The synthesis and chemistry of model compounds related to fluoropolybcers

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UNIVERSITY OF DURHAM

A THESIS

ENTITLED

THE SYNTHESIS AND CHEMISTRY OF MODEL COMPOUNDS RELATED TO FLUOROPOLYMERS

SUBMITTED BY

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TO MY PARENTS

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Finally, I owe a particular debt of gratitude to my family and friends for their continual advice and encouragement.

MEMORANDUM

The work described in this thesis was carried out at the University of Durham between October 1985 and May 1988. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

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

R.D. Chambers, G.C. Apsey, M. Salisbury, and G. Moggi, J. Fluorine Chem., 1987, 35 46.

R.D. Chambers, M. Salisbury, G.C. Apsey, T.F. Holmes, and S. Modena, J. Chem.Soc., Chem. Commun., 1988, 679.

R.D. Chambers, M. Salisbury, G.C. Apsey, and G. Moggi, J. Chem.Soc., Chem. Commun., 1988, 680.

G.C. Apsey, R.D. Chambers, M. Salisbury, and G. Moggi, J. Fluorine Chem., in press.

and has been presented by the author at the following meetings:

Graduate Symposium, Durham University March 1987.

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by

GLENN APSEY

ABSTRACT

The objectives of this research project were to synthesize and investigate the chemistry of model compounds related to the hexafluoropropene/vinylidene fluoride copolymer system. A number of compounds of this type were prepared which underwent a series of reactions in order to obtain definitive information about the chemical processes occuring during the cross-linking of the copolymer system with bis-nucleophiles. Further studies with the model compounds also indicated potential sites in the cured copolymers through which chemical degradation could take place, during their use in aggressive environments.

Other investigations with the model compounds, together with unsaturated compounds derived from these systems, led to the observation of some very unusual chemistry. Lewis acid induced dehydrofluorination reactions with antimony pentafluoride led to the formation of a number of observable carbocations and a unique contiguous dication. This methodology was further developed in the treatment of saturated homopolymers, in which dehydrohalogenation by antimony pentafluoride led to formation of polyacetylene derivatives displaying intense colouration.

In order to circumvent the formation of potential sites of chemical instability during the curing process with nucleophiles, a methodology was investigated in which cross-linking could occur via a free radical mechanism involving homolytic bond cleavage of sterically demanding groups. A number of monomers containing a bulky pendant group were prepared and were investigated in order to determine their suitability to undergo copolymerisation with vinylidene fluoride. Copolymers obtained in this way were then examined to determine whether polymer radicals could be produced by thermally induced homolytic bond scission of sites involving the sterically crowded groups. The results obtained clearly demonstrated that this type of cross-linking process is entirely feasible.

CONTENTS

INTRODUCTION

CHAPTER ONE

FLUOROELASTOMERS

1.1 Introduction

Elastomeric materials are extremely important in the family of materials of construction, as their use permits increased flexiblity in design of mechanical systems. There are two remarkable properties which distinguish elastomers from other types of material. When an external force is applied elastomers undergo very large deformations in shape without disintegrating and on removal of the stress spontaneous recovery of their original dimensions occurs.[1-3]

The performance of an elastomer at low temperatures is only one of many properties which determine its utility. Its stability at elevated temperatures and chemical and/or physical interactions with its intended environment are also important factors, all of which are related to its chemical constitution. For a material to possess elastomeric properties it must consist of long flexible and linear molecules of high molecular weight, which have been cross-linked by a few intermolecular bonds to form an insoluable three-dimensional network.[1-3] The thermal stability of an elastomer often differs from that of the raw polymer, which is a consequence of the introduction of chemical heterogeneity by the cross-linking process. Even if the cross-links have the same chemical structure as the polymer chains, the structure at the junctions between chains and cross-links usually differs.

Cross-linked elastomers cannot be dissolved in any solvents but may swell in contact with liquids and vapours. In their numerous applications such as sealings, rings, gaskets and linings, elastomers need to be resistant to the solvents to which they come into contact.[4]

However, many elastomers have unsatisfactory resistances to hydrocarbon fuels and oils, as well as to chlorinated solvents.[2,4] Hydrocarbon elastomers in particular are most susceptible to degradation in these liquids.

In searching for a means of improving the thermal, chemical and oxidative stability of elastomeric materials investigations have focused mainly on reducing the amount of unsaturation and on introducing other elements to the hydrocarbon systems. The interest in fluorine - containing elastomers followed from the discoveries of poly (chloro-trifluoroethylene) and poly (tetrafluoroethylene), since these polymers display great superiority over their non-fluorinated analogues in their resistance to many organic solvents.

Homopolymers of simple fluoroalkenes are often crystalline in nature as a consequence of regular and repeating monomer units in the polymer backbone.[2,12] A high degree of crystallinity in a polymer is undesirable for elastomeric behaviour since, such regions do not confer flexibility on the material.[12] However, copolymers of fluoroalkenes possess sufficient structural irregularities to prevent crystallization. Hence, copolymers of vinylidene fluoride with chlorotrifluoroethylene and with hexafluoropropene are non-crystalline elastomers which form the bases of commercially available elastomers introduced in the 1950s. Materials based on these polymer systems are easily the most successful of the fluoroelastomers and have dominated the market since their introduction. Many detailed reviews on fluoroelastomers are available in which their preparation and properties are discussed together with their use in specialized applications.[2,5,12-16]

A brief outline of the synthesis and copolymerisation of fluorovinyl monomers together with a more detailed discussion of fluoroelastomers, is given overleaf.

1.2 Preparation and Polymerisation of Fluorovinyl Monomers

Synthetic routes to the fluoralkenes which are most frequently used in the preparation of fluoroelastomers are outlined in Table 1.1. The processes which are most widely employed in the synthetic routes include halogen exchange, dehydrohalogenation and hydrofluorination reactions.[17-19]

The preparation of fluorelastomers is usually achieved by a free-radical emulsion polymerisation process.[2,12] The initiators employed are frequently either ammonium or potassium persulphate since they are useful sources of radicals for low temperature polymerisations.[13,14] Perfluorinated emulsifying agents such as ammonium perfluoro-octanoate are preferred in order to minimize chain transfer reactions. The temperature range for the polymerisation process is from 30 to 125°C and since the monomers are gases, the pressure is regulated so it is between 50 and 1500 psi.

The polymerisation is carried out by either a batch or continuous process. Control of the copolymer composition is achieved by altering the monomer ratios. The molecular weight of the products is dependent on both the monomer/initiator ratio and the presence of chain transfer reagents such as carbon tetrachloride, methanol or diethyl malonate.[42,43] A typical polymerisation recipe is given in Table 1.2.

Table 1.1

	Alkene	References
1	$CF_2 = CF_2$ (TFE)	7,19,20

$$CHCl_3 \xrightarrow[60^\circ C]{HF/SbCl_5} CHF_2Cl \xrightarrow[\text{Pt tube}]{\underline{ca}\ 700^\circ C} CF_2 = CF_2$$

2	$CF_3CF = CF_2$ (HFP)	21-23

$$CF_2 = CF_2 \xrightarrow{759\text{-}800^\circ C} CF_3CF = CF_2$$

3	$CF_2 = CFCl$ (CTFE)	24,25

$$CCl_3CCl_3 \xrightarrow[150^\circ C]{HF/SbCl_5} CF_2ClCFCl_2 \xrightarrow[100^\circ C]{Zn/MeOH} CF_2 = CFCl$$

4	$CH_2 = CF_2$(VDF or VF_2)	26-29

$$CH_3CCl_3 \xrightarrow[180^\circ C]{HF/SbCl_5} CH_3CF_2Cl \xrightarrow[550^\circ C]{\text{Ni tube}} CH_2=CF_2$$

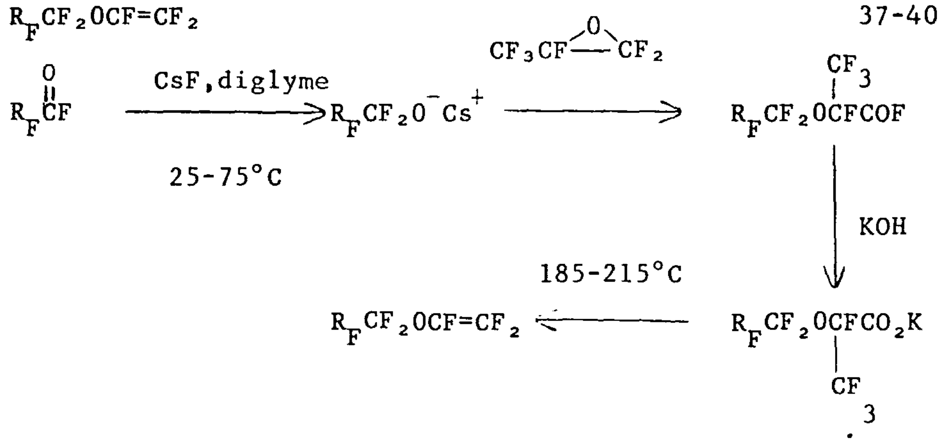
5	$CFH=CFCF_3$(HPFP)	30-32

$$CF_3CF=CF_2 \xrightarrow{H_2/Pd} CF_3CFHCF_2H \xrightarrow{\text{base}} CF_3CF = CFH$$

6	$CF_2 = CHCF_3$	33-36

$$CF_3CF=CF_2 \xrightarrow[\text{peroxide}]{MeOH} CF_3CFHCF_2CH_2OH \xrightarrow[2)NaOH/\Delta]{1)Na_2Cr_2O_7} CF_3CH=CF_2$$

7	$R_FCF_2OCF=CF_2$	37-40



$$\begin{tikzcd}
R_F\overset{O}{\overset{\|}{C}}F \arrow[r, "\text{CsF, diglyme}", "25\text{-}75^\circ C"'] & R_FCF_2O^-Cs^+ \arrow[r, "CF_3CF\overset{O}{\wedge}CF_2"] & R_FCF_2O\overset{CF_3}{\overset{|}{C}}FCOF \arrow[d, "KOH"] \\
 & R_FCF_2OCF=CF_2 & R_FCF_2O\underset{\underset{CF_3}{|}}{C}FCO_2K \arrow[l, "185\text{-}215^\circ C"']
\end{tikzcd}$$

On removal of the polymer latex from the reactor vessel it is coagulated by adding salt or acid. The resultant crumb is washed and then dried.

Table 1.2

Component	Grams
Water	340
Vinylidene fluoride (VDF)	61
Hexafluoropropene (HFP)	39
Dibasic potassium phosphate	3.6
Potassium persulphate	1.2
Perfluoro-octanoic acid	0.9
Carbon tetrachloride	0.1

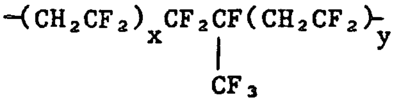
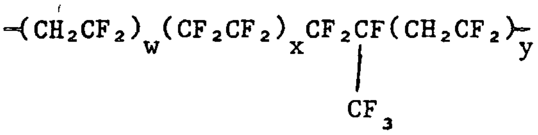
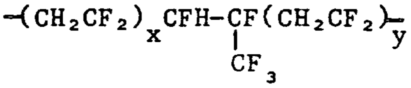
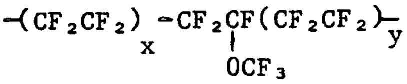
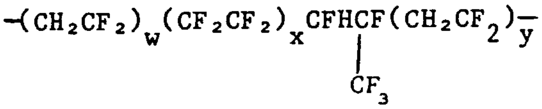
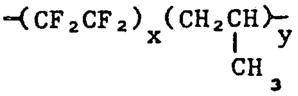
1.3 Fluorocarbon Elastomers

The principal commercial fluoroelastomers based on carbon-carbon polymer chains are listed in Table 1.3, together with their major structural units. The actual chemical structures of the raw polymers, on which the fluoroelastomers are based, are a function of a number of different factors including the monomer ratios, their relative reactivities and the degree of regioselectivity of the polymerisation reactions.[44-47]

1.31 Curing of Fluoroelastomers

Raw fluoropolymers may possess some elastomeric properties due to some degree of inter-chain entanglements and this effect is augmented by pendant groups situated along the polymer backbone. However, thermal agitation or the application of sufficient stress to the polymers can overcome any elastomeric properties which may be present. This results in the permanent plastic flow of polymer molecules past one another unless this is restricted by cross-links between the chains at selected sites along their lengths, to give a three-dimensional network. It is necessary however, to optimize the number and distribution of cross-links between polymer chains since too many will give materials which are rigid, whereas insufficient intermolecular links will produce

Table 1.3

Monomers	Trade Name/ Manufacturer	Major Structural Units	
$CH_2=CF_2/$ $CF_3CF=CF_2$	Fluorel 3M (USA) Viton A du Pont (USA) Tecnoflon Montefluos (Italy)	 $-(CH_2CF_2)_x CF_2\underset{\displaystyle CF_3}{\underset{\vert}{C}}F(CH_2CF_2)_y-$	48-50
$CH_2=CF_2/CF_2=CF_2$ $CF_3CF=CF_2$	Viton B du Pont (USA)	 $-(CH_2CF_2)_w(CF_2CF_2)_x CF_2\underset{\displaystyle CF_3}{\underset{\vert}{C}}F(CH_2CF_2)_y-$	50
$CH_2=CF_2/$ $CF_3CF=CFH$	Tecnoflon SL Montefluos (Italy)	 $-(CH_2CF_2)_x CFH-\underset{\displaystyle CF_3}{\underset{\vert}{C}}F(CH_2CF_2)_y-$	
$CH_2=CF_2$ $/CF_2=CFCl$	Kel-F Elastomer 3M (USA)	$-(CH_2CF_2)_x(CF_2CFCl)_y-$	51
$CF_2=CF_2$ $/CF_3OCF=CF_2$	Kalrez du Pont (USA)	 $-(CF_2CF_2)_x-CF_2\underset{\displaystyle OCF_3}{\underset{\vert}{C}}F(CF_2CF_2)_y-$	50,52
$CF_2=CF_2/CH_2=CF_2$ $/CF_3CF=CFH$	Tecnoflon T Montefluos (Italy)	 $-(CH_2CF_2)_w(CF_2CF_2)_x CFH\underset{\displaystyle CF_3}{\underset{\vert}{C}}F(CH_2CF_2)_y-$	
$CF_2=CF_2/$ $CH_2=CHCH_3$	Aflas Asahi Glass (Japan)	 $-(CF_2CF_2)_x(CH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}H)_y-$	53

materials that are devoid of elastomeric characteristics.[12]

The curing of raw fluoropolymers is generally carried out according to the stages outlined below:

i) The raw polymer is formulated with a curing agent, an acid acceptor and a filler, on conventional processing equipment.[2,13,15,54] Both the nature and proportions of the compounding ingredients are determined by the end uses of the fluorocarbon elastomers but a typical recipe is outlined in Table 1.4. Metallic oxides are essential for satisfactory cures and while their function is not completely understood they are known to remove any acids, such as HF, produced during the curing process. Studies have demonstrated that an increase in the magnesium oxide content (up to 15 pph) actually increases the cross-link density of fluoroelastomers based on vinylidene fluoride.[55]

Table 1.4

Component	pph
Elastomer	100
MgO or $Ca(OH)_2$	6-20
Filler, reinforcing or non-reinforcing	0-60
Curatives/accelerators	0-6
Process aids	0-2

Fillers are used in variable quantities to meet a number of criteria for specific applications of fluorocarbon elastomers. Medium thermal carbon black is the most frequently used filler, which serves to increase the tensile strength of cured materials while also reducing their costs. However, too high a proportion of MT carbon black can have detrimental effects on both the ageing and low temperature properties of fluoroelastomers.[15,41] For materials which are required to be heat resistant fine silica fillers are often used instead of carbon black but this is at the expense of resistance to fluids and compression set.[56]

ii) The compounded polymer is formed into the desired shape at a suitable temperature and then subjected to a press-cure for 10-60 minutes between 100-150°C. The purpose of the press-cure is to introduce some cross-links between the polymer molecules and to release trapped air and other volatiles which thereby prevents formation of a porous product.[57]

iii) The partially cured material is then heated in an air oven for 15-24 hours at ca 200°C. A considerable increase in the cross-link density usually occurs and more volatile materials are emitted. For nucleophilic cures water is the major volatile. It is produced by the reaction of HF with the basic metal oxide, e.g:[57]

$$2HF + MgO \longrightarrow MgF_2 + H_2O$$

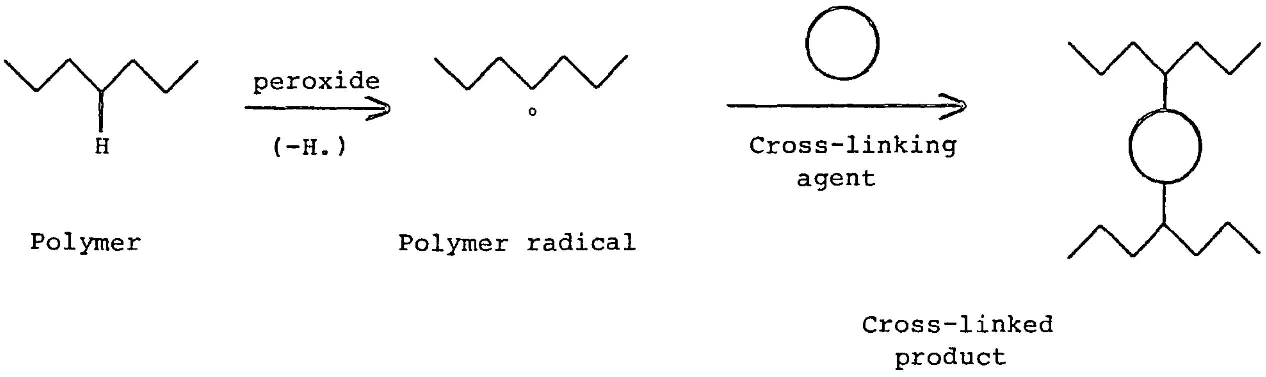
The physical properties of fluoroelastomers are generally improved by an oven post-cure, and in particular there is an increase in tensile strength and compression set resistance.

1.32 Formation of Cure-Sites

Materials such as natural rubber have unsaturated sites along their chain lengths through which intermolecular bonding can occur.[58] For fluorinated polymers cure-sites have to be created by either one of the following methods:

i) For certain fluorine containing polymers unsaturated sites can be produced, by dehydrohalogenation for example, and the development of cross-links can then be achieved by the chemical reaction of these active sites with nucleophiles, such as amines or bis-hydroxy compounds.

ii) For fluoropolymers containing suitable C-H bonds cure-sites can be created by peroxide induced abstraction of hydrogen atoms. It is believed that the resultant polymer radicals may then combine with each other, or with a radical trap, to produce cross-links (see Scheme 1.1).



Scheme 1.1

iii) Optimum amounts of a special monomer can be incorporated into a polymerisation system, so that the resultant fluoropolymer contains active sites through which cross-linking can occur.

Each of the three techniques have been used to produce fluoroelastomers that are commercially available. However, the choice of which methodology to use depends on not only the chemical nature of the fluoropolymer, but its intended application also. Polymers of tetrafluoroethylene and perfluoromethylvinyl ether can only be cross-linked by the incorporation of cure-sites, since they are highly resistant to most chemicals.

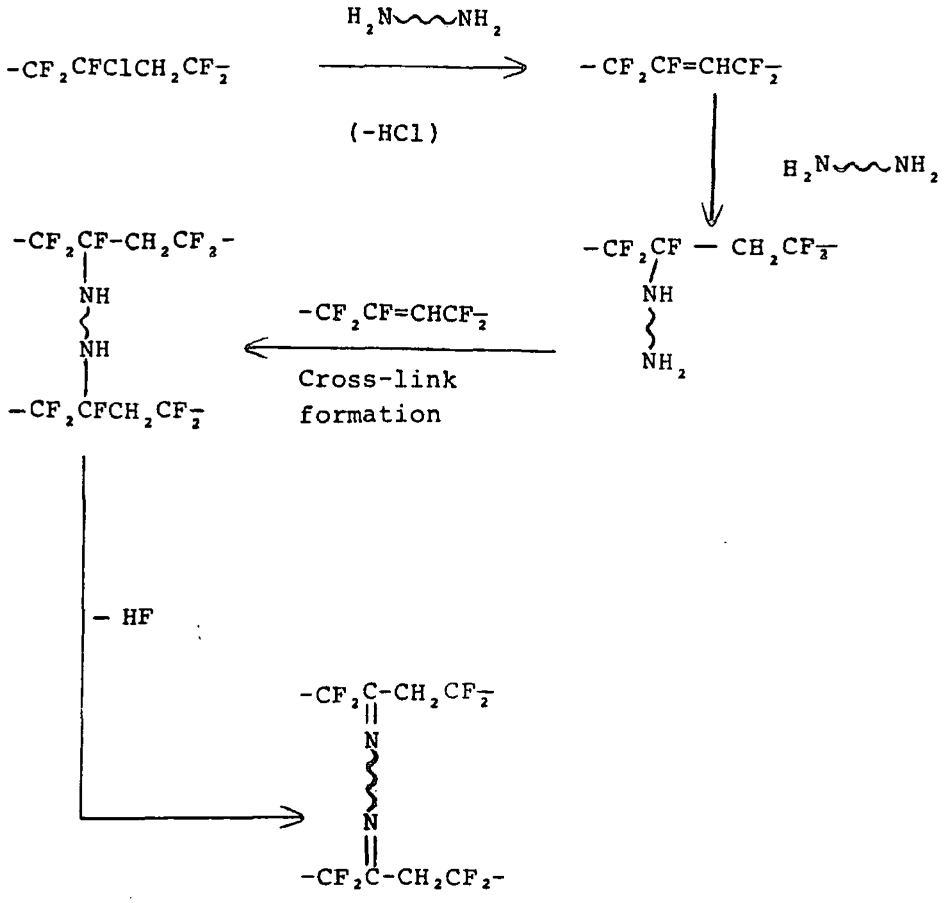
A more detailed discussion of the cross-linking procedures is given below.

1.33 Cross-linking by Amines

For copolymers of vinylidene fluoride the mechanism of cross-linking by amines involves initial dehydrohalogenation to produce unsaturated sites, which are then attacked by the curing agent. Details of the subsequent reactions are not completely understood.

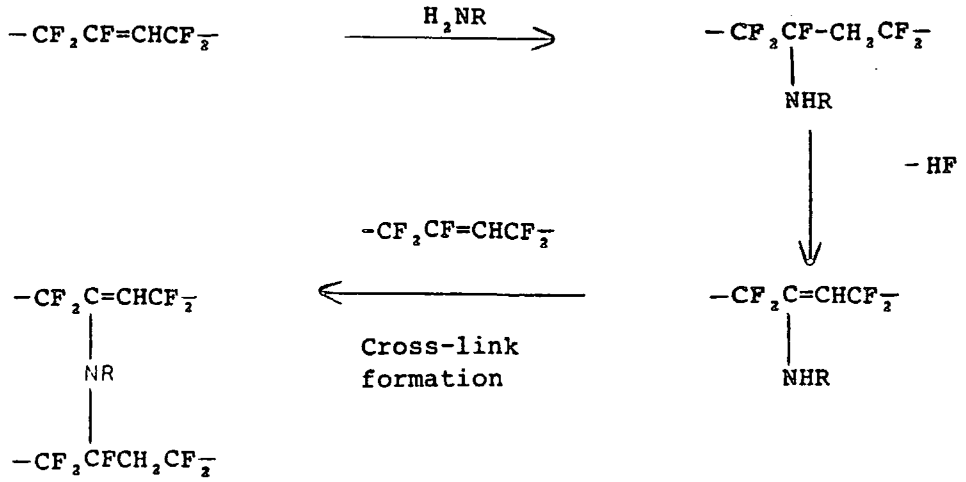
a) $CF_2CFCl/CH_2=CF_2$ Copolymers

Polymers based on $CF_2=CFCl$ and $CH_2=CF_2$ can be cross-linked in solution by primary diamines at room temperature.[57] Initially dehydrochlorination occurs, which proceeds much more rapidly than dehydrofluorination. It is believed that this is followed by addition of the amine to the unsaturated sites, with concomitant loss of HF (See Scheme 1.2).[51]



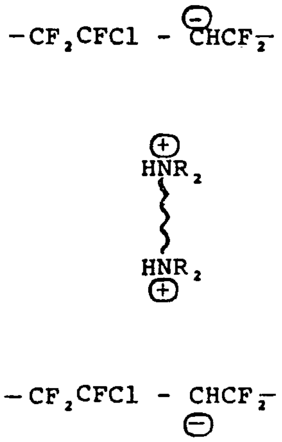
Scheme 1.2

Primary monoamines also cross-link $CF_2{=}CFCl/CH_2{=}CF_2$ copolymers at room temperature and it has been postulated that the mechanism for this process is the one outlined in Scheme 1.3, based on studies with model compounds.[59]



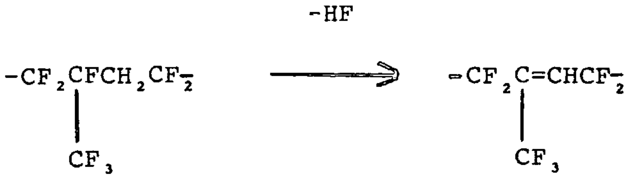
Scheme 1.3

These mechanisms, involving nucleophilic attack of amines on unsaturated sites, cannot account for the fact that the copolymers are cross-linked by secondary and tertiary monoamines and by tertiary diamines at elevated temperatures. To overcome this problem, however, the rather unlikely formation of quaternary sites was proposed,[57] e.g.,



b) $CF_3CF=CF_2/CH_2=CF_2$ Copolymers

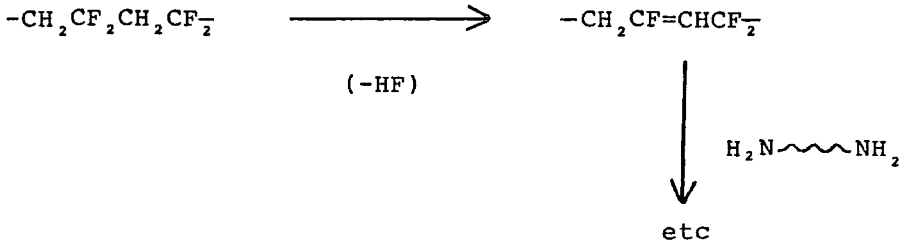
Dehydrofluorination of these copolymers by amines occurs preferentially at tertiary sites, although less readily than the dehydrochlorination of $CF_2=CFCl/CH_2=CF_2$ polymers.



$$-CF_2CF(CF_3)CH_2CF_2- \xrightarrow{-HF} =CF_2C(CF_3)=CHCF_2-$$

It is believed that the free amines add across the unsaturated sites to give a product from which elimination of HF could occur, as for the $CF_2=CFCl/CH_2=CF_2$ copolymer system. This is supported by studies with model compounds and by the fact that four moles of HF are eliminated for each molar equivalent of cross-link which is formed.[55] However, there is a lack of definitive evidence for the mechanism of this process.

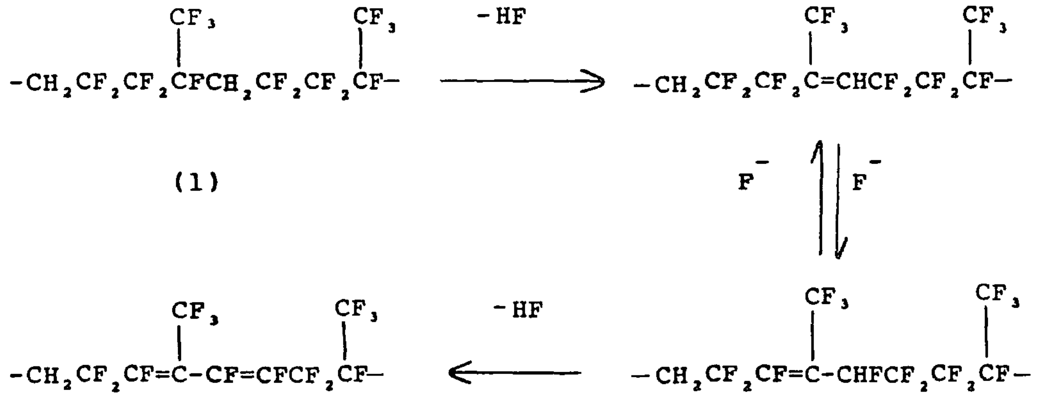
Sequences of vinylidene fluoride units are present in $CF_3CF=CF_2/CH_2=CF_2$ copolymers and elimination of HF from these sites could ultimately lead to the formation of cross-links, by a similar route to that outlined in Scheme 1.2, e.g.[55,60]



In order to determine the differences in rates of dehydrofluorination of the sequences $-CH_2CF_2CH_2CF_2-$ and $-CH_2CF_2CF_2(CF_3)CH_2CF_2-$, Schmiegel treated solutions of $CF_3CF=CF_2/CH_2=CF_2$ and vinylidene fluoride polymers in dimethylacetamide (DMAC) with different types of base/bis-nucleophile systems. It was found that $CF_3CF=CF_2/CH_2=CF_2$ copolymers were gelled much more rapidly than $CH_2=CF_2$ homopolymers. For example, treatment with hexamethylene diamine led to gellation in under 4 minutes for $CF_3CF=CF_2/CH_2=CF_2$ copolymers, , whereas $CH_2=CF_2$ homopolymers only afforded a firm gel after more than 10 days.

Further studies carried out by Schmiegel demonstrated that the dehydrofluorination step proceeds relatively slowly compared to nucleophilic attack on unsaturated sites.[50]

Solution studies of $CF_3CF=CF_2/CH_2=CF_2$ copolymers in DMAC, after treatment with tetra-n-butylammonium hydroxide, have indicated that preferential elimination of HF occurs from tertiary sites and that units of the type (1) are the most active.[50] Further investigations led to the proposal that the displaced fluoride ion may participate in reactions with the unsaturated sites, leading ultimately to further dehydrofluorination of the polymer chains (see Scheme 1.4).



Scheme 1.4

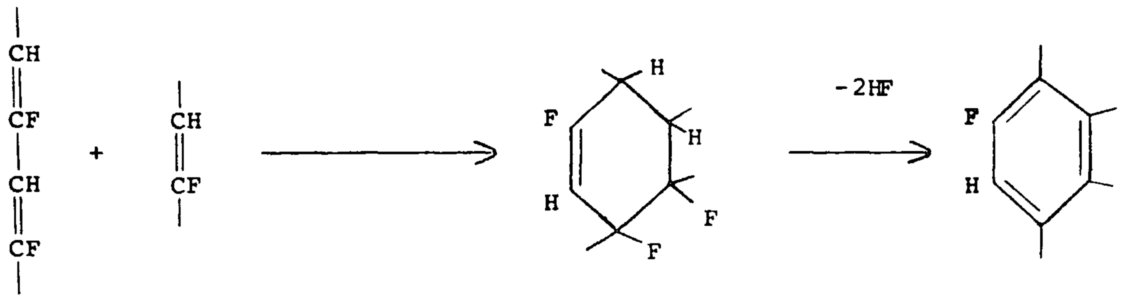
c) Curing Agents

During the compounding of the raw fluoropolymers it is important that premature cross-linking ('scorch') is avoided. In practice aliphatic amines are extremely reactive and cause scorching, so that compounds which generate amines on heating are used instead.[60-62] A number of delayed action curing agents have been developed to overcome the scorch problem and these include Schiff bases of alphatic diamines, such as bis-cinnamylidene hexamethylene diamine $(PhCH=CHCH=N(CH_2)_3)_2$ and carbonates such as hexamethylene diamine carbonate ($H_3\overset{+}{N}(CH_2)_6NHCO_2^-$). Water is required to produce the free amine and this is accomplished by the chemical reaction between the basic metal oxide and HF. The metal oxide also reacts with any amine hydrofluoride which is present, to produce the free amine, e.g.

$$MgO + 2R\overset{+}{N}H_3\overset{-}{F} \longrightarrow MgF_2 + H_2O + 2RNH_2$$ [57]

The presence of water can have a significant effect on the stability of the cured material since it can cleave the intermolecular bonds. Consequently, water must be carefully removed during the post-cure process.

The function of the post-cure is not only to remove volatile materials. It also serves to significantly increase the degree of cross-links. The role of the acid acceptors during this process is not completely understood since copolymers of vinylidene fluoride cannot be effectively cross-linked unless they are included in the curing formulation. This applies to curing by amines, bis-hydroxy compounds and peroxides.[60] Indeed, heating raw copolymers of $CF_3CF=CF_2$ and $CH_2=CF_2$ with magnesium oxide alone can bring about some degree of cross-linking.[63] This observation, together with the fact that magnesium oxide can act as a dehydrofluorinating agent, have led to proposals that unsaturated sites can react to form cross-links during the post-cure stage, e.g.[60]



Scheme 1.5

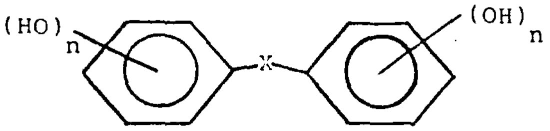
However, it is highly unlikely that this type of cross-linking mechanism occurs since related conjugated materials failed to react in the absence of amines.[51]

d) Properties of Amine Cured Fluoroelastomers

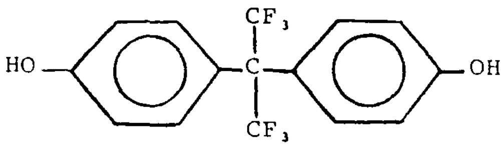
A significant increase in the physical and thermal properties of fluoroelastomers based on vinylidene fluoride is obtained during the oven post-curing cycle. Many of the centres of instability are removed so that the cured materials are largely stable to heat and have increased resistance to oxidation and weathering. The limitations of amine cured fluorelastomers, however, are their susceptibility to degradation by various solvents and gases, which can attack any remaining sites of unsaturation.[64] Consequently, the proportion of fluoropolymers which are cross-linked by amines has progressively diminished over the last two decades.

1.34 Cross-linking by Bisphenols

Currently the curing of vinylidene fluoride copolymers is largely carried out using a bisphenolin conjunction with a cross-linking accelerator and an acid acceptor.[65,66] The preferred cross-linking accelerator is a quaternary phosphonium salt of the type $R_1R_2R_3\overset{+}{P}R_4\ \overset{-}{X}$, although related arsenic or antimony compounds can be used also.[66] Typically, however, benzytriphenylphosphonium chloride is used. Bisphenols of the form (2) are the cross-linking agents used most frequently, where X



(2)



Bisphenol AF

is preferably an electron-withdrawing group such as a carbonyl, sulphonyl or perfluorinated alkylene.[66] Usually, hexafluorisopropylene - bis-(4-hydroxybenzene) (Bisphenol AF) is the preferred compound and a typical curing system is shown in Table 1.5. Both the press-cure (several minutes at 170-190°C) and the oven post-cure processes (24h at 230-260°C) are carried out at temperatures above those used for cross-linking by amines.

Table 1.5

Component	pph
Elastomer	100
MT Black	30
$Ca(OH)_2$	6
MgO	3
Bisphenol AF	1.5-2.5
$Ph_3\ P^+\ CH_2Ph\ Cl^-$	0.4-0.5

Copolymers of vinylidene fluoride and hexafluoropropene, chlorotrifluoroethylene or pentafluoropropene and terpolymers of vinylidene fluoride, tetrafluoroethylene and hexafluoropropene or pentafluoropropene can be cross-linked using the phenol curing system.[66] Most investigations of the cross-linking process have concentrated on studies with the $CF_3CF{=}CF_2/CH_2{=}CF_2$ copolymer system and a discussion of the results is given below.

a) $\underline{CF_3CF{=}CF_2/CH_2{=}CF_2}$ Copolymers

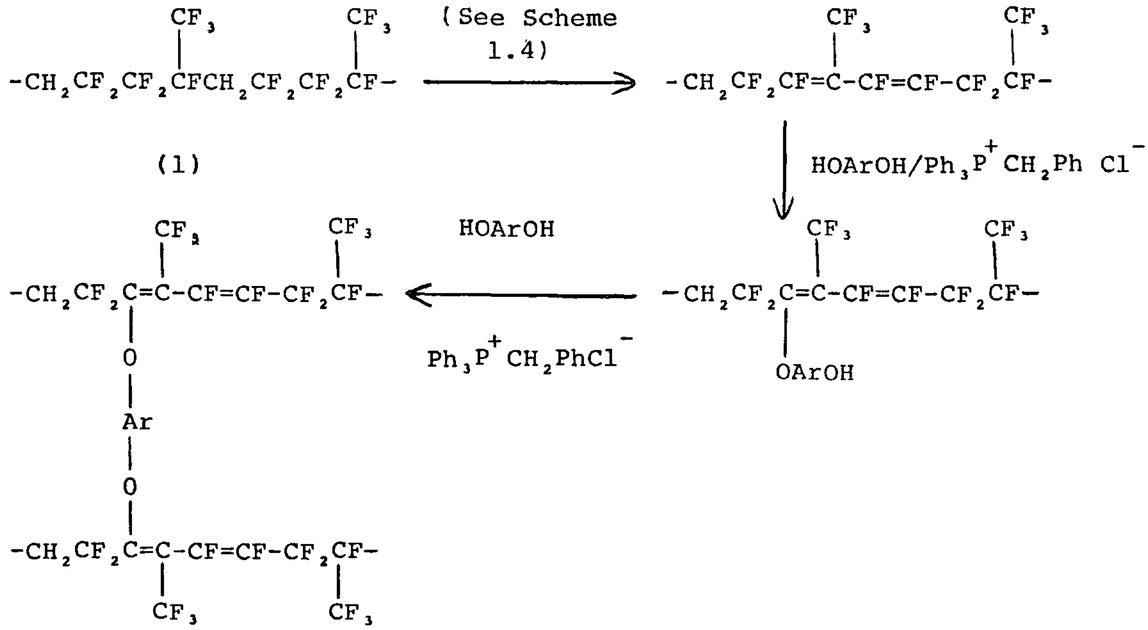
Schmiegel investigated the curing of these copolymers with Bisphenol AF and made several observations:[50]

i) If the cross-linking accelerator, e.g. $Ph_3\overset{+}{P}\ CH_2Ph\ \overset{-}{Cl}$, is omitted from the curing recipe no cure occurs.

ii) If Bisphenol AF is omitted, only <u>ca</u> 7% of the cure-state of the complete formulation is attained.

iii) The cross-link density is directly related to the level of Bisphenol AF.

These observations, together with studies based on ^{19}FNMR analysis of polymer solutions, after treatment with base/bis-nucleophile systems, led to the proposal that the most likely cross-linking mechanism is the one outlined in Scheme 1.6. However, these studies only apply to the initial stages of the curing process, since the formation of cross-links cause the polymer solutions to gel and consequently hinder the spectroscopic analysis. It is known that there is a significant increase in the degree of cross-linking during the post-cure stage, and there is evidence that bond breakage is followed by bond reformation, to give a more stable three-dimensional network.[12]



Scheme 1.6

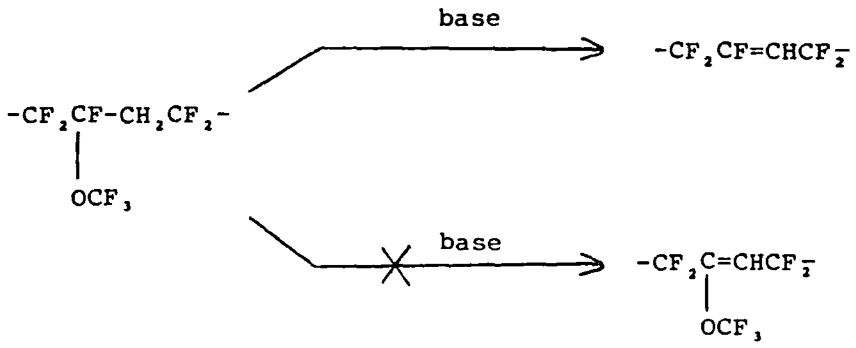
During the cross-linking process Bisphenol AF is probably converted to the corresponding bisphenolate by either magnesium oxide or the quaternary phosphonium salt.

$$PhCH_2P^+Ph_3Cl^- + HOArOH \longrightarrow PhCH_2P^+Ph_3\ ^-OArOH + HCl$$

The phenolate can then attack the polymer either eliminating HF or adding to any unsaturated units.[50] The quaternary phosphonium salt serves to accelerate these reactions, possible by conferring some surface phase transfer properties on the system. Schmiegel has proposed that the phosphonium ion undergoes conversion from bisphenolate to fluoride or bifluoride during the course of the curing process.[48] Ultimately, it is converted to triphenylphosphonium oxide.

b) Polymers containing $CF_3OCF=CF_2$ and $CH_2=CF_2$

Terpolymers based on vinylidene fluoride, perfluoromethylvinyl ether and tetrafluoroethylene or hexafluoropropene have been developed as they can be used at lower temperatures than $CH_2=CF_2/CF_3CF=CF_2$ and $CH_2=CF_2/CF_2=CF_2/CF_3CF=CF_2$ polymers, but still possess good resistance to chemical attack. However, these materials cannot be effectively cross-linked by nucleophilic curatives since there are considerable porosity problems with the vulcanizates.[50] The unsuitability of this curing methodology is most likely to be due to emission of insoluble volatile materials from the fluoroelastomer compound during the cross-linking process. In fact, it was demonstrated that trifluoromethanol is eliminated in preference to HF when solutions of these polymers are treated with base (see Scheme 1.7).[50]



Scheme 1.7

Furthermore, the decomposition of trifluoromethanol according to the process:

$$CF_3OH \longrightarrow CF_2=O + HF$$

leads to the evolution of HF, which on reaction with metal oxides will produce water. It is understandable, therefore, that the formation of these insoluble volatiles is instrumental in causing the observed porosity problems. This situation, however, can be circumvented by incorporating a cure-site monomer into these polymers (See Section 1.36).

c) Properties of Bisphenol Cured Fluoroelastomers

The major utility of the bisphenol curing process is in the manufacture of fluoroelastomers having a combination of high thermal stability and low compression set for applications such as O-rings, shaft seals and tubing.[66] In addition the compounded articles have improved storage stability and processability relative to amine formulations.

Bisphenol cured fluoroelastomers are resistant to a wide range of chemicals including acids, salt solutions, hydrocarbon solvents, fuels and oils. However, they are degraded by certain polar solvents such as methyl ethyl ketone, amines and low molecular weight esters and alchols.[13]

1.35 Cross-Linking by Peroxides

a) $CH_2{=}CF_2$ Copolymers

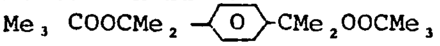
In principle, copolymers containing vinylidene fluoride can be cross-linked by peroxides via the abstraction of hydrogen atoms from the polymer chains and reaction of the resultant radicals probably with either each other or a suitable cross-linking agent. (See Scheme 1.1.)[14,15,57,67,68] In practice however, it is necessary to add magnesium oxide to the system in order to attain a practical degree of cure. Furthermore, the abstraction of a hydrogen atom is a high energy process which requires very active peroxides and the use of such compounds often leads to scorching problems.

Fluoroelastomers based on vinylidene fluoride, which have been cured in this way, are thermally less stable than amine or bis-phenol vulcanizates and have poor resistance to compression set and creep.

b) $CH_3CH{=}CH_2/CF_2{=}CF_2$ Copolymers

Copolymerisation of tetrafluoroethylene and propene produces amorphous polymers in which there is a high degree of alternation of the monomer units.[53,69,70] These polymers cannot be cured by most cross-linking agents, including polyamines and polyhydroxyaromatics, since there are no active cure sites. However, the combination of a peroxide and a cross-linking coagent can bring about an effective cure-state.[71] A typical curing recipe is shown in Table 1.6.

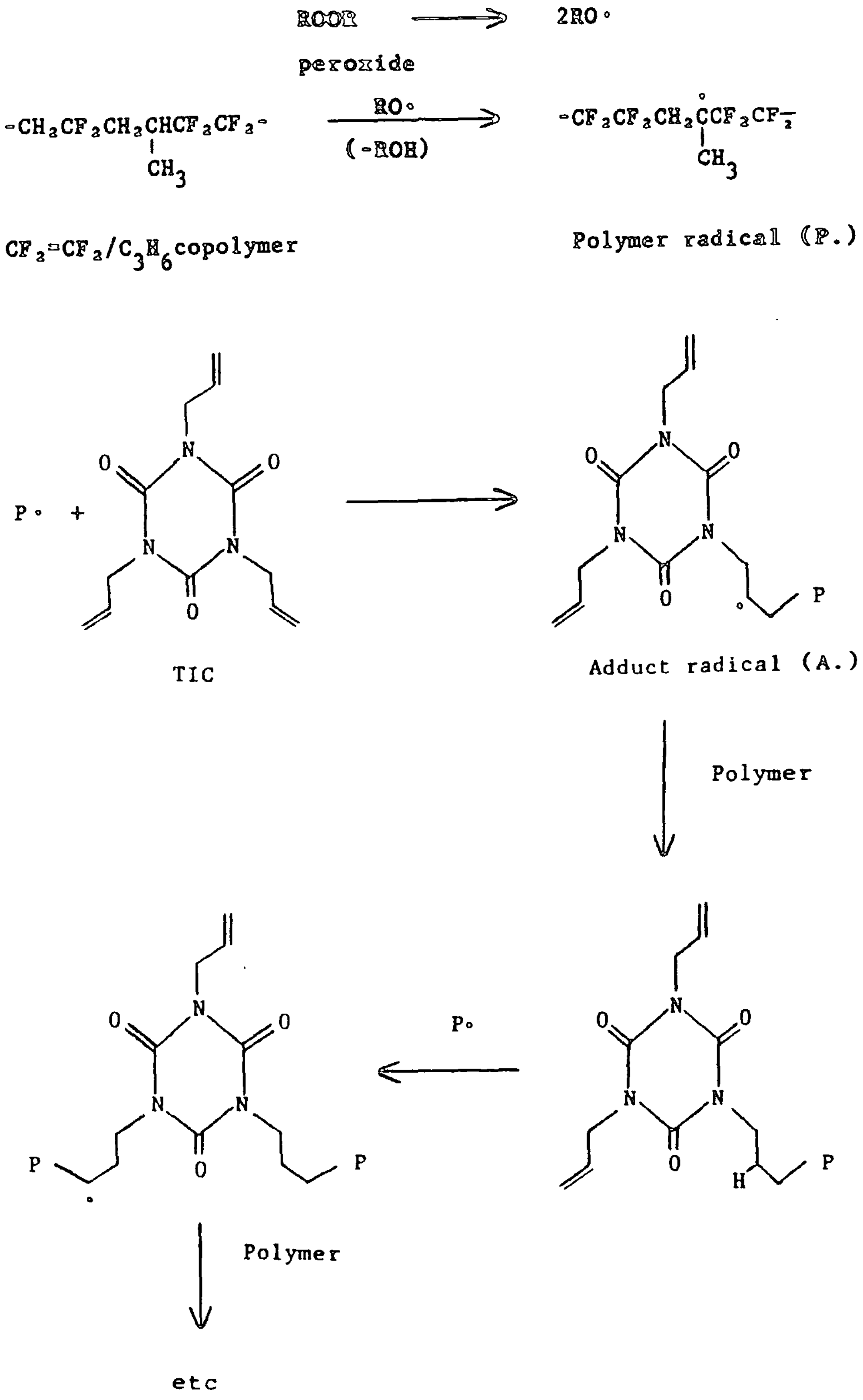
Table 1.6

Component	pph
Copolymer	100
MT carbon black	35
 $\mathrm{Me_3\ COOCMe_2}-\langle\mathrm{O}\rangle-\mathrm{CMe_2OOCMe_3}$	2
Triallyl isocyanurate (TIC)	3

Press-Cure: 30 mins at 160°. Post-cure: 2h at 200°C

The most satisfactory cure-states are obtained with α,α' - bis - (t - butylperoxy) - p - diisopropylbenzene as the peroxide and triallyl isocyanurate (TIC) as the coagent.[71]

It was postulated that the cross-linking reaction proceeds by the mechanism outlined in Scheme 1.8[71] The mechanism involves peroxide induced abstraction of hydrogen from the tertiary carbons, giving polymer radicals which participate in the cross-linking process. It is most likely that the methylene groups of TIC are susceptible to abstraction of hydrogen also, although this was not stated.[71]

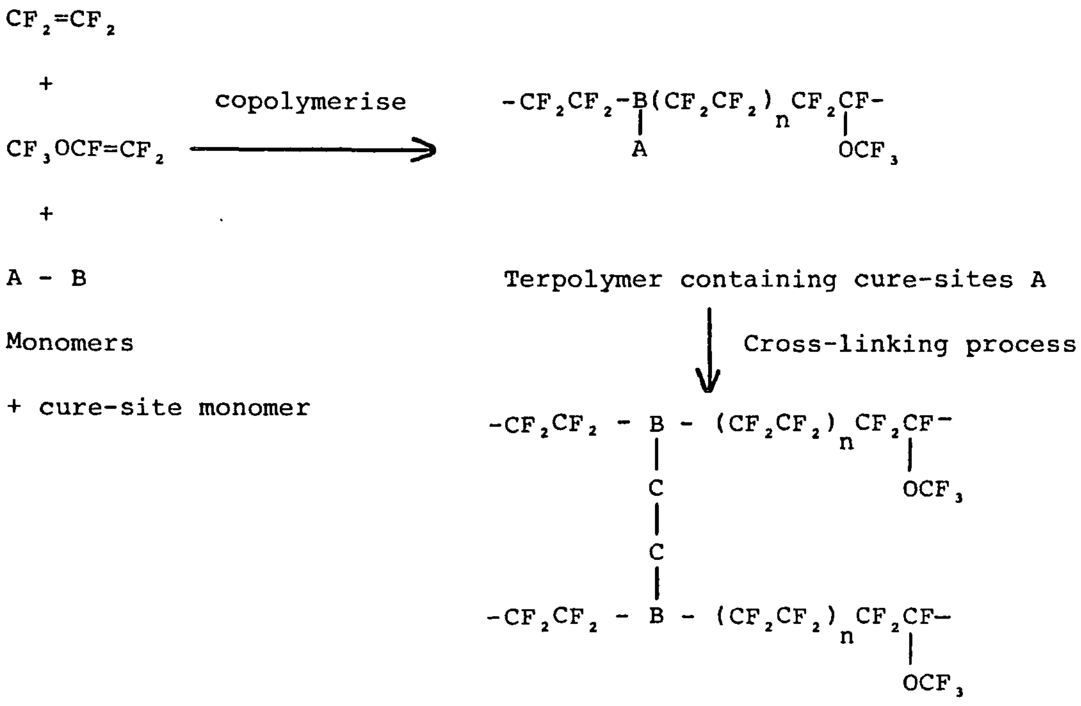


Scheme 1.8

Elastomers of tetrafluoroethylene and propene which have been cured in this manner show good physical properties and are highly resistant to heat (no loss in tensile strength after 60 days at 200°C) and to chemicals, including acids, alkalis and steam.[71] Due to their lower fluorine content, however, they are not as resistant as $CH_2{=}CF_2/CF_3CF{=}CF$ copolymers to swelling by hydrocarbon fuels and oils.

1.36 Incorporation of Cure-Site Monomers

The use of amine and peroxide formulations for the cross-linking of copolymers based on vinylidene fluoride is often problematic, since highly active materials are required which frequently give rise to processing difficulties. Furthermore, copolymers of tetrafluoroethylene and perfluoromethylvinyl ether cannot be cross-linked using nucleophilic curatives, due to their extreme chemical inertness. These difficulties can be overcome by incorporating optimum amounts of a special monomer, containing an active site through which cross-linking can occur. For example, the cure-site monomer A-B can be incorporated into the $CF_2=CF_2/CF_3OCF=CF_2$ copolymer as shown in Scheme 1.9.



Scheme 1.9

This cross-linking methodology is suitable for all fluoropolymers in principle, provided that the cure-site monomer can satisfy several criteria, as follows:

i) During the polymerisation step, the reactivity of the cure-site monomer must not appreciably differ from that of the other monomers, since the cross-link density will contribute to the mechanical properties of the cured product.

ii) The cure-site must not participate in the free radical polymerisation step, since this could lead to substantial chain branching or complete inhibition of the process.

iii) The cure-site must be reactive towards the curing agents so that the cross-links are stable extensions of the polymer system, thereby avoiding the introduction of weak bonds through which chemical and/or thermal degradation could occur.

iv) The cure-site monomer must be relatively easy to synthesize in order to minimise its cost and must also be fairly non-toxic.

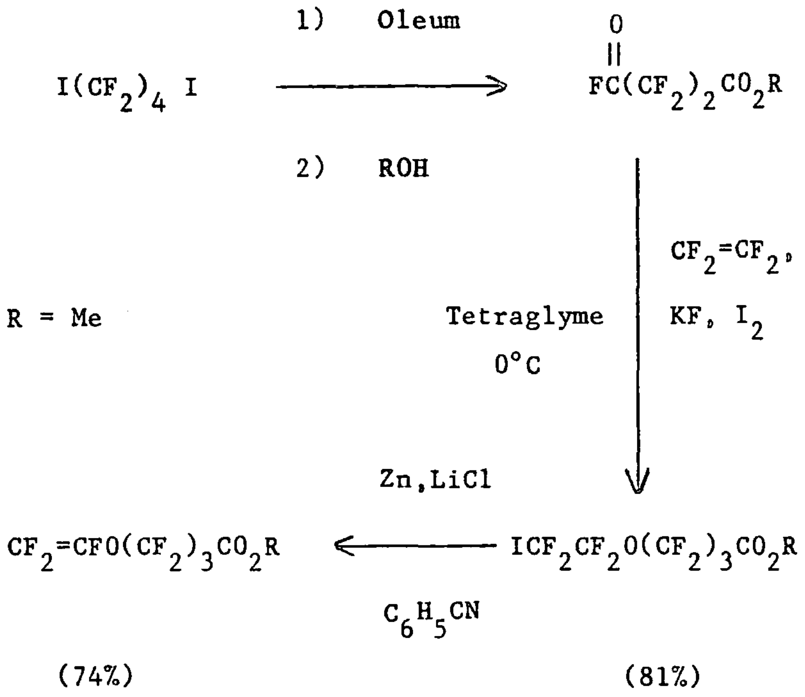
Cure site monomers displaying enhanced receptivity to attack by either free radicals or nucleophilic cross-linking agents have been developed and a discussion of some specific examples is given below:

a) Cure-Sites Responsive to Nucleophilic Cross-linking Agents

Perfluorovinyl ethers of the form $CF_2=CFOR_FA$ are easily incorporated into fluoropolymer chains and several different types have been used as cure-site monomers, e.g. $A = CO_2R$ or OC_6F_5 and $R_F = (CF_2)_n$ or $[CF_2CF(CF_3)O]_nCF_2CF(CF_3)$ where n = 1, 2 or 3.[72,73] Synthetic routes to these compounds are shown in Schemes 1.10 and 1.11.

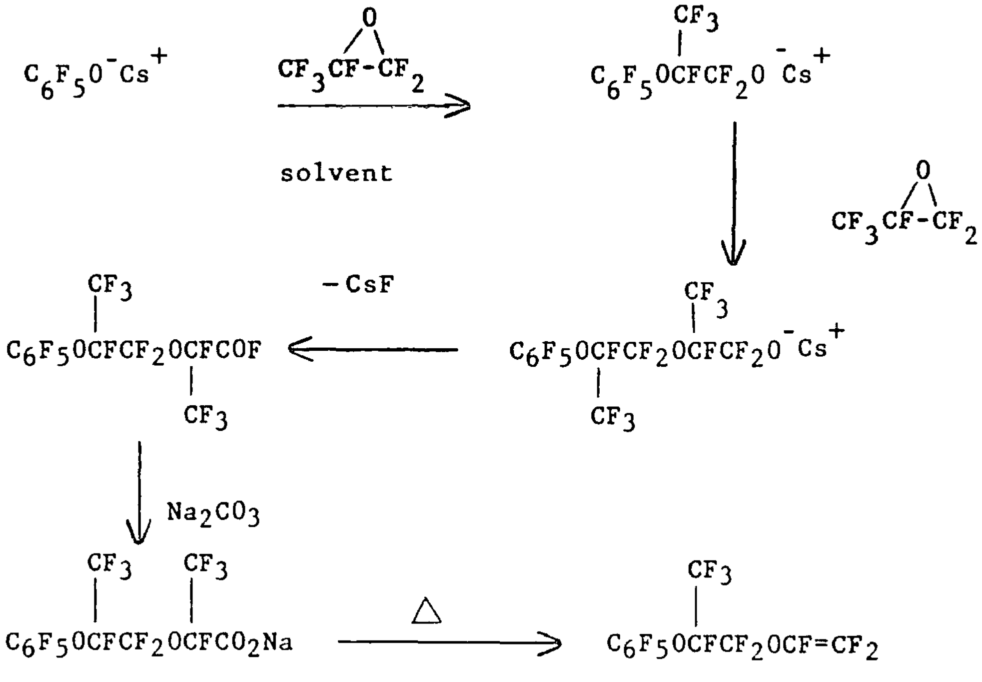
Typically, about 1–4% of the cure-site monomers are incorporated into the fluoropolymer systems and cross-linking is achieved by reaction with nucleophilic reagents such as polyfunctional amines, glycols or phenols. For example, polymers containing a cure-site monomer of the form $CF_2=CFO(CF_2)_nCO_2R$ are presumably cross-linked according to Scheme 1.12.[72]

Synthesis of $CF_2 = CFO(CF_2)_3CO_2R$ [38]

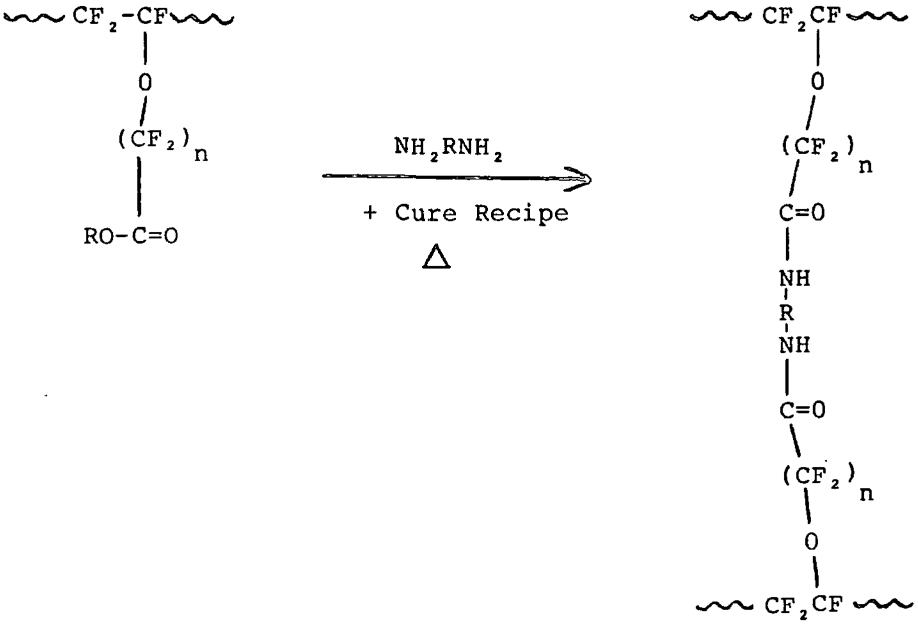


Scheme 1.10

Synthesis of $CF_2=CFOCF_2CF(CF_3)OC_6F_5$ [72]



Scheme 1.11



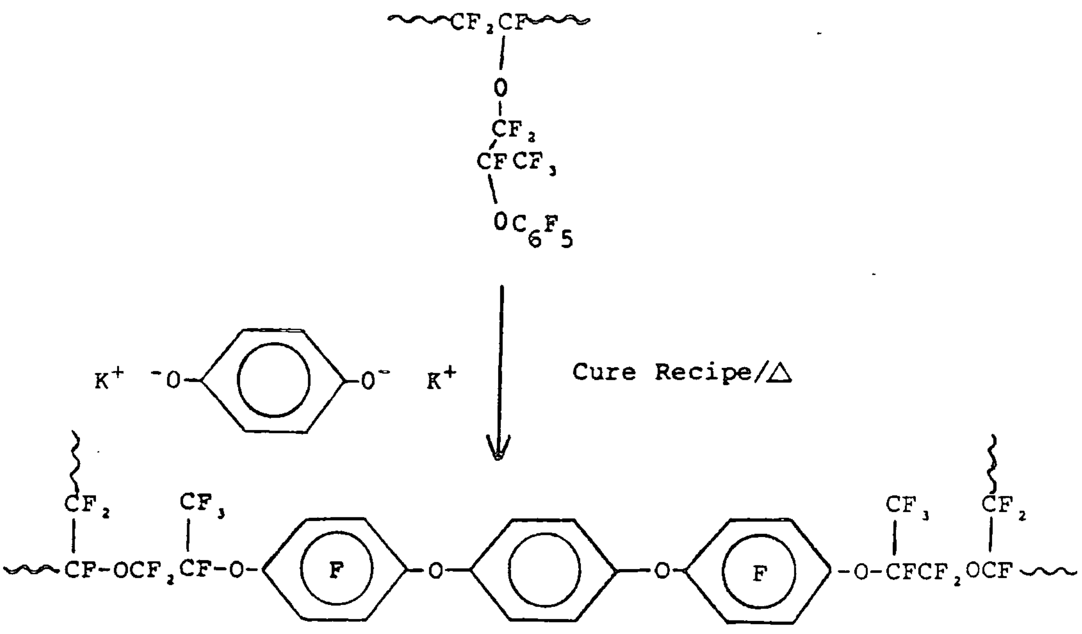
Scheme 1.12

Fluoropolymers containing the active pentafluorophenoxy site are cross-linked by polyamines, such as hexamethylenediamine and tetraethylenepentamine, or salts of polyhydroxyaromatics, e.g. hydroquinone, Bis-phenol A, etc (See Scheme 1.13 for the postulated mechanism).[72,74] A typical curing formulation is shown in Table 1.7.

Table 1.7

Component	pph
Polymer	100
Carbon black	10
MgO	4
Cross-linking salt	3
Polyether accelerator	3

Press-cure: 30 mins at 177°C. Post-cure: Several days at a steadily increasing temp. 150-300°C.



Scheme 1.13

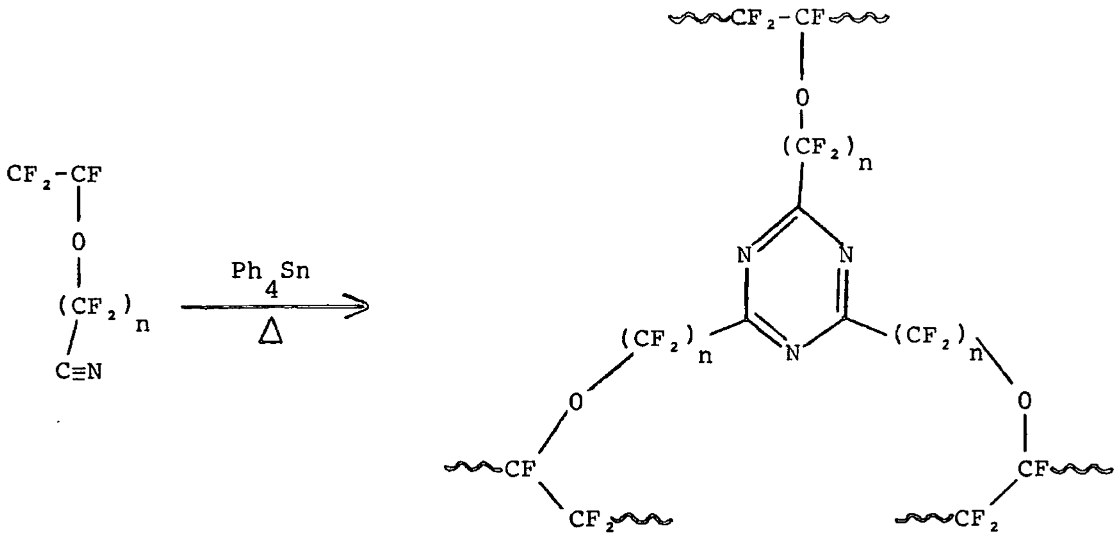
Satisfactory cures are obtained in this way but for polymer chains linked by an ester group (See Scheme 1.12), the possibility of cross-link interchange is reflected in the vulcanizates possessing low compression set resistances.[72] Also, materials containing perfluorophenoxy linkages lose some degree of thermal stability.

b) Nitrile Cure-Sites

Monomers in which the active cure-site is a nitrile group have been used for the cross-linking of fluoropolymers, since they can be easily synthesized by modification of the ester group of the perfluorovinyl ethers discussed in section 1.35a, e.g.[12,75]

$$CF_2{=}CFO(CF_2)_nCO_2CH_3 \xrightarrow[2)P_2O_5/\Delta]{1)NH_3} CF_2{=}CFO(CF_2)_nCN$$

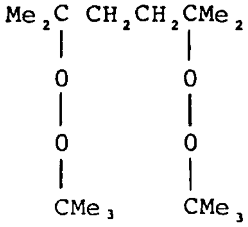
For a typical curing process, the fluoropolymer containing pendant nitrile groups (100pph) is formulated with carbon black (10pph) and tetraphenyl tin (3-6pph). The polymer compound is subjected to a press-cure for 0.5-18h at 160-210°C followed by an air oven post-cure at 200-290°C over several days. The mechanism of cross-linking is believed to be that in which the nitrile groups are converted into triazine units, e.g:



c) Cure-Sites Responsive to Free Radical Cross-Linking Agents

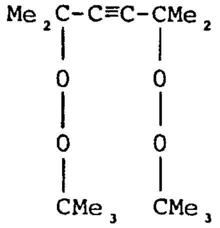
Over the last decade or so cure-site monomers have been developed which, on incorporation into a fluoropolymer, greatly enhance the response to curing by peroxides. This susceptibility to free radical attack is provided by the introduction of bromine containing monomers, such as bromotrifluoroethylene, 3-bromopentafluoroprop-1-ene and 4-bromo- 3,3,4,4- tetrafluorobut-1-ene, amongst others.[64,76,77]

In order to reach an effective state of cure, the fluoropolymer containing the copolymerized cure-site monomer must be compounded with an organic peroxide, a suitable cross-linking coagent and a combination of acid acceptors (See Table 1.8). The peroxides which give the most favourable response are 2,5 - dimethyl - 2,5- di-t- butylperoxyhexane (3) and the analogous hex-3-yne derivative(4).[64]



$Me_2C(OOCMe_3)CH_2CH_2C(OOCMe_3)Me_2$

(3)



$Me_2C(OOCMe_3)-C{\equiv}C-C(OOCMe_3)Me_2$

(4)

Di-tert-butylperoxide also gives good cures but problems with is volatility are restrictive to its utility.

Table 1.8

Component	pph
Copolymer	100
MT carbon black	15-30
Austin black	0-10
Acid acceptor, e.g. MgO and/or $Ca(OH)_2$	3-5
Peroxide	1-6
TIC	1-6

Initial Cure: 1-60 mins at 149-204°C. Post-cure (for maximum heat resistance): 1-48h at 180-300°C.

A number of compounds were examined for their suitability as cross-linking coagents but triallylisocyanurate (TIC) was found to be the most useful.[64] Although other coagents such as triallylcyanurate and diallylacrylamide are similarly effective in forming cross-links, the cured articles possess inferior resistance to compression set and thermal degradation.[77]

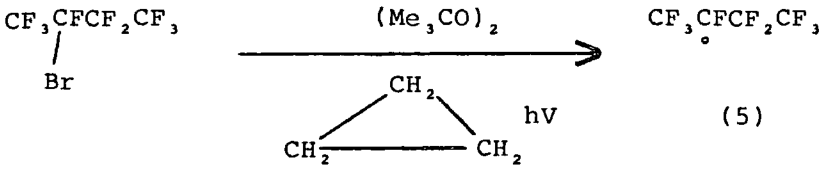
There are several advantages in using this type of curing system:

i) A wide range of fluoropolymers can be cross-linked in this way, many of which would not respond to nucleophilic curatives.

ii) The curing process is rapid and can be carried out at atmospheric pressure. This is in contrast to cross-linking with polyfunctional nucleophilic reagents, in which the compounded fluoropolymers have to be subjected to a press-cure in order to avoid the formation of porous products.

iii) More useful physical properties and increased resistance to chemical degradation can be obtained. Nucleophilic cures have the inherent disadvantage of producing vulcanizates which contain reactive sites. This undesirable feature is avoided using the peroxide curing system.

Studies were carried out in order to determine the mechanism by which the peroxide induced cross-linking of polymers containing bromotrifluoroethylene occurs. The simplest way of generating a fluorinated alkyl radical from a fluoroalkylbromide involves the abstraction of bromine. Thus, using 2-bromononafluorobutane as a model for bromine containing fluoropolymers, treatment with UV light and di-t-butyl peroxide in cyclopropane gave an intense ESR spectrum due to formation of the radical. (5)[77]



(5)

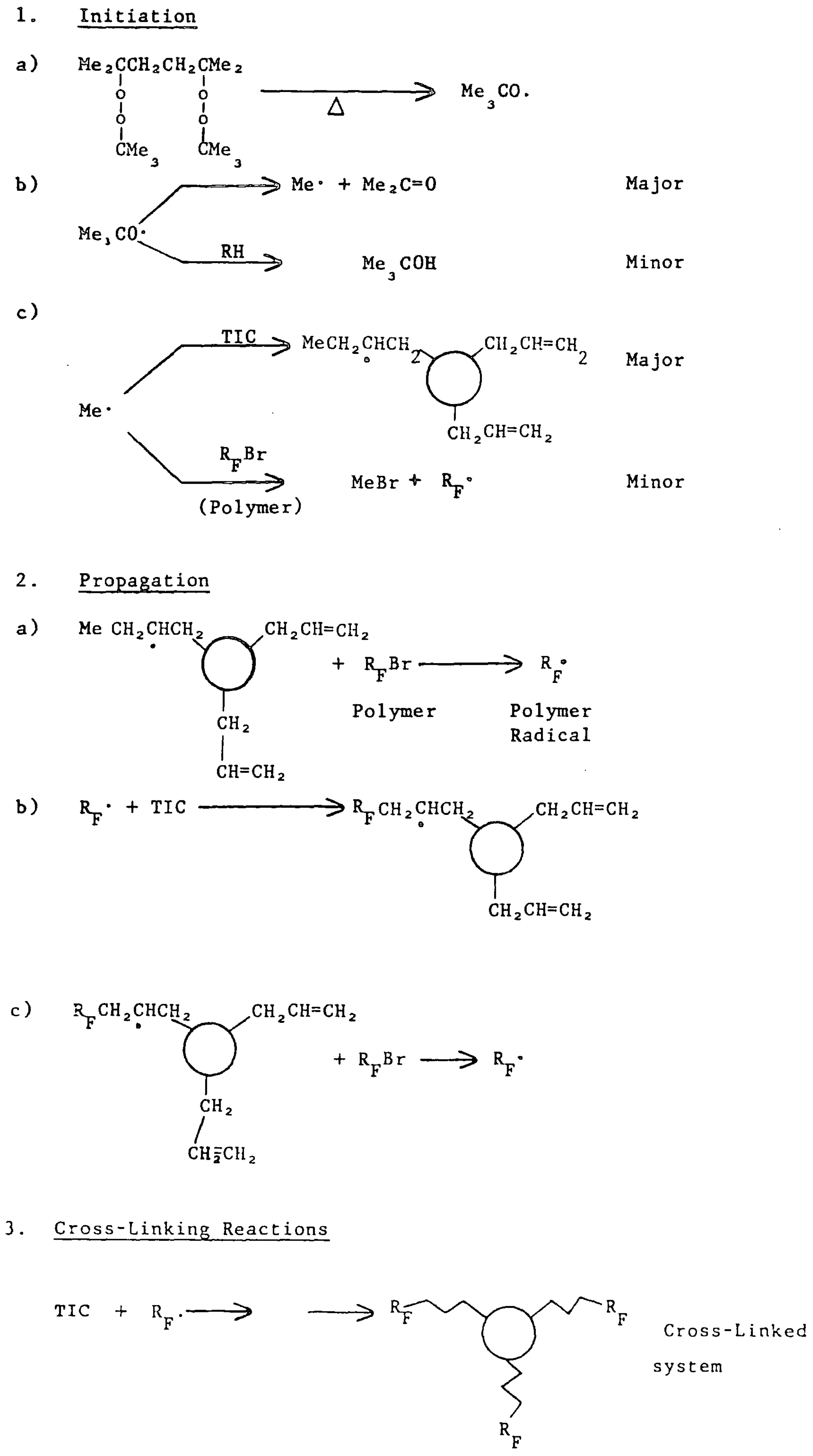
Further investigations to determine the nature and amount of volatiles produced during the curing process indicated the manner in which peroxide decomposition and cross-link formation probably occur (See Table 1.9 and Scheme 1.14).[77]

Table 1.9

Relative Amounts of Volatile Materials Generated During Curing

Compound	Amount Produced (%)	Observations
Water	54	The only product when peroxide is omitted
Acetone	31	
Methane	9	
t-Butyl alcohol	3	
Isobutene	1	
Methyl bromide	1	50-100% greater on omission of TIC
Others	1	

Ingredients: Polymer 100; Carbon black 30; $Ca(OH)_2$ 4; peroxide 4; TIC 4.


1. Initiation
a)
Me₂CCH₂CH₂CMe₂
O
O
CMe₃
CMe₃
Δ
Me₃CO.
b)
Me₃CO·
Me· + Me₂C=O
Major
RH
Me₃COH
Minor
c)
Me·
TIC
MeCH₂CHCH₂
CH₂CH=CH₂
CH₂CH=CH₂
Major
R_FBr
(Polymer)
MeBr + R_F·
Minor
2. Propagation
a)
Me CH₂CHCH₂
CH₂CH=CH₂
CH₂
CH=CH₂
+ R_FBr
R_F·
Polymer
Polymer Radical
b)
R_F· + TIC
R_FCH₂CHCH₂
CH₂CH=CH₂
CH₂CH=CH₂
c)
R_FCH₂CHCH₂
CH₂CH=CH₂
CH₂
CH=CH₂
+ R_FBr
R_F·
3. Cross-Linking Reactions
TIC + R_F·
R_F
R_F
R_F
Cross-Linked system

Scheme 1.14

1.4 Fluoroelastomers Based on Polymers with Heteroatom Backbones

There are three major classes of fluoroelastomer based on polymers containing heteroatom backbones:

i) Perfluoroalkylenetriazine elastomers

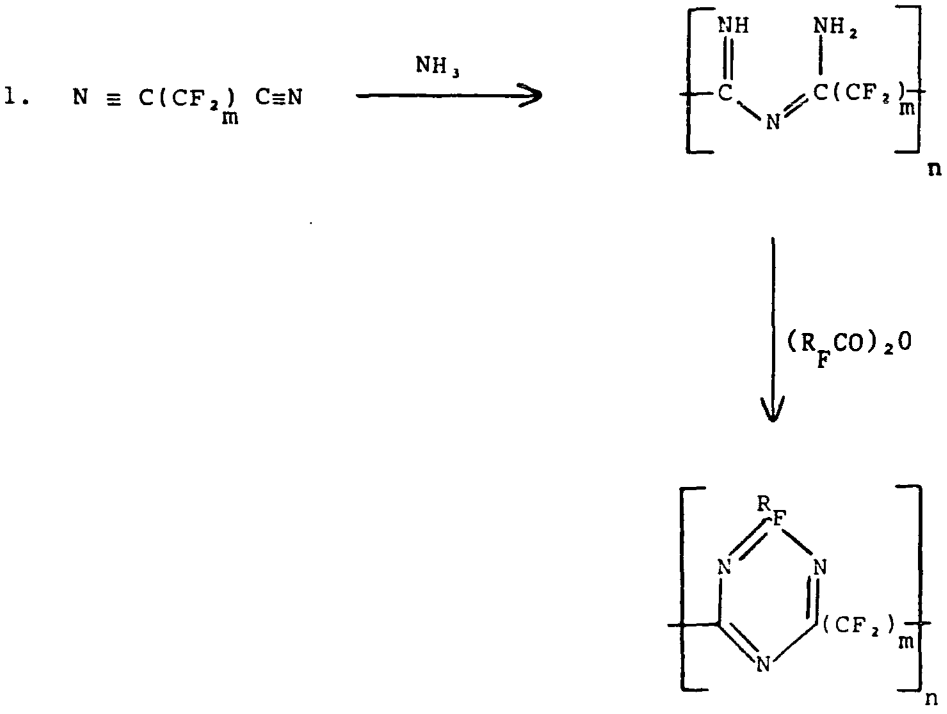
ii) Nitroso rubbers

iii) Fluorothiocarbonyl elastomers

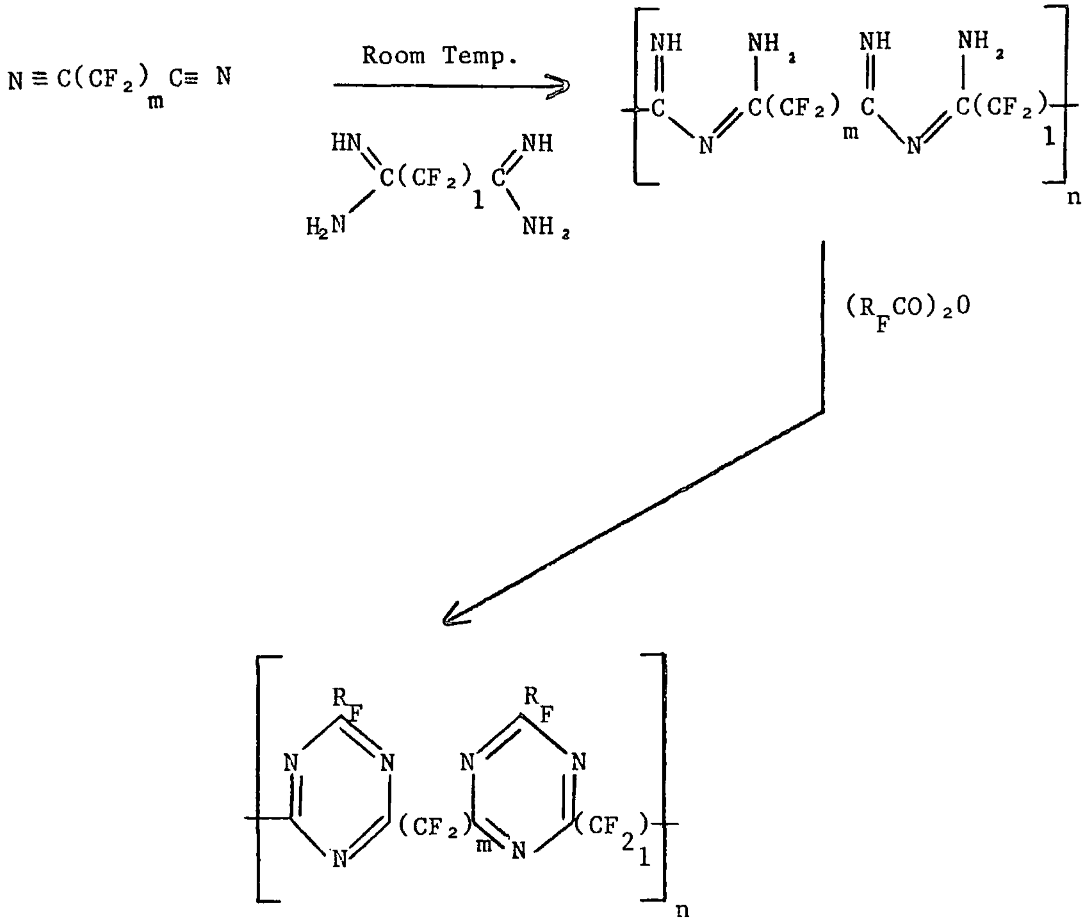
A dicussion of each class is given below:

1.41 Perfluoroalkylenetriazine Elastomers

It has been known for some time that tris(perfluoroalkyl)-s-triazines are very resistant to thermal and chemical degradation.[78-80] This prompted interest in the synthesis of polymers based on this unit, since it was hoped that these materials would display similar stability in aggressive environments.[81] The most successful routes to linear poly(alkylenetriazine)s are outlined in Scheme 1.15 involving the synthesis of poly(imidoylamidine) polymers, which then undergo ring closure reactions along their chain lengths by treatment with an acid anhydride.[82]

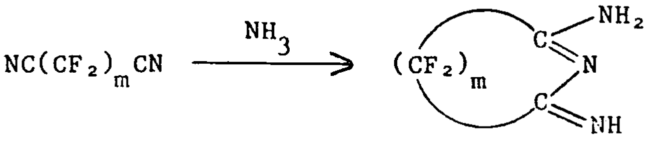


2.



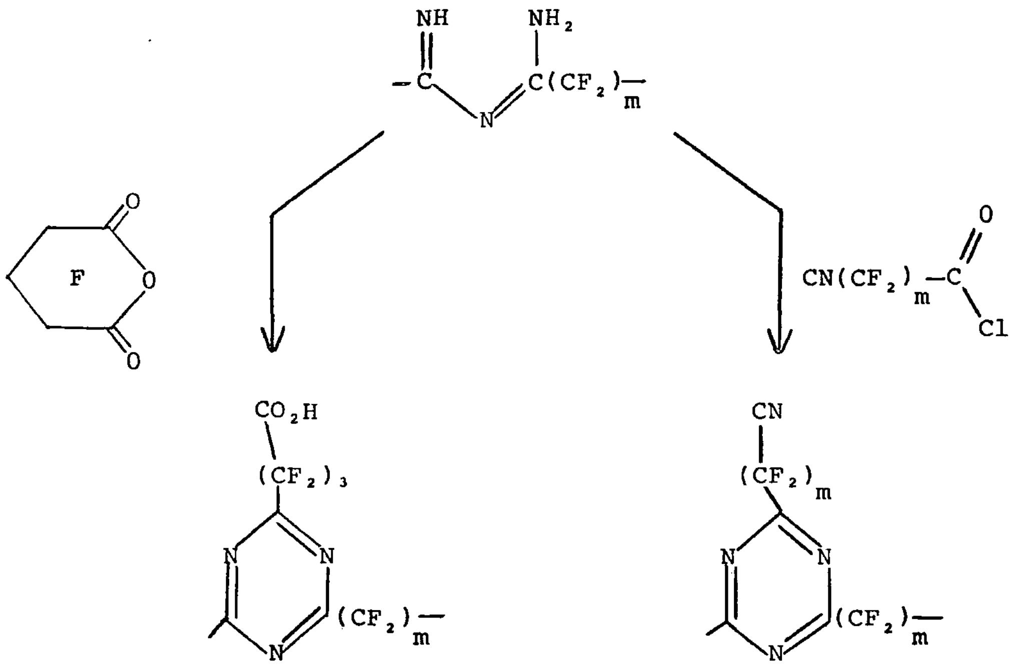
Scheme 1.15

Since the triazine units are sterically demanding, it is necessary that the perfluoroalkylene links between the rings contain at least five carbon atoms (l and m $\geqslant$ 5). Otherwise the materials do not display good elastomeric properties and problems arise in preparing the requisite poly(imidoylamidine)s, since the dinitriles tend to cyclise when treated with ammonia, e.g.:[81]



m = 2,3,4

In order to cross-link the triazine polymers, cure-sites need to be incorporated and this is achieved by adding a small amount of a cyclic anhydride or a ω - cyanoacyl chloride to the poly(imidoylamidine) during the ring closure step. This leads to a proportion of triazine rings having pendant carboxyl or nitrile cure-sites (See Scheme 1.16)[83,84]



Scheme 1.16

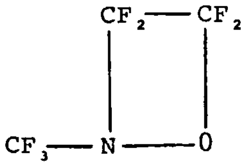
The carboxyl groups can be converted to their silver salts and subsequent heat treatment leads to cross-linking formation.[57] Polymers containing nitrile cure-sites are cross-linked by metal oxides, e.g. silver oxide or lead oxide. It is believed that these materials catalyze the formation of triazine rings (cf. section 1.36b).[57,83]

Poly(perfluoroalkylenetriazine) polymers are not commercially available mainly as a consequence of the difficulty in carrying out reproducible syntheses, together with the high cost of requisite perfluorinated starting materials.

1.42 Nitroso Rubbers

Many copolymers belonging to the family of nitroso rubbers have been prepared and they have been the focus of much interest, mainly because of their potential value as chemically resistant elastomers for low temperature applications, especially in the aerospace industry. A number of detailed reviews on nitroso rubbers have been published.[85-87]

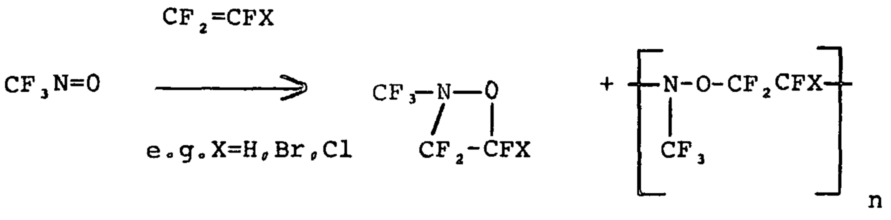
The best material in this class has been found to be the copolymer of tetrafluoroethylene and perfluoronitrosomethane which was first prepared in 1955.[88-90] It was discovered that on mixing equal amounts of the two monomers, spontaneous reaction occurred giving a viscous polymeric oil and heptafluoro-2-methyl -1,2-oxazetidine (6). The yields of the



(6)

products were found to be dependent on temperature. Low temperatures tend to favour polymer formation (65% at 45°C), whereas at high temperatures (> 100°C) the heterocycle is the only product. Detailed studies demonstrated that the polymerisation process proceeds via free-radical intermediates, whereas the heterocycle (6) is formed by a homogeneous bimolecular reaction.[91-93] Further work indicated that a significant proportion of the copolymers prepared in this manner consist of chains of relatively low molecular weight ($\bar{M}_v < 5000$) and that this may be the cause of their low tensile strengths.[94]

Other fluoroalkenes can be copolymerised with perfluoronitrosomethane in an analogous way.[95-97] For unsymmetrical alkenes, addition to the N=O bond to form the heterocyle (7) proceeds with reversed regioselectivity to that observed for the free radical polymerisation process, so the copolymer is largely composed of the structure (8).



(7) (8)

The nature of the fluoroalkene has a marked effect on the rate of the polymerisation reactions and it was found that the relative reactivities of the monomers decreases as the fluorine content is lowered.[91] Conversely, altering the structure of the nitroso monomer does not have a significant effect on the rate of reaction provided the nitroso group is directly bonded to a difluoromethylene unit.

The $CF_2=CF_2/CF_3NO$ copolymer, which is usually referred to as nitroso rubber, cannot be cross-linked using traditional curing systems due to its chemical inertness. However, termonomers containing cure-sites can be incorporated and it was found that the most useful are of the nitroso type.[87] The preferred active cure-site is a carboxyl group, which allows for the introduction of cross-links by a number of reagents, including metal oxides, chromium tris(perfluorocarboxylate)s and epoxy compounds.[57,99] Thus, the most successful material in this class is the terpolymer of tetrafluoroethylene, perfluoronitrosomethane and perfluoro (nitrosobutyric acid), $HO_2C(CF_2)_3NO$, which is known as carboxy nitroso rubber (CNR) and is available on pilot-plant scale.[99]

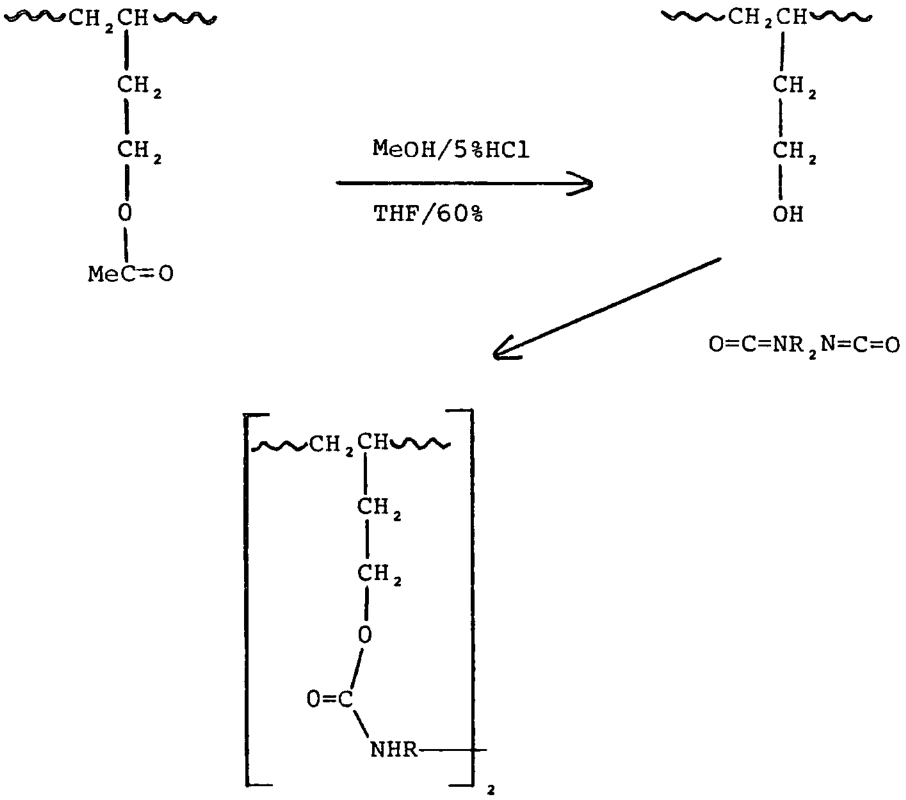
1.43 Fluorothiocarbonyl Elastomers

Considerable interest has centred on fluorinated thiocarbonyl compounds since they can undergo facile polymerisation to yield materials possessing unusual properties.[12,100,101] The most intensely studied material in this class is poly(thiocarbonyl fluoride), $(CF_2S)_n$ although polymers of thioacyl fluorides ($R_FCF{=}S$) and of fluorothioketones (R_FCSR_F) have been investigated also. A detailed review on fluorothiocarbonyl compounds is available.[102]

Thiocarbonyl fluoride can undergo polymerisation by either free radical or anionic chain mechanisms.[100,101] The raw polymer is a tough, highly resilient material which displays elastomeric properties and can be pressed into films or moulded into required shapes.[102] It has an extremely low glass transition temperature (T_g = -118°C), but potential applications are limited by the fact that it gradually crystallizes on storage at room temperature (T_m=35°C) and that depolymerisation occurs at temperatures above 175°C. The chemical resistance of the polymer is generally good. It is unaffected by boiling sodium hydroxide solution or short term contact with boiling nitric acid. However, it is severely degraded by amines.[102]

Although poly(thiocarbonyl fluoride) displays elastomeric properties attempts were made in order to cure it. Compounding of the polymer with benzoyl peroxide and divinylbenzene followed by a press-cure at 100°C yielded a vulcanizate which showed good compression set and abrasion resistances.[102] However, the undesirable properties inherent in the raw polymer are still present in the cured material, such as the poor resistance to amines and slow crystallization at room temperature.

Crystallization of the thiocarbonyl fluoride polymer can be avoided by incorporation of small amounts of a vinyl comonomer into the system, such as 3-butenyl acetate or allyl chloroformate.[101,103] Copolymers containing the former compound can be modified so that the pendant groups contain a functional hydroxyl group and by treatment with di-isocyanates cross-links can be formed (presumably by the mechanism given in Scheme 1.17). Curing of copolymers containing allyl chloroformate can be carried out by a press-cure operation at 100°C, using zinc oxide (<u>ca</u> 2-5 mol%).



Scheme 1.17

Due to limitations in their resistance to chemical and thermal degradation, the fluorothiocarbonyl elastomers have never attained commercial availability.

1.5 Fluoroelastomers Based on Polymers with Inorganic Backbones

The two major types of fluoroelastomer in this category are fluorosilicones and fluoroalkoxyphosphazenes

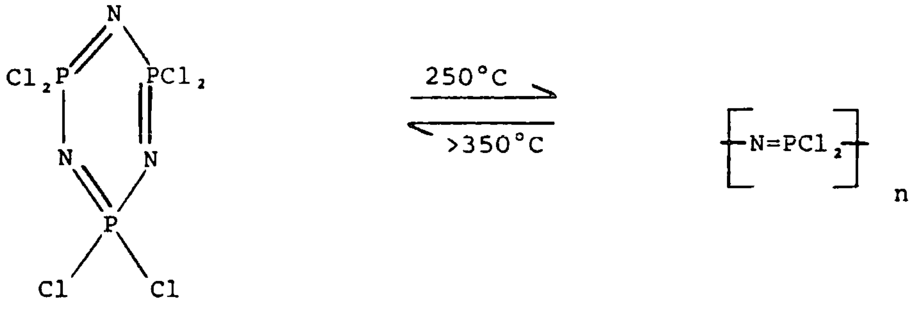
1.51 Fluoroalkoxyphosphazenes

Compounds containing the basic unit $-N=\overset{/}{\underset{\backslash}{P}}-$ are called phosphazenes and both cyclic and linear types have been known for some time. They are obtained by the reaction of ammonium chloride or ammonia with phosphorus pentachloride.[104-106]

$$nNH_4Cl + nPCl_5 \longrightarrow \left[N=PCl_2\right]_n + 4nHCl$$

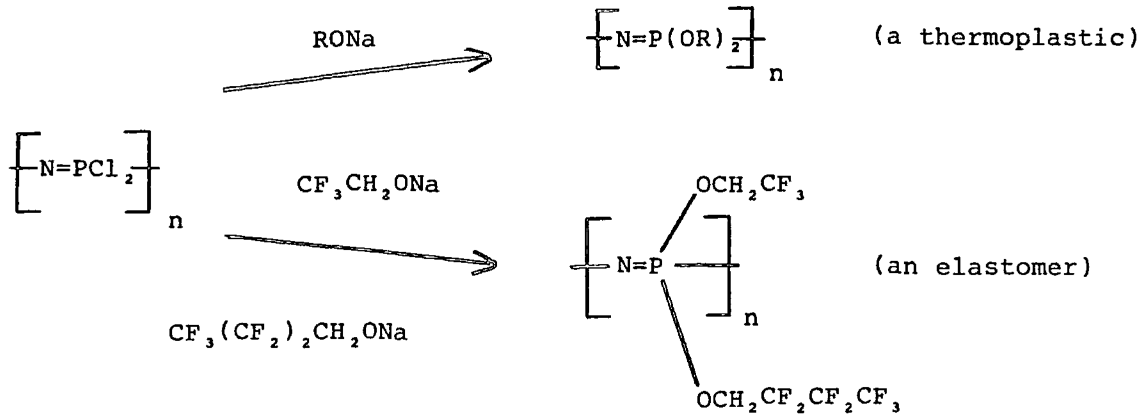
By regulating the reaction conditions the yields of the most useful cyclic products, where n=3 and 4, can be optimized (<u>ca</u> 60% and 25% respectively).[107,108]

Ring opening polymerisation of the cyclic oligomers occurs between 230 - 250°C and it was found that the rate decreases with increasing ring size.[104,109] The most satisfactory polymers are obtained by heating the trimer (9) under vacuum at 250°C.[110]



(9)

Poly(dichlorophosphazene) prepared in this way is amenable to displacement of its chlorine atoms, since it can undergo treatment with a nucleophilic reagent while dissolved in a suitable solvent such as benzene, toluene or THF. (See Scheme 1.18)[110-115]



Scheme 1.18

A significant number of different alkoxyphosphazene polymers can be synthesized by varying the alkoxide, or by utilizing more than one alkoxide materials with different pendant groups can be formed. Thus, reaction of two fluoroalkoxides of different carbon chain lengths with poly(dichlorophosphazene) produces a fluoroelastomer. Much of the available literature refers to fluoroelastomers carrying the pendant groups OCH_2CF_3 + OCH_2 $(CF_2)_3$ CHF_2 and OCH_2CF_3 + OCH_2-$(CF_2)_2$ CF_3.[112,116-118] Elastomers based on materials of this type are commercially available under the trademark PNF (Firestone, USA).

In order to optimise the physical properties of poly(fluoroalkoxyphosphazene) polymers for particular applications they can be cured by the use of organic peroxides, sulphur or high-energy radiation.[117,119] A basic formulation consists of the polymer (100 pph), a reinforcing filler (e.g. silica or carbon blacks) (30 pph), magnesium oxide (6 pph), a stabilizer (e.g. zinc - 8- quinolinolate (1-2 pph) and a curing agent (1-6 pph).

Compared to poly (alkoxyphosphazene) polymers the fluoroalkoxy derivatives are more resistant to chemical and thermal degradation. The major advantage of these materials over fluorocarbon elastomers is their ability to function at much lower temperatures. For example the glass transition temperature of the raw fluoroalkoxyphosphazene polymer containing the pendant groups CF_3CH_2O and $HCF_2(CF_2)_3\,CH_2O$ is - 68°C.[117]

1.52 Fluorosilicones

The sites to which fluorine can be bonded in polyalkylsiloxanes are limited due to the susceptibility of α and β substituents to undergo hydrolytic or thermal degradation.

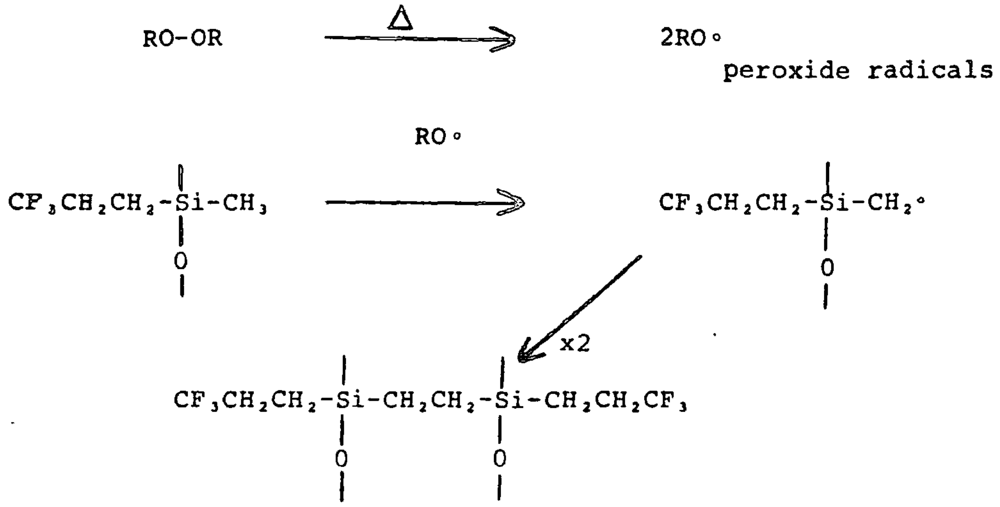
$$R_3Si\text{-}CF_3 \longrightarrow nR_3SiF + (CF_2)_n$$

$$R_3Si\text{-}CH_2CF_3 \longrightarrow R_3SiF + CH_2{=}CF_2$$

Consequently the most useful site in which fluorine can be bonded is γ to silicon, so that polymers of the form $[CH_3Si(CH_2CH_2R_F)O]_n$ have been prepared, where $R_F = CF_3$, C_2F_5 or $n\text{-}C_3F_7$.[120-123] Since the nature of the perfluoroalkyl group does not significantly affect the properties of polyfluoroalkylsiloxanes investigations have centred on developing the polymer in which $R_F{=}CF_3$. Materials based on this polymer are commercially available and are designated 'Silastic' LS (Dow Corning, USA).

As for other fluoroelastomers, the fluorosilicones can be formulated to provide specific properties for a number of applications.[15] They are usually compounded with <u>ca</u> 1 pph of a peroxide curing agent, as well as upto 50 pph of silica fillers and hydroxy containing silicone oils.[123] The mechanism of cross-linking involves the combination of polymer radicals to create new carbon-carbon bonds. Formation of the polymer radicals is achieved by the peroxide, either by abstraction of hydrogen from methyl groups or addition to a vinyl cure-site (See Scheme 1.19).[15]

Although the incorporation of fluorine into the poly(alkylsiloxane)s is rather limited, the cured materials are significantly more resistant to swelling by solvents than their hydrocarbon analogues. Furthermore, the inherent thermal stability and low temperature characteristics of silicone elastomers are retained on the introduction of fluorine.[14]



Scheme 1.19

1.6 Properties and Applications of Fluoroelastomers

As a broad class fluoroelastomers display a remarkable resistance to chemical and thermal degradation, flame propagation, oxidation and weathering. The chemical resistance of the materials is usually dependent upon their fluorine content so that elastomers based on tetrafluoroethylene and perfluoromethylvinyl ether are unaffected by most chemicals and solvents.

The selection of a fluoroelastomer for a given application is often a compromise between a number of different factors, including its cost and the optimum properties which it confers upon the system. Fluoroelastomers are utilized in specialized applications where high performance is required since their relatively high cost precludes widespread use but their excellent mechanical properties and high resistance to degradation in aggressive environments is outstanding when compared to other classes of elastomer. Fluoroelastomers are most widely used in industry for sealing applications such as O-rings, but they also find major use as diaphragms for pumps, industrial rolls, tubing, coatings and pipe expansion joints.

The characteristics of some fluoroelastomers are given in Table 1.10.

Table 1.10

Elastomer	Continuous Service Temp/°C	Fluid and Chemical Resistance		Useful Properties
		Good	Poor	
$CF_3OCF=CF_2$/ $CF_2=CF_2$	315	Almost all solvents and liquids	Some highly fluorinated solvents	Unmatched chemical, solvent and oxidation resistance
$CF_3CF=CF_2$/ $CH_2=CF_2$	200	hydrocarbons	ketones	Excellent weather resistance
		inorganic acids	esters	Low compression set
		chloro solvents	amines	Low permeability to gase
$CF_2=CFCl$/ $CH_2=CF_2$	175	Generally less resistant than $CH_2=CF_2$/ $CF_3CF=CF_2$ elastomers		High tensile strength High resistance to oxidising agents
$CF_2=CF_2$/ $CH_3CH=CH_2$	200	inorganic acids and bases	benzene	Low permeability to gase
		H_2O_2		Good resistance to compression set
Triazine Elastomers	345	Hydrocarbons strong acids	amines caustic solutions	High tensile strengths at elevated temperatures
Nitroso rubber CNR	200	ozone	amines	Excellent weather resistance
		hydrocarbons		Low temp.serviceability (ca-40°C)
		HNO_3		Non-flammable even in oxygen
Fluorosilicones Silastic LS	260	Strong acids Most common Solvents	ketones esters	Good mechanical properti at high temperatures. Low temp.flexibility (ca-54°C)
Phosphonitrilic elastomers PNF	174	hydrocarbons dilute acids and alkalis	esters ketones ethers	non-flammable Low temp.flexibility (down to ca-68°C)

CHAPTER TWO

SYNTHESIS AND SPECTROSCOPIC EXAMINATION OF SATURATED MODEL COMPOUNDS

2.1 Introduction

It is often difficult to determine the nature of chemical reactions occurring in a bulk polymer system with any degree of certainty. Consequently, model studies offer an opportunity to provide a framework of understanding on which to base more firmly, discussions of chemistry carried out on the polymer. This research project is concerned with the synthesis and chemistry of model compounds related to the $CH_2=CF_2/CF_3CF=CF_2$ copolymer system. Investigations have mainly concentrated on discovering the mechanism by which the cross-linking of these copolymers occurs, especially using nucleophilic curatives such as Bisphenol AF (See Section 1.34). These studies have led to the discovery of some interesting and unusual reactions of the model compounds and further work has been carried out in order to demonstrate the potential chemistry of this copolymer system.

2.2 Structure and Routes to the Saturated Model Compounds

For $CH_2=CF_2/CF_3CF=CF_2$ copolymers the structural arrangements (10),(10a),(11) and (11a) are present, although (10) and (11) predominate.[49] The ratio of (10):(10a) and (11):(11a) is constant but the ratio of [(10)+(10a)] : [(11)+(11a)] obviously varies with monomer ratios. Therefore, model compounds which incorporate structures (10) and (11) have been synthesized. The simplest model compounds are of the type

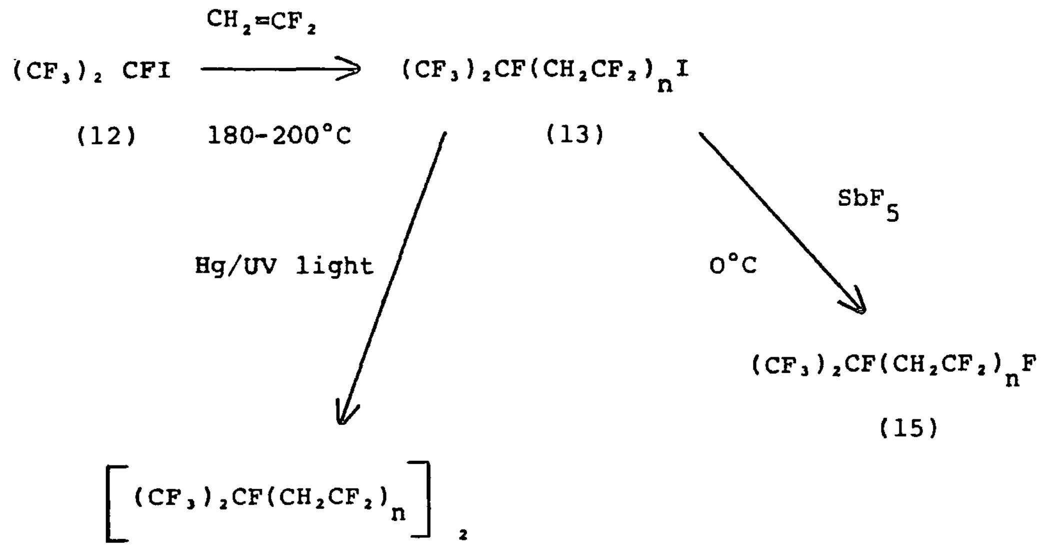
$\left[CH_2CF_2CH_2CF_2\right]_{0.95}$ $\left[CH_2CF_2CF_2CH_2\right]_{0.05}$

(10) (10a)

$\left[CF_2CF(CF_3)CH_2CF_2\right]_{0.93}$ $\left[CF(CF_3)CF_2CH_2CF_2\right]_{0.07}$

(11) (11a)

(14) and (15) and they have been prepared by the route outlined in Scheme 2.1.



(14)

Scheme 2.1

More complex model compounds have been obtained by further development of this synthetic approach and these are discussed below.

2.3 Synthesis of Fluoroalkyl Iodides

2.31 Heptafluoro-2-iodopropane (12)

Heptafluoro-2-iodopropane (12) can be synthesized from hexafluoropropane by formal addition of iodine fluoride to the carbon-carbon double bond.[124] The most convenient preparative system, which was developed earlier in our laboratory, involves the use of a mixture of iodine and iodine pentafluoride in proportions equivalent to IF stoichiometry.[125-126]

$$CF_3CF{=}CF_2 \xrightarrow[150^\circ C/24h]{IF_5/I_2} (CF_3)_2CFI$$

(12)

During the course of this work the reactions were carried out in a stainless steel autoclave under autogenous pressure and gave yields between 94 and 98%.

2.32 $(CF_3)_2CF(CH_2CF_2)_nI$ (13)

Heptafluoro-2-iodopropane is a useful source of tertiary fluorine since at elevated temperatures homolytic cleavage of the C-I bond occurs. Thus, it can undergo successive addition to suitable fluoroalkenes and by using vinylidene fluoride, the carbon backbone of the model compounds can be constructed in this way.[127-129] The reaction is outlined in Scheme 2.2 in which free-radical addition of the propagating fluoroalkyl radical to vinylidene fluoride proceeds preferentially at the methylene unit. This largely leads to telomer radicals of the form (16) in which the unpaired electron is situated on a difluoromethylene carbon rather than the relatively less stabilising methylene carbon.[130] However, each of the telomer iodides produced in this way contain _ca_ 5% of the corresponding regio-isomer $R_FCF_2CH_2I$.

Initiation $\quad (CF_3)_2CFI \xrightarrow[\Delta]{} (CF_3)_2CF\bullet + I\bullet$

(12)

Propagation $\quad (CF_3)_2\dot{C}F + (n+1)CH_2{=}CF_2 \longrightarrow (CF_3)_2CF(CH_2CF_2)_nCH_2\dot{C}F_2$

(16)

Chain Transfer

$$(CF_3)_2CF(CH_2CF_2)_nCH_2\dot{C}F_2 + (CF_3)_2CFI$$

$$\longrightarrow (CF_3)_2CF(CH_2CF_2)_nCH_2CF_2I + (CF_3)_2\dot{C}F$$

(13)

Scheme 2.2

Since heptafluoro-2-iodopropane is an efficient chain transfer agent the telomer iodide products usually contained between one and five vinylidene fluoride units. The actual yields of each compound were regulated by varying the alkene:telogen ratio, together with the duration and temperature of the reaction (See Table 2.1).

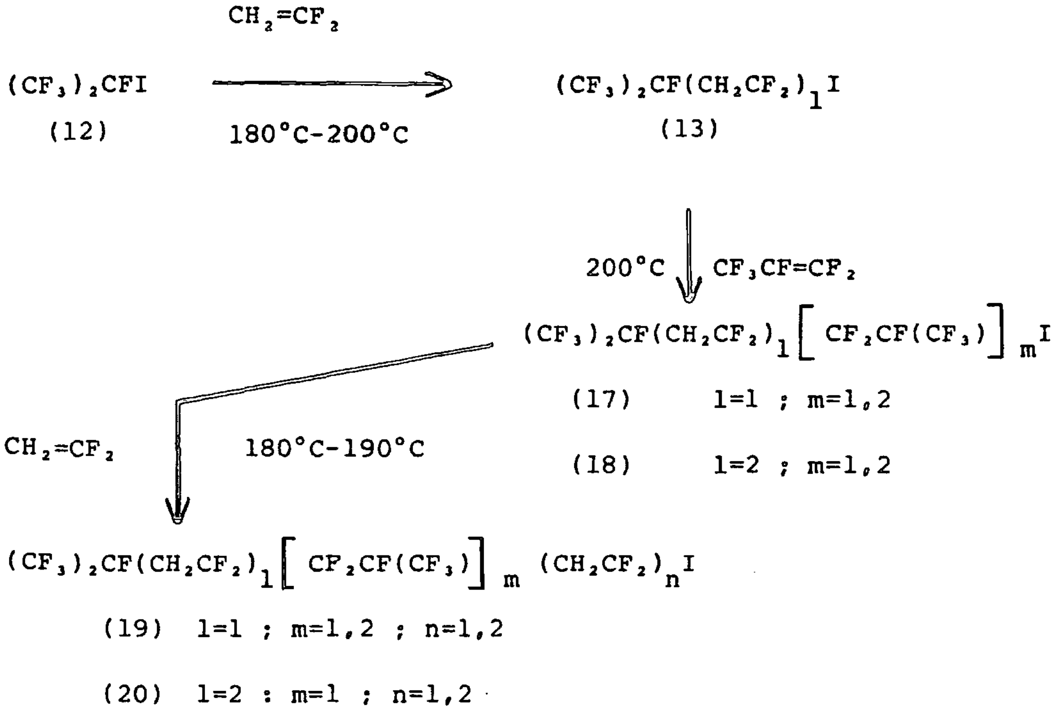
Table 2.1

Alkene/Telogen ratio	Time/h	Temp/°C	Approx. molar composition of (13)/%				
			n=1	n=2	n=3	n=4	n=5
3.6	36	190	9	27	36	23	3
1.9	24	185	44	37	10	5	
1.0	24	185	75	21	2		

Although the telomerisation reactions were initially carried out in nickel or stainless steel autoclaves, it was found that Hastelloy tubes (principally composed of nickel (51%), chromium (17%), molybdenum (17%), iron (7%) and tungsten (5%)) gave products which were the most iodine free.

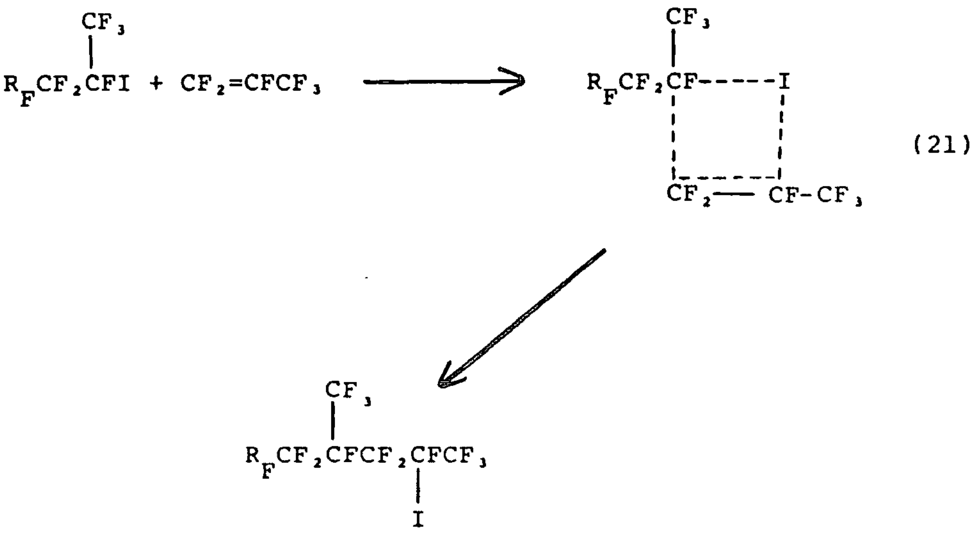
2.33 $(CF_3)_2CF(CH_2CF_2)_l\left[CF_2CF(CF_3)\right]_m(CH_2CF_2)_n\,I$ (19-20)

More complex telomer iodides were synthesized by a series of additions to vinylidene fluoride and hexafluoropropene, as outlined in Scheme 2.3. The products were separated by fractional distillation after each step.



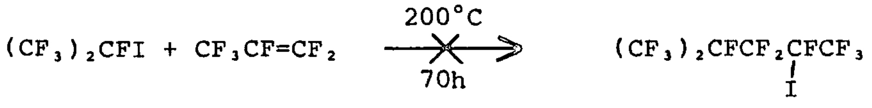
Scheme 2.3

Free-radical additions to HFP proceeded by attack on the difluoromethylene unit. Significant amounts of telomer iodides containing the sequence HFP-HFP were produced, e.g. (17) and (18) where m = 2. Since HFP does not undergo facile homopolymerisation[131] it has been suggested that these products are formed via a cyclic transition state of the type (21) shown in Scheme 2.4.[132]



Scheme 2.4

In contrast to these observations, however, no reaction occurred on heating heptafluoro-2-iodopropane (12) with HFP under identical conditions, i.e. the corresponding telomer (22) was not found.



$$\underset{(12)}{(CF_3)_2CFI} + CF_3CF{=}CF_2 \xrightarrow[70h]{200°C} \underset{(22)}{(CF_3)_2CFCF_2\underset{\displaystyle I}{C}FCF_3}$$

2.34 $(CF_3)_2CF(CHFCF_2)_nI$ (23)

The telomerization reaction between heptafluoro-2-iodopropane and trifluoroethylene gave a range of telomer iodide products, where n depended on the reaction conditions as for the analogous process employing vinylidene fluoride.[133]

$$\underset{(12)}{(CF_3)_2CFI} \xrightarrow[185°C,24h]{CHF=CF_2} \underset{(23)}{(CF_3)_2CF(CHFCF_2)_nI} \quad \begin{array}{l} n=1\ (25\%) \\ n=2\ (38\%) \\ +\text{ Higher telomers} \\ \text{for alkene/telogen} = 2.6 \end{array}$$

The reactions were slightly more complex than that involving vinylidene fluoride and heptafluoro-2-iodopropane for two reasons:

i) Addition of the propagating fluoroalkyl radicals to trifluoroethylene is not regiospecific,[134,135] i.e. both steps 1. and 2. occur.

$$R_F\cdot + CHF{=}CF_2 \begin{array}{l} \xrightarrow{1} R_FCHFCF_2\cdot \quad (24) \\ \xrightarrow[2]{} R_FCF_2CHF\cdot \quad (25) \end{array}$$

The ratio (24)/(25) is <u>ca</u> 5

ii) For each trifluoroethylene unit in the telomer iodides there is one chiral centre. Hence, for a given value of n there can be $2^{(n-1)}$ observable diastereoisomers for each regioisomer.

2.4 Synthesis of Model Compounds

2.41 Fluorodeiodination of the Telomer Iodides

Many reagents are available which can effect the fluorodeiodination of fluoroalkyl iodides, e.g.:

$$C_2F_5CFICH_2C_3F_7 \xrightarrow[130^\circ C]{HF} C_2F_5CF_2CH_2C_3F_7 \qquad (53\%)^{136}$$

$$CF_3CF_2CF_2CF_2CFICF_3 \xrightarrow[260^\circ C-290^\circ C]{CoF_3} CF_3(CF_2)_4CF_3 \qquad (75\%)^{132}$$

$$CF_3CF_2CH_2CF_2I \xrightarrow[140^\circ C]{Hg_2F_2} CF_3CF_2CH_2CF_3 \qquad (48\%)^{137}$$

$$R_FCH_2CF_2I \xrightarrow[\text{Room temp.}]{SbCl_2F_3} R_FCH_2CF_3 \qquad (71\%)^{127,138}$$

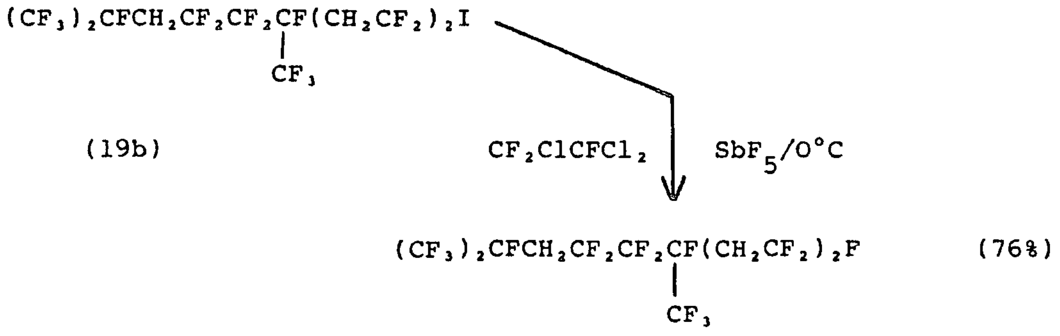
$$R_F = (CF_3)_2\ CF \text{ or } CF_3CF_2CF_2$$

For our purposes the most convenient fluorinating agent is antimony pentafluoride.[139] The reactions were carried out at 0°C using an excess of the reagent and in order to ensure efficient mixing of the system, arklone ($CF_2ClCFCl_2$) was used as the solvent. Mixtures of telomer iodides can be converted to the corresponding model compounds in this way. However, model compounds of higher molecular weight (i.e. n=3,4,5) are not as easily separated by fractional distillation as their corresponding telomer iodides. Consequently, it is preferable to firstly separate the iodides and then fluorinate each individually.

$$(CF_3)_2CF(CH_2CF_2)_nI \xrightarrow[CF_2ClCFCl_2]{SbF_5/0°C} (CF_3)_2CF(CH_2CF_2)_nF$$

(13) (15)

n = 2 (70%)
n = 3 (68%)
n = 4 (60%)
n = 5 (58%)



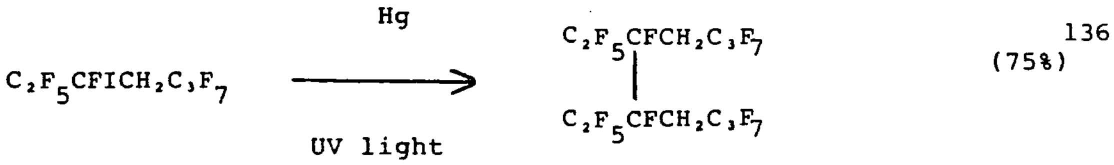
$$(CF_3)_2CFCH_2CF_2CF_2CF(CF_3)(CH_2CF_2)_2I \xrightarrow[CF_2ClCFCl_2]{SbF_5/0°C} (CF_3)_2CFCH_2CF_2CF_2CF(CF_3)(CH_2CF_2)_2F$$

(19b) (26) (76%)

At temperatures above ca 10°C the model compounds undergo further reaction with SbF_5, yielding unsaturated products (See Section 3.23).

2.42 Coupling Reactions of the Telomer Iodides

Much work has been published on the free-radical coupling of fluoroalkyl iodides, e.g.



$$C_2F_5CFICH_2C_3F_7 \xrightarrow[\text{UV light}]{Hg} C_2F_5CF(CH_2C_3F_7)-CF(CH_2C_3F_7)C_2F_5 \quad (75\%)^{136}$$

$$(CF_3)_2\ CFI \xrightarrow[\text{UV light}]{Hg} (CF_3)_2CFCF(CF_3)_2 \quad (97\%)^{125}$$

$$C_2F_5CFClI \xrightarrow[\text{UV light}]{Hg} C_2F_5CFCl-CFClC_2F_5 \quad (68\%)^{140}$$

This type of reaction can be applied to the synthesis of model compounds as demonstrated by Chambers and co-workers, who coupled the telomer iodide (13a) as follows:[127]

$$\underset{(13a)}{(CF_3)_2CFCH_2CF_2I} \xrightarrow[\text{UV light}]{\text{Hg}} \underset{(14a)}{[(CF_3)_2CFCH_2CF_2]_2} \quad (75\%)$$

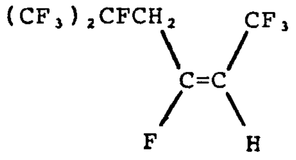
Comparable yields of (14a) have been obtained on repeating the reaction. The products (27) and (28) were formed also.

$$\underset{(13a)}{(CF_3)_2CFCH_2CF_2I} \xrightarrow[\text{UV light}]{\text{Hg}} \underset{(14a)}{[(CF_3)_2CFCH_2CF_2]_2} \ (71\%) + \underset{(27)}{(CF_3)_2CFCH{=}CF_2} \ (11\%) + \underset{(28)}{(CF_3)_2CFCH_2CF_2H} \ (12\%)$$

Similar treatment of the higher telomer (13b) led to the formation of the corresponding coupled product (14b), but in lower yield. Two other products (29) and (30) were also identified.

$$\underset{(13b)}{(CF_3)_2CFCH_2CF_2CH_2CF_2I} \xrightarrow[\text{UV light}]{\text{Hg}} \underset{(14b)}{[(CF_3)_2CF(CH_2CF_2)_2]_2} \ (41\%) + \underset{(29b)}{(CF_3)_2CFCH_2CF_2CH{=}CF_2} \ (34\%)$$

+



(17%)

(30)

2.5 Spectroscopic Examination of the Model Compounds and the HFP/VDF Copolymer System

2.51 Introduction

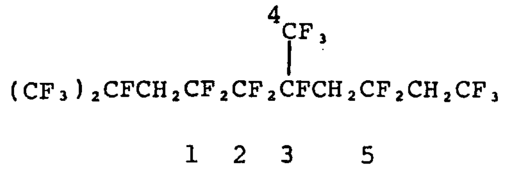
The model compounds that have been discussed in this chapter contain the pertinent structural features of HFP/VDF copolymers. Hence, by acquiring NMR spectroscopic data for the model compounds it should be possible to correlate their chemical shift values with those for the copolymers. In this way the model compounds can provide information about chemical processes occurring in the copolymer system.

Due to the complexity of the ^{1}H and ^{13}C NMR spectra, investigations have solely concentrated on acquiring ^{19}F NMR data. ^{19}F NMR Spectroscopy is particularly suited to this kind of correlation study since the regions of CF_3, CF_2 and CF fluorine resonances are essentially non-overlapping and encompass a wide chemical shift range.

