	69.96	0.67	49	123.00	1.96
6	30.85	2.01	28	71.02	0.46	50	125.04	0.83
7	31.95	2.53	29	73.00	0.83	51	128.95	0.67
8	35.16	0.67	30	75.05	1.45	52	138.97	0.77
9	38.97	1.86	31	76.06	0.83	53	142.97	0.62
10	39.87	1.08	32	77.05	0.98	54	145.02	0.88
11	40.96	1.96	33	78.94	1.03	55	157.04	0.72
12	43.11	1.91	34	80.94	1.86	56	160.97	1.86
13	44.10	1.19	35	83.08	0.67	57	163.03	0.62
14	45.15	13.89	36	84.08	0.41	58	173.01	7.49
15	48.95	3.20	37	85.03	1.39	59	174.07	0.62
16	50.94	2.48	38	86.96	0.57	60	175.02	2.43
17	53.05	0.52	39	88.96	0.93	61	193.00	0.52
18	55.15	1.76	40	90.98	0.98	62	207.01	6.45
19	56.16	1.03	41	92.98	0.67	63	208.01	0.52
20	57.12	1.45	42	95.04	1.19	64	210.96	1.03
21	63.09	3.41	43	104.04	0.77	65	212.96	0.46
22	64.11	0.83	44	105.04	0.77			

No.60 TRANS-1,1,1,4,4,4-HEXAFLUORO-2-METHOXY-3-METHOXYMETHYL-2-BUTENE (123)

SJ154X 56 S.L.JONES 15/4 10-DEC-84

CAL:CALM30 STA: MW=238 8:9

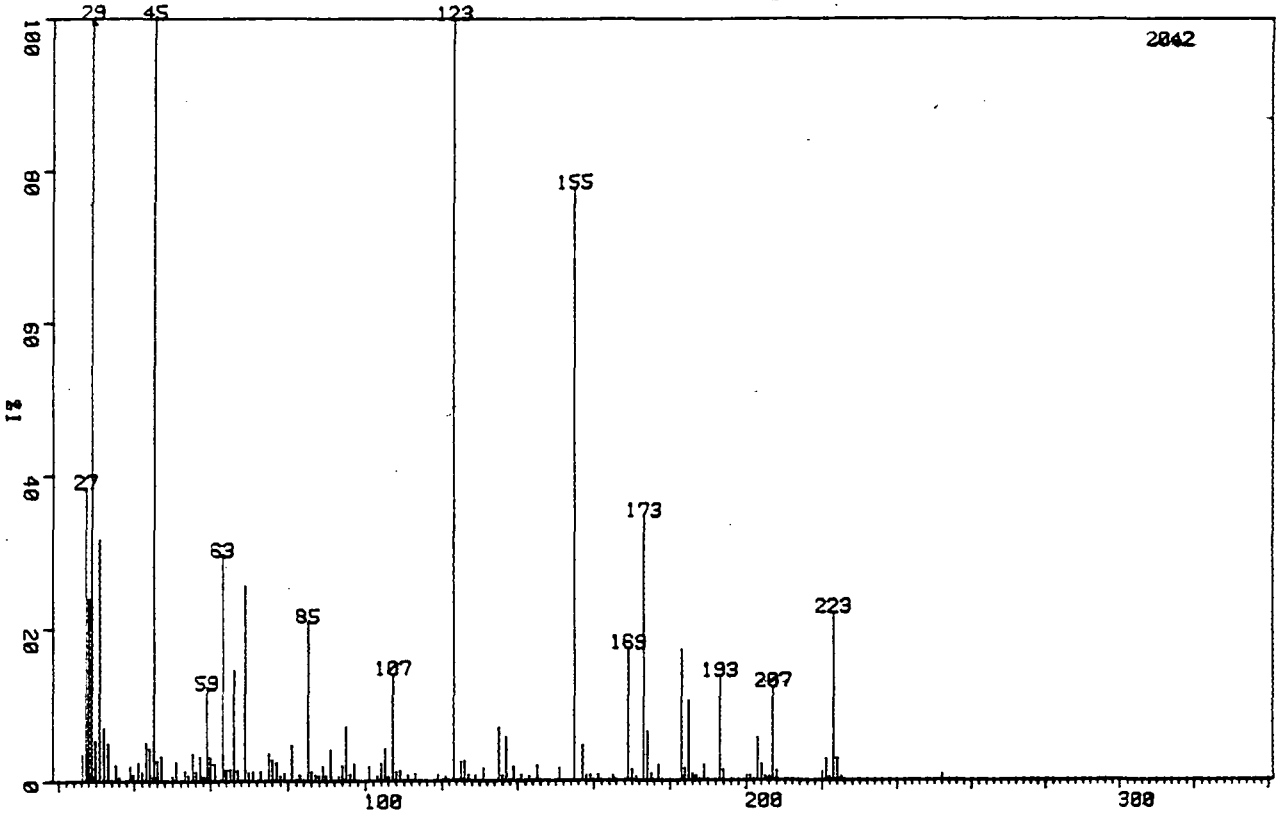


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.07	14.14	23	73.01	2.06	45	155.02	1.93
2	28.94	12.34	24	75.02	3.30	46	157.04	11.15
3	30.85	3.80	25	77.01	2.06	47	169.00	47.10
4	31.95	2.68	26	80.93	7.35	48	169.98	3.68
5	33.07	2.06	27	85.03	3.74	49	173.01	16.64
6	35.16	1.50	28	88.94	2.80	50	175.02	2.74
7	38.98	2.06	29	90.92	4.30	51	177.03	4.42
8	40.96	3.36	30	95.03	5.92	52	188.98	3.55
9	43.11	3.61	31	96.97	2.06	53	203.02	1.56
10	44.12	1.93	32	105.01	4.61	54	207.02	24.74
11	45.15	61.50	33	107.00	13.02	55	207.99	2.43
12	46.15	1.68	34	108.93	1.50	56	223.06	3.12
13	48.95	2.43	35	110.91	1.56			
14	50.94	3.55	36	112.97	3.24			
15	55.15	2.24	37	122.99	40.31			
16	57.12	2.49	38	124.02	2.06			
17	59.00	3.05	39	125.01	1.56			
18	63.09	23.74	40	130.98	1.50			
19	64.11	1.87	41	137.02	2.49			
20	65.11	1.68	42	138.96	3.55			
21	66.10	11.53	43	144.99	3.86			
22	68.92	20.37	44	153.01	3.30			

No.61 TRANS-1,1,1,4,4,4-HEXAFLUORO-2-ETHOXY-3-METHOXYMETHYL-2-BUTENE (124)

SJ154X 77 S.L.JONES 15/4 10-DEC-84

CAL:CALM30 STA: MW=252 11:9

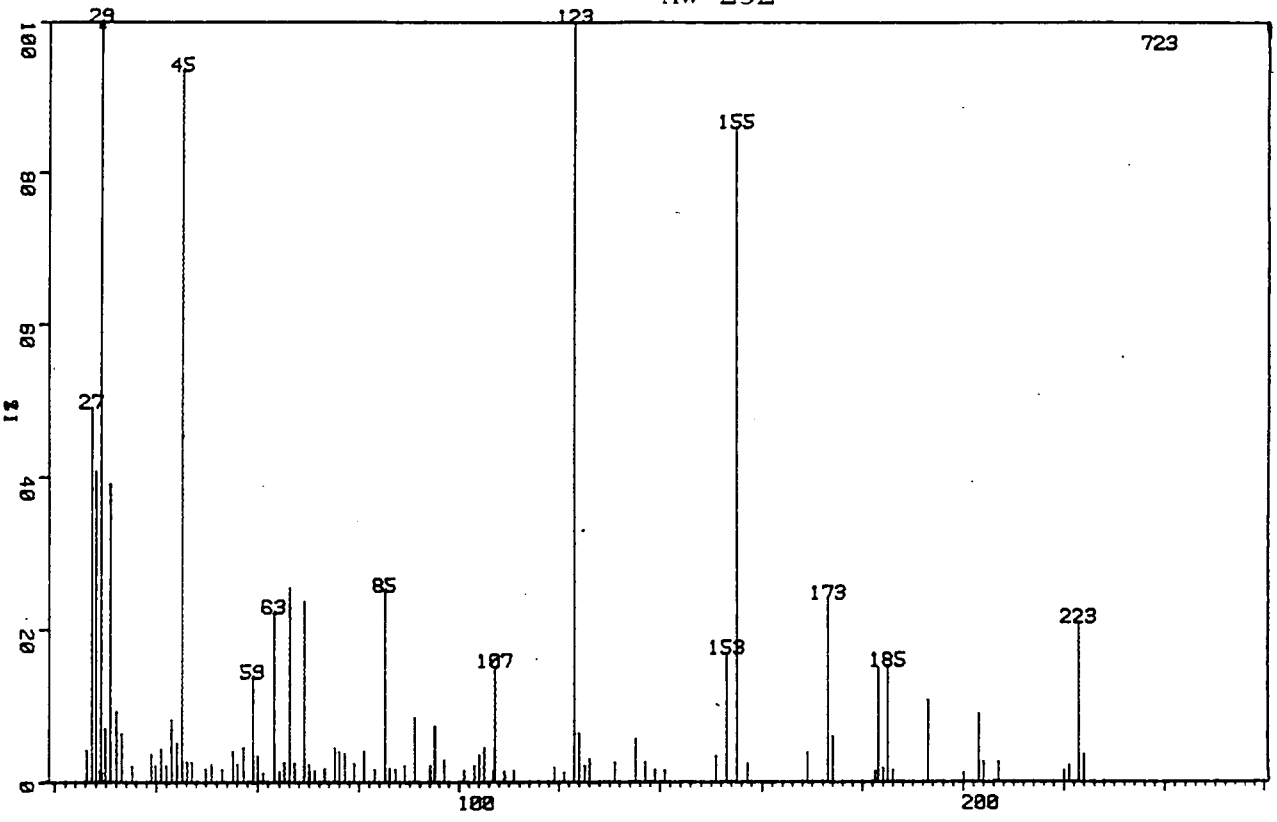


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.23	1.73	23	66.10	7.30	45	169.04	8.67
2	27.17	19.17	24	68.95	12.82	46	173.05	17.26
3	28.07	11.94	25	75.05	1.81	47	174.03	3.20
4	28.96	100.00	26	76.06	1.37	48	177.07	1.03
5	29.79	2.64	27	77.05	1.20	49	183.10	8.57
6	30.84	15.80	28	80.94	2.32	50	185.04	5.25
7	31.96	3.44	29	85.05	10.40	51	189.03	1.03
8	33.07	2.44	30	90.94	2.05	52	193.02	6.81
9	35.16	1.03	31	94.05	1.00	53	203.02	2.78
10	40.95	1.20	32	95.05	3.59	54	204.03	1.05
11	43.09	2.54	33	97.02	1.12	55	207.03	6.15
12	44.11	2.15	34	104.03	1.17	56	221.05	1.39
13	45.15	49.87	35	105.03	2.12	57	223.06	11.04
14	46.14	1.34	36	107.03	7.01	58	224.05	1.44
15	47.09	1.64	37	123.04	49.79			
16	50.93	1.25	38	125.04	1.22			
17	55.14	1.78	39	126.05	1.29			
18	57.11	1.59	40	135.05	3.47			
19	58.99	6.03	41	137.02	2.86			
20	59.93	1.56	42	145.02	1.00			
21	60.98	1.12	43	154.81	38.75			
22	63.07	14.73	44	157.06	2.30			

No.62 CIS-1,1,1,4,4,4-HEXAFLUORO-2-ETHOXY-3-METHOXYMETHYL-2-BUTENE (125)

SJ154X 101 S.L.JONES 15/4 10-DEC-84
CAL:CALM30 STA: 14:36

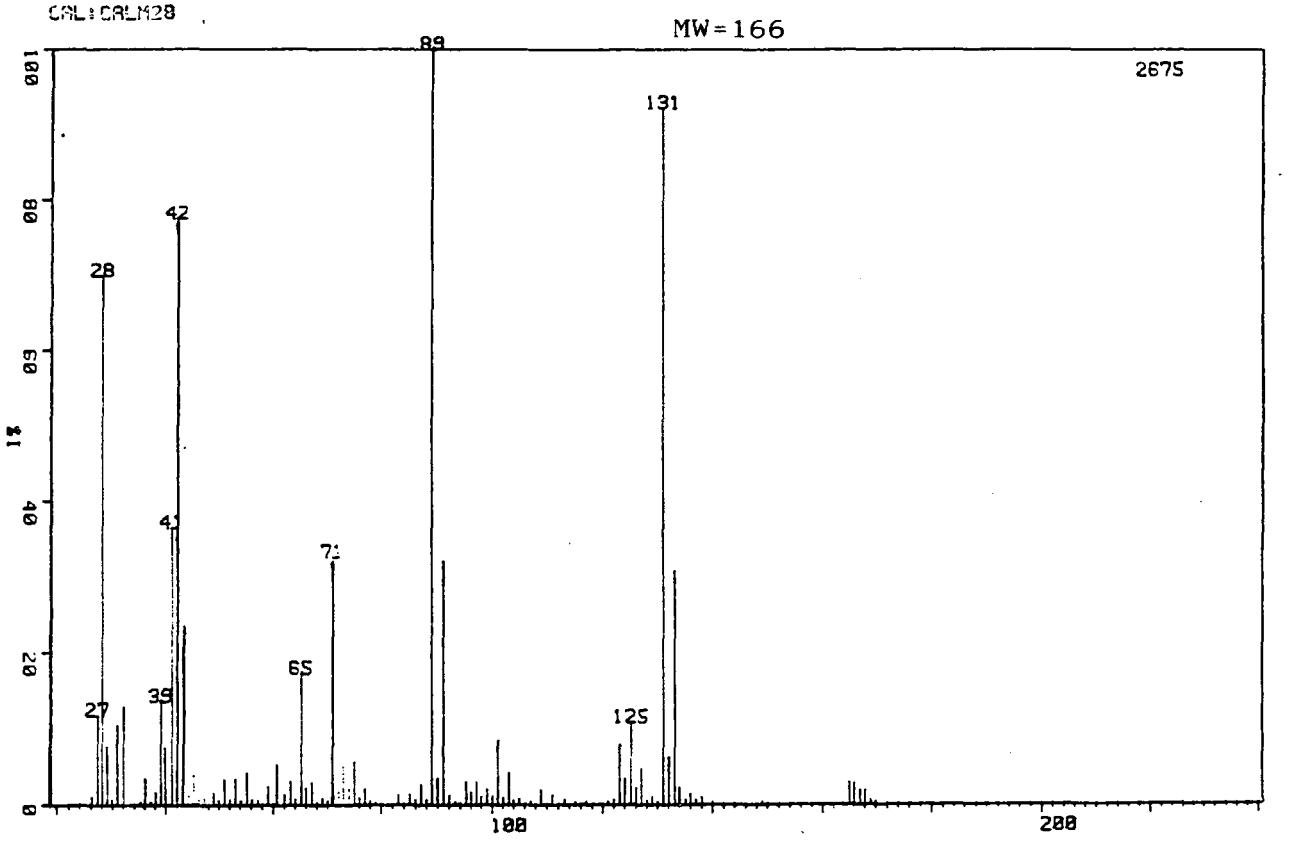
MW=252



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.23	1.62	23	68.96	9.24	45	173.04	9.41
2	27.17	19.19	24	75.06	1.78	46	174.04	2.32
3	28.07	15.95	25	76.07	1.57	47	183.08	5.84
4	28.96	100.00	26	77.05	1.46	48	185.01	5.95
5	29.79	2.76	27	80.95	1.57	49	193.02	4.16
6	30.84	15.30	28	85.07	9.78	50	203.00	3.51
7	31.96	3.62	29	90.95	3.30	51	204.03	1.03
8	33.07	2.49	30	95.05	2.86	52	207.03	1.03
9	38.96	1.41	31	97.02	1.14	53	222.99	8.16
10	40.95	1.68	32	104.04	1.41	54	224.02	1.41
11	43.10	3.19	33	105.05	1.78			
12	44.11	2.00	34	107.09	5.89			
13	45.15	36.59	35	123.04	39.08			
14	46.14	1.03	36	124.05	2.49			
15	47.09	1.03	37	126.11	1.19			
16	55.14	1.57	38	131.02	1.03			
17	57.12	1.78	39	135.08	2.22			
18	58.99	5.35	40	137.05	1.03			
19	59.94	1.35	41	150.99	1.35			
20	63.08	8.70	42	153.03	6.59			
21	65.13	1.03	43	155.02	33.68			
22	66.09	9.95	44	169.05	1.51			

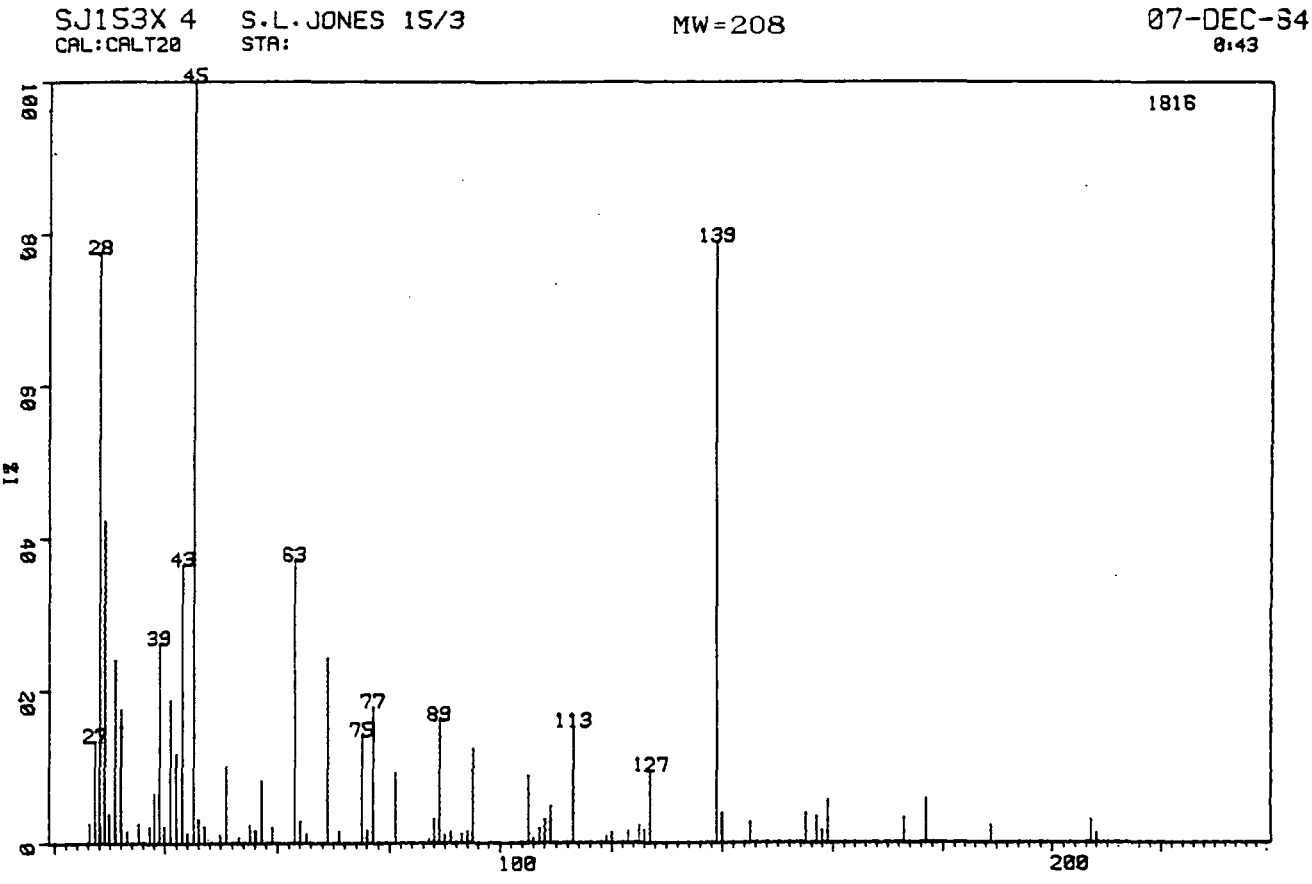
No.63 2-(1,2-DICHLOROETHENYL)OXOLANE (126)

SJ106 3 S.L.JONES 13-JUL-83
CAL:CALM28



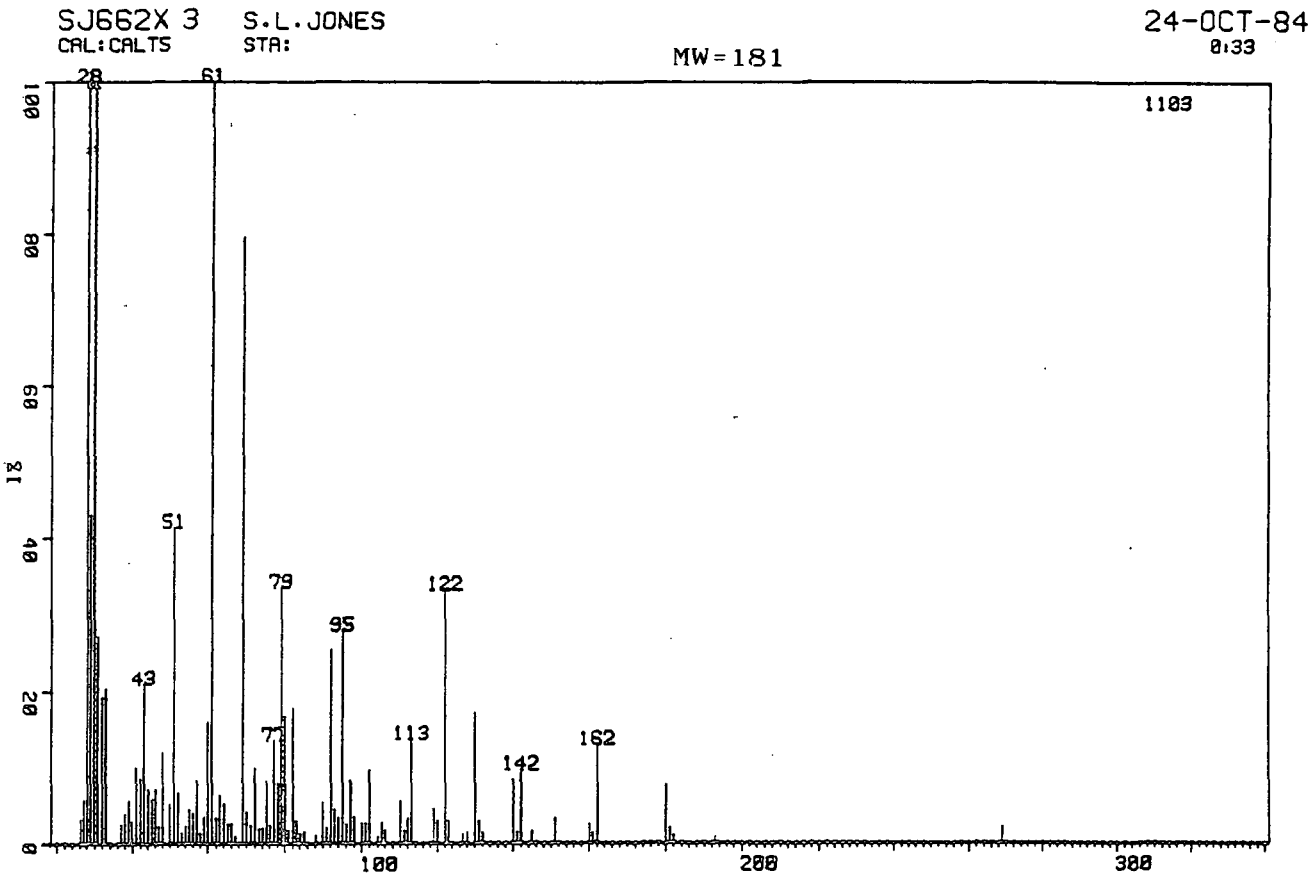
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.31	1.12	23	63.11	3.14	45	99.95	1.08
2	27.24	11.78	24	65.13	17.27	46	101.01	8.49
3	28.13	69.87	25	66.09	2.09	47	103.08	4.07
4	29.00	7.59	26	67.08	2.88	48	108.95	1.94
5	30.92	10.47	27	70.99	32.67	49	110.97	1.31
6	32.01	12.90	28	72.03	1.72	50	123.02	7.81
7	36.15	3.44	29	73.03	5.01	51	124.03	3.33
8	38.07	1.68	30	74.09	2.06	52	125.04	10.80
9	39.01	13.53	31	75.05	5.53	53	126.05	2.28
10	39.90	7.48	32	77.03	2.06	54	127.04	4.79
11	41.00	36.52	33	82.99	1.27	55	129.00	1.05
12	42.09	77.57	34	85.02	1.42	56	131.07	92.19
13	43.16	23.51	35	87.02	2.65	57	132.09	6.28
14	44.18	1.16	36	88.92	100.00	58	133.11	30.80
15	45.19	3.89	37	89.89	3.44	59	134.11	2.28
16	48.98	1.61	38	90.95	32.07	60	136.04	1.46
17	51.00	3.36	39	92.01	1.23	61	137.99	1.05
18	53.11	3.40	40	95.05	3.03	62	165.09	2.92
19	55.17	4.19	41	96.02	1.64	63	166.09	2.77
20	59.06	2.39	42	97.05	2.99	64	167.07	1.91
21	60.62	5.27	43	97.99	1.12	65	168.07	1.91
22	62.06	1.42	44	98.99	2.06			

