Model compounds related to fluoroelastomers

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UNIVERSITY OF DURHAM

A THESIS

Entitled

MODEL COMPOUNDS RELATED TO FLUOROELASTOMERS

Submitted by

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(University College)

A Candidate for the Degree of Doctor of Philosophy

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To My Late Father

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Last, but not least, I would like to express my gratitude to my mother and family for their encouragement during the time of this research.

MEMORANDUM

The work described in this thesis was carried out at the University of Durham between October 1982 and August 1985 and is original except where stated by reference. This work has not previously been submitted, either wholly or in part, for a degree at this or any other university.

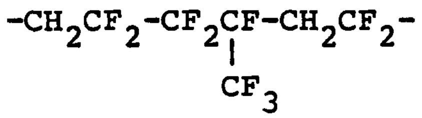
MODEL COMPOUNDS RELATED TO FLUOROELASTOMERS

by

MARTIN SALISBURY

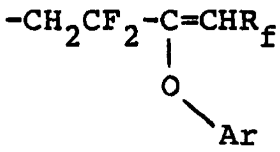
ABSTRACT

The aims of the research described in this thesis were to explore the chemistry of some model compounds related to fluorohydrocarbon polymers, in particular the copolymer of (I), especially to obtain definitive information about mechanisms of cross-linking and polymer degradation and to explore new approaches to cross-linking.



$$-CH_2CF_2-CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F-CH_2CF_2-$$

(I)

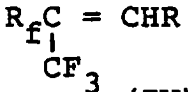


(II)

A range of model compounds of the form (III) and (IV) were synthesized and the results obtained demonstrate that arylether cross-links of the form (II) are stable in the presence of various bases at elevated temperatures. This indicates that these links are not responsible for the instability of copolymers cured in this way.

$(R_f)_2CFCH_2F$

(III)



$$R_f\underset{\displaystyle CF_3}{\underset{|}{C}} = CHR$$

(IV)

$R = (CF_2CH_2)CF_3$, coupled

$R_f = CF_3$ $n = 1,2$

Models of the form (III) and (IV) show surprisingly low reactivity under typical curing conditions, indicating that either the polymers themselves are more reactive or reaction occurs by an unexpected mechanism.

In pursuit of the likely cross-linking mechanism it was shown that polymers of the forms (I) and $(CF_2CH_xF_{2-x})_n$, x=1,2, are highly susceptible to elimination of HF in the presence of Lewis acids, *e.g.* SbF_5 to yield highly unsaturated materials. Model chemistry involving SbF_5 resulted in novel eliminations of HF, *e.g.*

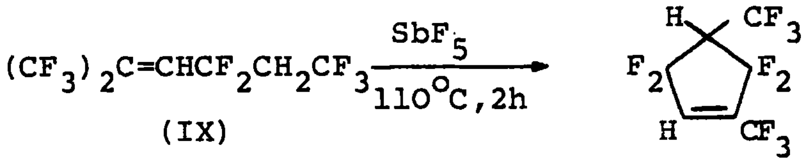
$$\underset{(V)}{[(CF_3)_2CFCH_2CF_2]_2} \xrightarrow[120^oC,2h]{SbF_5} \underset{(VI)}{[(CF_3)_2C{=}CHCF_2]_2} \quad \text{(quant.)}$$

the formation of some stable long-lived carbocations, *e.g.*

$$(CF_3)_2CFCH_2CF_2CH_2CF_2CH_2CF_3 \xrightarrow[20^{o}C]{SbF_5} (CF_3)_2CFCH_2\overset{+}{\overline{CFCHCF}}CH_2CF_3$$

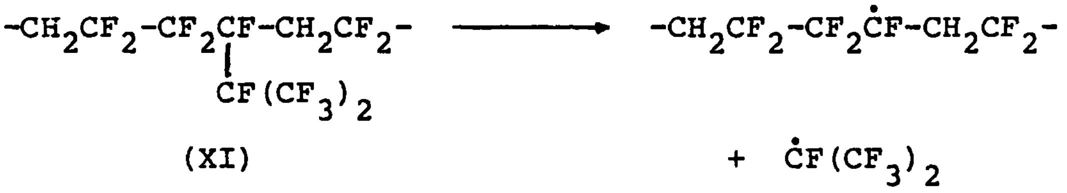
(VII) (VIII)

and other novel chemistry, *e.g.* a 1,5 elimination of HF



(IX) (X)

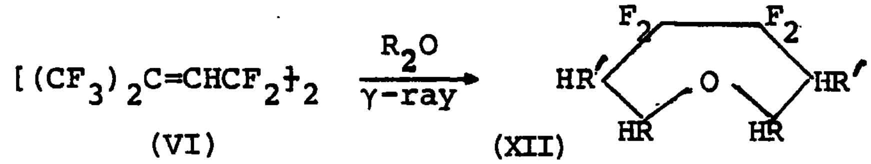
A new approach to cross-linking was also developed involving the incorporation into the copolymer (I) of crowded comonomer units, *e.g.* when copolymers containing the structures (XI) where heated radicals were found *via* homolytic cleavage to promote cross-linking:



$$-CH_2CF_2-CF_2\underset{\displaystyle CF(CF_3)_2}{CF}-CH_2CF_2- \longrightarrow -CH_2CF_2-CF_2\dot{C}F-CH_2CF_2- + \dot{C}F(CF_3)_2$$

(XI)

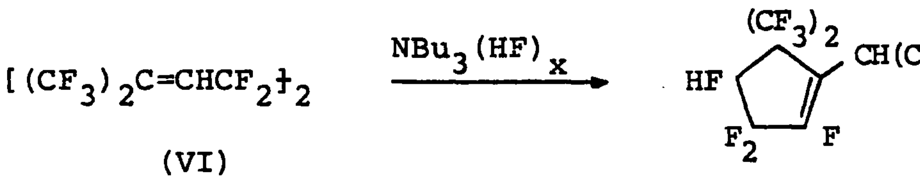
General examination of the model compounds yielded new reactions including a route to seven-membered cyclic ethers,



(VI) (XII)

R = Me, Et
R′= $CH(CF_3)_2$

and an unexpected ring closure reaction catalysted by $NBu_3,(HF)_x$,



(VI) (XIII)

The reactivity of the models was also examined in the areas of nucleophilic attack, base-catalysed elimination of HF, addition of 1,3-dipoles, the formation of long-lived carbanions and one-electron transfer chemistry. The results obtained considerably broaden the chemistry of this class of compound.

CONTENTS

INTRODUCTION

GENERAL INTRODUCTION

ORGANOFLUORINE CHEMISTRY

Organofluorine chemistry is a particularly useful and interesting branch of organic chemistry for a number of reasons;[1]

(i) It is possible to replace, extensively, hydrogen in hydrocarbon compounds with fluorine, without generating steric crowding (Van der Waals radii; H 1.20Å, F 1.35Å). Therefore, in principle, a whole new organic chemistry is possible, which is entirely synthetic, based on C-F rather than C-H skeletons.

(ii) Fluorocarbon systems give rise to some very novel chemistry because of the high electronegativity of fluorine. For example, often the chemistry of functional groups is altered

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad K = 1.26 \times 10^{-5}$$

$$CF_3COOH \rightleftharpoons CF_3COO^- + H^+ \qquad K = 1.8$$

In addition, the C-F chemical bond is comparatively strong (107-121 Kcal mol^{-1} *cf*. 98 Kcal mol^{-1} for C-H)[2] and this, in conjunction with its associated non-bonding electron pairs, gives rise to a well protected carbon skeleton in most highly fluorinated compounds.

(iii) A range of biologically active partially fluorinated organic compounds have wide applications in the fields of medicine, pharmacy and pest control.[3,4]

(iv) Organofluorine chemistry is of major interest and promise to industry[5,6] for the discovery of new materials which have greater thermal and chemical resiliance while at the same time exhibiting desirable physical properties, *e.g.* elasticity, low surface friction, *etc*.

Clearly, therefore, there is extensive scope for research into all of these areas for the purpose of expanding our understanding of organic chemistry[7] and for producing new materials and new effects that may be exploited by industry.

CHAPTER ONE

FLUOROPOLYMERS

I.A. Fluoropolymers and Industry

The vast advances in technology, which have been made over the last forty years, in the fields of automation,[8] electronics and space exploration have resulted in a high demand for materials of a very specialised nature; for example, elastomeric materials which retain their rubbery properties over a wide range of temperatures while, at the same time, are resistant to aggressive chemicals, solvents, radiation and weathering. It is in this type of role that fluoropolymers have great value.

I.B. Fluoropolymers *via* Fluorinated Alkenes

I.B. (i) Availability of Fluorinated Alkenes

Near the end of the last century Swarts pioneered the halogen exchange reaction[9]

$$C_nCl_{2n+2} \xrightarrow[SbCl_5]{SbF_3} C_nCl_{2n+2-a}F_a$$

This discovery provided later workers with a route to many fluorinated alkenes[10-12] as exemplified below:

$$CCl_3CCl_3 \xrightarrow[110^{o}C]{HF,\ SbCl_3,\ Cl_2} CCl_{3-n}F_nCCl_{3-n}F_n$$ [13,14]

$$CF_2ClCFCl_2 \xrightarrow{Zn,\ CH_3OH} CF_2 = CFCl$$

This and the syntheses of the other industrially important fluoroalkenes are summarised in Table 1.1.

TABLE 1.1 Syntheses of Fluoroalkenes

Alkene	Synthesis	References to other reported routes
$F_2C{=}CF_2$	$CF_2HCl \xrightarrow{650^{\circ}C} CF_2{=}CF_2{+}HCl$	(15)
$F_2C{=}CFCl$	$CF_2ClCFCl_2 \xrightarrow{Zn,\ CH_3OH} CF_2{=}CFCl$	(16-18)
$FHC{=}CH_2$	$CH{\equiv}CH{+}HF \xrightarrow[Hg^{2+}]{500^{\circ}C} CHF{=}CH_2$	(19-21)
$F_2C{=}CH_2$	$CH_3CF_2Cl \xrightarrow{870^{\circ}C} CH_2{=}CF_2$	(22,23)
$CF_3CF{=}CF_2$	$CF_2{=}CF_2 \xrightarrow[\text{steel tube}]{750\text{-}810^{\circ}C} CF_2{=}CFCF_3$	(24,25)
$CF_3CF{=}CFH$	$CF_3CF{=}CF_2 \xrightarrow{Pd/H_2} CF_3CFHCF_2H \xrightarrow{base} CF_3CF{=}CFH$	(26)
$CF_3CH{=}CF_2$	$CF_3CFHCF_2CH_2OH \xrightarrow[\text{(ii) NaOH}\Delta]{\text{(i) Oxidn.}} CF_3CH{=}CF_2$	(27)

I.B. (ii) The Effect of Fluorine in Free-Radical Additions

Polymerisations of the fluorinated alkenes, shown in Table 1.1 proceed *via* free radical addition mechanisms,

e.g. $F_2C = CFCl \xrightarrow{\text{Initiator}} -\!\!(CF_2CFCl)\!\!-_n$

and this is the principle process used in industry for forming fluoropolymers.

