Free radical reaction of fluorine containing compounds

Abu-Nasrieh, Omar M.

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UNIVERSITY OF DURHAM

A THESIS

ENTITLED

FREE RADICAL REACTION OF FLUORINE CONTAINING COMPOUNDS

Submitted By

OMAR M. ABU-NASRIEH B.A

(GRAD.UATE SOCIETY)

A candidate for the degree of Master

of Science

Department of Chemistry

1989

To

my Father and Mother-in-Law
for their continuing support
during my university career
and my Wife, Sana, without
whose support this thesis
would not have seen the
light of day.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1988 and October 1989. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Professor R·D·Chambers for his considerable encouragement, advice and discussions during the course of this research project.

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

I would also like to thank many technical staff for their assistance: to Mrs·M·Cocks for analysis; Messrs R·Hart and G·H·Aswell for their cheerful and expert glassblowing; and to many others.

I am grateful to colleagues in the laboratory for helpful and incentive discussion, special thanks go to Mr T F Holmes as well as to Robert, Andy, Martin, Steve and Mike.

Last but not least, my thanks go to my wife and my father and mother-in-law for their considerable support and encouragement.

Free-Radical Reaction of Fluorine Containing Compounds

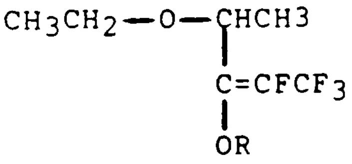
by

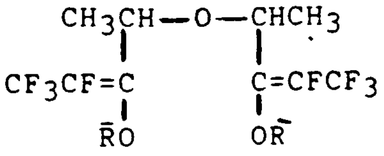
O. M. Abu-Nasrieh

ABSTRACT

This thesis is concerned with the free-radical addition of oxygen containing compounds of the adducts produced.

Free-radical additions of ether compounds to fluoroalkenes have been done by previous workers and the chemistry of some of these adducts has been investigated. The following new compounds have been synthesised and identified by g.l.c., mass spect., i.r., and NMR spectroscopy



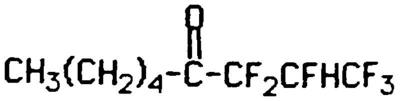


RO = CH_3O, C_3H_7O, C_4H_9 . $\bar{R}O$ = CH_3O, C_2H_5, C_3H_7, C_4H_9.

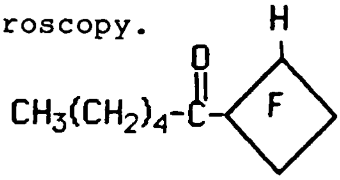
These arose from reaction of the α-(1,2,3,3,3-pentafluoro-1-propenyl) diethylether and α,α'-bis(1,2,3,3-pentafluoro-1-propenyl) diethylether which were prepared by dehydrofluorination of diethylether/hexafluoropropene mono-adduct and diethylether/hexafluoropropene di-adduct respectively.

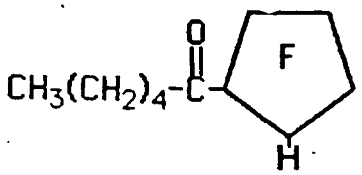
Free-radical additions of mono-functional aldehyes and di-functional aldehydes to fluoroalkenes has produced new ketone compounds with a good yield.

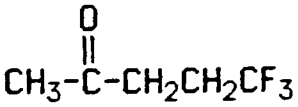
The following new compounds have been synthesised and identified by mass spect., NMR spectroscopy.



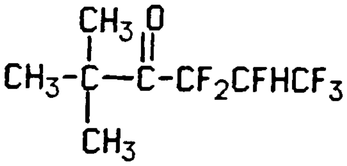
$CH_3(CH_2)_4-\overset{O}{\overset{\|}{C}}-CF_2CFHCF_3$



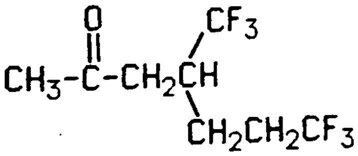


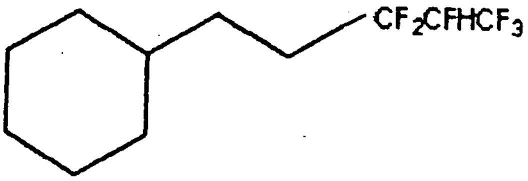


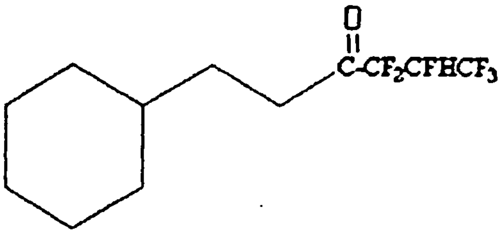
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CF_3$

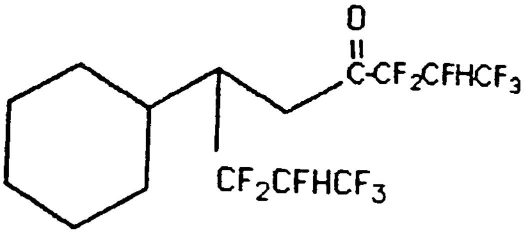


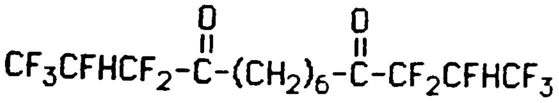
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CF_2CFHCF_3$



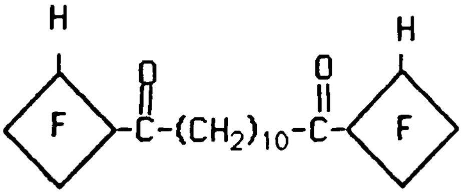


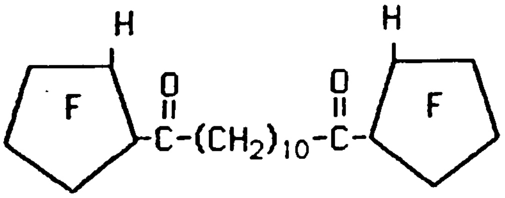


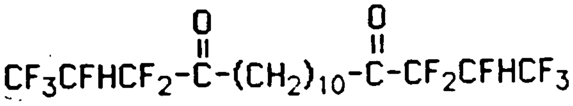




$CF_3CFHCF_2-\overset{O}{\overset{\|}{C}}-(CH_2)_6-\overset{O}{\overset{\|}{C}}-CF_2CFHCF_3$

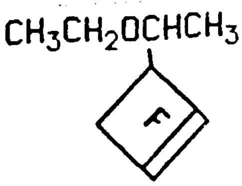






$CF_3CFHCF_2-\overset{O}{\overset{\|}{C}}-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-CF_2CFHCF_3$

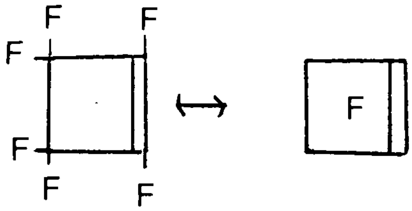
The dehydrofluorination of ether/hexafluorocyclobutene mono-adduct has been investigated and a new diene was produced.



NOMENCLATURE

1. To denote that a compound is fully fluorinated, either a capital 'F' or the prefix 'perfluoro' is included before the chemical name. If a capital 'F' or the prefix 'perfluro' is included in the middle of a chemical name, this denotes that the part of the compound following the 'F' or 'perfluoro' is fully fluorinated.

2. A capital 'F' within a ring denotes that all unmarked substituents are fluorine, e.g.



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INTRODUCTION

CHAPTER ONE

FREE RADICAL ADDITION REACTIONS

I A Introduction

An extensive number of books and papers have been published on the subject of organo flourine compounds and their unique chemistry 1 - 6, because the replacement of hydrogen by fluorine in organic molecules can lead to compounds which display unique physical and chemical properties. These properties result from a variety of factors, notably (a) the small size of fluorine (Van der Waals radius, 1.35 A), (b) the high electronegativity of fluorine (Pauling Scale, 4.0), (c) the presence of unshared electron pairs on fluorine and (d) the high bond strength of C-F (116 Kcal/mole sq). Properties such as high thermal and chemical stability, and biological activity have resulted in a diversity of applications for organic fluorine compounds. These compounds do not occur naturally but have found a wide range of applications.

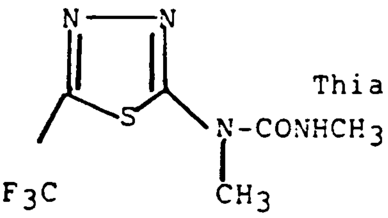
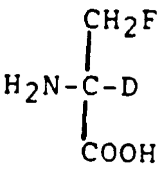
Table 1 summarises a number of the applications of highly fluorinated compounds and gives an example of each. All the compounds in this category have high thermal and chemical stability, importantly, and low toxicity.

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

Table 1 Highly fluorinated compounds

APPLICATION	COMPOUNDS
Fire Extinguishers	Bromofluoroalkenes e.g. CF_3Br
Blood Substitutes	Perfluorinated cycloalkanes
Polymers	Polytetrafluoroethylene
e.g. lubricants	P.T.F.E.
Refrigerants	Chlorofluorocarbons e.g. CF_2Cl_2

Table 2 Low fluorinated compounds

APPLICATION	COMPOUNDS
Plant protection	 Thiazafluon
Pharmaceuticals	 $H_2N-\underset{COOH}{\overset{CH_2F}{C}}-D$ 'DFA' a cell wall active antibiotic

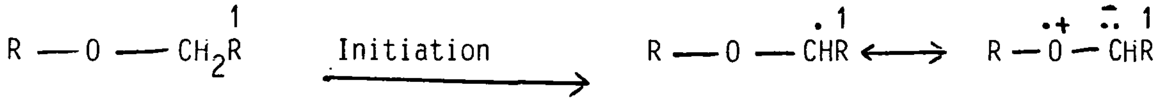
Clearly, development of techniques for introducing of fluorine or fluorocarbon groups into organic molecules is of great significance.

I B Free-Radical Additions To Fluorinated Alkenes.

In this laboratory, we have a continuing interest in free-radical addition reactions of carbon centred radicals to fluorinated alkenes 7,8. Radicals stabilised by an adjacent oxygen (e.g. ethers, alcohols) or nitrogen (e.g. amines, amides) are nucleophilic in character and are therefore ideally set up to react with electrophilic fluorinated alkenes. Thus, such reactions in effect utilize carbon-hydrogen bonds as a functional group.

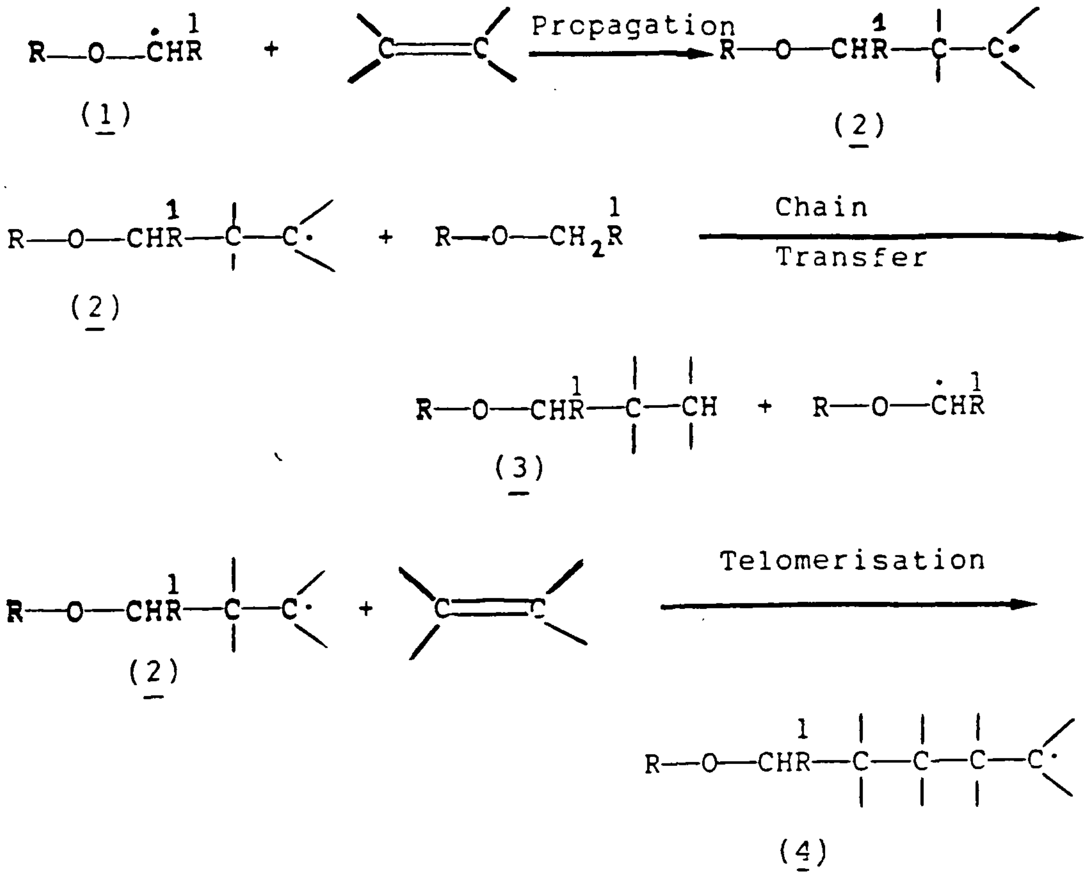
1. Mechanism of Free-Radical Addition

The generalised process for the free-radical reactions can be described as shown below using normal terminology describing the various steps. Scheme 1 below uses the free-radical addition of an ether to an alkene in order to explain the mechanistic steps.



$$R-O-CH_2R^1 \xrightarrow{\text{Initiation}} R-O-\dot{C}HR^1 \longleftrightarrow R-\overset{\cdot+}{O}-\overset{-}{\ddot{C}}HR^1$$

(1)



(i) Initiation step consists of the abstraction of a hydrogen atom from the ether substrate to give a radical (1) which will be stabilized due to the lone pair of electrons on the oxygen.

(ii) Propagation step consists of the addition of radical (1) to an alkene which will be from an intermediate radical (2)

The orientation of addition of radical (1) to an unsymmetrically substituted alkene depends on a complex interplay of steric effects, polar effects, stability of the produced radical, and sgtrength of the forming bond 7.

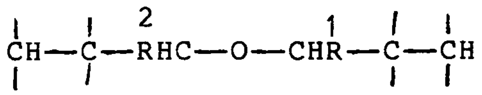
(iii) Chain - Transfer step consists of the abstraction of a hydrogen atom from the ether substrate by the radical (2) to form the product (3) This step also regenerates the initial radical (1)

(iv) Telomerisation step is a frequent side reaction where the radical (2) adds to another alkene molecule to form telomers (4) rather than abstract a hydrogen atom from either substrate.

The nature of the alkene and the ratio of ether to an alkene are very important to know which step will occur.

(v) Chain - Termination Step is termed a mono-adduct (3) and further alkene molecule will form di-adduct if the ether contains more than one easily abstractable hydrogen atom.

e.g. If $R = \overset{2}{R}CH_2$ then di-adduct (5) could be formed.



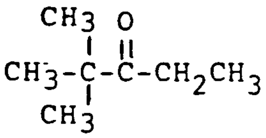
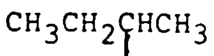
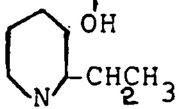
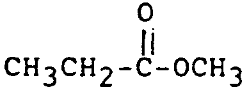
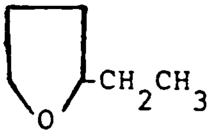
$$-\overset{|}{\underset{|}{C}}H-\overset{|}{\underset{|}{C}}-\overset{2}{R}HC-O-CH\overset{1}{R}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}H-$$

2. Intermolecular Addition Reactions.

Many free-radical addition reactions have been reported since the 1940's and addition of alkane, aldehyde, ketone, amine and ethers to hydrocarbon olefins via free-radical reaction are well established 7,8.

Table 3 summarises a number of free-radical addition reactions to ethylene.

Table 3 Free-Radical Addition to Ethylene

Substrate	Method of Initiation	Product	Reference
$CHCl_3$	Bz_2O2	$CCl_3CH_2CH_3$	[9,10]
Trimethyl-acetaldehyde	gamma	 $CH_3-C(CH_3)_2-C(=O)-CH_2CH_3$	[11]
Ethanol	DTBP	 $CH_3CH_2CH(OH)CH_3$	[12]
Piperidine	DTBP		[13]
Methyl formate	DTBP	 $CH_3CH_2-C(=O)-OCH_3$	[14,15]
Tetrahydrofuran	Thermal		[16]

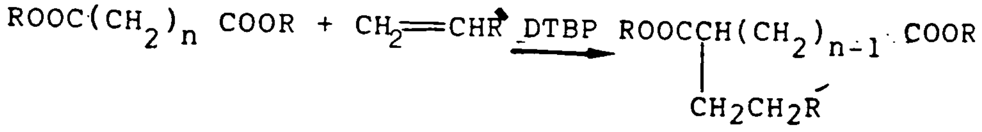
But the addition to fluorinated olefins has been known since 1948, 17. In most common radical systems involvvling nucleophilic radicals, electron deficient fluorinated olefins are ideal for addition reactions and their use has been reported 18. Some complexity with many olefins (e.g. tetrafluoroethane) is a frequent side reaction where the substrate radical adds to another fluoroolefin molecule to form telomers. The addition of hexafluoropropene does not give any telomeric product, so,

$R + CF_2{=}CF_2 \longrightarrow RCF_2-\dot{C}F_2$ Addition step.

$R-CF_2-\dot{C}F_2 + CF_2{=}CF_2 \longrightarrow R-CF_2CF_2CF_2-\dot{C}F_2$ Telomerisation step.

it is an ideal olefin for the synthesis of functional fluorocarbons.

Some reactions have been reported on the addition of electrophilic radical to hydrocarbon olefins, for example, the addition of di-carboxylic acid 19.



$$ROOC(CH_2)_n\,COOR + CH_2{=}CHR' \xrightarrow{DTBP} ROOC\underset{\displaystyle CH_2CH_2R'}{\underset{|}{C}}H(CH_2)_{n-1}\,COOR$$

R= H, CH_3,Et

(6)

R'= Alkyl

n= 1,2,4,7,8 .

3. Intramolecular Addition Reactions

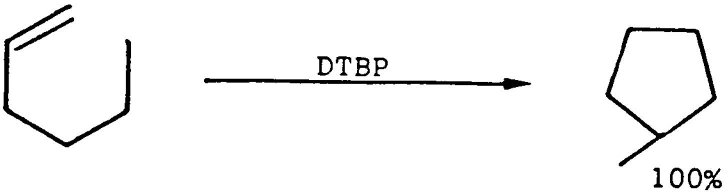
Free-radical addition to carbon-carbon double bonds can also occur by a process of intramolecular addition reactions, to produce cyclic products. Radical cyclization is becoming increasingly important in mechanistic and synthetic organic chemistry.

The dominant system in this sort of reaction is the forming of 5 -or 6-membered ring.

The size of ring formed is controlled by both thermodynamic and kinetic factors and having a strong background in these factors is very important in order to choose the conditions which are suitable for the required ring size.

Production of a 6-membered ring involves addition of the unsubstituted end of the double bond and it will produce a more stable secondary radical.

The variability of ring size produced can be built by the cyclization of a series of stabilized 5-hexenyl radicals.



[20]

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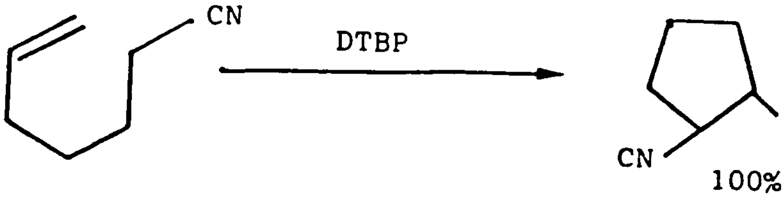
(7)



[20]

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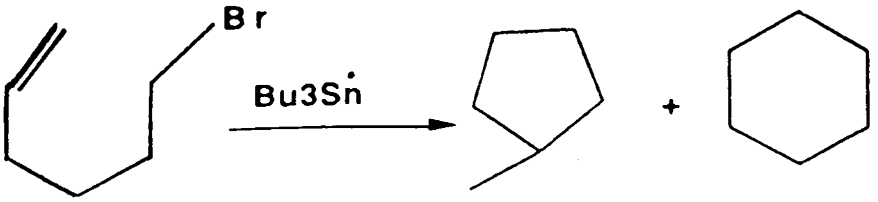
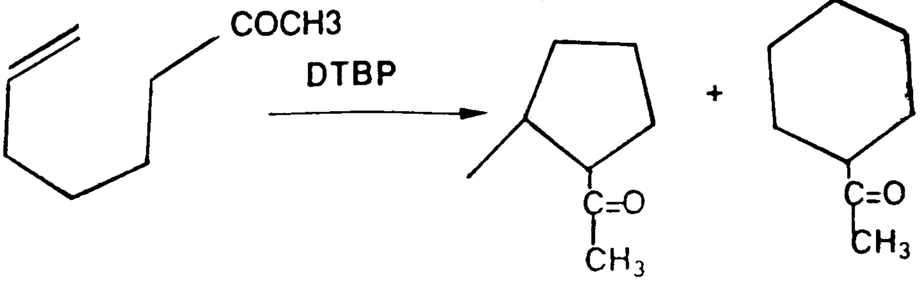
(8)



(9) (10)

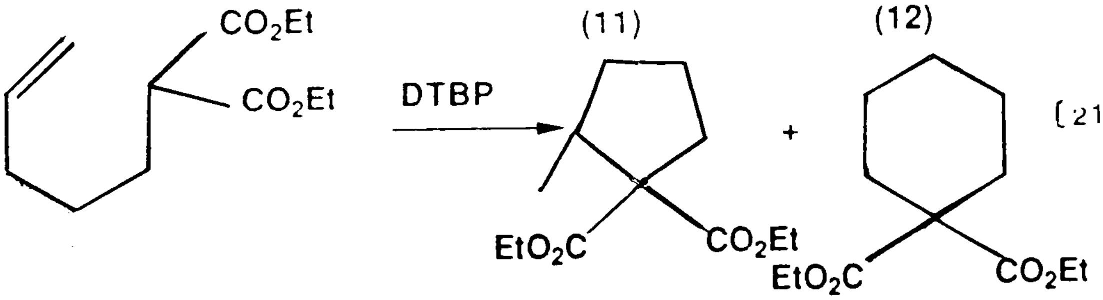
94% 6%

[21]



(11) (12)

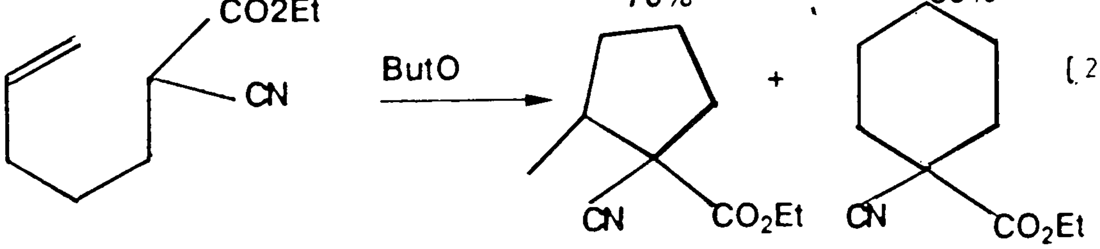
[20]



(13) (14)

70% 30%

[21]



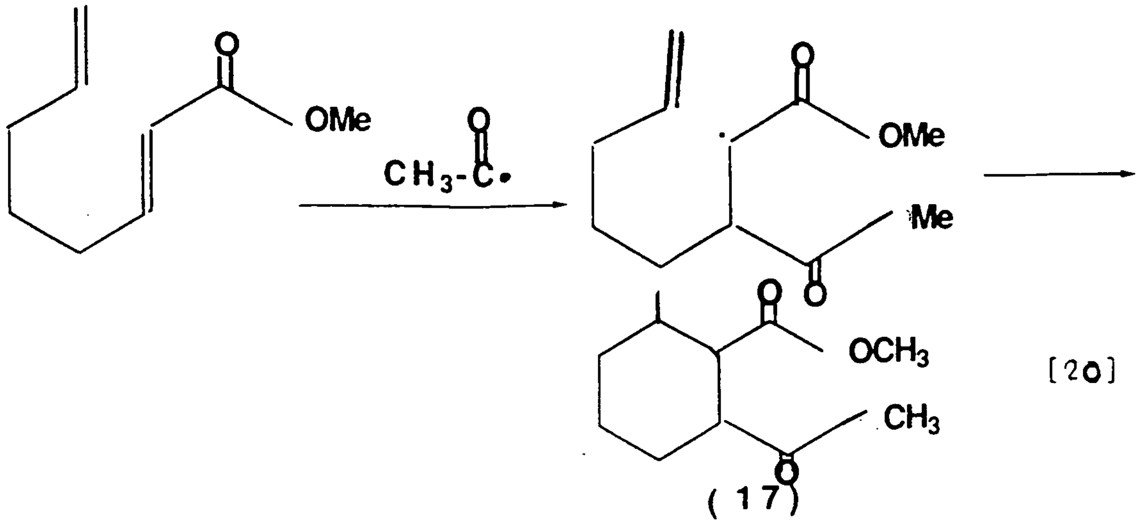
(15) (16)

16% 84%

[20]

The above examples show an increasing preferential formation of 6-membered ring with increasing stability of the radicals and decreasing reactivity of the radicals, because the radical stabilized with electron-with drawing substituents adjacent to the unpaired electron.

The cyclization process could happen by the adition of a radical to a suitable diene, for example, the addition of acetaldehyde to ester 20 (17)



(17)

[20]

4. Factors Influencing Free-Radical Addition.

(a) Steric Effects.

It has been observed that steric effects have an important function in a number of free-radical addition reactions, for example, the stereochemistry of the chain-transfer step in the addition reactions of free-radicals to norbornylene 22. It seems to be controlled by the availability of unhindered solid angle of approach which permits chain transfer readily from the exo side, but not easily from the endo side and in common, cis addition frequently occurs in this case.

(18)

(b) Temperature.

It has been observed that changes in temperature have a deep effect on a free-radical reaction.

This effect comes from the low activation energies of many propagation steps where an increase in temperature may increase the rate violently. On the other hand, a change in temperature may often open the door to competition by other reactions. For example, if the propagation step is reversible, an increase in temperature will decrease the concentration of the free-radical intermediate and slow the reaction down as far as the rate of formation of product in chain transfer step.

(c) Resonance.

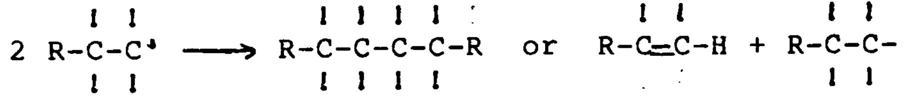
It was found that if the radical product in the propagation step is quite stable then it will exhibit a reluctance to continue on into chain transfer, either with the substrate R-H or with olefin in telomer formation. This reluctance comes from two sources: (a) a higher activation energy for chain transfer is the usual consequence of high radical stability and (b) the inability of a highly stabilized radical to acquire energy sufficient to break a relatively strong R-H bond.

It is obvious that the radical acquires enough stability through normal resonance and hyperconjugation. The free electron is highly delocalized in conjugated structures and if the system provides sufficient delocalization, the radical may become so stable that it refuses to react at all. Similarly, the evidence of electron spin resonance (ESR) spectroscopy indicates that hyperconjugation is extraordinarily effective in stabilizing radicals.

(d) Energy state

It is becoming increasingly evident that the energy 22 considerations in free-radical reactions have been too often neglected in the past, and that small differences in the energies of various intermediates or the steps that produce them in a chain process may have a profound effect on the course of the reaction. For example, the addition of R' to an olefin will produce radicals containing the entire energy of the new R-C bond. If this energy cannot be spread out through the structure of the intermediate radical fairly quickly, or dissipated by collisons, then the bond will dissociate to starting material R• and olefin. The reversiblility, as a reflection of a lack of effective energy dissipation, will vary with the structure of the olefin. Thus some additions of R• to olefin will be highly reversible and others not at all.

Again, the resonance energy of the intermediate radical R-C-C•, will determine the reactivity and lifetime of that radical. If there is considerable resonance stabilization, then R-C-C' will build up in the termination step of the chain process by dimerization or disproportionation



$$2\ R\text{-}C\text{-}C^{\bullet} \longrightarrow R\text{-}C\text{-}C\text{-}C\text{-}C\text{-}R \quad \text{or} \quad R\text{-}C{=}C\text{-}H + R\text{-}C\text{-}C\text{-} \qquad [22]$$

If $\mathrm{R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C'}}}$ is very reactive, and therefore very short-lived, the termination will probably take a different path, such as the dimerization of R with a corresponding change in the kinetics of the process.

$$R. + R. \longrightarrow R_2$$

Here, too, energy states and energy dissipation function, for the dimerization of R. when R is an atom or a small molecule, leave R with a considerable excess of energy, and often this sort of dimerization requires either a third body to carry off the energy or it takes place on the wall of the container, with different kinetics for each.

$$R\cdot + R\cdot + M \longrightarrow R_2 + M \qquad [22]$$
$$R\cdot + \text{wall} \longrightarrow \tfrac{1}{2} R_2$$

All of these, plus other considerations must go into the process of comprehending the details of an addition reaction mechanism. The total reaction can then be summed up thermodynamically in an energy-reaction coordinate diagram, of which Figure 1 is an example.

In the understanding of an addition reaction, the activation energies, heats of reactions, and entropy changes of each step and in both directions, will then constitute a fairly good description.

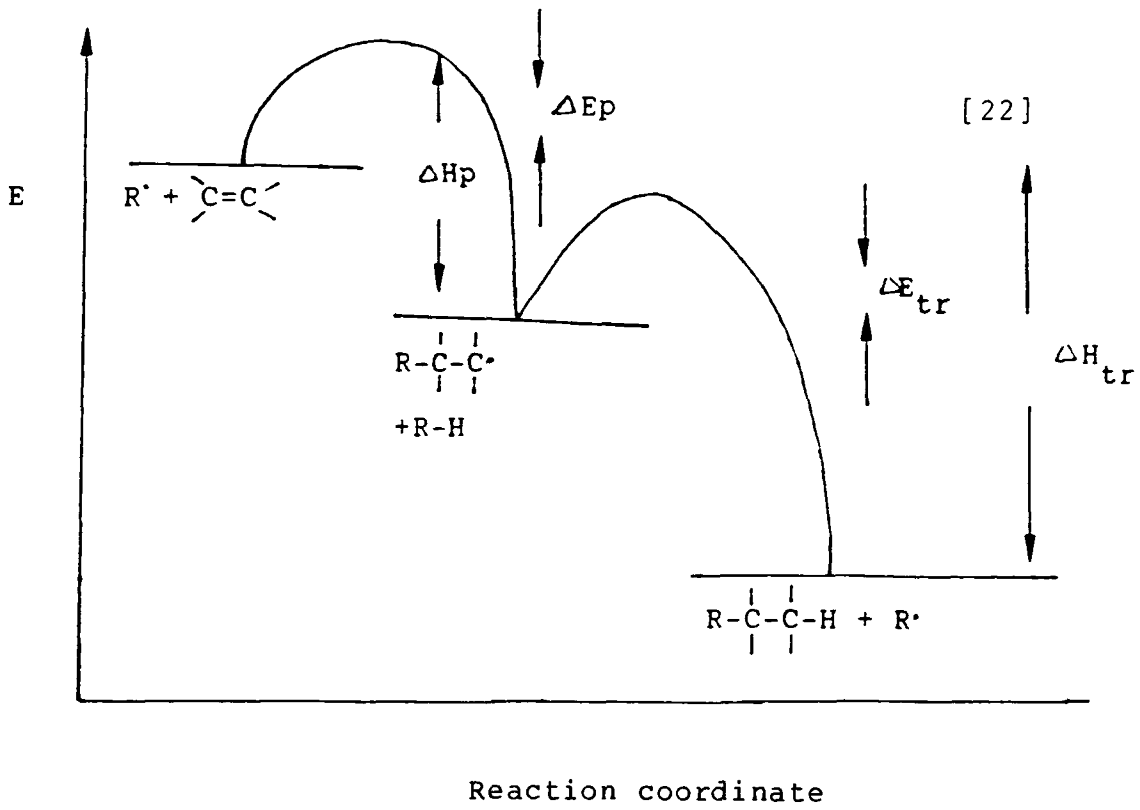


Figure 1: Energy-reaction coordinate diagram

(e) Polar Effect

Polar effects in a free-radical additions have not often been observed. That is coming for many reasons. First, the free radical, lacking a formal charge, is less subject to the dipolar action of the solvent; and second, many of the free radicals that have been studied are most extensively 22 reactive that the types of solvents that may be employed are severely limited. Also, solvent effects may tend to cancel out in that the the solvation of an intermediate radical such as R-C-C•, which will reduce the activation energy needed to produce it, may be counterbalanced by solvation of the attacking radical R• with consequent loss of its reactivity. In any case, relatively few examples of polar effects in radical addition reactions are documented.

CHAPTER TWO

FREE-RADICAL ADDITIONS OF OXYGEN CONTAINING COMPOUNDS TO FLUORINATED ALKENES

CHAPTER 2

FREE RADICAL ADDITIONS OF OXYGEN CONTAINING COMPOUNDS TO FLOURINATED ALKENES.

II A INTRODUCTION.

The majority of recent work on free radical addition reactions of functional compounds to fluoroalkenes has concentrated on oxygen-functional substrates. A variety of oxygen containing systems have been added and have been documented in the past 18, 28, 29, 31-38. The work in this study is the addition of ethers, and aldehydes to fluorinated alkenes and the chemistry of these adducts.

II B ADDITION OF-ETHERS.

An excellent series of papers 23-27 reporting the results of investigating the addition of ethers to fluorinated alkenes via a chain mechanism was described on page two. The reaction may be initiated thermally by the use of chemical initiators, by high energy radiation such as gammar rays, or photo-chemically.

In the formation of the ether radical (1) is energetically favourable due to the stabilisation of the resulting radical by the adjacent oxygen atom. This stabilization comes from the interactions shown in Figure 2.

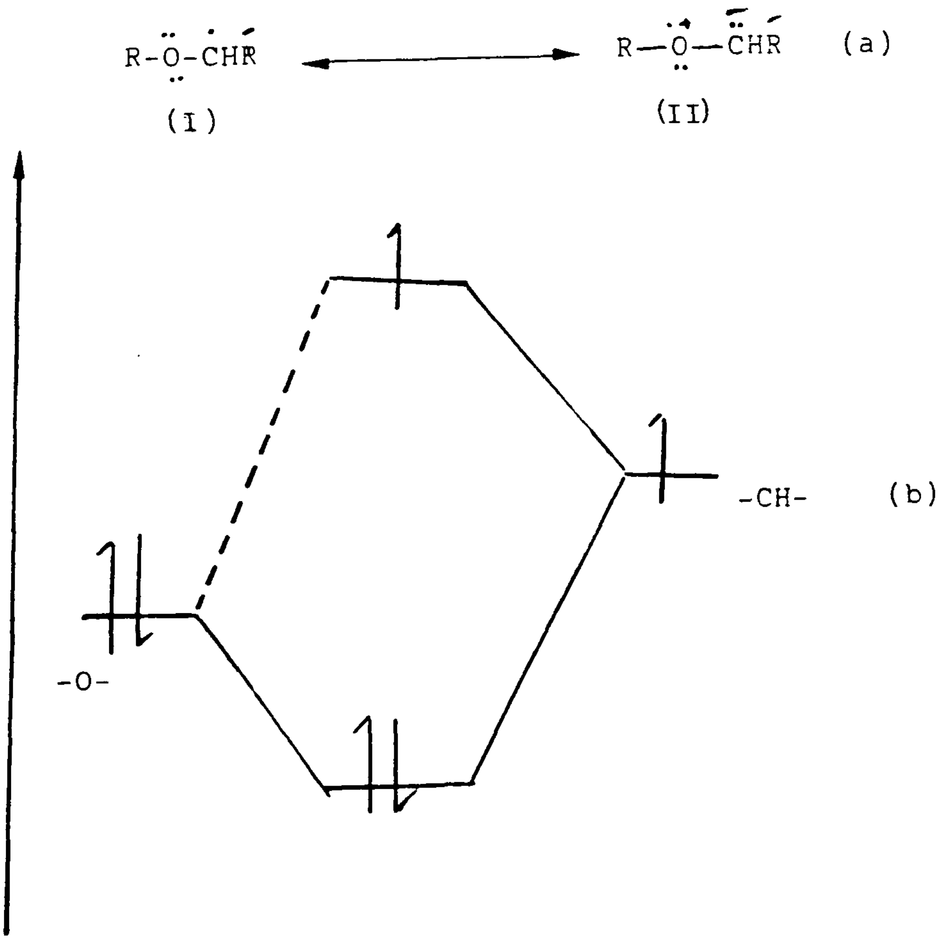
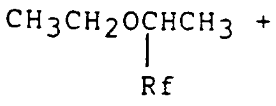
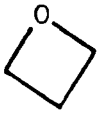
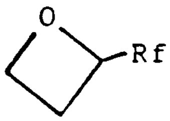


Figure 2

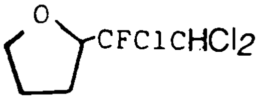
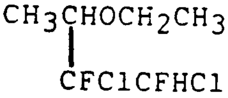
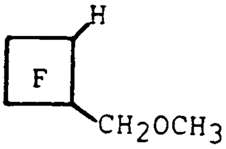
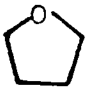
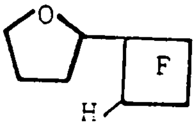
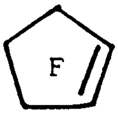
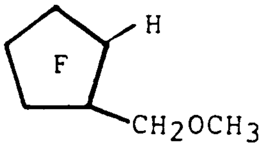
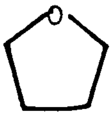
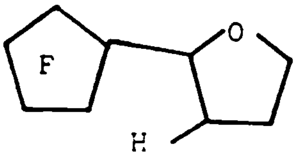
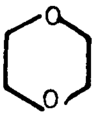
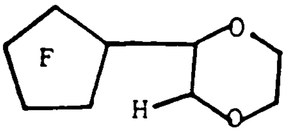
The propagation step which consists the addition of α ether radical (1) to fluoroalkenes is generally favourable. Considering Figure 1, it is obvious from the structures (i) and (ii) that α- ether radical (1) has a nucleophilic character. So, we find that the ether radicals react readily with fluoroolefins. In the chain transfer step the abstraction of a hydrogen atom from the eher substrate by the radical (2) takes place to form the product (3), but if this step is hindered then a 'short chain' mechanism will result with low conversion to product.

A variety of reactions of ethers with fluoroalkenes have been reported and in the results are summarized in Table 4.

Table 4 The Addition of Ethers Via Free-Radical

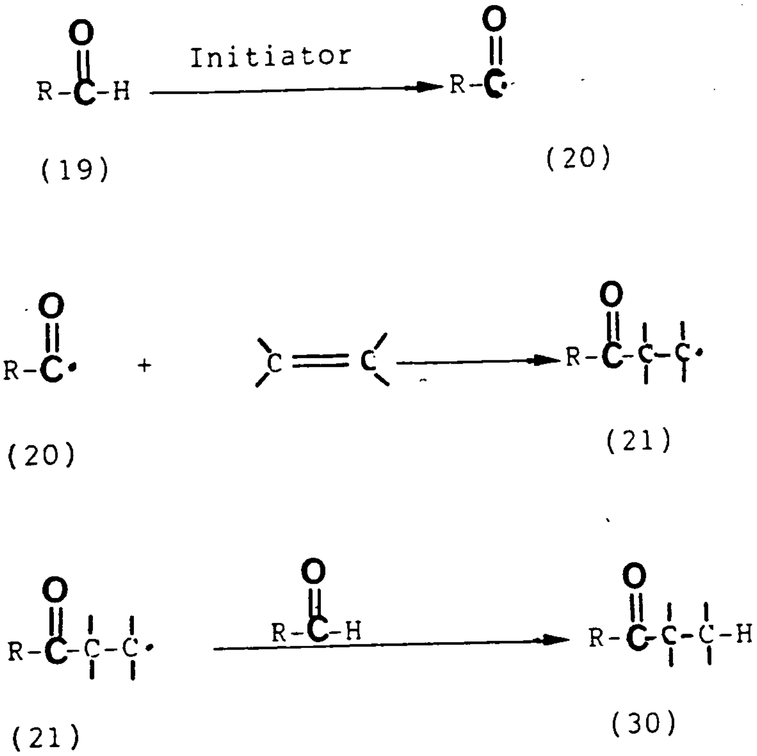
Alkene	Ether	Method of Initiation	Product	Reference
$CF_3CF=CF_2$	$(CH_3)_2O$	gamma	$CH_3OCH_2CF_2CFHCF_3$	28
"	$(C_2H_5)_2O$	gamma	 $CH_3CH_2O\underset{\underset{Rf}{\vert}}{C}HCH_3$ +  $CH_3\underset{\underset{Rf}{\vert}}{C}HO\underset{\underset{Rf}{\vert}}{C}HCH_3$	28
"		gamma		28

Rf= CF_2CFHCF_3

Alkene	Ether	Method of Initiation	Product	reference
$CF_3CF=CF_2$	$RfCF_2OEt$	gamma	$RfCF_2OCH(CH_3)CF_2CFH-CF_3$ $Rf= CHF_2$, CHFCl, $CHCL_2$	30
$CFCl=CCl_2$		gamma		24
$CFCl=CFCl$	$(C_2H_5)_2O$	gamma	 $CH_3\underset{\mid \atop CFClCFHCl}{C}HOCH_2CH_3$	24
	$(CH_3)_2O$	gamma, DBP		29
//		gamma		28
	$(CH_3)_2O$	gamma		29
//		gamma		28
//		gamma		28

II C ADDITION OF ALDEHYDES

The addition of an aldehyde to an olefin results in the formation of a ketone.



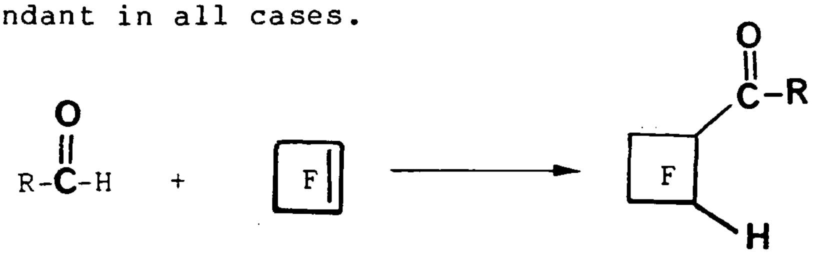
The reactivity is accounted for by stabilization, involving the adjacent oxygen lone pair of electrons in an analogous manner to that with ethers.

A series of reactions of aldehydes with fluorinated alkenes results in fluorinated ketone which have been obtained by gamma radiation-initiated 23, 24, 39-45 and peroxide 46-47.

In some cases, the yield of 1:1 adducts are fairly good.

With simple olefins such as ethylene, telomer formation does occur.

Cyclic olefins react readily with aldehydes, for example, hexafluorocyclobutene reacted readily with aldehydes 43, the yield of 1:1 adduct increasing the size of R. As in the corresponding alcohol additions 43 two stereoisomers of (31) were produced and once again the trans isomer was more abundant in all cases.

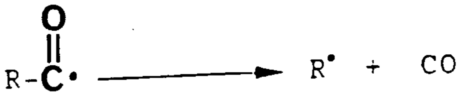


[43]

R= CH_3, C_2H_5, C_3H_7.

(31)

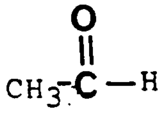
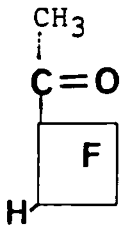
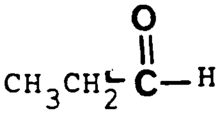
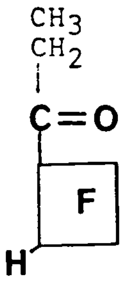
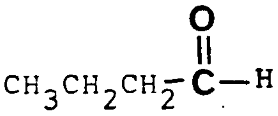
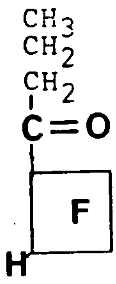
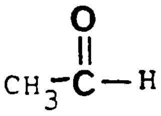
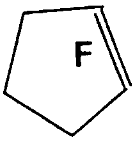
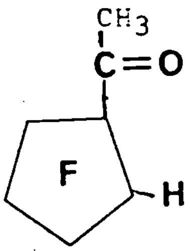
A side reaction which tends to lower the yields of ketone is the decarbonylation of an acyl radical.



$$R\text{-}\overset{O}{\overset{\|}{C}}\cdot \longrightarrow R^{\cdot} + CO$$

Substitution of the α-carbon atom increases the possibility of the elimination of carbon monoxide from the acyl radical. In some cases, such as tri-methylacetaldehyde, breakdown is complete. The elimination is temperature-dependent and becomes appreciable even with the normal aldehydes at temperatures above 100^{0}C 43.