No.64 1,1,1,4,4,4-HEXAFLUORO-2-METHOXYMETHYL-2-BUTENE (127)



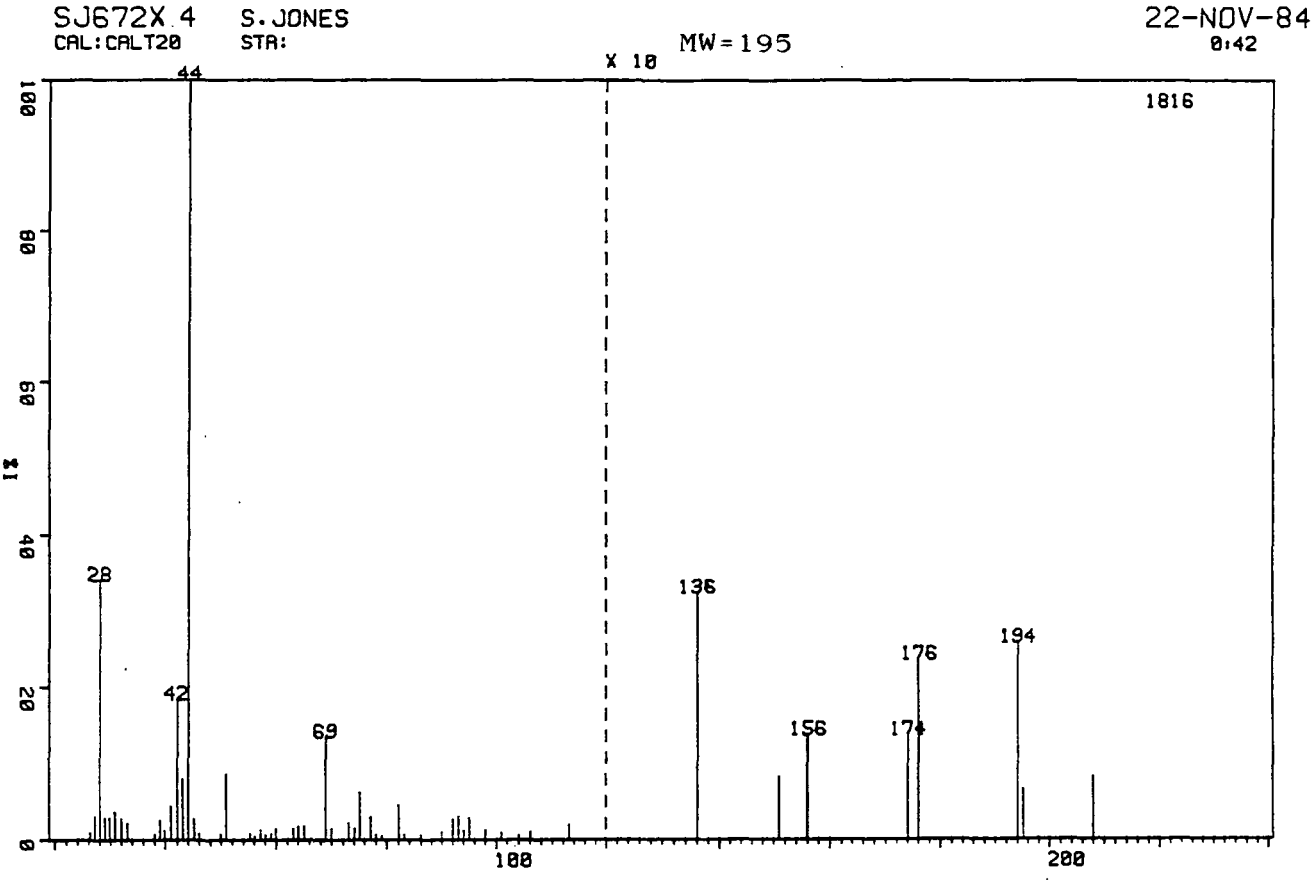
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.30	2.59	23	47.10	2.20	45	105.02	8.87
2	27.23	13.38	24	50.94	10.13	46	107.01	1.98
3	28.11	77.53	25	55.11	1.71	47	107.99	3.14
4	28.13	2.26	26	55.15	2.37	48	108.96	4.90
5	28.96	42.24	27	56.09	1.54	49	122.99	15.25
6	29.00	5.01	28	56.15	1.65	50	123.00	1.60
7	29.80	3.85	29	57.08	8.20	51	125.00	2.31
8	30.86	4.74	30	57.13	4.74	52	126.01	1.71
9	30.88	24.01	31	59.00	2.09	53	127.01	9.47
10	31.96	17.57	32	63.08	37.11	54	138.97	79.07
11	33.07	1.54	33	64.09	2.86	55	139.95	3.91
12	35.16	2.53	34	68.94	24.34	56	144.99	2.75
13	37.09	2.20	35	71.03	1.60	57	154.99	3.96
14	38.04	6.55	36	75.05	14.10	58	156.98	3.52
15	38.96	26.21	37	76.04	1.65	59	157.97	1.65
16	39.86	2.15	38	77.04	17.84	60	158.95	5.67
17	40.94	18.78	39	80.95	9.25	61	172.97	3.25
18	42.03	11.73	40	87.99	3.19	62	176.98	5.84
19	43.07	3.03	41	88.96	16.08	63	188.94	2.31
20	43.11	36.51	42	90.98	1.54	64	206.97	3.03
21	45.14	100.00	43	94.06	1.54			
22	46.13	3.19	44	95.03	12.33			

No.65 2,2,3,4,4,4-HEXAFLUOROBUTYLAMINE (129)



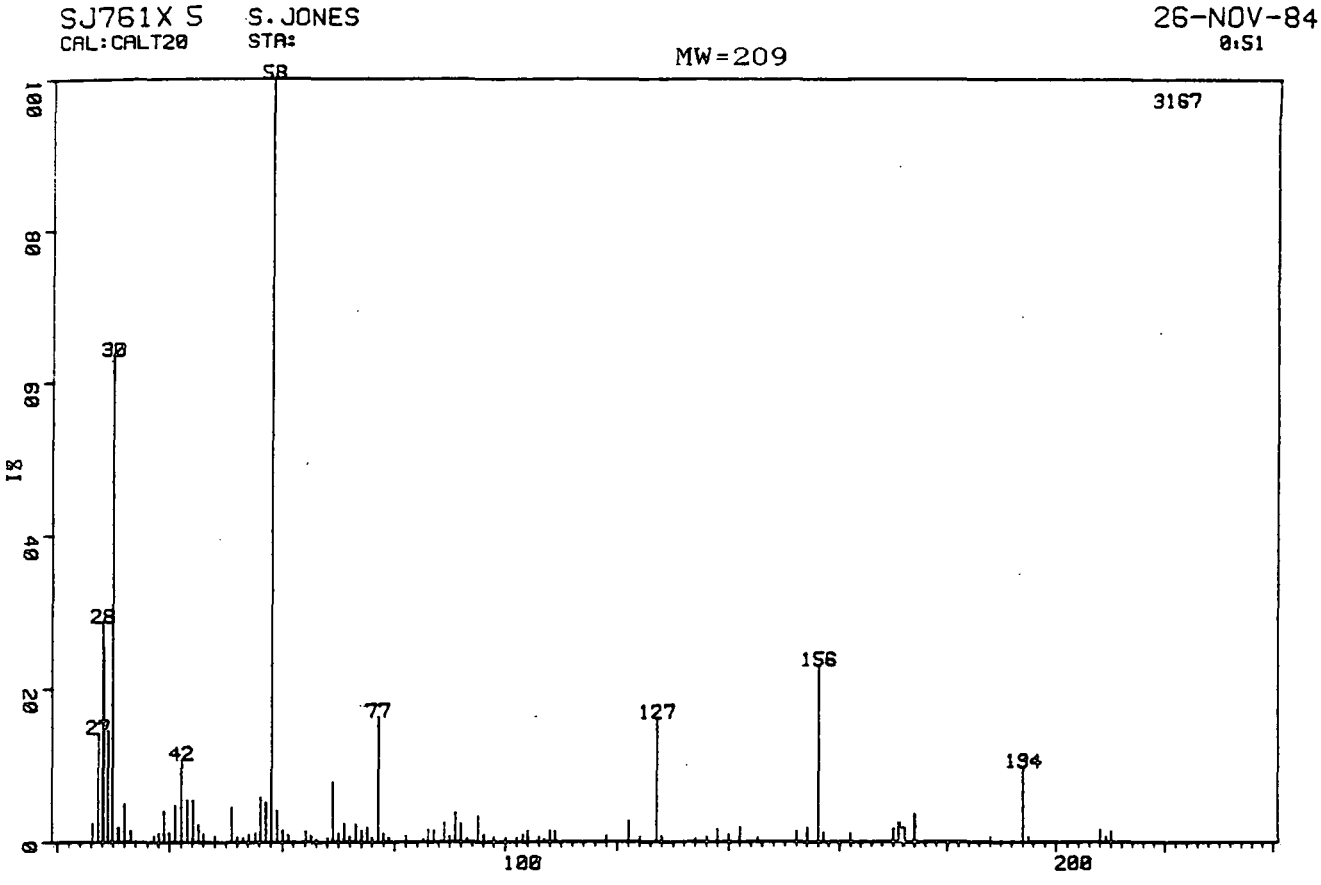
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.21	1.01	23	57.02	1.36	45	97.03	2.69
2	27.14	1.86	24	57.07	2.69	46	98.01	1.12
3	28.03	68.94	25	58.93	1.09	47	102.00	3.16
4	28.91	14.02	26	59.87	5.18	48	109.93	1.80
5	29.75	100.00	27	60.93	32.62	49	112.01	1.04
6	30.77	8.87	28	61.98	1.09	50	113.00	4.47
7	31.87	6.24	29	63.01	2.04	51	118.97	1.48
8	32.98	6.63	30	64.05	1.69	52	122.00	10.85
9	37.96	1.27	31	68.95	25.97	53	129.95	5.59
10	38.88	1.83	32	69.89	1.33	54	139.93	2.72
11	40.84	3.25	33	72.04	3.22	55	142.00	3.16
12	41.93	2.78	34	75.07	2.69	56	150.95	1.04
13	43.00	6.83	35	77.06	4.41	57	161.99	4.23
14	44.01	2.31	36	78.03	2.57	58	179.92	2.48
15	45.04	1.89	37	78.99	10.94			
16	46.03	2.31	38	79.94	5.44			
17	47.97	3.87	39	82.00	5.77			
18	49.80	1.66	40	89.90	1.75			
19	50.86	13.49	41	92.02	8.25			
20	51.95	2.19	42	93.03	1.45			
21	55.08	1.45	43	94.07	1.06			
22	56.04	1.27	44	95.05	9.11			

No.66 (2,2,3,4,4,4-HEXAFLUOROBUTYL)METHYLAMINE (128)



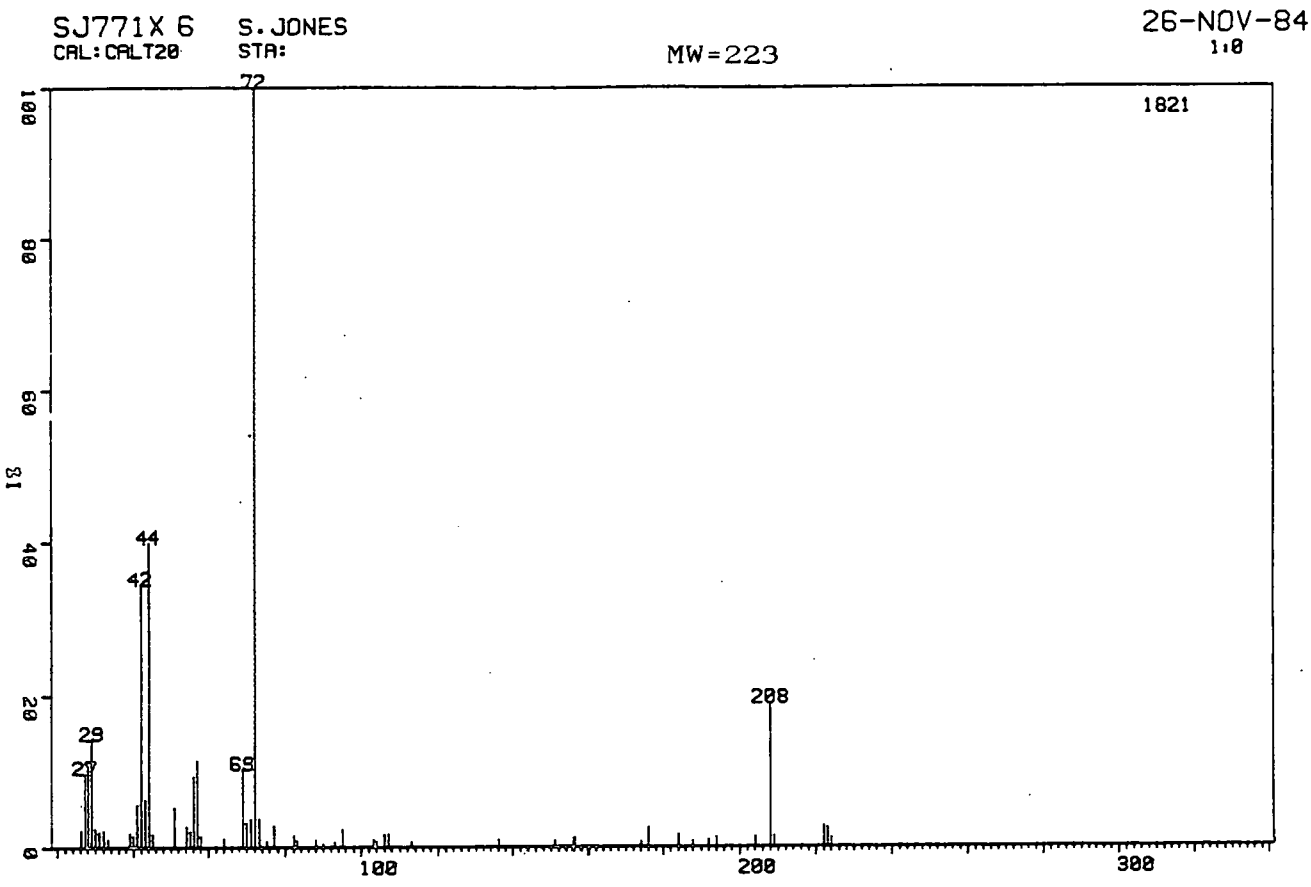
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.28	0.94	23	57.13	0.72	45	94.07	1.27
2	27.22	3.14	24	58.10	0.66	46	95.04	2.92
3	28.11	34.09	25	59.00	0.83	47	98.05	1.27
4	28.98	2.86	26	59.93	1.49	48	100.95	0.94
5	29.82	2.92	27	63.06	1.49	49	104.06	0.61
6	30.85	3.69	28	64.10	1.76	50	106.08	1.05
7	31.96	2.81	29	65.09	1.82	51	113.02	1.98
8	33.07	2.15	30	68.96	13.44	52	136.09	3.25
9	38.03	0.77	31	69.90	0.66	53	150.99	0.83
10	38.96	2.53	32	69.99	1.49	54	156.09	1.38
11	39.85	1.27	33	73.10	2.26	55	174.12	1.38
12	40.93	4.41	34	74.10	1.54	56	176.11	2.37
13	42.02	18.45	35	75.11	6.28	57	194.07	2.59
14	43.09	7.93	36	77.04	3.03	58	195.10	0.66
15	44.14	100.00	37	78.00	0.77	59	208.05	0.83
16	45.14	2.70	38	78.97	0.55			
17	46.11	0.83	39	81.97	4.52			
18	49.87	0.77	40	83.03	0.66			
19	50.94	8.59	41	86.06	0.66			
20	55.15	0.83	42	89.93	1.05			
21	56.12	0.44	43	92.02	2.64			
22	57.08	1.32	44	93.05	3.08			

No.67 (2,2,3,4,4,4-HEXAFLUOROBUTYL)ETHYLAMINE (131)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	2.49	23	55.20	1.26	45	95.08	3.41
2	27.23	14.27	24	56.15	1.01	46	104.09	1.45
3	28.11	28.77	25	56.19	5.90	47	108.02	1.52
4	28.12	25.42	26	57.14	3.19	48	109.00	1.36
5	29.00	14.62	27	57.18	5.24	49	122.08	2.78
6	29.83	63.62	28	58.14	100.00	50	127.06	16.17
7	30.86	1.93	29	59.07	4.10	51	138.08	1.71
8	30.89	1.86	30	59.98	1.52	52	142.06	1.86
9	30.91	1.20	31	64.17	1.42	53	152.13	1.42
10	31.98	5.05	32	68.97	7.89	54	154.13	1.89
11	33.08	1.55	33	69.99	1.17	55	156.07	23.08
12	38.06	1.17	34	71.01	2.46	56	157.06	1.23
13	38.98	4.10	35	73.10	2.37	57	162.07	1.17
14	39.87	1.26	36	74.11	1.52	58	170.07	1.74
15	40.96	4.93	37	75.05	1.99	59	171.12	2.56
16	42.05	10.86	38	77.04	16.39	60	172.10	1.86
17	43.12	5.56	39	78.01	1.11	61	174.08	3.66
18	44.17	5.56	40	86.09	1.64	62	194.11	9.91
19	45.15	2.34	41	87.08	1.52	63	208.08	1.71
20	46.15	1.07	42	88.99	2.56	64	210.07	1.42
21	50.98	4.64	43	91.01	3.85			
22	54.17	1.01	44	92.06	2.37			

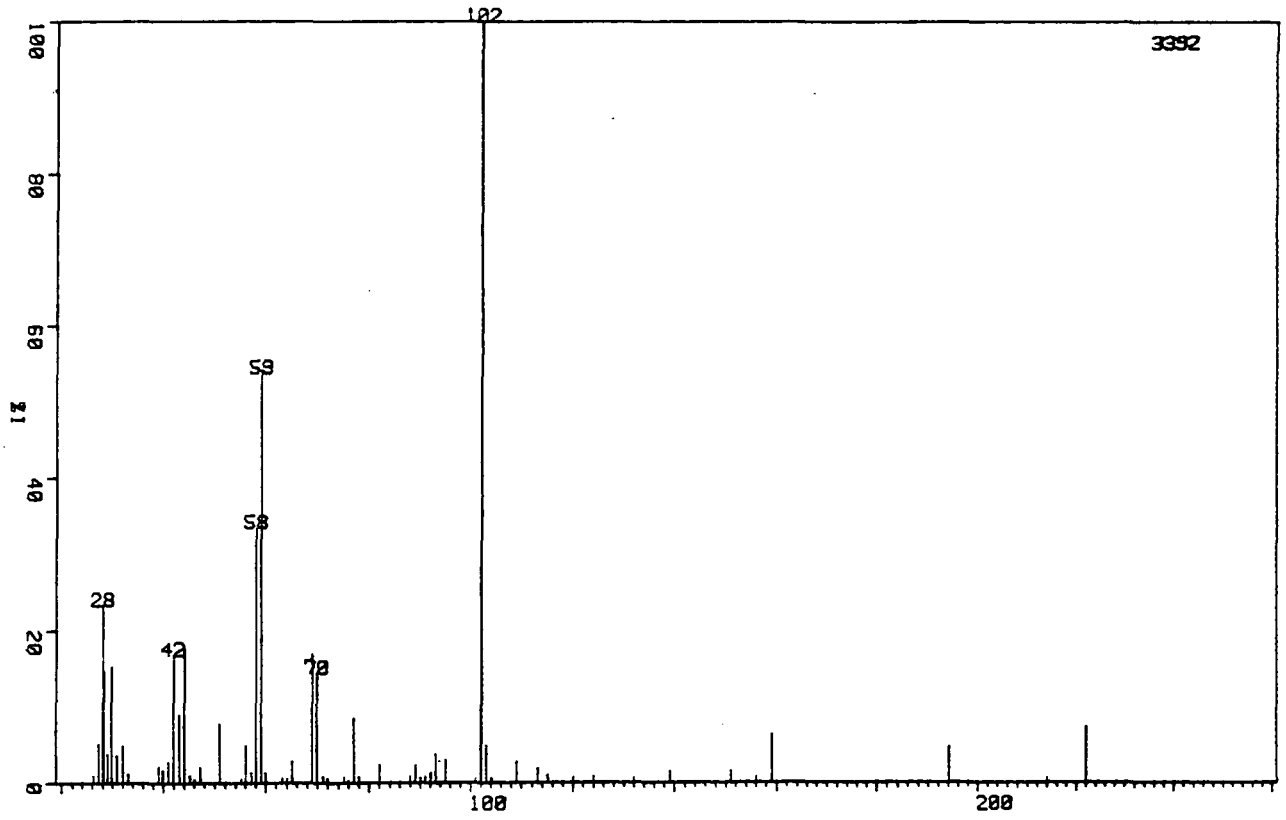
No.68 (2,2,3,4,4,4-HEXAFLUOROBUTYL)ETHYLMETHYLAMINE (130)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.28	2.25	23	57.17	11.48	45	151.07	0.88
2	27.22	9.77	24	58.13	1.48	46	156.17	1.26
3	28.11	10.82	25	64.15	1.15	47	174.17	0.77
4	28.96	0.60	26	69.00	10.32	48	176.13	2.64
5	28.99	14.28	27	70.01	3.24	49	184.16	1.65
6	29.82	2.47	28	71.08	3.73	50	188.08	0.82
7	30.85	1.81	29	72.14	100.00	51	192.09	0.93
8	30.88	2.03	30	73.14	3.73	52	194.11	1.32
9	31.96	2.20	31	75.10	0.82	53	204.16	1.43
10	33.07	1.04	32	77.05	2.91	54	208.07	18.89
11	38.97	1.92	33	82.01	1.59	55	209.05	1.48
12	39.86	1.48	34	83.04	0.88	56	222.13	2.75
13	40.95	5.66	35	88.08	0.93	57	223.14	2.53
14	42.04	34.49	36	89.96	0.49	58	224.12	1.21
15	43.12	6.32	37	93.08	0.66			
16	44.16	39.92	38	95.10	2.42			
17	45.14	1.04	39	103.16	1.04			
18	45.17	1.65	40	104.10	0.77			
19	50.97	5.27	41	106.10	1.70			
20	54.16	2.75	42	107.07	1.76			
21	55.19	2.14	43	113.06	0.71			
22	56.18	9.39	44	136.15	0.99			

No.69 METHYL-N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)CARBAMATE (132)

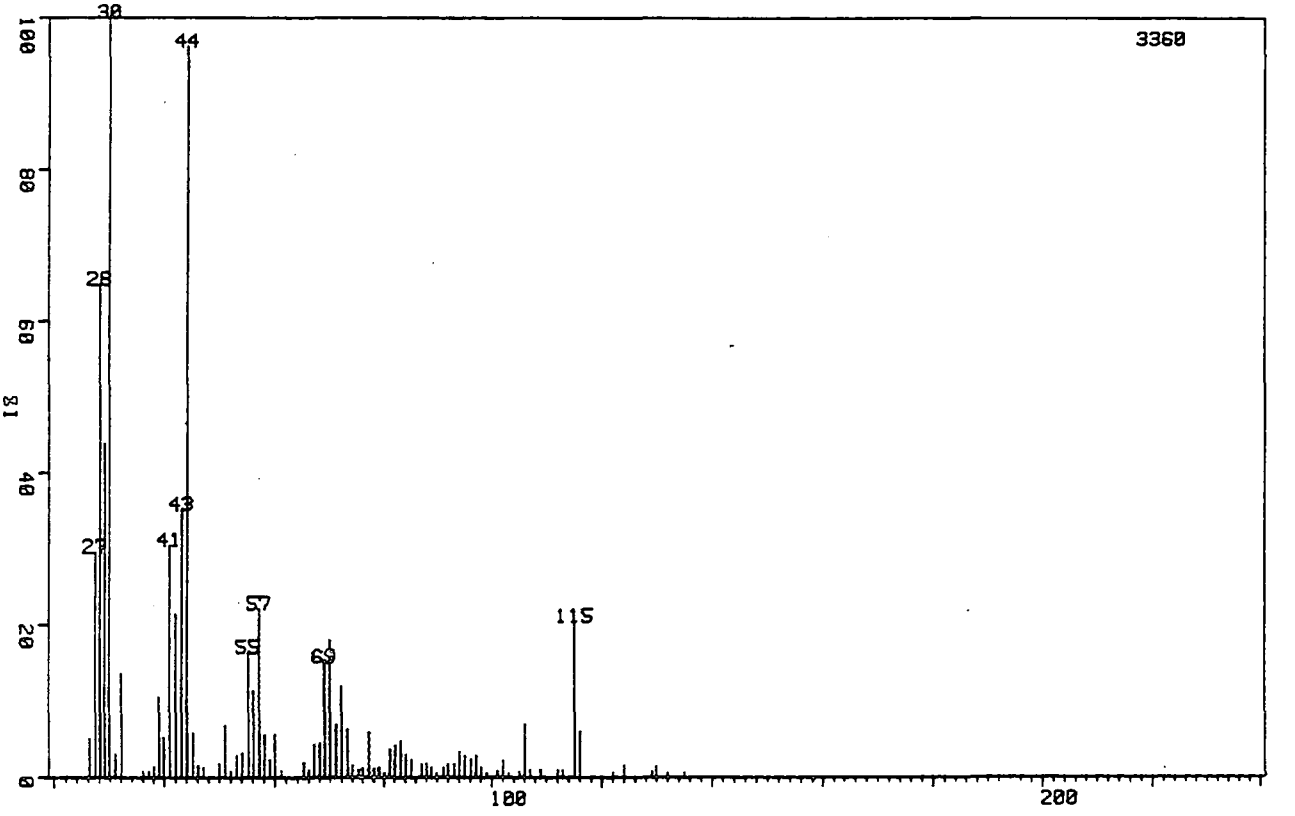
SJ911X.S S.L.JONES EI 17-JAN-85
CAL:CALT31 STA: MW=253 0:51