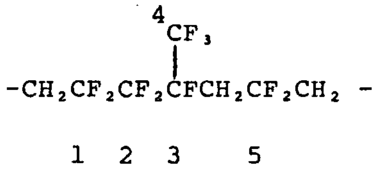
2.52 Correlation Between The Model Compounds and the Copolymer System

A 1:9 ratio of HFP to VDF was irradiated with γ- rays at ambient temperature for four days. The resultant copolymer was dissolved in N, N-dimethylformamide (DMF) and its high field ^{19}F NMR spectrum acquired. Comparison with the ^{19}F chemical shift values for the model compound (26) in DMF led to assignment of the different groups in the copolymer as shown in Table 2.3.

Table 2.3



$$(CF_3)_2CFCH_2\underset{1}{CF_2}\underset{2}{CF_2}\underset{3}{\overset{\overset{4}{CF_3}}{\overset{|}{C}}}FCH_2\underset{5}{CF_2}CH_2CF_3$$



$$-CH_2\underset{1}{CF_2}\underset{2}{CF_2}\underset{3}{\overset{\overset{4}{CF_3}}{\overset{|}{C}}}FCH_2\underset{5}{CF_2}CH_2-$$

Model (26)		Polymer (*ca* 60% $CH_2=CF_2$)	
Shift/ppm	Assignment	Shift/ppm	
- 76.0	4 - CF_3	- 76.0	
- 97.2	5 - CF_2	- 92.4 to - 95.5	(4)*
- 110.1	1 - CF_2	- 109.2 to - 110.7	(2)
- 118.6	2 - CF_2	- 117.4 to - 118.4	(4)
- 185.0	3 - CF	- 185.0	

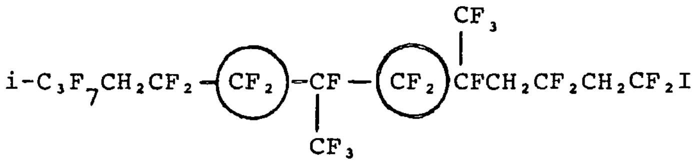
*The figure in brackets indicates the number of signals occurring within the chemical shift range.

It can be seen that there is a very good correlation between the chemical shifts for the copolymer and the model (26), although there is some difference between the values for the 5 - CF_2 groups. This is due to a difference in adjacent groups for the model (26) $-CH_2-CF_3$ and the copolymer $- CH_2CF_2 -$. The S_F value for the 5-CF_2 group of the copolymer, however, is in closer agreement with the model compound $(CF_3)_2 CF(CH_2CF_2)_3 CH_2CF_3$ (15d) in which the signals for the CF_2 units are between -92.3 and -95.4 ppm.

It can also be seen from Table 2.3 that there is a chemical shift range over which some of the groups in the copolymer resonate. Within each range there are a number of signals, each depending on the specific nature of the neighbouring units. By a consideration of the relative intensities of these signals, together with reference to the chemical shift values for the model compounds, most of them can now be assigned.

2.53 Assignment of the Structural Units in the Copolymer

In order to facilitate assignment of the NMR signals, it was firstly determined whether HFP units are present in the copolymer. By comparison of the ^{19}F NMR spectrum of the telomer (19d) (see Section 2.33 for its preparation) in DMF with that of the copolymer in DMF, it was found that there can be no repeating HFP units in the copolymer system.

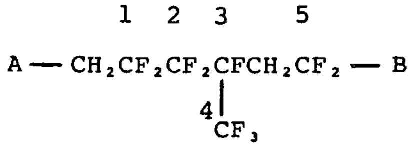


$$i\text{-}C_3F_7CH_2CF_2-\boxed{CF_2}-\underset{CF_3}{\underset{|}{CF}}-\boxed{CF_2}\overset{CF_3}{\overset{|}{C}}FCH_2CF_2CH_2CF_2I$$

(19d)

This conclusion was derived from the fact that the highlighted CF_2 groups in the diasteroisomers of (19d) form a complex set of AB systems between -102 and -115 ppm, which are not observed in the ^{19}F NMR spectrum of the copolymer.

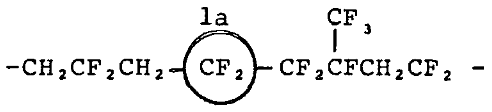
Referring to Table 2.3, there are two signals within the chemical shift range assigned for the 1-CF_2 group. These two signals must depend upon the precise arrangement of units directly attached to the structure (31), i.e. A and B, which represent either VDF or HFP units.



$$A-CH_2\overset{1}{CF_2}\overset{2}{CF_2}\overset{3}{\underset{4|\,CF_3}{CF}}CH_2\overset{5}{CF_2}-B$$

(31)

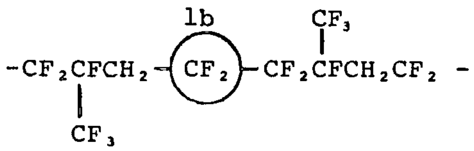
The δ_F value for the 1 - CF_2 group should be more sensitive to changes in the unit A rather than B, due to its greater proximity. Since A can be a VDF or an HFP unit the two resonances within this range can be assigned as follows:



$-CH_2CF_2CH_2-\overset{1a}{\textcircled{CF_2}}-CF_2\overset{CF_3}{\overset{|}{C}}FCH_2CF_2-$

(31a)

$\delta_F^{1a} = -109.2$ ppm

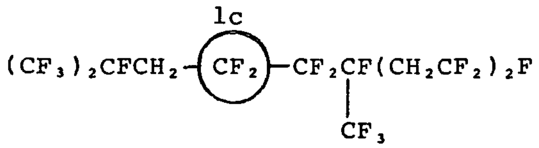


$-CF_2\underset{CF_3}{\underset{|}{C}}FCH_2-\overset{1b}{\textcircled{CF_2}}-CF_2\overset{CF_3}{\overset{|}{C}}FCH_2CF_2-$

(31b)

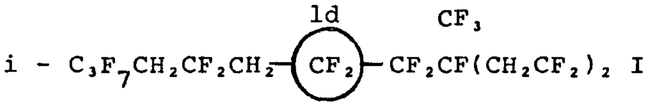
$\delta_F^{1b} = -110.7$ ppm

These assignments are supported by the fact that the copolymer in the study contained ca. 60% VDF and, in accordance, the integral for the signal at - 109.2 ppm was correspondingly larger than that at - 110.7 ppm. However, the use of model compounds in assigning structures (31a) and (31b) is somewhat limiting. For example, δ_F^{1c} is - 110.1 ppm for model (26), which is close the resonances



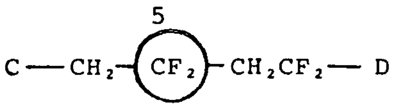
$(CF_3)_2CFCH_2-\overset{1c}{\textcircled{CF_2}}-CF_2\underset{CF_3}{\underset{|}{C}}F(CH_2CF_2)_2F$ (26)

for both (31a) and (31b). In addition, the δ_F value for 1d - CF_2 in compound (20b) occurs at - 111.1 ppm and therefore shows poor correlation with the assignments given above.



$i-C_3F_7CH_2CF_2CH_2-\overset{1d}{\textcircled{CF_2}}-CF_2\overset{CF_3}{C}F(CH_2CF_2)_2I$ (20b)

For the 5 - CF_2 group there are four distinct resonances in the spectrum of the copolymer. The exact chemical shift values are dependent on the contiguous units C and D in (32) which can be either HFP or VDF.



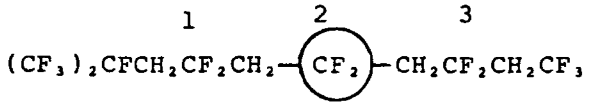
$C-CH_2-\overset{5}{\textcircled{CF_2}}-CH_2CF_2-D$ (32)

Since the copolymer contains ca 60% VDF the signals have been assigned on the basis of their relative intensities (See Table 2.4).

Table 2.4

Shift/ppm	Relative Intensity	Assignment
- 95.5	ca 3	$-CH_2CF_2CH_2-\overset{5a}{\textcircled{CF_2}}-CH_2CF_2CH_2CF_2-$*
- 93.7	3	$-CH_2CF_2CH_2-\overset{5b}{\textcircled{CF_2}}-CH_2CF_2CF_2CF(CF_3)-$
		OR
- 93.3		$-CF_2CF(CF_3)CH_2-\overset{5c}{\textcircled{CF_2}}-CH_2CF_2CH_2CF_2-$
- 92.4	1	$-CF_2CF(CF_3)CH_2\ \underset{5d}{\textcircled{CF_2}}\ CH_2CF_2CF_2CF(CF_3)-$

*This assignment is further supported by the ^{19}F NMR spectrum of the model compound (15d), in which there is close correlation with the δ_F value for the 2 - CF_2 group.

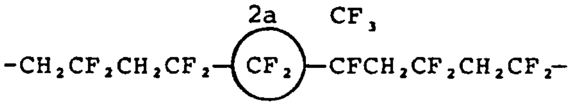


$$\overset{1}{(CF_3)_2CFCH_2}CF_2CH_2-\overset{2}{\textcircled{CF_2}}-\overset{3}{CH_2}CF_2CH_2CF_3$$

(15d)

δ_F/ppm - 92.4 -95.4 -95.0

Assignment of the four resonances for the 2-CF_2 group of the copolymer is more difficult since they overlap to a certain extent. Consequently the use of signal integration is limited and the only structural unit which has been definitively assigned is (33).



$$-CH_2CF_2CH_2CF_2-\overset{2a}{\textcircled{CF_2}}-\overset{CF_3}{C}FCH_2CF_2CH_2CF_2-$$

(33)

δ_F^{2a} = - 118.4 ppm

Further work is under way in order to resolve the NMR signals for this group.

2.6 Gamma Ray Polymerisation of Vinylidene Fluoride

During the course of our investigations we became interested in determining the effect of temperature on the polymerisation of vinylidene fluoride using γ - ray initiation. Samples of VDF were irradiated with γ-rays at room temperature, 0°C and - 78°C. The resultant polymers obtained at each temperature were then dissolved in DMF and their high field ^{19}F NMR spectra acquired. Each of the spectra consisted of five resonances of which four have been assigned to the various CF_2 groups.[141,142]

$-CF_2CH_2\overset{1}{C}F_2CH_2CF_2-$	$\delta_F^{1} = -92.6$ ppm
$-CH_2CH_2\overset{2}{C}F_2CH_2CF_2-$	$\delta_F^{2} = -95.8$ ppm
$-CF_2CH_2\overset{3}{C}F_2CF_2CH_2-$	$\delta_F^{3} = -114.6$ ppm
$-CH_2CH_2\overset{4}{C}F_2CF_2CH_2-$	$\delta_F^{4} = -117.0$ ppm

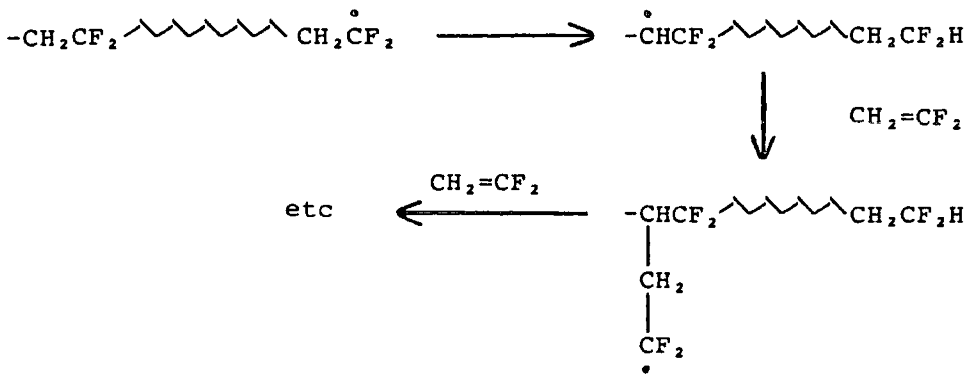
Intensity measurements of the resonances gave a direct estimation of the percentage of head-to-tail arrangement of the monomer units in the homopolymer, prepared at different temperatures. The results are displayed in Table 2.5.

Table 2.5

Origin of PVDF	Head-to-Tail (%)
Room Temp.	87
0°C	89
- 78°C	92
Room Temp. + Precipitation*	90

*Solution of the polymer was concentrated under vacuum to precipitate out some of the material. ^{19}F NMR studies were carried out on the remaining solution.

As expected, the degree of regioselectivity increases as the temperature at which polymerisation is carried out becomes lower, so that the degree of head-to-tail addition of the monomer is seen to increase as the temperature is dropped. However, the percentage values given in Table 2.5 are lower than those obtained for poly(vinylidene fluoride) (PVDF) formed by peroxide initiated polymerisations, which are typically about 5-6% irregular.[143] In fact a further signal was observed at -93.1 ppm in the ^{19}F NMR spectra of the VDF polymers prepared by gamma ray initiation. This resonance overlapped with that at -92.6 ppm and is indicative of the formation of branched chains during the polymerisation process.[144] A possible mechanism for the formation of branched chains is presented in Scheme 2.5. This mechanism requires that for every branched chain which is formed, a terminal difluoromethyl group is also produced. However, resonances due to this group were not observed in the ^{19}F NMR spectra of the VDF homopolymers.



Scheme 2.5

It is possible that polymer radicals of the type $RCF_2\dot{C}H_2$, formed by head-to-head addition of monomer units, could undergo a similar process to that outlined in Scheme 2.5. This would result in the formation of terminal methyl groups, which could not be detected by this type of study.

2.7 Conclusions

A number of model compounds have been synthesized which contain the pertinent structural units of VDF/HFP copolymers. NMR spectroscopy has demonstrated that there is good correlation between the models and the copolymers. Furthermore, the spectroscopic investigations have proved conclusively that there are no sequences of HFP units in the copolymer system. Since the model compounds are liquids they can be easily manipulated and analysed, so that they present an excellent opportunity to determine the nature of chemical processes occurring during the cross-linking of these copolymers.

CHAPTER THREE

MODEL STUDIES RELATED TO THE CROSS-LINKING OF VDF/HFP COPOLYMERS

3.1 Introduction

It is believed that during the cross-linking of HFP/VDF copolymers with nucleophilic curatives, the initial step involves elimination of hydrogen fluoride (see section 1.33b). Therefore, attempts have been made to prepare some compounds which would usefully serve as models for unsaturated sites that might be produced by base induced elimination of hydrogen fluoride from the structural units (10) and (11) in the polymer system.

$-CH_2CF_2CH_2CF_2-$ (10)

$-CF_2CF(CF_3)CH_2CF_2-$ (11)

3.2 Synthesis of Unsaturated Model Compounds

3.21 Base Induced Elimination of HF from Saturated Model Compounds

Fluoride ion can function as a strong base[146] so that heating the saturated model compounds (15b) and (15c) with caesium fluoride, in sulpholane at 150°C, gave good yields of the corresponding alkenes (34) and (35). It is significant that this system was unable to promote elimination of hydrogen fluoride from a site involving difluoromethylene.

$$(CF_3)_2\,CFCH_2CF_2(CH_2CF_2)_nF \xrightarrow[150^\circ]{\text{CsF, SULPHOLANE}} (CF_3)_2\,C{=}CHCF_2(CH_2CF_2)_nF$$

n=1 (15b) (34) (79%)

n=2 (15c) (35) (70%)

The structural unit $(CF_3)_2\,C{=}CH-$ was easily identified by NMR spectroscopy since the trifluoromethyl groups were non-equivalent and gave rise to signals at lower field shift values than for the corresponding groups in the saturated models. In addition the vinylic hydrogen gave rise to a triplet (J=13Hz) at 6.5 ppm in the ^1H NMR spectrum which is characteristic of such an atom in this environment.[147]

3.22 Fluoride Ion Induced Reaction of $(CF_3)_2CF(CH_2CF_2)_nCH{=}CF_2$ (29)

The fluorohydrocarbon alkenes (29) were easily prepared from their corresponding telomer iodides (13) by elimination of hydrogen iodide, using a base such as triethylamine or tri-n-butylamine.

$$(CF_3)_2CF(CH_2CF_2)_nCH_2CF_2I \xrightarrow[\text{room temp.}]{NBu_3 \text{ or } NEt_3} (CF_3)_2CF(CH_2CF_2)_nCH{=}CF_2$$

(13) (29) (81-97%)

n=0,1,2,

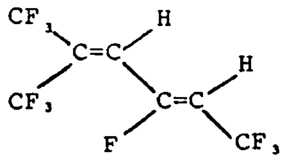
These compounds are useful intermediates in the synthesis of unsaturated models. Thus, treatment of (29a) and (29b) with fluoride ion in sulpholane gave the alkenes (36) and (37) respectively.

$$(CF_3)_2CF{-}CH{=}CF_2 \xrightarrow[100^{\circ}C,\ 2h]{CsF,\ SULPHOLANE} (CF_3)_2C{=}CHCF_3 \quad (96\%)$$

(29a) (36)

$$(CF_3)_2CFCH_2CF_2CH{=}CF_2 \xrightarrow[150^{\circ}C,\ 7h]{CsF,\ SULPHOLANE}$$

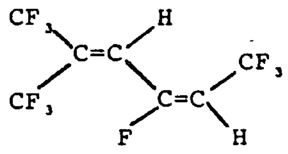
(29b)



(64%)

(37a)

+



(34%)

(37b)

However, similar treatment of (29c) with fluoride ion gave several products, presumably as a consequence of further reaction of the diene (38).

$$(CF_3)_2CF(CH_2CF_2)_2{-}CH{=}CF_2 \xrightarrow[150^{\circ}C]{CsF,\ SULPHOLANE} (CF_3)_2C{=}CHCF_2CH_2CF{=}CHCF_3 \longrightarrow \text{Several products}$$

(29c) (38)

These products were not characterised.

3.23 Lewis Acid Induced Reactions

Usually, Lewis acids are not used to carry out dehydrohalogenation reactions since the unsaturated products are often susceptible to electrophilic attack. However, a number of unsaturated model compounds can be prepared in this way, using antimony pentafluoride as the Lewis acid.

$$(CF_3)_2\,CFCH_2CF_3 \xrightarrow[120^{\circ}C,\,3h]{SbF_5} (CF_3)_2\,C{=}CHCF_3 \qquad (80\%)^{133}$$

(15a) (36)

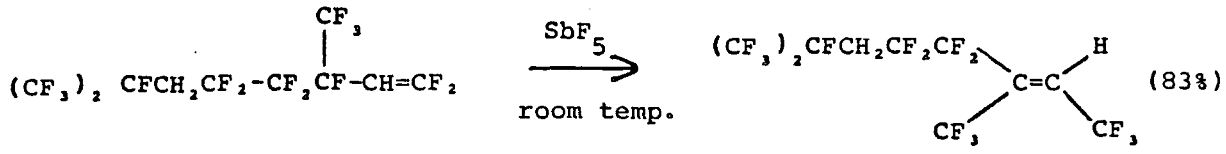
$$\left[(CF_3)_2CFCH_2CF_2\right]_2 \xrightarrow[120^{\circ}C,\,3h]{SbF_5} \left[(CF_3)_2\,C{=}CHCF_2\right]_2 \qquad (86\%)^{133}$$

(14a) (39)

In addition, it was found that antimony pentafluoride can be employed in rearrangement reactions, e.g.

$$(CF_3)_2\,CF{-}CH{=}CF_2 \xrightarrow[\text{room temp.}]{SbF_5} (CF_3)_2\,C{=}CH{-}CF_3 \qquad (\text{Quant.})$$

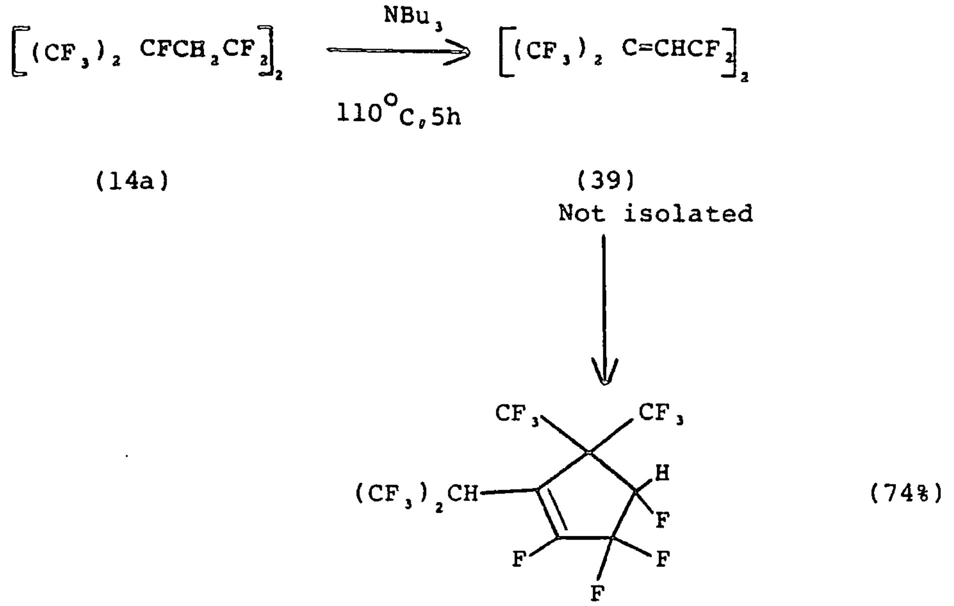
(29a) (36)



(40) (41)

The Z-stereoisomer of (41) was formed exclusively, reflecting the preference to keep the sterically demanding groups as spatially distant as possible. The identity of (41) was largely determined by NMR spectroscopy which showed a coupling constant of 11 Hz between the fluorines of the vinylic CF_3 groups.

This methodology for producing unsaturated models is useful in that the reactions proceed in high yield. Furthermore, the unsaturated models (39) and (41) can only be prepared in this way. For example, the 1,5-diene (39) cannot be synthesized by base induced elimination of hydrogen fluoride from the saturated model (14a). Attempts to produce it, using either fluoride ion or tri-n-butylamine led to exclusive formation of the cyclopentene derivative (42).[133]

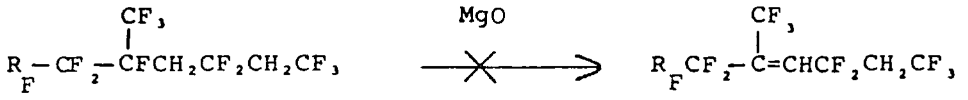


(42)

Longer chain saturated models of the type (15) also underwent elimination of hydrogen fluoride on treatment with antimony pentafluoride. However, many of the products were not inert to further electrophilic attack and led to remarkably stable carbocations or other unusual reactions. This chemistry is discussed in chapter five.

3.3 Treatment of Saturated Model Compounds with Curing Agents

The saturated model compounds (14) and (15) showed no evidence of elimination of hydrogen fluoride when heated to elevated temperatures in the presence of typical mixtures that are used for cross-linking raw HFP/VDF copolymers.[133] Typical mixtures involve addition of carbon black $Ca(OH)_2$, MgO, $Ph_3P^+CH_2Ph\ Cl^-$, and $p\text{-}(HOC_6H_4)_2(CF_3)_2$ (Bisphenol AF)[50]. During the course of this work, treatment of the more appropriate saturated model (26) with MgO at high temperature also failed to bring about a dehydrofluorination reaction. The metal oxide is known to be able to bring about some degree of cross-linking of HFP/VDF copolymers.[63]



$$R_F\text{-}CF_2\text{-}\overset{\displaystyle CF_3}{\overset{|}{C}}FCH_2CF_2CH_2CF_3 \xrightarrow[210^\circ C,\,24h]{MgO} R_FCF_2\text{-}\overset{\displaystyle CF_3}{\overset{|}{C}}{=}CHCF_2CH_2CF_3$$

(26) (43)

$R_F=(CF_3)_2CFCH_2CF_2$

Quite clearly, there is a marked difference between the activity of the polymer system and that of the model compounds and this could be attributed to a) a contact problem in the case of the models, or b) enhanced reactivity of solid - solid interaction which occurs in the polymer system, or c) intrinsic instability of the polymers towards elimination of hydrogen fluoride, which is not characteristic of lower molecular weight systems of similar structure. The most significant is probably a) because treatment of models of type (15) with D.B.U. in D.M.A.C., i.e. a homogeneous system, at room temperature, led to rapid dehydrofluorination in a manner similar to that which has previously been observed with the polymer.[50]

$$(CF_3)_2\ CFCH_2CF_2(CH_2CF_2)_nF \xrightarrow[\text{room temp.}]{\text{D.B.U., D.M.A.C.}} (CF_3)_2\ C{=}CHCF_2(CH_2CF_2)_nF$$

n=1 (15b) (34) (39%)

n=2 (15c) (35) (38%)

It has been argued[50] that in reaction of base with polymer sites (10) and (11), preferential elimination of hydrogen fluoride occurs from positions involving the 'tertiary' fluorine. We have reached the same conclusion by observing the reactions of model compounds with bases in solution. For example, reaction of (15b) with D.B.U. gave (34) exclusively. Other examples of reactions of models with bases that led exclusively to eliminations of hydrogen fluoride from sites involving 'tertiary' fluorine, have been discussed in section 3.2.

Further attempts to react saturated model compounds with the curing agents, by adding D.M.A.C. to the system, were unsuccessful.

$$\underset{(15c)}{(CF_3)_2\ CFCH_2CF_2(CH_2CF_2)_2F} \ \not\xrightarrow[140^{\circ}\text{C, 24h}]{\text{MgO,D.M.A.C.}}\ \underset{(35)}{(CF_3)_2\ C{=}CHCF_2(CH_2CF_2)_2F}$$

$$(CF_3)_2CFCH_2CF_2(CH_2CF_2)_2F \xrightarrow{i} \text{No Reaction}$$

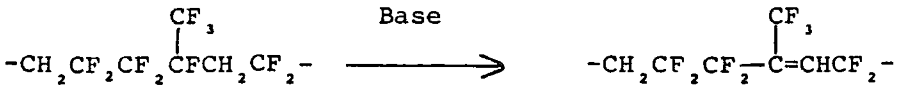
(15c) i Bisphenol AF, $Ph_3P^+CH_2Ph\ Cl^-$,

D.M.A.C., 140°C, 24h.

3.4 Reactions of Unsaturated Model Compounds with Nucleophiles

3.41 Reactivity of the $-C(CF_3)=CH-$ Site

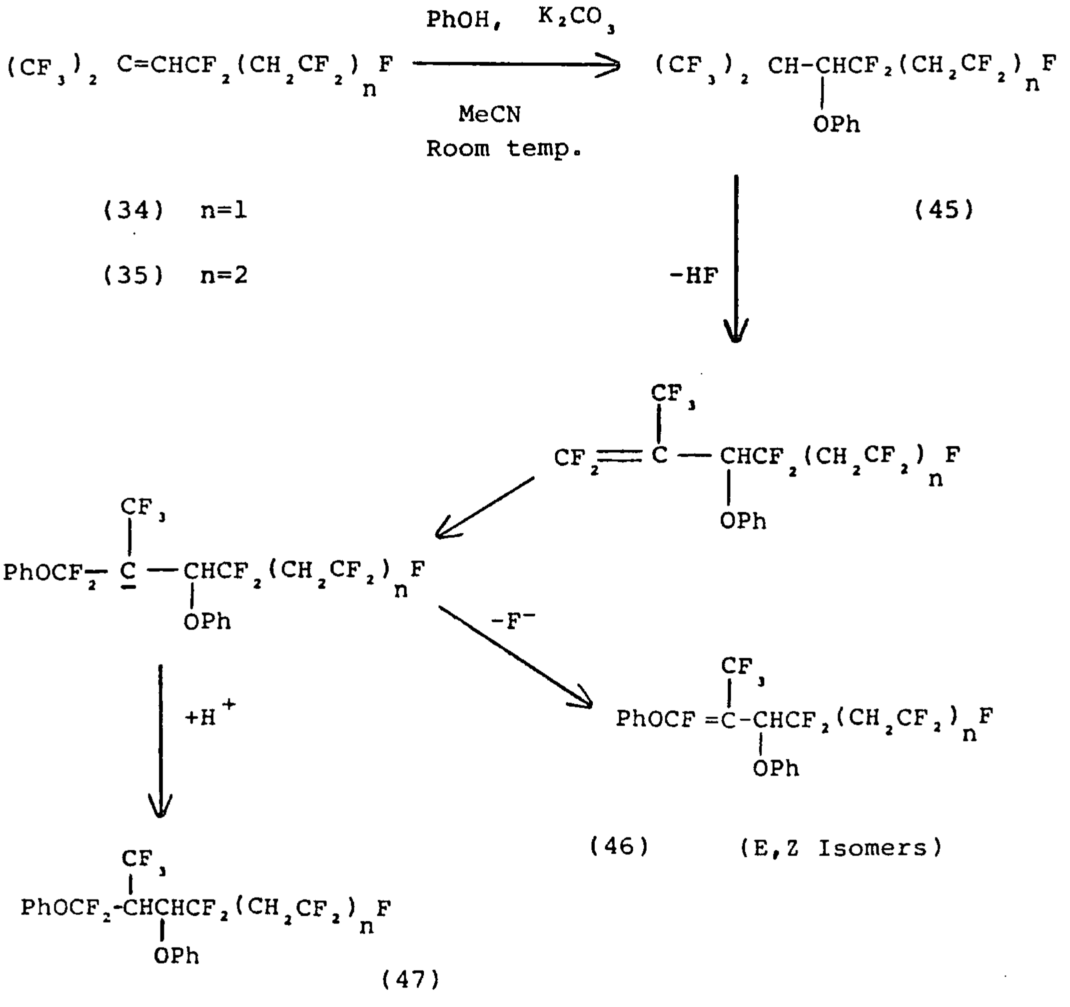
Having established the type of unsaturated site most readily produced in the copolymer system, further reactions have been carried out with model compounds involving the site $-C(CF_3)=CH-$ which is contained in (44). The reactions involve nucleophilic attack of phenoxide



$$-CH_2CF_2CF_2\overset{CF_3}{\overset{|}{C}}FCH_2CF_2- \xrightarrow{\text{Base}} -CH_2CF_2CF_2-\overset{CF_3}{\overset{|}{C}}=CHCF_2-$$

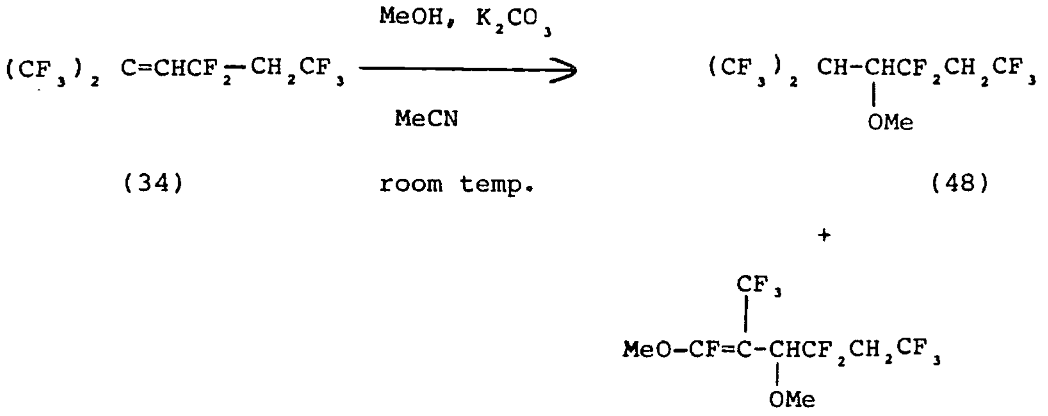
(11) (44)

or methoxide and are discussed below.



Scheme 3.1

Treatment of models (34) and (35) with phenol demonstrates that reaction occurs extremely readily with systems containing sites $-C(CF_3){=}CH-$ giving the product of addition (45), but it is important to note the formation of both (46) and (47) since this demonstrates that attack at the double bond can occur with allylic displacement of fluoride. A new unsaturated site is formed which reacts further with phenol to give (46) and (47). This observation has great significance for the elastomer cross-linked with Bisphenol AF. Similar treatment of the model (34) with methanol gave the products (48) and (49).

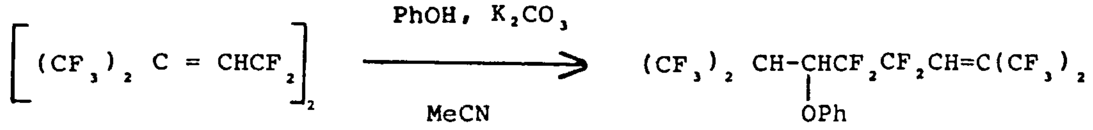


$$(CF_3)_2C{=}CHCF_2{-}CH_2CF_3 \xrightarrow[\text{MeCN, room temp.}]{\text{MeOH, }K_2CO_3} (CF_3)_2CH{-}CH(OMe)CF_2CH_2CF_3 + MeO{-}CF{=}C(CF_3){-}CH(OMe)CF_2CH_2CF_3$$

(34) (48)

(49) (E,Z - Isomers)

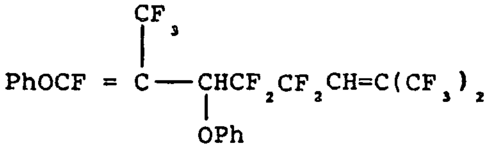
The 1,5-diene (39) contains two sites which are susceptible to attack by nucleophiles. Using an equimolar mixture of phenol and (39) the principal product was the adduct (50).



$$\left[(CF_3)_2C = CHCF_2\right]_2 \xrightarrow[\text{MeCN, room temp., 8h}]{\text{PhOH, }K_2CO_3} (CF_3)_2CH{-}CH(OPh)CF_2CF_2CH{=}C(CF_3)_2$$

(39) (50)

Using an excess of phenol to diene (39), two major products were obtained. Mass spectrometry indicated that these products were formed by further addition of phenol to (50) accompanied by dehydrofluorination, i.e. the E- and Z- isomers of (51) (m/z 574).

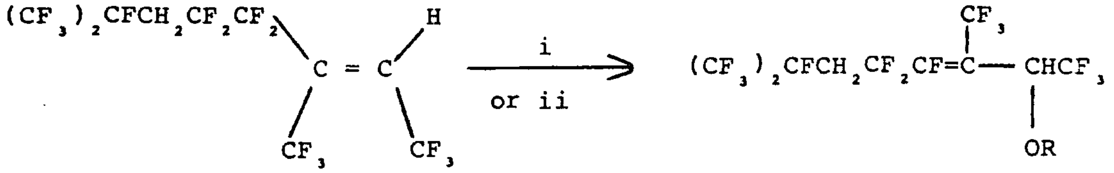


$\mathrm{PhOCF=C(CF_3)-CH(OPh)CF_2CF_2CH=C(CF_3)_2}$

(51) (E, Z - Isomers)

The isomers of (51) were not fully characterised, however, as they could not be separated from other minor products.

Compound (41) is a more appropriate model for sites of unsaturation (44) generated in the main polymer structure (11) and reactions of (41) illustrate further the allylic displacement process described above.



(41)

(52) (E,Z Isomers)

i, PhOH, MeCN, K_2CO_3, room temp.

ii, MeOH, MeCN, K_2CO_3, room temp.

Product (52) was obtained from allylic displacement of fluoride ion and this obviously occurs more readily with (41) than with (34) or (35) because the process involves loss of fluoride in the former case from a difluoromethylene site. It is well known that a carbon-fluorine bond is weaker in a difluoromethylene group than in a trifluoromethyl.[148] Indeed it is worth stressing that no addition product was obtained from (41) and undoubtedly an analogous process, i.e. forming and retaining unsaturated sites, will predominate with the polymer system. Therefore cross-linking with Bis-phenol AF will always generate vinylic fluorine sites which will obviously be a major source of chemical instability.

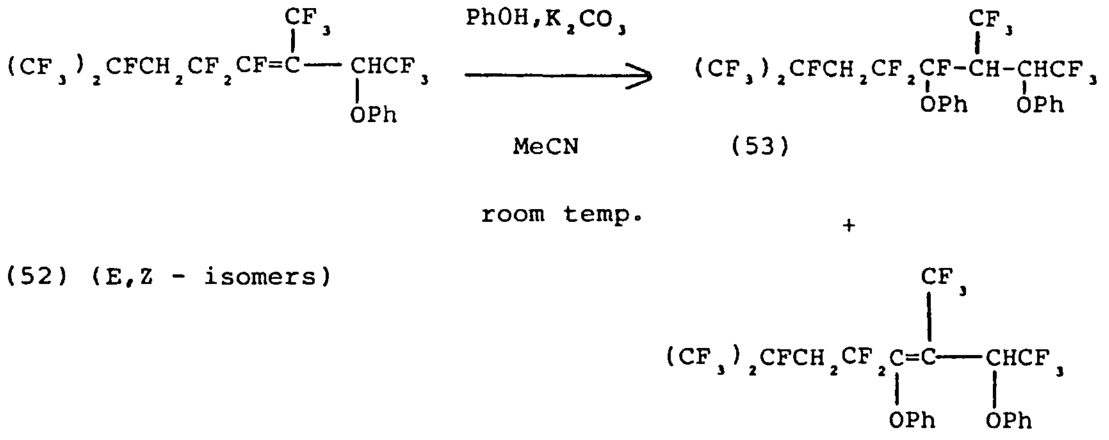
Schmiegel[50] recognised the production of sites in the polymer with fluorine attached at vinylic positions but found it necessary to suggest equilibration with fluoride ion in order to produce these sites, i.e.

$$\mathrm{-CF_2C(CF_3) = CH-} \xrightleftharpoons{F^-} \mathrm{-CF = C(CF_3)CHF-}$$

This equilibrium is, however, unlikely because attachment of perfluoroalkyl is thermodynamically preferred over fluorine at double bonds[149] and the allylic displacement process that has been described above adequately demonstrates how these vinylic sites attached to fluorine may be produced.

3.42 Response of the $-CF_2CF{=}C(CF_3)-CH(OAr)-$ Unit to Nucleophilic Attack

The susceptibility of the vinylic site in compound (52) to nucleophilic attack has been clearly demonstrated. Under the conditions used to generate (52) from the unsaturated model (41), adding an excess of phenol led to further reaction of (52) in which both addition to the double bond and substitution of the vinylic fluorine occurred to yield the products (53) and (54). G.C.-Mass spectrometry was used to investigate the reaction since the products gave definitive mass spectra (m/z 614 (53) and 594 (54).



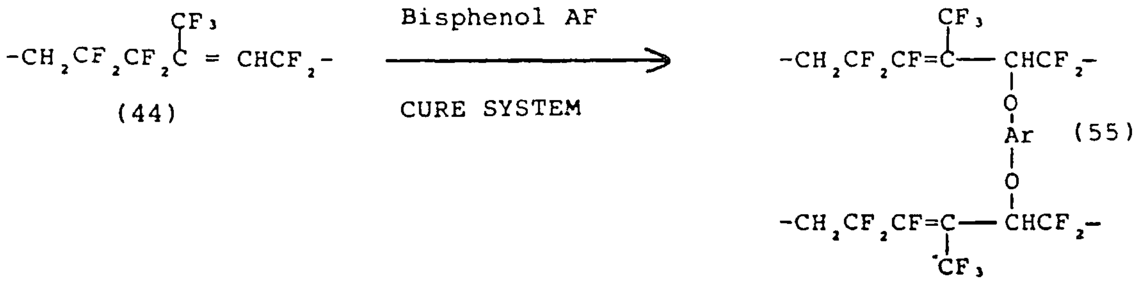
$$(CF_3)_2CFCH_2CF_2CF{=}C(CF_3)-CH(OPh)CF_3 \xrightarrow[\text{MeCN, room temp.}]{PhOH,\,K_2CO_3} (CF_3)_2CFCH_2CF_2CF(OPh)-CH(CF_3)-CH(OPh)CF_3 + (CF_3)_2CFCH_2CF_2C(OPh){=}C(CF_3)-CH(OPh)CF_3$$

(52) (E,Z - isomers)

(53)

(54) (E,Z - isomers)

It is worth stressing that the ether linkage on compound (52) remained intact during the reaction, Hence, for VDF/HFP elastomers cured by Bisphenol AF, the source of chemical instability will be the vinylic sites in (55) rather than the actual cross-link.



$$-CH_2CF_2CF_2C(CF_3){=}CHCF_2- \xrightarrow[\text{CURE SYSTEM}]{\text{Bisphenol AF}} -CH_2CF_2CF{=}C(CF_3)-CH(CF_2-)-O-Ar-O-CH(CF_2-)-C(CF_3){=}CFCF_2CH_2-$$

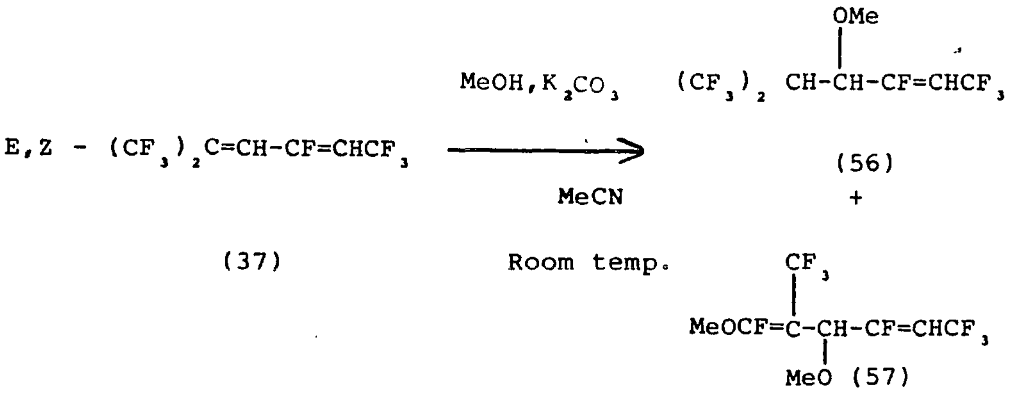
(44)

(55)

It is also worth noting that the vinylic sites in (55) are unlikely to be modified by Bisphenol AF to any significant extent during the curing process. This is because the ratio of the curing agent to raw copolymer is generally ca 1:50.[50]

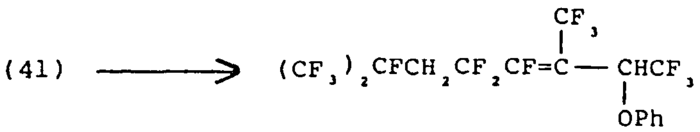
3.43 $(CF_3)_2C{=}CH{-}CF{=}CHCF_3$ (37) with Methanol

If dehydrofluorination of contiguous VDF units occurs during the curing of the polymer with Bisphenol AF, unsaturated sites of the type -CF=CH- will be formed. In order to determine the relative reactivities of the unsaturated sites $-C(CF_3){=}CH-$ and -CF=CH- towards nucleophilic attack the diene (37) was treated with methanol at room temperature. Under these conditions it was found that the -CF=CH- unit was inert to nucleophilic attack, whereas the $-C(CF_3){=}CH-$ site reacted to give the products (56) and (57) in a manner similar to that observed for the models (34) and (35).



3.44 $(CF_3)_2CFCH_2CF_2CF_2{-}C(CF_3) = CHCF_3$ (41) with Phenol

The unsaturated model (41) was treated with phenol in slightly modified systems to the one described in section 3.41, all at ambient temperature as follows:



(52)

i) $PhOH$, Na_2CO_3, MeCN
ii) $PhOH$, K_2CO_3 DMF
iii) PhO^-Na^+, DMF
iv) PhOH, MeCN

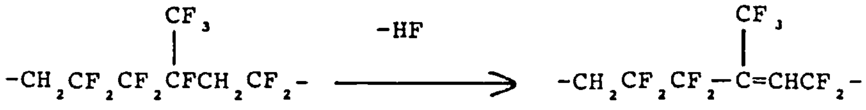
With systems i) and ii) conversion of (41) to (52) was observed whereas iii) gave little and iv) no reaction. The solvent, DMF or acetonitrile, was responsible for dissolving the solid phenol and ensuring increased contact between the reactants. The presence of carbonate was essential for reaction to occur, although the choice of counter-ion, Na^+ or K^+, did not affect the process. Since little reaction was observed on treating (41) with system iii), in contrast with ii), it appears that there must have been a lack of phase contact between phenoxide and the model in the former case.

Under exactly analogous conditions phenol was more reactive towards (41) than methanol and this reflects the fact that the nucleophile which attacks (41) must be either methoxide or phenoxide rather than the corresponding OH compound. This is because formation of phenoxide from phenol will occur more readily than that of methoxide from methanol.

3.5 Conclusions

Some definite conclusions can be drawn on the basis of these investigations with model compounds, that relate to bisphenol cured elastomer:

1. Unsaturated sites are initially generated predominantly through elimination of the 'tertiary' fluorine, i.e.,

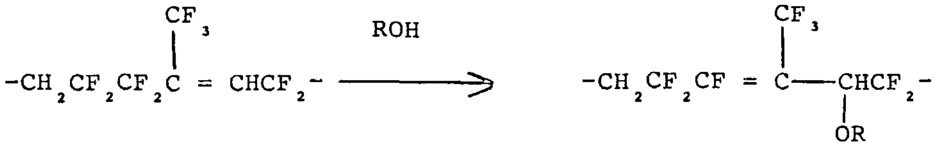


$$-CH_2CF_2CF_2\overset{CF_3}{\overset{|}{C}}FCH_2CF_2- \xrightarrow{-HF} -CH_2CF_2CF_2-\overset{CF_3}{\overset{|}{C}}{=}CHCF_2-$$

(11) (44)

In addition, merely heating the copolymer system may generate fluoride ion which can eliminate hydrogen fluoride, principally with loss of tertiary fluorine.

2. With the model compounds, unsaturated sites of the form (44) are susceptible to attack by alcohols and phenols under mild conditions, i.e.,



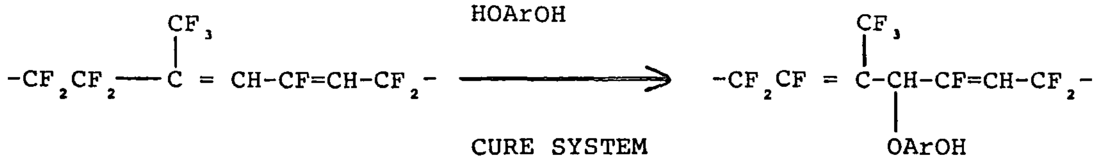
$$-\mathrm{CH_2CF_2CF_2}\overset{\mathrm{CF_3}}{\overset{|}{\mathrm{C}}}=\mathrm{CHCF_2}- \xrightarrow{\mathrm{ROH}} -\mathrm{CH_2CF_2CF}=\overset{\mathrm{CF_3}}{\overset{|}{\mathrm{C}}}-\underset{\underset{\mathrm{OR}}{|}}{\mathrm{CHCF_2}}-$$

(44) (58)

Hence, such unsaturated sites present in the copolymer system should also be susceptible to attack by nucleophiles in a similar way, i.e. during the curing process with bisphenols.

3. The remaining vinylic site in (58), rather than the aryl link, will be the most significant source of chemical instability of bisphenol cured elastomers. Consequently, the use of such elastomers in environments where aqueous alkalis, amines or other nucleophiles are present, could be life limiting.

4. If any sites of the form (59) are initially present in the copolymer during the bisphenol curing process, they ought to be susceptible to nucleophilic attack but only in a chemoselective manner i.e.,



$$-\mathrm{CF_2CF_2}-\overset{\mathrm{CF_3}}{\overset{|}{\mathrm{C}}}=\mathrm{CH{-}CF{=}CH{-}CF_2}- \xrightarrow[\text{CURE SYSTEM}]{\mathrm{HOArOH}} -\mathrm{CF_2CF}=\overset{\mathrm{CF_3}}{\overset{|}{\mathrm{C}}}-\underset{\underset{\mathrm{OArOH}}{|}}{\mathrm{CH}}-\mathrm{CF{=}CH{-}CF_2}-$$

(59) (60)

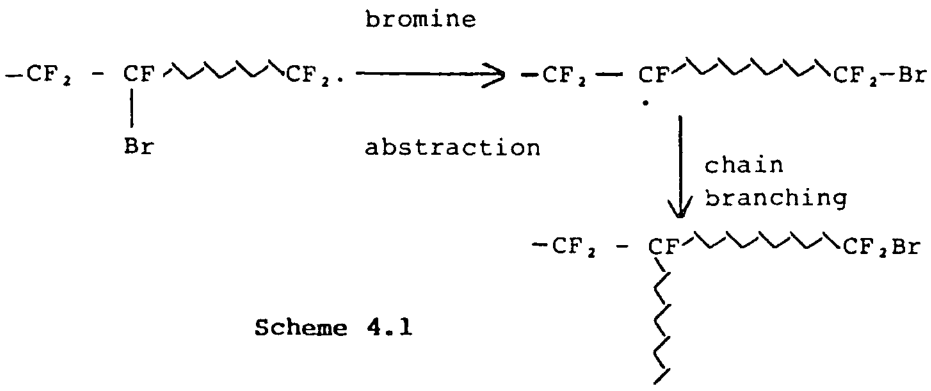
CHAPTER FOUR

DEVELOPMENT OF A NEW FREE RADICAL CROSS-LINKING PROCESS

4.1 Introduction

The studies outlined in chapter three have demonstrated the mechanism by which the cross-linking of $CF_3CF=CF_2/CH_2=CF_2$ copolymers probably occurs using the bisphenol curing system. Furthermore, it was shown that relatively reactive vinylic sites remain in the bisphenol cured elastomers and that such sites will be a source of long term instability towards nucleophiles, e.g. steam, amines, etc. A possible way in which to circumvent these undesirable features of nucleophilic cures is to carry out the cross-linking of the $CF_2CF=CF_2/CH_2=CF_2$ copolymer system by a free radical process.

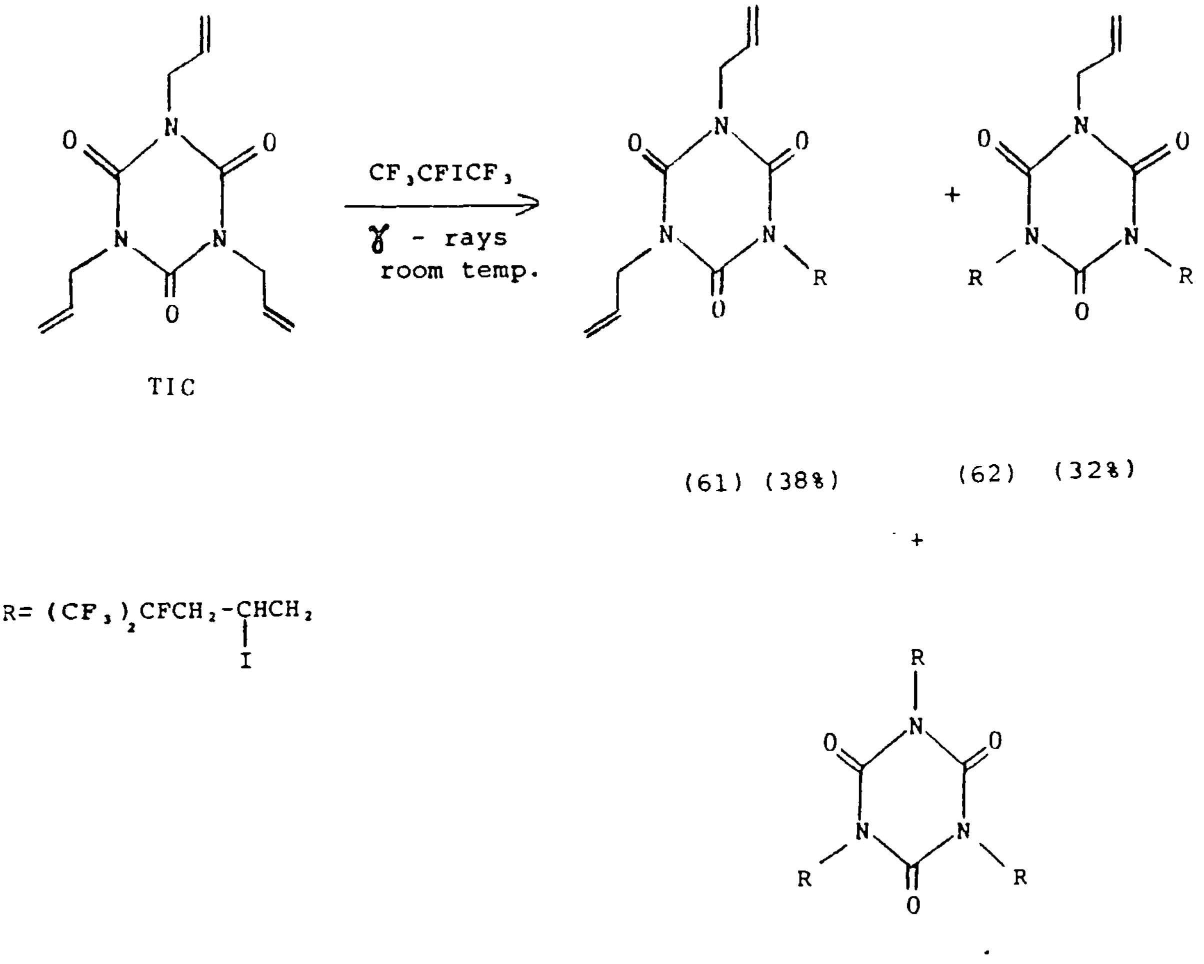
A number of fluorocarbon elastomers, which have been produced by a free radical cross-linking process, are commercially available. Fluropolymers containing bromine cure-sites have received much attention in recent years as they can be cured using a suitable peroxide and a cross-linking coagent, such as triallyl isocyanurate (TIC).[77,142] Although there are a number of advantages in using this type of curing system (See section 1.36b), the incorporation of bromine containing monomers can be problematic. This is because during polymerisation scission of carbon-bromine bonds can occur, which results in chain branching and/or inhibition of the process, e.g. with bromotrifluoroethylene;



Scheme 4.1

4.2 Cross-Linking of Bromine Containing Fluoropolymers

The curing of fluoropolymers containing bromotrifluoroethylene was studied by Apotheker and co-workers[77] who proposed a mechanism by which cross-link formation occurs (see Scheme 1.14). In order to obtain more definitive experimental evidence for the postulated cross-linking mechanism, the reaction between a perfluoroalkyl halide of the form R_FCFXR_F and the coagent TIC has been examined. Since fluoropolymers containing bromotrifluoroethylene have a highly fluorinated backbone containing pendant tertiary bromine atoms, the alkyl halide can be envisaged as approximating to this structure. The perfluoroalkyl halide of the type R_FCFXR_F which was most easily obtainable was heptafluoro-2-iodopropane (12). On irradiating a mixture of TIC and (12) with γ - rays at ambient temperature, three products were obtained as follows:



TIC

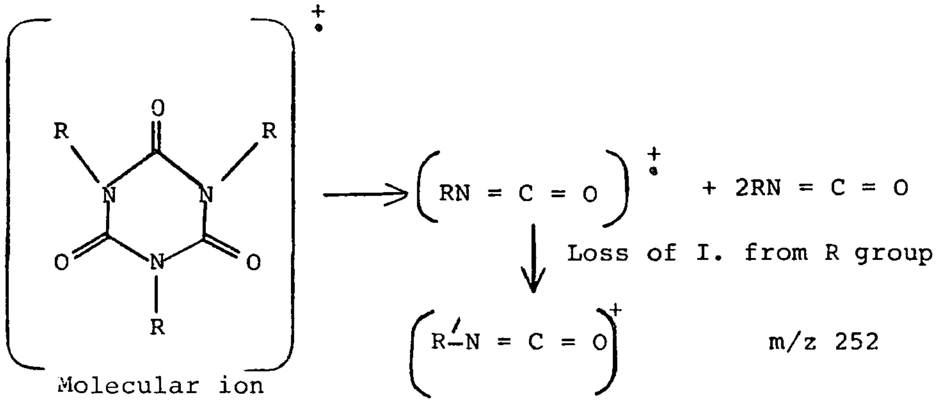
(61) (38%)

(62) (32%)

(63) (8%)

$R = (CF_3)_2CFCH_2\text{-}CH(I)CH_2$

Structural identification of the products was achieved by G.C.-mass spectrometry and by NMR spectroscopy (see appendix for spectra). The mass spectra (electron impact mode) of compounds (61) and (62) both included a base peak arising from the M^{+} - I fragment ion, at m/z 418 and 714 respectively. In contrast, this fragment ion was not observed in the mass spectrum of (63). Instead, a base peak was observed at m/z 252 which has been attributed to fragmentation of the isocyanurate ring of the molecular ion accompanied by loss of iodine, i.e.

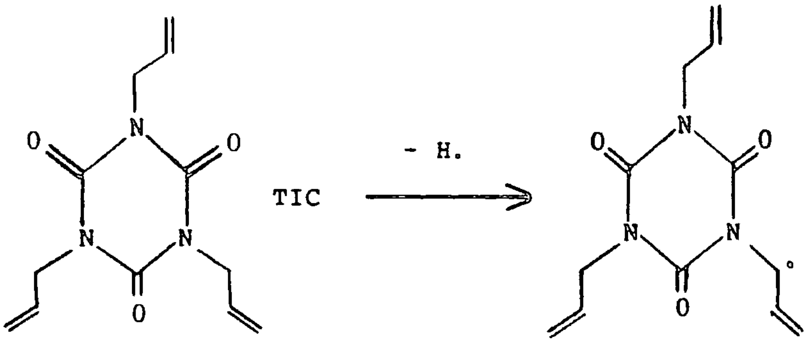


R = $(CF_3)_2CFCH_2CHICH_2$

The NMR shifts and couplings for the allyl groups of compounds (61-63) are essentially similar to those for TIC. By comparing the NMR shift data for the $(CF_3)_2CFCH_2$ group of the saturated model compounds described in chapter two with the NMR spectra obtained for (61), (62) and (63), it was possible to determine the direction of addition of heptafluoro-2-iodopropane to TIC, i.e. $(CF_3)_2CFCH_2CHICH_2$- was formed rather than $(CF_3)_2CFCH(CH_2I)CH_2$- .

The corresponding bromo compound of (12), 2-bromoheptafluoropropane, is a better model for the polymer system and ought to give analogous products to (61), (62) and (63), although the yields in each case would be expected to be lower since the C-Br bond will not undergo homolytic scission as readily as the C-I bond. Hence the reaction between (12) and TIC has clearly demonstrated the way in which cross-linking of bromine containing fluoropolymers must occur with TIC and is in agreement with the postulated mechanism (see Scheme 1.14).[77]

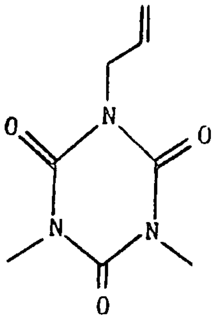
In principle, it is possible that during the cross-linking process abstraction of hydrogen from a methylene group of TIC could occur, to give a relatively stable radical intermediate of type (64).



(64)

In fact studies carried out by Apotheker and co-workers[77] demonstrated that of the t-butoxy radicals that were formed by thermal decomposition of the peroxide, 36% led to hydrogen abstraction reactions which ultimately produced either methane, t-butanol or isobutene, the latter formed by dehydration of t-butanol (see Scheme 1.14 and Table 1.9). This figure increases to ca 43% if the formation of other volatiles, ethylene, propylene and propane, are taken into account since they must be produced by a series of reactions that may include hydrogen abstraction from TIC. Hence, of the t-butoxy radicals that were produced, just over half were able to initiate the cross-linking process.

The reaction between TIC and heptafluoro-2-iodopropane (12) described above, has clearly shown that free radical addition to the alkene units of TIC occurs readily. This was also demonstrated by irradiation of a solution of TIC in acetone with γ- rays. TIC underwent rapid polymerisation[143,144] yielding a material which was highly soluble in acetone. Three major resonances in its solution state ^{1}H NMR spectrum were almost identical to those observed for TIC, so they have been attributed to the allyl unit within structure (65). This follows from the fact that on heating the material under vacuum, no TIC was transferred to a cold trap. Further work is under way to determine the overall structure of the material.

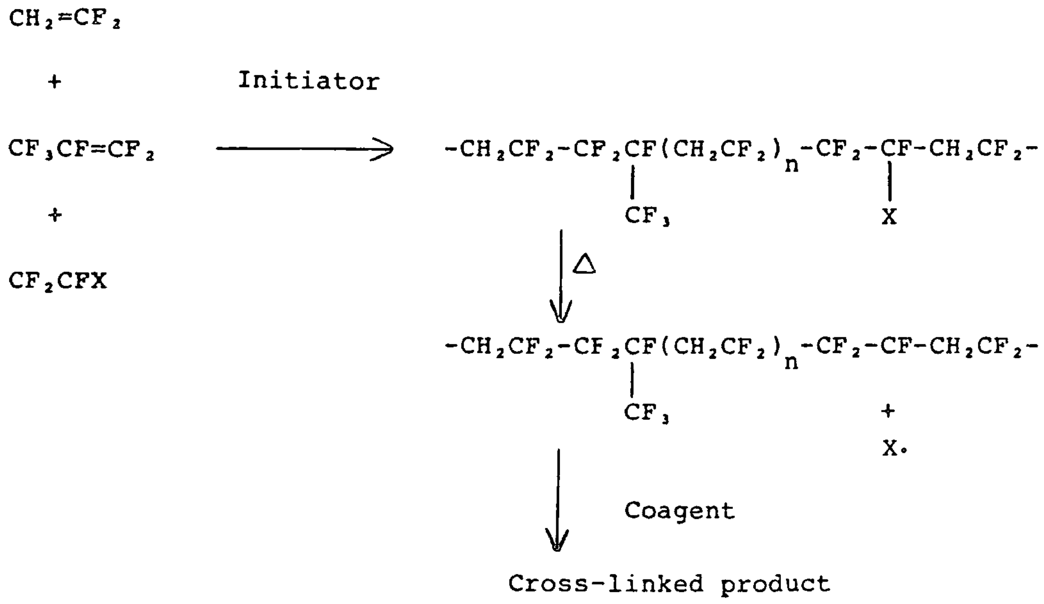


(65)

Similar irradiation of a mixture of HFP and TIC in actone with γ- rays gave a polymer in which HFP had been incorporated. Elemental analysis has shown that there are ca six TIC units to each of HFP in the polymer. Further analytical studies have been hampered by the fact that the polymer is virtually insoluble in all of the common organic solvents which have been examined to date, including DMF, hexane and chloroform.

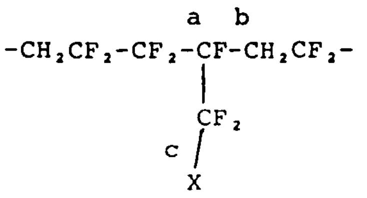
4.3 Cross-linking Via Sterically Crowded Cure-Sites

In order to avoid the occurrence of chain transfer processes during the incorporation of cure-site monomers that are responsive to free radical reactions, a new approach to the cross-linking of fluoropolymers has been investigated. This involves the incorporation of a sterically crowded monomer into the polymer system which can undergo facile and specific homolytic bond scission at elevated temperatures, yielding polymer radicals which would be active towards cross-linking in the presence of a suitable coagent such as TIC (see Scheme 4.2).[133]



Scheme 4.2

There are many possible sterically crowded groups which can be envisaged for the group X but there are a number of important requirements which must be overcome, as outlined in Section 1.36. In addition it is preferable that the group X is not directly bonded to the polymer backbone but, instead, is separated by at least one carbon unit, e.g. a CF_2 group. This is advantageous in that steric crowding is then minimized at the point where the crowded alkene is attached to the polymer backbone, thus reducing the risk of chain scission, i.e. cleavage of bonds a and b in (66).

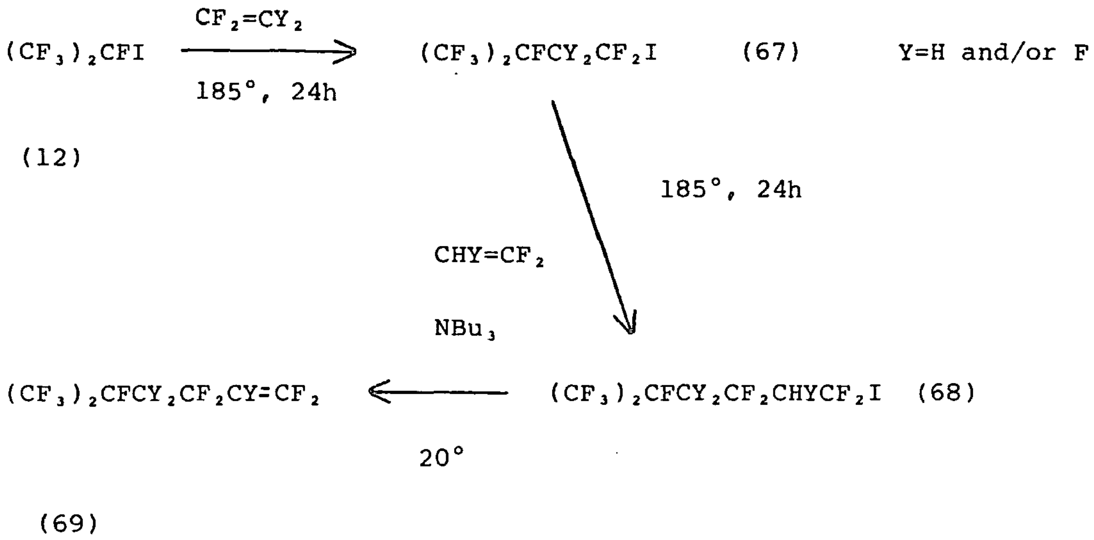


$$-CH_2CF_2-CF_2\overset{a}{-}CF\overset{b}{-}CH_2CF_2- \quad (CF_2\overset{c}{-}X \text{ on } CF)$$

(66)

4.4 Synthesis and Incorporation of $i\text{-}C_3F_7CY_2CF_2CY=CF_2$(69)

Initially, the synthesis and incorporation of some alkene compounds derived from 2-iodoheptafluoropropane, i.e. $X=(CF_3)_2CF$, was carried out. The syntheses were achieved in good yields using the route given below in Scheme 4.3 (cf. Section 2.2).



Scheme 4.3

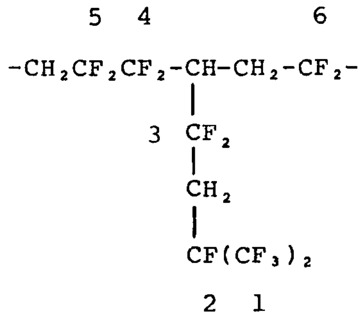
Copolymerisation reactions with vinylidene fluoride and each of the alkenes were carried out in sealed and evacuated Carius tubes, with irradiation by γ- rays. This method of initiation is advantageous not only in that the copolymerisations can be carried out at ambient temperature but, more importantly, that the resultant copolymers are produced in high purity which thereby facilitates their structural analysis.

The copolymers displayed high solubility in DMF and were therefore analysed by solution state ^{19}F NMR in order to determine the degree of incorporation of (69). Each of the copolymer systems that were prepared are discussed below.

4.41 $CH_2=CF_2/(CF_3)_2CFCH_2CF_2CH=CF_2$ (29b)

A mixture of $(CF_3)_2CFCH_2CF_2CH=CF_2$ (29b) and vinylidene fluoride in 1:9 ratio was irradiated with γ- rays for 2 days. By comparing the ^{19}F chemical shifts for the groups in alkene (29b) with the ^{19}F NMR spectrum of the copolymer, it was determined that the comonomer (29b) had largely been incorporated as structure(70). The degree of molar incorporation of (29b) was determined as 7% by assigning the resonances in the ^{19}F NMR spectrum due to vinylidene fluoride units in the copolymer (see Section 2.6) and obtaining their overall intensity measurement relative to that for a CF_2 group within structure (70).

Together with the resonances assigned to structure (70) (See Table 4.2) in the ^{19}F NMR spectrum of the copolymer, a number of other resonances were observed also. For example, resonances at -59.9 and -66.0 ppm of equal intensity indicate that $(CF_3)_2$—C=C sites may be present in the copolymer and that the incorporation of (29b) is not merely a simple process leading to exclusive formation of structure (70).



$-CH_2CF_2CF_2-CH(CF_2CH_2CF(CF_3)_2)-CH_2-CF_2-$

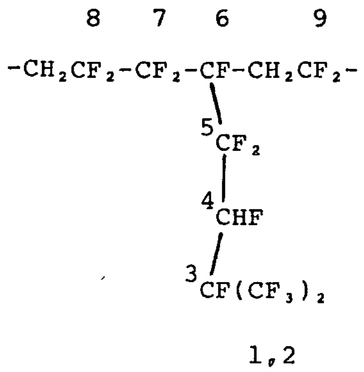
(70)

Table 4.2

δ_F/PPM	Assignment
- 78.0	1
- 81.8	3
- 89.9	6
-111.2	4 or 5
-112.6	4 or 5
-186.2	2

4.42 $CH_2=CF_2/i-C_3F_7CHFCF_2CF=CF_2$(69b)

On irradiation of a 1:8 mixture of (69b) to vinylidene fluoride for 2 days, a copolymer was obtained which contained _ca_ 12% molar composition of (69b), incorporated as the structural unit (71) (Table 4.3).



$-CH_2CF_2-CF_2-CF(CF_2CHFCF(CF_3)_2)-CH_2CF_2-$

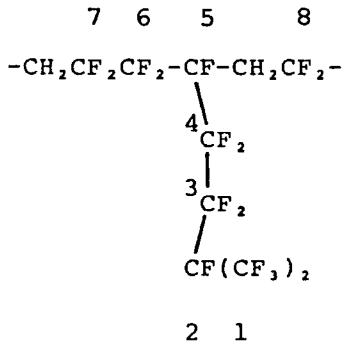
(71)

Table 4.3

δ_F/PPM	Assignment
- 72.3	1 or 2
- 74.5	1 or 2
- 93.0	9
-109.9	8
-116.6	5 or 7
-117.1	5 or 7
-184.9	3,6
-206.8	4

4.43 $CH_2=CF_2/i-C_3F_7CF_2CF_2CF=CF_2$(69a)

The copolymer obtained on irradiation of a 1:8 mixture of (69a) and vinylidene fluoride contained 10% molar composition of the structural unit (72).



$-CH_2CF_2CF_2-CF(CF_2CF_2CF(CF_3)_2)-CH_2CF_2-$

(72)

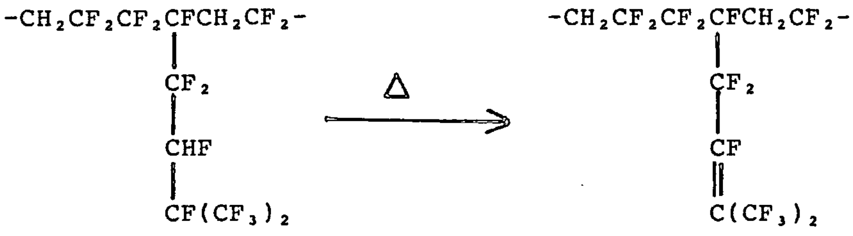
Table 4.4

δ_F/PPM	Assignment
- 72.0	1
- 93.5	8
-109.8	7
-112.8	3,4,6
-114.5	
-116.5	
-185.5	2 or 5
-186.0	2 or 5

4.44 Suitability of the i-C_3F_7 Group for Cross-Linking Purposes

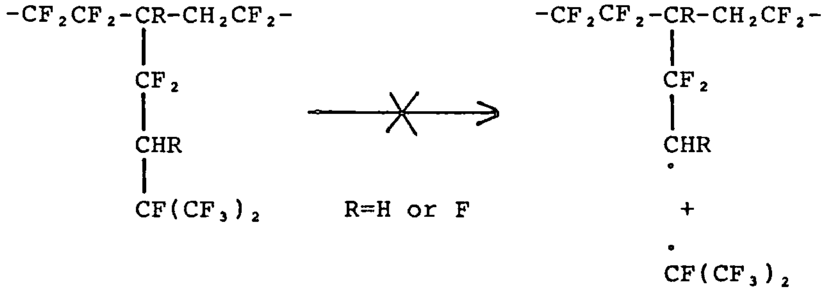
A convenient way in which to follow chemical and/or physical changes in a material involves the use of differential scanning calorimetry (DSC). The material to be examined is slowly and steadily heated to elevated temperatures under an atmosphere of dry argon. Any endothermic or exothermic processes are detected by a change in the specific heat capacity of the material, which is plotted against temperature on a chart recorder. Since only small samples are required for analysis, typically on the milligram scale, this technique is highly suitable for the examination of polymers containing crowded sites since it would be expected that cleavage of the weak bonds and resultant relief in steric crowding will be an exothermic process.

On investigation of the homopolymer of VDF by DSC, no exothermic or endothermic process was observed in the temperature range 30-300°C. However, the copolymer of VDF and the alkene (69b) showed a steadily increasing exotherm from 70°C upwards. This is unlikely to be due to specific homolytic cleavage of the i-C_3F_7 group since a relatively sharp exotherm would be expected. Instead, the observed exotherm may be due to elimination of hydrogen fluoride, as follows:



(71) (73)

This process did not occur with the copolymer of VDF and alkene (29b), which instead showed an endothermic melting point in the region 150-170°C. In fact for the copolymers containing (29b) and (69b) specific homolytic bond scission of the type (74) ⟶ (75) was not observed, so that the isopropyl group is not sufficiently crowded for our purposes.



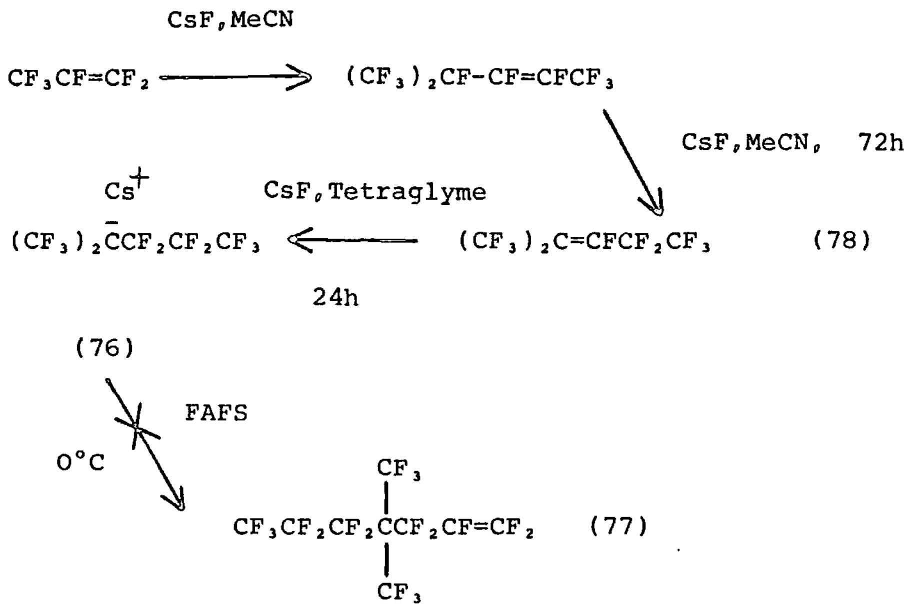
(75)

(74)

The investigations have clearly demonstrated that alkenes of the type (69) possess suitable sites for incorporation into VDF polymers, although the presence of hydrogen atoms in the monomers can lead to the occurrence of side reactions during the copolymerisation process. In addition, the investigations have been useful in developing a suitable methodology for the preparation and analysis of copolymers containing bulky pendant groups.

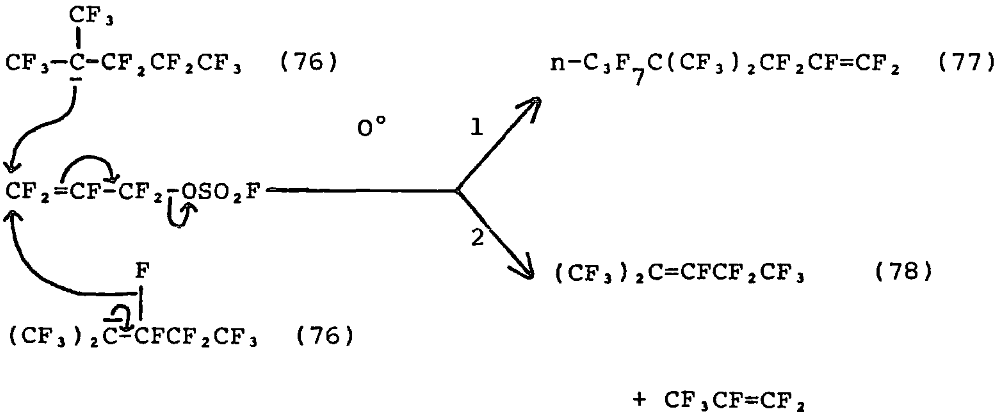
4.5 Attempted Synthesis of n-$C_3F_7C(CF_3)_2CF_2CF{=}CF_2$(77)

Having demonstrated that alkenes of the type $R_FCF_2CF{=}CF_2$ can be copolymerized with VDF, attempts were made to synthesize comonomers in which the R_F group is more sterically crowded than the heptafluoroisopropyl group. Initially the route to the alkene (77) was investigated (See Scheme 4.4).



Scheme 4.4.

For the reaction of the carbanion (76) with perfluoroallylfluorosulphate (FAFS)[146] there are two possible processes which could occur, resulting from either a

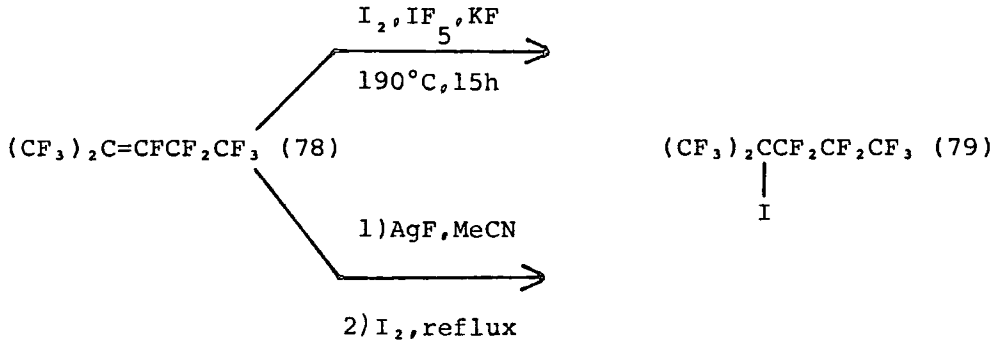


Scheme 4.5

simple quenching reaction or a donation of fluoride ion (see Scheme 4.5). The reaction was carried out at 0°C since any significant rise in temperature would be expected to favour route 2 over route 1. However, the former pathway occurred exclusively instead of the reaction which led to the required product (77).[147]

4.6 Routes to Some Crowded Alkenes via n-$C_3F_7C(CF_3)_2I$(79)

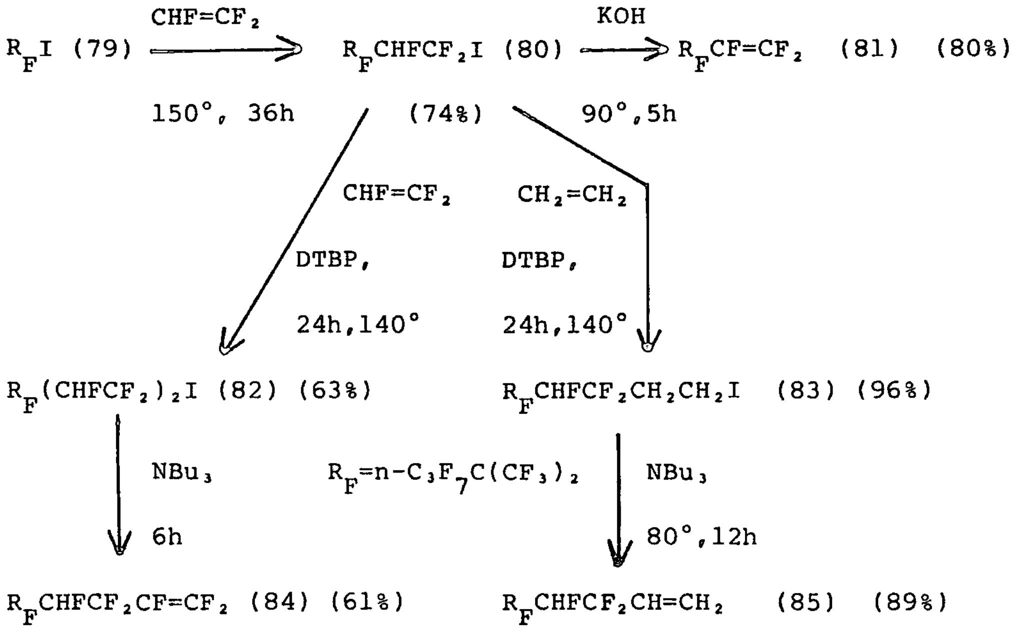
Two routes to perfluoro-2-iodo-2-methylpentane (79) have been described by von Werner et al which both involve formal addition of iodine fluoride to the double bond of perfluoro-2-methylpent-2-ene (78).[148]



Scheme 4.6

Both of these routes were examined but no reaction occurred using the $IF_5/I_2/KF$ system. However, the second system employing silver (I) fluoride gave the iodide (79) in 66% yield. The use of silver fluoride rather than caesium fluoride for the formation of (79) was important in that the iodide ions produced in the reaction were efficiently removed from solution as silver iodide, which could then be recovered. Iodide ions rapidly attack (79) with consequent reformation of the starting alkene (78).

The relatively low thermal stability, i.e. weak carbon-iodine bond, of the iodide (79) can be exploited in carrying out some free radical additions to certain fluoroalkenes. In this way the crowded alkene compounds (81),(84) and (85) were synthesized in good yields by the route outlined in Scheme 4.7.

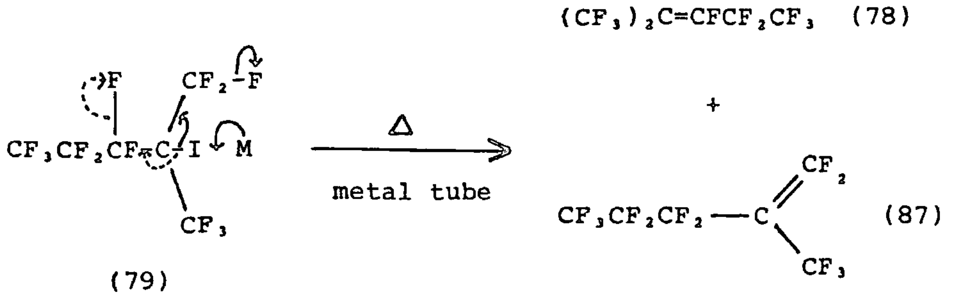


Scheme 4.7

Perfluoro-2-bromo-2-methylpentane, the bromo derivative of (79) was unsuitable for free-radical reaction with trifluoroethylene even using peroxide or gamma ray initiation.

The thermal reaction between the crowded iodide (79) and trifluoroethylene, when carried out in a glass vessel, gave (80) as the major product with only small amounts of (82) formed also. Only ca 2% of (80) was due to its regioisomer R_FCF_2CHFI (86) which demonstrates that the process is of high regioselectivity. Typically, for reactions that involve free radical addition to trifluoroethylene, 10-15% of the propagating radicals attack the difluoromethylene moiety of the double bond.[149]

Partial decomposition of the crowded iodide (79) according to Scheme 4.8 occurred when conversion to (80) was carried out in a stainless steel tube, or to a lesser extent, a nickel tube. However, these side reactions can be avoided by carrying out the process in a glass vessel or a Hastelloy tube.

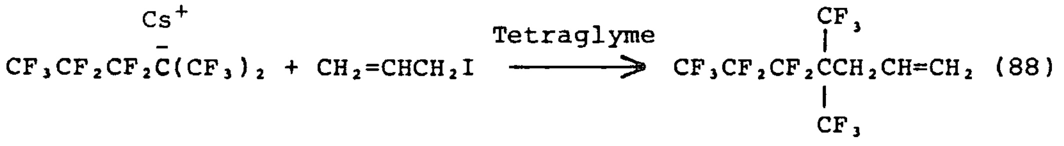


Scheme 4.8

Telomerisation reactions with (80) were carried out using a peroxide initiator. With trifluoroethylene (82) was the major product but higher telomers were also formed. Reaction between (80) and ethylene, however, yielded (83) exclusively.

4.7 Quenching of Carbanion (76) with Allyl Iodide

The carbanion (76), formed by addition of fluoride ion to F-2-methylpent-2-ene (78) in tetraglyme, was quenched with allyl iodide to give the crowded alkene (88).[147]



$$\underset{(76)}{CF_3CF_2CF_2\overset{Cs^+}{\bar{C}}(CF_3)_2} + CH_2{=}CHCH_2I \xrightarrow{\text{Tetraglyme}} CF_3CF_2CF_2\overset{CF_3}{\underset{CF_3}{C}}CH_2CH{=}CH_2 \quad (88)$$

(76)

4.8 Copolymerisation Studies

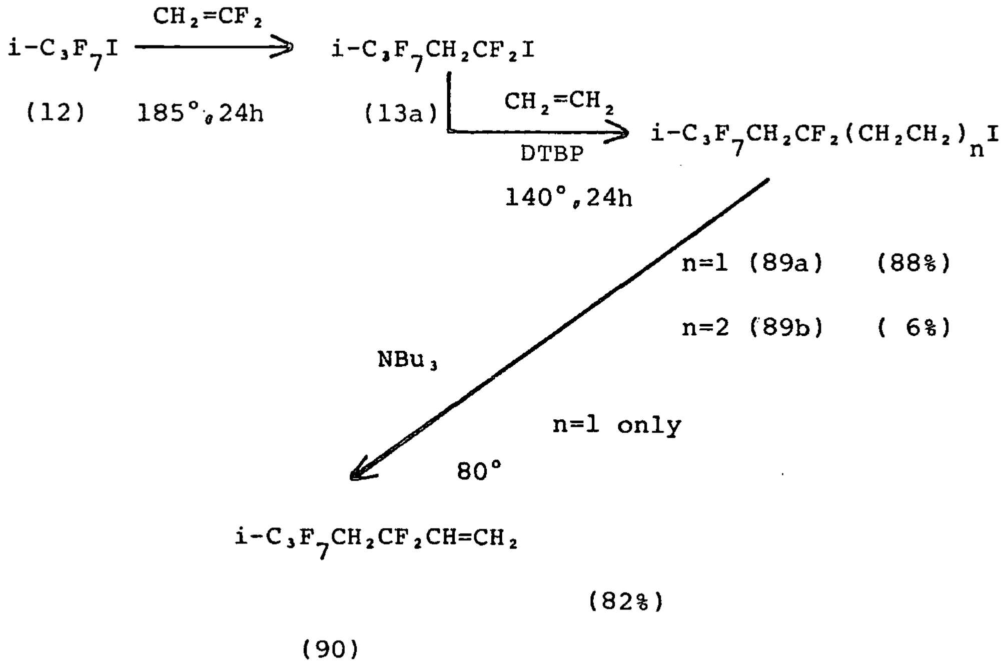
Mixtures of each of the alkenes (81), (84), (85) and (88) with vinylidene fluoride were irradiated with γ- rays as described in Section 4.4. Each of the systems are discussed below.

4.81 $CH_2{=}CF_2$ With $n\text{-}C_3F_7C(CF_3)_2CF{=}CF_2$(81)

On irradiating a 9:1 mixture of vinylidene fluoride to (81) with γ - rays for 72h, analysis of the resultant polymer showed that the incorporation of (81) was minimal. This result is most likely to be due to the difficulty of a propagating polymer radical in approaching alkene (81), due to the sterically demanding perfluoroalkyl group of the latter. Therefore, for alkene (81) the crowded perfluoroalkyl uni is spatially too close to the site of polymerisation.

4.82 $CH_2=CF_2$ with n $-C_3F_7C(CF_3)_2CHFCF_2CH=CH_2$ (85)

Irradiation of both a $CH_2=CF_2$/(85) and a $CH_2=CF_2/CF_3CF=CF_2$/(85) mixture with γ-rays at room temperature failed to initiate polymerisation. Instead only a slight discolouration of each of the systems was observed and the starting monomers were recovered. Copolymerisation also failed to occur at temperatures up to 140°C with mixtures of alkene (90) and vinylidene fluoride, using either peroxide or γ-rays initiation. Alkene (90) was used for the studies at elevated temperatures rather than (85) since the former contains the relevant $-CF_2CH=CH_2$ unit but can be prepared more easily. The route used to synthesize (90) is shown in Scheme 4.9.



Scheme 4.9

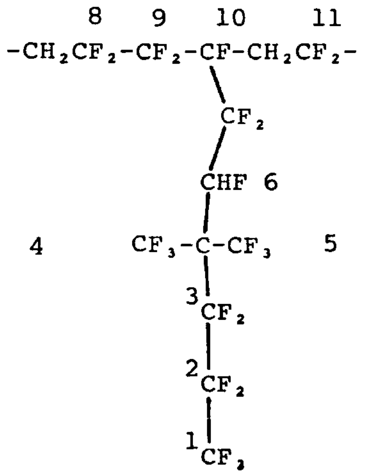
These results are rather surprising not only in that alkenes (85) and (90) failed to incorporate but also that they actually hindered the homopolymerisation of vinylidene fluoride.

4.83 $CH_2=CF_2$ with $n-C_3F_7C(CF_3)_2CH_2-CH=CH_2$ (88)

Irradiation of a 1:9 mixture of (88) and vinylidene fluoride with gamma rays failed to produce any polymeric material, as for the alkenes (85) and (90).

4.84 $CH_2=CF_2$ with $n-C_3F_7C(CF_3)_2CHFCF_2CF=CF_2$(84)

On irradiation of a 1:10 mixture of alkene (84) and vinylidene fluoride a copolymer was obtained that consisted of 22% molar composition of (84), which had been incorporated as the structural unit (91), as determined by ^{19}F NMR spectroscopy (Table 4.5).



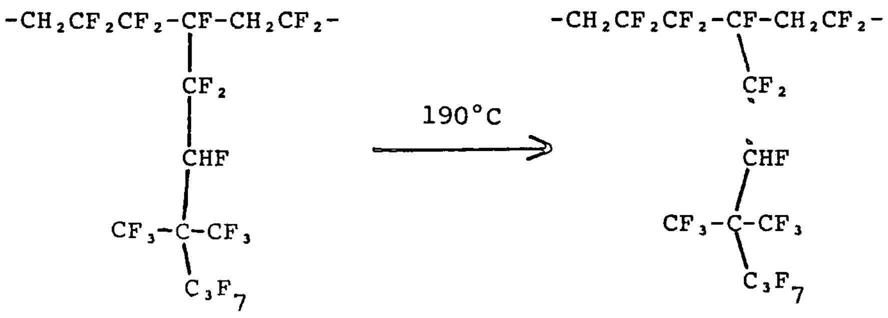
(91)

Table 4.5

δ_F/PPM	Assignment
- 58.8	4 or 5
- 59.1	4 or 5
- 79.7	1
-104.0	3
-106.8	7
-121.5	2
-114.5	8 or 9
-115.7	8 or 9
-187.3	10
-198.0	6

4.9 Thermal Stability of the $CH_2{=}CF_2/n\text{-}C_3F_7C(CF_3)_2CHFCF_2CF{=}CF_2$ Copolymer

The thermal stability of the copolymer of VDF and $n\text{-}C_3F_7C(CF_3)_2\text{-}CHFCF_2CF{=}CF_2$ (84) described in Section 4.84 was investigated by DSC. When a sample of the copolymer was progressively heated from 30° to 400°C two exotherms were observed, the first between 160 and 200°C and the second between 275 and 380°C. The latter was due to decomposition of the copolymer since tarring was observed but the first exotherm has been attributed to specific homolytic bond cleavage of the type (91) → (92).



(91) (92)

Confirmation that bond scission of this type had occurred was achieved by heating a sample of the copolymer to 190°C for 0.5 h under high vacuum. The system was backed up by a cold trap which was subsequently rinsed out with acetone. The only product transferred to the cold trap during the experiment was identified as (93) by NMR spectroscopy (e.g. δ_F = - 188.4 and - 197.5 ppm for the CHF groups (two diastereoisomers) Due to the crowded nature of (93), its mass spectrum (EI) showed complete fragmentation of the molecular ion. The highest observed masses were 463 (loss of H, CF_3 and C_3F_7) and 363 (loss of H and two C_3F_7 groups).

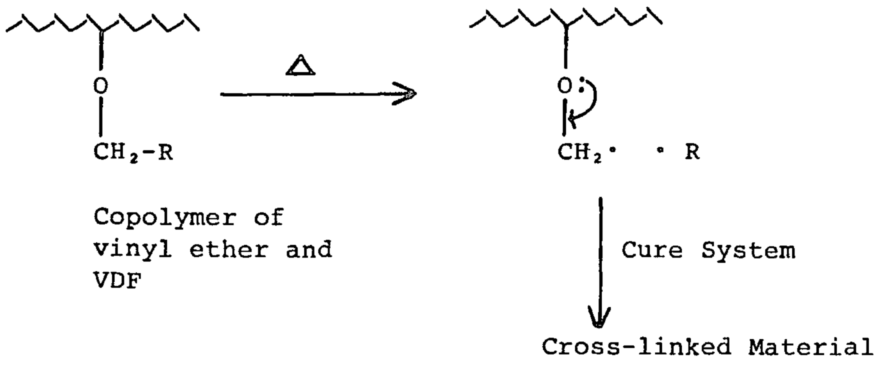
The observation of (93) provides clear evidence that specific bond scission of the copolymer had occurred, with concomitant formation of the radical $n\text{-}C_3F_7\,C(CF_3)_2\,\dot{C}HF$ (92a) and that alkene (84) is entirely suitable as a source of polymer radicals for cross-linking purposes.

$$CF_3CF_2CF_2C(CF_3)_2CHF. \longrightarrow \left[\,CF_3CF_2CF_2C(CF_3)_2CHF\,\right]_2$$

(92a) (93)

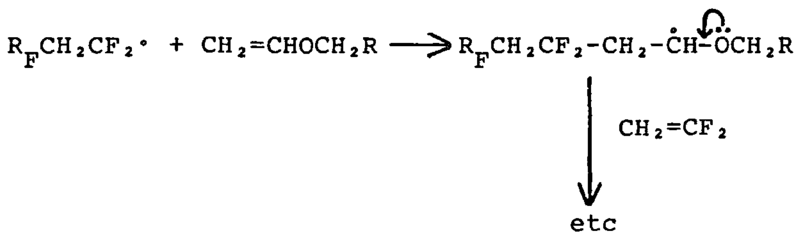
4.10 Attempted Synthesis of Vinyl Ethers Containing a Bulky Pendant Group

Vinyl ethers of the type $RCH_2OCF{=}CF_2$ and $RCH_2OCH{=}CH_2$, where R is a bulky alkyl or perfluoroalkyl group, ought to copolymerize with vinylidene fluoride (cf. Scheme4.2) so that it is possible for the resultant copolymers to undergo thermally induced homolytic bond scission as follows:



Scheme 4.10

The oxygen aton is strategically positioned so as to stabilize the polymer radicals which, under suitable conditions, ought to give rise to intermolecular cross-links. In addition, the oxygen atom can stabilize propagating polymer radicals during the copolymerisation process, i.e.:

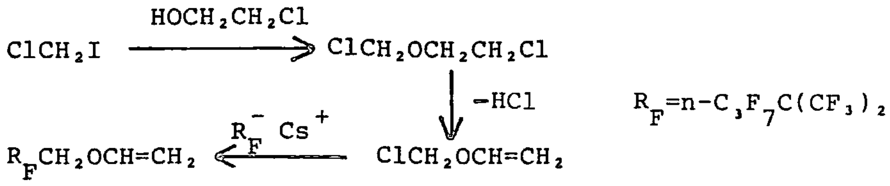


Scheme 4.11

Two routes to vinyl ethers of this type have been investigated as outlined below.

4.101 $R_FCH_2OCH{=}CH_2$ (94)

The route to the crowded alkene (94), as illustrated in Scheme 4.12, has been examined.



(94)

Scheme 4.12

However, it was found that little reaction occurred between 2-chloroethanol and chloroidomethane, even after modification of the conditions as follows:

i) $ClCH_2I$, $HOCH_2CH_2Cl$, $Na^{+-}OCH_2CH_2Cl$, 120°C

ii) $ClCH_2I$, $Na^{+-}OCH_2CH_2Cl$, DMF, 120°C

iii) $ClCH_2I$, $HOCH_2CH_2Cl$, DMF, K_2CO_3

4.102 $Me_3CCH_2OCF=CF_2$ (95)

A potential route to the crowded vinyl ether (95) involves reaction between neopentyl alchol and tetrafluoroethylene.

$$Me_3CCH_2OH \xrightarrow[\text{ii) TFE, DMF, } 50^\circ C]{\text{i) Na}} Me_3CCH_2OCF=CF_2 \qquad (95)$$

Neopentyl alchol was completely converted to the alkoxide using sodium metal in rigorously dried ether, in order that conversion to (95) would occur rather than formation of $Me_3CCH_2OCF_2CF_2H$ (96). However, although dry solvents were used throughout only (96) was produced in 46% yield.

Attempts to remove hydrogen fluoride from (96) to give the requisite vinyl ether (95) were unsuccessful. Treatment of (96) with SbF_5 at room temperature led to a vigorous reaction, the products of which gave a complex ^1H NMR spectrum. In addition, no reaction between (96) and D.B.U. was observed at temperatures up to 200°C.

4.11 Conclusions

It has been demonstrated that alkenes containing a crowded perfluoroalkyl group can be prepared by relatively simple synthetic routes but that the suitability of these compounds for copolymerisation with vinylidene fluoride is dependent on a number of factors.

1) It is important that the alkene moiety of the comonomer consists either of trifluorovinyl or a 1,1-difluorovinyl group. Alkenes of the form $R_FCF_2CH{=}CH_2$ or $R_FCH_2CH{=}CH_2$ failed to incorporate and this is rather surprising since Apotheker and coworkers observed that both 4-bromo - 2,3,4,4,-tetrafluorobut-1-ene and 6-bromo- 5,5,6,6,- tetrafluorohex-1-ene formed terpolymers with hexafluoropropene and vinylidene fluoride.[76,77]

2) The sterically demanding perfluoroalkyl group must not be directly bonded to the site of polymerisation since this will result in minimal incorporation. This crowding effect was observed for the alkene $n\text{-}C_3F_7C(CF_3)_2CF{=}CF_2$(81).

The alkene $n\text{-}C_3F_7C(CF_3)_2CHFCF_2CF{=}CF_2$(84) possesses the important features mentioned above and therefore easily underwent copolymerisation with vinylidene fluoride. Studies with the resultant copolymer have clearly demonstrated that the bulky, pendant perfluoroalkyl groups can be thermally cleaved to yield polymer radicals which, under suitable conditions, should be able to form a cross-linked network. This methodology offers a completely new approach to the cross-linking of HFP/VDF copolymers but without the limitation of leaving sites of instability in the cured products, as is found with nucleophilic curing systems.

CHAPTER FIVE

REMARKABLE CHEMISTRY OF THE MODEL COMPOUNDS WITH ANTIMONY PENTAFLUORIDE

5.1 Introduction

In Chapter three the use of antimony pentafluoride as a dehydrofluorinating agent in the synthesis of unsaturated model compounds was discussed. In the examples given, elimination of hydrogen fluoride occurred exclusively at sites involving 'tertiary' fluorine, i.e.,

$$(CF_3)_2CFCH_2(CF_2CH_2)_n\ CF_2R_F \xrightarrow[120^\circ C]{SbF_5} (CF_3)_2\ C{=}CH(CF_2CH_2)_nCF_2R_F$$ [133]

$n=0$ and $R_F=F$ or Coupled (80-86%)

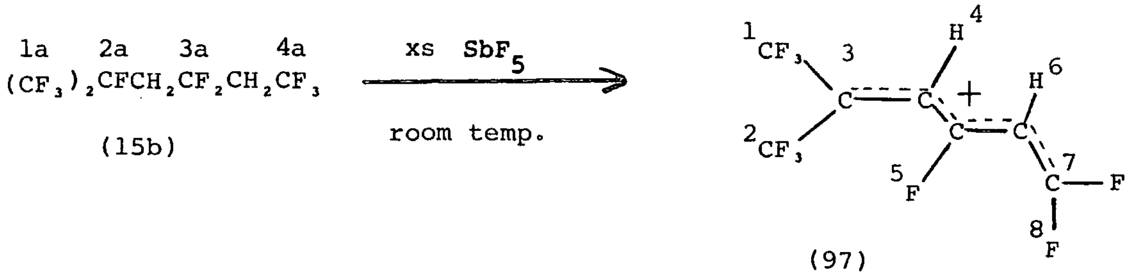
However it was found that saturated model compounds of longer chain length, i.e. $n \geqslant 1$, are susceptible to elimination of hydrogen fluoride by antimony pentafluoride at room temperature. Moreover, the products of dehydrofluorination are not alkenes but instead, remarkably stable allylic carbocations which in all examples discovered to date show no sign of decomposition on storing at room temperature for several weeks. This chemistry, together with its application to the synthesis of polyacetylene derivatives, is discussed in this chapter.

5.2 Preparation of Remarkably Stable Fluorinated Carbocations

Much work has been published on the synthesis and characterisation of stable fluorinated carbocations.[150-157] During the course of these studies fluorinated carbocations were prepared in each case by dissolving appropriate model compounds in an excess of antimony pentafluoride at room temperature (typically 6:1 excess). During the process antimony pentafluoride functions as both a Lewis acid and as the solvent.

5.21 Treatment of $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (15b) with SbF_5

When an excess of antimony pentafluoride was added to the saturated model (15b), significant changes in the NMR spectra were observed as outlined in table 5.1. The geminal CF_3 groups became non-equivalent, i.e. coupling was observed and, in addition, the resonances due to the CF_2 and terminal CF_3 group completely disappeared. In the ^{19}F NMR spectrum, signals downfield from the $CFCl_3$ reference became evident and increased with time, gaining maximum intensity after ca ½ hour. The NMR spectra clearly indicate the quantitative formation of an observable carbocation (97) (see tables 5.1 and 5.2).



(15b)

(97)

TABLE 5.1

Selected ^{19}F NMR DATA FOR (15b) and (97)

Model (15b)		Carbocation (97)	
δ_F/ppm	Assignment	δ_F/ppm	Assignment
- 80.4	1a	- 69.1	1
-188.2	2a	- 62.6	2
- 93.8	3a	+14.8	5
- 65.2	4a	+32.2	7,8
		+34.0	

(see appendix for full ^{19}F and ^{1}H NMR spectra)

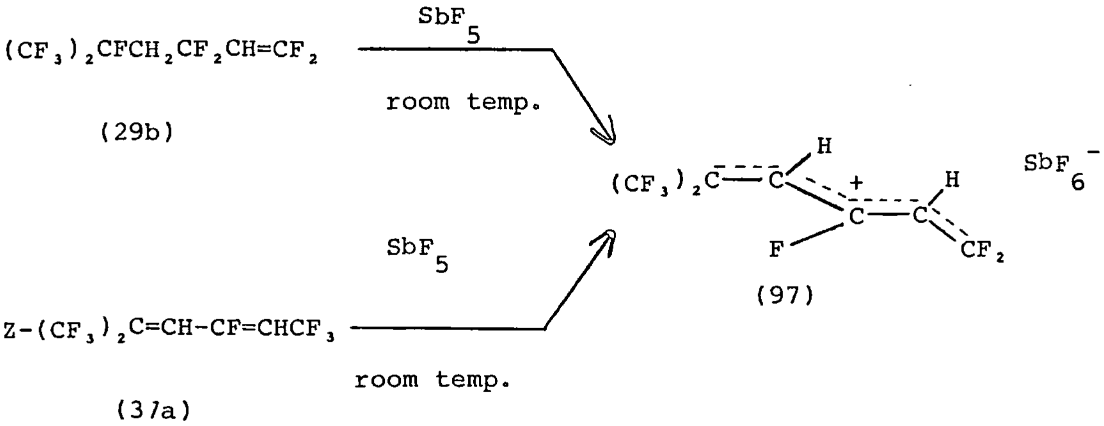
Table 5.2

^{13}C NMR DATA FOR CARBOCATION (97)

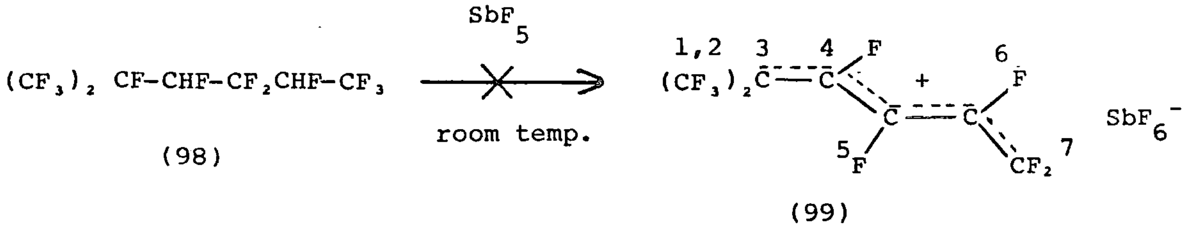
δ_C/ppm	COUPLING/Hz	ASSIGNMENT
96.1	D(J=20)	6
116.1	Q(J=278)	1,2
117.4	Q(J=277)	
125.2	S	4
146.0	Sept.(J=36)	3
177.4	T(J=365)	7
199.4	D(J=354)	5

The ^{19}F and ^{13}C NMR spectra of carbocation (97) show that the charge must be essentially delocalised as shown. This conclusion follows from the fact that the resonances associated with 5-CF and 7-CF_2 show massive downfield shifts from the values observed for similar model compounds. For example, the δ_C and δ_F values for the vinylic CF in Z-$(CF_3)_2$C=CH-CF=CHCF_3(37a) are 121.3 and -102 ppm respectively. In contrast the signals associated with the vinylic CH groups 4-CH and 6-CH in the ^{13}C NMR spectrum of carbocation (97) show upfield shifts when compared to compound (37a) in which these groups resonate at 129.3 and 109.0 ppm respectively. It would be expected that any charge development at the 3-C site in carbocation (97) will be disfavoured by the inductively electron withdrawing capability of the geminal trifluoromethyl groups. However, there must be some degree of charge development at this site since its signal in the ^{13}C NMR spectrum, at 146.0 ppm, is significantly shifted downfield from that for the corresponding group in (37a) at 127.8 ppm. The stereochemistry of carbocation (97) could not be elucidated from the NMR data but it must exist in the Z- configuration as determined by quenching reactions (see section 5.31).

Further evidence for the existence of carbocation (97) stems from the fact that it can also be prepared by treatment of either (29b) or (37a) with an excess of SbF_5 at room temperature, i.e.;



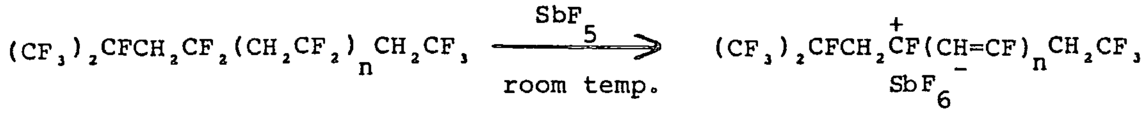
It is interesting to contrast the chemical behaviour of (15b) in SbF_5 with that of (98) in SbF_5. The former system gave carbocation (97) as described above but compound (98) was completely unaffected by SbF_5, i.e. carbocation (99) was not produced.



This observation is understandable since carbocation (99) would be relatively less stable than (97) due to the replacement of the hydrogens by fluorine at the 4-C and 6-C positions, i.e. adjacent to the charge centres. It is now well established that fluorine at a carbocation site $F-\overset{+}{C}\!\lessgtr \leftrightarrow \overset{+}{F}=C\lessgtr$ is stabilising whereas at a site adjacent to the positive charge $F\leftarrow C-\overset{+}{C}\lessgtr$, fluorine is inductively strongly destabilising.[158]

5.22 $(CF_3)_2CF(CH_2CF_2)_n\ CH_2CF_3$ (15) with SbF_5

The higher homologues of (15b) also yield observable allylic carbocations on treatment with an excess of antimony pentafluoride at room temperature.[133]



$$(CF_3)_2CFCH_2CF_2(CH_2CF_2)_nCH_2CF_3 \xrightarrow[\text{room temp.}]{SbF_5} (CF_3)_2CFCH_2\overset{+}{C}F(CH{=}CF)_nCH_2CF_3\ \ SbF_6^-$$

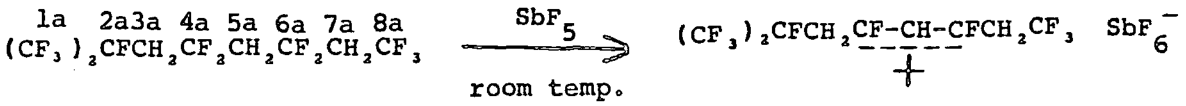
(15c)	n=1	(100)
(15d)	n=2	(101)
(15e)	n=3	(102)

For these model compounds, allylic carbocations can be produced by elimination of fluorine exclusively from CF_2 units. This is in contrast to model (15b) which only contains one difluoromethylene unit so, in order to form an allylic carbocation, there must also be loss of fluorine from a trifluoromethyl group. The structure of the carbocations (100),(101) and (102), is such that fluorine is directly attached to those carbon atoms bearing a partial positive charge i.e. a stabilising situation. In addition the destabilising effects of the electron withdrawing trifluoromethyl and heptafluoroisopropyl groups are diminished by the presence of a methylene unit between these groups and the charge centres.

The NMR spectra of carbocations (100), (101) and (102) clearly indicate the sites at which the overall positive charge is principally located (see appendix for complete spectral data). As an example, details of the ^{19}F and ^{13}C NMR spectra of carbocation (100) are outlined in tables 5.3 and 5.4 respectively. The fact that the charge is essentially localised on carbons 4-CF and 6-CF is clearly shown by the two doublet resonances at the relatively low field shift values of 209.3 and 210.5ppm in the ^{13}C NMR spectrum. In addition, the ^{19}F NMR signals for the CF_3 groups of the saturated model (15c) are virtually unchanged after treatment with SbF_5, whereas those for the CF_2 groups at -91.2 and -92.9 ppm are not observed. Instead, a resonance of integral two appears at + 58.5ppm which is approximately 150 ppm downfield from the signals for the CF_2 groups.

Table 5.3

Selected ^{19}F NMR Data for Model (15c) and carbocation (100)



$$\overset{1a}{(CF_3)_2}\overset{2a}{C}F\overset{3a}{C}H_2\overset{4a}{C}F_2\overset{5a}{C}H_2\overset{6a}{C}F_2\overset{7a}{C}H_2\overset{8a}{C}F_3 \xrightarrow[\text{room temp.}]{SbF_5} (CF_3)_2CFCH_2\underset{+}{\underline{CF-CH-CF}}CH_2CF_3 \quad SbF_6^-$$

(15c) (100)

δ_F/ppm	Assignment	δ_F/ppm	Assignment
- 63.6	8a	- 63.0	8
- 78.7	1a	- 79.4	1
-186.7	2a	-181.9	2
- 91.2	4a	+ 58.5	4,6
- 92.9	6a		

TABLE 5.4

^{13}C NMR data for carbocation (100)

δ_C/ppm	Coupling/Hz	Assignment
35.7	S	3
42.0	Q(J=36)	7
89.0	D(J=250)ofsept.(J=29)	2
111.7	S	5
117.4	Q(J=287)ofD(J=26)	1
118.7	Q(J=281)	8
209.3	D(J=368)	4,6
210.5	D(J=373)	

On comparing NMR data for ions (100), (101) and (102), an upfield trend for the ^{19}F and ^{13}C chemical shifts of the charged sites is observed (see table 5.5). These trends are understandable since charge is delocalised over a greater number of atoms.

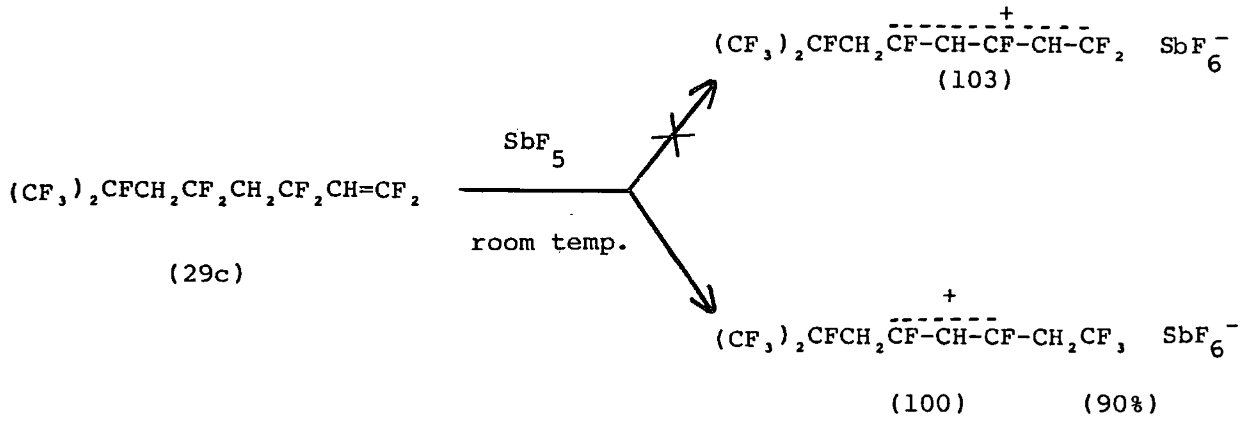
TABLE 5.5

Chemical shift values of carbocations at the charge centres

Carbocation	δ_F/ppm	δ_C/ppm
(100)	+58.5	209.3, 210.5
(101)	+8 to 0	190.1, 195.4
(102)	-13.3 to -30.0	178.6,183.8,185.5,191.2

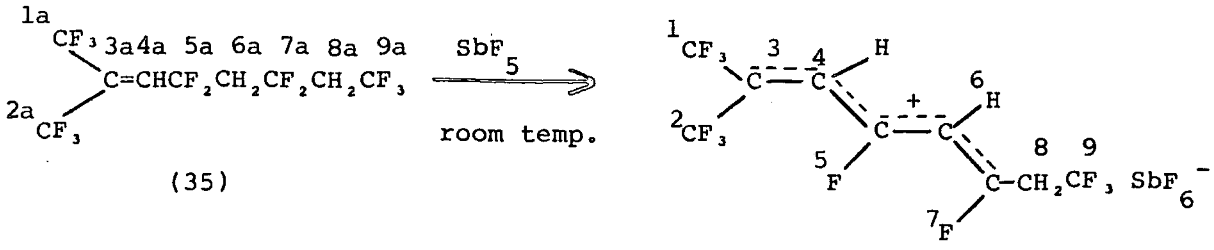
Notably the upfield trend for the ^{19}F resonances is more pronounced and this fact, together with a progressive broadening of the ^{13}C and ^{19}F signals, suggest that exchange processes are probably occurring at room temperature especially for ions (101) and (102).

It was expected that alkene (29c), on treatment with SbF_5 at room temperature, would yield carbocation (103). Instead, the major product was (100) in which formal addition of hydrogen fluoride to the double bond of (29c) had occurred. This observation is rather surprising in view of the fact that there is an increased delocalisation of charge in ion (103) over (100).



5.23 $(CF_3)_2C{=}CHCF_2CH_2CF_2CH_2CF_3$ (35) with SbF_5

Dehydrofluorination of the alkene (35) with SbF_5 at room temperature gave carbocation (104), which has been observed and characterised by NMR (see tables 5.6 and 5.7).



(35)

(104)

The ^{19}F NMR spectrum of the carbocation solution has a very large coupling constant of 207 Hz between the two fluorine atoms at the charge centres, so they are most likely to be spatially near to each other as in structure (104).

TABLE 5.6

Selected ^{19}F NMR data for compound (35) and carbocation (104).

(35)		(104)	
δ_F/ppm	Assignment	δ_F/ppm	Assignment
- 61.2	2a	- 62.3	2 or 9
- 64.7	9a	- 62.6	2 or 9
- 68.4	1a	- 68.8	1
- 92.7	5a	+ 24.5	5 or 7
- 94.3	7a	+57.4	5 or 7

TABLE 5.7

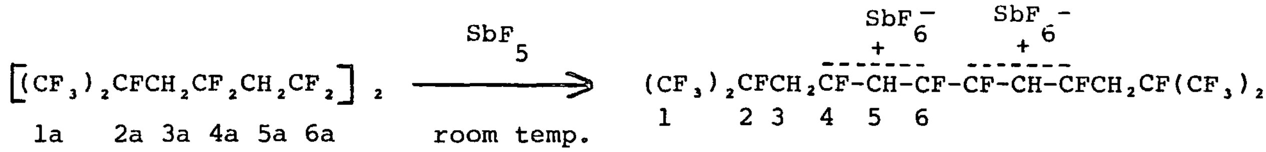
^{13}C NMR data for carbocation (104)

δ_C/ppm	Coupling/Hz	Assignment
43.9	Q(J=33)	8
114.6	S	6
126.7	S	4
117.4	Q(J=277)	1 or 2
118.2	Q(J=278)	1 or 2
120.5	Q(J=280)	9
149.4	sept(J=36)	3
195.1	D(J=367)	5 or 7
211.9	D(J=375)	5 or 7

It would be expected that delocalisation of the charge on to carbon C-3 of ion (104) would be energetically unfavourable due to the proximity of the inductively electron withdrawing perfluoromethyl groups. However, a pronounced downfield shift of 23.4 ppm was observed for the ^{13}C resonance of carbon C-3 on conversion of (35) to carbocation (104), so it is likely that there is some degree of charge development at this carbon atom in (104).

5.24 $[(CF_3)_2CFCH_2CF_2CH_2CF_2]_2$ (14b) with SbF_5

Reaction of (14b) with antimony pentafluoride gave the most remarkable result of all, since the NMR data clearly point to the formation of a unique dication (105) (see tables 5.8 and 5.9).



$$\underset{1a\quad 2a\;3a\;4a\;5a\;6a}{[(CF_3)_2CFCH_2CF_2CH_2CF_2]_2} \xrightarrow[\text{room temp.}]{SbF_5} \underset{1\qquad\quad 2\;3\quad 4\quad 5\quad 6}{(CF_3)_2CFCH_2\overset{SbF_6^-}{\overset{+}{\overline{CF-CH-CF}}}-\overset{SbF_6^-}{\overset{+}{\overline{CF-CH-CF}}}CH_2CF(CF_3)_2}$$

(14b) (105)

We are unaware of any previous report of a dication with adjacent charges of this type. The possibility that (105) is a monocation which is undergoing rapid exchange is inconsistent with the data because the ^{13}C NMR shifts for the charged sites C-4 and C-6 are even further downfield than for the ion (100), whereas shifts similar to those observed for (101) and (102) would be apparent for a monocation averaged over six carbon atoms. The coupling to fluorine, associated with the low field signals, is also quite inconsistent with rapid exchange.

TABLE 5.8

Selected ^{19}F NMR data for (14b) and dication (105)

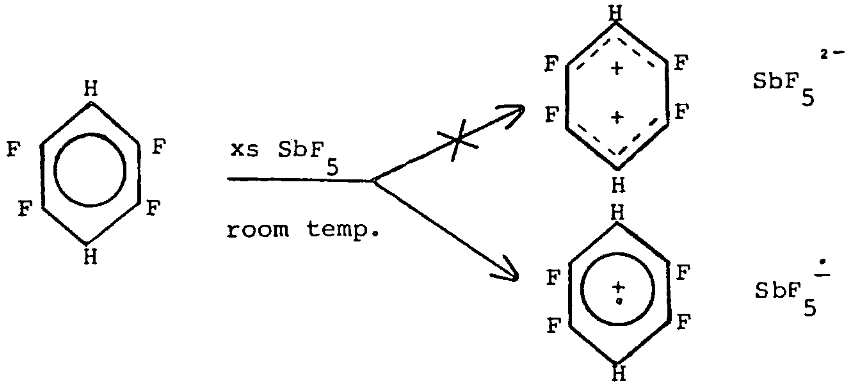
(14b)		(105)	
δ_F/ppm	Assignment	δ_F/ppm	Assignment
- 92.8	4a	+42.0	4 or 6
-116.8	6a	+40.6	4 or 6
- 78.5	1a	-79.0	1
-186.5	2a	-182.1	2

TABLE 5.9

^{13}C NMR data for dication (105)

δ_C/ppm	COUPLING/Hz	ASSIGNMENT
41.4	S	3
94.5	D(J=232)ofM(J=36)	2
122.1	S	5
123.1	Q(J=287)ofD(J=26)	1
210.4	D(J=372)	4
224.8	D(J=371)ofD(J=41)	6

Treatment of 1,2,4,5-tetrafluorobenzene with an excess of antimony pentafluoride was carried out in order to determine whether it would form the dication (106). However, the blue colouration of the solution, together with the fact that no signals were observed in both the ^{1}H and ^{19}F NMR spectra indicate formation of the radical cation (107) rather than (106). The presence of unpaired electrons prevents the acquisition of NMR spectra due to rapid relaxation of the excited nuclei.[159]



(106)

(107)

5.25 $(CF_3)_2C{=}CHCF_3$(36) AND $(CF_3)_2CFCH_2CF_3$ (15a) WITH SbF_5

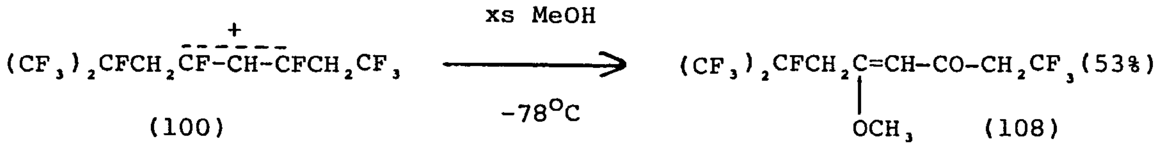
On dissolving either (36) or (15a) in an excess of antimony pentafluoride, the NMR spectra in each case were consistent with rapid exchange of fluoride ion between the Lewis acid and the model compounds. There were no significant changes in the ^1H and ^{19}F chemical shifts of each of the models in antimony pentafluoride, compared with those for the compounds alone. However, no coupling was observed between adjacent groups of the models and in addition a broad resonance was centred at -109 ppm in the ^{19}F NMR spectra, which is characteristic of SbF_6^- rather than SbF_5.[160]

5.3 REACTIONS OF THE CARBOCATIONS

Apart from the interesting properties of the carbocations described above, including their remarkable stability, they also provide a convenient route by which functional groups may be introduced into the saturated model compounds. The routes which have been investigated include quenching reactions and high temperature reactions of the carbocations.

5.31 QUENCHING REACTIONS

Reaction of carbocation (100) with methanol at low temperature gave (108) as the major product.[133]

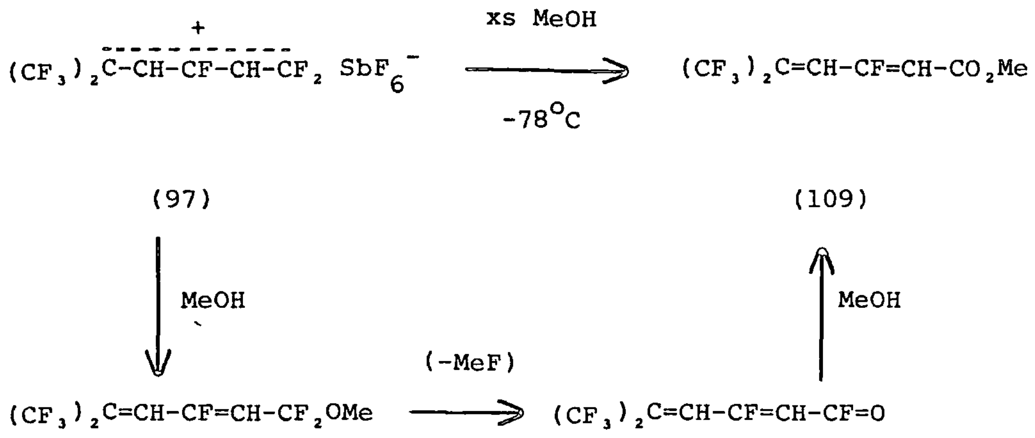


$$(CF_3)_2CFCH_2\overset{+}{\overline{CF-CH-C}}FCH_2CF_3 \xrightarrow[-78^{\circ}C]{\text{xs MeOH}} (CF_3)_2CFCH_2\underset{\overset{|}{OCH_3}}{C}{=}CH-CO-CH_2CF_3\ (53\%)$$

(100) (108)

Similar treatment of carbocation (97) with methanol gave (109) as the major product as determined by ^{19}F NMR and mass spectrometry (m/z 266(M^+), 235(M^+-OCH_3) and 207(M^+-CO_2CH_3)).