Free-radical addition, in general, may be represented by the scheme outlined in Figure 1.1.[28]

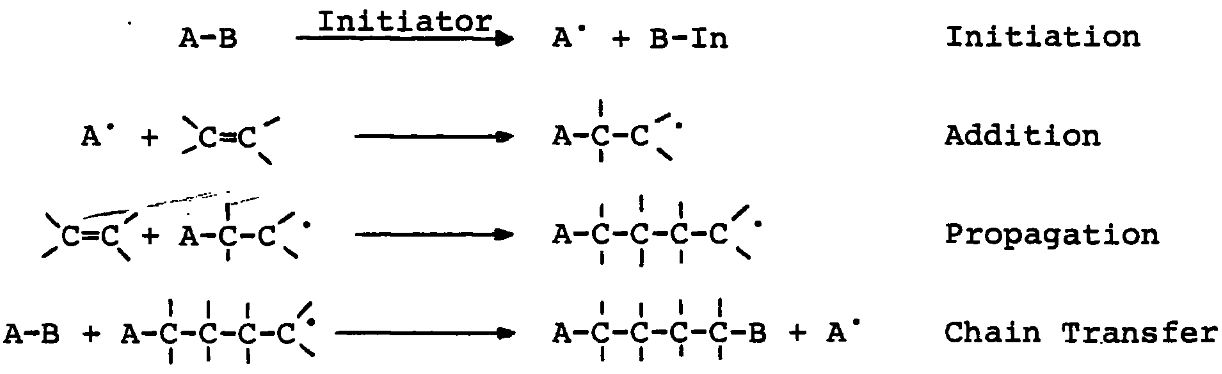


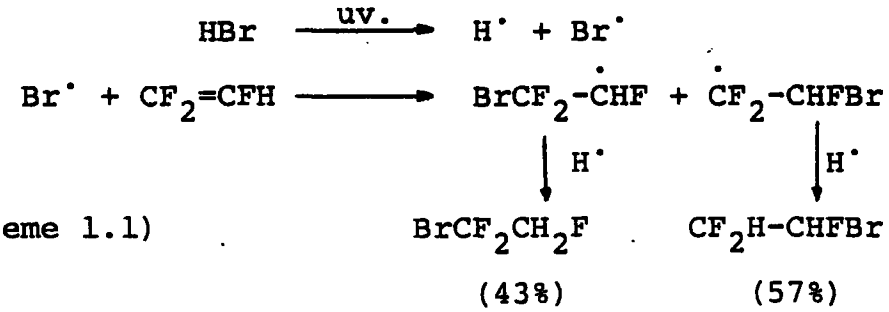
Figure 1.1 Free-Radical Addition

There are two extreme cases:

(i) If A-B is weakly bonded and in high concentration then addition only occurs, *i.e.* the chain transfer process competes successfully with the propagation step.

(ii) If A-B is more strongly bonded, and present only in catalytic amounts, propagation competes successfully with chain transfer and polymerisation occurs.

Free-radical additions to unsymmetrical fluoroalkenes are frequently non-regiospecific.[29] This is exemplified by the addition of hydrogen bromide to trifluoroethene (Scheme 1.1).



(Scheme 1.1)

However, with addition of carbon radicals, it has been established that the odd electron will tend to reside on the carbon atom with the following substituents in increasing order preference: H < F < Cl.[30]

This preference reflects the stability of the intermediate radical. This consideration is more important when the structure of the transition state most closely resembles the "reactants". For example, consider the separate reactions of chlorine and bromine atoms with propene. The relevant thermodynamic data for the process

$$X^{\bullet} + CH_2 = CHCH_3 \longrightarrow XCH_2\dot{C}HCH_3$$

is given in Table 1.2[31].

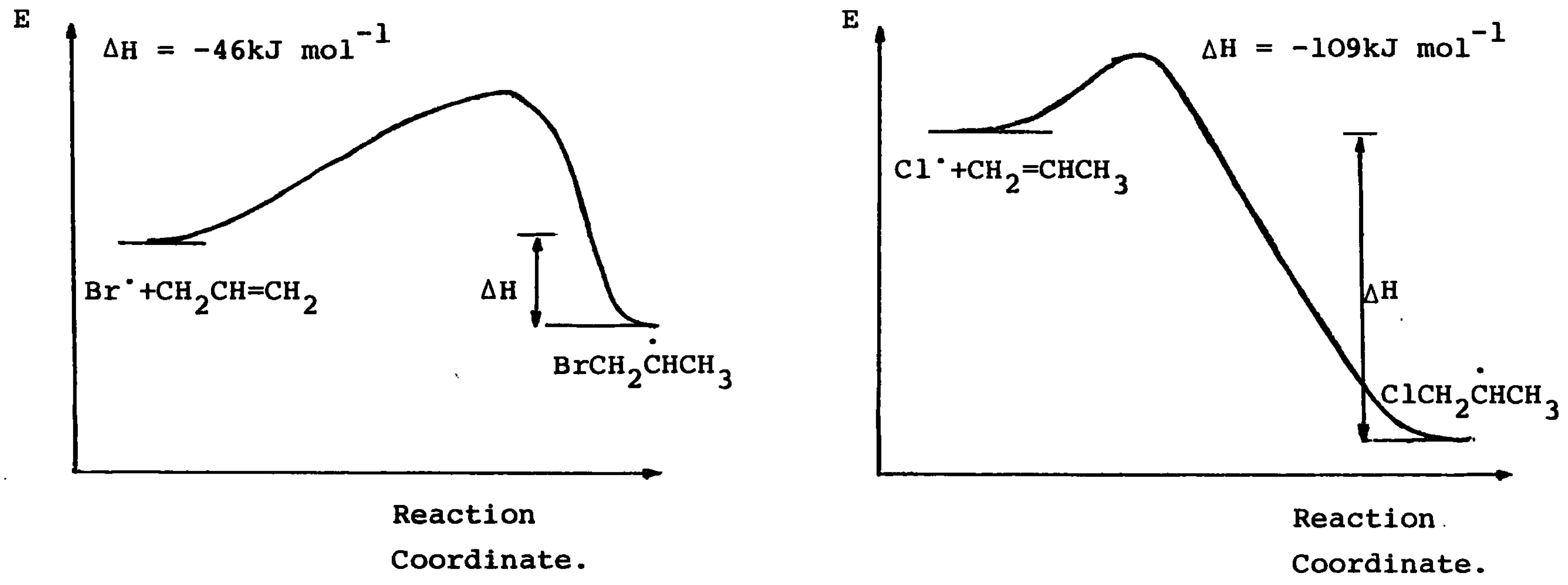
TABLE 1.2 Enthalpy values for $X^{\bullet} + CH_2 = CHCH_3 \longrightarrow XCH_2\dot{C}HCH_3$

$X^{\bullet}$	ΔH
$Br^{\bullet}$	$-46 kJ mol^{-1}$
$Cl^{\bullet}$	$-109 kJ mol^{-1}$

The energy profiles for these reactions are shown in Figure 1.2. In the case of addition of HCl, the transition state would most closely resemble the "reactants" in structure and may therefore be represented as

$$Cl^{\bullet} --- CH_2 = CHCH_3$$

Figure 1.2 Energy Profiles for $X^{\cdot} + CH_2 = CHCH_3 \longrightarrow XCH_2\dot{C}HCH_3$



Clearly, the reactivity of this system, *i.e.* free-radical addition of HCl, does not reflect the stability of an intermediate radical. (In fact this reaction is unknown because the radical transfer step $ClCH_2\dot{C}HCH_3 + HCl \longrightarrow ClCH_2CH_2CH_3 + Cl^{\bullet}$ is endothermic, $\Delta H = +21 kJ\ mol^{-1}$). In the case of free-radical addition of HBr, however, the transition state more closely resembles the "products" in structure and may be represented as

$$Br \text{---} CH_2 \overset{----}{\underset{----}{}} \dot{C}HCH_3$$

Therefore the rate of free-radical addition of HBr, which is facile, does to some extent reflect the stability of an intermediate radical.

The rate of free-radical addition is also affected by the strength of the chemical bond being formed. Consider the reactions

$$CCl_3 + CF_mH_n = CH_2 \longrightarrow Cl_3CCF_mH_n\dot{C}H_2$$

$$m + n = 2$$

The stability of the intermediate radical may be ignored because the odd electron resides on a $-CH_2-$ group in each case. The activation energy and Arrhenius A factors were compared for m = 0, 1 2.[32] It was found that while the Arrhenius factors remained almost constant, there was a steep increase in activation energy on going from m=0 to m=2. This increase must be due to the enthalpy of bond-formation.

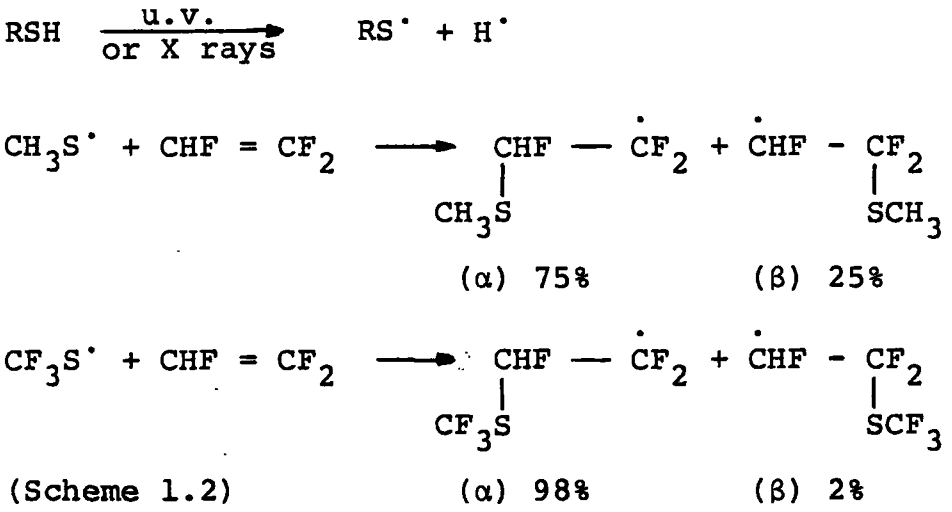
These observations arise from polar effects as illustrated by the reactions -

$$\text{(a)}\quad \dot{C}R_3 + CF_2 = CF_2 \longrightarrow CR_3CF_2\dot{C}F_2$$

$$R = \text{(i) } F \quad \text{(ii) } H$$

$$\text{(b)}\quad \dot{C}R_3 + CH_2 = CH_2 \longrightarrow CR_3CH_2\dot{C}H_2$$

Here, although $\dot{C}F_3$ radicals are always more reactive than $\dot{C}H_3$ radicals, the reaction (a) (i) is slower than the reaction (b) (i) and the reaction (b) (ii) is slower than the reaction (a) (ii). Consider the additions of thiols to trifluoroethene[33] (Scheme 1.2):



$$RSH \xrightarrow[\text{or X rays}]{\text{u.v.}} RS^{\bullet} + H^{\bullet}$$

$$CH_3S^{\bullet} + CHF = CF_2 \longrightarrow \underset{\underset{CH_3S}{|}}{CHF} - \dot{C}F_2 + \dot{C}HF - \underset{\underset{SCH_3}{|}}{CF_2}$$

$$(\alpha)\ 75\% \qquad (\beta)\ 25\%$$

$$CF_3S^{\bullet} + CHF = CF_2 \longrightarrow \underset{\underset{CF_3S}{|}}{CHF} - \dot{C}F_2 + \dot{C}HF - \underset{\underset{SCF_3}{|}}{CF_2}$$

$$(\alpha)\ 98\% \qquad (\beta)\ 2\%$$

(Scheme 1.2)

These results are rationalised in terms of the electrophilicity of the thioyl radicals and the polarity of trifluoroethene

$$\overset{\delta^-}{\underset{(\alpha)}{CHF}} = \overset{\delta^+}{\underset{(\beta)}{CF_2}}$$

The more electrophilic $\dot{S}CF_3$ radical is more strongly directed towards the negatively polarised carbon whilst the $\dot{S}CH_3$ radical, being less electrophilic, is less selective.