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	5.16	23	45.13	1.03	45	109.00	2.77
2	28.11	23.35	24	47.11	2.03	46	113.03	1.98
3	28.12	14.59	25	50.95	7.78	47	115.07	1.06
4	28.13	1.27	26	56.12	1.68	48	139.03	1.56
5	28.97	3.83	27	56.15	4.92	49	151.02	1.53
6	29.00	3.74	28	57.14	1.39	50	159.02	6.34
7	29.83	15.24	29	58.11	33.46	51	194.11	4.69
8	30.86	1.59	30	59.01	53.74	52	222.08	7.31
9	30.89	3.63	31	59.94	1.33			
10	31.97	4.86	32	65.11	2.80			
11	32.01	1.44	33	68.95	16.86			
12	33.08	1.12	34	69.92	14.39			
13	33.10	1.21	35	77.05	8.46			
14	38.97	2.09	36	81.99	2.45			
15	39.81	1.62	37	88.98	1.21			
16	39.86	1.39	38	89.02	2.33			
17	40.95	2.77	39	91.99	1.33			
18	42.03	16.83	40	92.03	1.00			
19	43.11	8.96	41	93.06	3.71			
20	44.09	1.33	42	95.05	3.07			
21	44.11	17.75	43	102.07	100.00			
22	44.15	2.15	44	103.09	4.83			

No.70 N-ETHYL-N'-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)UREA (133)

SJ921X 0 S.L.JONES EI 20-JAN-85
CAL:CALT31 STA: MW=266 0:26

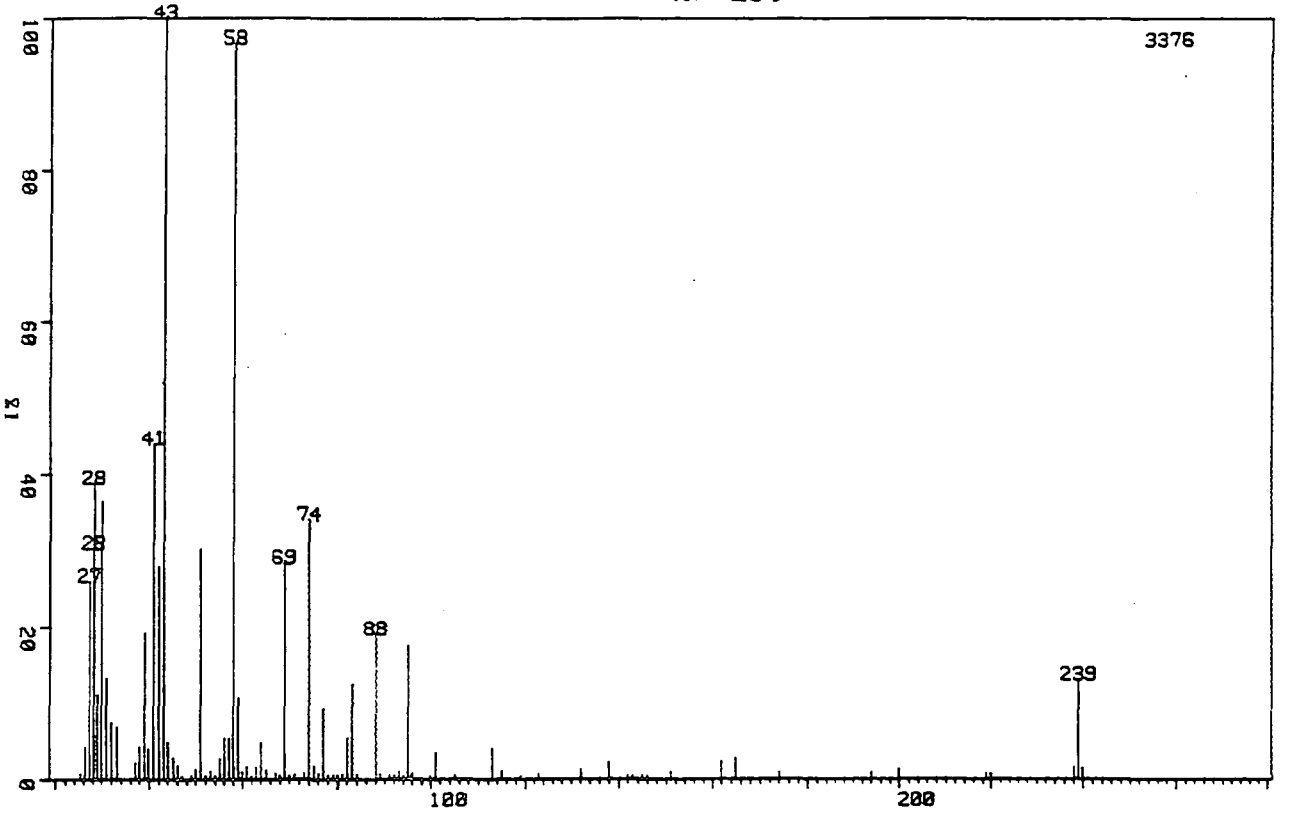


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.30	5.09	23	50.95	6.76	45	81.01	3.78
2	27.23	29.52	24	53.10	2.83	46	81.97	2.08
3	28.11	64.73	25	54.14	3.18	47	82.05	4.17
4	28.12	18.10	26	55.15	16.40	48	83.09	4.76
5	28.13	6.87	27	56.11	11.43	49	84.11	3.01
6	28.97	6.99	28	56.15	11.19	50	85.11	2.29
7	29.00	43.81	29	57.10	5.77	51	94.05	3.42
8	29.83	100.00	30	57.14	22.11	52	95.09	2.86
9	30.89	3.07	31	58.09	5.54	53	96.10	2.38
10	31.97	13.54	32	59.01	2.35	54	97.05	2.86
11	38.96	10.60	33	59.93	5.68	55	102.00	2.26
12	39.80	5.21	34	67.07	4.37	56	106.04	6.99
13	39.86	4.08	35	68.05	4.55	57	115.07	20.48
14	40.95	30.45	36	68.93	15.09	58	116.06	6.07
15	42.03	21.40	37	69.00	10.51			
16	42.04	10.57	38	69.90	18.07			
17	43.08	9.26	39	69.94	7.59			
18	43.11	35.21	40	70.98	6.96			
19	44.10	30.60	41	71.01	6.19			
20	44.12	8.33	42	72.03	11.90			
21	44.15	96.19	43	73.06	6.31			
22	45.14	5.86	44	77.04	5.98			

No. 71 (1H, 1H, 3H-HEXAFLUOROBUTYL)-N-METHYLCARBAMATE (134)

SJ951X 0 S.L.JONES EI 17-JAN-85
CAL:CALP17 STA: 2:27

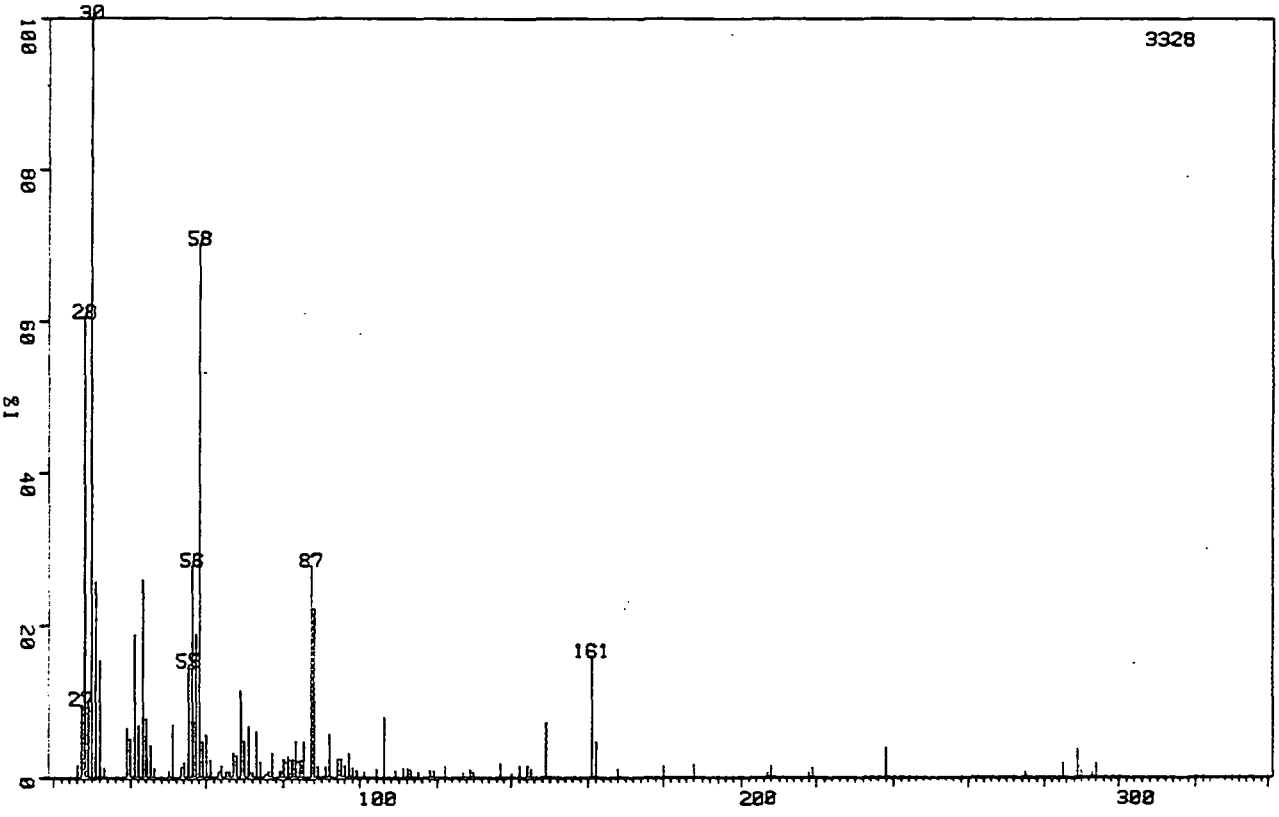
MW=239



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.28	4.27	23	46.10	1.81	45	83.00	12.53
2	27.21	26.07	24	49.84	1.39	46	88.00	19.08
3	28.09	30.33	25	50.90	30.33	47	92.98	1.13
4	28.11	38.83	26	53.06	1.10	48	95.00	17.51
5	28.12	5.92	27	55.11	2.75	49	100.90	3.50
6	28.96	11.11	28	56.06	5.36	50	112.97	4.03
7	28.98	7.82	29	56.11	2.10	51	115.00	1.13
8	29.82	36.49	30	57.04	5.42	52	131.90	1.27
9	30.87	13.27	31	57.09	4.00	53	137.94	2.25
10	31.96	7.43	32	58.01	96.65	54	150.85	1.04
11	33.06	6.87	33	58.05	1.60	55	161.90	2.40
12	37.08	2.10	34	58.95	10.78	56	164.96	2.78
13	38.03	4.24	35	59.88	1.01	57	199.86	1.36
14	38.95	19.19	36	60.91	1.69	58	237.92	1.69
15	39.79	3.17	37	63.01	1.69	59	238.92	13.00
16	39.84	4.03	38	64.03	4.80	60	239.89	1.57
17	40.92	44.05	39	65.05	1.16			
18	42.02	27.96	40	68.91	28.50			
19	43.09	100.00	41	74.02	34.12			
20	44.07	4.95	42	75.02	1.81			
21	44.13	3.47	43	77.00	9.24			
22	45.10	2.81	44	81.96	5.45			

No.72 N-METHYL-N'-(1H,1H,3H-HEXAFLUOROBUTYL)UREA (135)

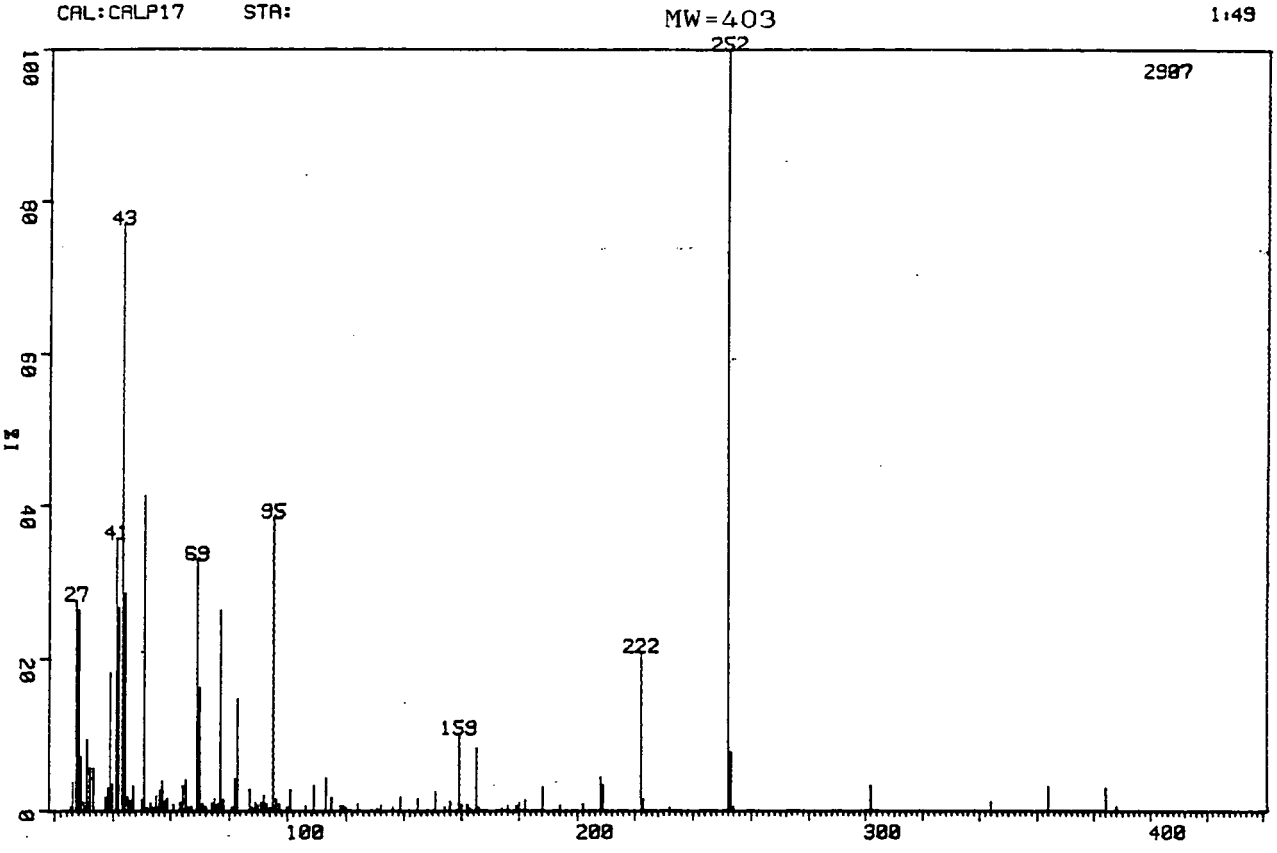
SJ971X 0 S.L.JONES EI 20-JAN-85
CAL:CALT31 STA: MW=238 0:43



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	9.59	23	55.15	14.63	45	85.09	4.78
2	28.11	60.55	24	56.11	27.85	46	87.02	27.79
3	28.12	33.02	25	56.15	7.30	47	88.00	22.15
4	28.96	4.54	26	57.12	18.87	48	91.97	5.77
5	28.98	9.37	27	58.06	70.16	49	94.03	2.40
6	28.99	8.47	28	59.01	4.78	50	95.00	2.07
7	29.82	100.00	29	59.93	5.71	51	95.08	2.37
8	30.86	2.07	30	60.99	2.25	52	97.08	3.19
9	30.91	25.69	31	67.07	3.22	53	106.00	7.96
10	31.97	15.38	32	68.04	2.91	54	148.96	7.18
11	32.03	3.25	33	68.94	11.54	55	160.97	15.87
12	38.96	6.46	34	69.00	7.21	56	161.99	4.66
13	39.80	5.08	35	69.97	4.72	57	238.04	3.91
14	40.95	18.75	36	71.05	6.70			
15	42.04	6.85	37	73.08	6.13			
16	43.10	25.96	38	74.07	2.13			
17	44.08	7.75	39	77.07	3.22			
18	44.11	5.02	40	79.94	2.43			
19	44.15	2.58	41	81.03	2.85			
20	45.14	4.24	42	82.08	2.49			
21	50.95	7.06	43	83.12	4.81			
22	54.13	2.01	44	84.11	2.31			

No.73 (1H,1H,3H-HEXAFLUOROBUTYL)-N-(1,1,1,2,3,3-HEXAFLUORO-4-PENTYL)CARBAMATE (136)

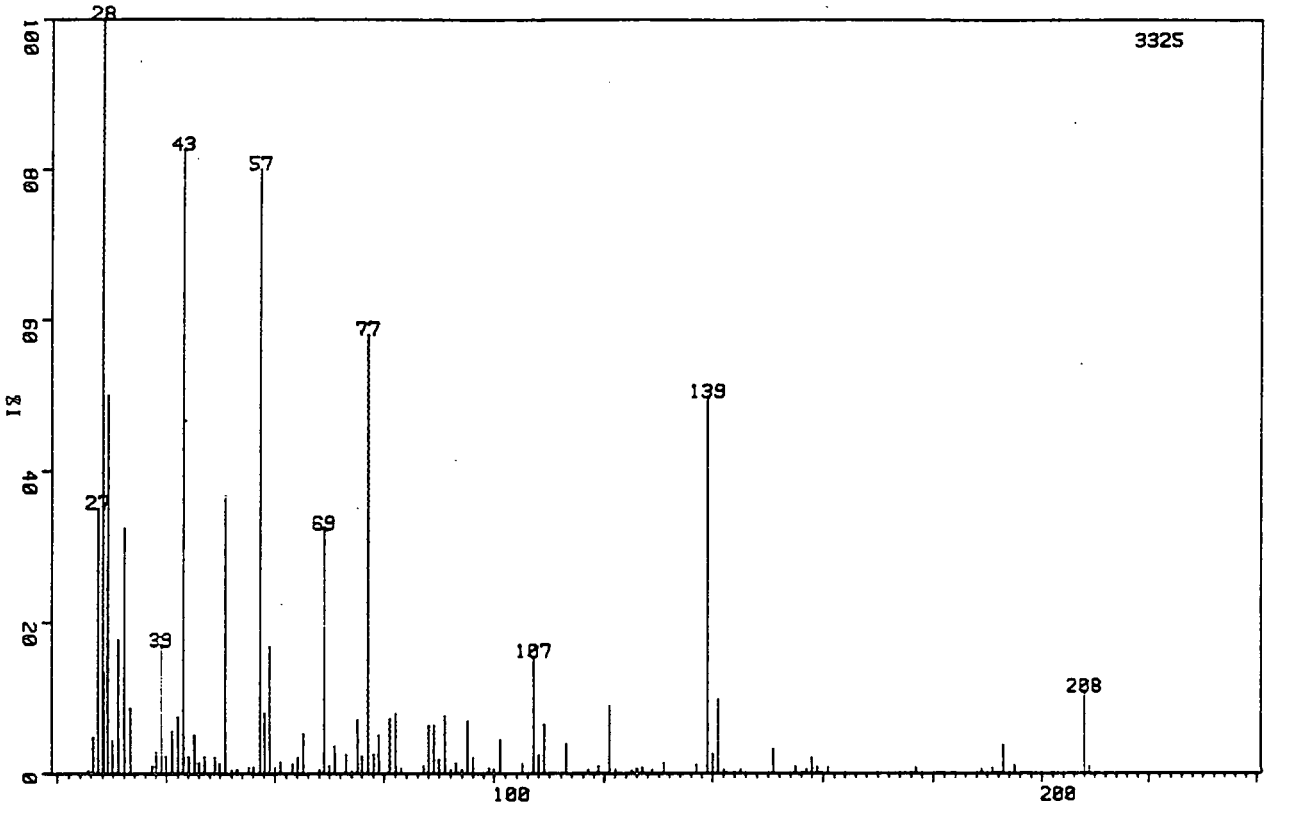
SJ961X 0 S.L.JONES EI 17-JAN-85
CAL:CALP17 STA: 1:49



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.29	3.82	23	50.92	41.35	45	114.99	1.79
2	27.23	27.66	24	55.13	2.03	46	138.90	1.86
3	28.11	26.42	25	56.09	2.72	47	144.97	1.62
4	28.12	14.28	26	56.13	1.51	48	150.89	2.61
5	28.96	3.99	27	57.11	3.99	49	158.93	10.18
6	29.00	7.16	28	58.98	1.65	50	164.95	8.26
7	30.88	9.43	29	64.06	3.37	51	181.95	1.55
8	31.97	5.74	30	65.09	4.09	52	187.97	3.16
9	33.08	5.71	31	68.95	32.99	53	207.94	4.54
10	37.10	1.86	32	69.91	16.24	54	208.91	3.47
11	38.04	3.13	33	75.05	1.65	55	221.90	20.92
12	38.96	18.16	34	77.04	26.38	56	222.96	1.51
13	39.80	2.30	35	78.01	1.51	57	251.90	100.00
14	39.86	3.51	36	81.97	4.23	58	252.94	7.77
15	40.94	35.78	37	83.01	14.83	59	301.86	3.37
16	42.03	26.69	38	87.04	2.92	60	363.85	3.27
17	43.11	77.02	39	91.97	2.06	61	383.87	3.13
18	44.10	28.62	40	95.01	38.53			
19	44.14	23.63	41	96.02	1.62			
20	45.13	1.86	42	100.93	2.79			
21	47.09	3.30	43	108.94	3.30			
22	49.87	1.51	44	112.96	4.40			

No.74 1,1,1,2,3,3-HEXAFLUORO-4-METHYL-4,5-EPOXYPENTANE (139)

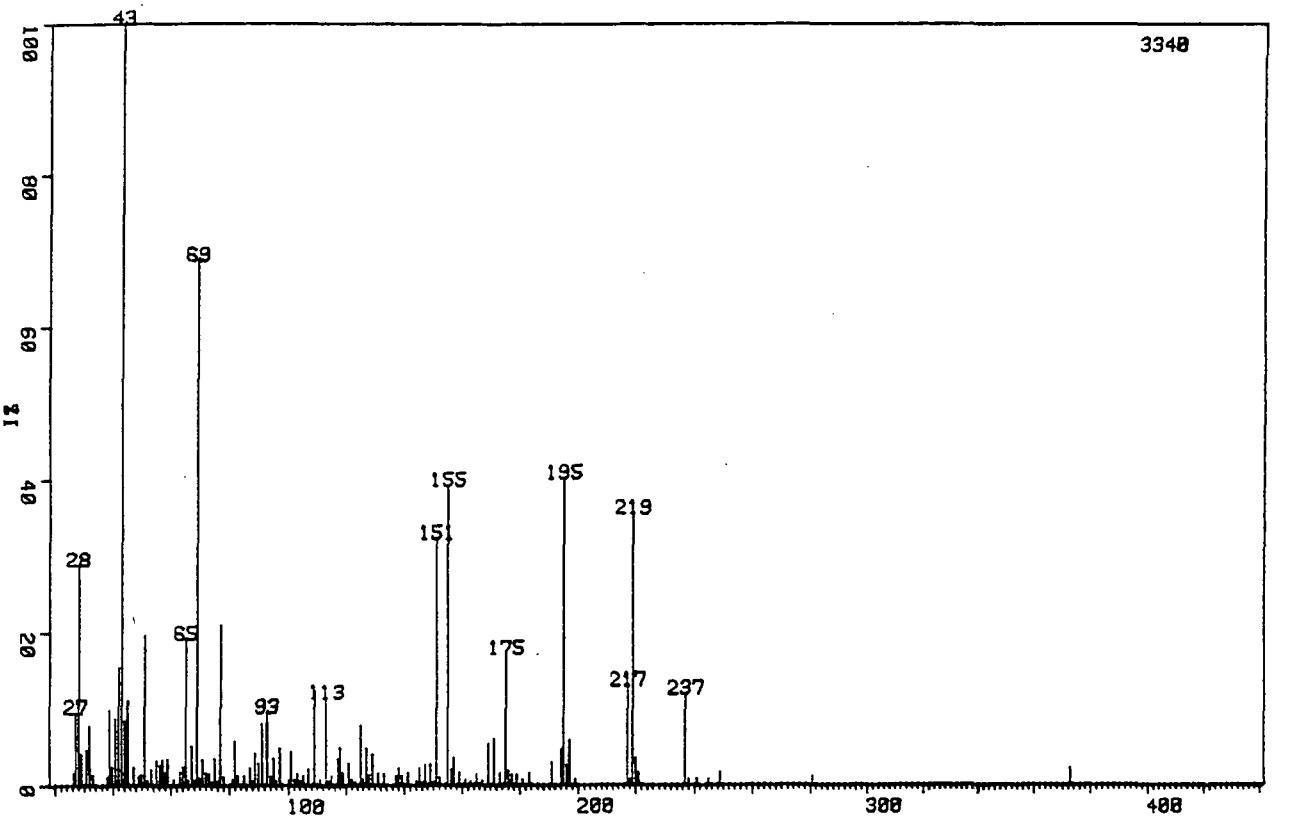
SJ118X 5 S.L.JONES 118/1 31-JUL-85
CAL:CALT1 STR: MW=208 0:50