Table 5 The Addition of Aldehydes Via Free-Radical

Aldehydes	Alkenes	Method of Initiation	Product	Ref.
 $CH_3-\overset{O}{\overset{\|}{C}}-H$		gamma, peroxide		27,53
 $CH_3CH_2-\overset{O}{\overset{\|}{C}}-H$		gamma		27
 $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-H$		gamma		27
 $CH_3-\overset{O}{\overset{\|}{C}}-H$		gamma, peroxide		53

DISCUSSION

CHAPTER 3

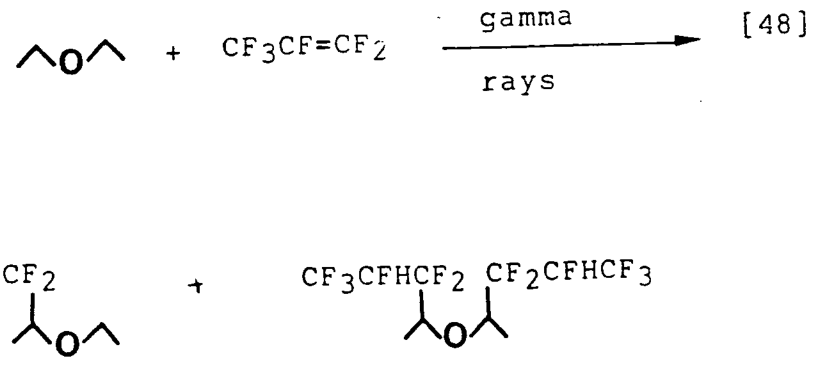
FREE RADICAL ADDITION OF ETHERS TO FLUORINATED ALKENES AND THE CHEMISTRY OF THESE ADDUCTS

Previous work on the addition of ethers to fluoroalkenes has been listed in Table 4. It was necessary to repeat a few of these reactions in order to prepare some ether adducts and to do some chemistry on these aducts.

III A ADDITION OF ETHERS TO FLUORINATED ALKENES

1. Addition of Diethylether to Hexafluoropropene.

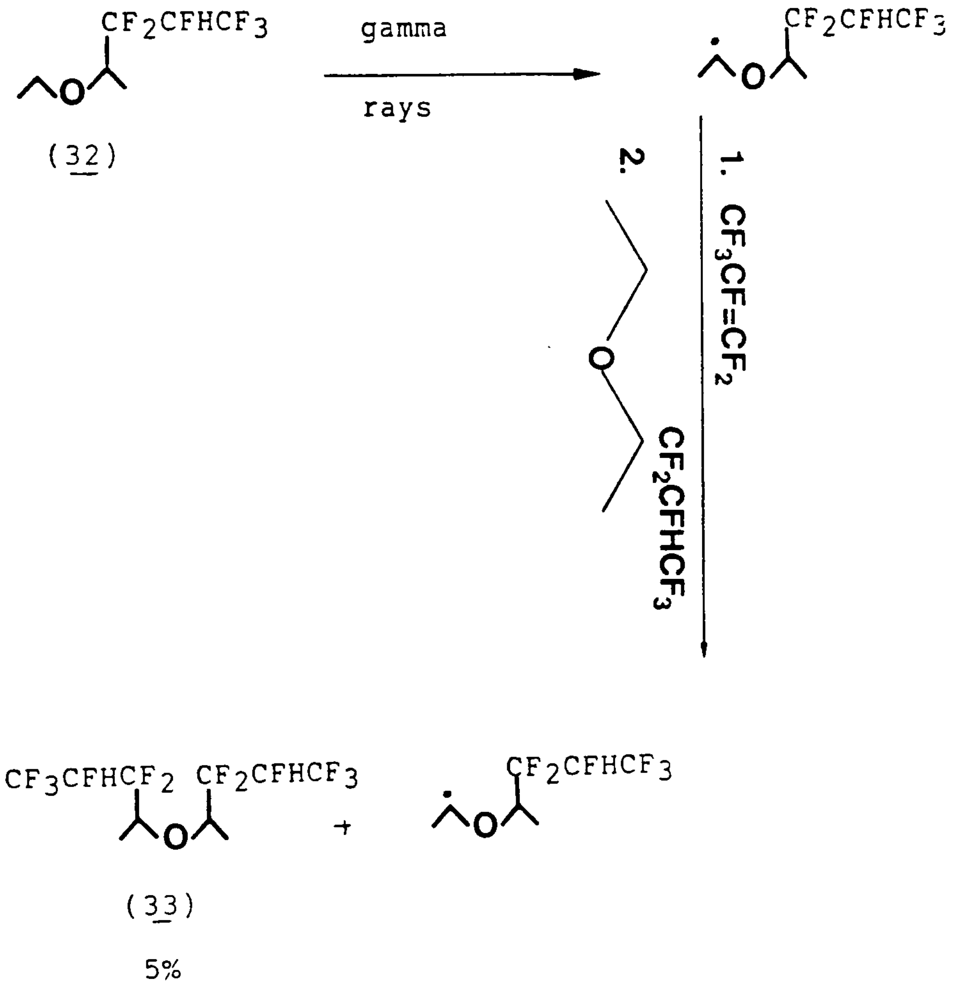
Diethylether reacted with hexafluoropropene and gave a mixture of mono-adduct (32) and di-adduct (33) in roughly equal proportions.



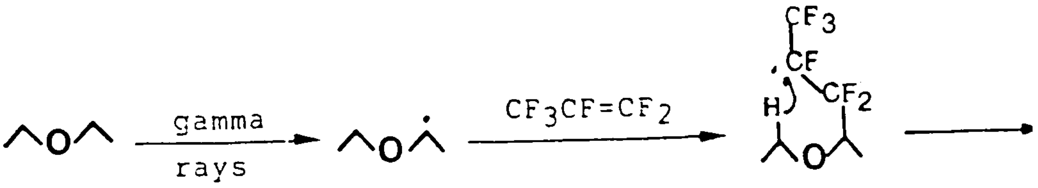
(32) 39%

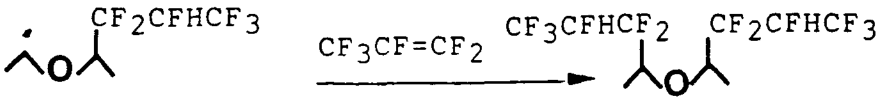
(33) 46%

A previous worker 48 has shown that the addition of adduct (32) to hexafluoropropene gave low conversion to the di-adduct (33).



It was believed that the production of di-adduct (33) in good yield is coming, from the intramolecular 1,5 hydrogen transfer.

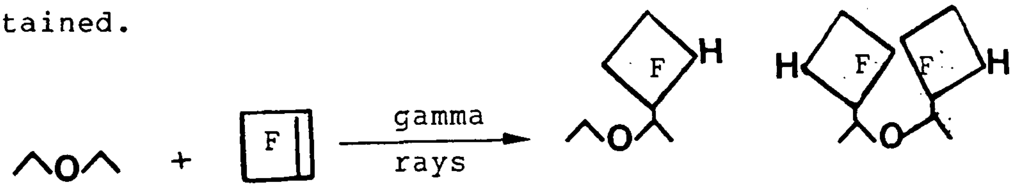




(33)

2. Addition of Diethylether to Hexafluorocyclobutene.

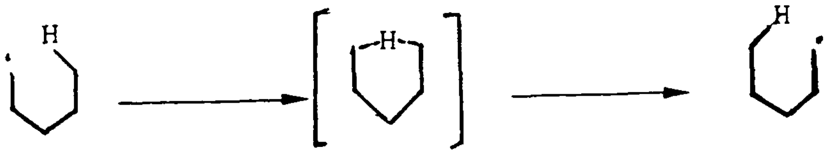
The addition of diethylether to hexafluorocyclobutene occurs very readily using γ-ray initiation. High yields were obtained. A mixture of trans-cis-isomers was also obtained.



(34) 77%

(35) 13%

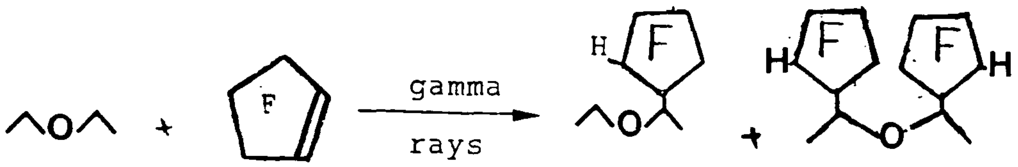
It was believed that F-cyclobutene does not favourably undergo the 1,5-hydrogen transfer step. The hydrogen transfer process, both inter-and intramolecular mechanism, is well documented 49 and is generally believed to occur through a linear transition state.



It is obvious that with F-cyclobutene, the strained 4-membered ring is not flexible enough to allow a linear transition state to form easily and hence mainly mono-adduct (34) is formed.

3. Addition of Diethylether to Octafluorocyclopentene.

The addition of diethylether to octafluorocyclopentene which was initiated by gamma rays and gave a high yield of products.



(36) 65%

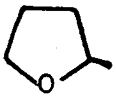
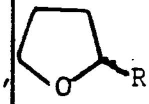
(37) 22%

It is clear that F-cyclopentene has more tendency than F-cyclobutene to undergo the 1,5-hydrogen transfer. So, we obtained a little more of the di-adduct in the addition of diethylether to octafluorocyclopentene.

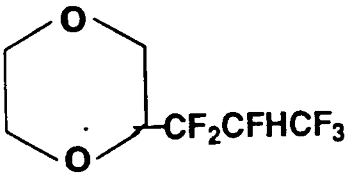
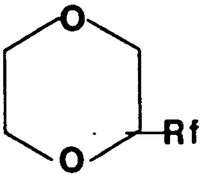
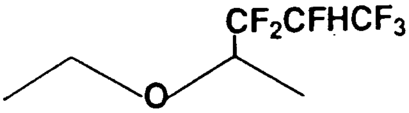
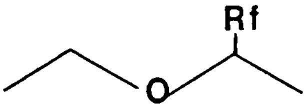
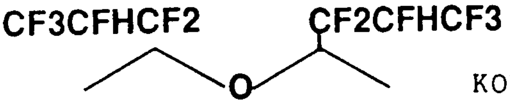
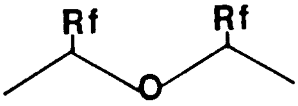
III B DEHYDROFLUORINATION

The dehydrofluorination of ether/hexafluoropropene mono-adducts have been prepared by other workers 31, 35, 49 with varying yields (Table 6)

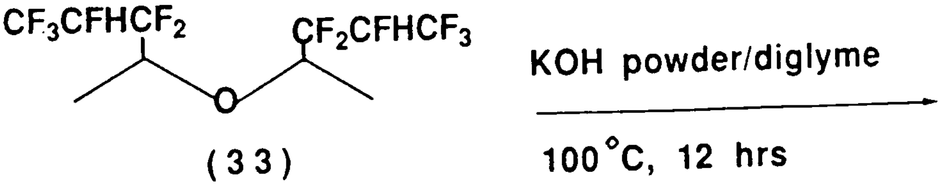
Table 6

Ether adducts	Conditions	Product	Ref.
- CF_2CFHCF_3 (38)	KOH Powder, 150°C,7.5hr	Rf 47% (39)	[49]
- (38)	KOH Powder, reflux, 2hrs	(39), 75%	[31]
- (38)	KOH Powder, diglyme, 120°C,8 hrs	(39),75%	[35]
- (38)	Na/t-butyl alcohol,25°C 7 hrs.	(39)	[35]

Rf= CF =CFCF$_3$

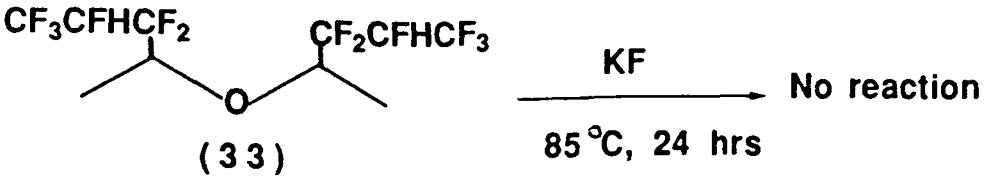
Ether adduct	Conditions	Product	Ref.
 (40)	KOH Powder 150°C,7.5 hrs .	 (41) 21%	[49]
 (32)	KOH Pellets 85°C,7hrs	 (42) 78%	[50]
 (33)	KOH Pellets 85°C,15hrs,. 130°C, 1hrs	 (43) 60%	[50]

In this study some attempts to dehydrofluorinate (33) di-adducts using potassium fluoride, potassium hydroxide in diglyme, sodium/t-butanol and triethylamine yielded very low conversion to product, or just starting materials were recovered.

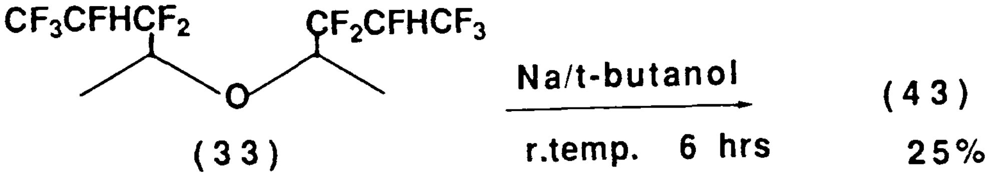


(33)

(43)
20%

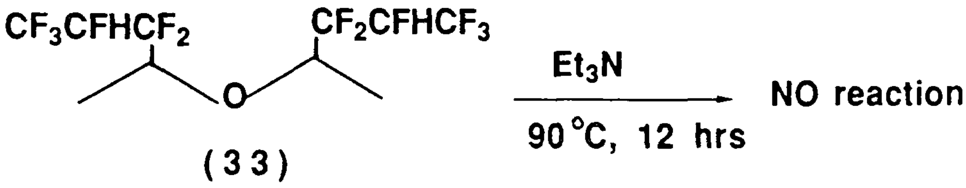


(33)



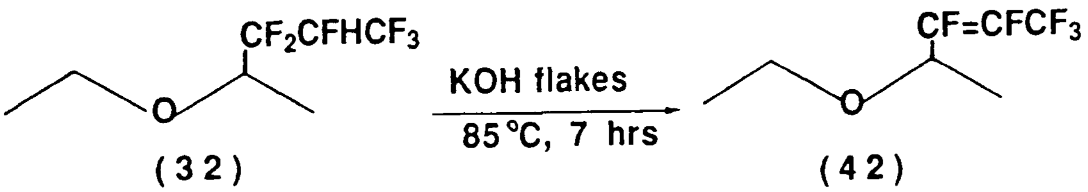
(33)

(43)
25%



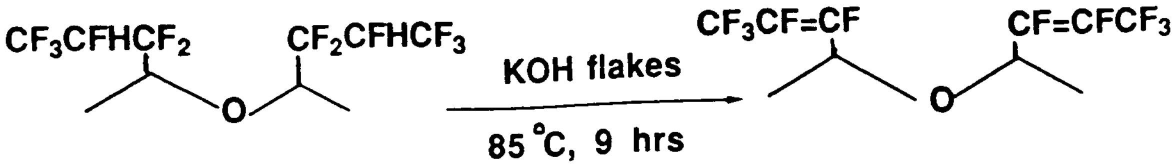
(33)

We obtained dehydrofluorination of the mono-adduct (32) and di-adduct (33) by using potassium hydroxide pellets which was improved by a previous worker 50, in order to get enough material of these adducts to do some chemistry on them.



(32)

(42)
70%

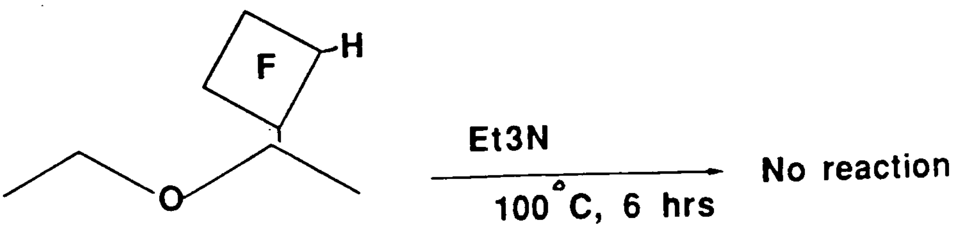


(43)

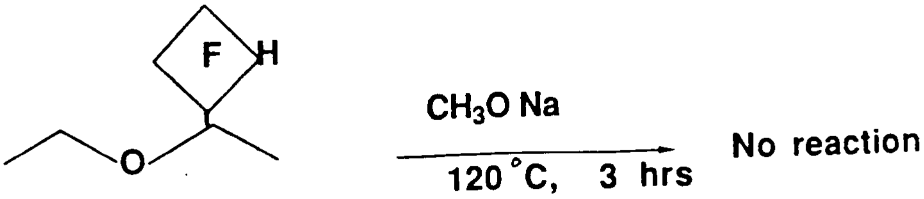
70%

Also, in this study a successful attempt to dehydrofluorinate diethylether/hexafluorocyclobutene mono-adduct (34) was carried out by heating the mono-adduct (34) with caesium fluoride in a sealed system.

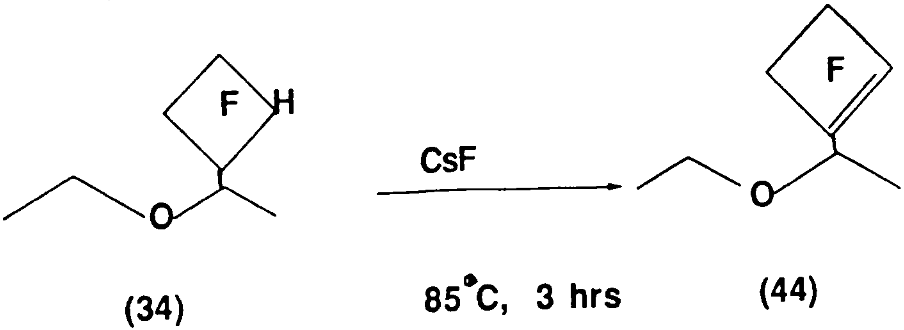
In contrast, other attempts to dehydrofluorinate (34) using triethylamine and sodium methoxide proved unsuccessful, even at elevated temperatures.



(34)



(34)



(34)

(44)

45%

III C NUCLEOPHILIC REACTIONS OF FLUOROOLEFIN ADDUCTS

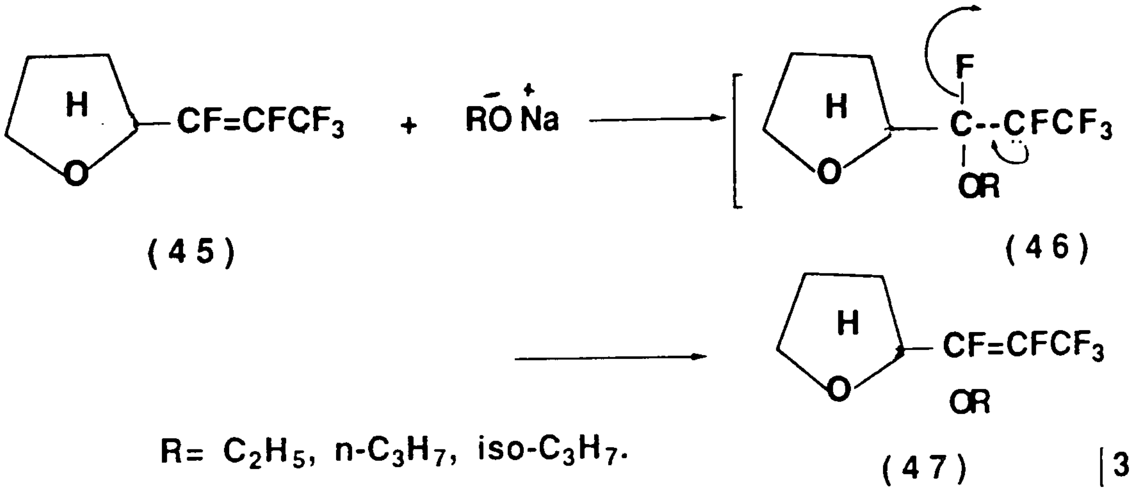
1. Introduction

Nucleophilic reactions of perfluoro- and chloroolefins containing two to four carbon atoms in the molecule have been reported in numerous publications 51. These olefins combine readily, preferably in the presence of basic catalysts, with alcohols, thiols, and phenols to give saturated ethers as major or sole products.

Some unsaturated ethers formed by replacement of vinylic fluorine by alkoxy or aryloxy groups were obtained occasionally in the reactions of alcohols with fluoroolefins 1,35. The tendency of unsaturated ethers to form at the expense of adducts, observed in the reactions with perfluoroisobutene 1, increases with the rise in basicity of the attacking alkoxy anion, viz.,

$$C_2H_5O < n\text{-}C_3H_7O < iso\text{-}C_3H_7O < n\text{-}C_4H_9O$$

It has been reported 6 that, in nucleophilic reactions with internally branched perfluoroolefins, there is a definite tendency to form unsaturated products as a result of the rising stability of the carbanionic intermediate involved (46)



R= C_2H_5, n-C_3H_7, iso-C_3H_7.

[35]

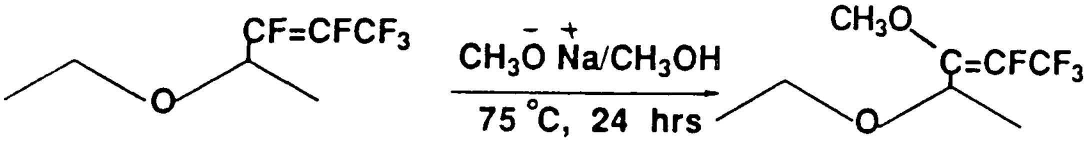
The reversal of the distribution of products in the above reactions as compared with the analogous reactions of perfluoropropene, which yielded saturated adducts mainly 1,52 can be rationalised in terms of the relative abilities of the possible carbanionic intermediate (46) to eject the fluoride ion and producing unsaturated adducts (47), rather than of their stabilities.

This study set out to describe the results of the reactions of various alcohols with α- (1,2,3,3,3-pentafluoro-1-propenyl) diethylether (42) and α,α′ - bis (1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43) which were prepared by dehydrofluorination of 1-methyl-2,2,3,4,4-hexafluorobutyl ether (32) and di(1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (33) respectively.

2. Nucleophilic reactions of α-(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (42) with sodium alkoxide

α - (1,2,3,3,3-pentafluoro-1-propenyl) diethylether (42) reacted with sodium alkoxide in parent alcohol solutions to give mixtures of isomers Z and E of 1-alkoxy-1-(1-ethoxyethyl)-tetrafluoropropene as a sole product in a good yield.

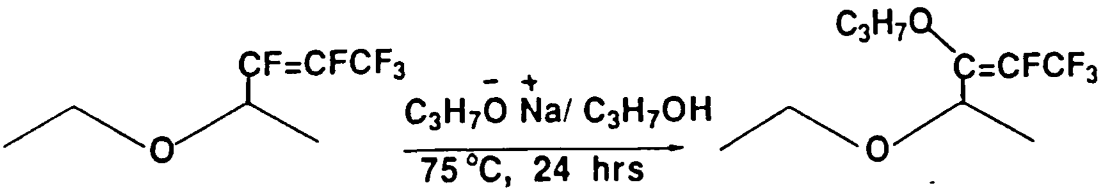
With sodium methoxide in solution (42) gave 1-methyl-methoxy-1-(1-ethoxyethyl)-tetrafluoropropene (48) as sole product.



(42) (48)

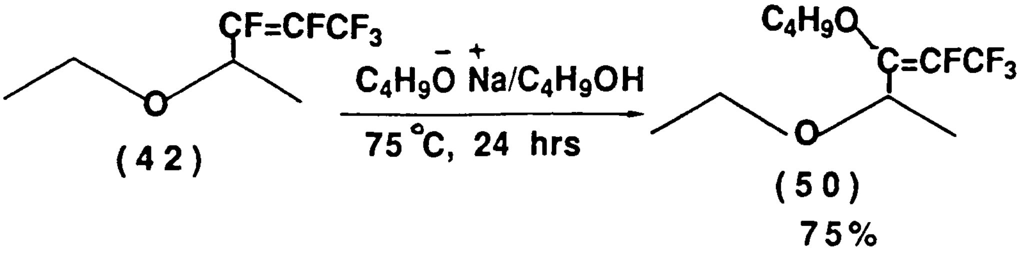
73%

Similarly sodium propoxide (42) gave 1-propoxy-1-(1-ethoxy-ethyl)-tetrafluoropropene (49)



(42) (49) 75%

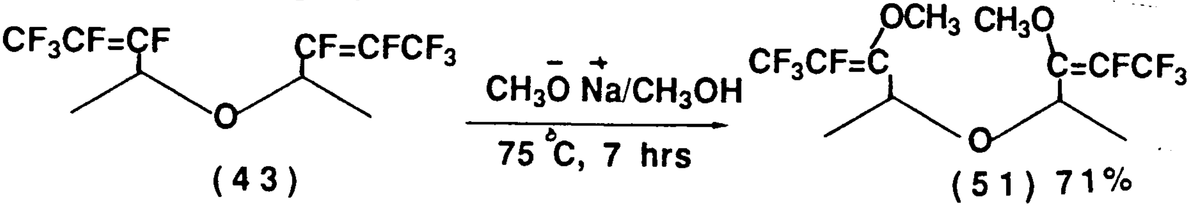
with sodium butoxide (42) gave 1-butoxy-1-(1-ethoxyethyl)-tetrafluoropropene (50)



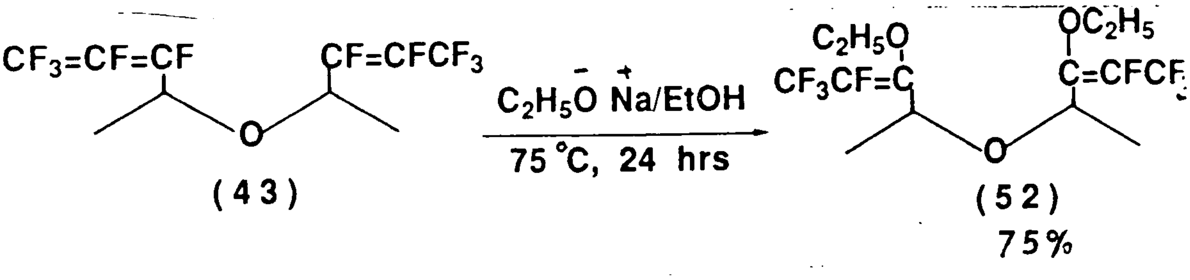
3. Nucleophilic reactions of α,ᾱ- bis (1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43) with sodium alkoxide.

α, ᾱ-Bis(1,2,3,3,3,-pentafluoro-1-propenyl) diethylether (43) reacted with sodium alkoxide in parent alcohol solutions to give a complex mixture of isomers Z and E of α,ᾱ -bis(1-alkoxy-tetrafluoro-1-propenyl) diethylether as a sole product.

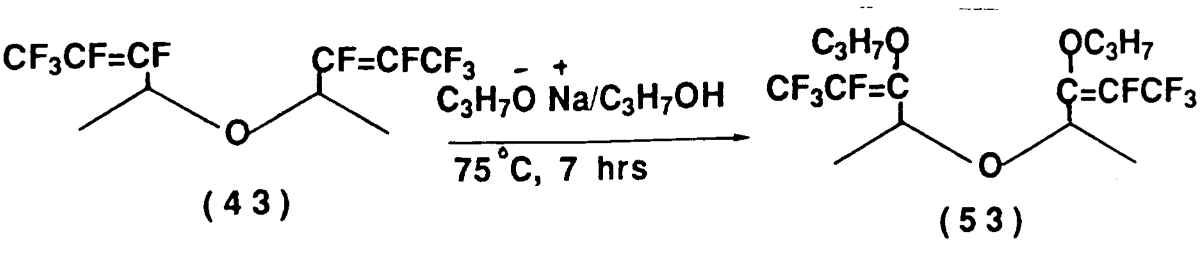
With sodium methoxide (43) gave α,ᾱ -bis-(1-methoxy-tetrafluoro-1-propenyl) diethylether (51) as sole product



With sodium ethoxide (43) gave α, ᾱ -bis(1-ethoxy-tetrafluoro-1-propenyl) diethylether (52)



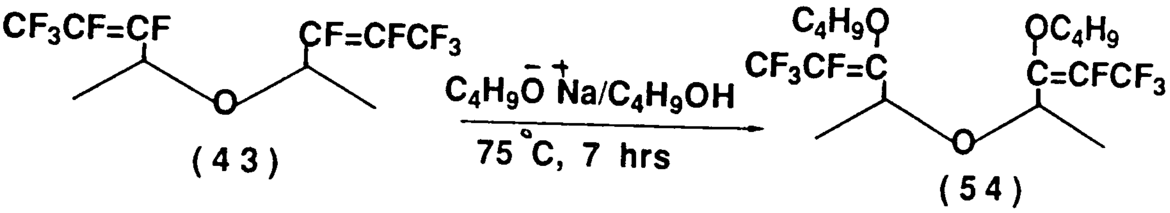
with sodium propoxide, (43) gave α,ά -bis(1-propoxy-tetrafluoro-1-propenyl) diethylether (53)


(43)

(53)

75%

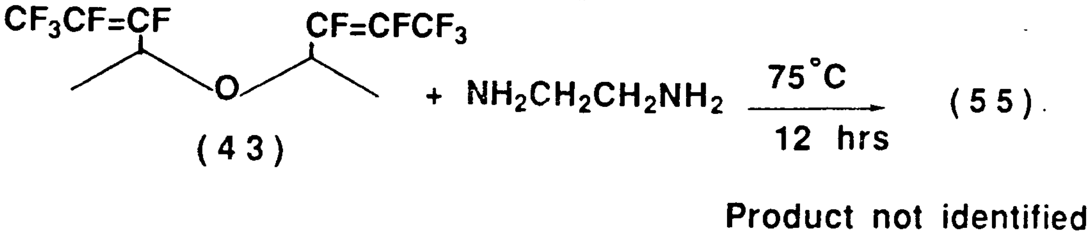
with sodium butoxide (43) gave α,ά -bis(1-butoxy-tetrafluoro-1-propenyl) diethylether (54)


(43)

(54)

74%

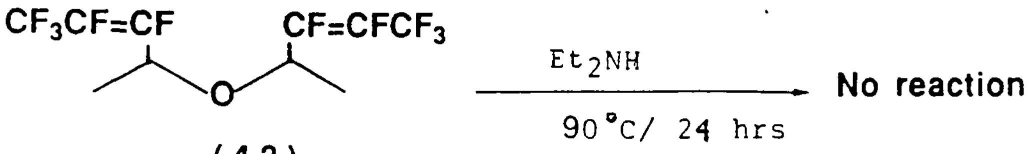
4. <u>Miscellaneous attempted nucleophilic reactions of α, ά -bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43) with nitrogen containing compounds.</u>


(43)

(55)

α, ά-bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43) reacted with ethylenediamine to give a complex product which was not identified.

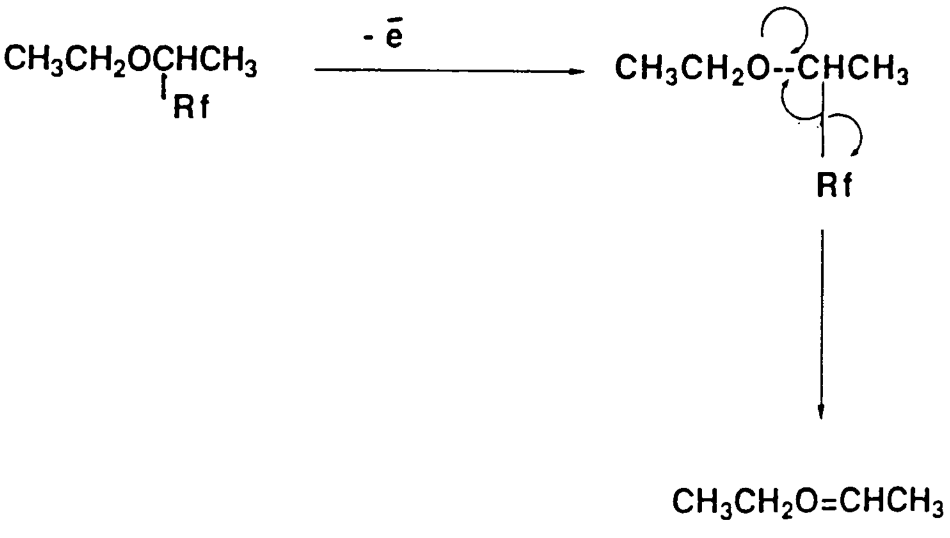
No product was obtained from the reaction of (43) with diethylamine.



(43)

III D IDENTIFICATION OF THE PRODUCTS

The most useful techniques for the characterization of the ether adducts were mass spectroscopy and NMR spectroscopy. The mass spectra consisted of very small molecular ion peaks and with di-adducts the molecular ion peak was often missing. The principal fragmentation was the cleavage of the carbon-oxygen bond and this process gives the base peak.



m/e 73 (100%)

The NMR spectra are very complex. The proton resonances are usually broad but the appearances of a doublet of multiplets at about 4.95 ppm (TMS reference) with a coupling constant of about 44 Hz is very characteristic of the CFH proton. The 1,1,2,3,3,3-hexaflouropropyl grouping from hexafluoropropene adducts give a similar fluorine-19 spectrum irrespective of the rest of the adducts structure. The trifluoromethyl resonances occur as multiplet at 73 to 78 ppm (CFCl3 reference). The difluoromethylene resonances occur usually at 119 to 130 ppm, and the tertiary fluorine resonances occur as multiplets at 212 to 220 ppm.

The polyfluorocycloalkene adducts were present as cis and trans isomers. The fluroine-19 chemical shift of the tertiary fluorine atoms in such adducts may be used to assign their sterochemistry 29. The chemical shifts of the CFR and CFH fluorine atoms were found to be consistently at higher field in the cis isomer than in trans isomer.

The dehydrofluorination adducts were present as cis and trans isomers. The fluorine-19 chemical shift of vinylic fluorines atom occur at 140 ppm, allylic fluorines atom occur at 160 ppm. No peaks occur at 210 to 220 ppm.

CHAPTER 4

FREE RADICAL ADDITION OF ALDEHYDES TO FLUORINATED ALKENES

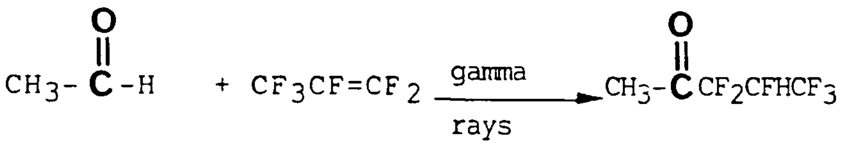
Previous work on the addition of aldehydes to fluoroalkenes has been listed in Table 5-p23.

In this study, we ran a series of reactions of mono-functional aldehyes and di-functional aldehydes with fluoroalkenes.

IV A ADDITION OF MONO-FUNCTIONAL ALDEHYDES TO FLUORINATED ALKENES.

1. Additions to Hexafluoropropene

A series of mono-functional aldehydes react with hexafluoropropene to form ketones usually in good yield. With acetaldehyde and C_3F_6, 3,3,4,5,5,5-hexafluoropentan-2-one (56) formed as sole product.

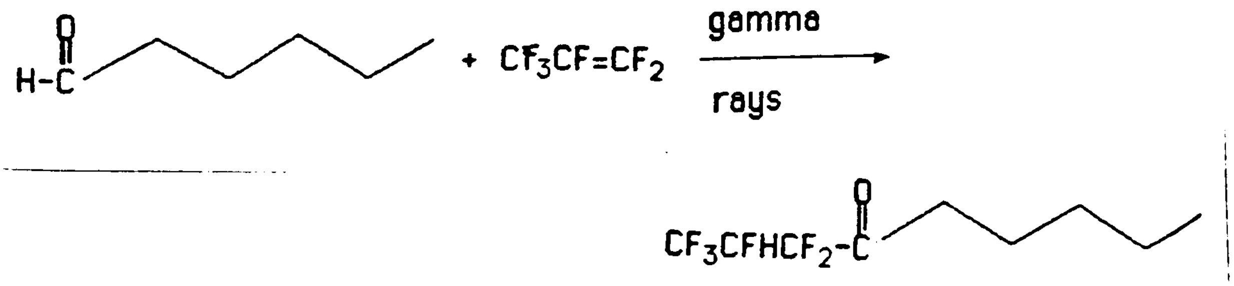


$$CH_3-\overset{\overset{O}{\|}}{C}-H + CF_3CF=CF_2 \xrightarrow[\text{rays}]{\text{gamma}} CH_3-\overset{\overset{O}{\|}}{C}CF_2CFHCF_3$$

(56)

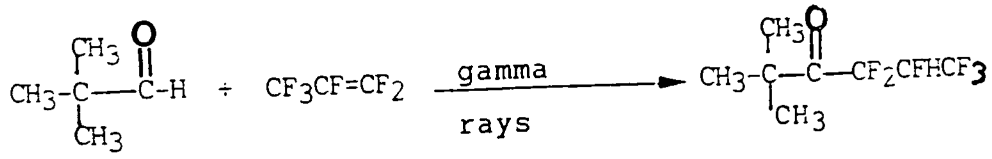
74%

Hexanal gave 1,1,1,2,3-hexafluorononа-4-one(57)



(57) 80%

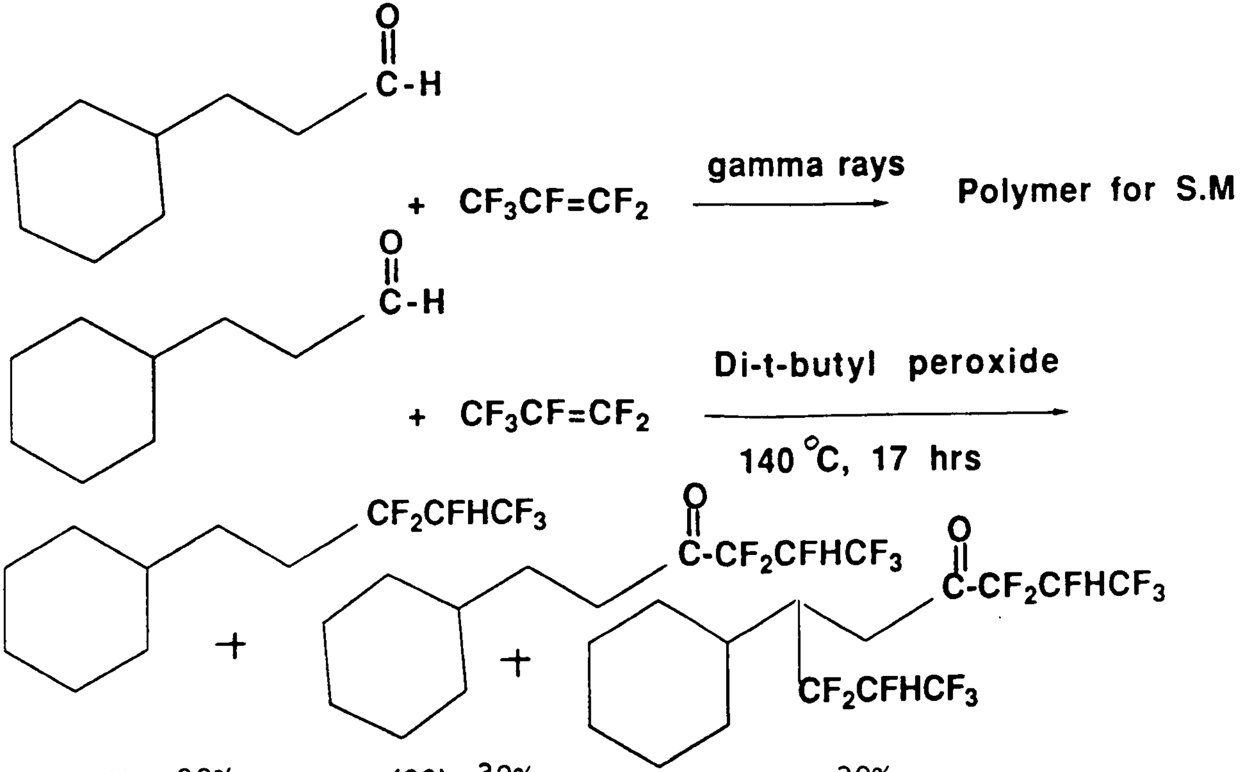
Trimethylacetaldehyde gave 2-H- hexafluoropropylt-butyl ketone (58)



(58)

81%

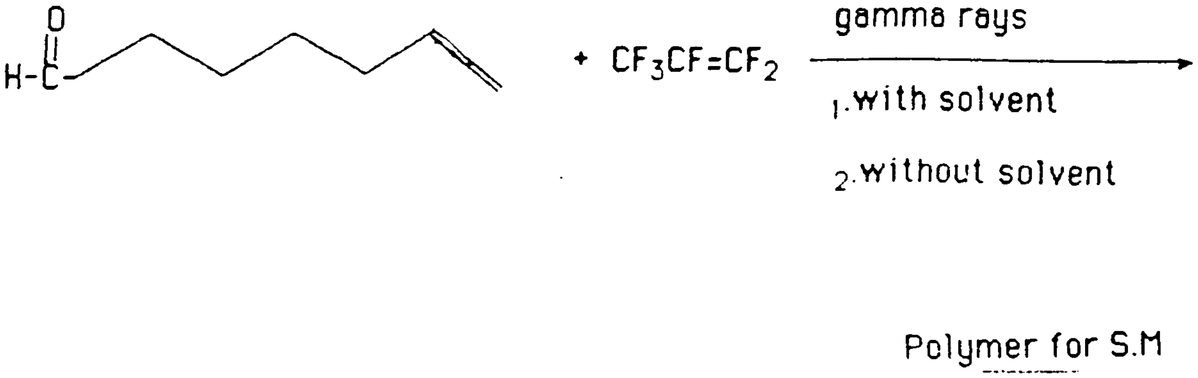
3-Cyclohexylpropanal gave a polymer from starting material which was initiated by gamma rays, but by peroxide it gave three products.



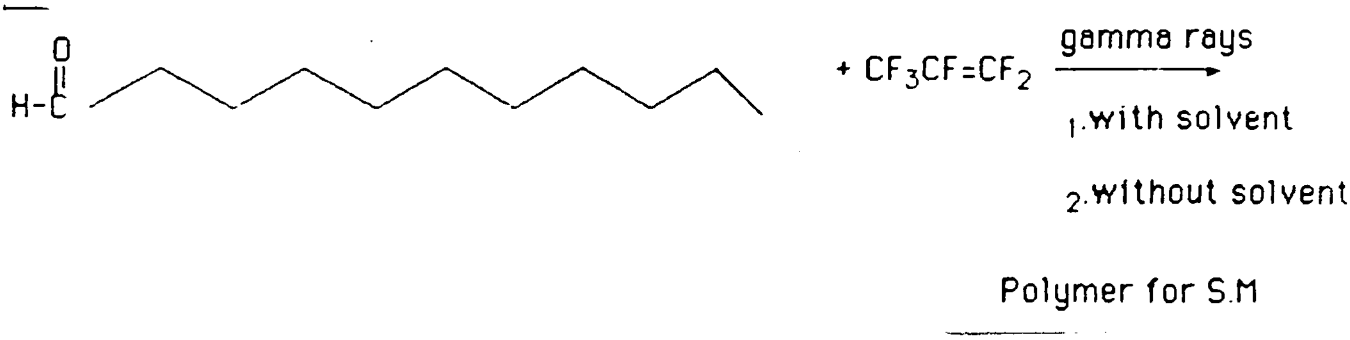
(59) 20% (60) 30% 39%

(61)

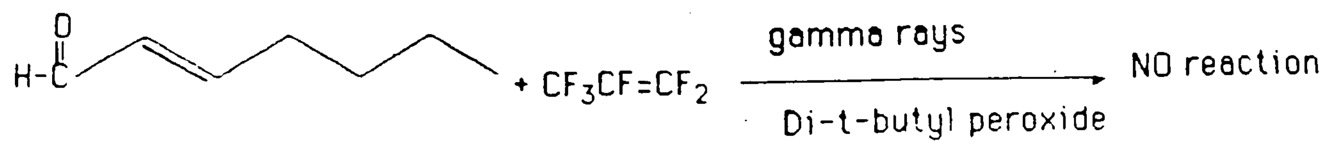
Attempted addition of C_3F_6 to 6-heptenal gave a polymer for starting material, was obtained with either solvent or without solvent.



Similarly, in the addition of C_3F_6 to monodecanal a polymer was obtained with either solvent or without solvent.

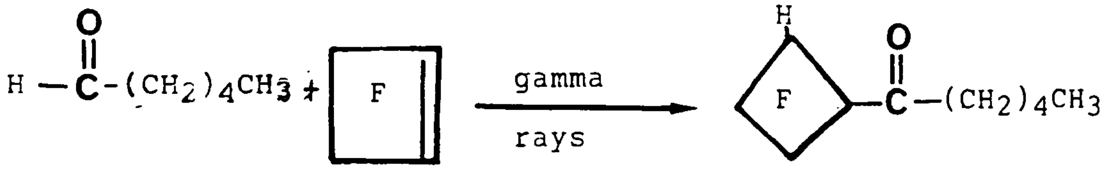


Attempted addition of C_3F_6 to trans-2-heptenal gave no product from either γ-rays or peroxide initiated reactions.



2. Addition to Hexafluorocyclobutene

Hexanal reacted with hexafluorocyclobutene and produced 2-Hydro-hexafluorocyclobutyl pentyl ketone (62) as the sole product.

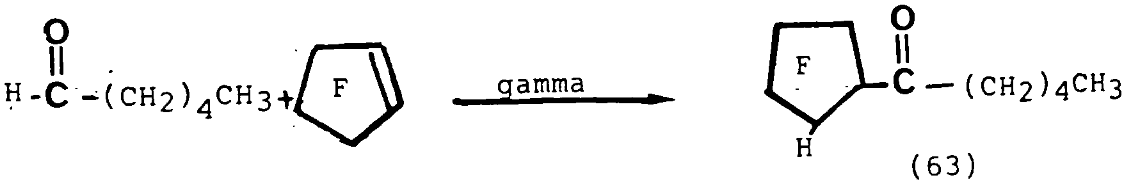


(62)

80%

3. Addition to Octafluorocyclopentene

Hexanal reacted with octafluorocyclopentene and produced 2-Hydro-octafluoropentyl pentyl ketone (63).