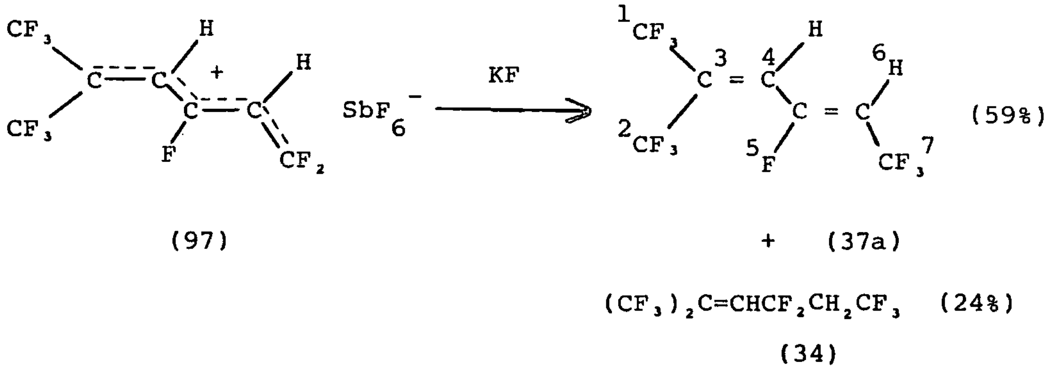
The proposed mechanism for its formation is outlined in scheme 5.1.



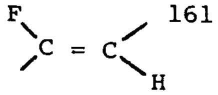
SCHEME 5.1

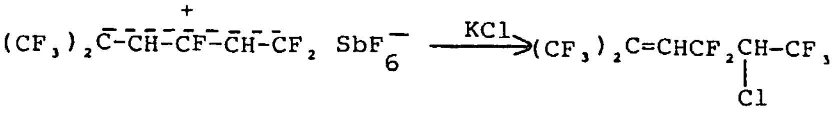
However (109) was rapidly converted to a number of other products, presumably by further attack of methanol. These products were not characterised.

Carbocation (97) has also been quenched with both fluoride and chloride ion. With potassium fluoride a mixture of the monoene (34) and diene (37a) was produced, the latter in the Z-configuration only.



(97) + (37a) (34)

The stereochemistry of (37a) was determined by NMR spectroscopy in which the magnitude of the coupling constant between 5-F and 6-H (J=28 Hz) is characteristic of the group  . In addition, the coupling of 18Hz between the 5-F and 7-F nuclei is indicative of their z-geometrical relationship. Treatment of carbocation (97) with potassium chloride afforded the unexpected alkene (110) as the major product.



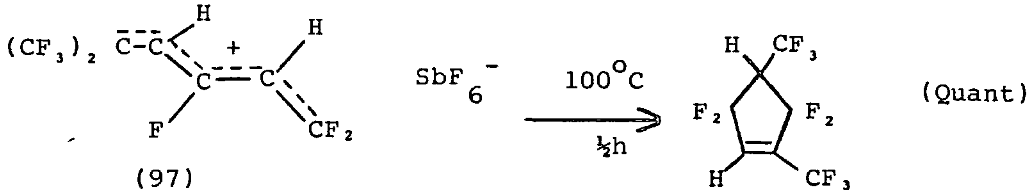
$$(CF_3)_2\overset{+}{C}\text{-}CH\text{-}CF\text{-}CH\text{-}CF_2\ SbF_6^- \xrightarrow{KCl} (CF_3)_2C{=}CHCF_2\underset{\displaystyle Cl}{\underset{|}{C}}H\text{-}CF_3$$

(97) (110)

The identity of (110) was established by mass spectrometry (m/z 311(M^+-F)) and by NMR spectroscopy in particular (see appendix).

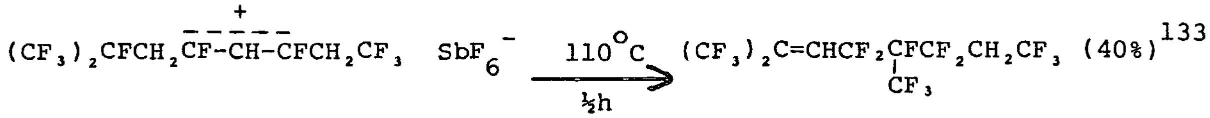
5.32 HIGH TEMPERATURE REACTIONS

Heating a number of the carbocations to over 100°C has led to some unusual observations as detailed below.



(97)

(111)



$$(CF_3)_2CFCH_2\overset{+}{\overline{CF-CH-CF}}CH_2CF_3\ SbF_6^- \xrightarrow[\frac{1}{2}h]{110^\circ C} (CF_3)_2C{=}CHCF_2\underset{CF_3}{\underset{|}{C}}FCF_2CH_2CF_3\ (40\%)^{133}$$

(100)

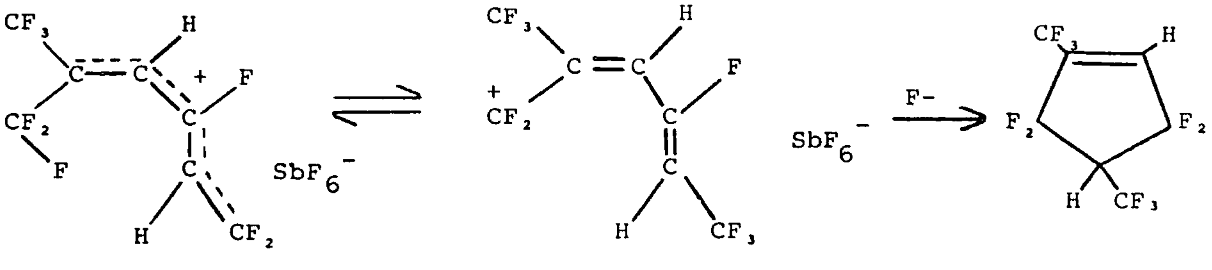
(112)

$$\overset{SbF_6^-}{}(CF_3)_2CFCH_2\overset{+}{C}F(CH{=}CF)_nCH_2CF_3 \xrightarrow[\frac{1}{2}h]{120^\circ C} \text{No change}$$

(101) n=2

(102) n=3

Conversion of (100) to (112) is a rather unusual process and clearly must proceed by an <u>intermolecular</u> mechanism.[133] Conversely, formation of the cyclopentene derivative (111) from (97) must be an <u>intramolecular</u> process. Carbocation (97) probably exists in equilibrium with another ion of type (113) under the reaction conditions. Once formed ion (113) must undergo rapid cyclisation and pick-up of fluoride ion from SbF_6^- to give product (111) (see scheme 5.2).



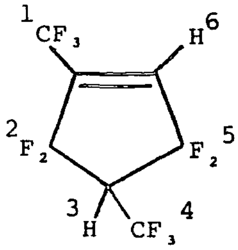
(97) (113) (111)

SCHEME 5.2

The structure of (111) was determined by mass spectrometry (m/z 276 M^+) and by NMR spectroscopy (see table 5.10).[133]

TABLE 5.10

NMR data for compound (111)



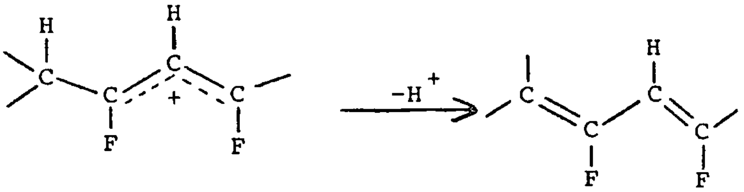
SHIFT/ppm	COUPLING/Hz	ASSIGNMENT
^{19}F spectrum		
- 66.5	M	4
- 66.9	S	1
- 99.2	AB(J=282)	2 or 5
-100.0	AB(J=268)	2 or 5
^{1}H spectrum		
3.6	M	3
6.8	S	6

Integrals as required.

Carbocations (101) and (102) showed no sign of decomposition after heating to 120°C for ½h. These observations are quite remarkable and are examples of only a few carbocations known to be so thermally stable.[162]

5.33 EXPOSURE OF CARBOCATIONS TO HIGH VACUUM

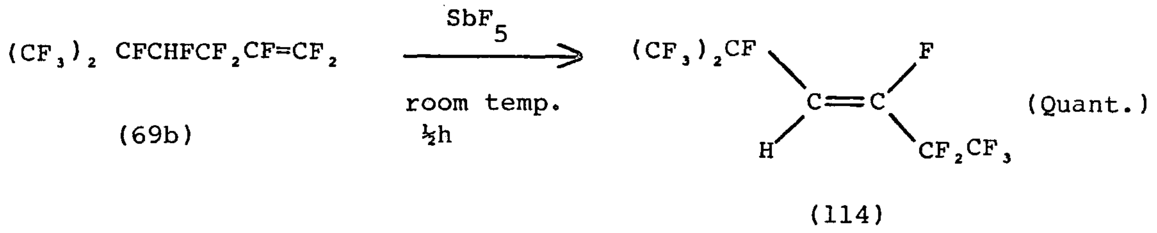
Ions (97) and (100) were exposed to high vacuum in order to determine whether conversion to other products would occur. For example, it was hoped that (100) might undergo proton loss to generate alkene products as follows:



However both ions (97) and (100) were stable to high vacuum at room temperature

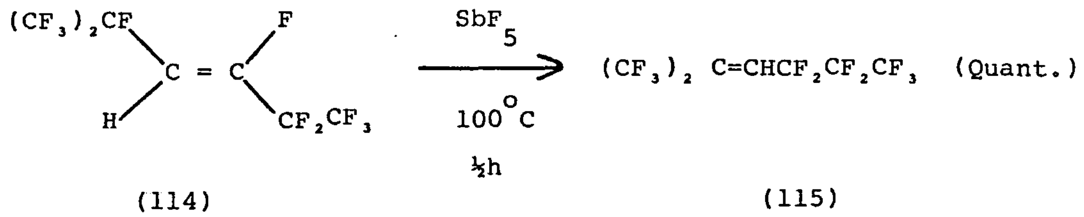
5.4 REARRANGEMENT OF 4H-PERFLUORO-5-METHYLHEX-1-ENE (69b) BY SbF_5

Fluorohydrocarbon compounds of the type $i\text{-}C_3F_7(CHF\ CF_2)_nF$, where n= 1 and 2, show no susceptibility to Lewis acid induced elimination of hydrogen fluoride at temperatures up to 150°C.[133] However, treatment of alkene (69b) with antimony pentafluoride ar room temperature gave a rearrangement reaction forming the internal alkene (114).



The Z isomer of (114) was formed exclusively as determined by NMR spectroscopy which gave a coupling constant of 29 Hz between the vinylic hydrogen and fluorine.

On heating alkene (114) to 100°C in antimony pentafluoride, quantitative rearrangement to the more thermodynamically stable alkene (115) occurred.



5.5 APPLICATION OF SbF_5 CHEMISTRY TO THE SYNTHESIS OF POLYACETYLENE DERIVATIVES

5.51 DEHYDROHALOGENATION OF SATURATED POLYMER SYSTEMS BY SbF_5

There is much current interest in conjugated polymers[163] and the effect of replacing hydrogen by fluorine on the properties of polyacetylene has been speculated upon.[164, 165] Polymerisation of difluoroacetylene has been claimed [154] and this is surprising in view of the inherent instability of difluoroacetylene.[166] The reactions of antimony pentafluoride which have been described in this chapter suggest an alternative approach to polyacetylene derivatives by effecting elimination from a saturated polymer system and it has been found that this process is remarkably effective.[133] When a thin film of polyvinylidene fluoride (116) was simply exposed under high vacuum to antimony pentafluoride as a vapour, the film rapidly darkened and went through black to a lustrous black appearance, all at room temperature (scheme 5.3). Similarly, polytrifluoroethylene (117) went through the same sequence but this system required heating to 80°C in neat antimony pentafluoride. In marked contrast a film of PVC (118) went instantly black when a vacuum tap was opened to allow vapour contact with antimony pentafluoride. It is clear that extensive elimination occurs in these systems but the products are not simply (119) - (121) since they contain antimony pentafluoride and certainly for dehydrofluorinated polyvinylidene fluoride, a number of charged sites must be present. This is evident from the fact that long-lived fluorinated carbocations can be observed in analogous less conjugated model systems (see section 5.2).

$$\underset{(116)}{\left(\mathrm{CH_2-CF_2} \right)_n} \longrightarrow \underset{(119)}{\left(\mathrm{CH{=}CF} \right)_n}$$

$$\underset{(117)}{\left(\mathrm{CHF-CF_2} \right)_n} \longrightarrow \underset{(120)}{\left(\mathrm{CF{=}CF} \right)_n}$$

$$\underset{(118)}{\left(\mathrm{CH_2-CHCl} \right)_n} \longrightarrow \underset{(121)}{\left(\mathrm{CH{=}CH} \right)_n}$$

Allowing the polymer films (116) - (118) to come into contact with trace amounts of antimony pentafluoride vapour, followed by exposure to high vacuum alone, did not lead to intense colouration. Continuous exposure to antimony pentafluoride was required for the formation of intensely coloured products, i.e. the action of antimony pentafluoride is not catalytic.

The treated films (119) and (121) were stored and manipulated under dry nitrogen. Their elemental compositions and infra-red spectra were obtained, the latter using a Nicolet 60 SX photoacoustic IR spectrometer since the films did not have to undergo any treatment prior to running of the spectra.

5.52 EXAMINATION OF THE COLOURED FILMS (119) and (121)

Elemental analyses of the coloured films derived from PVC and polyvinylidene fluoride indicate that the proportion of each element on a particular film differs from region to region. Furthermore antimony is present in the materials (typically 8-15%) and must exist either as SbF_6^- or as SbF_5 coordinated with the remaining halogen sites along the polymer chains, since the antimony species could not be removed by exposure to high vacuum.

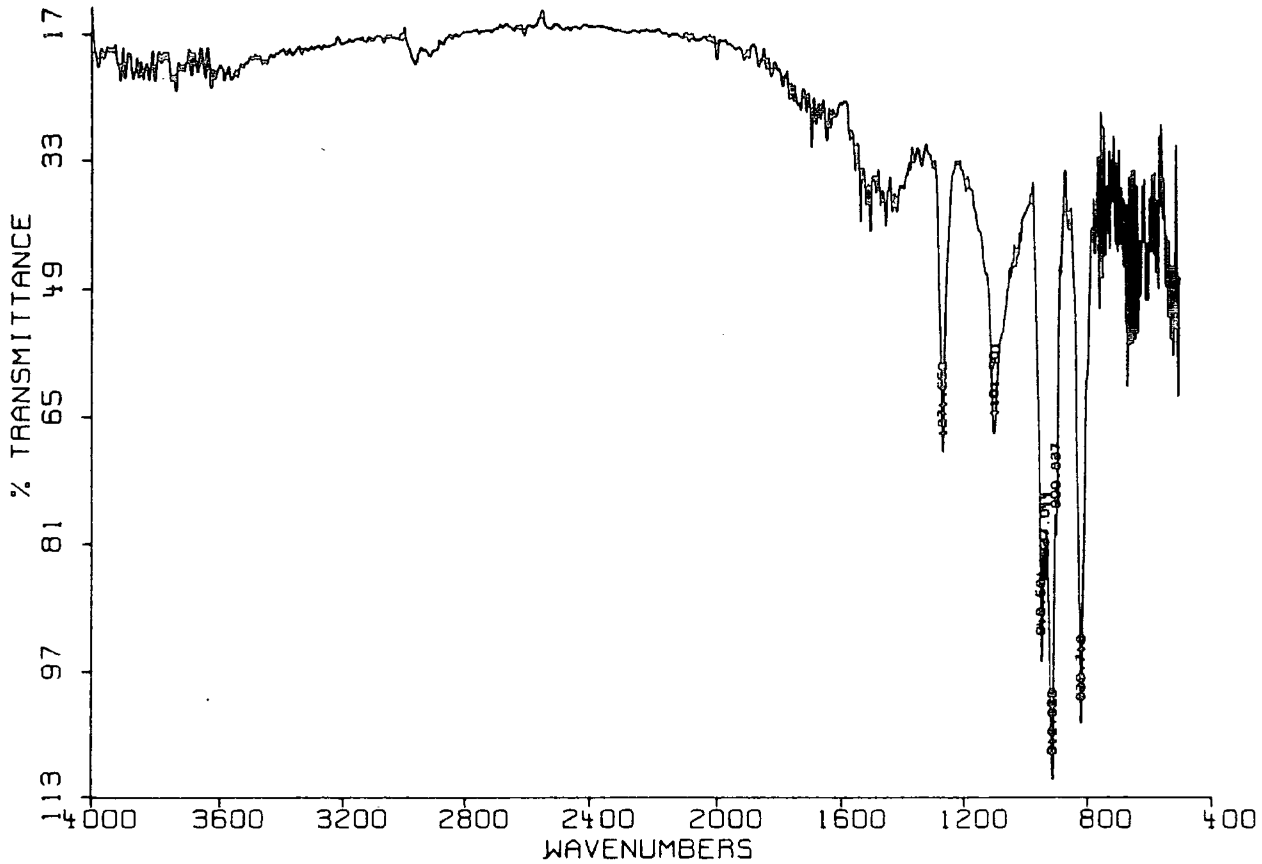
Comparing the photoacoustic IR spectra of the coloured films with those of the corresponding saturated homopolymers it is evident that there are significant differences in the spectra, indicating that there has been a bulk chemical change rather than just a surface effect. However, it must be noted that the coloured films probably contain charged sites which may significantly modify their vibrational characteristics as well as their chemical properties. For this reason the IR spectrum of the coloured film derived from PVC is not directly comparable with that of polyacetylene. Since the films also contain antimony pentafluoride the properties of these materials will be modified to a further extent, since the nature of dopant species and the homogeneity of doping are very important matters.[167] Consequently, caution must be exercised in noting any analogies or differences between the properties of these materials and polyunsaturated polymer systems described in the literature.

Each of the treated films are discussed below.

5.53 Dehydrochlorinated PVC

The photoacoustic FT-IR spectrum of a treated PVC film is shown in figure 5.1. Bands characteristic of PVC initially present at 1425, 1240 and 610 cm^{-1} have disappeared. The IR spectrum of the coloured film is essentially devoid of bands in the 2800-3200cm^{-1} region. Weak, broad bands are observed in the 1650-1450 cm^{-1} region, some of which may be due

FIGURE 5.1 IR SPECTRUM OF A PVC FILM AFTER TREATMENT WITH SbF_5 VAPOUR



to C=C bonds. Furthermore, bands at 1102 and 1272 cm^{-1} are indicative of possible fluorine incorporation into the polymer since there is an absence of an intense band in the region of the C-Cl stretching mode. Alternatively, an intense band at $821cm^{-1}$ could be C-Cl stretch but shifted in frequency from PVC since IR absorptions often occur at higher energies on fluorine incorporation into a material.[168]

Bulk elemental analyses have been carried out and are variable even for the same film. Some samples showed a high chlorine content but the IR spectrum shows that the bulk, rather than the surface had been affected by exposure to antimony pentafluoride. Consequently, it is assumed that a great deal of the eliminated chlorine must remain associated with the counter-ion, i.e. as $SbCl_6^-$ or as mixed ions, SbF_5Cl^- etc. Consistent with this conclusion is the fact that complex absorptions between 400 and 800 cm^{-1} are observed in the IR spectrum. Further evidence for the presence of mixed counter-ions stems from the fact that no chloride ion was detected in the materials (SbF_5 and HF) recovered from liquid air

FIGURE 5.2 IR SPECTRUM OF POLYVINYLIDENE FLUORIDE

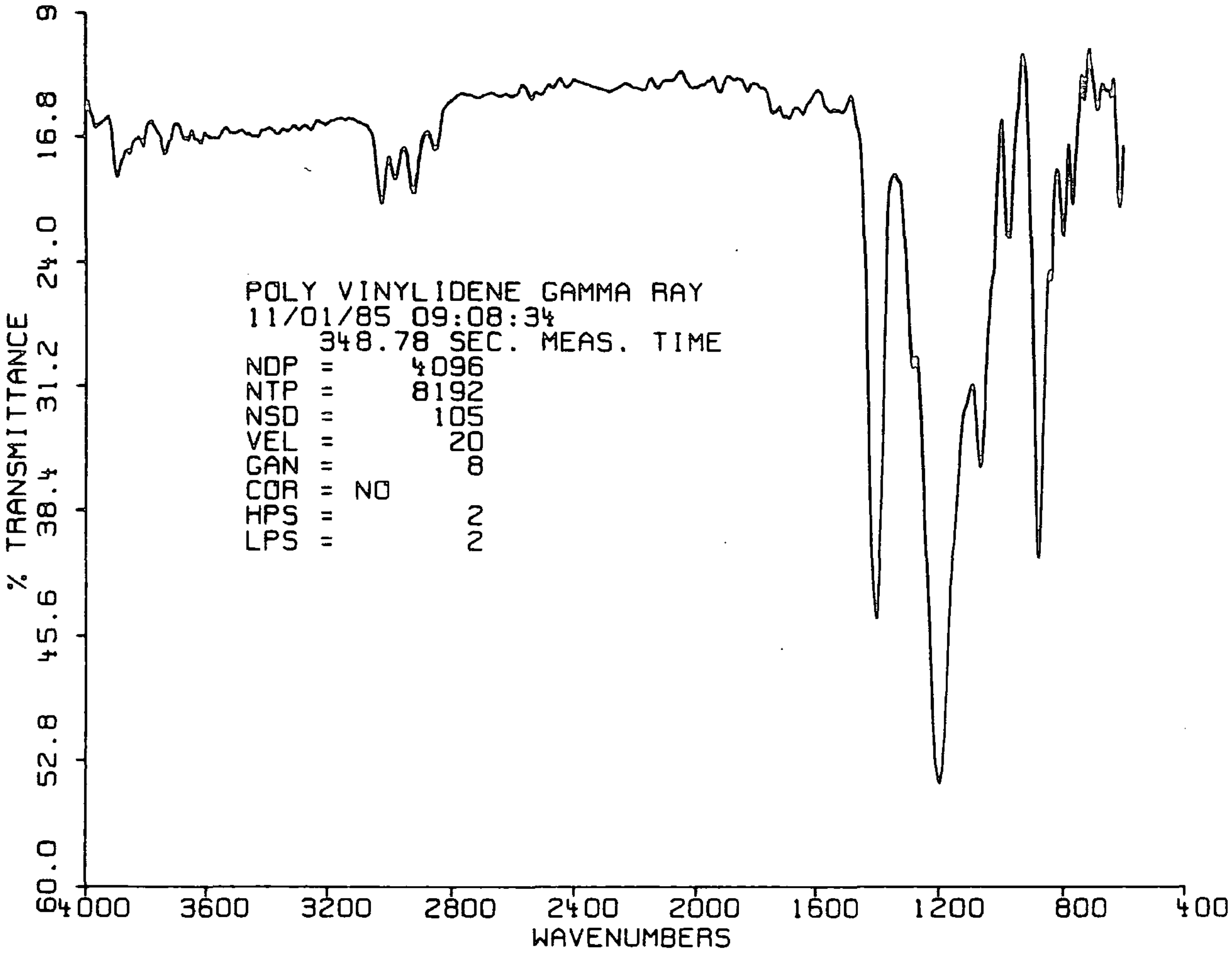
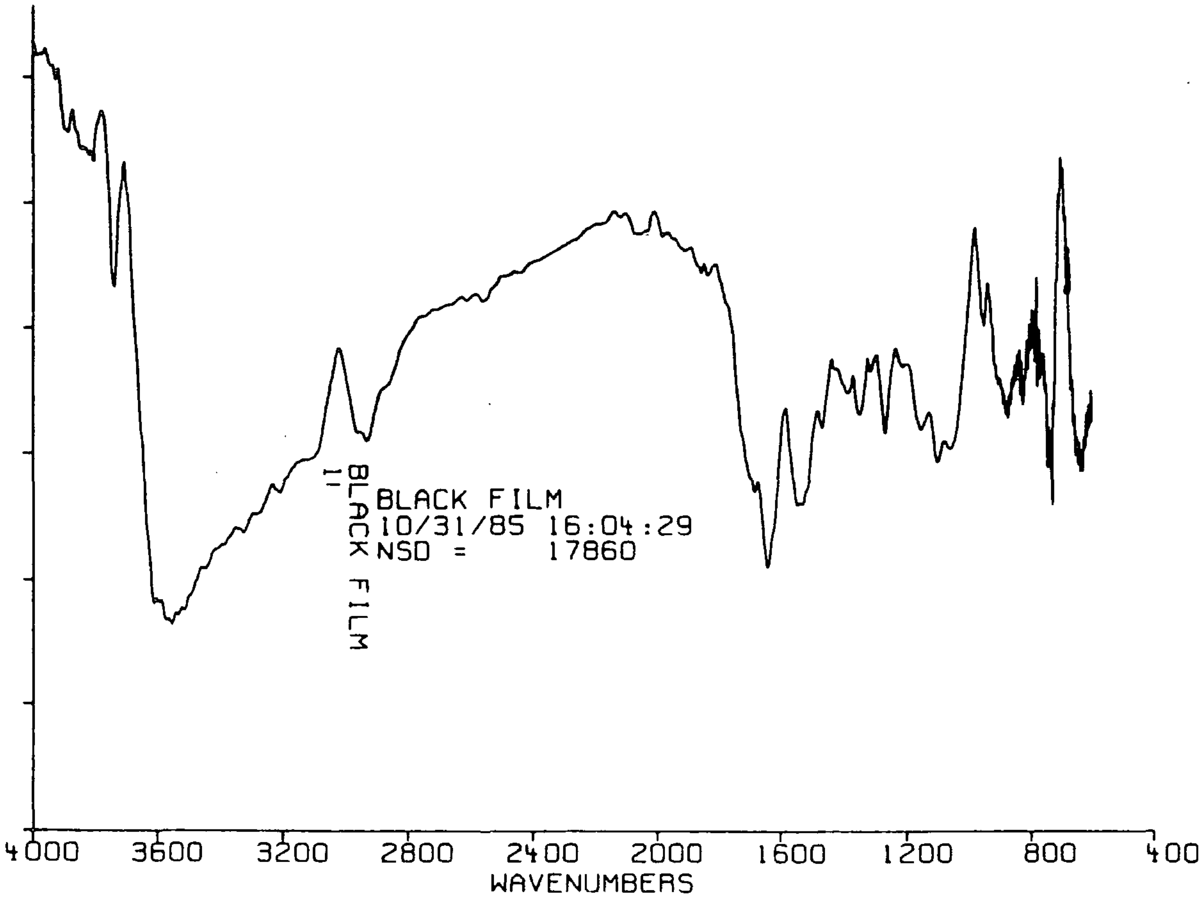


FIGURE 5.3 IR SPECTRUM OF DEHYDROFLUORINATED POLYVINYLIDENE FLUORIDE



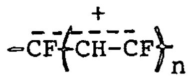
cooled traps after treatment of PVC with antimony pentafluoride vapour.

5.54 DEHYDROFLUORINATED POLYVINYLIDENE FLUORIDE

The photoacoustic IR spectrum of polyvinylidene fluoride produced by γ-ray initiation is shown in figure 5.2, in which there are intense bands at 1402 (CH_2 wagging) 1197 (CF_2 stretching) 1067 (CF_2 wagging) and 878 cm^{-1} (C-C stretching).[169,170] The characteristics of this spectrum contrast with that of a coloured film resulting from treatment of polyvinylidene fluoride with antimony pentafluoride vapour, given in figure 5.3, which clearly demonstrates that a bulk chemical change has occurred. Intense bands due to polyvinylidene fluoride at 1402, 1197, 1067 and 878 cm^{-1} have completely disappeared and broad strong absorptions appear at 1640, 1685 and 1530 cm^{-1}, which are indicative of the formation of both isolated and conjugated C=C bonds. The disappearance of the bands at 1402 and 1197 cm^{-1} especially indicates that both C-H and C-F bond breakage has occurred during the process.[170] In addition, the C-H band at 3022 cm^{-1} in the IR spectrum of polyvinylidene fluoride was not observed for a pyrolyzed sample[171] and is also not present in that of the coloured film. In fact, the IR spectrum of the coloured film bears a remarkable similarity to that observed for a base induced dehydrofluorinated product of polyvinylidene fluoride given in the literature.[172] The very broad and intense band between 2000 and 3600 cm^{-1} is also similar to that observed for polyacetylene doped with hydrogen fluoride.[173] Indeed the coloured film is expected to contain hydrogen fluoride following its displacement from the polymer backbone by antimony pentafluoride.

5.55 EVIDENCE FOR THE EXISTENCE OF CHARGED SITES

Kise and Ogata[172] reported that no significant change in the IR spectrum occurred after exposing a dehydrofluorinated polyvinylidene fluoride film to air for eight weeks. In contrast when a polyvinylidene fluoride film, after treatment and antimony pentafluoride, was exposed to air, a very strong band at 1760 cm^{-1} was the most striking feature of the IR spectrum of the resultant product (see figure 5.4). This indicates that carbonyl groups were formed on contact with air, probably by attack on charged sites of the type (122).



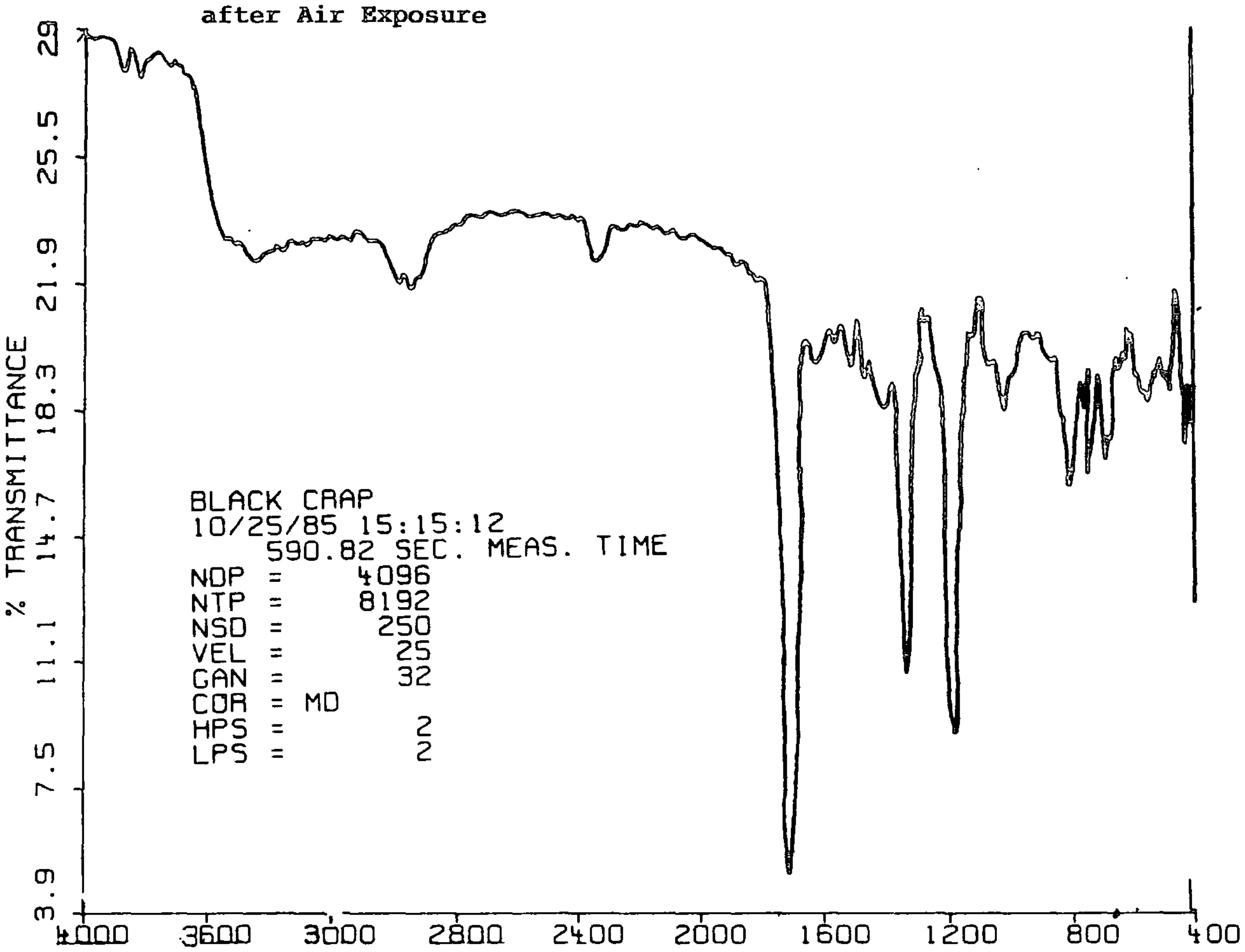
$$-\overline{CF}\!\left(\overset{+}{\overline{CH-CF}}\right)_n$$

(122)

Quenching of carbocations, derived from model compounds, with methanol gave rise to products containing carbonyl groups (see section 5.31).[133] Hence, the coloured films derived from PVC and polyvinylidene fluoride were treated with methanol vapour at room temperature, in order to determine whether a reaction would occur as a result of the presence of charged sites. The former system produced no colour change but the latter, derived from polyvinylidene fluoride, gave an immediate colour change to orange. The photoacoustic IR spectrum of the orange film is given in figure 5.5 and shows an intense band at 1650 cm^{-1} which is almost certainly due to carbonyl groups conjugated to C=C bonds. In addition, the intense absorptions between 1050 and 1200 cm^{-1} may be due to C-O stretching of methoxy groups. The absorption at 1650 cm^{-1} overlaps with a broad band covering the range 1550 - 1760 cm^{-1} which indicates that a number of different C=C groups are present.

The fact that the dehydrofluorinated films derived from polyvinylidene fluoride are modified by either air or methanol to give materials containing carbonyl groups, presents strong evidence for the existence of charged sites of the type (122). It would be expected that hydrogen atoms adjacent to charge centres will give rise to signals showing appreciable downfield shifts in the ^1H NMR spectrum, as observed for the carbocations described in section 5.2. Table 5.11 shows the ^1H NMR chemical shift ranges observed for the broad signals of carbocations (100)-(102). It can be seen from the table that as n increases, the resonances for the 1-CH_2 and 2-CH groups

FIGURE 5.4 IR spectrum of dehydrofluorinated polyvinylidene fluoride after Air Exposure



```
BLACK CRAP
10/25/85 15:15:12
          590.82 SEC. MEAS. TIME
NOP =        4096
NTP =        8192
NSD =         250
VEL =          25
GAN =          32
COR = MD
HPS =           2
LPS =           2
```

FIGURE 5.5 IR spectrum of dehydrofluorinated polyvinylidene fluoride after Exposure to MeOH Vapour

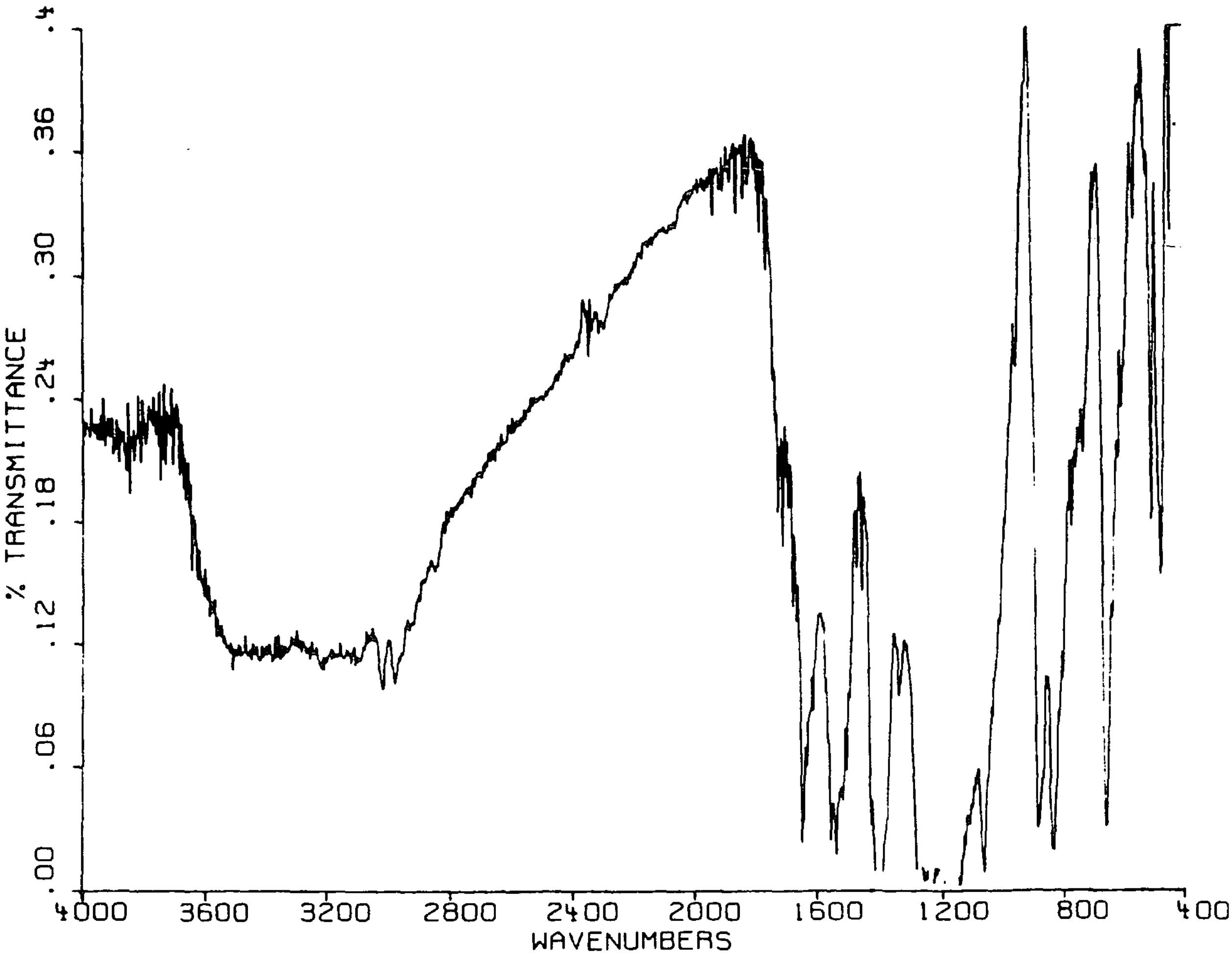
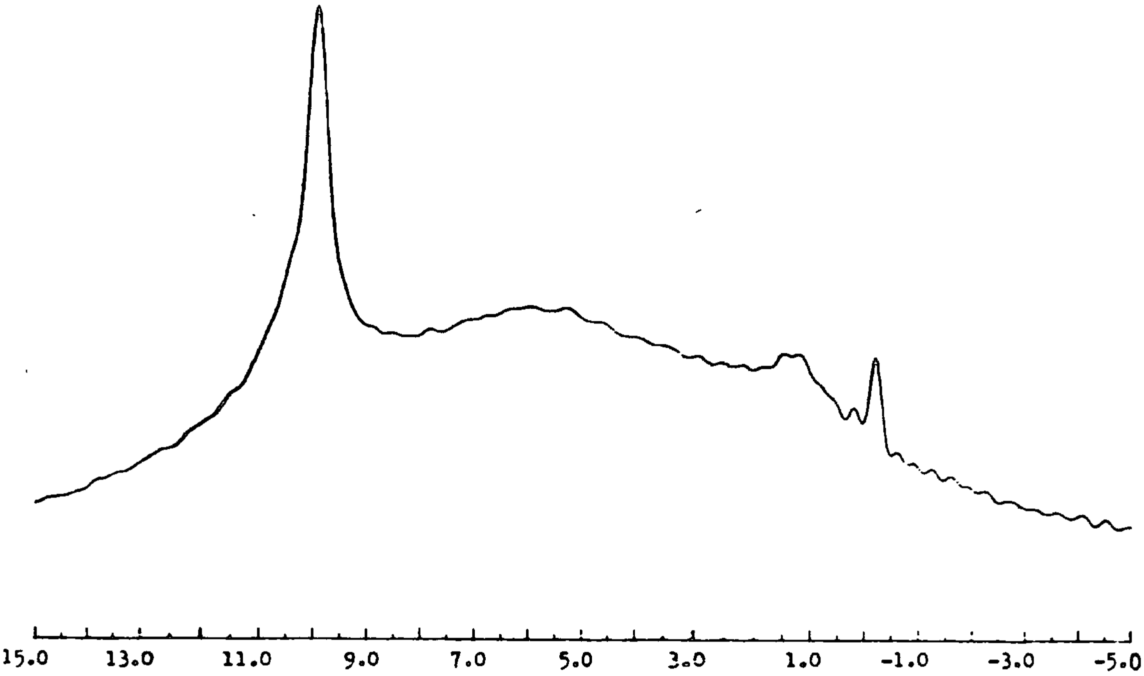
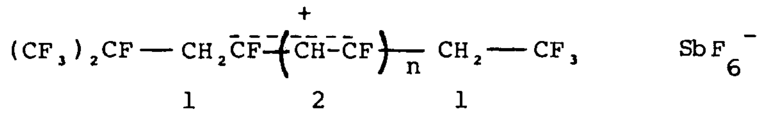


FIGURE 5.6 ^1H NMR SPECTRUM OF DEHYDROFLUORINATED PVDF.



progressively shift upfield and become closer. Hence, for ^1H NMR spectra of polyvinylidene fluoride films, after treatment with antimony pentafluoride, these resonances should be even closer. This accounts for the observed ^1H NMR spectrum presented in figure 5.6 and provides further evidence for the presence of charged sites of the type (122). The sharp resonance at ca 10.0ppm in the spectrum is due to the presence of hydrogen fluoride and was also observed in the ^1H NMR spectra of carbocations (100)-(102).

TABLE 5.11



$$(CF_3)_2CF-\underset{1}{CH_2}CF\left(\overset{+}{\underset{2}{CH}}-CF\right)_n\underset{1}{CH_2}-CF_3 \qquad SbF_6^-$$

	$^1\delta_H$/ppm	$^2\delta_H$/ppm
n=1 (100)	3.6 - 4.8	7.0 - 8.3
n=2 (101)	3.0 - 4.5	6.2 - 7.6
n=3 (102)	2.9 - 4.4	5.8 - 7.6

5.6 CONCLUSIONS

The Lewis acid induced rearrangement and dehydrofluorination reactions described in this chapter have illustrated new chemistry and have also led to a number of interesting products. Synthesis of unsaturated model compounds has been possible and these have been useful in carrying out mechanistic studies concerning cross-linking processes (see chapter three). In addition a number of remarkable, highly fluorinated carbocations have been prepared which are useful intermediates for functionalizing the saturated model compounds, via quenching reactions with nucleophiles. Notably the reactions with antimony pentafluoride yield unsaturated products in which the most sterically demanding groups are situated exclusively in the E configuration relative to each other.

This methodology for forming unsaturated products has been successfully extended to the synthesis of polyacetylene derivatives, by treating suitable saturated polymers with antimony pentafluoride. Currently there is much interest in the synthesis and investigation of polymers with conjugated π-electron backbones since they possess unusual electronic properties when compared to conventional polymers. The most successful attempts to prepare fluorinated polyacetylenes are limited to base induced dehydrofluorination of saturated homopolymers such as PVDF. These reactions require a solvent and often a phase transfer catalyst, such as tetrabutylammonium bromide, and are usually carried out at elevated temperatures (typically 90-100°C). By contrast, Lewis acid induced dehydrohalogenation of PVC and PVDF simply involves exposure to antimony pentafluoride vapour at room temperature. The resultant materials may well be difficult to completely characterise but this procedure offers an extremely simple methodology for generating polyconjugated films and it is clear that the electrical properties of these systems should be explored.

CHAPTER SIX

MISCELLANEOUS REACTIONS OF SOME FLUOROCARBON DERIVATIVES

6.1 Introduction

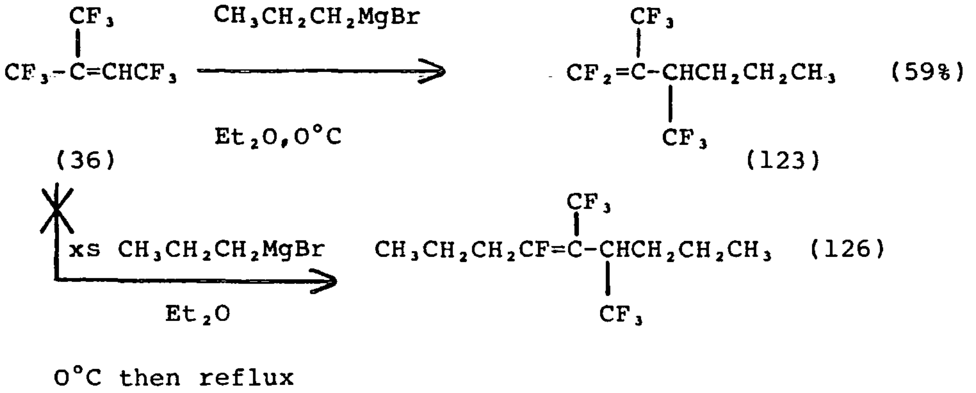
In Chapter three it was concluded that unsaturated units of the form $-(CF_3)C{=}CHCF_2-$ are the sites through which nucleophilic cross-linking of HFP/VDF copolymers occurs. Since it is likely that a proportion of these sites remain in the cured articles, which are often utilized in contact with aggressive chemicals, their response towards nucleophilic and free radical attack is described in this chapter.

Details of the synthesis of fluorocarbon derivatives containing the bulky F-2-methylpentyl group were presented in Chapter Four. The presence of this group has led to the observation of some unusual chemistry, the results of which are discussed in this chapter.

6.2 Nucleophilic Attack on $-(CF_3)C{=}CHCF_2-$ Sites

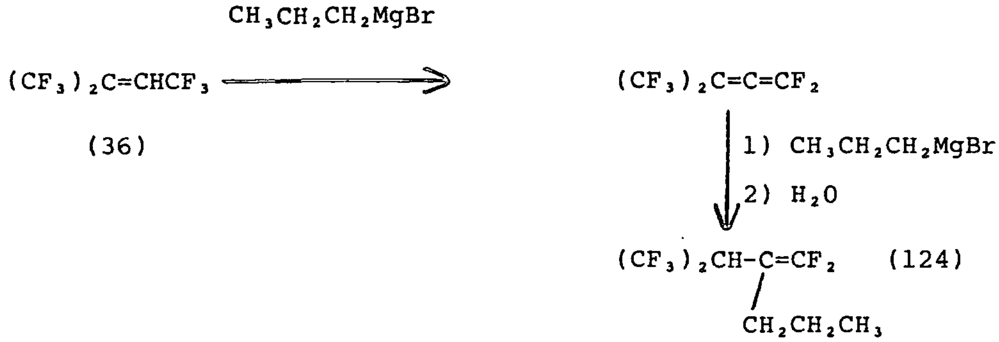
6.21 $(CF_3)_2C{=}CHCF_3$(36) with Grignard Reagents

Treatment of alkene (36) with a stoichiometric amount of propyl magnesium bromide in ether led to allylic displacement of fluoride ion to form (123) (See Scheme 6.1).



Scheme 6.1

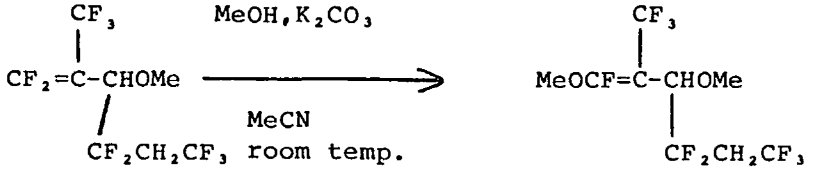
An alternative alkene (124), which could be formed by the mechanism outlined in Scheme 6.2, was not produced.



Scheme 6.2

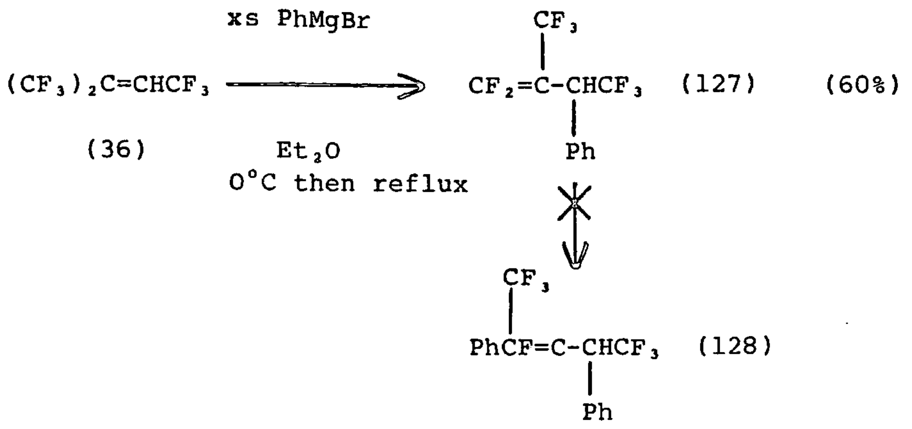
The trifluoromethyl groups in (124) would be magnetically equivalent and would give rise to one signal in the ^{19}F NMR spectrum, rather than the two resonances which were observed. Furthermore, two molar equivalents of Grignard reagent would be required to produce (124) but only a stoichiometric amount was used.

On treatment of (36) with two molar equivalents of propyl magnesium bromide, the major product was (123) (See Scheme 6.1). Compound (123) contained only ca 8% of other minor products which did not appear to include (126) as determined by G.C. - mass spectrometry. It is very surprising that (123) did not react with further amounts of Grignard reagent to produce (126), by analogy to the reaction between (125) and methanol described in Section 3.41, i.e.,



(125) (49) (E and Z isomers)

Similar treatment of (36) with an excess of phenyl magnesium bromide gave (127) as the major product. Further reaction of (127) with Grignard reagent to give (128) was not observed.

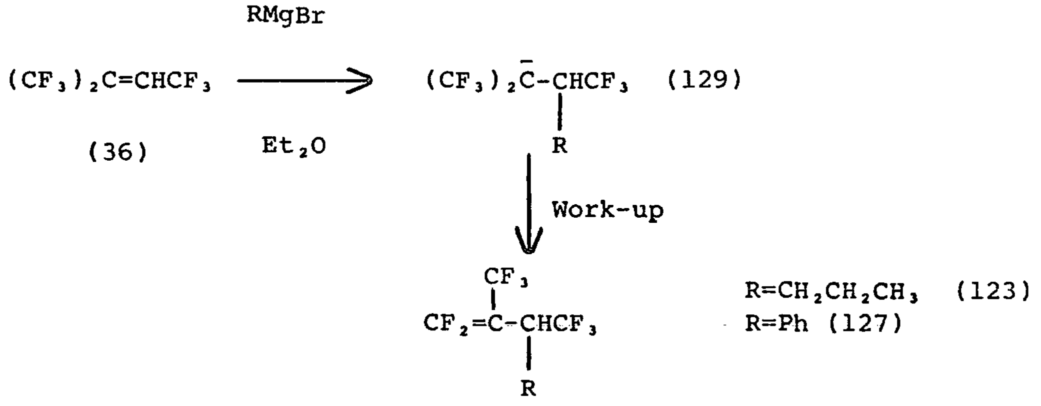


$$\underset{(36)}{(CF_3)_2C{=}CHCF_3} \xrightarrow[\text{Et}_2\text{O, 0°C then reflux}]{\text{xs PhMgBr}} CF_2{=}\overset{\displaystyle CF_3}{\overset{|}{C}}\text{-}\underset{\displaystyle Ph}{\underset{|}{C}}HCF_3 \quad (127) \quad (60\%)$$

$$\cancel{\big\downarrow} \quad Ph\overset{\displaystyle CF_3}{\overset{|}{C}F}{=}C\text{-}\underset{\displaystyle Ph}{\underset{|}{C}}HCF_3 \quad (128)$$

Scheme 6.3

A possible explanation for these observations is that the reaction between Grignard reagent and alkene (36) produced a carbanion intermediate (129), which only yielded the products (123) or (127) on carrying out the work-up procedure. Formation of (129) would hinder any further reaction to give (126) or (128).



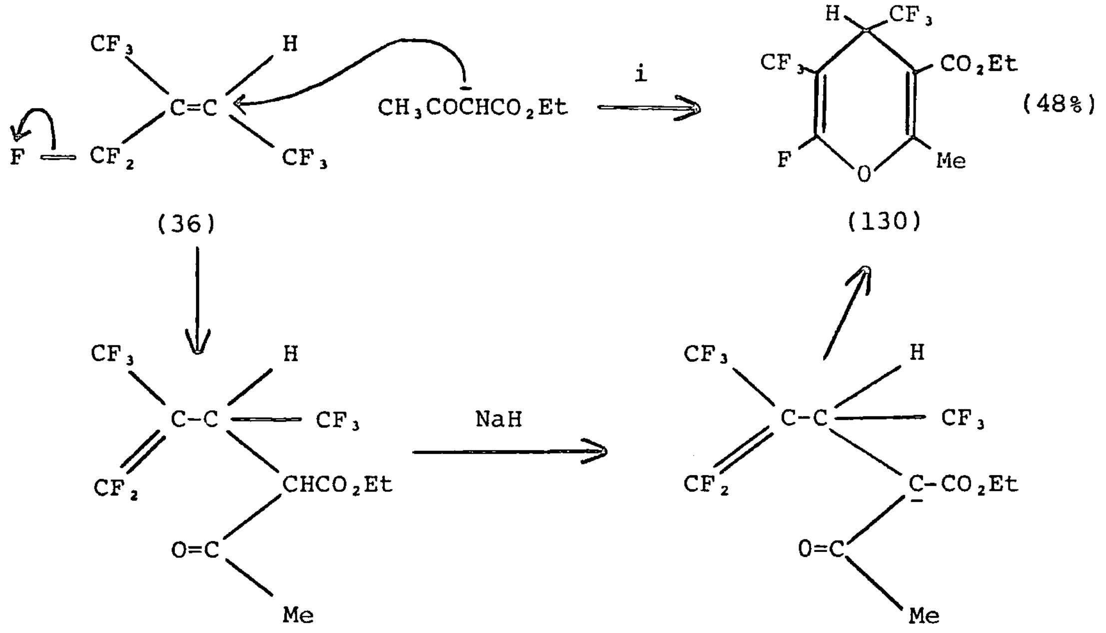
$$\underset{(36)}{(CF_3)_2C{=}CHCF_3} \xrightarrow[\text{Et}_2\text{O}]{\text{RMgBr}} (CF_3)_2\bar{C}\text{-}\underset{\displaystyle R}{\underset{|}{C}}HCF_3 \quad (129)$$

$$\xrightarrow{\text{Work-up}} CF_2{=}\overset{\displaystyle CF_3}{\overset{|}{C}}\text{-}\underset{\displaystyle R}{\underset{|}{C}}HCF_3 \qquad R{=}CH_2CH_2CH_3 \ (123), \quad R{=}Ph \ (127)$$

Scheme 6.4

6.22 $(CF_3)_2C{=}CHCF_3$(36) with Ethyl Acetoacetate

On addition of alkene (36) to a mixture of ethyl acetoacetate and sodium hydride in tetraglyme, the pyran derivative (130) was the only product. The probable mechanism for its formation is presented in Scheme 6.5.[175]

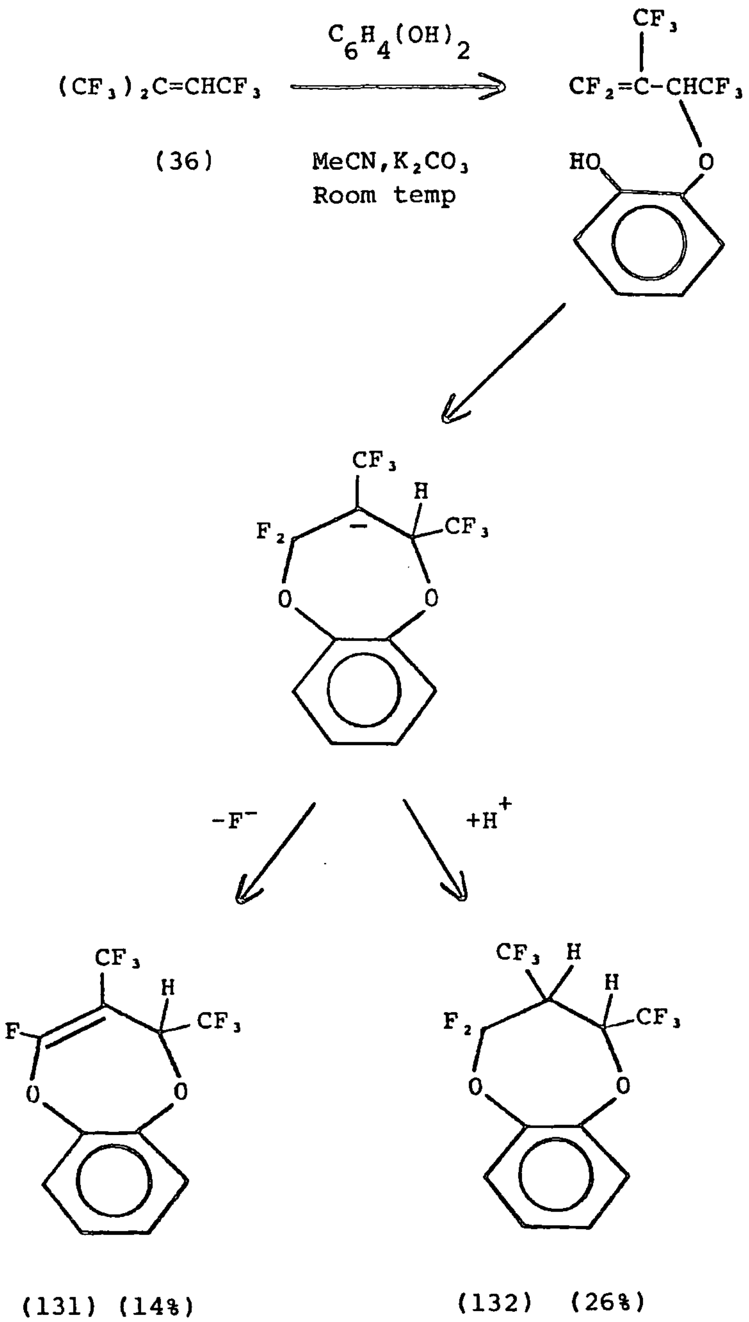


i $CH_3COCH_2CO_2Et$, xs NaH, tetraglyme, room temp., 19h.

Scheme 6.5

6.23 $-(CF_3)C=CHCF_2-$ With Catechol

The response of $-(CF_3)C=CHCF_2-$ groups to nucleophilic attack by alcohols was described in Section 3.41 and further related studies have been carried out. For example, treatment of (36) with catechol gave a cyclization reaction leading to predominant formation of (131) and (132). The mechanism for their formation is presented in Scheme 6.6 .



Scheme 6.6

Structural elucidation of the products was achieved principally by mass spectrometry (m/z 302 (131) and 322 (132), IR spectrometry (ν_{max} (C=C) 1700 cm^{-1}) and NMR spectroscopy (δ_F(vinyl F) -61.5 ppm (131) and δ_F (CF_2) -61.0 ppm and -67.1 ppm (132) (two diastereoisomers)).

6.3 Free Radical Attack on $-(CF_3)C{=}CHCF_2-$ Sites

It is known that fluoroalkenes of the type $R_FCF{=}CF_2$ are susceptible to free radical addition reactions.[176] For example, irradiation of a mixture of alkene (133) and methanol with γ- rays gave (134) in moderate yield.

$$(CF_3)_2CFCF{=}CF_2 \xrightarrow[\gamma\text{- rays}]{MeOH} (CF_3)_2CFCHFCF_2CH_2OH \quad (57\%)$$

(133) (134)

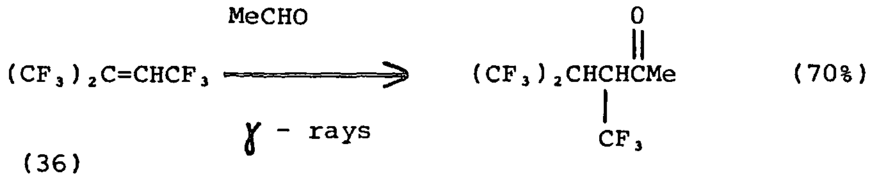
Alkene (133) was synthesized from heptafluoro-2-iodopropane (12) by the route given in Scheme 6.7.

$$(CF_3)_2CFI \xrightarrow[185°C]{CHF{=}CF_2} (CF_3)_2CFCHFCF_2I \xrightarrow[\text{Room temp.}]{NBu_3} (CF_3)_2CFCF{=}CF_2 \quad (76\%)$$

(12) (23a) (133)

Scheme 6.7

Sites of the type $-(CF_3)C{=}CHCF_2-$ also undergo free radical reactions as exemplified by treatment of (36) with ethanal, which yielded (135).

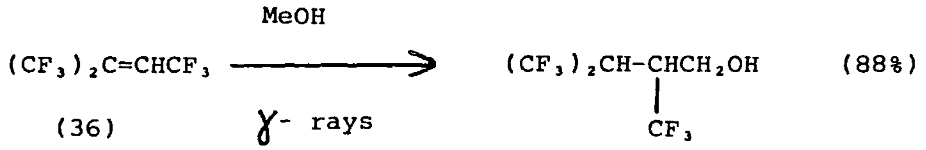


$$(CF_3)_2C{=}CHCF_3 \xrightarrow[\gamma\text{ - rays}]{MeCHO} (CF_3)_2CHCH(CF_3)C(=O)Me \quad (70\%)$$

(36)

(135)

In a similar way, irradiation of a mixture of (36) and methanol with γ- rays afforded the alcohol (136).

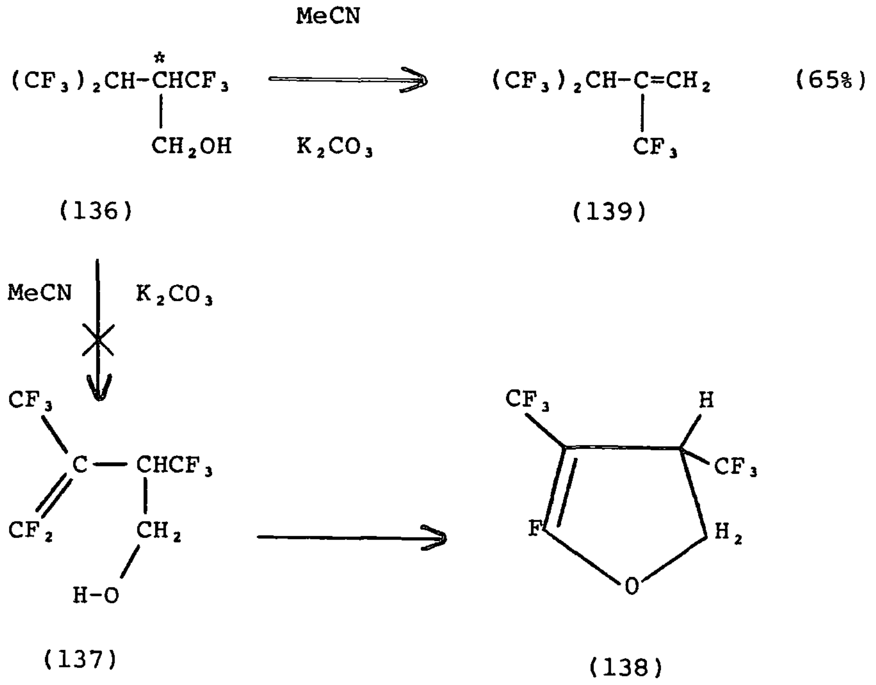


$$(CF_3)_2C{=}CHCF_3 \xrightarrow[\gamma\text{- rays}]{MeOH} (CF_3)_2CH{-}CH(CF_3)CH_2OH \quad (88\%)$$

(36)

(136)

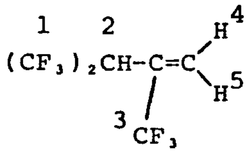
An attempt was made to cyclize alcohol (136) according to Scheme 6.8, in which initial elimination of hydrogen fluoride is followed by intramolecular nucleophilic attack of alkoxide on the double bond of (137).



Scheme 6.8

However, the furan derivative (138) was not produced. The only product was alkene (139) which was formed by elimination of water from (136). This result is surprising since it appears to indicate that the most base sensitive site is the asterisked group of (136) rather than the 2H-hexafluoropropyl unit. The identity of (139) was achieved by mass spectrometry (m/z 246(M^+)) and by NMR spectroscopy in particular (See Table 6.1).

Table 6.1 NMR data for alkene (139)

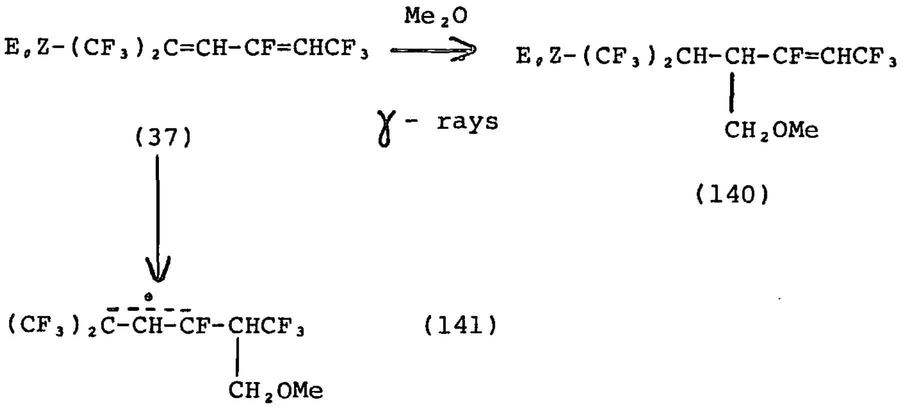


$$\overset{1}{(CF_3)_2}\overset{2}{CH}-\underset{{}^{3}CF_3}{C}=C(H^4)(H^5)$$

δ/ppm	Coupling/Hz	Assignment
^{19}F spectrum: $CDCl_3$		
- 66.9	D(J=8) of Q(J=1)	1
- 70.4	Sept. (J=1)	3
^{1}H spectrum: $CDCl_3$		
3.8	Sept. (J=8)	2
6.2	S	4 or 5
6.3	S	4 or 5

Integrals as required.

The free radical reactions described above have clearly demonstrated that $-(CF_3)C{=}CHCF_2-$ sites are susceptible to attack by free radicals. However, it was also found that when such sites are conjugated to an alkene group, as with (37), then this is sufficient to offset any reaction. Hence, irradiation of a mixture of (37) and dimethyl ether with γ- rays gave no chemical change.



$$E,Z\text{-}(CF_3)_2C{=}CH\text{-}CF{=}CHCF_3 \xrightarrow[\gamma\text{- rays}]{Me_2O} E,Z\text{-}(CF_3)_2CH\text{-}\underset{\displaystyle CH_2OMe}{\underset{|}{CH}}\text{-}CF{=}CHCF_3$$

(37) (140)

$$\big\downarrow$$

$$(CF_3)_2\overline{C\text{-}\overset{\bullet}{CH}\text{-}CF}\text{-}\underset{\displaystyle CH_2OMe}{\underset{|}{C}}HCF_3$$

(141)

Scheme 6.9

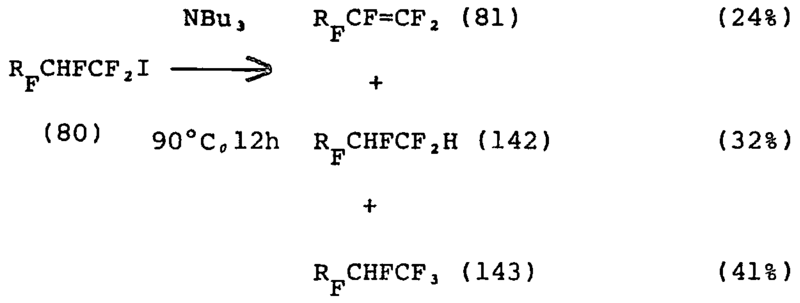
This result may be due to formation of the relatively stable allylic radical (141) which could then hinder the reaction.

6.4 Novel Reactions with Compounds Containing the F-2-Methylpentyl Group

6.41 2H-Perfluoro-1-iodo -3,3-dimethylhexane (80) with Tri-n-Butylamine

Normally the formal elimination of hydrogen iodide from fluorohydrocarbon iodides containing the $-CHFCF_2I$ group can be achieved relatively easily using tri-n-butylamine at ambient temperature (see Section 4.4). However, the crowded iodide (80) failed to react readily until the temperature was maintained at 90°C. This has been attributed to the difficulty of the large tertiary amine in approaching the hydrogen of (80) due to chronic steric repulsions.

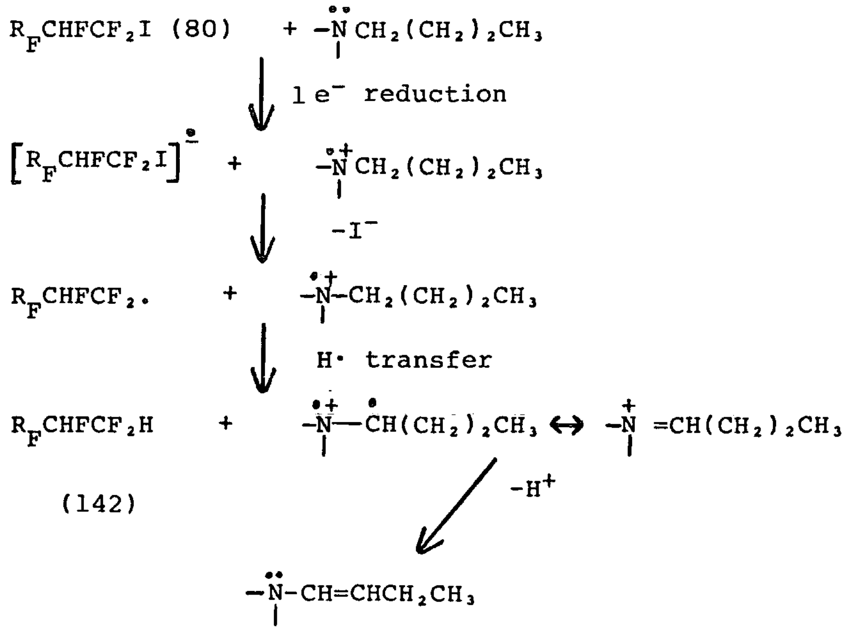
When iodide (80) was treated with the amine at 90°C, two products were observed in addition to the expected alkene (81).



$$R_FCHFCF_2I\ (80) \xrightarrow[90^\circ C,\ 12h]{NBu_3} R_FCF{=}CF_2\ (81)\ (24\%) + R_FCHFCF_2H\ (142)\ (32\%) + R_FCHFCF_3\ (143)\ (41\%)$$

$R_F{=}CF_3CF_2CF_2C(CF_3)_2$

The products (142) and (143) were not derived from alkene (81) since the latter remained unchanged after heating to 90°C with tri-n-butylamine. Consequently, it is likely that (142) was produced by reduction of iodide (80) according to Scheme 6.10. One electron reductions of this type have been reported and are now well established.[177, 133]

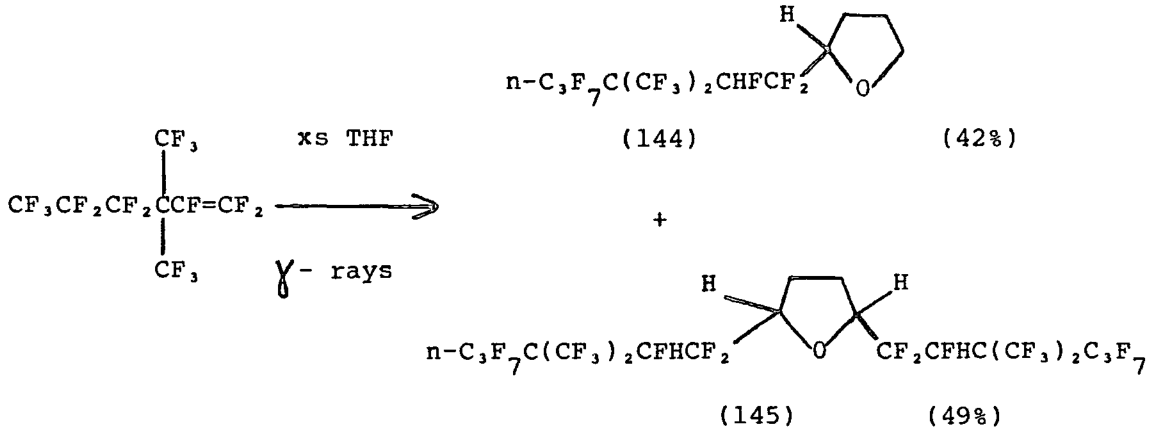


Scheme 6.10

The formation of (143) suggests that hydrogen fluoride was produced during the reaction presumably as a result of partial decomposition of (80). This would lead to formation of tertiary amine hydrofluoride which is known to be an active source of fluoride ion[178] and could therefore attack alkene (81) to give (143).

6.42 Free Radical Addition of the THF to Perfluoro-3,3-Dimethylhex-1-Ene (81)

Irradiation of a mixture of perfluoro-3,3-dimethylhex-1-ene (81) and THF with γ- rays afforded the products (144) and (145).

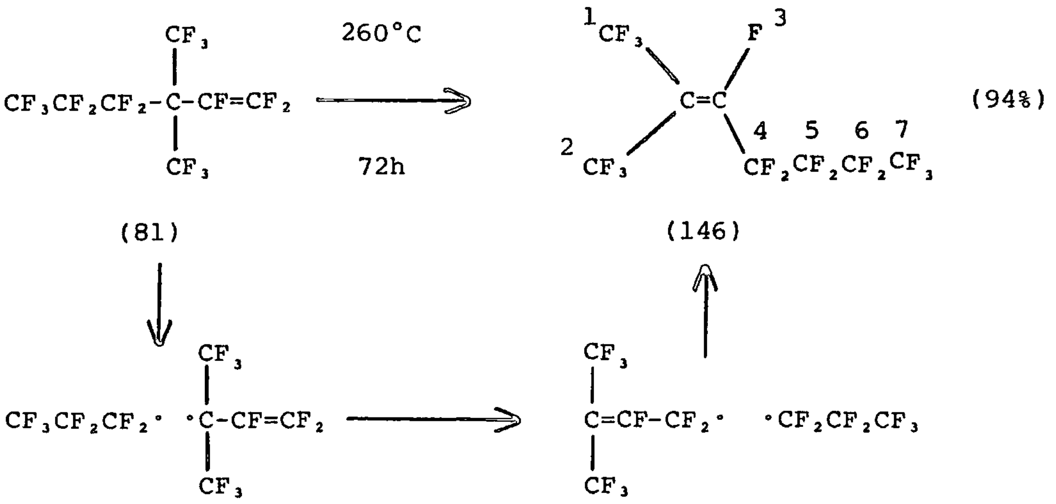


Hence, the crowded perfluoro-2-methylpentyl group of (81) did not suppress free radical addition to the double bond. Compound (145) contains four chiral centres so there should be eight observable isomers. However, only three were produced and this must reflect the preference to form diastereoisomers in which the large groups are spatially distant from each other.

The structures of the products were determined principally by mass spectrometry (for (144) m/z 472 (M$^+$) and for (145) m/z 853 (M$^+$-F) and NMR spectroscopy (see appendix). For product (145) the two fluorocarbon groups are attached to different ring carbon atoms, as indicated by ^{1}H NMR spectroscopy in which the ratio of methine to methylene protons is 1:2. This result is in agreement with studies carried out by Jones.[179]

6.43 Pyrolysis of Perfluoro-3,3-Dimethylhex-1-ene (81)

The crowded alkene (81) underwent complete conversion to perfluoro-2-methylhept-2-ene (146) on exposure to high temperature. The proposed mechanism for the reaction is presented in Scheme 6.11.



Scheme 6.11

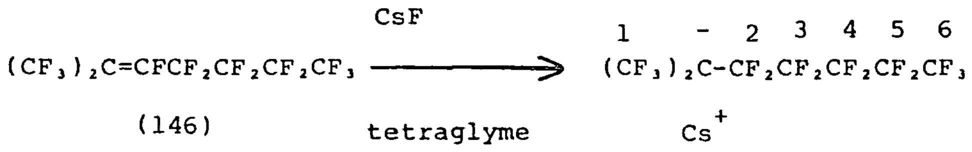
Identification of alkene (146) was achieved by mass spectrometry (m/z 381 (M^+-F)), IR spectrometry (ν_{max} (C=C) 1705 cm^{-1}) and NMR spectroscopy (See Table 6.2).

Table 6.2 NMR data for alkene (146)

δ_F/ppm	Integral	Assignment
- 60.0	3	2
- 62.7	3	1
- 84.6	3	7
- 99.2	1	3
-116.6	2	4
-124.8	2	5
-129.4	2	6

6.44 Preparation of Perfluoro-2-Methylheptyl Anion (147)

On stirring alkene (146) with an excess of caesium fluoride in tetraglyme an orange coloured solution was obtained. Its ^{19}F NMR spectrum indicated that quantitative formation of perfluoro-2-methylheptyl anion (147) had occurred.



$$\underset{(146)}{(CF_3)_2C{=}CFCF_2CF_2CF_2CF_3} \xrightarrow[\text{tetraglyme}]{\text{CsF}} \overset{1}{(CF_3)_2}\overset{-}{C}\text{-}\overset{2}{CF_2}\overset{3}{CF_2}\overset{4}{CF_2}\overset{5}{CF_2}\overset{6}{CF_3}\ \ Cs^+$$

(147)

The ^{19}F NMR data are summarized in Table 6.3.

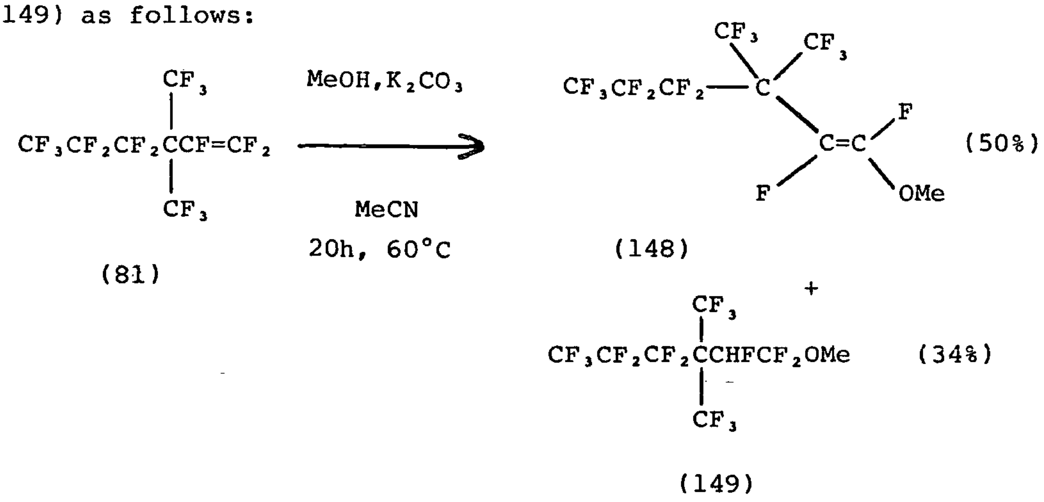
Table 6.3 ^{19}F NMR data for anion (147)

δ_F/ppm	Coupling	Integral	Assignment
- 41.7	M	6	1
- 81.8	M	3	6
- 91.9	M	2	2
-112.6	M	2	3
-122.0	M	2	4
-126.5	M	2	5

The ^{19}F NMR shifts for the fluorine atoms adjacent to the anionic charge centre are in close agreement with those observed for similar perfluoroalkyl carbanions prepared by Bayliff.[147]

6.45 Reaction of Perfluoro-3,3-Dimethylhex-1-ene (81) with MEthanol

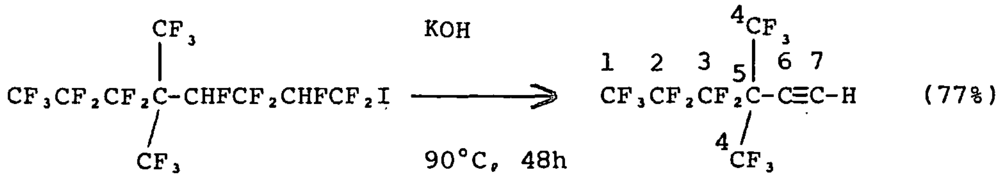
Treatment of alkene (81) with methanol gave the products (148) and (149) as follows:



The structural nature of the products was determined mainly by mass spectrometry (for (148) m/z 412 (M^+) and for (149) m/z 413 (M^+-F)) and by NMR spectroscopy (See appendix). Nucleophilic substitution of fluoride by methoxide ion gave the E isomer of (148) exclusively, as determined by its ^{19}F NMR spectrum which showed a large coupling constant, J_{FF}=119Hz, between the two vinylic fluorines. Typically, such coupling constants range between 100 and 140 Hz for vinylic fluorines situated in a trans configuration, whereas similar fluorines situated cis to each other generally give rise to values between 10 and 60 Hz.[160]

6.46 Preparation of 1H-Perfluoro-3,3Dimethylhex-1-yne (150)

2H,4H-Perfluoro-1-iodo-5,5-dimethyloctane (82) was treated with potassium hydroxide at 90°C in order to produce alkene (84) (See Section 4.6). Remarkably, however, the major product was 1H-perfluoro-3,3-dimethylhex-1-yne (150) rather than (84).



$$\mathrm{CF_3CF_2CF_2C(CF_3)_2{-}CHFCF_2CHFCF_2I} \xrightarrow[90^\circ\mathrm{C},\ 48\mathrm{h}]{\mathrm{KOH}} \mathrm{CF_3CF_2CF_2C(CF_3)_2{-}C{\equiv}C{-}H}\quad (77\%)$$

(82) (150)

Structural identification of (150) was achieved from the following data:

i) mass spectrometry; m/z 325 (M^+-F)

ii) IR spectrometry; ν_{max}(C≡C) 2142cm^{-1}, ν_{max} (C≡C-H) 3315cm^{-1}.

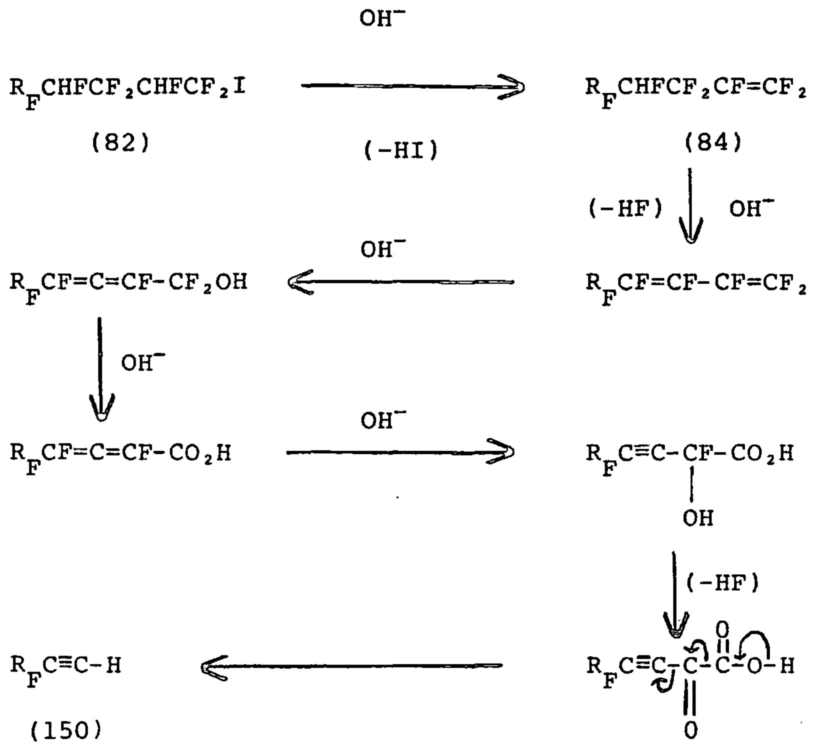
iii) NMR spectroscopy; δ_H(C≡C-H) 2.9ppm.

In addition the ^{13}C NMR spectrum of (150) is given in Table 6.4

Table 6.4 ^{13}C NMR data for alkyne (150).

δ_C/ppm	Coupling/Hz	Assignment
57.0	M(J=30)	5
65.8	S	6
80.7	S	7
109.1	T(J=272) of Q(J=38) of T(J=38)	2
113.4	T(J=273) of T(J=33)	3
117.6	Q(J=289) of T(J=33) of T(J=2)	1
120.4	Q(J=288)	4

On repeating the reaction for 5h and for 24h, two major volatile products (84) and (150) were obtained. Hence the first step in the formation of alkyne (150) must be dehydroiodination to give (84). The remaining steps in the reaction are not clear but the intermediate compounds must either be short-lived or involatile, since they were not present in the volatile reaction mixture. The type of mechanism which may be in operation is shown in Scheme 6.12.



$R_F=CF_3CF_2CF_2C(CF_3)_2$

Scheme 6.12

It appears that the formation of alkyne (150) is favoured by the presence of the bulky F-2-methylpentyl group in (82). This follows from the fact that similar treatment of iodide (23b) only gave alkene (69b) as the major product.

$$i\text{-}C_3F_7CHFCF_2CHFCF_2I \xrightarrow[90^\circ C]{KOH} i\text{-}C_3F_7CHFCF_2CF{=}CF_2$$

(23b) (69b)

A minor product resulting from dehydrofluorination of (69b) was also formed, as indicated by GC-mass spectrometry. The identity of this compound was not determined.

EXPERIMENTAL SECTION

INSTRUMENTATION

IR spectra: Unless stated IR spectra were recorded on a Perkin Elmer 457 grating IR spectrophotometer. Liquid samples were recorded as thin films between KBr plates and gaseous samples or volatile liquids in a cylindrical cell with KBr windows.

Mass Spectra: Mass spectra of pure samples were acquired on a VG 7070E spectrometer equipped with electron impact, chemical ionization and negative ionization modes. GC-mass spectra were recorded on a VG Micromass 12B spectrometer fitted with a Pye 104 gas chromotgraph or a VG 7070E spectrometer equipped with a capillary column gas chromograph.

Gas Liquid Chromotography: Gas liquid chromatographic analyses were carried out using either a Varian Aerograph Model 920 equipped with a gas density balance detector or Pye Unicam GCD chromatographs fitted with flame ionisation detectors. Column packings most frequently used were silicone elastomer (5% or 10%) on Chromasorb P (column O) diisodecylphthalate (10% or 20%) on Chromasorb P (column A) and Krytox (20%) on Chromasorb P (Column K). Alternatively GC analyses were carried out on a Hewlett Packard 5890A instrument equipped with a silicone elastomer coated fused silica capillary column. Preparative GC was performed on a Varian Aerograph Model 920 fitted with a Cathodometer detector, using columns A or O.

NMR Spectra: Routine ^{1}H and ^{19}F NMR spectra were recorded on a Perkin Elmer R24B spectrometer operating at 60MHz and a Varian EM360L spectrometer operating at 56.4 MHz respectively. High field spectra were recorded on a Bruker AC250 operating at 62.9 MHz (for ^{13}C) 250.1 MHz (for ^{1}H) and 235.3 MHz (for ^{19}F). Chemical shifts are quoted in ppm relative to TMS (for ^{1}H and ^{13}C) or $CFCl_3$ (for ^{19}F) as external reference, with downfield values expressed with a positive sign.

Elemental Analyses: Carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba 1106 elemented analyser. Analysis for halogens was performed as described in the literature.[181]

Fractional distillations: Fractional distillations of product mixtures were carried out using a Fischer Spaltrohr MMM 202 concentric tube system.

Reagents and Solvents

Unless otherwise stated, reagents were used as supplied. Hexafluoropropene, vinylidene fluoride, antimony pentafluoride, Bisphenol AF, triallyl isocyanurate (TIC) and perfluoroallylfluorosulphate (FAFS) were obtained from Montefluos SpA, Bollate, Italy.

Solvents were dried prior to use by standard methods and stored over molecular sieves (type 4A) under dry nitrogen.

CHAPTER SEVEN

EXPERIMENTAL TO CHAPTER TWO

SYNTHESIS AND SPECTROSCOPIC EXAMINATION OF MODEL COMPOUNDS

7.1 Preparation of Fluoroalkyl Iodides

7.11 Heptafluoro-2-iodopropane (12)[125]

A mixture containing hexafluoropropene (273g, 1.82 mol), iodine pentafluoride (81g, 0.36 mol) and iodine (185g, 0.73 mol) was sealed in a stainless steel autoclave (capacity 1175 ml) and rocked under autogenous pressure for 24 h at a temperature of 150°C. HFP (ca.4g) was recovered on opening the tube and further material (508g) was transferred under vacuum to a separate vessel. The product was washed with water, followed by alkaline sodium thiosulphate solution. Analysis by capillary G.C. showed one component which was identified as heptafluoro-2-iodopropane by comparison of its IR spectrum with that of an authentic sample.[125]

7.12 $(CF_3)_2CF(CH_2CF_2)_nI$ (13)[127,133,145]

a) A mixture containing heptafluoro-2-iodopropane (12) (41.0g, 0.14 mol) and vinylidene fluoride (32.8g, 0.51 mol) was sealed in a stainless steel tube (150ml) and rocked at 190°C for 36h under autogenous pressure. VDF (ca. 1g) was recovered on opening the tube, together with a purple liquid (69.4g). Capillary G.C. (100-250°C) showed the presence of five major components which were separated by fractional distillation. The fractions isolated were 2H,2H- nonafluoro-1-iodo-3-methylbutane (13a) (4.5g, 9%); b.p. 105°C; 4H,4H-undecafluoro-1-iodo-5-methylhexane (13b) (15.9g, 27%); 2H,2H,4H,4H,6H,6H-tridecafluoro-1-iodo-7-methyloctane (13c) (24.6g, 36%); b.p. 98°C (15 mmHg); 2,2,4,4,6,6,8,8 - octahydropentadecafluoro-1-iodo-9-methyldecane (13d) (17.6g, 23%); b.p. 106°C (5 mmHg); NMR spectrum no. 1; m/z 425 (M^+-I); and 2,2,4,4,6,6,8,8,10,10-

decahydroheptadecafluoro-1-iodo-11-methyldodecane (13e) (2.6g, 3%); NMR spectrum no. 2; m/z 469 (M^+-I-HF). Compounds (13a)-(13c) were identified by comparison of their NMR and mass spectra with authentic samples.[133]

The reaction was repeated at 185°C for 24h with heptafluoro-2-iodopropane (12) (70.1g, 0.24 mol) and VDF (29.3g, 0.46 mol). On opening the tube VDF (ca. 0.5g) was recovered and the telomer iodides were separated by distillation to give four fractions, (13a) (37.6g, 44%); (13b) (37.5g, 37%); (13c) (11.6g, 10%); and (13d) (6.5g, 5%).

7.13 $(CF_3)_2CF(CH_2CF_2)_l[CF_2CF(CF_3)]_m I$ (17-18)

a) The iodide $i\text{-}C_3F_7CH_2CF_2I$ (13a) (49g, 0.14 mol) was pipetted into a stainless steel autoclave (150ml) and HFP (35g, 0.23 mol) transferred under vacuum. The contents were rocked for 48h at 200°C and on cooling a liquid (69.3g) was recovered. Analysis of the liquid by capillary G.C. (100-220°C) showed three major peaks. Distillation of the mixture yielded three major fractions which were identified as (13a) (10.9g): b.p. 105°C; 5H,5H-pentadecafluoro-2-iodo-6-methylheptane (17a) (49.1g, 71%); b.p. 70-71°C (27 mmHg); (Found: C, 18.5; H, 0.4. $C_8H_2F_{15}I$ requires C, 18.8; H, 0.4%); NMR spectrum no. 3; mass spectrum no. 1; IR spectrum no. 1; and 7H,7H-heneicosafluoro-2-iodo-4,8-dimethylnonane (17b) (5.9g, 7%); b.p. 109-110°C (28 mm Hg); (Found: m/z 659.9787. $C_{11}H_2F_{21}I$ requires M^+ 659.8865); NMR spectrum no. 4; mass spectrum no. 2, IR spectrum no. 2.

b) A stainless steel autoclave (150ml) was charged with $(CF_3)_2CF(CH_2CF_2)_2I$ (13b) (31.1g, 73.3 mmol) and HFP (11.2g, 74.7 mmol). The tube was rocked for 48h at 200°C and on cooling HFP (ca. 1.5g) and a liquid (38.2g) were recovered. Distillation of the liquid afforded two major fractions. The first fraction was the starting material $(CF_3)_2CF(CH_2CF_2)_2I$ (13b) (17.1g) and the second fraction was identified as *5,5,7,7 - tetrahydroheptadecafluoro-2-iodo-8-methylnonane* (18a) (15.1g, 36%); b.p. 88-89°C (12mmHg); (Found: C,21.0; H,0.8, F, 56.4, $C_{10}H_4F_{17}I$ requires C,20.0;H, 0.7; F, 56.3%);NMR spectrum no. 5; mass spectrum no. 3; IR spectrum no. 3.

7.14 $(CF_3)_2CF(CH_2CF_2)_l[CF_2CF(CF_3)]_m(CH_2CF_2)_nI$ (19-20)

a) Vinylidene fluoride (15.5g, 0.24 mol) and (17a) (99.4g, 0.19 mol) were sealed in a stainless steel tube (125 ml capacity) and rocked at 185°C for 24h. On opening the tube a liquid (112.7g) was recovered and analytical G.C. showed that it contained two major components, which were separated by fractional distillation. The fractions isolated were *2H,2H,6H,6H-heptadecafluoro-1-iodo-3,7-dimethyloctane* (19a) (83.0g, 74%); b.p. 91-92°C (13mmHg); (Found: C, 20.5; H, 0.7; F, 56.9.$C_{10}H_4F_{17}I$ requires C, 20.9; H, 0.7; F, 56.3%); NMR spectrum no. 6; mass spectrum no. 4; IR spectrum no. 4; and *2,2,4,4,8,8-hexahydrononadecafluoro-1-iodo-5-9-dimethyldecane* (19b) (24.1g, 19%); b.p. 125°C/15mmHg; (Found: C, 22.6, H, 1.0; F, 56.9. $C_{12}H_6F_{19}I$ requires C, 22.6; H, 1.0; F, 56.6%); NMR spectrum no. 7; mass spectrum no. 5; IR spectrum no.5.

b) The iodide (18a) (12.3g,21.4 mmol) and vinylidene fluoride (2.7g, 42.2 mmol) were transferred to a stainless stell autoclave (150ml) which was subsequently rocked at 185°C for 24h. On opening the tube VDF (*ca* 1g) and a pale yellow liquid (12.3g) were recovered. Distillation of the liquid gave two major fractions which were identified as *2,2,6,6,8,8-hexahydrononadecafluoro-1-iodo-3,9-dimethyldecane* (20a) (6.0g, 44%); b.p. 106°C/5mmHg; (Found: C, 22.5; H, 1.0; F, 56.9. $C_{12}H_6F_{19}$ I requires C, 22.6; H, 1.0; F, 56.6%); NMR spectrum no. 8; mass spectrum no. 6; IR spectrum no. 6; and *2,2,4,4,8,8,10,10-*

octahydroheneicosafluoro-1-iodo-5,11-dimethyldodecane (20b) (3.4g, 23%); b.p. 131-132°C/3 mm Hg; (Found: C, 23.7; H, 1.0; I, 18.5. $C_{14}H_8F_{21}I$ requires C, 23.9; H, 1.2; I 18.1%); NMR spectrum no. 9; mass spectrum no. 7; IR spectrum no. 7.

c) A stainless steel autoclave (150ml) was charged with the iodide (17b) (16.1g, 24.4 mmol) and vinylidene fluoride (3.4g, 53.1mmol) and rocked at 190°C for 24h. On opening the tube VDF (1.5g) and a liquid (15.0g) were recovered. Distillation of the liquid yielded one fraction which was identified as 2,2,8,8-tetrahydrotricosafluoro-1-iodo-3,5,9-trimethyldecane (19c) (11.0g, 62%); b.p. 95°C/5mmHg: (Found: C, 21.7; H, 0.5; F, 60.9. $C_{13}H_{14}F_{23}$ I requires C, 21.6; H, 0.6; F, 60.4%); NMR spectrum no. 10; mass spectrum no. 8; IR spectrum no. 8. The liquid remaining in the distillation apparatus could not be distilled over. It was identified as 2,2,4,4,10,10-hexahydropentacosafluoro-1-iodo-5,7,11-trimethyldodecane (19d); (1.4g, 7%); (Found: C, 22.6; H, 0.8. $C_{15}H_6F_{25}$ I requires C, 22.9; H, 0.8%); NMR spectrum no. 11; mass spectrum no. 9; spectrum no. 9.

7.15 Heptafluoro-2-iodopropane (12) with HFP

A stainless steel autoclave (150ml) was cooled in liquid air and heptafluoro-2-iodopropane (12) (46.3g, 156.4 mmol) and HFP (24.9g, 166.0 mmol) transferred under vacuum. The contents were rocked at 200°C for 7h and on cooling HFP (ca. 14g) and a liquid (35.4g) were recovered. Analysis of the liquid by capillary G.C. showed the starting material (12) to the only major component, along with several very minor products which were not characterized.

7.16 $(CF_3)_2CF(CHFCF_2)_nI$ (23)[133]

A mixture of heptafluoro-2-iodopropane (12) (59.5g, 0.20 mol) and trifluoroethylene (42.4g, 0.52 mol), in a stainless steel autoclave (150 ml), was rocked at 185°C for 24h. On opening the tube trifluoroethylene (ca. 4g) and a purple liquid (84.6g) were recovered. Three fractions were isolated from the liquid by distillation. They were identified as (12) (3.4g); b.p. 38-41°C; 2H-decafluoro-1-iodo-3-methylbutane (23a) (19.3g, 25%); b.p. 103°C;[133] NMR spectrum no. 12; and 2H, 4H-tridecafluoro-1-iodo-4-methylhexane (23b) (35.3g, 38%); b.p. 143°C (540 mmHg);[133] NMR spectrum no. 13. The remaining undistilled material was not characterized.

NMR spectroscopy showed that 16% of product (23a) was due to its regioisomer $(CF_3)_2$ $CFCF_2CHFI$ (23c).

7.2 Fluorodeiodination of the Telomer Iodides[133]

7.21 Preparation of $(CF_3)_2CF(CH_2CF_2)_nF$(15)

a) A three necked round-bottomed flask (250ml) was fitted with a condenser, dropping funnel and mechanical stirrer. Under an atmosphere of nitrogen gas antimony pentafluoride (43.2g, 0.20mol) in arklone ($CF_2ClCFCl_2$) (25ml) was slowly added to $(CF_3)_2CF(CH_2CF_2)_2$ I (13b) (50.5g, 0.12 mol) in arklone (20ml) at 0°C with stirring. The mixture was stirred for a further 0.5h and then water (150ml) was added cautiously. The contents of the flask were warmed to room temperature and poured into more water (150ml). Repeated washing of the lower fluorocarbon layer was carried out using saturated sodium carbonate solution until effervescence had almost ceased. Finally, the fluorocarbon material was washed with water (100ml), dried using anhydrous $MgSO_4$ and distilled to remove the solvent. The remaining liquid was purified by distillation to give 3H,3H,5H,5H-dodecafluoro-2-methylhexane (15b) (26.2g, 70%); b.p. 104-105°C.

The product was identified by comparison of NMR and mass spectral data with those of an authentic sample.[133]

By following the procedure described above, other model compounds were prepared also.

b) Antimony pentafluoride (13.9g,64.1 mmol) and $(CF_3)_2CF(CH_2CF_2)_3I$ (13c) (16.2g, 33.2 mmol) gave 3,3,5,5,7,7-hexahydrotetradecafluoro-2-methyloctane (15c) (8.6g, 68%); b.p. 58-59°C (15mmHg); (Found: C, 28.7; H, 1.5; F, 69.4. $C_9H_6F_{14}$ requires C, 28.4; H, 1.6; F, 70.0%). The product was identified by comparison of its NMR spectrum with that of a sample given in the literature, although erroneous analysis and mass spectral data were quoted;[133] mass spectrum no. 10.

c) Antimony pentafluoride (25.1, 0.11mol) and $(CF_3)_2CF(CH_2CF_2)_4I$ (13d) (42.6g, 77.2 mmol) gave <u>3,3,5,5,7,7,9,9,-octahydrohexadecafluoro-2-methylhexane</u> (15d) (20.5g, 60%); (Found: C, 29.6; H, 1.7; F, 69.0. $C_{11}H_8F_{16}$requires C, 29.7; H, 1.8; F, 68.5%); NMR spectrum no. 14; mass spectrum no. 11.

d) Antimony pentafluoride (11.8g, 54.4mmol) and $(CF_3)_2CF(CH_2CF_2)_5I$ (13e) (15.2g, 24.7mmol) gave <u>3,3,5,5,7,7,9,9,11,11-decahydrooctadecafluoro-2-methyldodecane</u> (15e) (7.3g, 58%); (Found: C, 30.9; H, 1.9; F, 66.8. $C_{13}H_{10}F_{18}$ requires, C, 30.7; H, 2.0; F, 67.3%); NMR spectrum no. 15; mass spectrum no. 12.

7.22 Synthesis of $(CF_3)_2CFCH_2CF_2CF_2CF(CF_3)CH_2CF_2CH_2CF_3$(26)

Following the procedure outlined in Section 7.21a, antimony pentafluoride (13.7g, 63.2 mmol) and $(CF_3)_2CFCH_2CF_2CF_2CF(CF_3)(CH_2CF_2)_2I$ (196) (23.0g, 36.1 mmol) gave <u>3,3,7,7,9,9 - hexahydroeicosafluoro-2,6-dimethyldecane</u> (26) (14.6g, 76%); b.p. 81-82°C (5mmHg); (Found: m/z 511.0152. $C_{12}H_6F_{20}$ requires M^+-F 511.0166); NMR spectrum no. 16; mass spectrum no. 13; IR spectrum no. 10.

7.3 Coupling of the Telomer Iodides

7.31 $(CF_3)_2CFCH_2CF_2I$ (13a)[127,145]

A Carius tube was charged with mercury (128g) and $(CF_3)_2CFCH_2CF_2I$ (13a) (15.2g, 42.2 mmol). The sealed tube was shaken for 4 days while under exposure to UV light from a 1KW Hanovia lamp. After this time volatile material was transferred to a separate vessel under vacuum. Analysis by G.C showed one major and two minor components which were separated by fractional distillation. The fractions isolated were 2H-nonafluoro-3-methylbut-1-ene (27) (1.1g, 11%); b.p. 31°C; 3,3,4-trihydrononafluoro-2-methylbutane (28) (1.2g, 12%); b.p. 52-53°C; NMR spectrum no. 17; and 3,3,6,6,-tetrahydrooctadecafluoro-2,7-dimethyloctane (14a) (7.0g, 71%). The products were identified by comparison of their infrared spectra with those of authentic samples.[145]

7.32 $(CF_3)_2CFCH_2CF_2CH_2CF_2I$ (13b)[133]

A Carius tube was charged with mercury (60.4g) and the iodide (13b) (15.6g,36.8 mmol). The sealed tube was irradiated for 7 days with UV light from a 1KW Hanovia lamp. Volatile material was then transferred under vacuum to a separate vessel. Analysis by capillary G.C. (60°-170°C) showed three components and no starting material. The components were separated by fractional distillation which yielded 2,4,4-trihydroundecafluoro-5-methylhex-(E)-2-ene (30) (1.9g, 17%); b.p. 89°C; NMR spectrum no. 18; mass spectrum no. 14; IR spectrum no.11; 2,4,4,-trihydroundecafluoro-5-methylhex-1-ene (29b) (3.7g,34%); b.p. 92-93°C; NMR spectrum no. 19; mass spectrum no. 15; and 3,3,5,5,8,8,10,10-octahydrodocosafluoro-2,11-dimethyldodecane (14b) (4.5g, 41%). Products (29b) and (14b) were identified by comparison of spectra with those of authentic samples.[133,145]

7.4 ^{19}F NMR Data on a VDF/HFP Copolymer

A Carius tube was charged with VDF (3.9g, 60.9 mmol) and HFP (10.8g, 72.0 mmol), then sealed under vacuum. The tube was irradiated with γ-rays for 96h at ambient temperature. On opening the tube the solid material was dissolved in DMF over a period of 2 days. The high field NMR spectra for the copolymer and solutions of each of the models (15d) and (26) in DMF were recorded. Discussion of the spectroscopic data is given in Section 2.5.

7.5 Polymerisation of VDF at Different Temperatures

VDF (ca. 2.5g) was transferred under vacuum to each of three different Carius tubes, which were then sealed and irradiated with γ-rays. One tube was irradiated at room temperature for 2 days, the second at 0°C for 5 days and the third at -78°C for 10 days. On opening the tubes, each of the homopolymer samples were dissolved in DMF over a period of 2 days and their ^{19}F NMR spectra recorded. Accurate integrals of the observed signals in the spectra gave an estimation of the regioselectivity of addition during the polymerisation process at different temperatures. Discussion of the results is given in Section 2.6.

CHAPTER EIGHT

EXPERIMENTAL TO CHAPTER THREE

MODEL STUDIES RELATED TO THE CROSS-LINKING OF VDF/HFP COPOLYMERS

8.1 Fluoride Ion Induced Dehydrofluorination Reactions of Saturated Model Compounds

A mixture containing sulpholane (4 ml) caesium fluoride (1.8 g, 11.8 mmol) and $(CF_3)_2CF(CH_2CF_2)_2CH_2CF_3$(15c) (4.2 g, 11.0 mmol) was sealed in a Carius tube under vacuum and rocked at 150°C for 6 h. On opening the tube volatiles were transferred under vacuum and analysis by glc showed two components, one of which was the starting material (15c). Separation was effected by fractional distillation to give (15c) (0.5 g) and 3,5,5,7,7-pentahydroterdecafluoro-2-methyloct-2-ene (35) (2.8 g, 70%); b.pt. 55-56°C (15 mmHg); (Found: C, 30.2; H, 1.3; F, 68.9. $C_9H_5F_{13}$ requires C,30.0;H,1.4;F,68.6%); NMR Spectrum no. 20; mass spectrum no. 16,m/z (NI) 341 (M^--F, 7%); IR spectrum no. 12.

The procedure was repeated using $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (15b) (4.2 g, 13.3 mmol), sulpholane (4 ml) and caesium fluoride (2.7 g, 17.8 mmol). Analysis by glc showed one major component which was subsequently identified as 3.5.5-trihydroundecafluoro-2-methylhex-2-ene (34) (3.1 g, 79%) by comparison of its NMR and mass spectra with those of an authentic sample.[133]

8.2 Dehydroiodination Reactions of Telomer Iodides

Tri-n-butylamine (6.9 g, 37.1 mmol) and the iodide (19a) (21.2 g, 36.9 mmol) were stirred vigorously until the mixture became solid due to the formation of the amine hydroiodide. Volatile material was transferred under vacuum and subsequent distillation of this material yielded the alkene 2,6,6-trihydroheptadecafluoro-3,7-dimethyloct-1-ene (40) (14.1 g, 86%); b.pt. 71-72° (44 mmHg); (Found: C, 26.9; H, 0 .7; F, 72.7. $C_{10}F_{17}H_3$ requires C, 26.91; H, 0.68; F, 72.42%); NMR spectrum no. 21; mass spectrum no. 17, m/z (CI)427(M^+-F, 1%); ν_{max} (C=C) 1750 cm^{-1}(s).

The procedure was repeated with $(CF_3)_2CFCH_2CF_2I$ (13a)(15.4g, 42.8 mmol) and tri-n-butylamine (10.2g, 55.0 mmol) to give 2H-nonafluoro-3-methylbut-1-ene (29a) (9.6g, 97%), which was identified by comparison of its IR spectrum with that of an authentic sample.[145]

Tri-n-butylamine (7.0g, 37.8 mmol) and $(CF_3)_2CF(CH_2CF_2)_2I$ (13b)(15.2g, 35.8 mmol) gave 2H,4H,4H- undecafluoro-5-methylhex-1-ene (29b)(8.7g, 82%), which was identified by comparison of its IR spectrum with that of an a authentic sample.[145]

Tri-n-butylamine (6.2g, 33.4 mmol) and $(CF_3)_2CF(CH_2CF_2)_3I$ (13c)(16.3g, 33.4 mmol) gave 2H,4H,4H,6H,6H-tridecafluoro-7-methyloct-1-ene (29c)(9.8g, 81%);b.p. 59°C (23mm Hg), NMR spectrum no. 22; mass spectrum no, 18. The identity of the product was confirmed by comparison of its IR spectrum with that of an authentic sample.[145]

8.3 Synthesis of Unsaturated Model Compounds Using Fluoride Ion

8.31 $(CF_3)_2C{=}CHCF_3$ (36)

A Carius tube was charged with $(CF_3)_2CF{-}CH{=}CF_2$ (29a) (17.6g , 75.9 mmol), caesium fluoride (7.0g, 46.1 mmol) and sulpholane (6 ml). The tube was sealed and then rocked at 100°C for 3h. After cooling the tube, volatile material was transferred under vacuum to a separate vessel. The liquid was washed with water (2x50ml) and dried using anhydrous $MgSO_4$. Analysis by capillary G.C. showed one component only, which was identified as 3H- nonafluoro -2-methylbut-2-ene (36) (16.9g, 96%) by comparison of its NMR spectrum with that given in the literature.[133]

8.32 E- and Z- $(CF_3)_2C{=}CH{-}CF{=}CHCF_3$ (37)

A mixture containing sulpholane (8 ml), caesium fluoride (3.8 g, 25.0 mmol), and the alkene $(CF_3)_2CFCH_2CF_2CH{=}CF_2$ (7.0 g, 23.6 mmol) was sealed in a glass ampoule, then rocked at 150°C for 4h. On opening the tube, volatile material was transferred under vacuum. Analysis by glc showed two major components which were separated by fractional distillation and identified as (Z)-3,5-dihydrodecafluoro-2-methylhexa-2,4-diene (37a) (4.2 g, 64%); b.p. 109°C; (Found: m/z 275.9997. $C_7H_2F_{10}$ requires M^+ 276.0001); NMR spectrum no. 23; mass spectrum no, 19, m/z(EI) 276(M^+, 18%); IR spectrum no. 13; and (E)-3,5-dihydrodecafluoro-2-methylhexa-2,4-diene (37b) (2.2 g, 34%); b.p. 86°C; (Found: C, 30.1; H, 0.9; F, 68.4. $C_7H_2F_{10}$ requires C, 30.4; H, 0.7; F, 68.8%); NMR Spectrum no. 24; mass spectrum no. 20; IR Spectrum no.14.

8.4 Synthesis of Unsaturated Model Compounds Using SbF_5

8.41 $(CF_3)_2$ $C=CHCF_3$ (36)

An NMR tube was charged with antimony pentafluoride (2.8g, 12.9 mmol) and $(CF_3)_2CFCH=CF_2$ (29a) (0.5g, 2.2mmol). The tube was sealed and the contents agitated for a few minutes at room temperature. Changes in the chemical nature of the mixture were followed by ^1H and ^{19}F NMR spectroscopy. The spectra which were acquired indicated that conversion of (29a) to $(CF_3)_2$ $C=CHCF_3$ had occurred.

8.42 $(CF_3)_2$ $CFCH_2CF_2CF_2$ $C(CF_3) = CHCF_3$ (41)

A two-necked 50ml round-bottomed flask was fitted with a condenser and dropping funnel. Under an atmosphere of dry nitrogen the alkene (40) (14.8g, 33.2 mmol) was dropped into antimony pentafluoride (7.2g, 33.2 mmol). Stirring of the mixture was continued for 2h at room temperature. After this time water (15ml) was added carefully to the system; two layers were observed and the lower fluorocarbon material was washed with further quantities of water, dried using anhydrous $MgSO_4$ and distilled to give (Z)-2,6,6 - trihydrohepta-decafluoro -3,7- dimethyloct-2-ene(41) (12.3g, 83%); b.p. 73°C (47 mm Hg); (Found : C, 26.9; H, 0.8; F, 71.7. $C_{10}H_3F_{17}$ requires C, 26.9; H, 0.7; F, 72.4%); NMR spectrum no. 25; mass spectrum no. 21, m/z(EI) 427(M^+-F, 2%); IR spectrum no. 15.

8.43 $[(CF_3)_2\ C{=}CHCF_2]_2$ (39)

Antimony pentafluoride (6.7g, 30.9 mmol) and $[(CF_3)_2CFCH_2CF_2]_2$ (14a) (7.2g, 15.4 mmol) were stirred in a round-bottomed flask fitted to a condenser, under an atmosphere of nitrogen gas, for 4h at 120°C. After cooling the system, water was added carefully to destroy any remaining SbF_5. The fluorocarbon layer was then washed with quantities of saturated Na_2CO_3 solution until no effervescence was observed and finally dried using $MgSO_4$. Analysis of the liquid by capillary G.C. showed one component which was identified as 3H, 6H- hexadecafluoro-2,7-dimethylocta-2,6-diene (39) (5.2g, 79%) by comparison of its IR spectrum with that of an authentic sample.[133]

8.5 Treatment of Saturated Model Compounds with Typical Curing Agents

8.51 $(CF_3)_2\ CFCH_2CF_2CF_2CF(CF_3)(CH_2CF_2)_2F$ (26) with MgO

Magnesium oxide (1.4g, 34.7 mmol) and (26) (4.7g, 8.9 mmol) were sealed in a Carius tube and rocked for 24h at 210°C. On opening the tube a volatile liquid (4.5g) was recovered which was identified as the starting material (26).

8.52 $(CF_3)_2\ CF(CH_2CF_2)_2CH_2CF_3$ (15c) with MgO

The saturated model (15c) (0.4g, 1.1 mmol), magnesium oxide (0.02g, 0.5mmol) and DMAC (0.7g) were sealed in a 'Rotaflo' tube and heated to 140°C for 24h. Analysis by capillary G.C. and NMR spectroscopy showed that no reaction had occurred and that only the starting material (15c) was present.

8.53 $(CF_3)_2\ CF(CH_2CF_2)_2CH_2CF_3$ (15c) with Bisphenol AF

A mixture of the saturated model (15c), (0.5g, 1.3mmol), DMAC (1.0g), Bisphenol AF (0.2g, 0.6 mmol), and benzyltriphenylphosphonium chloride (0.2g, 0.5 mmol) was heated in a 'Rotaflo' tube for 24h at 140°C. After cooling the system was analysed by G.C. and NMR spectroscopy which showed that no reaction had occurred.

8.6 Dehydrofluorination of Saturated Models by D.B.U.

8.61 $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (15b)

To a solution of the saturated model compound (15b) (0.7 g, 2.2 mmol) in dimethylacetamide (1 ml), D.B.U. (0.3g, 2.0 mmol) was added at room temperature. An immediate exothermic reaction was observed and analysis by ^1H and ^{19}F NMR spectroscopy showed that elimination of hydrogen fluoride had occurred, exclusively at the 'tertiary' fluorine site, to yield the alkene 3H,5H,5H - undecafluoro-2-methylhex-2-ene (34) (39%). The identity of the product was confirmed by comparison of its NMR data with that given in the literature.[133]

8.62 $(CF_3)_2CF(CH_2CF_2)_2CH_2CF_3$ (15c)

Similar treatment of the saturated model compound (15c) (0.5g, 1.3 mmol) is D.M.A.C. (1.0g) with D.B.U. (0.2g, 1.3 mmol) yielded the alkene 3,5,5,7,7-pentahydroterdecafluoro-2-methyloct-2-ene (35) (38%).

The ^{19}F NMR spectra of the treated model compounds (15b) and (15c) showed a singlet resonance at-153.9 ppm in each case and this is probably due to the presence of the amidine hydrofluoride.

8.7 Reactions of Unsaturated Model Compounds with Nucleophiles

8.71 $(CF_3)_2C{=}CHCF_2CH_2CF_3$ (34) with Methanol

A mixture of the alkene (34) (3.5g, 11.8 mmol) methanol (0.6g, 18.8 mmol), acetonitrile (3 ml) and potassium carbonate (1.6g, 11.6 mmol) was stirred at room temperature for 30h. The system was washed with water (3 x 10 ml) and then dried using anhydrous $MgSO_4$ to give a liquid (3.7 g). Analysis by capillary G.C. showed 2 major components which were isolated by preparative scale G.C. (30% SE30, column temp. 160°C, injector temp. 160°C, flow rate 120 mm/min). The two products, in order of increasing retention time, were identified as <u>2,3,5,5-tetrahydro-undecafluoro-3-methoxy-2-methylhexane</u> (48); (Found: C, 29.5; H, 2.1; F,63.3. $C_8H_7F_{11}O$ requires C, 29.3; H, 2.2; F, 63.7%); NMR spectrum no. 26; mass spectrum no. 22, m/z (EI) 327 (M^+-H, 0.5 %) and 309 (M^+-F, 4%);

IR spectrum no. 16; and 3,5,5-trihydrononafluoro-1,3-dimethoxy-2-methylhex-1-ene(49) (E and Z isomers); (Found: m/z 301.0263 (M^+ -F). $C_9H_9F_9O_2$ requires M^+-F 301.0475); NMR spectrum no. 27; mass spectrum no. 23, m/z (EI)187 (M^+-$CF_2CH_2CF_3$, 100%); IR spectrum no. 17.

8.72 $(CF_3)_2$ $C{=}CHCF_2(CH_2CF_2)_2F$(35) with Phenol.

A mixture of the alkene (35) (1.8 g, 5.0 mmol), phenol (0.5 g, 5.0 mmol), acetonitrile (2 ml) and potassium carbonate (0.6 g, 4.3 mmol) was stirred for 24h at ambient temperature. After this time the system was washed with water (5 x 5 ml), then dried ($MgSO_4$). Analytical scale gas chromatography showed five major products. The component with the shortest retention time was isolated using preparative scale gas chromatography (30% SE30, column temp. 210°C) and identified as 2,3,5,5,7,7-hexahydro-3-phenoxyterdecafluoro-2-methyloctane(45b); (Found m/z 454.0572. $C_{15}H_{11}F_{13}O$ requires M^+ 454.0602); NMR spectrum no. 28; mass spectrum no. 24. Separation of the other components was not possible but they were identified as 3,5,5,7,7-pentahydro-1,3-diphenoxyundecafluoro-2-methyloct-1-ene(46b) (E and Z isomers); NMR spectrum no. 29; mass spectrum no. 25; m/z (EI) 415 (M^+-OPh, 16 %); IR spectrum no. 18 and 2,3,5,5,7,7-hexahydro-1,3-diphenoxydodecafluoro-2-methyloctane(47b) (two diastereoisomers); NMR spectrum no. 30; mass spectrum no. 26, m/z(EI) 528 (M^+, 12%); IR spectrum no. 18.

8.73 $(CF_3)_2$ $C{=}CHCF_2CH_2CF_3$ (34) with Phenol

The procedure was repeated using the alkene (34)(1.7g, 5.7 mmol), phenol (0.5g, 5.7 mmol), acetonitrile (2 ml) and potassium carbonate (0.9 g, 6.5 mmol), and stirred for 24h at room temperature. Analytical scale G.C. showed five major products, the most volatile of which was isolated by preparative G.C. (30% SE30, column temp. 175°, injector temp. 200°C) and identified as 2,3,5,5-tetrahydro-3-phenoxyundecafluoro-2-methylhexane(45a) ; NMR spectrum no. 31; mass spectrum no. 27. m/z (EI) 390 (M^+, 34%) and 257 (M^+-$CF_2CH_2CF_3$,43%). The other four components could not be separated but were identified as 3,5,5-trihydro -1, 3-diphenoxydecafluoro-2-methylhex-1-ene(46a) (E and Z isomers); NMR spectrum no. 32; mass spectrum no. 28; IR spectrum no. 19; and 2,3,5,5-tetrahydro-1,3-diphenoxydecafluoro-2-methylhexane(47a) (two diastereoisomers); NMR spectrum no. 33; mass spectrum no. 29, m/z 464 (M^+, 40%); IR spectrum no. 19.

8.74 $[(CF_3)_2\ C{=}CHCF_2]_2$ (39) and Phenol

The diene (39) (1.7g, 4.0mmol), phenol (0.4g, 4.2 mmol), potassium carbonate (0.5g, 3.6 mmol) and acetonitrile (2 ml) were stirred at room temperature for 10h. After this time the mixture was washed with water (5 x 5ml) and dried using anhydrous $MgSO_4$. Capillary G.C. showed the presence of two major components in the mixture, one of which was the starting material (39). The other compound was isolated by preparative G.C. (10% SE30, column temp. 190°C, injector temp. 220°C) and identified as 3,6,7-trihydro-6-phenoxyhexadecafluoro - 2,7-dimethyl oct-2-ene, (50); (Found: m/z 501.0057. $C_{16}H_8F_{16}O$ requires M^+-F 501.0336); NMR spectrum no. 34; mass spectrum no. 30, m/z (EI) 520 (M^+, 34%); IR spectrum no. 20.

The procedure was repeated using the diene (39) (1.5g, 3.5 mmol), phenol (0.7g, 7.4 mmol), potassium carbonate (0.6g, 4.3 mmol) and acetonitrile (2 ml) for 26h. Two major products were observed using capillary G.C. but they could not be purified since several minor components with similar boiling points were also present in the mixture. Consequently, the products were not fully characterised although their mass spectra are consistent with the E and Z isomers of 3,6-dihydro - 1,3-diphenoxytetradecafluor -2,7-dimethylocta - 1,6-diene (51) mass spectrum no. 31, m/z 574 (M^+,26%).

8.75 Z - $(CF_3)_2CFCH_2CF_2CF_2C(CF_3){=}CHCF_3$(41) with Methanol

A mixture of the alkene (41) (1.9 g, 4.3 mmol) methanol (0.3 g, 9.3 mmol), acetonitrile (1 ml) and potassium carbonate (0.4 g, 2.9 mmol) was stirred vigorously at room temperature for 24h. The mixture was washed with water and analysis by G.C. (capillary column, 70°C to 170°C) showed two major products and no starting material. The products could not be separated, so were isolated together by preparative scale G.C. (30% SE30, column temp. 140°C) and identified as 2,6,6-trihydro-2-methoxyhexadecafluoro-3,7-dimethyloct-3-ene (52a) (E-isomer) and (52b) (Z-isomer); Found: m/z 439.0370. $C_{11}H_6F_{16}O$ requires 439.0179 (M^+-F) ;

NMR spectrum no. 35; mass spectrum no. 32; IR spectrum no. 21.