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.37	4.84	23	57.08	80.09	45	100.96	4.48
2	27.30	35.13	24	58.04	8.03	46	107.03	15.46
3	28.17	100.00	25	58.97	16.81	47	107.99	2.44
4	28.19	13.47	26	60.94	1.53	48	108.96	6.47
5	29.02	26.95	27	64.06	2.20	49	122.98	3.97
6	29.05	50.02	28	65.08	5.32	50	120.92	8.99
7	29.86	4.36	29	68.94	32.39	51	138.96	49.80
8	29.88	1.80	30	70.97	3.67	52	139.93	2.62
9	30.94	17.77	31	73.03	2.56	53	140.95	9.80
10	32.03	32.57	32	75.05	7.19	54	150.91	3.22
11	33.13	8.66	33	76.06	2.32	55	157.96	2.08
12	38.07	2.83	34	77.04	58.14	56	192.91	3.73
13	38.99	16.90	35	78.02	2.62	57	207.91	10.83
14	39.82	2.32	36	78.98	5.08			
15	40.97	5.62	37	80.95	7.22			
16	42.02	7.52	38	81.99	8.00			
17	43.08	82.68	39	88.03	6.32			
18	44.12	2.26	40	88.98	6.41			
19	45.14	5.08	41	89.93	1.86			
20	47.10	2.26	42	90.98	7.67			
21	48.96	2.17	43	95.04	6.95			
22	50.93	36.81	44	96.05	2.11			

No.75 2H,7H,4,5-DIHYDROXY-4,5-DIMETHYLPERFLUOROOCTANE (140)

SJS91X 3 S.L.JONES 59/1 08-AUG-84
CAL:CALT2 STA: MW=390 0:32



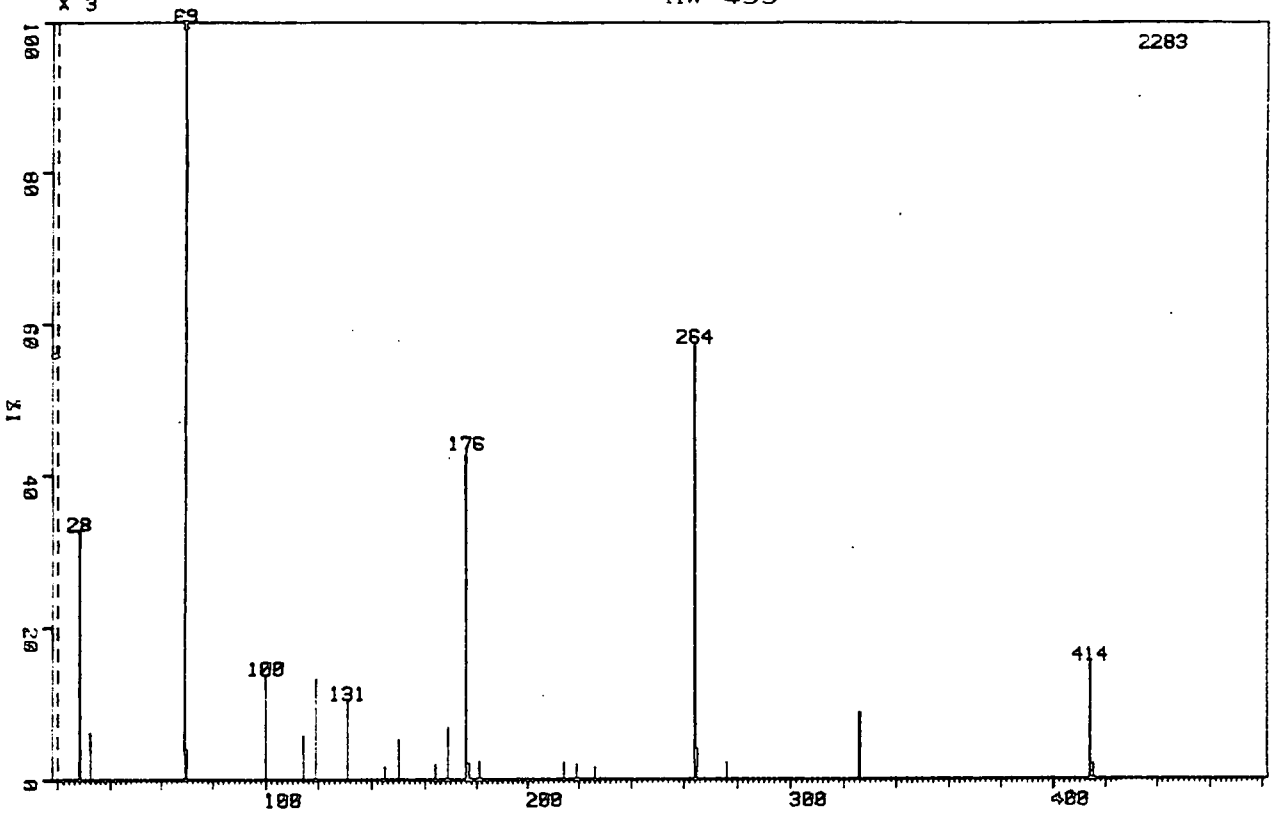
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.14	9.55	23	70.99	3.32	45	155.03	39.25
2	28.02	28.86	24	75.05	3.56	46	157.02	3.59
3	28.88	3.80	25	77.04	20.99	47	168.98	5.39
4	28.91	4.04	26	81.96	5.93	48	170.97	6.14
5	30.76	4.67	27	88.93	4.28	49	174.99	17.22
6	31.87	7.78	28	89.88	2.84	50	190.95	3.05
7	38.88	9.79	29	90.95	8.11	51	193.98	4.70
8	40.85	8.83	30	93.01	9.58	52	194.98	40.24
9	41.92	15.48	31	95.04	3.53	53	195.95	2.60
10	41.95	6.14	32	97.03	4.82	54	196.96	5.96
11	42.98	100.00	33	100.94	4.43	55	216.94	13.02
12	44.03	8.38	34	108.95	12.34	56	218.91	35.66
13	45.06	11.14	35	112.96	11.47	57	219.89	3.50
14	50.87	19.64	36	117.01	3.50	58	236.99	11.95
15	55.09	3.14	37	117.96	4.97			
16	56.10	2.57	38	120.94	2.96			
17	57.04	2.72	39	125.00	7.90			
18	57.08	3.32	40	126.98	4.79			
19	58.95	3.50	41	128.97	4.01			
20	65.08	19.16	42	147.04	2.57			
21	67.04	5.15	43	149.00	2.69			
22	68.96	68.95	44	150.98	32.34			

No.76 PERFLUORO-N-METHYL-2-PROPYLPYRROLIDINE (142)

SJ311 20 S.L.JONES 05-DEC-83

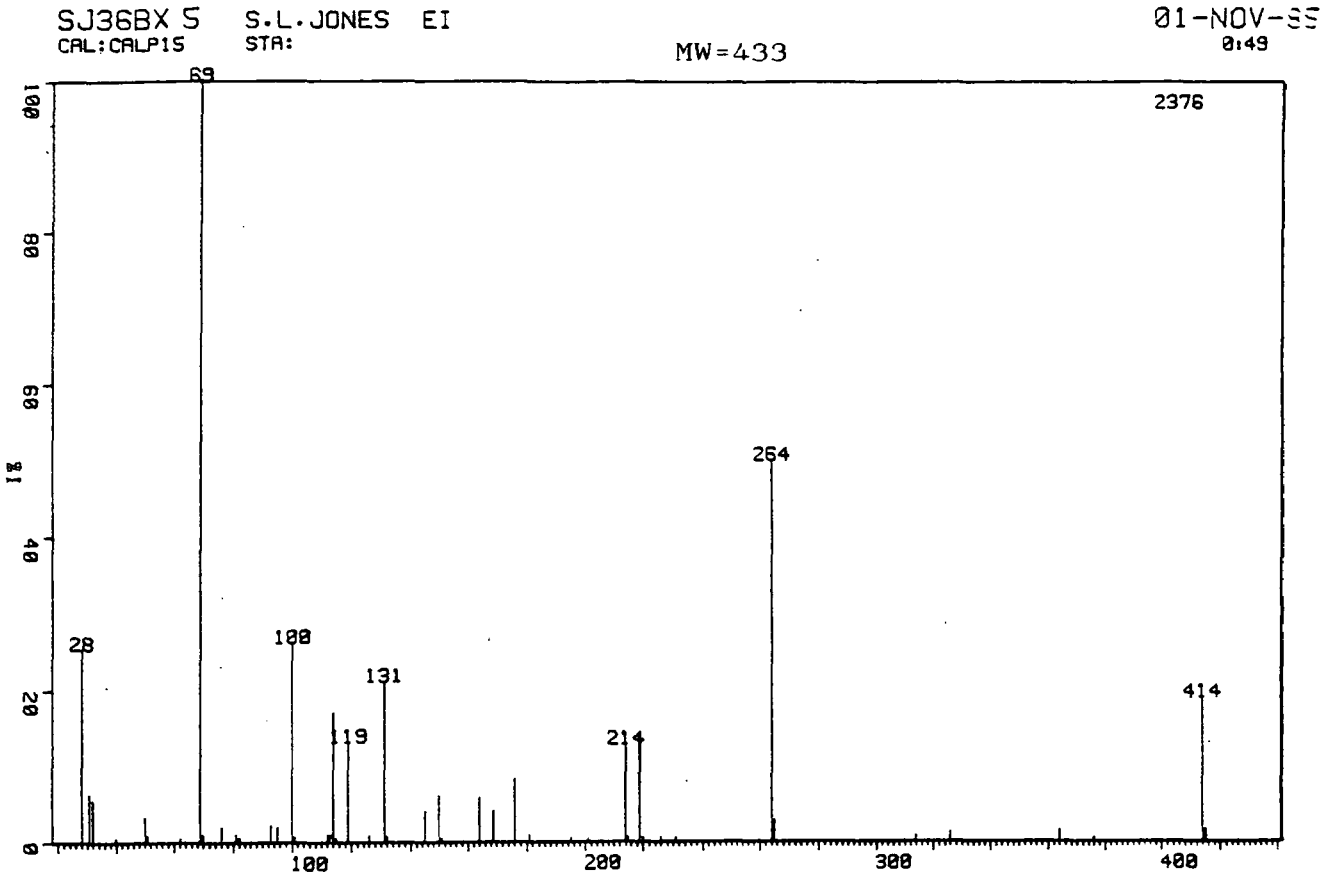
CAL:CALM28
X 3

MW=433



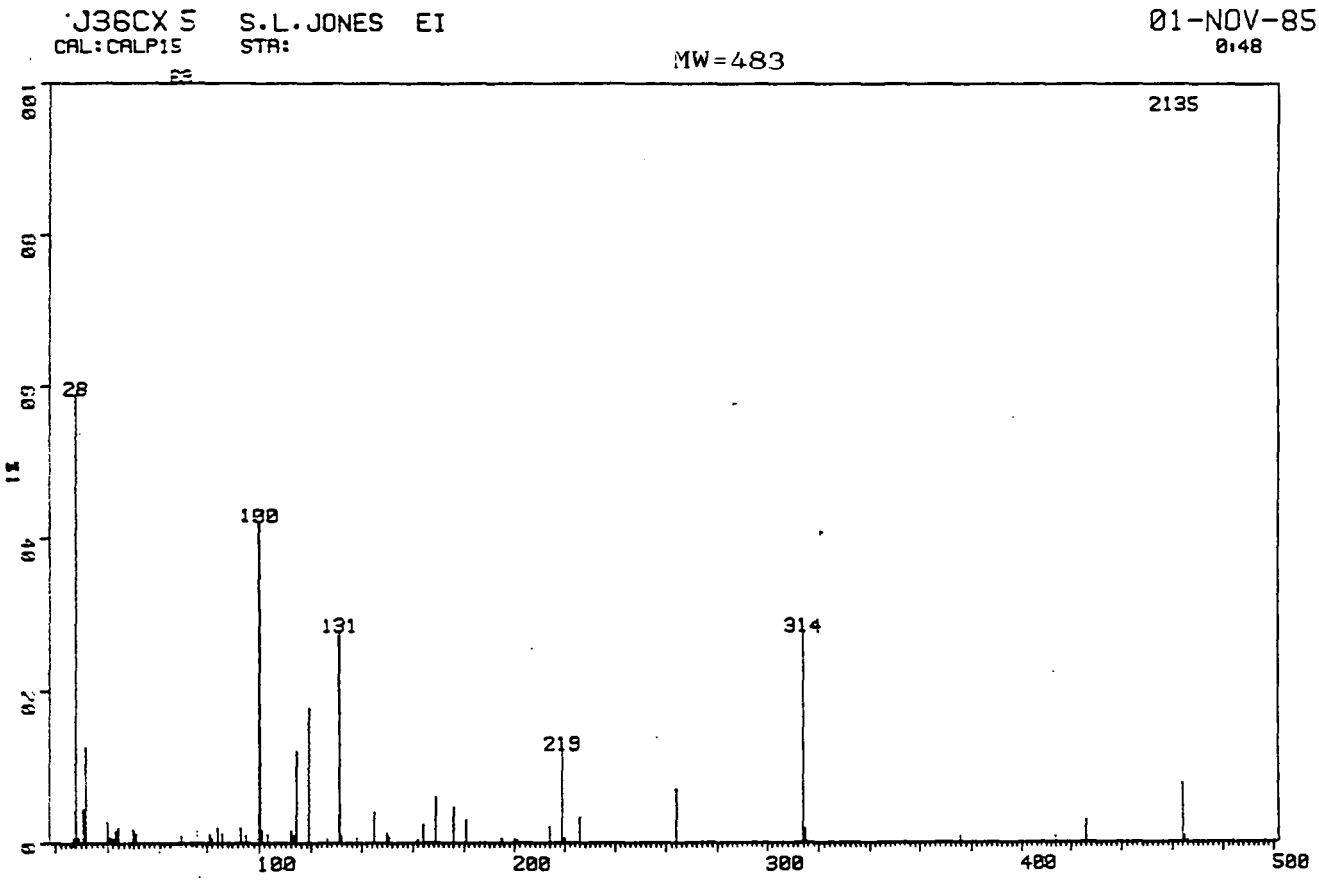
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.06	10.95	23	414.08	5.17
2	31.94	2.06	24	415.17	0.66
3	68.98	100.00			
4	69.92	1.31			
5	99.93	4.60			
6	114.07	1.97			
7	119.01	4.42			
8	131.00	3.50			
9	145.09	0.57			
10	150.00	1.75			
11	164.04	0.66			
12	169.02	2.32			
13	176.09	14.50			
14	177.07	0.70			
15	181.03	0.79			
16	214.09	0.74			
17	219.02	0.66			
18	226.12	0.53			
19	264.03	19.19			
20	265.06	1.31			
21	276.08	0.74			
22	326.09	2.93			

No.77 PERFLUORO-N-BUTYLPYRROLIDINE (145)



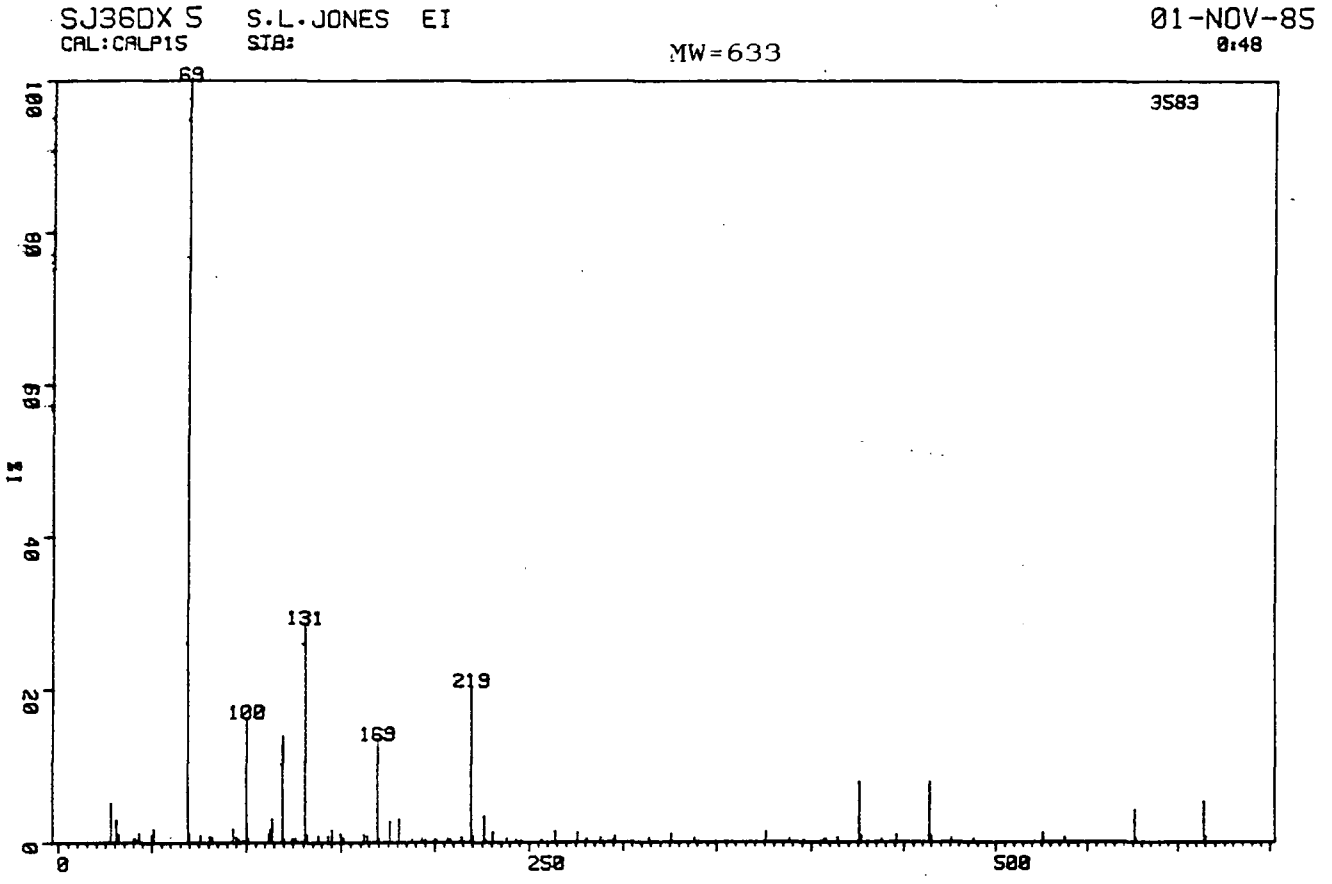
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.10	25.42	23	130.94	21.17	45	375.92	0.55
2	30.85	6.31	24	131.97	0.72	46	413.88	18.98
3	31.95	5.47	25	144.98	4.08	47	414.90	1.68
4	39.79	0.46	26	149.90	6.14			
5	49.86	3.32	27	150.92	0.46			
6	50.93	0.84	28	163.96	5.89			
7	61.99	0.46	29	168.91	4.08			
8	68.95	100.00	30	175.95	8.29			
9	69.89	1.05	31	180.90	0.97			
10	76.07	2.06	32	194.94	0.51			
11	80.96	1.09	33	200.90	0.46			
12	82.02	0.59	34	213.91	12.92			
13	93.02	2.27	35	214.92	0.63			
14	95.05	1.98	36	218.87	13.68			
15	99.92	26.22	37	219.89	0.63			
16	100.96	0.72	38	225.96	0.63			
17	111.99	1.05	39	230.92	0.51			
18	113.01	1.01	40	263.92	50.13			
19	114.02	17.13	41	264.93	2.82			
20	115.03	0.42	42	313.88	0.84			
21	118.95	13.26	43	325.92	1.22			
22	126.00	0.93	44	363.88	1.47			

No.78 PERFLUORO-N-BUTYLPIPERIDINE (146)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.22	0.61	23	99.91	42.20	45	200.91	0.42
2	28.10	58.92	24	100.89	1.73	46	213.95	2.11
3	28.95	0.66	25	100.98	1.08	47	218.91	12.27
4	30.85	4.50	26	102.97	1.17	48	219.90	0.66
5	30.87	0.61	27	112.01	1.59	49	225.96	3.42
6	31.96	12.60	28	113.03	0.94	50	263.92	7.03
7	39.79	2.81	29	114.05	12.04	51	313.88	27.73
8	40.94	0.70	30	118.96	17.75	52	314.90	1.87
9	42.03	0.52	31	126.01	0.52	53	375.87	0.89
10	43.10	1.64	32	130.96	27.73	54	413.86	0.89
11	44.07	2.01	33	131.99	0.94	55	425.87	2.95
12	49.86	1.83	34	137.99	0.70	56	463.87	7.73
13	50.93	1.26	35	145.00	4.03	57	464.87	0.80
14	68.94	100.00	36	149.92	1.26			
15	69.89	0.94	37	150.94	0.84			
16	76.07	1.59	38	161.93	0.42			
17	80.96	1.17	39	163.97	2.39			
18	82.01	0.61	40	168.92	6.04			
19	84.01	2.06	41	175.96	4.68			
20	86.01	1.26	42	180.91	3.04			
21	93.02	2.06	43	194.95	0.61			
22	95.05	1.03	44	199.89	0.56			

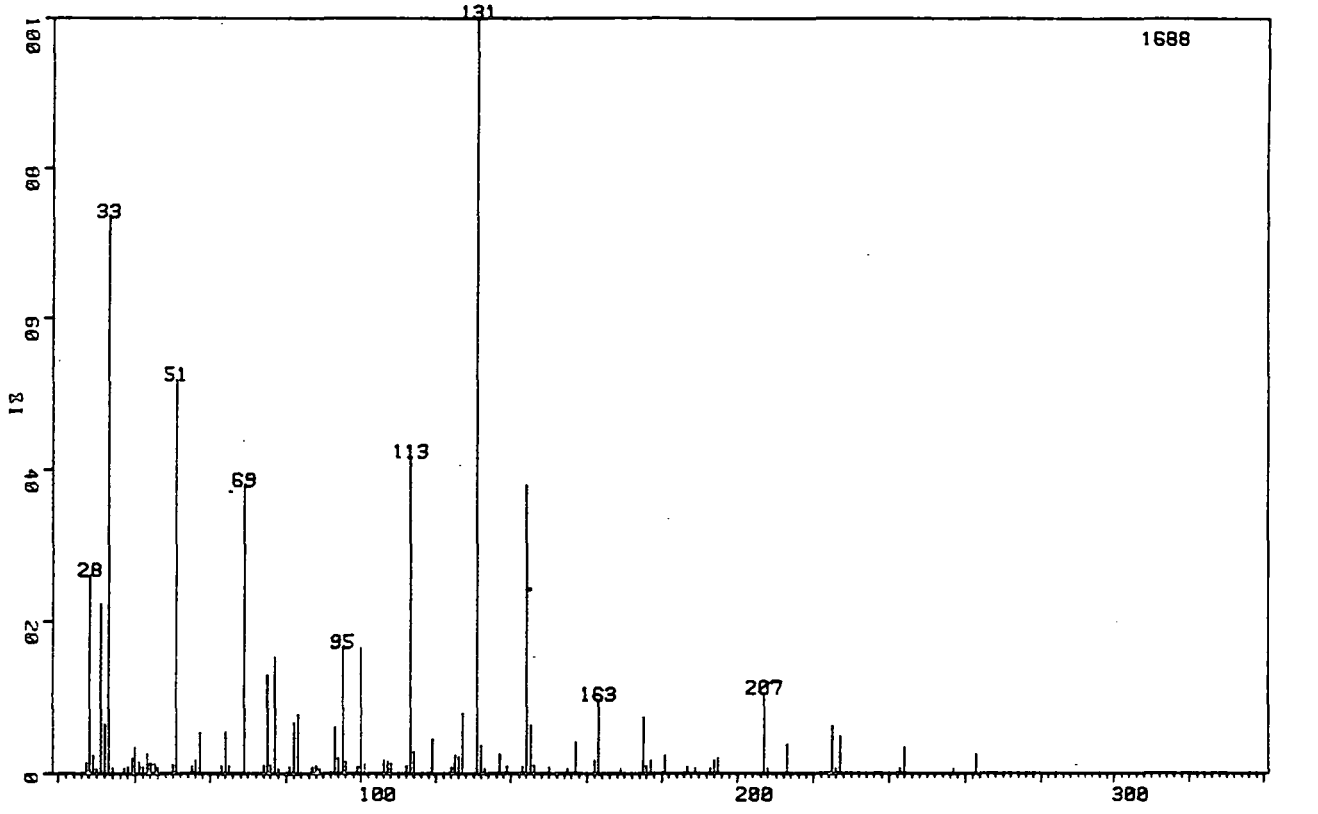
No.79 PERFLUORO-N-BUTYL-2-PROPYLPIPERIDINE (147)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.10	5.22	23	130.93	28.58	45	295.92	0.89
2	30.85	3.01	24	131.96	1.06	46	313.90	0.59
3	31.96	1.09	25	137.97	0.92	47	325.91	1.20
4	39.80	0.50	26	142.98	0.81	48	337.89	0.53
5	40.94	0.64	27	144.98	1.65	49	375.89	1.40
6	43.10	1.26	28	149.90	1.12	50	413.91	0.67
7	49.86	1.03	29	150.92	0.59	51	425.89	7.90
8	50.93	1.79	30	161.94	1.12	52	426.93	0.92
9	68.95	100.00	31	163.96	0.87	53	445.93	1.03
10	69.89	1.23	32	168.91	13.42	54	463.88	7.90
11	76.07	0.98	33	169.90	0.56	55	464.93	0.84
12	80.96	0.81	34	175.97	2.82	56	475.90	0.53
13	82.02	0.78	35	180.92	3.13	57	525.92	1.26
14	93.02	1.84	36	213.94	0.67	58	537.88	0.73
15	95.05	0.73	37	218.90	20.32	59	575.90	4.27
16	99.92	16.22	38	219.91	0.87	60	613.86	5.33
17	100.96	0.53	39	225.95	3.43	61	614.89	0.81
18	111.98	1.12	40	230.91	1.42			
19	113.01	1.65	41	237.93	0.50			
20	114.02	3.18	42	263.91	1.45			
21	118.95	13.95	43	275.89	1.34			
22	126.00	0.53	44	287.92	0.59			