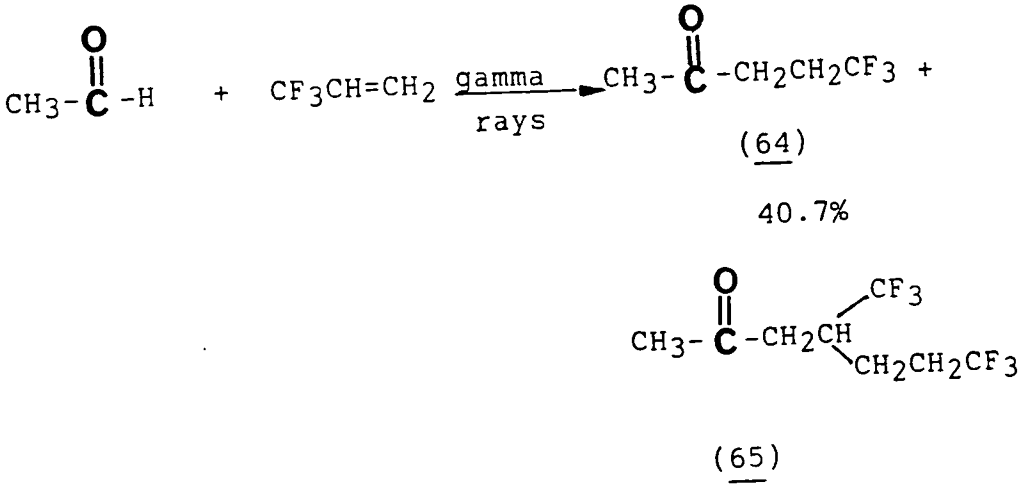


(63)

85%

4. Additions to 3,3,3-Trifluoropropene

Acetaldehyde reacted with 3,3,3-trifluoropropene and gave two major products, 5,5,5-trifluopentan-2-one (64) and 4-trifluoromethylheptan-2-one (65)



$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + CF_3CH{=}CH_2 \xrightarrow[\text{rays}]{\text{gamma}} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_2CF_3 + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH(CF_3)CH_2CH_2CF_3$$

(64)

40.7%

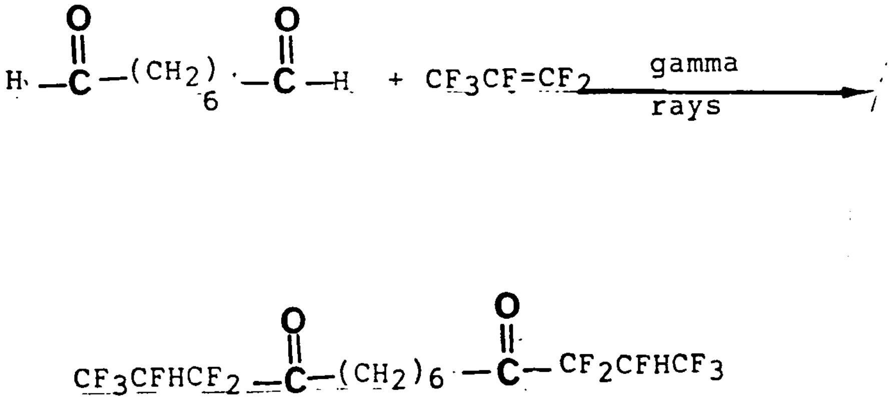
(65)

48.3%

IV B ADDITION OF DI-FUNCTIONAL ALDEHYDES TO FLUORINATED ALKENES

1. Additions to Hexafluoropropene

1,8-octanedial reacted with hexafluoropropene and produced 1,1,1,2,3,3,12,12,13,14,14,14-tetradecan-4,11-dione (66) as a sole product.

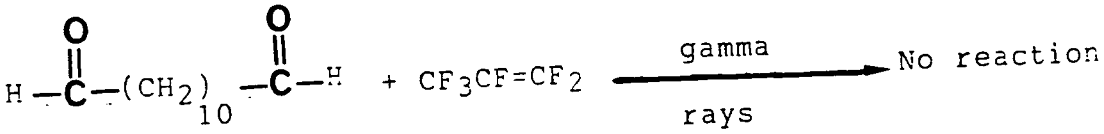


$$H\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_6\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + CF_3CF{=}CF_2 \xrightarrow[\text{rays}]{\text{gamma}} CF_3CFHCF_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_6\text{-}\overset{O}{\overset{\|}{C}}\text{-}CF_2CFHCF_3$$

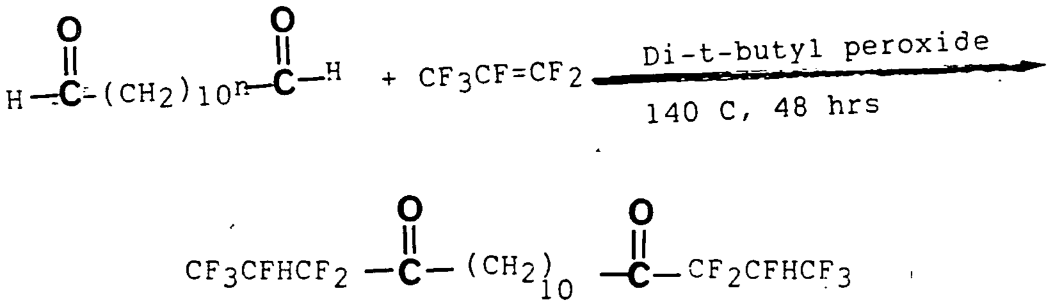
(66)

90%

No product was obtained from the x-ray initiated reaction of 1,12-dodecanedial with hexafluoropropene; but with peroxide a reaction occurred and formed 1,1,1,2,3,3,3,16,16,17,18,18,18-octadecan-4,15-dione (67).



$$H{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_{10}{-}\overset{O}{\overset{\|}{C}}{-}H + CF_3CF{=}CF_2 \xrightarrow[\text{rays}]{\text{gamma}} \text{No reaction}$$



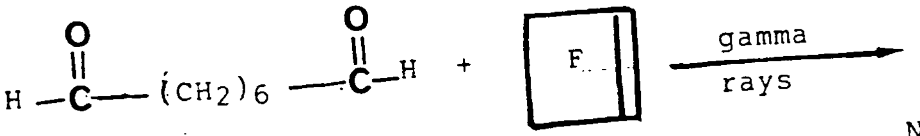
$$H{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_{10}{-}\overset{O}{\overset{\|}{C}}{-}H + CF_3CF{=}CF_2 \xrightarrow[\text{140 C, 48 hrs}]{\text{Di-t-butyl peroxide}}$$

$$CF_3CFHCF_2{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_{10}{-}\overset{O}{\overset{\|}{C}}{-}CF_2CFHCF_3$$

(67) 45%

2. <u>Additions to Hexafluorocyclobutene</u>

1,8-octanedial reacted with hexafluorocyclobutene, and yielded a high molecular weight product which was not identified.

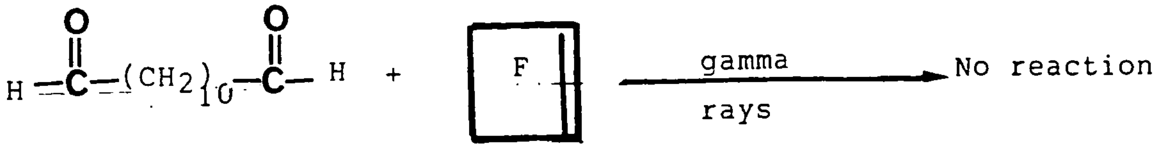


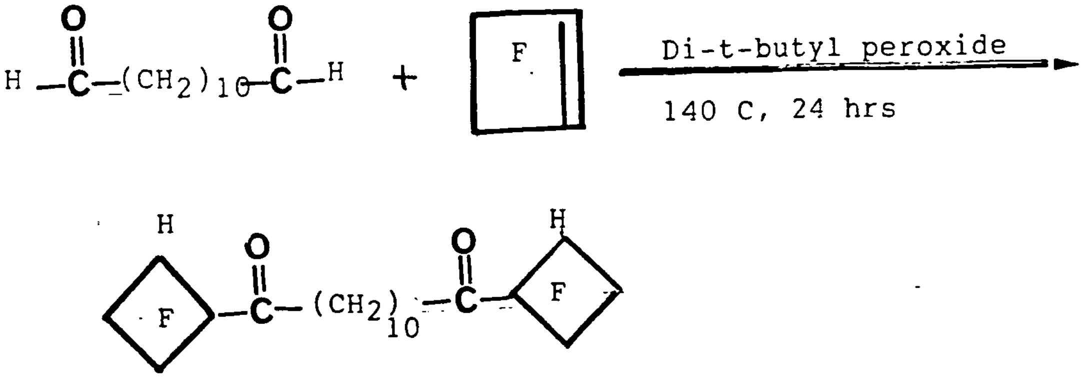
$$H{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_6{-}\overset{O}{\overset{\|}{C}}{-}H + \xrightarrow[\text{rays}]{\text{gamma}}$$

(68)

Not identified

No product was obtained from the γ-ray initiated reaction of 1,12-dodecanedial with hexafluorocyclobutene, but with peroxide, a reaction occurred and formed 1,12-di (2-Hydro-perfluorocyclobutyl) dodecanedione (69)



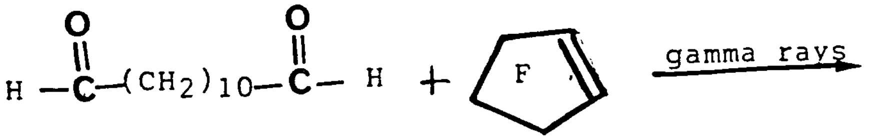


(69)

83%

3. Addition to Octafluorocyclopentene

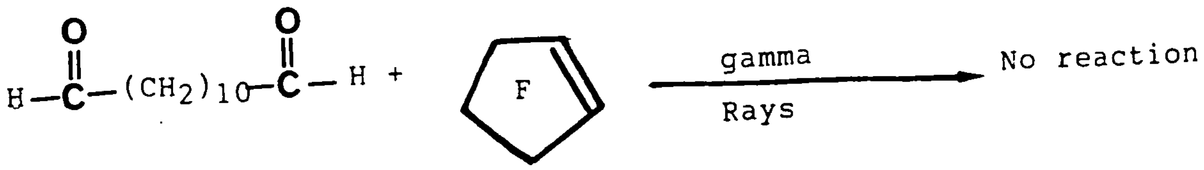
1,8-octanedial reacted with octafluorocyclopentene, and yielded a higher molecular weight product which was not identified.

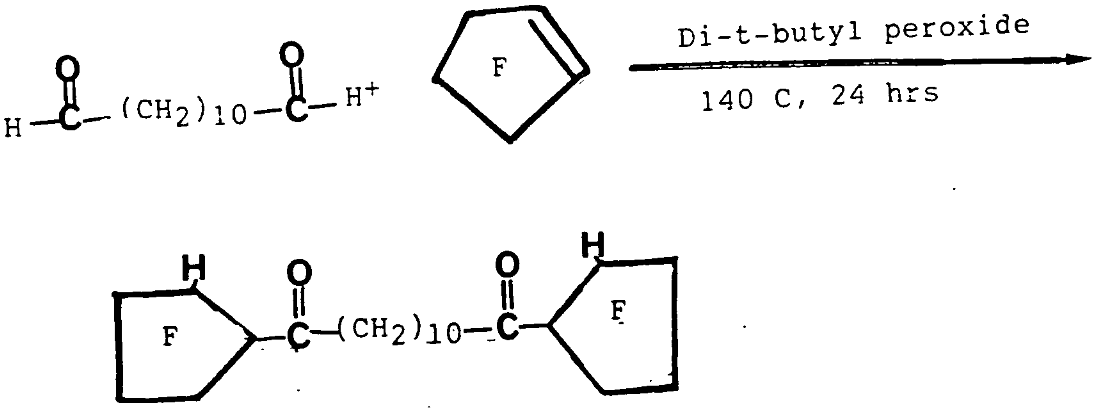


(70)

Not identified

No product was obtained from the γ-ray initiated reaction of 1,12-dodecanedial with octafluorocyclopentene, but with peroxide initiated, a product was obtained which was 1,12-di (2-Hydro-perfluorocyclopentyl) dodecanedione (71)





(71)

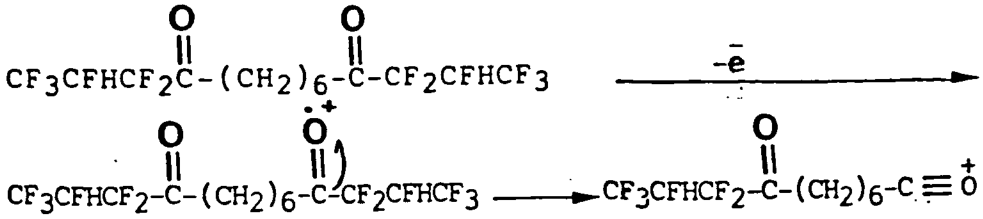
80%

IV C IDENTIFICATION OF PRODUCTS

The infra red spectra of aldehyde adducts (ketone) show the carbonyl stretching vibration at 1765 to 1789 cm^{-1}

The proton NMR spectra were useful in identifying CFH and the disappearance of aldehydic protons in the adducts.

The mass spectra show very small parent peaks and the base peak results usually from cleavage next to the carbonyl group with charge residing on the carbonyl fragment.



$$\mathrm{CF_3CFHCF_2\overset{O}{\overset{\|}{C}}-(CH_2)_6-\overset{O}{\overset{\|}{C}}-CF_2CFHCF_3} \xrightarrow{-\bar{e}}$$

$$\mathrm{CF_3CFHCF_2-\overset{O}{\overset{\|}{C}}-(CH_2)_6-\overset{\dot{O}^{+}}{\overset{\|}{C}}-CF_2CFHCF_3} \longrightarrow \mathrm{CF_3CFHCF_2-\overset{O}{\overset{\|}{C}}-(CH_2)_6-C\equiv\overset{+}{O}}$$

IV D Conclusions

The free-radical additions of aldehydes to fluorinated alkenes provided an excellent route to functional fluorocarbons. The reactions of mono-functional aldehydes and di-functional aldehydes with fluoroalkenes produced new ketone compounds. The adducts produced from these reactions can be converted into novel and interesting products with a whole new chemistry of their own.

EXPERIMENTAL

INSTRUMENTATION

Fractional distillation of product mixtures was carried out using Fischer-Spaltrohr HMS 255 and HMS 500, small and large concentric tube system.

Gas liquid chromatographic (g.l.c.) analyses were carried out on a Varian Aerograph Model 920 (gas density balance detector) gas chromatograph using columns packed with 20% di-isodecylphthalate on chromosorb P (column A), 20% Krytox on chromosorb P (column K), 5% Poly(ehtylene glycol) 20M on chromosorb W (column PEG20M) or 10% silicone elastomer 30 on chromosorb p (column 10% SE30). A Hewlett-Packard 5890A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column was also used. Preparative g.l.c. was carried out using a Varian Aerograph Model 920 (catharometer detector) gas chromatograph.

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 or a Carlo Erba 1106 Elemental Analyser. Analyses for halogens were performed as described in the literature.

Infrared (i.r.) spectra were recorded on either a Perkin-Elmer 457 or 577 Grating Spectrophotometer using conventional techniques.

Proton (^{1}H) n.m.r. spectra were recorded on a Varian EM360L spectrometer operating at 60 MHz, an Hitachi Perkin-Elmer R-24B spectrometer operating at 60 MHz or a Bruker AC250 spectrometer operating at 250 MHz.

Fluorine (^{19}F) n.m.r. spectra were recorded on a Varian EM360L spectrometer operating at 56.45 MHz or a Bruker AC250 spectrometer operating at 235.3 MHz.

Mass spectra of solid or one component liquid samples were recorded on a VG 7070E spectrometer. G.l.c. mass spectra were recorded on either a VG Micromass 12B spectrometer linked to a Pye 104 gas chromatograph or the VG 7070E spectrometer linked to a Hewlett-Packard 5790A gas chromatograph fitted with a 25 m cross-linked methyl silicone capillary column.

PURIFICATION OF REAGENTS

In general, hydrocarbon reagents were dried with anhydrous magnesium sulphate and distilled onto 4A molecular sieves. Diethylether with sodium. The hazards of ethers used gave a negative peroxide test

GAMMA RAY INITIATION

a. Cobalt-60 Gamma Ray Source

All gamma ray initiated reactions were carried out using cobalt-60 gamma rays. The source is housed in a purpose built irradiation chamber. Pellets of the source material are enclosed in a steel container which is located on the end of a steel hawser within a steel guiding tube. When not in use the source is located within a lead and concrete bunker. The source may be electrically or mechanically driven from the bunker via the steel guide tube to the irradiation site by winding the hawser. A number of safety procedures are incorporated in the winding mechanism such that access to the irradiation chamber through the gate is not possible unless the source is in the bunker. Samples to be irradiated are placed in a metal holder which positions them a set distance from the source.

b. Measurements of Dose Rates

(i) Fricke Dosimeter

The dose of radiation received by the samples was calculated using the Fricke dosimeter. The method involves the oxidation of an acid solution of ferrous ions to ferric, in the presence of oxygen and under the influence of the radiation. The increase in ferric ion concentration was determined spectrometrically. The dosimeter solution was prepared by adding concentrated AR sulphuric acid (22ml) to distilled water (600ml) with continual stirring. When cool, AR ferrous ammonium sulphate (0.56g) and AR sodium chloride (0.06g) were dissolved and the volume made up to one litre using distilled water. The solution was irradiated with gamma rays using the same conditions as used for the reactions. An optimum dose of 15 to 20 Krad is required for most accurate results because above a dose of 40 Krad the dissolved oxygen becomes depleted in the dosimeter solution.

(ii) Definitions

RAD:	The unit of absorbed dose, corresponds to any energy absorption of 100 erg/g of material.
G value:	The radiationchemical yield. The number of molecules of materials changed or of product formed, for each 100 eV of

radiation energy absorbed by the system.

(iii) Calculation

A worked example is given below to show how the dose rate may be calculated using the Fricke dosimeter. Fricke solution (20ml) was irradiated for 1.2 hours at 5 cm from the ^{60}Co gamma ray source. The absorbance of the irradiated solution was found to be 0.61 (at 304nm) when measured in a 1 cm cell at 24^0C.

$$1 \text{ rad} = 100 \text{ erg/g}$$

$$\Longrightarrow \quad 1 \text{ rad} = 6.242\text{x}10^{13} \text{ eV/g}$$

$$\therefore \quad 1 \text{ rad will convert } 6.242 \text{ x } 10^{13} \text{ x } \frac{G}{100} \text{ molecules/g}$$

$$6.242 \text{ x } 10 \text{ x } \frac{G}{Na} \text{ mol/g}$$

where N_a= Avogadro number.

$$= 1.036 \text{ x } G \text{ x } 10^{-12} \text{ mol/g}$$

$$\therefore \quad 1 \text{ rad will convert } 1.036 \text{ x } 10^{-3} \text{ x } G \text{ x}1.024 \text{ mol/dm}^3$$

-----------(1)

where 1.024g/cm^3 is the density of the dosimeter solution.

The variation of the molar extinction coefficient with temperature is given by the expression

$$\varepsilon_2 = \varepsilon_1[1+ 0.007(t_2- t_1)]$$

as ε_1= 2193 at t1=25 C for Fe^3 at 304nm, then ε_2= 2178

$$\text{Concentration} = \frac{\text{absorbance}}{\varepsilon_2} = \frac{0.61}{2178}$$

$\Longrightarrow$ Concentration of Fe^{3+} $=0.28 \times 10^{-3}$ mol/dm^{3}

Therefore the dose produces a change of

0.28×10^{-3} mol/dm^{3} ---------(2)

$$(1) \quad (2) \Longrightarrow \text{Dose} = 1000\text{x}\ \frac{0.28}{15.5\text{x}1.036\text{x}1.024}\ \text{Krad}$$

$$\Longrightarrow \text{Dose} = 17.0\ \text{Krad.}$$

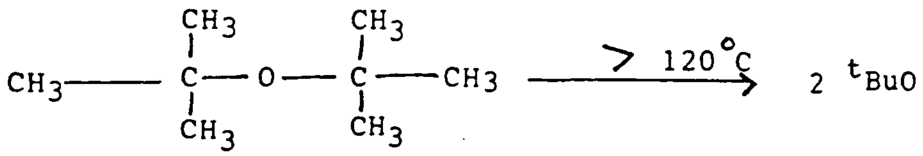
$$\text{Dose rate} = \frac{17.0}{1.2}\ \text{Krad/hr.}$$

$$\text{Dose rate} = 14.2\ \text{Krad/hr.}$$

The value of the dose is within the optimum range for the dosimeter. The dose rate was determined periodically throughout the duration of this work. The half life of cobalt-60 is 5.26 years.

Thermal Initiation.

One peroxide initiator has been used during this study. Di-t-butyl peroxide has a useful half life above 120°C,



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3 \xrightarrow{>120^{\circ}C} 2\ {}^{t}BuO$$

It was added to the reactant mixture at 1 to 5% (wt :wt) concentration.

CHAPTER 5

EXPERIMENTAL TO CHAPTER 3

V A GENERAL PROCEDURE

1. X-Ray Initiated Reactions

Solid and/or liquid reagents were introduced into a pyrex Carius tube (ca.100ml) and degassed. Any gaseous reagents were then transferred into the tube using normal vacuum line techniques. The tube was sealed with the reagents frozen (liquid air) and under vacuum. The tube was placed in a metal sleeve and, unless otherwise stated, was then irradiated with γ-rays to a total dose of ca.10 Mrad at a temperature of 18^{0}C. The Tube was opened while the contents were frozen (liquid air) and any gaseous species were transferred under vacuum.

2. Peroxide Initiated Reactions

Liquid and/or solid reagents and di-t-butylperoxide as initiator were introduced into a nickel tube (ca.150ml) which was then sealed with the reagents frozen (liquid air) and under vacuum. The tube was heated at the required temperature in a thermostatically controlled rocking furnace. The tube was opened while the contents were frozen (liquid air) and any gaseous species were transferred under vacuum.

V B ADDITION OF ETHERS

(a) Addition of Diethylether to Hexafluoropropene

A mixture of diethylether (11.0g, 150mmole) and hexafluoropropene (22.5g,150mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess from hexafluoropropene was collected and the residue was distilled, yielded two products: the first one which is 1-methyl-2,2,3,4,4,4,-hexafluorobutyl ethyl ether (32), (13.1g, 39%); (Found: C, 37.9; H, 4.6; F, 51.3%; M, 224. Calc. for $C_7H_{10}F_6O$: C, 37.5; H, 4.5; F, 50.9%; M, 224); n.m.r. spectrum 1, mass spectrum 1 and i.r. spectrum 1.

The other product which is di (1-methyl-2,2,3,4,4,4,-hexafluorobutyl) ether (33), (25.8g, 46%); (Found: C, 31.9; H, 2.4; F, 61.2%; (P-150), 224. Calc. for $C_{10}H_{10}F_{12}O$: C, 32.1; H, 2.6; F, 60.9%; M, 374); n.m.r. spectrum 2, mass spectrum 2 and i.r. spectrum 2.

(b) Addition of Diethylether to Hexafluorocyclobutene

A mixture of dry diethylether (21.7g, 239mmole) and hexafluorocyclobutene (15.0g,93mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess from hexa-fluorocyclobutene was collected and the residue distilled in vacuo, yielded two products: the first one is 1-methyl-2-H-perfluorocyclobutyl ethyl ether (34), (16.9g, 77%); (Found: C, 41.0; H, 4.5; F, 48.7%, M, 236. Calc. for $C_8H_{10}F_6O$: C, 40.7; H, 4.3; F, 48.3%; M, 236); n.m.r. spectrum 3, mass spectrum 3 and i.r. spectrum 3.

The second product is di(1-methyl-2-H-perfluorocyclobutyl) ether (35), (4.8g, 13%); (Found: C, 36.7; H, 2.6; F, 58.0%; (P-98), 300. Calc. for $C_{12}H_{10}F_{12}O$: C, 36.2; H, 2.5; F, 57.3%; M, 398); n.m.r. spectrum 4, mass spectrum 4 and i.r. spectrum 4.

(c) Addition of Diethylether to Octafluorocyclopentene

A mixture of diethylether (11.0g, 140mmole) and octafluorocyclopentene (10.3g, was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess from octafluorocyclopentene was collected and the residue was distilled in vacuo, yielded two products: the first one is 1-methyl-2-H-perfluorocyclopentyl ethyl ether (36), (9.1g, 65%); (Found: C, 40.1; H, 3.2; F, 53.6%; M+,286). Calc. for $C_9H_{10}F_8O$: C, 37.8; H, 3.1; F, 53.1%; M, 286); n.m.r. spectrum 5, mass spectrum 5 and i.r spectrum 5.

The second product is di (1-methyl-2-H-perfluorocyclopentyul) ether (37) (5.4g, 22%); (Found: C,34.0; H, 2.1; F, 61.4%; M+,286). Calc. for $C_{14}H_{10}F_{16}O$: C, 33.7; H, 2.0; F, 61.0%; M, 498); n.m.r. spectrum 6, mass spectrum 6 and i.r. spectrum 6.

V C DEHYDROFLUORINATIONS

(a) Di (1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (33)

(i) Using Potassium Hydroxide

A mixture of di (1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (33), (3.74g, 0.01 mole) and potassium hydroxide flakes (2.2g, 40 mmole) was heated in a sealed rotaflo at 85^{0}C for 7 hours. Volatile material in the rotaflo was transferred under vacuum to give α,α'-bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43), (2.5g, 70%) as a mixture of isomers; (Found: C, 35.6; H, 2.3; F, 57.4%; M+,334. Calc. for $C_{10}H_{8}F_{10}O$: C, 35.9; H, 2.3; F, 56.9%; M, 334); n.m.r. spectrum 8, mass spectrum 8 and i.r. spectrum 8.

(ii) Using Potassium Fluoride

A mixture of di(1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (33), (3.74g, 0.01mole) and potassium fluoride (2.30g, 0.04 mmole) was heated in a sealed rotaflo at 85^{0}C for 24 hours but the resulting liquid was shown to contain only starting materials by g.l.c. In addition only starting materials were recovered after heating the reactants to 100^{0}c for 8 hours and 130^{0}C for 8 hours in a sealed rotaflor (shown by g.l.c.)

(iii) Using Potassium Hydroxide in diglyme

A mixture of di(1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (33), (3.74g, 0.01mole), potassium hydroxide powder (2.2g, 0.04mole) and 100 ml diglyme was stirred at 100°C for 12 hours followed by 12 hours at 110°C Volatile material in the rotaflo was transferred under vacuum to give α, α'-bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43), (0.7g, 20%) which was identified by g.l.c.

(iv) Using Sodium t-butoxide

A mixture of di(1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (33), (3.74g, 0.01 mmole) and sodium t-butoxide which was prepared by addition of sodium metal (0.50g, 0.0195 mole) to absolute t-butanol (70 ml). The mixture was stirred at room temperature for 6 hours. The reaction mixture was diluted with H_2O and hydrochloric acid, in order to bring the pH to pH = 7.5. The organic layer was extracted with ether and dried over anhydrous MgSO4, evaporation of filtrate yielded compound α, α'-bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43), (0.8g, 25%) as a mixture of isomers which was identified by g.l.c.

(v) Using Triethylamine

A mixture of di(1-methyl-2,2,3,4,4,4-hexafluorobutyl) ether (33), (3.74g. 0.01mole) and triethylamine (4.0g, 0.04 ole) was stirred at room temperature for 24 hours but the resulting liquid was shown to contain starting material by g.l.c. In addition, only starting materials were recovered after heating the reactants to 90°C for 12 hours in a sealed rotaflo (shown by g.l.c.).

(b) 1-Methyl-2,2,3,4,4,4-hexafluorobutyl ethyl ether (32)

(i) Using Potassium Hydroxide

A mixture of 1-methyl-2,2,3,4,4,4-hexafluorobutyl ethyl ether (32), (2.2g, 100 mmole) and potassium hydroxide flakes (5.6g, 0.1 mmole) was heated in a sealed rotaflo at 85°C for 7 hours.

Volatile material in the rotaflo was transferred under vacuum to give α-(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (42), (1.4g, 70%) as a mixture of isomers; (Found: C, 40.8; H, 4.5; F, 46.0 %; M+, 204. Calc. for $C_7H_9F_5O$: C, 41.1; H, 4.4; F, 46.5%; M, 204); n.m.r. spectrum 7, mass spectrum 7 and i.r. spectrum 7.

(c) 1-Methyl-2-H-perfluorocyclobutyl ethylether

(i) Using Triethylamine

A mixture of 1-methyl-2-H-perfluorocyclobutyl ethyl ether (34), (5.0g, 21 mmole) and triethylamine (4.0g, 40 mmole) was stirred at room temperature for 24 hours but the resulting liquid was shown to contain starting material by g.l.c. In addition, only starting materials were recovered after heating the reactants to 100°C for 6 hours in a sealed rotaflo (shown by g.l.c.).

(ii) Using sodium methoxide

A mixture of 1-methyl-2-H-perfluorocyclpobutyl ethyl ether (34), (5.0g, 21 mmole) and sodium methoxide dried powder (2.2g, 40 mmole) was stirred at 70°C for 12 hours but the resulting liquid was shown to be starting material by g.l.c. In adition, only starting materials were recovered after heating the reactants to 120°C for 3 hours in a sealed rotaflo (shown by g.l.c.).

(iii) Using Caesium Fluoride

A mixture of 1-methyl-2-H-perfluorocyclobutyl ethyl ether (34), (5.0g, 21 mmole) and caesium fluoride (dried) (9.6g, 63 mmole) was heated to 85^{0}C for 3 hours. 80% conversion to product was obtained. A further 10 hours at 110^{0}C gave α-(2,3,3,4,4,-pentafluorocyclobutyl-1-ene) diethyl ether (44), (2.0g, 45%), (Found: C,44.1; H, 4.1; F, 44.2%; (P-15), 201. $C_8H_9F_5O$ requires C, 44.4; H, 4.1; F, 43.9%; M, 216); n.m.r. spectrum 9, mass spectrum 9 and i.r. spectrum 9.

V D NUCLEOPHILIC REACTIONS-OF FLUOROOLEFIN ADUCTS

1. Nucleophilic Reactions of α-(1,2,3,3,3-pentafluoro-1-propenyl) Diethylether (42) with Sodium Alkoxide

(i) With sodium methoxide.

In a round bottomed flask connected to reflux condenser containing sodium methoxide solution which was prepared by addition of sodium metal (1.0g, 40 mmole) to absolute methanol (12.8g, 400 mmole), α-(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (42), (2.0g, 10 mmole) was added in one portion at 75^{0}C and the reaction mixture was left stirring at 75^{0}C for 24 hours. The reaction mixture was diluted with H_2O and hydrochloric acid, in order to bring the pH to pH = 7.5. The organic layer was extracted by ether and dried over anhydrous MgS04, evaporation of filtrate yielded compound 1-methoxy-1-(1-ethoxyethyl) tetrafluoropropene (48), (1.6g, 73%); (Found: C, 43.9; H, 5.5; F, 35.6%; (P-14), (202). $C_8H_{12}F_8O_2$ requires C, 44.4; H, 5.5; F, 35.2%; M, 216); n.m.r. spectrum 10, mass spectrum 10 and i.r. spectrum 10.

(ii) With sodium propoxide

In a round bottomed flask connected to reflux condenser containing sodium propoxide solution which was prepared by addition of sodium metal (1.0g, 40 mmole) and absolute probonol (24.0g, 400 mmole). α-(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (42), (2.0g, 10 mmole) was added as one portion at 75^{0}C and the reaction mixture was left stirring at 75^{0}C for 24 hours. The reaction mixture was diluted with H_2O and hydrochloric acid, in order to bring the pH to pH = 7.5. The organic layer was extracted with ether and dried over MgSO4, evaporation of filtrate yielded 1-propoxy-1-(1-ethoxyethyl)-tetrafluoropropene (49), (1.8g, 75%); (Found: C, 48.8; H, 6.6; F, 30.7%; M, 244. $C_{10}H_{16}F_4O_2$ requires C, 49.2; H, 6.6; F, 31.1%; M, 244); n.m.r. spectrum 11, mass spectrum 11 and i.r. spectrum 11.

(iii) With sodium butoxide.

In a round bottomed flask connected to reflux condenser containing sodium butoxide which was prepared by addition of sodium metal (1.0g, 40 mmole) to absolute butanol (29.6g, 400 mmole). α-(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43), (2.0g, 10 mmole) was added as one portion at 75^{0}C and the reaction mixture was left stirring at 75^{0}C for 24 hours. The reaction mixture was diluted with H_2O and hydrochloric acid, in order to bring the pH to pH = 7.5. The organic layer was extracted with ether and dried over MgSO4, evaporation of filtrate yielded compound 1-butoxy-1-(1-ethoxyethyl)-tetrafluoropropene (50), (1.9g, 75%); (Found: C, 51.3; H, 7.4; F, 29.0%; (P-15), (243). $C_{11}H_{18}F_4O_2$ requires C, 51.1; H, 7.0; F, 29.4%; M, 258); n.m.r. spectrum 12, mass spectrum 12 and i.r. spectrum 12.

2. Nucleophilic Reactions of α,α'-bis(1,2,3,3,3-pentafluoro-1-propenyl) Diethylether With Sodium Alkoxide

(i) With sodium methoxide

In a round bottomed flask connected to reflux condenser containing sodium methoxide solution which was prepared by addition of sodium metal (1.0g, 40 mmole) to absolute methanol (11.4g, 400 mmole). α,α'-bis (1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43), (3,34g, 10 mmole) was added in one portion at 75^0C and the reaction mixture was diluted with H_2O and hydrochloric acid, in order to bring the pH to pH = 7.5. The organic layer was extracted with ether and dried over anhydrous MgSO4, evaporation of filtrate yielded α,α'-bis(1-methoxy-tetrafluoro-1-propenyl) diethylether (51), (2.5g, 71%); (Found: C, 39.8; H, 3.9; F, 42.4%; M, 354. $C_{12}H_{14}F_8O_3$ requires C, 40.2; H, 3.9; F, 42.3%; M, 354); n.m.r. spectrum 13, mass spectrum 13 and i.r. spectrum 13.

(ii) With sodium ethoxide.

In a round bottomed flask connected to reflux condenser, containing sodium ethoxide solution which was prepared by addition of sodium metal (1.0g, 40 mmole) to absolute ethanol (18.4g, 400 mmole). α,α-bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43) was added in one portion at 75 C and the reaction mixture was left stirring at 75 C for 7 hours. The reaction mixture was diluted with H O and hydrochloric acid, in order to bring the pH to pH = 7.5. The organic layer was extracted with ether and dried over anhydrous over MgSO4, evaporation of filtrate yielded compound α,α-bis(1-ethoxy-tetrafluoro-1-propenyl) diethylether (52), (2.9g, 75%; (Found: C, 44.0; H, 4.9; F, 40.5%; M, 386. $C_{14}H_{18}F_{8}O_{3}$ requires C, 43.5; H, 4.7; F, 39.4%; M, 386); n.m.r. spectrum 14, mass spectrum 14 and i.r. spectrum 14.

(iii) With sodium propoxide

In a round bottomed flask connected to a reflux condenser containing sodium propoxide solution which was prepared by addition of sodium metal (1.0g, 40 mmole) to absolute probanol (24.0g, 400 mmole). α,α-bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43), (3.34g, 10 mmole) was added in one portion at 75^{o}C and the reaction mixture was left for stirring at 75^{o}C for 7 hours. The reaction mixture was diluted with H_2O and hydrochloric acid, in order to bring the pH to pH = 7.5. The organic layer was extracted with ether and dried over anhydrous MgSO4, evaporation of filtrate yielded α,α-bis(1-propoxy-tetrafluoro-1-propenyl) diethylether (53), (3.1g, 75%; (Found: C, 46.5; H, 5.3; F, 37.4%; (P-42,372).

$C_{16}H_{22}F_4O_3$ requires C, 46.6; H, 5.3; F, 36.7%; M, 414); n.m.r. spectrum 15, mass spectrum 15 and i.r. spectrum 15.

(iv) With sodium butoxide.

In a round bottomed flask connected to reflux condenser containing sodium butoxide solution which was prepared by addition of sodium metal (1.0g, 40mmole) to absolute butanol (29.6g, 400 mmole). α,α'-bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether was added in one portion at 75°C and the reaction mixture left for stirring at 75°C for 7 hours. The reaction mixture was diluted with H_2O and hydrochloric acid, in order to bring the pH to pH = 7.5. The organic layer was extracted with ether and dried over anhydrous MgSO4, evaporation of filtrate yielded compound α,α'-bis(1-butoxy-tetrafluoro-1-propenyl) diethylether (54), (3.2g, 74%); (Found: C, 48.3; H, 5.8; F, 40.0%; (P-59), 383. $C_{18}H_{26}F_8O_3$ requires C, 48.8; H, 5.8; F, 34.4%; M, 442); n.m.r. spectrum 16, mass spectrum 15 and i.r. spectrum 16.

3. Nurcleophilic Reaction of α,α'-bis(1,2,3,3,3-pentafluoro-1-propenyl) Diethylether With Diethylamine

In a round bottomed flask connected to reflux condenser, containing diethylamine (2.9g, 400 mmole). α,α'-bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43), (3.34g, 10 mmole) was added in one portion at 150°C and the reaction mixture was left stirring at 90°C for 24 hours. The reaction mixture was diluted with H O and hydrochloric acid, in order to bring the PH to PH = 7.5. The organic layer was extracted by ether and dried over MgSO4, evaporation of filtrate but the resultant liquid was shown to contain only starting material by g.l.c.

4. Nucleophilic Reaction of $\alpha,\tilde{\alpha}$-bis(1,2,3,3,3-pentafluoro-1-propenyl) Diethylether (43) with Ethylenediamine

In a round bottomed flask connected to reflux condenser containing ethylenediamine (6.0g, 100 mmole), $\alpha,\tilde{\alpha}$-bis(1,2,3,3,3-pentafluoro-1-propenyl) diethylether (43), (3.34g, 10 mmole) was added in one portion at 75°C for 12 hours. The reaction mixture was diluted with H_2O and hydrochloric acid, in order to bring the PH to PH=7.5. The organic layer was extracted with ether and dried over anhydrous MgSO4; evaporation of filtrate yielded a compound (55) which could not be identified.

CHAPTER 6

EXPERIMENTAL TO CHAPTER 4

VI A THE ADDITION OF MONO-FUNCTIONAL ALDEHYDES TO FLUOROALKENES

1. Addition of Acetaldehyde to Hexafluoropropene

A mixture of acetaldehyde (9.0g, 200 mmole) and hexfluropropene (50.0g, 330 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess of hexfluoropropene was collected and the residue was distilled, yielded 3,3,4,5,5,5-hexafluoropenta-2-one (56), (28.5g, 74%); (Found: C, 31.1; H, 2.2; F, 58.6%; M+, 194. Calc. for $C_5H_4F_6O$: C, 30.9; H, 2.1: F, 58.8%; M, 194); n.m.r. spectrum 17, mass spectrum 17, and i.r. spectrum 17.

2. Addition of Hexana to Hexafluoropropene

A mixture of hexanal (5.0g, 50 mmole) and hexafluoropropene (23.0g, 150 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and excess of hexafluoropropene was collected and the residue distilled in vacuo, yielded 1,1,1,2,3,3-hexafluorononan-4-one (57), (10.0g, 80%); (Found: C, 43.2; H, 4.8; F, 45.7%; (P—17), 233. $C_9H_{12}F_6O$ requires C, 43.5; H, 4.8; F, 45.6%; M, 250); n.m.r. spectrum 18, mass spectrum 18 and i.r. spectrum 18.

3. Addition of Trimethylacetaldehyde to Hexafluoropropene

A mixture of trimethylacetaldehyde (6.0g, 70 mmole) and hexafluoropropene (28.0g, 186 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess hexafluoropropene was collected and the residue was distilled to yield 2-H-hexafluoropropyl t-butyl ketone (58), (14.0g, 81%); (Found: C, 40.9; H, 4.2; F, 48.7%; (P-15), 221. $C_8H_{10}F_6O$ requires C, 40.7; H, 4.2; F, 48.3%; M, 236); n.m.r. spectrum 19, mass spectrum 19 and i.r. spectrum 19.

4. Addition of 3-Cyclohexlpropanal to Hexafluoropropene

(i) γ-Ray Initiation

A mixture of 3-cyclohexylpropanal (8.0g, 57 mmole), and hexafluoropropene (53.6g, 357 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and most of the hexafluoropropene was recovered with a material which was believed to be polymer from starting materials.

(ii) Peroxide Initiation

A mixture of 3-cyclohexylpropanal (8.0g, 57 mmole), hexafluoropropene (51.6g, 350 mmole) and di-t-butyl peroxide (0.4g) was heated at 140°C in a thermostatically controlled rocking furnace for 24 hours. The tube was opened unde vacuum and the excess from hexafluoropropene was recovered and the residue was shown to contain three products by g.l.c., which were separated by preparative scale g.l.c. (column 10% SE 30, 90^{o}C), the first compound was identified as <u>1,1,1,2,3,3-hexafluoro-5-cyclohexyl-pentane</u> (59), (3.0g, 20%); (Found: C, 49.7; H, 6.0; F, 44%; M, 218. $C_{11}H_{16}F_{6}$ requires C, 50.3; H, 5.8; F, 43.5%; M, 262); n.m.r. spectrum 20, mass spectrum 20, and i.r. spectrum 20. The second product was identified as <u>1,1,1,2,3,3-hexafluoro-6-cylohexyl-hexan-4-one</u> (60), (5.0g, 30%); (Found: C, 51.6; H, 6.0; F, 40.4%; M+, 290 $C_{12}H_{16}F_{6}O$ requires C, 49.7; H, 5.5; F, 39.3%; M,290); n.m.r. spectrum 21, mass spectrum 21, and i.r. spectrum 21. The last product was identified as <u>1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-6-cyclohexyl-nonan-4-one</u> (61), (9.0g, 39%), (Found: C, 40.7; H, 4.1; F, 51.8%; M, 440. $C_{15}H_{16}F_{12}O$ requires C, 40.9; H, 3.6; F, 52.5%; M+,440); n.m.r. spectrum 22, mass spectrum 22 and i.r. spectrum 22.

5. <u>Addition of Hexanal to Hexafluorocyclobutene</u>

A mixture of hexanal (5.0g, 50 mmole) and hexafluorocyclobutene (17.0g, 104 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess hexafluorocyclobutene was collected and the residue was distilled in vacuo, yielded 2-Hydro-Hexafluorocyclobutyl pentyl ketone (62), (10.0g, 80%); (Found: C, 45.6; H, 4.5; F, 43.7%; $C_{10}H_{12}F_6O$ requires C, 45.8; H, 4.5; F, 43.5%; M, 262) n.m.r. spectrum 23, mass spectrum 23 and i.r. spectrum 23.

6. Addition of Hexanal to Octafluorocyclopentene

A mixture of hexanal (5.0g, 50 mmole) and octafluorocyclopentene (31.8g, 150 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess octafluorocyclopentene was recovered and the residue distilled in vacuo, yielded 2-Hydro-octafluorocyclopentyl pentyl ketone (63), (13,2g 85%); (Found: C, 42.8; H, 3.1; F, 49.4%; M+, 312. $C_{11}H_{10}F_8O$ requires C, 42.6; H, 3.2; F, 49.0%; M, 312); n.m.r. spectrum 24, mass spectrum 24 and i.r. spectrum 24.

7. Addition of Acetaldehyde to 3,3,3-Trifluoropropene

A mixture of acetaldehyde (14.0g, 318 mmole) and 3,3,3-trifluoropropene (17.0g, 180 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess 3,3,3-trifluoropropene was collected and the residue was distilled to give two products; the first one was 5,5,5-trifluoro-pentan-2-one (64), (7.5g 30%); (Found: C, 43.0; H, 5.2; F, 40.0%; M+,140. $C_5H_7F_3O$ requires C, 42.8; H, 5.0; F,40.7%; M, 140); n.m.r. spectrum 25, mass spectrum 25 and i.r.

spectrum 25. The second product was 4-trifluoromethyl-7,7,7-trifluoropheptan-2-one (65), (17.0g, 40%); (Found: C, 39.3; H, 4.2; F, 47.5%; M+, 236. $C_8H_{10}F_6O$ requires C, 40.7; H, 4.2; F, 48.3%; M, 236; n.m.r. spectrum 26, mass spectrum 26 and i.r. spectrum 26.

8. Attempted Addition of Monodecanal to Hexafluoropropene

(i) Without Solvent

A mixture of monodecanal (9.5g, 55 mmole) and hexafluoropropene (22.5g, 150 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and all the hexafluoropropene was recovered with a material which was believed to be polymer from starting materials.

(ii) In Acetone

A mixture of monodecanal (9.5g, 55 mmole), dry acetone (12,7g, 220 mmole) and hexafluoropropene (22.5g, 150 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and all the hexafluoropopene and acetone were recovered with a material which was belived to be polymer from starting materials.

9. Attempted Addition of Trans-2-heptenal to Hexafluoropropene

(i) γ-Ray Initiation

A mixture of trans-2-heptenal (10.0g, 89 mmole), and hexafluoropropene (52.5g, 350 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum. The product was shown to contain only starting materials by g.l.c.

(ii) Peroxide Initiation

A mixture of trans-2-heptenal (10.0g, 89 mmole) and hexafluoropropene (52.5g, 350 mmole) and di-t-butyl peroxide (0.4g) was heated at 140°C in a thermostatically controlled rocking furnace for 24 hours. The tube was opened under vacuum and the product was shown to contain only starting materials by g.l.c.