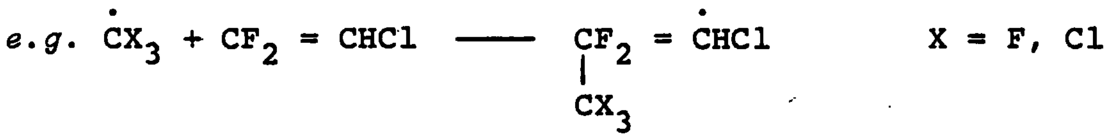
This trend is also observed in the addition of $\dot{C}F_3$ and $\dot{C}H_3$ to trifluoroethene.[31] However, in the series $\dot{C}F_3$, $\dot{C}F_2Br$, $\dot{C}FBr_2$, $\dot{C}Br_3$ there is little change in the electrophilicity of the radical and so only a small variation in the yields of the α- and β- adducts to trifluoroethene would be expected. In fact there is a considerable lowering of reactivity at the more substituted (β-) end as the radical becomes more bulky.

$$\dot{C}Br_3 + CHF=CF_2 \longrightarrow \underset{CBr_3}{\underset{|}{CHF}}\dot{C}F_2 + \dot{C}HF\underset{CBr_3}{\underset{|}{CF_2}}$$

(α) 80% (β) 20%

This result clearly demonstrates a steric hindrance effect due to the size of the Br atoms. This effect is even more pronounced in the series $\dot{C}F_3$, $\dot{C}F_2CF_3$, $\dot{C}F(CF_3)_2$, $\dot{C}(CF_3)_3$ where the yield of the β-adduct drops to 6%. For the straight chain perfluorocarbon radicals $\dot{C}F_3$ to $\dot{C}_8F_{17}$ there is, however, only a small change in selectivity which is important when consdering polymerisation processes.

Steric hindrance effects may compete with polar effects,



$$e.g.\ \dot{C}X_3 + CF_2=CHCl \longrightarrow \underset{CX_3}{\underset{|}{CF_2}}-\dot{C}HCl \qquad X = F, Cl$$

Here the electrophilic radicals $\dot{C}F_3$ and $\dot{C}Cl_3$ add preferentially to the positively polarised position because of steric repulsion by the large Cl atom at the negatively polarized position.

Since bond-strength, polarity, steric requirements and electrophilicity are strongly affected by the presence of fluorine in organic molecules, unusual effects are prevalent in organofluorine free-radical chemistry.

I.B. (iii) Mechanistic Aspects of Polymerisation

(a) Homopolymers

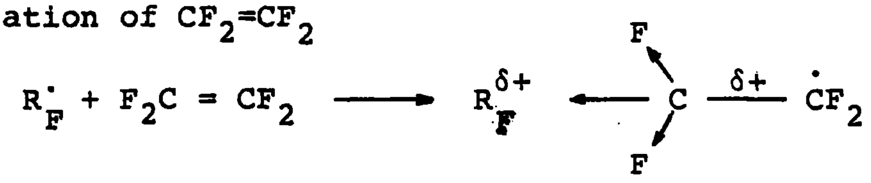
The import mechanistic considerations of polymerisation of fluoroalkenes by free radical processes are identified in terms of the ground rules described above for free radical addition reactions. The key step to consider is the propagation step

$$\begin{array}{l} RM^\bullet + M \longrightarrow RM_2^\bullet \\ \vdots \\ RM_r^\bullet + M \longrightarrow RM_{r+1}^\bullet \end{array} \qquad M \equiv \text{Monomer}$$

which involves the addition of polymer radicals $RM_r^\bullet$ to the monomer unit M. The reactivity of this type of process depends mainly upon (i) polar and (ii) steric factors.

(i) Polar Effects

The rate of polymerisation is lowered by the presence of electronegative substituents. For example in the polymerisation of CF_2=CF_2



$$R_F^\bullet + F_2C = CF_2 \longrightarrow R_F^{\delta+} \longleftarrow \underset{F}{\overset{F}{C}} \overset{\delta+}{\text{—}} \dot{C}F_2$$

an unfavourable dipole interaction occurs due to the electronegativity of $R_F^\bullet$ and the polar C-F bonds in CF_2=CF_2.

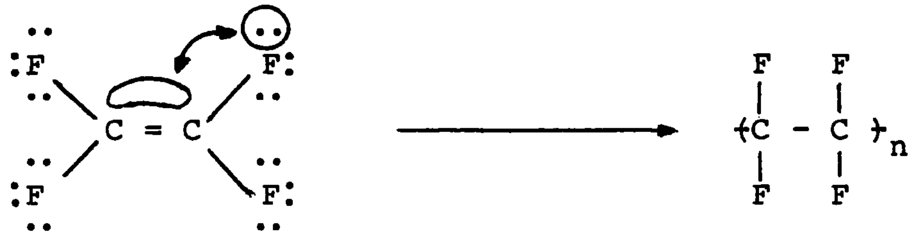
(ii) Steric Effects

In general the bulkier the substituents, either on the propagating radical $R\dot{C}X_2$ or the monomer CXY=C , the greater the energy barrier towards reaction. For example, the polymerisation of 1,2-disubstituted alkenes is usually difficult

$$R^{\cdot} + CHX = CHY \longrightarrow RCHX\dot{C}HY$$

$$RCHX\dot{C}HY + CHX = CHY \not\longrightarrow R\text{+}CHXCHY\text{+}_n^{\cdot}$$

In stark contrast to this second observation is the high heat of polymerisation of CF_2=CF_2 (18 Kcal mol^{-1} greater than C_2H_4). This is best accounted for in terms of the relief of π-electron repulsion in CF_2=CF_2 which has a destabilising effect



CF_3CF=CF_2, however, forms a homopolymer only under extreme conditions

$$CF_2 = CFCF_3 \xrightarrow[\text{14h, 3000 atm}]{(CF_3S)_2Hg,\ 225^{\circ}C} \text{+}CF_2CF(CF_3)\text{+}_n{}^{34}$$

These observations lead to the conclusion that steric considerations are unimportant when the only α-substituents, on both the propagating radical $R\dot{C}X_2$ and the alkene substrate, are fluorine. In fact none of the polymerisations of CH_2=CHF(VF), CH_2=CF_2(VF_2) or CHF=CF_2(VF_3) (to form PVF, PVF_2, PFV_3 resp.) are sterically hindered by the presence of fluorine substituents. Therefore in these systems polar effects are more dominant. While the rate of polymerisation falls as the number of substituents is increased, the main effect is on the regiochemistry of addition, resulting in head to tail arrangements of the monomer units. The reactions are not, however, completely regiospecific.

$R(CH_2CHF)^{\bullet}_{n} + CH_2 = CHF \longrightarrow R(CH_2CHF)^{\bullet}_{n+1}$ 26% irregular[35]

$R(CH_2CF)_2^{\bullet} + CH_2 = CF_2 \longrightarrow R(CH_2CF_2)^{\bullet}_{n+1}$ 10% irregular[36]

$R(CHFCF_2)^{\bullet}_{n} + CHF = CF_2 \longrightarrow R(CHFCF_2)^{\bullet}_{n+1}$ 10-15% irregular[37]

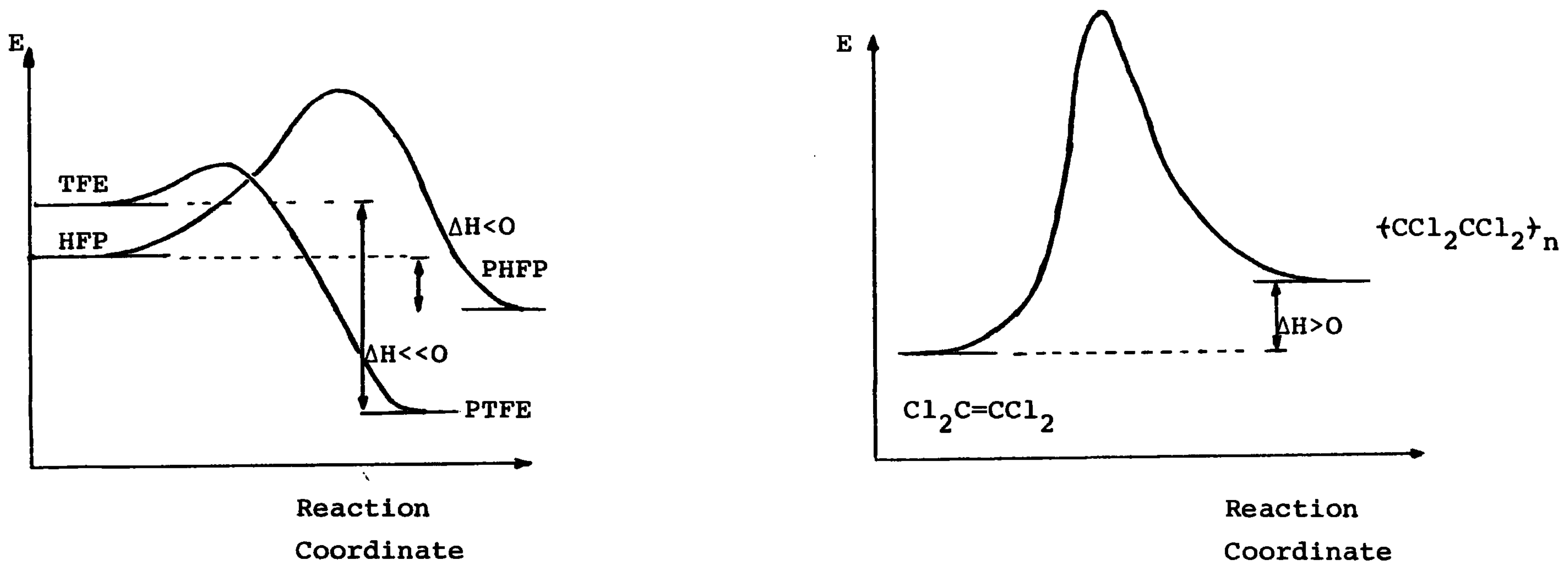
It would be logical to expect a thermodynamic advantage for the homopolymerisation of $CF_2CF = CF_2$ due to the relief of π-non-bonding electron pair repulsions, similar to that found with $CF_2 = CF_2$. However this is precluded by the steric hindrance of the $-CF_3$ group. It is useful to compare the energy profiles for these two processes with that of the homopolymerisation of $Cl_2C = CCl_2$, which under no conditions proceeds. These are shown in Figure 1.3. In homopolymerising $Cl_2C = CCl_2$ steric repulsions would also occur in the resultant homopolymer to further reduce the feasibility of reaction.