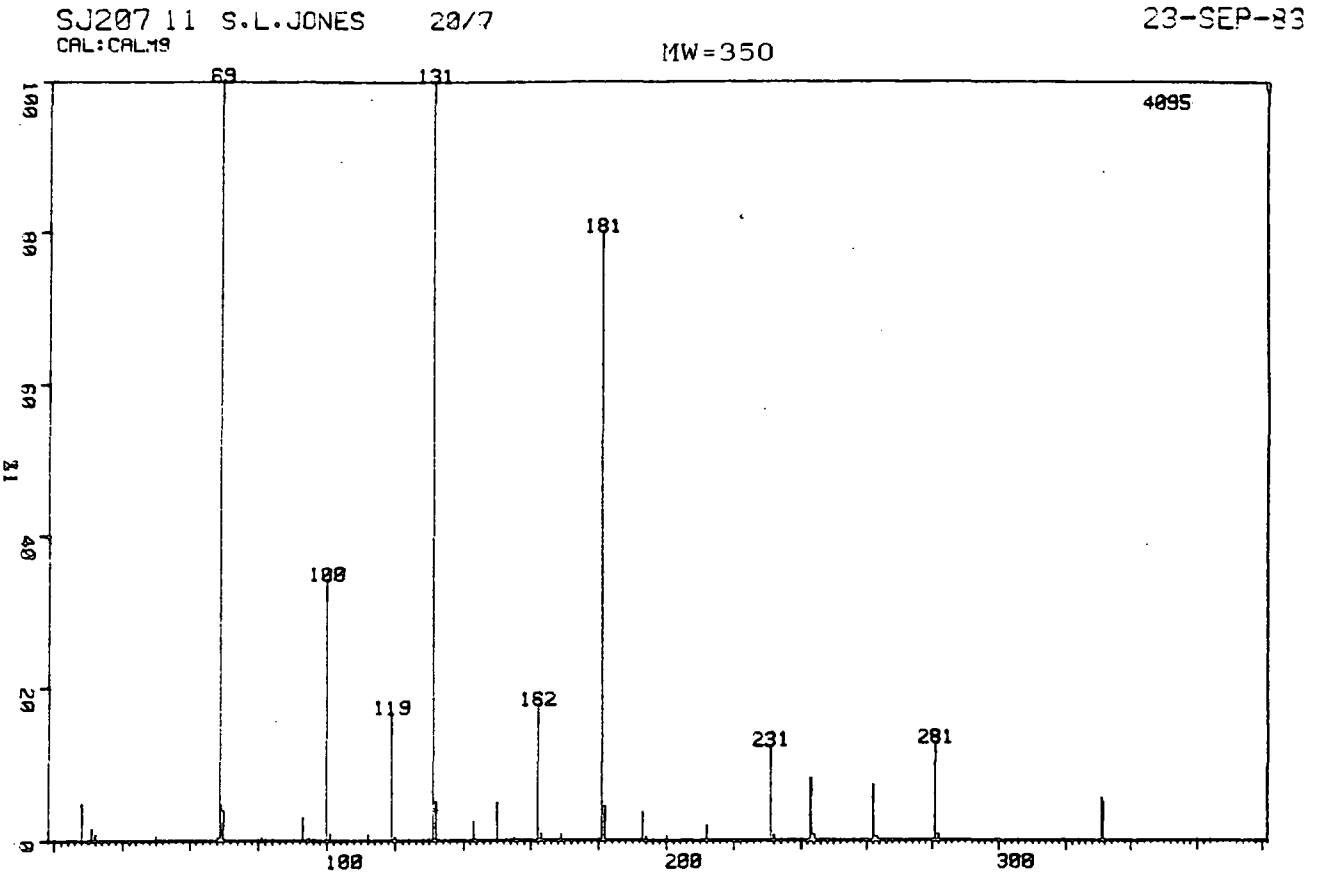
No.80 (2H-DECAFLUOROCYCLOHEXYL)FLUOROMETHANE (148)

SJ205X 10 S.L.JONES 20/5 22-JUL-85
CAL:CALT1 STA: MW=296 1:33



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.30	1.36	23	76.08	1.13	45	131.97	3.73
2	28.17	26.01	24	77.07	15.34	46	137.01	2.55
3	29.02	2.37	25	82.03	6.69	47	144.02	38.09
4	30.94	22.33	26	83.06	7.82	48	145.03	6.34
5	32.03	6.46	27	88.04	1.01	49	146.02	1.01
6	33.13	73.46	28	93.05	6.10	50	157.01	4.15
7	38.99	1.95	29	94.08	2.01	51	161.97	1.72
8	39.83	3.44	30	95.09	16.53	52	162.99	9.66
9	40.98	1.54	31	96.09	1.54	53	175.00	7.46
10	43.13	2.61	32	99.94	16.53	54	176.00	1.07
11	44.17	1.36	33	100.99	1.24	55	177.01	1.84
12	45.15	1.30	34	106.06	1.72	56	180.94	2.37
13	49.88	1.13	35	107.05	1.60	57	193.99	1.72
14	50.94	51.84	36	108.04	1.36	58	194.99	2.01
15	56.09	1.72	37	111.99	1.01	59	206.99	10.55
16	57.08	5.33	38	113.03	41.77	60	212.97	3.85
17	63.05	1.01	39	114.05	2.90	61	224.98	6.22
18	64.08	5.45	40	118.96	4.56	62	226.99	4.92
19	65.10	1.01	41	125.02	2.43	63	243.95	3.44
20	68.96	37.91	42	126.03	2.25	64	262.97	2.61
21	74.06	1.01	43	127.03	7.94			
22	75.08	12.97	44	130.95	100.00			

No.81 PERFLUOROMETHYLCYCLOHEXANE (149)

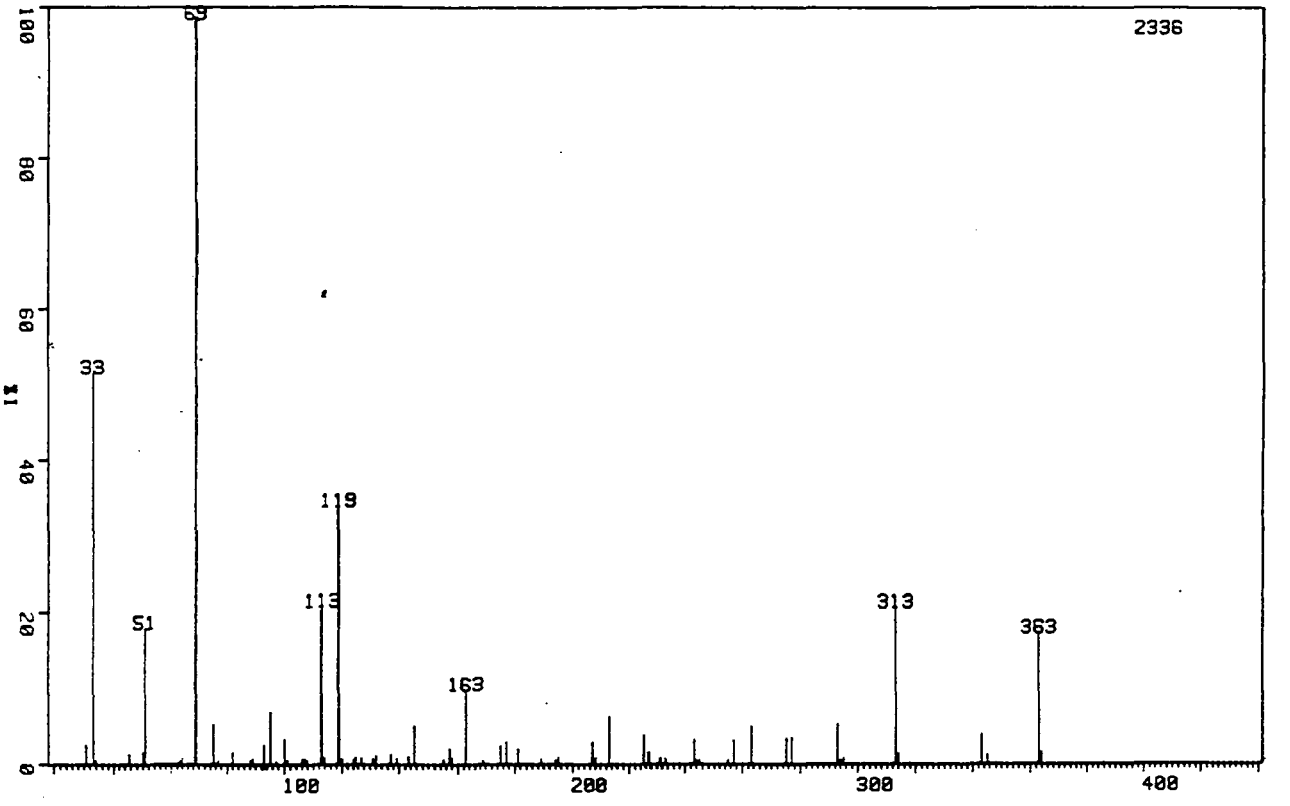


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.12	4.79	23	155.03	0.32
2	30.90	1.44	24	161.97	17.68
3	32.01	0.83	25	163.00	0.88
4	49.87	0.51	26	168.98	0.81
5	68.24	0.34	27	180.95	80.15
6	68.96	100.00	28	181.85	4.47
7	69.18	4.66	29	193.01	3.66
8	69.87	3.88	30	194.06	0.37
9	80.93	0.29	31	199.95	0.46
10	92.99	3.03	32	212.01	1.88
11	94.66	0.27	33	231.01	12.38
12	94.92	0.22	34	231.96	0.76
13	99.89	34.16	35	243.03	8.16
14	100.97	0.90	36	244.06	0.66
15	112.02	0.76	37	261.97	7.16
16	118.95	16.63	38	263.04	0.46
17	119.94	0.37	39	280.97	12.77
18	129.66	0.24	40	282.02	0.83
19	130.95	100.00	41	330.84	5.52
20	131.90	5.03	42	331.38	5.05
21	143.00	2.47			
22	149.92	4.96			

No.82 3-FLUOROMETHYLPERFLUORO-4H,3,4-DIMETHYLHEXANE (150)

SJ831X 4 S.L.JONES 10-MAY-85
CAL:CAL26 STA:E. 8:42

MW=434

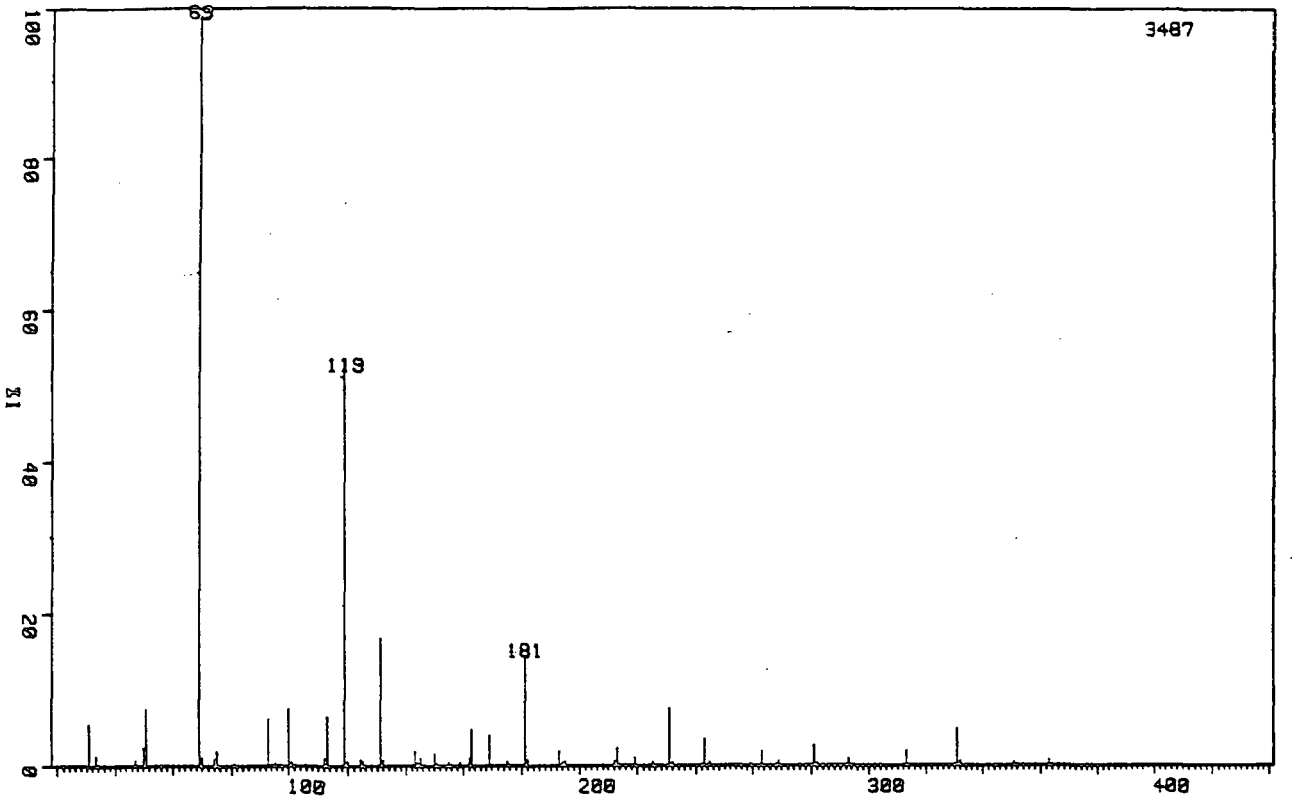


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	30.84	2.61	23	127.08	0.81	45	231.04	0.81
2	33.06	51.58	24	131.01	0.73	46	233.07	0.73
3	45.13	1.37	25	132.04	1.16	47	243.06	3.30
4	49.87	1.58	26	137.07	1.33	48	244.10	0.64
5	50.93	17.89	27	139.04	0.77	49	245.09	0.64
6	64.08	0.81	28	143.05	0.98	50	257.09	3.21
7	68.96	98.37	29	145.08	5.09	51	263.07	5.01
8	75.06	5.35	30	155.06	0.64	52	275.07	3.38
9	81.97	1.58	31	157.07	2.10	53	277.07	3.51
10	88.99	0.77	32	158.06	0.90	54	293.08	5.35
11	93.05	2.61	33	163.06	9.80	55	295.08	0.81
12	95.09	6.93	34	175.08	2.44	56	313.05	20.68
13	99.96	3.30	35	177.09	3.00	57	314.08	1.46
14	101.01	0.64	36	181.02	2.05	58	343.06	3.98
15	106.08	0.73	37	189.05	0.73	59	345.08	1.24
16	107.07	0.81	38	194.07	0.64	60	363.07	17.34
17	113.06	20.80	39	195.08	0.98	61	364.08	1.54
18	114.09	0.90	40	207.07	3.00			
19	119.01	33.95	41	208.05	0.90			
20	119.98	0.73	42	213.07	6.29			
21	124.08	0.64	43	225.09	3.90			
22	125.08	0.98	44	227.08	1.63			

No.83 PERFLUORO-3,3,4-TRIMETHYLHEXANE (151)

SJ832X 6 S.L.JONES 10-MAY-85
CAL:CAL26 STR:E. 8:59

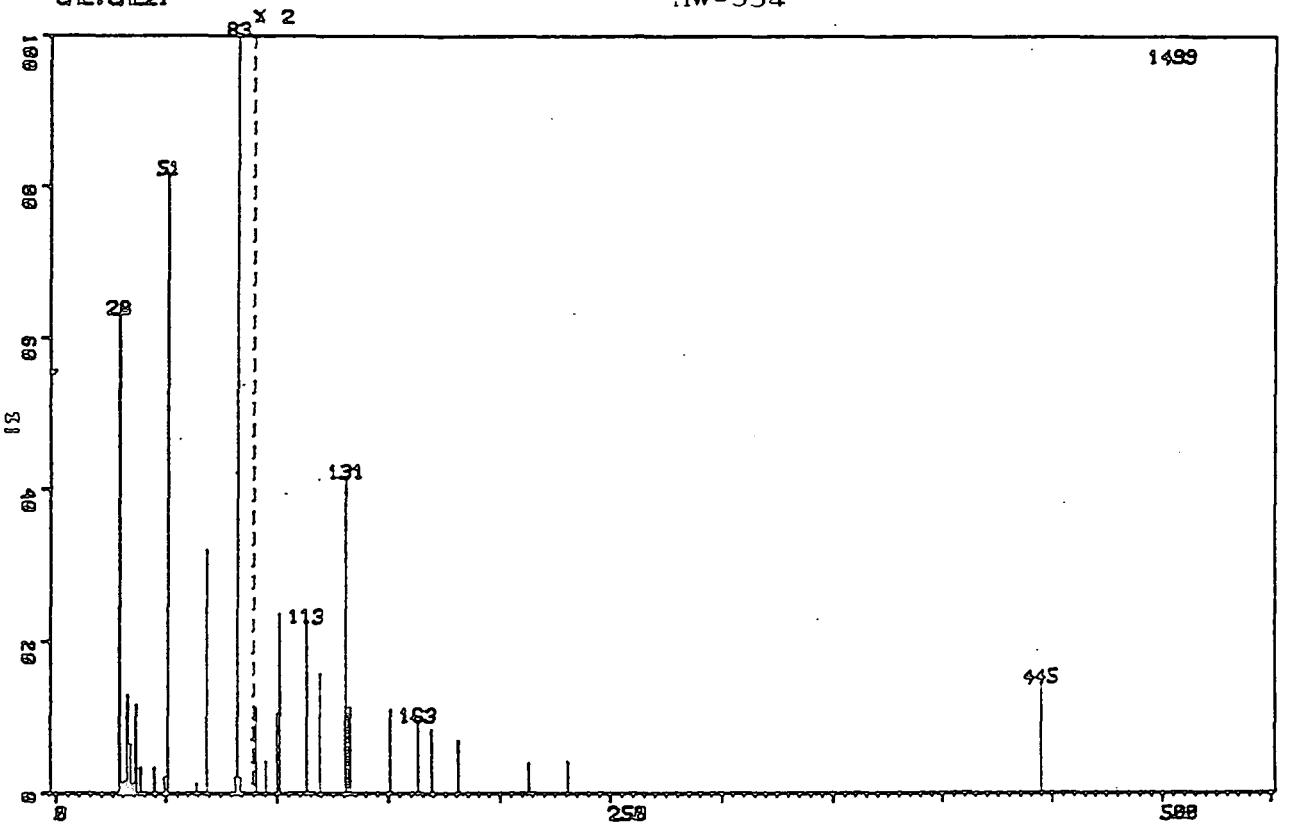
MW=488



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	30.84	5.53	23	132.02	0.75	45	232.04	0.37
2	33.06	1.32	24	143.04	1.95	46	243.04	3.44
3	47.05	0.75	25	144.05	0.43	47	245.06	0.40
4	49.86	2.44	26	145.06	1.06	48	259.00	0.40
5	50.93	7.51	27	149.94	1.58	49	263.02	1.98
6	68.94	98.65	28	150.97	0.34	50	268.99	0.60
7	69.89	1.12	29	155.04	0.54	51	280.98	2.67
8	74.04	0.86	30	158.99	0.40	52	282.02	0.34
9	75.05	1.95	31	162.02	1.06	53	293.02	0.92
10	80.90	0.23	32	163.04	4.73	54	313.02	1.98
11	93.03	6.17	33	168.99	4.01	55	331.02	4.85
12	95.07	0.26	34	175.06	0.60	56	332.01	0.43
13	97.04	0.20	35	180.99	14.31	57	350.98	0.49
14	99.94	7.54	36	182.02	0.75	58	363.00	0.75
15	100.99	0.43	37	193.02	1.98			
16	112.02	1.03	38	194.03	0.40			
17	113.05	6.54	39	195.05	0.54			
18	119.00	52.08	40	212.02	0.57			
19	119.96	0.63	41	213.03	2.35			
20	124.05	0.89	42	218.99	1.12			
21	125.07	0.57	43	225.05	0.54			
22	131.00	16.83	44	231.00	7.54			

No.84 PERFLUORO-1H,1H,11H-UNDECANE (152)

SJ252 7 S.L.JONES 25/2 21-OCT-83
CRL:CRL21 MW=534



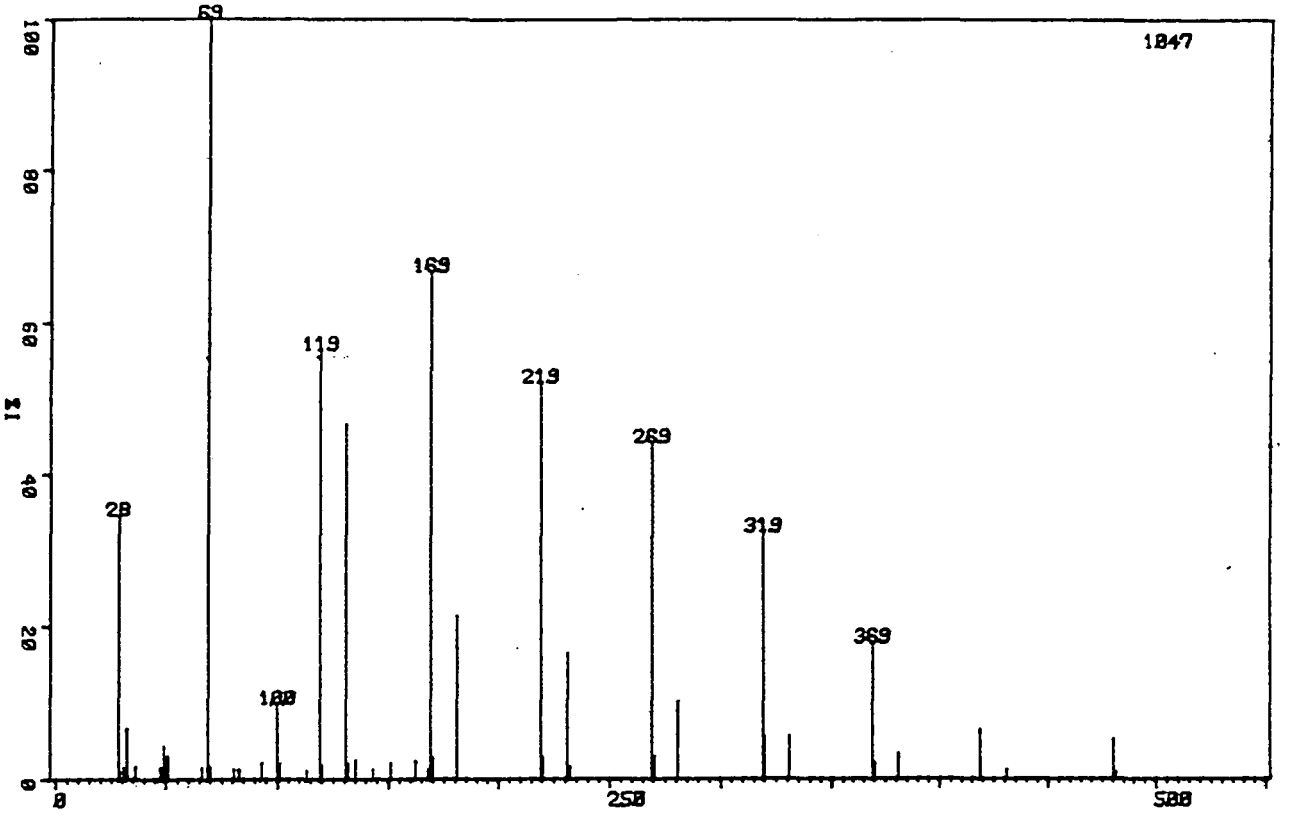
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.13	63.18	23	130.98	20.81
2	29.00	1.40	24	133.06	5.67
3	30.92	1.53	25	150.97	5.47
4	32.02	12.88	26	163.03	4.74
5	33.13	6.34	27	169.03	4.20
6	35.16	1.27	28	181.01	3.47
7	36.15	11.67	29	213.06	1.93
8	38.06	3.27	30	231.01	2.07
9	44.14	3.34	31	444.74	7.27
10	48.99	1.93			
11	50.95	81.59			
12	64.14	1.27			
13	68.97	31.95			
14	82.00	2.20			
15	83.03	100.00			
16	84.09	2.07			
17	91.02	5.60			
18	95.08	2.07			
19	99.93	5.27			
20	100.97	11.81			
21	113.00	11.27			
22	118.98	7.87			

No.85 PERFLUOROUNDECANE (153)