8.76 Z-$(CF_3)_2$ $CFCH_2CF_2CF_2$ $C(CF_3)$=$CHCF_3$ (41) with Phenol

The above reaction was repeated using phenol (0.4 g, 4.3 mmol), (41) (2.0, 4.5 mmol), K_2CO_3 (0.6 g, 4.5 mmol) and CH_3CN (1 ml). The mixture was stirred at room temperature for 4 h and analysis by capillary G.C. (90°C to 250°C) showed two major components, together with a number of minor products. The major products could not be separated from each other but they were isolated as a mixture using preparative scale G.C. (30% SE30, injector temp. 210°C, column temp. 210°C) and identified as 2,6,6-trihydro-2-phenoxyhexadecafluoro-3,7-dimethyloct-3-ene(52c) (E-isomer) and(52d) (Z-isomer); (Found: m/z 520.0296. $C_{16}H_8F_{16}O$ requires 520.0320 (M^+)); NMR spectrum no. 36; mass spectrum no. 33; IR spectrum no. 22.

The minor products could not be isolated but were analysed by GC-mass spectrometry. They have greater retention times than the E and Z isomers of (52) and their mass spectra are consistent with 2,6,6-trihydro-2,4-diphenoxypentadecafluoro-3,7-dimethyloct -3-ene (54) (E and Z isomers); mass spectrum no. 34; and 2,3,6,6-tetrahydro-2,4-diphenoxyhexadecafluoro-3-7-dimethyloctane(53) (Mixture of diastereoisomers); mass spectrum no. 35. By increasing the ratio of phenol to the alkene (41), these products could be formed in greater proportions relative to (52).

The following mixtures were stirred at room temperature for 12h and any reaction detected by analysis using capillary G.C.

a) Phenol (0.02g, 0.2 mmol), (41)(0.1g, 0.2 mmol), Na_2CO_3 (0.02g, 0.2 mmol), CH_3CN (1 ml)

b) Phenol (0.02g, 0.2 mmol), (41) (0.1g, 0.2 mmol), K_2CO_3 (0.03g, 0.2 mmol), DMF (1 ml)

c) PhO^-Na+ (1.3g, 11.2 mmol), (41)(4.8g, 10.8mmol), DMF (15ml)

d) Phenol (0.02g, 0.2 mmol), (41) (0.1g, 0.2 mmol), CH_3CN (1 ml)

With systems a) and b) conversion of (41) to (52) was observed. No reaction was observed for system d) and c) gave little change.

8.77 $(CF_3)_2$ C=CH-CF=CHCF$_3$ (37) with Methanol

A mixture of E- and Z-dienes (37) (2.0g, 7.2 mmol), methanol (0.3g, 9.4 mmol) potassium carbonate (0.6g, 4.3 mmol) and acetonitrile (1 ml) was stirred at room temperature for 24h. Capillary G.C. showed four major products and no starting material. The products could not be isolated but were separated into two mixtures, each containing two compounds, by preparative G.C. (30% SE30, column temp. 140°C, injector temp. 150°C). The first mixture was identified as 2,4,5-trihydro-4-methoxydecafluoro-5-methylhex-2-ene (56a)(Z-isomer) and (56b) (E-isomer); (Found: C, 31.5; H, 1.9; F;61.1. $C_8H_6F_{10}O$ requires C, 31.2; H, 2.0; F, 61.7%); NMR spectrum no. 37; mass spectrum no. 36; IR spectrum no. 23; and the second as 3,5-dihydro-1,3-dimethoxyoctafluoro-2-methylhexa-1, 4-diene (57) (mixture of isomers); (Found: m/z 269.0210. $C_9H_8F_8O_2$ requires M^+-OCH_3 269.0213); NMR spectrum no. 38; mass spectrum no. 37 ; IR spectrum no. 24.

CHAPTER NINE

EXPERIMENTAL TO CHAPTER FOUR

DEVELOPMENT OF A NEW FREE RADICAL CROSS LINKING PROCESS

9.1 Free Radical Reactions of TIC.

A Carius tube was charged with heptafluoro-2-iodopropane (12) (6.6g, 22.3 mmol) and TIC (2.8 g, 11.2 mmol). The materials were thoroughly degassed and the sealed tube was irradiated with γ-rays at room temperature for 72h. On opening the tube the iodide (12) (2.5g) was recovered by distillation of the material under reduced pressure. The remaining material (6.1g) was analysed by capillary G.C. which showed the presence of four components, one of which was TIC. Separation of the other compounds was not possible but their identity was determined by GC-mass spectrometry as follows; (1,1,2,3,3-pentahydroheptafluoro-2-iodo-4-methylpentyl) diallyl isocyanurate (61) (38%); mass spectrum no. 38, m/z (EI) 545 (M^+,4%), 418 (M^+-I, 100%) and 252 ($[RNCO]^+$-I, 27%) where R=$(CF_3)_2CFCH_2CHICH_2$; Bis (1,1,2,3,3-pentahydroheptafluoro-2-iodo-4-methylpentyl) allyl isocyanurate (62) (32%); mass spectrum no. 39, m/z (EI) 714(M^+-I, 100%) and 252 ($[RNCO]^+$-I, 34%); and tris(1,1,2,3,3-pentahydroheptafluoro-2-iodo-4-methylpentyl isocyanurate (63) (8%); mass spectrum no. 40, m/z(EI) 252 $[RNCO]^+$-I, 100%). See NMR spectrum no. 39.

A Carius tube was charged with a solution of TIC (3.4g, 13.7 mmol) in acetone (15ml). The materials were thoroughly degassed and the sealed tube irradiated with γ-rays for 96h. On opening the tube a polymer (3.4g) was recovered by removing the acetone under reduced pressure. The acetone was found to be virtually pure by ^1H NMR, i.e. it did not contain any dissolved TIC. On heating a portion of the polymer under high vacuum to ca 250^oC no physical change was observed and no volatile material was transferred to the cold trap. The ^1H NMR spectrum of the polymer in acetone was acquired and its pertinent features are as follows:

δ_H 4.5(2H, d, J=6 Hz), 5.3(2H, m), 5.9 (1H, tt, J=14 and 6Hz); (Found: C, 57.6; H, 5.7; $C_{12}H_{15}N_3O_3$ units require C, 57.8; H, 6.0%).

A Carius tube containing a degassed solution of TIC (3.3g, 13.3 mmol) and HFP (4.8g, 32.0 mmol) in acetone (25ml) was irradiated with γ-rays for 4 days. On opening the tube HFP (2.8g) and a polymer (4.9g) were recovered. The polymer was found to be virtually insoluble in acetone, DMF, hexane and chloroform. (Found: C, 54.1; H, 5.5; N, 14.3; F, 6.2 %).

9.2 Trifluoroethylene with i-$C_3F_7CF_2CF_2I$ (67a)

A 150ml stainless steel autoclave was evacuated and charged with i-$C_3F_7CF_2CF_2I$(67)(43.1g, 108.8 mmol) and trifluoroethylene (10.7g, 130.5 mmol). The tube was rocked at 185°C for 24h and after cooling, trifluoroethylene (ca. 5g) and a liquid (46.2g) were recovered. Fractional distillation of the liquid afforded three major fractions which were identified as the starting material (67a) (22.2g, 52%), b.p. 94°C; <u>2H-tetradecafluoro-1-iodo-5-methylhexane</u>(68a)(16.7g, 32%); b.p. 77-78°C (65mm Hg); (Found: C,17.9;H,0.2;F, 55.6. $C_7HF_{14}I$ requires C, 17.6; H, 0.2; F, 55.7 %); NMR spectrum no. 40; mass spectrum no. 41, m/z(EI) 478 (M^+, 43%); IR spectrum no. 25; and 2H, 4H-heptadecafluoro-1-iodo-7-methyloctane (68b) (1.7g, 3%); b.p. 87-90°C (40 mm Hg); NMR spectrum no. 41; mass spectrum no. 42; m/z (EI) 560 (M^+, 20%).

9.3 Dehydroiodination of Telomer Iodides

9.31 i-$C_3F_7CF_2CF_2CHF$-CF_2I (68a)

Tri-n-butylamine (4.7 ml, 19.7 mmol) and $(CF_3)_2CFCF_2CF_2CHFCF_2I$ (68a) (9.4g, 19.7 mmol) were stirred together at room temperature until the mixture became solid in nature. Volatile material was transferred under vacuum to a separate vessel, washed with water (2x10ml) and dried using anhydrous $MgSO_4$. Capillary G.C. showed one component ca 45% pure which was identified as <u>tetradecafluoro-5-methylhex-1-ene</u> (69a) (4.4g, 64%);

(Found: C, 23.7; F, 76.4. C_8F_{16} requires C, 24.0; F, 76.0%); NMR spectrum no. 42; IR spectrum no. 26.

9.32 i-C_3F_7 $CHFCF_2CHFCF_2I$ (23b)

The above procedure was repeated with tri-n-butylamine (12.0ml, 50.4 mmol) and $(CF_3)_2CF(CHFCF_2)_2I$ (23b) (23.2g, 50.4 mmol). Analysis by capillary G.C. showed one major component which was purified by distillation to yield 4H-tridecafluoro-5-methylhex-1-ene (69b) (11.9g, 71 %); b.p. 85-86°C; (Found: C, 25.2; H, 0.4; F, 74.9. C_7HF_{13} requires C, 25.3; H, 0.3; F, 74.4 %); NMR spectrum no. 43; mass spectrum no. 43; m/z(EI) 332 (M^+, 2%); IR spectrum no. 27.

9.4 Copolymerisation Reactions

Table 9.1 summarises the amounts of each of the alkenes, vinylidene fluoride,(29b), (69a) and (69b) which underwent copolymerisation reactions. In each case the alkenes were transferred under vacuum to a Carius tube. The tubes were sealed and the contents irradiated with γ-rays for 2 days at ambient temperature. After this time each of the tubes were opened and volatile materials removed by transfer under high vacuum to cold traps. A small portion of each of the resultant polymers were dissolved in DMF and their high field F NMR spectra obtained. Discussion of the structures of the copolymers is given in section 4.4. By calculating the amounts for each of the comonomers that were incorporated into the copolymers, from the data given in table 9.1, their percentage molar compositions were determined. However, the values obtained in this way are less accurate than those obtained by intensity measurements of the resonances in the ^{19}F NMR spectra of the copolymers, since it is not possible to completely separate VDF from the other comonomer, on their removal from the polymer after γ-ray irradiation.

TABLE 9.1

Quantity of Starting Materials (g)		Quantity of Volatiles Recovered (g)		Molar Composition of Incorporated Alkene (g)	
Alkene	VDF	Alkene	VDF	By calculation	By integration
(29b) 2.8	5.5	(29b) 1.9	2.9	7	7
(69b) 2.9	4.5	(69b) 1.6	3.3	17	12
(69a) 3.2	4.5	(69a) 1.4	2.8	16	10

9.5 Attempted Preparation of Octadecafluoro-4,4-dimethylhept-1-ene (77)

9.51 Synthesis of F-2-methylpent-2-ene (78)[147]

A 'Rotaflo' tube was charged with acetonitrile (130ml), caesium fluoride (6.9g, 45.4 mmol) and HFP (58.2g, 388.0 mmol). The mixture was agitated using a rotating arm for 3 days at ambient temperature. After this time the lower fluorocarbon layer was removed from the tube, washed with water (2x50ml) and dried using anhydrous $MgSO_4$. A good yield of F-2-methylpent-2-ene (78) (46.9g, 81%) was obtained in this way.

9.52 Reaction Between F-2-methylpentyl carbanion (76) and FAFS

Caesium fluoride (8.9g, 58.6 mmol), tetraglyme (35ml) and $(CF_3)_2C{=}CFCF_2CF_3$(10.8g 36.0 mmol) were stirred together at room temperature for 48h. Stirring of the mixture was then halted and the solution was separated from the excess caesium fluoride. The ^{19}F NMR spectrum of a small portion of the solution was then acquired in order to confirm the formation of F-2-methylpentyl carbanion (76). Under an atmosphere of dry nitrogen the carbanion solution was placed in a two-necked round-bottomed flask, fitted with a dropping funnel and condenser leading to a cold trap. The solution was then cooled to $0^{o}C$ and with constant stirring perfluoroallylfluorosulphate (FAFS) (10.4g 45.2 mmol) was added. Stirring was continued at $0^{o}C$ for 1h, then at room temperature for 2h. The volatiles were transferred off under vacuum (10.0g). Capillary G.C. showed one major component which was attributed to $(CF_3)_2C{=}CFCF_2CF_3$ and, together with a small amount of HFP recovered from the cold trap, it was concluded that the carbanion had acted as an active source of fluoride ion in its reaction with FAFS.

9.6 Preparation of F-2-Iodo-2-methylpentane (79)

a) A stainless steel autoclave (125ml) was charged with potassium fluoride (1.2g, 20.7 mmol) iodine (6.0g, 23.6 mmol), iodine pentafluoride (2.9g, 13.1 mmol) and F-2-methylpent-2-ene (78) (17.2g, 57.3 mmol) and rocked at 190° for 15h. After cooling to room temperature the contents of the tube were poured into ice/water. The lower fluorocarbon layer was washed with further quantities of water, then dried over molecular sieves (type 4A) and finally transferred under vacuum to a separate vessel to give a liquid (9.2g). Analysis by both G.C. and ^{19}F NMR spectroscopy showed the liquid to be starting material only.

On repeating the reaction with potassium fluoride (1.5g, 25.8 mmol), iodine (6.4g, 25.2 mmol), iodine pentafluoride (2.8g, 12.6 mmol), and F-2-methylpent-2-ene (30.3g, 101.0 mmol) in a Hastelloy vessel (150 ml), a liquid (24.1g) was recovered which was identified as principally the starting material (78).

In each reaction described above, the potassium fluoride was rigorously dried before use and the iodine pentafluoride was pre-treated with fluorine gas.

b) Under exclusion of light, silver (I) fluoride (9.1g, 67.0 mmol) and F-2-methylpent-2-ene (78) (20.1g, 67.0g) were stirred together in acetonitrile (65ml) for 48h at room temperature. A portion of the mixture was analysed by ^{19}F NMR spectroscopy in order to confirm conversion to the carbanion. Iodine (17.1g, 67.3 mmol) was then added to the mixture through a condenser. Stirring was continued for 1h at room temperature, then for 3h under reflux. After cooling, the liquid was filtered and the solid residue washed with acetonitrile; the acetronitrile solutions were combined and poured into water. The lower organic layer was separated washed with further quantities of water and finally dried with magnesium sulphate. The remaining liquid was analysed by ^{19}F NMR spectroscopy and identified as perfluoro-2-iodo-2-methylpentane (79) (19.7g, 66%);

(δ_F-63.2 (6F, m, J=12Hz, 1-CF_3),-82.8(3F,t,J=13, 4-CF_3), -101.4 (2F, m, 2-CF_2)-123.3(2F,m, 3-CF_2); m/z 446 (M^+). The silver iodide was recovered by washing the solid residue with water followed by drying.

9.7 Telomerisation Reactions

9.71 F-2-Iodo-2-Methylpentane(79) with Trifluoroethylene

A Carius tube was cooled with liquid air then perfluoro-2-iodo-2-methylpentane (79) (8.6g, 19.3 mmol) and trifluoroethylene (2.4g, 29.3 mmol) were transferred in under vacuum. The tube was sealed and rocked for 36h at 150°C. After cooling to room temperature gaseous material (0.6g) was recovered, together with a purple liquid (9.7g). Analysis of the liquid by capillary G.C. showed one major and four minor components. Using fractional distillation the major component was isolated and identified as 2H-hexadecafluoro-1-iodo-3,3-dimethylhexane (80) (7.5g, 74%); b.p. 87°C (66 mmHg); (Found: C, 17.9; H, 0.2; F, 58.3. $C_8HF_{16}I$ requires C, 18.2; H, 0.2; F, 57.6%); NMR spectrum no. 44; mass spectrum no. 44, m/z(EI) 401 (M^+-I, 35%); IR spectrum no. 28. The remaining four components were identified as 2H, 4H-nonadecafluoro-1-iodo-5,5-dimethyloctane (82) (mixture of diastereoisomers) and its two regioisomers (1.1g, 8%); b.p. 48-49°C (2mmHg); (Found: C, 19.9; H, 0.6. $C_{10}H_2F_{19}I$ requires C, 19.7; H, 0.3 %); NMR spectrum no. 45; mass spectrum no. 45, m/z(EI) 483(M^+-I, 4%); IR spectrum no. 29.

9.72 n-$C_3F_7C(CF_3)_2CHFCF_2I$ (80) with Trifluoroethylene

A Carius tube was charged with n-$C_3F_7C(CF_3)_2CHFCF_2I$ (80) (10.6g, 20.1 mmol), trifluoroethylene (1.9g, 23.1 mmol) and di-tert-butyl peroxide (6 drops). The tube was sealed under vacuum and the contents rocked at 140°C for 24h. After cooling a purple liquid (12.1g) was recovered but there was no remaining gaseous alkene. Analysis of the liquid by G.C. showed a number of components including some starting material. The major components as determined by G.C.-mass spectrometry were due to 2H,4H-nonadecafluoro-1-iodo-5,5-dimethyloctane (82) (two diastereoisomers + two regioisomers) which was separated by fractional distillation under reduced pressure; b.p. 90°C (14 mmHg) (7.7g, 63%). The remaining components in the mixture were due to higher telomers but they were not fully characterised.

9.73 Preparation of n-$C_3F_7C(CF_3)_2CHFCF_2CH_2CH_2I$ (83)

A Carius was charged with $C_3F_7C(CF_3)_2CHFCF_2I$ (80) (8.0g, 15.2 mmol), ethylene (0.5g, 17.9 mmol) and di-tert-butyl peroxide (8 drops). The tube was sealed and rocked at 140°C for 24h. After this time a liquid (8.1g) was recovered and analysis by capillary G.C. showed only one major component, which was identified as 1,1,2,2,4-pentahydrohexadecafluoro-1-iodo-5,5-dimethyloctane (83) (8.1g, 96%); (Found: C, 21.9; H, 0.7; F, 54.8. $C_{10}H_5F_{16}I$ requires C, 21.6; H, 0.9; F, 54.7%); NMR spectrum no. 46; mass spectrum no. 46, m/z(EI) 556(M^+, 26%); IR spectrum no. 30.

9.74 Preparation of $(CF_3)_2CFCH_2CF_2CH_2CH_2I$ (89a)

A nickel autoclave (100ml) was charged with $(CF_3)_2CFCH_2CF_2I$ (13a) (37.1g, 0.1 mmol), ethylene (3.2g, 0.1mol), and di-tert-butyl peroxide (0.2g). The tube was sealed and the contents rocked at 140° for 24h. On opening the tube a pale yellow liquid (38.8g) was collected but there was no remaining gaseous material. Analysis by G.C. showed one major and one minor component. Distillation of the mixture yielded a small fore-fraction boiling between 35-40°C.

The other fractions were identified as 1,1,2,2,4,4-hexahydrononafluoro-1-iodo-5-methylhexane (89a) (35.0g, 88%); b.p. 92°C (36mmHg); (Found: C, 22.0; H, 1.3. $C_7H_6F_9I$ requires C, 21.7; H, 1.6%); NMR spectrum no. 47; mass spectrum number 47, m/z(EI) 388 (M^+, 20%); IR spectrum no. 31; and 1,1,2,2,3,3,4,4,6,6-decahydrononafluoro-1-iodo-7-methyloctane (89b) (2.5g, 6%); (Found: C, 25.7; H, 2.1; F, 41.6. $C_9H_{10}F_9I$ requires C, 26.0; H, 2.4; F, 41.1%); NMR spectrum no. 48; mass spectrum no. 48, m/z(EI) 289 (M^+-I, 8%); IR spectrum no. 32.

9.8 Preparation of Sterically Crowded Alkene Compounds

9.81 $CF_3CF_2CF_2C(CF_3)_2CHFCF_2CH{=}CH_2$ (85)

Tri-n-butylamine (3.4 ml, 14.3 mmol) and the iodide (83) (7.8g, 14.0 mmol) were stirred at 80°C for 12h. Volatile material was then transferred under vacuum to a separate vessel, washed with water (2x20ml) and dried using anhydrous $MgSO_4$. Analysis by capillary G.C. showed that only one compound was present. Distillation was carried out in order to remove slight colouration of the compound which was subsequently identified as <u>1,1,2,4-tetrahydrohexadecafluoro-5,5-dimethyloct-1-ene</u> (85) (5.7g, 95%); b.p. 73°C (51 mmHg); (Found : C, 28.3; H, 0.9; F, 71.4. $C_{10}H_4F_{16}$ requires C, 28.0; H, 0.9; F, 71.0%); NMR spectrum no. 49; mass spectrum no. 49, m/z(EI) 409 (M^+-F, 1%); IR spectrum no. 33.

9.82 $CF_3CF_2CF_2C(CF_3)_2CF{=}CF_2$ (81)

Potassium hydroxide pellets (11.7g, 208.5 mmol) and n-C_3F_7-$C(CF_3)_2CHFCF_2I$ (80) (6.3g, 11.9 mmol) were heated to 90°C for 5h. After this time volatile material was transferred under vacuum to a separate vessel, washed with water (3x10 ml) and dried using anhydrous $MgSO_4$. Analysis by G.C. showed one component only, which was identified as <u>hexadecafluoro-3,3-dimethylhex-1-ene</u> (81) (3.8g, 80%); (Found: C, 23.7; F, 76.5. C_8F_{16} requires C, 24.0; F, 76.0%); NMR spectrum no. 50; mass spectrum no. 50, m/z(EI) 400 (M^+, 6%); IR spectrum no. 34.

9.83 $CF_3CF_2CF_2C(CF_3)_2CHFCF_2CF{=}CF_2$ (84)

A mixture of tri-n-butylamine (2.4ml, 10.1 mmol) and n-$C_3F_7C(CF_3)_2(CHFCF_2)_2I$ (82) (6.2g, 10.2 mmol) was stirred at room temperature for 6h. Volatile material was then transferred under vacuum to a separate vessel and analysis by capillary G.C. showed one major product, together with a small amount of starting material. The product was isolated by fractional distillation and identified as <u>4H-nonadecafluoro-5,5-dimethyloct-1-ene</u> (84) (3.0g, 61%); b.p. 76°C (66mmHg); (Found: C, 25.2; H, 0.5; F, 74.4.

$C_{10}HF_{19}$ requires C, 24.9; H, 0.2; F, 74.9%); NMR spectrum no. 51; mass spectrum no. 51, m/z (EI) 482(M^+,0.5%); IR spectrum no. 35.

9.84 $(CF_3)_2CFCH_2CF_2CH{=}CH_2$(90)

The above procedure was repeated with tri-n-butylamine (5.5g, 29.7 mmol) and $(CF_3)_2CFCH_2CF_2CH_2CH_2I$ (89)(11.6g, 29.9 mmol) at 80°C for 12h. Analysis of the volatile material by capillary G.C. showed only one component which was identified as 1,1,2,4,4-pentahydrononafluoro-5-methylhex-1-ene (90) (6.4g, 82%); (Found: C, 32.5; H, 1.8; F, 65.3. $C_7H_5F_9$ requires C, 32.3; H, 1.9; F, 65.8%); NMR spectrum no. 52; mass spectrum no. 52, m/z(EI) 241(M^+-F, 18%); IR spectrum no. 36.

9.85 $CF_3CF_2CF_2\ C(CF_3)_2CH_2CH{=}CH_2$ (88) [147]

Caesium fluoride (11.0g, 72.4 mmol) tetraglyme (30ml) and perfluoro-2-methylpent-2-ene (8.8g, 29.3 mmol) were stirred at room temperature for 24h. Analysis of the mixture by ^{19}F NMR spectroscopy showed conversion to F-2-methylpentyl carbanion (76). The carbanion solution was separated from excess caesium fluoride and allyl iodide (4.9g, 29.2 mmol) was then introduced to the system. After stirring for ½h the fluorocarbon layer was allowed to settle and was then removed from the vessel. Subsequent analysis of the material showed it to be 1,1,2,3,3-pentahydrotridecafluoro-4,4-dimethylhept-1-ene (88) by comparison of its NMR and mass spectral data with these of an authentic sample.[147]

9.9 Attempted Copolymerisations with Vinylidene Fluoride

Each of the alkenes listed below were transferred into separate Carius tubes together with vinylidene fluoride. The tubes were then sealed and the contents irradiated with γ-rays. The results for each system were as follows;

i) VDF (4.3g, 67.2 mmol) and (88) (2.6g, 7.2 mmol). Irradiated for 1 week at room temperature. No polymer was observed after this time.

ii) VDF (5.0g, 78.1 mmol) and (81) (3.5g, 8.8 mmol). Irradiated for 3 days at room temperature. On opening the tube only VDF (3.5g) and (81) (3.3g) were recovered. The ^{19}F NMR spectrum of a solution of the remaining polymer in DMF showed only a very small degree of incorporation of (81).

iii) VDF (3.2g, 50.0 mmol) and (85) (2.1g, 4.9 mmol). Irradiated for 1 week at room temperature; no polymeric material was observed.

iv) VDF (2.3g, 35.9 mmol), HFP(1.0g, 6.7 mmol) and (85) (1.5g, 3.5 mmol). Irradiated for 1 week at room temperature; no polymer formation was observed.

v) VDF (2.3g, 35.9 mmol) and (84) (1.8g, 3.7 mmol). Irradiated at room temperature for 4 days. On opening the tube VDF (1.4g) and (84) (0.2g) were recovered, together with a polymer. Analysis of a solution of the polymer in DMF by ^{19}F NMR showed 22% molar incorporation of (84).

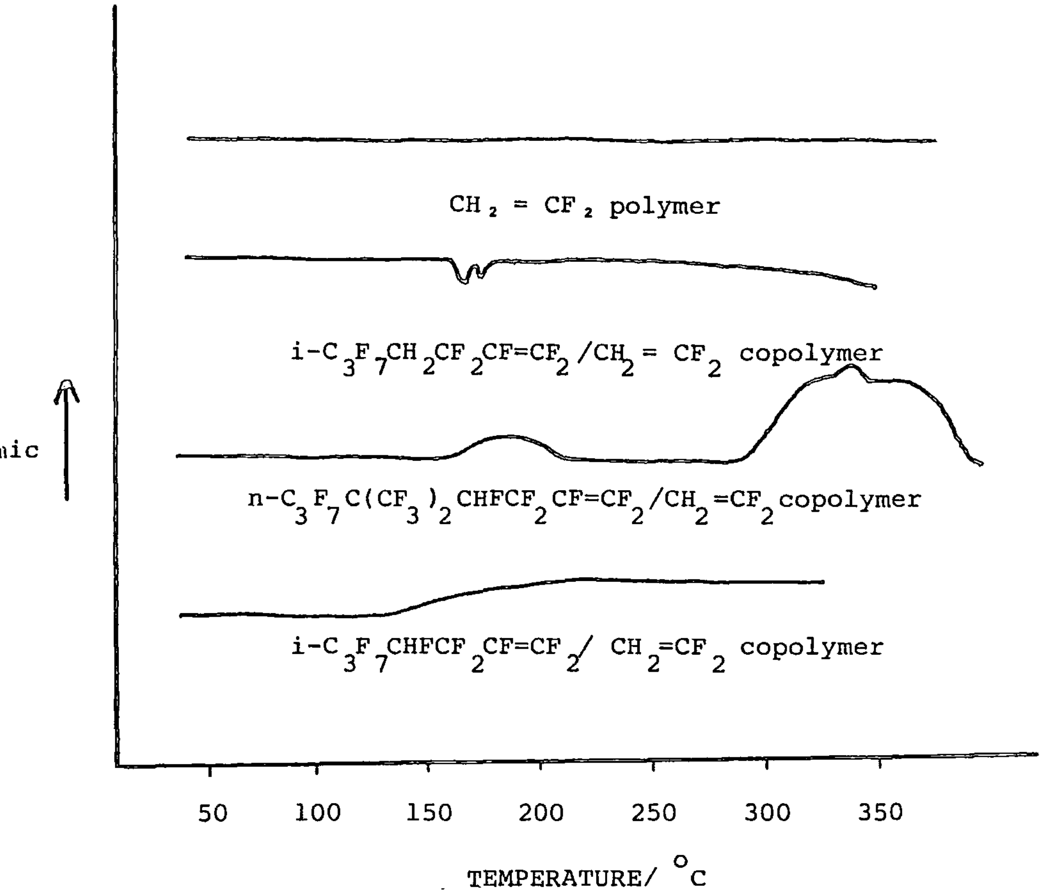
vi) VDF (3.2g, 50.0 mmol) and (90) (1.4g, 5.4 mmol). Irradiated for 1 week at room temperature; no polymer was observed.

vii) VDF (2.6g, 40.6 mmol) and (90) (1.1g, 4.2 mmol). Irradiated for 1 week at 80°C; no polymer was recovered.

viii) VDF (1.7g, 26.6 mmol), (85) (1.6g, 3.7 mmol) and di-tert-butyl peroxide (0.08g). Rocked in a Carius tube at 140°C for 24h. No chemical change was observed and the starting materials were completely recovered.

9.10 Thermal Analysis of Polymers by Differential Scanning Calorimetry

The technique of DSC involved heating each of the polymers (ca 0.02-0.05g), under an atmosphere of dry argon, from 30°C to over 300°C at a steady rate (typically 5°C min^{-1}). The resultant thermograms are depicted overleaf and are discussed in sections 4.44 and 4.9.



A sample of the VDF/$n\text{-}C_3F_7((CF_3)_2CHFCF_2CF{=}CF_2$ (84) copolymer (ca. 0.3g) was heated under high vacuum at 190°C for ½h. The apparatus included a cold trap which was rinsed out with acetone (2ml) after the experiment. Analysis of the acetone solution by capillary G.C. showed one product had been transferred from the copolymer and this was subsequently identified as 5H, 6H-octacosafluoro-4,4,7,7-tetramethyldecane (93); NMR spectrum no. 53.; mass specttrum no. 53, m/z(EI) 463 (M^+-(H, CF_3,C_3F_7),0.1%)and 363 (M^+-(H,C_3F_7, C_3F_7), 0.2%).

The remaining copolymer was virtually insoluble in DMF. This is in contrast to its high solubility before undergoing thermal treatment and probably reflects the formation of a cross-linked network.

9.11 Attempted Synthesis of Vinyl Ether Compounds

Nucleophilic Attack of Alkoxide on TFE

The ether used in this experiment was firstly dried over sodium wire, then distilled on to lithium aluminium hydride and finally distilled on to molecular sieves (type 4A). During these procedures the ether was kept under an atmosphere of dry nitrogen.

To a solution of neopentyl alcohol (2.7g, 30.6 mmol) in dry ether (30 ml), sodium metal (0.7g, 30.6 mmol) was added and the mixture was refluxed overnight under an atmosphere of dry nitrogen. The resultant suspension of sodium alkoxide was introduced into a Carius tube by use of a syringe and the ether was then removed under reduced pressure. DMF (20ml) and tetrafluoroethylene (3.0g, 30.0 mmol) were transferred into the Carius tube which was sealed and rocked at 50°C for 48h. On opening the tube, TFE (0.9g) was recovered and ether (50ml) added to the rest of the material. The ether solution was washed with water in order to remove the DMF and finally dried with anhydrous $MgSO_4$. Removal of the ether by distillation yielded the crude product, which was distilled to give one fraction that was identified as <u>2,2-dimethylpropyl-1,1,2,2-tetrafluoroethyl ether</u> (96) (2.6g, 46%); b.p. 72°C (262 mmHg); (Found: C, 45.0; H,6.4; F, 40.4. $C_7H_{12}F_4O$ requires C, 44.7; H, 6.4; F, 40.4 %); NMR spectrum no. 54; mass spectrum no. 54; m/z(EI) 173 (M^+-CH_3,12%).

9.112 Attempted Dehydrofluorination of Me_3CCH_2=CF_2CF_2H(96)

The ether (96) (0.5g, 2.7 mmol) was dissolved in DBU (0.5g, 3.3 mmol) and the solution sealed in an NMR tube, which was then heated to 200°C for 24h. However, analysis by ^1H NMR spectroscopy showed that no reaction had occurred.

Antimony pentafluoride (4.0g, 18.4 mmol) and the ether (96) (0.4g, 2.1 mmol) were sealed in an NMR tube. On warming to room temperature a vigorous reaction occurred. Analysis by ^1H NMR spectroscopy showed that the tertiary butyl group had been attacked by SbF_5 rather than a simple dehydrofluorination reaction.

9.113 Chloroiodomethane with 2-Chloroethanol

Sodium (0.9g, 39.1 mmol) was carefully added to 2-chloroethanol (9.7g, 120.5 mmol) and stirred until the metal had completely disappeared. Chloroiodomethane (10.0g, 56.7 mmol) was then added to the system and stirring continued. Little reaction was observed at temperatures up to 120°C for 24h as determined by G.C. and G.C.-mass spectrometry.

On repeating the procedure with $ClCH_2CH_2OH$(0.4g, 5.0 mmol), ICH_2Cl (0.9g, 5.1 mmol) K_2CO_3(0.7g, 5.1 mmol) and DMF (2ml), little reaction was observed also.

CHAPTER TEN

EXPERIMENTAL TO CHAPTER FIVE

REMARKABLE CHEMISTRY OF THE MODEL COMPOUNDS WITH ANTIMONY PENTAFLUORIDE

10.1 Preparation of Remarkably Stable Fluorinated Carbocations

A series of observable carbocations were prepared by dissolving appropriate fluorohydrocarbon compounds in antimony pentafluoride. In a typical procedure, a fluorohydrocarbon derivative listed in Table 10.1 was transferred under vacuum to an NMR tube, followed by a *ca* 6:1 molar excess of antimony pentafluoride. The NMR tube was sealed and allowed to warm to room temperature. Gentle rotation of the tube was then carried out for *ca*. 0.5h and the ^{13}C, ^{19}F and ^{1}H NMR spectra of the resultant solution acquired. In each case observable carbocations were produced in almost quantitative yield. The carbocations showed no detectable signs of decomposition after storage at room temperature for several weeks. A discussion of the NMR data is presented in Section 5.2.

Table 10.1

Fluorohydrocarbon Derivative (g,mmol)	Antimony Pentafluoride(g,mmol)	Carbocation Produced	NMR Spectrum No.
(15b)(0.9,2.8)	(3.6,16.6)	(97)	55
(15c)(0.4,1.0)	(1.1,5.1)	(100)[133]	56
(15d)(0.8,1.8)	(2.4,11.1)	(101)[133]	57
(15e)(1.1,2.2)	(4.7,21.7)	(102)	58
(14b)(1.6,2.7)	(4.6,21.2)	(105)	60
(35)(1.5,4.2)	(5.2,24.0)	(104)	59
(29b)(0.6,2.0)	(2.4,11.1)	(97)	55
(37a)(0.8,2.9)	(3.6,16.6)	(97)	55
(29c)(0.4,1.1)	(1.4,6.5)	(100)	56

Similar treatment of $(CF_3)_2CFCHFCF_2CHFCF_3$ (98) (0.4g,1.1mmol) with antimony pentafluoride (1.7g, 7.8mmol) at room temperature failed to eliminate hydrogen fluoride.

On mixing 1,2,4,5-tetrafluorobenzene (0.2g,1.3mmol) with antimony pentafluoride (1.7g,7.8mmol) at room temperature the solution became blue in colouration. This coupled to the fact that no signals were observed in either the ^1H or ^{19}F NMR spectrum of the solution led to the conclusion that the radical-cation (107) was formed.

10.2 $(CF_3)_2C{=}CHCF_3$(36) and $(CF_3)_2CFCH_2{-}CF_3$(15a) with SbF_5

No chemical change was observed on dissolving the saturated model $(CF_3)_2CFCH_2CF_3$ (15a)(5.4g, 21.0 mmol) in SbF_5 (13.9g, 64.0 mmol) as determined by ^1H and ^{19}F NMR spectroscopy. Similarly, treatment of the unsaturated model $(CF_3)_2C{=}CHCF_3$ (36) (0.5g, 2.2mmol) with SbF_5 (2.8g, 13.0mmol) gave no chemical change. The spectra of models (15a) and (36), however, indicate that rapid exchange of fluoride ion may be occurring at room temperature (see Section 5.25).

10.3 Quenching Reactions

10.31 Carbocation (97) with Methanol

A mixture of $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (15b) (6.8g, 21.5 mmol) and SbF_5 (28.0g, 129.2 mmol) was stirred in a round-bottomed flask (10ml) for 1h under an atmosphere of dry nitrogen. Formation of carbocation (97) was confirmed by analysis of the solution by ^{19}F NMR spectroscopy. The flask was then fitted with a water and a dry-ice condenser. The mixture was cooled by an acetone/dry-ice bath and sulphuryl chlorofluoride (20ml) added with constant agitation using a mechanical stirrer. This was followed by slow addition of methanol (30.0g, 0.94mol) and stirring was continued for a further 0.5h. After warming the contents of the flask to room temperature, diethyl ether (50ml) was added. The ether layer was washed with water (2x50ml) then dried ($MgSO_4$) and transferred under vacuum to a fresh vessel. AFter distilling off the ether the remaining solution was analysed by G.C. The major component was identified as methyl 2H,4H-heptafluoro-5-methylhexa-2,4-dienoate (109); NMR spectrum no. 61; mass spectrum no. 55, m/z (EI) 226(M^+,2%), 235 (M^+-OCH_3,100%) and 207 (M^+-

CO_2CH_3, 35%). Complete characterization of (109) was not possible since it underwent decomposition at room temperature.

10.32 Carbocation (97) with Potassium Fluoride

A mixture of (15b) (4.6g,14.6 mmol) and SbF_5 (18.8g, 86.7 mmol) was stirred for 1h at room temperature. Carbocation (97) was produced (as determined by ^{19}F NMR spectroscopy) and was quenched by addition of dry potassium fluoride (20.0g) to the system. A temperature of 0°C was maintained during the addition of KF. After a contact time of 0.5h the volatiles were transferred under vacuum to a separate vessel, washed with dilute sodium carbonate solution and dried using anhydrous $MgSO_4$. Analysis of the remaining liquid by capillary G.C. showed a small amount of starting material (15b) together with one major and one minor product. The products were isolated using preparative G.C. (30% SE30, column temp. 60°C, injector temp. 150°C) and identified as 3,5,5-trihydroundecafluoro-2-methylhex-2-ene (34) (24%) and (Z)-3,5-dihydrodecafluoro-2-methylhexa-2,4-diene (37a)(59%). The identity of (34) was determined by comparison of its IR and mass spectral data with those of an authentic sample.[133] An alternative route to diene (37a) was described in Section 8.32.

10.33 Carbocation (97) with Potassium Chloride

Carbocation (97) was produced by stirring the saturated model (15b) (8.5g,26.9 mmol) with SbF_5 (30.8g, 142.1 mmol) at room temperature for 6h. The carbocation solution was then carefully dropped on to potassium chloride (14.0g) at 0°C. After a contact time of 1h the volatiles were transferred under vacuum to a fresh vessel, washed with dilute sodium carbonate solution and finally dried ($MgSo_4$) to give a liquid (5.6g). Analysis by G.C. showed one major product and several minor components. The major product was isolated by preparative G.C. (20% DIDP, column temp. 90°C, injector temp. 150°C) and was identified as <u>3H,5H-5-chloro-undecafluoro-2-methylhex-2-ene</u> (110); (Found: C,25.5;H,0.6.$C_7H_2F_{11}Cl$ requires C, 25.4; H, 0.6%); NMR spectrum no. 62; mass spectrum no. 56, m/z (EI) 311 (M^+-F , 3%) and 213 (M^+- CH(Cl)CF_3, 100%); IR spectrum no. 37. The minor compounds were not characterized.

10.4 High Temperature Reactions of the Carbocations

The diene Z-$(CF_3)_2C=CH-CF=CHCF_3$ (37a) (1.1g, 4.0 mmol) was stirred with SbF_5 (1.3g, 6.0 mmol) at room temperature for 0.5h. Analysis of the solution by ^{19}F NMR spectroscopy indicated that formation of (97) had occurred. The carbocation solution was then stirred for 0.5h at 100°C and after cooling volatile material was transferred under vacuum to a separate vessel, washed with dilute sodium carbonate solution and finally dried using anhydrous $MgSO_4$. Analysis of the resultant liquid by G.C. showed one component which was identified as 2H,4H-decafluoro-1,4-dimethylcyclopentene (111) (1.0g,91%) by comparison of its NMR and mass spectral data with those of an authentic sample.[133]

The saturated model (15d) (0.8g,1.8 mmol) and SbF_5 (2.4g,11.1 mmol) were stirred together at room temperature. Formation of carbocation (101) was confirmed by NMR spectroscopy. On heating the solution to 120°C for 0.5h, no chemical change was detected in its NMR spectra. Carbocation (102), prepared in a similar way from (15e) (1.1g, 2.2 mmol) and SbF_5 (4.7g, 21.7 mmol), was also thermally stable over this temperature.

10.5 Exposure of Carbocations to High Vacuum

The saturated model compounds (15b)(0.5g,1.6mmol) and (15c) (0.4g, 1.1 mmol) were pipetted into separate NMR tubes and SbF_5 (2.2g, 10.2 mmol) added to each. After 0.5h the ^{19}F NMR spectra of the solutions were acquired to confirm conversion to carbocations (97) and (100). The carbocations were then exposed to a high vacuum (10^{-4} mm Hg) at room temperature, each backed up by a cold trap. For both systems only SbF_5 and HF were recovered from the cold traps after exposure for 1h, i.e. no organic material had been transferred. The ^{19}F NMR spectra of the carbocations were unchanged after this treatment.

10.6 Rearrangement of 4H-Perfluoro-5-Methylhex-1-ene (69b) by SbF_5

An NMR tube was charged with alkene (69b) (0.6g, 1.8 mmol) and SbF_5 (0.8g, 3.7 mmol), then sealed under vacuum. The tube was agitated for 0.5h and the ^{19}F and ^{1}H NMR spectra of the resultant solution was acquired. The NMR data indicate that quantitative rearrangement of (69b) to (Z)-3H-tridecafluoro-2-methylhex-3-ene (114) had occurred; NMR spectrum no. 63.

Alkene (69b) (3.1g,3.3 mmol) and SbF_5 (4.4g, 20.3 mmol) were stirred at 100°C for 0.5h. After cooling, volatile material was transferred under vacuum to a separate vessel. The liquid was poured into ice/water, then washed with sodium carbonate solution until effervescence had ceased and finally dried with anhydrous $MgSO_4$. Analysis by capillary G.C. showed one component which was identified as <u>3H-tridecafluoro-2-methylhex-2-ene</u> (115) (2.0g, 65%); (Found: C, 25.4; H, 0.4; F, 73.8. C_7HF_{13} requires C, 25.3; H, 0.3; F, 74.4%); NMR spectrum no. 64; mass spectrum no. 57, m/z (EI) 313 (M^+-F, 16%) and 213 (M^+-CF_2CF_3, 56%); IR spectrum no. 38.

10.7 Application of SbF_5 Chemistry to the Synthesis of Polyacetylene Derivatives

10.71 Preparation of Coloured Films[133]

The homopolymers listed in Table 10.2 were dissolved separately in their respective solvent over a period of 3 days and the resultant gels were then filtered to leave solutions of the polymers. Each of the polymers were deposited as a thin film on a clean round-bottomed flask (100ml) by progressive evaporation of the solvent. Traces of solvent were removed by exposure to high vacuum for 1h, then SbF_5 vapour was allowed to pass over each film until a strong colouration was observed. A sustained temperature of 170°C was required for colouration of poly-trifluoroethylene although extensive dehydrofluorination was also observed by heating a film to 80°C in neat SbF_5 solution. In each case the coloured materials were exposed to high vacuum (10^{-4} mmHg) for 1h in order to remove any SbF_5. Storage and manipulations of the films were carried out under a nitrogen atmosphere. A discussion of the IR and NMR data of the films is given in Section 5.5.

Table 10.2 Solvents used to prepare polymer films and conditions of reactions with SbF_5 vapour

Polymer	Solvent	Temp. of Reaction	Observations
$(CH_2CHCl)_n$	CH_2Cl_2	Room Temp.	Immediate intense colouration.
$(CH_2CF_2)_n$	DMF	Room Temp.	Intense colouration after ca. 1h.
$(CHFCF_2)_n$	$(CH_3)_2CO$	170°C	Strong colouration after several hours.

10.72 Exposure of the Coloured Films to Methanol

The coloured films derived from PVC and PVDF were exposed to high vacuum and allowed to come into contact with dry methanol vapour. The former system produced no colour change but the latter gave an immediate change terminating in an orange colouration. The photoacoustic IR spectrum of this product was recorded and is presented in Section 5.55.

CHAPTER ELEVEN

EXPERIMENTAL TO CHAPTER SIX

MISCELLANEOUS REACTIONS OF SOME FLUOROCARBON DERIVATIVES

11.1 $(CF_3)_2C{=}CHCF_3$(36) with Grignard Reagents

11.11 With Propyl Magnesium Bromide

Under an atmosphere of dry nitrogen, propyl bromide (3.0g, 24.4 mmol) was added slowly to magnesium metal (0.6g, 25.0 mmol) in dry ether (25ml) with stirring. The rate of addition was controlled so as to give a steady reflux of the ether. After all of the bromide had been added the system was allowed to reflux for a further 20 min to ensure complete conversion to propyl magnesium bromide. The Grignard solution was then cooled to 0°C and slow addition of alkene (36) (4.6g,19.8 mmol) was carried out. After stirring for 10 min. water (5ml) was added to destroy any remaining Grignard reagent, followed by sufficient 5% aqueous HCl to dissolve all inorganic salts. The ether layer was washed with further amounts of water and then dried with anhydrous $MgSO_4$. The ether was distilled off to leave the crude product which afforded one major fraction upon distillation that was identified as <u>1,1-difluoro-2,3-bis(trifluoromethyl)hex-1-ene</u> (123) (3.0g, 59%);b.p. 102°C; (Found: C,37.8; H, 3.4; F, 59.8. $C_8H_8F_8$ requires C, 37.5; H, 3.1; F, 59.4%); NMR spectrum no. 65; mass spectrum no. 58, M/Z (EI) 256 (M^+, 6%) and 187 (M^+-CF_3,30%); IR spectrum no. 39. The experiment was repeated using magnesium (1.1g, 45.8 mmol), ether (35ml) propyl bromide (5.6g, 45.5 mmol) and alkene (36)(4.7g, 20.3 mmol). After addition of the alkene to propyl magnesium bromide at 0°C, the system was held under reflux for 0.5h. After the work-up procedure, analysis of the crude product mixture (3.7g) by G.C. showed the major product to be (123). Approximately 8% of the mixture consisted of minor products which were not isolated.

11.12 With Phenyl Magnesium Bromide

To a dry round-bottomed flask (250ml), magnesium turnings (1.8g, 74.1 mmol) and diethyl ether (35ml) were added. The flask was fitted to a condenser and dropping funnel and, under an atmosphere of nitrogen, bromobenzene (11.9g, 75.8 mmol) was added slowly with stirring. After all of the bromide had been added the system was refluxed for 0.5h to ensure complete formation of phenyl magnesium bromide. The alkene (36) (8.3g, 35.8 mmol) was then added slowly to the ice-cooled solution of the Grignard reagent and the reaction mixture was refluxed for 15 min. Water (50ml) was added to the system, followed by sufficient 5% aqueous HCl to dissolve all inorganic salts (ca 75ml). The organic layer was separated, washed with water (30ml) and dried over $MgSO_4$. Ether removal was effected by distillation which also yielded a small fraction of benzene (b.p. 80-81°C). The major fraction was identified as 3H-octafluoro-3-phenyl-2-methybut-1-ene (127) (6.2g, 60%); b.p. 103°C (109mmHg); (Found: C, 45.8, H, 2.0; F, 52.0, $C_{11}H_6F_8$ requires C, 45.5; H, 2.1; F, 52.4%); NMR spectrum no. 66; mass spectrum no. 59, m/z (EI) 290 (M^+, 29%) and 221 (M^+-CF_3, 66%); IR spectrum no. 40. The remaining undistilled material (1.5g) consisted mainly of biphenyl.

11.2 $(CF_3)_2C=CHCF_3$(36) and Ethyl Acetoacetate[175]

To a mixture of sodium hydride (0.5g, 20.8 mmol) in tetraglyme (5ml), ethyl acetoacetate (3.0g, 23.1 mmol) was added carefully at 0°C. Alkene (36) (2.5g, 10.8 mmol) was then transferred to the system under vacuum. On warming to room temperature an exothermic reaction was observed. Stirring of the mixture was continued at room temperature for 19 h and after this time water (30ml) was added. The fluorocarbon layer was dissolved in ether and washing of the ether layer was carried out using water. The ether solution was then dried over anhydrous $MgSO_4$ and removal of ether was achieved by distillation. Analysis of the crude product by capillary G.C. showed one major product, together with some remaining ethyl acetoacetate. The product was isolated by distillation and identified as 3-ethoxycarbonyl-6-fluoro-2-methyl-4,5-bis(trifluoromethyl)-4H-pyran (130) (2.0g, 48%); b.p. 84°C (8 mmHg); (Found: C, 41.3; H, 3.1; F, 41.4. $C_{11}H_9F_7O_3$ requires C, 41.0; H, 2.8; F, 41.3%); NMR spectrum no. 67; mass spectrum no. 60, m/z (EI) 303 (M^+-F, 3%), 277 (M^+-OEt, 80%) and 253 (M^+-CF_3, 100%); IR spectrum no. 41.

11.3 $(CF_3)_2C=CHCF_3$(36) with Catechol

A mixture of catechol (2.7g, 24.5 mmol), acetonitrile (9 ml) potassium carbonate (3.1g, 22.4 mmol) and (36) (4.8g, 20.7 mmol) was stirred at room temperature for 3 days. After this time the system was extracted with ether (10 ml) and then washed with water. The ether layer was removed and washed further with water, followed by treatment with anhydrous $MgSO_4$. Removal of the ether was then carried out by distillation to yield a fluorocarbon material containing three major components, as determined by capillary G.C. Separation of the three products was not possible by fractional distillation. Instead, the products (2.6g) were isolated in one fraction boiling in the range 46-48°C (8 mmHg) and were subsequently identified as 6,7-benzo- 2-fluoro-3,4-bis(trifluoromethyl)-1,5-dioxacyclohept-2-ene(131) (0.9g, 15%); NMR spectrum no. 69; mass spectrum no. 61, m/z (EI) 302 (M^+, 73%) and 233 (M^+-CF_3, 10%); IR spectrum no. 42; and 6,7-benzo-2,2-difluoro-3,4-bis(trifluoromethyl)-1,5-dioxacycloheptane(132) (1.7g, 26%) (two diastereoisomers); NMR spectrum no. 69; mass spectrum no. 62, m/z (EI) 322 (M^+,100%) and 303 (M^+-F,3%); IR spectrum no. 42. The remaining material in the distillation flask was not characterized.

11.4 Synthesis of F-3-Methylbut-1-ene (133)

A mixture of tri-n-butylamine (6.2g, 33.4 mmol) and $(CF_3)_2CFCHFCF_2I$ (23a)(12.7g, 33.6 mmol) was stirred at room temperature for 6h. Volatile material was transferred under vacuum to a separate vessel, washed with water and then dried over anhydrous $MgSO_4$. The product was identified as decafluoro-3-methylbut-1-ene (133)(6.4g, 76%) by comparison of its NMR spectrum with that given in the literature.[180]

11.5 Free Radical Reactions of Fluoroalkenes

11.51 $(CF_3)_2CF-CF=CF_2$(133)

A Carius tube was charged with alkene (133) (6.4g, 25.6 mmol) and methanol (2.0g, 62.5 mmol). The tube was sealed and the contents irradiated with γ-rays for 11 days. On opening the tube the liquid material was washed with water (4x15ml) and dried over anhydrous $MgSO_4$. The resultant liquid consisted of one compound as determined by capillary G.C. and was identified as 1,1,3-trihydrodecafluoro-4-methylpentan-1-ol (134) (4.1g, 57°%); (Found: C, 25.7; H, 1.5; F, 67.2. $C_6H_4F_{10}O$ requires C, 25.5; H, 1.4; F, 67.4%); NMR spectrum no. 68; mass spectrum no. 63, m/z (EI) 263 (M^+-F, 2%); IR spectrum no. 43.

11.52 $(CF_3)_2C=CHCF_3$(36)

A mixture of alkene (36) (6.3g, 27.2 mmol) and methanol (2.1g, 65.6 mmol) was irradiated with γ-rays for 2 weeks. Analysis of the resultant solution by capillary G.C. showed two components were present, one of which was due to methanol. Thorough washing with water was carried out in order to remove the methanol and the remaining liquid was then dried over anhydrous $MgSO_4$. Subsequent analysis of the liquid identified it as 1,1,2,3-tetrahydrononafluoro-2,3-dimethylbutan-1-ol (136) (6.3g, 88%); (Found: C, 27.3; H, 2.1, F, 64.2. $C_6H_5F_9O$ requires C, 27.3; H, 1.9; F, 64.8%); NMR spectrum no. 70; mass spectrum no. 64, m/z 195 (M^+-CF_3, 5%); IR spectrum no. 44.

A mixture of ethanal (2.8g, 63.6 mmol) and (36) (5.9g, 25.4 mmol) was irradiated with γ-rays for 2 weeks. On opening the tube the remaining ethanal was removed by distillation (1.6g). Further distillation yielded one major fraction which was identified as 1,1,1,3,4-pentahydrononafluoro-

3,4-dimethylpentan-2-one (135) (4.9g, 70%); 43°C (700 mmHg); (Found: C, 30.7; H, 1.9; F, 62.6. $C_7H_5F_9O$ requires C, 30.4; H, 1.8; F, 62.0%); NMR spectrum no. 71; mass spectrum no. 65, m/z (EI) 261 (M^+-CH_3, 6%).

11.53 $(CF_3)_2C$=CH-CF=$CHCF_3$(37)

A Carius tube was charged with dimethyl ether (1.3g, 28.3 mmol) and E- Z- $(CF_3)_2C$=CH-CF=$CHCF_3$(37) (2.4g, 8.7 mmol). The materials were thoroughly degassed and then irradiated with γ-rays for 12 days. The tube was opened and the liquid analysed by capillary G.C. and by NMR spectroscopy, which both showed the presence of starting materials only.

11.6 Dehydration of $(CF_3)_2$CH-CH(CF_3)CH_2OH (136)

Potassium carbonate (2.5g, 18.1 mmol) was added to a solution of (136) (4.9g, 18.6 mmol) in acetonitrile (5 ml). The system was stirred at room temperature for 4 days. After this time K_2CO_3 and the solvent were removed by thorough washing with water. The remaining fluorocarbon material was dried with anhydrous $MgSO_4$ and analysis by capillary G.C. showed one major product and ca 10% remaining starting material. The product was isolated using preparative G.C. (10% SE 30, column temp. 90°C, injector temp. 160°C) and identified as 1,1,3-trihydrononafluoro-2,3-dimethylbut-1-ene (139)(3.0g, 65%); NMR spectrum no. 72; mass spectrum no. 66, m/z (EI) 246 (M^+, 91%) and 227 (M^+-F, 100%).

11.7 Novel Reactions with Compounds Containing the F-2-Methylpentyl Group

11.71 2H-Perfluoro-1-iodo-3,3-dimethylhexane (80) with Tri-n-butylamine

Tri-n-butylamine (2.3g, 12.4 mmol) and n-$C_3F_7C(CF_3)_2CHFCF_2I$ (80) (6.6g, 12.5 mmol) were stirred for 12h at 100°C. Volatile material was then transferred under vacuum to a separate vessel (3.3g). Analysis by capillary G.C. showed three major components the most volatile of which was separated by fractional distillation and identified as hexadecafluoro-3,3-dimethylhex-1-ene (81)(1.2g,24%); b.p. 68°C (245 mmHg) by comparison of its NMR spectrum with that of an authentic sample (See Section 9.82). The remaining two components could not be completely separated by distillation, so each was isolated by preparative G.C. (30% SE30, column temp. 50°C, injector temp 150°C). The compounds in order of increasing retention time were identified as 2H-heptadecafluoro-3,3-dimethylhexane (143) (41%); (Found: C, 22.7; H, 0.1; F, 76.7. C_8HF_{17}requires C, 22.9; H, 0.2; F, 76.9%); NMR spectrum no. 73; mass spectrum no. 67 (substantial breakdown of the molecular ion was observed for CI,EI and NI modes), m/z (EI) 351 (M^+-CF_3 12%); and 1H,2H-hexadecafluoro-3,3-dimethylhexane (142) (32%); (Found: C, 23.6; H, 0.5; F, 75.7. $C_8H_2F_{16}$ requires C, 23.9; H, 0.5; F, 75.6%); NMR spectrum no. 74; mass spectrum no. 68 (substantial breakdown of the molecular ion was observed for CI, EI and NI modes), m/z (EI) 331 (M^+- [H,CF_3,H] , 3%);IR spectrum no. 45.

On stirring a mixture of n-$C_3F_7C(CF_3)_2CF{=}CF_2$ (81) (0.4g, 1.0 mmol) and tri-n-butylamine (0.2g, 1.1 mmol) at 110°C for 48h, no chemical change was observed as determined by G.C. and by NMR analysis.

11.72 Addition of THF to Perfluoro-3,3-Dimethylhex-1-ene (81)

A thoroughly degassed mixture of tetrahydrofuran (2.0g, 27.7 mmol) and (81) (3.0g,7.5 mmol) in a sealed Carius tube was irradiated with γ- rays for 15 days at room temperature (initially a two phase system). On opening the tube a liquid (4.9g) was recovered and analysis by G.C. showed six major components which included THF but not the alkene (81). THF and other minor components were distilled off (42-43°C at 370 mmHg) and further distillation yielded two compounds which were identified as diastereoisomers of 2-(2H-hexadecafluoro-3,3-dimethylhexyl) tetrahydrofuran (144) (1.5g, 42%); b.p. 41-42° (10^{-3}mmHg); (Found: C, 30.8; H, 1.8; F, 63.9. $C_{12}H_8F_{16}O$ requires C, 30.5; H, 1.7; F, 64.4%); NMR spectrum no. 75; mass spectrum no. 69, m/z (EI) 471 (M^+- H, 1%); IR spectrum no. 46. The remaining three components of the product mixture could not be distilled over but instead they were transferred under high vacuum to a separate vessel and identified as diastereoisomers of 2,5-bis(2H-hexadecafluoro-3,3,-dimethylhexyl) tetrahydrofuran (145) (1.6g, 49%); (Found: C, 27.8; H, 0.9; F, 69.2. $C_{20}H_8F_{32}O$ requires C, 27.5; H, 0.9; F, 69.7%); NMR spectrum no. 77; mass spectrum no. 70, m/z (EI) 853 (M^+-F, 11%) and 471 (M^+-$[CF_2CFHC(CF_3)CF_2CF_2CF_3]$ 100%).

11.73 Pyrolysis of Perfluoro-3,3-Dimethylhex-1-ene (81)

Alkene (81) (3.2g, 8.0 mmol) was transferred under vacuum to a Carius tube which was subsequently evacuated and sealed. The tube was heated to 260°C for 72h and after cooling, a liquid (3.0g) was recovered. Analysis of the liquid by capillary G.C. showed only one major component which was identified as hexadecafluoro-2-methylhept-2-ene (146) (3.0g, 94%); (Found: C, 23.7; H, 0.0; F, 76.4. C_8F_{16} requires C, 24.0; H, 0.0; F, 76.0%); NMR spectrum no. 76; mass spectrum no. 71, m/z (EI) 381 (M^+-F, 40%); IR spectrum no. 47.

11.74 Preparation of F-2-Methylheptyl Anion (147)

A mixture of F-2-methylhept-2-ene (146) (1.4g, 3.5 mmol), caesium fluoride (0.9g, 5.9 mmol) and tetraglyme (5ml) was stirred at room temperature for 5h. Analysis of the resultant orange solution by NMR spectroscopy indicated that quantitative formation of heptadecafluoro-2-methylheptyl anion (147) had occurred; NMR spectrum no. 78.

11.75 Reaction of F-3,3-Dimethylhex-1-ene (81) with Methanol

A mixture of (81) (2.7g, 6.8 mmol) methanol (0.5g, 15.6 mmol), acetonitrile (3ml) and potassium carbonate (1.2g, 8.7 mmol) was stirred for 20 h at 60°C. After cooling, the material was washed with water (30ml) which gave rise to two liquid layers. The lower fluorocarbon layer was further washed with water, then dried over anhydrous $MgSO_4$ to give a liquid (2.4g). Analysis of the liquid by G.C. showed two major products had been formed. Separation of these compounds could not be achieved, so instead a small sample containing both of the products was obtained for analysis using preparative G.C. (10% SE30, column temp.

70°C, injector temp. 150°C). The compounds were subsequently identified as (E)-1-methoxypentadecafluoro-3,3-dimethylhex-1-ene (148) (50%); NMR spectrum no. 79; mass spectrum no. 72, m/z (EI) 412 (M^+, 11%); and 2H-1-methoxyhexadecafluoro-3,3-dimethylhexane (149) (34%); NMR spectrum no. 80; mass spectrum no. 73, m/z (EI) 413 (M^+-F, 24%).

11.76 Preparation of 1H-Perfluoro-3,3-Dimethylhex-1-yne (150)

In a sealed 'Rotaflo' tube, potassium hydroxide pellets (9.5g, 169.3 mmol) and n-$C_3F_7C(CF_3)_2CHFCF_2CHFCF_2I$ (82) (11.5g, 18.9 mmol) were heated at 90°C for 48h. After cooling, volatile material was transferred under vacuum to a separate vessel and G.C. analysis showed that it contained one major product and no remaining starting material. The product was purified by distillation and identified as <u>1H-tridecafluoro-3,3-dimethylhex-1-yne</u> (150) (5.0g, 77%); b.p. 84°C (618 mmHg); (Found: C, 27.6; H, 0.4; F, 72.4. C_8HF_{13} requires C, 27.9; H,0.3; F, 71.8%); NMR spectrum no. 81; mass spectrum no. 74, m/z (EI) 325 (M^+-F, 6%) and 275 (M^+-CF_3, 5%); IR spectrum no. 48.

On repeating the reaction with potassium hydroxide (4.2g, 74.9 mmol) and (82)(4.4g, 7.2 mmol) for 24h at 90°C, two major products were obtained which were identified as (84) and (150) by mass spectrometry and by IR spectrometry.

APPENDICES

APPENDIX ONE

NMR SPECTRA

1. 2,2,4,4,6,6,8,8-Octahydropentadecafluoro-1-iodo-9-methyldecane (13d)
2. 2,2,4,4,6,6,8,8,10,10-Decahydroheptadecafluoro-1-iodo-11-methyldodecane (13e)
3. 5H,5H-Pentadecafluoro-2-iodo-6-methylheptane (17a)
4. 7H,7H-Heneicosafluoro-2-iodo-4,8-dimethylnonane (17b)
5. 5,5,7,7-Tetrahydroheptadecafluoro-2-iodo-8-methylnonane (18a)
6. 2H,2H,6H,6H-Heptadecafluoro-1-iodo-3,7-dimethyloctane (19a)
7. 2,2,4,4,8,8-Hexahydrononadecafluoro-1-iodo-5,9-dimethyldecane (19b)
8. 2,2,6,6,8,8-Hexahydrononadecafluoro-1-iodo-3,9-dimethyldecane (20a)
9. 2,2,4,4,8,8,10,10-Octahydroheneicosafluoro-1-iodo-5,11-dimethyldodecane (20b)
10. 2,2,8,8-Tetrahydrotricosafluoro-1-iodo-3,5,9-trimethyldecane (19c)
11. 2,2,4,4,10,10-Hexahydropentacosafluoro – 1-iodo-5,7,11-trimethyldodecane (19d)
12. 2H-Decafluoro-1-iodo-3-methylbutane (23a)
13. 2H,4H-Tridecafluoro-1-iodo-5-methylhexane (23b)
14. 3,3,5,5,7,7,9,9-Octahydrohexadecafluoro-2-methylhexane (15d)
15. 3,3,5,5,7,7,9,9,11,11-Decahydrooctadecafluoro-2-methyldodecane (15e)
16. 3,3,7,7,9,9-Hexahydroeicosafluoro-2,6-dimethyldecane (26)
17. 3H,3H,4H-Nonafluoro-2-methylbutane (28)
18. 2H,4H,4H-Undecafluoro-5-methylhex-(E)-2-ene (30)
19. 2H,4H,4H-Undecafluoro-5-methylhex-1-ene (29b)
20. 3,5,5,7,7-Pentahydroterdecafluoro-2-methyloct-2-ene (35)
21. 2,6,6-Trihydroheptadecafluoro-3,7-dimethyloct-1-ene (40)
22. 2H,4H,4H,6H,6H-Tridecafluoro-7-methyloct-1-ene (29c)
23. (Z)-3,5-Dihydrodecafluoro-2-methylhexa-2,4-diene (37a)
24. (E)-3,5-Dihydrodecafluoro-2-methylhexa-2,4-diene (37b)
25. (Z)-2,6,6-Trihydroheptadecafluoro-3,7-dimethyloct-2-ene (41)

26. 2,3,5,5,-Tetrahydroundecafluoro-3-methoxy-2-methylhexane (48)
27. 3,5,5-Trihydrononafluoro-1,3-dimethyoxy-2-methylhex-1-ene (49)
28. 2,3,5,5,7,7-Hexahydro-3-phenoxyterdecafluoro -2-methyloctane (45b)
29. 3,5,5,7,7-Pentahydro-1,3-diphenoxyundecafluoro-2-methyloct-1-ene (46b)
30. 2,3,5,5,7,7-Hexahydro-1,3-diphenoxydodecafluoro-2-methyloctane (47b)
31. 2,3,5,5,-Tetrahydro-3-phenoxyundecafluoro-2-methylhexane (45a)
32. 3,5,5-Trihydro-1,3-diphenoxynonafluoro-2-methylhex-1-ene (46a)
33. 2,3,5,5,-Tetrahydro-1,3-diphenoxydecafluoro-2-methylhexane (47a)
34. 3,6,7-Trihydro-6-phenoxyhexadecafluoro-2,7-dimethyloct-2-ene (50)
35. 2,6,6,-Trihydro-2-methoxyhexadecafluoro-3,7-dimethyloct-3-ene (52a & b)
36. 2,6,6-Trihydro-2-phenoxyhexadecafluoro-3,7-dimethyloct-3-ene (52c & d)
37. 2,4,5-Trihydro-4-methoxydecafluoro-5-methylhex-2-ene (56)
38. 3,5-Dihydro-1,3-dimethyoxyoctafluoro-2-methylhexa-1,4-diene (57)
39. Heptafluoro-2-iodopropane adducts of triallyl isocyanurate (61), (62) and (63)
40. 2H-Tetradecafluoro-1-iodo-5-methylhexane (68a)
41. 2H,4H-Heptadecafluoro-1-iodo-7-methyloctane (68b)
42. Tetradecafluoro-5-methylhex-1-ene (69a)
43. 4H-Tridecafluoro-5-methylhex-1-ene (69b)
44. 2H-Hexadecafluoro-1-iodo-3,3-dimethylhexane (80)
45. 2H,4H-Nonadecafluoro-1-iod-5,5-dimethyloctane (82)
46. 1,1,2,2,4-Pentahydrohexadecafluoro-1-iodo-5,5-dimethyloctane (83)
47. 1,1,2,2,4,4-Hexahydrononafluoro-1-iodo-5-methylhexane (89a)
48. 1,1,2,2,3,3,4,4,6,6,-Decahydrononafluoro-1-iodo-7-methyloctane (89b)
49. 1,1,2,4-Tetrahydrohexadecafluoro-5,5-dimethyloct-1-ene (85)
50. Hexadecafluoro-3-3-dimethylhex-1-ene (81)
51. 4H-Nonadecafluoro-5,5-dimethyloct-1-ene (84)
52. 1,1,2,4,4-Pentahydrononafluoro-5-methylhex-1-ene (90)
53. 5H,6H-Octacosafluoro-4,4,7,7-tetramethyldecane (93)
54. 2,2,-Dimethylpropyl-1,1,2,2-tetrafluoroethyl ether (96)

55. Observable carbocation (97)

56. Observable carbocation (100)

57. Observable carbocation (101)

58. Observable carbocation (102)

59. Observable carbocation (104)

60. Observable carbocation (105)

6.1 Methyl 2H,4H-heptafluoro-5-methylhexa-2,4-dienoate (109)

62. 3H,5H-5-chloroundecafluoro-2-methylhex-2-ene (110)

63. (Z)-3H-Tridecafluoro-2-methylhex-3-ene (114)

64. 3H-Tridecafluoro-2-methylhex-2-ene (115)

65. 1,1-Difluoro-2,3-bis(trifluoromethyl)hex-1-ene (123)

66. 3H-Octafluoro-3-phenyl-2-methybut-1-ene (127)

67. 3-Ethoxycarbonyl-6-fluoro-2-methyl-4,5-bis(trifluoromethyl)-4H-pyran (130)

68. 1,1,3-Trihydrodecafluoro-4-methylpentan-1-ol (134)

69. 6,7-Benzo-2-fluoro-3,4-bis(trifluoromethyl)-1,5-dioxacyclohept-2-ene (131) and 6,7-Benzo-2,2-difluoro-3,4-bis(trifluoromethyl)-1,5-dioxacycloheptane (132)

70. 1,1,2,3-Tetrahydrononafluoro-2,3-dimethylbutan-1-ol (136)

71. 1,1,1,3,4-Pentahydrononafluoro-3,4-dimethylpentan-2-ene (135)

72. 1,1,3-Trihydrononafluoro-2,3-dimethylbut-1-ene (139)

73. 2H-Heptadecafluoro-3,3-dimethylhexane (143)

74. 1H,2H-Hexadecafluoro-3,3-dimethylhexane (142)

75. 2-(2H-Hexadecafluoro-3,3-dimethylhexyl)tetrahydrofuran (144)

76. Hexadecafluoro-2-methylhept-2-ene (146)

77. 2,5-Dis(2H-hexadecafluoro-3,3-dimethylhexyl)tetrahydrofuran (145)

78. Heptadecafluoro-2-methylhept-2-ylcaesium (147)

79. (E)-1-Methoxypentadecafluoro-3,3-dimethylhex-1-ene (148)

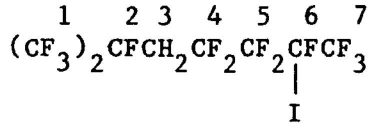
80. 2H-1-Methoxyhexadecafluoro-3,3-dimethylhexane (149)

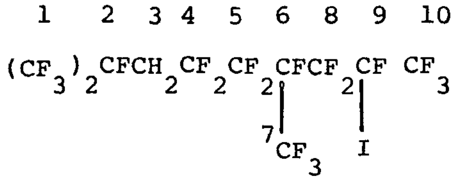
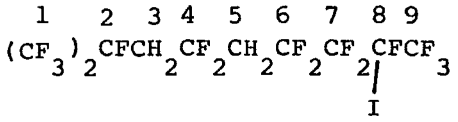
81. 1H-Tridecafluoro-3,3-dimethylhex-1-yne (150)

For the ^{13}C and ^{1}H NMR data presented below, the chemical shifts are expressed relative to TMS as external reference, whereas for the ^{19}F NMR data, the values are expressed relative to $CFCl_3$. All shifts occurring downfield from the reference are quoted with a positive sign.

Abbreviations used for the multiplicity of the resonances are S-singlet, D-doublet, T-triplet, Q-quartet, Sept.-septet and M-complex multiplet.

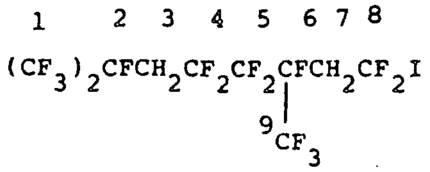
Unless otherwise stated, the samples were dissolved in $CDCl_3$ and their spectra recorded at the ambient temperature of the probe.

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
1. 1 2 3 4 5 6 7 8 9 10 $(CF_3)_2CFCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2I$			(13d)
^{19}F spectrum: neat			
-39.0	M	2	10
-78.0	D(J=6) of T(J=6)	6	1
-91.1	M	6	4,6,8
-186.4	M	1	2
^{1}H spectrum: neat			
3.3	M	-	3,5,7,9
2. 1 2 3 4 5 6 7 8 9 10 11 12 $(CF_3)_2CFCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2I$			(13e)
^{19}F spectrum: neat			
-39.0	M	2	12
-78.0	D(J=6)of T(J=6)	6	1
-91.2	M	8	4,6,8,10
-186.5	M	1	2
^{1}H spectrum: neat			
3.3	M	-	3,5,7,9,11
3.  1 2 3 4 5 6 7 $(CF_3)_2CFCH_2CF_2CF_2CF(I)CF_3$			(17a)
^{19}F spectrum: neat			
-75.1	D(J=9)of T(J=9)	3	7
-79.3	D(J=6)	6	1
-110.3	M	4	4,5
-145.7	M(J=13)	1	6
-187.6	M	1	2
^{1}H spectrum: neat			
2.8	D(J=17)of T(J=17)	-	3

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
4.	 $(CF_3)_2CFCH_2CF_2CF_2\underset{CF_3}{CF}CF_2\underset{I}{CF}CF_3$		(17b)
^{19}F spectrum			
- 70.2	D(J=108) of D(J=100)	3	10
- 72.7	M(J=8)	3	7
- 77.1	D(J=6)	3	1
-100.6 to -114.1	M	4	5,8
-110.6	M	2	4
-145.4	M	1	9
-181.6	D(J=80) of M(J=26)	1	6
-185.5	M	1	2
^{1}H spectrum			
2.9	M	-	3
5.	 $(CF_3)_2CFCH_2CF_2CH_2CF_2CF_2\underset{I}{CF}CF_3$		(18a)
^{19}F spectrum			
- 73.0	M	3	9
- 77.0	M	6	1
- 87.8	M	2	4
-107.8	AB(J=289)	2	7
-109.9	M	2	6
-144.1	M	1	8
-185.4	M	1	2
^{1}H spectrum			
2.9	M	-	3,5

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT

6.



$(CF_3)_2CFCH_2CF_2CF_2\underset{CF_3}{CF}CH_2CF_2I$

(19a)

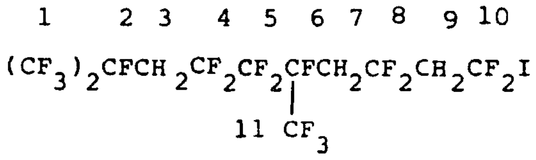
^{19}F spectrum: neat

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
- 39.2	M	2	8
- 78.2	D(J=9) of T(J=9)	3	9
- 79.7	D(J=7) of T(J=7)	6	1
-112.6	M	2	4
-121.2	M	2	5
-185.9	M	1	2,6
-187.5	M	1	

^{1}H spectrum: neat

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
3.3	M	-	3,7

7.



$(CF_3)_2CFCH_2CF_2CF_2\underset{CF_3}{CF}CH_2CF_2CH_2CF_2I$

(19b)

^{19}F spectrum: neat

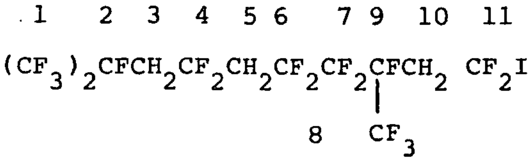
SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
- 40.0	M	2	10
- 77.5	D(J=9) of T(J=9)	3	11
- 79.3	D(J=7) of T(J=7)	6	1
- 91.5	M	2	8
-112.0	M	2	4
-120.5	M	2	5
-185.3	M	1	2,6
-187.4	M	1	

^{1}H spectrum: neat

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
3.2	M	-	3,7,9

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT

8.



$$(CF_3)_2CFCH_2CF_2CH_2CF_2CF_2\underset{\displaystyle CF_3}{\underset{|}{C}F}CH_2\ CF_2I$$

(20a)

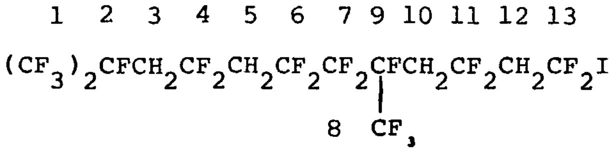
^{19}F spectrum: neat

- 38.4	M	2	11
- 77.7	M	3	8
- 78.8	D(J=6) of T(J=6)	6	1
- 90.2	M	2	4
-112.7	M	2	6
-121.0	M	2	7
-186.3	M	1	2,9
-187.3	M	1	

^{1}H spectrum: neat

2.2 - 3.9	M	-	3,5,10

9.



$$(CF_3)_2CFCH_2CF_2CH_2CF_2CF_2\underset{\displaystyle CF_3}{\underset{|}{C}F}CH_2CF_2CH_2CF_2I$$

(20b)

^{19}F spectrum: neat

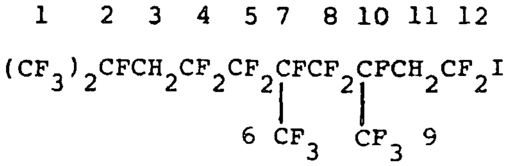
- 39.8	M	2	13
- 77.5	M	3	8
- 78.9	D(J=6) of T(J=6)	6	1
- 90.7	M	2	4
- 91.5	M	2	11
-112.8	M	2	6
-120.9	M	2	7
-186.1	M	1	2,9
-187.3	M	1	

^{1}H spectrum: neat

2.1 - 3.9	M	-	3,5,10,12

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT

10.



$$\mathrm{(CF_3)_2CFCH_2CF_2CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FCH_2CF_2I}$$

(19c)

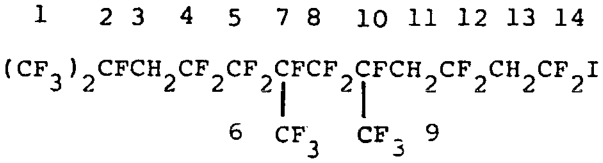
^{19}F spectrum

- 37.5	M	2	12
- 70.2	M	3	6
- 75.7	M	3	9
- 77.0	M	6	1
-110.5	M	2	4
-101.4 to -115.8	M	4	5,8
-187.7 to -183.1	M	2	7,10
-185.4	M	1	2

^{1}H spectrum

2.9	M	2	3
3.5	M	2	11

1.



$$\mathrm{(CF_3)_2CFCH_2CF_2CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FCH_2CF_2CH_2CF_2I}$$

(19d)

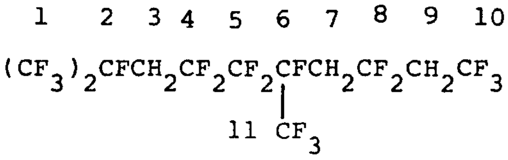
^{19}F spectrum

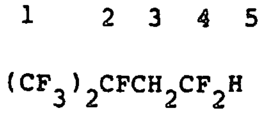
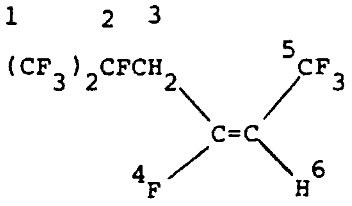
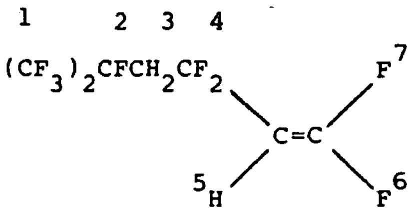
- 38.6	M	2	14
- 70.3	M	3	6
- 75.3	M	3	9
- 77.1	M	6	1
-89.4	M	2	12
-101.4 to -115.9	M	4	5,8
-110.6	M	2	4
-181.8 to -182.8	M	2	7,10
-185.5	M	1	2

^{1}H spectrum

2.9	M	4	3,13
3.3	M	2	11

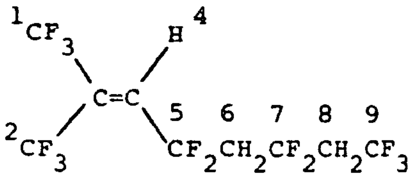
SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
12.	1,2 3 4 5 6		
	$(CF_3)_2CFCHFCF_2I$		(23a)
^{19}F spectrum			
- 54.7	AB(J=198)	2	6
- 72.6	M	3	1,2
- 76.0	M	3	
-186.4	M	1	3
-191.5	M	1	5
^{1}H spectrum			
5.2	D(J=46)ofD(J=17)ofD(J=8) of D(J=4)	-	4
13.	1,2 3 4 5 6 7 8 9		
	$(CF_3)_2CFCHFCF_2CHFCF_2I$		(23b)
^{19}F spectrum			
- 54.1	M	2	9
- 72.8	M	3	1,2
-75.8	M	3	
-117.6 to -124.4	M	2	6
-186.5	M	1	3
-192.1	M	1	8
-209.6	M	1	5
^{1}H spectrum			
4.8 - 5.6	M	-	4,7
14.	1 2 3 4 5 6 7 8 9 10		
	$(CF_3)_2CFCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_3$		(15d)
^{19}F spectrum: neat			
- 63.2	T(J=9) of T(J=9)	3	10
- 78.3	D(J=6) of T(J=6)	6	1
- 92.7	M	6	4,6,8
-186.2	M	1	2
^{1}H spectrum: neat			
2.6	M	-	3,5,7,9

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
15.	$\overset{1}{(CF_3)_2}\overset{2}{CF}\overset{3}{CH_2}\overset{4}{CF_2}\overset{5}{CH_2}\overset{6}{CF_2}\overset{7}{CH_2}\overset{8}{CF_2}\overset{9}{CH_2}\overset{10}{CF_2}\overset{11}{CH_2}\overset{12}{CF_3}$		(15e)
^{19}F spectrum: neat			
- 64.2	T(J=9) of T(J=9)	3	12
- 79.2	D(J=6) of T(J=6)	6	1
- 93.0	M	8	4,6,8,10
-187.4	M	1	2
^{1}H spectrum: neat			
2.5 - 3.4	M	-	3,5,7,9,11
16.	 $\overset{1}{(CF_3)_2}\overset{2}{CF}\overset{3}{CH_2}\overset{4}{CF_2}\overset{5}{CF_2}\overset{6}{C}F(\overset{11}{CF_3})\overset{7}{CH_2}\overset{8}{CF_2}\overset{9}{CH_2}\overset{10}{CF_3}$	(26)	
^{19}F spectrum: neat			
- 64.9	M(J=9)	3	10
- 78.3	D(J=9) of T(J=9)	3	11
- 80.2	D(J=6) of T(J=6)	6	1
- 93.2	M	2	8
-112.6	M	2	4
-121.1	M	2	5
-186.3	M	1	2,6
-188.2	M	1	
^{1}H spectrum: neat			
2.8	M	-	3,7,9

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
17.	 $\overset{1}{(CF_3)_2}\overset{2}{CF}\overset{3}{CH_2}\overset{4}{CF_2}\overset{5}{H}$	(28)	
^{19}F spectrum: neat			
- 80.8	M	6	1
-116.0	AB(J=56)	2	4
-188.5	M	1	2
^{1}H spectrum: neat			
4.1	M	-	3,5
18.		(30)	
^{19}F spectrum			
- 58.0	M	3	5
- 77.0	D(J=6) of D(J=5)	6	1
- 84.4	M	1	4
-182.6	M	1	2
^{1}H spectrum			
3.3	D(J=21) of D(J=21)	2	3
5.8	D(J=18) of Q(J=7)	1	6
19.		(29b)	
^{19}F spectrum: neat			
- 77.8	D(J=23) of D(J=23)	1	6
- 80.1	D(J=6) of T(J=6)	6	1
- 82.0	M	1	7
- 87.0	M	2	4
-188.1	M	1	2
^{1}H spectrum: neat			
2.9	D(J=17) of T(J=14)	2	3
4.8	M	1	5

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
^{13}C spectrum			
36.1	T(J=32) of D(J=19)		3
77.9	T(J=14) of T(J=17)		5
89.3	D(J=298) of Sept. (J=32)		2
115.6	T(J=242) of D(J=12)		4
120.2	Q(J=286) of D(J=28)		1
157.7	T(J=296) of T(J=7)		6

20.

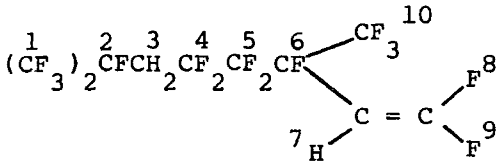


(35)

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
^{19}F spectrum: neat			
- 61.3	T(J=14) of Q(J=17)	3	2
- 64.7	T(J=9) of T(J=9)	3	9
- 68.4	Q(J=7)	3	1
- 92.8	M	2	5
- 94.4	M	2	7
^{1}H spectrum: neat			
2.6	M	4	6,8
6.4	T(J=13)	1	4
^{13}C spectrum			
40.9	M(J=30)		8
43.7	T(J=26) of T(J=26)		6
116.2	T(J=246)		5
117.3	T(J=239)		7
120.3	Q(J=275)		1 or 2 or 9
123.2	Q(J=278)		1 or 2 or 9
123.3	Q(J=277)		1 or 2 or 9
126.0	M		3
137.7	T(J032)		4

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT

21.



(40)

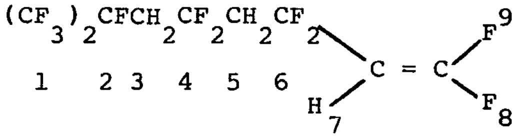
^{19}F spectrum: neat

- 75.5	M	2	8,9
- 80.3	M	3	10 Overlapping signal
- 80.3	D(J=7) of T(J=7)	6	1
-113.0	M	2	4
-123.6	M	2	5
-177.3	M	2	2,6

^{1}H spectrum: neat

2.6	D(J=17) of (T(J=17)	2	3
4.3	D(J=20) of D(J=20)	1	7

22.



(29c)

^{19}F spectrum: neat

- 77.7	M	1	8
- 79.3	D(J=6) of T(J=6)	6	1
- 81.7	M	1	9
- 88.3	M	2	6
- 92.9	M	2	4
-187.0	M	1	2

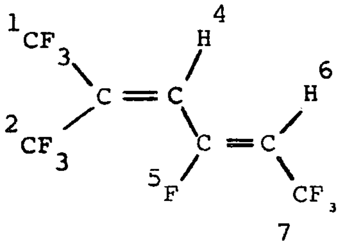
^{1}H spectrum: neat

2.5	M	4	3,5
4.3	M	1	7

22. ^{13}C spectrum

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
34.8	T(J=26) of D(J=20)		3
43.8	T(J=26) of T(J=26)		5
78.0	T(J=18) of T(J=14)		7
89.4	D(J=210)of sept.(J=33)		2
116.2	T(J=239)		6
117.5	T(J=246)		4
119.9	Q(J=286)of D(J=27)		1
157.5	T(J=299)of T(J=7)		8

23.



(37a)

^{19}F spectrum:neat

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
- 60.0	D(J=29) of Q(J=8)	3	2
- 61.3	D(J=18) of D(J=8)	3	7
- 67.0	Q(J=8)	3	1
-101.7	M	1	5

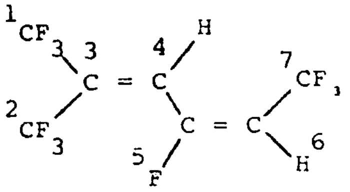
^{1}H spectrum:neat

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
5.6	D(J=28) of Q(J=8)	1	6
6.7	D(J=24)	1	4

^{13}C spectrum

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
109.0	Q(J=38) of D(J=10)		6
119.0	Q(J=272)		1 or 2 or 7
119.9	Q(J=274)		1 or 2 or 7
121.3	D(J=144)		5
122.3	Q(J=275)		1 or 2 or 7
127.8	M		3
129.3	D(J=26)		4

24.



(37b)

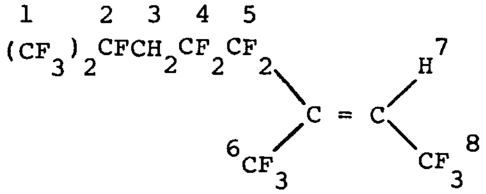
24. ^{19}F spectrum:neat

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
- 60.3	D(J=11) of D(J=8)	3	7
- 62.4	D(J=28) of Q(J=8)	3	2
- 68.1	Q(J=8)	3	1
- 98.0	M	1	5

^{1}H spectrum:neat

7.3	D(J=22)	1	4
5.8	Q(J=8) of D(J=7)	1	6

25.



(41)

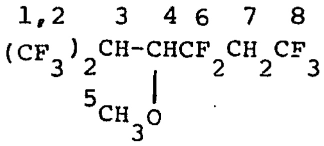
^{19}F spectrum

- 60.7	T(J=21) of Q(J=11)	3	6
- 61.6	Q(J=11) of D(J=8)	3	8
- 79.5	D(J=7) of T(J=7)	6	1
-111.3	M	2	4 or 5
-112.4	M	2	4 or 5
-188.0	M	1	2

^{1}H spectrum:neat

2.7	D(J=17) of T(J=17)	2	3
6.3	Q(J=8)	1	7

26.


$(CF_3)_2CH\text{-}\underset{\underset{^{5}CH_3O}{|}}{CH}CF_2CH_2CF_3$

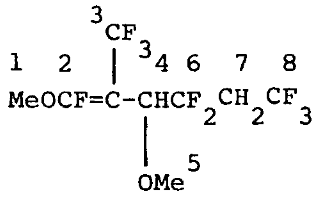
(48)

^{19}F spectrum

- 61.9	M	6	1,2
- 67.0	M	3	8
-106.4	AB(J=268)	2	6

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
^{1}H spectrum			
3.0	M	2	7
3.4	Sept.(J=8)	1	3
3.6	S	3	5
3.9	D(J=17) of D(J=7)	1	4

27.



$$\overset{1}{\mathrm{Me}}\mathrm{O}\overset{2}{\mathrm{CF}}=\overset{\overset{3}{\mathrm{CF_3}}}{\mathrm{C}}-\underset{\mathrm{OMe}^{5}}{\overset{4}{\mathrm{CH}}}\overset{6}{\mathrm{CF_2}}\overset{7}{\mathrm{CH_2}}\overset{8}{\mathrm{CF_3}}$$

(49) E and Z isomers (54% Z)

^{19}F spectrum			
- 56.5	D(J=19) of D(J=11)	3	3(Z)
- 57.7	D(J=9) of D(J=9)	3	3(E)
- 62.2	T(J=10) of T(J=10)	6	8(E and Z)
- 71.3	Q(J=19)	1	2(Z)
- 75.3	M	1	2(E)
-106.2	AB(J=267)	2	6(Z)
-106.5	AB(J=263)	2	6(E)
^{1}H spectrum			
2.9	M	4	7(E and Z)
3.4	S	6	5(E and Z)
3.9	S	6	1(E and Z)
4.2	D(J=18) of D(J=7)	1	4(E or Z)
4.3	D(J=17) of D(J=7)	1	4(E or Z)

28.

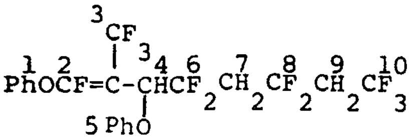
$$\overset{1,2}{(\mathrm{CF_3})_2}\overset{3}{\mathrm{CH}}\text{-}\overset{4}{\mathrm{CH}}(\mathrm{OPh})\overset{5}{\mathrm{CF_2}}\overset{6}{\mathrm{CH_2}}\overset{7}{\mathrm{CF_2}}\overset{8}{\mathrm{CH_2}}\overset{9}{\mathrm{CF_3}}$$

(45b)

^{19}F spectrum : $(CD_3)_2CO$			
- 61.0	M	3	1 or 2
- 62.0	M	3	1 or 2
- 66.1	T(J=10) of T(J=10)	3	10
- 90.2	M	2	8
-104.7	AB(J=264)	2	6

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
^{1}H spectrum: $(CD_3)_2CO$			
2.8	M	4	7,9
3.5	Sept.(J=8)	1	3
4.9	D(J=16) of D(J=7)	1	4
7.0-7.2	M	5	5

29.

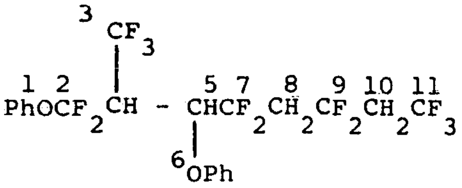


$$\overset{1}{Ph}O\overset{2}{C}F=\overset{\overset{3}{CF_3}}{C}-\underset{\underset{5}{PhO}}{\overset{4}{C}H}\overset{6}{CF_2}\overset{7}{CH_2}\overset{8}{CF_2}\overset{9}{CH_2}\overset{10}{CF_3}$$

(46b) (E and Z isomers) (1:1))

^{19}F spectrum: $(CD_3)_2CO$			
- 56.2	D(J=14) of D(14)	3	3(E or Z)
- 57.5	M	3	3(E or Z)
- 61.7	T(J=10) of T(J=10)	6	10(E and Z)
- 65.2	M	1	2(E or Z)
- 68.0	M	1	2(E or Z)
- 93.4	M	4	8(E and Z)
-103.5 to-108.2	M	4	6(E and Z)
^{1}H spectrum: $(CD_3)_2CO$			
3.0-3.4	M	4	7,9(E and Z)
5.7	M	1	4(E and Z)
7.1-7.5	M	10	1,5 (E and Z)

30.



$$\overset{1}{Ph}O\overset{2}{CF_2}\overset{\overset{3}{CF_3}}{CH}-\underset{\underset{6}{OPh}}{\overset{5}{C}H}\overset{7}{CF_2}\overset{8}{CH_2}\overset{9}{CF_2}\overset{10}{CH_2}\overset{11}{CF_3}$$

(47b) (Two diastereoisomers)

^{19}F spectrum: $(CD_3)_2CO$			
- 61.7	T(J=10) of T(J=10)	3	3,11
- 93.0	M	1	2
- 94.3	M	1	9
-103.5 to-108.2	M	1	7
^{1}H spectrum: $(CD_3)_2CO$			
3.0-3.4	M	5	4,8,10
5.6-5.8	M	1	5
7.1-7.5	M	10	1,6

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT

31. $(\overset{1,2}{CF_3})_2\overset{3}{CH}-\overset{4}{CH}(\overset{5}{OPh})\overset{6}{CF_2}\overset{7}{CH_2}\overset{8}{CF_3}$ (45a)

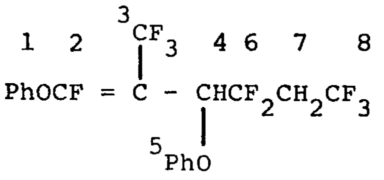
^{19}F spectrum

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
- 61.0	M	3	1 or 2
- 61.3	M	3	1 or 2
- 66.1	T(J=10) of T(J=10)	3	8
-105.6	AB(J=264)	2	6

^{1}H spectrum

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
3.0	M	2	7
3.6	Sept.(J=8)	1	3
5.0	D(J=15) of D(J=7)	1	4
7.0 - 7.3	M	5	5

32.



$\overset{1}{PhO}\overset{2}{CF}=\overset{\overset{3}{CF_3}}{\overset{|}{C}}-\underset{\underset{5}{PhO}}{\underset{|}{\overset{4}{CH}}}\overset{6}{CF_2}\overset{7}{CH_2}\overset{8}{CF_3}$ (46a) (E and Z isomers)

^{19}F spectrum

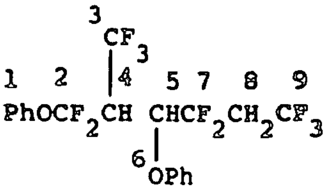
SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
- 56.4	M	3	3 (E or Z)
- 57.6	M	3	3 (E or Z)
- 61.6	T(J=9) of T(J=9)	6	8
- 65.4	Q(J=10)	1	2 (E or Z)
- 67.4	M	1	2 (E or Z)
-103.5 to -108.0	M	4	6

^{1}H spectrum

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
3.0 - 3.3	M	2	7
5.4 - 5.7	M	1	4
6.7 - 7.5	M	10	1,5

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT

33.



$PhOCF_2CH(CF_3)CH(OPh)CF_2CH_2CF_3$

(47a) (Two diastereoisomers)

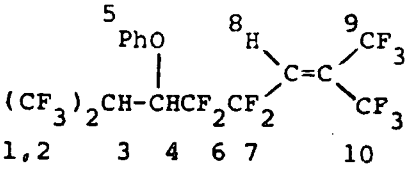
^{19}F spectrum

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
- 61.1	M	3	3
- 61.6	T(J=9) of T(J=9)	3	9
-100.6 to -103.3	M	2	2
-103.5 to -108.0	M	2	7

^{1}H spectrum

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
3.0 - 3.3	M	3	4,8
5.4 - 5.7	M	1	5
6.7 - 7.5	M	10	1,6

34.



(50)

^{19}F spectrum

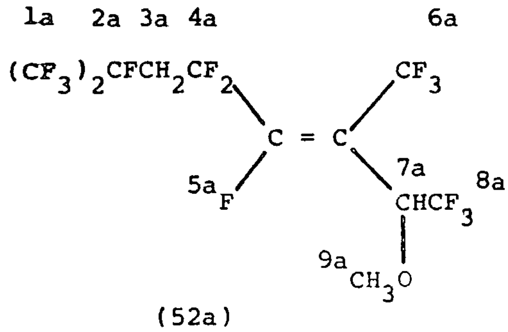
SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
- 59.4	M	3	9 or 10
- 61.2	M	3	9 or 10
- 65.9	M	3	1 or 2
- 66.1	M	3	1 or 2
-110.8	M	2	7
-121.5	AB(J=274)	2	6

^{1}H spectrum

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
3.6	Sept.(J=8)	1	3
5.3	D(J=18) of D(J=7)	1	4
6.8	T(J=14)	1	8
6.9 - 7.3	M	5	5

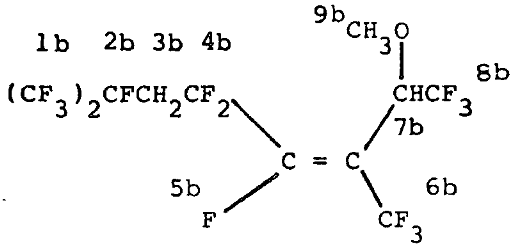
SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT

35.



(52a)

+



(52b)

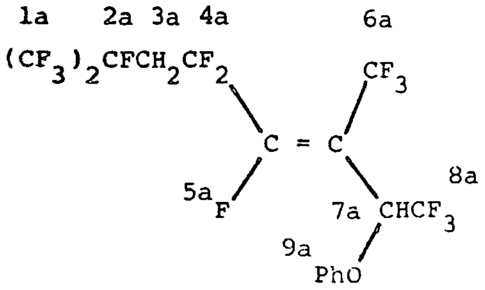
^{19}F spectrum

- 55.6	M	3	6a
- 58.6	D(J=22) of Q(J=8)	3	6b
- 73.8	M	3	8b
- 74.9	M	3	8a
- 77.6	M	12	1a,1b
- 92.1	AB(J=282)	2	4b
- 96.4	M	1	5a or 5b
- 98.4	M	1	5a or 5b
- 96.8	M	2	4a
-186.9	M	2	2a,2b

^{1}H spectrum

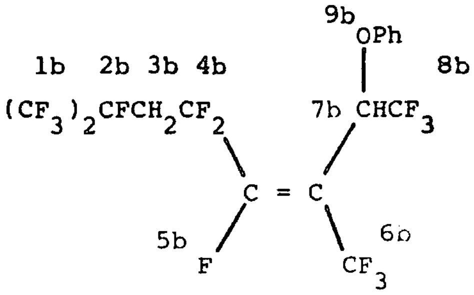
3.0	M	4	3a,3b
3.5	S	6	9a,9b
3.5	S		
4.6	Q(J=7)	1	7a
4.9	Q(J=7)	1	7b

36.



(52c)

+

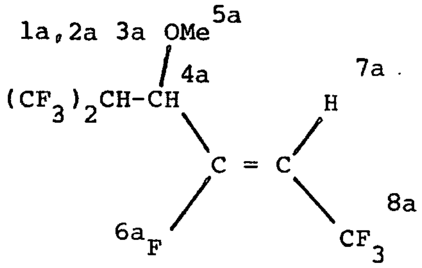


(52d)

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
^{19}F spectrum			
- 54.9	M	3	6a
- 57.6	D(J=21) of Q(J=7)	3	6b
- 73.8	M	3	8b
- 75.1	M	3	8a
- 77.8	M	12	1a,1b
- 94.3	AB(J=287)	2	4b
- 96.6	M	1	5a
- 96.8	M	1	5b
- 97.4	M	2	4a
-187.0	M	2	2a,2b
^{1}H spectrum			
2.9	M	4	3a,3b
5.5	Q(J=6)	1	7b
5.7	Q(J=6)	1	7a
7.0	M	5	9a
7.3	M	5	9b

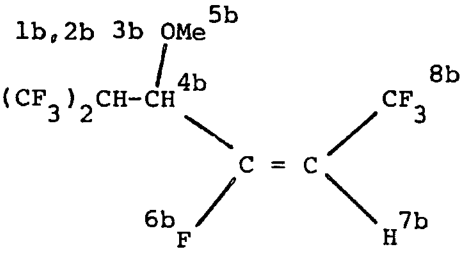
SHIFT/PPM COUPLING/HZ INTEGRAL ASSIGNMENT

37.



(56a)

+



(56b)

^{19}F spectrum

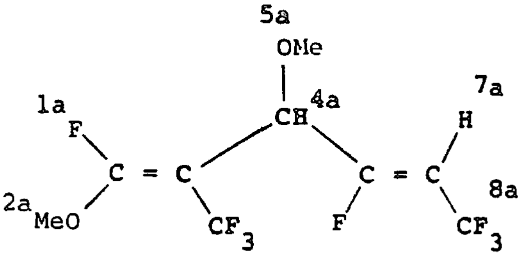
SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT
- 56.1	D(J=19) of D(J=8)	3	8b
- 58.7	D(J=17) of D(J=8)	3	8a
- 62.0	D(J=10) of Q(J=7)	3	1a or 2a
- 65.3	D(J=10) of Q(J=7)	3	1a or 2a
- 63.3	M	3	1b or 2b
- 64.6	M	3	1b or 2b
-105.5	D(J=33) of Q(J=17)	1	6a
-106.9	M	1	6b

^{1}H spectrum

3.3	M	2	3a,3b
3.4	S	3	5b
3.5	S	3	5a
4.3	Broad S	1	4a
4.6	D(J=25) of D(J=8)	1	4b
5.5	D(J=33) of Q(J=8)	1	7a
5.8	D(J=17) of Q(J=8)	1	7b

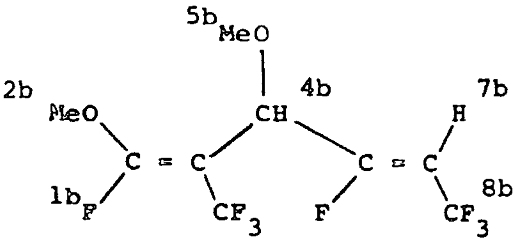
SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT

38.



(57a)

+



(57b)

^{19}F spectrum: neat

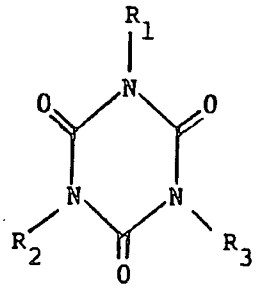
- 58.5	D(J=20)	3	3b
- 59.3	D(J=11)	3	3a
- 60.2	D(J=17) of D(J=8)	6	8a,8b
- 75.7	Q(J=20)	1	1b
- 80.3	Q(J=11)	1	1a
-105.4	D(J=33) of Q(J=17)	2	6a,6b

^{1}H spectrum: neat

3.5	S	3	4a,4b
3.9	S	3	2a,2b
4.7	Broad S	1	5a,5b
5.5	D(J=33) of Q(J=8)	1	7a,7b

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT

39.



Mixture containing (61),(62) and (63)

1 2 3 4 5 6 7 8

R_1, R_2, and R_3 = $CH_2CH{=}CH_2$ or $CH_2CHICH_2CF(CF_3)_2$

^{19}F spectrum

- 75.4 to - 77.6	M	-	8
- 185.2	M	-	7

^{1}H spectrum

3.0	M	2	6
4.2	M	2	4
4.5	M	2	1
4.7	M	1	5
5.3	M	2	3
5.8	M	1	2

40.

1 2 3 4 5 6 7

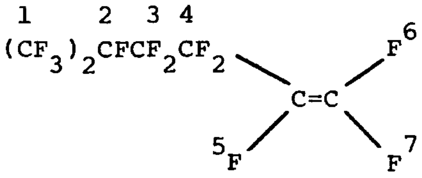
$(CF_3)_2CFCF_2CF_2CHFCF_2I$ (68a)

^{19}F spectrum

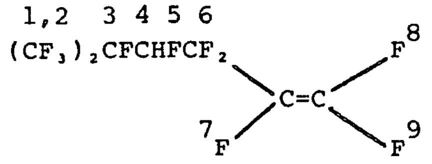
- 53.8	AB(J=191)	2	7
- 72.1	M	6	1
-115.9	M	2	3
-122.4	AB(J=282)	2	4
-186.4	M	1	2
-191.6	M	1	6

^{1}H spectrum

5.0	D(J=43)ofT(J=16) of T(J=3)	-	5

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
41. 1 2 3 4 5 6 7 8 9 10 $(CF_3)_2CFCF_2CF_2CHFCF_2CHFCF_2I$		(68b)	
^{19}F spectrum			
- 53.9	M	2	10
- 72.2	M	6	1
-116.2	M	2	3
-121.0 to -121.6	M	4	4,7
-186.4	M	1	2
-192.3	M	1	9
-210.3	M	1	6
^{1}H spectrum			
4.8 - 5.3	M	-	5,8
42. 		(69a)	
^{19}F spectrum			
- 72.4	M	6	1
- 87.4	D(J=45) of D(J=45)	1	7
-104.5	M	1	6
-116.4	M	2	3 or 4
-117.7	M	2	3 or 4
-186.9	M	1	2
-188.3	D(J= 120) of M	1	5

43.



(69b)

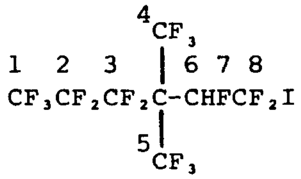
^{19}F spectrum

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSISGNMENT
- 73.2	M	3	1 or 2
- 76.4	M	3	1 or 2
- 89.7	D(J=54) of D(J=38)	1	9
-105.7	M	1	8
-114.9	AB(J=292)	2	6
-188.0	M	1	3
-189.8	D(J=80) of M	1	7
-209.6	M	1	5

^{1}H spectrum

5.3	D(J=43) of M	-	4

44.



$CF_3CF_2CF_2C(CF_3)_2\text{-}CHFCF_2I$

(80)

^{19}F spectrum: neat

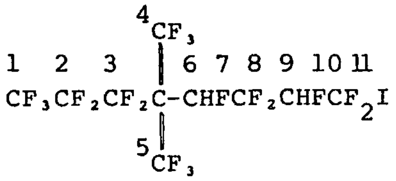
- 50.0	M	2	8
- 61.0	M	6	4,5
- 81.8	T(J=14)	3	1
-106.4	M	2	3
-124.4	M	2	2
-177.8	M	1	7

^{1}H spectrum: neat

5.9	D(J=39) of D(J=17) of D(J= 4)	-	6

SHIFT/PPM	COUPLING/HZ	INTEGRAL	ASSIGNMENT

45.



$$\overset{1}{\mathrm{CF_3}}\overset{2}{\mathrm{CF_2}}\overset{3}{\mathrm{CF_2}}\underset{{}^{5}\mathrm{CF_3}}{\overset{{}^{4}\mathrm{CF_3}}{\mathrm{C}}}\text{-}\overset{6}{\mathrm{CH}}\overset{7}{\mathrm{F}}\overset{8}{\mathrm{CF_2}}\overset{9}{\mathrm{CH}}\overset{10}{\mathrm{F}}\overset{11}{\mathrm{CF_2}}\mathrm{I}$$

(82)

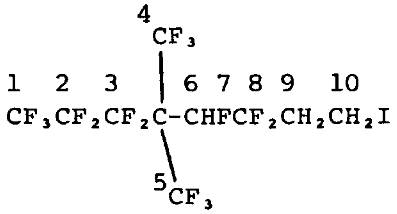
^{19}F spectrum

- 53.7	M	2	11
- 59.2	M	3	4 or 5
- 59.9	M	3	4 or 5
- 80.0	M	3	1
-105.2	AB(J=320)	2	3
-122.5	M	2	2
-113.9	AB(J=250)	2	8
-191.8	M	1	10
-199.7	M	1	7

^{1}H spectrum

5.7	M	-	6,9

46.



$$\overset{1}{\mathrm{CF_3}}\overset{2}{\mathrm{CF_2}}\overset{3}{\mathrm{CF_2}}\underset{{}^{5}\mathrm{CF_3}}{\overset{{}^{4}\mathrm{CF_3}}{\mathrm{C}}}\text{-}\overset{6}{\mathrm{CH}}\overset{7}{\mathrm{F}}\overset{8}{\mathrm{CF_2}}\overset{9}{\mathrm{CH_2}}\overset{10}{\mathrm{CH_2}}\mathrm{I}$$

(83)

^{19}F spectrum

- 59.1	M	3	4 or 5
- 60.1	M	3	4 or 5
- 80.0	T(J=13)	3	1
-105.1	AB(J=313)	2	3
-106.5	AB(J=261)	2	8
-122.3	M	2	2
-196.2	M	1	7

^{1}H spectrum

2.7	M,broad	2	9
3.2	D(J=8) of D(J=8)	2	10
5.4	D(J=41) of D(J=19) of D(J=4)	1	6

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT

47.

1 2 3 4 5 6

$(CF_3)_2CFCH_2CF_2CH_2CH_2I$ (89a)

^{19}F spectrum: neat

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
- 79.1	D(J=6) of T(J=6)	6	1
- 96.8	M	2	4
-187.2	M	1	2

^{1}H spectrum: neat

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
2.8-3.9	M	-	3,5,6

48.

1 2 3 4 5 6 7 8

$(CF_3)_2CFCH_2CF_2CH_2CH_2CH_2CH_2I$ (89b)

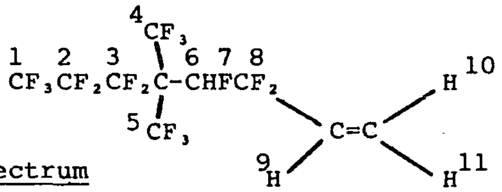
^{19}F spectrum: neat

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
- 78.8	D(J=6) of T(J=6)	6	1
- 95.6	M	2	4
-187.1	M	1	2

^{1}H spectrum: neat

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
2.0-4.0	M	-	3,5,6,7,8

49.



(85)

^{19}F spectrum

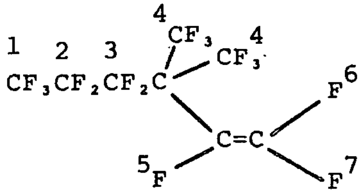
SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
- 59.2	M	3	4 or 5
- 59.9	M	3	4 or 5
- 80.1	T(J=14)	3	1
-105.1	AB(J=311)	2	3
-105.2	AB(J=268)	2	8
-122.4	M	2	2
-196.1	M	1	7

^{1}H spectrum

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
5.3	D(J=41) of D(J=16) of D(J=5)	1	6
5.7	M	1	10 or 11
5.8	M	1	10 or 11
6.0	M	1	9

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT

50.

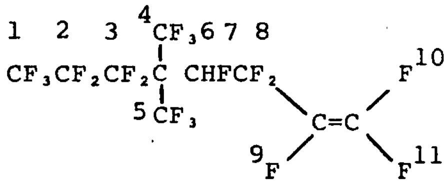


(81)

^{19}F spectrum

- 60.8	M	6	4
- 80.6	T(J=15)	2	1
- 87.6	T(J=47)	1	7
-100.5	M	1	6
-106.9	M	2	3
-124.7	M	2	2
-179.8	D(J=111) of M	1	5

51.



(84)

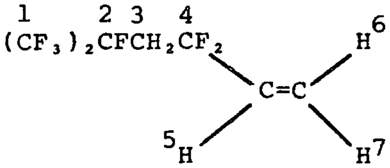
^{19}F spectrum: $(CD_3)_2CO$

- 60.3	M	3	4 or 5
- 60.6	M	3	4 or 5
- 81.2	T(J=14)	3	1
- 92.1	M	1	11
-105.3 to -107.0	M	2	3,10
-112.2	AB(J=289)	2	8
-123.0	M	2	2
-189.2	D(J=113) of M	1	9
-198.4	M	1	7

^{1}H spectrum: $(CD_3)_2CO$

6.3	D(J=39) of D(J=20)	-	6

52.



(90)

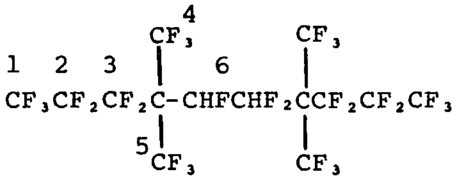
^{19}F spectrum: neat

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
- 79.4	D(J=6) of T(J=6)	6	1
- 96.4	M	2	4
-187.0	M	1	2

^{1}H spectrum: neat

2.4	D(J=18) of T(J=14)	2	3
5.1	S	1	7
5.4	M	2	5,6

53.



$CF_3CF_2CF_2C(CF_3)_2\text{-}CHFCHF_2C(CF_3)_2CF_2CF_2CF_3$

(93) (mixture of diastereoisomers)

^{19}F spectrum: $(CH_3)_2CO$

- 59.0	M	6	4,5
- 59.4	M		
- 79.9	M	3	1
-104.4 to -117.1	M	2	3
-121.7	M	2	2
-188.4	M	1	6
-197.5	M		

54.

1 2 3 4 5

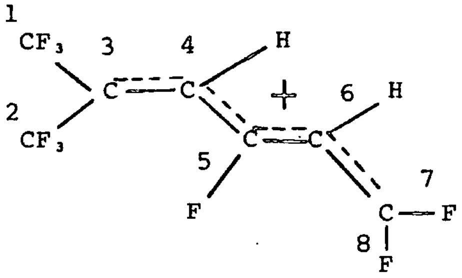
$Me_3CCH_2OCF_2CF_2H$ (96)

^{19}F spectrum: neat

- 42.9	T(J=9)	1	3
-110.0	M	1	4

^{1}H spectrum: neat

0.7	S	9	1
3.3	S	2	2
5.4	T(J=53) of T(J=3)	1	5

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
55. 	SbF_6^-	(97)	
^{19}F spectrum: SbF_5			
- 69.1	Q(J=8)	3	1
- 62.6	D(J=30) of Q(J=8)	3	2
+ 14.8	M Very broad	1	5
+ 32.2	M	1	7 or 8
+ 34.0	M	1	7 or 8
^{1}H spectrum: SbF_5			
7.3	M	-	4,6
^{13}C spectrum: SbF_5			
96.1	D(J=20)		6
116.6	Q(J=278)		1 or 2
117.4	Q(J=277)		1 or 2
125.2	S		4
146.0	Sept. (J=36)		3
177.4	T(J=365)		7
199.4	D(J=354)		5
56. $(CF_3)_2CFCH_2\overset{+}{\overline{CF\text{-}CH\text{-}CF}}CH_2CF_3$ 1 2 3 4 5 6 7 8	SbF_6^-	(100)	
^{19}F spectrum: SbF_5			
- 63.0	M	3	8
- 79.4	D(J=6)	6	1
-181.9	M	1	2
+ 58.5	M	2	4,6
^{1}H spectrum: SbF_5			
4.2	M	4	3,7
7.6	M	1	5

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
^{13}C spectrum: SbF_5			
35.7	S		3
42.0	Q(J=36)		7
89.0	D(J=250) of Sept. (J=29)		2
111.7	S		5
117.4	Q(J=287) of D(J=26)		1
118.7	Q(J=281)		8
209.3	D(J=368)		4 or 6
210.5	D(J=373)		4 or 6

57. $(CF_3)_2CFCH_2\overset{+}{\overline{CF\text{-}CH\text{-}CF\text{-}CH\text{-}CF}}CH_2CF_3 \quad SbF_6^-$ (101)

1 2 3 4 5 6 7 8 9 10

^{19}F spectrum: SbF_5

- 64.1	S	3	10
- 79.3	D(J=6)	6	1
-183.1	M	1	2
-8 to 0	Broad	3	4,6,8

^{1}H spectrum: SbF_5

3.7	M	2	3,9
6.8	M	1	5,7

^{13}C spectrum: SbF_5

34.6	S		3
40.5	Q(J=31)		9
90.2	D(J=248) of Sept. (J=34)		2
108.0	S		5 or 7
108.8	S		5 or 7
118.8	Q(J=287) of D(J=26)		1
121.1	Q(J=278)		10
190.1	M		4,6,8
195.4	M		

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT

58. $(CF_3)_2CFCH_2\overset{+}{\overline{CF-CH-CF-CH-CF-CH-CF}}CH_2CF_3 \quad SbF_6^-$ (102)

1 2 3 4 5 6 7 8 9 10 11 12

^{19}<u>F spectrum</u>: SbF_5

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
- 64.8	M	3	12
- 79.4	M	6	1
-183.4	M	1	2
-13.3 to -30.0	M	4	4,6,8,10

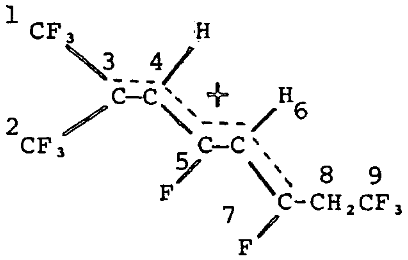
^{1}<u>H spectrum</u>: SbF_5

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
3.0 to 4.4	M	4	3,11
5.8 to 8.1	M	3	5,7,9

^{13}<u>C spectrum</u>: SbF_5

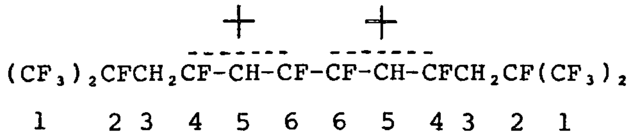
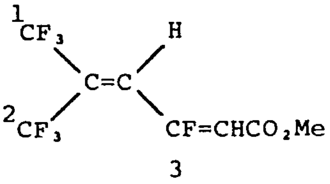
SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
34.0	S		3
39.6	M		11
90.3	D(J=216) of M		2
106.1	S		5,7,9
107.0	S		
107.7	S		
119.7	Q(J=286) of D(J=27)		1
122.1	Q(J=279)		12
178.6	M		4,6,8,10
183.8	M		
185.5	M		
191.2	M		

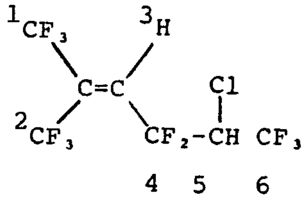
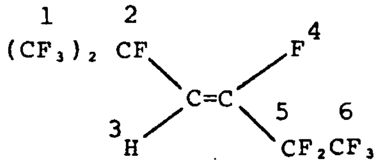
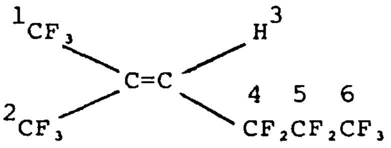
9.



SbF_6^- (104)

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
^{19}F spectrum: SbF_5			
+ 57.4	D(J=207) of M	1	5 or 7
+ 24.5	D(J=207) of M	1	5 or 7
- 62.3	M	3	2 or 9
- 62.6	M	3	2 or 9
- 68.8	Q(J=5)	3	1
^{1}H spectrum: SbF_5			
4.2	M	2	8
7.5	D(J=25)	1	4
7.6	D(J=26) of D(J=26)	1	6
^{13}C spectrum: SbF_5			
43.9	Q(J=33)		8
114.6	S		6
126.7	S		4
117.4	Q(J=277)		1 or 2
118.2	Q(J=278)		1 or 2
120.5	Q(J=280)		9
149.4	Sept. (J=36)		3
195.1	D(J=367)		5 or 7
211.9	D(J=375)		5 or 7

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
0.	 $(CF_3)_2CFCH_2\overset{+}{\overline{CF\text{-}CH\text{-}CF}}\text{-}\overset{+}{\overline{CF\text{-}CH\text{-}CF}}CH_2CF(CF_3)_2$ 1 2 3 4 5 6 6 5 4 3 2 1	$2SbF_6^-$	(105)
^{19}F spectrum: SbF_5			
+ 42.0	M	1	4 or 6
+ 40.6	M	1	4 or 6
- 79.0	D(J=6)	6	1
-182.1	M	1	2
^{1}H spectrum: SbF_5			
3.5	M	2	3
6.9	M	1	5
^{13}C spectrum: SbF_5			
41.4	S		3
94.5	D(J=232) of M(J=36)		2
122.1	S		5
123.1	Q(J=287) of D(J=26)		1
210.4	D(J=372)		4
224.8	D(J=371) of D(J=41)		6
61.		(109)	
^{19}F spectrum: neat			
- 59.2	D(J=33) of Q(J=8)	3	2
- 65.7	Q(J=8)	3	1
- 99.1	M	1	3

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
2.			
		(110)	
^{19}F spectrum			
- 58.9	T(J=23) of Q(J=8)	3	2
- 65.6	Q(J=8) of D(J=2)	3	1
- 69.0	T(J=10) of D(J=6)	3	6
- 98.0	AB(J=275)	2	4
^{1}H spectrum			
4.6	T(J=17) of Q(J=6)	1	5
6.8	T(J=13)	1	3
3.			
		(114)	
^{19}F spectrum: SbF$_5$			
- 79.7	D(J=5)	6	1
- 86.3	M	3	6
-113.9	M	1	4
-125.4	D(J=13)	2	5
-188.8	M	1	2
^{1}H spectrum: SbF$_5$			
5.4	D(J=29) of D(J=21)	-	3
64.			
		(115)	

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT

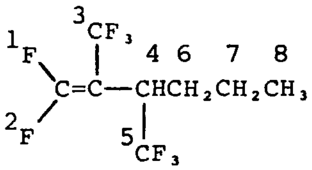
^{19}F spectrum: neat

- 61.1	M	3	2
- 68.5	Q(J=8)	3	1
- 82.9	T(J=9)	3	6
-113.5	M	2	4
-130.2	M	2	5

^{1}H spectrum: neat

6.7	T(J=13)	-	3

5.



(123)

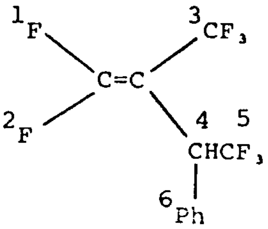
^{19}F spectrum

- 59.4	M, broad	3	3
- 68.2	M, broad	1	1 or 2
- 69.8	M	3	5
- 72.2	M, very broad	1	1 or 2

^{1}H spectrum

1.0	T(J=7)	3	8
1.4	M	2	7
1.8	M	2	6
3.1	M	1	4

66.



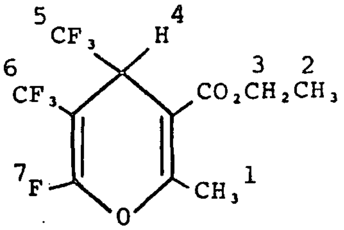
(127)

^{19}F spectrum

- 59.9	D(J=22) of D(J=10) of D(J=3)	3	3
- 66.6	D(J=11) of D(J=9) of D(J=3)	3	5
- 69.5	Q(J=22)	1	1
- 71.1	M	1	2

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
^{1}H spectrum			
4.4	Q(J=9) of D(J=3)	1	4
7.4	S	5	6

57.



(130)

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
^{19}F spectrum			
- 59.2	D(J=14) of Q(J=5)	3	6
- 74.2	M	3	5
- 79.8	Q(J=14) of D(J=7)	1	7
^{1}H spectrum			
1.3	T(J=7)	3	2
2.5	S	3	1
4.3	Q(J=11) of Q(J=7)	2	3
4.5	D(J=7) of Q(J=7)	1	4

3.