Steric effects strongly determine regiochemistry in certain homopolymerisations. For example polychloro- and polybromo-trifluoroethene (PCTFE and PBTFE resp.) are 98-99% regiospecific[38] (*cf.* PVF_2 and PVF_3 due to polar effects).

$CF_2 = CFCl \longrightarrow -CF_2CFCl - CF_2CFCl - CF_2CFCl -$

$CF_2 = CFBr \longrightarrow -CF_2CFBr - CF_2CFBr - CF_2CFBr -$

Figure 1.3 Reaction Profiles for the Homopolymerisations $CF_2=CF_2$, $CF_3CF=CF_2$, $Cl_2C=CCl_2$

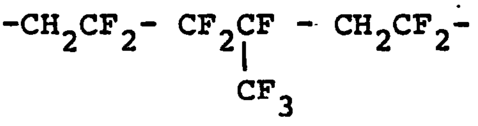


(b) Copolymers

Copolymers are produced by mixing together two or more comonomers in the presence of a free-radical initiator. Therefore an alkene which will not homopolymerise becomes useful if it can be copolymerised with one which has less steric barriers to reaction, *e.g.* $CF_3CF = CF_2$.

(i) Copolymers Derived from $CF_3CF{=}CF_2$ and $CH_2{=}CF_2$

The actual structure of the copolymer of $CF_3CF{=}CF_2$ and $CH_2{=}CF_2$ depends upon the reactivities of the comonomers and is, therefore, also subject to the factors affecting reactivity that were described above for homopolymerisation. For example, since $CF_3CF{=}CF_2$ does not homopolymerise, the maximum content of $CF_3CF{=}CF_2$ in the copolymer with $CH_2{=}CF_2$ is 50% because it is reasonable to expect that no $CF_3CF{=}CF_2$ sequences will occur. In fact, the structure



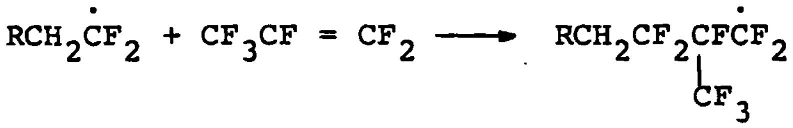
$$-CH_2CF_2-\ CF_2\underset{\displaystyle CF_3}{\underset{|}{CF}}-\ CH_2CF_2-$$

accounts for 93% of the $CF_3CF{=}CF_2$ in the copolymer.[39] Conversely $CH_2{=}CF_2$ sequences do occur due to its greater reactivity. In considering the structure of $CH_2{=}CF_2$ sequences it is reasonable to assume that the regiochemistry does not differ from that of the $CH_2{=}CF_2$ homopolymer and that >90% regioselectivity occurs.[36] Therefore the most important structural units to consider are those involving a $CF_3CF{=}CF_2$ unit adjacent to a $CH_2{=}CF_2$ unit.

Consider radical attack upon $CF_3CF{=}CF_2$ by a polymer radical terminating in a $-CH_2\dot{C}F_2$ unit. Attack upon $CF_3CF{=}CF_2$

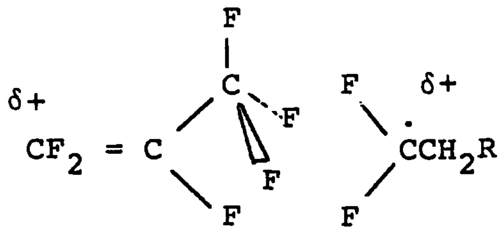
can therefore occur in two ways:

(i) $RCH_2\dot{C}F_2 + CF_2 = CFCF_3 \longrightarrow RCH_2CF_2CF_2\dot{C}FCF_3$

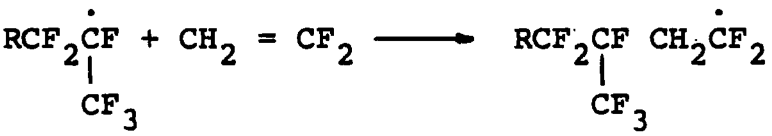
(ii) 

$$RCH_2\dot{C}F_2 + CF_3CF = CF_2 \longrightarrow RCH_2CF_2\underset{CF_3}{C}F\dot{C}F_2$$

$RCH_2\dot{C}F_2$ is an electrophilic radical and therefore the most favourable approach occurs at the least electrophilic carbon of $CF_3CF = CF_2$:

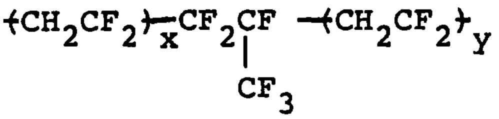


However the steric hindrance between the $-CF_3$ group and the propagating $RCH_2\dot{C}F_2$ radical results in attack at the positively polarised carbon of $CF_3CF = CF_2$ and a new propagating radical of the form $RCF_2\dot{C}FCF_3$ which reacts preferentially with $CH_2 = CF_2$:



$$RCF_2\underset{CF_3}{\dot{C}}F + CH_2 = CF_2 \longrightarrow RCF_2\underset{CF_3}{C}F\ CH_2\dot{C}F_2$$

Therefore the predominant structure of $CH_2 = CF_2/CF_3CF = CF_2$ copolymers is



$$-\!\!\left(CH_2CF_2\right)\!\!-_x CF_2\underset{CF_3}{C}F -\!\!\left(CH_2CF_2\right)\!\!-_y$$

Structural irregularities such as head to head bonding are relatively minor.

(ii) $CH_2=CF_2$/Pentafluoropropene Copolymers

1H-pentafluoropropene $CF_3CF=CFH$ and 2H-pentafluoropropene $CF_3CH=CF_2$ will form copolymers with $CH_2=CF_2$. These copolymers have structures exactly analogous to the $CH_2 = CF_2/CF_3CF = CF_2$ copolymer.

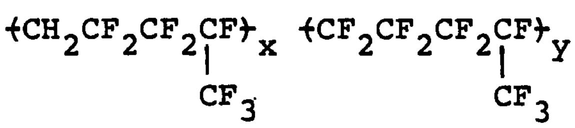
(iii) $CH_2 = CF_2/CF_2 = CFCl$ (CTFE)

These copolymers may contain sequences of PVF_2 and PCTFE because each monomer is itself able to form a homopolymer. The predominant polar effects in PVF_2 and steric effects in PCTFE have a strong influence upon the structure of the copolymer with the result that the copolymer, for the most part, may be represented

$$(CH_2CF_2)_x\text{—}(CF_2CFCl)_y\text{—}(CH_2CF_2CF_2CFCl)_z$$

(iv) Terpolymers

The structural features prevailing in terpolymers incorporating $CF_2 = CF_2$, *e.g.* the $CF_2 = CF_2/CH_2 = CF_2/CF_3CF=CF_2$ system, are determined by analogy with the copolymer $CH_2 = CF_2/CF_3CF = CF_2$ because the incorporation of $CF_2 = CF_2$ does not introduce any additional polar or steric considerations. Thus the important structural units of such a terpolymer are



$$(CH_2CF_2CF_2\underset{\displaystyle CF_3}{\underset{|}{C}F})_x \quad (CF_2CF_2CF_2\underset{\displaystyle CF_3}{\underset{|}{C}F})_y$$

I.3.(iv) Polymerisation Methods

Free-radical addition polymerisation is the principle polymerisation process employed in industrial fluorine chemistry since cationic catalysts do not promote reaction and anionic catalysts (*e.g.* lithium alkyls) react vigorously to remove fluorine. There are four main methods for the radical polymerisation of fluoroalkenes.

(i) Bulk polymerisation involves reaction of the pure monomer(s) with the initiator. This produces a very pure polymer but presents serious engineering problems due to heat dissipation and the development of hot spots.

(ii) Solution polymerisation involves mixing an inert solvent with the monomer. This overcomes the problem of heat dissipation and the need to handle viscous melts.

(iii) Suspension polymerisation involves an aqueous phase in which the monomer is suspended as droplets. The droplet size is important in determining the final physical properties of the polymer and can be controlled by the addition of suspension agents such as poly(vinyl alcohol), gelatine or water soluble cellulose derivatives.

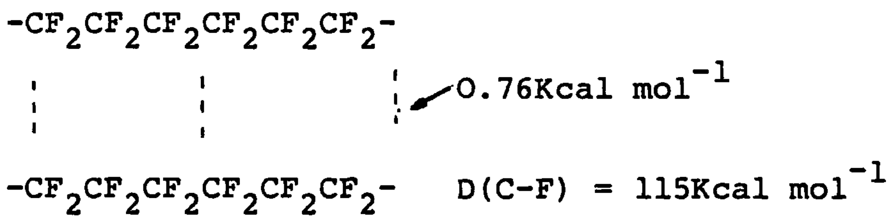
(iv) Emulsion polymerisation employs a continuous aqueous phase which helps to dissipate heat. Small micelles in which the monomer dissolves are formed by the action of an emulsifying agent, *e.g.* sulphonate esters of long chain fatty acids. Polymerisation occurs within the micelles which swell as more monomer and initiator diffuse inside from the aqueous phase.

I.B. (v) Properties of Fluoropolymers

(a) Homopolymers

(i) Polytetrafluoroethene (PTFE)

The C-F bonds in PTFE are among the strongest known at 115Kcal mol^{-1} (*c.f.* 50-100Kcal mol^{-1} for most other organic single bonds). However the interactive forces between PTFE polymer chains are very small at 0.76Kcal mol^{-1} (*c.f.* 1-10 Kcal mol^{-1} for most organic solids). This variation in bond-strength makes PTFE a very unusual solid material.



$$\begin{array}{l} -CF_2CF_2CF_2CF_2CF_2CF_2- \\ \;\vdots \qquad\quad \vdots \qquad\qquad\quad \vdots \swarrow 0.76\text{Kcal mol}^{-1} \\ -CF_2CF_2CF_2CF_2CF_2CF_2- \quad D(C\text{-}F) = 115\text{Kcal mol}^{-1} \end{array}$$

The structure of PTFE is remarkable in that the fluorine atoms are packed closely due to their size. Non-bonding electron pair repulsions between the fluorine atoms cause the polymer to twist into a helical form about its own axis (see Figure 1.4).[41]

The fluorine atoms in PTFE consequently shield the carbon skeleton from chemical attack with the result that PTFE has extreme chemical resiliance.[42] Only alkali metals, chlorine trifluoride and fluorine at high temperature and pressure degrade PTFE.[43]

PTFE is also remarkable in that it has exceptional qualities of electrical resistivity, non-flammability, weathering,

FIGURE 1.4 THE STRUCTURES OF POLYTETRAFLUOROETHENE (PTFE) AND POLYETHENE (PE)