SJ253 S S.L.JONES
CAL:CAL24

MW=588

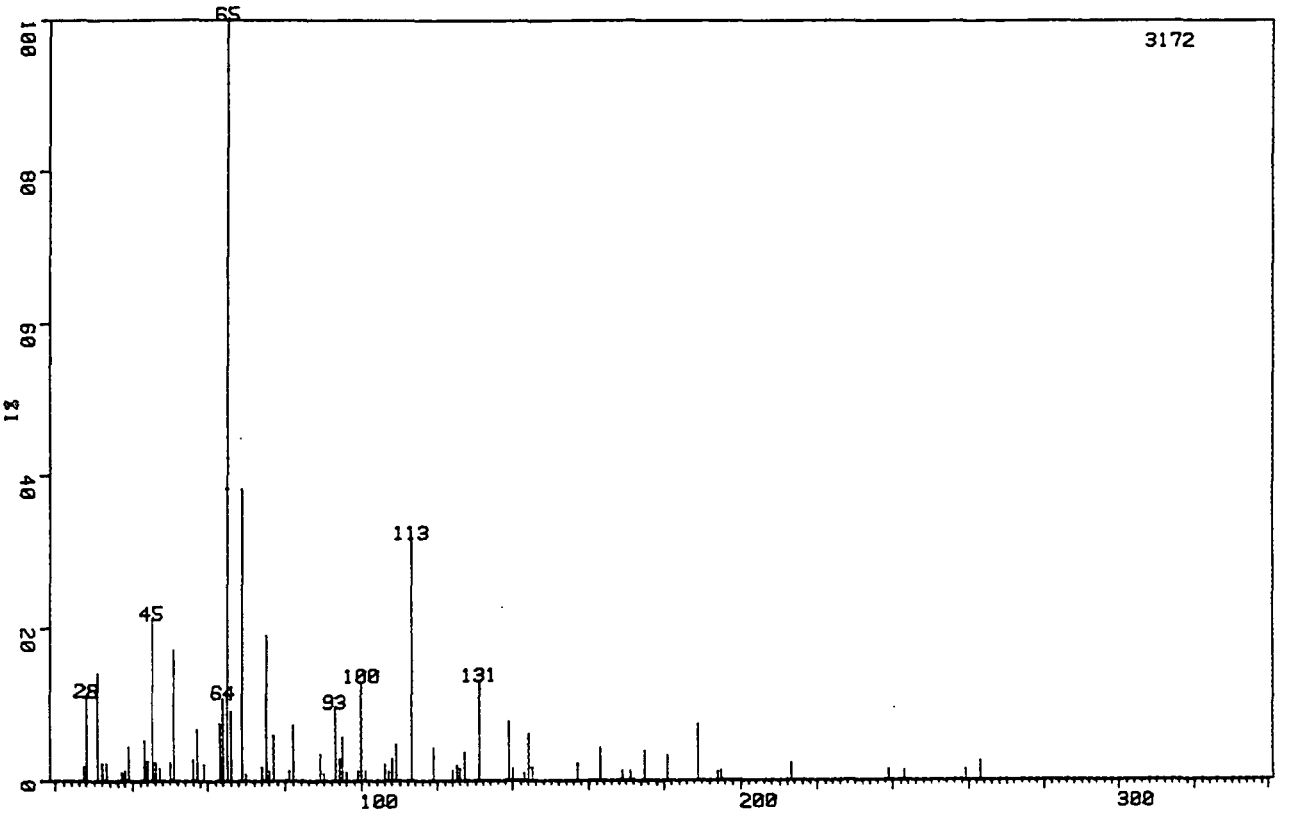
24-OCT-83



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.12	34.57	23	132.09	2.01	45	381.14	3.25
2	28.99	1.05	24	135.14	2.48	46	418.75	6.40
3	30.92	1.53	25	143.08	1.34	47	431.09	1.24
4	32.02	6.59	26	151.02	2.10	48	480.43	5.16
5	36.16	1.62	27	162.12	2.29	49	481.41	0.86
6	47.13	1.43	28	167.87	1.15			
7	48.09	1.34	29	169.00	66.76			
8	49.00	4.39	30	170.06	2.77			
9	51.00	3.06	31	181.11	21.30			
10	66.17	1.43	32	219.07	52.24			
11	68.97	100.00	33	219.48	1.72			
12	69.18	1.05	34	220.11	2.77			
13	69.89	1.62	35	231.09	16.43			
14	80.94	1.34	36	232.13	1.43			
15	83.07	1.24	37	269.09	44.32			
16	93.05	2.20	38	270.15	2.96			
17	99.92	9.84	39	281.04	10.12			
18	101.00	2.01	40	318.98	32.57			
19	113.08	1.15	41	319.78	5.44			
20	119.01	56.64	42	331.03	5.64			
21	120.00	1.81	43	369.04	17.86			
22	131.03	46.70	44	370.15	2.01			

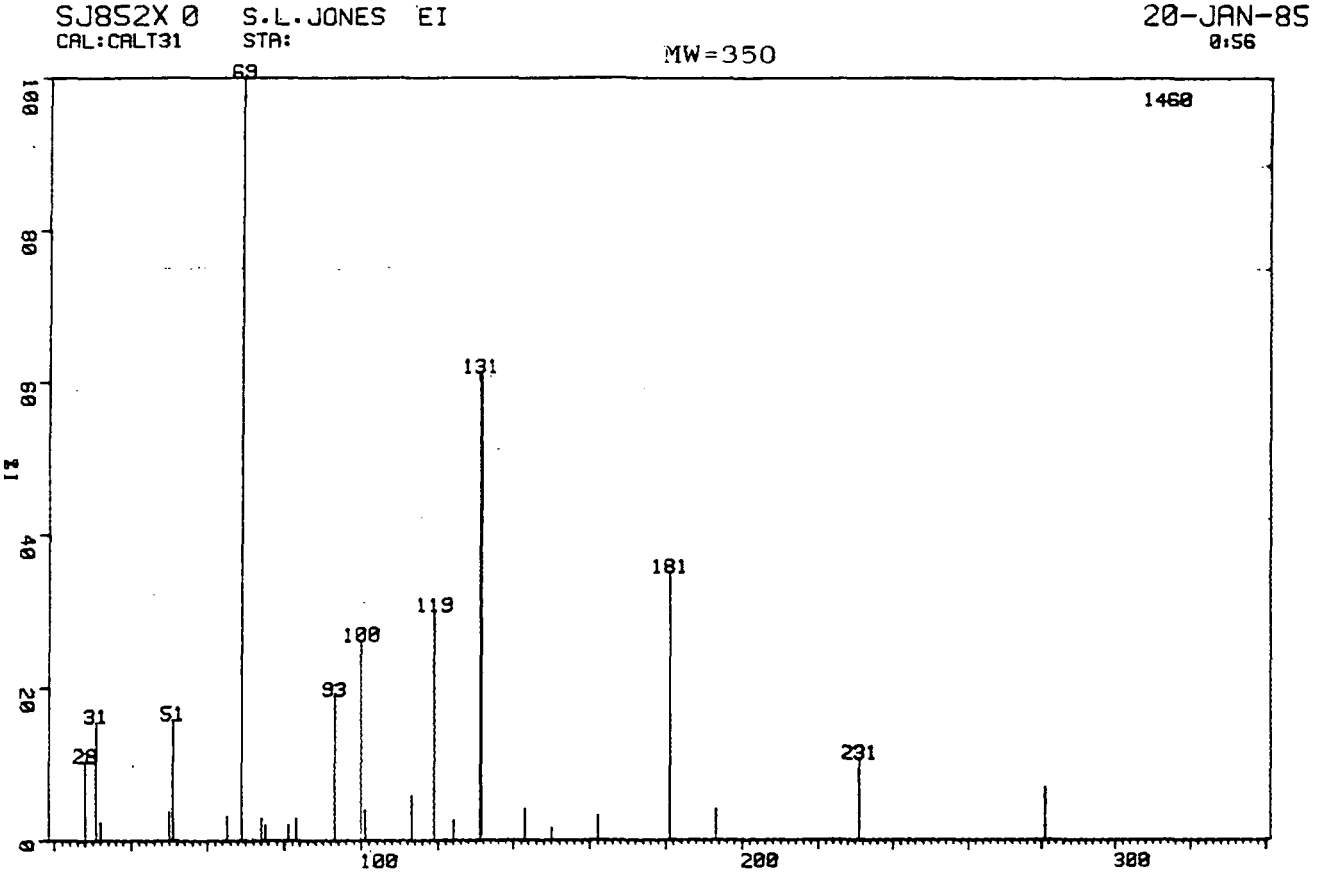
No.86 1-(2H-OCTAFLUOROCYCLOPENTYL)-1,1-DIFLUOROETHANE (154)

SJ851X 0 S.L.JONES EI 20-JAN-85
CAL:CALT31 STA: MW=278 0:35



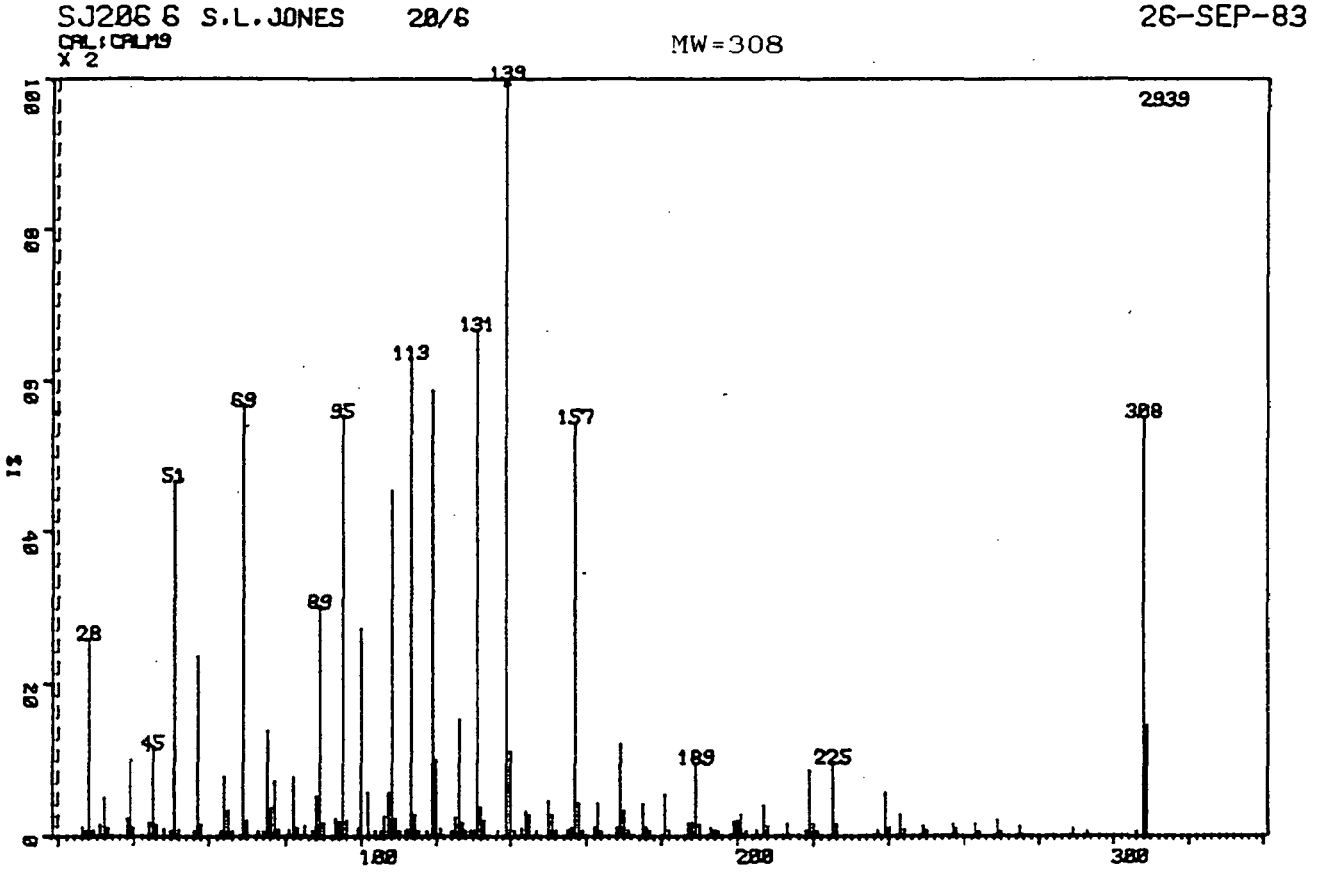
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.23	1.89	23	68.96	38.30	45	126.07	1.64
2	28.11	11.07	24	74.05	1.80	46	127.06	3.78
3	30.86	14.12	25	75.06	19.14	47	130.99	13.11
4	31.97	2.30	26	76.07	1.20	48	139.02	7.79
5	33.08	2.33	27	77.06	6.05	49	140.00	1.67
6	38.04	1.42	28	80.95	1.29	50	144.05	6.15
7	38.96	4.51	29	82.00	7.31	51	145.06	1.80
8	43.07	5.26	30	88.98	3.59	52	157.05	2.24
9	43.11	1.89	31	93.01	9.55	53	163.05	4.29
10	44.10	2.62	32	94.04	2.90	54	169.02	1.39
11	45.12	21.19	33	95.06	5.80	55	171.04	1.23
12	46.12	2.43	34	98.97	1.36	56	175.05	3.88
13	47.10	1.67	35	99.92	12.99	57	180.99	3.31
14	49.87	2.43	36	100.98	1.32	58	189.03	7.31
15	50.94	17.15	37	106.05	2.18	59	194.04	1.20
16	56.10	2.77	38	107.04	1.20	60	195.06	1.23
17	57.08	6.65	39	108.03	2.99	61	213.06	2.24
18	59.00	2.18	40	109.01	4.82	62	239.03	1.48
19	63.08	7.57	41	113.03	31.75	63	243.02	1.36
20	64.10	10.84	42	119.00	4.35	64	259.07	1.54
21	65.09	100.00	43	124.05	1.39	65	263.04	2.62
22	66.09	9.08	44	125.06	2.02			

No.87 PERFLUOROETHYLCYCLOPENTANE (155)



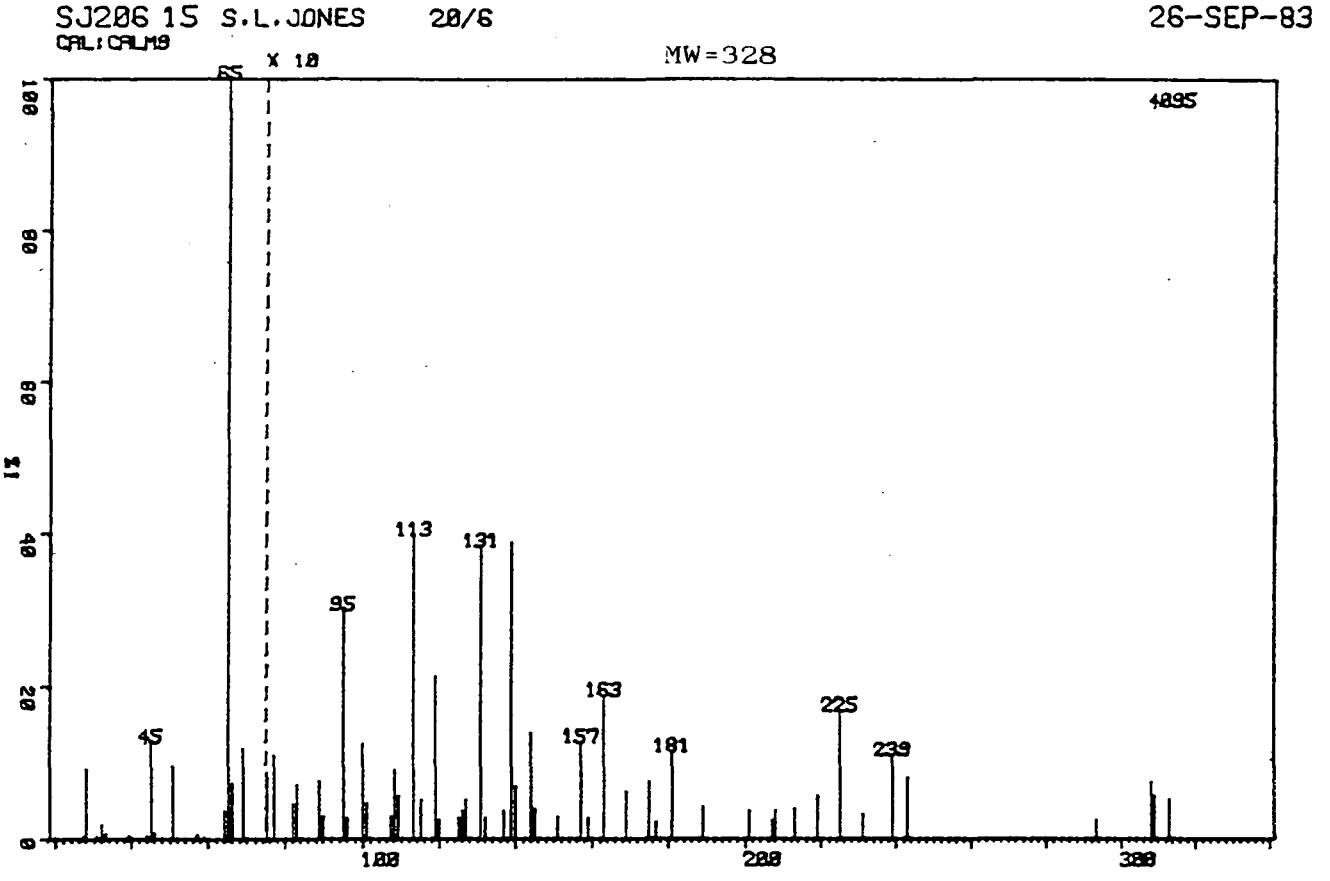
NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.11	10.41	23	193.05	4.04
2	30.86	15.55	24	231.00	10.68
3	31.97	2.40	25	281.03	6.99
4	49.87	3.84			
5	50.94	15.89			
6	65.12	3.22			
7	68.96	100.00			
8	74.06	2.95			
9	75.07	2.05			
10	80.95	2.12			
11	83.04	2.95			
12	93.02	19.04			
13	99.92	26.23			
14	100.97	3.90			
15	113.04	5.96			
16	119.00	30.14			
17	124.05	2.67			
18	131.00	61.30			
19	143.05	4.11			
20	150.00	1.64			
21	162.04	3.29			
22	181.02	35.07			

No.88 1-(2H-DECAFLUOROCYCLOHEXYL)-1-FLUOROETHENE (156)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.12	12.90	23	106.05	1.26	45	169.04	6.09
2	32.00	2.55	24	107.04	2.96	46	170.04	1.70
3	38.07	1.16	25	108.02	22.76	47	175.08	2.14
4	38.99	5.14	26	108.99	1.16	48	181.04	2.76
5	45.14	5.82	27	113.03	31.44	49	189.01	4.80
6	50.94	23.34	28	114.03	1.43	50	201.01	1.43
7	57.08	11.81	29	118.98	29.33	51	207.05	1.97
8	64.10	3.95	30	119.79	5.00	52	219.03	4.39
9	65.09	1.74	31	125.08	1.19	53	225.06	4.83
10	68.94	28.34	32	126.09	7.66	54	238.93	2.82
11	69.90	1.02	33	131.00	33.34	55	243.06	1.40
12	75.08	6.91	34	132.03	1.87	56	269.01	1.05
13	76.08	1.80	35	133.03	1.02	57	306.09	0.31
14	77.07	3.64	36	138.84	100.00	58	308.04	27.59
15	81.99	3.84	37	139.93	5.58	59	308.96	7.28
16	88.01	2.59	38	144.08	1.60			
17	88.98	15.01	39	145.10	1.33			
18	93.01	1.16	40	149.99	2.35			
19	95.05	27.63	41	151.03	1.33			
20	96.06	1.09	42	157.06	27.25			
21	99.92	13.61	43	158.06	2.21			
22	101.68	2.96	44	163.03	2.21			

No.89 1-(2H-DECAFLUOROCYCLOHEXYL)-1,1-DIFLUOROETHANE (157)

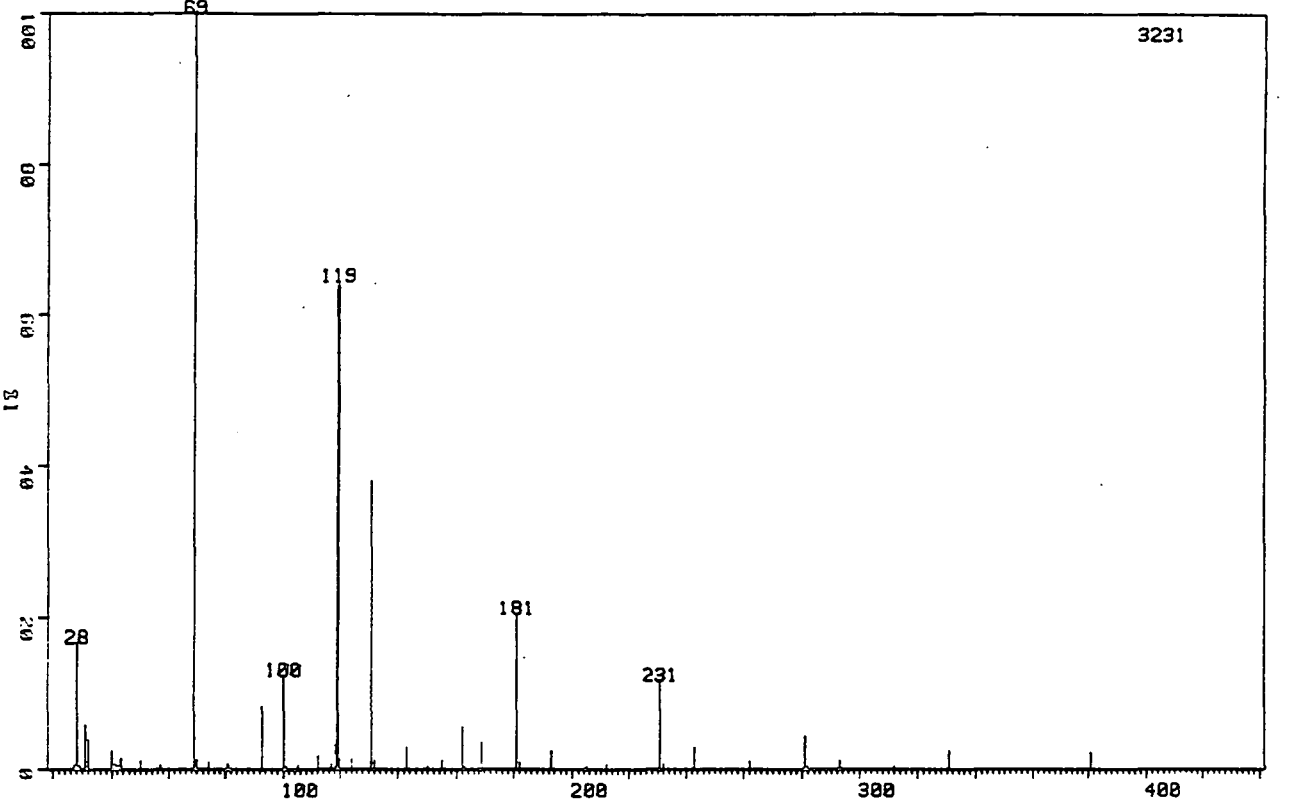


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.24	0.34	23	89.91	0.29	45	157.00	1.27
2	28.12	9.11	24	95.02	3.00	46	158.96	0.27
3	30.90	0.34	25	96.01	0.27	47	163.02	1.88
4	32.01	1.90	26	99.88	1.25	48	169.00	0.61
5	33.12	0.68	27	100.97	0.46	49	175.05	0.73
6	39.00	0.42	28	107.05	0.29	50	180.97	1.15
7	44.13	0.29	29	108.02	0.90	51	189.01	0.42
8	45.15	12.72	30	109.01	0.56	52	200.95	0.37
9	46.15	0.81	31	113.03	3.98	53	208.00	0.37
10	50.94	9.62	32	115.05	0.51	54	213.02	0.39
11	57.10	0.59	33	118.95	2.12	55	219.00	0.56
12	59.00	0.27	34	125.05	0.27	56	225.00	1.68
13	64.10	3.66	35	126.02	0.37	57	231.01	0.32
14	65.09	100.00	36	127.03	0.51	58	239.02	1.10
15	65.35	2.10	37	130.96	3.83	59	242.99	0.81
16	66.10	7.16	38	131.95	0.27	60	308.03	0.76
17	68.93	11.79	39	137.00	0.37	61	309.00	0.56
18	75.03	0.81	40	138.98	3.88	62	313.01	0.51
19	77.03	1.10	41	139.95	0.68			
20	81.97	0.46	42	144.01	1.39			
21	82.99	0.71	43	145.04	0.39			
22	88.94	0.76	44	150.94	0.29			

No.90 PERFLUOROETHYLCYCLOHEXANE (158)