10. Attempted Addition of 6-Heptenal to Hexafluoropropene

(i) Without Solvent

A mixture of 6-heptenal (5.0g, 50 mmole) and hexafluoropropene (15.0g, 100 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and most of hexafluoropropene was recovered with a material which was belived to be polymer from starting materials.

(ii) In Acetone

A mixture of 6-heptenal (5.0g, 50 mmole), dry acetone (11.6g, 200 mmole) and hexafluoropropene (15.0g, 100 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the most of hexafluoropropene and acetone were recovered with a material which was believed to be polymer from starting materials.

VI B THE ADDITION OF DI-FUNCTIONAL ALDEHYDES TO FLUOROALKENES

1. Addition of 1,8-Octanedial to Hexafluoropropene

A mixture of 1,8-octanedial (4.3g, 30 mmole) and hexafluoropropene (15.0g, 100 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess hexafluoropropene was collected and the residue distilled in vacuo, yielded 1,1,1,2,3,3,12,12,13,14,14,14-tetradecan--4,11-dione (66), (12,0g, 90%); (Found: C, 38.2; H, 3.4; F, 50.9%; (P-151), 291. $C_{14}H_{14}F_{12}O_2$ requires C, 38.0; H, 3.2; F, 51.6%; M, 442); n.m.r. spectrum 27, mass spectrum, and i.r. spectrum 27.

2. Addition of 1,12-Dodecanedial to Hexafluoropropene

(i) γ-Ray Initiation

A mixture of 1,12-dodecanedial (3.0g, 15 mmole) and hexafluoropropene (48.0g, 320 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the product was shown to contain only starting materials by n.m.r. spectroscopy.

(ii) Peroxide Initiation

A mixture of 1,12-dodecanedial (5.0g, 25 mmole), hexafluoropropene (26.0g, 170 mmole) and di-t-butyl peroxide (0.2g) was heated at 140°C in a thermostatically controlled rocking furnace for 48 hours. The reaction tube was opened under vacuum and the excess hexafluoropropene was recovered and the product was collected by filtration and purified by sublimation to give 1,1,1,2,3,3,3,16,16,17,18,18,18-octadecan-4,15-dione (67), (5.7g, 45%); Found: C, 43.8; H, 4.6; F, 45.5%; M+, 498. $C_{18}H_{22}F_{12}O_2$ requires C, 43.3; H, 4.4; F, 45.8%; M, 498); n.m.r. spectrum 28, mass s spectrum 28 and i.r. spectrum 28.

3. Addition of 1.8-Octanedial to Hexafluorocyclobutene

A mixture of 1,8-octanedial (4.3g, 30 mmole) and hexafluorocyclpbutene (19.1g, 120 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess hexafluorocyclobutene was collected with a material which was belived to be polymer.

4. Addition of 1,12-Dodecanedial to Hexafluorocyclobutene

(i) ℽ-Ray Initiation

A mixture of 1,12-dodecanedial (3.5g, 18 mmole) and hexafluorocyclobutene (16.0g, 99 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the product was shown to contain only starting materials by n.m.r. spectroscopy.

(ii) Peroxide Initiation

A mixture of 1,12-dodecanedial (2.0g, 10 mmole), hexafluorocyclobutene (7.0g, 43 mmole) and di-t-butyl peroxide (0.1g) was heated at 140°C, in a thermostatically controlled rocking furnace for 24 hours. The reaction tube was opened under vacuum and the excess hexafluorocyclobutene was recovered and the product was collected by filtration and purified by sublimation to give 1,12-di(2-Hydro-perfluorocyclobutyl) dodecandione (69), (4.3g, 83%); (Found: C, 45.3; H, 3.9; F, 43.1%; (P-165), 357. $C_{20}H_{22}F_{12}O_2$ requires C, 45.9; H, 4.2; F, 43.6%; M, 522); n.m.r. spectrum 29, mass spectrum 29 and i.r. spectrum 29.

5. Addition of 1,8-Octanedial to Octafluorocyclopentene

A mixture of 1,8-octanedial (5.0g, 35 mmole) and octafluorocyclopentene (46.0g, 217 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the excess octafluorocyclopentene was collected with a material which was believed to be polymer.

6. Addition of 1,12-Dodecanedial to Octafluorocyclopentene

(i) γ-Ray Initiation

A mixture of 1,12-dodecanedial (5.0g, 25 mmole) and octafluorocyclopentene (21.4g, 101 mmole) was irradiated for the period of five days. The reaction tube was opened under vacuum and the product was shown to contain only starting material by n.m.r. spectroscopy.

(ii) Peroxide Initiation

A mixture of 1,12-dodecanedial (2.5g, 12.6 mmole) octafluorocyclopentene (8.0g, 37.7 mmole) and di-t-butyl peroxide (0.15g) was heated at 140°C in a thermostatically controlled rocking furnace for 24 hours. The reaction tube was opened under vacuum and the excess octafluorocyclopentene was recovered and the product was collected by filtration and purified by sublimation to give 1,12-di (2-Hydro-perfluorocyclopentyl) dodecandione (71), (6.2g, 80%); Found: C, 41.0; H, 3.1; F, 40.2%; M, 622. $C_{22}H_{22}F_{16}O_2$ requires C, 42.4; H, 3.5; F, 48.8%; M. 622); n.m.r. spectrum 30, mass spectrum 30 and i.r. spectrum 30.

APPENDIX I- NMR SPECTRA

COMPOUND ENDEX

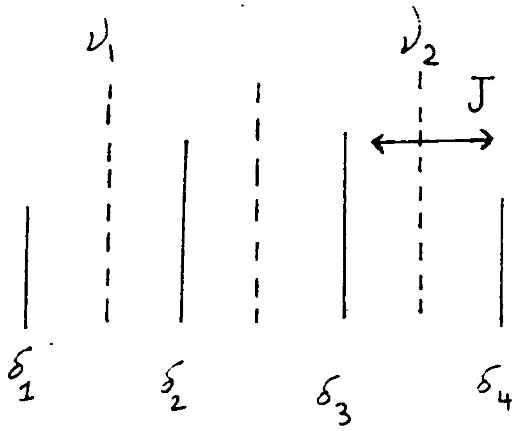
1. 1-methyl-2,2,3,4,4,4-hexafluorobutyl ethyl ether (32)
2. di(1-methyl-2,2,3,4,4,4-hexafluorobutyl)ether (33)
3. 1-methyl-2-H-perfluorocyclobutyl)ethyl ether (34)
4. di(1-methyl-2-H-perfluorocyclobutyl)ether (35)
5. 1-methyl-2-H-perfluorocyclopentyl ethyl ether (36)
6. di(1-methyl-2-H-perfluorocyclopentyl)ether (37)
7. α-(1,2,3,3,3-pentafluoro-1-propenyl)diethylether (42)
8. α,α'-bis(1,2,3,3,3-pentafluoro-1-propenyl)diethylether (43)
9. α-(2,3,3,4,4-pentafluorocyclobutyl)diethylether (44)
10. 1-methoxy-1-(1-ethoxyethyl)tetrafluoropropene (48)
11. 1-propoxy-(1-ethoxyethyl)-tetrafluoropropene (49)
12. 1-butoxy-1-(1-ethoxyethyl)-tetrafluoropropene (50)
13. α,α'-bis(1-methoxy-tetrafluoro-1-propenyl)diethylether (51)
14. α,α'-bis(1-ethoxy-tetrafluoro-1-propenyl)diethylether (52)
15. α,α'-bis(1-propoxy-tetrafluoro-1-propenyl)diethylether (53)
16. α,α'-bis(1-butoxy-tetrafluoro-1-propenyl)diethylether (54)
17. 3,3,4,5,5,5-hexafluoropentan-2-one (56)
18. 1,1,1,2,3,3,3-hexafluorononan-4-one (57)
19. 2-H-hexafluoropropyl t-butyl ketone (58)
20. 1,1,1,2,3,3-hexafluoro-5-cyclohexyl-pentane (59)
21. 1,1,1,2,3,3-hexafluoro-6-cyclohexyl-hexan-4-one (60)
22. 1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-6-cyclohexyl-nonan-4-one (61)
23. 2-Hydro-hexafluorocyclobutyl pentyl ketone (62)

24. 2-Hydro-octafluorocyclopentyl pentyl ketone (63)
25. 5,5,5-trifluoro-pentan-2-one (64)
26. 4-trifluoromethyl-7,7,7-trifluoroheptan-2-one (65)
27. 1,1,1,2,3,3,12,12,13,14,14,14-dodecafluoro-tetradecan-4,11-dione (66).
28. 1,1,1,2,3,3,3,16,16,17,18,18,18-dodecafluoro-octadodecan-4,15-dione (67)
29. 1,12-di(2-Hydro-perfluorocyclobutyl)dodecandione (69)
30. 1,12-di(2-Hydro-perfluorocyclopentyl)dodecandione (71)

ABBREVIATIONS

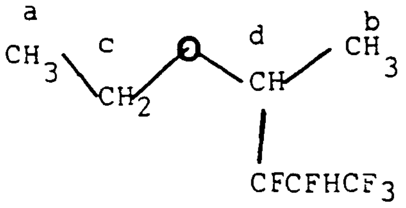
The following abbreviations are used for the splitting patterns of the NMR resonances;

S = singlet
D = doublet
T = triplet
Q = quartet
AB = AB quartet



Chemical shift quoted as 'centre of gravity' or ± v/2 from the mid point of the pattern, calculated from $(\delta_1-\delta_3)=(\delta_2-\delta_4)=\sqrt{(\Delta v)^2+J^2}$

P = pentet
Sx = sextet
Sp = septet
Oc = octet
M = multiplet



No.1

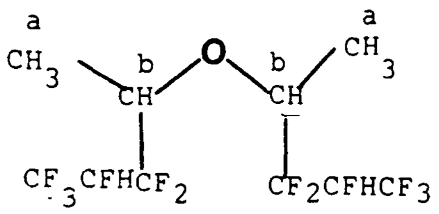
(32)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	0.88	T	3
CH_3(b)	0.97	D	3
CH_2(c)	3.3	M	2
CH(d)	3.5	M	1
CFH	4.87	M	1

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-76.6 → -77.1	M	3
CF_2	-121.3 → -127.0	M	2
CFH	-215.6 → -218.8	M	1



No.2

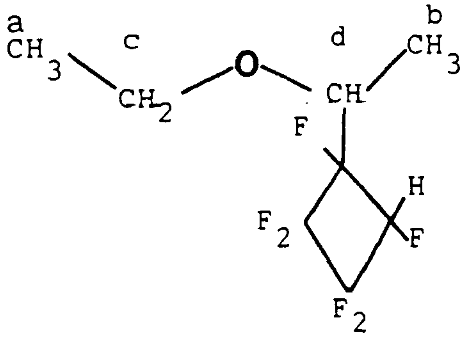
(<u>33</u>)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	1.09	D	6
CH(b)	3.72	M(broad)	2
CFH	4.78	M	2

^{19}F.n.m.r

	Chemical Shift In P.p.m	Multiplicity	Relative Intensity
CF_3	-76.5 → -77.0	M	6
CF_2	-117.0 → -129.7	M	4
CFH	-213.5 → -216.5	M	2



No.3

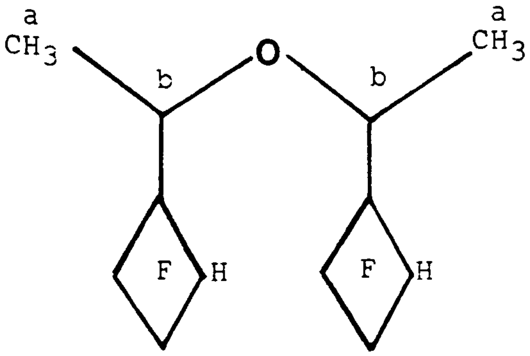
(34)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	1.12	M	3
CH_3(b)	1.26	D	3
CH_2(c)	3.34 → 3.64	D(M)	3
CH (d)	3.7 → 3.85	M	1
CFH	4.9 → 5.2	M	1

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_2	-121.7 → -134.5	M	4
CFR	-188.5	D	1
CFH	-215.5	D(D)	1



(35)

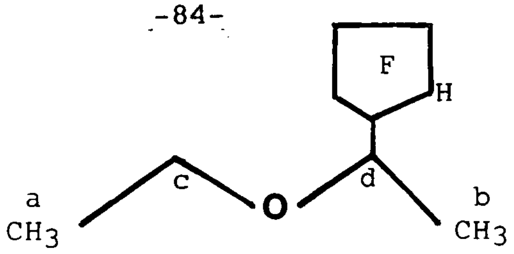
No.4

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	1.36	M	6
CH(a)	3.9 → 4.19	M	2
CFH	4.9 → 5.25	M	2

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_2	-115.4 → -136.0	M	16
CFR	-188.4	M	4
	-200.4	M	4
CFH	-212.4	M	4
	-222.8	M	4



No.5

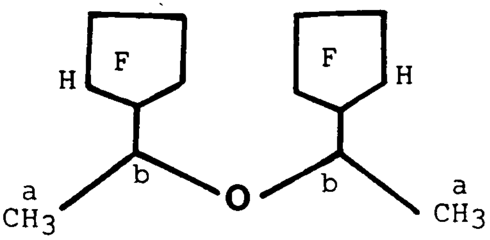
(36)

^1H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	1.2	Q	3
CH_3(b)	1.4	D	3
CH_2(c)	3.2 → 3.5	D(M)	2
CH (d)	3.6 → 3.8	D(M)	1
CFH	4.7 → 5.0	D(M)	1

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_2	-115.98 → -134.50	M	6
CFR	-189.5 -191.3 -195.14	M	1
CFH	-209.33 -210.64 -224.36 -228.53	D(M)	1



No.6

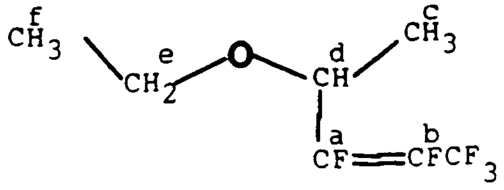
(37)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensit
CH_3(a)	1.44	M	6
CH(b)	4.0 → 4.3	M	2
CFH	5.0 → 5.2	D(M)	2

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relativ Intensit
CF_2	-116.5 → -134.3	M	12
CFR	-189.7 -193.3 -194.5	M	2
CFH	-210.0 -226.5 -230.0	M	2



No.7

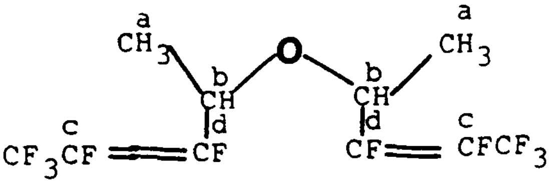
(42)

^{19}F.n.m.r

	Chemical Shift In P.P.m	Multiplicity	Relative Intensity
CF_3	-65.75	S	3
CF(a)	-140.3	S	1
CF(b)	-155.4	S	1

^{1}H.n.m.r

	Chemical Shift In P.P.m	Multiplicity	Relative Intensity
CH_3(f)	1.19	T	3
CH_3(c)	1.40	D	3
CH_2(e)	3.34	Q	2
CH(d)	4.30	Q	1



No.8

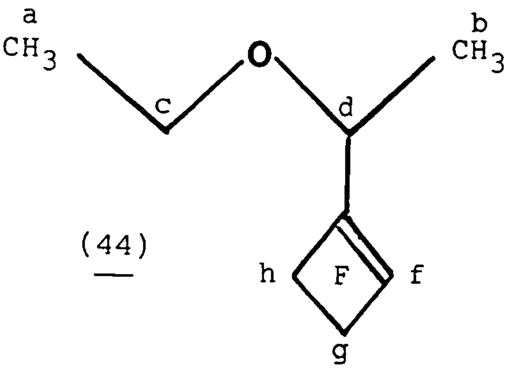
(43)

^{1}H.n.m.r

	Chemical Shift In P.P.m	Multiplicity	Relative Intensity
CH_3(a)	1.4	D	6
CH(b)	4.5	Q	2

^{19}F.n.m.r

	Chemical Shift In P.P.m	Multiplicity	Relative Intensity
CF_3	-66.8	S	6
CF(c)	-140.1	S	2
CF(d)	-153.8	S	2



(44)

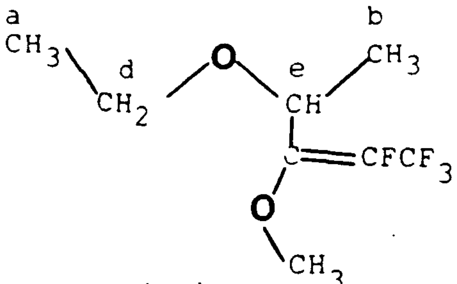
No.9

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	1.12	T	3
CH_3(b)	1.3	D	3
CH_2(c)	3.4 → 3.5	Q	2
CH (d)	4.2	Q	1

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF(f)	-113.1	T	1
CF_2(g)	-116.0	Q	2
CF_2(h)	-118.3	T	2



(48)

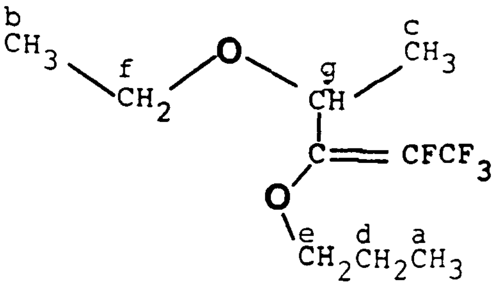
No. 10

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	1.14 → 1.36	M	3
CH_3(b)	1.5 → 1.6	M	3
CH_3(c)	3.7 → 4.0	M	3
CH_2(d)	3.3 → 3.55	M	2
CH (e)	4.1 → 4.47	M	1

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-62.9 → -67.4	M	3
CF	-156.6 → -160.79	M	1



No.11

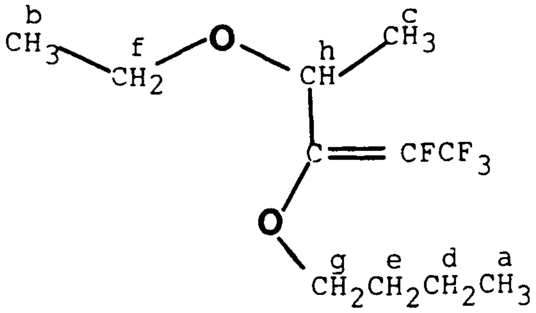
(49)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	1.74	T	3
CH_3(b)	1.95	T	3
CH_3(c)	2.1	D	3
CH_2(d)	2.4 → 2.55	M	2
CH_2(f)	4.1 → 4.25	M	2
CH_2(e)	4.8 → 4.90	M	2
CH (g)	4.91 → 5.03	M	1

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-61.8 → -66.13	M	3
CF	-154.9 → -161.40	M	1



No.12

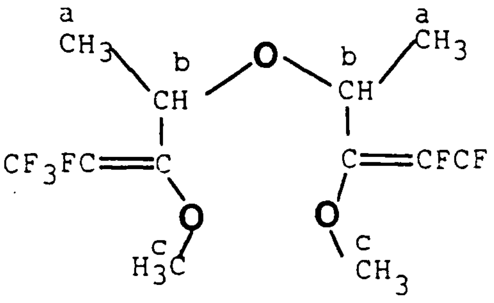
(50)

^{1}H.n.m.r.

	Chemical Shift In p.p.m	Multiplicity	Relative Intensit
CH_3(a)	0.95	M	3
CH_3(b)	1.20	T	3
CH_3(c)	1.32	D	3
CH_2(d)	1.42	M	2
CH_2(e)	1.65	M	2
CH_2(f)	3.40	M	2
CH_2(g)	4.0	M	2
CH (h)	4.2	M	1

^{19}F.n.m.r.

	Chemical Shift In p.p.m	Multiplicity	Relative Intensit
CF_3	-62.7 → -67.1	M	3
CF	-155.7 → -160.9	M	1



No.13

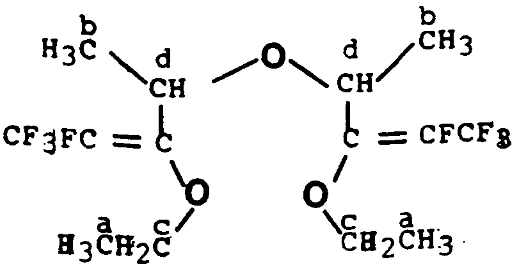
(51)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	1.09 → 1.41	M	6
CH(b)	4.2 → 4.4	M	2
CH_3(c)	3.5 → 4.01	M	6

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-62.4 → -67.5	M	6
CF	-155.2 → -160.2	M	2



No.14

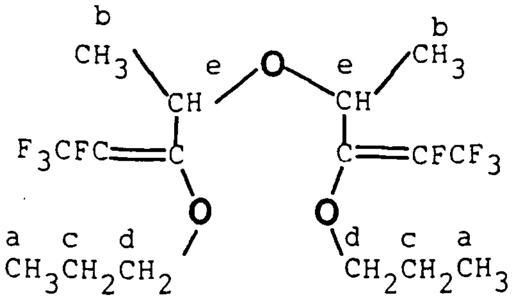
(52)

^{1}H.n.m.r

	Chemical shift In p.p.m	Multiplicity	Relative Intensit
CH_3(a)	1.01	T	6
CH_3(b)	1.27	D	6
CH_2(c)	4.2	Q	4
CH (d)	3.4	Q	2

^{19}F.n.m.r

	Chemical shift In p.p.m	Multiplicity	Relative Intensit
CF_3	-63.15 → -67.0	M	6
CF	-155.11 → -160.4	M	2



No.15

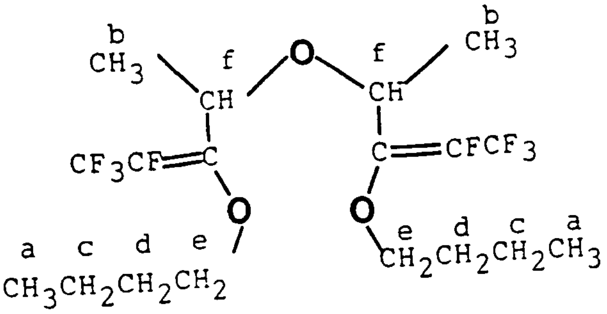
(53)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	0.98	T	6
CH_3(b)	1.29 → 1.35	M	6
CH_2(c)	1.57 → 1.72	M	4
CH_2(d)	4.0 → 4.4	M	4
CH (e)	4.5 → 4.9	M	2

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-63.1 → -67.4	M	6
CF	-155.2 → -160.6	M	2



No.16

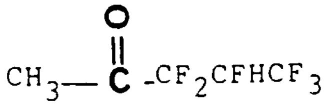
(54)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a)	0.96	T	6
CH_3(b)	1.29 → 1.40	M	6
CH_2(c)	1.4 → 1.48	M	4
CH_2(d)	1.51 → 1.67	M	4
CH_2(e)	3.6 → 4.05	M	4
CH (f)	4.1 → 4.5	M	2

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-62.2 → -67.3	M	6
CF	-155.0 → -160.1	M	2



$CH_3-C(=O)-CF_2CFHCF_3$

(56)

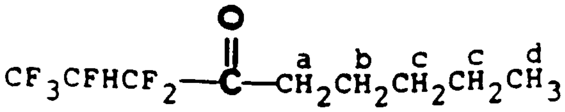
No.17

^{1}H.n.m.r.

	Chemical shift In p.p.m	Multiplicity	Relative Intensity
CH_3	1.90	S	3
CFH	5.2	M	1

^{19}F.n.m.r.

	Chemical shift In p.p.m	Multiplicity	Relative Intensit
CF_3	-75.0	M	3
CF_2	-117.0	M	2
CFH	-215.9	M	1



$$CF_3CFHCF_2-\overset{\overset{O}{\|}}{C}-\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_3$$

(57)

No.18

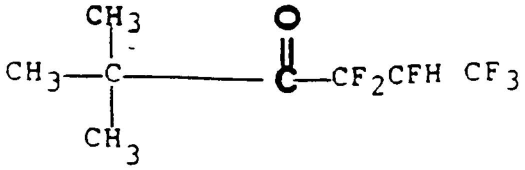
^1H.n.m.r

	Chemical shift In p.p.m	Multiplicity	Relative INtensit
CFH	5.0	M	1
CH_2(a)	2.5	T	2
CH_2(b)	1.6	M	2
CH_2(c)	1.18	M	2
CH_3(d)	0.81	T	3

^{19}F.n.m.r

	Chemical shift In p.p.m	Multiplicity	Relative Intensit
CF_3	-75.4	M	3
CF_2	-116.8	Q	2
CFH	-217.0	M	1

No.19



$$(CH_3)_3C-C(=O)-CF_2CFHCF_3$$

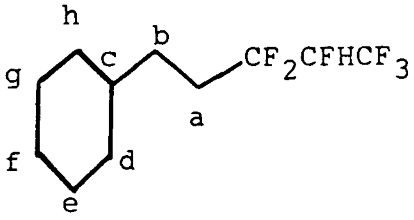
(58)

^{1}H.n.m.r

	Chemical shift In p.p.m	Multiplicity	Relative Intensity
CH_3	1.1	S	9
CFH	5.0	M	1

^{19}F.n.m.r

	Chemical shift In p.p.m	MUltiplicity	Relative INtensity
CF_3	-75.4	M	3
CF_2	-117.0	Q	2
CFH	-217.1	M	1



No.20

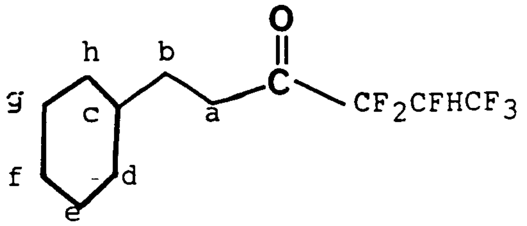
(59)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Muliplicity	Relative Intensity
CH_2(a)	2.1 → 3.36	M	2
CH_2(f)	0.98	M	2
CH_2(g) CH_2(e)	1.16 → 1.3	M	4
CH_2(d)	1.48	M	4
CH_2(b) CH_2(h) CH (c)	1.74	broad	5

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-74.6	D	3
CF_2	-107 → -111.9	D(d)	2
CFH	-210.9	D	1



No.21

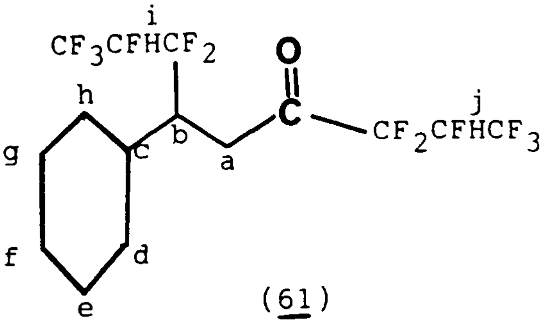
(60)

^1H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_2(f)	0.95	Q	2
CH_2(g) CH_2(e)	1.19 → 1.24	M	4
CH_2(d)	1.43 → 1.55	M	
CH_2(b) CH_2(h) CH (c)	1.67	broad	5
CH_2(a)	2.78	T	2
CFH	5.1 → 5.38	D(M)	1

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-74.6 → -75.2	M	3
CF_2	-116.0 → -124.7	D(d)	2
CFH	-216.3	D	1



No.22

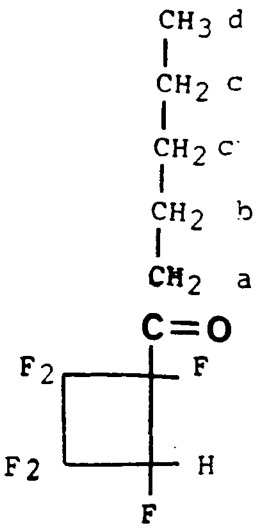
(61)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_2(f)	0.97	M	2
CH_2(g) CH_2(e)	1.17 → 1.26	M	4
CH_2(d) CH_2(h) CH (c)	1.29 → 2.32	M	5
CH (b)	2.39	D(T)	1
CH_2(a)	2.87	M	2
CFH (i)	4.6 → 4.9	D(M)	1
CFH (j)	5.0 → 5.5	D(M)	1

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-74.1	Q	6
CF_2	-116.07 → -124.8	M	4
CFH	-206.5 → -216.4	M	2



No.23

(62)

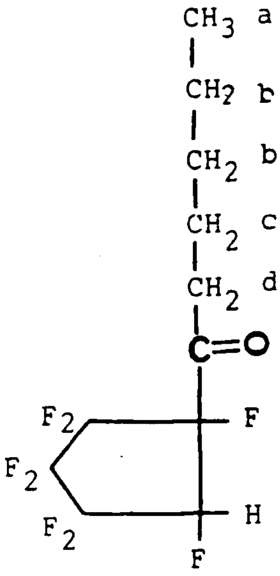
^{1}H.n.m.r.

	Chemical Shift In P.P.m	Multiplicity	Relative Intensity
$CH_3(d)$	0.82	T	3
$CH_2(c)$	1.17	M	4
$CH_2(b)$	1.47	M	2
$CH_2(a)$	2.40	M	2
CFH	5.0	M	1

^{19}F.n.m.r.

	Chemical Shift In P.P.m	Multiplicity	Relative Intensity
CFR	-175.0 -197.81	M	1
CFH	-213.57 -223.0	M	1

No.24



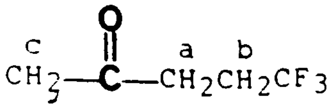
(63)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensit
CH_3(a)	0.91	T	3
CH_2(b)	1.15 → 1.26	M	4
CH_2(c)	1.47 → 1.61	M	2
CH_2(d)	2.24 → 2.82	M	2
CFH	4.91 → 5.65	M	1

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_2	-114.6 → 127.7	M	6
	-128.18 → -137.9	M	6
CF	-176.70 -193.84	S	1
CFH	-216.2 -227.90	D	1



$$\overset{c}{CH_3}-\overset{\overset{O}{\|}}{C}-\overset{a}{CH_2}\overset{b}{CH_2}CF_3$$

No.25

(64)

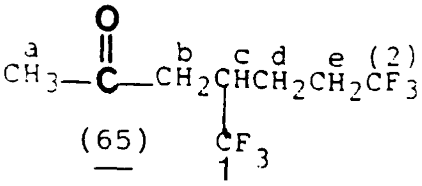
^{1}H.n.m.r

7

	Chemical shift In p.p.m	Multiplicity	Relative Intensity
$CH_3(c)$	1.99	S	3
$CH_2(b)$	2.25	T	2
$CH_2(a)$	2.7	M	2

^{19}F.n.m.r

	Chemical shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-67.8	S	3



$$\overset{a}{CH_3}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{b}{CH_2}\overset{c}{C}H(\underset{1}{CF_3})\overset{d}{CH_2}\overset{e}{CH_2}\overset{(2)}{CF_3}$$

(65)

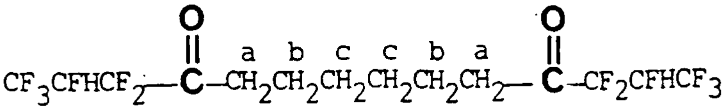
No.26

^{1}H.n.m.r

	Chemical shift In p.p.m	Multiplicity	Relative Intensity
CH_3(a) CH (b)	2.08	M	5.
CH_2(e)	2.7 → 2.8	D(b)	2
CH (c)	2.4	Q	1
CH_2(d)	1.4 → 1.8	M	2

^{19}F.n.m.r

	Chemical shift In p.p.m	Multiplicity	Relative Intensity
CF_3(1)	-71.08	S	3
CF_3(2)	-67.90	S	3



$$CF_3CFHCF_2-\overset{\overset{O}{\|}}{C}-\overset{a}{CH_2}\overset{b}{CH_2}\overset{c}{CH_2}\overset{c}{CH_2}\overset{b}{CH_2}\overset{a}{CH_2}-\overset{\overset{O}{\|}}{C}-CF_2CFHCF_3$$

No.27

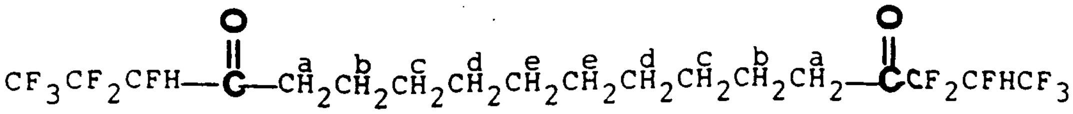
(66)

^1H.n.m.r.

	Chemical shift In p.p.m	Multiplicity	Relative Intensity
CH_2(a)	3.4	T	4
CH_2(b)	2.5	M	4
CH_2(c)	1.8	M	4
CFH	6.2	M	2

^{19}F.n.m.r.

	Chemical shift In p.p.m.	Multiplicity	Relative Intensity
CF_3	-75.07	M	6
CF_2	-117.0	M	4
CFH	-217.0	M	2



$$CF_3CF_2CFH-\overset{\overset{O}{\|}}{C}-\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2\overset{e}{C}H_2\overset{e}{C}H_2\overset{d}{C}H_2\overset{c}{C}H_2\overset{b}{C}H_2\overset{a}{C}H_2-\overset{\overset{O}{\|}}{C}CF_2CFHCF_3$$

(<u>67</u>)

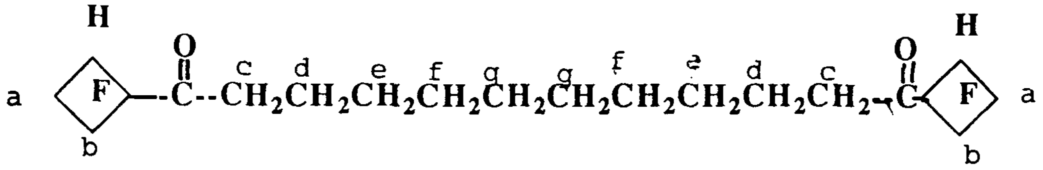
No.28

<u>^{1}H.n.m.r</u>

	Chemical shift In p.p.m	Multiplicity	Relative Intensity
CH_2(a)	2.71	T	4
CH_2(b)	1.64	M	4
CH_2(c)	1.4	M	12
CH_2(d)			
CH_2(e)			
CFH	5.1 → 5.4	D(M)	2

<u>^{19}F.n.m.r</u>

	Chemical shift In p.p.m	Multiplicity	Relative Intensity
CF_3	-75.0	M	6
CF_2	-117.9	M	4
CFH	-217.2	M	2



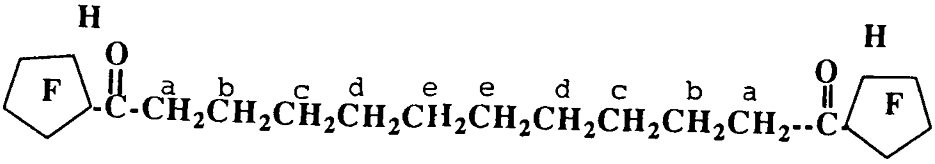
(69)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_2(e) CH_2(f) CH_2(g)	1.28	M(broad)	12
CH_2(c) CH_2(d)	2.3 → 2.78	M	8
CFH	5.1 → 5.5	M	2

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_2(a)	-116.8 → -121.9	M	4
CF_2(b)	-126.2 → -131.2	M	4
CFR	-172.6 -194.5 → -197.8	M	2
CFH	-212.9 → -216.6 -218.3 → -221.6	M	2



(71)

^{1}H.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CH_2(c) CH_2(d) CH_2(e)	1.27 → 1.48	M(broad)	12
CH_2(b)	2.0 → 2.18	M(broad)	4
CH_2(a)	2.67	M(broad)	4
CFH	5.0 → 5.5	D(M)	2

^{19}F.n.m.r

	Chemical Shift In p.p.m	Multiplicity	Relative Intensity
CF_2	-114.4 → -133.1 -176.2	M	12
CFR	-184.83 → -193.2	M	2
CFH	-208.0 → -215.6 -225.0 → -227.11	M	2

APPENDIX II- MASS SPECTRA

COMPOUND ENDEX

1. 1-methyl-2,2,3,4,4,4-hexafluorobutyl ethyl ether (32)
2. di(1-methyl-2,2,3,4,4,4-hexafluorobutyl)ether (33)
3. 1-methyl-2-H-perfluorocyclobutyl)ethyl ether (34)
4. di(1-methyl-2-H-perfluorocyclobutyl)ether (35)
5. 1-methyl-2-H-perfluorocyclopentyl ethyl ether (36)
6. di(1-methyl-2-H-perfluorocyclopentyl)ether (37)
7. α-(1,2,3,3,3-pentafluoro-1-propenyl)diethylether (42)
8. α,α′-bis(1,2,3,3,3-pentafluoro-1-propenyl)diethylether (43)
9. α-(2,3,3,4,4-pentafluorocyclobutyl)diethylether (44)
10. 1-methoxy-1-(1-ethoxyethyl)tetrafluoropropene (48)
11. 1-propoxy-(1-ethoxyethyl)-tetrafluoropropene (49)
12. 1-butoxy-1-(1-ethoxyethyl)-tetrafluoropropene (50)
13. α,α′-bis(1-methoxy-tetrafluoro-1-propenyl)diethylether (51)
14. α,α′-bis(1-ethoxy-tetrafluoro-1-propenyl)diethylether (52)
15. α,α′-bis(1-propoxy-tetrafluoro-1-propenyl)diethylether (53)
16. α,α′-bis(1-butoxy-tetrafluoro-1-propenyl)diethylether (54)
17. 3,3,4,5,5,5-hexafluoropentan-2-one (56)
18. 1,1,1,2,3,3,3-hexafluorononan-4-one (57)
19. 2-H-hexafluoropropyl t-butyl ketone (58)
20. 1,1,1,2,3,3-hexafluoro-5-cyclohexyl-pentane (59)
21. 1,1,1,2,3,3-hexafluoro-6-cyclohexyl-hexan-4-one (60)
22. 1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-6-cyclohexyl-nonan-4-one (61)
23. 2-Hydro-hexafluorocyclobutyl pentyl ketone (62)

24. 2-Hydro-octafluorocyclopentyl pentyl ketone (63)

25. 5,5,5-trifluoro-pentan-2-one (64)

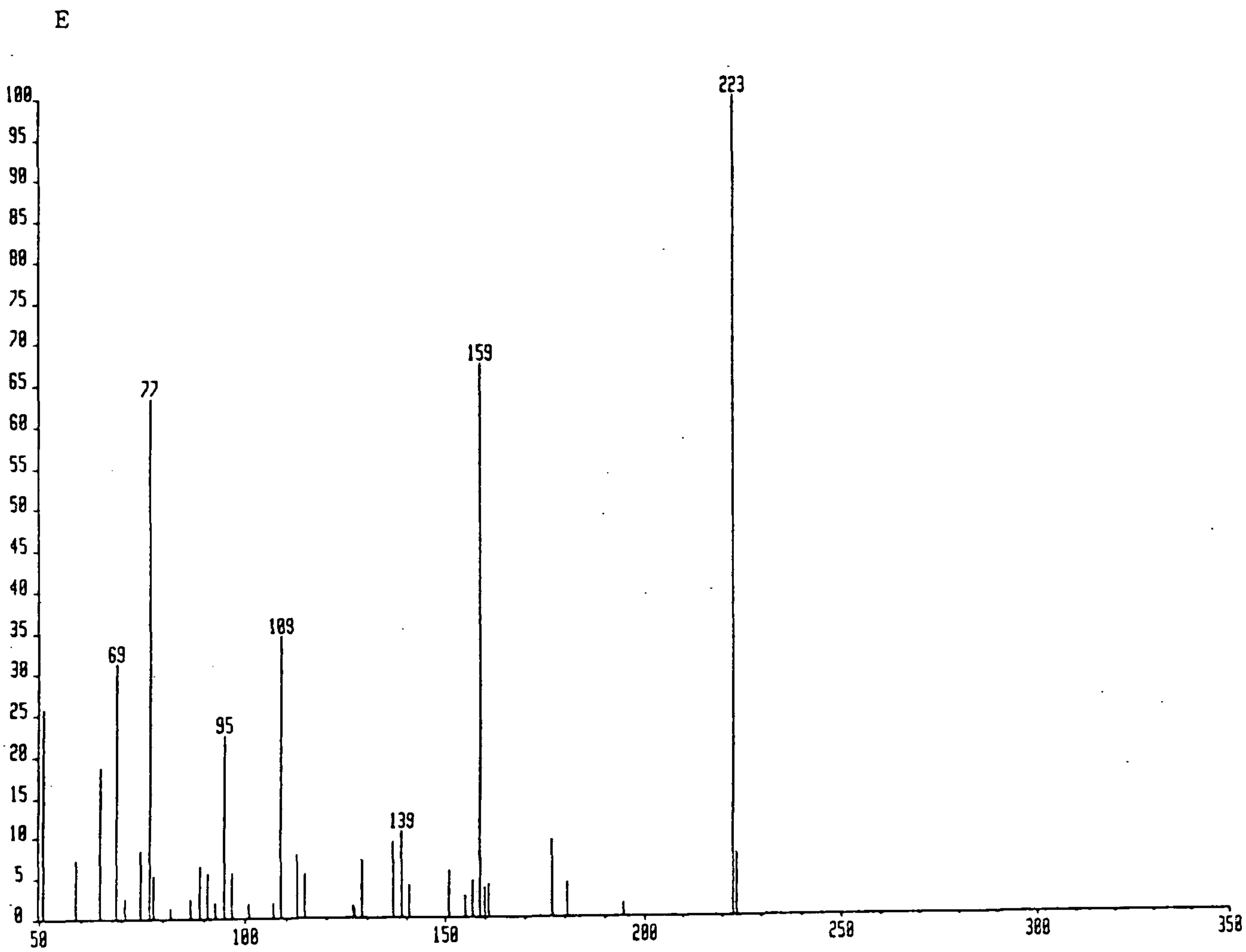
26. 4-trifluoromethyl-7,7,7-trifluoroheptan-2-one (65)

27. 1,1,1,2,3,3,12,12,13,14,14,14-dodecafluoro-tetradecan-4,11-dione (66).