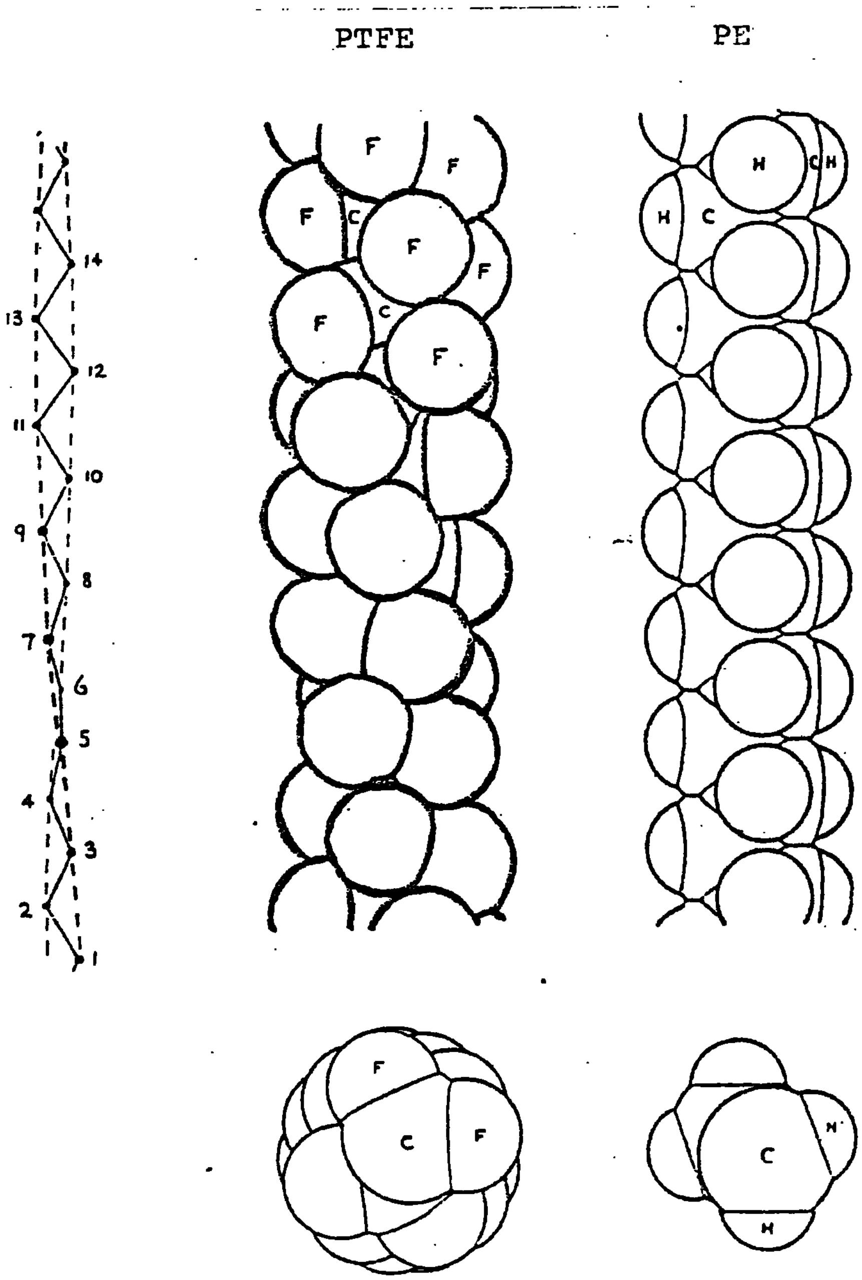


TABLE 1.3 The Properties of Some Important Homopolymers

	PCTFE	PVF	PVF_2	PVF_3	ALL
Structure	$+CF_2CFCl+_n$ >98%	$+CH_2CHF)_n$ 74%	$+CH_2CF_2+_n$ 90%	$+CHFCF_2+_n$ 85-90%	
Physical Properties:					
Optical	Thin films and annealed samples are milky and translucent (PVF films are transparent)				
Mechanical	Good creep resistance		Excellent resistance to abrasion		Good. Approach polyamides and polyesters
Melting Pt.	MPT>202°C	MPt>192°C	MPt 171°C		All are thermoplastic, *i.e.* soften then flow when heated
Thermal Stability in air (50% weight loss after 30 mins.	380°C	389°C	446°C	*c.a.*420°C	PVF_n produce HF on degradation. PCTFE undergoes chain scissions.
Chemical Inertness	Excellent	Good, except to NaOH, $PhNH_2$ and NR_3			Much higher than other engineering plastics.
Solvents (Resistance to swelling)	Excellent	Moderate	Poor in polar solvents	Good except $(CH_3)_2C{=}O$ DMF and Cyclopentanone	No better than other polyamides

low surface friction and non-adhesiveness. The main disadvantage of PTFE is that, as a dense and highly crystalline polymer, it is not viable for processes which require manipulation. The properties of the other important homopolymers are summarized in Table 1.3.

(b) Copolymers

(i) $CH_2=CF_2/CF_3CF=CF_2$ Copolymers

Neither of the homopolymers PVF_2 and poly(hexafluoropropene) are elastomers, *i.e.* after deformation these materials do not revert rapidly to their original dimensions. This is a very desirable property which is a characteristic of $CH_2=CF_2/CF_3CF=CF_2$, $CH_2=CF_2/CF_3CH=CF_2$ and $CH_2=CF_2/CF_3CF=CFH$ copolymers.

The thermal stabilities of these copolymers are high. For example at 370°-390°C 25% weight loss from $CH_2=CF_2/CF_3CF=CF_2$ copolymers occurs over 2 hours depending upon composition.[44]

These copolymers are subjected to a curing process (or vulcanization) in order to enhance their elastomeric properties and for better service life over a wider range of temperatures. The cure introduces inter-chain crosslinks which endows the copolymer with greater rigidity. This is particularly useful at higher temperatures when elastomericity due to inter-chain entanglements is lost.

TABLE 1.4 The Chemical Resistance of $CH_2=CF_2/CF_3CF=CF_2$, $CH_2=CF_2$/Pentafluoropropene Copolymers

Chemicals which have no effect	Chemicals which degrade
All Fuels, Oils, Lubricants, Hydraulic fluids, Chlorinated Solvents, Ozone, Mineral Acids, Steam, Aqueous Salt Solutions	Low Mol wt. Esters, Ethers and Ketones, Aldehydes, Amines, Organic Acids, Conc. Aqueous Alkali

The chemical inertness of the cured copolymers is high and this is summarized in Table 1.4.

(ii) $CH_2=CF_2/CF_2=CFCl$ Copolymers

This elastomer has somewhat less thermal stability than the other copolymers of $CH_2=CF_2$. At 350°C 25% weight loss occurs in 2 hours. This reduction in thermal stability is attributed to the fact that the C-Cl bond energy is 81Kcal mol^{-1} (*c.f.* Δ(C-F) = 115Kcal mol^{-1} in PTFE). The chemical inertness of this copolymer system is lowered towards reagents which will tend to eliminate HCl, *e.g.* amines and NaOH. Resistance to steam and mineral acids is excellent.

(iii) $CH_2{=}CF_2/CF_2{=}CF_2/CF_3CF{=}CF_2$ Terpolymers

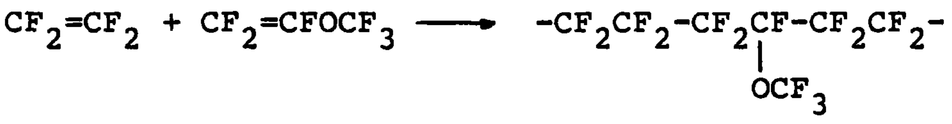
The introduction of $CF_2{=}CF_2$ into $CH_2{=}CF_2$ copolymers results in greater chemical and thermal stability but at the expense of physical properties at lower temperatures. For example the glass transition temperature of the raw terpolymer is $-17^{o}C$ whereas that of the $CH_2{=}CF_2/CF_3CF{=}CF_2$ copolymer is $-20^{o}C$.[45]

(iv) $CF_2{=}CF_2/CF_3CF{=}CF_2$ and $CF_2{=}CF_2/CF_2{=}CFOR_F$ Copolymers

In an effort to reduce the crystallinity of PTFE, copolymers of $CF_2{=}CF_2$ with $CF_3CF{=}CF_2$ are produced containing pendant $-CF_3$ groups

$$CF_2{=}CF_2 + CF_2{=}CFCF_3 \longrightarrow -CF_2CF_2CF_2\underset{\underset{\displaystyle CF_3}{|}}{C}FCF_2CF_2-$$

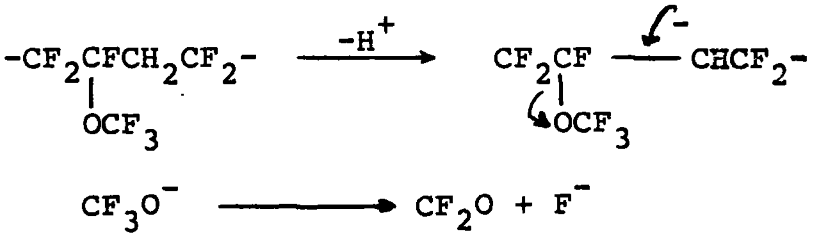
However this was found to introduce crowding at the tertiary sites, resulting in a reduction of thermal stability in comparison with PTFE. If, on the other hand, the $-CF_3$ group is attached to the polymer chain by an oxygen atom there is less crowding and higher thermal stability. Therefore $CF_2{=}CF_2$ is copolymerized with perfluoromethyl vinyl ether (PFMVE).[46-48]



$$CF_2{=}CF_2 + CF_2{=}CFOCF_3 \longrightarrow -CF_2CF_2-CF_2\underset{\underset{\displaystyle OCF_3}{|}}{C}F-CF_2CF_2-$$

The result is a series of elastomers (PFMVE content >20%) which are melt processable[5] and have chemical and thermal stability approaching the excellence of PTFE.

The cross-linking of these copolymers is achieved only by incorporation of a third comonomer (Section I.D.(iv)). $CF_3OCF{=}CF_2$ is not used in copolymers with $CH_2{=}CF_2$ because the process



$$-CF_2\underset{OCF_3}{\underset{|}{C}F}CH_2CF_2- \xrightarrow{-H^+} CF_2\underset{OCF_3}{\underset{|}{C}F} \overset{\curvearrowleft -}{—} CHCF_2-$$

$$CF_3O^- \longrightarrow CF_2O + F^-$$

is a major pathway leading to polymer degradation.

I.B. (vi) The Uses and Applications of Fluoropolymers[49]

The applications of the copolymers described above are summarized in Table 1.5.

I.C. Miscellaneous Fluoroelastomers

The structure, preparation and properties of the more interesting and/or commercially successful fluoroelastomers, are summarized in Table 1.6.

I.D. Cross-linking of Copolymers of 1,1-Difluoroethene

I.D. (i) Introduction

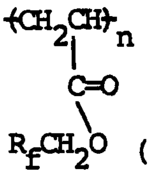
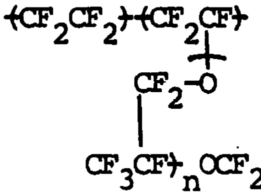
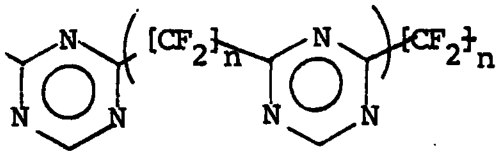
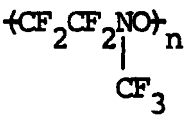
Copolymers of 1,1-difluoroethene, in the raw state, consist of long linear chain-like molecules. In this form these materials may exhibit elastomeric properties due to inter-chain entanglements, *e.g.* due to pendant $-CF_3$ groups.