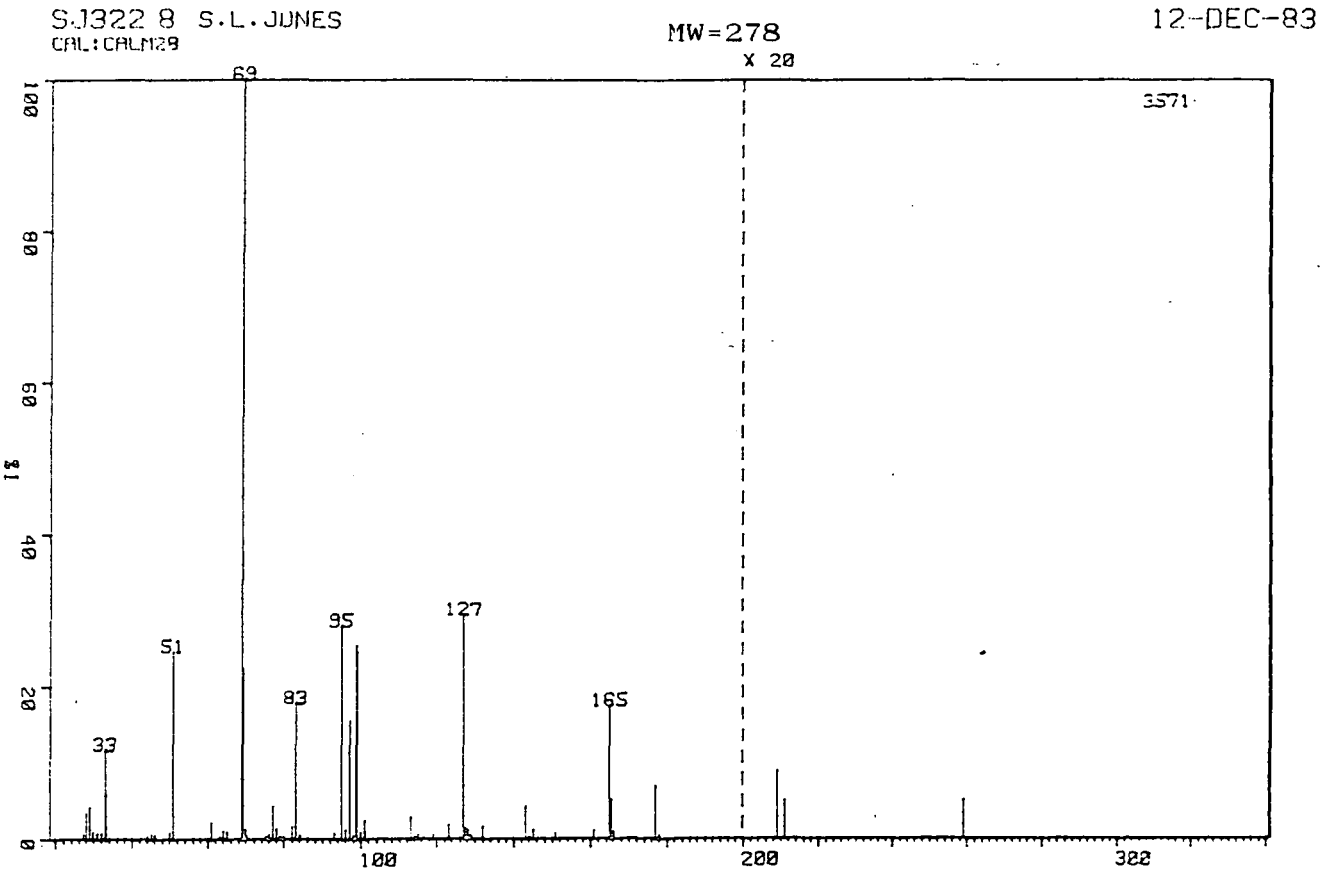
S2012X 5 S.L.JONES 20/12 22-JUL-85
CAL:CALT1 STR: 0:50

MW=400



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.29	0.46	23	119.92	1.39	45	311.90	0.31
2	28.17	16.65	24	124.01	1.36	46	330.85	2.57
3	29.05	0.43	25	130.93	38.10	47	380.81	2.26
4	30.93	5.91	26	131.96	1.21			
5	32.03	3.87	27	142.98	2.94			
6	39.82	2.45	28	149.90	0.34			
7	40.97	0.74	29	154.99	1.15			
8	42.06	0.43	30	161.94	5.66			
9	43.12	1.45	31	162.96	0.34			
10	49.87	1.21	32	168.91	3.62			
11	57.12	0.53	33	180.90	20.55			
12	68.95	100.00	34	181.92	0.93			
13	69.89	1.15	35	192.94	2.45			
14	74.07	0.99	36	204.93	0.34			
15	80.97	0.77	37	211.89	0.65			
16	93.05	8.33	38	230.89	11.70			
17	99.95	12.35	39	231.93	0.71			
18	100.98	0.34	40	242.93	2.88			
19	105.06	0.46	41	261.91	1.11			
20	112.00	1.76	42	280.87	4.49			
21	117.00	0.59	43	281.92	0.31			
22	118.95	64.47	44	292.94	1.15			

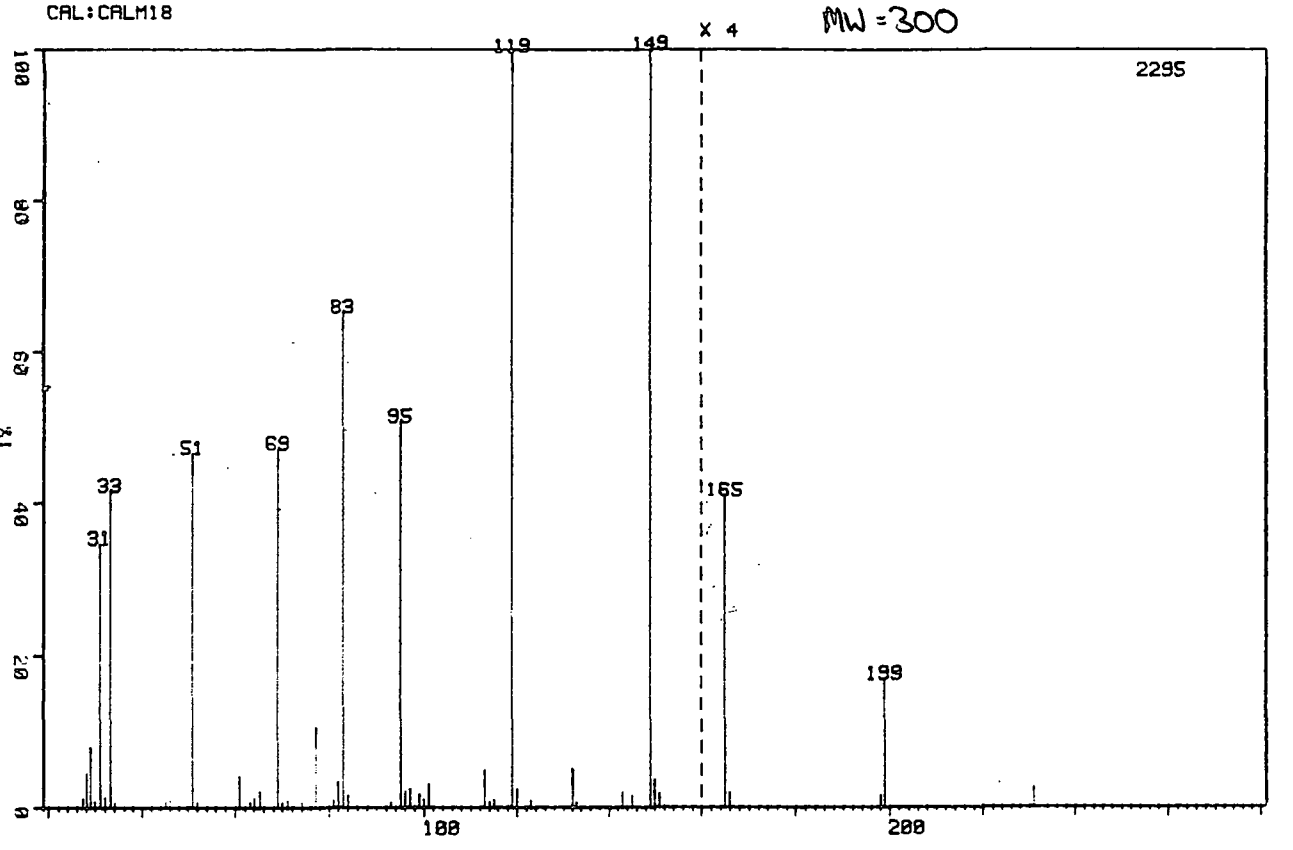
No.91 1H,1H,3H-HEXAFLUOROBUTYLTRIFLUOROACETATE (159)



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.19	0.59	23	75.05	0.42	45	123.08	1.79
2	28.06	3.36	24	76.07	0.62	46	127.05	29.38
3	28.93	4.14	25	77.06	4.23	47	127.57	1.40
4	29.78	0.98	26	78.02	1.43	48	128.03	1.09
5	30.85	0.64	27	78.96	0.31	49	129.00	0.42
6	31.94	0.73	28	79.91	0.34	50	132.06	1.71
7	33.06	11.65	29	82.02	1.60	51	143.08	4.14
8	33.12	5.88	30	83.03	17.75	52	144.10	0.31
9	44.10	0.48	31	84.07	0.48	53	145.13	1.20
10	45.13	0.70	32	93.04	0.76	54	150.96	0.76
11	46.15	0.53	33	95.04	27.98	55	160.97	1.09
12	49.87	0.81	34	96.05	1.15	56	165.04	17.39
13	50.95	24.59	35	97.03	15.46	57	165.43	5.04
14	60.96	2.21	36	97.99	0.45	58	166.04	0.84
15	63.07	0.34	37	98.91	25.43	59	177.04	6.89
16	64.12	1.09	38	99.01	24.61	60	178.08	0.36
17	65.09	0.95	39	99.91	0.92	61	209.05	0.45
18	68.96	100.00	40	101.01	2.46	62	211.07	0.25
19	69.11	21.73	41	113.03	2.80	63	259.06	0.25
20	69.13	22.40	42	114.06	0.34			
21	69.84	1.23	43	115.08	0.50			
22	70.07	0.42	44	119.00	0.53			

No. 92 PERFLUORO-1-ETHOXY-1H, 1H, 3H-BUTANE (160)

SJ323 3 S.L.JONES 18-JAN-84
CAL:CALM18

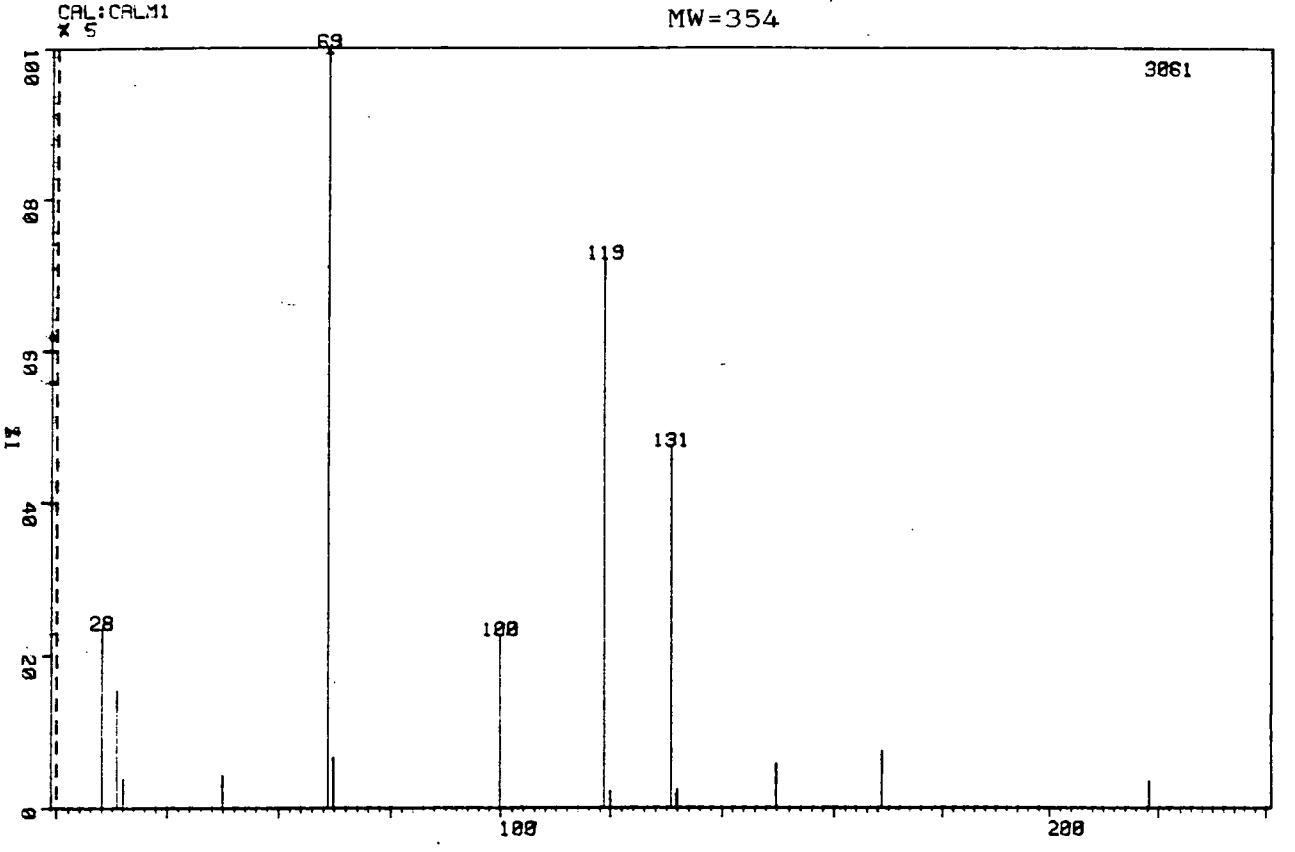


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.24	1.09	23	81.96	3.18	45	150.92	1.79
2	28.12	4.49	24	83.01	65.19	46	164.98	10.24
3	28.99	7.84	25	84.04	1.48	47	165.98	0.48
4	29.83	0.78	26	93.03	0.65	48	197.93	0.39
5	30.91	34.64	27	95.05	50.68	49	198.89	4.23
6	32.01	1.35	28	96.05	2.09	50	230.95	0.65
7	33.11	41.57	29	97.01	2.48			
8	34.17	0.44	30	98.97	1.74			
9	45.14	0.65	31	99.93	1.05			
10	46.14	0.96	32	100.96	3.01			
11	50.94	46.49	33	113.00	4.84			
12	52.02	0.44	34	114.03	0.78			
13	60.97	4.10	35	115.05	1.05			
14	63.06	0.61	36	118.94	99.65			
15	64.09	1.13	37	119.91	2.40			
16	65.11	2.14	38	123.02	0.92			
17	68.93	47.10	39	131.94	5.01			
18	69.86	0.52	40	132.97	0.70			
19	71.01	0.87	41	142.97	1.96			
20	74.06	0.48	42	144.98	1.53			
21	77.04	10.63	43	148.93	100.00			
22	80.93	0.96	44	149.91	3.57			

No.93 PERFLUOROETHOXYBUTANE (162)

SJ324 6 S.L.JONES 32/4 02-MAR-76

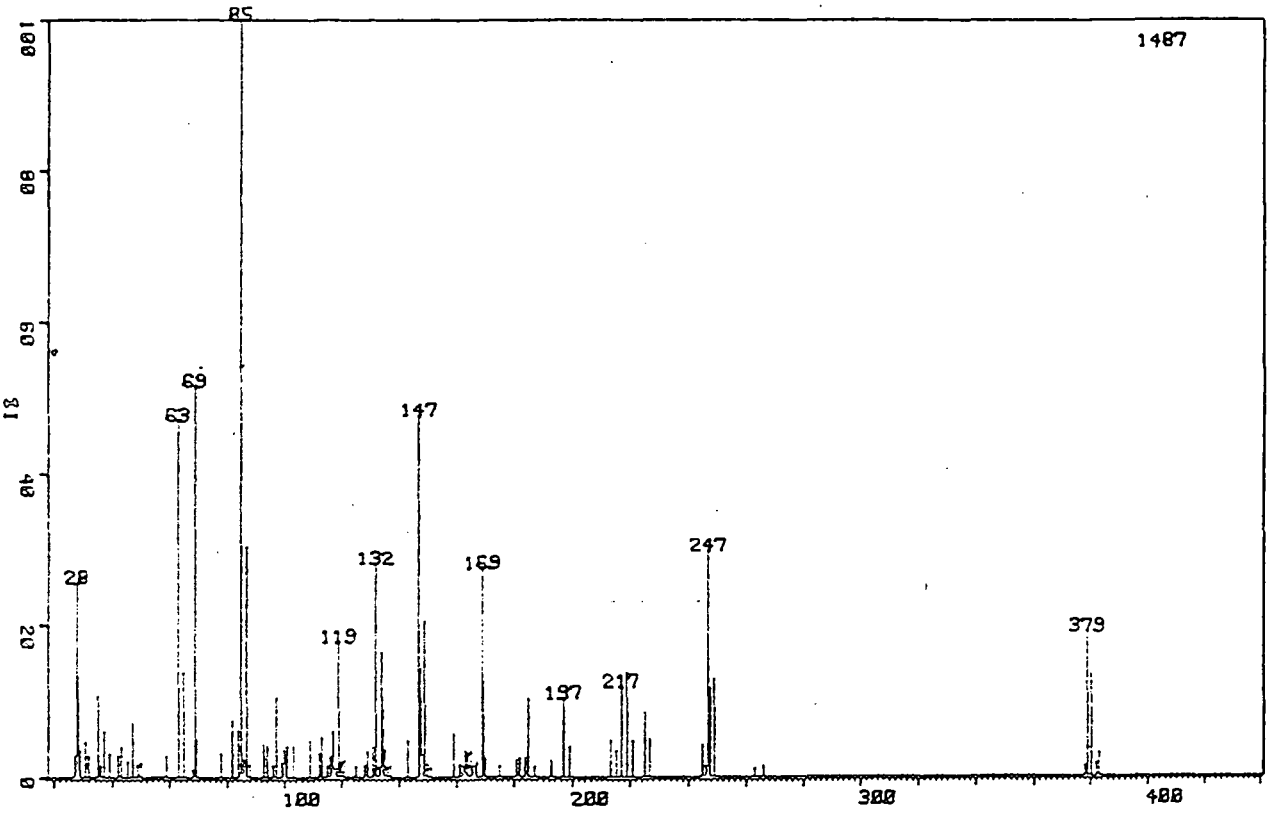
CAL:CALM1 MW=354



NO.	MASS	%HT. BASE
1	28.13	4.67
2	30.90	3.07
3	32.01	0.75
4	49.84	0.85
5	68.87	100.00
6	69.84	1.31
7	99.80	4.51
8	118.82	14.44
9	119.85	0.42
10	130.78	9.51
11	131.71	0.36
12	131.92	0.46
13	149.72	1.14
14	168.71	1.47
15	218.39	0.69

No.94 2,5,5-TRICHLOROPERFLUORO-2-PROPYLOXOLANE (163)

SJ9 5 S.L.JONES 11-MAY-83
CAL:CALM4 MW=414

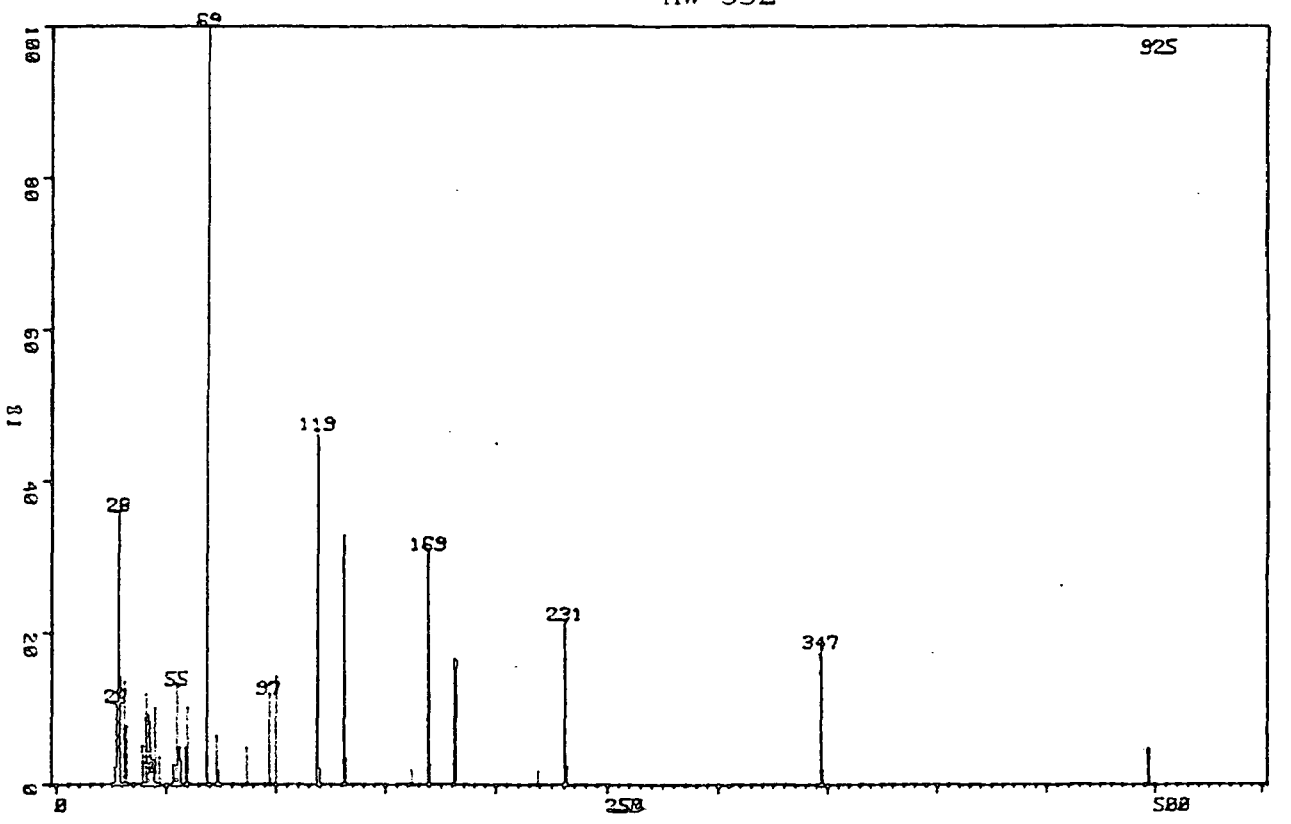


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	28.05	25.62	23	100.93	4.10	45	168.98	27.44
2	28.09	13.32	24	103.02	4.10	46	169.21	12.51
3	28.95	3.43	25	108.98	4.91	47	184.98	10.42
4	30.84	4.71	26	112.01	3.16	48	196.98	10.36
5	35.10	10.69	27	112.99	5.25	49	198.90	4.10
6	37.08	6.12	28	116.95	6.12	50	212.93	4.91
7	38.97	3.16	29	118.97	17.82	51	214.95	3.43
8	43.11	4.03	30	128.93	3.36	52	216.90	11.84
9	47.07	7.20	31	130.95	3.97	53	218.85	13.85
10	63.02	47.14	32	131.96	28.11	54	220.87	4.84
11	65.05	13.79	33	133.97	16.48	55	225.05	8.47
12	68.97	51.58	34	134.15	8.81	56	226.98	5.04
13	69.08	5.04	35	134.97	3.63	57	245.03	4.24
14	77.96	3.23	36	143.04	4.91	58	247.04	29.79
15	81.90	7.53	37	146.99	47.75	59	247.53	11.77
16	83.95	6.19	38	147.21	14.32	60	249.00	12.91
17	85.00	100.00	39	148.00	3.03	61	378.84	19.03
18	87.00	30.46	40	148.92	20.51	62	380.37	13.38
19	93.01	4.37	41	158.95	5.85	63	382.96	3.16
20	93.99	4.10	42	162.94	3.56			
21	97.04	10.56	43	163.93	3.16			
22	99.96	3.70	44	164.98	3.43			

No.95 2-CHLOROPERFLUORO-2,5-DIPROPYLOXOLANE (164)