28. 1,1,1,2,3,3,3,16,16,17,18,18,18-dodecafluoro-octadodecan-4,15-dione (67)

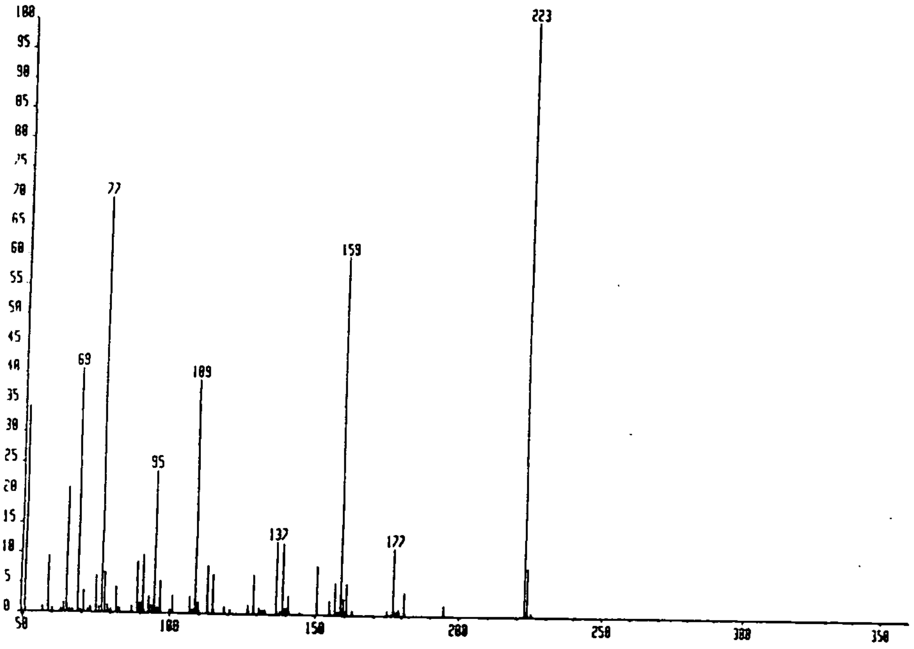
29. 1,12-di(2-Hydro-perfluorocyclobutyl)dodecandione (69)

M.Wt= 224 **No.1**



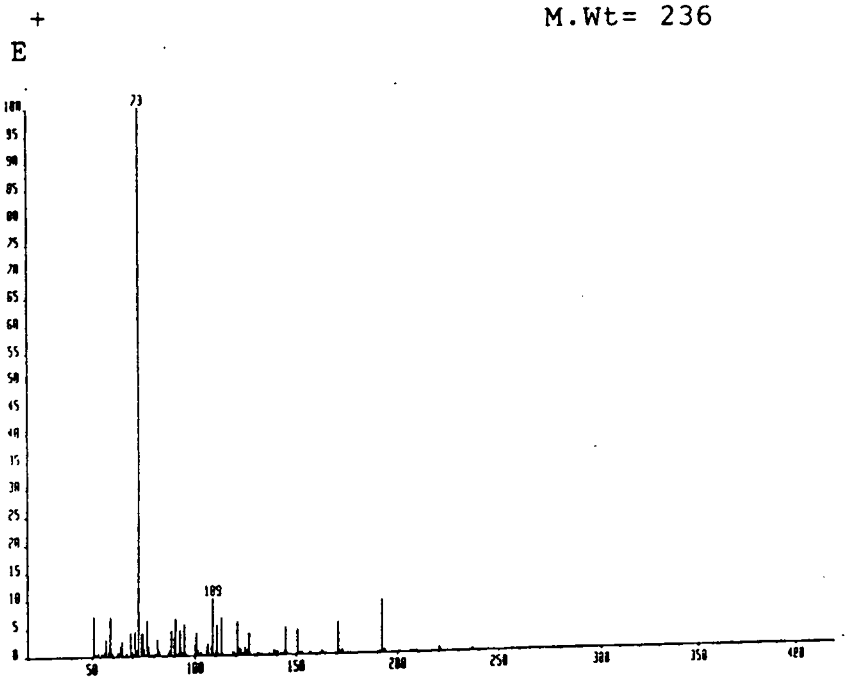
Mass	% Base
50.91	25.69
58.93	7.06
64.91	18.51
68.89	31.12
70.93	2.39
74.91	8.23
76.89	63.22
77.90	5.20
81.88	1.23
86.89	2.22
88.88	6.42
90.89	5 43
92.86	1.75
94.86	22.42
96.88	5.43
100.85	1.63
106.87	1.69
108.86	34.33
112.83	7.76
114.84	5.31
126.81	1.28
126.86	0.99
128.83	7.01
136.82	9.22
138.82	10.45
140.79	3.85
150.79	5.66
154.79	2.51
156.82	4.50
158.80	67.37
159.83	3.56
160.78	4.03
176.80	9.40
180.78	4.09
194.78	1.46
222.76	100.00

E^{+} M.Wt= 374 No. 2



Mass	% Base
50.91	34.05
56.91	0.91
58.93	9.22
59.93	0.62
62.92	0.43
63.91	1.49
64.91	20.83
65.91	0.51
66.90	0.44
68.88	40.54
69.88	0.32
70.92	3.62
71.93	0.38
72.48	0.30
72.91	0.95
74.90	6.05
75.90	0.95
76.89	69.65
77.90	6.71
78.90	1.18
79.88	0 44
81 87	4.24
82.88	0.83
86 90	0.99
88.88	8.47
89.88	1.70
90 89	9.53
92.87	2 78
93.88	1.27
94.86	23.71
95 88	0.89
96.88	5.23
99.85	0.41
100.85	2.84
106.87	2.73
107.85	0.56
108.86	38.76
109.87	1.75
112.83	7.82
114.85	6.55
118.85	1.06
120.88	0.56
126.85	1.43
128.82	6.40
130.81	0.97
131.80	0.54
132.83	0.59
136.82	12.01
137.84	0.44
138.82	11.73
139.84	1.06
140.80	2.99
144.80	0.22
150.79	8.04
154.79	2.30
156.82	5.31
157.82	0.41
158.81	59 67
162.80	0.54
174 81	0.75
175.80	0.22
176.80	11.03
177.80	0 54
178.81	0 86
180.76	3.75
194.77	1.62
222.77	100.00
223.77	8.02
224.81	0.46

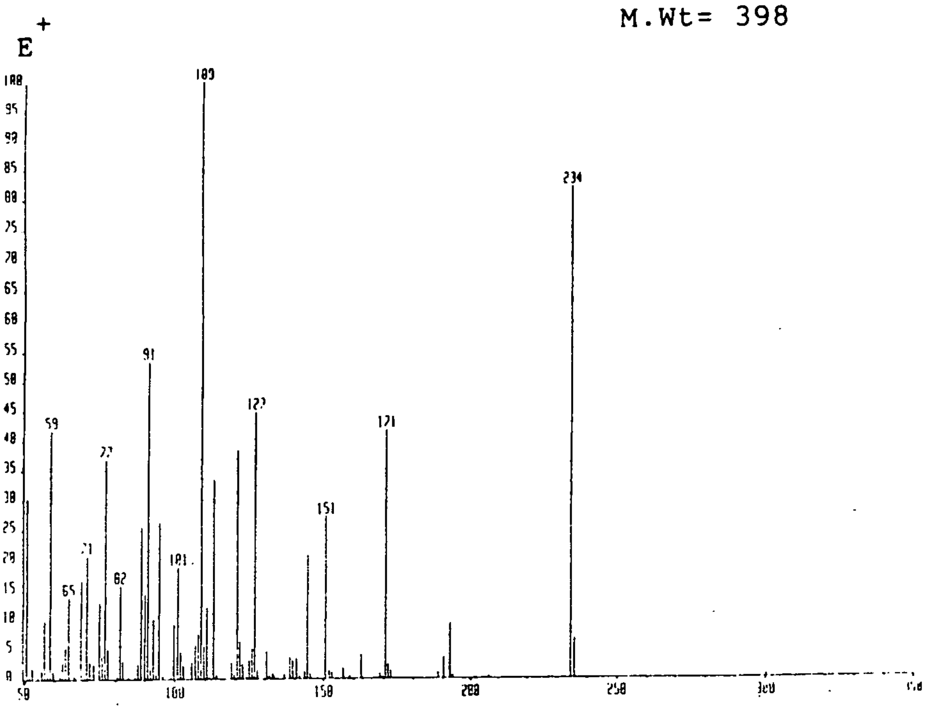
M.Wt= 236 No. 3



Mass	% Base
50.91	7.16
51.93	0.37
52.94	0.38
54.92	0.35
55.92	0.53
56.92	2.90
57.93	0.68
58.92	6.97
59.93	0.63
62.91	0.63
63.91	1.64
64.91	2.52
66.89	0.36
68.88	3.98
69.91	0.60
70.91	4.31
71.92	0.96
72.94	100.00
73.95	3.92
74.89	3.97
75.90	1.22
76.89	6.24
77.90	1.66
78.91	0.20
80.87	0.24
81.87	2.81
82.89	0.77
86.89	0.24
87.88	0.92
88.88	4.40
89.89	2.92
90.89	6.58
91.89	0.40
92.86	4.38
93.86	0.65
94.86	5.56
95.87	0.18
99.84	1.74
100.86	3.96
101.87	0.83
102.88	0.54
103.86	0.11
104.86	0.16
105.86	1.46
106.86	2.12
107.86	1.42
108.85	10.10
109.86	0.73
110.83	5.39
111.83	0.22
112.82	6.71
118.84	0.61
119.83	0.22
120.84	6.00
121.85	0.87
122.82	1.20
123.84	0.35
124.83	1.29

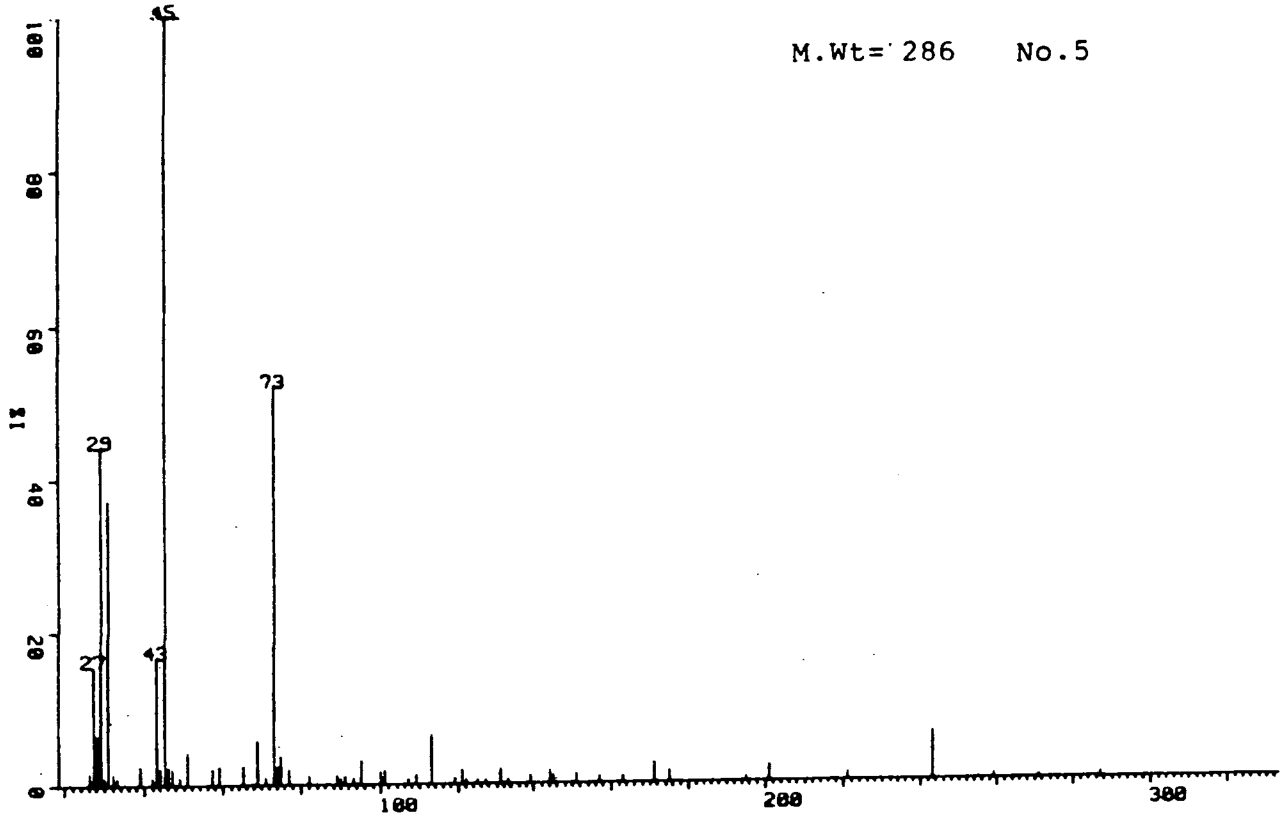
Mass	% Base
130.81	0 37
132.84	0 18
136.81	0.15
138.83	0 89
139.83	0 49
140.83	0 63
142.82	0.11
143.81	0 36
144.80	4.69
145.80	0 17
150.81	4 25
151.82	0.31
152.80	0 23
156.80	0 30
162.79	0.43
170.80	5 57
171.81	0 35
172.78	0 57
190.78	0 21
192.74	9 30
193.76	0 45
200.80	0 13
206.76	0.33
208.78	0.14
220.76	0 78
236.79	0 33

M.Wt= 398 No. 4



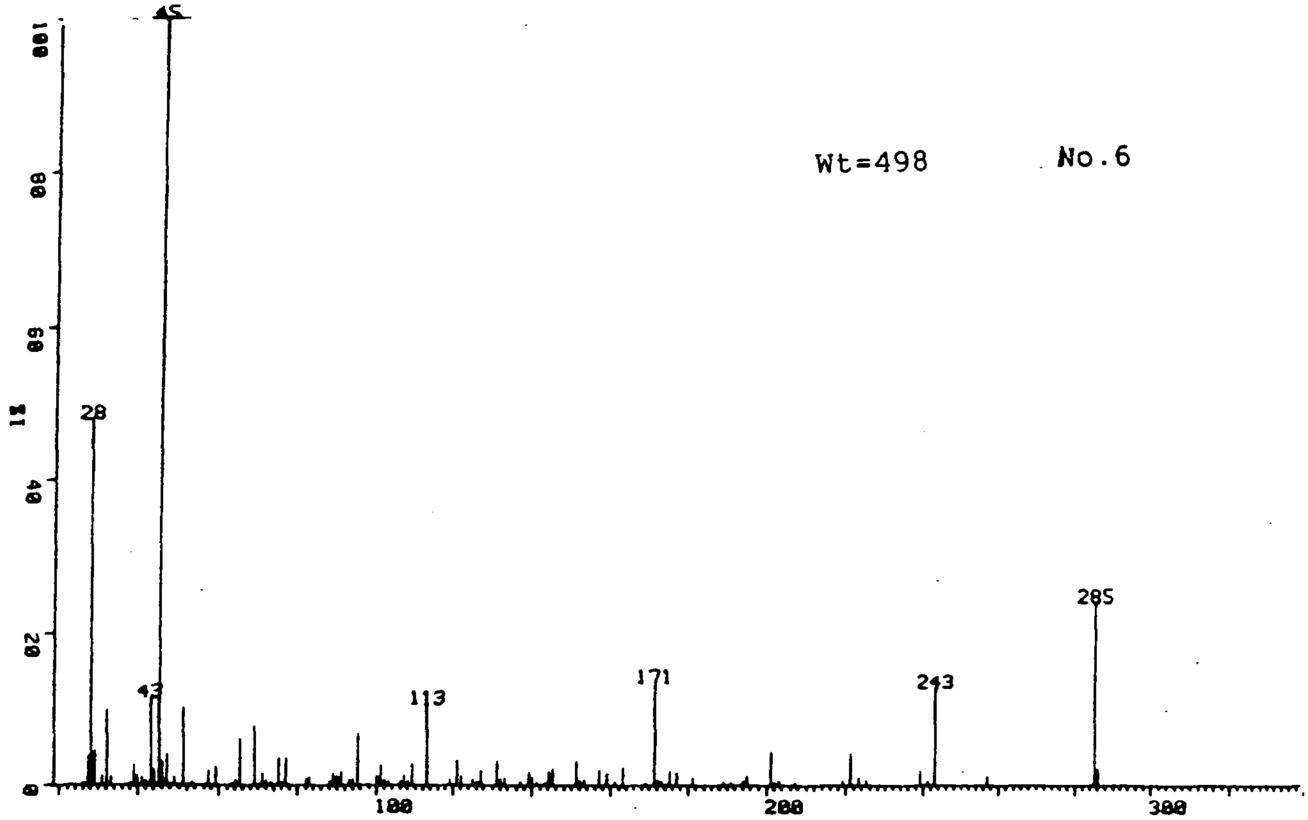
Mass	% Base
50.84	30.13
51.86	1.07
52.87	1.87
54.85	0.31
55.84	1.32
56.83	9.81
57.84	1.52
58.84	41.80
59.85	1.41
61.83	0.52
62.82	2.94
63.81	5.26
64.82	13.77
66.79	0.50
68.79	16.69
69.81	1.45
70.81	20.77
71.82	2.90
72.80	2.47
74.78	12.87
75.80	3.96
76.79	36.83
77 80	5.10
80.77	0.52
81.76	15.76
82.78	3.08
84.51	0.22
86.75	0.31
87.76	2.65
88.76	25.44
89.76	14.42
90.77	53.34
91.78	1.75
92.74	9.93
93.73	1.47
94.74	26.14
95.76	0.52
98.74	0.30
99.71	9.13
100.73	18.83
101.74	4.54
102.74	2.27
105.72	2.70
106.72	5.81
107.72	7.45
108.71	100.00
109 72	5.45
110.69	12.03
111.67	0.41
112.68	33.37
113.68	0.61
118.68	2.79
119.69	0.75
120.69	38.38
121.70	6.15
122.67	2.40

Mass	% Base
127.68	1.56
130.64	4.60
131.67	0.39
132.65	0.81
132.88	0.49
133.15	0.30
136.65	0.62
138.65	3.62
139.66	3 07
140.66	3.41
141.65	0.39
143.62	1.17
144.62	20.73
145.64	0.69
150.62	27.17
151.63	1.40
152.63	1.02
156.60	1.66
158.64	0.24
162.60	3.99
168.62	0.73
169.62	0.30
170.60	41.60
171 60	2.32
172.57	1.22
188.56	0 94
190.55	3 54
192.52	9.20
193.53	0.43
206.50	0.35
234.49	81 83
235.50	6.51
300.36	0.46



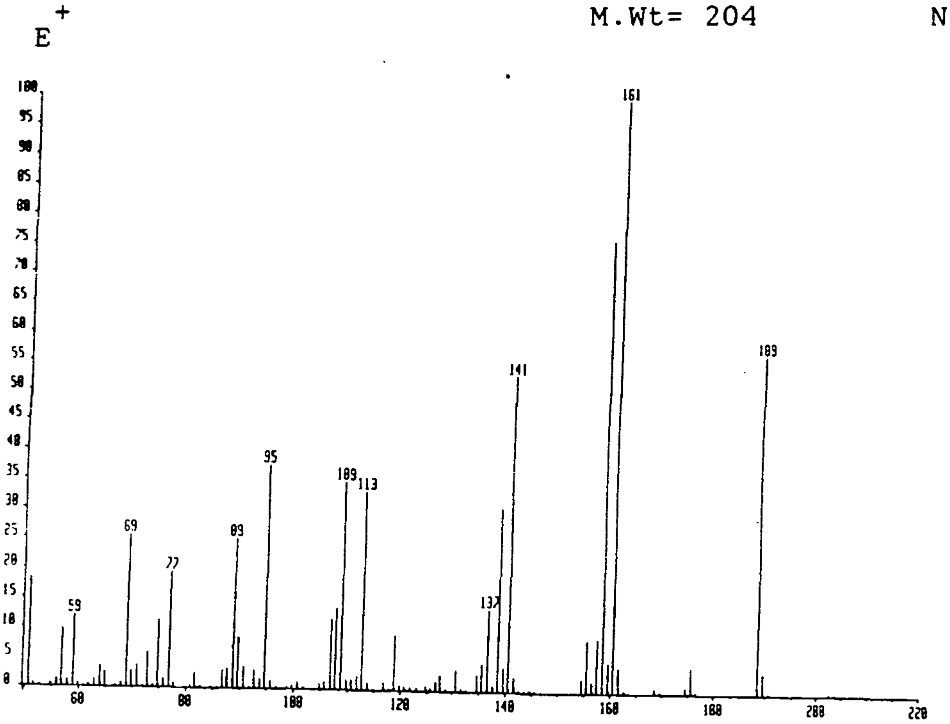
M.Wt= 286 No.5

MASS	%INT. BASE	MASS	%INT. BASE
[illegible]	1.65	37.90	0.87
27.[illegible]	15.[illegible]0	90.98	1.10
28.11	[illegible]	93.01	0.96
28.13	4.08	95.05	3.17
28.[illegible]	[illegible]	99.91	1.70
29.00	44.[illegible]	100.98	1.88
29.81	0.87	102.04	[illegible].75
29.83	0.5[illegible]	105.01	1.24
30.88	37.43	1[illegible]3.04	0.61
31.9[illegible]	1.3[illegible]	115.01	0.83
33.08	1.01	1[illegible]1.03	1.9[illegible]
[illegible]	[illegible].38	[illegible]	0.64
4[illegible].01	1.1[illegible]	125.08	0.64
43.08	16.[illegible]5	127.08	0.60
4[illegible].1[illegible]	0.60	131.01	1.27
44.1[illegible]	[illegible]	1[illegible]3.09	0.69
45.19	100.00	139.04	1.15
[illegible]	[illegible]	144.08	1.70
4[illegible].[illegible]1	[illegible].11	15[illegible].09	1.01
4[illegible]	1.0[illegible]	151.05	1.38
[illegible]	[illegible]	152.07	0.96
[illegible]	[illegible].16	153.09	1.06
[illegible]9.9[illegible]	[illegible].48	171.07	[illegible].71
[illegible]5.1[illegible]	[illegible].5[illegible]	175.10	1.61
[illegible]1.9[illegible]	[illegible].92	195.12	0.60
[illegible]1.00	0.96	201.05	2.16
73.11	52.11	2[illegible]1.10	1.10
74.11	[illegible].43	243.10	6.42
75.03	3.76	259.10	0.83
[illegible].01	2.06	271.12	0.50
81.9[illegible]	1.1[illegible]	287.15	0.28
8[illegible].9[illegible]	1.[illegible]		



Mass	Base%	Mass	Base%	Mass	Base%	Mass	Base%
26.30	0.47	68.96	7.90	131.02	3.30	207.11	0.41
27.23	3.83	70.99	1.62	132.07	1.09	219.11	0.74
28.11	47.86	72.05	0.68	133.08	1.18	221.10	4.48
28.13	1.24	73.11	0.41	137.07	0.56	223.08	1.21
28.97	4.63	75.08	3.66	139.05	1.89	225.09	0.80
29.00	1.09	76.08	0.53	140.02	1.21	239.08	2.03
30.86	1.33	77.06	3.57	141.06	0.38	241.10	0.50
30.89	0.62	82.02	1.00	143.07	0.35	243.09	13.06
31.97	9.97	83.07	1.15	144.09	1.92	257.13	1.24
33.08	1.21	88.03	0.50	145.10	2.33	285.16	24.15
38.05	0.35	89.00	1.77	151.04	3.21	286.13	2.27
38.97	2.74	89.95	1.33	152.07	0.83		
39.81	1.42	91.02	1.89	153.09	0.83		
40.96	1.09	93.05	0.97	157.07	2.09		
42.02	0.68	94.06	0.91	159.05	1.74		
42.06	0.47	95.08	6.81	161.05	0.62		
43.09	11.68	99.95	1.36	163.07	2.48		
43.12	1.56	101.02	2.65	169.05	0.38		
44.10	1.03	102.06	0.88	171.07	13.68		
44.13	2.21	103.10	0.50	172.10	0.86		
45.16	100.00	106.06	0.71	173.09	0.56		
46.15	3.18	107.06	1.33	175.08	2.06		
47.12	4.10	108.05	0.62	177.08	1.89		
48.98	1.12	109.02	2.83	181.04	1.09		
50.96	10.29	113.07	10.85	189.05	0.59		
53.12	0.47	119.03	0.91	191.07	0.38		
57.11	1.95	121.05	3.21	194.09	0.62		
59.03	2.45	122.09	1.39	195.09	1.30		
63.11	0.41	125.10	0.94	201.07	4.54		
64.13	0.88	126.10	0.50	202.10	0.47		
65.12	6.28	127.07	2.03	203.09	0.77		

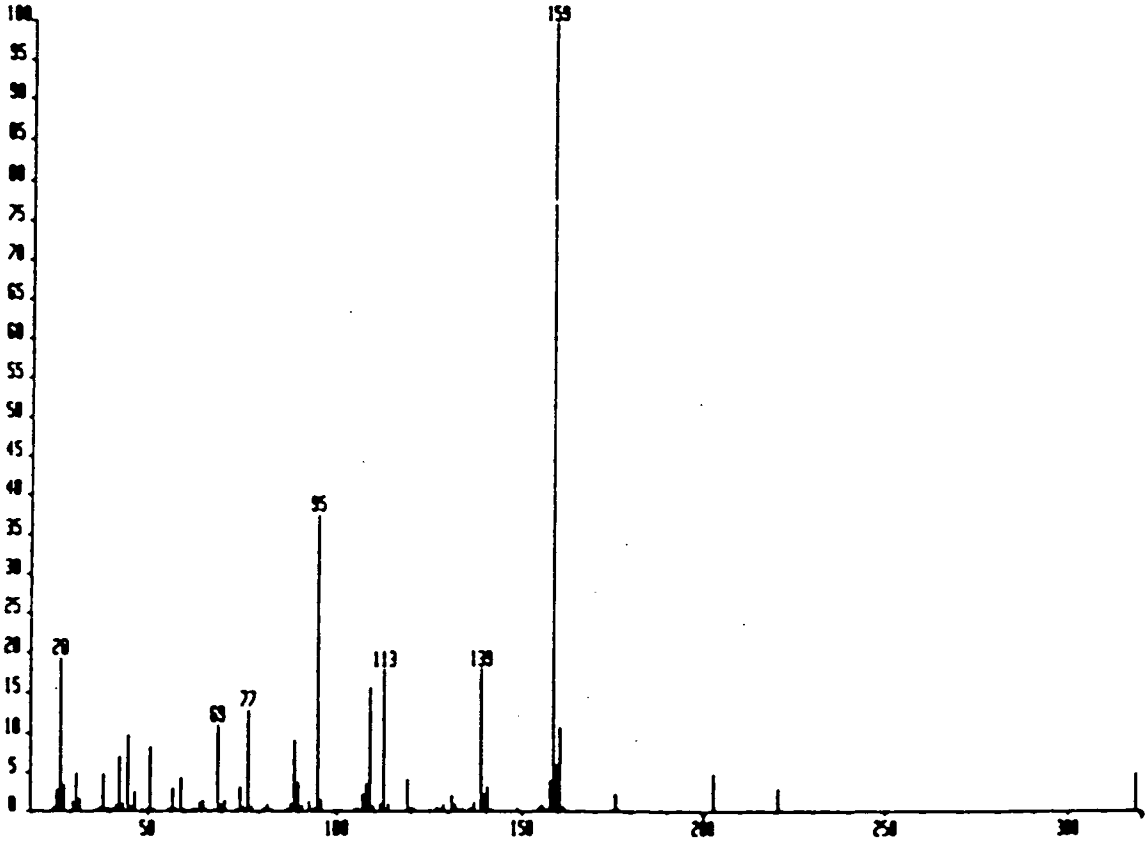
M.Wt= 204 No. 7



Mass	% Base
50.85	18.13
51.86	0.41
52.85	0.15
54.85	0.50
55.85	1.27
56.84	9.59
57.84	1.09
58.85	11.75
59.85	0.45
61.82	0.38
62 83	1.24
63.82	3.40
64.83	2.46
66.81	0.21
67.81	0.60
68.79	25.34
69.82	2.52
70 82	3.56
71.83	0.18
72.83	5 61
73 81	0 34
74.79	11.07
75.79	1 31
76 80	19.32
77 80	0.71
80.77	0.50
81.77	2.43
82.77	0.19
84.80	0.12
86.78	2.95
87 76	3.16
88 77	24 91
89 77	8.27
90.76	3.52
91.76	0.15
92.74	2.93
93.74	1.57
94.75	37.26
95.75	1.17
96.75	0.18
98.74	0.30
99.72	0.44
100.75	1.11
101.73	0.19
104.76	0.70
105.72	1.21
106.73	11.47
107.72	13.41
108.72	34.50
109.73	1.48
110.70	1.71
111.69	2.28
112.69	33.00
113.70	1.11
116.69	1.14
118.69	9.14
119.69	0.80
120.70	0.60
121.68	0.38
123.05	0.53

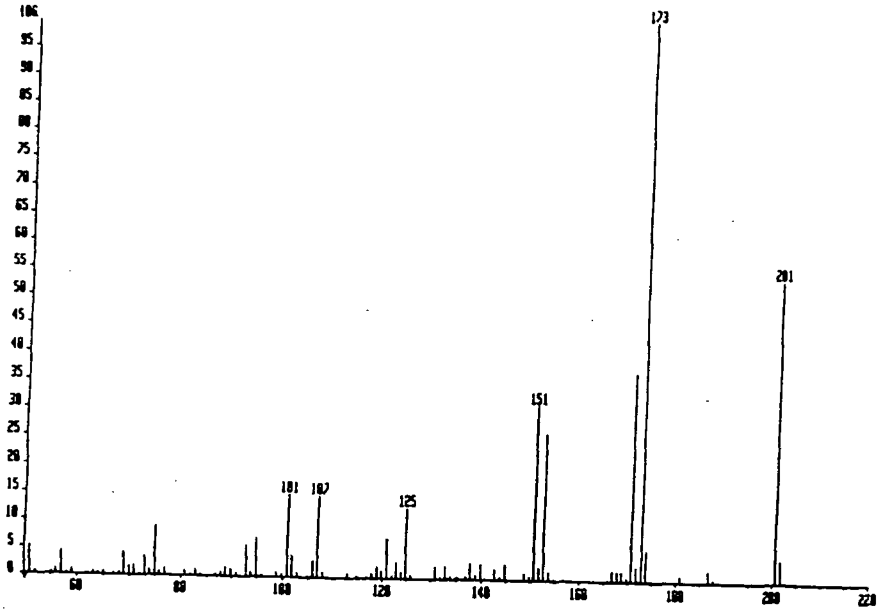
Mass	% Base	
124.68	0 69	
125.67	0 36	
126 60	1 44	
127.60	2 53	
128.67	0.26	
130.65	3.46	
131.66	0 23	
134.71	2.67	
135.66	4 57	
136.67	13 70	
137.71	0 85	F
138.65	30.40	F
139.65	3 88	
140.63	52 94	
141.63	2 36	
142 63	0 22	
144.64	0 29	
145.65	0 14	
154.61	2 21	
155 62	8 66	
156 63	1 83	
157 61	8.90	F
158.61	76 15	F
159 62	5 04	F
160.60	100 00	F
161 61	4 21	
162.62	0.29	
168.62	0.81	
169.64	0 13	
174.60	0 90	
175 59	4.19	
176 61	0 17	
188.56	56 81	
189 57	3.27	
190.57	0.16	
202.57	0 13	
203.57	0.15	

EI^+ M.Wt=334 No.8



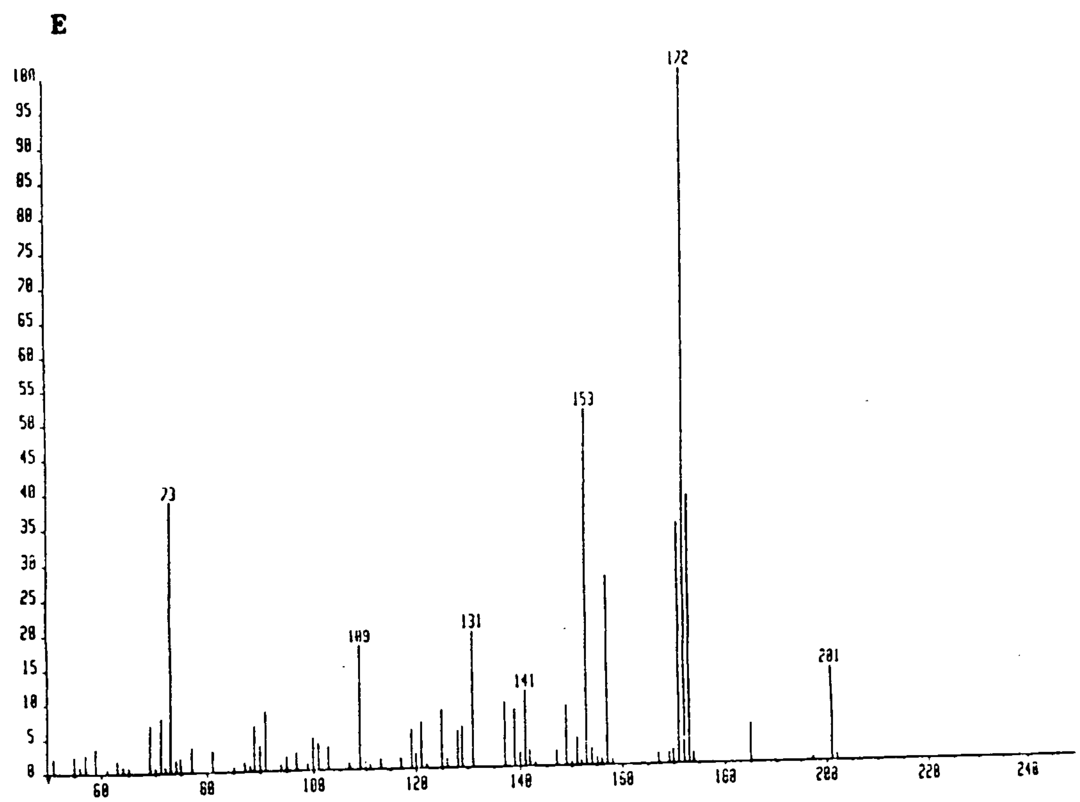
Mass	% Base
25 61	0. 41
26 62	2. 75
27 60	19 27
28. 60	3. 39
28. 63	0 12
30. 60	1 26
31. 59	4. 90
32. 62	1. 45
36 62	0. 15
37. 64	0 50
38 65	4 77
39 59	0 35
39 66	0. 33
40 67	0 34
41 65	0 69
41 68	0 17
42 67	7. 04
43 65	0 92
44 69	9 77
45 69	0 61
46 66	0 14
46 70	2. 45
48 70	0 14
49 71	0 32
50 71	8. 15
51 74	0. 17
55. 75	0 34
56 77	2 93
56. 81	0 19
56 83	0. 18
57. 78	0. 33
58 80	4 30
59 81	0. 13
61. 79	0. 19
62. 82	0. 26
63 84	1. 06
64. 28	0. 19
64 85	1 23
65 80	0. 14
67 86	0 15
67. 87	0 15
68. 87	10 85
69. 92	0 79
70. 94	1. 14
73. 97	0. 18
75. 01	3 05
76 04	0 38
77 07	12 73
78 10	0 51
81 13	0 24
82. 13	0 75
83 12	0 14
87 08	0 23
88 07	0 96
89 06	9 13
90 06	3 66
91 04	0 55
92 99	1 22
93 99	0 40
94 98	37 43
95 98	1 36
99 91	0 21
100 93	0 22
104 93	0 29
104 96	0 14
105 88	0 26
106 89	2 13
107 88	3 49
108 88	15 40
109 87	0 61
111 82	0 88
112 82	17 66
113 82	0 72
118 80	4 06
119 81	0 29
120 81	0 29
124 78	0 19
124 82	0 11
126 80	0. 42
127 77	0 19
128 68	0 80
130. 75	1 94
131. 68	0. 77
131. 77	0 15
132. 79	0 16
133. 67	0 23
135 68	0 25
135. 79	0 27
136 79	1 00
138 79	17 83
139 79	2 05
140 77	3 01
141 76	0 18
148 81	0 29
154 76	0 37
155 76	0 73
156 76	0 34
157. 76	4 00
158 47	0 11
158 76	100 00
159 76	5 91
160 74	10 80
161 74	0 49
174 70	0 18
175 72	2 16
176 73	0 14
202 68	0 24
220 67	0 14
318 51	0 24

M.Wt=216 No.9



Mass	% Base
50.92	5.01
74.88	8.81
92.85	5.60
94.86	6.79
100.86	14.91
106.85	14.71
120.85	7.07
124.82	12.72
150.79	31.37
152.77	26.15
170.78	37.31
172.76	100.00
173.76	5.67
200.76	53.86

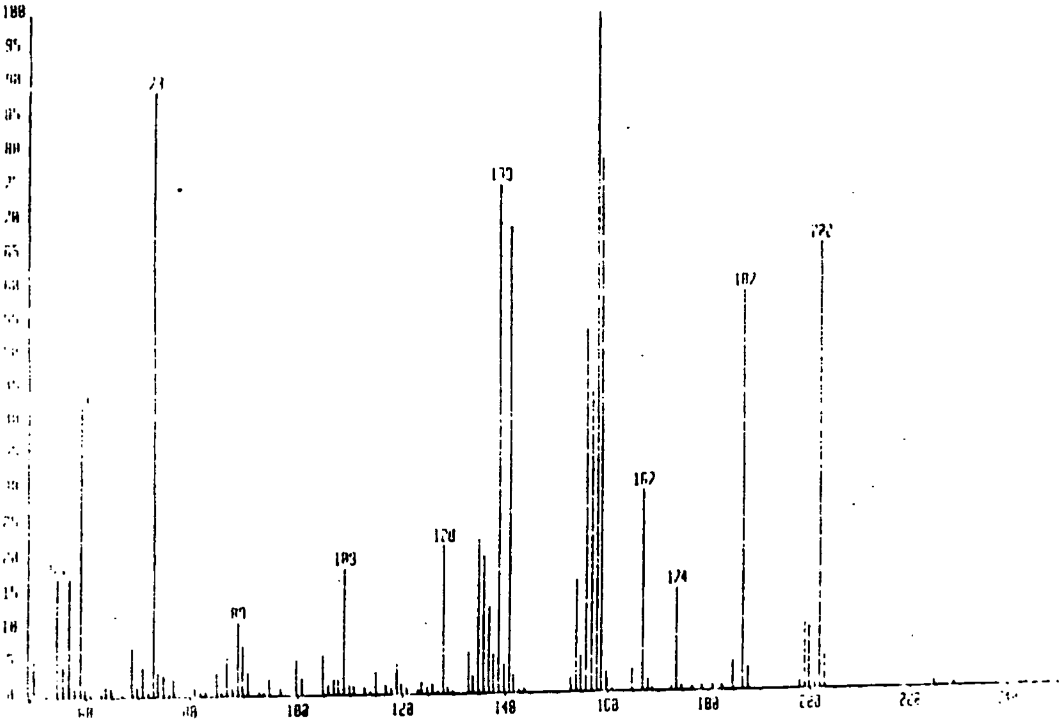
M.Wt= 216 No. 10



Mass	% Base
51.01	2.10
55.02	2.40
56.03	0.85
57.03	2.64
59.04	3.47
61.03	0.52
63.03	1.87
64.02	0.85
65.03	0.70
69.01	6.84
70.03	0.67
71.05	7.78
72.06	0.82
73.07	38.60
74.08	1.65
75.02	2.92
77.03	3.44
81.01	3.04
85.05	0.67
87.04	1.22
88.03	0.77
89.04	6.59
90.04	3.41
91.02	8.66
94.03	0.80
95.03	2.02
97.01	2.97
99.05	0.90
100.01	4.97
101.04	3.82
103.07	3.37
107.04	0.97
109.02	17.84
110.03	1.07
111.02	0.55
113.03	1.35
117.03	1.45
119.05	5.61
120.04	7.05
121.05	6.69
122.06	0.52
125.04	8.26
126.04	1.15
128.01	5.36
129.05	5.24
131.03	19.91
137.05	9.18
139.05	8.11
140.05	1.90
141.07	10.98
142.03	2.25
143.04	0.50
147.11	2.70
149.07	9.63
150.08	0.50
151.07	3.87
152.08	0.80
153.04	51.32
154.05	2.50
155.03	1.07

Mass	% Base
156.05	0.82
157.06	27.77
158.07	0.79
167.08	1.55
169.10	1.95
170.08	1.90
171.09	34.48
172.09	100.00
173.07	38.67
174.08	1.45
185.09	5.49
197.13	0.42
201.08	13.62
203.11	0.80

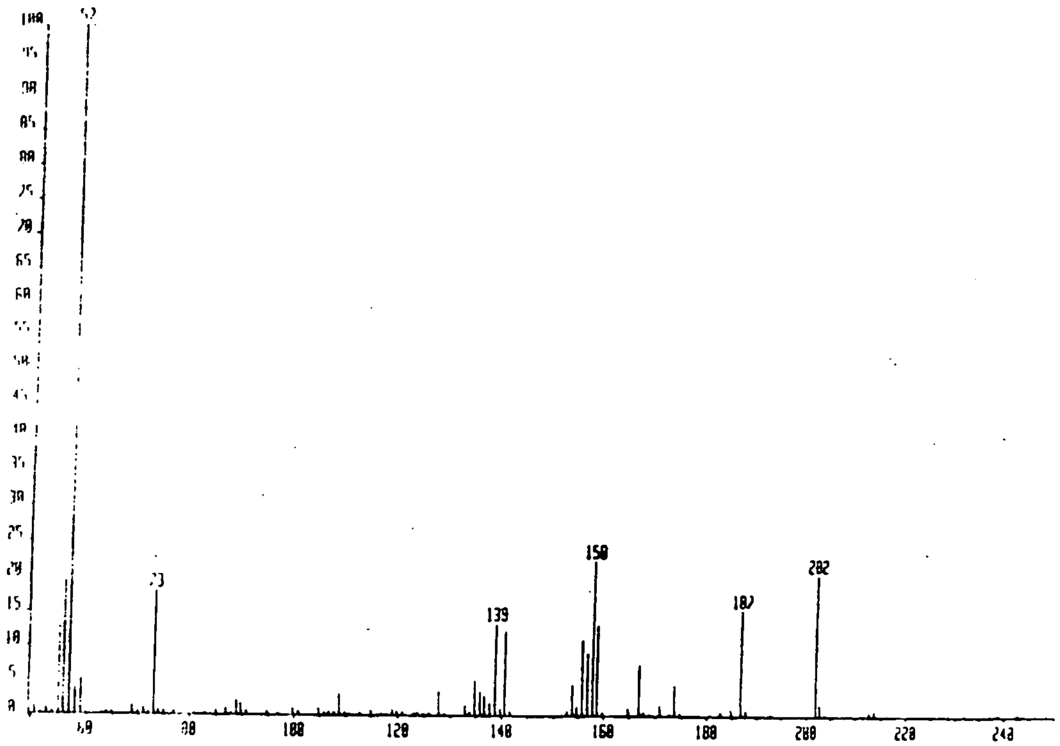
E^+ M.Wt= 244 No. 11



Mass	% Base
50.92	5.30
52.91	0.31
54.92	17.40
55.93	4.51
56.93	12.42
57.94	1.19
58.94	42.09
59.94	1.25
60.94	0.36
62.91	0.53
63.91	1.48
64.92	1.28
66.90	0.11
68.89	2.25
68.96	0.33
69.91	1.39
70.91	4.12
71.93	0.63
72.94	88.13
73.95	3.47
74.90	1.09
75.90	0.34
76.90	2.41
80.87	1.23
81.88	0.44
82.88	0.51
84.90	1.34
85.89	0.42
86.90	5.58
87.88	1.05
88.88	10.00
89.89	7.77
90.87	3.38
92.86	0.45
93.86	0.77
94.86	2.42
96.85	1.02
99.84	5.20
100.87	2.47
104.88	5.91
105.86	1.47
106.86	2.28
107.85	2.16
108.81	18.48
109.83	1.44
110.84	1.16
112.85	1.00
113.85	0.34
114.85	3.41
116.84	1.39
117.85	0.88
118.83	4.34
119.84	1.50
120.85	0.97
[illegible]	[illegible]

Mass	% Base
124.84	0.83
125.83	1.59
126.84	0.10
127.80	21.72
128.81	1.06
129.82	0.33
132.87	6.00
133.81	2.62
134.83	22.12
134.95	0.25
135.88	0.29
135.81	20.05
136.82	12.51
137.81	[illegible] 70
138.80	74.03
139.81	4.27
140.79	68.61
141.80	2.50
142.81	1.40
143.82	1.50
152.10	2.44
153.80	26.12
154.81	5.25
155.80	51.45
156.81	44.77
157.81	100.00
158.79	70.36
159.79	2.91
160.80	6.28
164.83	1.20
166.81	29.09
167.82	1.11
169.82	0.31
172.80	0.51
173.90	15.01
174.81	0.52
176.83	0.19
178.81	0.22
180.80	0.78
182.81	0.72
184.80	4.22
186.78	58.61
187.79	3.31
197.80	1.55
198.80	0.59
199.81	0.01
200.81	0.81
201.78	65.21
202.79	4.00
224.87	0.78
228.78	1.04
243.80	0.36

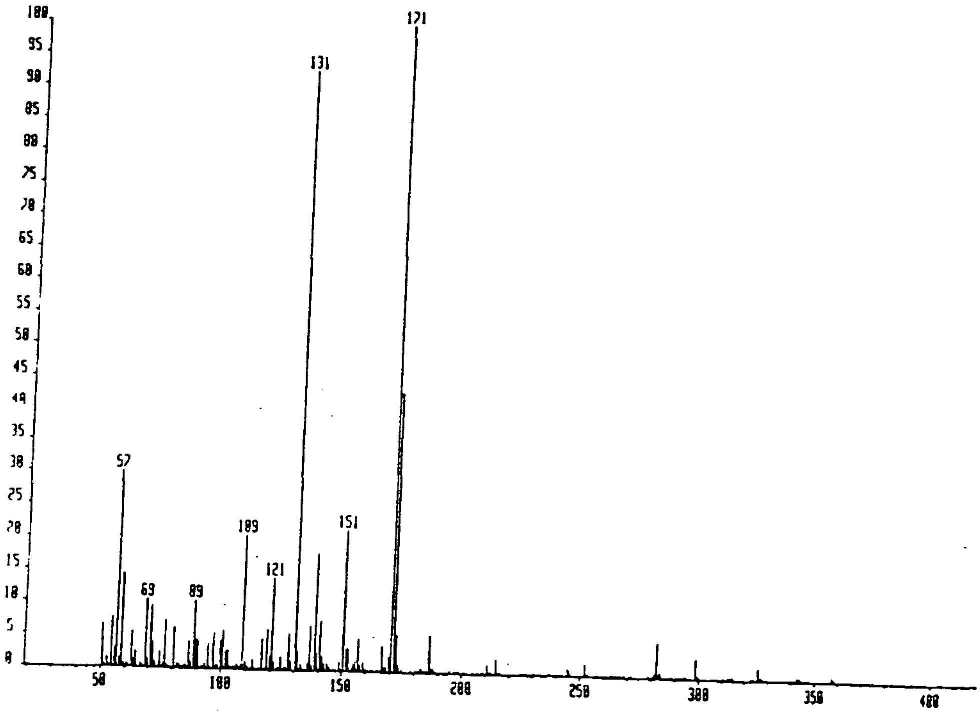
E+ M.Wt= 258 No.12



Mass	% Base
50.91	1.15
52.93	1.11
53.94	0.25
54.94	13.94
55.95	19.24
56.96	100.00
57.96	3.06
58.97	4.94
59.93	0.12
63.90	0.26
64.91	0.24
68.88	1.15
69.90	0.24
70.91	0.91
71.93	0.17
72.94	17.90
73.94	0.64
74.89	0.53
76.89	0.52
80.86	0.27
82.94	0.14
84.89	0.59
86.89	[illegible]
[illegible]	0.14
88.87	1.96
89.87	1.47
90.86	0.52
94.86	0.45
96.88	0.16
99.83	0.60
100.88	0.49
104.86	0.05
105.85	0.26
106.85	0.45
107.84	0.30
108.9	2.96
109.82	0.27
110.81	0.18
112.84	0.26
114.82	0.60
116.82	0.20
117.83	0.21
118.81	0.27
119.83	0.42
120.81	0.45
122.82	0.14
123.84	0.12
123.79	0.29
124.93	0.13
125.87	0.27
127.70	3.33
128.80	0.21
132.86	1.40
133.81	0.51
134.81	5.07
[illegible]	[illegible]
136.81	2.72

Mass	% Base
140.77	[illegible]
141.76	0.41
[illegible]	[illegible]
[illegible]	4.[illegible]
[illegible]	1.[illegible]
155.76	[illegible]
[illegible]	3.99
157.75	22.42
158.[illegible]	13.27
159.[illegible]	0.52
164.81	1.12
166.79	[illegible]
167.[illegible]	1.41
168.[illegible]	0.15
170.[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
174.[illegible]	[illegible]
180.[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
186.[illegible]	[illegible]
187.[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
242.[illegible]	[illegible]