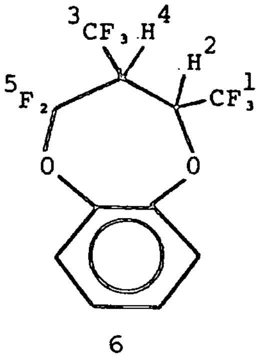
1,2 3 4 5 6 7 8
$(CF_3)_2CFCHFCF_2CH_2OH$

(134)

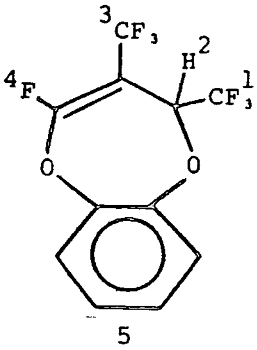
SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
^{19}F spectrum			
- 73.4	M	3	1 or 2
- 76.3	M	3	1 or 2
-121.1	AB (J=274)	2	6
-187.8	M	1	3
-211.7	M	1	5
^{1}H spectrum			
2.7	Broad	1	8
4.0	M	2	7
5.4	D(J=42) of D(J=18) of D(J=9) of D(J=5)	1	4

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT

69.



(132) +



(131)

Mixture containing 35% (131) and 65% (132)

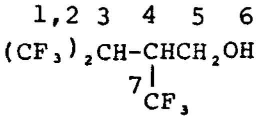
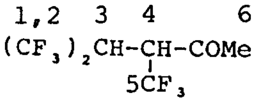
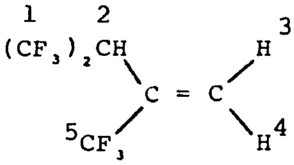
a denotes shifts for (131); b and c denotes shifts for the stereoisomers of (132)

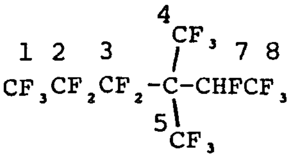
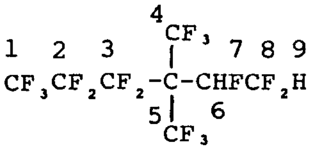
^{19}F spectrum

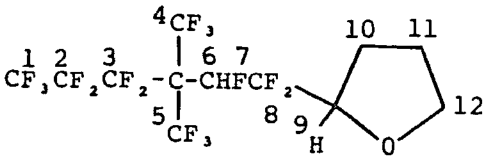
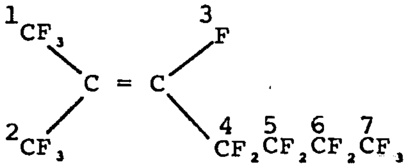
- 58.2	D(J=18) of Q(J=4)	3	3a
- 61.0	AB(J=168)	2	5c
- 61.5	Q(J=18) of D(J=5)	1	4a
- 62.6	M	3	3b
- 66.6	M	3	3c
- 67.1	AB(J=153)	2	5b
- 73.3	M	3	1a
- 74.3	M	3	1b
- 77.2	M	3	1c

^{1}H spectrum

3.6	M	2	4b,4c
4.8	D(J=6) of Q(J=6)	1	2c
4.9	Q(J=7)	1	2a
5.2	D(J=6) of Q(J=6)	1	2b
7.1	M	12	5a,6b,6c

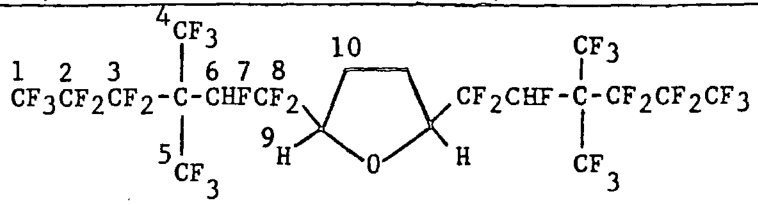
SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
	 $\overset{1,2}{(CF_3)_2}\overset{3}{CH}-\underset{{}^{7}CF_3}{\underset{\vert}{\overset{4}{C}H}}\overset{5}{CH_2}\overset{6}{OH}$	(13b)	
^{19}F spectrum			
- 62.4	M	1	7
- 65.6	M	1	1 or 2
- 66.9	M	1	1 or 2
^{1}H spectrum			
2.1	broad	1	6
3.1	M	1	4
3.6	sept.(J=9)ofD(J=1)	1	3
4.1	D(J=17)ofQ(J=9)	2	5
	 $\overset{1,2}{(CF_3)_2}\overset{3}{CH}-\underset{5CF_3}{\underset{\vert}{\overset{4}{CH}}}-\overset{6}{COMe}$	(135)	
^{19}F spectrum			
- 62.8	M	1	1,2,5
- 63.7	M	1	
- 64.1	M	1	
^{1}H spectrum			
2.5	S	3	6
3.7	Q(J=8)ofD(J=7)	1	4
4.0	M	1	3
		(139)	
^{19}F spectrum			
- 66.9	D(J=8)ofQ(J=1)	2	1
- 70.4	sept. (J=1)	1	5
^{1}H spectrum			
3.8	sept.(J=8)	1	2
6.2	S	1	3 or 4
6.3	S	1	3 or 4

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
73	 $\overset{1}{CF_3}\overset{2}{CF_2}\overset{3}{CF_2}-\underset{\underset{5}{CF_3}}{\overset{\overset{4}{CF_3}}{C}}-\overset{7}{CHF}\overset{8}{CF_3}$	(143)	
^{19}F spectrum: neat			
- 62.9	M	6	4,5
- 74.4	M	3	8
- 83.6	T(J=14)	3	1
-107.9	M	2	3
-125.4	M	2	2
-204.7	M	1	7
^{1}H spectrum: neat			
5.6	D(J=40)of M	-	6
74	 $\overset{1}{CF_3}\overset{2}{CF_2}\overset{3}{CF_2}-\underset{\underset{5}{CF_3}}{\overset{\overset{4}{CF_3}}{C}}-\overset{7}{C}\underset{6}{H}F\overset{8}{CF_2}\overset{9}{H}$	(142)	
^{19}F spectrum: $(CD_3)_2CO$			
- 60.9	M	3	4 or 5
- 61.6	M	3	4 or 5
- 81.3	T(J=14)	3	1
-106.1	M	2	3
-122.8	M	2	2
-128.0	AB(J=300)	2	8
-212.5	M	1	7
^{1}H spectrum: $(CD_3)_2CO$			
6.0	D(J=41)ofD(J=8)of D(J=2)	1	6
6.7	T(J=5)ofD(J=10)ofD(J=2)	1	9

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
			(144)
^{19}F spectrum			
- 59.5	M	3	4 or 5
- 59.7	M	3	4 or 5
- 80.2	M	3	1
-105.3	AB(J=300)	2	3
-114.4	AB(J=264)	2	8
-122.8	AB(J=265)		
-122.6	M	2	2
-200.2	M	1	7
^{1}H spectrum			
2.0	M	4	10,11 Overlapping signals
2.1	M		
3.9	M	2	12
4.3	M	1	9
5.8	D(J=39)ofD(J=22)	1	6
76 			(146)
^{19}F spectrum			
- 60.0	M	3	2
- 62.7	D(J=26)ofM	3	1
- 84.6	M	3	7
- 99.2	M	1	3
-116.6	M	2	4
-124.8	M	2	5
-129.4	M	2	6

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT

77.



(145)

(mixture of diastereoisomers)

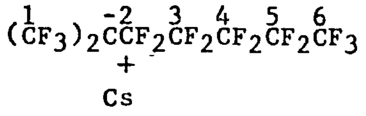
^{19}F spectrum

-59.4	M	3	4 or 5
-60.0	M	3	4 or 5
-80.2	M	3	1
-105.2	AB(J=294)	2	3
-114.4	AB(J=226)	2	8
-122.6	AB(J=277)		
-122.4	M	2	2
-122.7	M		
-200.2	M	1	7
-200.9	M		

^{1}H spectrum

2.3	M	2	10
4.6	M	1	9
5.6	M	1	6

78.

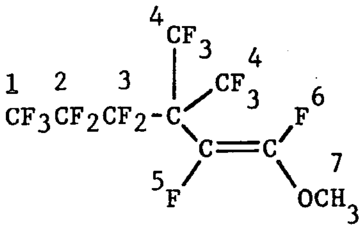
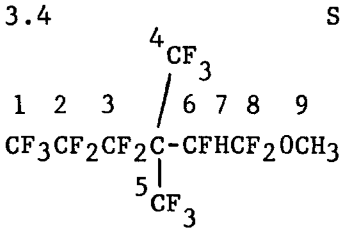


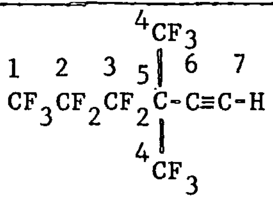
$(\overset{1}{C}F_3)_2\underset{\substack{+\\ Cs}}{\overset{-}{C}}\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_2\overset{6}{C}F_3$

(147)

^{19}F spectrum: Tetraglyme

-41.7	M	6	1
-81.8	M	3	6
-91.9	M	2	2
-112.6	M	2	3
-122.0	M	2	4
-126.5	M	2	5

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
79. 		(148)	
^{19}F spectrum			
-60.7	M	6	4
-80.8	M	3	1
-106.8	M	2	3
-124.5	M	2	2
-174.6	M	1	6
-179.3	D(J=119) of M	1	5
^{1}H spectrum			
3.4	S	-	7
80.  $CF_3CF_2CF_2C(CF_3)(CF_3)-CFHCF_2OCH_3$		(149)	
^{19}F spectrum			
-59.3	M	3	4 or 5
-60.2	M	3	4 or 5
-79.7	AB(J=147)	2	8
-80.5	M	3	1
-105.3	AB(J=300)	2	3
-122.6	M	2	2
-199.5	M	1	6
^{1}H spectrum			
3.7	S	3	9
5.4	D(J=41) of D(J=4) of D(J=4)	1	7

SHIFT/PPM	COUPLING/Hz	INTEGRAL	ASSIGNMENT
81.  $CF_3CF_2CF_2C(CF_3)_2{-}C{\equiv}C{-}H$		(150)	
^{19}F spectrum : $(CD_3)_2CO$			
-65.7	T(J=9) of T(J=9)	6	4
-81.3	T(J=12)	3	1
-109.6	M	2	3
-123.4	M	2	2
^{1}H spectrum : $(CD_3)_2CO$			
2.9	S	-	7
^{13}C Spectrum			
57.0	M(J=30)		5
65.8	S		6
80.7	S		7
109.1	T(J=272) of Q(J=38) of T(J=38)		2
113.4	T(J=273) of T(J=33)		3
117.6	Q(J=289) of T(J=33) of T(J=2)		1
120.4	Q(J=288)		4

APPENDIX TWO

MASS SPECTRA

The mass spectra of the compounds listed below were obtained by either electron impact (EI), chemical ionization (CI) or negative ion chemical ionization (NI) methods. Unless stated the mode of ionization was by electron impact.

1. 5H,5H-Pentadecafluoro-2-iodo-6-methylheptane (17a)
2. 7H,7H-Heneicosafluoro-2-iodo-4,8-dimethylnonane (17b)
3. 5,5,7,7-Tetrahydroheptadecafluoro-2-iodo-8-methylnonane (18a)
4. 2H,2H,6H,6H-Heptadecafluoro-1-iodo-3,7-dimethyloctane (19a)
5. 2,2,4,4,8,8-Hexa-hydrononadecafluoro-1-iodo-5,9-dimethyldecane (19b)
6. 2,2,6,6,8,8-Hexahydrononadecafluoro-1-iodo-3,9-dimethyldecane (20a)
7. 2,2,4,4,8,8,10,10-Octahydroheneicosafluoro-1-iodo-5,11-dimethyldodecane (20b)
8. 2,2,8,8-Tetrahydrotricosafluoro-1-iodo-3,5,9-trimethyldecane (19c)
9. 2,2,4,4,10,10-Hexahydropentacosafluoro-1-iodo-5,7,11-trimethyldodecane (19d)
10. 3,3,5,5,7,7-Hexahydrotetradecafluoro-2-methyloctane (15c)
11. 3,3,5,5,7,7,9,9-Octahydrohexadecafluoro-2-methylhexane (15d)
12. 3,3,5,5,7,7,9,9,11,11-Decahydrooctadecafluoro-2-methyldodecane (15e)
13. 3,3,7,7,9,9-Hexahydroeicosafluoro-2,6-dimethyldecane (26)
14. 2H,4H,4H-Undecafluoro-5-methylhex-(E)-2-ene (30)
15. 2H,4H,4H-Undecafluoro-5-methylhex-1-ene (29b)
16. 3,5,5,7,7-Pentahydroterdecafluoro-2-methyloct-2-ene (35) (NI)
17. 2,6,6-Trihydroheptadecafluoro-3,7-dimethyloct-1-ene (40) (CI)
18. 2H,4H,4H,6H,6H-Tridecafluoro-7-methyloct-1-ene (29c)
19. (Z)-3,5-Dihydrodecafluoro-2-methylhexa-2,4-diene (37a)
20. (E)-3,5-Dihydrodecafluoro-2-methylhexa-2,4-diene (37b)
21. (Z)-2,6,6,-Trihydroheptadecafluoro-3,7-dimethyloct-2-ene (41)
22. 2,3,5,5-Tetrahydroundecafluoro-3-methoxy-2-methylhexane (48)

23. 3,5,5-Trihydrononafluoro-1,3-dimethoxy-2-methylhex-1-ene (49)
24. 2,3,5,5,7,7-Hexahydro-3-phenoxyterdecafluoro-2-methyloctane (45b)
25. 3,5,5,7,7-Pentahydro-1,3-diphenoxyundecafluoro-2-methyloct-1-ene (46b)
26. 2,3,5,5,7,7-Hexahydro-1,3-diphenoxydodecafluoro-2-methyloctane (47b)
27. 2,3,5,5-Tetrahydro-3-phenoxyundecafluoro-2-methylhexane (45a)
28. 3,5,5-Trihydro-1,3-diphenoxynonafluoro-2-methylhex-1-ene (46a)
29. 2,3,5,5-Tetrahydro-1,3-diphenoxydecafluoro-2-methylhexane (47a)
30. 3,6,7-Trihydro-6-phenoxyhexadecafluoro-2,7-dimethyloct-2-ene (50)
31. 3,6-Dihydro-1,3-diphenoxytetradecafluoro-2,7-dimethylocta-1,6-diene (51)
32. 2,6,6,-Trihydro-2-methoxyhexadecafluoro-3,7-dimethyloct-3-ene (52a)
33. 2,6,6-Trihydro-2-phenoxyhexadecafluoro-3,7-dimethyloct-3-ene (52c)
34. 2,6,6-Trihydro-2,4-diphenoxypentadecafluoro-3,7-dimethyloct-3-ene (54)
35. 2,3,6,6-Tetrahydro-2,4-diphenoxyhexadecafluoro-3,7-dimethyloctane (53)
36. (Z)-2,4,5-Trihydro-4-methoxydecafluoro-5-methylhex-2-ene (56a)
37. 3,5-Dihydro-1,3-dimethoxyoctafluoro-2-methylhexa-1,4-diene (57)
38. (1,1,2,3,3-Pentahydroheptafluoro-2-iodo-4-methylpentyl) diallyl isocyanurate (61)
39. Bis(1,1,2,3,3-Pentahydroheptafluoro-2-iodo-4-methylpentyl) allyl isocyanurate (62)
40. Tris(1,1,2,3,3-Pentahydroheptafluoro-2-iodo-4-methylpentyl) isocyanurate (63)
41. 2H-Tetradecafluoro-1-iodo-5-methylhexane (68a)
42. 2H,4H-Heptadecafluoro-1-iodo-7-methyloctane (68b)
43. 4H-Tridecafluoro-5-methylhex-1-ene (69b)
44. 2H-Hexadecafluoro-1-iodo-3,3-dimethylhexane (80)
45. 2H,4H-Nonadecafluoro-1-iodo-5,5-dimethyloctane (82)
46. 1,1,2,2,4-Pentahydrohexadecafluoro-1-iodo-5,5-dimethyloctane (83)
47. 1,1,2,2,4,4-Hexahydrononafluoro-1-iodo-5-methylhexane (89a)
48. 1,1,2,2,3,3,4,4,6,6-Decahydrononafluoro-1-iodo-7-methyloctane (89b)

49. 1,1,2,4-Tetrahydrohexadecafluoro-5,5-dimethyloct-1-ene (85)

50. Hexadecafluoro-3,3-dimethylhex-1-ene (81)

51. 4H-Nonadecafluoro-5,5-dimethyloct-1-ene (84)

52. 1,1,2,4,4-Pentahydrononafluoro-5-methylhex-1-ene (90)

53. 5H,6H-Octacosafluoro-4,4,7,7-tetramethyldecane (93)

54. 2,2,-Dimethylpropyl-1,1,2,2-tetrafluoroethyl ether (96)

55. Methyl 2H,4H-heptafluoro-5-methylhexa-2,4-dienoate (109)

56. 3H,5H-5-Chloroundecafluoro-2-methylhex-2-ene (110)

57. 3H-Tridecafluoro-2-methylhex-2-ene (115)

58. 1,1,-Difluoro -2,3-bis(trifluoromethyl)hex-1-ene (123)

59. 3H-Octafluoro—3-phenyl-2-methylbut-1-ene (127)

60. 3-Ethoxycarbonyl-6-fluoro-2-methyl-4,5-bis(trifluoromethyl)-4H-pyran (130)

61. 6,7-Benzo-2-fluoro-3,4-bis(trifluoromethyl)-1,5-dioxacyclohept-2-ene (131)

62. 6,7-Benzo-2-difluoro-3,4-bis(trifluoromethyl)-1,5-dioxacycloheptane (132)

63. 1,1,3-Tetrahydrodecafluoro-4-pentan-1-ol (134)

64. 1,1,2,3-Tetrahydrononafluoro-2,3-dimethylbutan-1-ol (136)

65. 1,1,1,3,4-Pentahydrononafluoro-3,4-dimethylpentan-2-one (135)

66. 1,1,3-Trihydrononafluoro-2,3-dimethylbut-1-ene (139)

67. 2H-Heptadecafluoro-3,3-dimethylhexane (143)

68. 1H,2H-Hexadecafluoro-3,3-dimethylhexane (142)

69. 2-(2H-Hexadecafluoro-3,3-dimethylhexyl)tetrahydrofuran (144)

70. 2,5-Bis(2H-hexadecafluoro-3,3-dimethylhexyl)tetrahydrofuran (145)

71. Hexadecafluoro-2-methylhept-2-ene (146)

72. (E)-1-1Methoxypentadecafluoro-3,3-dimethylhex-1-ene (148)

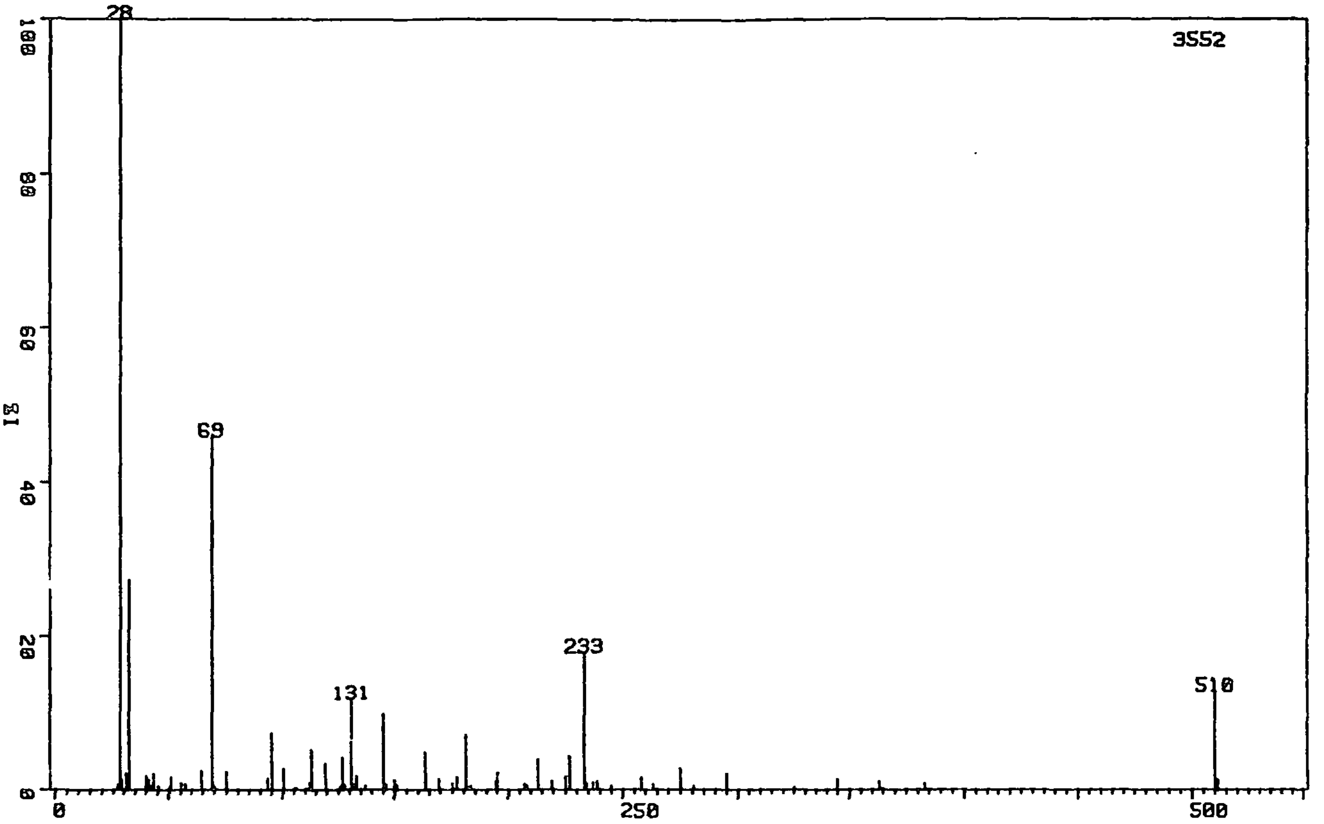
73. 2H-1-Methoxyhexadecafluoro-3,3-dimethylhexane (149)

74. 1H-Tridecafluoro —3,3-dimethylhex-1-yne (150)

GAM9 2 G.APSEY CAL:CALT9 STA:

No 1

01-OCT-86 8:26



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     31.97  27.34
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     40.95   1.41
     43.08   1.04
     43.12   2.11
     50.95   1.63
     64.13   2.39
     68.99  45.92
     75.11   2.34
     93.08   1.55
     95.12   7.40
     99.95   2.76
    113.07   5.21
    119.00   3.43
    126.99   4.19
    131.04  11.91
    133.11   1.83
    145.11   9.91
    150.01   1.24
    163.09   4.93
    169.04   1.44
    176.98   1.66
    181.06   7.18
    194.09   1.10
    195.10   2.22
    213.09   3.94
    219.05   1.10
    225.11   1.77
    226.98   4.36
    233.10  17.93
    238.95   1.18
    257.98   1.63
    275.10   2.84
    295.13   2.11
    345.18   1.32
    363.16   1.10
    510.32  12.84
    511.30   1.38
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Bpm=69   I=1Cv   Hm=662   TIC=[illegible]            Acnt:          Sys:MPSE                                  HMR:
6.MPSEY                                                  EC= 115°  Col:[illegible]                           MASS:
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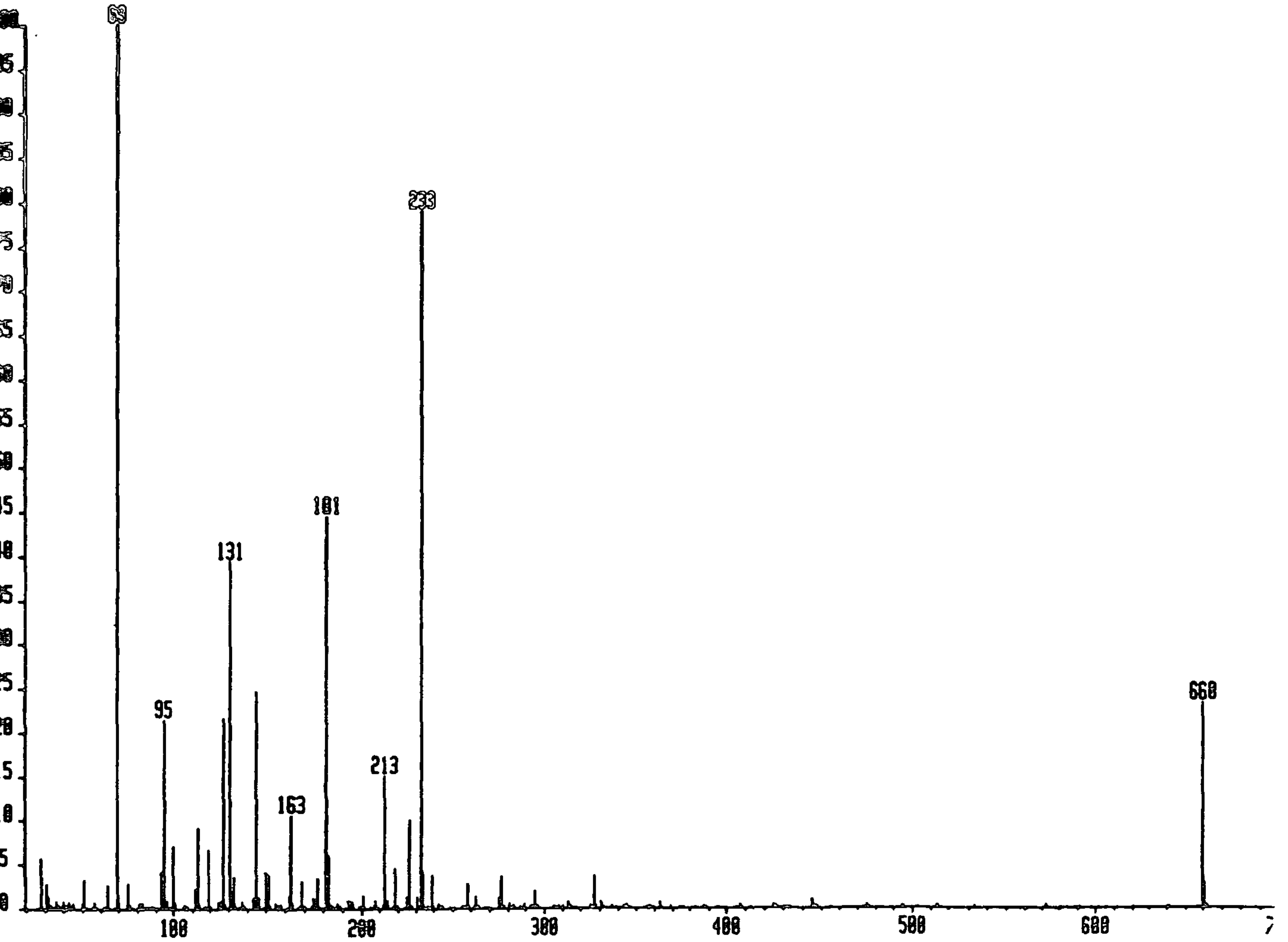

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  55.95       0.14              150.98        3.65           239.86        0 12
  56.96       0.55              151.98        0.11           242.95        0.49
  61.96       0.13              154.96        0.38           243 95        0.11
  63.98       2.52              155.96        0.11           244 96        0.20
  68.99     100.00 0            156.98        0.37           256 96        0 18
  69.99       1.34              157.88        0.29           257.86        2 69
  73.99       0.31              161.96        1.35           258.86        0 10
  75.00       2.66              162.97       10.47           261 95        0.20
  76.01       0.29              163.98        0.48           262.96        1 14
  81.00       0.48              167.97        0.19           274 95        1 04
  82.00       0.45              168.96        2 98           275.96        0 10
  83.01       0.44              169.94        0.10           276 86        3 54
  92.98       3.96              174.96        0.98           277.87        0 11
  93.99       0.43              175.98        0.18           280.95        0.40
  94.99      21.35              176.87        3.24           282 97        0.30
  96 00       0.67              180 96       44.51           286 95        0 11
  98.98       0.14              181 96        1 83           288 87        0 45
  99.98       6.91              182 97        5 92           292.94        0 10
 100.98       0.67              183 98        0 23           294.97        1 83
 104.98       0.11              186.96        0 38           295.97        0 13
 105.98       0.27              188 87        0 13           312 96        0 58
 106.99       0.15              192 96        0 71           313.97        0 35
 111.98       2.05              193 96        0 68           324.97        0 31
 112.98       9.05              194 96        0.56           326 87        3 49
 113.99       0.33              198.96        0 13           327.87        0.15
 116.97       0.20              199 95        0 18           330 97        0 63
 118.97       6 48              200.96        1 37           344 98        0 32
 119.98       0.14              204 95        0 20           356.97        0 18
 123.97       0.55              206.97        0 36           362.97        0 59
 124.98       0.60              207 86        0 70           406 99        0.24
 125.99       0.76              211 95        0 36           424.98        0 29
 126 88      21.50              212 95       14 [illegible]  425 98        0.10
 127.90       0.22              213 96        0 77           444 97        0 92
 130.97      39.24              218 95        4 48           447.00        0.19
 131.97       1.27              219 96        0 18           474.98        0 23
 132.98       3.40              224 96        1 19           494.96        0.20
 134.00       0.10              226.86        7.94           512.97        0.16
 136.98       0.67              227 86        0 18           532.98        0 11
 142.97       1.05              230.95        1 20           571.90        0.30
 143.98       0.85              232.97       79.02           659.90       23.09 F
 144.98      24.56              233.97        4 19           660.93        2.64 F
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GA51X092◦ ¤1 Bgd=69 9-NOV-87 15:4◦8:06:23 70E EI◦
BpM=0 I=10v ▭=575 TIC=412512889 Acnt: Sys:RPSE HMR:
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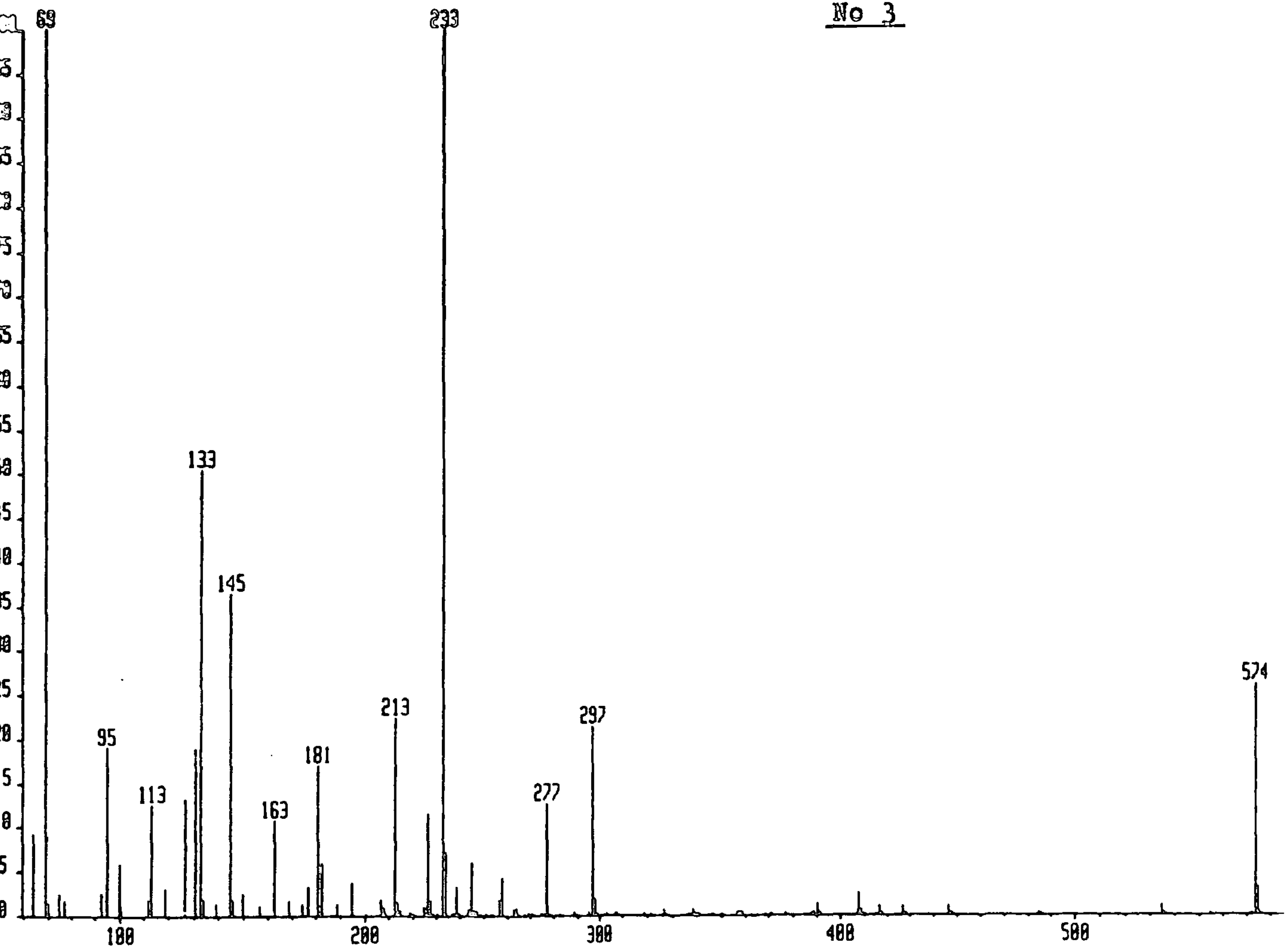
No 3



Mass	% Base
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31.90	1.43
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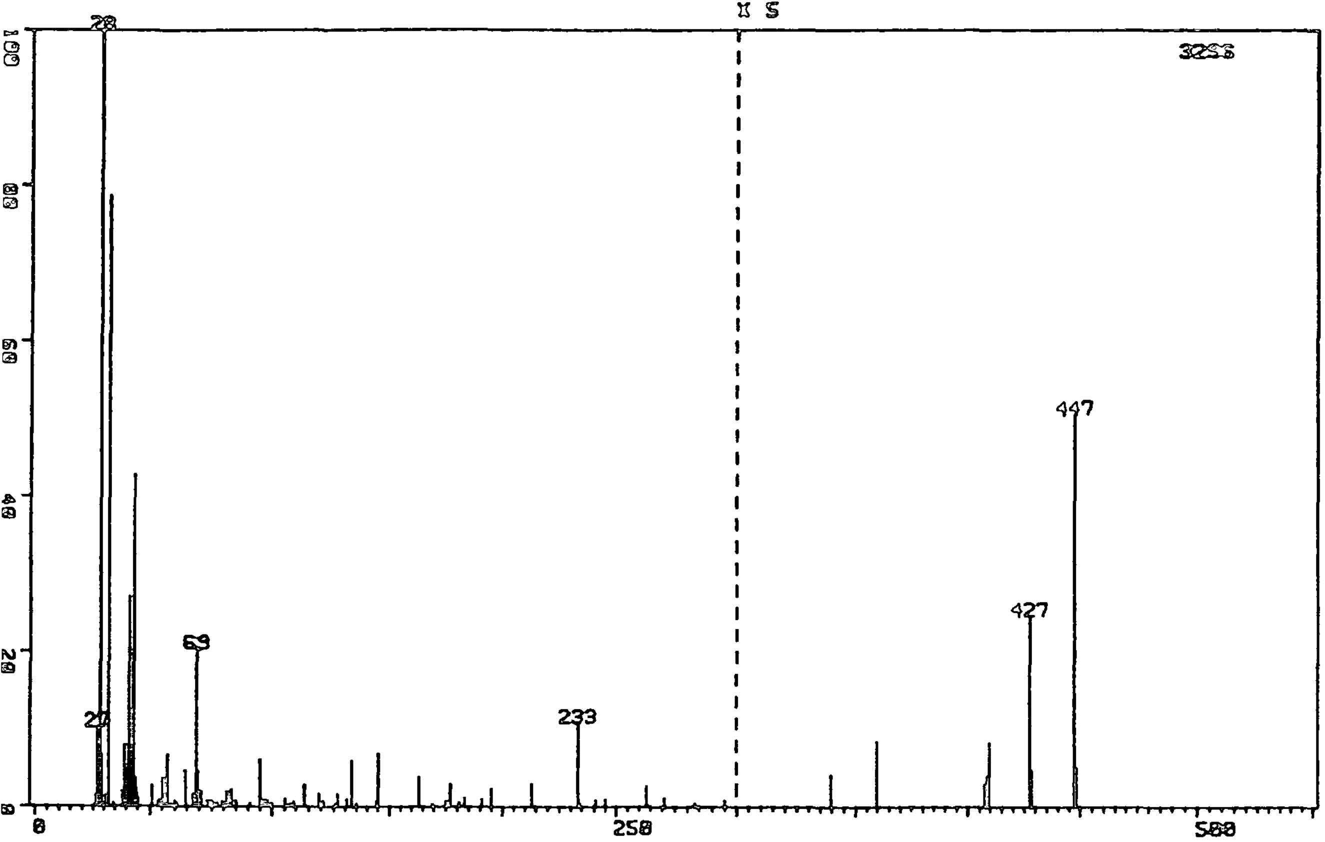
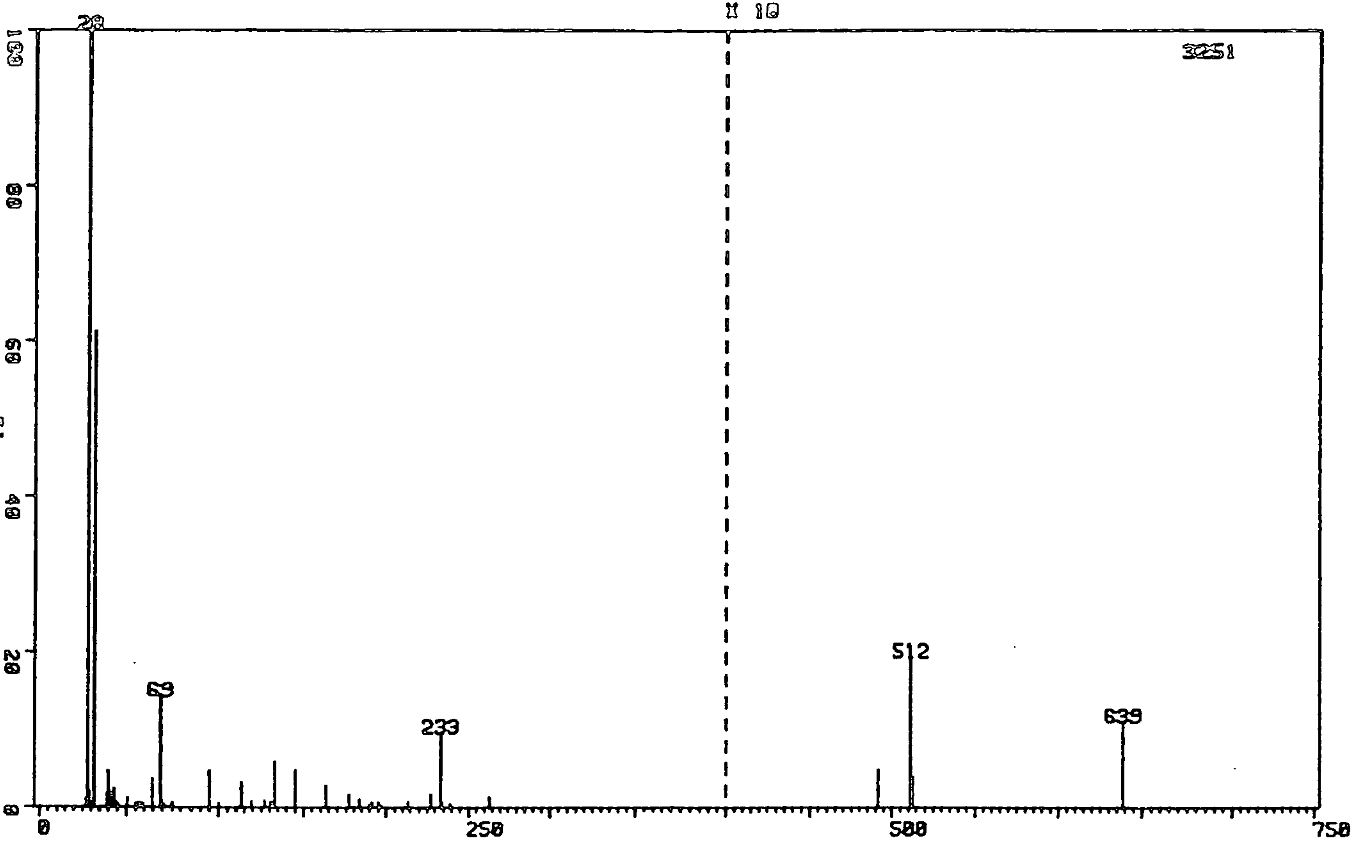
44.94	1.95
50.91	5.56
56.94	1.19
58.96	4.88
63.95	9.14
68.95	100.00 O
69.96	1.33
74.97	2.33
76.99	1.66
92.97	2.44
94.98	18.99
99.96	5.83
100.98	1.02
111.96	1.66
112.97	12.40
118.97	3.02
126.89	13.15
130.96	18.97
132.97	50.49
133.97	1.72
138.98	1.34
144.97	36.49
145.96	1.56
149.95	2.35
156.97	1.06
162.96	10.69
168.96	1.62
174.96	1.15
176.87	3.12
180.95	16.94
182.94	5.85
188.97	1.26
194.96	3.49
206.96	1.61
212.95	22.43
213.95	1.37
226.86	11.62
227.96	1.70
232.96	100.00 O
244.96	5.97
256.96	1.60
257.99	4.21
276.95	12.93
296.97	21.39
297.98	1.73
390.85	1.23
406.94	0.35
407.96	2.30
408.96	0.43
409.96	0.05
416.88	0.81
417.87	0.08
426.95	0.82
427.96	0.18
446.99	0.89
448.01	0.11
484.86	0.16
485.88	0.03
534.87	1.07
535.87	0.14
554.89	0.14
571.78	0.02
572.18	0.03
572.47	0.05
573.85	25.97 F
574.87	2.98 F
575.86	0.15

GAMG 10 G.APSEY E.I. **No 4** 01-OCT-86
CRL:CRLT9 STA: 1:34



MASS	%HT. BASE
26.29	1.46
27.23	10.29
28.10	100.00
28.12	2.28
28.96	3.31
28.99	6.52
30.86	1.43
30.88	1.37
31.97	78.64
38.04	1.97
38.97	7.98
39.81	5.13
39.87	1.76
40.95	27.06
42.05	12.47
43.08	2.28
43.12	42.72
44.09	3.61
44.16	1.55
45.14	1.09
50.96	2.70
55.18	3.67
57.17	6.64
64.14	4.70
67.13	1.67
68.08	1.24
68.97	20.39
69.04	4.64
69.99	1.06
71.06	2.03
81.08	1.97
82.13	1.18
83.13	2.25
95.03	6.19
95.10	1.15
105.11	1.00
112.99	2.85
118.94	1.64
126.91	1.61
130.97	1.06
133.03	6.01
145.07	6.80
163.09	3.89
176.98	2.88
183.11	1.21
213.12	2.91
233.13	10.92
245.14	1.06
263.11	2.64
270.99	1.18
359.27	1.70
409.37	1.67
427.42	4.95
447.46	10.13
448.48	1.00

GAM7 3 G.APSEY E.I. No 5 01-OCT-86
CAL:CALT9 STA: 0:35

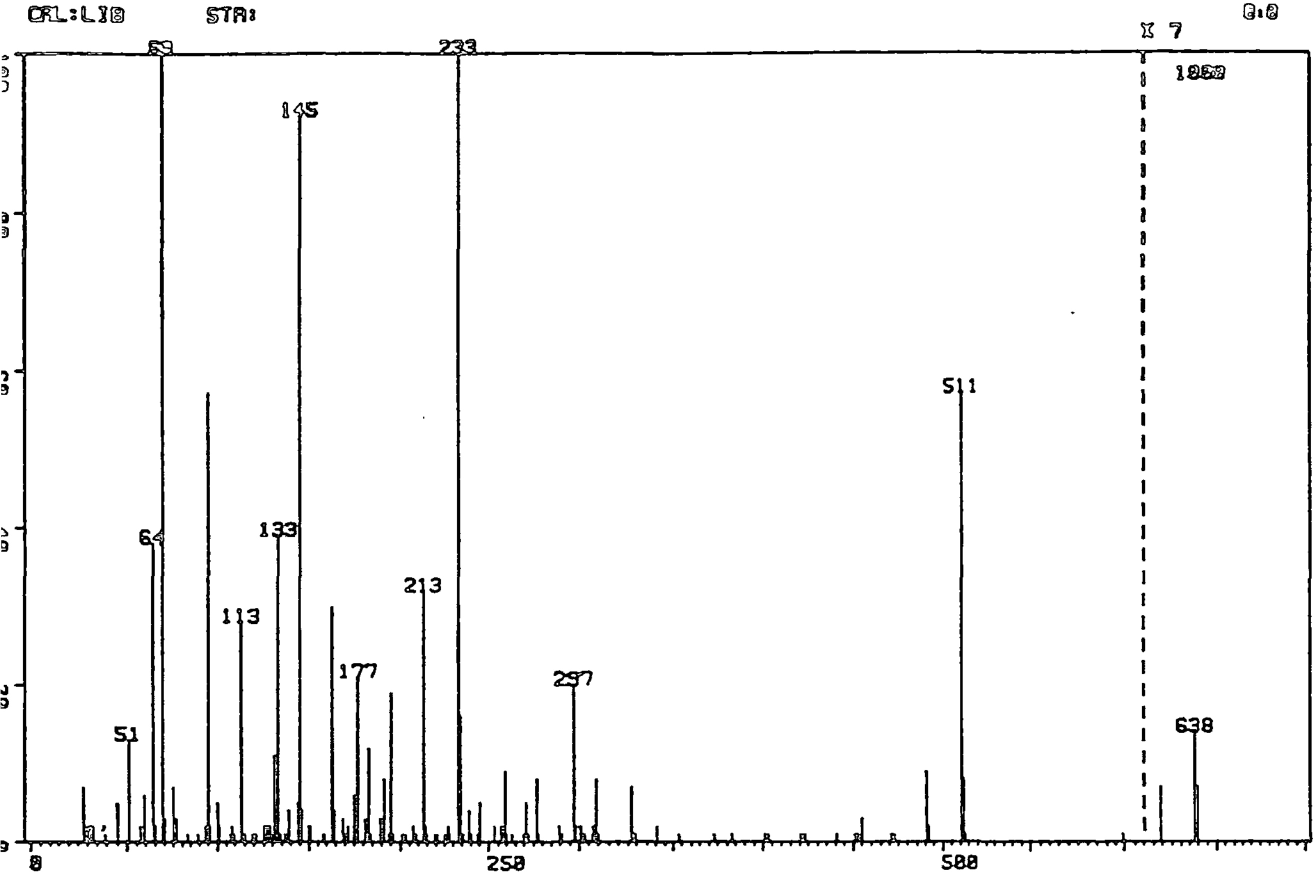


MASS	%HT. BASE
27.23	1.14
28.10	100.00
28.96	2.03
31.97	61.15
38.96	1.02
39.81	4.64
40.95	1.41
43.08	1.51
43.12	2.46
50.96	1.17
64.14	3.66
68.99	14.30
95.12	4.77
113.08	3.26
133.10	5.94
145.12	4.80
163.10	2.92
177.02	1.75
183.15	1.14
227.12	1.72
233.10	9.69
263.11	1.32
511.69	1.94
638.82	1.11

GASSX 0
CAL:LIB   STA:

No 6

19-SEP
0:0



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MASS     % BASE
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  30.90     2.12     189.91     0.21     245.93    0.61     327.92    6.60     454.80    3.04
  31.98     1.61     190.86     7.86     246.93    0.16     328.93    0.62     455.79    0.28
  33.00     1.61     191.87     0.15     248.94    0.05     332.91    0.21     470.89    1.09
  39.01     1.18     192.93     0.28     250.92    0.18     334.91    0.04     471.89    0.81
  45.00     4.63     193.94     0.81     251.88    0.08     334.98    0.05     472.90    0.47
  50.98    12.27     194.38     0.06     252.84    1.68     336.91    0.06     473.95    0.06
  56.99     2.02     194.94    18.38     253.84    0.08     338.91    0.34     489.57    0.03
  59.01     6.09     195.95     0.94     256.93    2.02     339.92    0.05     490.21    0.04
  63.99    37.44     198.94     0.13     257.99    0.31     340.82    1.47     490.40    0.07
  65.00     1.85     199.94     0.13     258.47    0.09     341.86    0.11     490.88    9.01
  68.97   100.00 O   200.94     0.49     258.94    9.16     342.90    0.06     491.88    1.73
  69.98     2.35     201.93     0.04     259.95    0.74     344.92    0.04     492.89    0.15
  74.98     6.96     201.99     0.04     262.91    0.97     346.90    0.17     500.14    0.02
  76.99     2.91     202.86     0.49     263.93    0.28     350.93    0.04     500.61    0.03
  82.98     1.01     202.99     0.05     264.92    0.28     352.91    0.32     500.86    0.05
  88.99     1.22     204.56     0.04     268.92    0.53     353.83    0.16     510.94   56.66 F
  92.96     1.56     204.69     0.03     269.95    0.11     356.90    0.14     511.97    7.30 F
  93.97     1.24     204.89     0.06     270.16    0.05     358.90    0.12     512.44    0.04
  94.98    57.10     205.95     0.02     270.39    0.03     362.91    0.26     512.97    0.50
  95.98     2.03     206.94     1.57     270.53    0.04     366.83    0.18     548.81    0.03
  99.96     4.77     207.93     0.21     270.83    4.69     370.86    0.11     568.78    0.04
 100.98     1.99     208.88     1.07     271.84    0.46     372.92    0.51     578.00    0.05
 112.96    27.78     209.78     0.05     272.93    0.09     373.94    0.04     590.84    0.19
 113.97     1.23     209.89     0.06     274.90    0.16     380.89    0.07     618.79    0.49
 114.98     0.54     210.01     0.04     275.92    0.05     381.90    0.04     619.77    0.04
 116.96     0.07     210.94     0.11     276.93    7.50     382.91    0.45     619.89    0.03
 126.86    12.03 F   211.42     0.03     277.93    0.50     383.92    0.07     637.79    1.77
 126.98     1.93 F   212.93    31.86     281.94    0.04     384.83    0.09     638.80    0.20
 127.87     1.34     213.93     2.02     282.91    0.19     385.82    0.25
 127.98     0.13     214.94     0.76     286.91    0.23     386.88    0.12
 128.89     0.60     215.95     0.05     287.91    0.29     388.91    0.04
 129.86     0.13     217.91     0.10     288.12    0.03     390.83    0.07
 130.95    11.18     218.93     1.18     288.28    0.06     395.81    0.07
 131.91     0.59     219.94     0.52     288.91    1.63     400.90    0.36
 132.97    39.32     220.87     0.88     289.92    0.19     401.91    0.18
 133.95     1.28     224.92     1.04     290.83    1.03     402.90    0.80
 135.07     0.19     225.93     0.20     291.85    0.07     432.89    0.18
 144.96    92.03     226.91     1.36     294.91    0.19     434.78    0.21
 145.96     4.00     227.95     1.08     296.93   19.71     435.78    0.07
 162.94    29.72     228.88     0.05     297.94    1.59     440.90    0.78
 176.85    21.10     228.97     0.07     298.92    0.09     441.92    0.24
 177.90     0.25     230.74     0.02     300.91    1.29     450.57    0.04
 180.93     2.69     230.91     0.23     301.90    0.14     450.89    1.14
 182.94    11.90     231.08     0.04     302.83    1.06     451.85    0.69
                     231.23     0.03     303.83    0.04     452.29    0.05
                     231.29     0.06     306.92    1.60     452.43    0.04
                     232.97   100.00 FO  307.92    2.11     452.88    0.39
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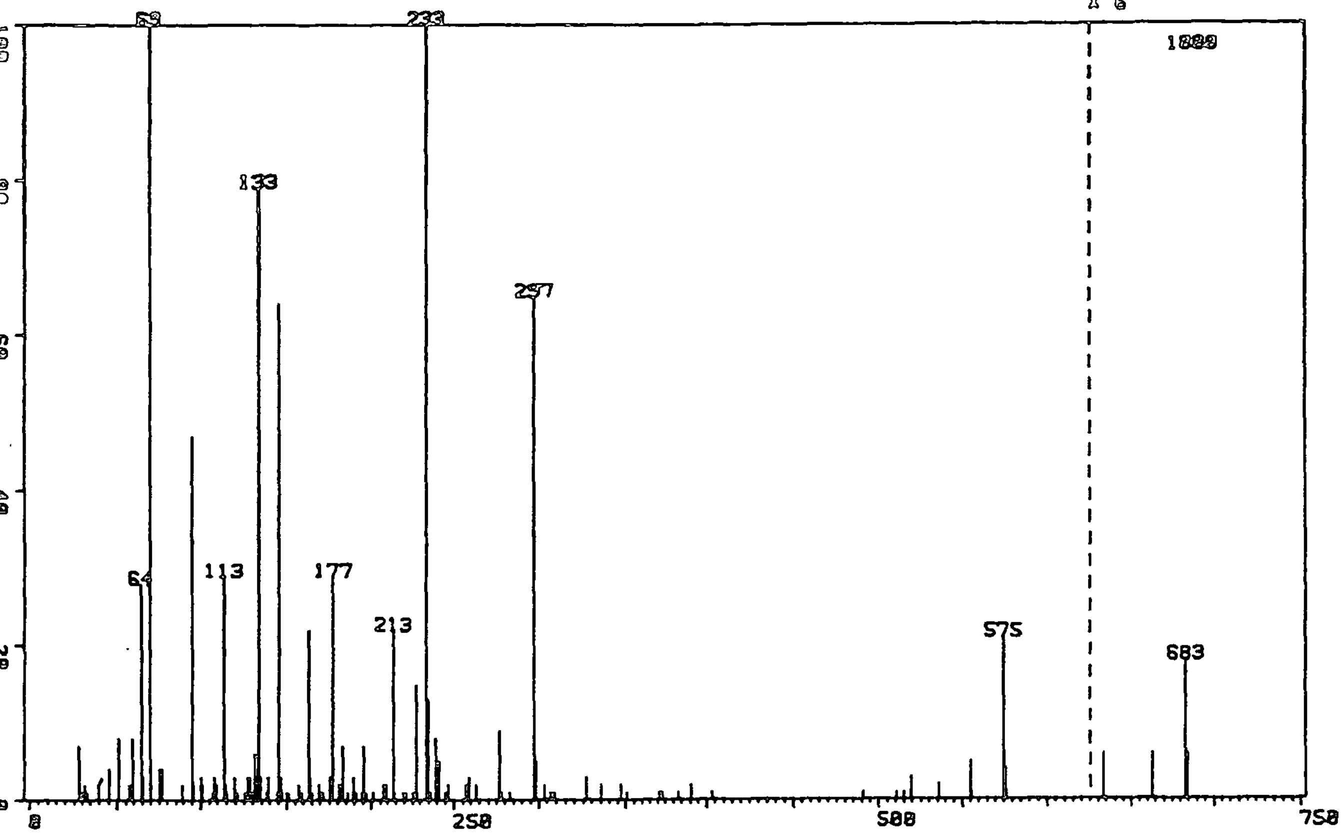
GASS 0 No 7 19-SEP

CAL:LIB STA: 8:0



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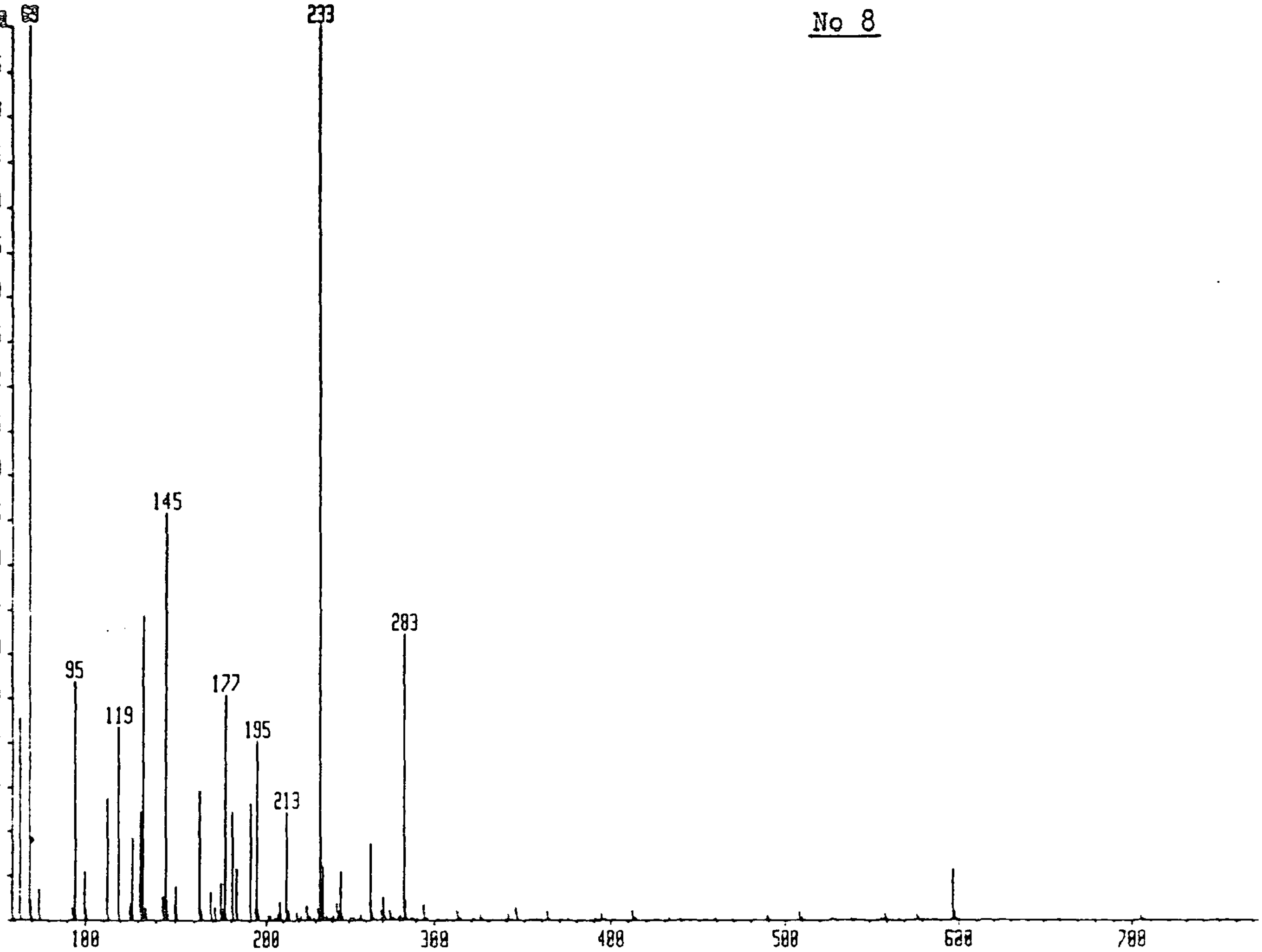
31.98	1.84	132.97	78.40	214.95	0.16	312.92	0.06
33.00	1.22	133.96	2.67	226.94	15.16	314.87	0.12
39.01	2.15	144.96	64.06	227.95	1.26	318.91	0.09
45.00	3.64	145.96	2.83	228.92	0.06	320.93	0.11
50.99	7.43	146.97	0.54	228.98	0.04	322.95	0.21
57.00	1.41	147.97	0.04	230.93	0.14	326.92	2.72
59.01	7.83	149.95	0.81	231.06	0.03	327.93	0.31
63.99	20.11	150.96	0.90	231.15	0.02	332.93	0.14
65.00	3.18	151.87	0.05	231.34	0.03	334.83	1.98
68.98	100.00 O	151.97	0.08	231.51	0.06	335.83	0.14
69.98	1.50	152.87	0.25	232.92	100.00 FO	338.91	0.13
74.98	3.25	152.99	0.04	233.94	12.46 F	340.84	0.11
77.00	3.97	153.25	0.03	234.20	0.03	346.92	1.63
80.99	2.19	153.40	0.04	234.92	0.28	518.87	2.41
94.98	46.71	153.52	0.04	235.93	0.64	519.87	0.30
95.98	1.61	153.62	0.04	236.45	0.07	534.28	0.05
99.96	2.63	153.68	0.03	236.93	0.14	535.82	1.29
100.98	1.40	153.95	0.11	237.93	0.12	537.80	0.08
101.99	0.16	154.94	0.05	238.94	7.47	554.87	4.36
105.97	0.18	155.95	0.07	239.94	0.67	555.88	0.69
106.98	0.46	156.94	1.55	240.84	4.70	556.81	0.08
107.98	2.66	157.92	0.47	256.93	1.41	556.97	0.06
108.99	1.61	158.92	1.12	258.66	2.38	573.26	0.03
109.99	0.08	159.95	0.09	259.95	0.15	573.58	0.06
111.96	0.29	160.95	0.06	262.92	1.77	574.90	20.99 F
112.96	28.87	161.92	0.04	263.94	0.18	575.93	3.43 F
113.97	1.37	162.94	21.60	264.93	0.11	576.93	0.24
114.98	1.23	174.87	2.68	267.95	0.12	618.84	0.03
115.99	0.06	175.91	0.66	268.93	0.20	632.80	0.22
116.93	0.06	176.47	0.04	270.85	0.30	662.79	0.06
116.97	0.06	176.86	28.30	272.95	0.20	682.82	2.20
117.02	0.04	177.89	0.28	274.92	0.07	683.81	0.35
117.19	0.02	180.94	1.53	276.92	8.53		
118.96	2.99	182.94	6.92	277.93	0.75		
119.98	0.36	194.95	6.53	280.91	0.03		
120.99	0.58	195.95	1.00	282.92	1.18		
123.96	0.10	196.47	0.06	296.90	65.26		
124.97	0.68	196.96	0.83	297.50	0.03		
125.97	1.18	198.94	0.14	297.91	4.78		
126.86	6.34 F	199.95	0.10	298.90	0.17		
126.90	2.75 F	200.94	0.34	300.88	0.17		
127.96	2.33	202.86	0.31	301.93	0.05		
128.90	0.78	206.91	2.22	302.93	2.12		
129.87	0.14	207.90	0.48	303.94	0.30		
130.95	5.40	208.89	1.58	304.92	1.21		

```
CX01120      x1     Bgd=59    9-NOV-87  16:1-0 07:42   70E          EI+
BpM=0       I=10v    Hm=705   TIC=435151000                Acnt:          Sys:APSE                                       HMR:
                                                        GC= 135⁰   Cal:PFK2                                        RASS:
```

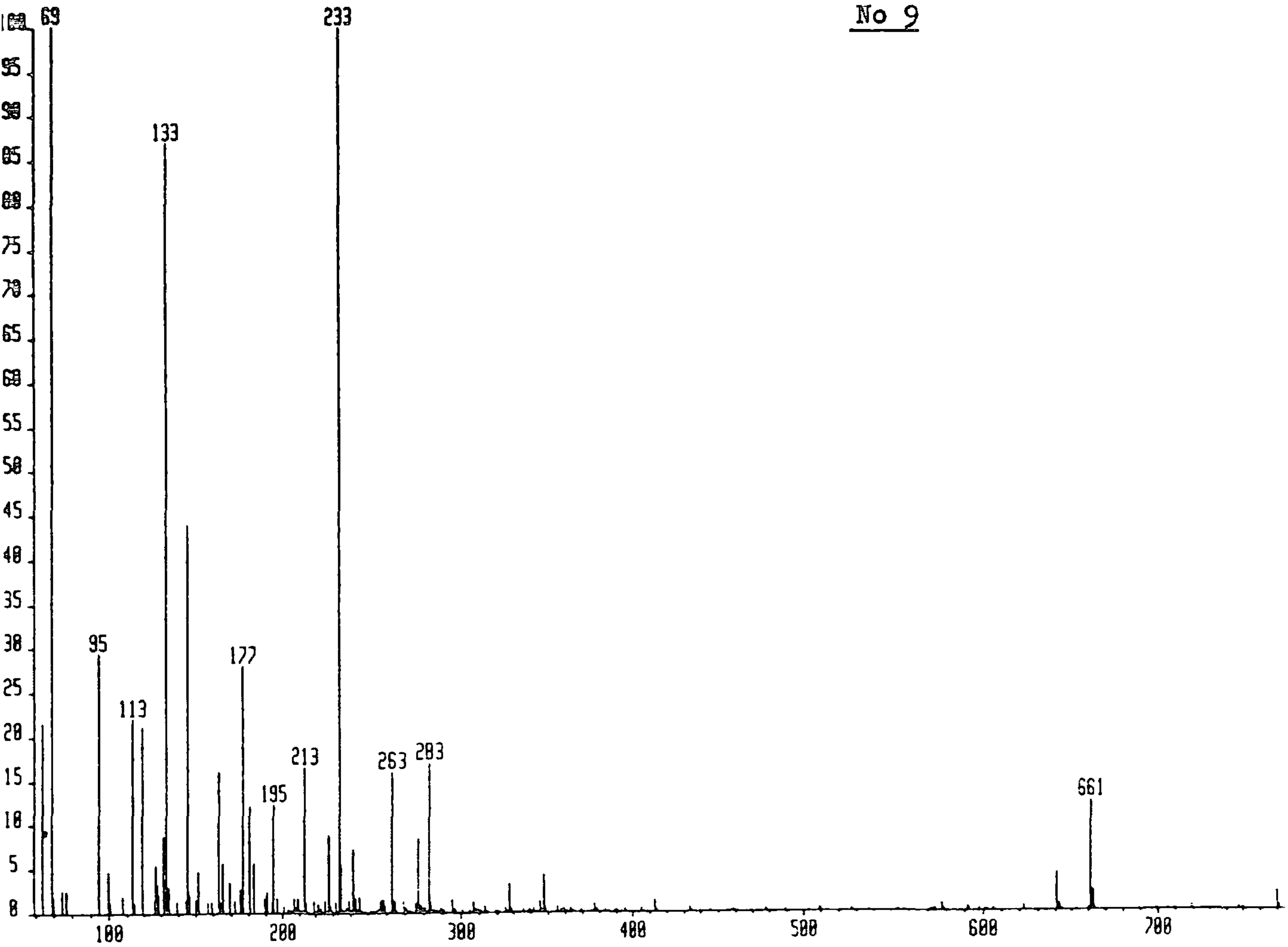
No 8



Mass	% Base
27.91	8.08
30.90	1.63
31.90	2.06
44.94	2.73
50.91	4.35
63.95	22.84
68.95	100.00 0
69.95	2.02
74.97	3.45
92.97	1.24
94.98	26.81
99.97	5.34
100.97	1.04
112.97	13.67
118.96	21.80
124.97	1.06
125.98	1.81
126.88	9.22
130.96	12.18
132.98	34.23
134.00	1.15
143.96	2.50
144.97	45.83
145.97	2.05
149.95	1.43
150.96	3.63
162.96	14.49
163.96	1.09
167.96	0.16
168.95	3.16
169.96	0.13
170.87	0.10
171.88	1.29
172.89	0.03
173.94	0.05
174.96	3.99
175.97	1.00
176.86	25.35
177.87	0.29
180.95	11.93
181.96	0.57
182.97	5.69
193.95	1.13
194.96	20.21
195.96	1.06
198.96	0.05
200.95	0.44
202.87	0.29
204.94	0.14
205.96	0.08
206.96	0.65
207.84	0.03
207.95	0.06
208.86	1.90
209.84	0.04
211.94	0.19
212.95	12.21
213.96	0.98
217.96	0.07
218.95	0.68
219.97	0.04
220.87	0.31
223.93	0.04
224.10	0.04
224.29	0.02
224.34	0.04
224.43	0.04
224.56	0.03
224.70	0.04
224.95	1.54
225.96	0.18
226.86	0.37
228.96	0.15
230.95	1.12
231.71	0.03
232.96	100.00 0
233.44	0.04
233.54	0.04
233.97	5.91
234.97	0.14
236.96	0.32
237.95	0.03
238.01	0.04
238.87	0.19
240.87	0.38
242.95	1.74
262.95	8.49
263.95	0.94
264.94	0.07
268.94	0.93
269.93	0.05
270.86	2.36
271.86	0.30
274.95	0.93
275.96	0.13
276.85	0.05
278.95	0.24
279.46	0.06
280.94	0.37
281.89	0.03
281.98	0.05
282.45	0.04
282.96	32.10
283.96	2.09
284.96	0.06
286.96	0.11
288.91	0.08
290.86	0.10
292.94	0.04
294.96	1.59
295.96	0.10
300.95	0.04
301.85	0.05
302.88	0.20
304.96	0.05
306.96	0.13
312.95	0.85
313.95	0.12
320.86	0.22
321.86	0.07
324.95	0.50
325.96	0.12
326.94	0.04
330.86	0.05
330.94	0.05
332.95	0.07
336.94	0.04
338.91	0.07
340.87	0.56
412.94	0.91
413.96	0.11
424.94	0.04
426.97	0.03
432.94	0.15
438.95	0.04
452.93	0.05
459.02	0.10
468.97	0.16
488.96	0.42
489.99	0.09
508.97	0.71
509.97	0.08
526.97	0.10
527.99	0.05
538.96	0.14
540.88	0.06
556.97	0.10
557.95	0.06
558.96	0.56
559.98	0.09
566.85	0.05
576.96	0.52
577.95	0.10
596.43	0.02
596.97	5.66
597.96	0.80
598.98	0.06
685.00	0.04
704.90	0.28
705.87	0.04

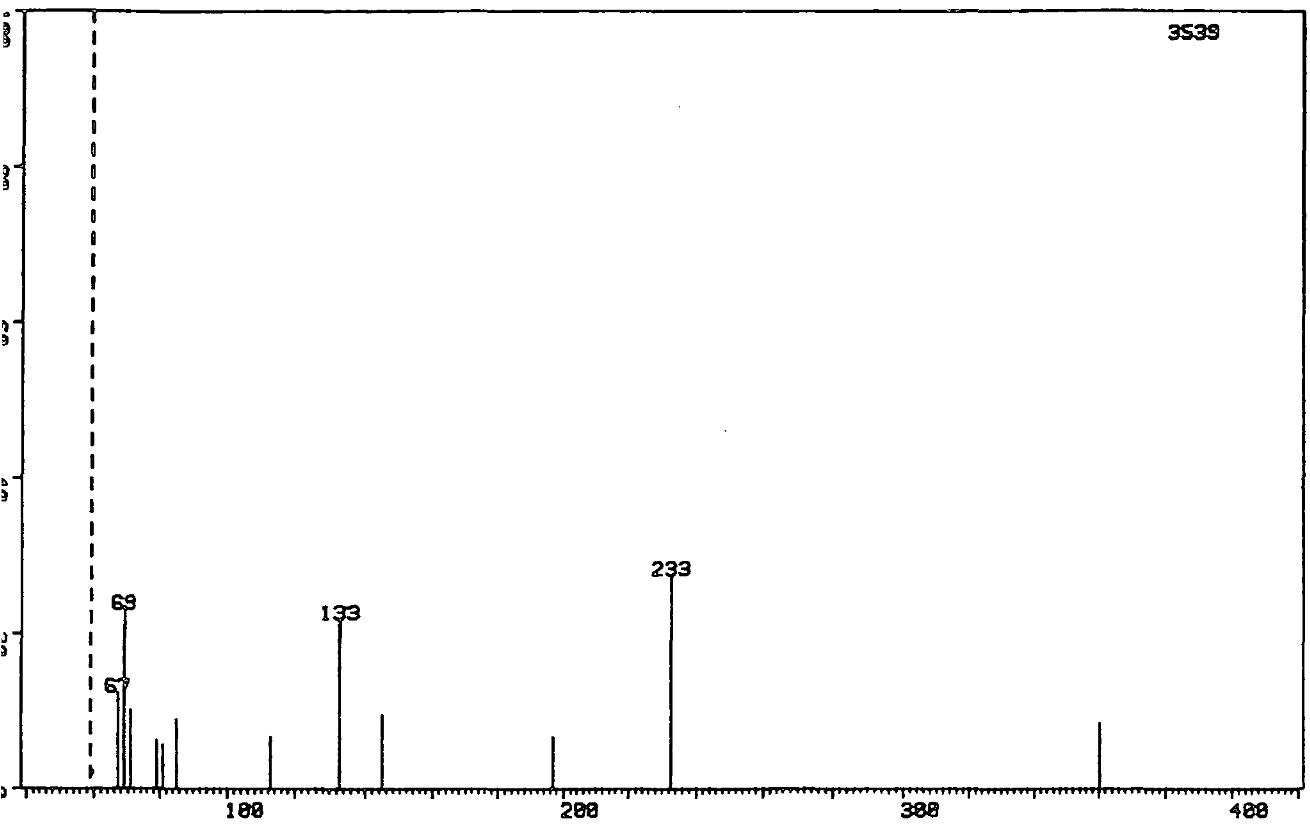
```
GAS4X0151o      x1    Bgd=147   10-NOV-87 08:5+0:10:27   70E          EI+
BpM=0      I=10v    Ha=770   TIC=506152888              Acnt:             Sys:APSE                                  HRR:
                                                           EC= 163°  Cal:PFK2                                  MASS:
```

No 9



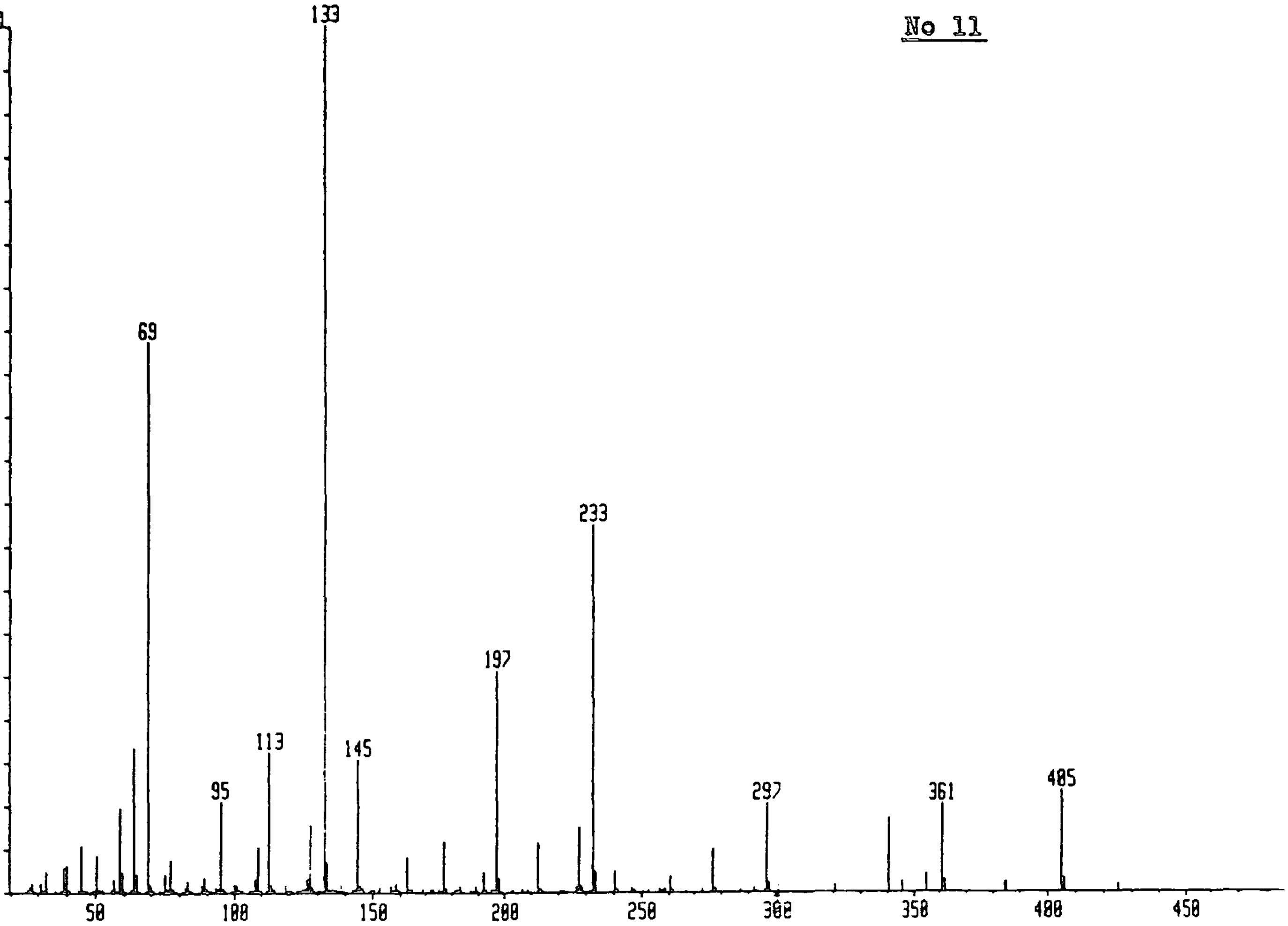
Mass	% Base						
27.94	7.11	164.14	1.03	238.19	0.21	341.16	0.29
30.94	1.12	164.41	0.02	239.20	1.21	343.24	0.05
31.94	1.71	165.15	5.47	240.20	0.13	345.26	1.02
38.99	1.06	166.16	0.27	241.11	7.14	346.26	0.09
44.99	2.78	168.15	0.12	242.11	0.22	347.28	4.13
50.98	5.93	169.14	3.33	243.18	1.53	413.30	1.17
59.03	3.03	170.15	0.29	244.19	0.29	414.30	0.11
64.03	21.44	171.13	0.08	244.43	0.03	433.31	0.51
69.03	100.00 O	172.06	1.16	244.60	0.05	577.40	0.69
70.04	1.64	173.07	0.09	245.20	1.63	578.43	0.09
75.06	2.42	174.11	0.03	262.21	0.05	591.42	0.48
77.08	2.31	174.16	0.04	262.88	0.03	592.42	0.11
95.09	29.37	175.15	2.53	263.20	15.91	597.40	0.11
100.08	4.58	177.06	27.91	264.20	1.12	601.21	0.03
101.09	1.00	178.08	0.31	275.21	0.85	601.40	0.04
108.11	1.78	181.14	12.05	276.21	0.09	602.31	0.03
113.10	21.93	182.15	0.57	277.22	8.36	602.48	0.04
114.11	1.11	182.62	0.03	283.22	16.91	605.35	0.09
119.10	21.06	183.16	5.54	284.22	1.11	622.27	0.49
126.12	1.34	191.08	2.19	285.17	0.08	641.46	4.16
127.01	5.33 F	192.10	0.05	295.23	1.35	642.45	0.66
127.13	3.18 F	193.14	0.30	296.23	0.10	643.40	0.06
128.11	1.88	194.16	1.01	297.24	0.28	659.45	0.18
131.10	8.53	194.62	0.02	301.25	0.12	661.44	12.33 F
133.12	86.96	194.70	0.02	305.19	0.07	662.47	2.14 F
134.12	2.84	194.82	0.05	307.24	1.05	663.47	0.16
139.14	1.26	195.17	12.13	308.26	0.33	699.41	0.02
144.12	1.35	196.17	0.68	308.56	0.03	705.40	0.05
145.13	43.91	197.18	1.53	308.71	0.04	709.50	0.03
146.13	1.90	212.16	0.19	309.26	0.30	719.44	0.25
150.12	1.34	213.17	16.50	311.24	0.08	747.52	0.10
151.12	4.54	214.18	1.08	313.23	0.56	749.43	0.10
152.12	0.18	225.18	1.22	314.22	0.07	769.52	1.89
153.05	0.21	226.18	0.14	314.33	0.02		
155.12	0.12	227.19	8.72	315.15	0.05		
156.13	0.09	233.19	99.88	315.23	0.03		
157.14	1.07	233.76	0.03	319.25	0.10		
158.11	0.16	233.88	0.02	321.21	0.07		
159.15	1.16	234.19	5.29	325.25	0.45		
160.17	0.05	235.16	0.18	326.23	0.07		
162.13	0.26	236.14	0.09	327.25	3.06		
163.14	15.83	[illegible]	[illegible]				

GAMIX 10   OG.APSEY   EI   No 10   03-MAR-85
CAL:CALT31   STA: 1:34



MASS	%HT. BASE
67.04	0.62
68.90	0.34
68.96	1.16
70.97	0.51
78.93	0.31
80.94	0.28
85.05	0.45
112.88	0.34
132.85	1.10
144.89	0.48
196.75	0.34
232.65	1.38
360.42	0.42

```
GA880365o      ¤1    Bgd=359   21-SEP-88 11:5+8:06:29   70E          Cl◦
BpA=0     I=10v    Ho=424   TIC=286496992              Acnt:COI      Sys:OPCH                                   HAR
                                                               GC= 93⁰    Cal:PFK267                                 MASS
                                                                               ◦¤0◦0
```



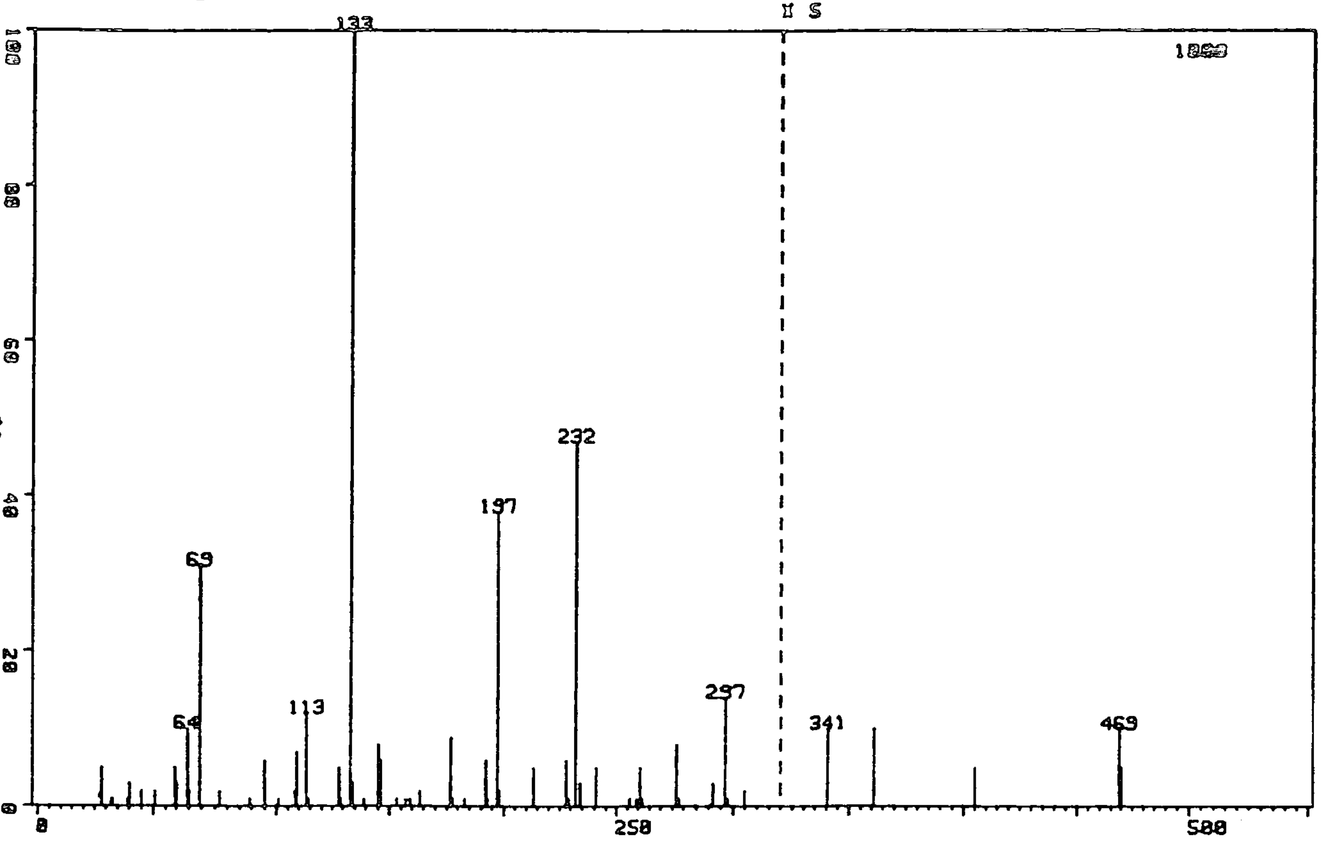
No 11

```
ass        % Base
 32.92        2.20      360.69       0.50
 38.92        2.66      361.71       0.06
 39.93        2.99      384.29       0.05
 44.90        5.31      384.80       0.05
 50.89        4.08      404.86       0.58
 56.89        1.36      405.89       0.07
 58.90        9.67      424.96       0.04
 59.90        2.08
 63.87       16.74
 64.88        1.99
 68.84       63.48
 74.84        1.90
 76.85        3.62
 82.84        1.19
 88.84        1.56
 94.82       10.49
107.81        1.44
108.81        5.14
112.79       16.25
126.79        1.36
127.79        7.69
132.78      100.00 0
133.77        3.36
144.76       15.26
162.73        3.87
 76.74        5.78
 91.73        2.26
 96.70       25.55
 97.70        1.53
 12.69        5.60
 27.71        7.45
 32.69       42.47
 33.69        2.33
 40.72        2.25
 60.74        1.60
 76.70        4.88
 96.67       10.18
 00.62        0.04
 20.64        0.03
 40.67        0.42
 45.75        0.05
 54.70        0.10
```

GA40 0
CAL:L18 STR:

No 12

19-SEP
0:0

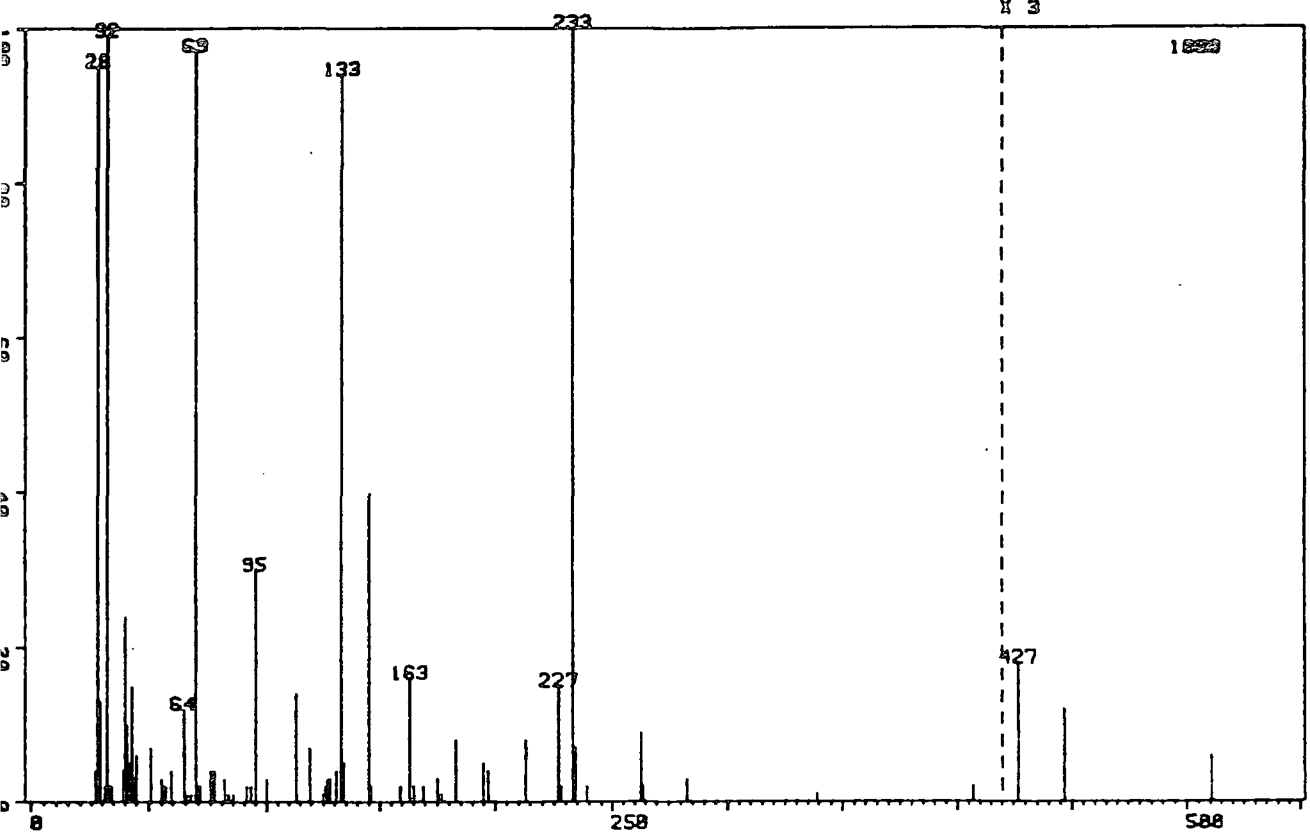


Mass	% Base				
27. 99	4 34	162. 93	2. 27	304 93	1 35
31. 97	1. 05	163. 93	0. 12	305. 95	0 07
32. 99	1. 01	164. 94	0. 13	316. 93	0. 18
39. 00	1 24	168. 93	0. 30	322 90	0. 11
40. 01	2 61	171. 95	0. 16	324 92	0. 32
44. 99	2. 41	172. 96	0. 49	340. 89	1. 83
50. 97	1 72	174. 93	0. 07	341. 90	0 13
59. 00	4 66	176. 94	8. 98	355 92	0. 20
60. 00	2 96	177. 94	0. 50	360. 89	1. 98
63. 98	9 56	182. 93	0. 68	361 88	0 18
64. 98	1. 52	188. 93	0. 39	404. 89	0 87
68. 96	31 05	190. 96	0. 07	405. 89	0. 10
76. 98	1 90	191. 96	5. 53	418 93	0. 11
88. 98	1 03	192. 97	0. 36	424. 93	0. 07
94. 97	5 77	194. 93	0. 22	468. 89	1. 10
100. 97	0 37	196. 94	37 71	469. 89	0 13
101. 97	0 10	197 95	2. 06		
102. 99	0 22	202. 95	0 08		
107. 97	1 85	206. 93	0. 39		
108. 98	6 68	208. 93	0. 28		
109. 97	0 25	212. 91	4 78		
112. 95	12 35	213. 91	0 19		
113. 95	0 49	216. 95	0. 31		
114. 95	0 18	220 92	0 12		
118. 94	0 33	222 94	0 31		
120. 96	0 21	226 92	0 29		
122. 98	0 08	227. 93	5 56		
125. 94	0 12	228 93	0 39		
126. 96	0 95	232 91	46 69		
127. 97	4 95	233 91	2 52		
128. 97	0 58	240 93	4 73		
131. 94	0 14	241 93	0 31		
132. 85	0 07	246 92	0 27		
132. 95	100 00	252. 93	0 09		
133. 95	3 18	255 95	0 67		
136. 93	0 13	256 91	0 32		
138. 95	0 51	258. 91	0 49		
143. 93	0 11	260 93	4 85		
144. 94	8 36	261 93	0 41		
145. 94	0 32	272. 92	0 30		
146. 96	0 29	276. 90	7 81		
149. 94	0 13	277. 91	0 58		
150. 94	0 09	284 93	0 18		
152. 96	0 84	290 92	0 16		
156. 94	0 52	291 92	2 49		
157. 95	0 08	292 92	0 19		
158. 95	0 81	296. 90	13 52		
159. 95	0 07	297 91	1 03		

6A10X 0
CAL:LIB STA:

No 13

19-SEP
0.0

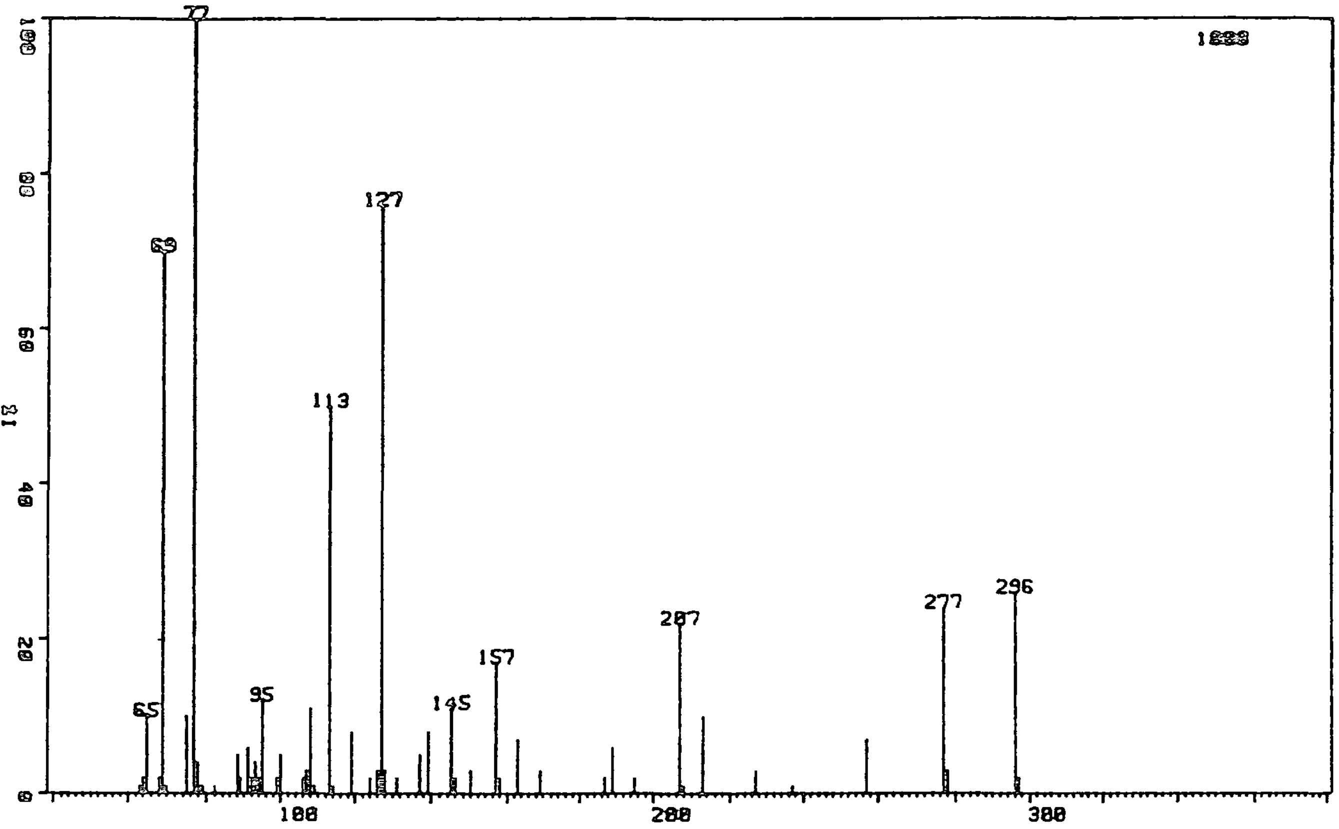


MASS	%HT. BASE
27.23	4.08
28.10	94.79
28.97	12.61
29.00	3.74
30.87	2.17
30.89	2.17
31.97	99.10
33.08	2.00
34.11	1.72
38.97	4.11
39.82	23.87
40.97	9.46
42.06	4.50
43.13	14.39
44.10	3.15
45.14	6.31
45.16	1.04
50.98	7.18
55.20	2.73
56.19	1.04
57.12	1.38
57.18	3.35
59.05	3.89
64.16	11.43
65.14	1.10
67.11	1.32
68.94	97.16
69.02	4.05
69.89	1.66
70.00	1.15
71.08	2.11
75.08	3.77
77.08	3.43
81.07	2.42
83.14	1.24
85.14	1.04
91.00	1.52
92.99	1.38
95.03	30.18
95.11	1.55
99.87	3.24
113.04	14.13
118.95	7.21
119.04	1.27
125.05	1.13
126.05	1.27
127.05	2.48
128.03	2.93
131.02	4.25
133.09	93.69
134.10	4.28
145.08	39.61
146.09	1.49
159.08	1.80
163.10	16.19
165.11	1.63
169.01	1.58
175.08	2.25
177.09	1.10
183.10	7.85
195.08	4.48
197.09	3.97
213.09	8.47
227.13	15.29
228.09	1.32
233.11	100.00
234.10	6.53
239.05	1.30
263.11	9.12
264.08	1.41
283.16	2.67
339.27	1.15
407.47	1.55
427.54	5.26
447.59	3.91
511.79	1.07

GAX29 0
CAL:L18 STR:

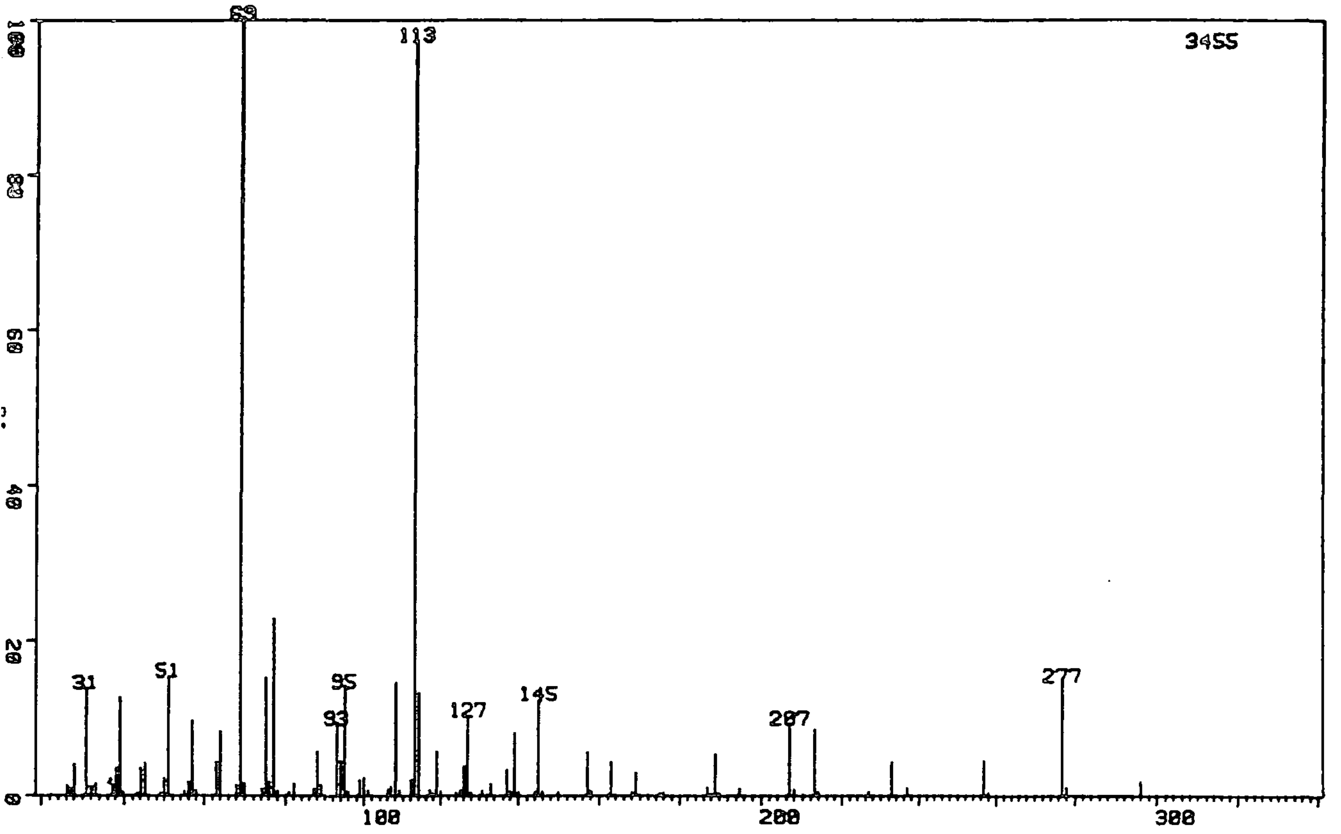
No 14

19-SEP
0:0



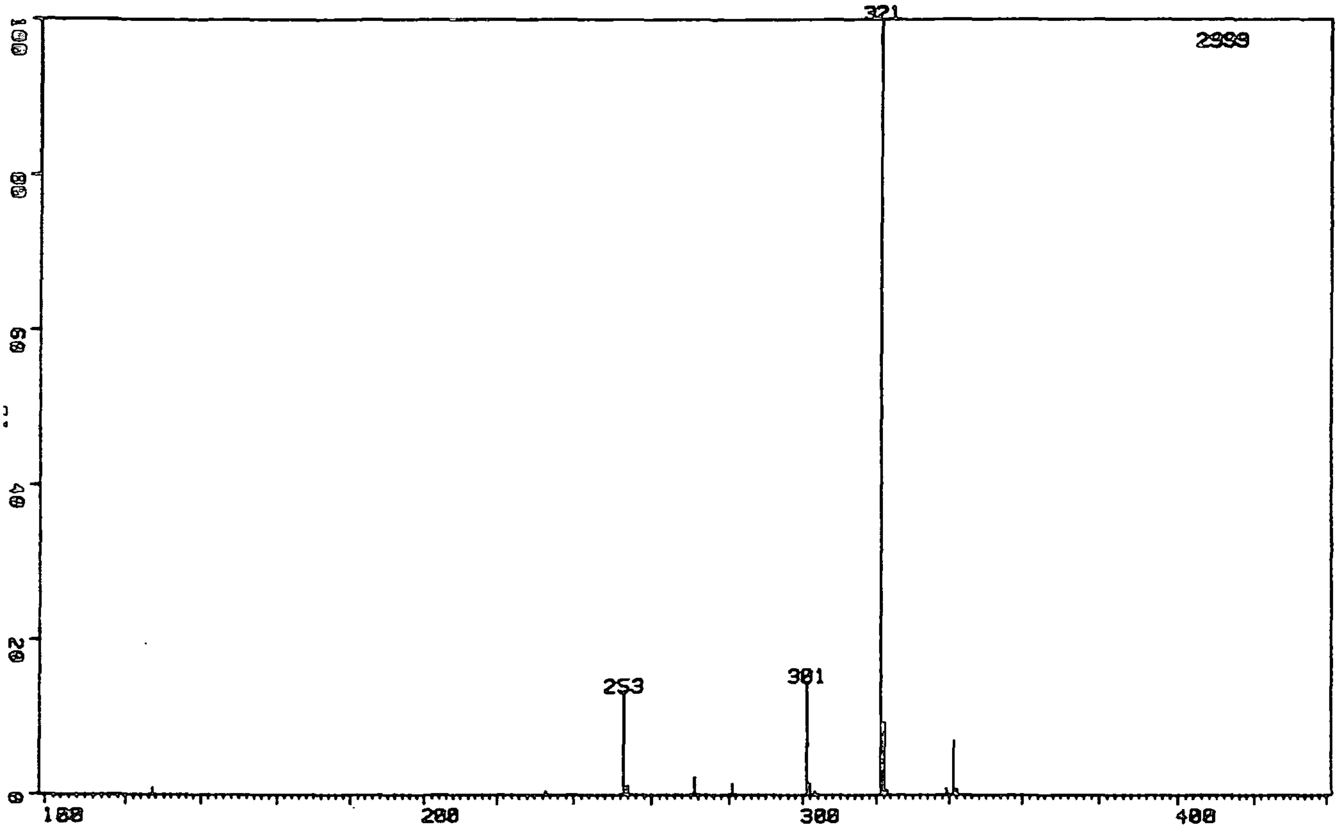
Mass	% Base
63.03	1.13
63.98	1.56
64.03	3.76
65.04	9.67
68.03	1.40
69.01	69.86
70.04	1.23
75.03	9.74
77.05	100.00
78.05	3.99
79.08	1.03
82.03	1.16
82.07	1.60
88.04	4.52
89.05	2.19
91.08	5.88
92.09	1.46
93.03	3.46
94.04	2.19
95.04	11.47
99.04	2.26
100.02	4.69
106.04	1.93
107.05	2.29
108.06	10.27
109.07	1.06
113.04	49.72
114.05	1.20
119.04	7.54
124.08	1.40
126.06	2.29
127.06	75.87
128.07	2.53
131.04	1.33
137.05	4.35
139.07	7.51
145.06	10.97
146.06	1.69
150.05	3.02
157.07	16.48
158.07	1.26
163.06	7.08
169.07	2.99
187.07	1.43
189.09	5.92
195.08	1.40
207.09	21.67
208.09	1.23
213.07	9.37
227.10	2.36
237.10	1.16
257.11	6.35
277.13	24.09
278.13	2.33
296.13	25.26
297.14	1.73

GA14X 39 G.APSEY CAP.COL **No 15** 16-MAY-86
CAL:CALP21 STA: 2:4



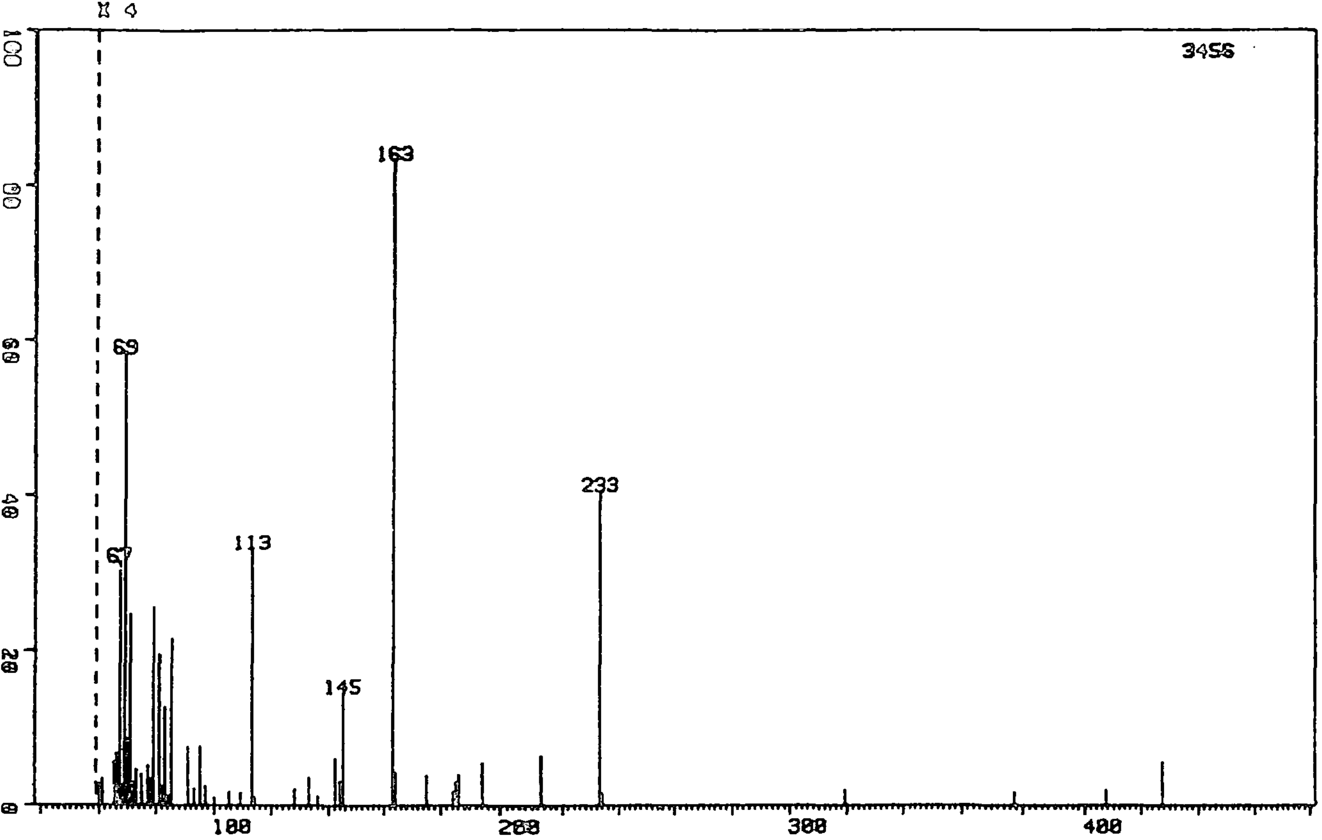
MASS	%HT. BASE
26.28	1.22
27.21	0.93
28.09	4.14
30.85	13.81
31.96	1.16
33.07	1.59
37.09	1.42
38.03	3.50
38.96	12.68
39.80	0.49
39.85	0.43
43.04	0.35
44.09	3.50
45.11	4.25
48.95	0.29
49.86	2.26
50.92	15.46
55.07	0.52
56.07	1.82
57.06	9.78
58.02	0.69
63.03	4.37
64.06	8.31
68.01	1.39
68.95	100.00
69.89	1.56
74.06	0.98
75.07	15.28
76.07	1.77
77.06	22.89
78.03	0.69
80.95	0.49
81.99	1.62
87.02	0.90
88.00	5.64
88.97	1.42
92.99	9.26
94.02	4.54
95.03	14.01
96.03	0.55
98.95	2.11
99.89	2.34
100.97	0.67
106.03	0.90
107.02	1.19
108.01	14.67
108.98	0.67
111.96	2.03
112.99	97.22
114.02	13.31
116.99	0.81
117.99	0.26
118.96	5.76
119.93	0.64
123.99	0.38
125.01	0.78
126.01	3.79
127.00	10.30
127.99	0.43
130.92	0.67
132.98	1.53
136.97	3.33
137.97	0.52
138.94	8.10
139.92	0.43
143.97	0.49
144.97	12.36
145.98	0.55
149.87	0.55
156.98	5.64
157.97	0.61
162.95	4.49
167.95	0.46
168.92	3.04
174.94	0.38
175.96	0.38
186.91	1.13
187.92	0.32
188.90	5.41
189.89	0.38
194.93	0.98
206.88	9.26
207.90	0.81
212.91	8.54
213.92	0.55
226.91	0.49
232.88	4.40
236.91	1.13
256.85	4.63
257.90	0.46
276.87	14.79
277.91	1.13
295.89	1.91

GAMSX 3 G.APSEY NEG. I-BU **No 16** 18-AUG-86
CRL:CRLN9 STR: 0:34



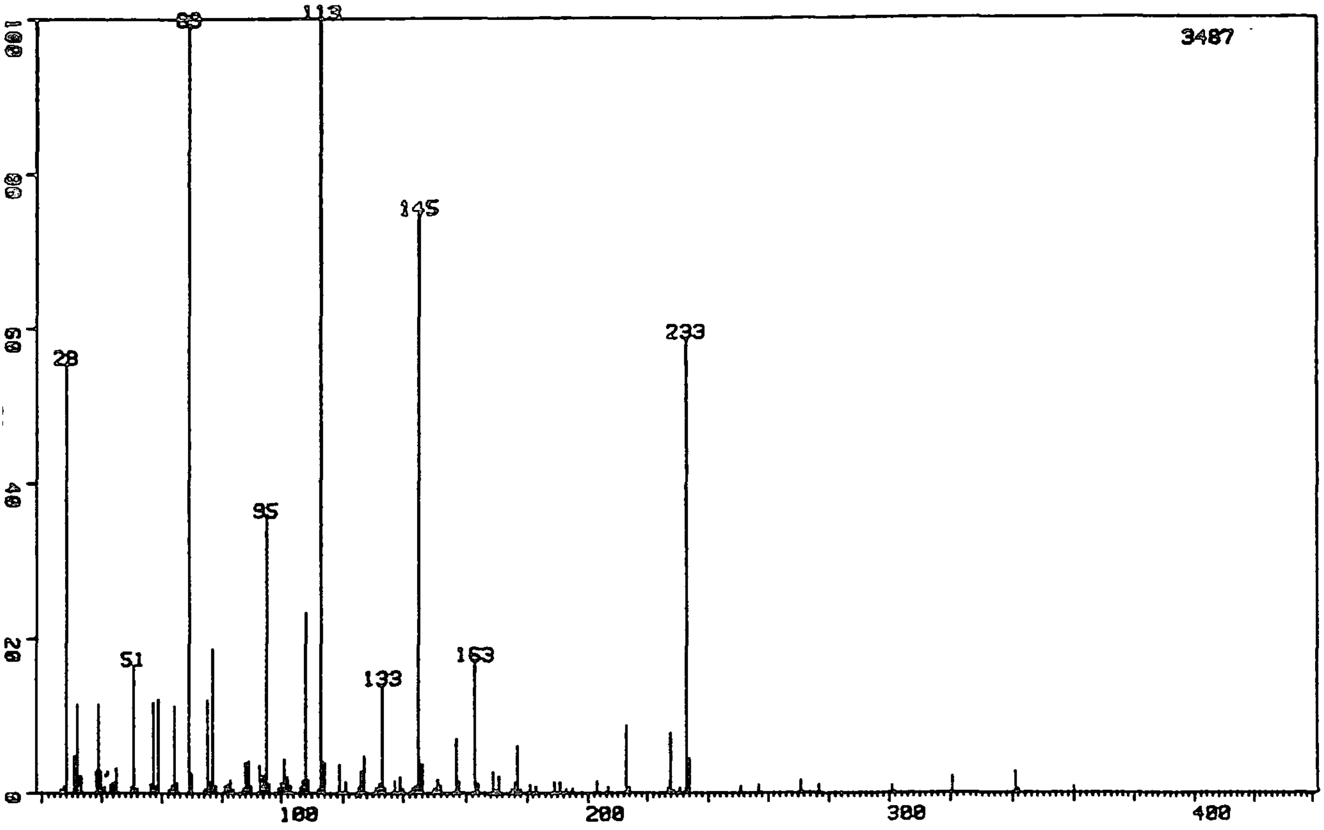
MASS	%HT. BASE
127.03	0.97
232.83	0.43
252.90	13.30
253.96	1.17
270.98	2.30
280.98	1.43
301.05	14.64
302.08	1.43
303.13	0.37
321.12	100.00
322.12	9.30
323.09	0.57
339.13	0.87
341.13	7.04
342.12	0.73

GAM8 S   G.APSEY I-BU C.I.   No 17   01-OCT-86
CAL:CALTS   STA: 1:13



MASS	%HT. BASE
65.12	1.39
66.09	1.68
67.08	7.87
68.94	2.03
69.02	14.55
69.96	2.14
71.03	6.16
73.10	1.13
77.08	1.27
79.02	6.37
81.04	4.86
83.13	3.18
85.14	5.38
90.98	1.88
95.02	1.91
112.99	8.30
142.13	1.53
144.98	3.65
162.97	20.80
164.00	1.04
193.91	1.36
212.93	1.59
232.95	10.16
427.34	1.39

GA17X 3S G.APSEY CAP.COL <u>No 18</u> 18-JUN-86
CAL:CALP21 STA: 2:15

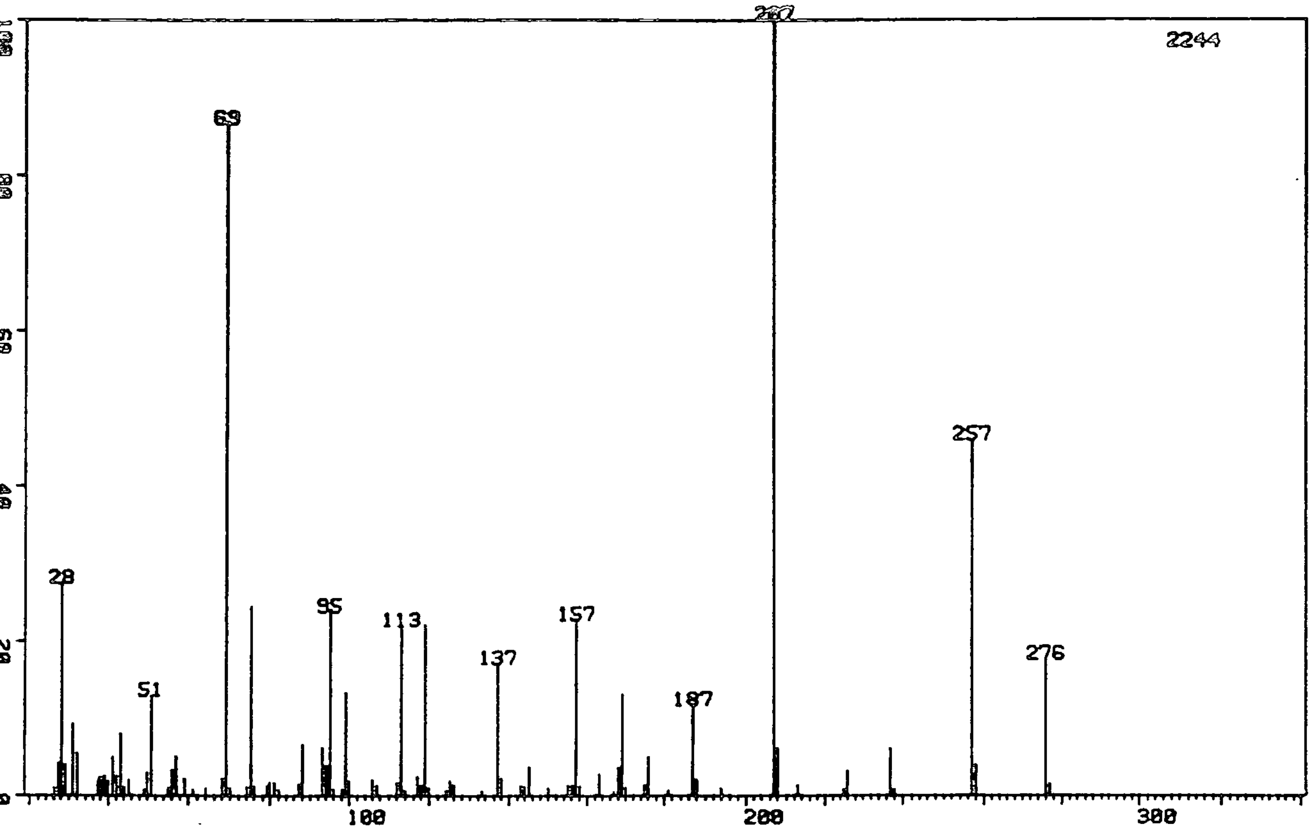


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.28	0.40	99.87	1.29	192.91	0.40
27.21	0.86	100.95	4.36	194.92	0.52
28.09	55.41	102.00	2.06	202.91	1.46
30.85	4.76	103.03	0.98	206.89	0.72
31.96	11.47	106.01	0.77	212.89	8.72
33.07	2.15	107.00	1.61	213.94	0.52
38.03	2.75	107.99	23.37	226.92	0.52
38.96	11.44	108.96	1.61	227.89	7.77
39.79	2.72	111.96	0.43	228.92	0.34
39.85	0.52	112.98	100.00	230.88	0.57
40.94	0.72	113.99	3.99	232.92	58.73
43.10	1.09	118.92	3.70	233.92	4.42
44.08	1.32	120.95	1.49	250.86	0.89
45.11	3.18	124.97	0.60	256.89	1.06
49.85	0.80	125.98	2.72	270.89	1.63
50.91	16.52	126.97	4.73	276.91	1.12
51.98	0.49	130.89	0.60	300.83	0.95
56.07	1.12	131.96	1.20	320.84	2.21
57.05	11.76	132.97	14.08	340.84	2.72
58.02	0.83	133.98	0.52	341.91	0.43
58.96	12.02	136.97	1.55	359.83	0.80
61.99	0.43	138.94	2.04		
63.03	1.06	139.92	0.43		
64.06	11.24	142.95	0.63		
65.07	1.23	143.95	1.03		
68.93	99.08	144.96	74.85		
69.88	2.52	145.96	3.70		
74.05	0.49	149.86	0.43		
75.06	12.02	150.90	1.75		
76.06	1.35	151.94	0.98		
77.04	18.64	156.92	7.11		
78.01	0.98	157.91	1.43		
80.94	0.92	162.90	17.18		
81.97	1.09	163.92	1.18		
83.03	1.52	168.86	2.72		
84.06	0.37	169.90	0.34		
87.01	0.43	170.90	2.18		
87.98	3.87	174.91	0.46		
88.95	4.16	175.93	1.35		
89.91	0.89	176.93	6.11		
92.98	3.64	177.93	0.37		
94.00	2.27	180.86	1.06		
95.01	35.79	182.94	0.89		
96.02	1.18	188.92	1.29		
98.92	0.43	190.91	1.35		

GA7X 3 G.APSEY E.I.
CAL:CALT31 STA:

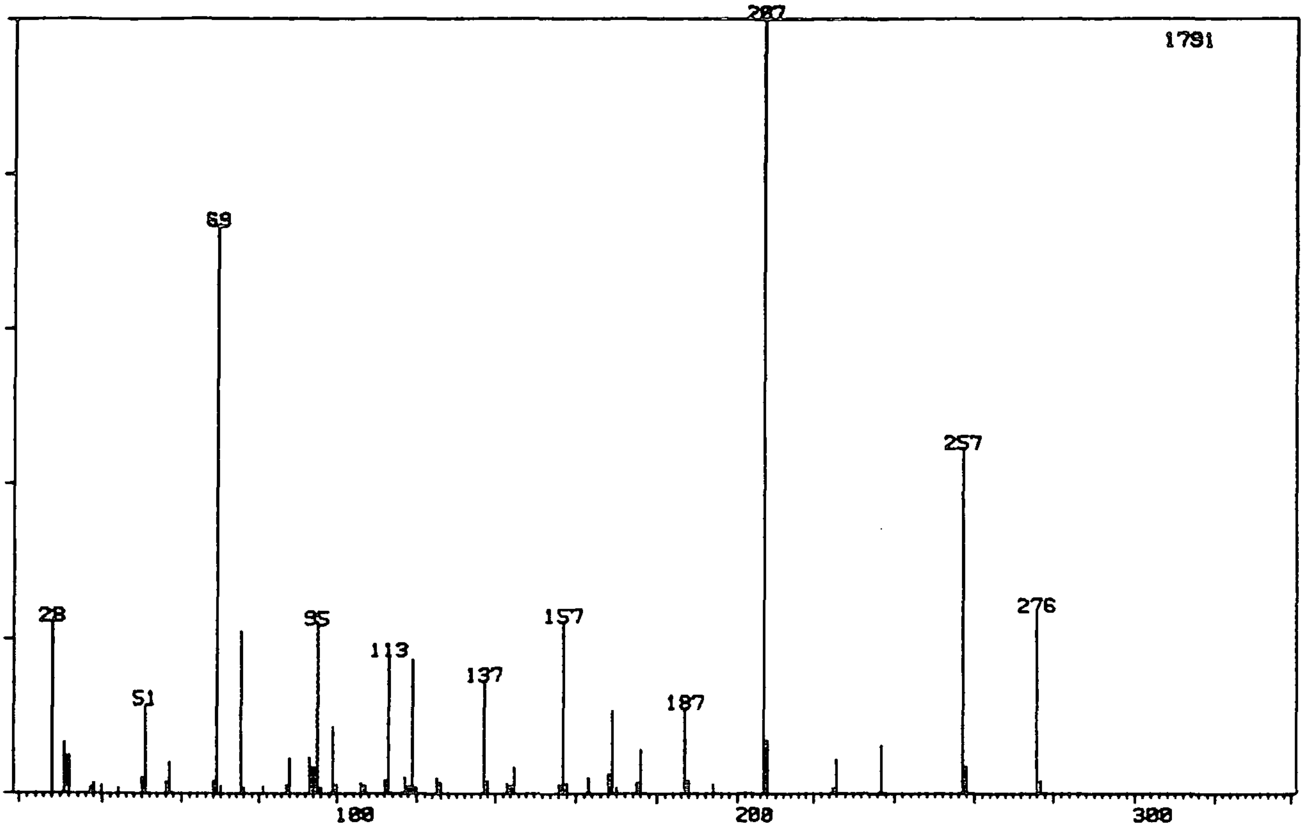
No 19

13-FEB-85
8:33



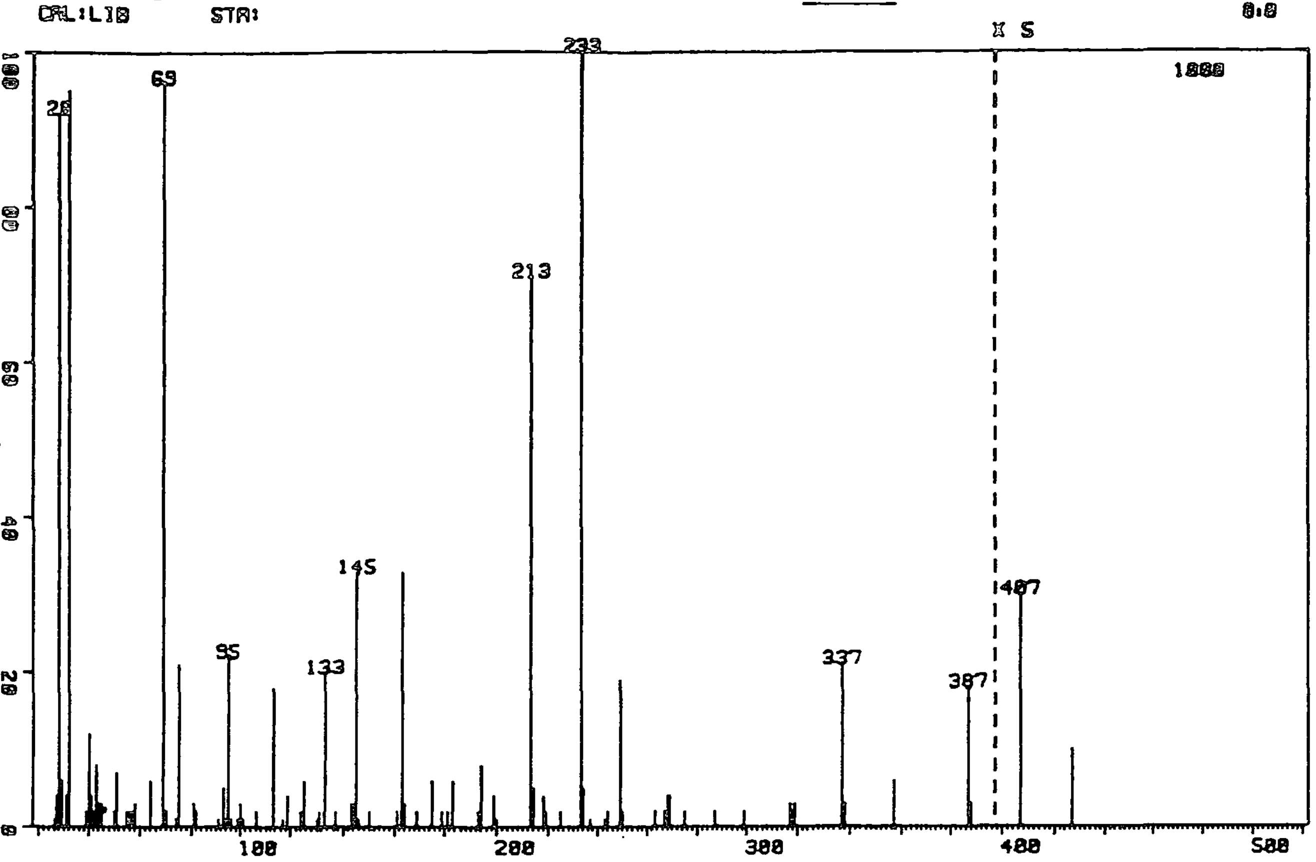
MASS	%HT. BASE
26.30	1.02
27.23	4.28
28.11	27.45
28.13	0.89
28.97	0.94
29.00	4.01
30.87	9.27
31.97	5.57
37.09	1.43
38.04	2.32
38.96	2.63
39.80	1.92
40.94	4.95
42.04	2.54
43.07	1.20
43.11	8.02
44.09	1.11
45.14	2.09
48.96	0.85
49.87	3.03
50.94	12.97
55.09	0.62
55.15	1.07
56.09	3.30
57.08	5.12
57.13	1.38
59.01	2.23
60.96	0.85
64.09	0.94
68.03	2.27
68.97	86.59
69.92	0.94
74.06	1.07
74.14	1.11
75.04	24.51
76.04	1.20
78.93	1.29
79.88	1.74
80.96	1.65
81.99	0.80
87.03	1.52
88.00	6.68
93.00	6.28
94.03	3.88
95.04	23.84
96.04	0.89
97.99	0.80
98.96	13.37
99.92	1.83
106.03	2.01
107.03	1.29
111.99	1.74
113.01	22.06
114.04	0.67
117.01	2.45
118.01	1.29
118.98	22.19
119.95	1.07
124.02	0.67
125.04	1.87
126.03	1.43
133.03	0.58
137.01	17.11
138.01	2.27
143.00	1.25
144.02	1.11
145.03	3.70
149.94	0.94
155.02	1.29
156.01	1.34
157.00	22.77
157.99	1.20
162.99	2.76
166.98	0.49
167.97	3.65
168.96	13.10
169.95	1.02
174.99	1.43
175.98	5.04
180.94	0.67
186.96	11.72
187.96	2.09
193.95	0.94
206.94	100.00
207.94	6.15
212.93	1.29
224.94	0.85
225.95	3.21
236.91	6.19
237.90	0.85
256.91	45.94
257.89	3.97
275.92	17.60
276.92	1.56

GA19X 56 G.APSEY E.I. No 20 08-JUL-86
CAL:CALP4 STR: 2:58



MASS	%HT. BASE
28.10	22.28
30.86	6.53
31.97	4.86
37.10	0.84
38.04	1.28
39.80	1.12
44.10	0.78
49.87	2.01
50.93	11.56
56.09	1.56
57.07	4.02
68.02	1.62
68.96	73.26
69.90	0.95
75.06	21.05
76.07	0.73
80.96	0.95
87.03	1.01
88.00	4.58
93.01	4.63
94.03	3.35
95.04	21.89
96.05	0.84
98.95	8.60
99.91	1.12
106.03	1.40
107.03	1.06
111.98	1.73
113.01	17.81
117.00	2.07
117.99	0.89
118.96	17.36
119.93	0.84
125.01	1.95
126.02	1.40
136.98	14.63
137.97	1.56
142.97	1.23
143.98	1.06
144.99	3.35
155.98	1.12
156.98	22.28
157.97	1.28
162.97	2.07
167.95	2.57
168.93	10.78
169.92	0.73
174.97	1.40
175.96	5.58
186.94	11.06
187.94	1.68
193.94	1.17
206.94	100.00
207.93	6.87
224.93	0.73
225.91	4.47
236.89	6.25
256.93	44.61
257.91	3.46
275.91	23.62
276.92	1.56

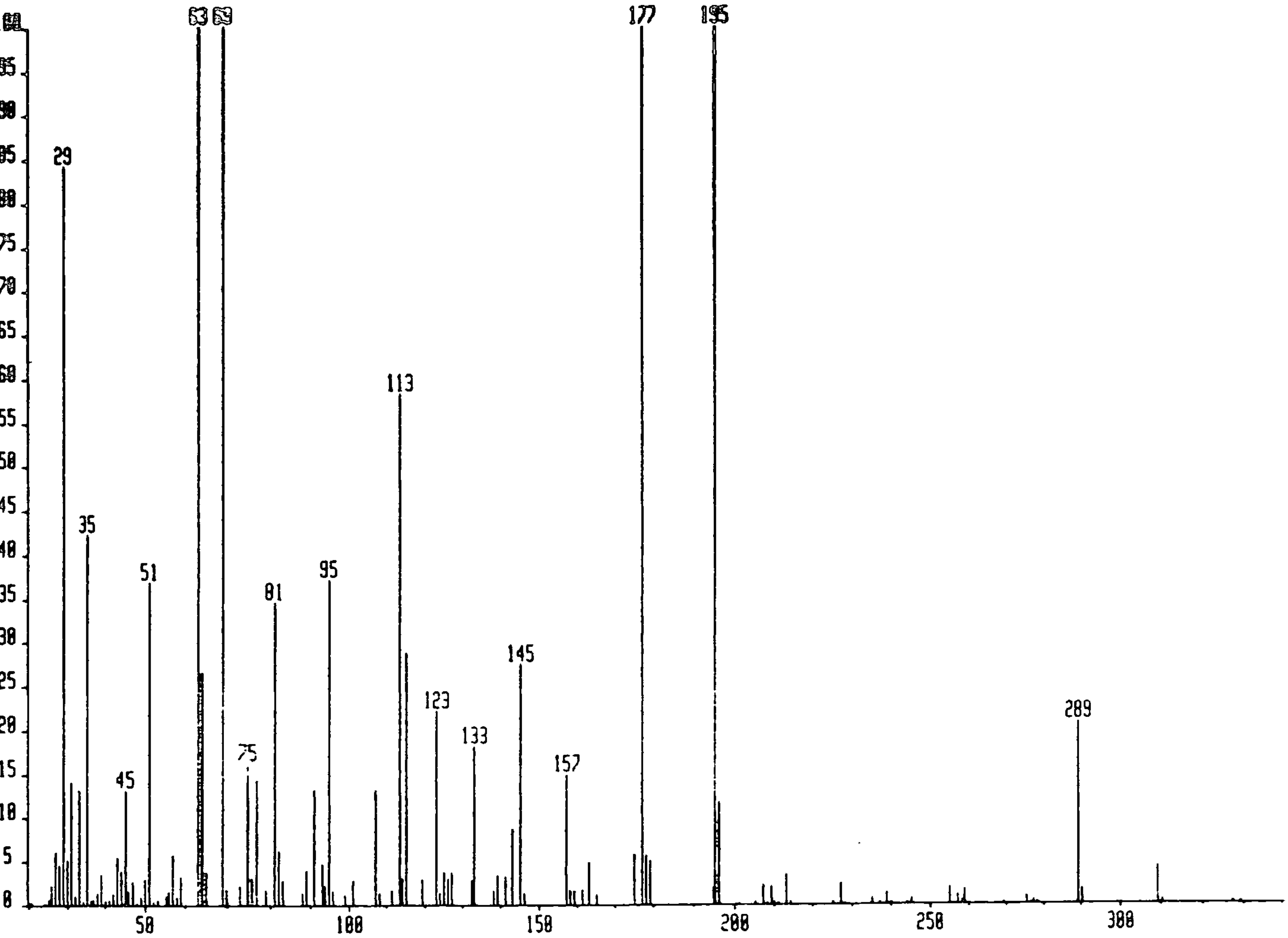
GA11X 0 **No 21** 19-SEP
CAL:L10 STR: 0:0



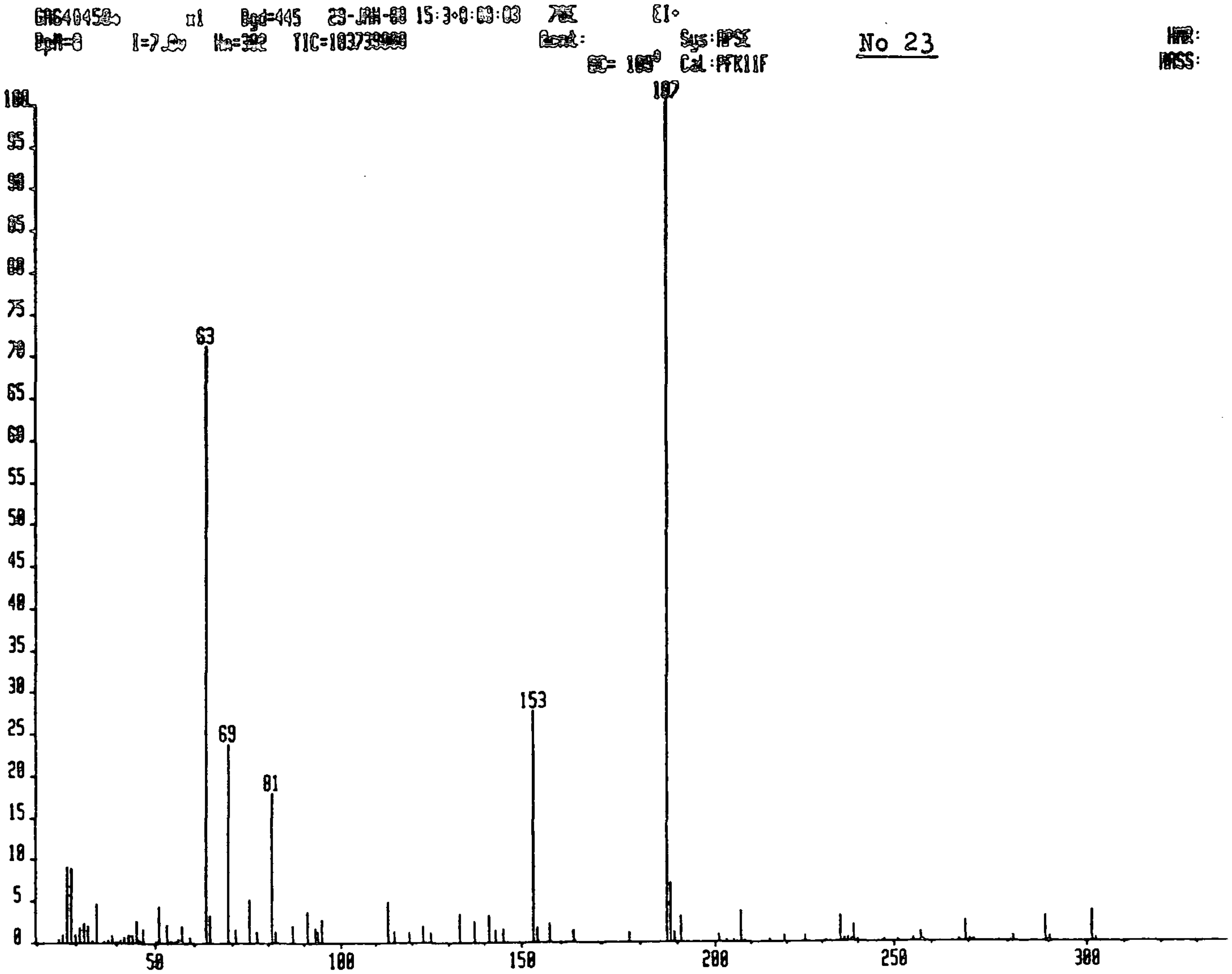
MASS	%HT. BASE
26.30	1.15
27.23	3.42
28.10	91.90
28.97	5.55
29.00	1.64
30.86	4.08
31.97	95.38
38.97	1.39
39.81	11.79
40.96	3.97
42.06	1.42
43.09	7.41
43.13	6.13
44.10	2.43
45.14	2.27
49.90	1.56
50.98	6.56
55.20	1.50
56.14	1.45
56.19	1.07
57.18	2.05
58.11	3.04
64.16	6.21
69.01	95.82
69.08	2.60
69.95	1.67
74.10	1.23
75.09	21.01
81.01	2.76
82.05	2.08
91.03	1.18
93.03	5.25
94.06	1.42
95.01	1.18
95.07	21.66
96.07	1.18
98.98	1.15
99.93	3.04
101.01	1.09
106.03	2.19
113.03	17.37
117.03	1.18
118.98	3.64
124.05	1.81
125.06	5.99
129.90	1.07
131.05	1.34
133.11	19.26
137.08	2.05
143.09	2.49
144.12	1.97
145.10	32.36
146.09	1.50
150.03	2.00
161.05	1.20
163.09	32.36
164.11	2.60
169.02'	1.94
175.10	5.25
179.06	1.26
181.07	2.00
183.12	6.13
193.09	1.39
194.11	7.66
199.04	3.80
200.06	1.20
213.14	70.46
214.10	5.17
218.10	4.02
219.09	1.53
225.13	1.26
233.12	100.00
234.09	4.73
237.10	1.15
243.12	1.09
244.10	1.45
249.06	18.35
250.07	1.56
263.12	1.94
267.11	2.19
268.08	3.04
269.07	3.42
275.12	1.61
287.10	1.72
299.10	2.11
317.18	2.63
318.14	1.97
319.10	2.30
337.13	20.87
338.12	2.35
357.15	5.36
387.19	17.20
388.17	2.49
407.25	5.31
427.29	1.81

GA6401920 x1 Bgd=170 29-JAN-88 15:3+0:03:26 70E EI+
BpM=0 I=10v Hm=329 TIC=703521024 Acnt: Sys:APSE HMR:
GC= 63° Cal:PFK11F MASS:

No 22



Mass	% Base						
26 04	2 01	91. 11	13 21	155. 15	0. 07	255. 23	1 77
27 05	5 99	93. 11	4. 61	157. 01	0. 07	257 22	0 92
28 03	4 40	94. 12	2 04	157. 17	14. 78	258. 26	0 23
29 04	84 15	95 12	37. 11	158. 18	1. 44	259. 25	1 49
30 04	4 97	96. 13	1 55	159. 16	1. 44	260. 28	0 05
31 04	11 82 F	99. 12	1 03	160. 16	0. 12	269. 25	0 15
31. 06	13 88 F	100 12	0 31	161. 16	1. 67	270. 35	0. 06
33 06	12 97 F	101 13	2 62	162. 17	0. 14	275. 24	0 67
33. 08	1 82 F	113. 13	58. 17	163. 16	4. 72	276. 30	0 07
35 08	42 18	113. 30	0. 07	175 19	5. 61	277. 23	0 23
38 07	1 22	114. 14	2. 74	176. 19	0. 52	278. 24	0. 17
39. 08	3 48	115. 03	0. 20	176. 33	0. 06	288 99	0 16
42. 07	1 14	115. 14	28 76	176. 48	0. 14	289 27	20 57
43. 08	5 30	119. 14	2. 77	176. 95	0. 84	290 27	1 54
44. 07	3 73	120 15	0. 19	177. 21	100. 00 0	309 29	4 14
45 08	13 04	121. 16	0. 70	177. 49	0. 05	310 28	0 27
46. 08	1 47	122. 15	0. 13	177. 54	0. 04	327 25	0 22
47 06	2 45	123. 02	0. 13	177 57	0. 03	329 30	0 13
50 07	2 94	123. 14	22. 10	178. 21	5. 52		
51 07	36 79	124. 14	1. 25	179. 17	4 87		
56 08	1 39	125. 15	3. 61	194 90	1. 78 F		
57 09	5 58	126. 16	2. 79	195. 21	100. 00 0		
59 10	3 09	127. 16	3. 54	195. 44	0. 06		
63 03	3 27	128 17	0. 15	195. 60	0. 08		
63 09	100 00 0	131. 15	0 45	196. 02	0. 06		
64 09	26 50	132. 15	2. 60	196. 22	11. 58		
65 10	3 67	133 03	0. 10	197. 21	0 65		
68 98	1 24	133. 15	18. 09	201. 20	0. 05		
69 07	100 00 0	141. 14	3. 11	205. 21	0. 13		
70 09	1 60	142 15	0. 39	207 20	2. 01		
73 09	2 03	143 04	0. 05	208. 21	0 14		
75 09	16 22	143. 16	8. 65	209. 22	1 86		
76 11	2 92	144 16	0. 88	210. 22	0. 18		
77 11	14 16	145 01	0 20	211. 20	0 11		
79 09	1 57	145. 15	27 36	213. 19	3 26		
81 11	34 51	146. 16	1 22	214 20	0 21		
82 10	6 08	147. 14	0. 28	215. 22	0 05		
83 11	2 62	150. 15	0. 11	225. 23	0. 20		
88 12	1 23	151. 17	0. 18	227. 22	2. 20		
89. 14	3 84						



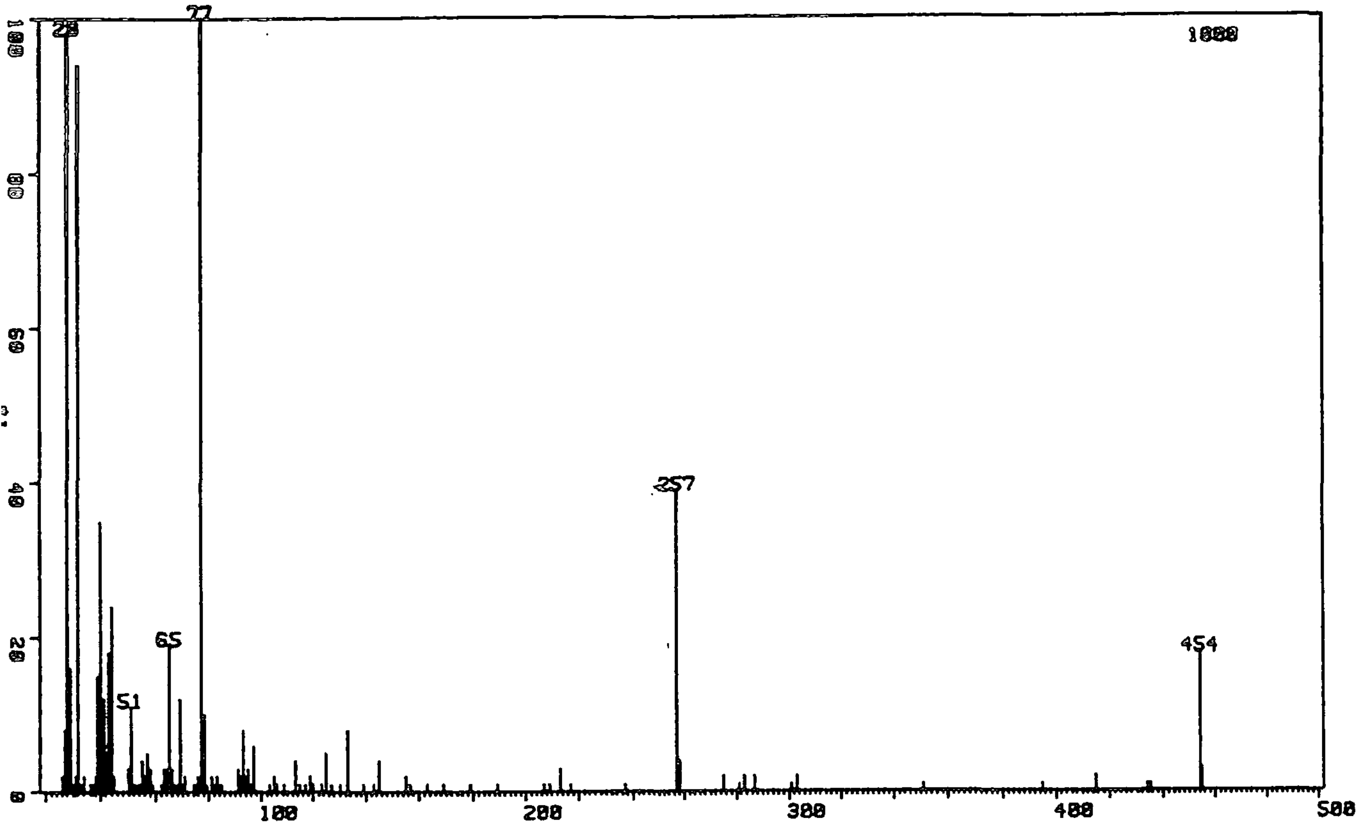
No 23

Mass	% Base
28.04	9.03
29.04	8.93
31.04	1.64 F
31.06	1.80 F
32.03	2.22
33.06	1.91
35.08	4.59
45.08	2.46
47.06	1.59
51.07	4.32
53.07	2.10
57.09	1.96
63.10	71.13
64.09	3.14
69.07	23.72
71.07	1.45
75.09	5.00
77.11	1.21
81.11	17.77
82.10	1.26
87.13	1.93
91.11	3.52
93.12	1.58
94.12	1.23
95.12	2.63
101.13	0.19
105.14	0.94
106.13	0.34
107.14	0.53
108.14	0.67
109.15	0.19
110.12	0.18
111.13	0.53
113.13	4.77
114.14	0.22
115.15	1.16
119.13	1.05
120.15	0.11
121.11	0.08
122.13	0.22
123.14	1.78
124.15	0.17
124.38	0.05
124.56	0.18
124.86	0.05
124.89	0.07
124.98	0.18
125.14	1.08
125.30	0.13
125.41	0.22
125.52	0.14
125.65	0.11
125.70	0.14
125.79	0.08
125.84	0.12
126.16	0.55
127.16	0.35
128.17	0.07
131.15	0.32
133.15	3.32
134.17	0.05
135.17	0.10
136.15	0.18
137.14	2.43
138.16	0.22
139.17	0.47
141.14	3.04
142.16	0.15
143.14	1.33
144.16	0.43
145.16	1.52
151.17	0.20
153.03	0.20
153.17	27.53
154.17	1.66
155.17	0.95
156.15	0.11
157.18	2.09
158.18	0.20
159.15	0.14
163.16	1.35
167.16	0.11
168.19	0.10
169.16	0.57
170.19	0.07
171.16	0.94
172.17	0.30
173.16	0.08
175.16	0.54
176.18	0.15
177.19	1.11
181.18	0.20
185.19	0.60
186.74	0.05
186.99	0.85
187.22	100.00
187.35	0.07
187.61	0.09
188.22	6.95
189.22	1.08
191.18	2.93
192.18	0.22
195.22	0.19
201.22	0.71
203.21	0.22
205.18	0.13
206.20	0.06
207.20	3.63
208.20	0.22
213.20	0.05
215.23	0.12
219.23	0.60
225.22	0.64
231.24	0.19
235.21	2.91
236.22	0.26
237.23	0.46
238.23	0.15
239.24	1.74
240.27	0.08
247.26	0.15
251.25	0.20
255.23	0.26
257.23	1.04
258.24	0.10
267.26	0.21
269.25	2.37
270.27	0.13
271.27	0.17
281.29	0.62
289.26	2.95
290.26	0.39
301.29	3.56
302.30	0.29

6A14X 0
CAL:LIB STA:

No 24

19-SEP
0:0

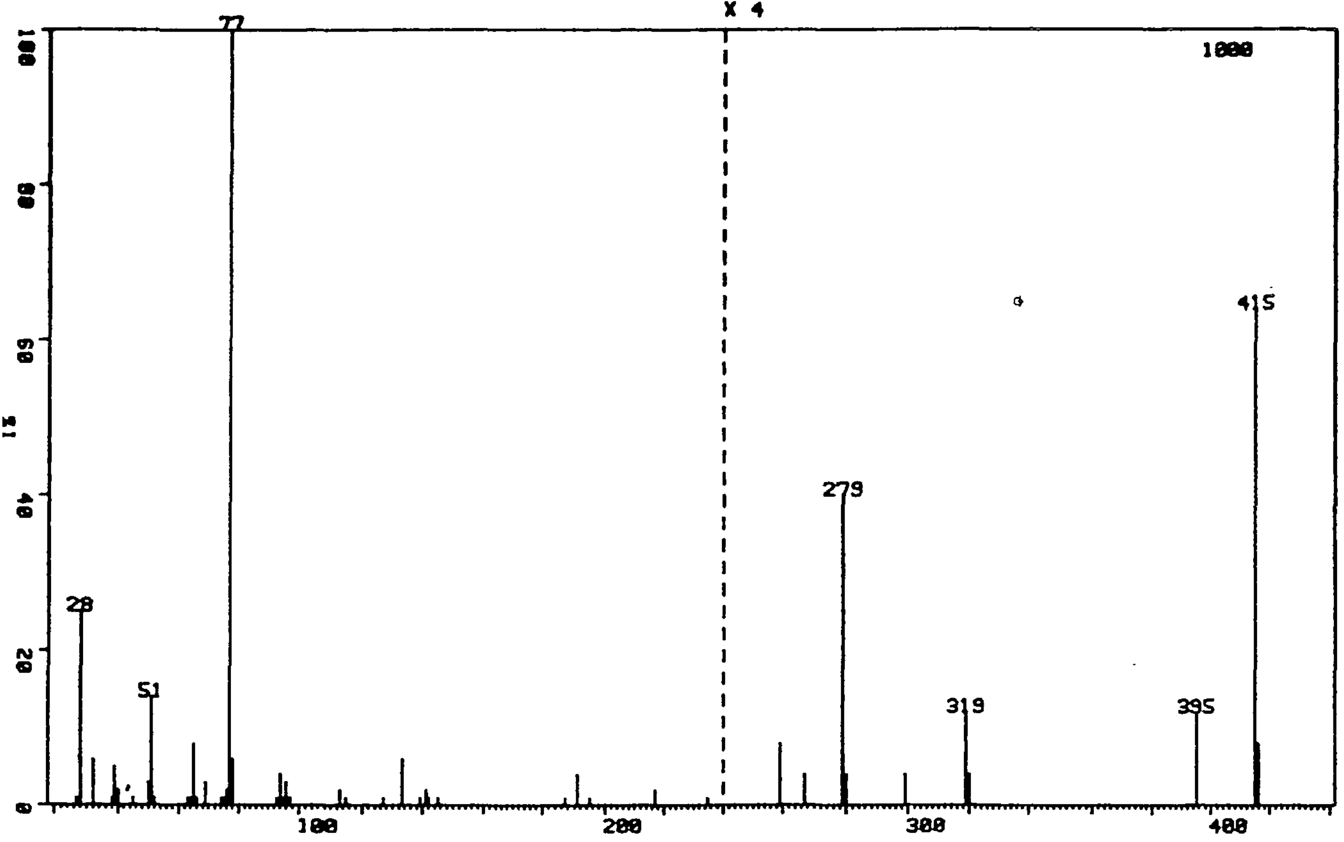


MASS	%HT. BASE				
26.30	1.57	65.11	19.19	122.98	0.59
27.23	7.53	66.08	2.81	125.04	4.78
28.11	97.98	67.07	1.32	127.02	0.81
28.97	15.84	68.05	0.56	129.83	0.67
29.00	3.26	68.93	11.60	130.99	0.42
29.80	1.29	69.00	2.98	131.93	0.48
29.81	0.53	69.95	1.21	133.04	8.06
30.87	1.07	71.03	2.36	133.15	0.70
30.69	2.42	73.08	0.34	134.13	0.42
31.97	93.82	74.07	0.81	138.99	0.76
33.08	0.62	75.07	1.38	143.05	0.56
33.11	0.51	76.08	2.02	145.04	3.62
34.11	1.99	77.07	100.00	145.12	0.31
36.11	1.10	78.05	9.94	151.04	0.37
37.10	0.81	79.01	1.43	155.07	1.60
38.01	0.34	80.97	0.90	157.06	1.12
38.05	2.33	81.04	1.57	163.04	1.07
38.97	15.03	82.04	0.70	167.07	0.42
39.81	35.28	82.09	0.81	169.02	0.53
39.87	1.88	83.07	0.45	179.04	0.76
40.96	11.66	83.13	1.54	181.03	0.37
42.01	0.70	84.12	0.67	189.05	1.10
42.05	4.86	85.10	1.26	207.13	0.81
43.08	9.13	90.95	3.06	209.07	0.51
43.12	17.61	91.98	1.85	213.07	3.15
44.10	24.38	93.00	7.75	217.12	0.79
44.16	0.59	94.03	11.80	237.09	1.24
45.13	1.77	95.01	2.84	255.11	0.48
47.07	0.31	96.01	0.56	257.13	38.65
49.90	3.26	96.07	0.42	258.10	3.99
50.97	10.84	96.91	0.59	275.11	1.74
52.05	0.87	97.02	6.24	281.08	0.62
53.11	1.07	103.03	0.51	283.10	1.71
54.15	0.76	104.05	0.42	287.07	1.43
55.14	0.59	105.06	2.36	301.09	0.53
55.18	3.71	106.06	0.87	303.16	1.85
56.18	1.57	108.96	0.65	319.08	0.42
57.10	0.76	109.02	0.84	351.19	0.53
57.16	4.69	110.96	0.37	371.19	0.31
58.09	2.78	111.06	0.42	395.27	0.59
58.12	0.53	112.99	3.88	415.24	1.43
59.04	0.96	115.05	0.93	434.22	1.04
62.06	0.76	117.05	0.96	435.20	1.21
63.11	2.78	118.99	2.25	454.24	17.98
64.11	2.89	119.99	0.81	455.24	3.12

6A29 0
CAL:LIB STA:

No 25

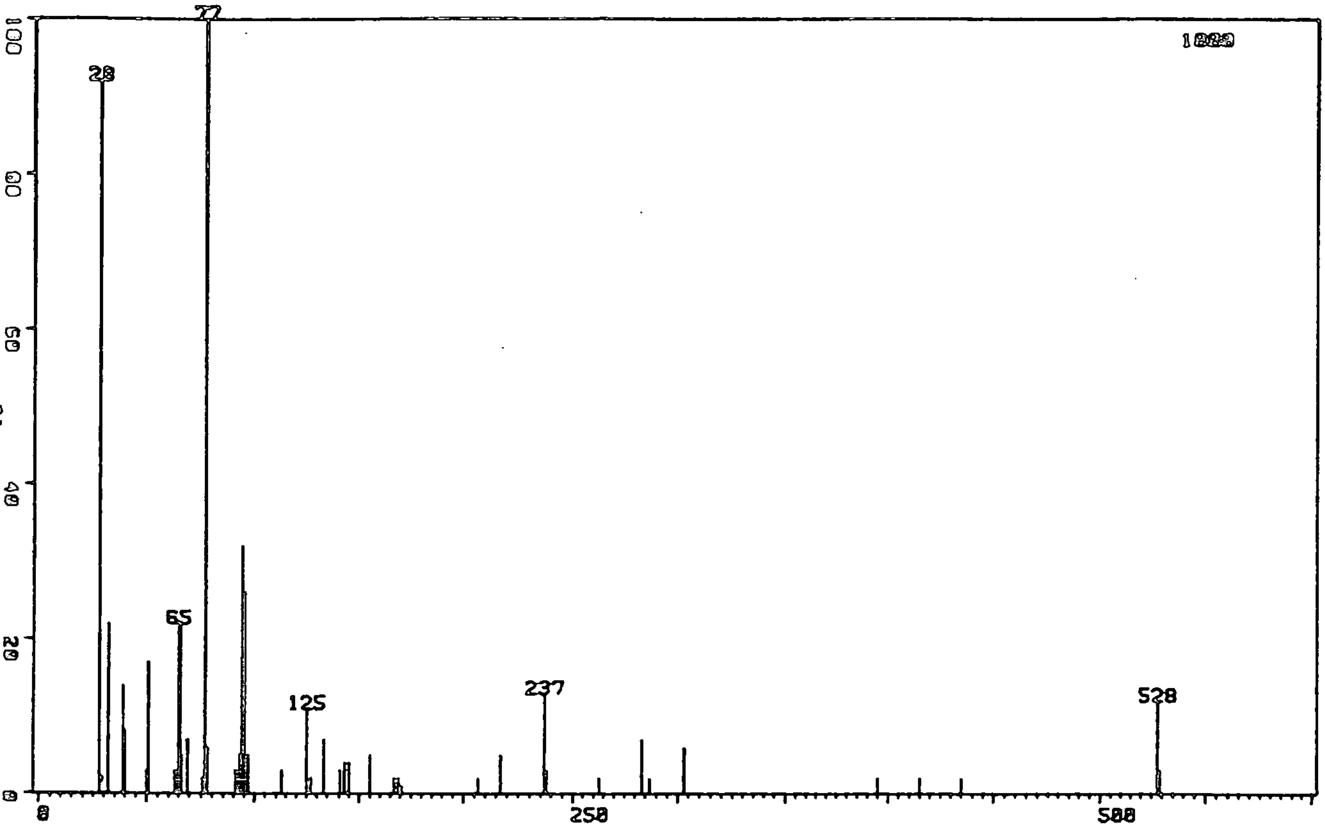
19-SEP-80
0:0



MASS	%HT. BASE
27.21	0.77
28.09	25.15
31.96	5.45
38.03	0.69
38.96	4.50
39.79	2.08
45.11	0.55
49.87	3.07
50.94	14.18
52.02	0.58
63.06	1.02
64.09	0.69
65.12	8.00
66.09	1.17
68.94	2.52
74.05	0.48
75.05	0.73
76.06	2.01
77.04	100.00
78.02	5.41
93.03	1.17
94.06	3.91
95.04	0.44
96.05	2.27
97.04	0.91
113.00	1.64
115.06	0.88
127.04	0.48
133.00	5.45
139.00	0.51
141.01	2.01
142.06	0.55
145.04	0.69
167.01	0.51
187.01	0.37
190.97	3.69
195.05	0.62
217.04	1.54
235.00	0.80
258.98	1.35
267.04	0.69
278.99	9.90
279.97	1.13
299.00	0.84
319.03	2.63
320.00	0.40
395.10	2.34
415.06	16.19
416.06	2.16

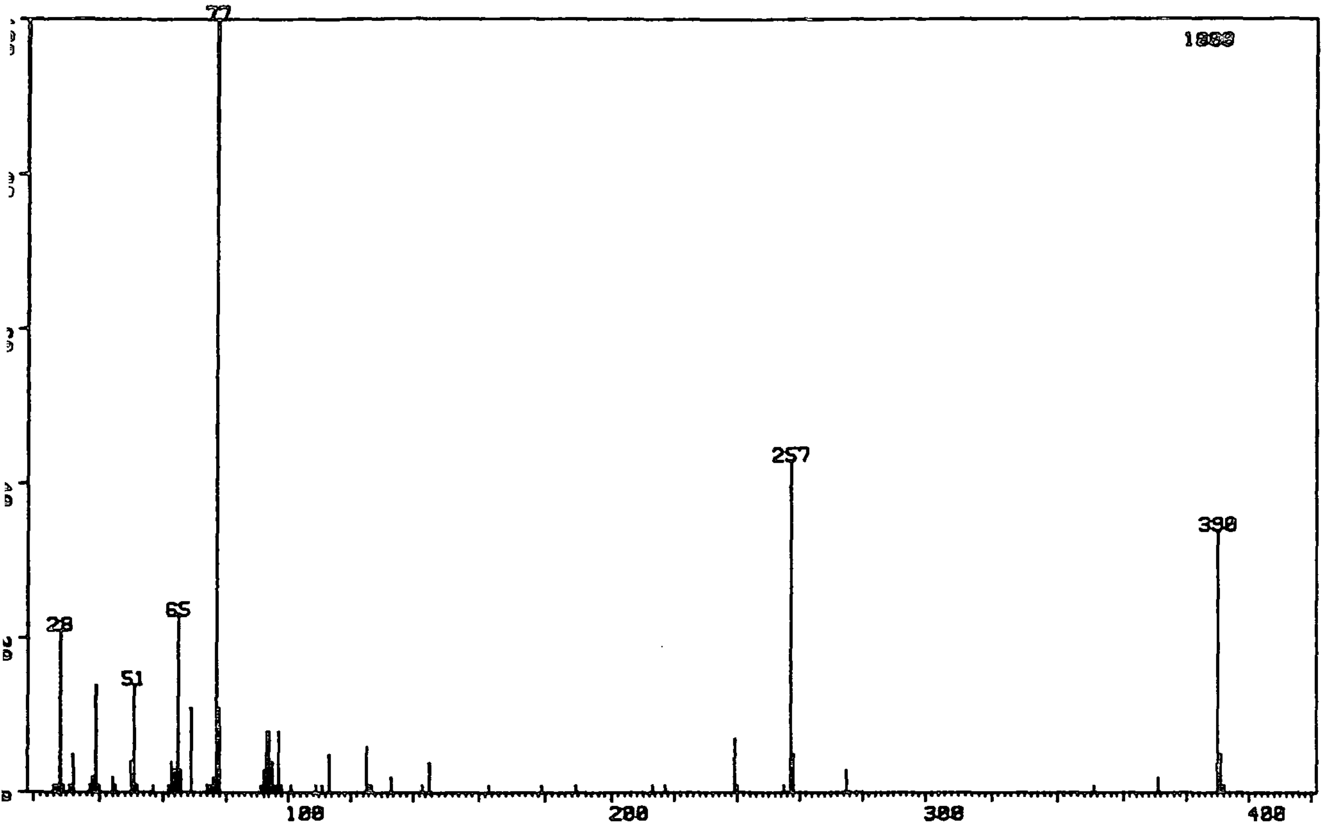
6A29 0 No 26 19-SEP

CAL:LIB STR: 0:0



MASS	%HT. BASE
28.09	91.76
31.96	21.98
38.96	13.46
39.79	8.24
49.87	2.75
50.94	16.21
63.07	2.47
64.08	1.92
65.12	21.98
66.09	4.81
68.94	6.32
76.06	2.06
77.04	100.00
78.02	5.49
90.99	2.34
93.03	4.67
94.05	31.32
95.06	25.69
96.06	2.61
97.04	5.08
112.99	2.47
125.05	10.85
127.04	2.20
133.00	6.46
141.02	3.02
143.02	4.26
145.03	3.43
155.03	4.26
167.00	1.92
168.99	1.65
171.00	1.24
207.00	2.20
217.02	4.53
237.02	12.36
238.02	2.34
263.03	1.92
293.05	6.73
297.03	1.92
303.06	6.18
395.10	1.37
415.02	2.06
435.05	1.79
528.07	11.81
529.14	2.61

GR28 0 **No 27** 19-SEP
CAL:LIB STA: 0:0



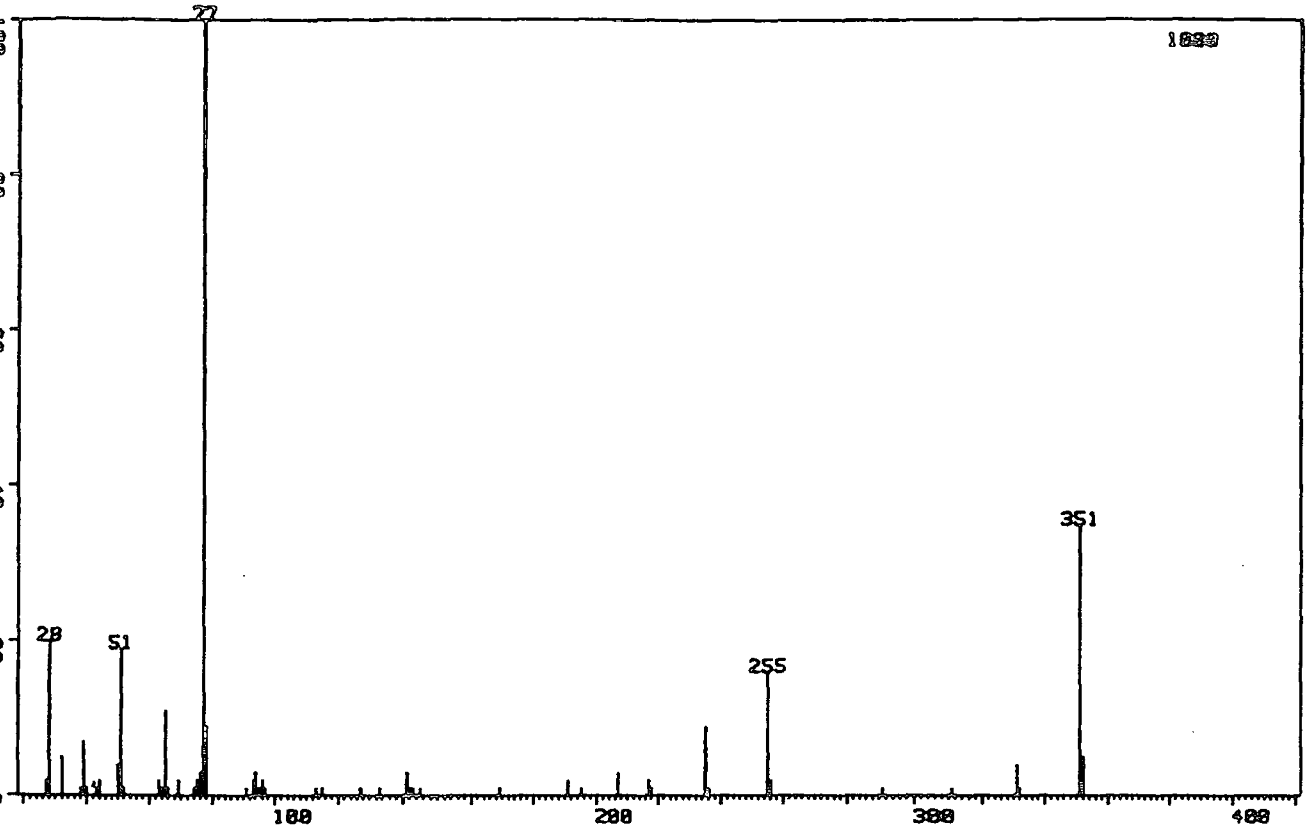
MASS	%HT. BASE
26.28	0.50
27.21	1.14
28.09	20.56
28.95	0.79
30.85	0.44
31.96	5.05
37.08	0.41
38.03	2.07
38.96	13.73
39.79	1.37
39.85	0.70
44.07	1.64
45.11	0.99
49.86	3.97
50.94	13.76
52.02	0.96
53.03	0.35
55.09	0.38
57.07	0.44
62.01	0.70
63.06	3.48
64.09	2.69
65.11	22.43
66.08	3.12
68.93	10.51
69.89	0.32
74.04	0.85
75.04	1.17
76.05	1.84
77.04	100.00
78.01	10.34
81.96	0.29
83.02	0.32
90.96	0.96
91.99	2.31
93.01	8.06
94.04	7.68
95.03	3.39
96.03	0.50
97.03	7.48
98.01	0.58
100.93	0.47
108.97	0.61
110.93	0.44
112.98	4.44
115.00	0.44
118.95	0.41
122.98	0.44
125.03	5.93
126.01	0.50
127.00	0.76
132.97	2.13
138.95	0.41
142.98	1.23
144.98	4.06
148.96	0.35
158.96	0.44
162.94	0.88
168.95	0.38
178.91	0.79
186.98	0.32
188.95	0.55
208.94	0.38
212.94	0.61
216.98	0.50
218.95	0.38
228.95	0.38
238.95	6.34
239.93	0.76
254.95	0.67
256.97	43.20
257.98	4.44
274.93	2.60
286.98	0.32
350.96	1.23
370.91	1.49
389.90	33.64
390.95	4.38
391.97	0.50

GA70 0

CAL:LIB STA:

No 28

0:0

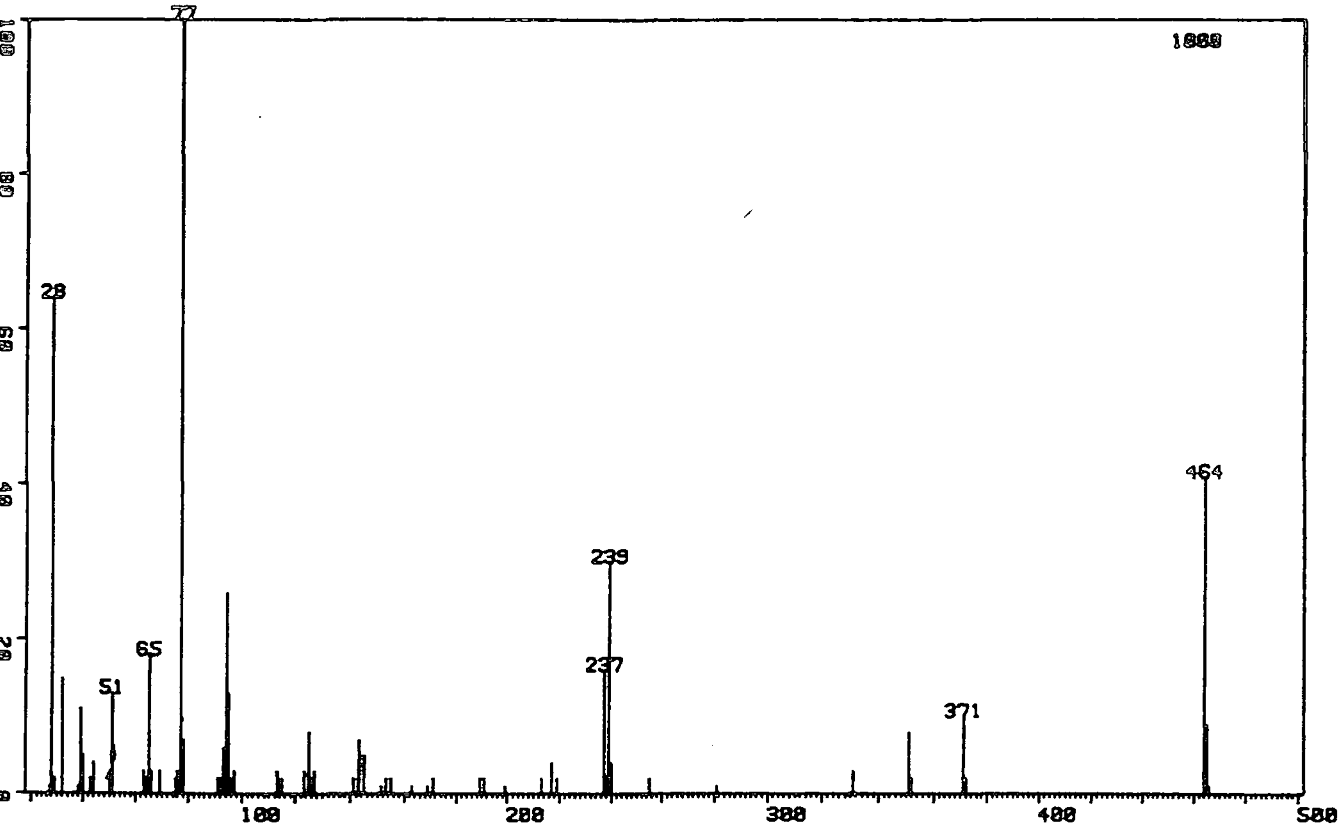


MASS	%HT. BASE
27.21	1.29
28.09	19.87
31.96	5.20
38.03	0.91
38.96	6.63
39.79	1.58
39.85	0.50
40.94	0.29
43.10	0.53
44.07	1.46
49.87	4.00
50.94	18.35
52.01	0.88
55.10	0.32
62.02	0.32
63.06	1.26
64.09	1.02
65.11	10.43
66.09	1.11
68.93	1.99
74.04	0.91
75.04	1.26
76.05	2.72
77.04	100.00
78.01	8.88
90.98	0.56
93.02	1.34
94.04	2.80
95.04	0.50
96.03	1.75
97.03	0.56
112.99	0.91
115.04	1.08
118.94	0.26
127.00	0.58
132.99	1.02
140.98	3.07
142.02	0.76
142.98	0.44
145.01	0.96
152.01	0.35
167.00	0.38
168.96	0.61
190.91	1.64
195.00	0.85
206.96	2.66
216.98	1.87
217.98	0.53
234.94	9.14
235.96	1.23
238.95	0.32
254.95	16.16
255.96	1.26
282.97	0.38
290.94	0.91
310.97	0.88
330.94	3.71
331.94	0.58
350.96	34.33
351.98	5.17

GA28Z 0
CAL:LIB STA:

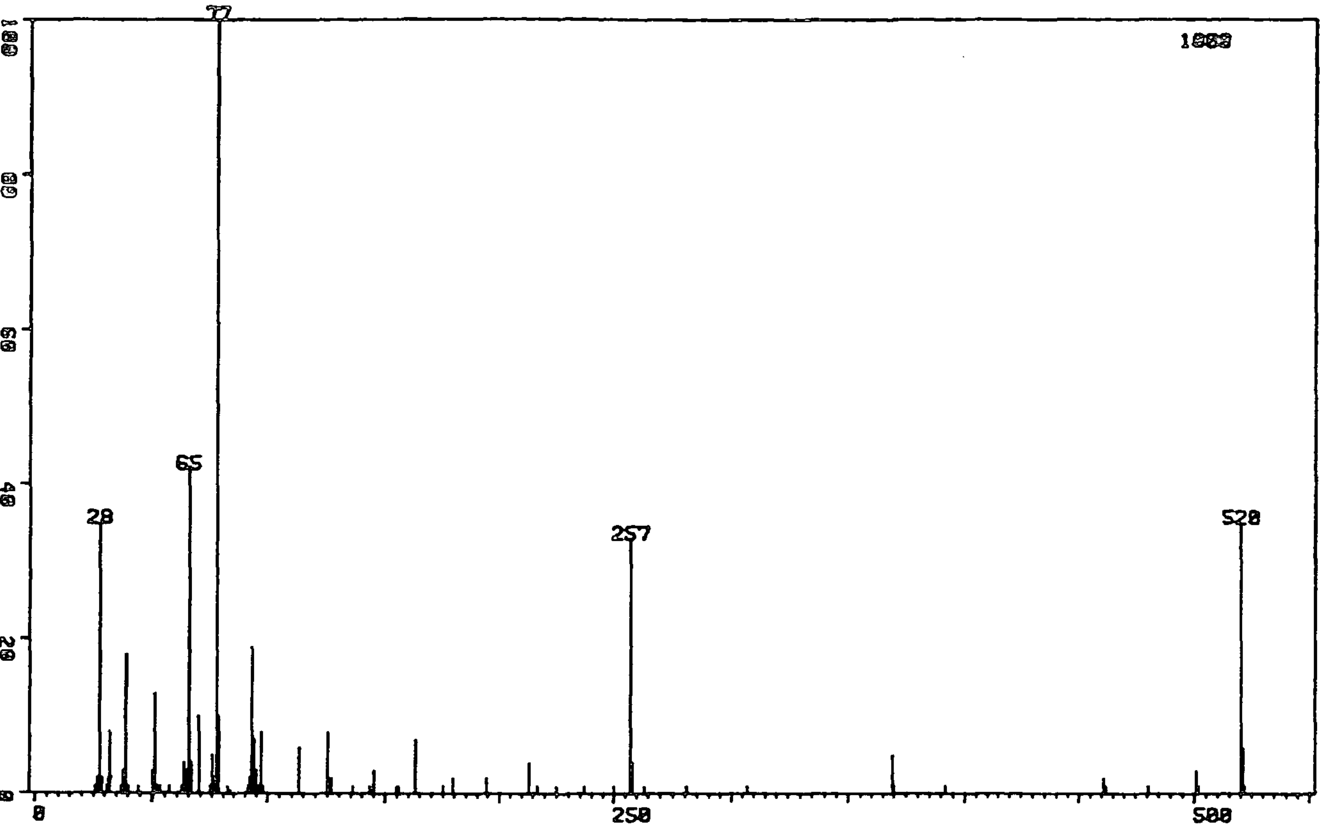
No 29

19-SEP
0:0



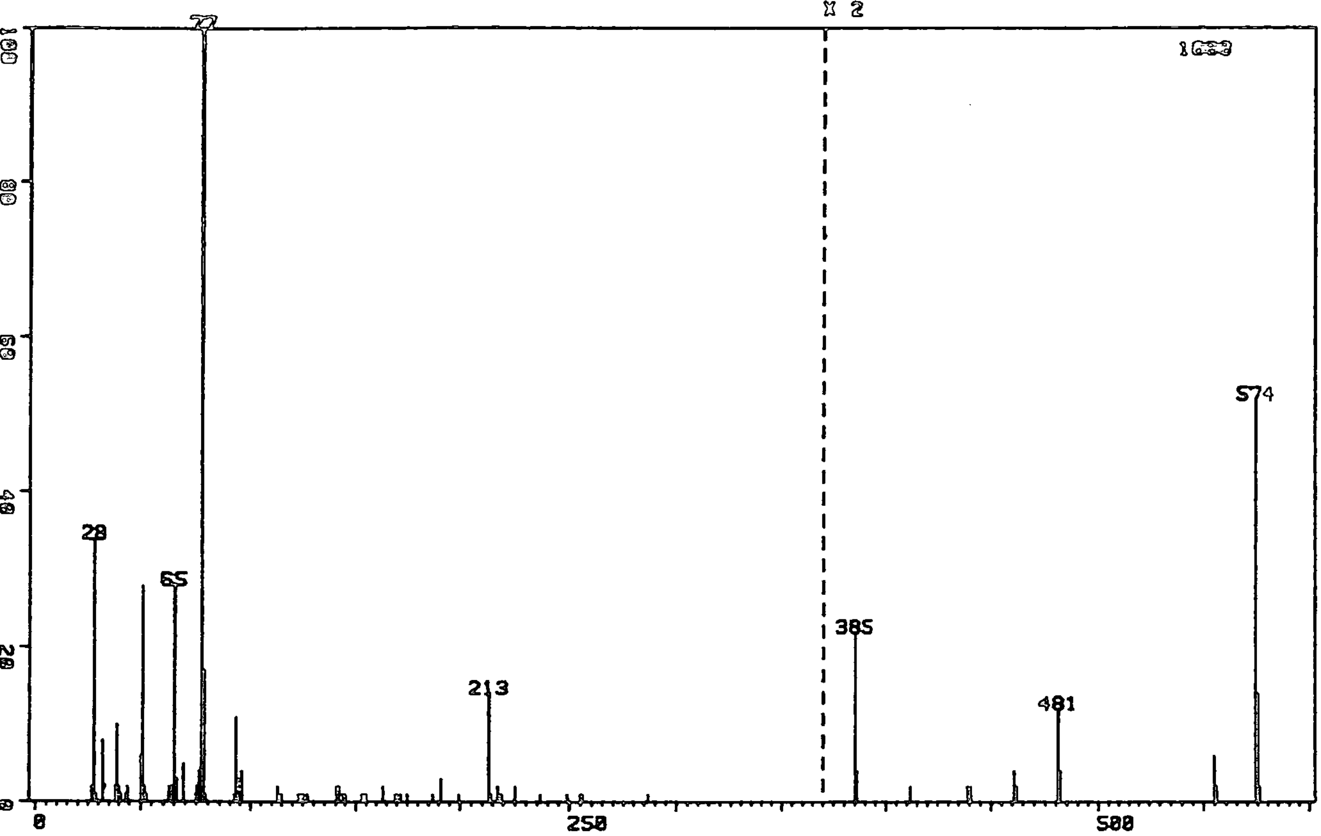
MASS	%HT. BASE
27.21	1.01
28.09	63.88
28.95	1.84
31.95	15.17
38.03	1.01
38.95	10.29
39.79	4.69
43.10	1.29
44.06	3.77
49.87	3.22
50.94	12.32
63.06	3.03
64.09	1.93
65.10	17.37
66.08	2.39
68.93	2.76
75.05	1.56
76.05	2.67
77.04	100.00
78.01	6.80
90.97	1.56
91.98	1.38
93.01	5.61
94.03	26.01
95.05	12.78
96.04	1.93
97.03	3.22
112.97	2.57
115.01	1.75
122.98	2.39
125.03	8.18
126.01	1.56
127.00	2.48
141.00	1.93
142.98	6.89
144.99	4.96
150.96	1.10
153.02	1.75
155.00	1.84
162.96	1.01
168.95	0.83
170.97	1.56
188.95	1.75
190.97	1.75
198.98	0.83
212.93	1.75
216.96	3.95
218.95	1.38
236.96	15.90
237.96	1.75
238.95	29.41
239.93	3.77
254.92	1.47
280.96	0.92
330.91	2.67
350.93	7.54
351.95	1.29
370.91	9.93
371.96	1.47
463.97	40.35
465.00	8.46
465.97	1.19

6A26 0　　　　　　　　　　**No 30**　　　　　　　　　　19-SEP
CAL:LIB　　STA:　　　　　　　　　　　　　　　　　　　0:0



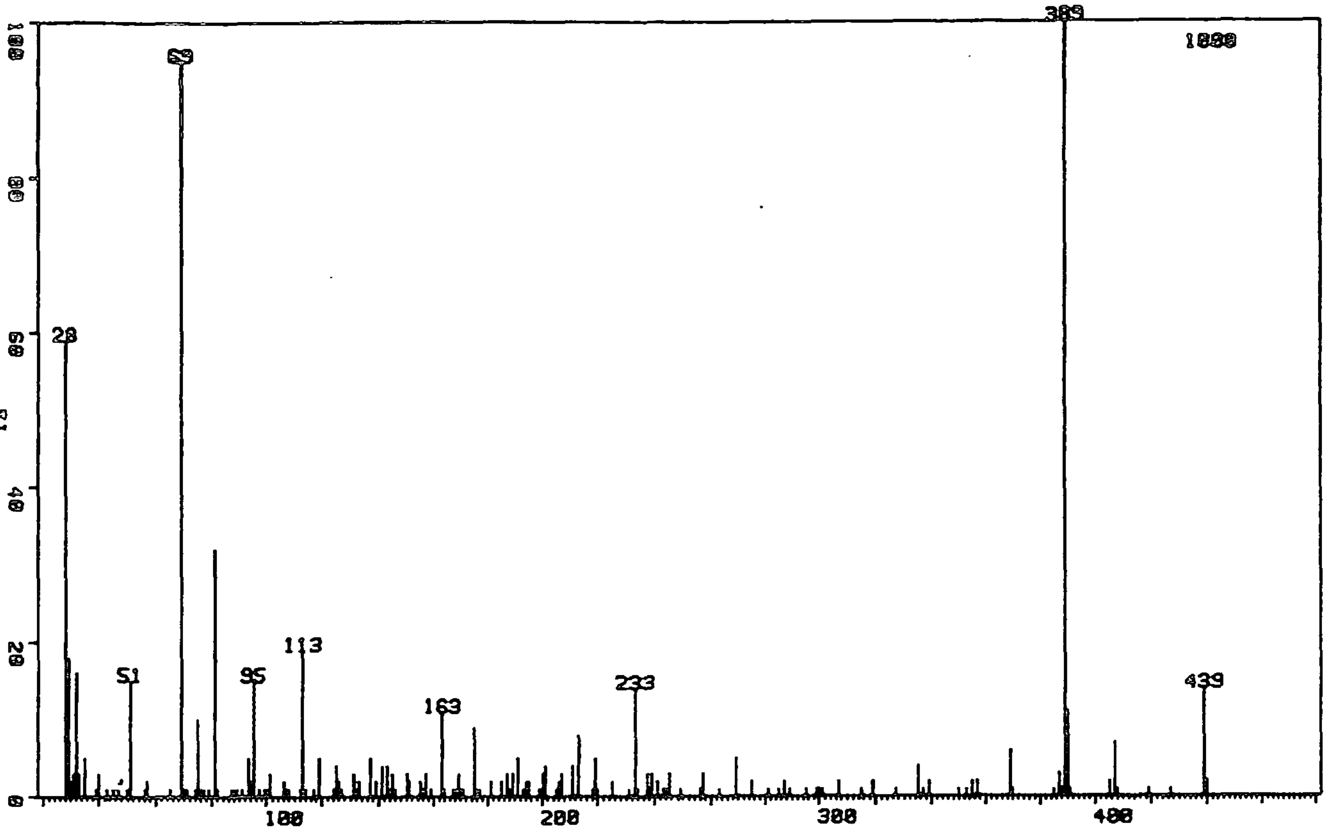
MASS	%HT. BASE
26.27	0.43
27.21	1.39
28.09	34.70
28.95	1.30
30.84	0.61
31.95	8.08
37.08	0.49
38.03	2.66
38.95	18.06
39.79	1.71
39.85	1.13
43.09	0.38
44.06	0.58
49.86	3.18
50.93	13.17
52.00	0.90
53.03	0.49
57.06	0.58
62.00	0.98
63.05	3.42
64.08	3.21
65.10	41.68
66.10	3.88
68.92	9.93
74.03	0.84
75.02	4.60
76.04	1.79
77.03	100.00
78.00	10.04
78.96	0.43
81.95	0.75
83.00	0.32
90.91	0.43
90.96	0.49
91.97	1.77
93.00	18.49
94.02	6.95
95.01	3.10
96.03	0.55
97.02	7.67
97.99	0.58
112.96	5.35
118.93	0.32
123.96	0.32
125.00	7.84
125.99	0.81
126.98	2.08
131.93	0.43
135.99	0.75
142.97	0.58
143.96	0.38
144.97	2.69
145.97	0.32
154.97	0.67
155.98	0.61
162.93	6.25
168.92	0.35
174.93	0.84
178.89	1.30
188.94	0.43
193.95	2.05
206.95	0.35
212.91	3.99
213.95	0.38
216.96	0.78
218.94	0.43
224.95	0.96
228.94	0.41
236.96	0.61
250.40	0.49
256.95	32.88
257.93	3.27
259.93	0.38
262.96	0.41
280.91	0.43
306.94	0.78
368.98	4.98
369.89	0.55
391.92	0.64
460.90	1.56
461.92	0.32
480.89	1.19
500.91	2.89
501.93	0.75
519.89	34.27
520.97	6.08
521.98	0.69

6A262 0 **No 31** 19-SEP
CAL:L10 STA: 0:0



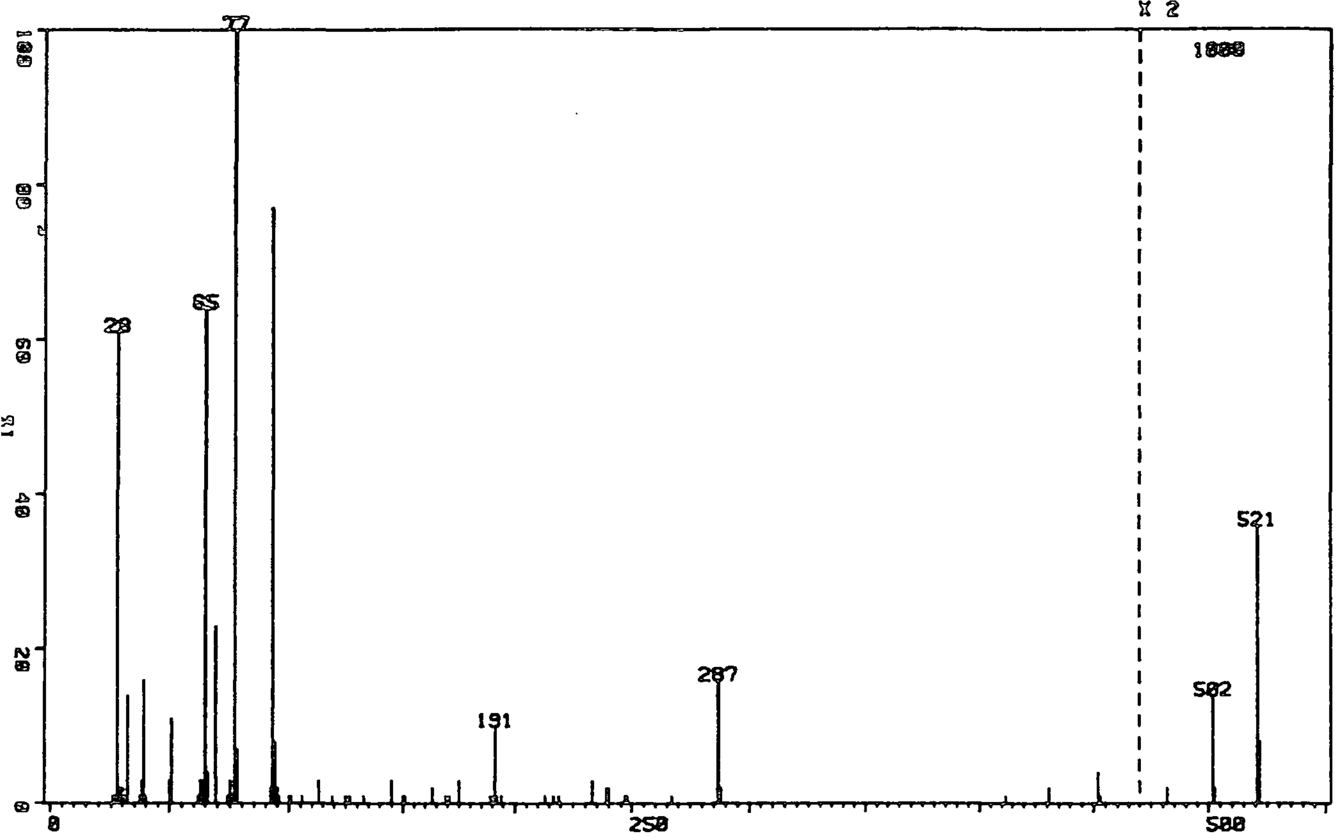
MASS	%HT. BASE
27.21	1.56
28.09	33.25
28.95	0.65
31.95	8.02
38.03	1.50
38.95	10.11
39.79	1.53
39.85	0.74
40.93	0.47
43.09	0.47
44.06	1.30
49.86	5.34
50.93	28.18
52.01	1.27
53.03	0.44
62.00	0.56
63.05	2.18
64.08	2.09
65.10	27.33
66.08	2.62
68.92	4.45
69.89	0.27
74.03	1.21
75.04	1.68
76.05	3.74
77.03	100.00
78.00	16.72
78.97	0.59
91.97	0.80
93.00	11.17
94.03	2.90
95.03	0.74
96.03	3.69
97.03	0.29
112.97	1.39
115.04	0.50
122.97	0.65
124.99	0.53
126.99	1.03
140.97	1.74
142.01	1.59
143.96	0.65
144.99	0.88
152.98	0.77
154.03	0.59
155.99	0.44
158.95	0.41
162.93	1.92
168.97	0.74
169.94	0.71
171.90	0.77
174.93	0.50
180.89	0.35
186.96	0.74
190.89	2.74
193.95	0.41
196.97	0.41
198.95	0.68
206.95	0.38
212.93	13.41
213.95	0.50
216.96	1.62
217.94	0.32
218.96	1.00
222.93	0.47
224.94	1.39
234.97	0.47
236.96	0.68
248.89	0.53
252.93	0.32
254.98	0.88
255.99	0.59
268.93	0.32
286.98	0.74
364.87	0.44
384.88	10.85
385.91	1.30
402.98	0.27
408.93	0.47
411.94	0.53
438.93	0.53
440.91	1.15
458.96	0.44
460.95	1.80
461.92	0.56
477.90	0.35
480.89	5.96
481.95	1.36
554.95	2.27
555.97	0.50
573.95	26.06
574.95	6.40
576.00	0.83

6A21 0 No 32 19-SEP
CAL:L10 STA: 0:0



MASS	%HT. BASE						
28.10	58.33	106.09	2.12	187.09	2.60	300.12	0.49
28.97	18.23	107.09	0.68	188.08	1.01	301.12	0.68
29.81	1.99	108.08	0.59	189.06	2.77	305.08	0.33
30.88	2.25	112.06	0.59	191.06	4.69	307.07	2.15
31.98	15.33	113.10	19.24	193.08	0.62	315.10	0.49
33.09	2.90	114.12	0.81	194.10	1.50	317.10	0.36
35.17	4.62	117.07	0.75	195.12	1.56	319.08	1.46
38.98	0.81	119.02	4.46	199.05	1.07	327.15	0.68
39.82	2.57	120.01	0.42	200.04	2.99	335.15	3.68
43.10	0.98	123.08	0.46	201.10	3.78	337.08	0.94
43.13	0.49	124.07	1.17	205.13	0.75	339.11	2.18
45.15	0.98	125.09	3.35	206.09	1.89	350.05	0.49
47.09	0.65	126.09	1.73	207.08	2.67	350.46	0.36
49.89	0.72	127.09	0.62	209.02	0.46	353.13	0.88
50.97	14.55	131.05	2.38	211.04	4.10	355.11	2.12
56.13	0.65	132.10	0.72	212.06	0.42	357.06	2.08
57.12	2.08	133.09	1.43	213.08	7.55	369.07	5.20
59.03	0.49	137.10	4.39	218.08	1.04	370.07	0.94
63.12	82.29	138.08	0.49	219.05	4.98	373.10	0.33
64.11	2.57	139.06	1.92	220.06	0.75	385.15	0.52
65.10	1.01	141.05	3.52	225.11	2.12	387.08	2.73
68.94	94.27	143.09	3.35	231.07	0.25	388.12	0.42
69.88	0.94	144.11	1.20	233.09	13.38	389.13	100.00
70.97	0.68	145.09	10.09	234.11	0.72	390.12	10.42
74.07	0.52	146.10	0.52	237.08	2.41	391.11	0.65
75.09	9.73	149.02	0.33	238.07	1.07	405.10	1.33
76.09	0.91	150.00	2.57	239.05	2.99	407.08	6.58
77.09	1.24	151.05	1.76	241.06	1.99	408.06	1.04
78.99	1.17	155.10	1.33	243.07	0.55	419.11	0.98
81.00	31.74	156.09	0.42	244.09	0.91	427.12	0.46
82.05	1.11	157.08	2.51	245.11	2.90	439.16	13.54
83.08	0.39	159.04	0.85	249.07	0.68	440.11	1.92
87.08	0.62	163.09	10.64	250.08	0.42		
88.06	1.14	164.11	0.62	256.12	0.88		
89.02	0.81	167.09	0.52	257.07	2.77		
91.01	0.81	168.06	0.98	263.08	0.28		
93.07	5.01	169.04	3.09	269.07	4.72		
94.10	1.27	170.04	1.07	270.08	0.36		
95.12	14.84	171.08	0.59	275.12	1.27		
96.09	0.46	175.09	9.15	281.11	0.49		
97.05	0.75	176.11	0.78	285.12	0.25		
99.00	1.20	177.08	0.52	287.10	2.08		
99.96	0.91	181.05	1.63	289.08	0.68		
101.02	2.57	183.09	0.42	295.15	1.14		
105.08	0.36	185.09	1.40	299.08	0.46		

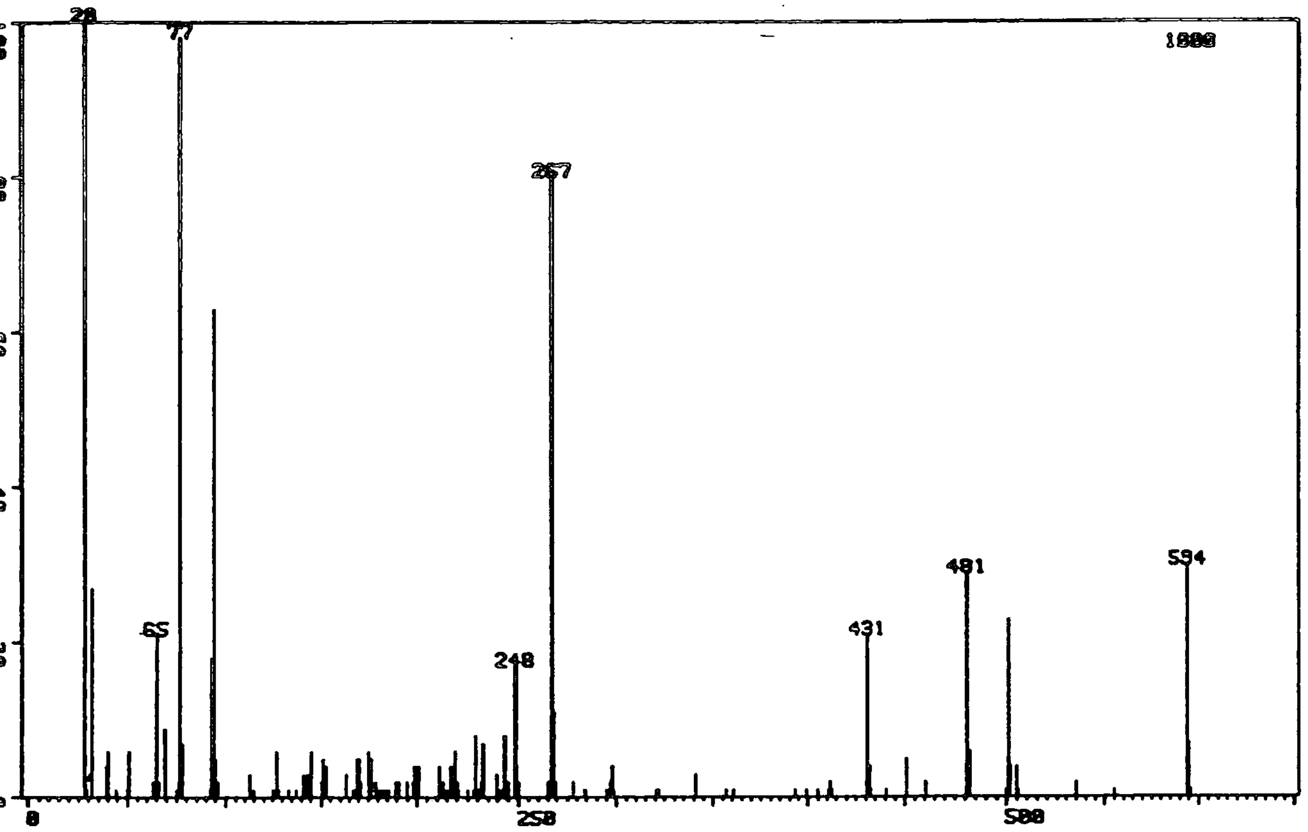
6A23 0 No 33 19-SEP
CAL:LIB STA: 0:0



MASS	%HT. BASE		
26.29	0.41	151.08	0.97
27.22	1.08	163.10	1.82
28.10	60.61	169.07	1.14
28.96	0.76	171.12	1.03
30.86	0.56	175.11	2.26
31.97	13.98	181.06	0.32
37.11	0.64	189.06	0.62
38.05	2.29	191.06	9.94
38.97	16.18	192.07	0.56
39.82	2.61	194.09	0.56
39.88	0.85	199.07	0.32
43.13	0.38	211.11	0.38
44.10	0.38	213.13	1.06
49.90	2.40	217.12	0.85
50.98	10.76	218.09	0.32
52.06	0.44	219.04	1.23
62.06	0.97	233.10	2.90
63.11	3.43	239.08	1.41
64.12	3.05	240.07	1.29
65.10	63.77	247.14	0.85
66.08	4.22	248.10	0.94
68.93	22.98	267.12	1.20
74.05	0.56	287.15	15.86
75.05	2.34	288.10	1.73
76.07	1.03	337.23	0.44
77.06	100.00	412.41	0.41
78.03	6.71	431.41	1.96
81.99	0.32	451.54	3.25
92.02	2.20	452.54	0.56
93.06	76.79	481.53	1.23
94.09	7.97	501.61	6.51
95.07	2.17	502.62	1.20
96.09	0.47	520.68	17.82
99.93	0.50	521.69	3.31
101.00	0.73		
106.06	0.38		
113.06	2.34		
119.01	0.76		
125.09	0.97		
127.11	0.56		
133.07	0.53		
143.59	0.44		
145.09	2.81		
150.02	0.76		

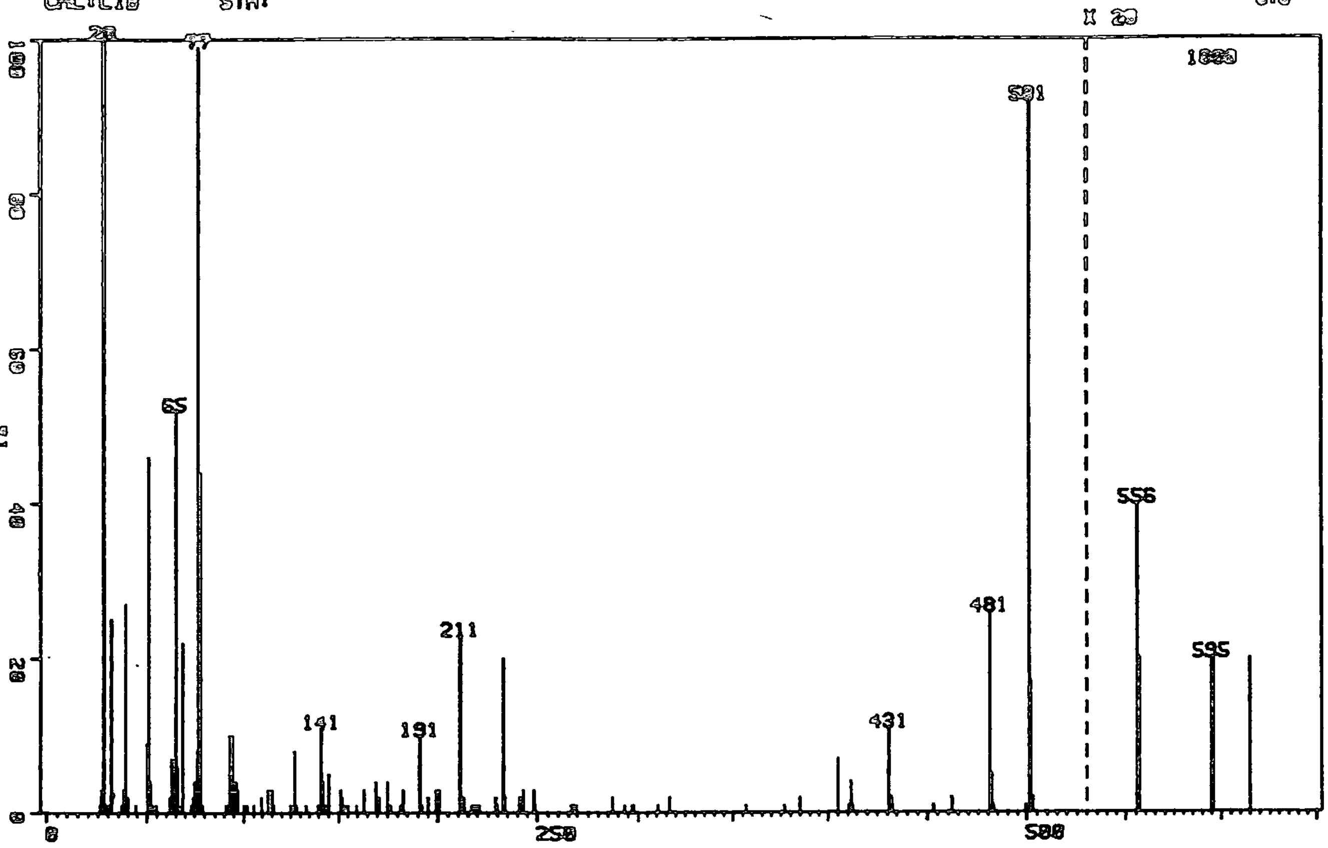
6A250 0 No 34 21-SEP

CAL:LIB STR: 0:0



MASS	%HT. BASE								
28.10	100.00	146.08	0.35	220.05	1.33	297.08	1.28	463.07	0.49
28.97	0.84	147.08	0.26	221.09	1.02	298.08	3.25	479.13	0.32
31.98	26.89	149.05	0.49	223.11	0.64	299.07	0.67	481.14	28.78
38.06	0.49	150.00	1.62	224.11	0.46	301.12	0.35	482.09	5.40
38.98	3.68	151.05	4.61	225.06	1.19	303.11	0.38	483.11	0.58
39.82	5.28	152.09	0.84	226.08	0.44	312.12	0.32	500.14	0.52
43.13	0.49	153.13	3.54	228.06	0.96	313.15	0.52	501.08	22.51
44.11	0.93	163.02	2.70	229.04	7.43	321.13	0.70	502.14	3.39
49.91	0.96	164.06	0.52	231.05	1.16	322.13	0.81	505.12	3.31
50.98	5.43	167.06	0.75	232.08	2.12	323.07	0.44	506.11	0.67
62.08	0.38	168.05	0.64	233.07	6.24	335.05	0.35	535.14	1.45
63.12	2.20	169.01	4.93	234.09	0.38	337.08	0.38	536.14	0.38
64.13	1.71	170.03	4.70	235.11	0.44	339.05	0.49	555.24	0.67
65.12	20.42	171.07	1.31	237.09	0.61	341.13	2.41	594.29	29.94
66.08	1.94	175.06	5.40	239.06	2.76	343.13	0.52	595.27	6.70
68.94	9.05	176.08	0.61	240.08	0.55	352.11	0.44	596.26	0.87
74.06	0.55	177.08	4.50	241.07	0.73	353.06	0.29		
75.06	1.13	178.07	0.41	243.13	7.40	357.05	0.93		
76.08	1.89	179.07	1.60	244.12	1.25	361.09	0.78		
77.06	97.91	181.05	0.87	245.08	1.25	363.10	0.49		
78.04	6.30	182.09	1.19	246.10	0.55	373.13	0.41		
92.03	1.02	183.09	0.84	247.03	0.29	380.12	0.29		
93.08	17.61	185.11	0.67	248.02	16.59	381.17	0.58		
94.10	62.66	186.10	0.67	249.02	4.21	385.10	0.55		
95.11	4.79	187.02	0.49	250.03	1.89	387.12	0.41		
96.08	1.42	189.01	1.94	251.03	0.67	389.09	0.55		
99.93	0.38	190.99	1.65	255.07	0.58	392.13	0.55		
100.99	0.67	193.07	0.55	257.03	0.46	393.12	1.42		
109.03	0.64	195.07	1.65	263.09	0.46	399.06	0.84		
113.05	2.49	196.09	0.46	264.09	0.64	405.09	0.96		
114.08	0.35	197.08	0.32	265.08	1.62	411.14	0.90		
115.12	1.13	198.07	1.51	266.08	0.38	412.10	2.09		
118.99	0.55	199.05	3.92	267.08	79.34	413.08	1.19		
120.00	0.38	200.03	1.31	268.08	10.79	431.12	20.89		
125.07	1.02	201.06	4.09	269.05	1.33	432.10	3.45		
127.08	5.57	202.09	0.64	270.06	0.38	433.10	1.25		
128.08	0.70	207.07	0.55	273.14	0.44	441.03	0.61		
131.02	0.49	209.07	0.32	274.15	0.29	442.11	0.26		
133.08	0.96	211.06	3.39	275.10	0.38	450.15	0.32		
137.06	0.78	212.09	0.44	277.09	0.46	451.16	4.64		
139.04	0.38	213.09	2.00	278.10	1.36	452.12	0.55		
141.09	2.26	214.13	0.35	284.12	0.75	453.10	0.49		
142.13	1.36	215.12	1.13	285.08	0.49	459.08	0.67		
143.07	2.76	217.08	3.34	292.10	0.52	461.50	2.12		
144.06	0.64	218.06	0.67	293.12	0.61	462.40	0.32		
145.06	5.57	219.03	5.89	295.06	0.93	462.76	0.32		

GA2SZ 0 **No 35** 19-SEP
CAL:LIB STA: 0:0

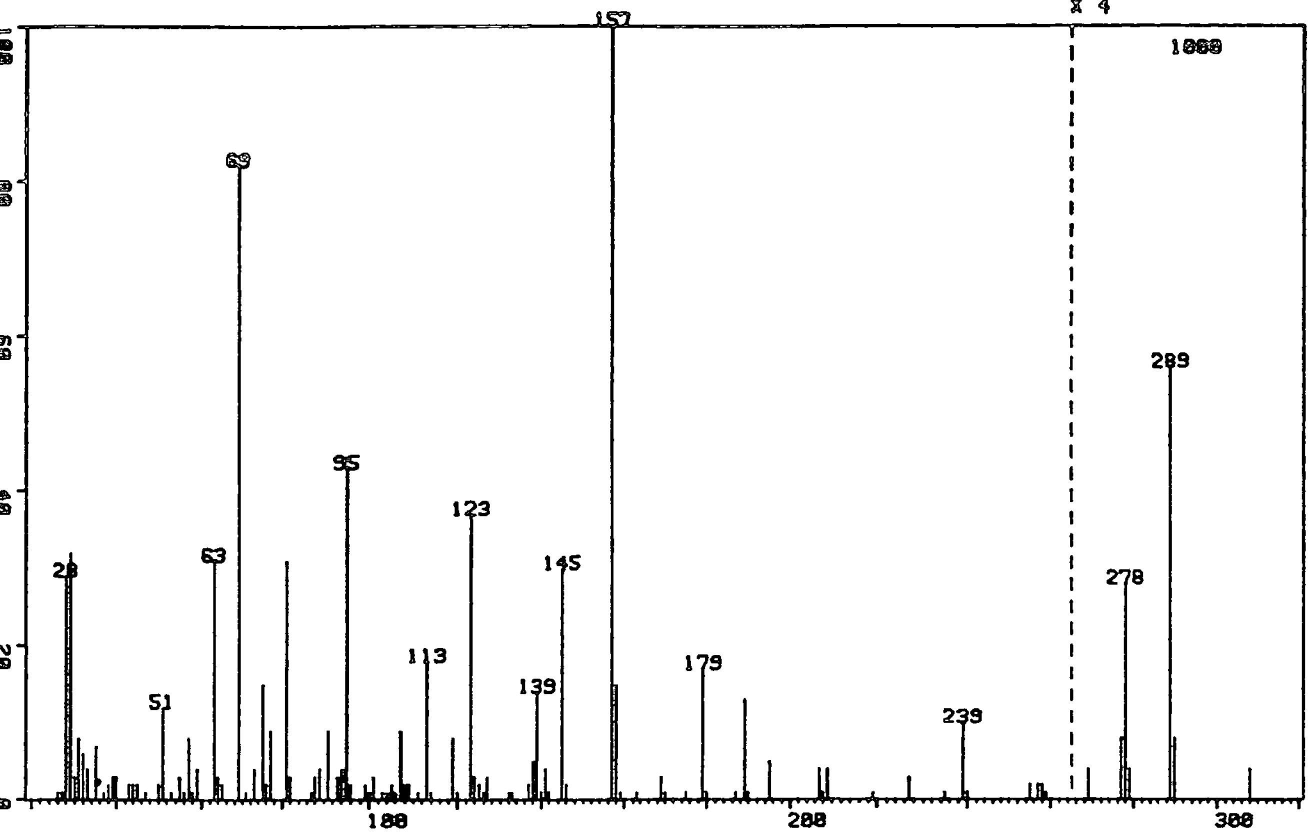


MASS	%HT. BASE						
26.29	0.73	100.98	0.50	191.05	9.60	322.15	0.56
27.22	3.11	102.06	0.50	192.06	0.50	335.13	0.53
28.10	100.00	105.09	0.62	193.10	0.26	337.06	0.35
28.96	0.79	109.02	1.88	195.12	1.82	357.13	0.73
30.87	0.59	113.05	3.14	196.11	0.38	377.15	1.03
31.97	24.30	115.12	2.58	199.07	2.90	385.18	1.47
37.11	0.53	116.10	0.73	200.05	0.67	386.17	0.29
38.06	3.08	119.00	0.44	201.08	2.93	405.21	6.78
38.98	26.29	125.07	0.56	211.08	22.54	406.20	0.44
39.82	3.76	127.07	7.34	212.10	1.32	411.23	0.56
39.88	1.85	128.07	0.67	213.09	1.56	412.21	3.84
40.97	0.44	129.04	0.38	215.17	0.38	413.23	0.79
43.13	0.41	133.07	0.67	217.12	1.00	431.23	10.59
44.11	0.67	137.05	0.47	219.06	0.91	432.27	1.91
45.15	0.41	138.07	0.32	220.07	0.50	433.22	0.79
49.91	8.74	139.05	0.88	221.09	1.03	453.30	0.59
50.98	46.01	140.05	0.47	229.09	1.79	461.04	0.26
52.07	3.29	141.09	11.03	230.11	0.73	462.07	1.67
53.09	0.70	142.13	3.29	231.08	0.38	481.35	25.97
55.15	0.85	143.06	0.67	233.08	19.98	482.37	4.78
57.12	0.41	144.05	0.41	234.10	1.29	483.40	0.53
62.08	1.44	145.06	4.87	235.14	0.29	499.44	0.44
63.12	7.19	149.05	0.44	239.09	0.26	500.46	0.35
64.13	4.69	149.98	0.47	241.07	2.14	501.43	92.02
65.11	51.64	151.05	2.90	243.16	3.20	502.45	16.34
66.09	5.78	152.09	1.26	244.11	0.41	503.47	1.41
68.01	0.62	153.11	0.79	247.10	0.35	555.66	1.26
68.94	21.57	155.09	0.76	248.10	2.32	556.68	0.32
69.88	0.38	159.06	1.20	249.09	1.47	594.79	0.91
73.03	0.85	163.07	2.96	250.08	0.41	595.87	0.50
74.06	1.41	168.10	0.70	251.11	0.41	614.98	0.67
75.07	3.70	169.07	3.49	255.16	0.32		
76.08	8.13	170.08	2.32	263.14	0.38		
77.05	98.83	171.08	1.38	267.15	0.79		
78.04	43.81	172.08	0.38	268.09	0.76		
78.99	1.26	175.11	3.58	269.06	1.20		
83.06	0.35	176.09	0.41	287.18	1.56		
91.01	0.67	177.09	0.76	291.15	0.41		
92.05	0.76	179.07	0.44	293.17	1.12		
93.07	9.45	180.05	0.44	297.12	1.03		
94.10	10.10	181.07	0.44	298.09	0.70		
95.10	2.64	182.07	0.88	311.09	0.56		
96.11	3.29	183.07	3.02	313.13	0.38		
97.07	2.90	187.10	0.44	317.11	1.44		
99.91	0.67	189.05	0.35	318.09	0.38		

GA24 0
CAL:LIB STA:

No 36

19-SEP-80
0:0

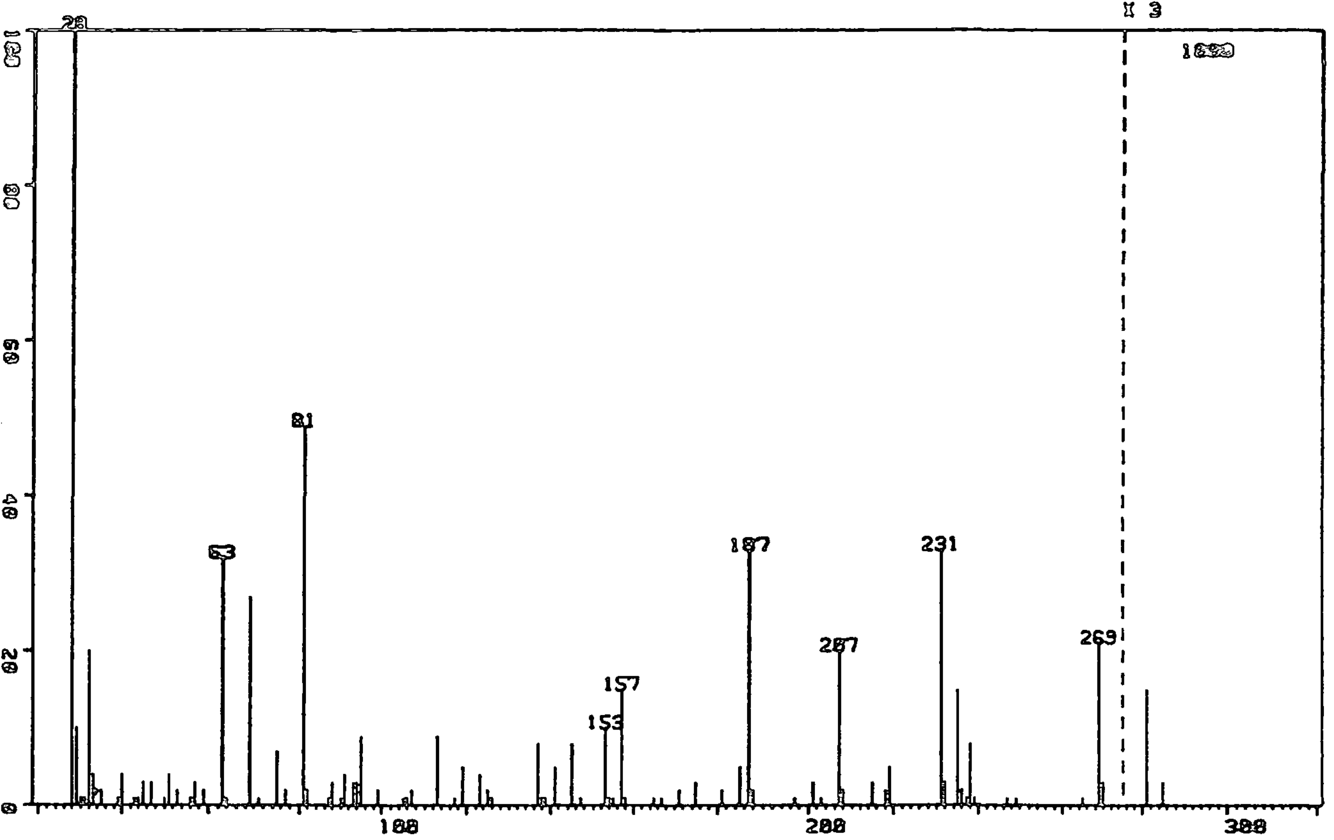


MASS	%HT. BASE				
26.29	0.59	89.00	3.61	163.09	0.92
27.22	1.04	90.99	9.44	169.05	3.17
28.10	28.37	93.05	3.25	170.06	0.71
28.96	32.19	94.08	3.99	175.13	1.04
29.80	2.31	95.09	43.08	179.03	16.66
30.88	7.49	96.09	1.78	180.02	0.71
31.97	5.80	99.01	2.13	185.10	0.38
33.08	3.37	99.97	0.56	187.09	0.86
35.17	7.25	101.03	2.49	189.06	12.31
37.11	0.68	103.08	0.50	190.05	0.86
38.05	1.51	104.10	0.47	195.13	4.32
38.97	2.84	105.11	1.42	207.10	3.34
39.82	1.01	106.07	0.59	208.11	0.44
43.09	1.45	107.07	8.49	209.08	4.05
44.11	1.78	108.05	1.66	219.11	0.44
45.14	1.57	109.03	1.83	227.12	2.34
47.08	1.07	111.01	0.68	235.12	1.04
47.12	0.44	112.04	0.33	239.08	9.32
48.98	0.38	113.06	17.99	240.09	0.68
49.89	1.27	114.08	0.74	255.14	1.66
50.96	12.07	117.07	0.33	257.10	1.69
53.08	1.21	119.02	8.05	258.10	1.42
55.14	2.93	120.01	0.86	259.06	1.15
56.12	1.15	121.04	0.41	269.09	0.50
57.11	8.11	123.07	36.42	277.13	1.36
58.07	0.59	124.09	2.40	278.08	6.66
59.02	3.43	125.10	1.86	279.09	0.50
63.12	31.71	126.09	1.18	289.12	13.93
64.10	2.51	127.09	2.99	290.10	1.33
65.09	1.60	132.06	0.98	308.15	0.33
68.02	0.53	133.10	0.72		
68.96	81.39	137.09	2.01		
69.91	1.21	138.10	4.35		
70.95	0.74	139.05	13.25		
73.05	3.46	140.04	0.77		
74.07	0.53	141.04	4.14		
75.07	15.15	142.08	0.50		
76.08	1.54	145.12	29.79		
77.06	8.25	146.09	1.27		
80.99	31.12	150.01	0.33		
82.02	2.75	151.07	0.38		
83.07	0.47	157.10	100.00		
87.07	0.98	158.09	14.88		
88.04	2.37	159.05	1.12		

GA242 0
CAL:L10 STA:

No 37

19-SEP-80
0.0

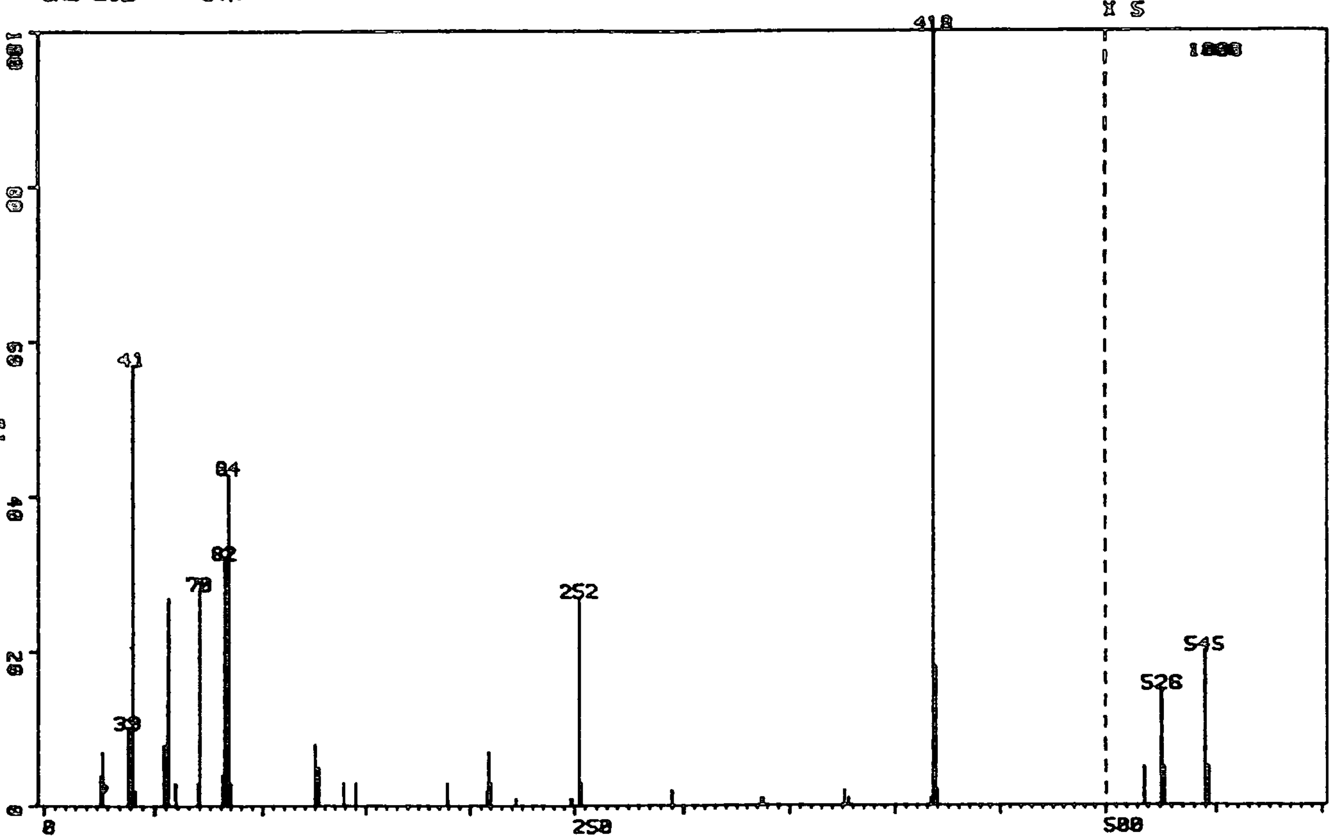


MASS	%HT. BASE
28.10	100.00
28.97	9.86
29.81	1.20
30.87	2.94
30.89	1.20
31.98	20.19
33.10	4.03
35.17	2.22
38.98	0.78
39.82	3.55
43.10	1.20
44.11	0.66
45.16	2.88
47.09	2.58
49.91	0.78
50.96	3.61
53.09	1.62
56.13	0.60
57.11	2.82
59.02	1.62
63.12	31.67
64.11	0.84
68.96	26.38
70.96	0.84
75.08	7.09
77.07	1.56
80.99	49.22
82.03	1.32
87.08	0.90
88.04	2.34
89.94	0.66
90.99	3.25
93.08	2.82
94.08	2.46
95.10	8.95
98.99	2.22
105.09	0.72
106.08	1.14
107.09	1.62
113.08	8.59
117.09	0.60
119.04	5.11
123.09	4.09
125.12	1.62
126.09	1.14
137.07	7.63
138.06	1.14
139.05	0.90
141.04	4.51
145.10	7.93
147.07	0.66
153.09	10.10
154.11	0.78
155.09	1.14
157.08	14.36
158.07	0.84
165.08	1.02
167.10	0.66
169.06	1.26
171.07	1.50
175.12	3.06
181.07	1.38
185.09	4.57
187.12	32.99
188.07	2.10
197.09	1.14
201.10	2.58
203.08	0.78
207.07	20.19
208.08	1.38
215.10	2.58
218.07	1.44
219.08	5.11
231.13	32.63
232.14	3.06
235.05	14.90
236.07	1.32
237.07	1.08
238.05	7.45
239.04	1.08
247.12	0.72
249.06	0.78
265.12	1.20
269.06	20.85
270.10	2.40
281.13	4.33
285.11	0.78

GA68 0
CAL:LIB STA:

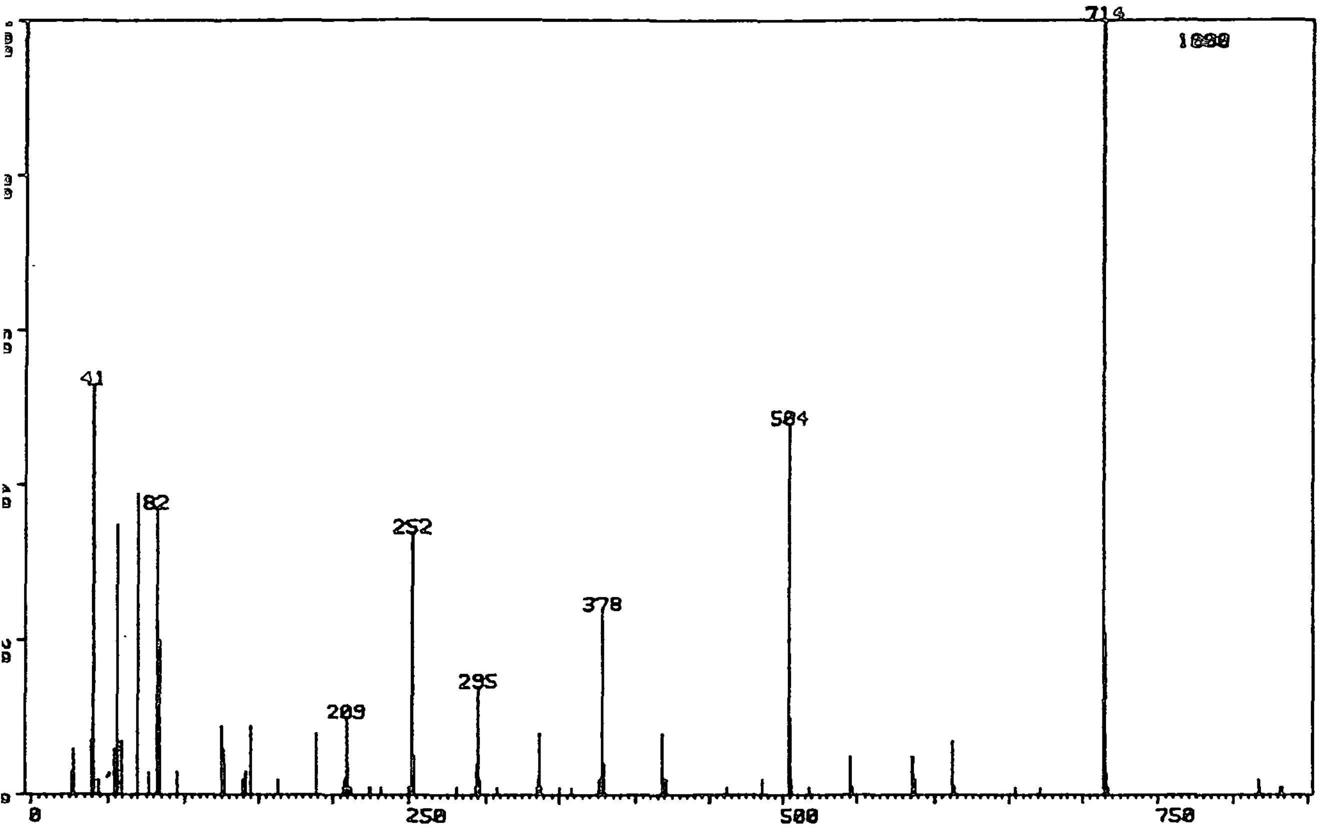
No 38

19-SEP-80
0.0



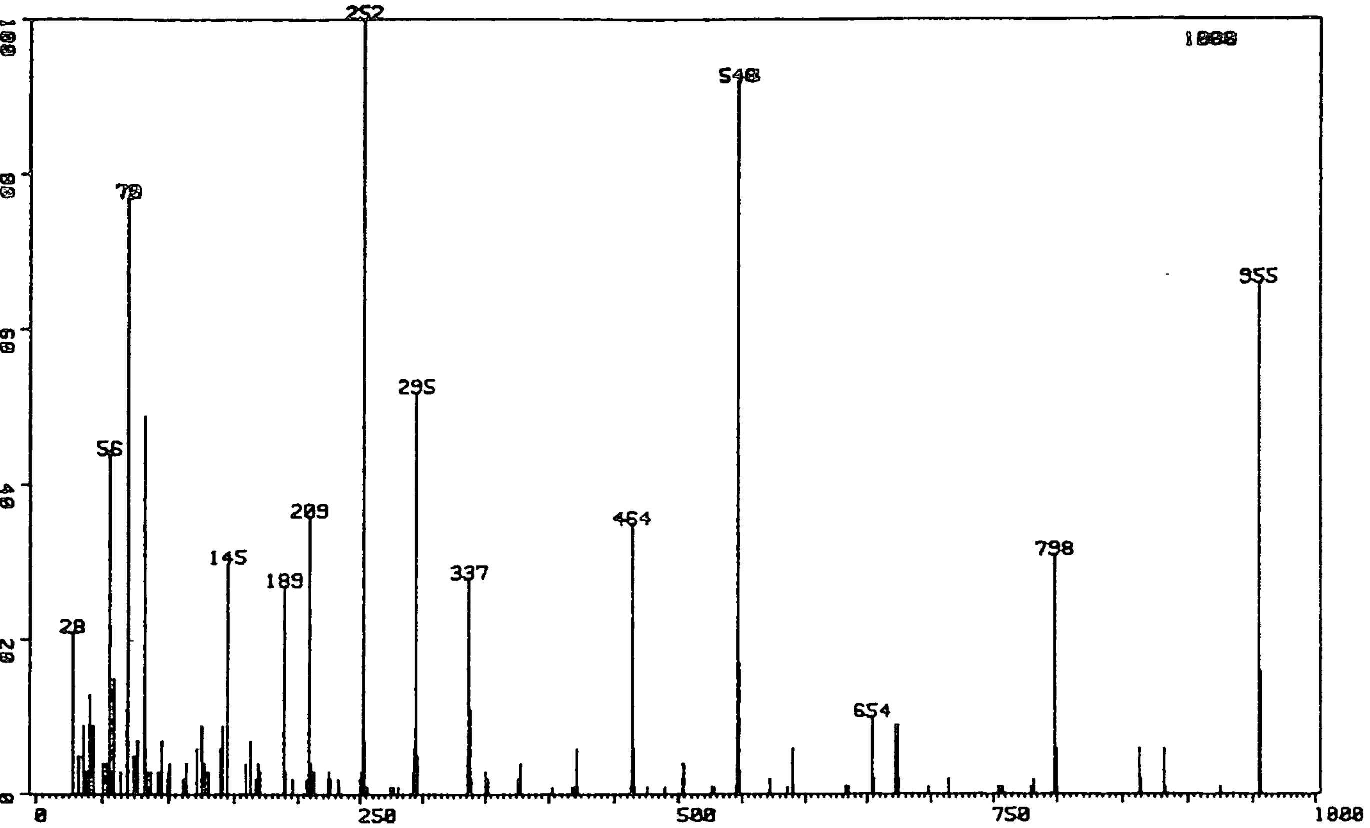
Mass	% Base	
27.00	3.46	
27.99	7.04	F
28.00	4.01	F
39.00	9.69	
41.02	56.77	
42.01	2.06	
54.01	7.69	
55.01	4.71	
55.99	27.17	F
56.03	5.40	F
59.00	2.87	
68.97	2.67	
69.96	27.95	
81.03	4.07	
81.99	31.28	
83.00	17.11	
84.01	43.17	
85.00	2.26	
124.98	7.71	
125.99	3.77	
126.99	4.85	
138.99	2.91	
144.95	3.10	
188.94	2.41	
206.92	0.06	
206.98	0.16	
207.99	1.27	
208.98	6.83	
209.98	2.55	
211.00	0.26	
211.93	0.27	
222.00	1.18	
222.99	0.21	
223.95	0.21	
224.94	0.12	
225.97	0.26	
231.94	0.29	
233.92	0.05	
234.01	0.33	
235.02	0.11	
237.95	0.07	
237.99	0.09	
248.02	0.44	
249.00	1.02	
249.97	0.35	
250.93	0.23	
251.93	26.90	
252.93	2.26	
253.85	0.07	
253.96	0.14	
263.99	0.06	
276.94	0.08	
280.95	0.06	
280.99	0.11	
291.98	0.09	
292.94	0.11	
293.88	0.14	
294.93	1.32	
295.90	0.20	
306.98	0.21	
307.86	0.35	
308.03	0.06	
318.97	0.09	
319.69	0.05	
319.76	0.07	
319.79	0.07	
319.85	0.08	
319.90	0.09	
320.02	0.09	
320.15	0.05	
320.27	0.07	
320.38	0.07	
320.45	0.08	
320.50	0.08	
320.54	0.06	
320.63	0.07	
320.78	0.07	
320.90	0.10	
320.97	0.06	
321.03	0.08	
321.13	0.08	
321.22	0.06	
321.30	0.08	
321.37	0.08	
321.41	0.09	
321.46	0.07	
321.60	0.07	
321.77	0.08	
321.96	0.11	
322.07	0.05	
322.41	0.06	
331.85	0.12	
333.88	0.22	
334.94	0.32	
335.87	0.22	
336.83	1.21	
337.91	0.56	
338.96	0.08	
338.99	0.05	
348.00	0.43	
349.01	0.08	
349.96	0.11	
357.95	0.46	
359.83	0.23	
361.91	0.10	
375.91	1.27	
376.80	0.12	
376.95	0.28	
377.94	0.86	
378.98	0.14	
397.99	0.11	
398.97	0.28	
400.02	0.09	
401.99	0.07	
402.85	0.12	
416.97	0.47	
417.30	0.07	
417.97	100.00	
418.46	0.07	
418.54	0.08	
418.98	17.76	
419.98	2.23	
420.98	0.17	
517.85	0.28	
525.87	3.03	
526.87	0.51	
527.94	0.08	
544.85	4.13	
545.85	0.73	
546.87	0.11	

GA68X 0 No 39 19-SEP-80
CAL:L10 STA: 0:0



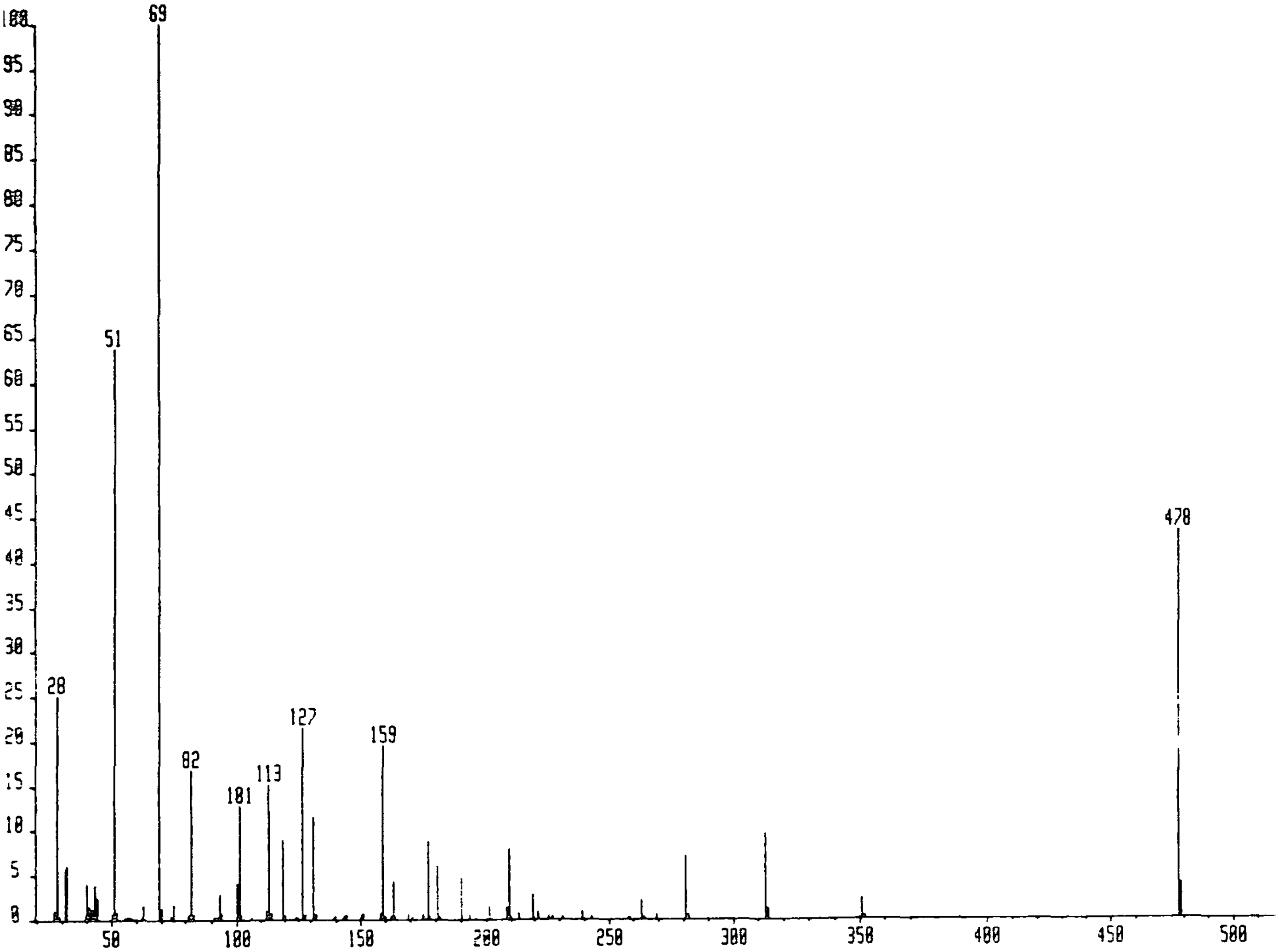
Mass	% Base						
26.99	2.87	253.84	0.37	357.48	0.14	567.99	0.38
27.99	5.84	253.98	0.14	357.95	0.61	585 94	4.31
39.00	6.35	255.85	0.11	358.88	0.12	586.95	1.12
41.02	52.80	266.01	0.30	358.96	0.26	587.96	1.67
43.99	2.24	274.96	0.41	359.86	0.27	589.00	0.35
54.01	5.52	276.97	0.20	359.93	0.14	611.75	6.97
55.01	2.62	278.90	0.09	361.98	0.20	612.75	0.96
55.99	34.98 F	280.77	0.10	372.98	0.15	629.78	0.14
56.03	4.12 F	280.95	0.62	373.02	0.13	653.88	0.67
59.00	7.19	281.64	0.13	375.94	2.19	671.81	0.78
68.97	4.34	281.94	0.33	376.95	2.10	672.83	0.17
69.96	38.73	282.58	0.11	377.94	23.35	693.82	0 12
76.99	2.50	282.92	0.19	378.95	3.25	693.93	0.15
81.99	37.02	282.99	0.20	379.98	0.44	713.97	100.00 F
83.00	11.36	292.93	0.67	402.76	0.13	715.00	21 61 F
84.00	19.50	293.92	3.64	402.80	0.11	716.03	2.82
94.97	2.54	294.93	13.90	402.86	0.19	717.07	0.33
124.98	8.94	295.90	1.53	403.99	0.27	817.16	1.94
126.00	5.73	296.92	0.18	417.98	7.71	817.98	0 38
126.97	3.93	298.99	0.33	418.99	1.58	832.49	1.00
138.97	2.09	306.87	0.14	419.73	0.13	833.27	0.24
140.90	2.69	306.98	0.45	419.77	0.16		
144.95	8.78	307.73	0.16	420.00	0.22		
162.94	2.02	307.93	0.92	420.81	1.48		
188.94	7.52	308.92	0.15	421.78	0.26		
205.97	0.15	308.99	0.16	422.84	0.21		
206.96	0.59	321.93	0.27	447.76	0.43		
207.98	1.52	331.87	0.17	461.76	0.56		
208.94	9.26	332.95	0.18	463.69	0.09		
209.87	4.12	333.89	0.48	463.83	0.37		
210.88	0.25	334.97	0.54	483.84	0.16		
211 94	0.53	335.88	1.39	485.84	1.91		
212.85	0.19	336.83	8.22	486.88	0.27		
221.01	0.37	337.89	0.73	501.86	0.09		
223.95	0.59	349.93	1 09	502.98	0.14		
224.95	0.78	350.94	0.16	503 84	47.76		
225.98	0.33	354 10	0.10	504.37	0.13		
226.99	0.13	354.44	0.09	504.84	10.04		
231.95	0.66	354.49	0.16	505.84	1.40		
232.97	0.23	354.56	0.14	506.85	0 14		
238.00	0.17	354 63	0 12	517.86	0.73		
248.99	0.40	354 67	0.15	525.94	0.22		
249.94	0.72	354.97	0.41	543.89	0.26		
250.93	1.11	356.91	0.27	545.91	4.30		
251.94	33.56	357.18	0.19	546.92	0.72		
252.88	5.12	357.27	0.14	547.99	0.13		

GA68Z 0 No 40 19-SEP-80
CALiLIB STR: 0:0



Mass	% Base						
27.98	20.65	207.96	0.94	503.82	3.58	798.04	30.83
31.96	5.22	208.92	35.49	504.75	0.47	798.94	6.13
35.95	8.48	209.92	3.31	504.89	0.41	799.85	0.73
37.95	2.85	211.92	1.82	525.88	0.59	863.52	5.28
39.00	2.70	212.82	2.61	527.96	0.44	864.26	1.73
41.01	12.91	223.93	2.11	544.90	0.53	864.98	2.14
43.97	8.68	224.94	2.61	545.88	91.49	882.16	5.72
50.98	3.61	225.95	2.05	546.88	16.54	882.87	0.88
54.00	3.84	231.93	2.08	547.89	2.85	925.14	0.47
55.99	44.18	232.92	0.67	571.68	1.41	954.98	65.74
56.99	2.61	249.91	1.47	585.92	0.94	955.69	16.13
59.00	14.29	250.91	2.90	589.65	6.13	956.40	2.49
63.93	2.52	251.92	100.00	590.58	0.32		
68.96	10.74	252.92	7.07	590.70	0.53		
69.95	76.27	253.65	0.44	603.72	0.38		
73.96	4.25	253.72	0.79	632.30	0.65		
76.98	6.42	253.89	0.35	632.45	0.50		
81.99	49.08	253.93	0.76	632.59	0.44		
82.99	5.54	255.83	0.82	632.66	0.53		
84.00	3.02	274.92	1.23	632.82	0.62		
86.97	2.93	276.92	0.91	633.02	0.47		
91.95	2.58	280.93	0.88	633.28	0.85		
94.96	6.63	292.90	2.41	633.71	0.76		
98.97	2.17	293.90	5.40	634.05	0.59		
99.96	2.93	294.92	51.42	634.16	0.56		
100.97	3.40	295.85	4.69	634.26	0.59		
110.97	2.02	335.82	3.64	634.32	0.38		
112.95	3.96	336.81	28.10	634.60	0.44		
120.97	5.49	337.90	10.71	634.81	0.53		
124.97	8.86	338.92	1.35	635.00	0.41		
126.84	2.49	349.91	2.35	635.12	0.53		
126.96	4.11	351.81	1.70	635.29	0.50		
129.96	2.35	375.92	2.20	653.81	9.74		
138.95	5.40	376.93	0.47	654.81	1.73		
140.89	8.48	377.85	3.61	671.79	8.51		
144.94	29.89	402.80	0.91	672.78	1.85		
158.95	3.81	417.98	0.65	673.79	8.89		
162.92	6.54	420.78	5.69	674.80	1.61		
166.86	2.17	421.76	0.62	697.58	1.06		
168.94	3.29	462.73	0.56	713.95	1.55		
170.95	2.58	462.80	0.67	753.84	0.85		
188.93	26.87	463.78	34.91	753.97	0.53		
189.93	2.79	464.79	5.28	756.04	0.62		
195.83	2.20	465.79	0.79	757.64	0.50		
206.94	2.11	475.91	0.85	779.61	0.76		
207.88	0.35	489.76	0.94	779.73	0.44		
207.92	0.56	502.90	1.85	781.56	1.53		