SJ911 8 S.L.JONES 9/11 04-MAR-83
CAL:CALM24

MW=532

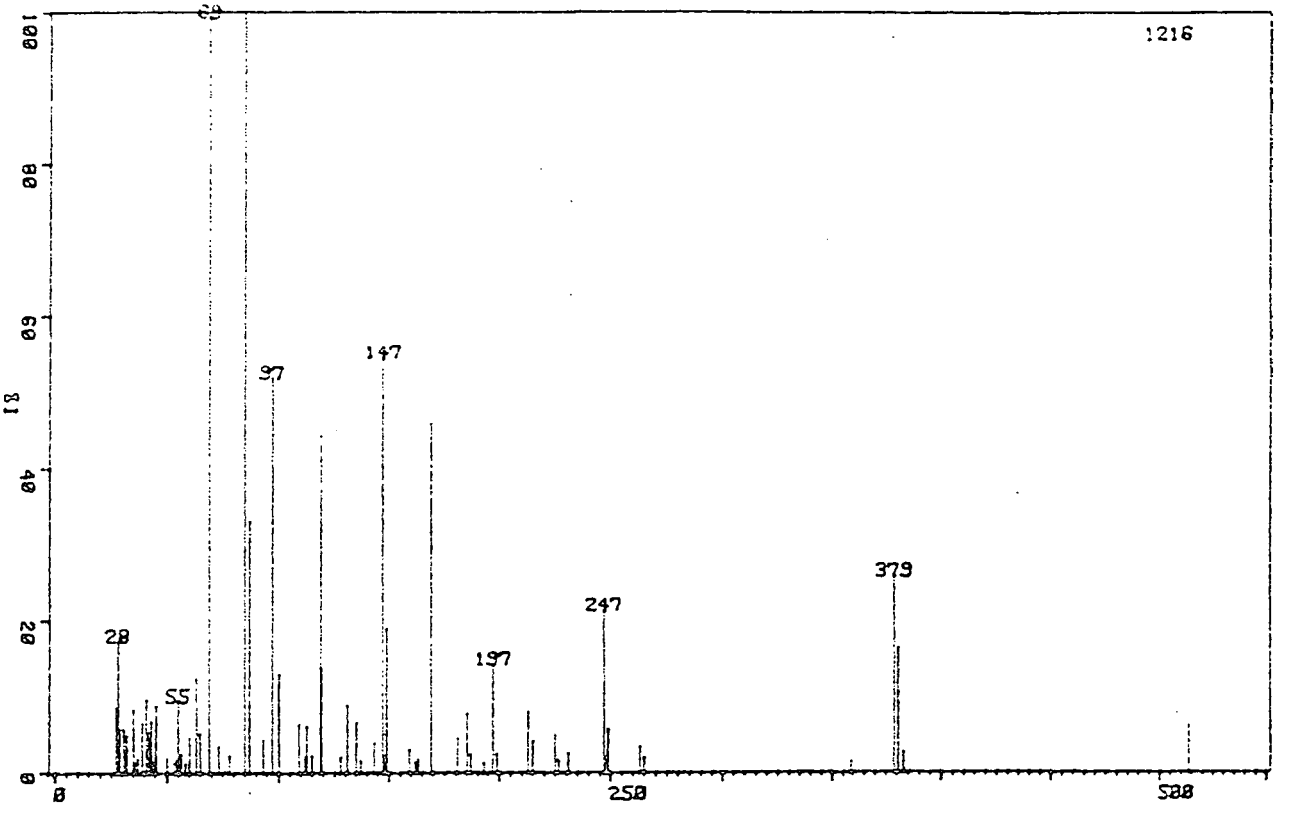


NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	26.32	2.27	23	74.08	1.84
2	27.25	10.92	24	87.05	4.86
3	28.14	36.11	25	97.02	12.00
4	29.02	14.16	26	99.95	14.38
5	30.93	13.51	27	118.95	47.03
6	32.03	7.68	28	119.96	2.05
7	39.01	5.19	29	130.98	33.08
8	40.99	12.00	30	131.99	3.46
9	42.06	9.19	31	161.94	1.95
10	43.13	8.22	32	168.98	31.24
11	44.13	3.24	33	169.94	2.70
12	45.17	10.27	34	180.95	16.76
13	47.09	3.78	35	218.92	1.84
14	53.10	2.70	36	230.98	21.95
15	54.14	2.49	37	231.99	2.49
16	55.16	13.19	38	346.95	18.16
17	56.17	4.97	39	347.87	1.95
18	57.12	3.03	40	496.88	4.86
19	59.04	4.86			
20	59.93	10.16			
21	68.97	100.00			
22	73.06	6.38			

No.96 2,5-DICHLOROPERFLUORO-2,5-DIPROPYLOXOLANE (165)

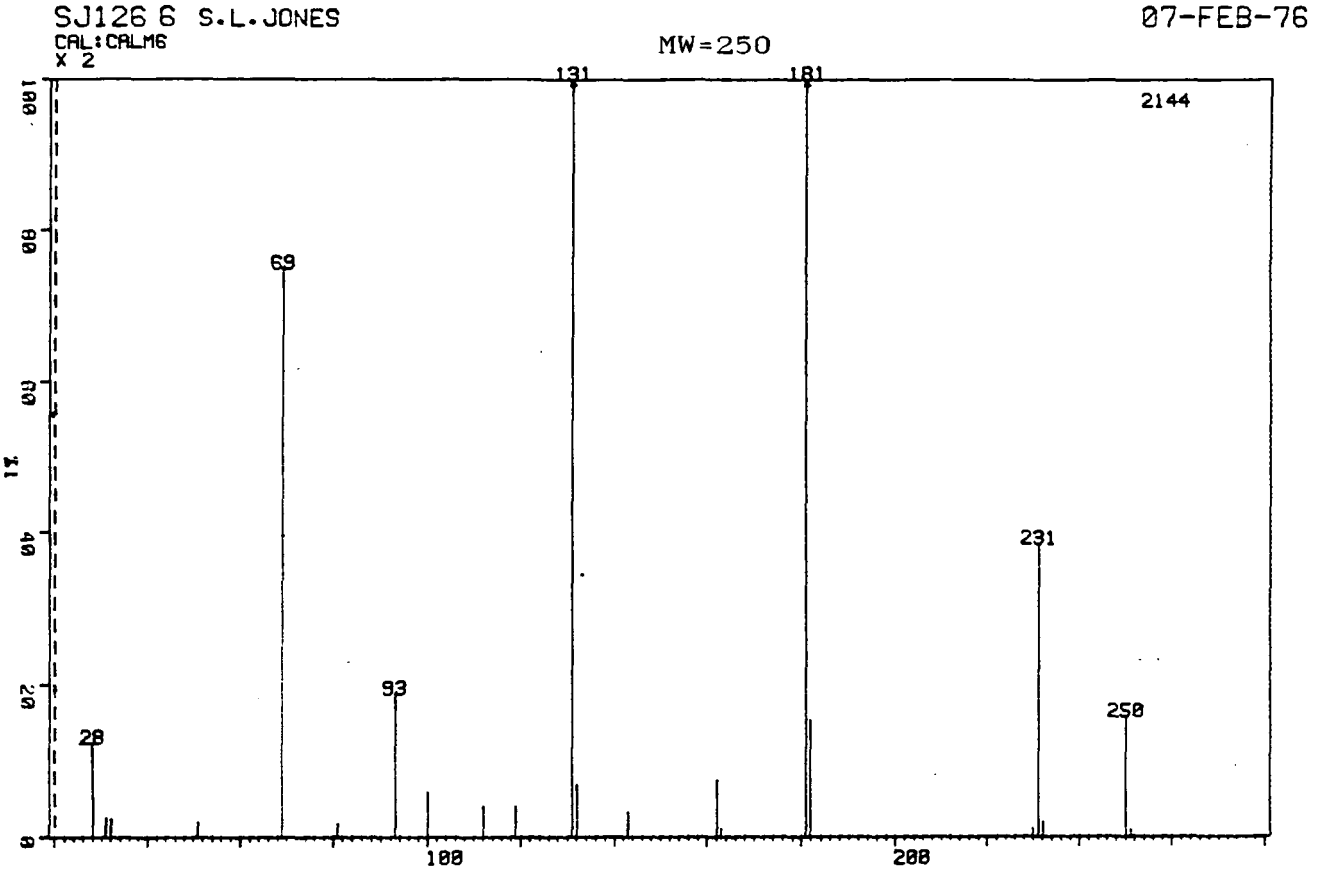
SJ911 14 S.L.JONES 9/11 04-MAR-83
CAL:CALM24

MW=548



NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE	NO.	MASS	%HT. BASE
1	27.26	8.63	23	77.97	2.22	45	168.95	46.05
2	28.14	17.27	24	85.00	100.00	46	180.96	4.52
3	29.02	5.76	25	86.98	33.14	47	184.97	7.73
4	30.94	5.84	26	93.02	4.28	48	186.97	2.38
5	32.02	4.85	27	97.02	51.89	49	196.93	14.14
6	35.17	8.31	28	99.95	12.91	50	198.84	2.47
7	37.11	1.89	29	108.93	6.33	51	212.93	8.06
8	39.02	6.58	30	111.97	2.06	52	214.95	4.19
9	41.00	9.62	31	112.96	6.09	53	225.01	5.02
10	42.06	5.26	32	115.03	2.22	54	227.00	1.73
11	43.14	6.74	33	118.97	44.41	55	231.07	2.55
12	45.17	8.80	34	119.12	13.73	56	246.98	21.30
13	49.87	1.97	35	127.98	2.06	57	247.96	2.06
14	53.12	1.40	36	130.95	8.88	58	248.94	5.76
15	54.18	1.64	37	134.98	6.58	59	262.96	3.37
16	55.16	9.29	38	136.97	1.56	60	264.90	1.97
17	56.16	2.47	39	142.99	3.87	61	378.85	25.74
18	59.95	4.61	40	146.97	54.61	62	380.71	16.37
19	63.04	12.42	41	147.99	2.22	63	383.01	2.71
20	65.07	5.18	42	148.93	18.91	64	513.72	6.09
21	68.97	99.26	43	158.96	3.04			
22	73.07	3.45	44	162.98	1.81			

No.97 PERFLUORO-2-PENTENE



NO.	MASS	%HT. BASE
1	28.07	6.20
2	30.84	1.26
3	31.95	1.21
4	50.93	0.98
5	68.95	37.50
6	80.90	0.89
7	93.00	9.42
8	99.93	2.99
9	111.98	2.01
10	118.96	2.01
11	130.94	92.54
12	131.91	3.40
13	142.98	1.59
14	161.95	3.73
15	162.96	0.51
16	180.90	100.00
17	181.77	7.70
18	229.84	0.51
19	231.02	19.26
20	232.08	0.93
21	249.98	7.88
22	251.05	0.47

COLLOQUIA AND CONFERENCES

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

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

(B) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out;

(C) details of the postgraduate induction course.

(A) RESEARCH COLLOQUIA, SEMINARS AND LECTURES

1. Durham University Chemistry Department Colloquia

1982

13 October * Dr. W.J. Feast (University of Durham), "Approaches to the synthesis of conjugated polymers".

14 October * Prof. H. Suhr (University of Tubingen, FRG), "Preparative Chemistry in non-equilibrium plasmas".

27 October Dr C.E. Housecroft (Oxford High School/Notre Dame University), "Bonding capabilities of butterfly-shaped Fe_4 units implications for C-H bond activation in hydrocarbon complexes".

28 October Prof. M.F. Lappert, F.R.S., (University of Sussex), "Approaches to asymmetric synthesis and catalyses using electron-rich olefins and some of their metal complexes".

15 November Dr. G. Bertrand (University of Toulouse, France), "Crutius rearrangement in organometallic series. A route for hybridised species".

24 November * Pfo. G.G. Roberts (Applied Physics, University of Durham), "Langmuir-Blodgett films: Solid state polymerisation of diacetylenes".

2 December * Dr. G.M. Brooke (University of Durham), "The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoroaryl and -heteroaryl systems".

8 December Dr. G. Wooley (Trent Polytechnic), "Bonds in transition metal-cluster compounds".

1983

12 January Dr. D.C. Sherrington (University of Strathclyde), "Polymer-supported phase transfer catalysts".

9 February — Dr. P. Moore (University of Warwick), "Mechanistic studies in solution by stopped flow F.T.-N.M.R. and high pressure NMR line broadening".

21 February — Dr. R. Lynden-Bell (University of Cambridge), "Molecular motion in the cubic phase of NaCN".

2 March * Dr. D. Bloor (Queen Mary College, University of London), "The solid-state chemistry of diacetylene monomers and polymers".

8 March — Prof. D.C. Bradley, F.R.S. (Queen Mary College, University of London), "Recent developments in organo-imido-transition metal chemistry".

9 March — Dr. D.M.J. Lilley (University of Dundee), "DNA, Sequence, Symmetry, Structure and Supercooling".

11 March * Prof. H.G. Viehe (University of Louvain, Belgium), "Oxidations on sulphur", "Fluorine substitutions in radicals". (The W.K.R. Musgrave Lecture).

16 March * Dr. I. Gosney (University of Edinburgh), "New extrusion reactions: Organic synthesis in a hot-tube".

25 March — Prof. F.G. Baglin (University of Nevada, U.S.A.), "Interaction induced Raman spectroscopy in supra-critical ethane".

21 April — Prof. J. Passmore (University of New Brunswick, U.S.A.), "Novel selenium-iodine cations".

4 May — Prof. P.H. Plesh (University of Keele), "Binary ionisation equilibria between two ions and two molecules. What Oswald never thought of".

10 May * Prof. K. Burger (Technical University of Munich, FRG), "New reaction pathways from trifluoromethyl-substituted heterodienes to partially fluorinated

heterocyclic compounds".

11 May * Dr. N. Isaacs (University of Reading), "The Application of high pressures to the theory and practice of organic chemistry".

13 May Dr. R. de Koch (Caloin College, Grand Rapids, Michigan/Free University, Amsterdam), "Electronic structural calculations in organometallic cobalt cluster molecules. Implications for metal surfaces"

16 May * Prof. R.J. Lagow (University of Texas, U.S.A.), "The chemistry of polylithium organic compounds. An unusual class of matter".

18 May Dr. D.M. Adams (University of Leicester), "Spectroscopy at very high pressures".

25 May Dr. J.M. Vernon (University of York), "New heterocyclic chemistry involving lead tetraacetate".

15 June Dr. A. Pietrzykowski (Technical University of Warsaw/University of Strathclyde), "Synthesis, structure and properties of Aluminoxanes".

22 June Dr. D.W.H. Rankin (University of Edinburgh), "Floppy molecules - the influence of phase on structure".

5 July * Prof. J. Miller (University of Camfinas, Brazil), "Reactivity in nucleophilic substitutions reactions".

5 October Prof. J.P. Maier (University of Basel, Switzerland), "Recent approaches to spectroscopic characterization of cations".

12 October * Dr. C.W. McLeland (University of Port Elizabeth, Australia), "Cyclization of aryl alcohols through the intermediacy of alkoxy radicals and aryl radical cations".

19 October — Dr. N.W. Alcock (University of Warwick), "Aryl tellerium (IV) compounds, patterns of primary and secondary bonding".

26 October * Dr. R.H. Friend (Cavendish Laboratory, University of Cambridge), "Electronic properties of conjugated polymers".

30 November — Prof. I. Cowie (University of Stirling), "Molecular interpretation of non-relaxation processes in polymer glasses".

14 December — Prof. R.J. Donovan (University of Edinburgh), "Chemical and physical processes involving the ion-pair states of the halogen molecules".

1984

10 January * Prof. R. Hester (University of York), "Nanosecond laser spectroscopy of reaction intermediates".

18 January — Prof. R.K. Harris (University of East Anglia), "Multi-muclear solid state magnetic resonance".

8 February — Dr. B.T. Heaton (University of Kent), "Multinuclear n.m.r. studies".

15 February * Dr. R.M. Paton (University of Edinburgh), "Heterocyclic syntheses using nitrile sulphides".

7 March * Dr. R.T. Walker (University of Birmingham), "Synthesis and biological properties of some 5-substituteduracil derivatives; yet another example of serendipity in antiviral chemotherapy".

21 March — Dr. P. Sherwood (University of Newcastle), "X-ray photoelectron spectroscopic studies of electrode and other surfaces".

23 March (Informal colloquim) Dr. A. Ceulemans (Catholic University of Leuven), "The development of field-type models of the bonding in molecular clusters".

2 April * Prof. K. O'Driscoll (University of Waterloo), "Chain ending reactions in free radical polymerisation".

3 April Prof. C.H. Rochester (University of Dundee), "Infrared studies of adsorption at the solid-liquid interface".

25 April * Dr. R.M. Acheson (Department of Biochemistry, University of Oxford), "Some heterocyclic detective stories".

27 April Dr. T. Albright (University of Houston), "Sigmatropic rearrangements in organometallic chemistry".

14 May * Prof. W.R. Dolbier, Jr., (University of Florida), "Cycloaddition reactions of fluorinated allenes".

16 May Dr. P.J. Garratt (University College, London), "Syntheses with dilithiated vicinal diesters and carboximides".

31 May Dr. A. Haaland (University of Oslo), "Electron diffraction studies of some organometallic compounds".

11 June * Dr. G.B. Street (I.B.M. San José), "Conducting polymers derived from pyrroles".

19 September * Dr. C. Brown (I.B.M. San José), "New superbase reactions - organic compounds".

21 September * Dr. H.W. Gibson (Signal UOP Research Centre, Des Plaines, Illinois), "Isomerization of polyacetylene"

19 October * Dr. A. Germain (Université du Languedoc, Montpellier), "Anodic oxidation of perfluoro organic compounds in perfluoroalkane sulphonic acids".

24 October Prof. R.K. Harris (University of Durham), "N.M.R. of solid polymers".

7 November Dr. H.S. Munro (University of Durham), "New information from ESCA data".

7 November Prof. W.W. Porterfield (Hampden-Sydney College, U.S.A), "There is no borane chemistry (only geometry)".

21 November Mr. N. Everall (University of Durham), "Pico-second pulsed laser raman spectroscopy".

27 November * Dr. W.J. Feast (University of Durham), "A plain man's guide to polymeric organic metals".

28 November Dr. T.A. Stephenson (University of Edinburgh), "Some recent studies in platinum metals chemistry".

5 December * Mr. P.J. Lux (University of Durham), "IR and GC studies of the interaction of CH_3OH with high silica zeolites".

12 December * Dr. K.B. Dillon (University of Durham), "^{31}P NMR studies of some anionic phosphorus complexes".

1985

11 January * Emeritus Prof. H. Suschitzky (University of Salford), "Fruitful fissions of benzofuroxanes and isobenzimadazoles (umpoung of o-phenyl-enediamine)".

13 February * Dr. G.W.J. Fleet (University of Oxford), "Syntheses of some alkaloids from carbohydrates".

13 February * Dr. D.J. Mincher (University of Durham), "Stereo-selective syntheses of some novel anthracyclinones related to the anti-cancer drug adriamycin and to the steffimycin antibiotics".

27 February Dr. R.E. Mulvey (University of Durham), "Some unusual lithium complexes".

7 March * Dr. P.J. Rodgers (I.C.I plc, Agricultural Division, Billingham), "Industrial polymers from bacteria".

12 March Prof. K.J. Packer (B.P. Research Centre), "NMR investigations of the structure of solid polymers".

14 March * Prof. A.R. Katritzky, F.R.S. (University of Florida), "Some adventures in heterocyclic chemistry".

21 March Dr. M. Poliakoff (University of Nottingham), "New methods for detecting organometallic intermediates in solution".

28 March * Prof. H. Ringsdorf (Organic Chemistry Institute, University of Mainz), "Polymeric liposomes as models for biomembranes and cells?"

24 April Dr. M.C. Grossel (Bedford College, University of London), "Hydroxypyridone dyes - bleachable one-dimensional metals?"

1 May * Dr. D. Parker (I.C.I. plc, Petrochemical and Plastics Division, Wilton), "Applications of radioisotopes in industrial research".

7 May Prof. G.E. Coates (formerly of University of Wyoming, U.S.A.), "Chemical education in Britain and America: Successes and deficiencies".

8 May Prof. D. Tuck (University of Windsor, Ontaario), "Lower oxidation state chemistry of indium".

8 May * Prof. G. Williams (University College of Wales, Aberystwyth), "Liquid crystalline polymers".

9May Prof. R.K. Harris (University of Durham), "Chemistry in a spin: nuclear magnetic resonance".

14 May Prof. J. Passmore (University of New Brunswick), "The synthesis and characterisation of some novel selenium-iodine cations, aided by ^{77}Se NMR spectroscopy".

15 May * Dr. J.E. Packer (University of Auckland, New Zealand), "Studies of free radical reactions in aqueous solution using ionising radiation".

17 May Prof. I.D. Brown (Institute for Materials Research, McMaster University, Canada), "Bond valence as a model for inorganic chemistry".

21 May Dr. D.L.H. Williams (University of Durham), "Chemistry in colour".

22 May Dr. R. Grimmett (University of Otago, Dunedin, New Zealand), "Some aspects of nucleophilic substitution in imidazoles".

22 May * Dr. M. Hudlicky (Virginia State University, Blacksburg), "Preferential elimination of hydrogen fluoride from vicinal bromoflurocompounds".

4 June * Dr. P.S. Belton (Food Research Institute, Norwich), "Analytical photoacoustic spectroscopy".

13 June Dr. D. Woollins (Imperial College, University of London), "Metal-sulphur-nitrogen complexes".

14 June * Prof. Z. Rappoport (The Hebrew University, Jerusalem), "The rich mechanistic world of nucleophilic vinylic substitution".

19 June — Dr. T.N. Mitchell (University of Dortmund), "Some synthetic and NMR-spectroscopic studies of organotin compounds".

26 June — Prof. G. Shaw (University of Bradford), "Synthetic studies on imidazole nucleosides and the antibiotic coformycin"

12 July * Dr. K. Laali (Hydrocarbon research Institute, University of South California) "Recent developments in superacid chemistry and mechanistic considerations in electrophilic aromatic substitutions; a progress report".

2. DURHAM UNIVERSITY CHEMICAL SOCIETY LECTURES

1982

14 October * Mr. F. Shenton (County Analyst, Durham), "There is death in the pot".

28 October — Prof. M.F. Lappert, F.R.S. (University of Sussex), "The chemistry of some unusual subvalent compounds of the main group IV and V elements".

4 November — Dr. D.H. Williams (University of Cambridge), "Studies on the structures and modes of action of antibiotics".

11 November — Dr. J. Cramp (I.C.I. Ltd.), "Lasers in Industry".

25 November * Dr. D.H. Richards, P.E.R.M.E. (Ministry of Defence), "Terminally functional polymers, their synthesis and uses".

1983

27 January * Prof. D.W.A. Sharp (University of Glasgow), "Some redox reactions in fluorine chemistry".

3 February ✲ Dr. R. Manning (Department of Zoology, University of Durham), "Molecular mechanisms of hormone action".

10 February Sir Geoffrey Allen, F.R.S. (Unilever Ltd.), "U.K. Research Ltd.".

17 February (R.S.C. Centenary Lecture), Prof. A.G. MacDiarmid (University of Pennsylvania), "Metallic covalent polymers: $(SN)_x$ and $(CH)_x$ and their derivatives".

3 March Prof. A.C.T. North (University of Leeds), "The use of a computer display system in studying molecular structures and interactions".

20 October ✲ Prof. R.B. Cundall (University of Salford), "Explosives".

3 November Dr. G. Richards (University of Oxford) "Quantum pharmacology".

10 November ✲ Dr. J. Harrison (Stirling Organic), "Applied chemistry and the pharmaceutical industry".

24 November ✲ Prof. D.A. King (University of Liverpool), "Chemistry in two dimensions".

1 December ✲ Dr. J.D. Coyle (The Open University), "The problem with sunshine".

1984

26 January ✲ Prof. T.L. Blundell (Birkbeck College, London), "Biological recognition: Interactions of macromolecular surfaces".

2 February Prof. N.B.H. Jonathan (University of Southampton), "Photoelectron spectroscopy - a radical approach".

16 February ✲ Prof. D. Phillips (The Royal Institution), "Luminescence and photochemistry - a light entertainment".

23 February — Prof. F.G.A. Stone, F.R.S. (University of Bristol), "The use of carbene and carbyne groups to synthesis metal clusters". [The Waddington Memorial Lecture].

1 March — * Prof. A.J. Leadbetter (Rutherford Appleton Labs.), "Liquid crystals".

8 March — * Prof. D. Chapman (Royal Free Hospital School of Medicine, University of London), "Phospholipids and biomembranes: basic structure and future techniques".

28 March — [R.S.C. Centenary Lecture], Prof. H. Schmidbaur (Technical University of Munich, FRG), "Ylides in coordination sphere of metals: synthetic, structural and theoretical aspects".

18 October — * Dr. N. Logan (University of Nottingham), "N_2O_4 and rocket fuels".

25 October — * Dr. W.J. Feast (University of Durham), "Syntheses of conjugated polymers. How and why?"

8 November — Prof. B.J. Aylett (Queen Mary College, London), "Silicon - dead common or refined?"

15 November — * Prof. B.T. Golding (University of Newcastle-upon-Tyne), "The vitamin B_{12} mystery".

22 November — * [R.S.C. Tilden Lecture], Prof. D.T. Clark, (I.C.I. New Science Group), "Structure, bonding, reactivity and synthesis as revealed by ESCA".

29 November — * Prof. C.J.M. Stirling (University College of North Wales), "Molecules taking the strain".

6 December — * Prof. R.D. Chambers (University of Durham) "The unusual world of fluorine".

1985

24 January ✲ Dr. A.K. Covington (University of Newcastle-upon-Tyne), "Chemistry with chips".

31 January Dr. M.L.H. Green (University of Oxford), "Naked atoms and negligée ligands".

7 February (Joint Lecture with Society of Chemical Industry) Prof. A. Ledwith (Pilkington Bros.), "Glass as a high technology material".

14 February ✲ Dr. J.A. Salthouse (University of Manchester), "Son et lumière"

21 February Prof. P.M. Maitlis, F.R.S. (University of Sheffield), "What use is rhodium?"

7 March Dr. P.W. Atkins (University of Oxford), "Magnetic reactions".

(B) RESEARCH CONFERENCES ATTENDED

Graduate Symposium, Durham, April 1983.

Graduate Symposium, Durham, April 1984.

4th International Symposium on "Organic Free Radicals", St Andrews, 9-13 July 1984.

A poster was presented by the author entitled "Free Radical Additions in the Synthesis of Poly- and Per-fluorinated Ethers".

International Symposium on "Chemistry of Carbanions", Durham, 16-20 July 1984.

18th Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, 19 December 1984.

A Meeting for Discussion on "Inorganic and Organic Radicals: Their Biological and Clinical Relevance", The Royal Society, London, 30-31 January 1985.

Graduate Symposium, Durham, April 1985.

A paper was presented by the author entitled "Functional Fluorocarbons via Free Radical Additions to Hexafluoropropene".

(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.

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

Chromatography and microanalysis - Mr. T.F. Holmes.

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

Mass spectroscopy - Dr. M. Jones.

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

Glassblowing techniques - Mr. R. Hart and Mr. G. Haswell.

Safety matters - Dr. M.R. Crampton.

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