M.Wt=358 No.13



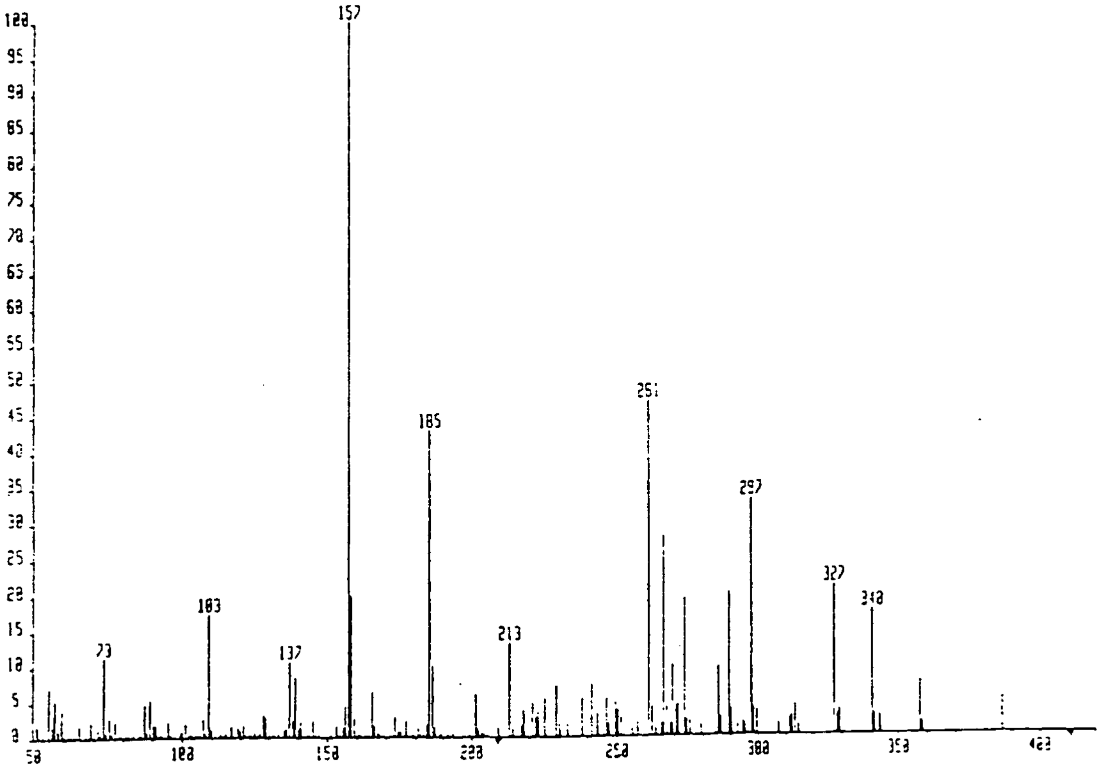
Mass	% Base	
50.94	6.33	
52.95	1.40	
54.96	7.50	
55.96	2.86	
56.96	29.87	
57.96	1.35	
58.97	14.28	
59.97	0.50	
62.95	5.30	
63.94	1.10	
64.95	2.33	
68.92	10.43	
69.94	1.23	
70.96	9.40	
71.97	3.71	
72.95	0.89	
74.93	2.41	
75.93	0.45	
76.93	7.29	
80.92	6.08	
81.92	0.65	
82.94	0.51	
86.93	4.06	
87.93	0.96	
88.92	10.33	
89.93	4.34	
90.92	4.08	
93.91	0.82	
94.91	3.72	
96.89	5.33	
98.94	0.54	
99.88	4.18	F
100.91	5.73	F
101.95	2.70	
102.94	2.78	
104.91	0.47	
106.90	0.69	
107.90	0.57	
108.89	20.64	
109.89	1.13	
112.90	1.47	
116.92	4.55	
118.90	6.09	
119.90	1.95	
120.91	14.06	
121.91	1.22	
124.90	1.90	
126.90	0.51	
127.87	5.53	
128.88	1.38	
130.88	92.62	
131.89	2.84	
132.90	0.82	
135.88	1.12	
136.89	6.78	
137.90	0.72	
138.88	17.75	
139.89	2.51	
140.89	7.52	
141.87	2.05	

Mass	% Base	
142.89	1.08	
143.88	1.06	
148.90	1.35	
150.89	21.68	
151.90	3.21	
152.87	3.38	
154.86	0.93	
155.88	1.53	
156.89	4.83	
157.93	0.87	
158.89	1.28	
166.88	3.83	
167.88	0.64	
168.86	0.81	F
169.86	2.19	F
170.51	1.66	F
170.93	100.00	FO
171.89	43.22	F
172.88	5.69	
173.88	1.08	
182.87	0.59	
186.86	5.58	
187.87	0.61	
210.86	1.36	
214.89	2.26	
244.86	0.82	
251.84	1.73	
281.82	0.54	
282.82	5.39	
283.83	0.69	
298.81	2.98	
325.82	1.83	
342.82	0.42	
357.83	0.61	

E+

M.Wt= 386

No. 14



Mass	% Base
51.10	1.71
53.12	0.18
55.11	6.98
56.13	1.47
57.13	5.33
58.14	1.02
59.13	3.88
60.13	0.17
63.12	0.20
64.12	0.22
65.13	1.72
67.13	0.21
69.11	2.17
70.13	0.26
71.16	1.08
72.16	0.23
73.18	11.39
74.18	0.59
75.14	2.73
76.15	0.41
77.14	2.32
79.15	0.14
81.13	0.26
82.13	0.21
83.16	0.25
85.17	0.23
86.18	0.12
87.16	4.64
88.16	0.53
89.16	5.25
90.16	1.72
91.16	1.73
93.15	0.18
95.15	2.07
96.17	0.14
97.15	0.90
99.22	0.49
100.14	0.87
101.16	1.99
102.20	0.26
103.19	0.33
105.19	0.30
106.17	0.28
107.18	2.58
108.17	0.42
109.16	17.57
110.16	1.09
111.16	0.44
113.16	0.43
114.17	0.13
115.19	0.57
117.19	1.55
118.20	0.13
119.19	1.51
119.75	0.15

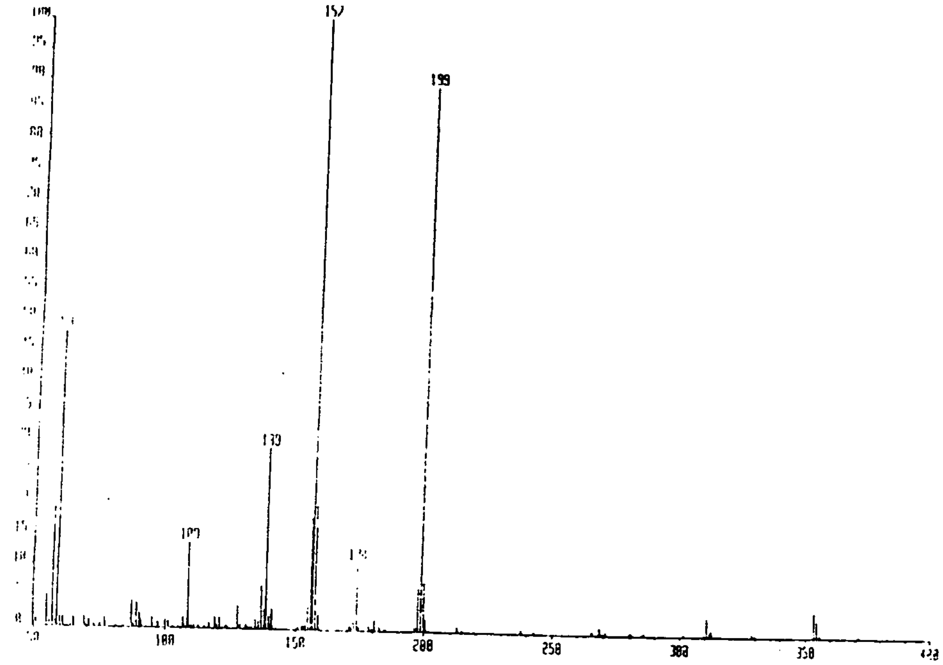
Mass	% Base
120.18	0.84
121.19	1.69
122.20	0.16
123.20	0.28
124.19	0.17
125.20	0.38
127.21	0.33
128.17	3.25
129.18	2.70
130.23	0.35
131.21	0.16
133.23	0.71
135.21	0.91
136.20	1.42
137.21	10.78
138.22	2.32
139.21	8.43
140.22	1.12
141.20	2.10
143.22	0.19
145.22	2.34
146.22	0.12
147.21	0.33
149.21	0.19
151.24	0.27
153.22	1.57
154.23	0.37
155.24	1.15
156.21	4.44 F
157.23	100.00 F
158.24	20.02
159.23	2.51
160.24	0.12
161.26	0.12
163.27	0.52
165.27	6.38
166.28	1.46
167.26	0.44
169.25	0.12
171.27	0.17
172.24	0.18
173.25	2.83
174.26	0.77
175.26	0.61
176.27	0.17
177.26	2.27
178.27	0.12
179.27	0.35
181.28	1.23
182.29	0.12
183.29	0.46
184.28	1.70 F
185.30	43.36 F
186.31	10.17

Mass	% Base
187.31	1.39
189.28	0.40
191.26	0.15
193.30	0.39
199.31	0.35
201.33	6.02
202.33	1.08
203.33	0.42
204.32	0.26
205.34	0.15
213.29	0.67
218.30	0.13
221.32	0.25
222.31	0.14
223.32	0.18
225.34	0.27
229.38	0.36
238.31	0.25
241.32	0.37
243.34	0.18
245.34	0.25
246.32	0.27
249.36	0.25
250.33	0.18
251.33	0.13
261.31	2.36
262.33	0.20
266.37	1.42
267.38	0.20
269.35	0.50
270.36	0.21
271.33	0.22
273.37	0.98
274.39	0.11
285.37	0.49
286.38	0.12
289.39	1.02
290.40	0.19
294.41	0.10
296.41	0.12
297.41	1.65
298.43	0.13
299.41	0.17
311.42	0.12
312.44	0.14
313.43	0.21
327.46	1.06
328.49	0.14
329.47	0.18
340.48	0.89
341.49	0.14
343.47	0.13
357.53	0.37
386.59	0.25

E^+

M.Wt= 414

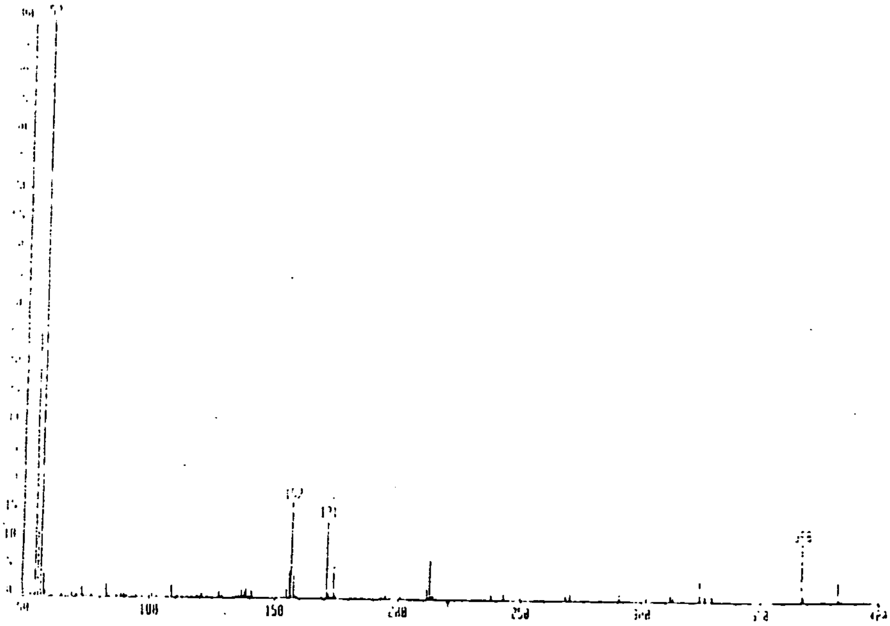
No. 15



Mass	% Base
50.89	1.18
54.91	4.06
55.90	1.07
56.91	19.20
57.91	0.90
58.92	48.09
59.92	1.46
60.91	1.44
63.88	0.18
64.89	1.50
68.89	1.46
69.89	0.19
70.88	1.10
72.80	0.27
74.86	0.55
76.86	1.48
80.83	0.16
83.89	0.14
86.89	4.12
87.85	0.21
87.90	0.22
88.94	3.78
89.85	2.19
90.85	1.27
94.82	1.65
96.87	0.88
99.81	1.13
100.83	1.03
102.85	0.12
104.85	0.14
106.82	1.67
107.82	0.15
108.79	13.72
109.80	0.46
110.83	0.41
112.70	0.25
114.81	0.36
116.79	0.07
118.80	1.75
119.80	0.55
120.80	1.64
121.81	0.16
122.80	0.25
123.39	0.11
123.49	0.16
123.57	0.13
123.76	0.25
127.75	3.57
128.78	0.64
130.82	0.60
131.79	0.15
132.78	0.11
134.78	1.31
135.77	1.16
136.77	6.89
137.78	3.02
[illegible]	

Mass	% Base
152.75	0.60
153.75	0.80
154.76	3.80
155.74	18.01
156.75	100.00
157.76	19.29
158.77	2.37
170.76	0.57
171.75	0.25
172.73	1.35
173.73	10.96
174.74	0.56
178.76	0.80
179.76	0.75
180.74	1.70
182.72	0.59
184.72	0.35
196.72	0.58
197.73	6.87
198.73	89.37
199.74	7.83
200.72	1.83
201.69	0.20
212.70	0.67
214.71	0.19
237.64	0.41
242.67	0.23
265.61	0.47
268.60	1.19
269.60	0.10
270.58	0.41
279.63	0.37
280.61	0.22
284.58	0.19
285.59	0.22
301.55	0.26
309.56	0.18
310.57	2.76
311.56	0.61
312.55	0.82
320.53	0.40
329.53	0.20
353.55	4.07
354.56	2.62
355.56	0.27
371.56	0.13

E⁺ M.Wt= 442 NO.16

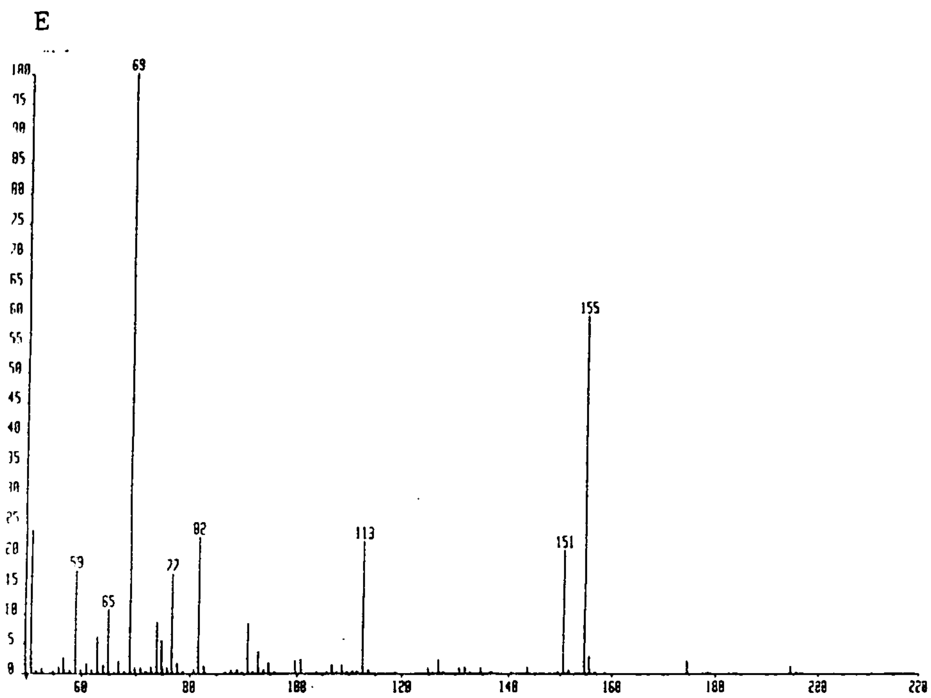


Mass	% Base
50.91	0.31
52.93	0.42
54.95	46.32
55.95	11.85
56.96	100.00
57.96	4.12
58.92	0.95
64.91	0.25
68.93	0.96
70.92	0.39
72.94	1.87
74.90	0.16
76.89	0.30
82.94	2.31
83.94	0.16
86.89	0.33
88.87	0.73
89.87	0.56
90.87	0.36
94.85	0.30
99.83	0.26
100.90	0.66
106.85	0.20
108.92	2.16
110.88	0.13
116.84	0.15
118.83	0.31
119.83	0.15
120.83	0.72
127.79	0.91
128.80	0.33
134.81	0.37
135.81	0.27
136.81	1.38
137.81	0.89
138.81	1.67
139.81	0.25
140.80	1.19
152.80	0.14
153.79	0.22
154.79	1.47
155.78	4.77
156.79	16.77
157.79	3.93
158.79	0.33
168.81	0.15
170.79	13.82
171.80	0.79
172.78	0.36
173.77	5.63
174.79	0.37
182.77	0.15
184.76	0.18
192.79	0.23
194.79	0.65

Mass	% Base
242.70	0.12
270.64	[illegible]
290.65	0.12
311.59	0.11
324.64	0.[illegible]
326.62	0.13
367.60	1.03
368.62	0.11
382.63	0.36

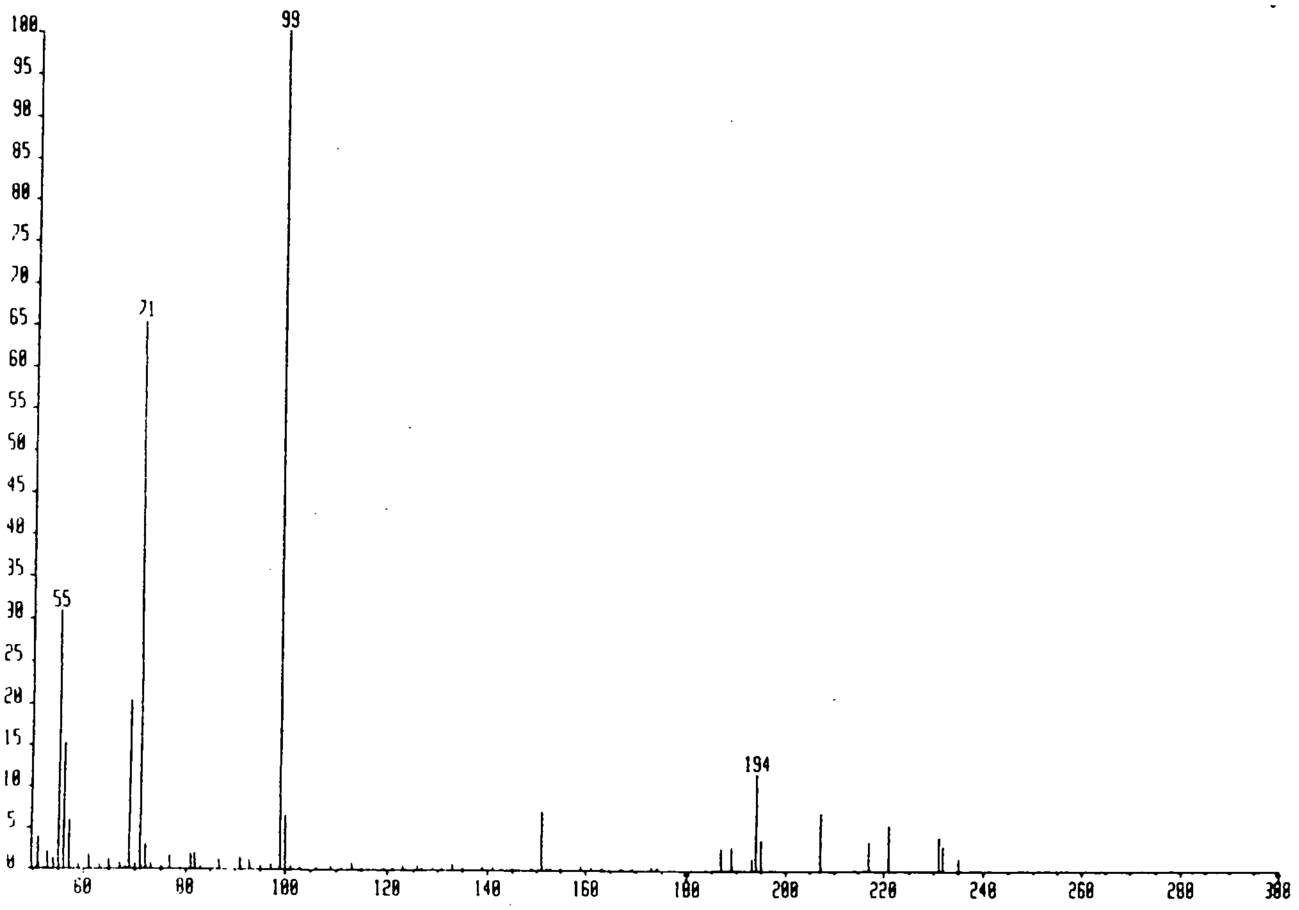
M.Wt= 194

No.17



Mass	% Base
50.83	23.66
51.84	0.32
52.83	0.72
54.82	0.23
55.83	1.04
56.83	2.55
57.84	0.42
58.86	17.18
59.84	0.57
60.82	1.69
61.81	0.53
62.81	6.03
63.82	1.43
64.82	10.73
65.82	0.16
66.80	1.99
67.80	0.30
68.79	100.00
69.79	0.97
70.78	0.94
71.79	0.28
72.83	1.07
73.85	8.67
74.78	5.38 F
74.86	0.94 F
75.79	0.94
76.79	16.62
77.77	1.61
78.80	0.33
80.77	0 61
81.76	22.79
82.77	1.22
87.76	0.43
88.76	0.56
89.76	0 10
90.74	8.41
91.74	0.27
92.73	3.63
93.73	0.62
94.74	1 75
95.76	0.13
99.71	2.07
100.72	2.20
103.72	0.19
105.71	0.12
106.71	1.43
107.72	0.17
108.71	1.33
109.70	0.19
110.70	0.24
111.68	0.37
112.68	22.06
113.69	0.68
118.68	0.11
124.69	0.88
125.68	0.18
126.68	2.28
130.65	0.92
131.65	0.99
132.66	0.14
134.65	0.90
140.64	0.14
143.65	1.05
149.59	0 26
150.61	20 69
151.61	0 63
154.63	59 80
155.62	2 92
156.62	0.17
158.60	0.10
174.58	2.09
178.56	0 11
194.54	1.24