TABLE 1.5 Properties and Applications of Fluoropolymers Derived from Fluoroalkenes

Material	Properties	Uses and Applications
PTFE	High electrical resistivity. Chemical Inertness. Resistance to Weathering. Low coeff. of friction.	Almost half of the PTFE made is used in Electrical Engineering. Also used for gaskets, packings, seals, pipe linings. Solar energy systems. Cooking and Photocopying.
PCTFE	Chemical Inertness Mechanical Props and Transparency.	As PTFE (though more costly). Windows for use with cryogenic fluids.[50]
PVF PVF_2	) Resistance to) Sunlight.) Processability Piezoelectric Props*	Cast into films as weather-resistant coatings for buildings. Pumps, valves, piping. Microphones, transducers, *etc*.[51]
HFP/VF_2	Resistance to Compression Set. Chemical Inertness	Sealing applications. Also used in gas chromatography as a Stationary phase
TFE/PFMVE	Processability over a wide Temperature Range. Extreme Chemical Resistance	Seals,[52] electrical connectors, gaskets, diaphragms.

* A piezoelectric material develops a potential difference upon deformation.

TABLE 1.6 Miscellaneous Fluoropolymers

Material	Structure and Preparation	Properties/Uses
Poly(fluoroalkylacrylates)	 $\left(CH_2\underset{\substack{\vert \\ C=O \\ \backslash \\ R_fCH_2O}}{CH}\right)_n$ (i) $CH_2=CHCOOH$ + R_fCH_2OH ⟶ Monomers (ii) $K_2S_2O_8$ aq. emulsion polymn.	Useful temp. range -40 to +200°C. Good O_3 u.v. and oil resistance. Used in car industry.[53]
Copolymers of TFE with F-sulphonated vinyl ethers	 $\left(CF_2CF_2\right)\left(CF_2\underset{\substack{\vert \\ CF_2-O \\ \vert \\ CF_3CF)_nOCF_2CF_2SO_2F}}{CF}\right)$ Monomer made by electrochem. fluorination.[28]	Ion selective. Used in chloro alkali cells.[54]
Polythiocarbonyl Fluoride	$\left(CF_2S\right)_n$ Rapid anionic polymerisation of $CF_2 = S$	Very resiliant. Stable to $cHNO_3$, $cNaOH$[55] but degraded by amines. Non-commercial but of great chemical interest.[56]
Poly(F-alkylene-triazines)	 Made by condensn. of fluorobisamidines[57-62]	Thermally stable at 362°C. Stable to acids.[59]
Nitroso Fluoropolymers	 $\left(CF_2CF_2\underset{\substack{\vert \\ CF_3}}{N}O\right)_n$ Copolmn. of TFE/CF_3NO, 0°C[63-68]	Useful low temp. properties.
Fluorosilicone polymers	$\left[Si(CH_2CH_2R_F)(CH_3)O\right]_n$	Very stable. Used in electrical applicns.

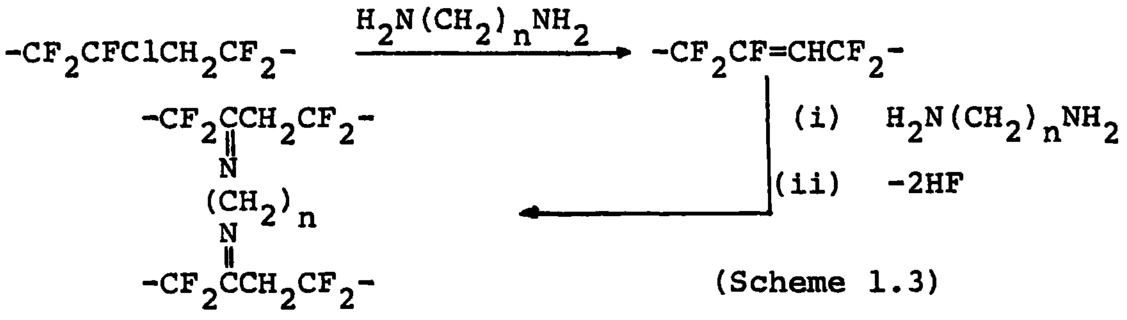
However, the temperature range of this type of effect is, in general, limited. In order to extend their elastomeric range, these copolymers are subjected to a curing process which introduces chemical bonding between the polymer molecules resulting in a stable three dimensional network.

This process is usually followed by an air-oven post-cure at elevated temperature. This second process may modify the bonding achieved in the initial cure and some sources postulate that this is the more important stage[69] in cross-linking.

An ideal cross-link should be a natural, stable extension of the copolymer structure so that reductions in chemical and thermal stability are minimised. Practically, however, this is rarely the case.

In general, there are two approaches to the cross-linking of $CH_2{=}CF_2$ copolymers.

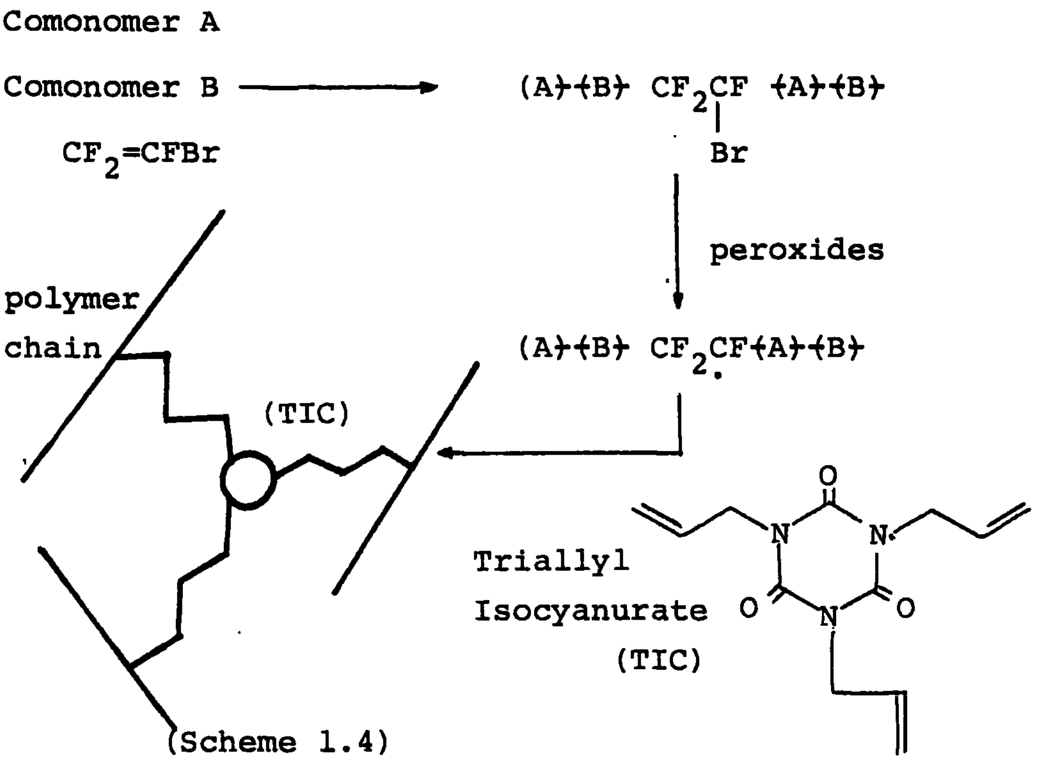
(i) Dehydrohalogenation of the polymer chain (in the presence of an acid-acceptor, *e.g.* MgO) yields sites of unsaturation, which are then linked chemically using a cross-linking agent of functionality 2 or greater. This type of cure most often involves polyamines and bisphenols.[70] For example the mechanism shown in scheme 1.3 is postulated for the curing of $CH_2{=}CF_2/CF_2{=}CFCl$ copolymers with diamines:[71]



$$\mathrm{-CF_2CFClCH_2CF_2-} \xrightarrow{\mathrm{H_2N(CH_2)_nNH_2}} \mathrm{-CF_2CF{=}CHCF_2-} \xrightarrow[\mathrm{(ii)\ -2HF}]{\mathrm{(i)\ H_2N(CH_2)_nNH_2}} \begin{array}{c} \mathrm{-CF_2CCH_2CF_2-} \\ \| \\ \mathrm{N} \\ \mathrm{(CH_2)_n} \\ \mathrm{N} \\ \| \\ \mathrm{-CF_2CCH_2CF_2-} \end{array}$$

(Scheme 1.3)

(ii) A third comonomer which itself provides the active site for cross-linking is included in the copolymerisation. For example bromotrifluoroethene (BTFE) is used as shown in scheme 1.4: [72]



(Scheme 1.4)

The second approach has been fully developed only recently[73,74] whereas a great deal of research has been directed towards a fuller understanding of the mechanisms involved in the first approach.[69]

Other materials included in a typical curing process are summarized in Table 1.7. The role of the acid-acceptor is not completely understood and has been the subject of detailed investigation as has the role and effect of the fillers.[75-78]

The properties of the cured fluoroelastomers are improved by air oven post-curing, usually at *c.a.* 230°C. For example diamine, bisphenol and peroxides vulcanizates show 50% increases in tensile strength. The post-cure also removes H_2O, a biproduct of the cure.

TABLE 1.7 Cure Ingredients and Additives

Material	Approx. Amount Used (by weight)	Purpose
Raw Polymer	100	
Basic Metal Oxides, *e.g.* MgO, CaO	6-20	Absorption of HX(X=Cl, F) released during the generation of unsat.sites
Fillers, *e.g.* Carbon Black, Austin Black, Silica, Calcium Silicate	Up to 60	Improve tensile strength, increase hardness and decrease cost, but reduce low temperature performance.
Accelerators *e.g.* Crown Ethers, Poly(ethylene ether glycol)	3	Improves certain cure parameters in bisphenol cures but exact role is unknown

I.D. (ii) Cross-Linking Involving Amines

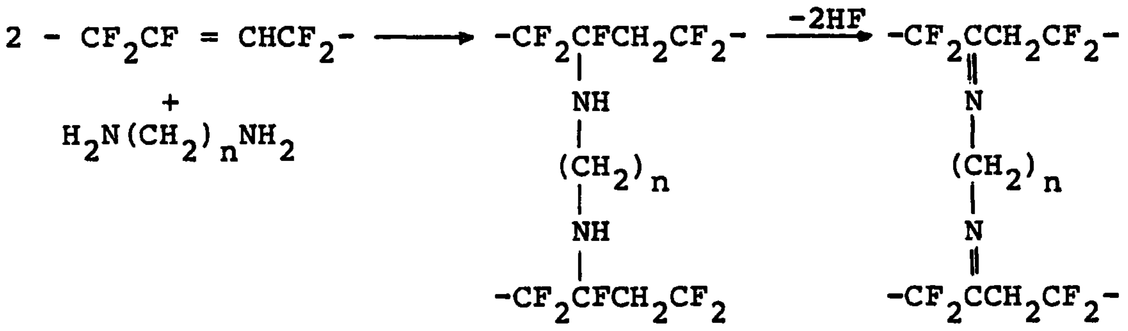
(a) Mechanistic Aspects

$CH_2=CF_2/CF_2=CFCl$ copolymers are cross-linked by primary mono- and diamines and by secondary diamines at room temperature and 50-60°C respectively.[71]