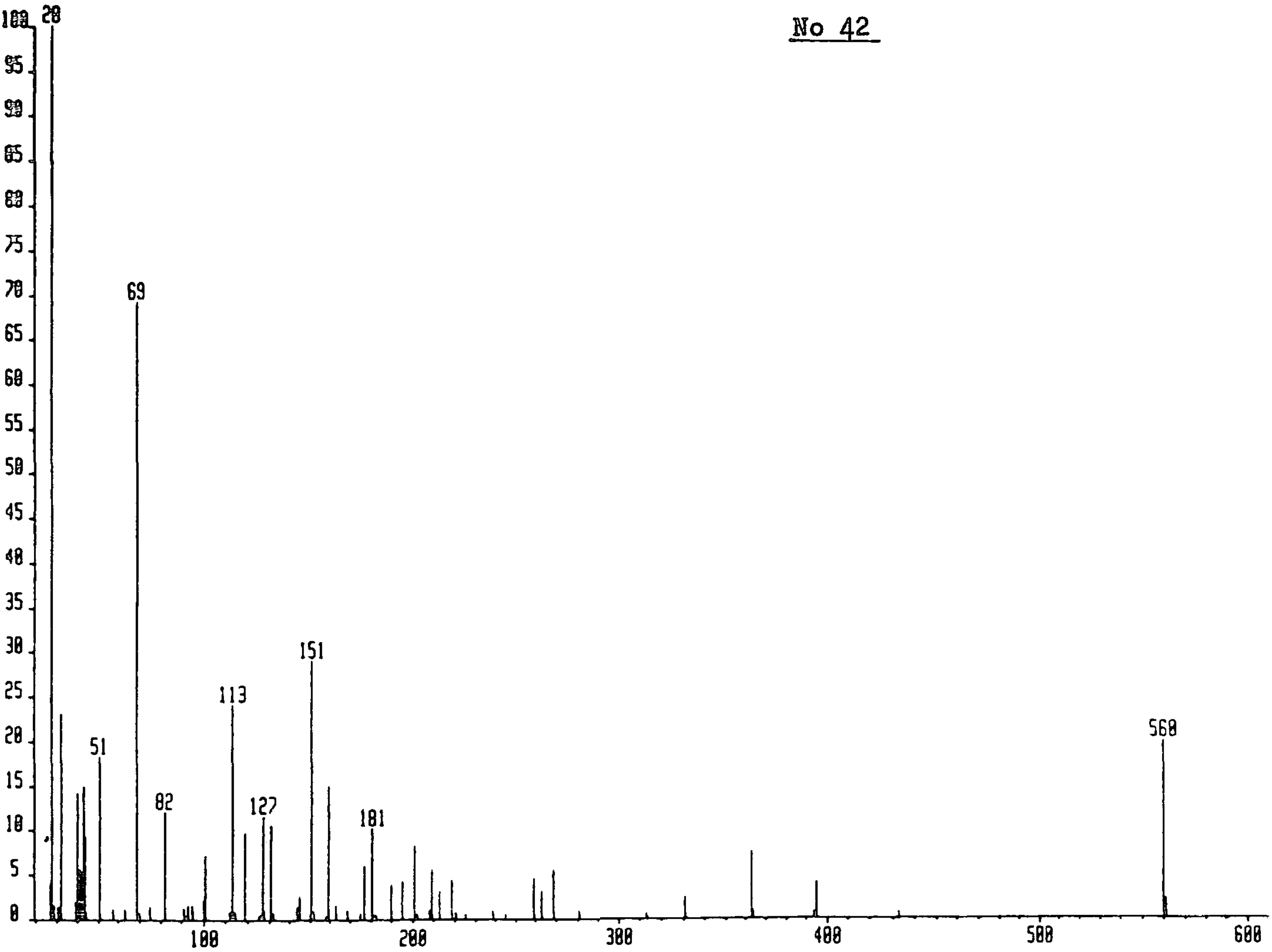
GA31867ο ¤1 Bgd=64 11-MAR-87 10:31+0:04:15 70E
BpM=69 I=7.2v Ho=480 TIC=213960000 Acnt: No 41 HAR
To¤%: MASS:



Mass	% Base				
27.02	0.84	112.97	15.10	218.92	2.56
28.00	25.04	113.97	0.58	220.84	0.79
29.00	0.15	116.96	0.05	224.93	0.24
29.03	0.30	118.96	8.84	226.83	0.22
30.99	5.57	119.96	0.24	230.92	0.19
31.98	5.86 F	123.96	0.20	238.83	0.75
32.00	0.82 F	124.98	0.21	242.92	0.33
39.01	0.39	126.87	21.61	243.94	0.09
39.95	3.81	127.88	0.47	257.45	0.16
41.03	1.29	130.96	11.57	257.52	0.10
42.04	1.04	131.96	0.51	257.59	0.11
42.99	0.10	138.87	0.19	257.77	0.15
43.05	3.79	139.87	0.23	257.99	0.08
43.98	2.27	142.96	0.32	258.39	0.13
49.98	0.57	143.98	0.48	262.92	2.05
50.99	63.80	145.85	0.08	263.90	0.10
51.99	0.78	149.95	0.37	268.91	0.40
54.98	0.06	150.96	0.59	280.88	7.09
55.04	0.13	157.85	0.63	281.90	0.37
55.99	0.14	158.87	19.39	312.89	9.45
57.06	0.26	159.87	0 22	313.90	1.08
58.06	0.10	161.95	0.25	350.86	2.21
61.98	0.18	162.95	4.17	351.87	0.13
62.99	1.40	163.95	0.16	388.77	0.69
68.98	100.00	168.95	0.46	477.73	43.16
69.98	1.12	169.85	0.05	478.73	3.76
73.98	0.33	170.87	0.14	479.74	0.10
74.99	1.63	174.95	0.41		
80.98	0.48	176.85	8.60		
81.99	16.73	177.85	0.17		
82.99	0.37	180.94	5.88		
91.04	0.14	181.94	0.19		
92.04	0.11	189.86	4 62		
92.97	2.68	192.94	0.43		
93.98	0.53	195.85	0.26		
99.97	3.94	200.93	1.37		
100.98	12.71	207.84	1.09		
101.98	0.32	208.84	7.73		
105.98	0.19	209.85	0.13		
111.96	0.92	212.94	0.61		

GA3181080 ¤1 Bgd=100 11-MAR-87 10:31+0:06:55 70E EI+ 14.1 HAR:
BpM=28 I=1.0v Ho=861 TIC=62940000 Acnt: Sys:APSEY MASS:
Tonl: Col:PFKGC

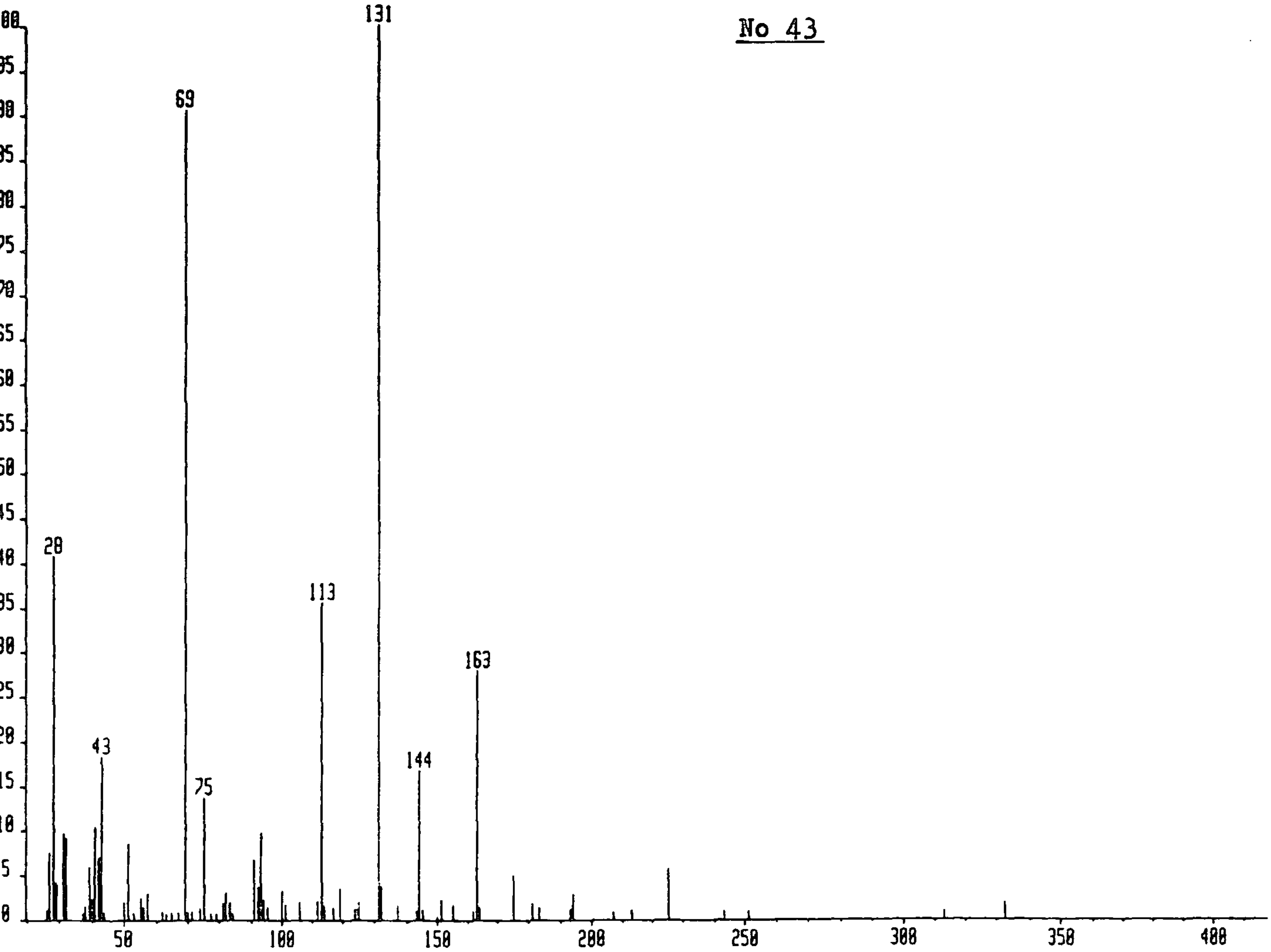
No 42



Mass	% Base		
27.02	3.82	144.98	2.46
28.00	100.00	149.96	0.41
29.00	1.40	150.97	28.94
29.03	0.75	151.98	0.68
30.99	1.30	157.88	0.36
31.02	0.33	158.88	14.86
31.99	23.00	162.97	1.51
39.02	1.94	168.96	0.88
39.96	14.06	174.95	0.64
41.03	5.47	176.87	5.96
42.04	5.11	180.95	10.13
43.05	14.87	181.96	0.47
43.98	9.14	182.96	0.22
44.05	0.66	189.86	3.70
50.99	18.07	194.96	4.13
57.06	1.06	200.95	8.25
62.99	1.04	201.96	0.42
68.98	69.06	207.85	0.80
69.99	0.62	208.86	5.46
74.99	1.35	212.94	2.98
81.99	11.92	218.94	4.34
91.04	1.10	220.86	0.63
92.04	0.34	224.94	0.48
92.98	1.48	238.85	0.69
95.00	1.41	244.98	0.39
99.97	1.99	258.85	4.39
100.98	6.98	262.94	3.00
111.97	0.75	268.92	5.32
112.98	24.03	280.92	0.78
113.98	0.68	312.90	0.50
118.97	9.64	330.91	2.37
124.98	0.35	362.91	7.32
126.00	0.45	363.91	0.77
126.88	11.55	393.92	0.58
127.88	0.93	394.91	3.89
130.97	10.49	432.89	0.64
131.97	0.51	559.77	19.69
143.97	1.26	560.77	2.05

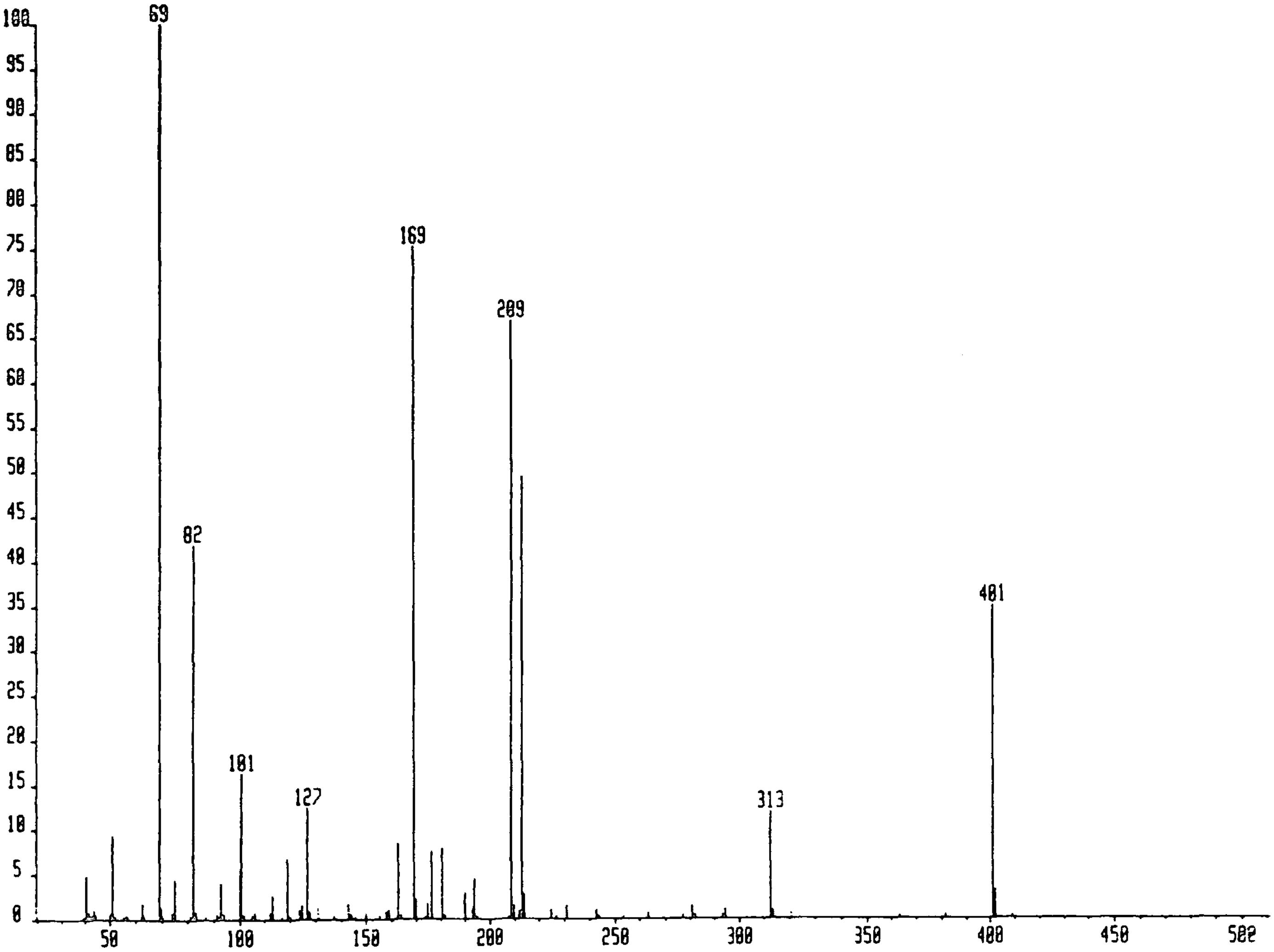
GAX220100 x1 Bpd=1 27-FEB-87 18:38+0:01:07
BpM=0 I=1.4v Hm=332 TIC=48010000 Acnt: Sys:EI HAR:
Text:6.APSEV PT=0 Cal:CALT24 MASS:

No 43



Mass	% Base				
26.02	0.98	83.04	1.82	313.18	0.88
27.03	7.54	83.12	0.56	332.20	1.72
28.01	40.75	84.12	0.64		
28.03	1.20	91.09	6.64		
29.04	3.98	92.10	3.56		
31.00	9.67	93.03	9.67		
32.00	9.03	94.04	2.14		
37.02	0.54	96.05	1.33		
38.02	1.44	100.03	3.23		
39.03	5.97	101.04	1.61		
39.97	2.09	106.05	1.82		
40.04	1.08	112.04	2.02		
41.05	10.40	113.05	35.60		
42.05	6.92	114.06	1.41		
43.03	2.27	117.05	1.28		
43.06	18.34	119.05	3.42		
44.00	0.78	124.05	1.15		
44.01	0.69	125.06	1.80		
44.07	0.55	131.05	100.00		
50.01	1.83	132.06	3.66		
51.02	8.55	137.07	1.52		
53.05	0.66	143.07	0.88		
55.07	2.32	144.07	16.70		
56.02	1.11	145.07	0.95		
56.08	1.29	150.06	0.33		
57.09	2.94	151.07	2.18		
62.03	0.88	155.07	1.52		
63.02	0.55	162.07	0.79		
65.06	0.72	163.08	27.90		
67.08	0.76	164.08	1.24		
69.02	90.69	175.09	4.87		
69.09	1.50	181.08	1.72		
70.03	0.67	183.11	1.36		
71.11	0.88	193.09	1.01		
74.02	1.10	194.10	2.79		
75.03	13.61	207.15	0.72		
77.05	0.57	213.11	0.94		
79.09	0.52	225.12	5.55		
81.03	1.67	243.13	0.80		

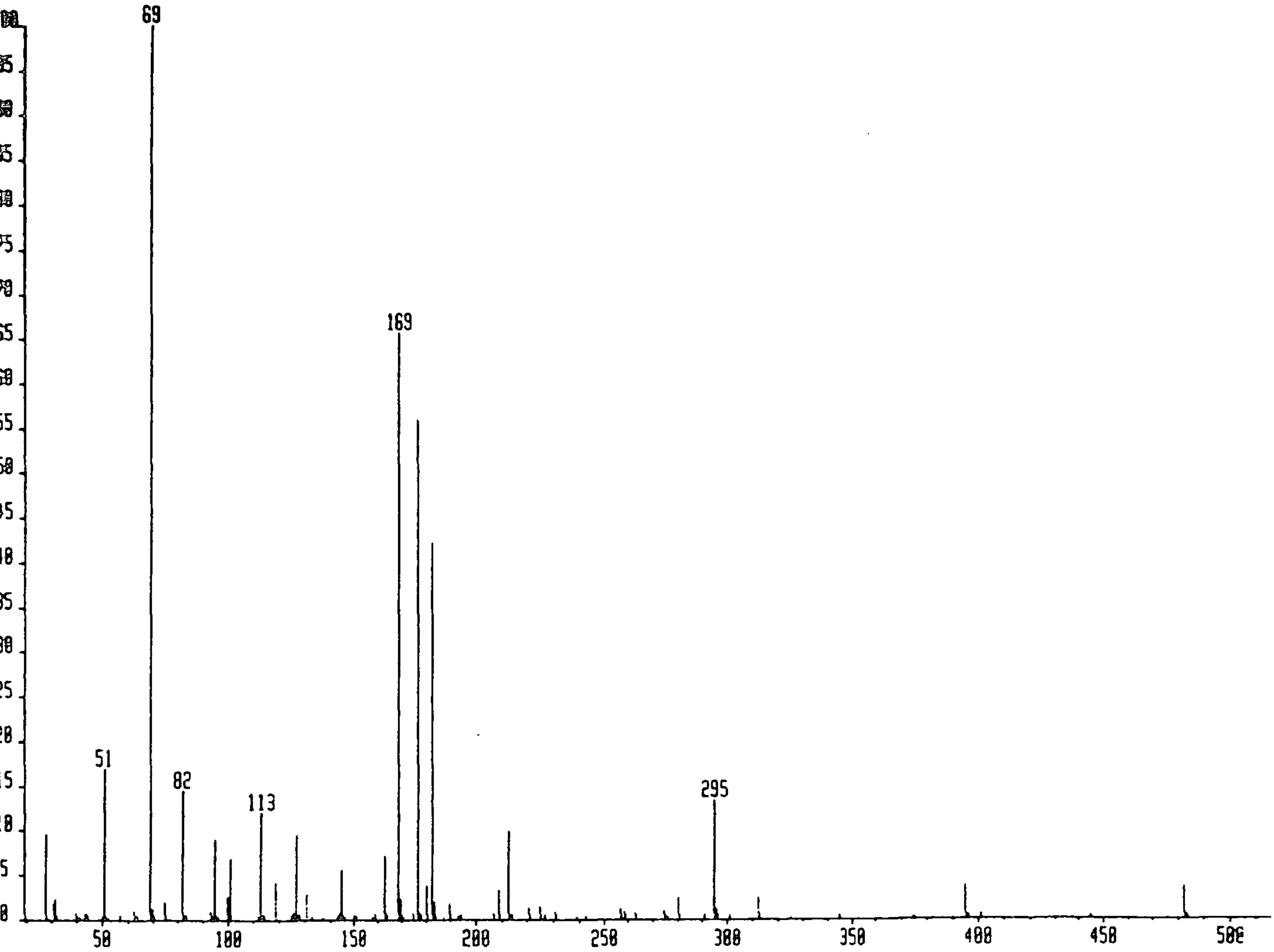
GA33075o x1 Bgd=69 28-MAR-87 15:46+0:04:43 70E EI+
BpM=69 I=10v Ho=509 TIC=352236898 Acnt: Sys:RPSEY **No 44** HAR:
Text: Cal:PFK20 MASS:



Mass	% Base				
50.13	0.45	119.91	0.14	213.85	2.57
51.12	9.14	123.90	0.89	224.84	0.93
52.12	0.13	124.91	1.43	225.84	0.06
55.07	0.11	126.81	12.36	226.75	0.13
55.12	0.16	127.81	0.77	230.83	1.26
56.06	0.32	130.89	1.08	231.82	0.05
56.12	0.09	135.88	0.08	242.82	0.84
57.12	0.17	136.90	0.33	243.82	0.14
61.99	0.13	142.89	1.62	253.64	0.10
62.99	1.53	143.89	0.42	262.83	0.56
63.44	0.16	145.80	0.15	263.83	0.08
68.94	100.00 0	149.87	0.58	276.71	0.25
69.02	0.09	154.88	0.31	280.80	1.33
69.93	1.20	155.86	0.06	281.81	0.28
70.01	0.10	155.91	0.09	292.79	0.34
73.92	0.58	157.79	0.66	293.79	0.79
74.92	4.36	158.80	0.98	312.79	11.85
75.92	0.10	161.87	0.17	313.80	0.72
80.89	0.35	162.88	8.32	320.71	0.52
81.90	41.84	163.88	0.30	338.69	0.09
82.91	0.72	168.86	74.89	362.79	0.11
85.90	0.10	169.87	2.06	381.75	0.23
86.91	0.16	173.87	0.12	400.74	34.88
90.97	0.41	174.88	1.57	401.74	2.96
91.98	0.12	175.88	0.09	408.62	0.16
92.91	3.87	176.78	7.41	508.65	0.08
93.92	0.49	177.77	0.07		
99.91	5.41	180.87	7.83		
100.92	16.24	181.87	0.28		
101.92	0.35	189.77	2.70		
104.92	0.25	190.80	0.07		
105.92	0.55	192.85	1.02		
111.91	0.59	193.86	4.35		
112.92	2.48	194.85	0.18		
113.05	0.07	207.76	0.18		
113.91	0.07	208.76	66.82		
116.91	0.12	209.77	1.31		
118.90	6.64	211.84	0.70		
118.99	0.06	212.85	49.35		

```
6A350910        x1    Bgd=84    14-APR-87 10:01+0:07:35  70E         EI+
BpA=69    I=13ovs  Ha=404   TIC=37359000                 Acnt:        Sys:APSEY                          HA9
Text:                                                                 Cal:PFK9                           MASS
```

No 45

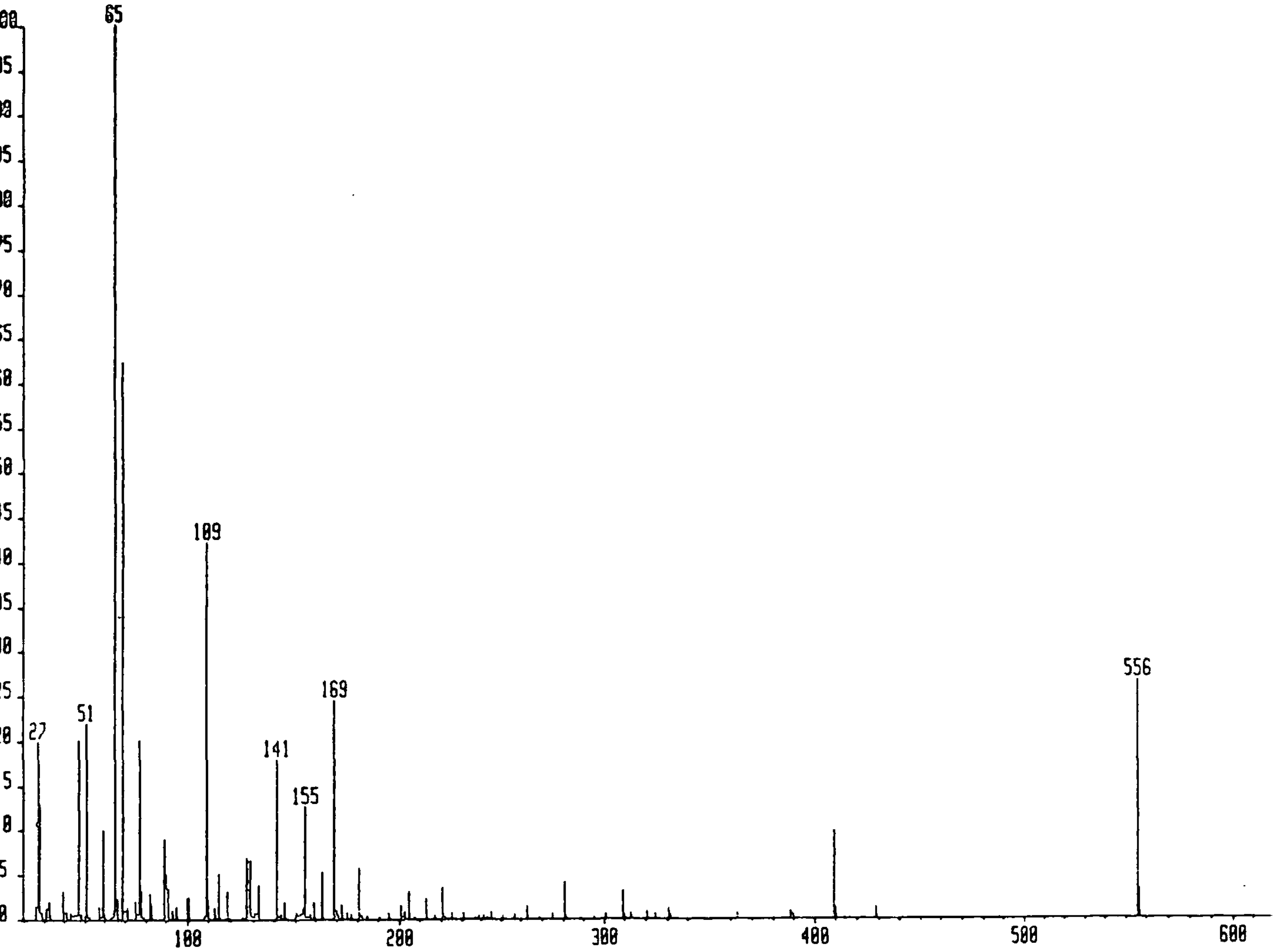


Mass	% Base
28.00	9.57
30.99	1.68
31.98	2.17
39.95	0.58
43.99	0.57
50.99	16.89
62.99	0.83
68.98	100.00
69.98	0.98
74.99	1.83
81.98	14.41
92.97	0.92
94.99	8.92
99.97	2.50
100.98	6.73
112.97	11.90
118.98	4.20
125.97	0.67
126.87	9.54
130.96	2.69
143.96	0.56
144.96	5.43
158.87	0.56
162.95	7.05
163.95	0.57
168.94	65.61
169.94	2.16
174.94	0.62
176.85	55.82
177.85	0.57
180.94	3.74
182.96	42.16
183.96	1.83
189.86	1.54
206.94	0.57
208.85	3.15
212.93	9.79
220.84	1.14
224.93	1.22
230.93	0.74
256.93	0.95
258.83	0.65
262.91	0.61
274.91	0.81
280.90	2.35
294.90	13.27
295.91	1.04
312.89	2.31
394.88	3.72
482.84	3.52

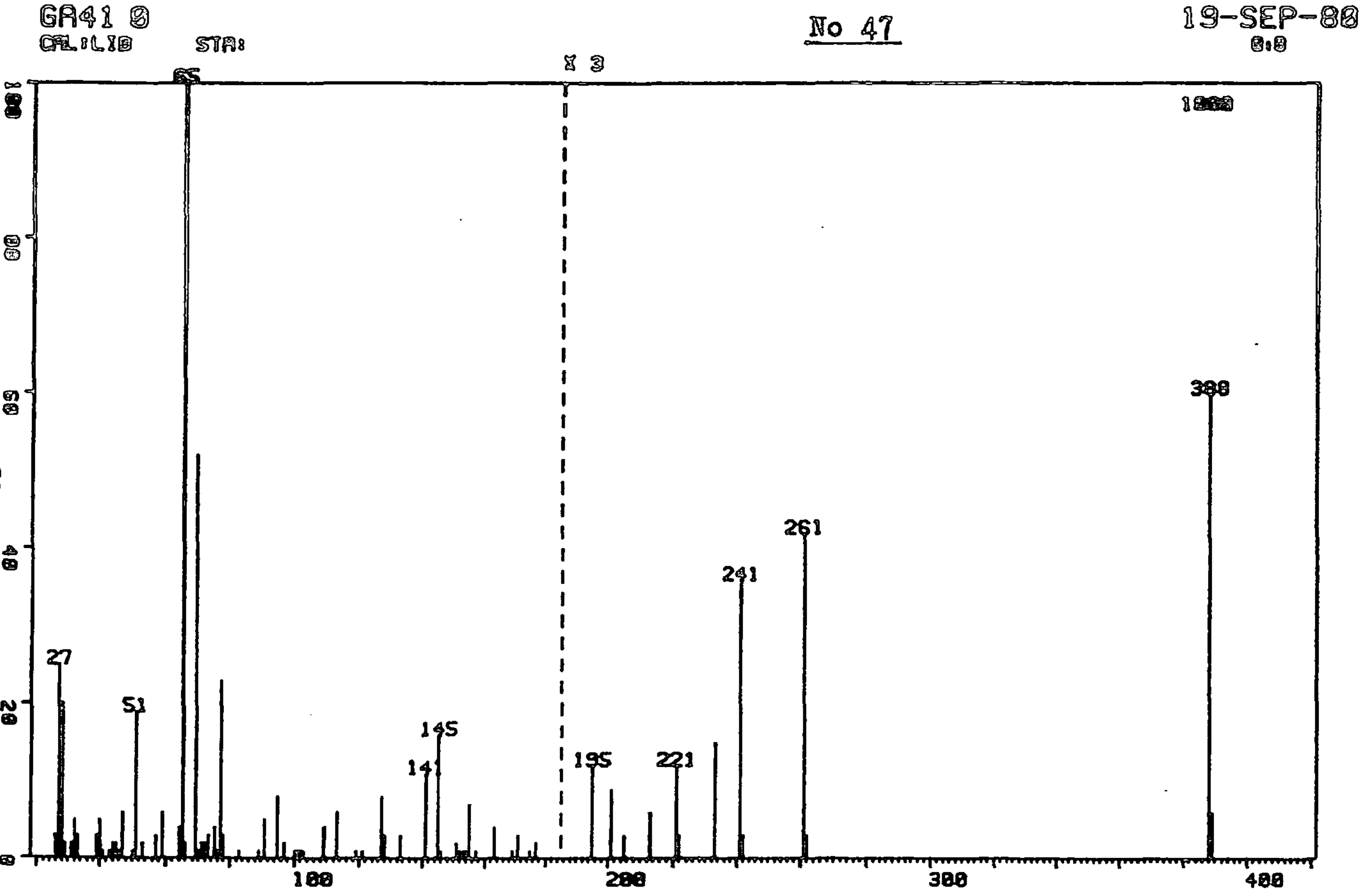
GA360116◦ x1 Bgd=1CS 14-APR-87 10:44◦0:09:30 70E EI◦
BpA=65 I=9.5mvs Hm=557 TIC=33580000 Acnt: Sys:APSEY
Text: Cal PFK9

No 46

Hm:
MASS:



Mass	% Base		
26.00	1.38	127.84	3.04
27.01	19.82	128.96	6.47
28.00	12.86	130.91	0.58
29.02	0.66	132.93	3.78
30.98	1.12	140.84	17.81
31.97	1.84	144.92	1.92
32.99	1.88	150.92	0.62
39.00	3.07	153.83	1.03
39.94	0.53	154.85	12.45
41.01	0.71	158.82	1.70
43.03	0.62	162.89	5.14
47.00	20.02	168.89	24.50
50.97	21.82	169.89	0.92
56.98	1.30	172.82	1.50
59.00	9.90	174.89	0.58
63.98	0.90	180.88	5.55
64.98	100.00	194.89	0.51
65.99	2.18	200.89	1.51
68.96	62.36	202.80	0.75
69.96	0.81	204.81	3.03
70.99	1.14	212.87	2.22
74.98	1.07	220.89	3.40
76.97	19.98	224.86	0.94
77.98	3.08	230.86	0.57
81.98	2.79	244.86	0.66
82.97	1.43	262.84	1.32
88.97	8.96	280.81	4.09
89.98	4.90	308.83	3.03
90.99	3.26	312.80	0.58
92.94	0.85	320.82	0.70
94.96	1.32	330.92	1.01
99.94	2.28	362.78	0.61
100.95	2.23	388.78	0.69
108.96	42.20	408.79	9.68
109.96	2.00	409.79	1.06
112.94	1.10	428.76	1.20
114.95	5.01	555.64	26.49
118.92	3.08	556.64	2.97
126.83	6.72		

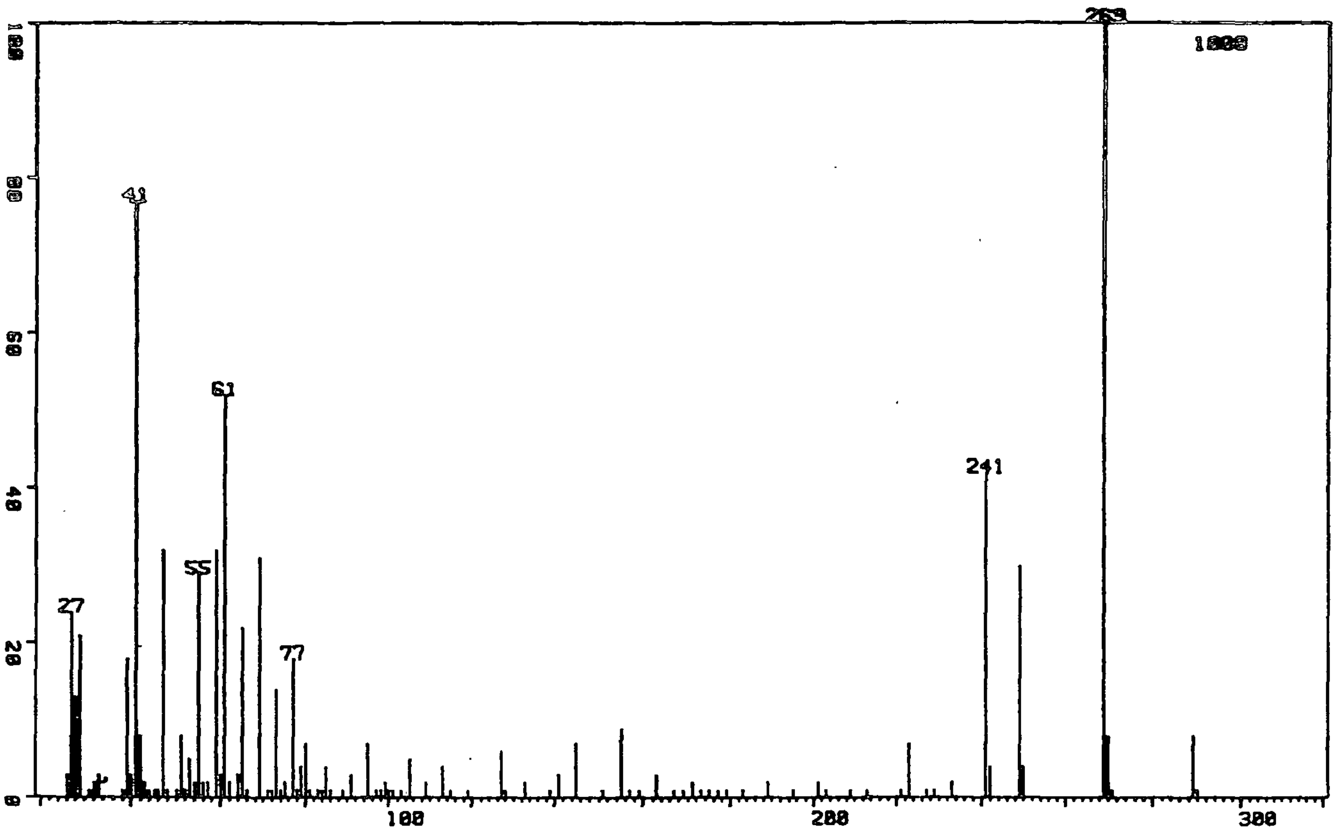


Mass	% Base
25.81	2.81
26.82	24.70
27.82	19.73
28.85	1.47
30.83	1.50
31.83	4.87
32.86	3.15
37.90	0.29
38.92	2.56
39.86	4.70
40.95	1.18
42.98	0.76
43.92	1.82
44.96	1.57
45.97	1.18
46.98	6.18
49.99	0.51
50.99	18.48
52.01	0.30
53.03	1.43
56.00	0.34
57.02	2.41
59.05	5.36
64.05	3.45
65.06	100.00
66.06	2.01
69.06	51.29
70.06	0.59
71.08	1.25
72.09	2.09
73.10	2.97
75.06	3.57
76.06	0.76
76.09	0.27
77.07	22.91
78.07	2.39
83.07	0.57
89.08	0.72
91.10	4.30
93.06	0.44
95.08	8.12
97.10	2.06
100.07	0.72
101.09	1.21
102.10	0.69
103.11	1.04
109.10	3.45
113.08	5.44
119.08	0.91
121.10	0.62
127.01	7.48
128.00	2.54
129.11	0.37
132.10	0.42
133.10	3.05
141.01	10.48
145.10	16.06
146.10	0.57
151.12	1.57
152.12	0.51
153.13	0.67
154.02	0.67
155.04	6.93
157 11	0 89
159.02	0.45
163.10	3.99
169 10	0 59
171 14	2.27
172.13	0 30
175.11	1 04
177.12	1 82
181 12	0 45
195.12	3 67
201.14	2 98
203 04	0 27
205 06	1 08
213.12	1.77
215 13	0 24
221.15	3.35
222.15	0 61
233.13	4 35
241.16	12 23
242.16	0 99
261 17	13 34
262.17	1 08
388 11	20.08
389 11	1.47

GA41Z 0 CAL:LIB STA:

No 48

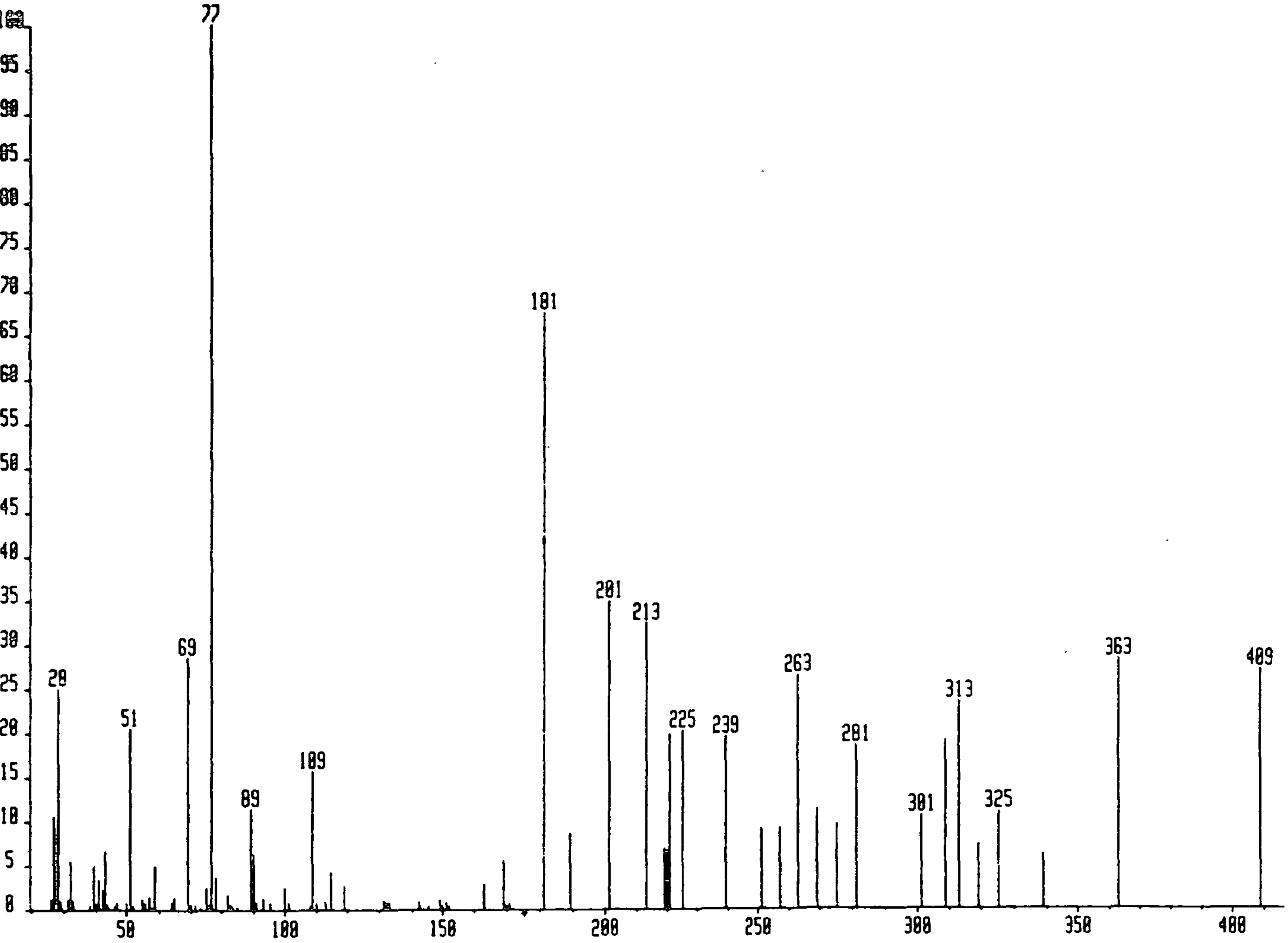
19-SEP-80 0:0



Mass	% Base
25 81	2. 29
26. 82	23. 88
27. 81	6. 94 F
27. 83	12. 36 F
28. 85	20. 90
29. 86	0. 41
30. 83	0. 63
31. 82	1. 55
32 86	2. 48
36. 88	0 20
37 90	0. 84
38. 92	17. 93
39. 86	1. 67
39. 93	2. 67
40. 95	77 02
41 96	7 85
42 98	1. 42
43. 92	0. 85
44. 95	0. 87
45. 97	0. 66
46. 98	31. 64
47. 99	0. 71
49. 99	0. 62
50 99	7 26
52 02	1 08
53. 03	4 64
54 04	1 57
55 05	29 23
56 06	2. 14
57. 03	1. 71
58 03	0. 28
59 04	31. 51
60 05	2. 57
61 07	51 47
62 07	1 69
63 05	0 24
64 05	2 96
65 06	21 97
66 08	0 68
67 10	0 35
69 05	30 30
70. 07	0 43
71 08	0 88
72 09	1 13
73. 10	13. 52
74. 09	0. 72
75 05	1. 79
76. 06	0. 36
77 06	18. 24
78 07	0. 95
79. 09	3. 68
80. 10	6. 89
81. 10	1. 05
83. 07	0. 97
84 08	0. 50
85. 10	3 73
86 10	0. 96
89. 08	0 74
90 08	0. 40
91 10	2 76
93. 07	0. 21
95. 08	6. 30
96. 10	0. 34
97. 11	0. 91
98. 13	0. 54
99. 13	2. 09
100. 10	0. 62
101. 09	0. 90
102. 10	0. 38
103. 11	1. 23
104. 12	0. 29
105. 12	4. 64
106. 13	0. 32
109. 10	1. 44
111. 13	0. 38
113. 08	3. 89
114. 09	0. 29
115 11	0. 70
119. 09	0. 73
121. 11	0. 43
127. 02	5. 41
128. 01	1. 21
132. 11	0 35
133. 10	1. 85
139. 10	0. 71
141. 02	2. 80
145. 10	7. 11
146. 11	0. 32
151. 12	0. 80
152. 12	0. 31
153. 01	0. 29
153. 12	0. 36
154. 02	0. 42
155. 03	8. 30
157. 11	0. 69
158. 11	0. 22
159. 13	0. 92
163. 10	2 91
165 13	0 35
167 04	0. 87
169. 07	1. 06
171. 13	1. 42
173. 04	0. 83
175. 10	0. 51
177. 13	1. 14
179. 15	0. 53
180. 16	0. 33
181. 13	0. 45
183. 13	0. 59
187. 05	0. 33
189. 13	1. 35
195. 12	0. 95
201. 13	1. 66
203. 15	0. 54
209. 14	1. 07
213. 10	0. 93
216. 07	0. 24
221 14	0. 62
223. 16	6. 54
224 16	0 48
227. 13	0. 64
228. 14	0. 25
229. 16	1. 06
230. 54	0. 32
233. 14	1. 34
241. 15	41. 35
242. 16	3. 25
243. 17	0. 40
249 19	29. 87
250. 33	3. 40
251. 18	0. 21
267. 17	0. 36
268. 19	0. 27
269. 20	100 00
270. 20	9 79
271. 20	0. 41
289. 21	7. 72
290. 22	0. 80

GAX2709°   x1   Bgd=1   22-APR-07 15:04+0 01 07 70E   EI+
BpM=0   I=1.8v   Hm=446   TIC=37075000   Acnt: Sys:ACE   HAR:
Text 6.APSEY   Cal:PFK16   MASS:

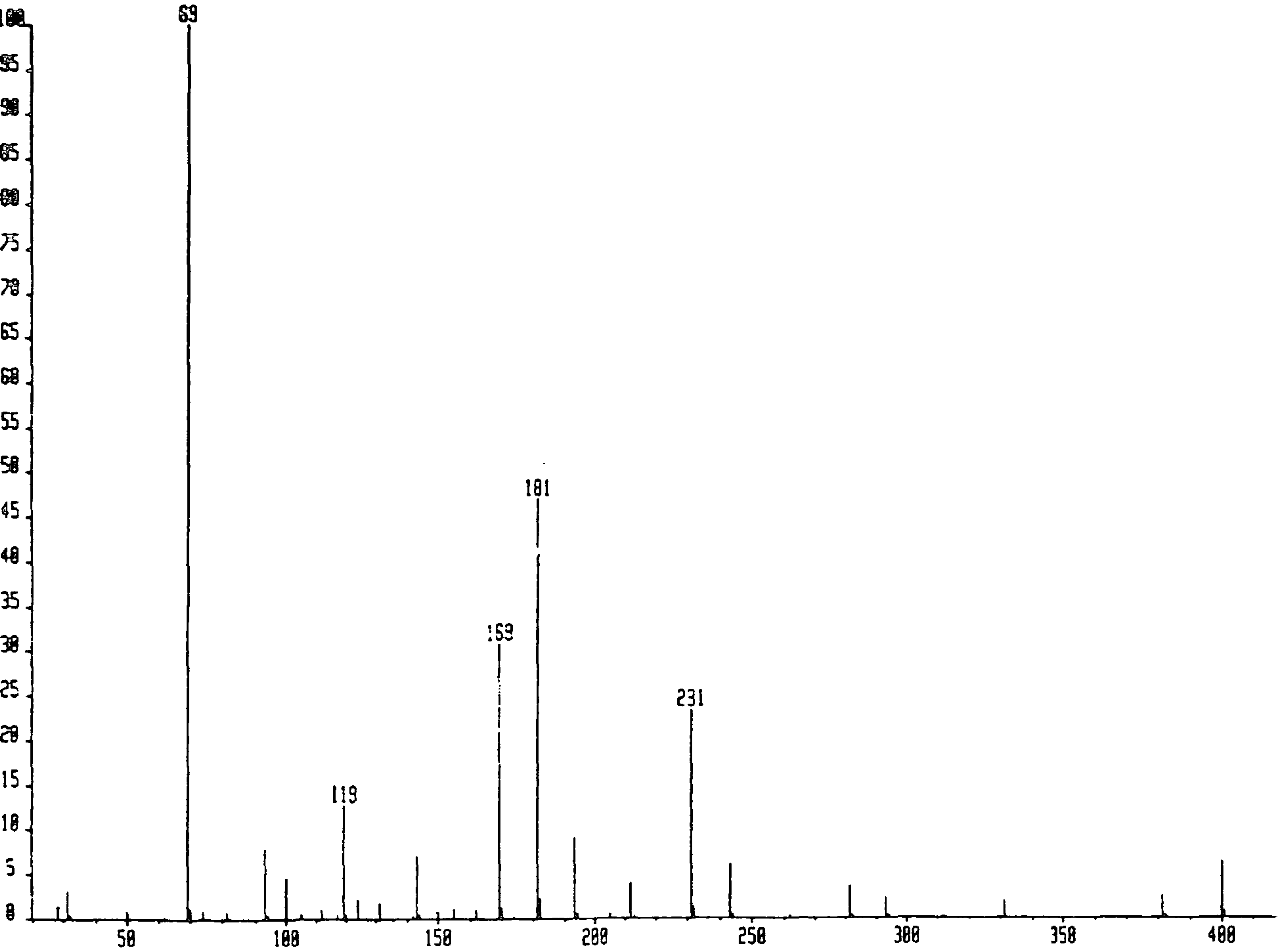
No 49



Mass	% Base
26.02	1.09
27.03	10.43
28.01	24.93
29.05	0.81
31.00	1.09
32.00	5.47
33.02	0.89
39.02	4.88
41.04	3.24
42.05	2.01
43.06	6.54
47.03	0.71
50.02	0.59
51.01	20.40
55.06	0.97
56.07	0.56
57.02	1.34
57.08	1.14
59.04	4.85
64.02	0.75
65.03	1.29
69.01	28.58
69.08	0.59
75.01	2.36
77.02	100.00
78.03	3.46
82.00	1.58
89.03	11.28
90.03	6.17
91.06	0.77
93.01	1.19
95.02	0.52
100.00	2.30
101.02	0.61
109.04	15.63
110.05	0.53
113.02	0.75
115.03	4.16
119.00	2.56
131.01	0.93
132.03	0.53
133.02	0.56
142.15	0.79
149.04	1.07
151.04	0.66
163.02	2.76
169.00	5.41
171.03	0.62
181.00	2.25
201.07	1.16
213.01	1.08
221.01	0.66
224.99	0.67
239.03	0.65
263.00	0.88
280.94	0.61
309.03	0.63
313.00	0.78
363.05	0.94
408.93	0.90

```
GA370180+        x1     Bgd=7     14-APR-87 11:53+0 01:49  78E          EI+
BpM=69    I=21uvs  Hm=401   TIC=32030000                  Acnt:          Sys:APSEY                       HAR:
Text:                                                                    Cal:PFK9                        MASS:
```

No 50

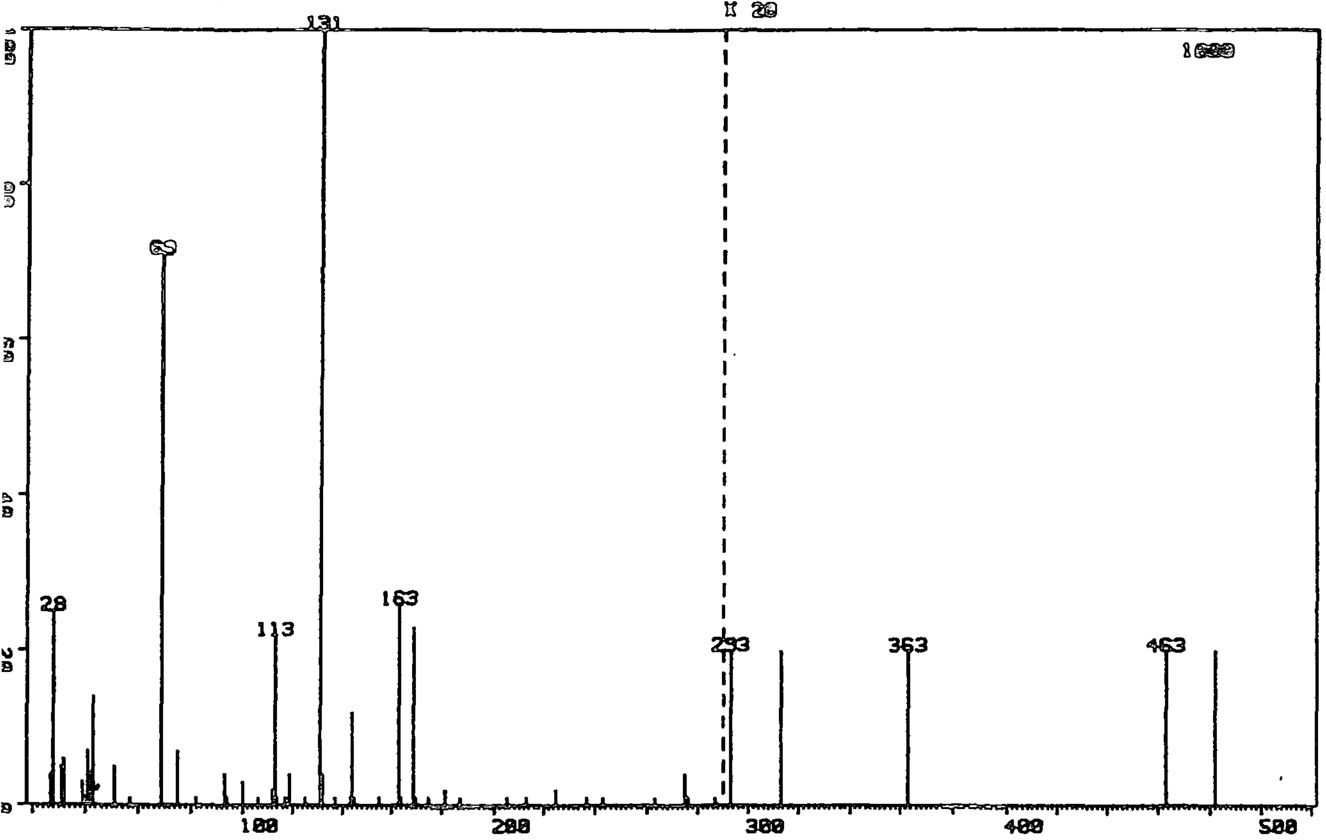


Mass	% Base
28.00	1.23
30.99	3.04
49.98	0.70
68.98	100.00
69.98	1.07
73.98	0.93
80.98	0.54
92.98	7.81
99.98	4.52
111.97	0.92
118.97	12.63
123.97	2.04
130.97	1.64
142.97	6.88
149.95	0.71
154.96	1.07
161.96	0.83
168.96	30.74
169.96	0.98
180.96	46.85
181.97	1.97
192.96	8.85
211.96	3.85
230.96	23.32
231.96	1.20
242.96	5.92
280.96	3.51
292.96	1.94
330.96	1.76
380.96	2.27
399.97	6.21
400.98	0.55

GAX39 0
CAL:LIB STA:

No 51

19-SEP-80
0:0

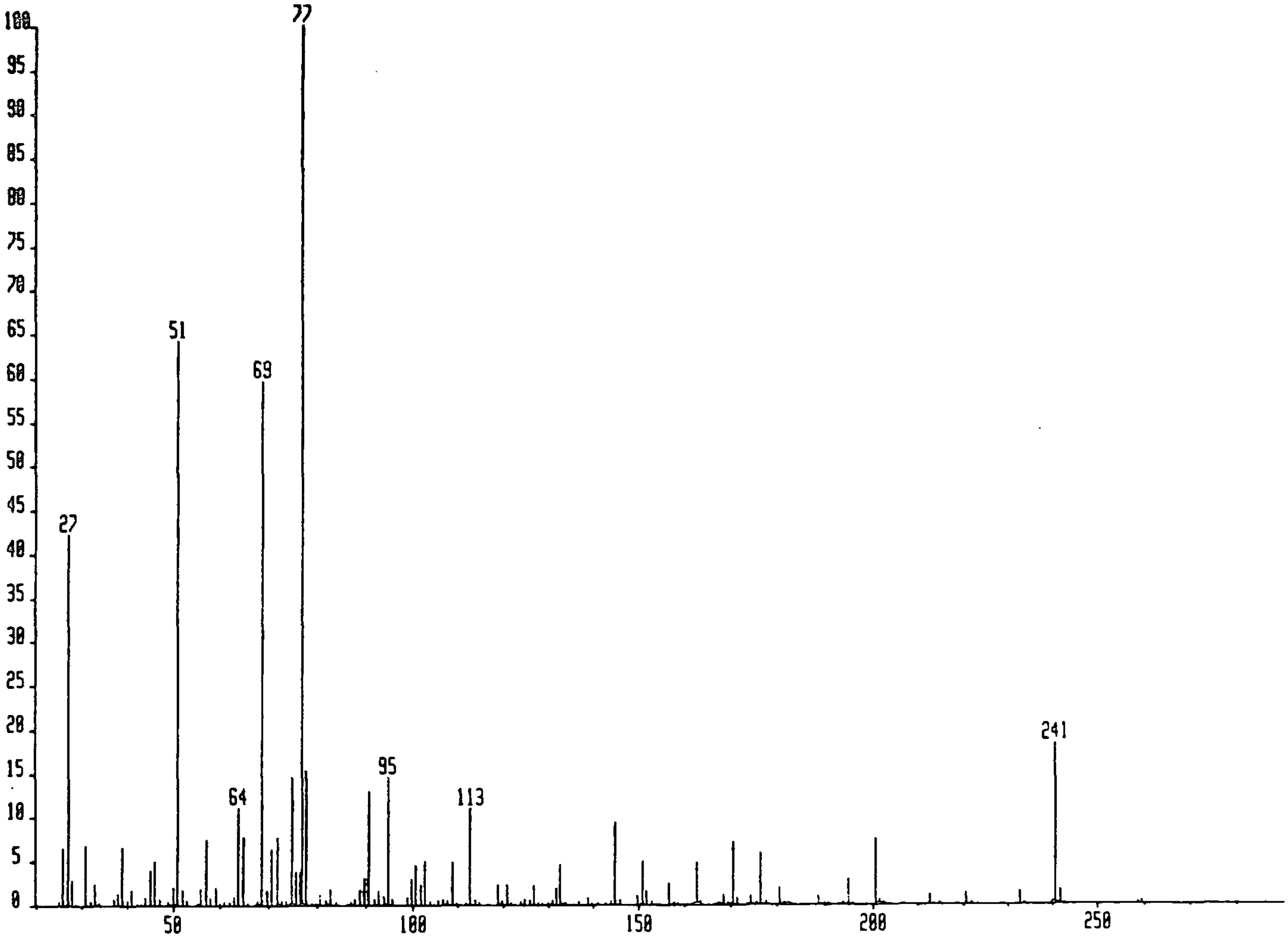


Mass	% Base
26. 82	3. 35
27. 81	24. 47
30. 82	4. 26
31. 82	5. 64
38. 91	2. 70
39. 86	1. 30
40. 95	6. 31
41. 96	3. 87
42. 97	14. 02
50. 98	4. 69
57. 07	1. 22
69. 04	70. 67
75. 04	6. 91
82. 06	1. 20
93. 05	3. 92
94. 07	1. 10
100. 06	3. 19
101. 06	0. 33
105. 13	0. 22
106. 07	0. 58
112. 06	2. 00
113. 06	21. 76
114. 08	0. 69
117. 07	0. 54
119. 07	4. 02
119. 16	0. 26
124. 07	0. 32
125. 07	0. 55
130. 77	0. 09
130. 79	0. 08
131. 07	100. 00
132. 07	3. 30
134. 18	0. 09
137. 09	0. 84
138. 20	0. 08
143. 07	0. 48
144. 08	11. 40
145. 09	0. 70
149. 11	0 13
150. 08	0. 35
155. 08	0. 62
162. 08	0. 23
163. 10	26. 17
164. 09	1. 23
168. 09	0 21
169. 09	23. 05
170. 09	0. 82
175. 09	0. 87
181. 09	2. 02
182. 11	0. 13
186. 10	0. 17
187. 11	0. 87
193. 10	0. 29
194. 10	0. 28
205. 10	0. 57
207. 18	0. 11
213. 11	0. 95
225. 11	1. 88
237. 14	0. 24
243. 12	0. 66
255. 07	0 10
255. 12	0. 10
263. 12	0. 20
275. 13	3 59
276. 06	0 06
276. 13	0. 23
281. 14	0. 36
287 13	0 35
293 11	0 18
293. 17	0 14
313. 15	0. 31
363. 15	0 11
463. 15	0 12
482. 16	0 16

```
GA810116o       x1   Bgd=111   21-SEP-88 14:2o0:02:04   70E         C1o
BpM=0      I=10v   Ma=259   TIC=376115000            Acnt:COI        Sys:OPEN
                                                          GC= 40⁰    Cal:PFK267
```

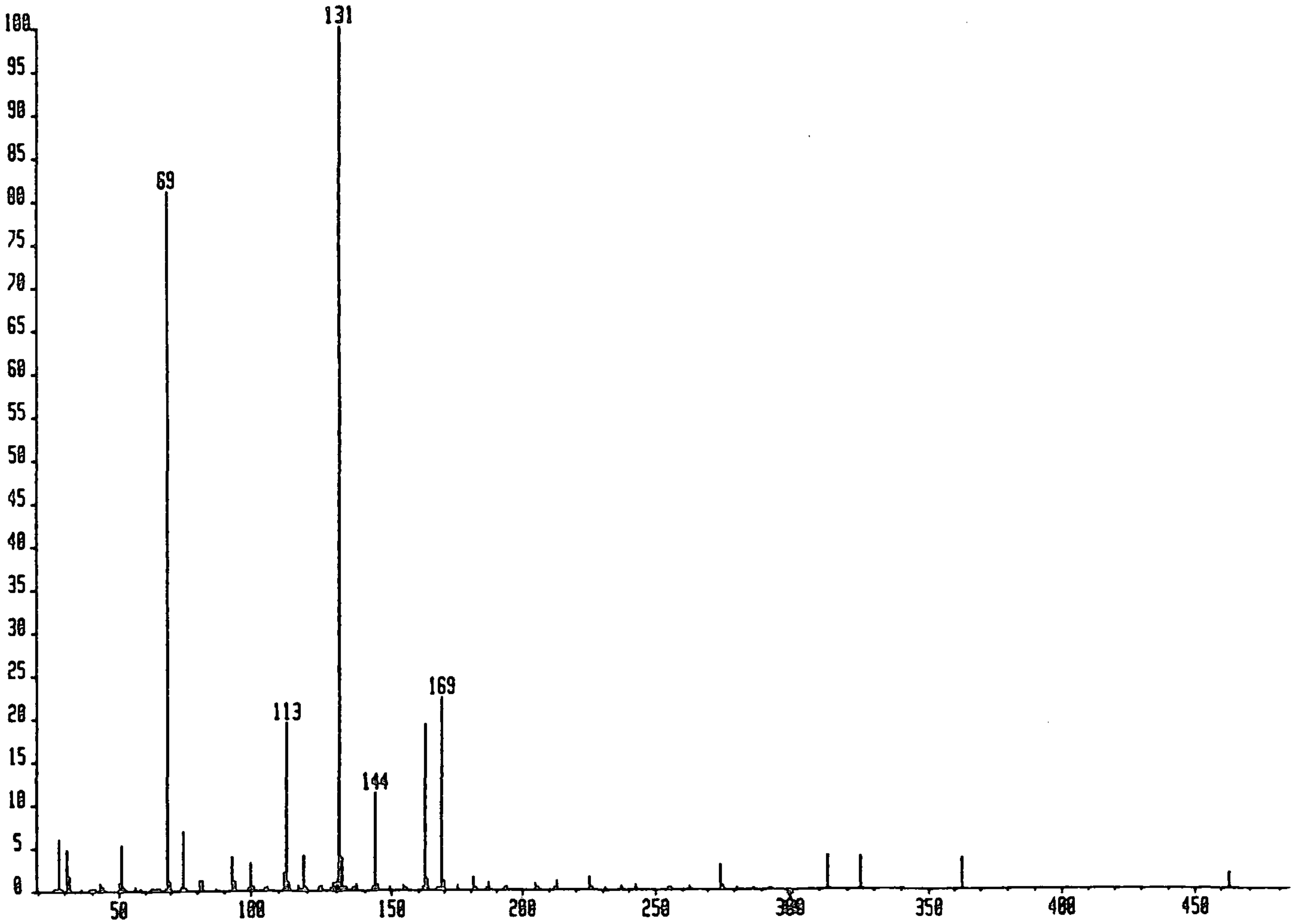
No 52

HRR
MASS



```
Mass       % Base
  25.91       6 41     118.72       2.17     233 51      0.03
  26.92      42.20     120.74       2.28     233.61      0 06
  27.92       2.78     126.72       2.12     238.53      0.05
  30 88       6.72     131.71       1.72     239.64      0 11
  32.89       2.40     132.71       4.43     239.80      0 05
  37.88       1.25     144.68       9.29     239.88      0.04
  38.89       6.45     150.69       4.96     239.99      0.08
  40.90       1.66     151.69       1.52     240.62     18 24
  44.86       3.78     156.66       2.40     241.08      0.06
  45.87       4.82     162.64       4.77     241 27      0 04
  49.85       1 91     168.63       1.07     241.63      1.41
  50.85      64.19     170.65       7.14     242 67      0 05
  51.86       1.66     176.65       5.77     258 63      0 09
  55.84       1.71     180.65       1.79     259.65      0 32
  56 84       7 44     194.63       2.82
  58 85       1 94     200.63       7.37
  63 82      11.08     200.87       0.03
  64 83       7.69     200.96       0.05
  68.79      59.72     201.02       0.06
  69.81       1.56     201 27       0.05
  70.82       6.38     201 30       0 05
  71.83       7.69     201 62       0 52
  74.79      14.48     201 81       0.05
  75.80       3.71 F   201 89       0.07
  76.71       3 52 F   201 93       0 06
  76.79     100.00 0   202 07       0 07
  77.80      15.20     202 47       0 13
  80.79       1.10     202 85       0 05
  82.80       1.80     202 91       0 05
  88.78       1 65     202 97       0 04
  89 79       2.96     203 01       0 06
  90.79      12.95     203 49       0 04
  92.75       1.43     206 64       0.06
  94.76      14.46     212 60       1 09
  99.74       2.88     213 55       0 04
 100.76       4 43     214 62       0 12
 101.76       2.16     218 63       0 05
 102.77       4.88     220 63       1 13
 108.75       4 70     221 64       0.08
 112.72      10.91     232 60       1 37
```

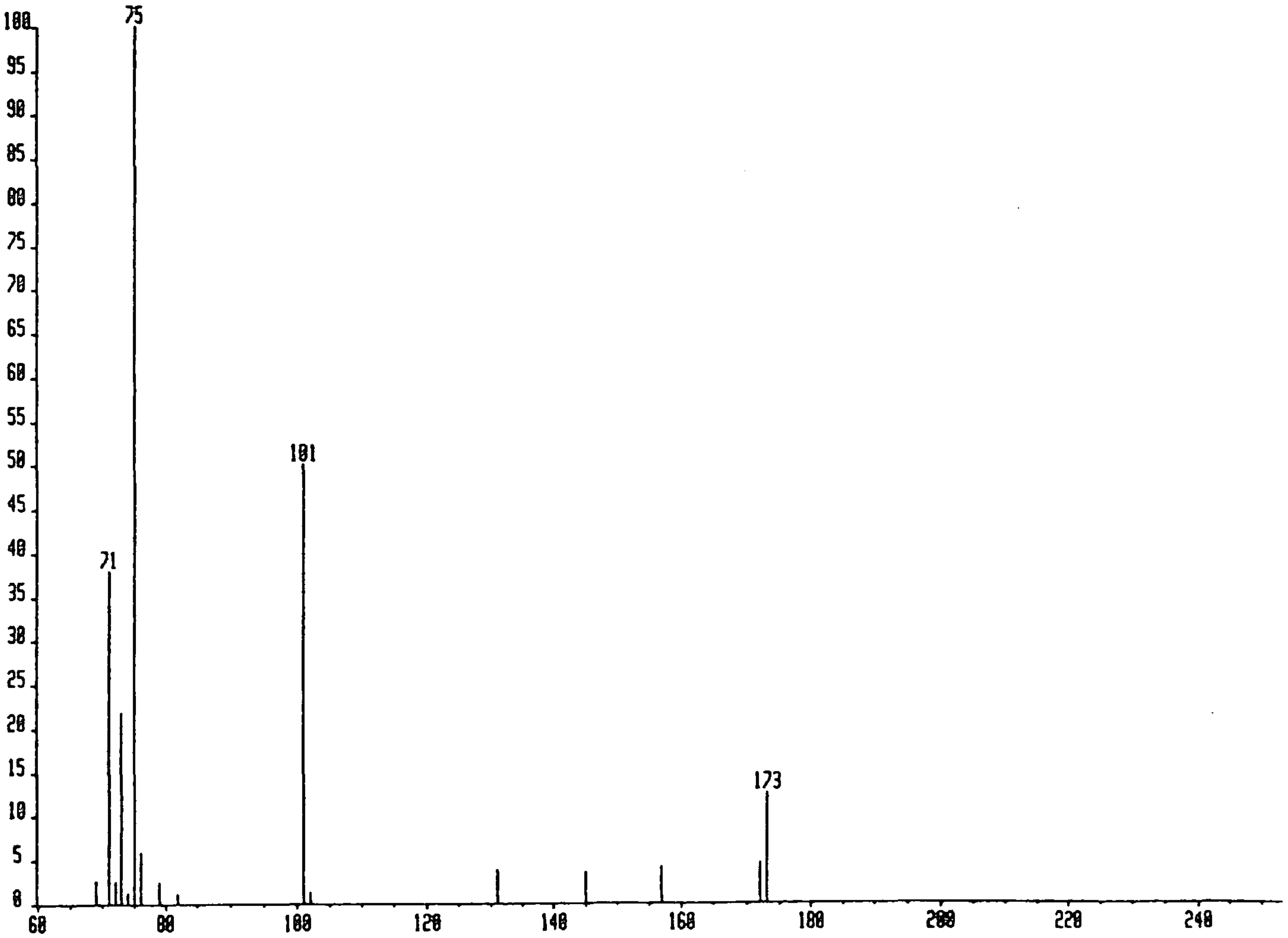
GA770139o x1 Bgd=135 26-JUL-88 15:0+0:02:28 70E EI+
BpA=0 I=4.Sv Ha=462 TIC=104327000 Acnt: Sys:RPSE
GC= 53⁰ Cal:PFK267 No 53 MASS



Mass	% Base		
27.99	5.98	143.93	11.23
30.98	4.67	144.93	0.50
50.99	5.17	149.92	0.24
68.97	81.11	154.91	0.49
74.97	6.86	155.94	0.11
92.96	3.85	161.91	0.25
99.96	2.99	162.75	0.20
100.95	0.33	162.92	19.23
104.95	0.19	163.92	1.01
105.95	0.33	166.92	0.10
111.94	1.77	167.92	0.20
112.84	0.17	168.74	0.20
112.95	19.39	168.91	22.21
113.95	0.71	169.91	0.84
116.94	0.44	174.92	0.48
117.96	0.06	180.90	1.29
118.94	3.86	181.91	0.08
119.94	0.13	185.90	0.14
123.94	0.25	186.91	0.70
124.94	0.52	212.87	0.84
127.84	0.15	224.86	1.32
128.85	0.69	225.87	0.12
129.80	0.07	230.88	0.09
129.86	0.13	236.89	0.25
130.18	0.08	242.88	0.40
130.30	0.08	254.89	0.10
130.32	0.05	255.89	0.10
130.35	0.05	262.93	0.24
130.39	0.13	274.90	2.69
130.44	0.11	275.90	0.33
130.48	0.10	280.88	0.19
130.54	0.11	286.87	0.23
130.77	1.14	292.86	0.13
130.93	100.00	312.84	0.25
131.92	3.67	324.85	0.24
133.83	0.33	362.85	0.24
135.84	0.25	462.85	0.11
136.94	0.66		
142.92	0.35		
143.75	0.10		
143.79	0.13		

```
GA53X033o      x1    Bgd=32    9-NOV-87  16:4◦0:02:16   70E          EI◦
0pA=0 ·   I=10v    Ma=175   TIC=574052992             Acnt:           Sys:APSE                         HMR:
                                                           GC= 81⁰   Cal:PFK2                         MASS:
```

No 54

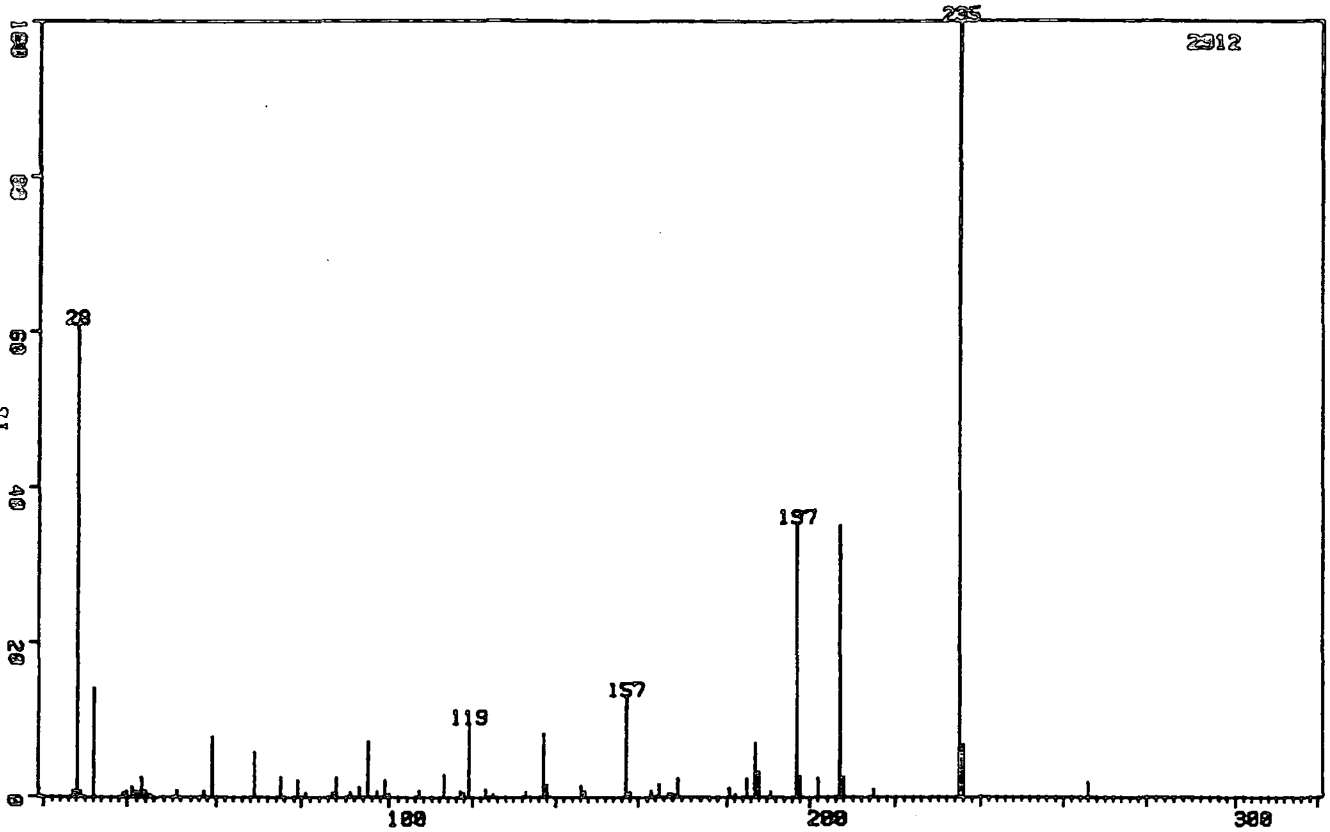


```
Mass       % Base
  25.93      2.11        71.05      37.98
  26.93     34.33        72.05       2.41
  27.94      6.17        73.03      21.80
  28.95     91.90        74.03       1.14
  29.35      0.19        75.03     100.00 O
  29.95      2.08        76.04       5.74
  30.93      7.72        77.01       0.22
  31.92      0.60        78.97       2.39
  32.93      0.83        80.00       0.11
  36.93      0.52        80.99       0.29
  37.94      1.83        81.99       1.05
  38.95     26.27        87.06       0.20
  39.96      3.56        88.07       0.22
  40.97     95.46        89.06       0.33
  41.39      0.13        93.00       0.38
  41.97      5.40        98.98       0.16
  42.98     45.39        99.98       0.41
  43.98      1.68       100.98      50.09
  44.96      6.33       101.99       1.19
  45.96      0.19       128.89       0.17
  46.95     21.98       131.00       3.71
  47.95      0.53       131.93       0.18
  48.94      0.20       144.01       0.13
  49.94      0.95       145.01       3.38
  50.93     17.95       146.02       0.18
  51.95      0.58       157.02       3.94
  52.96      4.16       158.02       0.26
  53.97      1.07       171.04       0.43
  54.98     90.69       172.05       4.52
  55.99     23.91       173.05      12.47
  57.02    100.00 O     174.06       0.94
  58.00     14.31
  58.97      1.27
  59.96      0.11
  60.46      0.57
  60.98      0.58
  62.96      0.13
  64.99      0.20
  67.00      0.42
  69.02      2.48
  70.03      0.36
```

GA9 2S6 G.APSEY CAP.COL. E.I.
CAL:CALP17 STA:

No 55

18-FEB-85
13:22

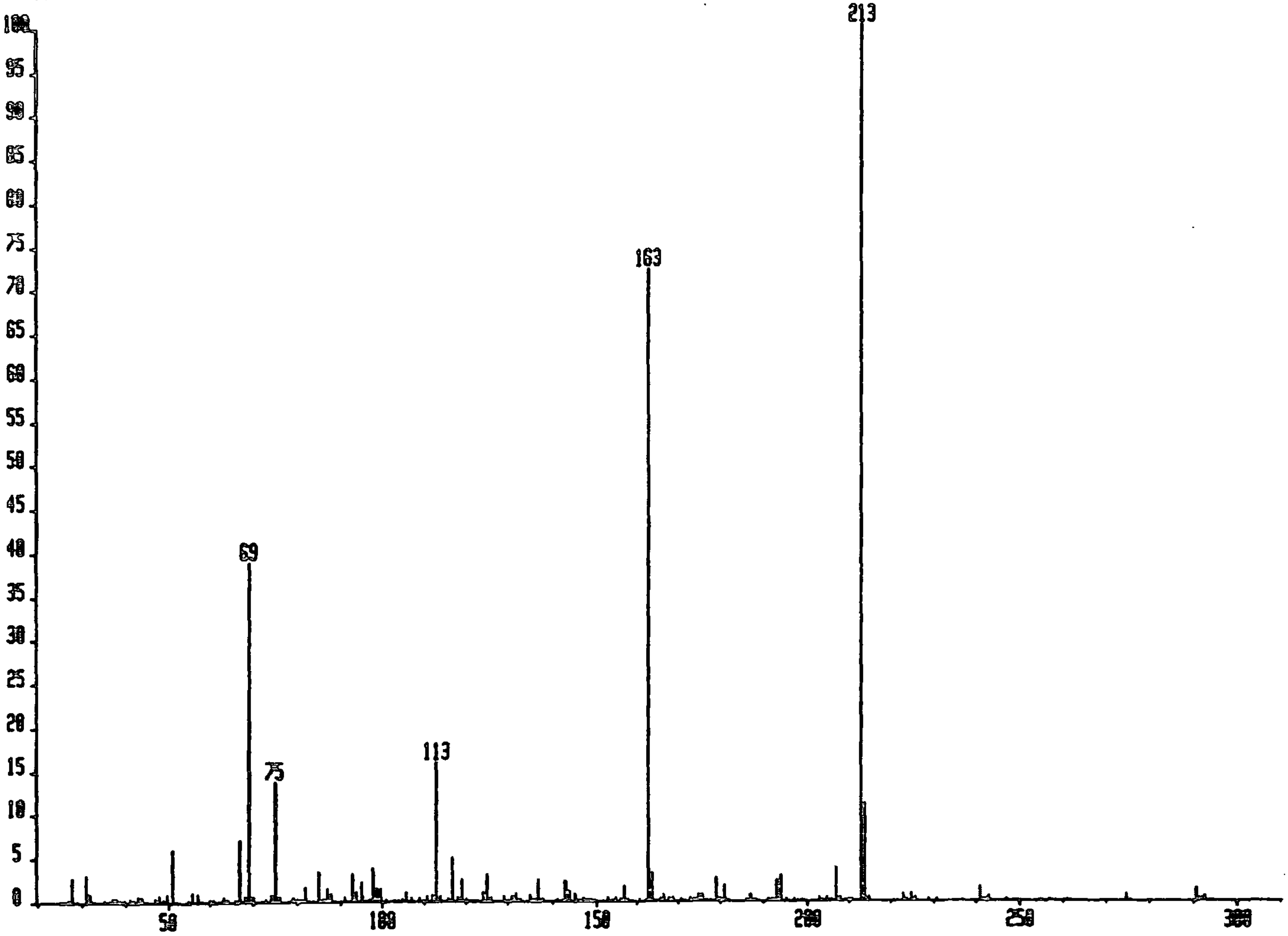


MASS	%HT. BASE
27.23	0.79
28.11	60.99
28.97	0.72
29.00	0.72
31.98	14.01
38.97	0.58
39.81	0.79
40.95	1.34
42.04	0.82
43.12	2.58
44.09	0.89
45.14	0.41
50.93	0.93
57.08	0.62
57.13	0.79
58.97	7.86
68.96	5.91
69.04	0.45
75.07	2.61
78.96	2.16
80.95	0.58
87.03	0.58
88.01	2.51
90.95	0.65
93.00	1.30
95.04	7.25
97.02	0.82
98.96	2.27
99.92	0.38
107.02	0.89
113.00	2.99
117.00	0.82
117.99	0.62
118.96	9.58
122.99	1.03
125.01	0.41
133.01	0.65
136.98	8.31
137.97	1.58
145.98	1.44
146.98	0.82
156.97	13.19
157.96	0.72
162.95	0.89
164.97	1.68
166.96	0.52
167.95	0.45
168.93	2.44
180.89	1.17
182.28	0.31
184.97	2.44
186.95	7.11
187.95	3.23
190.91	0.86
196.96	35.44
197.95	2.60
201.95	2.44
206.94	35.13
207.93	2.58
214.92	1.13
234.90	100.00
235.92	6.83
265.92	1.99

GRS8042o x1 Bgd=1 12-AUG-87 10:1·0:02:49 70E EI+
BpM=0 I=16v Ha=313 TIC=237860000 Cont: Sys:GPSE
HAPPY GPPY GC= 35° Cal:PFK

No 56

HMR:
MASS:

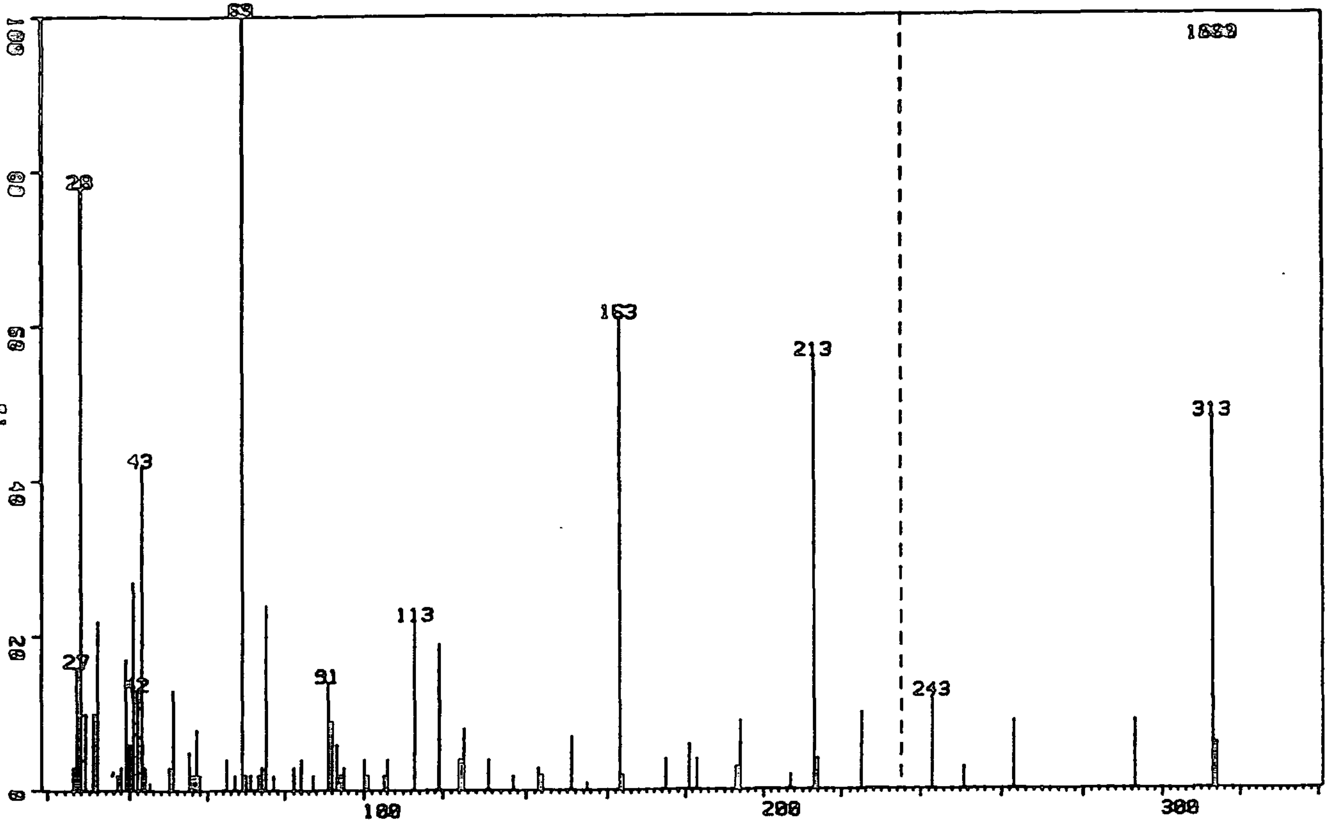


Mass	% Base
27. 00	0. 14
27. 98	2. 62
30 97	2. 96
31. 96	0. 67
34. 94	0. 14
36. 97	0. 34
37 98	0. 30
39. 92	0. 21
41 00	0. 23
42 00	0. 21
43 01	0. 66
43 96	0 42
46 92	0 27
47 93	0. 63
48 94	0. 14
49 95	0 71
50 95	5. 96
54 95	0 21
55 95	0 95
56 96	0. 70
62. 95	0. 47
63 95	0. 15
65 91	0. 10
66. 91	6 95
67 94	0. 44
68 93	38 85
69 93	0 44
72. 92	0 14
73 93	0. 58
74 93	13 67
75 94	0. 51
78 91	0. 26
79 92	0. 17
80 92	0 17
81 92	1. 55
84 89	3. 19
85 91	0. 13
86. 90	1. 28
87. 93	0. 80
90. 90	0. 24
92. 91	2. 98
93. 92	0. 84
94. 93	2. 11
96. 88	0. 11
97. 89	3. 70
98. 92	1. 32
99. 89	1. 38
100. 91	0. 18
104. 90	0. 21
105. 91	0. 85
106. 92	0. 24
108. 87	0. 29
110. 88	0. 41
111. 90	0 52
112. 90	15. 80
113. 91	0 51
115 87	0 13
116. 88	4 85
117. 89	0 29
118. 89	2 43
123 89	0 96 F
124 89	2 92 F
125 90	0 35
128 86	0 41
130 88	0 38
131 89	0 70
134 85	0 52
135 88	0 12
136 89	2 32
137 87	0 15
142 88	2 22
143 88	1 60
144 88	0 29
146 84	0 22
152 85	0 26
154 86	0 24
155 88	0 22
156 89	1. [illegible]
162 87	72 30
163 88	3 11
166. 84	0 56
167 87	0 31
168 85	0 32
170 84	0 12
172. 84	0 24
174 86	0 63
175 87	0 61
178 83	2 47
179 83	0 11
180. 83	1 60
186 86	0 62
190 83	0 21
192 84	2 16
193. 84	2 82
194 86	0 21
196 81	0 11
202 81	0 27
204 83	0 29
206. 84	3 77
207 85	0 25
212 92	100 00 FO
213 84	10 92 F
214 85	0 24
222 81	0. 55
224 83	0 72
225 83	0 25
228 80	0 12
230 81	0 17
240 80	1 54
241. 80	0 13
242 79	0 51
246 79	0 11
274 81	0 59
290 77	1 28
292 77	0 41
310 78	2 77
311 78	0 21
312 78	0 87

GAX2S 0
CAL:LIB STA:

No 57

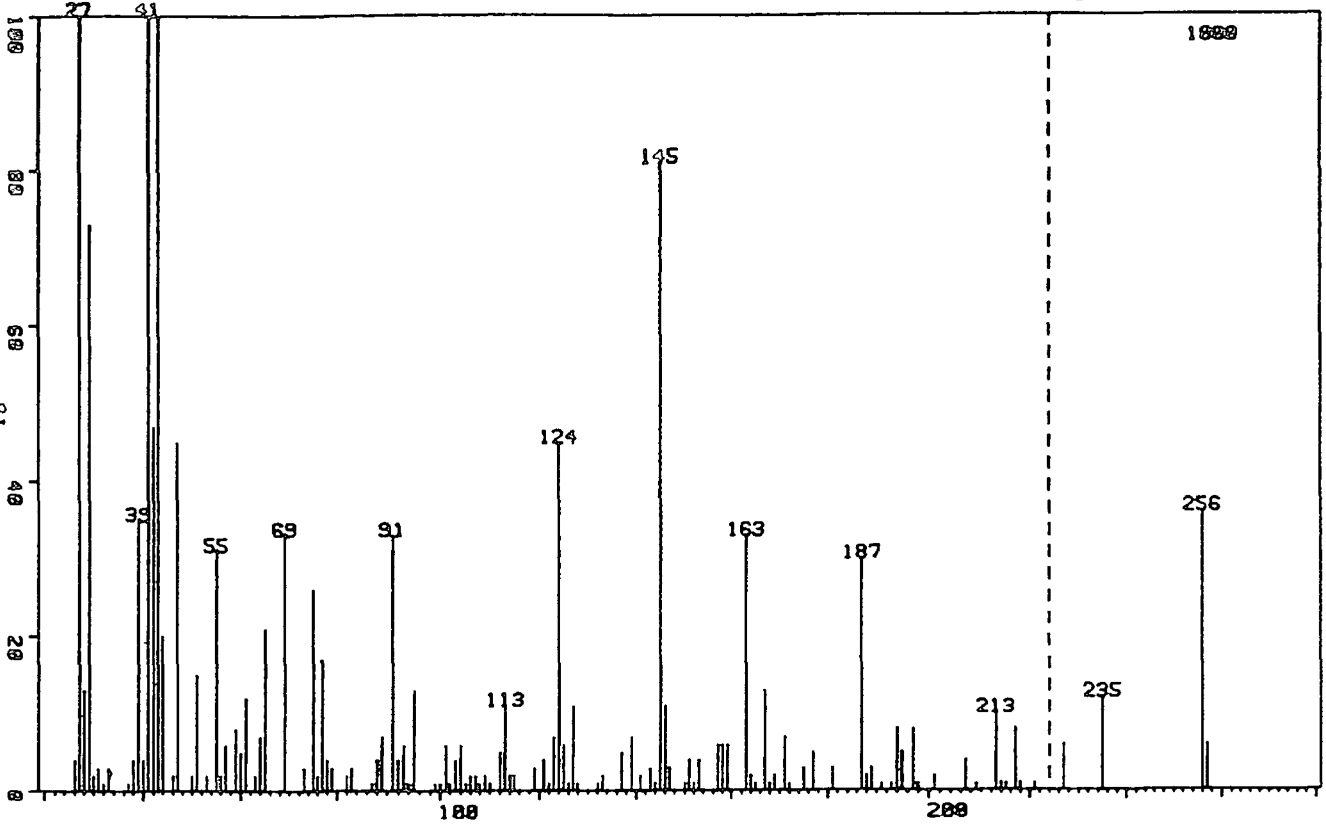
19-SEP-80
0:0



Mass	% Base
26.02	2.38
27.03	16.21
28.01	78.12
28.04	4.17
29.05	9.52
31.01	9.47
31.02	0.86
32.00	21.58
37.02	1.55
38.02	2.85
39.03	17.13
39.97	5.67
40.04	2.01
41.05	26.74
42.06	12.90
43.03	5.95
43.06	41.58
44.00	2.57
44.07	1.27
45.04	1.09
50.02	2.92
51.02	12.99
55.07	4.95
56.02	2.13
56.08	2.18
57.09	7.66
58.06	1.37
65.06	3.26
67.08	1.85
69.02	100.00
69.09	3.24
70.02	0.90
70.10	1.62
71.11	1.60
73.07	1.48
74.03	2.34
75.03	23.89
77.06	1.53
82.03	2.78
82.07	1.53
84.12	3.29
87.03	1.44
91.09	13.61
92.10	9.12
93.03	5.30
93.11	1.13
94.04	1.67
95.05	1.94
96.12	2.32
100.04	3.54
101.05	1.83
105.12	1.83
106.05	3.38
113.05	21.39
119.05	18.27
119.14	1.34
124.05	3.84
125.06	7.52
131.06	3.54
137.07	1.99
143.07	2.38
144.07	2.01
151.07	6.55
155.07	1.13
163.08	60.50
164.09	2.08
175.10	3.98
181.09	6.07
183.10	4.17
193.10	2.55
194.10	9.12
207.14	2.01
213.11	55.92
214.12	3.59
225.13	10.00
243.12	3.98
261.14	1.13
263.14	2.41
293.17	2.38
313.19	15.54
314.20	1.37

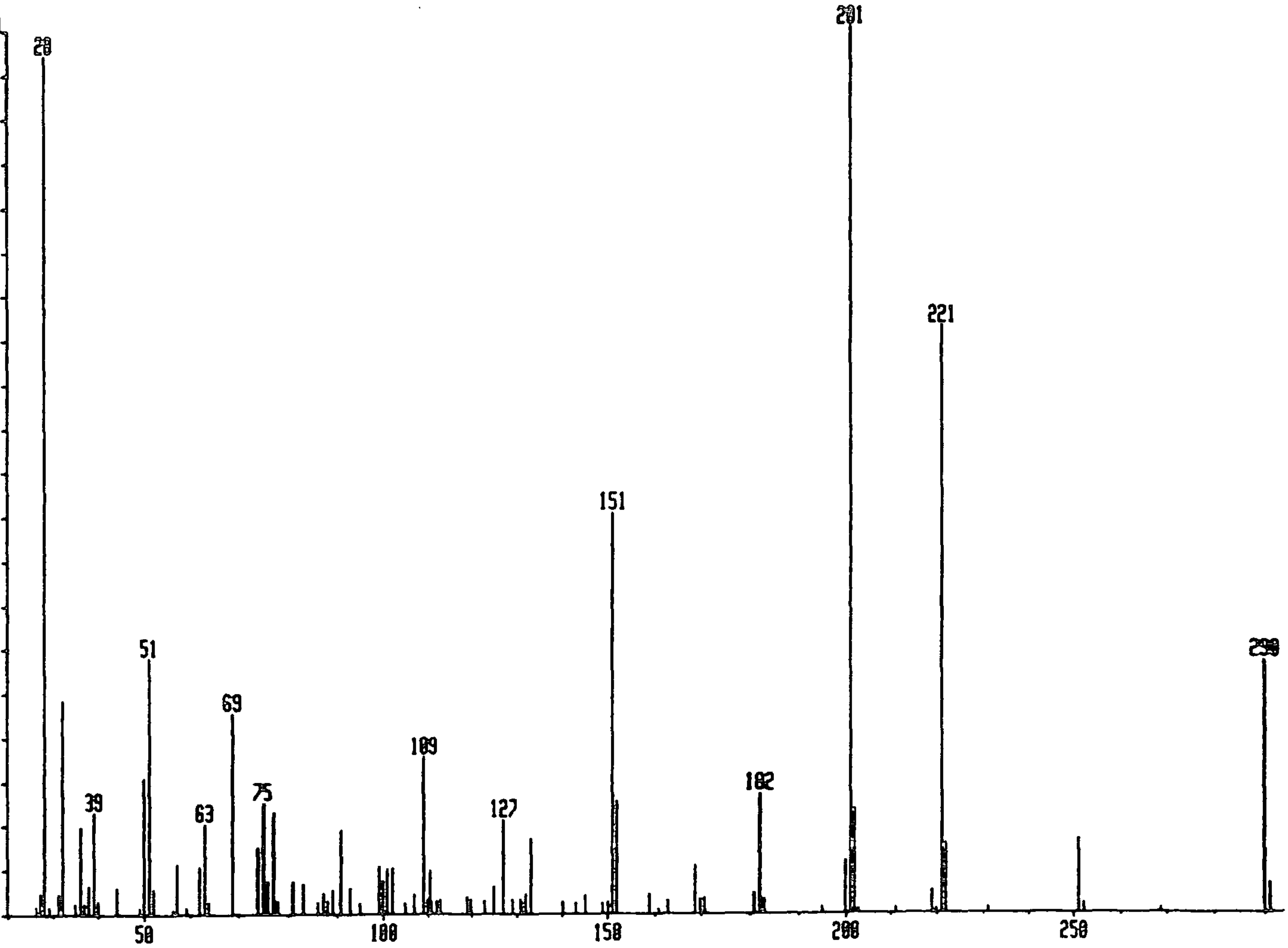
GAS8 0 No 58 19-SEP-80

CAL:LIB STA: 0:0



MASS	% BASE				
26.03	4.03	95.05	13.05	194.09	8.30
27.04	100.00 D	99.05	1.60	195.10	4.68
28.02	4.69 F	100.04	0.84	196.11	0.29
28.05	12.90 F	101.06	5.51	196.49	0.04
29.06	72.75	102.07	1.10	196.55	0.04
30.06	1.56	103.08	4.15	196.80	0.05
31.02	2.82	104.09	5.80	197.13	7.55
32.01	1.15	105.08	0.66	197.26	0.03
33.03	2.79	106.05	1.73	197.51	0.04
37.02	1.11	107.06	1.60	197.79	0.03
38.03	4.11	108.06	1.04	198.13	0.74
39.04	34.59	109.07	2.18	199.10	0.17
40.05	4.34	112.04	4.29	201.11	1.46
41.06	100.00 D	113.05	10.36	202.10	0.10
42.06	47.23	114.07	1.25	205.13	0.37
43.08	100.00 D	115.09	1.57	207.10	3.47
44.07	19.64	121.08	3.77	208.11	0.42
46.04	1.52	122.09	1.22	209.12	0.66
47.05	44.94	123.10	6.83	210.12	0.17
50.03	1.88	124.10	44.92	212.07	0.07
51.03	15.09	125.07	5 87	213.10	10.40
53.06	1.73	126.07	1 14	217.18	7.48
55.08	30.99	127.08	11.04	217.38	0.06
56.03	1.26 F	137.07	4.81	218.15	0.69
56.09	1.55 F	138.07	0 49	219.12	0.08
57.04	5.86	139.08	6.49	221.12	0.99
59.06	7.38	145.07	81.15	222.13	0.07
60.07	5.10	146.08	10 46	225.10	0.11
61.07	12.16	147.10	2 60	226.11	0.35
63.05	1.61	163.07	33.30	227.12	1.08
64.04	6.55	164.08	1.38	228.13	0.14
65.05	21.26	165.10	1.12	235.15	1.35
69.03	33.29	166.11	0.22	236.15	0.33
73.08	3.28	166.88	0 06	237.16	0.10
75.04	26.14	167.12	12.67	239.10	0 03
76.04	2.29	167.26	0 03	241.15	0.38
77.06	16.65	167.40	0 05	242.21	0.04
78.06	3.89	168.12	1.02	255.14	0.08
79.07	2.72	169.08	1.38	255.29	0.04
82.04	2.18	170.08	0 25	256.17	5.99
83.06	2.41	171.09	7 21	257.17	0.70
87.05	1.23	175.06	2 75		
88.05	4.41	176.07	0 45		
89.06	7.01	176.95	0 06		
91.07	32.53	177.09	4.88		
92.08	4.09	187.14	29 82		
93.04	5.74	187.44	0 08		
94.05	1.21	188.14	2.11		

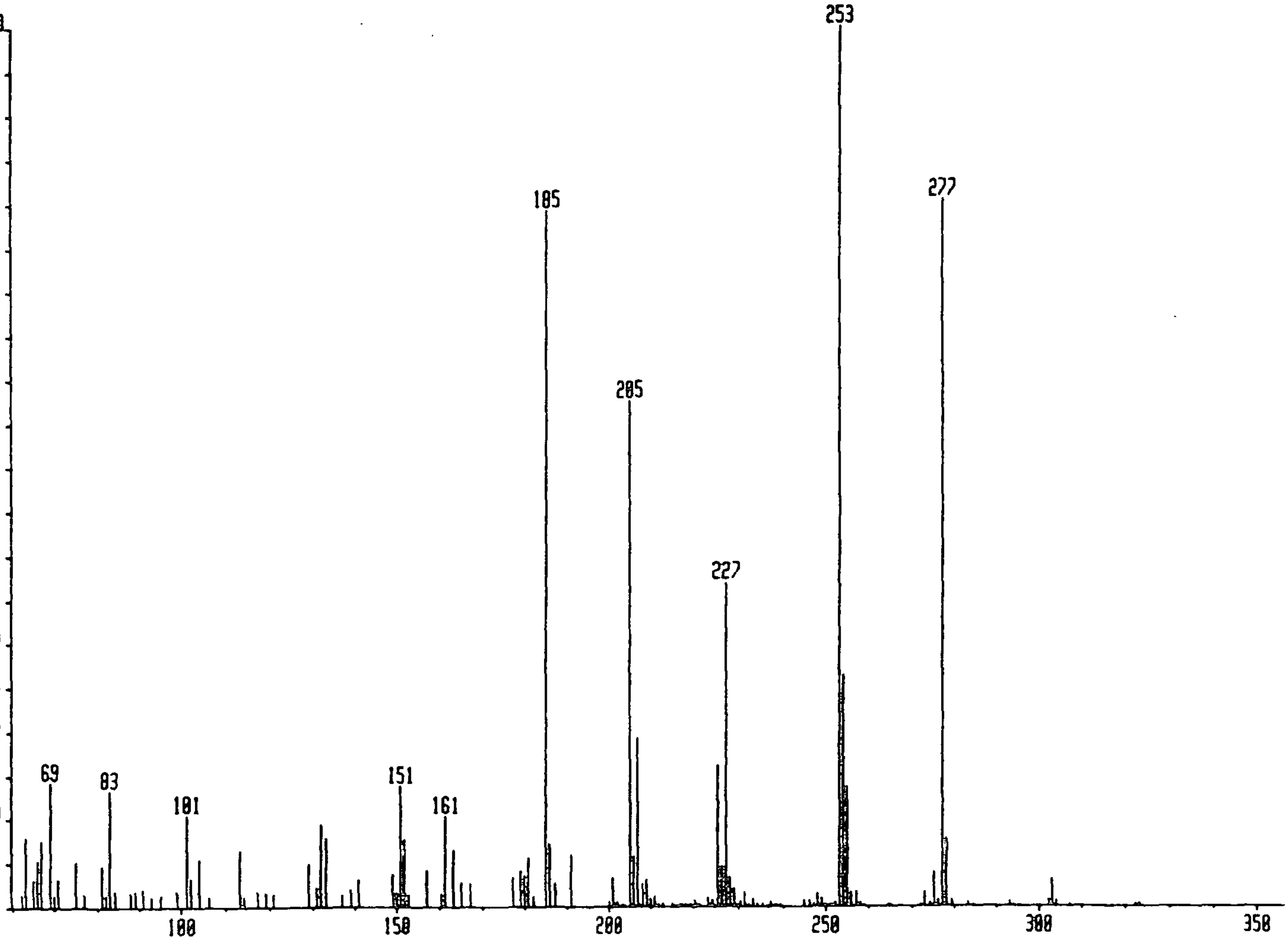
GR530116○ x1 Bgd=114 15-JAN-88 15:1○8:09:02 70E EI○
BpM=0 I=1.7v Hm=291 TIC=82111600 Rcnt: Sys:GPSE HRE:
GC= 98° Cal:PFK11 No 59 MASS:



ass	% Base				
27. 02	2. 15	114. 05	0. 56	200. 06	5 72
28. 01	96. 97	115. 54	0. 26	201. 06	100 00
31. 01	2. 14	119. 04	1. 72	202. 06	11 77
32. 00	24. 12	120. 06	1. 47	203. 06	0 34
35. 99	9. 78	123. 03	1. 27	211. 04	0. 39
37. 98	3. 18	124. 03	0. 64	219. 05	2 39
38. 03	2. 61	125. 04	2. 98	220. 06	0. 34
39. 03	11. 43	126. 05	0. 32	221. 06	66 27
44. 00	2. 88	127. 06	10. 50	222. 07	7. 65
50. 02	15. 22	128. 06	0. 93	231. 04	0 45
51. 03	28. 85	128. 93	1. 50	251. 08	8 16
52. 04	2. 73	130. 93	1. 52	252. 08	0. 85
57. 03	5. 43	131. 05	1. 12	269. 04	0 51
62. 03	5. 26	131. 93	2. 10	290. 07	28. 50
63 04	10. 06	132. 05	1. 03	291. 07	3 24
69. 01	22. 64	133. 07	8. 42		
74. 03	7. 44	133. 93	0. 59		
75. 03	12. 45	134 07	0. 53		
76 04	3. 50	135 54	0. 46		
77. 05	11. 45	135. 93	0. 47		
81. 03	3. 58	137. 02	0 34		
83. 05	3. 32	138. 05	0 47		
87. 03	2. 16	140. 07	1. 22		
89. 06	2. 53	143 03	1 07		
91. 03	9. 37	145. 05	1. 92		
93. 02	2. 85	149 05	1. 00		
99. 03	5. 18	150 05	1. 17		
00. 03	3. 61	151 06	45 27		
00. 53	0. 38	152. 07	12. 65		
01. 04	4. 86	153 07	0 81		
02. 07	5. 03	159. 07	2. 06		
05. 03	1. 06	161 04	0. 41		
06. 03	0. 72	163. 04	1 36		
07. 05	2. 14	169 05	5 36		
09. 07	17. 63	170 06	1 45		
10. 05	1. 51	171. 07	1 68		
10. 54	4. 77	181. 05	2. 29		
11. 04	1. 13	182 06	13 41		
12. 03	1. 36	183. 06	1. 44		
13. 03	1. 45	195 06	0 53		

```
GA57X0601o     x1     Bgd=581   11-DEC-87 15:5+0:10:42   70E          EI+
BpA=29    I=1Gv    Hn=324   TIC=637241824              Acnt:           Sys RPSE                                      HRR:
                                                              GC= 135⁰  Cal PFK412                                   MASS:
```

No 60

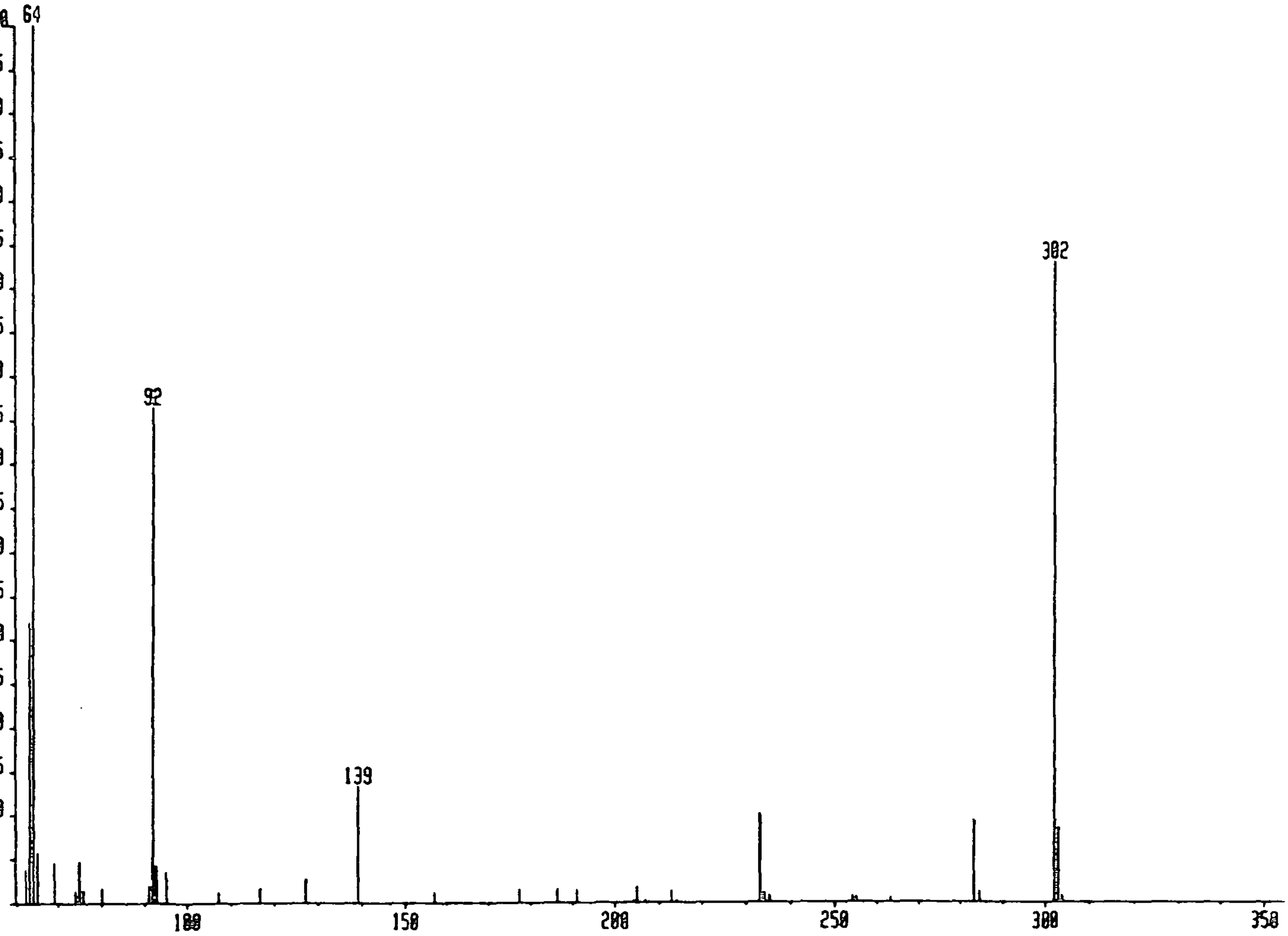


```
IASS      X OASE
  26.03       2.38         129.07      4.79        177.09      3.27        253.22     100.00 FO
  27.04      25.33         129.49      0.05        177.34      0.06        254.17      26.18 F
  28.02       3.93 F       129.52      0.06        177.72      0.05        254.57       0.04
  28.05       2.41 F       129.58      0.16        178.09      0.64        255.14      13.49
  29.02       2.79 F       130.07      0.61        178.27      0.03        255.48       0.03
  29.06     100.00 FO      131.06      2.05        179.09      3.94        256.14       1.45
  30.06       3.01 F       132.08      9.33        179.72      0.05        256.94       0.05
  32.01       1.08         132.80      0.03        179.81      0.08        257.13       1.52
  38.03       1.93         132.83      0.05        180.10      3.48        258.14       0.24
  39.04       8.03         133.09      7.66        180.56      0.11        259.11       0.05
  42.03       1.04         133.19      0.06        180.61      0.05        264.36       0.07
  43.04      26.45         133.28      0.04        180.72      0.08        264.51       0.05
  45.02       2.54 F       133.65      0.04        180.86      0.06        264.77       0.08
  45.05       7.99 F       133.75      0.06        181.09      5.44        264.87       0.05
  51.04       3.07         134.06      0.61        185.07     79.13 F      265.45       0.05
  53.03       1.77         135.08      0.20        186.06      7.11 F      272.05       0.06
  57.04       5.92         135.98      0.21        187.08      2.49 F      272.13       0.08
  62.05       1.28         136.08      0.20        205.12     57 51        273.14       1.46
  63.06       7.82         137.07      1.24        205.65      0.10        274.16       0.26
  65.05       2.94         138.08      0.22        205.79      0.09        275.15       3.68
  66.05       5.21         139.08      1.72        206.11      5 65        275.90       0.06
  67.05       7.41         139.19      0.06        206.27      0 05        276.17       0 54 F
  69.03      14.04         139.42      0.03        207.11     19.17        277.15      80.36 F
  70.06       1.17         140.09      0.12        207.32      0 08        278.15       7 57
  71.06       3.18         141.09      2.91        207.40      0.08        279.15       0.59
  75.04       5.06         151.09     13.65        207.51      0 03        283.19       0.31
  77.06       1.34         151.40      0.07        208.12      2.31        284.21       0.07
  81.05       4.60         151.57      0 05        209 12      2 90        293.15       0 47
  82.05       1.15 F       151.72      0.06        225 12     16.02        294.14       0 03
  83.07      13.23         151.76      0.03        225.43      0.05        294.19       0 05
  84.07       1.84         151.84      0.06        225.48      0.07        295.17       0.05
  88.05       1.52         151.89      0.05        225.59      0.05        302.19       0 57
  89.06       1.69         152.09      7.52        225 75      0.03        303.20       3.04
  91.07       1.96         160.09      1.30        225.86      0.05        304.21       0.38
  93.04       1.02         160.86      0.03        225.90      0.06        307.18       0.08
  95.06       1.23         161.10     10.23        226.12      4.45        322.20       0.08
  99.06       1.68         161.29      0.05        226.35      0.05        32[illegible].21       0.26
 100.06       0.42         162.10      0.89        226.52      0.06
 101.07      10.43         163.08      6.31        227.12     36.90
 102.07       3.12         164.09      0.52        228.13      3.25
 103.08       0.53         165.08      2.66        228.91      0.03
```

GA660592○ ¤1 Bgd=587 11-MAR-88 12:0+0:10:32 70E EI+
BpM=0 I=4.5v Mo=304 TIC=117540000 Acnt: Sys:RPSE
GC= 134⁰ Cal:PFK43

<u>No 61</u>

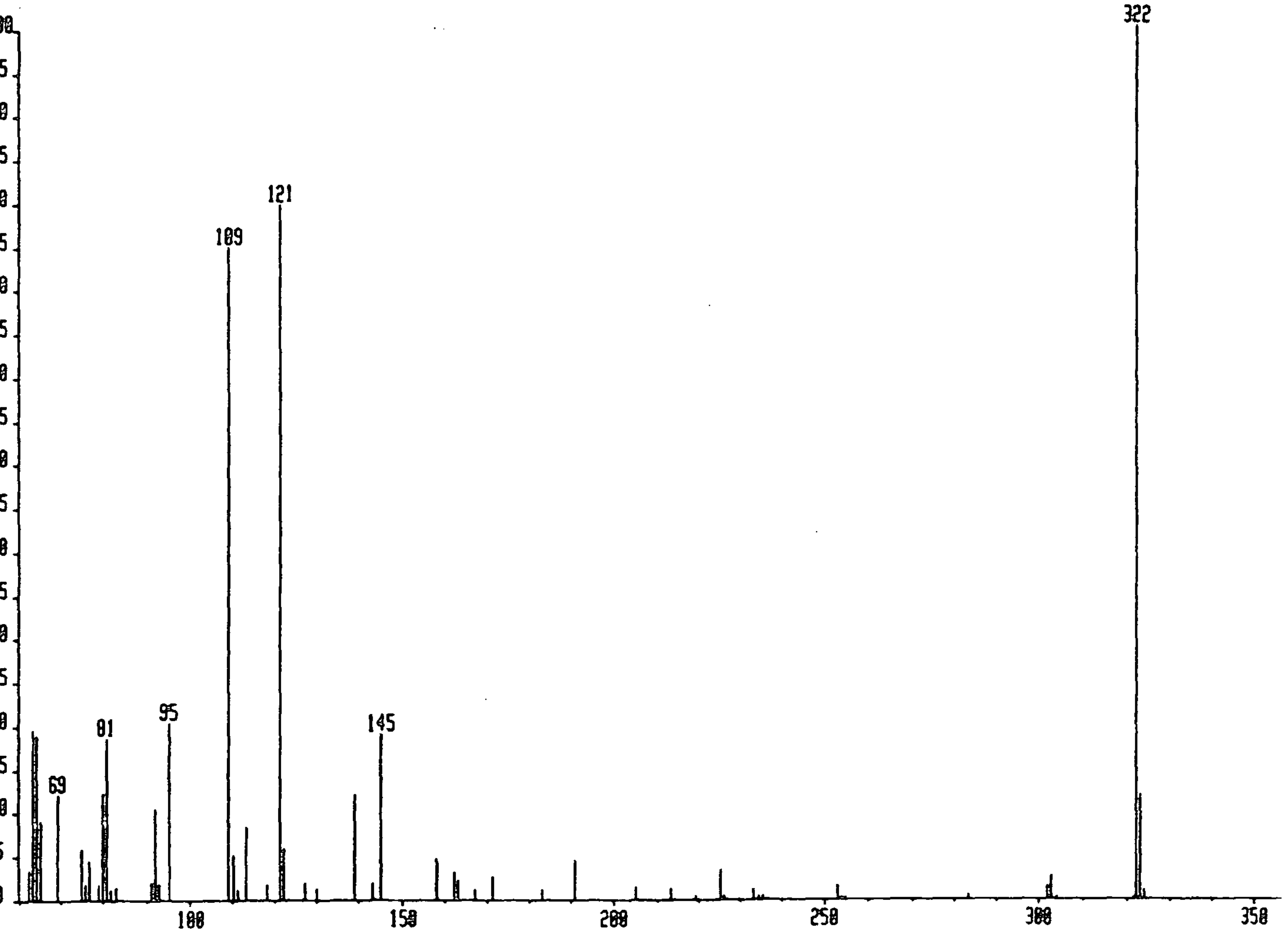
MAR:
MASS:



Mass	% Base
26.04	1.04
28.03	2.60
37.04	1.25
38.05	7.53
39.05	2.03
50.06	4.19
51.06	2.44
52.08	2.54
53.05	2.19
62.07	3.70
63.08	31.90
64.09	100.00
65.09	5.64
69.06	4.39
74.08	1.24
75.08	4.67
76.09	1.32
80.09	1.52
91.08	1.73
92.09	56.29
93.09	4.13
95.10	3.47
101.10	0.13
106.10	0.12
107.10	1.05
108.11	0.81
109.10	0.13
111.10	0.43
112.10	0.19
113.09	0.99
115.12	0.20
116.59	1.52
117.09	0.10
117.11	0.10
119.11	0.22
120.12	0.10
121.12	0.56
125.10	0.45
126.10	0.12
127.13	2.49
137.12	0.86
138.13	0.22
139.11	13.01
140.12	0.89
141.10	0.63
143.11	0.28
145.12	0.35
151.10	0.12
156.11	0.13
157.13	1.09
158.14	0.19
163.11	0.39
164.13	0.32
167.13	0.43
169.12	0.36
176.13	0.16
177.13	1.34
185.14	0.78
186.14	1.37
187.13	0.07
191.11	1.36
194.13	0.33
204.14	0.22
205.16	1.65
207.14	0.22
213.14	1.26
214.16	0.22
233.16	9.87
234.16	0.94
235.16	0.66
254.16	0.46
255.17	0.47
263.15	0.32
283.18	9.22
284.18	1.08
301.77	0.12
302.18	72.56
303.18	8.24
304.19	0.56

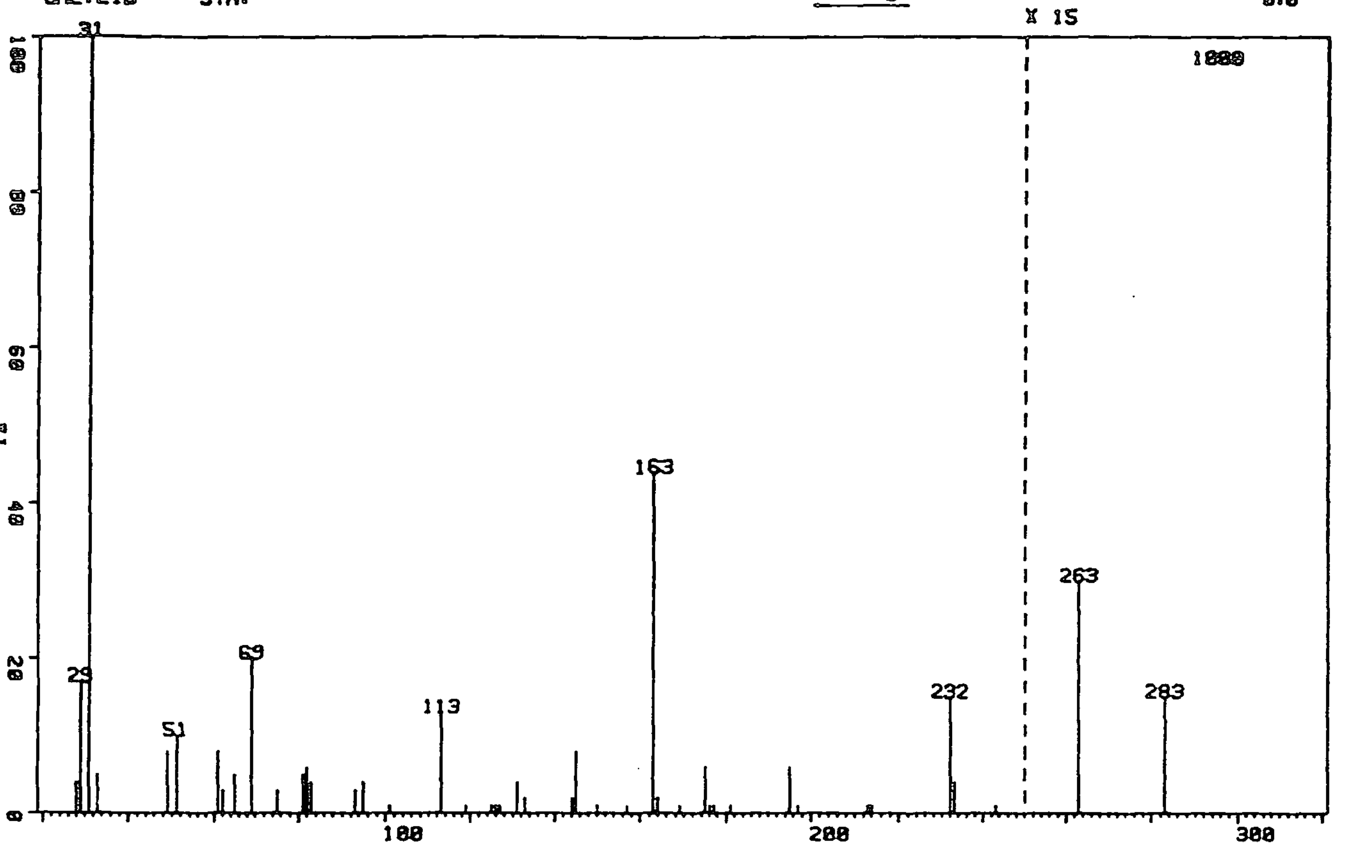
```
GA660582o        ≡l    Bgd=573   11-MAR-88 12:0+0:10:21   70E          EI+
BpA=0     I=3.3v   Ma=324   TIC=131221080                  Acnt:           Sys:APSE                      HAR:
                                                                    GC= 132°  Cal:PFK43                     MASS:
```