M.Wt=250 NO.18



```
BpM=0      [illegible]     [illegible]     TIC=52594[illegible]          Acnt            Sys OMAR
FA3 0 1MSEC                                                                   GC= 80   Cal PFK26
          Mass        % Base
           50 98        3 79
           52 00        0 22
           53 01        2 18
           54 02        1 17
           55 02       30 77
           56 03       15 11
           57 04        5 88
           59 00        0 57
           61 02        1 62
           62 99        0 50
           65 00        1 14
           67 02        0 82
           68 97       20 36
           70 02        0 63
           71 06       65 44
           72 06        3 02
           73 01        0 65
           75 01        0 36
           76 99        1 53
           79 02        0 25
           81 04        1 83
           81 98        1 84
           83 01        0 31
           87 03        1 02
           90 98        1 24
           92 98        1 11
           94 98        0 38
           97 03        0 47
           99 05      100 00
          100 05        6 33
          101 01        0 23
          103 01        0 22
          109 00        0 36
          112 97        0 89
          123 01        0 30
          125 98        0 26
          126 99        0 34
          130 99        0 28
          132 98        0 81
          138 98        0 23
          140 99        0 30
          143 03        0 21
          150 96        7 32
          158 99        0 23
          160 97        0 22
          163 02        0 30
          166 99        0 24
          173 02        0 24
          173 99        0 25
          187 01        0 25
          189 01        0 28
          193 99        1 16
          195 01        0 36
          207 02        0 70
          217 01        0 34
          221 03        0 55
          231 04        0 40
          232 05        0 28
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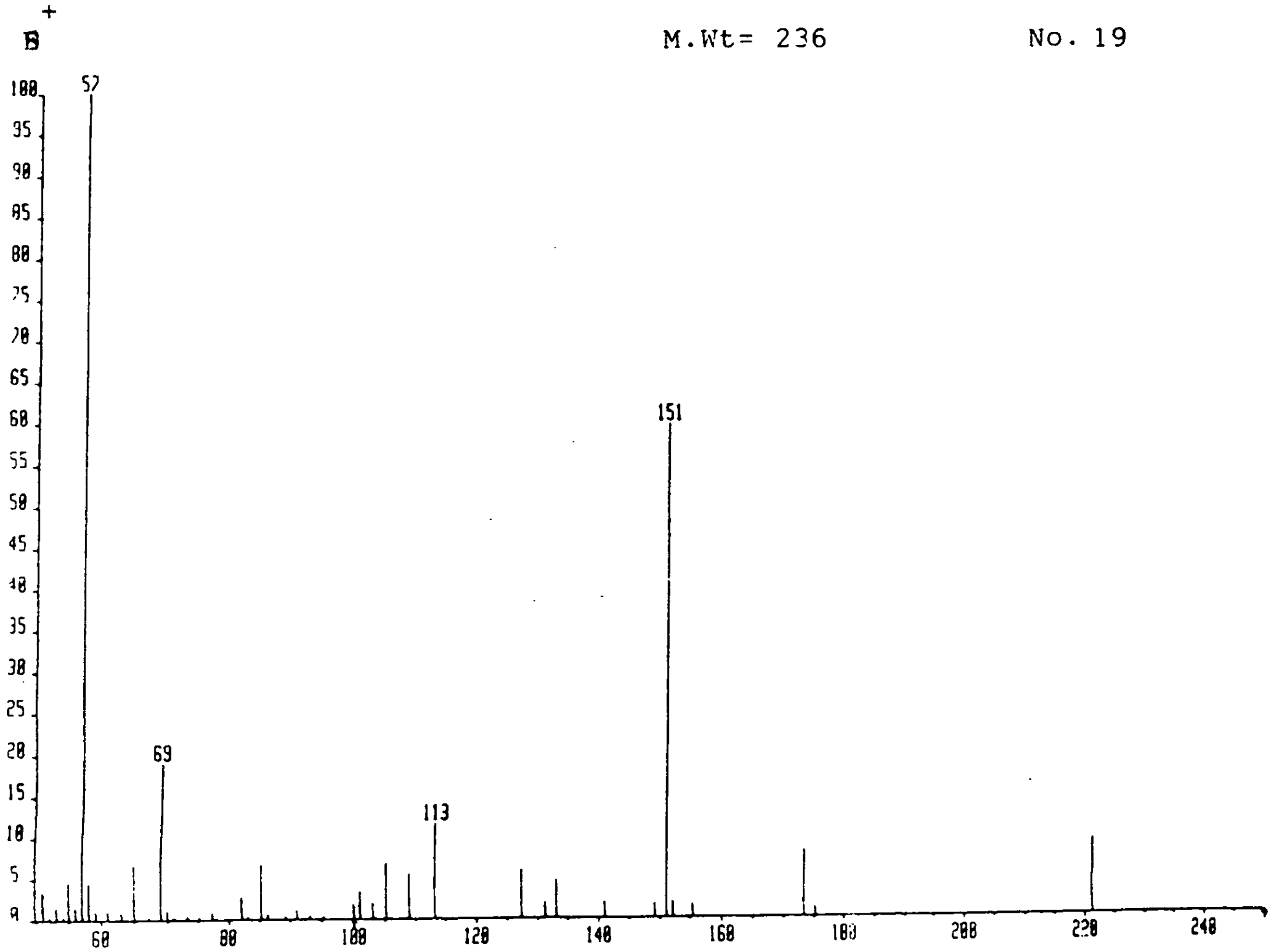
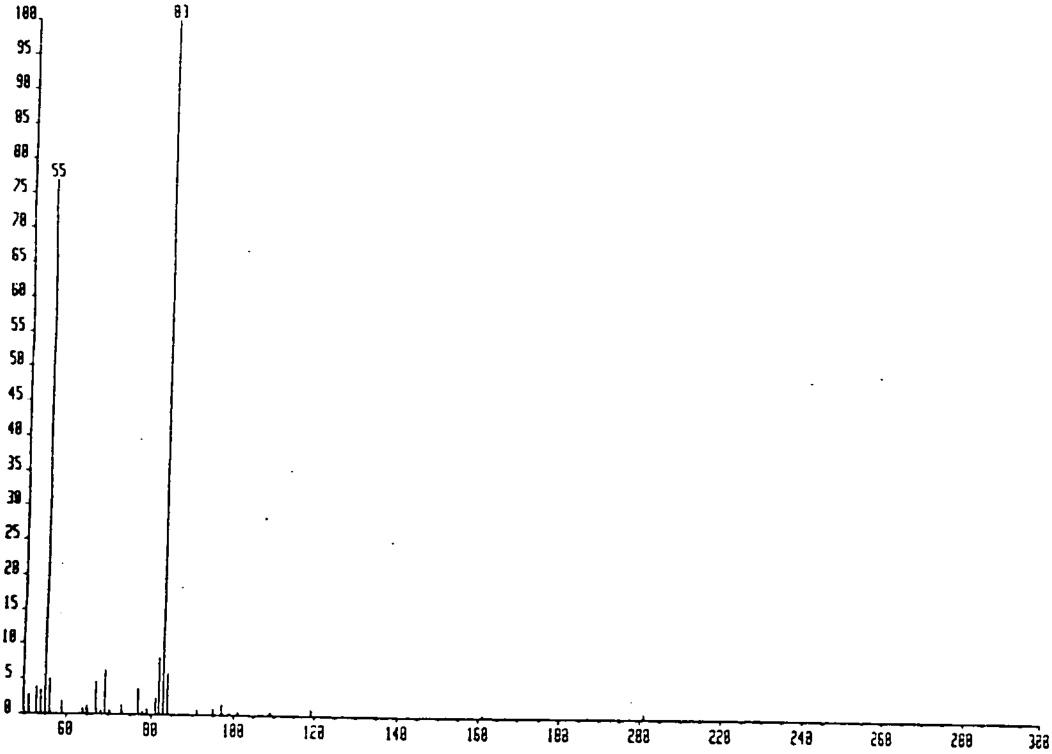
M.Wt= 236

No. 19



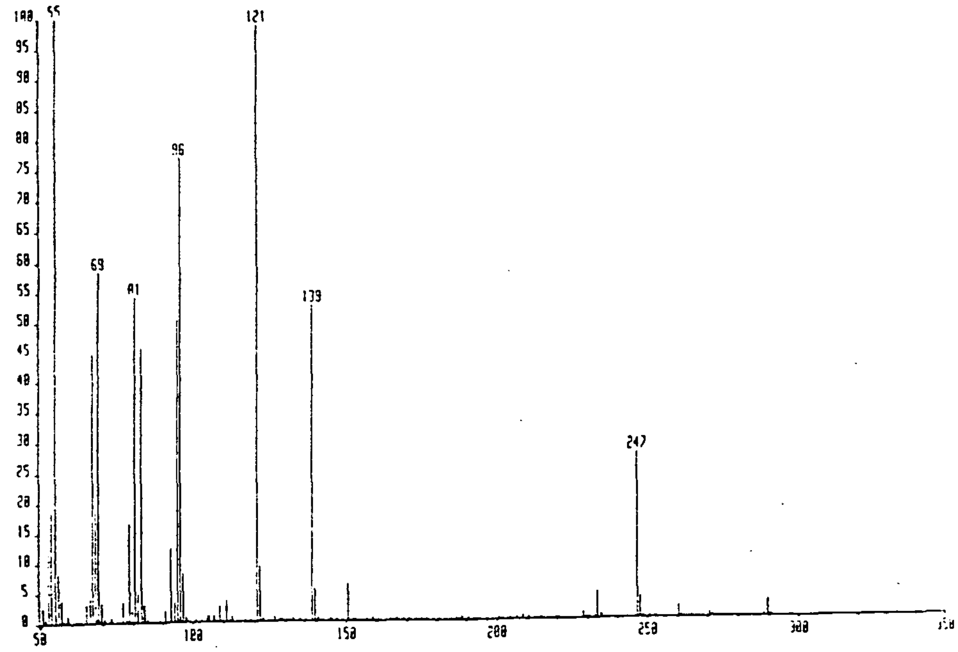
Mass	% Base
51.07	3.22
53.10	1.30
55.13	4.39
56.13	1.41
57.14	100.00
58.15	4.22
65.11	6.51
69.09	18.95
82.11	2.56
85.18	6.50
91.14	1.12
100.13	0.17
101.15	0.32
103.17	0.19
105.19	0.67
109.16	0.53
113.15	1.16
115.19	0.07
119.19	0 07
127.19	0.58
129.22	0.09
131.17	0.18
133.20	0.46
135.22	0.08
137.20	0.07
139.21	0.09
141.19	0.19
149.26	0.16
151.20	5.99
152.20	0.19
153.25	0.09
155.24	0.15
167.28	0.09
173.27	0.81
175.26	0.10
221.34	0.91

M.Wt=262 No.20



Mass	% Base
50.97	4.64
53.01	1.75
54.02	2.58
55.02	58.44
56.03	4.08
59.00	1.12
64.99	1.01
67.01	2.74
68.02	0.67
69.02	5.96
70.04	0.58
76.98	1.10
79.01	0.83
81.02	2.29
82.03	8.64
83.04	100.00
84.04	6.26
97.04	0.49
108.98	0.31
126.94	0.45
200.96	0.79
218.91	0.61

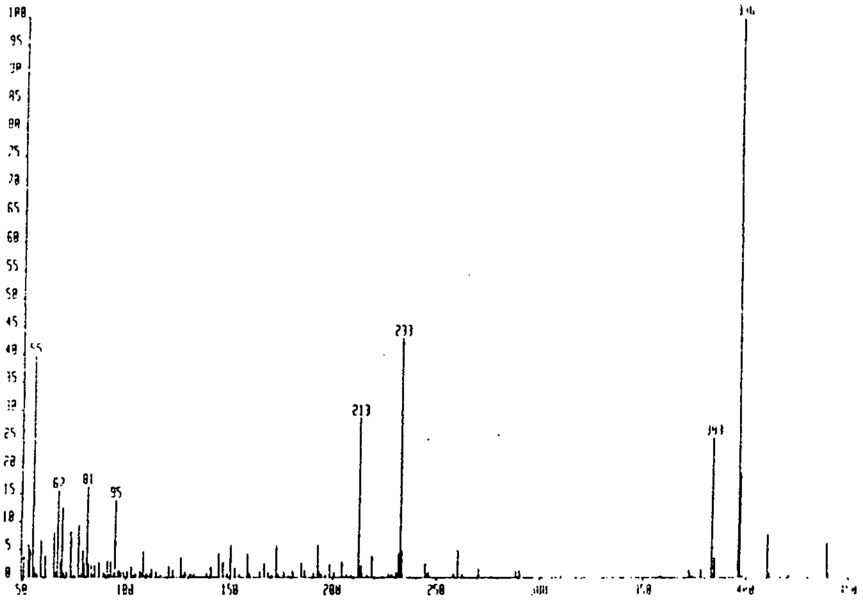
E^+ M.Wt= 290 No.21



Mass	%Base
50 97	2 41
51 45	0 11
51 09	0 92
52 09	11 76
53 10	19 70
54 92	100 00 0
55 91	8 21
56 90	3 12
57 91	0 15
58 99	1 09
60 30	0 14
61 00	0 14
62 85	0 14
63 96	0 11
64 87	2 97
65 99	3 87
66 88	44 59
67 87	18 41 f
68 75	3 91 f
68 92	14 27 f
69 92	58 20 f
69 29	0 15
69 89	3 14
70 88	0 69
72 85	0 50
74 84	0 17
76 89	7 11
77 83	5 67
78 76	16 41
79 86	7 10
80 87	54 11
81 86	4 79
82 80	49 69
83 70	7 91
84 85	0 43
88 91	0 13
90 82	1 84
91 84	0 30
92 95	12 74
93 39	3 11 f
94 97	50 29 f
95 87	76 81 f
96 86	7 96
97 89	0 80
98 84	0 21
100 79	0 37
102 81	0 34
104 80	0 74 f
105 16	1 13 f
106 81	0 86
107 84	0 17
108 84	2 61
109 83	0 17
110 86	3 46
111 86	0 33
112 75	0 81
114 78	0 27
116 77	0 21
118 82	0 79
120 84	98 46 f

Mass	%Base
121 83	8 21 f
122 03	0 52
126 75	0 82
127 77	0 19
128 77	9 74
130 73	0 18
131 72	0 19
132 73	0 43
134 76	0 12
136 77	0 15
138 82	57 12
139 81	5 24
143 76	3 46
144 73	0 24
146 74	0 17
150 67	6 27
151 69	0 16
156 71	0 10
158 59	0 11
160 70	0 22
164 71	0 13
166 72	0 27
168 73	0 10
170 70	0 11
172 70	0 15
174 68	0 21
178 68	0 11
184 67	0 17
186 65	0 13
187 64	0 13
188 67	0 [illegible]
192 67	0 27
193 62	0 11
194 64	0 11
196 66	0 11
198 64	0 14
200 63	0 11
206 61	0 10
208 61	0 14
210 64	0 13
212 62	0 11
214 61	0 25
220 69	0 14
228 61	0 81
229 63	0 14
232 63	0 15
233 63	0 25
233 99	4 33
234 99	0 53
246 58	27 59
247 59	3 55
248 61	0 26
250 65	0 14
252 62	0 11
260 58	1 06
261 57	0 21
270 69	0 55
271 69	0 12
289 54	0 12
289 58	2 14

E^+ M.Wt= 440 No. 22

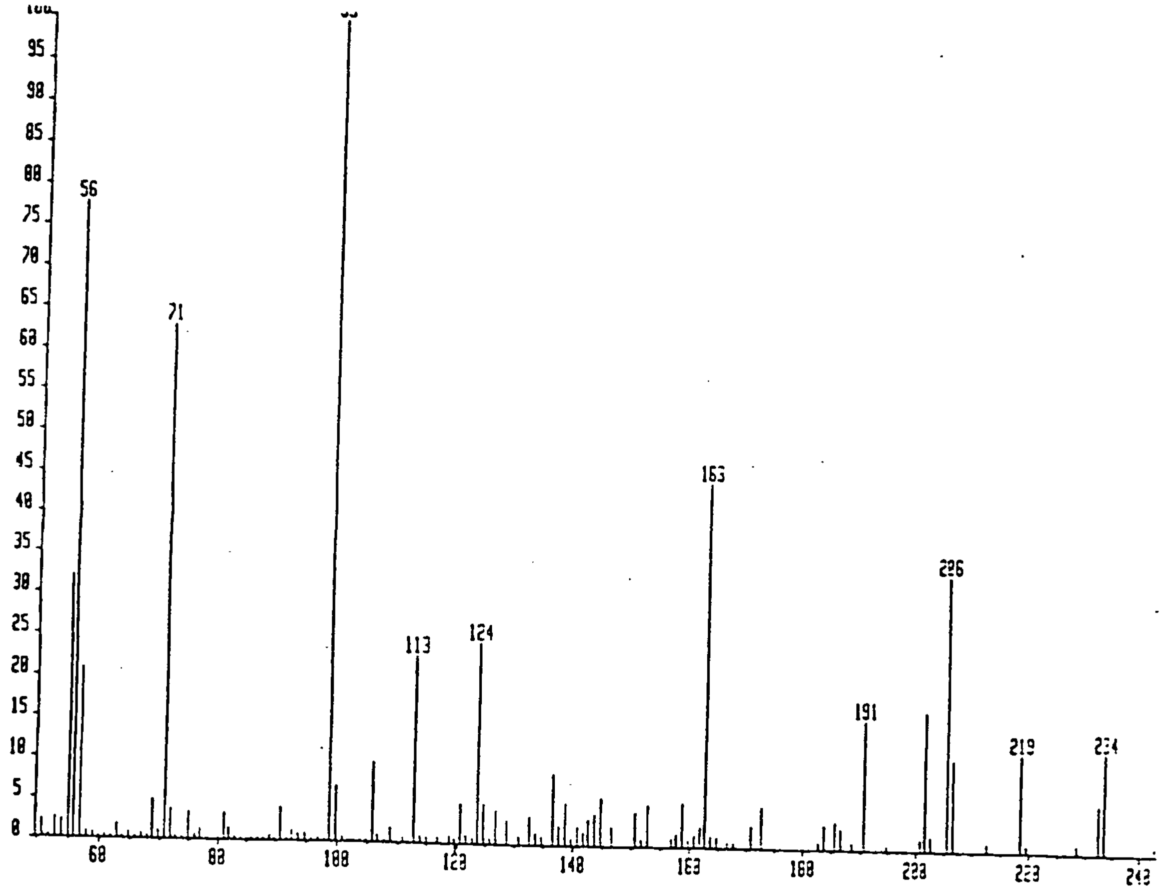


Mass	% Base
50.88	3.61
52.91	5.72
53.91	4.86
54.90	39.53
55.91	1.60
56.91	0.65
56.95	0.35
58.89	6.52
60.91	3.76
64.88	8.08
65.90	0.82
66.90	15.48
67.91	2.76
68.84	12.37 F
68.91	10.17 F
69.88	0.82
70.87	0.89
72.88	8.25
74.91	0.32
76.85	9.30
77.87	0.61
78.88	4.68
79.89	2.25
80.89	16.15
81.88	2.27
82.88	2.09
83.86	0.32
84.87	2.05
86.87	2.51
88.83	0.95
89.83	0.50
90.85	2.91
91.85	0.34
92.87	2.72
93.87	0.78
94.87	13.84
95.87	0.99
96.85	1.15
97.86	0.76
98.86	0.89
100.80	1.08
102.82	1.83
103.83	0.34
104.84	0.63
106.86	1.08
107.86	0.58
108.84	4.49
109.83	0.56
110.83	0.48
111.83	0.63
112.78	1.42
112.86	0.30
114.81	0.86
116.81	0.37
120.78	1.97
122.80	1.25
126.77	3.56
127.79	0.37
128.77	0.95

Mass	% Base
131.70	0.37
132.70	0.56
138.75	0.63
140.75	1.68
144.74	4.21
146.76	2.67
148.77	0.56
150.71	5.76
152.74	1.49
154.72	0.52
158.72	4.02
159.75	0.67
164.73	1.07
166.75	2.46
168.76	0.73
170.71	0.34
172.73	5.66
173.73	0.48
176.70	0.95
178.72	0.72
180.73	1.01
184.69	2.51
186.72	1.15
190.70	0.71
192.71	5.81
193.71	0.89
194.11	0.43
194.40	0.34
194.65	0.45
196.70	0.39
198.70	2.35
200.69	0.71
204.67	2.72
206.67	0.48
208.65	0.34
212.68	28.84
213.68	2.16
216.67	0.37
218.66	3.76
226.65	0.56
228.64	0.48
230.64	0.91
231.67	4.21
232.64	43.14
233.66	4.69
244.63	2.40
245.65	0.61
246.63	0.91
258.62	0.54
260.68	4.79
262.62	0.52
270.60	1.45
288.64	1.08
290.60	1.15
310.53	0.48
358.45	0.30
372.49	1.34
373.57	0.25
[illegible]	[illegible]

Mass	% Base
384.45	3.69
396.41	100.00
397.42	18.91
398.43	0.91
410.41	7.02
411.43	0.80
420.53	0.45
439.43	6.27
440.45	0.71

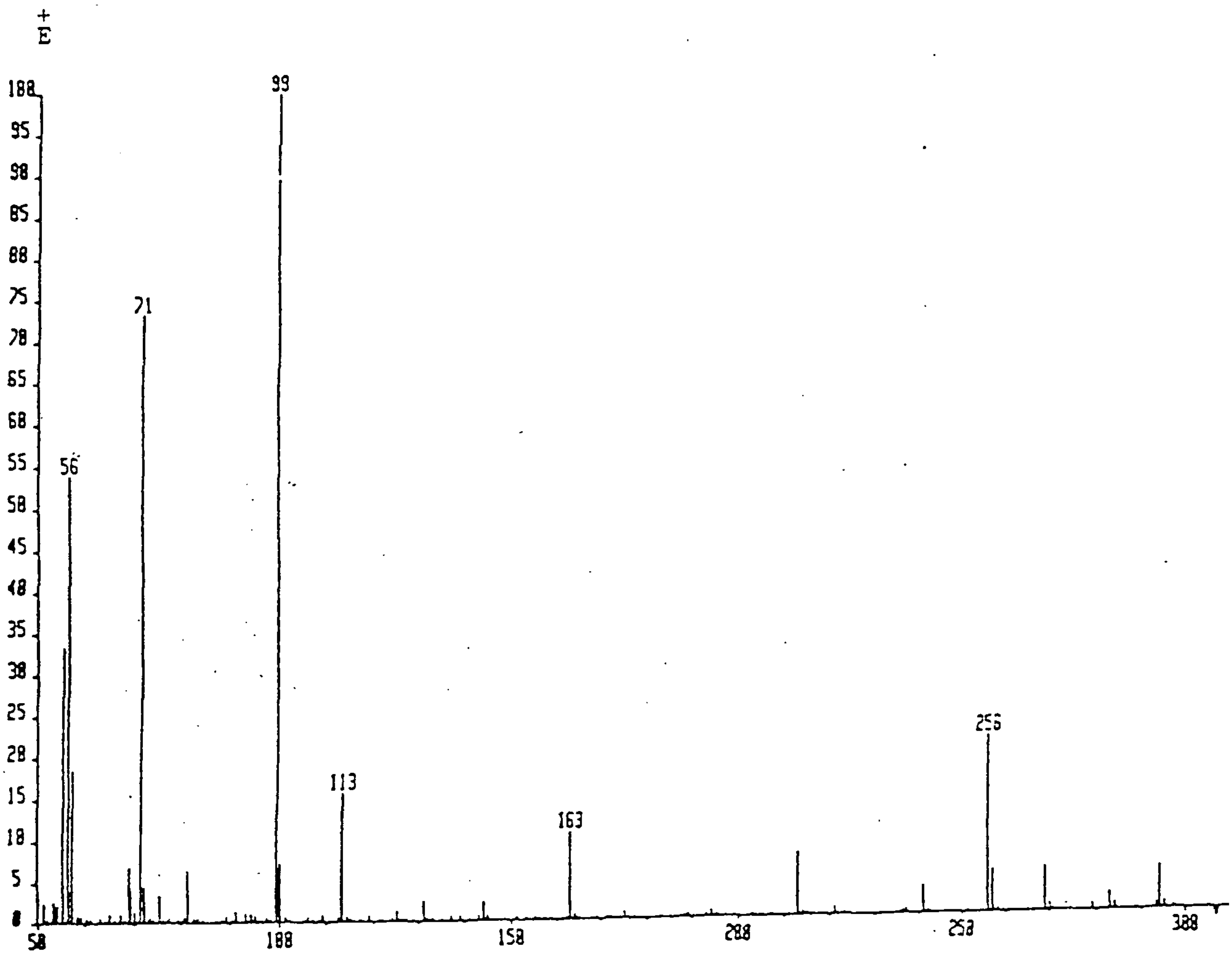
M.Wt=262 No.23



Mass	% Base
50 90	2.10
51.92	0.26
52 93	2 43
53 93	2 11
54 94	31 89
55 95	77 50
56 95	20 77
57 94	0 69
58 92	0 55
60 92	0 32
62 88	1 66
64 90	0 69
66 92	0 65
67 92	0 26
68 86	4 71 f
68 93	3 47 f
69 92	0 84
70 95	62 88
71 94	3 58
72 90	0 35
74 86	3 40
75 87	0 48
76 88	1.14
80 90	3 15
81.86	1.38
82.88	0 37
88 86	0 32
90 83	3 89
92 82	1 16
93 83	0 81
94 84	0 91
96 88	0 29
98 90	100 00
99 89	6 79
100 86	0 47
105 83	0 69
106 83	0 70
108 81	1 65
110 86	0 45
112 85	22 77
113 81	0 74
114 84	0 54
116 81	0 36
118 82	0 69
119 83	0 44
120 82	0 48
123 85	2 43
124 79	0 49
126 81	0 45
128 84	0 29
132 80	0 33
136 78	0 87
137.79	0 23
138 78	0 32
140 81	0 22
142 76	0 32
143 78	0 39

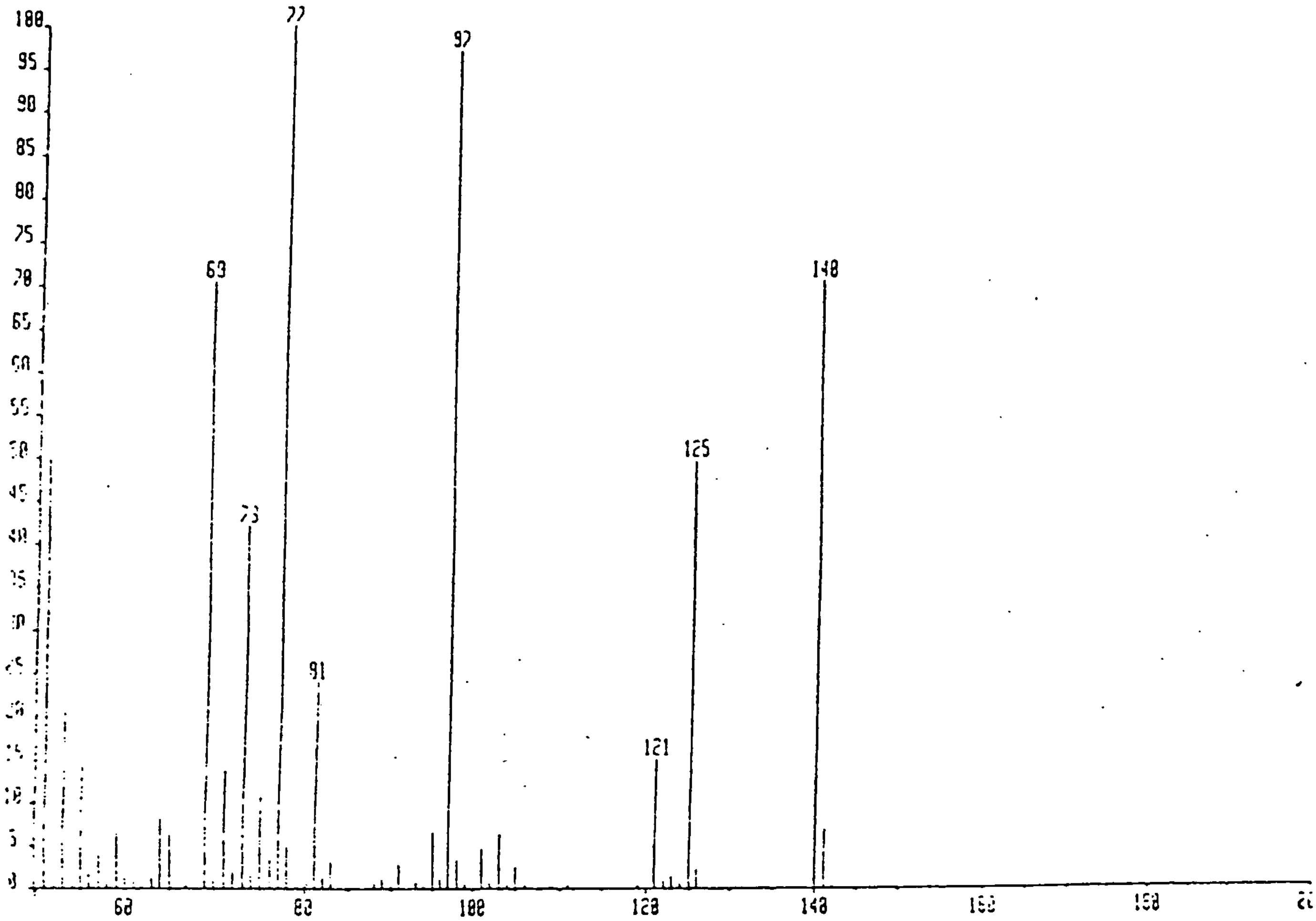
Mass	% Base
152 75	0 50
158 76	0 54
161 79	0 24
162 72	4 44
170 74	0 25
172 72	0 51
183 73	0 29
185 71	0 33
186 72	0 24
190 68	1 57
201 70	1 62
205 68	3 33
206 69	1 11
218 68	1 19
232 68	0 59
233 68	1 22
243 69	2 79
244 70	0 33

M.Wt= 312 No.24



Mass	%Base	Mass	%Base	Mass	%Base	Mass	%Base
51.05	2.26	88.09	0.14	144.11	2.12	257.22	5.06
52.07	0.27	89.09	0.54	145.13	0.40	258.24	0.36
53.08	2.50	90.08	0.12	151.14	0.17	269.22	5.17
54.09	1.95	91.07	1.21	155.14	0.26	270.24	0.83
55.10	33.18	93.07	0.93	156.14	0.12	279.26	0.59
56.11	53.75	94.08	0.88	157.14	0.15	283.25	2.03
57.11	18.34	95.09	0.63	162.13	0.10	284.25	0.76
58.12	0.77	96.12	0.13	163.13	10.53	293.30	0.59
59.08	0.55	97.14	0.44	164.14	0.51	294.31	5.05
60.07	0.39	98.15	0.16	169.15	0.14	295.32	0.76
61.09	0.30	99.15	100.00	171.16	0.17	297.31	0.30
63 06	0.46	100.15	6.93	175.14	0.68	311.32	0.24
64.07	0.13	101.13	0.48	177.17	0.11	312 36	0.12
65.08	0.91	106.09	0.49	183.18	0.18	313.36	0.29
66.10	0.22	107.10	0.21	188.18	0.13		
67.11	0.94	108.10	0.17	189.18	0.32		
68.09	0.30	109.08	0.65	193.17	0.38		
69.05	6.71 F	112.08	0.23	194.17	0.61		
69.12	4.00 F	113.08	15.40	195.21	0.13		
70.10	1.28	114.09	0.49	203.20	0.19		
71.14	73.17	117.11	0.13	207.21	0.11		
72.15	4.18	119.10	0.49	213.17	7.40		
73.10	0.38	124.10	0.26	214.18	0.37		
75.07	3.23	125.10	1.04	215.22	0.12		
76.08	0.16	126.11	0.20	221.16	0.72		
77.09	0.43	127.13	0.21	223.19	0.16		
79.12	0.18	131.09	2.35	236.20	0.28		
80.13	0.40	132.11	0.11	237.21	0.40		
81.13	6.26	133.14	0.15	241.18	3.14		
82.10	0.48	137.12	0.46	242.21	0.20		
83.11	0.40	139.13	0.47	251.23	0.20		
84.12	0.18	143 11	0 41	256 21	21 22		
[illegible]	[illegible]						

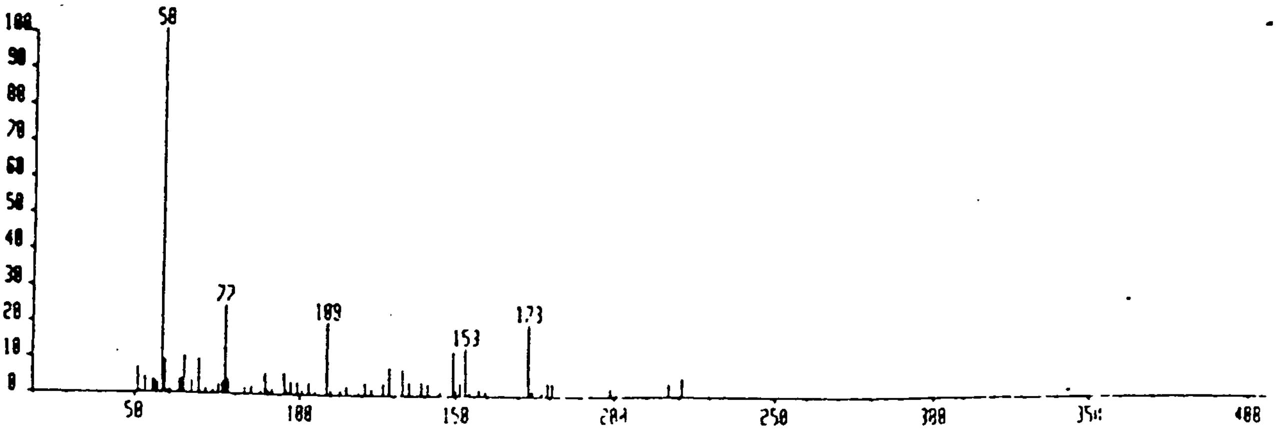
E^+ M.Wt= 140 No. 25



Mass	%Base
51.01	50.21
52.02	1.70
53.03	20.53
54.04	1.03
[illegible]	[illegible]
[illegible]	1.44
57.02	4.75
58.03	0.52
59.03	0.35
[illegible]	1.20
[illegible]	0.65
[illegible]	0.12
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	1.21
[illegible]	[illegible]
[illegible]	1.77
[illegible]	[illegible]
[illegible]	1.39
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

Mass	%Base
95.02	0.54
96.02	1.09
[illegible]	0.15
97.03	[illegible]
98.04	3.33
99.03	0.51
101.04	4.57
102.04	0.64
103.04	0.37
104.05	[illegible]
105.02	[illegible]
106.04	0.29
109.04	1.15
111.02	[illegible]
119.05	[illegible]
121.05	[illegible]
122.06	[illegible]
123.03	[illegible]
124.04	0.43
125.04	49.57
126.04	2.17
140.06	70.47 <
141.06	[illegible]
142.08	0.12
183.11	0.35

E+ M.Wt=236 No. **26**

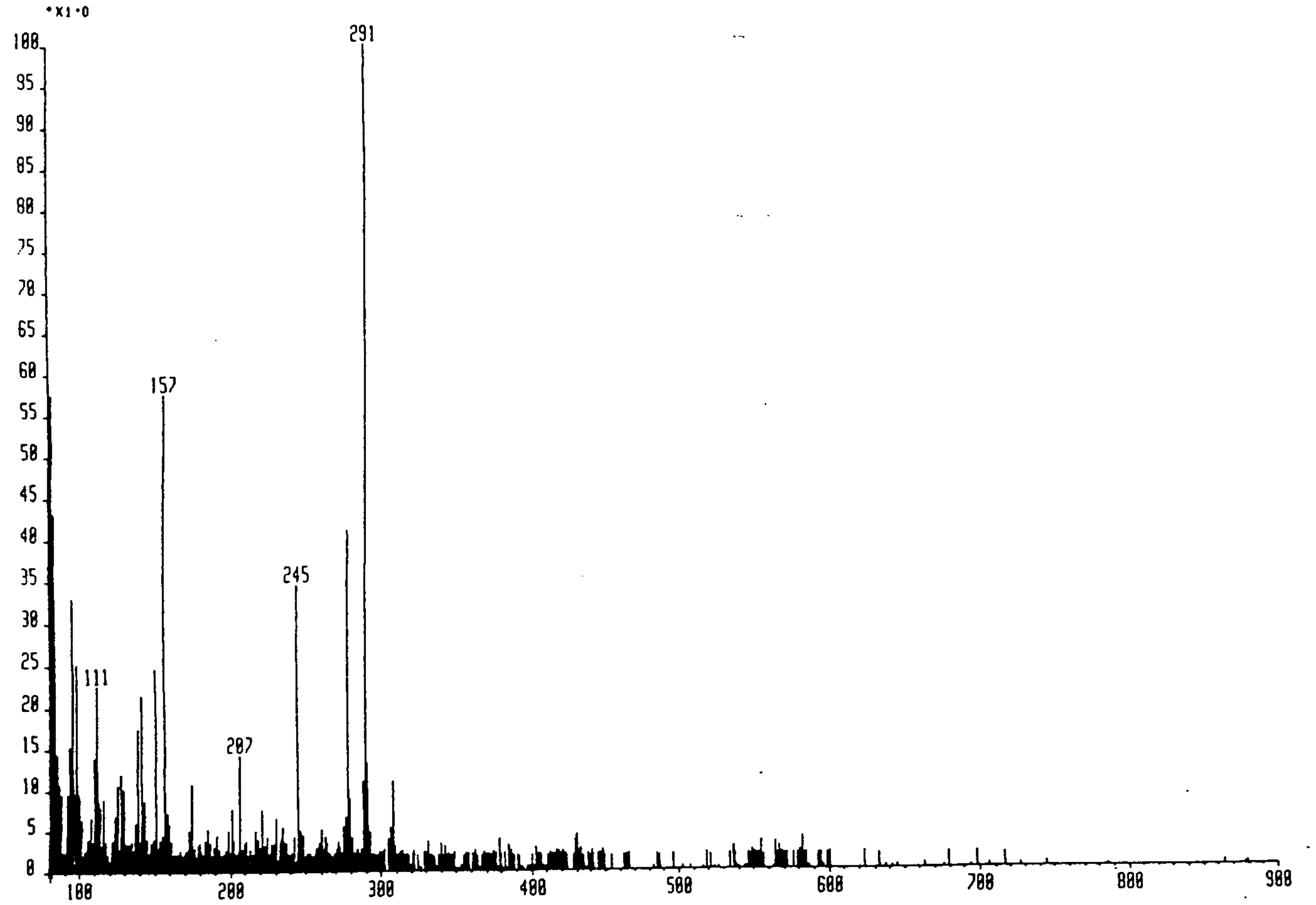


Mass	% Base
50 93	7 42
52 00	0 55
53 01	1 59
54 01	0 29
55 01	3 34
56 00	0 21
57 00	4 38
57 83	3 00 F
58 01	100 00 F
58 99	6 79 F
59 02	10 40 F
60 01	1 65
61 00	3 01
61 99	0 10
62 99	0 61
63 98	4 51
64 99	11 76
66 00	0 30
67 01	0 33
68 96	10 94
69 97	2 98
71 01	2 96
72 01	1 23
73 01	1 63
74 98	1 96
75 98	0 63
76 99	24 23
77 99	1 36
79 01	0 37
80 93	0 15
82 99	1 40
84 00	0 23
85 01	1 71
87 02	[illegible]
88 00	[illegible]
88 99	5 31
89 99	0 76
90 99	[illegible]
94 97	2 63
95 98	3 34
96 99	1 27
98 98	2 98
100 99	[illegible]
101 99	3 01
102 99	2 49
104 [illegible]	[illegible]
105 [illegible]	[illegible]
106 99	[illegible]
107 [illegible]	[illegible]
108 98	[illegible]
109 98	[illegible]
110 [illegible]	[illegible]
112 [illegible]	[illegible]
114 97	[illegible]
118 96	[illegible]
121 [illegible]	[illegible]
122 98	[illegible]
123 [illegible]	[illegible]
126 98	[illegible]
127 99	[illegible]

Mass	% Base
129 00	7 33
130 00	0 38
131 01	0 11
132 99	7 01
134 00	0 60
135 09	1 07
135 65	0 11
136 97	0 39
138 99	1 35
140 99	0 28
144 97	0 64
147 00	0 36
149 01	12 24
150 02	0 94
151 01	2 98
152 99	19 40
153 99	0 89
157 00	1 25
158 00	0 14
159 00	3 11
160 99	0 12
167 02	0 29
169 02	0 64
171 00	0 10
172 99	13 40
174 00	1 11
177 01	0 69
179 01	0 69
181 02	2 97
195 03	0 13
197 03	3 00
199 03	1 74
200 04	0 25
201 00	0 63
215 02	2 98
217 02	1 34
218 02	0 12
220 99	4 13
222 00	0 26
236 02	0 18
237 02	0 20

M.Wt=440

NO.27



Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base
79 87	9 73	122 29	0 41	171 66	0 21	207 04	1 79	241 65	0 63	292 61	4 69	344 59	1 98	402 91	0 29
80 88	57 37	122 84	6 62	171 76	0 76	207 14	1 80	242 63	4 16	293 47	0 29	345 73	1 93	403 59	0 84
81 86	8 93	123 83	3 36	171 90	1 75	207 66	2 60	243 66	1 01	293 60	1 86	346 53	0 23	403 75	1 78
82 80	42 97	124 83	10 42	171 92	1 75	207 79	0 26	244 64	34 35	293 68	0 20	346 63	1 81	404 59	1 90
82 97	0 21	125 83	2 61	172 74	4 82	208 15	0 29	245 65	4 37	294 61	2 00	347 48	0 25	405 55	1 92
83 87	14 28	126 82	11 82	173 75	1 07	208 69	2 40	246 62	4 84	295 59	1 90	347 60	0 58	406 56	1 68
84 86	10 64	127 82	3 42	174 76	10 55	209 71	3 31	247 65	2 46	296 66	1 37	348 57	2 13	407 68	0 49
85 85	3 41	128 83	10 03	175 77	2 80	210 68	3 70	248 43	0 24	297 58	1 81	350 53	0 21	408 50	0 24
86 35	1 74	129 83	3 39	176 71	1 71	211 63	0 46	248 64	4 27	297 62	1 74	352 64	0 61	410 50	1 79
86 86	9 43	130 80	3 16	177 75	0 55	211 73	1 75	249 65	1 71	298 68	2 21	354 60	1 70	412 59	2 05
87 86	1 55	131 78	1 82	178 40	0 32	212 71	2 54	250 66	1 95	299 64	1 78	355 63	1 80	412 77	1 71
88 84	2 24	132 80	3 14	178 71	3 06	213 69	0 54	251 64	1 79	300 61	2 28	356 59	2 20	413 64	1 95
89 84	2 16	133 83	3 49	179 73	0 32	213 78	1 87	252 67	2 16	301 58	2 13	357 63	1 91	414 53	1 84
90 84	9 37	134 81	2 13	179 82	3 39	213 84	0 26	253 69	1 82	302 63	2 63	358 40	0 21	415 43	1 86
91 86	2 91	135 83	2 49	180 69	2 21	214 05	0 26	254 64	1 73	302 77	3 22	358 56	1 90	415 79	0 28
92 86	15 16	136 80	5 78	180 80	0 20	214 51	1 89	255 64	1 93	304 56	3 81	360 53	1 91	416 58	2 40
93 45	1 76	137 81	5 32	181 74	1 82	214 66	2 00	255 74	0 23	305 62	1 90	360 66	1 73	418 57	2 29
93 87	6 44	138 81	17 34	181 83	0 29	214 80	1 80	256 64	2 78	306 58	5 17	360 72	1 76	419 61	1 93
94 87	32 80	138 93	0 33	182 70	3 69	215 32	1 74	257 64	1 79	307 61	2 47	361 52	1 77	420 59	2 30
95 42	1 76	139 81	3 48	183 60	1 72	215 67	1 87	258 62	3 36	308 58	10 91	362 64	2 46	421 57	1 83
95 72	0 20	140 81	21 41	183 74	1 95	216 66	4 92	259 66	2 32	309 61	2 93	363 63	1 75	422 57	1 95
95 74	1 76	141 81	3 71	184 71	5 03	217 65	1 93	260 63	5 01	310 62	1 90	363 74	1 85	423 56	1 70
95 86	9 46	142 80	8 52	185 71	1 85	217 74	1 81	261 65	2 56	311 64	1 75	364 56	1 74	427 65	1 74
96 87	25 02	143 54	0 22	186 69	3 28	218 65	3 77	262 63	4 06	312 47	1 67	365 56	0 26	428 55	1 81
97 87	9 45	143 80	1 75	187 70	1 81	219 63	2 78	263 61	3 33	312 62	2 25	365 66	0 23	429 52	3 64
98 85	8 93	144 78	3 75	186 70	2 95	219 74	0 20	264 65	1 77	313 57	0 42	366 58	1 72	430 58	4 21
99 84	3 98	145 82	2 07	188 83	[illegible]	220 40	1 70	265 69	2 05	313 61	1 74	367 70	1 73	431 57	2 25
100 84	6 28	146 79	3 28	189 67	[illegible]	220 64	[illegible] 44	266 65	1 84	314 64	2 36	367 78	1 72	432 59	2 53
101 84	1 80	147 78	0 91	189 72	[illegible]	221 65	2 67	267 63	0 66	315 58	1 85	367 94	1 74	434 61	0 54
102 84	2 49	148 78	3 77	190 71	[illegible]	222 66	2 96	267 83	1 73	316 60	2 00	367 99	1 75	434 80	0 20
103 84	1 71	149 11	0 24	190 95	[illegible]	223 49	1 86	268 65	1 98	317 63	2 01	368 60	2 30	434 99	1 70
104 85	3 74	149 79	1 93	191 66	0 14	223 68	2 56	269 61	2 15	318 58	1 62	370 60	1 93	438 48	1 98
105 84	2 73	150 72	24 50	191 72	[illegible]	224 65	4 08	270 62	2 55	320 52	0 62	371 57	1 98	438 65	1 74
106 00	0 21	151 77	2 60	192 34	[illegible]	225 69	[illegible] 98	271 50	1 72	320 64	0 21	372 59	0 65	440 50	2 35
106 31	1 74	152 78	3 58	192 39	1 47	226 72	3 21	271 65	3 45	321 52	2 00	373 50	1 80	441 48	1 83
106 43	0 26	153 79	1 52	192 69	2 54	227 70	2 13	272 62	2 79	322 56	2 49	373 59	1 82	444 50	1 85
106 85	6 52	154 79	4 28	193 65	[illegible]	228 66	3 23	273 69	2 12	324 54	1 75	374 61	2 20	445 71	1 91
107 26	3 46	155 78	2 08	193 73	[illegible]	229 66	1 96	274 03	1 74	324 61	0 21	376 63	2 12	446 62	1 97
107 33	0 28	155 89	0 22	194 71	1 96	229 81	1 71	274 63	5 26	326 58	0 26	377 54	0 25	447 57	1 72
107 85	3 38	156 79	57 50	195 70	0 22	230 64	6 40	275 61	2 24	326 65	0 26	378 59	3 79	448 61	2 38
108 70	1 74	156 95	1 80	196 68	2 48	231 65	1 15	276 61	6 45	328 60	2 21	379 55	1 93	449 55	1 79
108 85	13 84	157 55	0 21	196 82	1 79	232 64	3 36	277 62	3 17	329 47	0 24	379 68	0 28	454 56	1 67
109 86	4 43	157 79	7 03	197 75	0 34	232 78	1 78	277 93	1 67	329 55	0 23	382 53	2 16	454 64	0 21
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111 85	8 29	159 79	1 70	199 67	2 19	233 61	3 96	278 63	8 72	330 59	2 07	385 15	1 72	464 60	0 34
112 84	7 69	160 76	3 44	200 67	[illegible] 63	234 64	5 25	279 63	1 69	331 58	3 46	385 54	1 79	464 68	1 76
113 84	2 99	161 82	1 81	201 39	1 75	234 94	0 27	280 30	4 01	332 59	1 87	386 60	2 50	466 62	1 90
114 58	0 20	162 76	1 91	201 98	3 62	235 68	3 43	280 64	1 96	333 59	0 30	387 56	1 74	482 53	0 29
114 84	8 82	163 78	2 01	202 [illegible]	[illegible]	236 54	0 36	281 66	2 09	334 55	1 98	388 55	1 76	482 62	0 24
115 84	2 63	164 76	1 78	[illegible] 94	1 74	236 68	[illegible] 13	282 58	2 53	335 53	0 20	390 55	0 43	485 43	1 76
116 83	3 44	165 81	1 95	[illegible] 31	[illegible]	236 92	[illegible] 26	284 61	1 93	335 65	1 72	390 69	1 75	486 90	1 74
117 83	0 97	166 74	2 43	[illegible]	[illegible]	237 00	[illegible]	285 61	2 59	336 54	0 26	391 56	1 72	496 46	1 75
118 83	1 96	167 74	1 85	[illegible] 51	[illegible]	237 [illegible]	0 20	286 62	2 10	338 58	1 87	393 56	0 47	502 77	0 25