The first step in the cross-linking by all amines is the removal of either HCl or HF[79,80]

$$-CF_2CFClCH_2CF_2- \xrightarrow{\text{Amines}} -CF_2CF{=}CHCF_2-$$

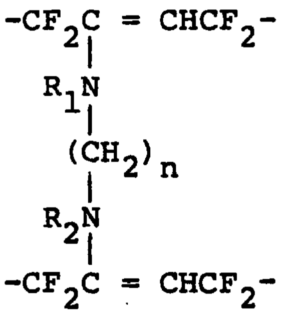
This was verified by the isolation of amine hydrochlorides and hydrofluorides. In the case of primary diamines this step is followed by addition of the amine and concomitant elimination of hydrogen fluoride



$$2\ -CF_2CF=CHCF_2- \;+\; H_2N(CH_2)_nNH_2 \longrightarrow \begin{array}{c} -CF_2CFCH_2CF_2- \\ | \\ NH \\ | \\ (CH_2)_n \\ | \\ NH \\ | \\ -CF_2CFCH_2CF_2 \end{array} \xrightarrow{-2HF} \begin{array}{c} -CF_2CCH_2CF_2- \\ \| \\ N \\ | \\ (CH_2)_n \\ | \\ N \\ \| \\ -CF_2CCH_2CF_2- \end{array}$$

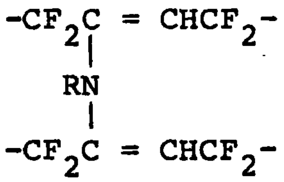
With (a) secondary diamines and (b) primary monoamines the final step clearly does not apply although dehydrofluorination of the polymer chain at the cross-link site may occur rapidly after the addition step to give cross-links of the form

(a)



$$\begin{array}{c} -CF_2C=CHCF_2- \\ | \\ R_1N \\ | \\ (CH_2)_n \\ | \\ R_2N \\ | \\ -CF_2C=CHCF_2- \end{array}$$

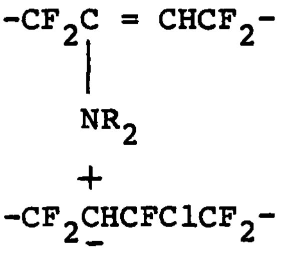
(b)



$$\begin{array}{c} -CF_2C=CHCF_2- \\ | \\ RN \\ | \\ -CF_2C=CHCF_2- \end{array}$$

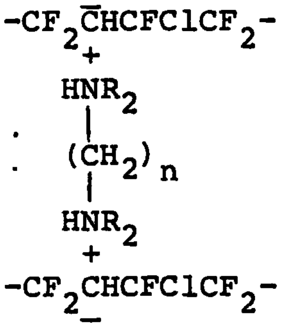
However, gelation of polymer solutions was also observed using (c) secondary monoamines (R_2NH) at 50-60°C and (d) tertiary diamines ($R_2N(CH_2)_nNR_2$) at 90-100°C. These observations would seem to indicate the involvement of quaternary ammonium salts.

(c)



$$\begin{array}{c} -CF_2C=CHCF_2- \\ | \\ NR_2 \\ + \\ -CF_2\underset{-}{C}HCFClCF_2- \end{array}$$

(d)



$$\begin{array}{c} -CF_2\overset{-}{C}HCFClCF_2- \\ + \\ HNR_2 \\ | \\ (CH_2)_n \\ | \\ HNR_2 \\ + \\ -CF_2\underset{-}{C}HCFClCF_2- \end{array}$$

The acidity of the hydrogen atoms is attributable to the strong electronegative effect of the neighbouring perhaloalkyl groups.

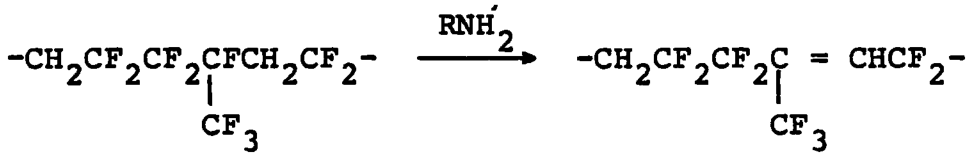
The fact that tertiary mono amines produce cross-links at 180-190°C presents an interesting mechanistic problem which has not been explained.

$CH_2=CF_2/CF_3CF=CF_2$ Copolymers

The $CH_2=CF_2/CF_3CF=CF_2$ copolymer system is less responsive than the $CH_2=CF_2/CF_2=CFCl$ system. Only primary amines achieve cross-linking below 190°C. The mechanisms proposed for this process are conflicting.

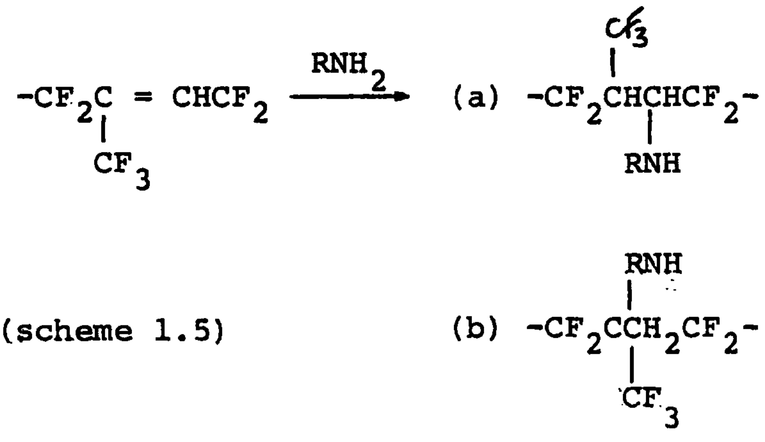
In comparison with the $CH_2=CF_2/CF_2CFCl$ system, elimination of HF occurs less readily than that of HCl, consequently higher temperatures are required in order to cure $CH_2=CF_2/CF_3CF=CF_2$ systems. Also, preferential elimination of HF occurs at tertiary sites

e.g.



$$-CH_2CF_2CF_2\underset{CF_3}{\underset{|}{C}}FCH_2CF_2- \xrightarrow{RNH_2'} -CH_2CF_2CF_2\underset{CF_3}{\underset{|}{C}} = CHCF_2-$$

Addition of the amine to this type of unsaturated site may occur in two ways (scheme 1.5)

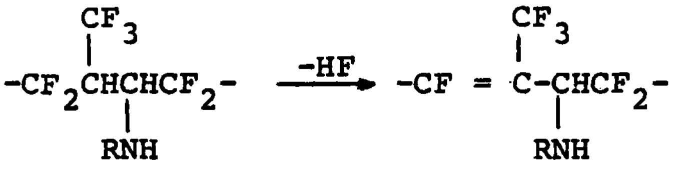


$$-CF_2\underset{CF_3}{\underset{|}{C}} = CHCF_2 \xrightarrow{RNH_2} \text{(a)}\ -CF_2\overset{CF_3}{\overset{|}{C}}H\underset{RNH}{\underset{|}{C}}HCF_2-$$

$$\text{(b)}\ -CF_2\underset{CF_3}{\underset{|}{\overset{RNH}{\overset{|}{C}}}}CH_2CF_2-$$

(scheme 1.5)

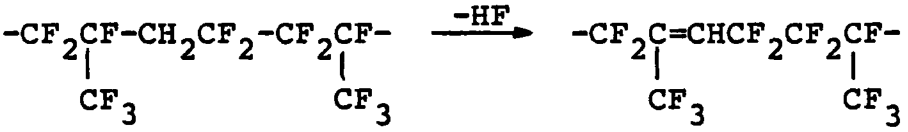
The structure (a) is the more feasible produce of nucleophilic addition because of the activating effect of the $-CF_3$ group. The experimental observation that 4 moles of HF are eliminated per mole of cross-links formed[77] is further evidence supporting the structure (a) since it is much more likely to lose HF than structure (b).



$$-CF_2\underset{RNH}{CH}\overset{CF_3}{C}HCF_2- \xrightarrow{-HF} -CF=\overset{CF_3}{C}-\underset{RNH}{C}HCF_2-$$

(a) (c)

A study using ^{19}F nmr spectroscopy of dehydrofluorination of $CH_2=CF_2/CF_3CF=CF_2$ copolymers in solution using $nBu_4N^+OH^-$ indicated that sites in which a $-CH_2CF_2-$ unit is isolated between two $-CF_2CF(CF_3)-$ units are the most easily dehydrofluorinated.[49]



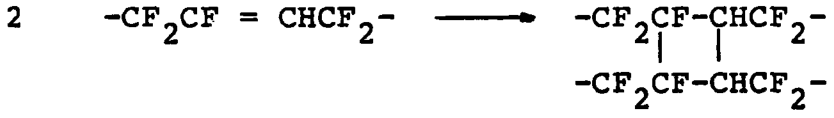
$$-CF_2\underset{CF_3}{C}F-CH_2CF_2-CF_2\underset{CF_3}{C}F- \xrightarrow{-HF} -CF_2\underset{CF_3}{C}=CHCF_2CF_2\underset{CF_3}{C}F-$$

Consequently solutions of copolymers of $CF_2=CFCF_3$ gel more quickly than those not containing $-CF_2CF(CF_3)-$.[49] This is apparent from the data shown in Table 1.8.

TABLE 1.8 Gel Rates of Certain Copolymers by $H_2N(CH_2)_6NH_2$ in DMAC at 20°C

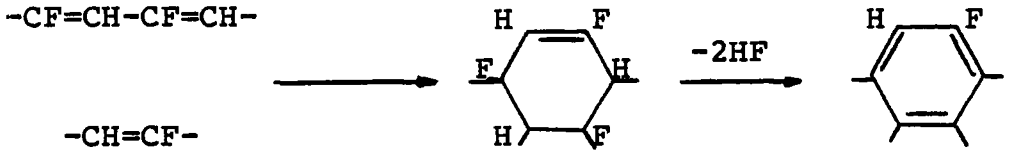
Copolymer (mol fractions)	Time to form a firm gel
$CH_2=CF_2(0.61)CF_3CF=CF_2(0.17)CF_2=CF_2(0.22)$	1.22 min.
$CH_2=CF_2(0.78)CF_3CF=CF_2(0.22)$	3.75 min.
$CH_2=CF_2(0.74)CF_3CF=CF_2(0.16)CF_2=CF_2(0.10)$	4.75 min.
$CH_2=CF_2(0.82)CF_2=CF_2(0.18)$	>2 hour
$CH_2=CF_2$ (1.00)	>10 days

Some sources have proposed the interaction of unsaturated sites alone to form cross-links



$$2 \quad -CF_2CF=CHCF_2- \longrightarrow \begin{array}{c} -CF_2CF-CHCF_2- \\ \;\;\;\;| \quad\;\; | \\ -CF_2CF-CHCF_2- \end{array}$$

although it has been shown that this reaction does not occur when hydrogen is attached to the double-bond.[81] Alternatively a Diels-Alder mechanism has been proposed.



However conjugated materials failed to cross-link in the absence of amines.[71] Yet differential thermal analysis of $CH_2=CF_2/CF_3CF=CF_2$ systems treated with the acid-acceptor MgO alone indicate a certain amount of cross-linking.[75] Therefore reaction between unsaturated sites cannot be wholly discounted.

More definitive information from model studies should clarify the exact nature of this cross-linking process (Section I.E.) although this area of research has lapsed due to recent developments of more stable cross-linking processes.