No 62



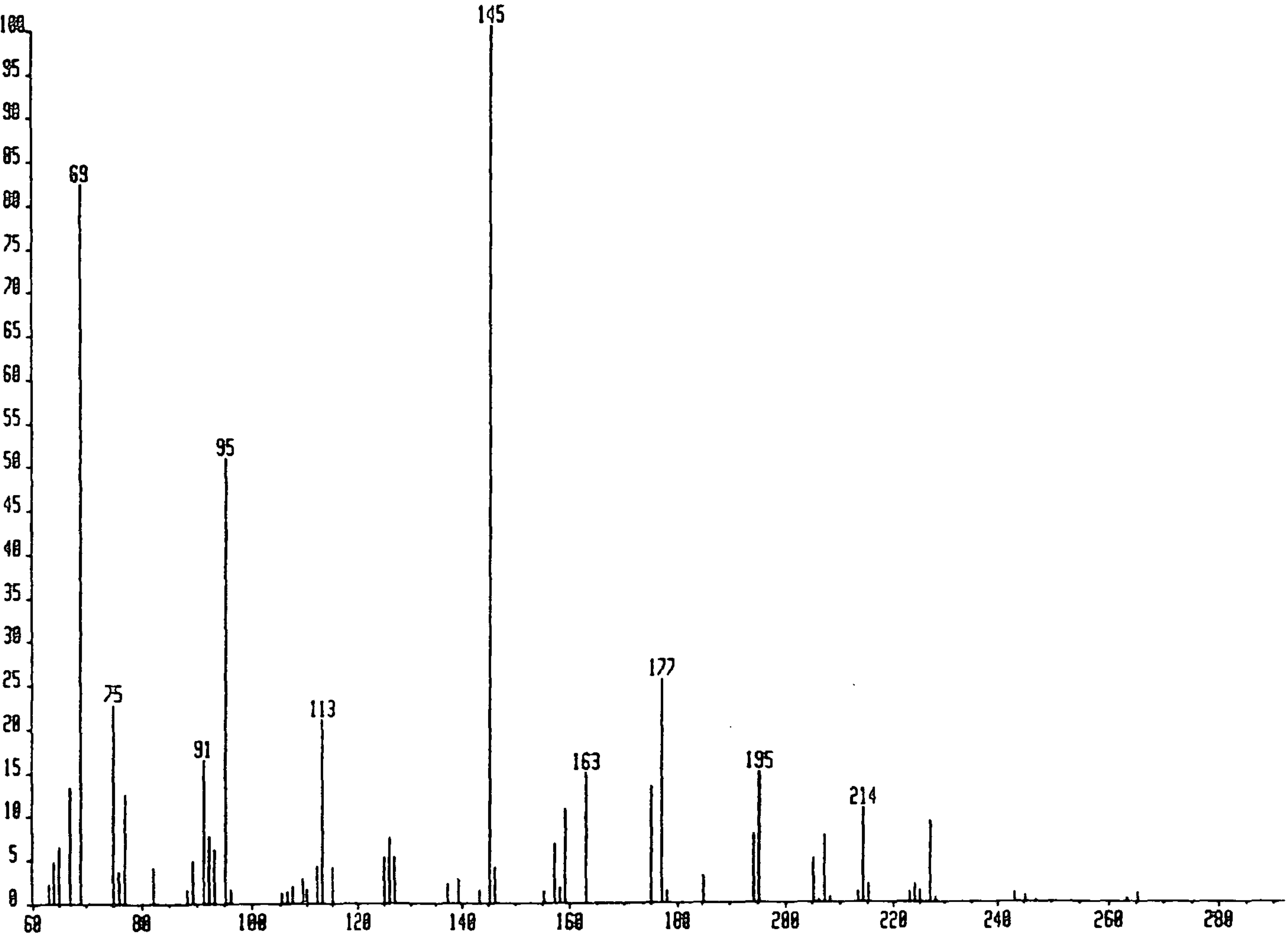
lass	% Base				
26. 04	4. 61	115. 14	0. 29	189. 15	0. 90
27. 05	1. 30	118. 13	1. 56	191. 12	4. 41
28. 03	1. 11	119. 13	0. 98	192. 16	0. 14
29. 03	3. 21	120. 13	0. 37	193. 16	0. 56
37. 04	1. 41	121. 13	79. 70	194. 15	0. 32
38. 06	6. 40	122. 14	5. 79	205. 16	1. 34
39. 06	4. 63	123. 14	0. 50	213. 14	1. 13
50. 06	7. 31	125. 11	0. 76	219. 20	0. 28
51. 07	11. 63	126. 13	0. 74	225. 18	3. 30
52. 08	23. 89	126. 60	0. 38	226. 21	0. 30
53. 05	3. 79 F	127. 14	1. 78	233. 19	0. 98
53. 09	2. 95 F	130. 13	1. 12	234. 24	0. 29
54. 06	1. 41	132. 14	0. 12	235. 21	0. 29
57. 07	1. 38	133. 14	0. 54	253. 20	1. 46
62. 08	3. 24	134. 15	0. 96	254. 21	0. 18
63. 09	19. 34	136. 16	0. 24	255. 19	0. 16
64. 09	18. 77	139. 13	12. 00	255. 22	0. 12
65. 10	8. 86	140. 13	0. 65	283. 23	0. 40
69. 06	11. 97	143. 14	1. 78	302. 20	1. 30
75. 08	5 65	145. 12	18. 94	303. 22	2. 51
76. 10	1 60	146. 13	0. 67	304 29	0. 16
77. 11	4. 30	157. 13	0. 23	321 64	0. 16
79. 09	1. 56	157. 17	0. 14	322. 22	100. 00
80. 09	12. 20	158. 14	4. 63	323. 22	11. 81
81. 10	18. 53	159 15	0. 81	324. 23	0. 95
82. 09	1. 05	162. 14	3. 17		
83. 11	1 33	163. 11	2. 07		
91. 08	1. 93	165. 15	0. 16		
92. 10	10 43	165. 17	0. 19		
93. 11	1. 71	167. 15	1. 03		
95. 10	20. 32	171. 14	2. 51		
101. 11	0 57	172. 17	0. 23		
102. 12	0 68	173. 12	0. 16		
107. 11	0. 62	173. 17	0. 23		
108. 11	0. 98	177. 18	0. 52		
109. 11	74. 77	183. 16	1. 05		
110. 12	5 03	185. 12	0. 10		
111. 12	1 05	185. 17	0. 19		
112. 13	0. 37	186. 15	0. 14		
113. 09	8. 31	186. 18	0. 10		
114. 12	0. 41	187. 18	[illegible]		

GA69 0 19-SEP-80
CAL:LIB STR: No 63 0:0



Mass	% Base
27.98	4.19
28.97	16.71
30.99	100.00
32.99	5.33
48.98	8.15
50.98	9.95
60.97	7.98
61.98	2.72
64.98	4.77
68.95	20.27
74.96	2.91
80.97	4.49
81.96	5.98
82.96	4.08
92.95	2.67
94.96	3.95
100.95	0.76
103.00	0.06
103.95	0.08
105.95	0.19
106.96	0.35
107.96	0.11
110.93	0.13
110.96	0.16
111.93	0.26
112.94	12.61
113.95	0.40
114.96	0.24
118.93	0.81
122.94	0.10
123 91	0.11
123.94	0.18
124.94	0.51
125.95	0.55
126.95	1.02
128.84	0.15
130.92	3.59
131.84	0.18
131.93	0.26
132.94	2.33
136.93	0.16
140.92	0.12
142.93	0.29
143.92	1.57
144.93	7.66
145.94	0.31
149.91	0.86
150.92	0.37
156.93	1.00
158.91	0.12
158.94	0.09
161.92	0.10
162.92	44.35
163.92	1.93
168.90	0.52
172.92	0.27
173.93	0.13
174.91	6.17
175.92	0.57
176.93	0.56
180.91	0.58
181.90	0.09
190.89	0.09
192.91	0.23
193.91	0.30
194.91	5.59
195.90	0.31
196.89	0.73
212.90	0.59
213.90	0.54
222.90	0.24
231.89	15.42
232.90	4.23
233.91	0 22
240.90	0.31
242.91	0 47
250.90	0 22
260.89	0.07
260.92	0.12
262.92	2.11
263.94	0 15
280.92	0.10
282.91	0 37

GA6502135 x1 Bgd=203 11-MAR-88 11:2+0:03:47 70E EI+
BpM=0 I=16v Hm=265 TIC=225782000 Rcnt Sys:RPSE **No 64** HRR:
GC= 66° Cal:PFK43 MASS:

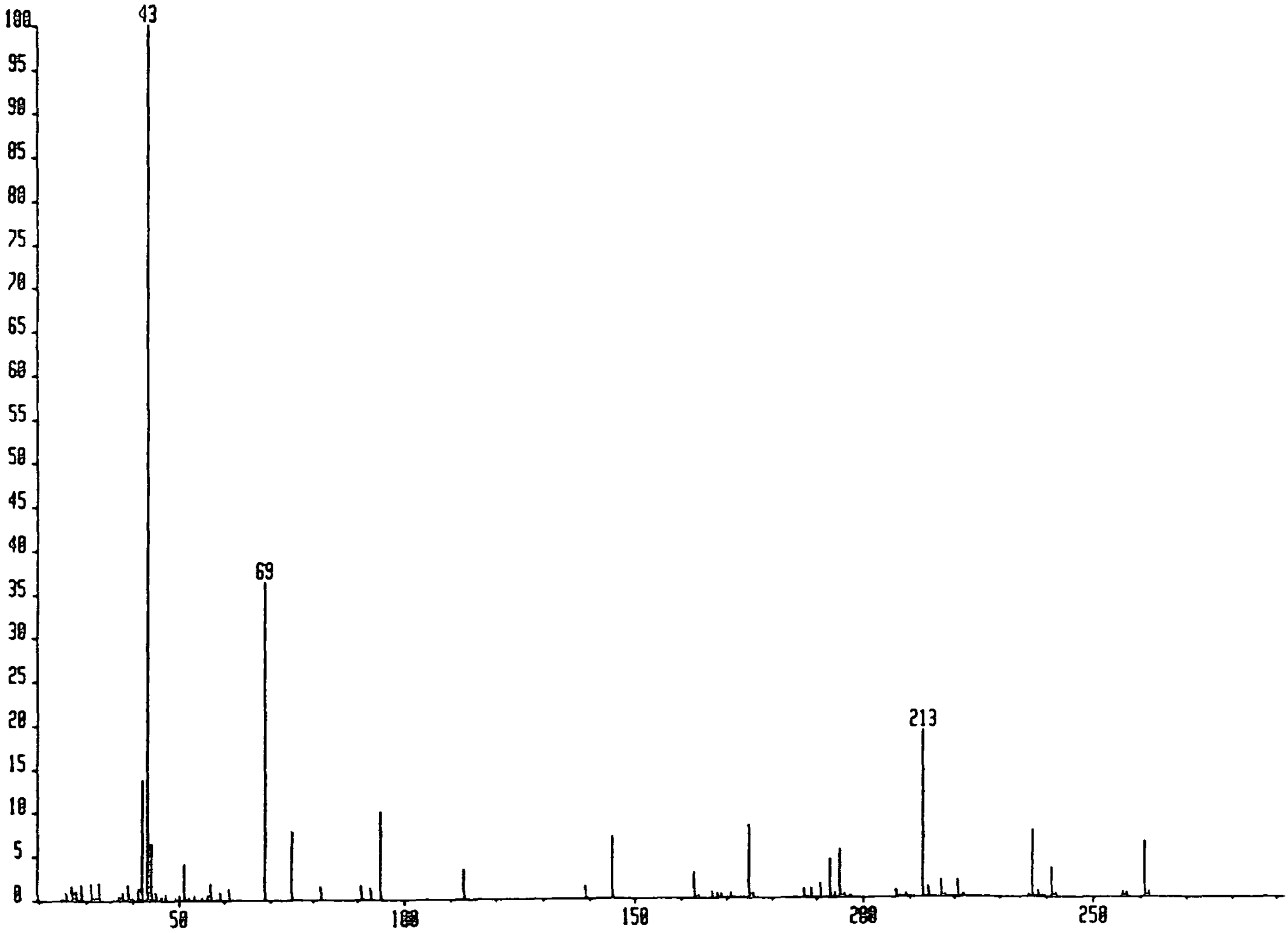


Mass	% Base
27.06	1.84
29.04	21.62
30.05	3.32
31.07	100.00 O
32.06	3.97
33.06	2.07
39.07	2.20
43.07	1.25
45.07	1.06
49.06	5.08
51.06	8.82
57.08	2.86
64.09	1.50
65.10	2.05
67.09	4.27
69.08	26.76
75.10	7.37
76.10	1.17
77.11	4.06
82.10	1.29
89.12	1.55
91.10	5.30
92.10	2.46
93.11	1.96
95.12	16.53
100.11	0.13
101.12	0.11
105.14	0.33
106.13	0.36
107.13	0.56
108.14	0.32
109.15	0.88
110.12	0.50
111.13	0.18
112.13	1.34
113.12	6.82
114.14	0.26
115.14	1.32
119.14	0.25
123.15	0.22
124.14	0.20
125.15	1.71
126.15	2.42
127.16	1.67
132.06	0.05
132.14	0.30
133.16	0.06
137.15	0.69
139.17	0.89
143.14	0.44
144.15	0.16
145.15	32.56
146.15	1.32
155.15	0.37
157.16	2.18
158.18	0.55
159.18	3.48
160.20	0.19
163.16	4.84
164.18	0.22
173.19	0.16
175.17	4.31
176.19	0.23
177.19	8.29
178.20	0.39
181.19	0.10
185.19	0.98
193.19	0.08
194.18	2.52
195.19	4.80
196.21	0.27
205.21	1.58
206.22	0.06
207.20	2.46
208.23	0.14
213.21	0.35
214.20	3.48
215.22	0.63
223.21	0.34
224.21	0.62
225.23	0.40
227.22	3.01
228.23	0.15
243.23	0.29
245.25	0.17
247.19	0.04
247.24	0.06
263.28	0.11
265.26	0.29

```
GA6804C5        x1     Bgd=30    17-DEC-87 16:3+0:02:49   7GZ        EI+
BpA=0     I=10v    Ho=261   TIC=201695000             Rcnt:          Sys:APSE
                                                          GC= 46°    Cal:PFK11
```

No 65

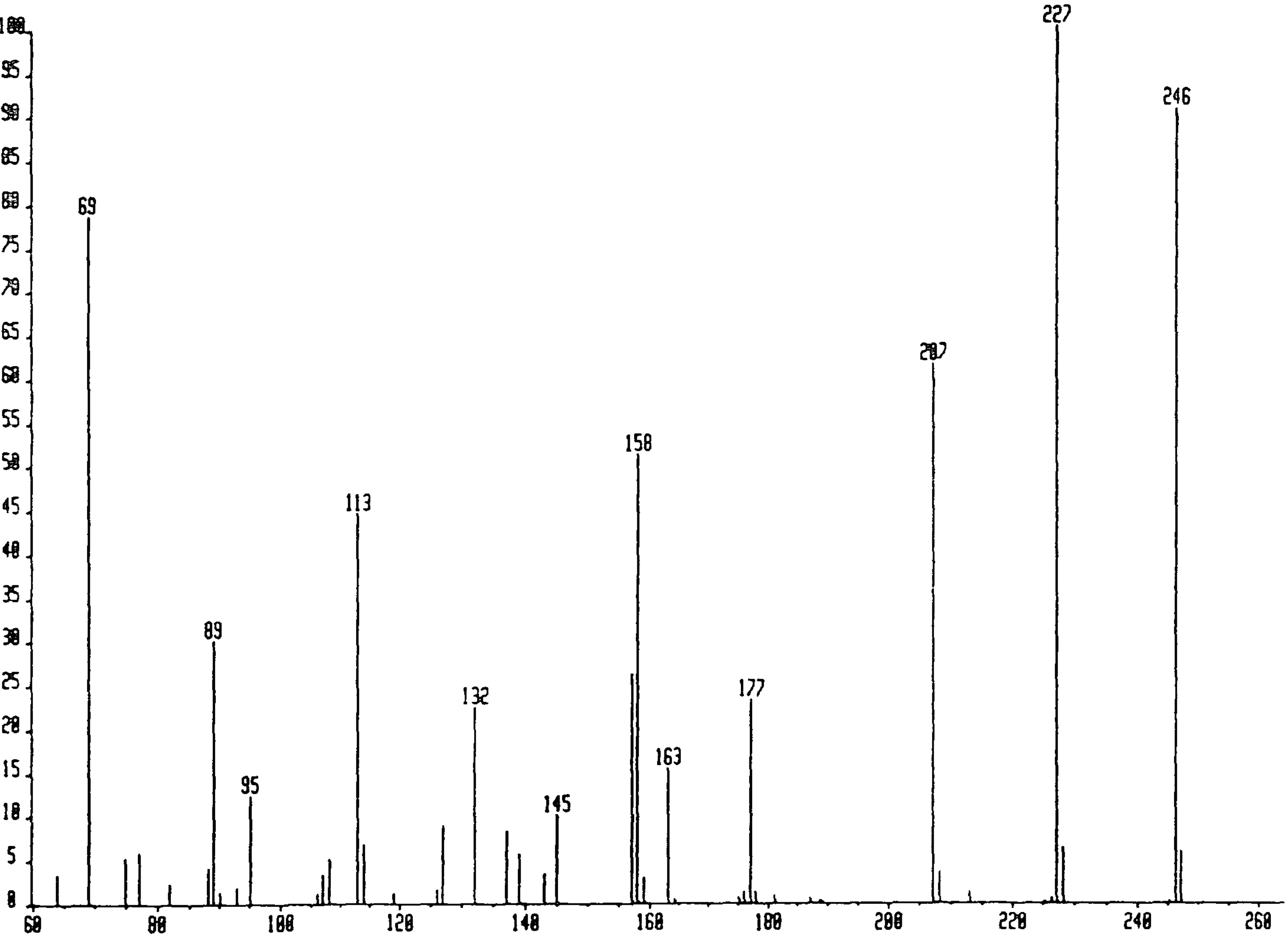
HRR:
MASS:



MASS	X BASE				
42.01	13.60	139.02	1.36	238.01	0.59
43.02	100.00 O	140.02	0.11	239.00	0.03
44.02	6.36	141.00	0.26	240.97	3.22
51.01	4.05	142.99	0.76	241.98	0.24
69.00	36.23	144.00	0.34	256.00	0.47
75.00	7.63	145.01	6.95	257.01	0.46
95.01	9.93	146.01	0.32	260.98	6.27
100.00	0.15	147.00	0.07	261.99	0.43
101.01	1.00	150.00	0.04		
102.02	0.10	151.01	0.27		
105.00	0.05	157.00	0.31		
106.00	0.21	158.01	0.05		
107.01	0.19	159.01	0.50		
108.02	0.12	162.99	2.79		
109.02	0.23	174.99	8.08		
110.00	0.76	175.99	0.46		
111.99	0.11	185.00	0.06		
113.00	3.29	187.01	0.90		
114.00	0.14	188.02	0.07		
115.01	0.13	189.01	0.96		
119.01	0.68	190.01	0.06		
120.02	0.11	190.99	1.43		
121.02	0.65	192.00	0.07		
122.03	0.05	192.98	4.27		
123.01	0.88	193.99	0.45		
124.00	0.37	195.00	5.33		
125.00	0.65	196.00	0.24		
126.01	0.51	197.00	0.09		
127.02	0.32	207.01	0.78		
128.02	0.27	208.01	0.06		
128.90	0.16	209.01	0.29		
129.03	0.04	212.98	18.89		
129.11	0.04	213.99	1.03		
129.28	0.03	217.00	1.82		
129.32	0.02	218.01	0.12		
129.40	0.04	220.97	1.80		
129.90	0.04	221.98	0.11		
130.91	0.13	227.02	0.05		
131.90	0.16	235.99	0.21		
132.00	0.21	237.00	7.60		

```
GA67023o        x1    Bgd=1    14-MAR-88 10 2-0 01:37   70E        EI+
BpM=0     I=3.1v   Ma=247   TIC=145293000              Acnt:          Sys:APSE                                    HAR:
                                                               GC= 44°   Cal:PFK83A                                  MASS:
```

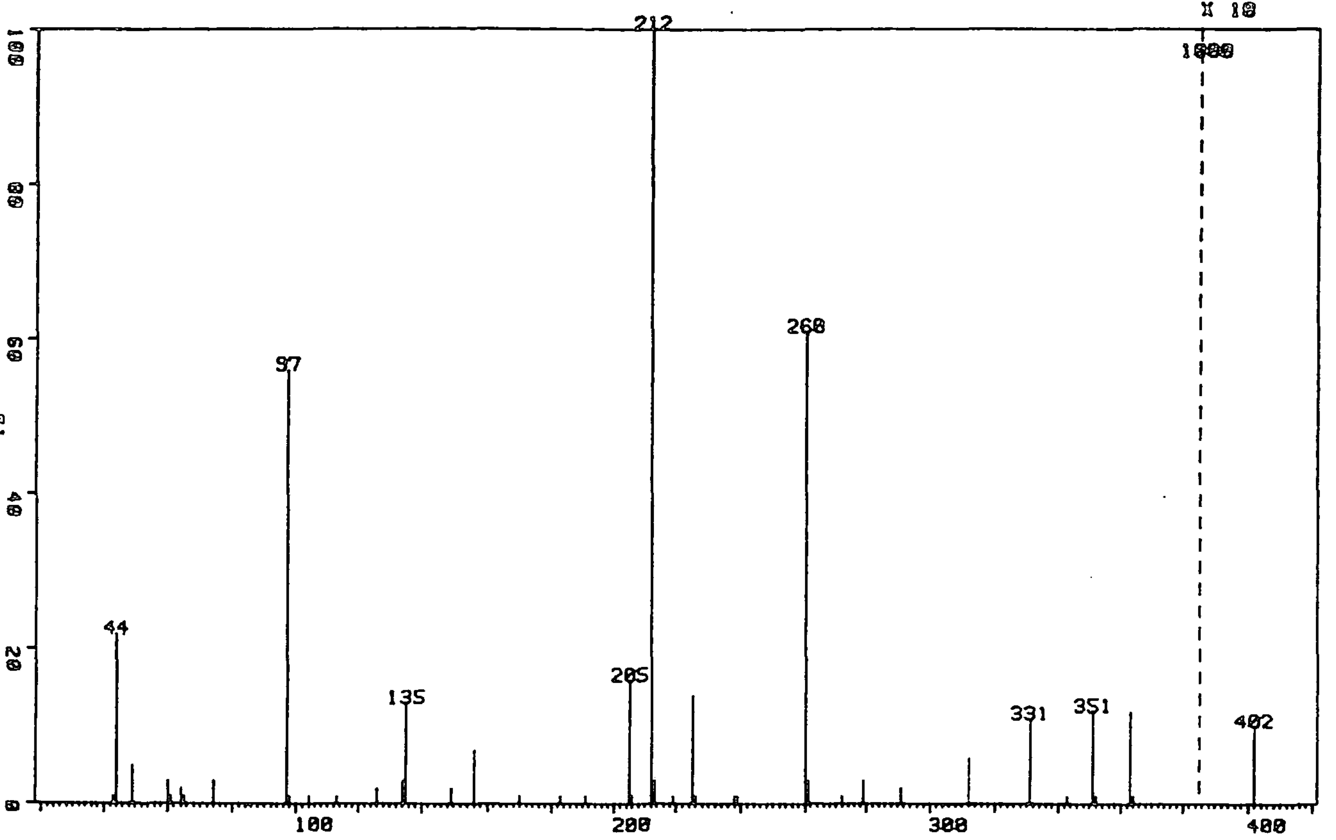
No 66



```
Mass      % Base
  69.04     78.57
  89.08     30.09
  95.07     12.23
 113.08     44.55
 132.09     22.56
 145.11     10.01
 157.11     26.19
 158.12     51.35
 163.11     15.48
 177.14     23.21
 207.13     61.57
 208.15      3.43
 213.15      1.25
 225.16      0.14
 226.16      0.48
 227.16    100.00
 228.17      6.23
 245.20      0.10
 246.19     90.68
 247.19      5.76
```

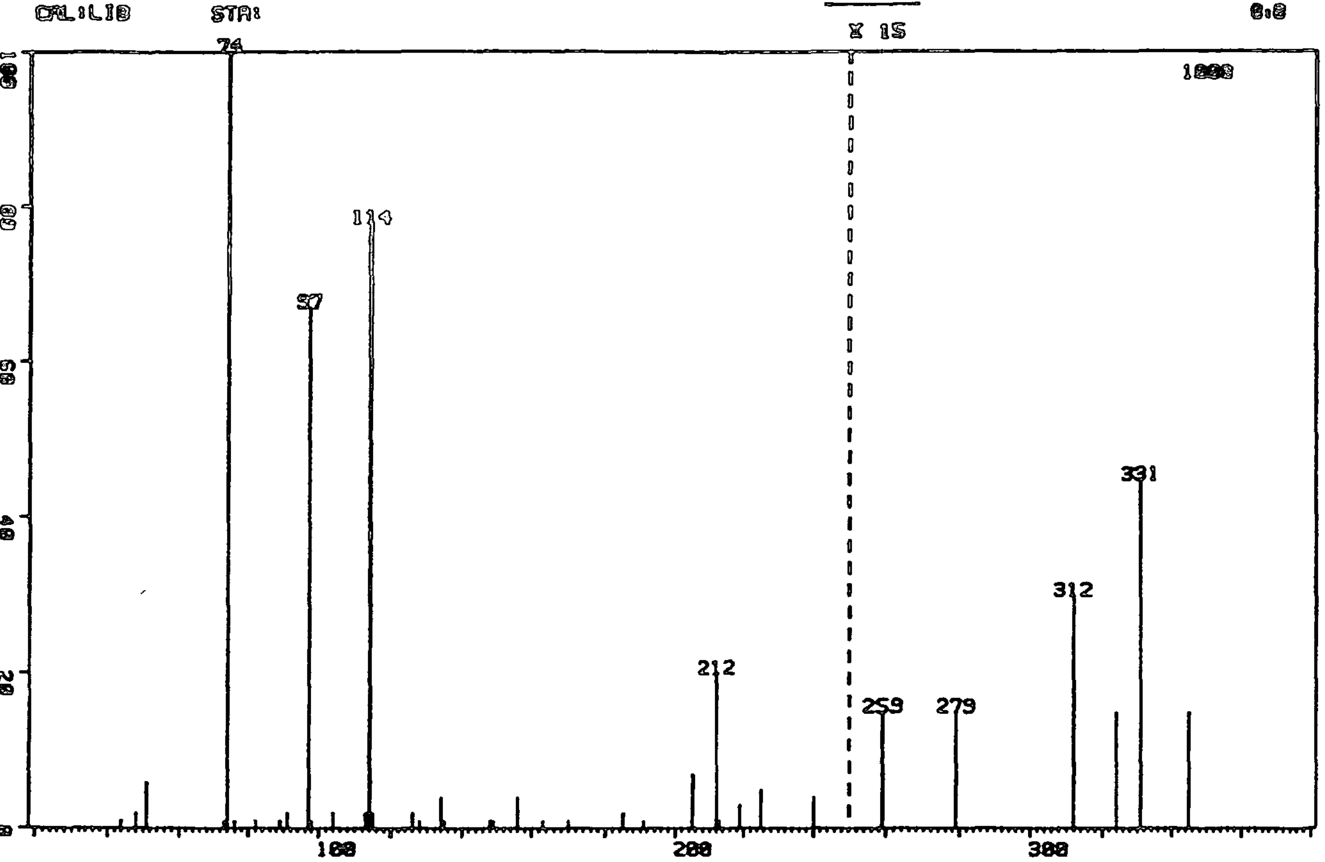
GR44 0 No 67 19-SEP-80

CAL:LIB STA:



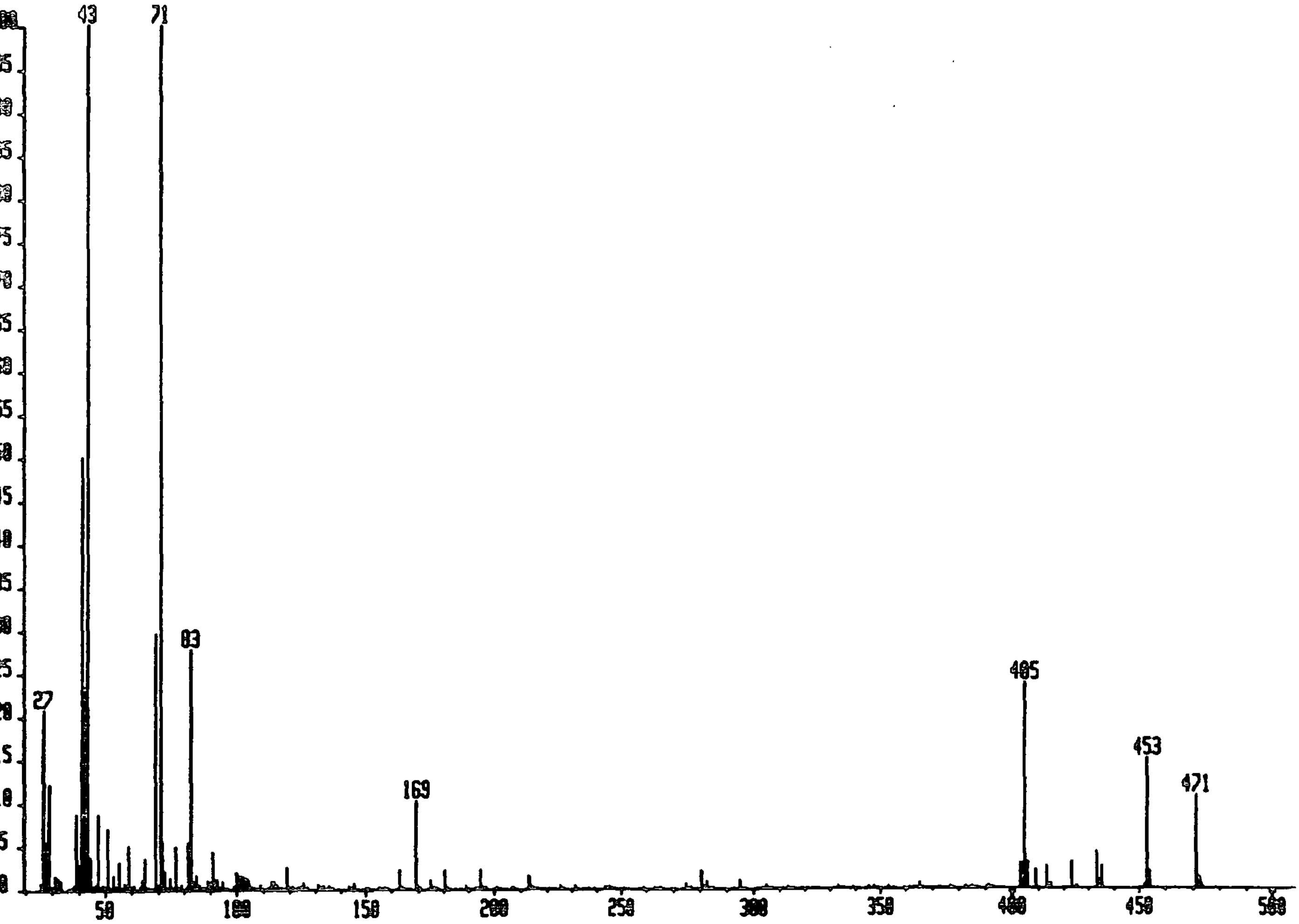
Mass	% Base
42.58	0.28
43.93	21.55
45.29	0.10
48.01	0.24
49.36	4.71
54.71	0.16
59.98	2.32
61.40	0.57
62.72	0.35
64.03	1.42
65.25	0.33
74.28	3.21
96 76	56.04
97.99	0.55
104.10	0.92
112.56	0.88
125.66	1.32
126.85	0.16
133.90	3.16
135.08	12.73
136.25	0 16
147.86	0 16
149.03	1.37
155.92	6.90
161.64	0.25
162 79	0.35
169 60	0.75
183 12	0.88
184.25	0 16
190.94	0.93
205 36	15.46
206.47	0 54
211.95	100.00
213.04	2 96
218 52	0 79
225.06	13 78
226 14	0 50
238.06	0 81
239.15	0.47
258.44	0.30
259 51	60 98
260 58	2.99
272.25	1.10
278.59	2.72
291.22	1.33
311.04	0.23
312.08	5.41
313.11	0.24
330.67	11.17
331.70	0.64
343.01	0.88
351.18	11.96
352.21	0.67
363.39	11.55
364 40	0.74
401.68	0.16

GA44X 0 No 68 19-SEP-80
CAL:LIB STA: 0:0



Mass	% Base		
43.92	1.28	170.72	0.03
48.01	2.40	176.37	0.20
49.36	0.30	183.10	0.38
50.73	6.39	184.22	0.10
52.08	0.05	185.35	1.95
59.97	0.13	186.48	0.07
64.02	0.07	190.92	0.59
65.26	0.16	196.48	0.08
66.57	0.13	198.72	0.17
72.98	0.57	198.84	0.02
74.27	100.00	204.23	0.04
75.55	1.06	205.34	7.30
80.61	0.14	206.45	0.29
81.88	0.33	211 92	20.25
88.11	0.05	213 02	0.61
89.36	1.05	218 50	3 30
90.61	1.65	219.60	0 23
96.75	66.46	225 03	4 98
97.98	0.70	226 12	0.22
102.86	0.13	231 56	0.06
104.09	2.41	238 03	0 19
105.31	0.10	239 12	0.24
111.33	0.14	240 21	3 88
112.54	1.69	241 29	0.20
113.75	77.58	253 10	0.10
114.95	1.61	258 41	0.07
118.52	0.09	259 48	1.08
119.72	0.03	260 55	0 04
125.64	1.61	272 23	0.37
126.83	0.31	273 31	0 02
128.02	0.55	278 56	0 84
132.72	0.02	279 62	0 03
133.89	3.74	291 19	0.29
135.06	0.60	292 25	0 03
139.72	0.06	293 30	0 12
140.90	0.25	309 98	0 02
142.07	0.07	311 00	0 11
147.85	0.28	312 06	1 51
149.01	0.94	313 09	0 11
153.61	0.03	324 48	0 88
155.90	3.80	325 51	0 06
157.05	0.07	330 65	2 78
161.62	0.20	331 68	0 18
162.77	0.50	332 71	0 03
163.92	0.11	345 04	0 64
169.58	0.61	346 05	0.04

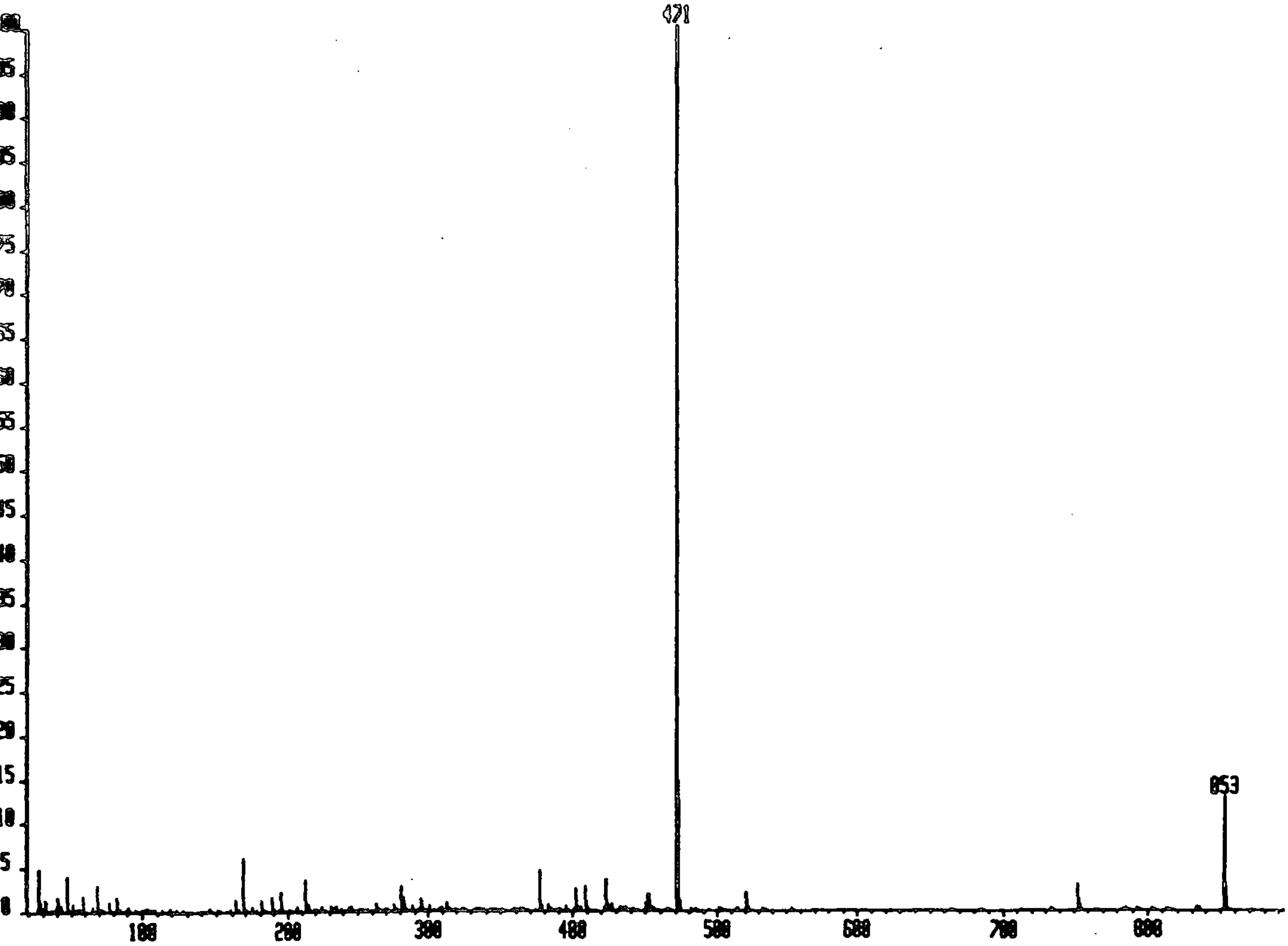
GR450168 x1 Scn=169 7-AUG-87 10:10:11:09 70E EI+
BpM=0 I=10v Hm=473 TIC=330026916 Rcnt: Sys:GPSE
G.APSEY GC= 125° Cal:PFK031 No 69
HRR:
MASS:
+1020+0 1020+0+



Mass	% Base						
50.94	6.90	95.01	0.70	180.98	2.06		
51.96	0.15	99.01	0.30	181.97	0.11		
52.98	1.49	99.99	1.86	189.00	0.30		
53.99	0.25	101.01	1.37	192.97	0.17		
55.00	3.01	102.04	1.32	193.99	0.20		
55.99	0.20	103.03	1.20	195.00	2.19		
56.98	0.60	104.04	1.03	196.01	0.15		
57.98	0.13	105.05	0.74	197.02	0.13		
58.99	5.00	106.01	0.12	206.99	0.18		
59.99	0.25	107.02	0.14	212.98	1.34		
61.01	0.52	109.02	0.48	224.98	0.23		
62.99	0.33	111.99	0.15	230.97	0.34		
63.99	0.99	113.01	0.75	242.98	0.12		
65.00	3.47	114.04	0.79	245.00	0.17		
66.03	0.18	115.03	0.42	262.98	0.21		
68.02	0.22	118.99	2.36	265.00	0.15		
69.00	29.61	120.02	0.20	274.99	0.46		
70.02	0.51	121.03	0.25	277.00	0.13		
71.06	100.00 0	123.04	0.15	280.98	2.03		
72.05	5.43	123.99	0.11	281.98	0.14		
73.05	1.99	125.00	0.67	283.00	0.76		
74.04	0.17	127.02	0.14	294.99	0.88		
75.01	1.24	130.98	0.51	305.05	0.29		
76.02	0.18	132.01	0.11	313.01	0.22		
77.03	4.83	133.03	0.26	345.01	0.16		
78.03	0.20	135.04	0.29	346.99	0.12		
79.04	0.43	136.99	0.17	353.05	0.12		
81.03	0.25	142.98	0.29	365.02	0.12		
82.01	5.24	145.01	0.57	377.02	0.21		
83.02	27.73	149.99	0.19	385.05	0.19		
84.03	0.78	151.01	0.14	403.05	0.13		
85.05	1.46	155.03	0.22	405.06	1.18		
86.06	0.43	157.00	0.16	406.06	0.14		
88.02	0.13	162.99	2.18	409.03	0.10		
89.03	0.86	163.99	0.12	413.04	0.12		
90.03	0.77	168.98	10.11	423.06	0.14		
91.03	4.26	169.99	0.37	433.05	0.20		
92.04	0.21	171.01	0.18	435.07	0.12		
93.00	0.99	174.97	0.91	453.06	0.74		
94.01	0.16	177.01	0.19	471.08	0.53		

GAM68223 n1 Bgd=219 7-AUG-87 10:3+0:15:10 70E EI+
DpH=0 I=16v Ma=471 TIC=152527000 Acnt: Sys:APSE HMR:
G.APSEY GC= 170° Cal:PFK031 MASS:

No 70

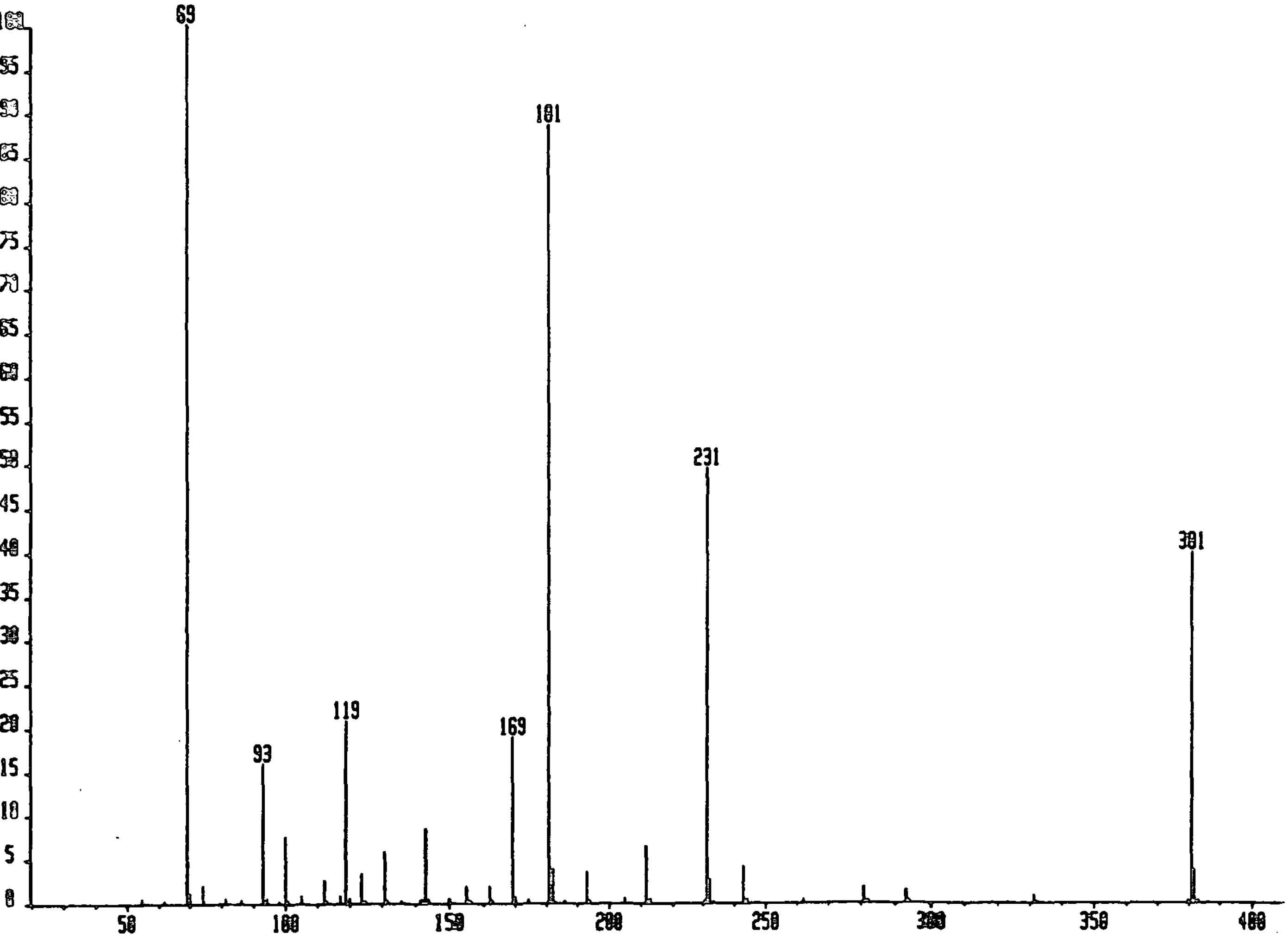


Mass	% Base								
50.94	6.98	99.01	0.60	280.96	2.39	813.05	0.14		
51.96	0.13	99.99	1.54	281.97	0.18	832.99	0.31		
52.98	0.81	101.01	1.81	282.98	1.15	835.01	0.14		
53.99	0.17	102.02	0.29	283.99	0.11	853.11	11.05 F		
54.97	4.32	103.02	3.58	288.98	0.49	854.24	2.43 F		
55.97	0.37	104.04	5.05	294.98	1.02				
56.98	0.40	123.03	1.65	376.99	4.16				
57.98	0.11	124.01	0.16	378.01	0.42				
58.99	17.92	125.00	0.36	383.00	0.56				
59.99	0.76	127.01	0.65	385.02	0.14				
61.00	0.32	129.02	0.10	391.00	0.18				
62.98	0.15	130.99	0.46	394.99	0.38				
63.99	1.01	132.01	0.27	401.00	0.13				
65.00	4.65	133.02	0.56	403.01	2.39				
66.01	0.13	134.02	0.19	404.02	0.28				
68.02	0.41	136.99	0.13	405.03	0.18				
68.99	27.87	139.01	0.21	409.02	2.53				
70.02	0.63	141.01	0.38	410.03	0.28				
71.03	1.12	142.99	0.25	421.02	0.29				
72.03	1.51	145.00	1.19	423.03	3.21				
73.03	0.68	146.02	0.14	424.03	0.40				
75.00	0.71	147.01	0.14	427.01	0.48				
76.01	0.15	149.99	0.20	433.02	0.36				
77.02	10.55	151.00	0.39	435.02	0.24				
78.03	0.41	152.02	0.22	436.99	0.25				
79.02	0.50	156.99	0.17	451.02	0.74				
81.03	0.16	159.01	0.23	452.03	0.11				
82.00	1.31	162.98	4.31	453.03	1.58				
83.02	27.58	163.99	0.22	454.04	0.22				
84.03	1.14	165.01	0.42	455.03	0.13				
85.05	0.60	166.02	0.12	471.09	100.00 F0				
87.03	0.17	168.97	15.79	472.04	14.19 F				
88.02	0.14	169.98	0.50	473.05	1.18 F				
89.03	1.59	171.00	0.43	485.04	0.19				
90.02	1.08	174.98	0.87	501.01	0.19				
91.03	5.44	175.99	0.16	502.02	0.22				
92.03	0.38	177.00	0.14	521.03	1.87				
93.00	0.64	180.96	[illegible]	753.11	2.55				
94.00	0.11	212.97	3.37	754.11	0.48				
95.00	1.39	213.98	0.25	785.09	0.12				
96.01	0.12	215.00	0.63	803.09	0.18				

GA190125○ x1 Bgd=110 11-AUG-87 11:1○0:01:38 7CE EI○
BpA=69 I=6.4v Ha=384 TIC=170707680 Acnt: Sys:APSE
GC= 35⁰ Cal:PFK690

No 71

HAR:
MASS:

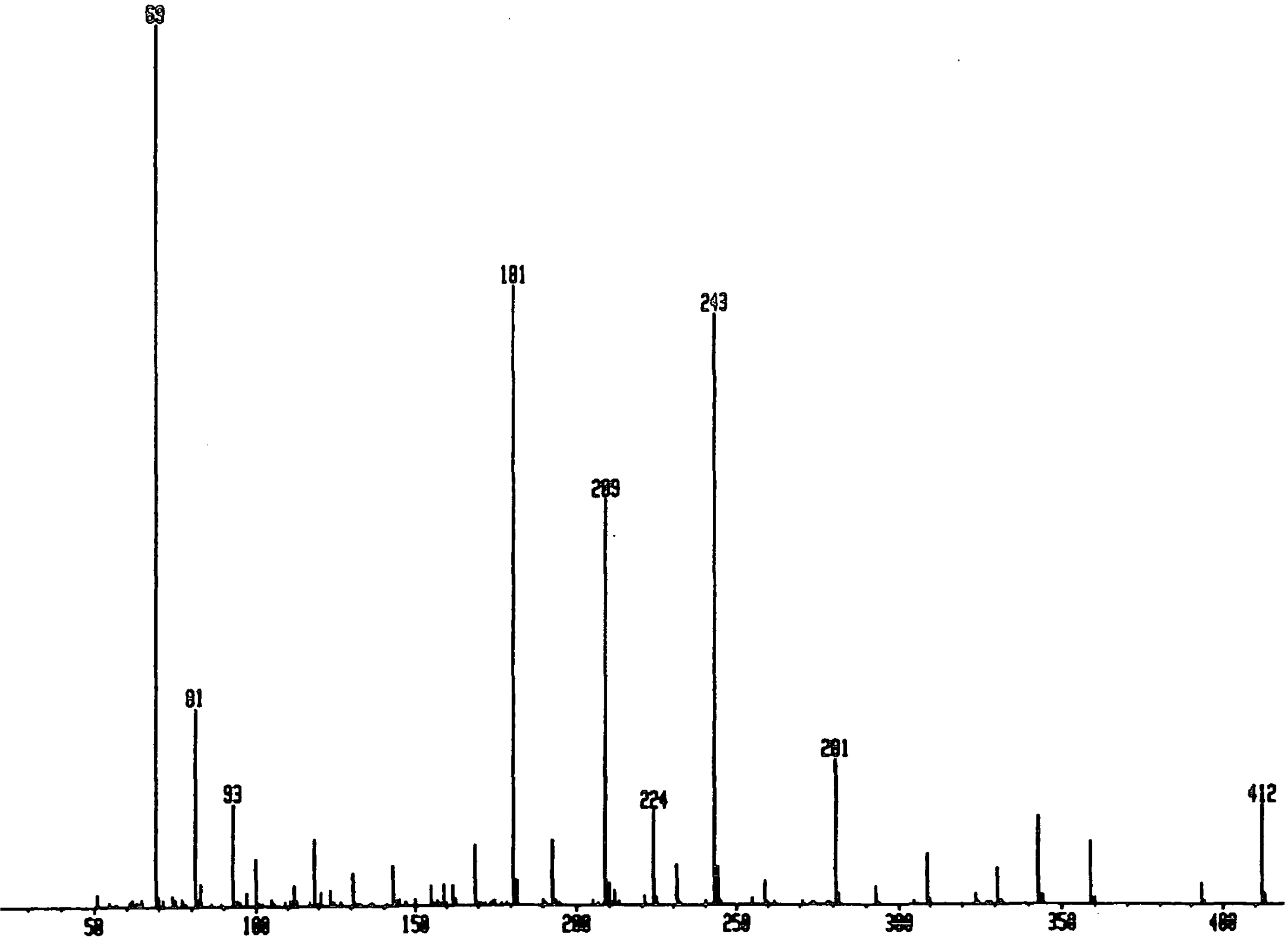


Mass	% Base
54.94	0.39
61.97	0.22
68.99	100.00
69.99	0.99
74.00	1.90
81.01	0.45
86.02	0.24
93.01	15.79
94.02	0.51
98.02	0.12
100.01	7.54
101.01	0.17
105.02	0.77
112.02	2.46
117.01	0.81
119.00	20.81
120.01	0.46
124.01	3.19
125.02	0.16
131.01	5.83
132.02	0.19
136.02	0.17
141.98	0.22
143.00	8.42
144.02	0.34
150.02	0.47
155.00	1.79
156.00	0.13
162.01	1.73
169.00	18.84
170.00	0.58
174.01	0.29
181.01	88.45
182.01	3.67
193.01	3.36
194.03	0.20
205.00	0.47
212.00	6.38
213.01	0.32
230.99	49.45
232.00	2.55
242.99	3.96
244.00	0.25
262.02	0.32
281.01	1.58
282.03	0.11
292.99	1.40
331.03	0.76
381.01	39.88 F
382.02	3.51 F
383.04	0.16

A400300 x1 Bgd=305 11-AUG-87 10:5+0:05:05 70E EI+
=69 I=4.2v Ha=413 TIC=1347 Rcnt: Sys:APSE
GC= 64⁰ Cal:PFK690

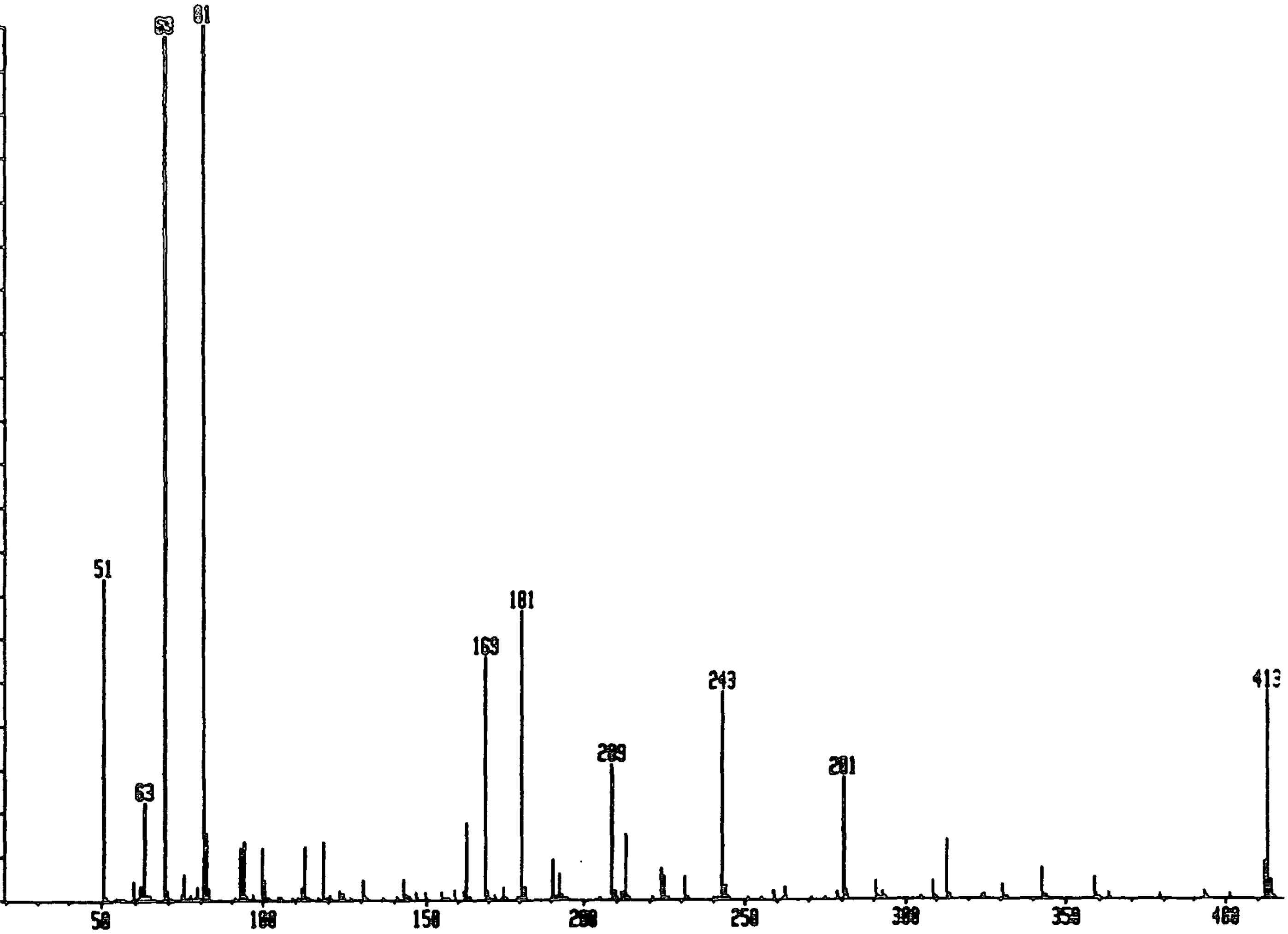
No 72

HRR:
MASS:



ss	% base						
0 92	1 19	121 00	1 35	208 97	45 87	331 98	0 27
4 93	0 23	124 00	1.70	209.29	0.11	343.00	9.96
6.96	0 17	125 00	0 24	209.34	0.11	344.00	0.83
0.97	0 25	127 03	0 27	209.98	2.39	358.97	6.95
1 97	0 61	131.01	3 60	210.97	0.15	359.97	0.54
2.98	0 30	132 02	0.13	211 97	1.45	392.99	2.17
3 99	0 19	132 99	0 18	212.98	0.25	393.98	0.24
5 00	0 58	133 02	0 17	220.98	0 82	411.98	11.05
8.99	100 00	136 99	0 14	224.00	10.48	412.98	1.05
9 99	0 92	137 05	0.12	225.00	0.77		
0 99	0 54	141.02	0.12	230.97	4.46		
4 00	1 04	143.00	4.45	231.97	0.21		
5 01	0.60	144 00	0 31	239.96	0.25		
7 03	0 77	145 02	0.56	242.28	0.11		
8 00	0 11	147 00	0 24	242.99	66.89		
8 03	0 14	150 00	0 58	243.41	0.12		
8.06	0 11	155 00	2 02	244.00	4.18		
1 03	22 33	158 98	2 22	245 01	0 31		
2 03	0 58	161 98	2.10	255.01	0 57		
3 02	2 43	162.99	0.58	258 98	2.50		
6 00	0 14	168 99	6 73	259 97	0 18		
9 03	0 11	169 99	0.19	261 96	0 23		
3 00	11 39	170.98	0 19	262.08	0 11		
4 01	0 43	171.99	0.18	270 97	0 37		
5 02	0.25	173 91	0.11	273 95	0 14		
7 00	1 26	174 00	0.25	274.05	0 13		
0 00	5 13	175 00	0.48	278 38	0 17		
1 01	0 14	177 02	0.14	278.97	0 11		
2 00	0 17	178 88	0.12	279.09	0.12		
5 01	0 60	180.99	70.06	280 98	16.31		
6 00	0 12	182.00	2.72	281.98	1 06		
6 03	0.11	189.99	0.48	293 00	1 97		
9 02	0 24	191.01	0 14	294.01	0.15		
9.08	0 11	193.00	7.28	305.02	0.25		
1 02	0.41	194.00	0.51	308 98	5 70		
2 01	2 20	195.00	0 22	324.01	0.97		
3 01	0 40	204.99	0.48	327.43	0.11		
7 00	0 31	207 01	0.19	327.96	0.17		
9.00	7 36	208.46	0 11	328.52	0.12		
0 00	0 18	208 49	0 11	330 98	4 05		

GA480385> xl Bgd=339 11-AUG-87 10:5+0:65:02 70E EI+
BpM=81 I=4.5> Ms=415 TIC=156372880 Rcnt: Sys:FPSE Cal:PFK690 **No 73** Hm:
EC= 64⁰ MASS:



ss	% Base						
50. 92	36. 67	106. 02	0. 23	180 26	0 13	271 05	0 10
51. 93	0. 36	109. 01	0. 13	180 29	0. 10	278. 98	0 71
54. 93	0 13	109. 05	0. 10	180 35	0 10	280 98	13 82
55. 95	0. 13	111. 02	0. 13	180 63	0 11	281. 98	0. 85
56. 95	0 13	112. 01	1. 15	180 99	33 05	290. 98	1 99
56. 96	0 10	113. 02	5. 97	182 00	1 39	291. 96	0. 13
59. 96	2. 04	114. 02	0. 18	190 00	0 16	292. 99	0. 81
60. 97	0. 19	114. 07	0. 12	191 00	4 47	308. 98	1. 97
61. 98	1. 47	117 00	0 16	191 66	0 10	309 98	0 16
62. 99	11. 16	119 00	6. 49	192 01	0 24	313 02	6 74
63. 99	0 39	120 00	0. 13	193 00	2 87	314 02	0 46
65 00	0. 46	120. 99	0. 51	194 00	0 46	324 01	0 33
65. 96	0 10	124. 00	0. 89	195 96	0 10	325. 02	0. 38
65. 98	0 12	125. 00	0. 57	204 95	0 19	330. 98	1 43
68. 83	0 13	127. 03	0. 11	208 97	15 48	331. 97	0. 11
68 98	98 82	131. 00	2. 04	209 98	0 94	343. 00	3 46
69. 99	0. 94	137. 00	0. 14	211 98	0 70	344. 00	0 31
70. 99	0. 22	141. 00	0 32	212 99	7 34	358. 97	2 42
74. 00	0 51	143. 00	2. 15	213 99	0 35	359. 98	0 20
75. 01	2 75	144. 00	0. 39	220 99	0 29	363 00	0 57
76. 02	0. 10	145. 01	0 26	224 00	3 43	378. 98	0 38
77. 03	0 44	147 00	0 71	225 00	2 49	392 99	0 81
78. 02	0. 11	149 99	0 79	226 00	0 13	400. 97	0 46
79. 00	1. 30	155 00	0 79	230 97	2 59	411. 97	4 09
80. 02	0 16	155 99	0 11	231 88	0 10	412 97	23 71
81 02	100 00	157 00	0 17	231 97	0 16	413 34	1 33
82. 02	7 52	158 98	0 96	240 95	0 17	413. 99	2. 07
83 02	1 19	161 98	0 93	241 04	0 10	414. 99	0 13
91 00	0 10	162 99	8 72	242 99	23 65		
91. 03	0 13	163 95	0 32	244 00	1 50		
93 00	5 73	168 99	27 71	245 01	0 10		
94. 03	6. 48	169 99	0 83	250 99	0 22		
95. 03	0 28	172 00	0. 40	255 00	0 20		
97. 00	0. 52	173 97	0 12	258 95	0 94		
00. 00	5 85	173 99	0 12	261 97	0 13		
01. 01	2. 04	175 01	1 26	262 01	0 13		
01. 98	0. 10	179 28	0 10	262 05	0 10		
02. 01	0 10	179 33	0 10	262 97	1 30		
05. 01	0 31	179 64	0 23	270 98	0 12		

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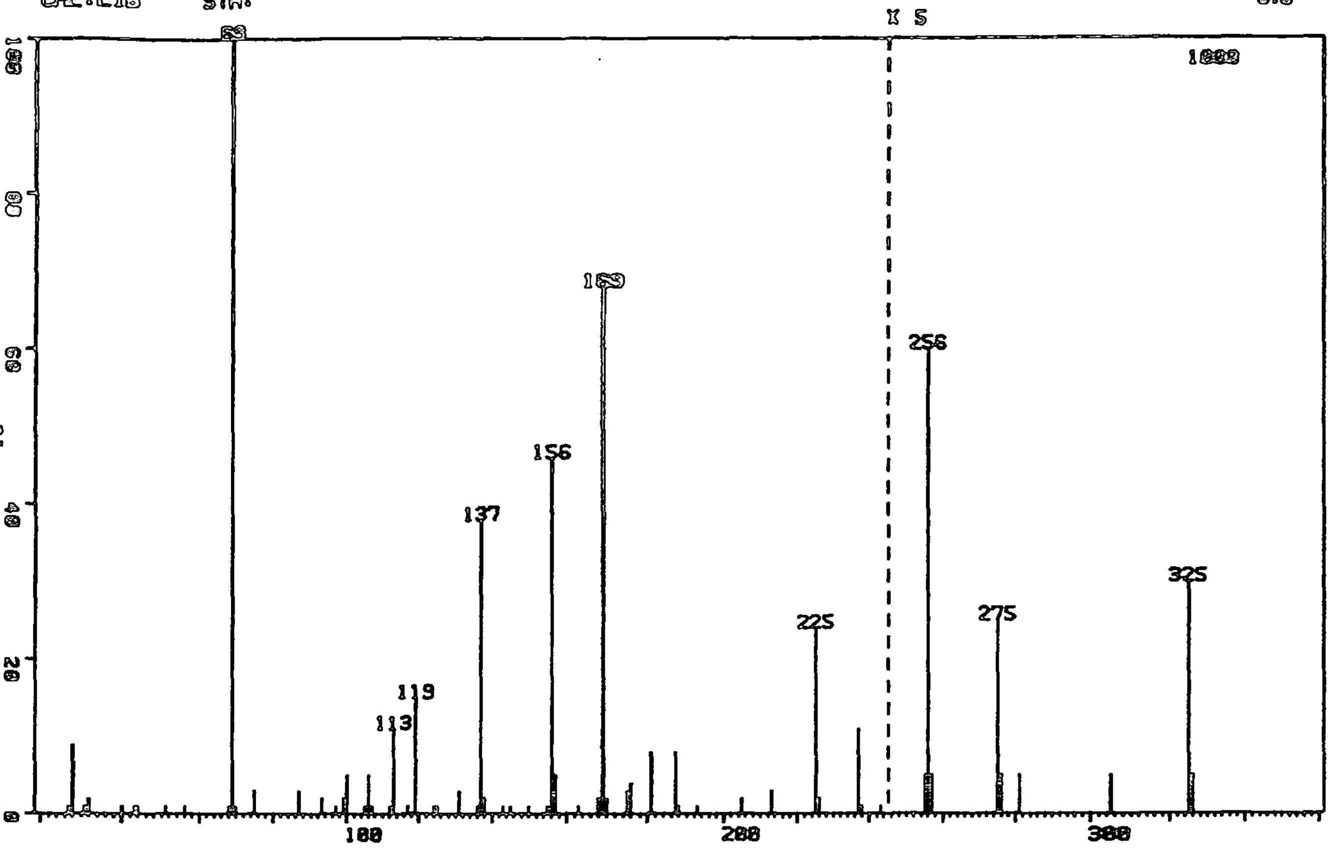

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28.98	0.07
30.98	0.71
31.97	2.01
36.98	0.36
39.93	1.03
41.01	0.24
42.01	0.18
43.02	0.60
43.96	0.39
44.98	0.09
49.96	0.37
50.97	0.61
55.97	0.62
56.97	0.07
56.98	0.06
59.01	0.07
63.97	0.10
67.96	0.81
68.95	100.00 M
69.95	1.08
73.95	0.14
74.95	2.44
75.96	0.05
77.94	0.07
78.95	0.08
79.95	0.15
80.94	0.15
85.94	0.23
86.95	2.76
87.95	0.18
92.93	2.14
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94.94	0.13
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97.92	0.13
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106.94	0.41
108.92	0.08
111.92	1.01
112.93	10.77 M
113.93	0.34
116.92	1.14
117.92	0.36
118.92	14.83 M
119.92	0.29
123.91	0.43
124.92	1.29
125.92	0.14
128.91	0.13
130.90	2.59
132.92	0.14
135.91	0.28
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137.91	1.87
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156.90	5.18 M
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205.86	0.17
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213.87	0.14
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256.84	0.88
274.83	5.34 M
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280.82	0.47
304.80	0.61
324.80	6.17 M
325.80	0.52

APPENDIX THREE

INFRA-RED SPECTRA

1. 5H,5H-pentadecafluoro-2-iodo-6-methylheptane (17a)
2. 7H,7H-heneicosafluoro-2-iodo-4,8-dimethylnonane (17b)
3. 5,5, 7,7-tetrahydroheptafluoro-2-iodo-8-methylnonane (18a)
4. 2H,2H,6H,6H-heptadecafluoro-1-iodo-3,7-dimethyloctane (19a)
5. 2,2,4,4,8,8-hexahydrononadecafluoro-1-iodo-5,9-dimethyldecane (19b)
6. 2,2,6,6,8,8-hexahydrononadecafluoro-1-iodo-3,9-dimethyldecane (20a)
7. 2,2,4,4,8,8,10,10-octahydroheneicosafluoro-1-iodo-5,11-dimethyldodecane (20b)
8. 2,2,8,8-tetrahydrotricosafluoro-1-iodo-3,5,9-trimethyldecane (19c)
9. 2,2,4,4,10,10-hexahydropentacosafluoro-1-iodo-5,7,11-trimethyldodecane (19d)
10. 3,3,7,7,9,9-hexahydroeicosafluoro-2 ,6-dimethyldecane (26)
11. 2H,4H,4H-undecafluoro-5-methylhex-(E)-2-ene (30)
12. 3,5,5,7,7-Pentahydroterdecafluoro-2-methyloct-2-ene (35)
13. (Z)-3,5-Dihydrodecafluoro-2-methylhexa-2,4-diene (37a)
14. (E)-3,5-Dihydrodecafluoro-2-methylhexa-2,4-diene (37b)
15. (Z)-2,6,6-Trihydroheptadecafluoro-3,7-dimethyloct-2-ene (41)
16. 2,3,5,5-Tetrahydroundecafluoro-3-methoxy-2-methylhexane (48)
17. 3,5,5-Trihydrononafluoro-1,3-dimethoxy-2-methylhex-1-ene (49)
18. 3,5,5,7,7-Pentahydro-1,3-diphenoxyundecafluoro-2-methyloct-1-ene (46b) and2,3,5,5,7,7-hexahydro-1,3-diphenoxydodecafluoro-2-methyloctane (47b)
19. 3,5,5-Trihydro-1,3-diphenoxynonafluoro-2-methylhex-1-ene (46a) and 2,3,5,5-tetrahydro-1,3-diphenoxydecafluoro-2-methylhexane (47a)
20. 3,6,7-Trihydro-6-phenoxyhexadecafluoro-2,7-dimethyloct-2-ene (50)
21. 2,6,6-Trihydro-2-methoxyhexadecafluoro-3,7-dimethyloct-3-ene (52a)
22. 2,6,6-Trihydro-2-phenoxyhexadecafluoro-3,7-dimethyloct-3-ene (52c)
23. 2,4,5-Trihydro-4-methoxydecafluoro-5-methylhex-2-ene (56a)
24. 3,5-Dihydro-1,3-dimethoxyoctfluoro-2-methylhexa-1,4-diene (57)
25. 2H-Tetradecafluoro-1-iodo-5-methyhexane (68a)

26. Tetradecafluoro-5-methylhex-1-ene (69a)

27. 4H-Tridecafluoro-5-methylhex-1-ene (69b)

28. 2H-Hexadecafluoro-1-iodo-3,3-dimethylhexane (80)

29. 2H,4H-Nonadecafluoro-1-iodo-5,5-dimethyloctane (82)

30. 1,1,2,2,4-Pentahydrohexadecafluoro-1-iodo-5,5-dimethyloctane (83)

31. 1,1,2,2,4,-Hexahydrononafluoro-1-iodo-5-methylhexane (89a)

32. 1,1,2,2,3,3,4,4,6,6-Decahydrononafluoro-1-iodo-7-methyloctane (89b)

33. 1,1,2,4-Tetrahydrohexadecafluoro-5,5-dimethyloct-1-ene (85)

34. Hexadecafluoro-3,3-dimethylhex-1-ene (81)

35. 4H-Nonadecafluoro-5,5-dimethyloct-1-ene (84)

36. 1,1,2,4,4-Pentahydrononafluoro-5-methylhex-1-ene (90)

37. 3H,5H-5-Chloroundecafluoro-2-methylhex-2-ene (110)

38. 3H-Tridecafluoro-2-methylhex-2-ene (115)

39. 1,1-Difluoro-2,3-bis(trifluoromethyl)hex-1-ene (123)

40. 3H-Octafluoro-3-phenyl-2-methylbut-1-ene (127)

41. 3-Ethoxycarbonyl-6-fluoro -2-methyl-4,5-bis(trifluoromethyl)-4H-pyran (13

42. 6,7-Benzo-2-fluoro-3,4-bis(trifluoromethyl)-1,5-dioxacyclohept-2-ene (131) and 6,7-Benzo-2,2-difluoro-3,4-bis(trifluoromethyl)-1,5-dioxacycloheptane (132)

43. 1,1,3-Trihydrodecafluoro -4-methylpentan-1-ol(134)

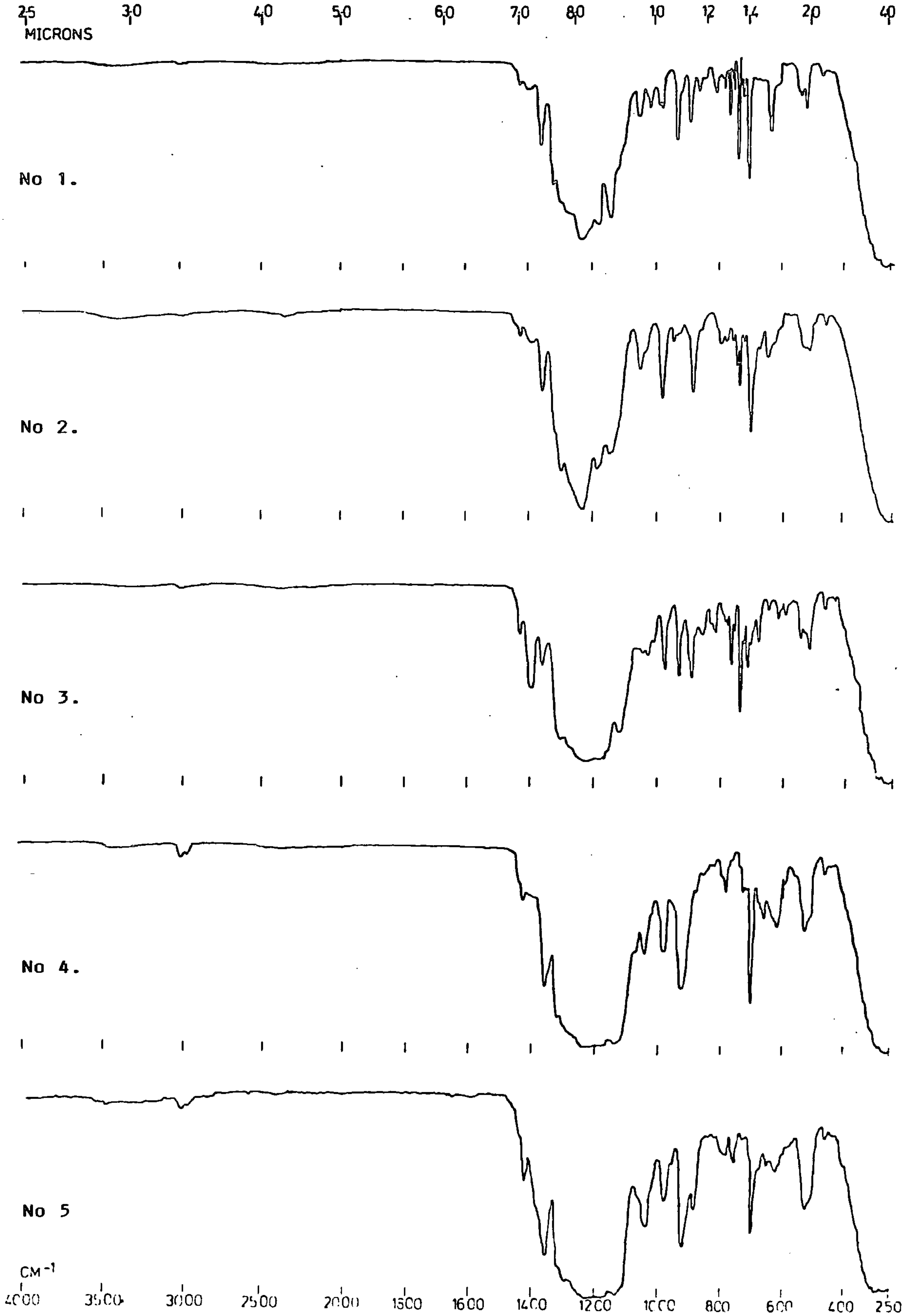
44. 1,1,2,3-Tetrahydrononafluoro-2,3-dimethylbutan-1-ol(136)

45. 1H,2H-Hexadecafluoro-2,3-dimethylhexane (142)

46. 2-(2H-Hexadecafluoro-3,3-dimethylhexyl)tetrahydrofuran (144)

47. Hexadecafluoro -2-methylhept-2-ene (146)

48. 1H-Tridecafluoro-3,3-dimethylhex-1-yne (150)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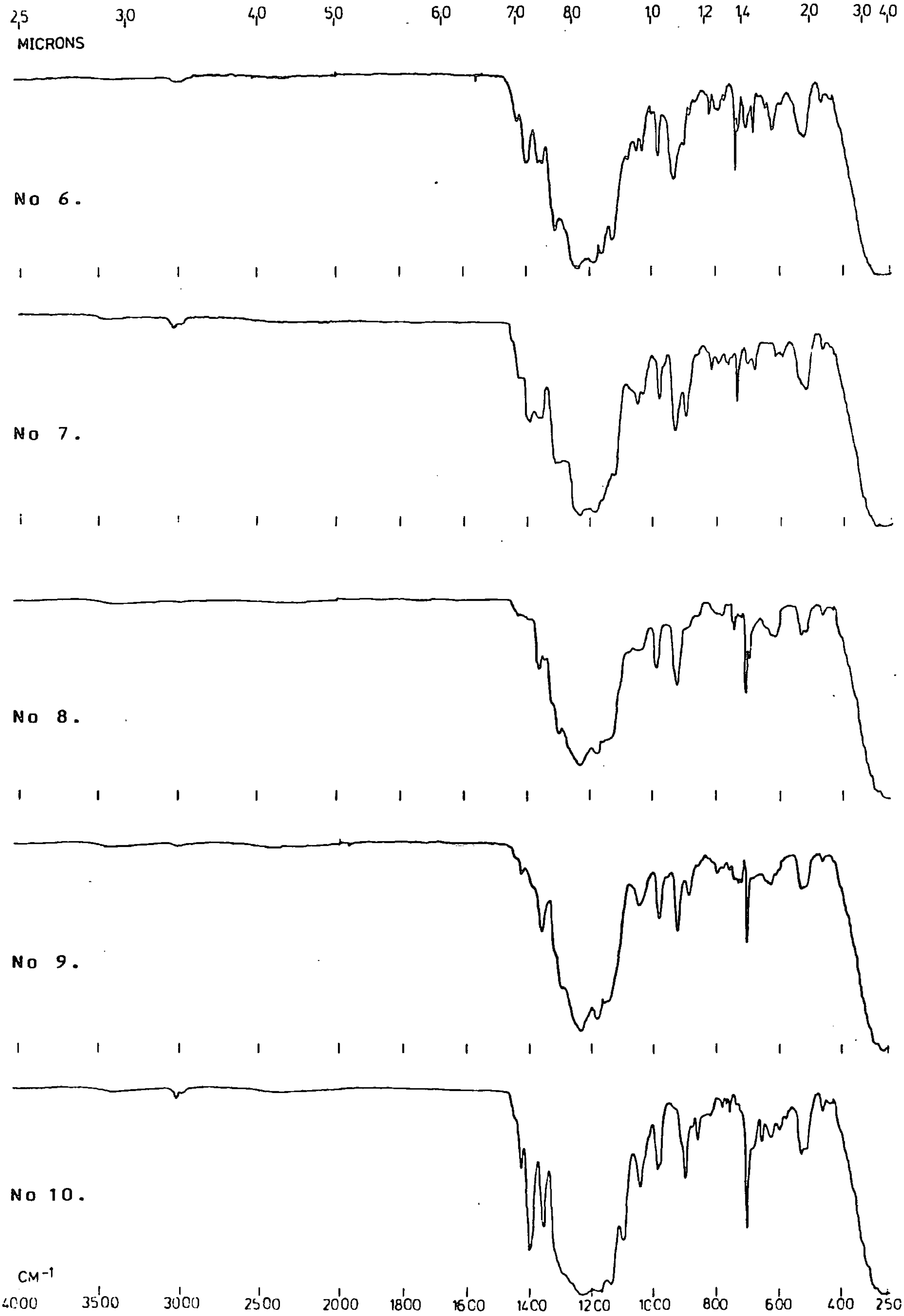
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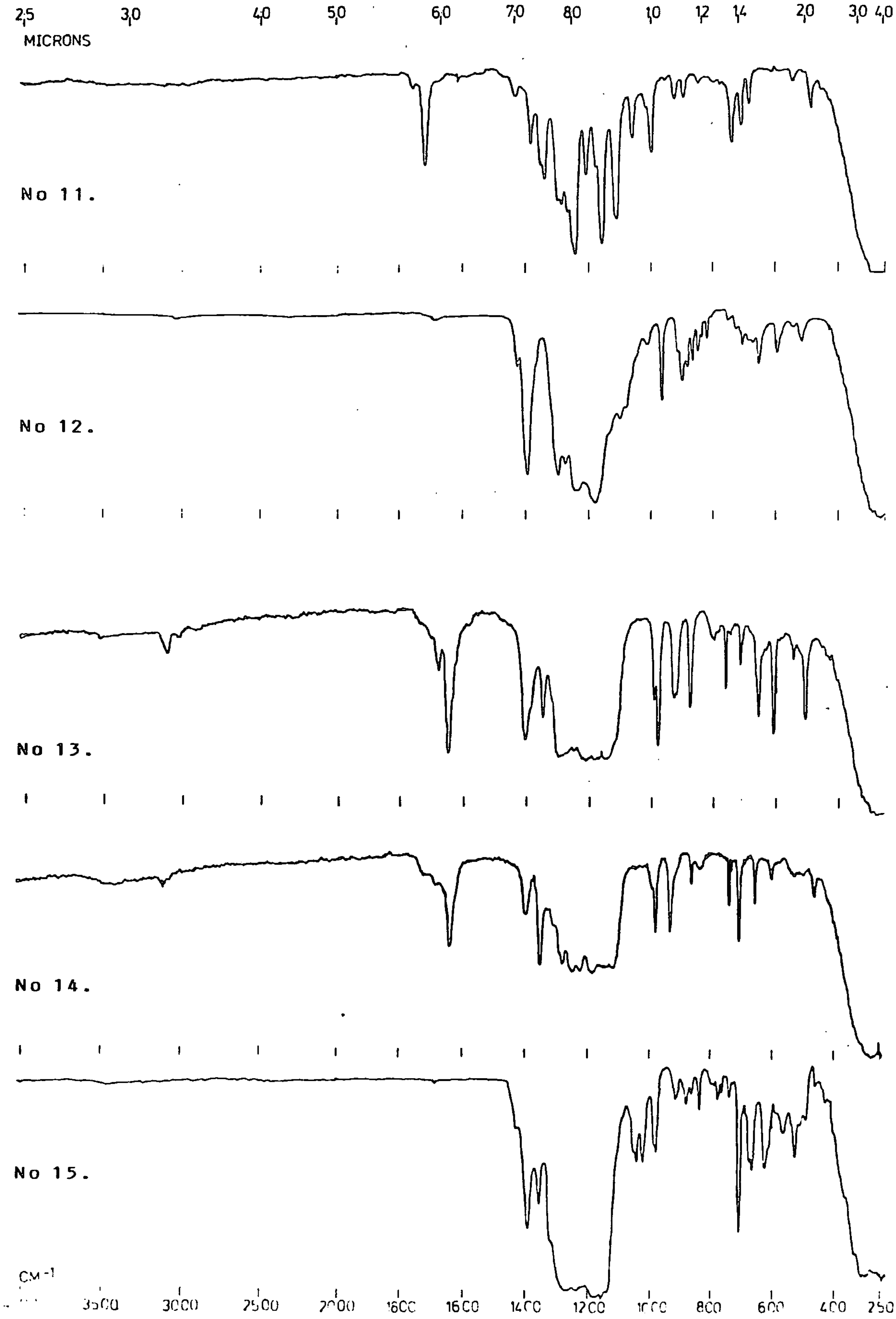

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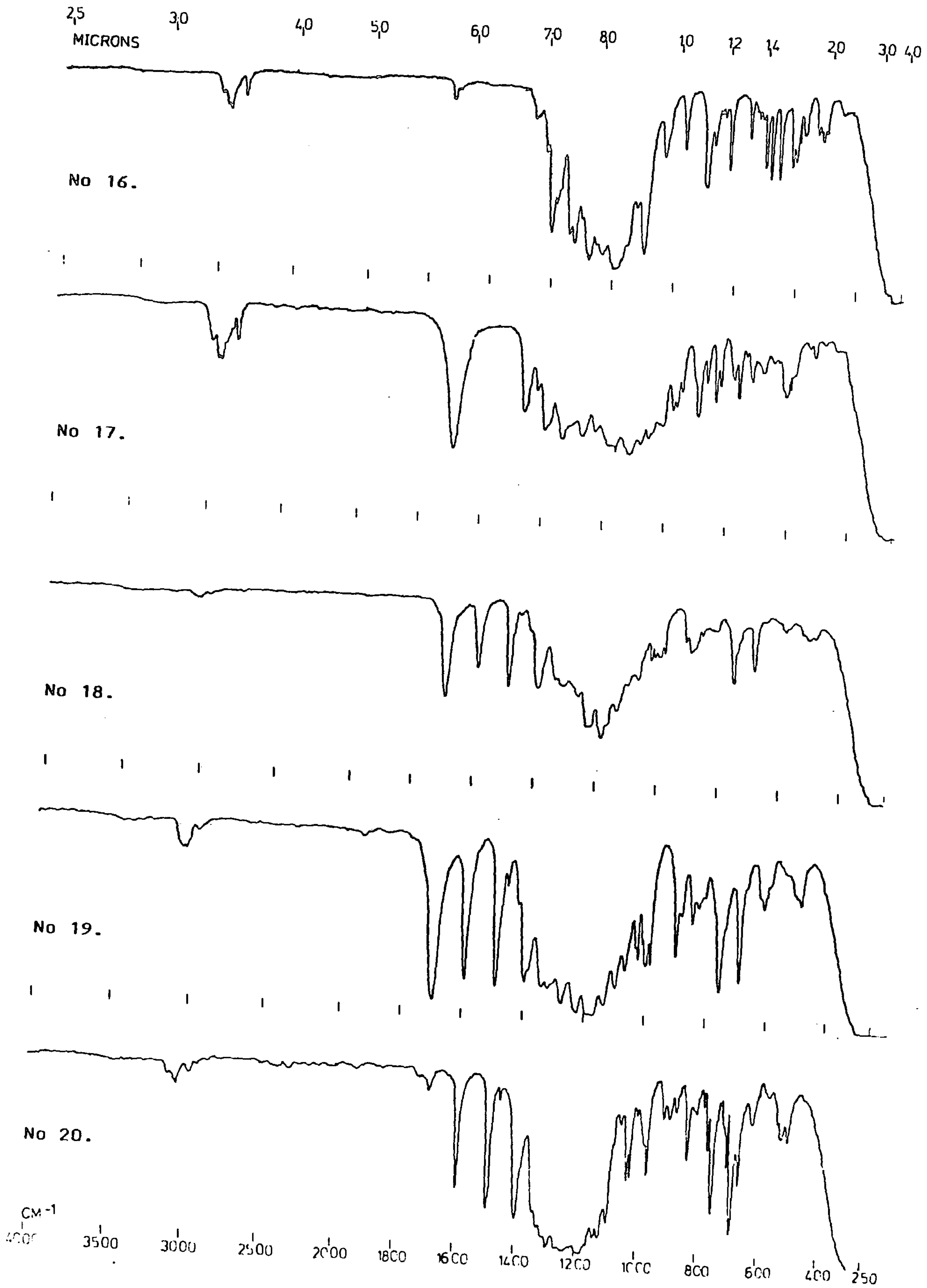
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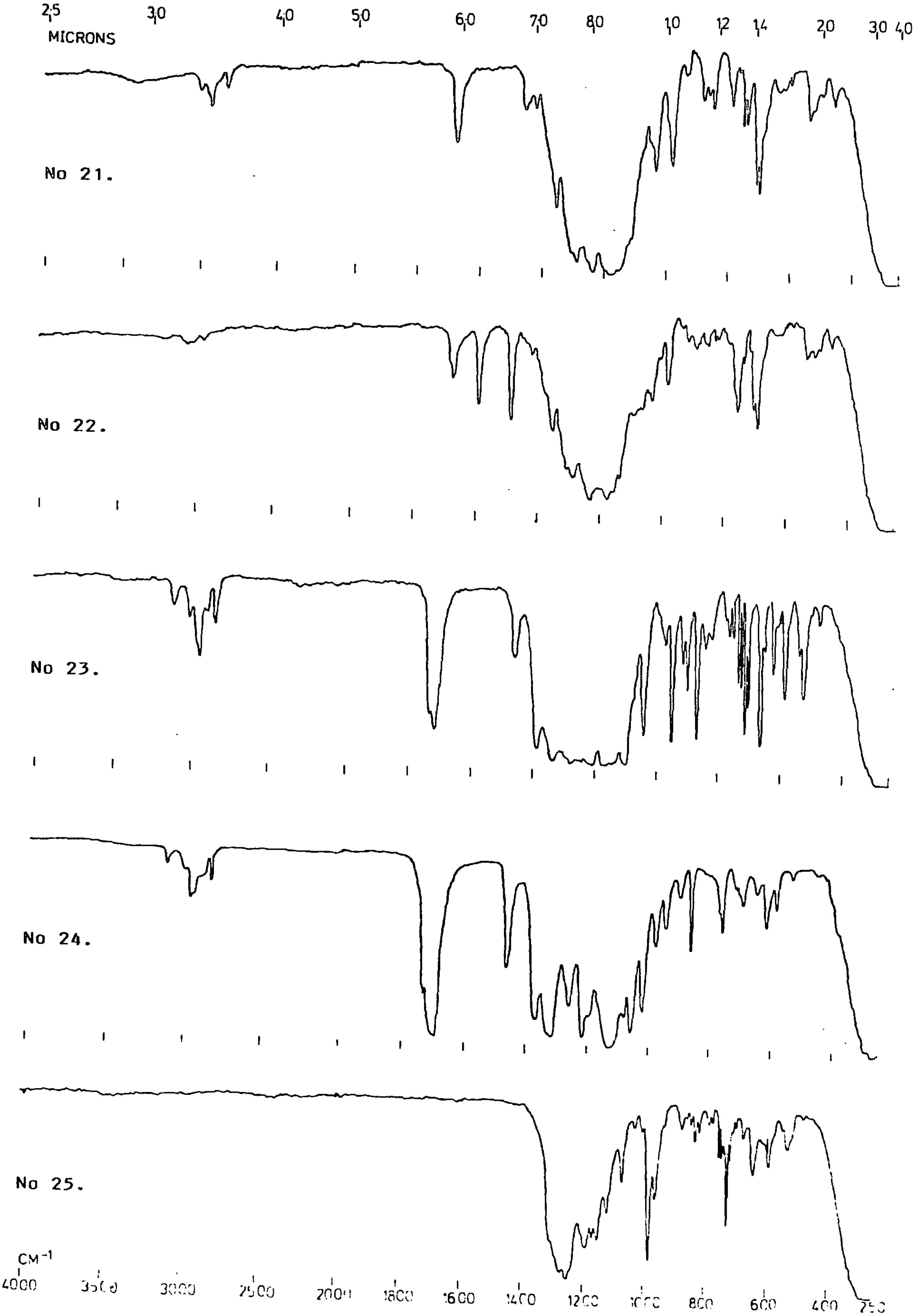
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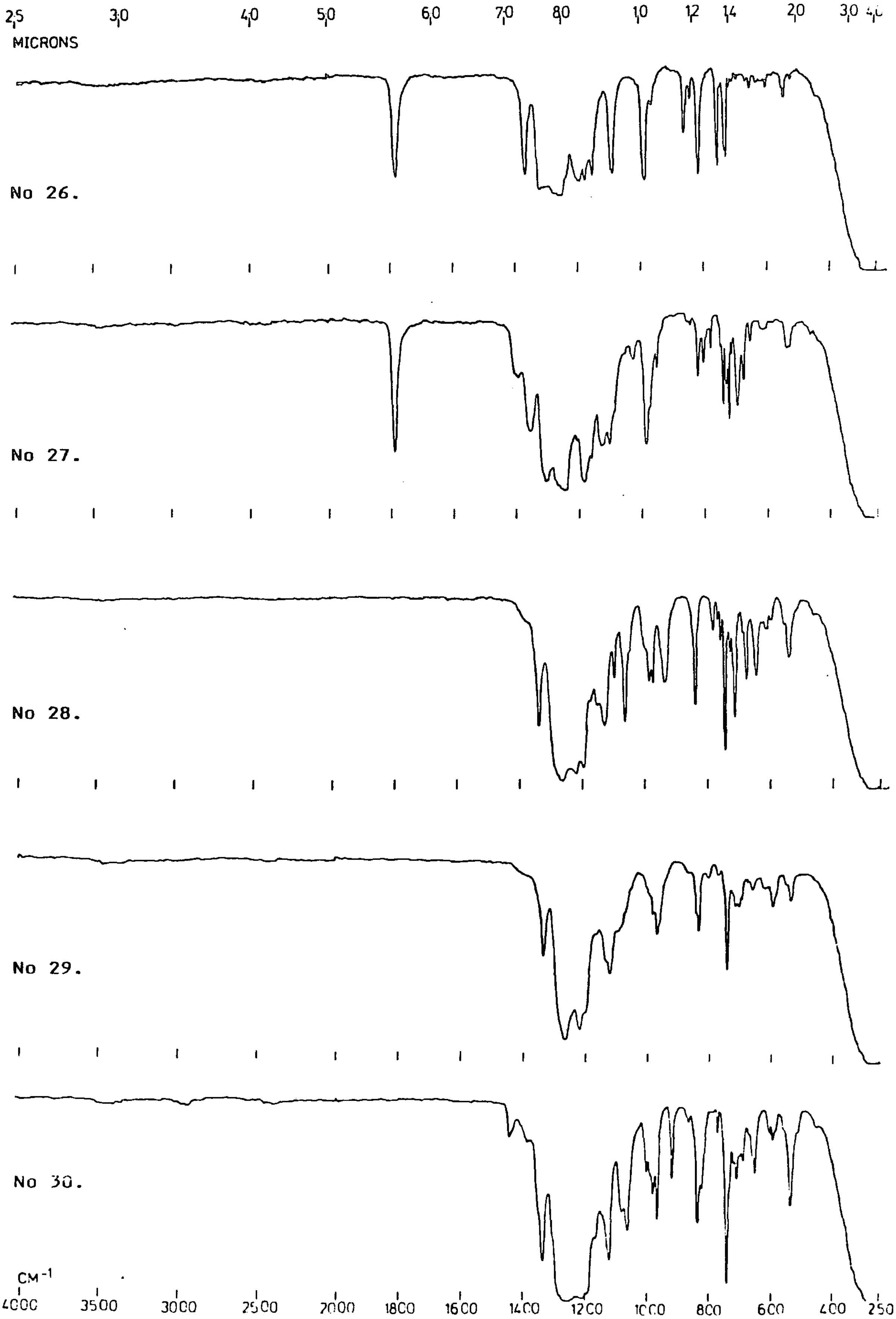
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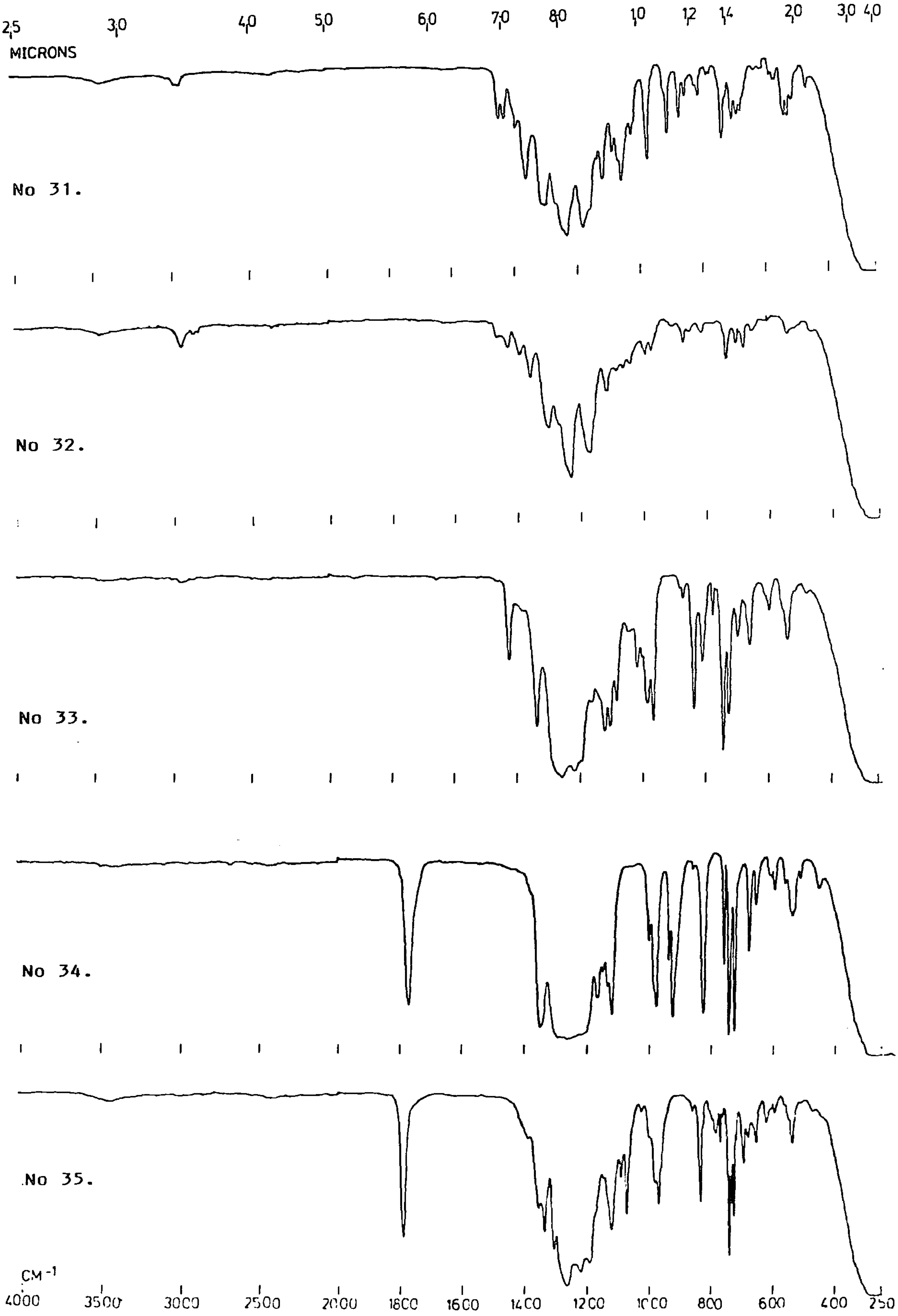
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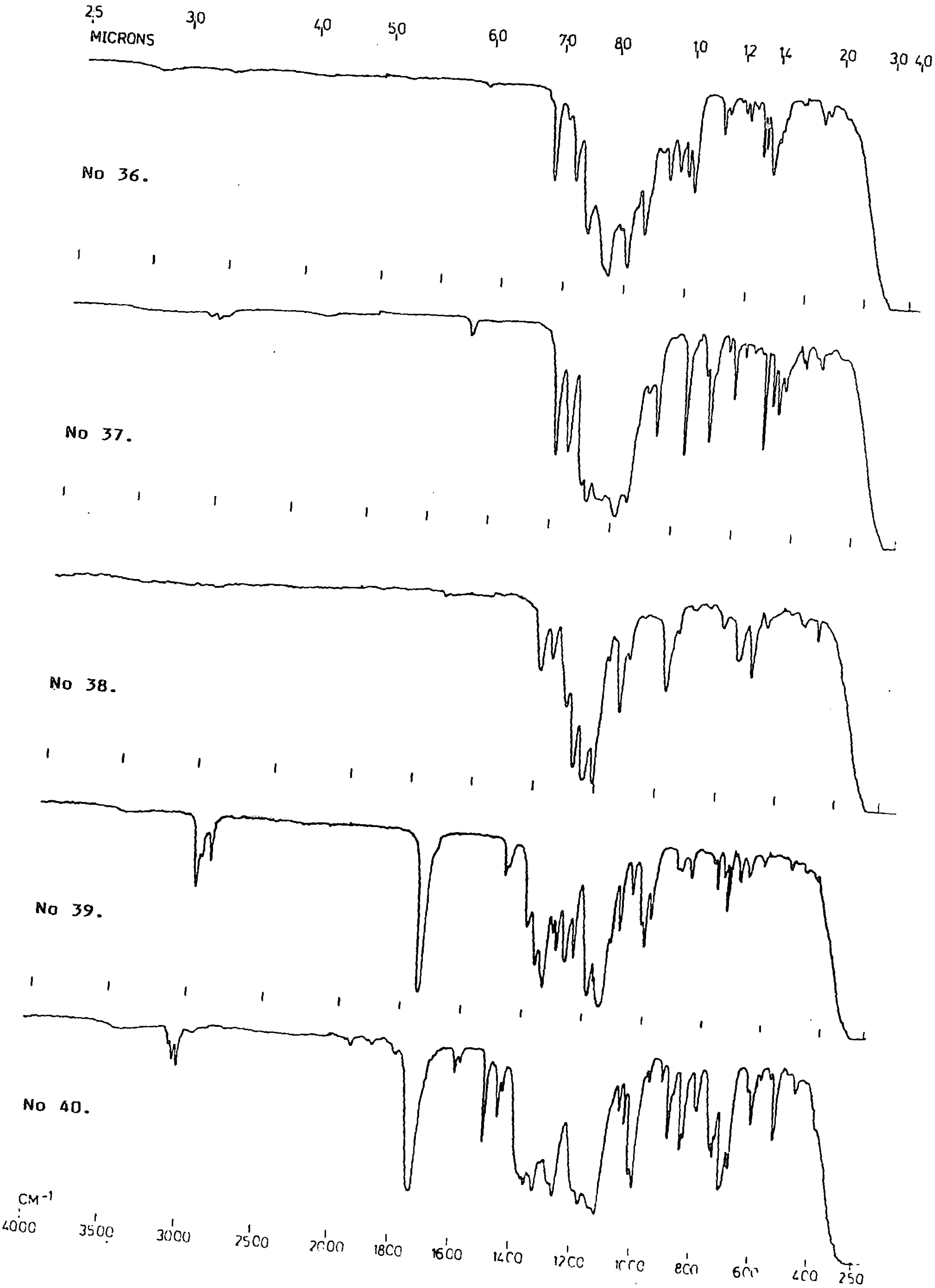
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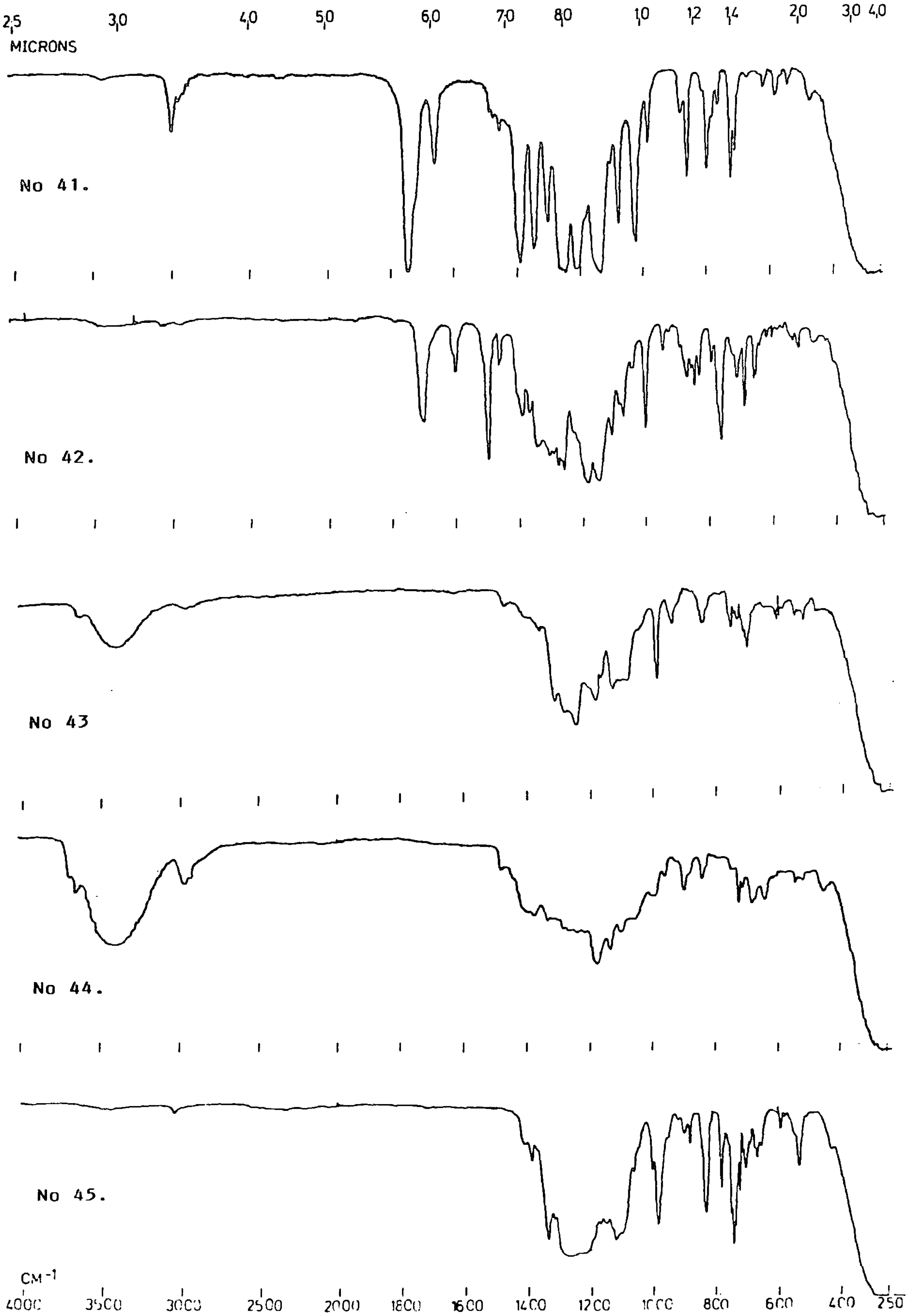

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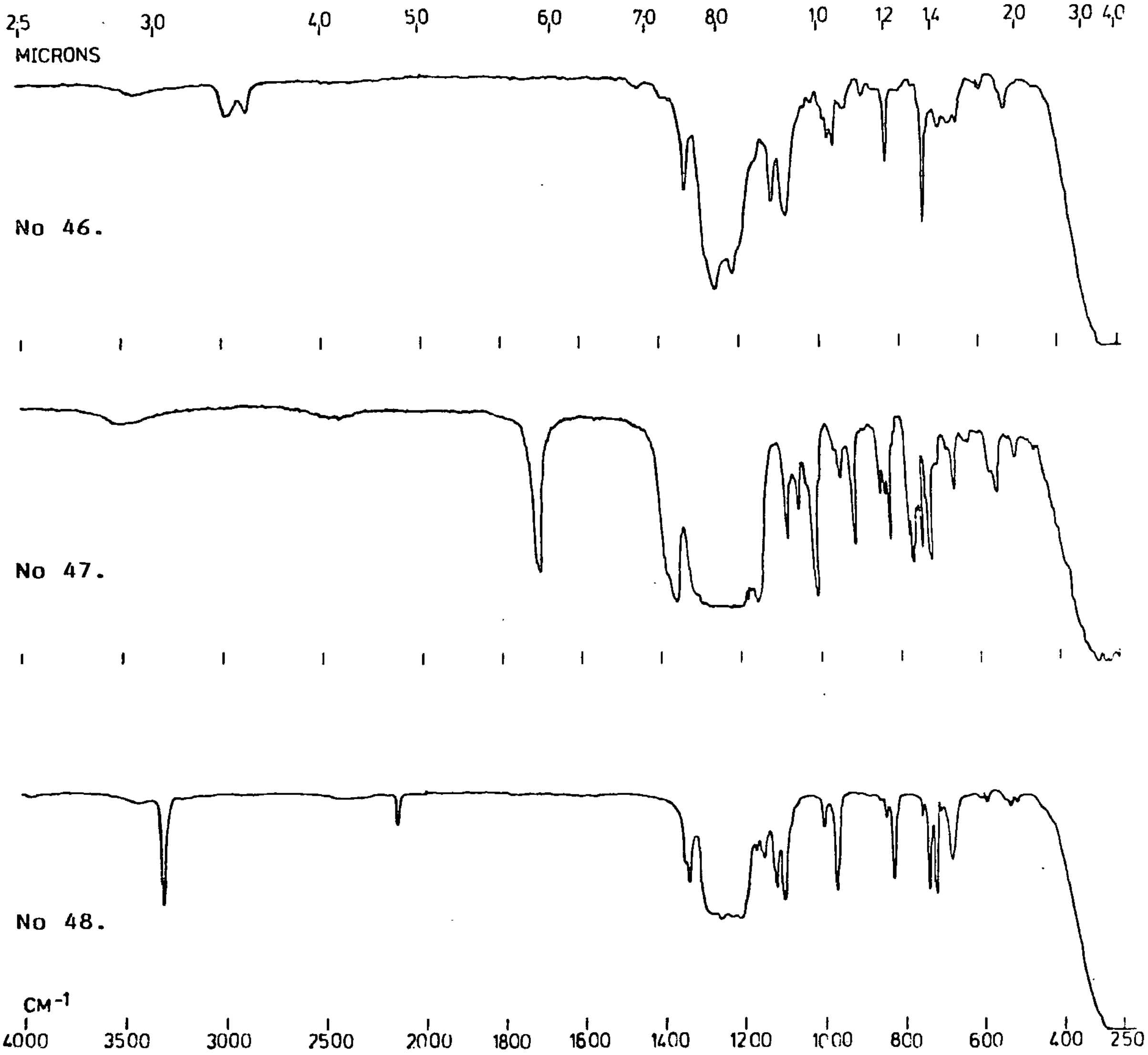
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APPENDIX FOUR
LECTURES, COLLOQUIA AND CONFERENCES

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

1 all research colloquia, research seminars and lectures, arranged by the Department of Chemistry during the period of the residence as a postgraduate student.

2 all research conferences attended, and papers presented by the author, during the period when the research for the thesis was carried out.

1 Lectures and Colloquia organised by the Department of Chemistry during the period October 1985 - July 1988

17.10.85 * Dr. C.J. Ludman (University of Durham)
"Some Thermochemical Aspects of Explosions"

24.10.85 * Dr. J. Dewing (UMIST)
"Zeolites - Small Holes, Big Opportunities"

30.10.85 Dr. S.N. Whittleton (University of Durham)
"An Investigation of a Reaction Window"

31.10.85 * Dr. P. Timms (University of Bristol)
"Some Chemistry of Fireworks"

5.11.85 Prof. M.J. O'Donnell (Indiana-Purdue University, U.S.A.)
"New Methodology for the Synthesis of Amino Acids"

7.11.85 Prof. G.Ertl (Munich, W.Germany)
"Heterogeneous Catalysis"

14.11.85 * Dr. S.G.Davies (University of Oxford)
"Chirality Control and Molecular Recognition"

20.11.85 Dr. J.A.H. McBride (Sunderland Polytechnic)
"A Heterocyclic Tour on a Distorted Tricycle - Biphenylene"

21.11.85 Prof. K.H. Jack (University of Newcastle)
"Chemistry of Si-Al-O-N Engineering Ceramics"

28.11.85 * Dr. B.A.J. Clark (Kodak Ltd)
"Chemistry and Principles of Colour Photography"

28.11.85 Prof. D.J. Waddington (University of York)
"Resources for the Chemistry Teacher"

15. 1.86 Prof. N. Sheppard (University of East Anglia)
"Vibrational and Spectroscopic Determinations of the Structures of Molecules Chemisorbed on Metal Surfaces"

23. 1.86	Prof. Sir Jack Lewis (University of Cambridge) "Some More Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls"
29. 1.86 *	Dr. J.H. Clark (University of York) "Novel Fluoride Ion Reagents"
30. 1.86	Dr. N.J. Phillips (University of Loughborough) "Laser Holography"
12. 2.86	Dr. J. Yarwood (Univeristy of Durham) "The Structure of Water in Liquid Crystals"
12. 2.86 *	Dr. O.S. Tee (Concordia University, Montreal, Canada) "Bromination of Phenols"
13. 2.86 *	Prof. R. Grigg (Queen's University, Belfast) "Thermal Generation of 1,3-Dipoles"
19. 2.86 *	Prof. G. Procter (University of Salford) "Approaches to the Synthesis of Some Natural Products"
20. 2.86	Dr. C.J.F.Barnard (Johnson Matthey Group) "Platinum Anti-Cancer Drug Development"
26. 2.86	Ms. C.Till (University of Durham) "ESCA and Optical Emission Studies of the Plasma Polymerisation of Perfluoroaromatics"
27. 2.86	Prof. R.K.Harris (University of Durham) "The Magic of Solid-State NMR"
5. 3.86	Dr. D.Hathway (University of Durham) "Herbicide Selectivity"
5. 3.86 *	Dr. M. Schroder (University of Edinburgh) "Studies on Macrocyclic Compounds"
6. 3.86 *	Dr. B. Iddon (University of Salford) "The Magic of Chemistry"
12. 3.86	Dr. J.M. Brown (University of Oxford) "Chelate Control in Homogeneous Catalysis"
14. 5.86	Dr. P.R.R. Langridge-Smith (University of Edinburgh) "Naked Metal Clusters - Synthesis, Characterisation, and Chemistry"
9. 6.86	Prof. R.Schmutzler (Braunschweigh, W.Germany) "Mixed Valence Diphosphorus Compounds"
23. 6.86	Prof. R.E.Wilde (Texas Technical University, U.S.A.) "Molecular Dynamic Processes from Vibrational Bandshapes"
16.10.86 *	Prof. N.N. Greenwood (University of Leeds) "Glorious Gaffes in Chemistry"
23.10.86 *	Prof. H.W.Kroto (University of Sussex) "Chemistry in Stars, Between Stars and in the Laboratory"

29.10.86	Prof. E.H.Wong (University of New Hampshire, U.S.A.) "Coordination Chemistry of P-O-P Ligands"
5.11.86	Prof. Döpp (University of Duisburg) "Cyclo-Additions and Cyclo-Reversions Involving Capto-Dative Alkenes"
6.11.86 *	Dr. R.M. Scrowston (University of Hull) "From Myth and Magic to Modern Medicine"
13.11.86 *	Prof. Sir Geoffrey Allen (Unilever Research) "Biotechnology and the Future of the Chemical Industry"
20.11.86 *	Dr. A. Milne and Mr. S. Christie (International Paints) "Chemical Serendipity - A Real Life Case Study"
26.11.86	Dr. N.D.S. Canning (University of Durham) "Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis"
27.11.86 *	Prof. R.L.Williams (Metropolitan Police Forensic Science) "Science and Crime"
3.12.86	Dr. J. Miller (Dupont Central Research, U.S.A.) "Molecular Ferromagnets:Chemistry and Physical Properties"
8.12.86	Prof. T.Dorfmüller (University of Bielefeld, W.Germany) "Rotational Dynamics in Liquids and Polymers"
22. 1.87	Prof. R.H. Ottewill (University of Bristol) "Colloid Science:A Challenging Subject"
28. 1.87	Dr. W. Clegg (University of Newcastle -upon-Tyne) "Carboxylate Complexes of Zinc Charting a Structural Jungle"
4. 2.87	Prof. A. Thomson (University of East Anglia) "Metalloproteins and Magneto-optics"
5. 2.87 *	Dr. P. Hubberstey (University of Nottingham) "Demonstration Lecture on Various Aspects of Alkali Metal Chemistry"
11. 2.87 *	Dr. T. Shepherd (University of Durham) "Pteridine Natural Products:Synthesis and Use in Chemotherapy"
12. 2.87 *	Dr. P.J.Rodgers (I.C.I., Billingham) "Industrial Polymers from Bacteria"
17. 2.87	Prof. E.H.Wong (University of New Hampshire, U.S.A.) "Symmetrical Shapes from Molecules to Art and Nature"
19. 2.87	Dr. M. Jarman (Institute of Cancer Research) "The Design of Anti-Cancer Drugs"
4. 3.87	Dr. R. Newman (University of Oxford) "Change and Decay:A Carbon-13 CP/MAS NMR Study of Humification and Coalification Processes"

5. 3.87 * Prof. S.V.Ley (Imperial College)
"Fact and Fantasy in Organic Synthesis"

9. 3.87 Prof. F.G.Bordwell (Northeastern University, U.S.A.)
"Carbon Anions, Radicals, Radical Anions and Radical Cations"

11. 3.87 Dr. R.D.Cannon (University of East Anglia)
"Electron Transfer in Polynuclear Complexes"

12. 3.87 Dr. E.M. Goodger (Cranfield Institute of Technology)
"Alternative Fuels for Transport"

17. 3.87 Prof. R.F.Hudson (University of Kent)
"Aspects of Organophosphorus Chemistry"

18. 3.87 Prof. R.F.Hudson (Univeristy of Kent)
"Homolytic Rearrangements of Free-Radical Stability"

3. 4.87 * Prof. G.Ferguson (University of Guelph, Canada)
"X-Ray Crystallography for the Organic Chemist"

6. 5.87 Dr. R. Bartsch (University of Sussex)
"Low Co-ordinated Phosphorus Compounds"

7. 5.87 Dr. M. Harmer (I.C.I. Chemicals and Polymer Group)
"The Role of Oranometallics in Advanced Materials"

11. 5.87 Prof. S.Pasynkiewicz (Technical University, Warsaw)
"Thermal Decomposition of Methyl Copper and Its Reactions with Trialkylaluminium"

27. 5.87 * Dr. M. Blackburn (University of Sheffield)
"Phosphonates as Analogues of Biological Phosphate Esters"

24. 6.87 * Prof. S.M.Roberts (University of Exeter)
"Synthesis of Novel Anti-Viral Agents"

26. 6.87 * Dr. C.Krespan (E.I. Dupont de Nemours)
"Nickel (0) and Iron (0) as Reagents in Organofluorine Chemistry"

15.10.87 * Dr. M.J.Winter (University of Sheffield)
"Pyrotechnics"

22.10.87 * Prof. G.W.Gray (University of Hull)
"Liquid Crystals and their applications"

29.10.87 * Mrs S. van Rose (Geological Museum, London)
"Chemistry of Volcanoes"

4.11.87 Mrs M. Mapletoft (Durham Chemistry Teachers' Centre)
"Salter's Chemistry"

5.11.87 Dr. A.R.Butler (University of St.Andrews)
"ChineseAlchemy"

12.11.87 * Prof. D.Seebach (E.T.H., Zurich)
"From Synthetic Methods to Mechanistic Insight"

26.11.87 *	Dr. D.H.Williams (University of Cambridge) "Molecular Recognition"
11.87	Dr. J.Davidson (Herriot-Watt University) "Metal Promoted Oligomerization Reactions of Alkynes"
3.12.87	Dr. J. Howard (I.C.I., Wilton) "Chemistry of Non-Equilibrium Processes"
10.12.87	Dr. C.J. Ludman (University of Durham) "Explosives"
16.12.87	Mr R.M.Smart (I.C.I.) "The Interaction of Chemicals with Lipid Bilayers"
19.12.87	Prof. P.G.Sammes (Smith, Kline and French) "Chemical Aspects of Drug Development"
21. 1.88	Dr. F.Palmer (University of Nottingham) "Luminescence"
28. 1.88	Dr. A.G.Cairns-Smith (University of Glasgow) "Clay Minerals and the Origin of Life"
9. 2.88	Mr Lacey (Durham Chemistry Teachers' Centre) "Double Award Science"
11. 2.88	Prof. J.J.Turner (University of Nottingham) "Catching Organometallic Intermediates"
18. 2.88	Dr. K. Borer (University of Durham Industrial Research Labs) "The Brighton Bomb - A Forensic Science View"
15. 2.88	Prof. A. Underhill (University of Bangor) "Molecular Electronics"
3. 3.88	Prof. W.A.G.Graham (University of Alberto, Canada) "Rhodium and Iridium Complexes in the activation of Carbon-Hydrogen Bonds"
7. 3.88	Prof. H.F.Koch (Ithaca College, U.S.A.) "Does the E2 Mechanism Occur in Solution?"
16. 3.88	L.Bossons (Durham Chemistry Teachers' Centre) "GCSE Practical Assessment"
7. 4.88	Prof. M.P. Hartshorn (Unviersity of Canterbury, New Zealand) "Aspects of Ipso-Nitration"
13. 4.88	Mrs E. Roberts (SATRO Officer for Sunderland) "Links between Industry and Schools"
18. 4.88	Prof. C.A.Nieto de Castro (University of Lisbon and Imperial College) "Transport Properties of Non-Polar Fluids"
25. 4.88	Prof. D.Birchall (I.C.I. Advanced Materials) "Environmental Chemistry of Aluminium"
27. 4.88	Dr. R. Richardson (University of Bristol) "X-ray Diffraction from Spread Monolayers"

27. 4.88		Dr. J.A.Robinson (University of Southampton) "Aspects of Antibiotic Biosynthesis"
28. 4.88		Prof. A.Pines (University of California, Berkeley, U.S.A.) "Some Magnetic Moments"
11. 5.88		Dr. W.A.McDonald (I.C.I. Wilton) "Liquid Crystal Polymers"
11. 5.88		Dr. J. Sodeau (University of East Anglia) "Spray Cans, Smog and Society"
8. 6.88		Prof. J.P. Majoral (Université Paul Sabatier) "Stabilization Complexation of Short-Lived Phosphorus Species"
29. 6.88		Dr. M.E.Jones (Durham Chemistry Teachers' Centre) "GCSE Chemistry Post-mortem"
29. 6.88	*	Prof. G.A.Olah (University of Southern California, U.S.A.) "New Aspects of Hydrocarbon Chemistry"
6. 7. 88		Dr. M.E.Jones (Durham Chemistry Teachers' Centre) "GCE Chemistry A-Level Post-mortem"

* Indicates colloquia attended by the author.

2. Conferences Attended

1. Sheffield Symposium on 'Modern Aspects of Stereochemistry', Sheffield, December 1985.

2. Graduate Symposium, Durham, April 1986.

3. 'Fluoropolymers' Conference, UMIST, January 1987.

4. Graduate Symposium, Durham, March 1987.

5. Sheffield Symposium on 'Modern Aspects of Stereochemistry', Sheffield, December 1987.

6. Graduate Symposium, Durham, April 1988.

7. 12th International Symposium on Fluorine Chemistry, Santa Cruz, California, August 1988.

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