118 94	1 75	167 85	0 31	[illegible]	[illegible]	237 14	[illegible] 75	287 61	10 84	339 59	0 29	394 67	0 22	507 52	0 32
119 16	0 22	167 90	1 74	205 69	[illegible]	[illegible]	[illegible]	288 58	3 43	340 48	3 40	396 60	0 48	518 54	1 38
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119 83	1 13	168 62	0 21	206 20	[illegible]	238 63	[illegible]	289 60	100 00	341 62	0 47	398 73	0 21	521 40	1 71
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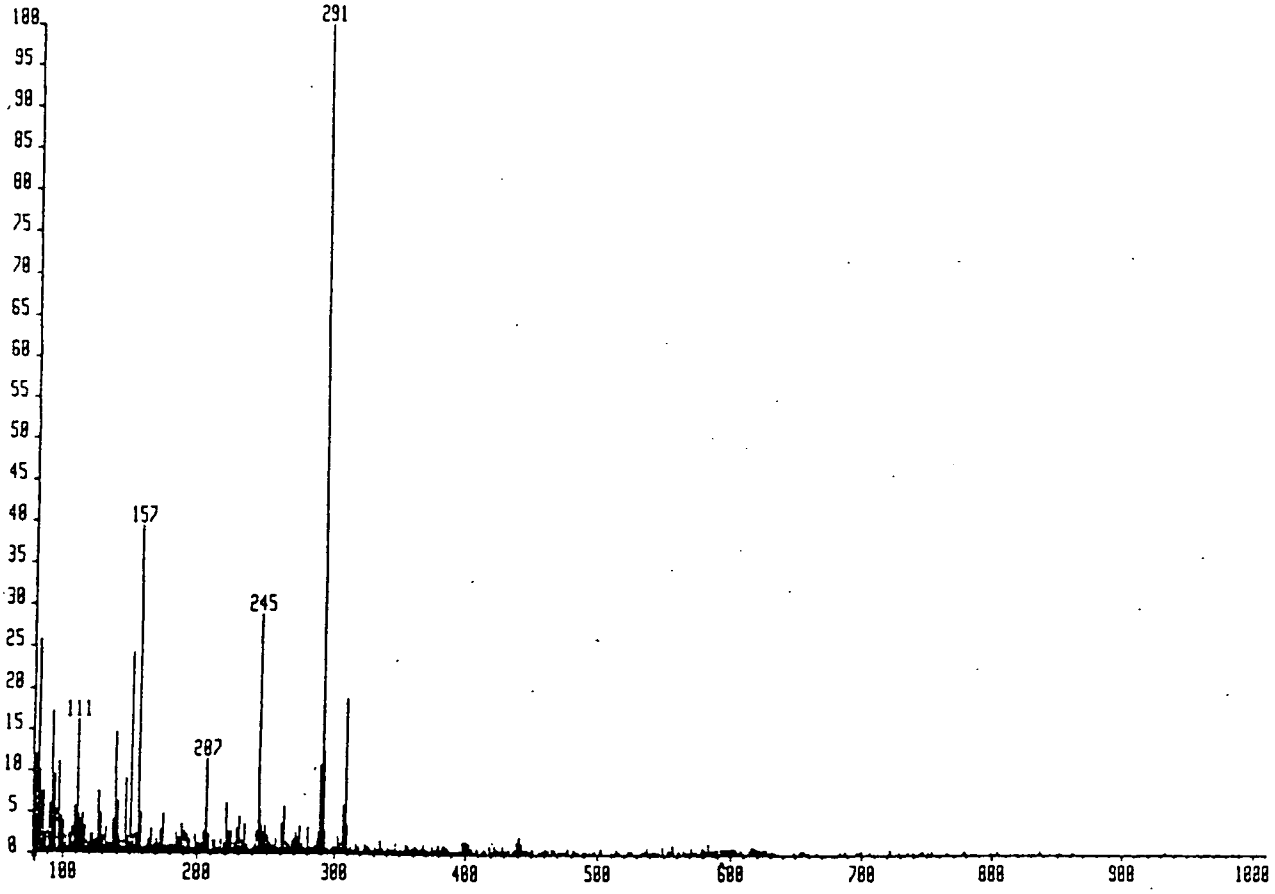

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80 62	0 24
81 01	7 95 F
81 36	11 78 F
81 99	4 40 F
82 05	3 72 F
82 20	0 42
83 06	25 66
84 04	10 31 F
84 09	2 25 F
85 04	7 30
85 91	0 48
86 04	1 31
87 04	7 40
88 03	2 10
89 02	2 40
90 02	0 51
90 99	5 93 F
91 05	4 97 F
92 04	1 91
93 05	17 13
93 68	0 57
94 05	3 23
94 41	0 31
95 05	9 46
95 63	0 25
96 05	5 18
97 06	10 89
98 06	2 60
99 05	4 36
100 06	1 58
101 04	3 76
101 71	0 22
102 03	0 60
103 03	2 01
104 03	0.37
104 41	0 27
104 70	0 21
105 05	2 30
105 20	0 25
105 42	0 56
106 03	1 72
107 06	3 08
107 15	0 35
107 28	0 31
108 07	1 12
109 06	5 63
110 06	2 94
111 07	16 07
111 20	0 30
112 07	4 61
113 01	3 92 F
113 08	3 13 F
114 05	1 89
115 06	4 77
116 06	1 72
117 04	3 19
118 04	0 21
119 02	1 42
119 10	0 24

Mass	% Base
120 03	0
121 36	2
121 95	0
122 05	1
122 67	0
123 07	2
124 37	1
125 38	1
126 36	1
126 95	0
127 04	7
127 78	0
128 06	1
129 07	4
129 33	0
129 37	0
129 45	0
130 39	1
131 03	1
131 21	0
132 04	0
133 03	3
133 31	0
134 03	1
135 05	1
136 06	0
136 69	0
137 05	3
138 07	3
139 06	14 4
139 85	0
140 07	2
140 39	0
140 78	0
141 06	6
142 08	1 9
143 07	1 4
144 05	0
144 12	0 3
145 03	1 4
146 08	0
147 06	9 0
148 06	1 7
149 03	1 5
149 32	0 2
149 62	0 2
150 02	1 0
150 99	24 2
151 73	0 3
152 03	1 1
153 06	2 1
154 06	0 6
155 05	2 3
156 07	1 6
157 07	29 3
157 40	0 2
158 08	3 9
158 26	0 2
159 04	4 9
159 60	0 3

Mass	% Base
160 04	0 56
160 24	0 40
161 02	0 47
162 06	0 79
163 03	0 51
164 06	1 22
165 05	1 72
167 01	2 82
167 45	0 24
168 08	0 57
168 63	0 30
169 02	1 06
169 39	0 38
170 04	0 69
170 09	0 23
170 76	0 21
171 04	1 65
172 00	1 07
173 02	2 69
174 00	0 91
174 07	0 21
175 07	4 75
176 07	0 67
177 02	0 84
177 19	0 54
178 32	0 53
179 01	0 89
181 03	1 02
182 05	0 48
183 02	0 94
183 99	0 68
185 04	2 39
186 02	0 47
187 01	1 76
188 02	1 72
189 01	3 46
190 04	0 60
191 01	2 53
192 05	0 36
193 01	2 25
193 98	0 73
194 21	0 39
194 32	0 29
195 03	1 64
195 99	0 38
196 93	0 24
197 04	0 63
197 40	0 33
198 03	0 46
199 02	2 07
200 02	0 51
200 67	0 38
201 08	1 24
201 80	0 21
202 02	0 27
203 03	1 25
204 02	0 75
204 32	0 27
205 01	2 52
206 02	1 39

Mass	% Base
207 01	11 4
207 32	0 3
207 99	0 9
208 20	0 2
209 01	2 2
210 00	0 3
211 02	1 5
211 15	0 3
212 02	0 3
213 04	1 45
213 23	0 2
213 87	0 2
214 02	0 3
214 67	0 2
215 00	0 7
216 07	0 2
217 00	1 74
218 01	0 25
219 05	1 19
220 05	0 95
221 00	5 99
222 00	1 01
222 47	0 24
223 02	2 57
223 97	0 22
224 03	0 26
225 02	2 52
225 15	0 24
225 90	0 21
226 03	0 34
227.05	1.22
228 08	0 21
228 27	0 23
229 00	2 96
230 01	0 66
231.00	4 39
232.04	0 66
233 03	1 47
234 02	1 05
234 67	0 26
235 00	3 43
236 02	0 82
237.03	1.05
237.60	0 38
238 02	0 37
238 22	0 22
238 79	0 24
238 94	0 33
239.07	0 27
240 05	0 26
241.04	0 63
242 02	0 87
242.18	0.22
242.99	2 50
244.01	0.62
245.03	28 73
246 02	5 21
247.01	3 38
247.39	0 33
248.01	2.38

Mass	% Base
249 02	3 40
250 07	0 92
250 74	0 21
251 01	2 07
251 28	0 23
252 02	1 12
253 00	1 28
254 02	0 21
255 01	0 96
256 03	0 28
257 02	1 65
258 04	0 44
259 04	0 62
260 05	0 64
261 03	3 55
262 04	0 99
262 43	0 52
263 03	5 58
264 01	0 50
264 99	1 29
265 19	0 22
266 07	0 38
266 96	1 06
267 99	0 32
268 12	0 28
269 04	1 44
270 02	1.57
271 05	1 89
271 76	0 20
272 04	2 42
272 32	0 31
273 04	1 74
273 35	0 26
273 48	0 21
274 00	1 84
274 45	0 66
274 97	3 16
275 54	0 39
277 03	1 11
277 89	0 20
278 09	0 22
278 70	0 26
279 03	0 58
279 81	0 30
280 01	0 52
281 01	2 96
281 64	0.29
282 05	0 55
282 98	0 72
284 15	0 60
285 01	0 85
286 09	0 31
287 02	1 56
288 04	2 42
288 27	0 32
289 01	10 54
290 03	3 48
291 01	100 00
292 03	12 31
293 01	2 59

Mass	% Base
294 06	0 35
295 02	0 54
297 02	0 3
298 12	0 43
299 06	0 74
300 03	0 45
301 05	0 74
303 02	1 94
305 02	1 23
306 02	0 47
307 00	5 63
308 03	1 18
309 02	18 86
309 25	0 42
309 38	0 47
310 04	3 5
311 06	0 52
313 01	0 77
315 09	0 36
317 09	1 07
319 95	0 82
320 05	0 23
322 06	0 44
322 99	1 09
324 05	0 24
324 67	0 24
324 95	0 88
325 89	0 78
326 90	0 39
328 00	0 28
328 96	0 36
331 14	0 71
333 06	0 48
335 05	1 49
335 52	0 27
336 07	0 65
336 70	0 66
336 95	0 22
337 10	0 41
338 98	0 28
340 92	0 80
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343 05	0 31
345 00	0 50
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348 54	0 22
349 09	0 33
351 11	0 44
353 08	0 32
355 00	1 90
356 10	0 24
357 00	0 89
358 04	0 39
359 05	0 57
360 13	0 32
360 99	0 84
361 18	0 23
362 05	0 51

Mass	% Base
447 36	0
447 99	0
451 08	0
459 03	0
463 35	0
461 14	0
462 93	0
465 21	0
467 24	0
477 12	0
481 17	0
482 12	0
489 24	0
498 19	0
501 96	0
502 13	0
503 04	0
514 06	0
522 77	0
524 91	0
526.22	0
536 05	0
537 26	0
543 02	0
549 13	0
553 10	0
554 11	0
556 91	1
561 08	0
564 53	0
565 09	0
565 34	0
571 26	0
573 76	0
575 16	0
578 12	0
579.11	0
580 24	0
583 20	1
587 33	0
588 22	0
594 37	0
596 27	0
601 34	0
602 28	0
615 62	0
617 46	0
618 29	0
626 55	0
632 52	0
633 54	0
653 47	0
653 79	0
655 41	0
656 86	0
687 39	0
696 37	0
698 75	0
700 40	0
721 71	0

Mass	% Base
363 35	0
365 34	0 4
366 36	0
367 10	0
368 37	1
368 97	0 4
370 23	0
370 74	0 4
372 12	0
374 37	0
374 61	0
375 35	0
375 89	0
377 16	0
379 36	0
380 12	1
381 99	0
383 38	0
383 99	1
385 06	0
385 33	0
386 34	0
386 99	0
387 07	0
387 96	0
388 98	0
391 15	0
395 15	0
396 10	0
398 12	1
398 95	1
401 04	1
403 36	1
404 97	0
406 18	0
408 33	0
408 96	0
414 34	0
414 91	0
419 12	0
420 06	0
422 03	0
423 04	0
425 19	0
427 12	0
429 33	0
430 03	0
431 19	0
432 17	
433 15	
436 73	
437 09	
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441 91	
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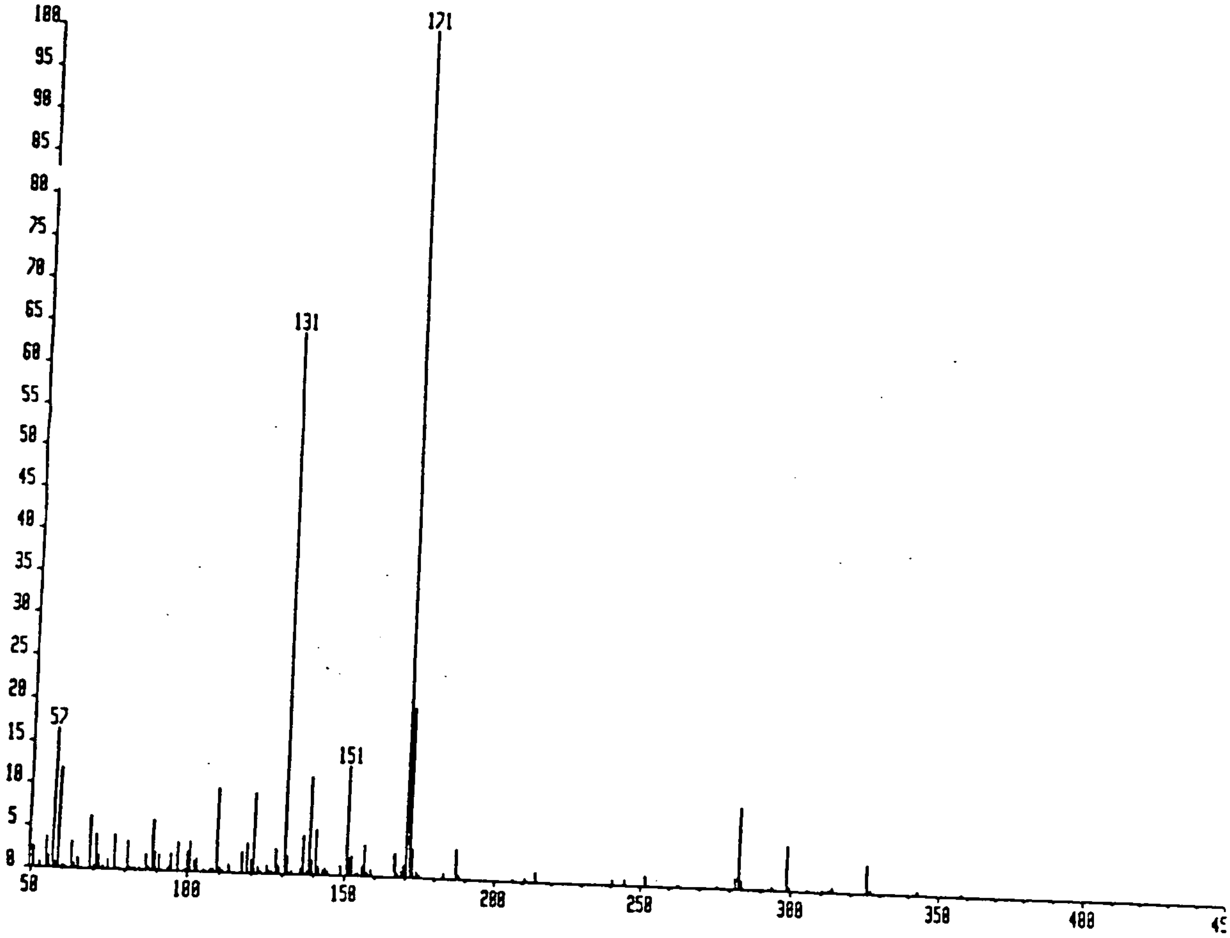

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58.95	11.77
68.89	6.03
88.89	5.84
108.85	9.71
120.86	9.30
130.83	64.06
138.83	11.46
140.83	5.15
150.82	12.96
170.81	100.00
171.82	19.84
262.72	0.11
275.73	0.14
281.70	1.13
282.70	9.45
283.71	0.90
293.70	0.31
298.67	5.14
299.69	0.32
305.67	0.11
310.65	0.15
312.66	0.19
313.70	0.40
325.69	3.22
326.67	0.36
342.69	0.23
357.70	0.17

APPENDIX III- INFRA RED

COMPOUND ENDEX

1. 1-methyl-2,2,3,4,4,4-hexafluorobutyl ethyl ether (32)
2. di(1-methyl-2,2,3,4,4,4-hexafluorobutyl)ether (33)
3. 1-methyl-2-H-perfluorocyclobutyl)ethyl ether (34)
4. di(1-methyl-2-H-perfluorocyclobutyl)ether (35)
5. 1-methyl-2-H-perfluorocyclopentyl ethyl ether (36)
6. di(1-methyl-2-H-perfluorocyclopentyl)ether (37)
7. α-(1,2,3,3,3-pentafluoro-1-propenyl)diethylether (42)
8. α,α'-bis(1,2,3,3,3-pentafluoro-1-propenyl)diethylether (43)
9. α-(2,3,3,4,4-pentafluorocyclobutyl)diethylether (44)
10. 1-methoxy-1-(1-ethoxyethyl)tetrafluoropropene (48)
11. 1-propoxy-(1-ethoxyethyl)-tetrafluoropropene (49)
12. 1-butoxy-1-(1-ethoxyethyl)-tetrafluoropropene (50)
13. α,α'-bis(1-methoxy-tetrafluoro-1-propenyl)diethylether (51)
14. α,α'-bis(1-ethoxy-tetrafluoro-1-propenyl)diethylether (52)
15. α,α'-bis(1-propoxy-tetrafluoro-1-propenyl)diethylether (53)
16. α,α'-bis(1-butoxy-tetrafluoro-1-propenyl)diethylether (54)
17. 3,3,4,5,5,5-hexafluoropentan-2-one (56)
18. 1,1,1,2,3,3,3-hexafluorononan-4-one (57)
19. 2-H-hexafluoropropyl t-butyl ketone (58)
20. 1,1,1,2,3,3-hexafluoro-5-cyclohexyl-pentane (59)
21. 1,1,1,2,3,3-hexafluoro-6-cyclohexyl-hexan-4-one (60)
22. 1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-6-cyclohexyl-nonan-4-one (61)
23. 2-Hydro-hexafluorocyclobutyl pentyl ketone (62)

24. 2-Hydro-octafluorocyclopentyl pentyl ketone (63)
25. 5,5,5-trifluoro-pentan-2-one (64)
26. 4-trifluoromethyl-7,7,7-trifluoroheptan-2-one (65)
27. 1,1,1,2,3,3,12,12,13,14,14,14-dodecafluoro-tetradecan-4,11-dione (66).
28. 1,1,1,2,3,3,3,16,16,17,18,18,18-dodecafluoro-octadodecan-4,15-dione (67)
29. 1,12-di(2-Hydro-perfluorocyclobutyl)dodecandione (69)
30. 1,12-di(2-Hydro-perfluorocyclopentyl)dodecandione (71)


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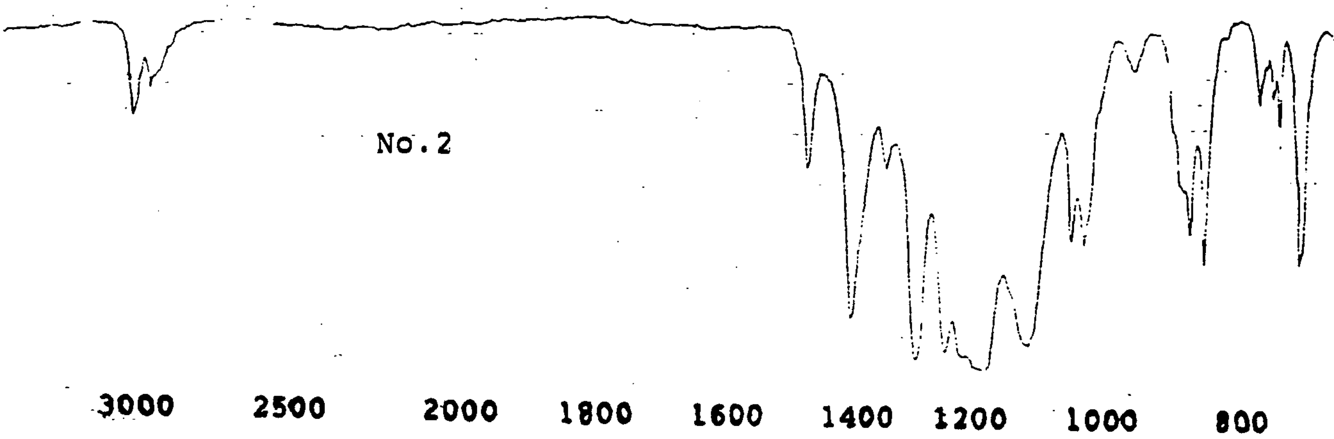
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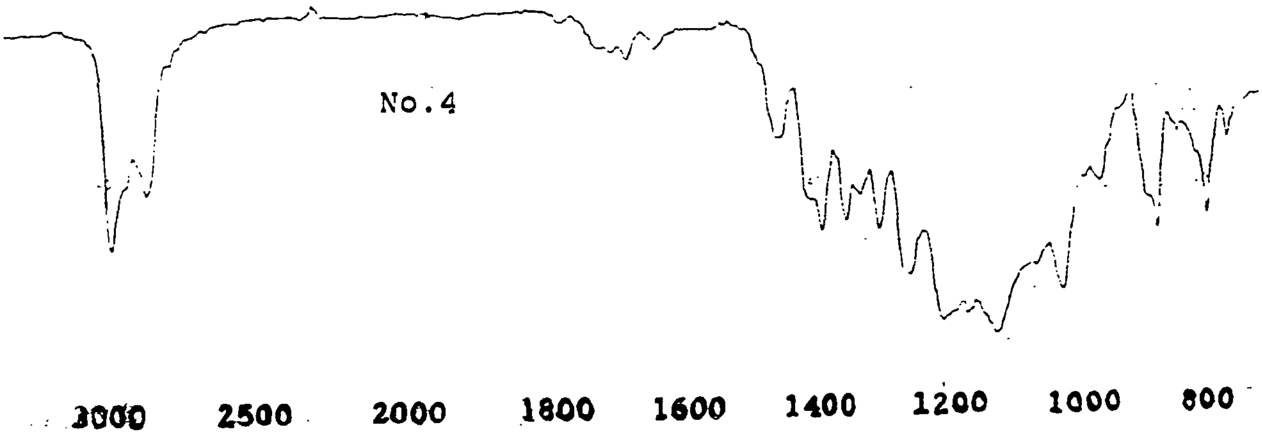
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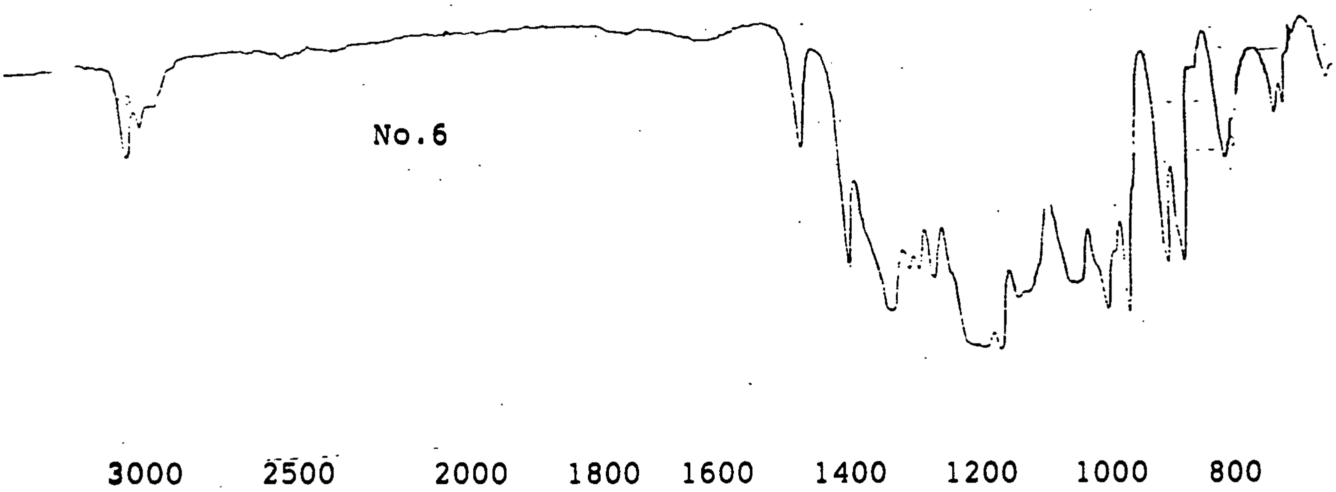
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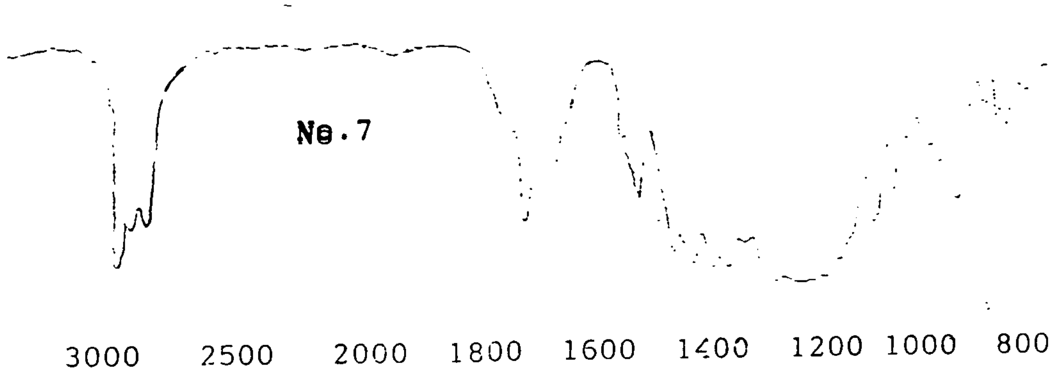
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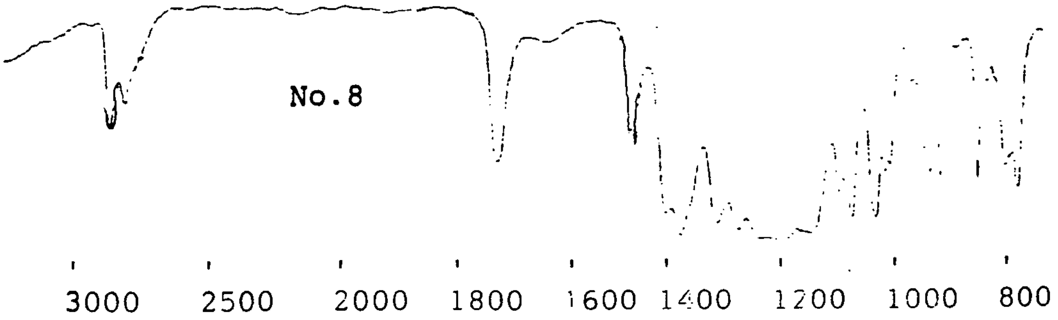
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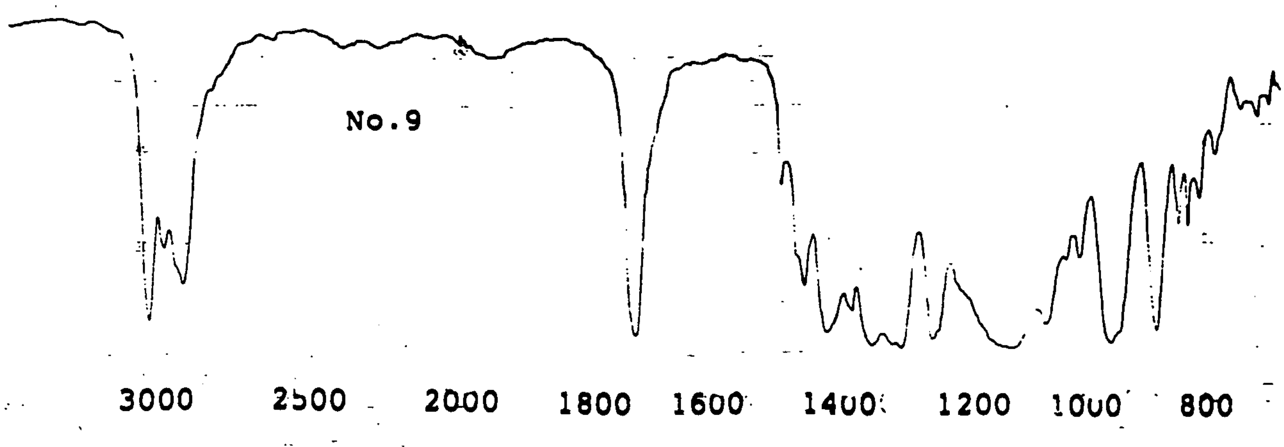
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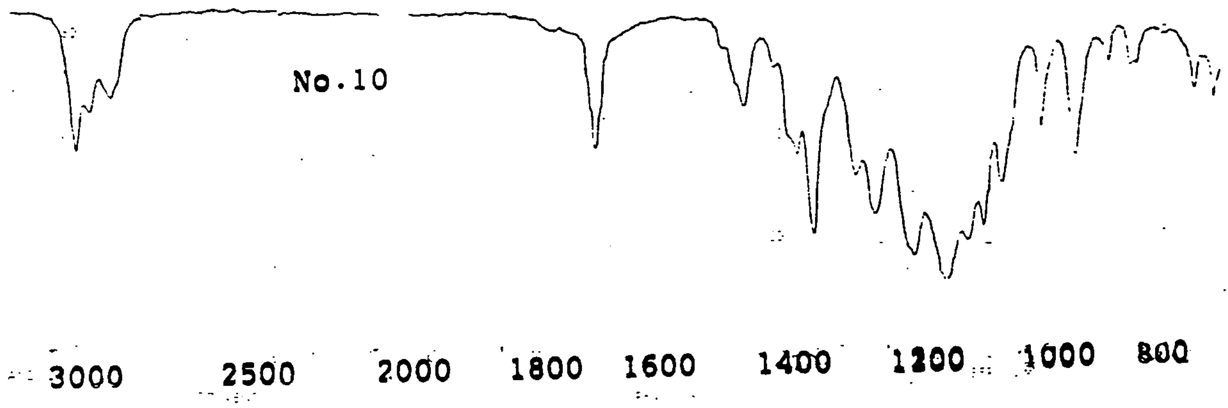
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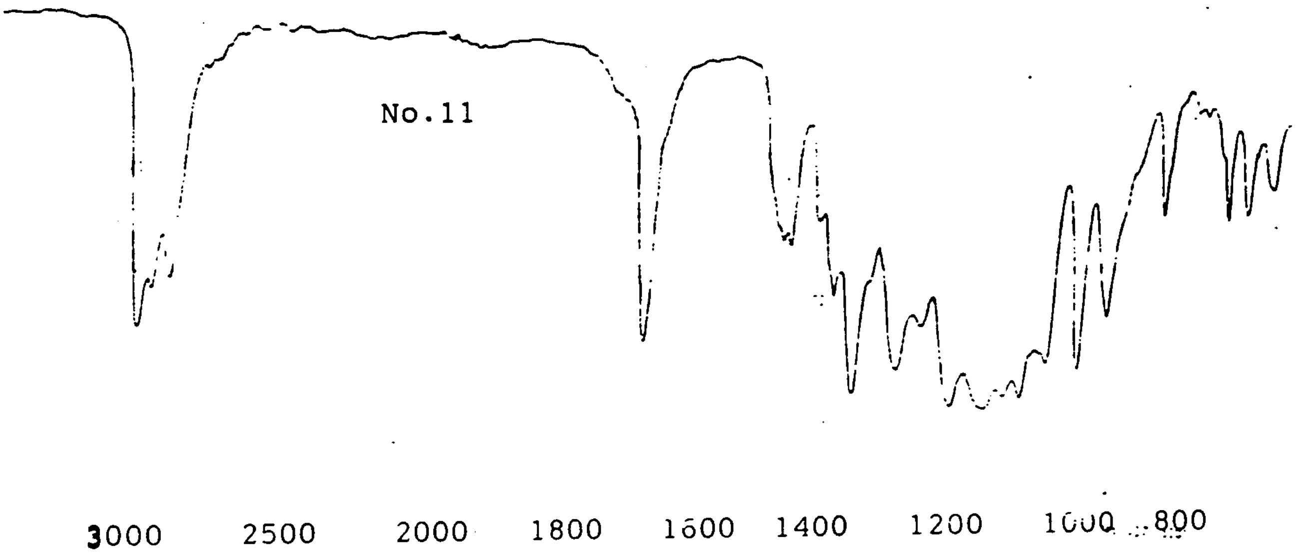
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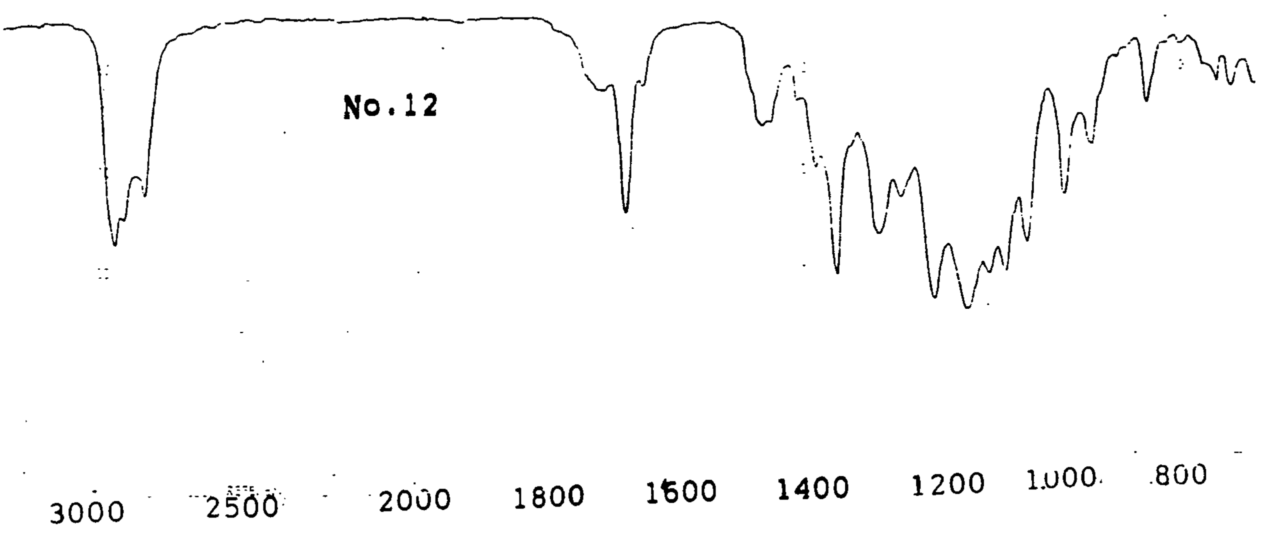
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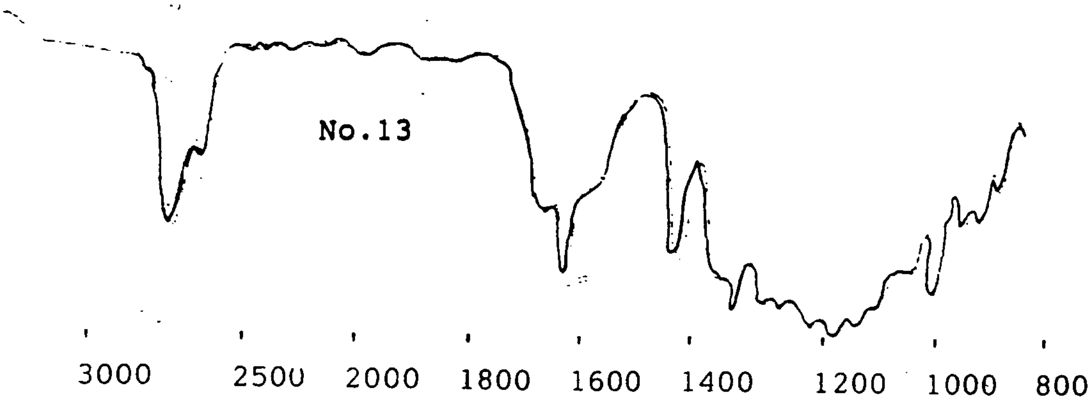

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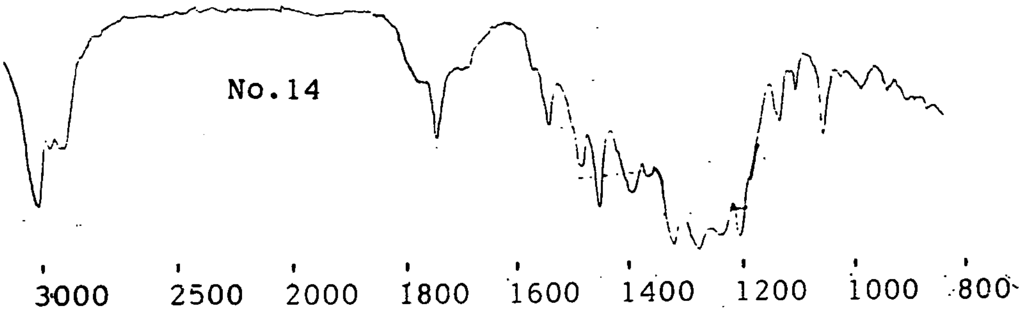

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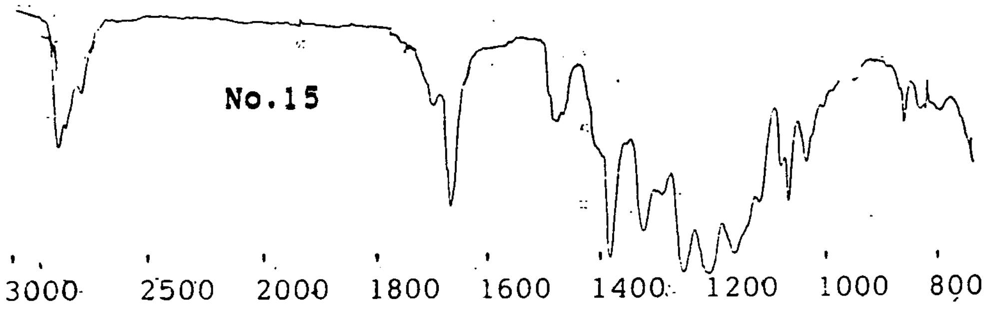

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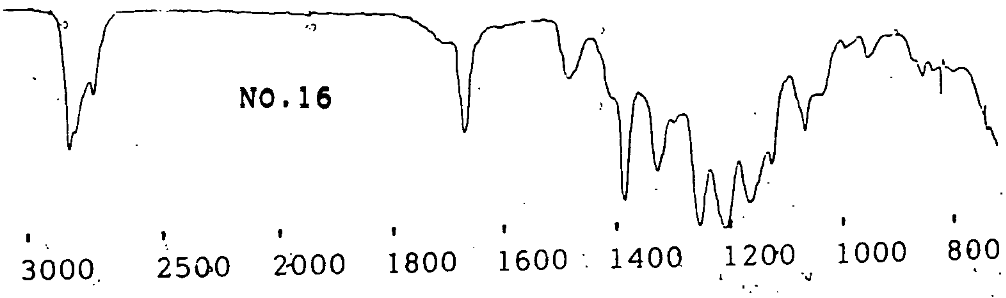

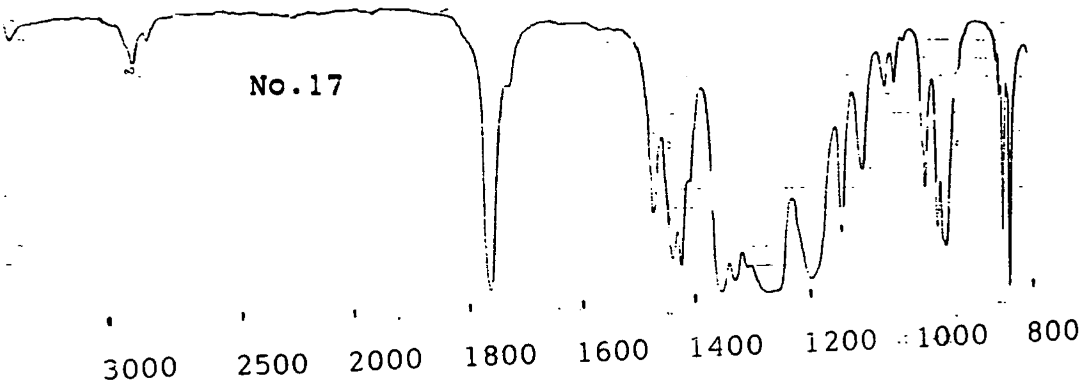

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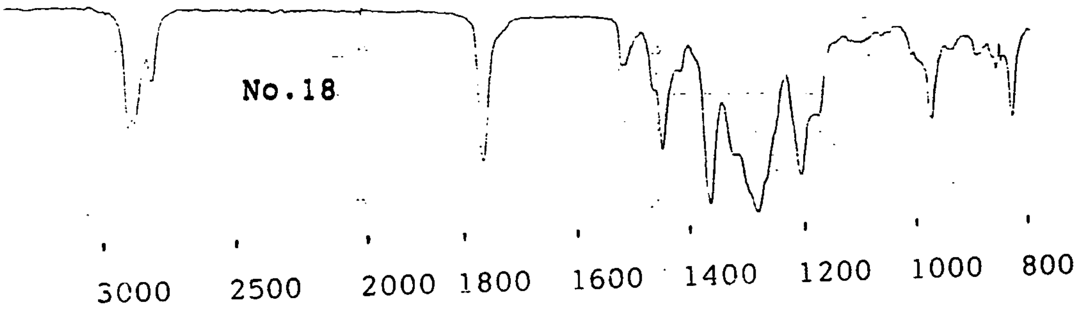

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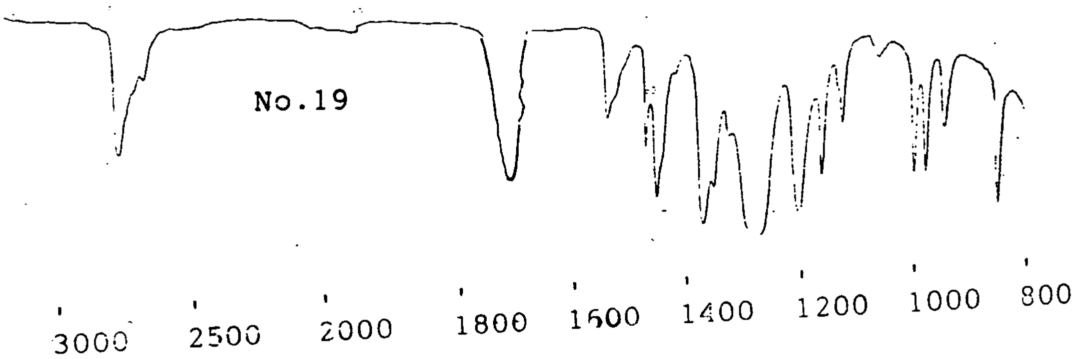

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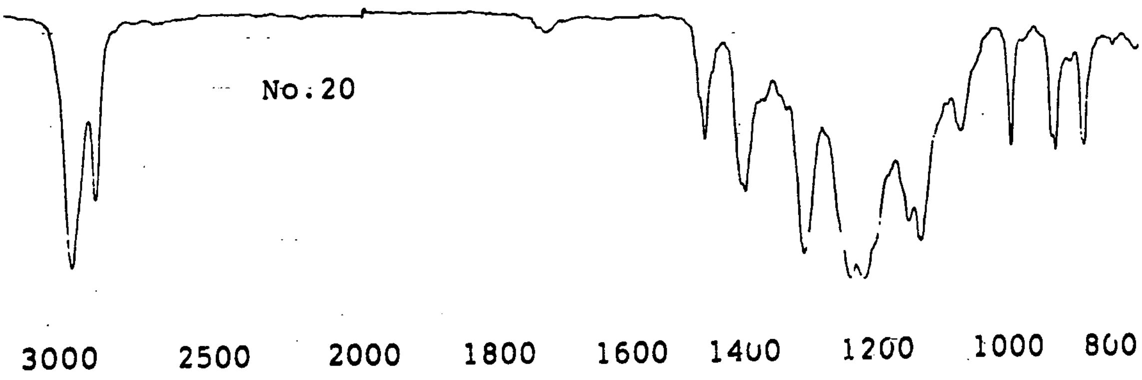

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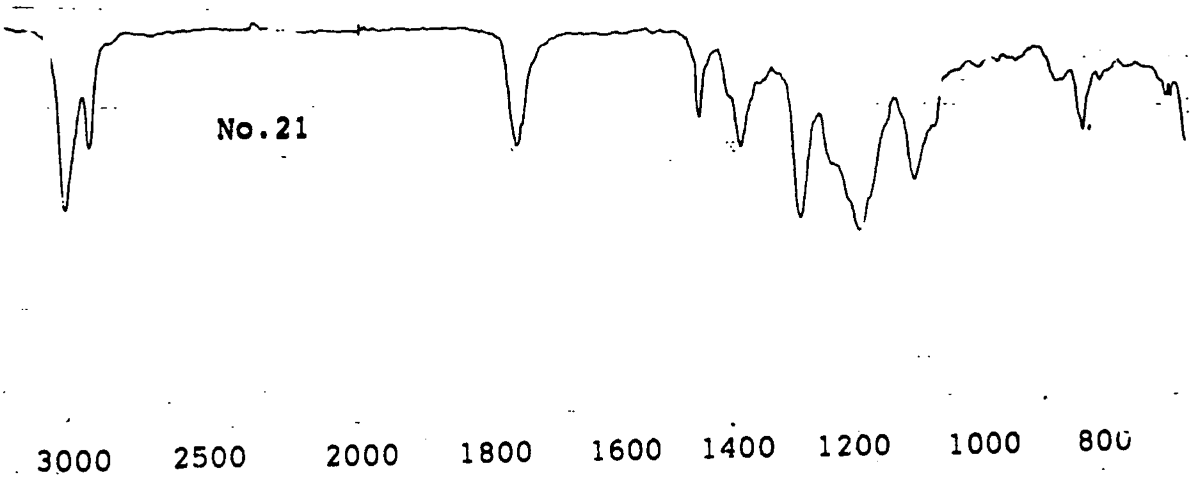
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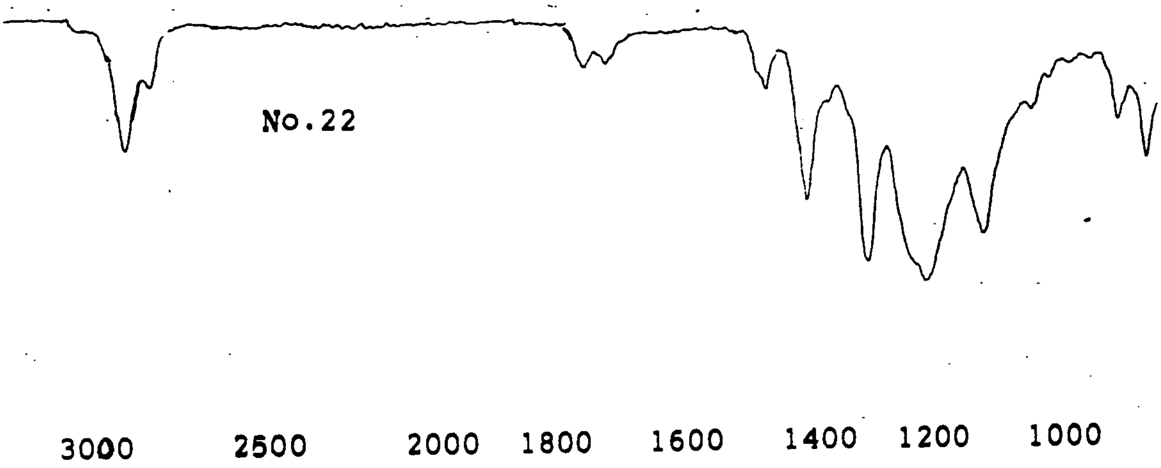
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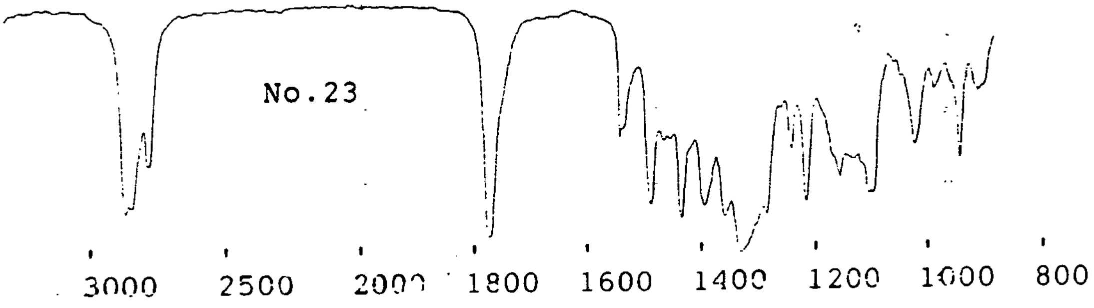
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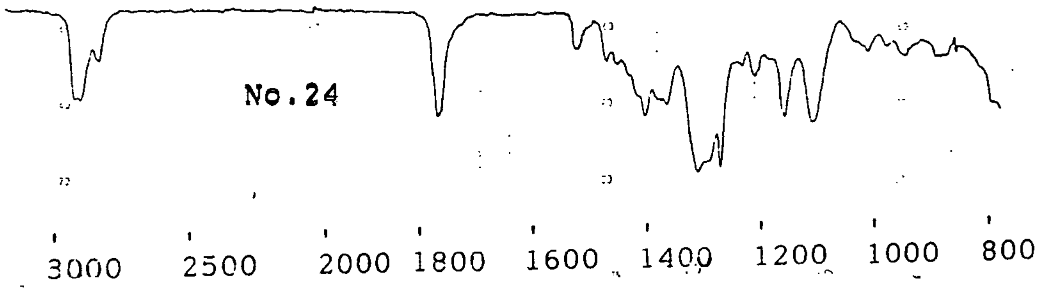
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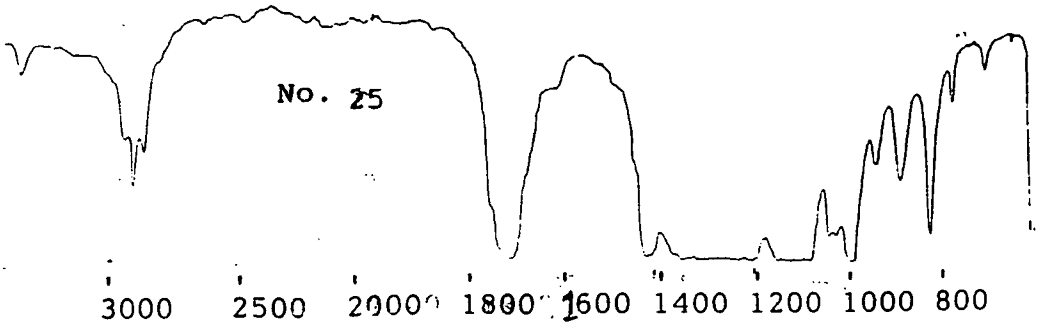
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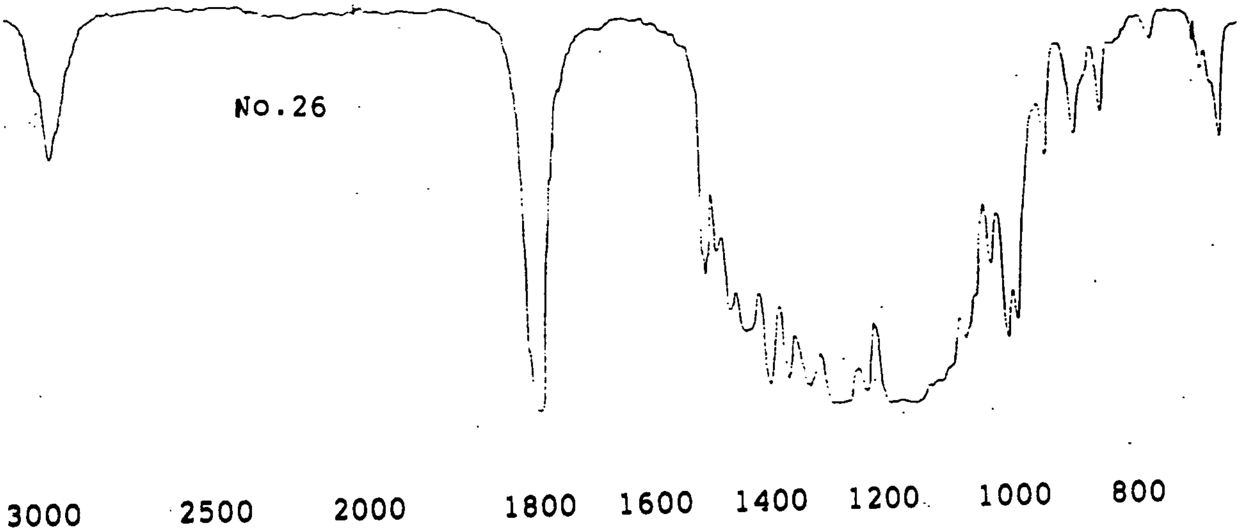
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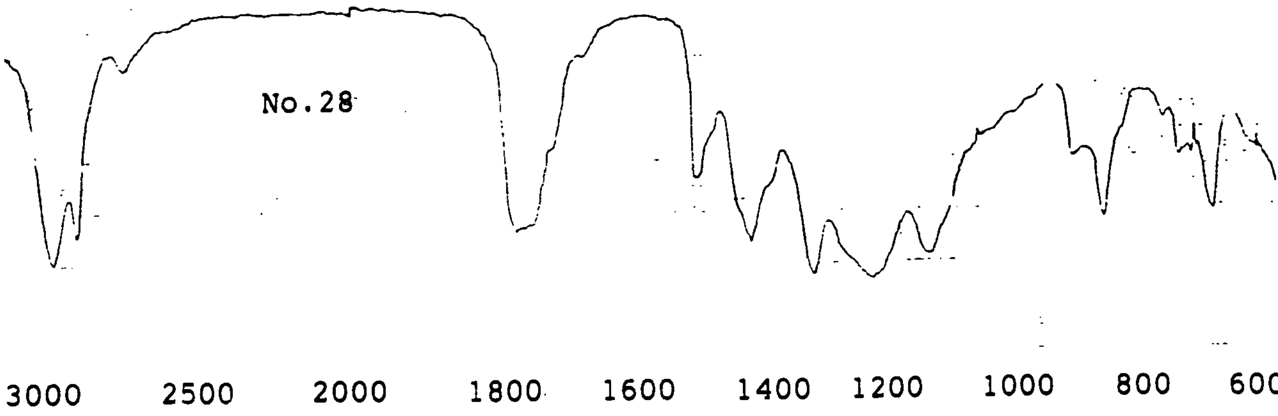
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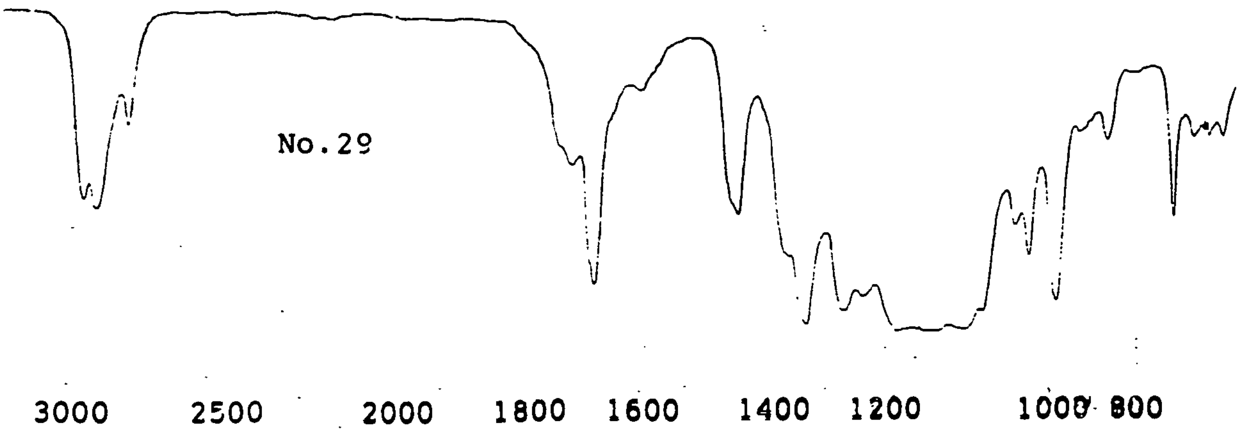
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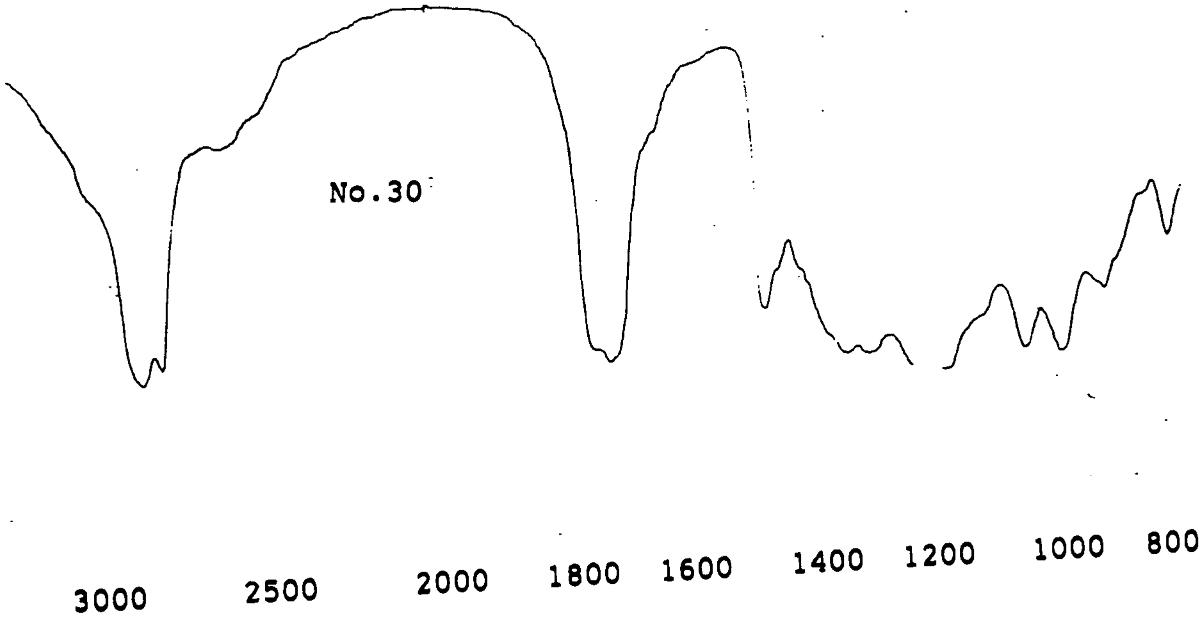
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APPENDIX IV

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

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

(b) lectures organised by Durham University Chemical Society;

(c) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out;

(d) details of the postgraduate induction course.

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKER

6th OCTOBER 1988 TO 1th OCTOBER 1989

6.10.88 Prof.R. Schmutzler (Technische Universitat Braunschweig) Fluorophosphines Revisited-New Contributions to an Old Theme

*18.10.88 Dr.J.Dingwall (Ciba Geigy)
Phosphorus-Containing Amino Acids: Biologically Active Natural and Unnatural Products

* 18.10.88 Dr.C.J.Ludman (University of Durham)
The Energetics of Explosives

18.10.88 Mr.F.Bollen
Durham Chemistry Teachers' Centre Lecture About Use of SATIS in the Classroom

* 21.10.88 Prof.P.Von Rague Schleyer (Universitat Erlangen Nurnberg) The Fruitful Interplay Between Calculation and Experimental Chemistry

* 27.10.88 Prof.C.W.Rees (Imperial College, London)
Some very Heterocyclic Compounds (The Musgrave Lecture)

* Seminars which were attended.

9.11.88 Dr.G.Singh (Teeside Polytechnic)
Towards Third Generation Anti-Leukaemics

10.11.88 Prof. J.I.G. Cadogan (British Petroleum)
From Pure Science to Profit

*16.11.88 Dr.K.A. Mclauchlin (University of Oxford)
The Effect of Magnetic Fields on Chemical Reactions

24.11.88 Dr.R.R. Baldwin and Dr. R.W. Walker (Hull University)
Combustion: Some Burning Problems

*1.12.88 Dr.R. Snaith (Cambridge University)
Egyptian Mummies: What, Where, Why and How?

.12.88 Dr.G. Hardgrove (St. Olaf. College, U.S.A.)
Polymers in the Physical Chemistry Laboratory

* 9.12.88 Dr.C. Jager (Friedrich-Schiller University)
NMR Investigations of Fast Ion Conductors of
the NASICON Type (Informal Research Seminar)

14.12.88 Dr.C. Mortimer (Lancashire Polytechnic)
The Hindenburg Disaster-An Excuse For Some
Experiments Durham Chemistry Teachers' Centre-
Schools Christmas Lecture

*25.1.89 Dr. L.Harwood (University of Oxford), 'Suythetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry Under Pressure.

*26.1.89 Prof. K.R.Jennings (University of Warwick), Chemistry of the Masses'.

*1.2.89. Mr. T. Cressey and Mr.D. Waters (Durham Chemistry Teachers' Centre), 'GCSE Chemistry 1988: A Coroner's Reports'.

*2.2.89 Prof. L.D. Hall (Addenbrookes'Hospital), ' NMR- A Window to the Human Body'.

13.2.89 Prof. R.R. Schrock (M.I.T.), 'Recent Advances in Living Metathesis'.

15.2.89 Dr. A.R. Butler (St. Andrews University), 'Cancer in Linxiam: The Chemical Dimension'.

*9.2.89 Prof. J. Baldwin (University of Oxford), '??' .

*16.2.89 Prof. J.B. Aylett (Queen Mary College), 'Silicon-based Chips: The Chemists Contribution'.

*22.2.89 Dr. G. Macdougall (Edinburgh University), 'Vibrational Spectroscopy of Model Catalytic System'.

*23.2.89 Dr. B. F.G. Johnson (University of Cambridge), 'The Binary Carbonyls'.

* 1.3.89 Dr. R.J. Errington (University of Newcastle-upon-Tyne), 'Polymetalate Assembly in Organic Solvents'.

* 9.3.89 Dr. I. Marko (Sheffield University), 'Catalytic Asymmetric Osmylation of Olefins'.

14.3.89 Mr. P. Revell (Durham Chemistry Teachers' Centre), Implementing Broad and Balanced Science 11-16'.

15.3.89 Dr. R. Aveyard (University of Hull), 'Surfactants at your Surface'.

* 20.4.89 Dr. M. Casey (University of Salford), 'Sulphoxides in Stereoselective Synthesis'.

* 27.4.89 Dr. D. Crich (University College London), 'Some Novel Uses of Free Radicals in Organic Synthesis'.

* 3.5.89 Mr. A. Ashman (Durham Chemistry Teachers' Centre), THe Chemical Aspects of the National Cuiculum'.

* 3.5.89 Dr. P.C.B. Page (University of Liverpool),'Stereocontrol of Organic Reactions Using 1,3-dithiane-1-Oxide'

*10.5.89 Prof. P.B. Wells (Hull University), 'Catalyst Characterisation and Activity'.

* 11.5.89 Dr. J. Frey (Southampton University, 'Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl'.

* 16,5.89 Dr. R. Stibr (Czechoslovak Academy of Sciences) 'Recent Developments in the Chemistry of Intermediate-Sited Carboranes'.

* 17.5.89 Dr. C.J. Moody(Imperial College),'Reactive Intermediates in Heterocyclic Synthesis'.

23.5.89 Prof. P. Paetzold (Aachen),'Iminoboranes XB NR: Inorganic Acetylenes?'.

14.6.89 Dr. M.E. Jones (Durham Chemistry Teachers' Centre), 'GCSE and A-level Chemistry 1989'.

* 15.6.89 Prof J.Pola (Czechslovak Academy of Sciences), 'Carbon Dioxide Laser Induced Chemical Reactions- New Pathways in Gas-Phase Chemistry'.

28.6.89 Dr. M.E. Jones (Durham Chemistry Teachers'Centre), 'GCSE and A-level Chemistry 1989'.

* 11.7.89 Dr. D. Nicholls (Durham Chemistry Teachers'Centre),' Liquid Air Demonstration'.

POSTGRADUATE INDUCTION COURSE.

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

Departmental Organisation:- Dr.M.R.Crampton.

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

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

Atomic Adsorption Spectrometry and Inorganic Analysis:- Mr.R.Coult. Library Facilities:- Mr.R.B.Woodward.

Mass spectrometry:- Dr.M.Jones.

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

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

RESEARCH CONFERENCES ATTENDED

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6. 'Preparation, Properties, and Industrial Applications of Organofluorine Compounds', ed., R.E.Banks, Ellis Horwood, Chichester, 1982.
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