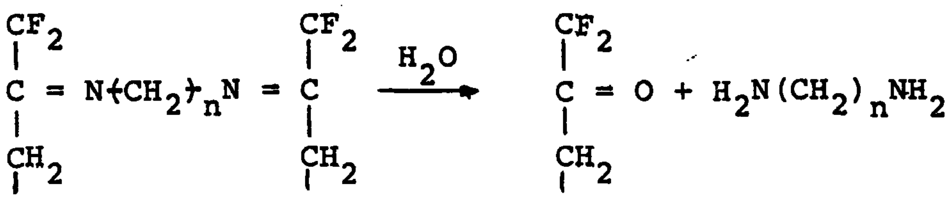
(b) Stability Considerations

In practice amines are very reactive towards $CH_2=CF_2$ copolymers, causing scorching. Therefore their Schiff bases are used. In order to generate the free amine water is required and this is overcome by the reactions

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

$$MgO + 2RNH_3\overset{+}{}\overset{-}{F} \longrightarrow MgF_2 + 2RNH_2 + H_2O$$

However the presence of water, particularly in the post-cure where it is slowly removed, promotes hydrolysis of the cross-links.[77]



$$\begin{array}{ccccc} CF_2 & & CF_2 & & CF_2 \\ | & & | & & | \\ C & = N(CH_2)_nN = & C & \xrightarrow{H_2O} & C = O + H_2N(CH_2)_nNH_2 \\ | & & | & & | \\ CH_2 & & CH_2 & & CH_2 \\ | & & | & & | \end{array}$$

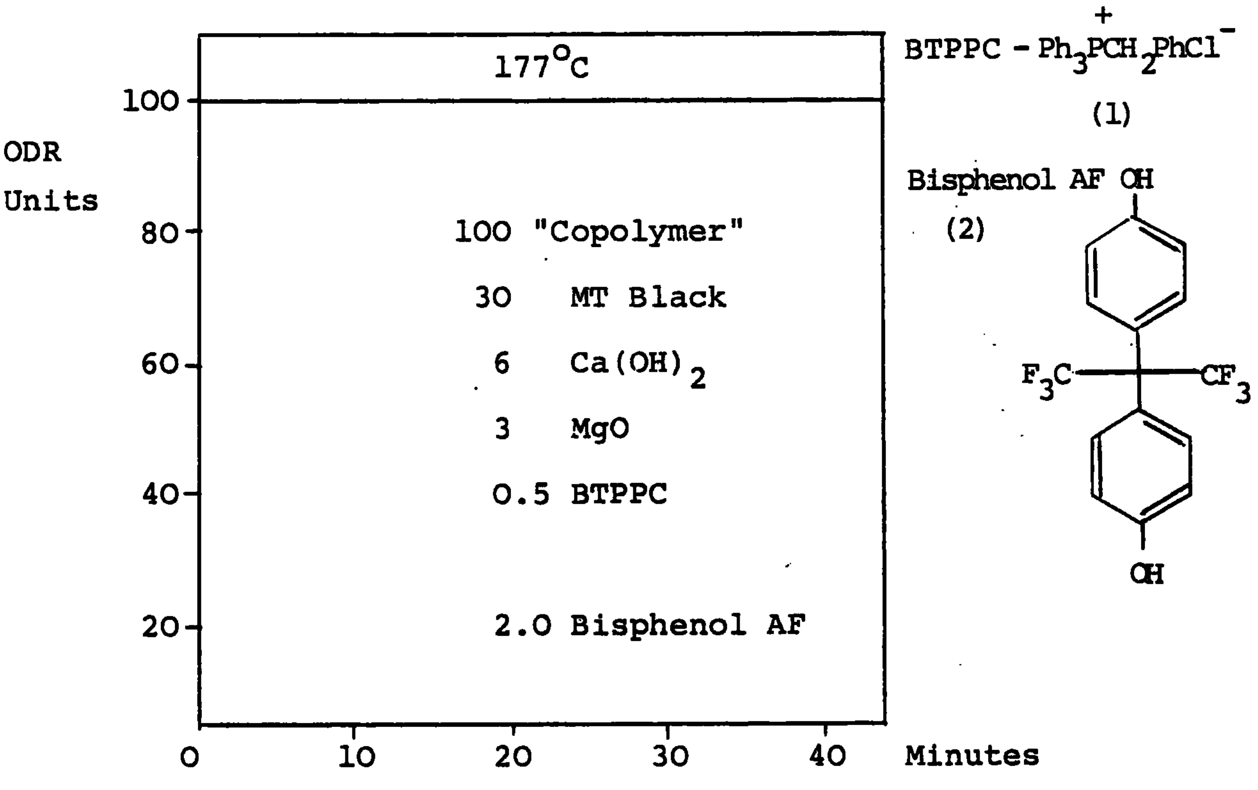
This process also occurs during the end-use of the polymer. Furthermore, unsaturated sites generated during the curing process, which have not been converted to cross-links, are susceptible to attack by aggressive reagents and therefore also lead to degradation. Consequently amine cross-linking is used for only a small percentage of the $CH_2=CF_2$ copolymers produced.

I.D. (iii) Cross-Linking Involving Bisphenols

(a) Compounding

Figure 1.9 outlines a standard cure system for a $CH_2=CF_2/CF_3CF=CF_2$ copolymer with a molar ratio 3.5:1 in favour of $CH_2=CF_2$.[49] The progress of the cure was followed using oscillating disc rheometry as shown in Figure 1.5. (This technique correlates the amount of cross-linking with the "stiffness" of the copolymer[82]).

FIGURE 1.5 ODR Graph of $CH_2=CF_2/CF_3CF=CF_2$ Copolymer Cure using Bisphenol AF



The remarkable features of this curing process are

(i) 75% of the cure occurs within 1 minute

(ii) No cure occurs in the absence of BTPPC (1)

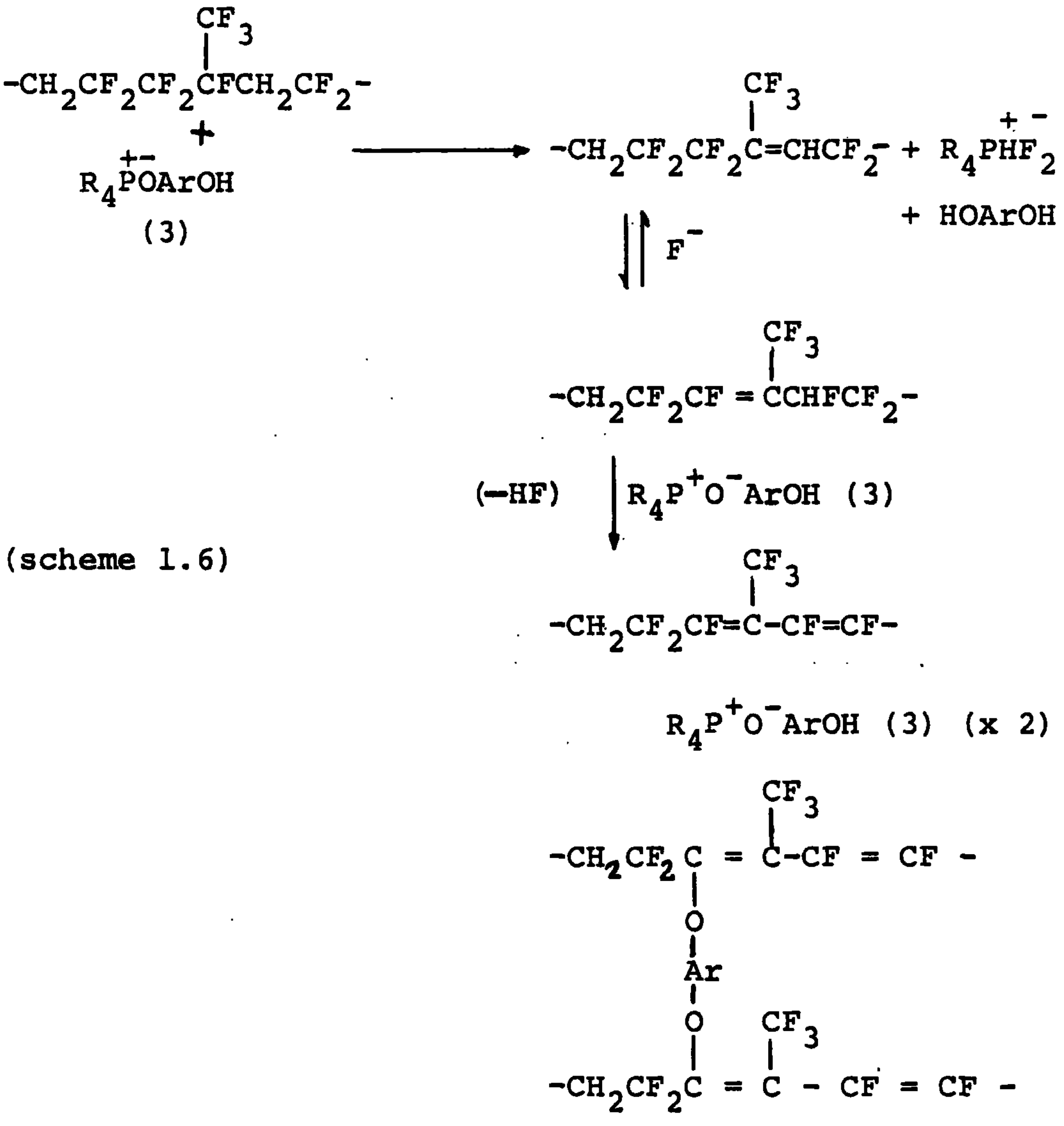
(iii) A distinct induction period of *c.a.* 5 minutes exists in which no cross-links are formed.

(b) Mechanistic Considerations

It is postulated that the bisphenol (2), on contact with the quaternary phosphonium chloride (1), forms a salt(3) with the elimination of hydrogen chloride [49]

$$\underset{(1)}{Ph_3\overset{+}{P}CH_2Ph\overset{-}{Cl}} + \underset{(2)}{HOArOH} \longrightarrow Ph\,\overset{+}{P}CH_2Ph\,\overset{-}{O}ArOH \;(3) + HCl$$

This new phosphonium salt (3) necessarily functions as both base, in eliminating HF from the saturated copolymer, and nucleophile in forming cross-links. The mechanism proposed by Smeigel is shown in scheme 1.6.



(scheme 1.6)

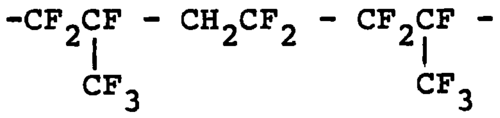
In considering the curing of VF_2 copolymers (and terpolymers) with HFP and TFE it is instructive to examine:

(i) the reactivity of these systems towards base.

(ii) the behaviour of the resultant unsaturated systems towards the bisphenolate salt (1).

(i) <u>Reactivity Towards Base</u>

The three systems to consider are (a) $CH_2{=}CF_2/CF_3CF{=}CF_2$ (b) $CH_2{=}CF_2/CF_2{=}CF_2$ and (c) $CH_2{=}CF_2/CF_2{=}CF_2/CF_3CF{=}CF_2$. ^{19}F nmr. studies have shown that the sites in (a) most sensitive to removal of HF are [49]



$$-CF_2\underset{CF_3}{\underset{|}{CF}} - CH_2CF_2 - CF_2\underset{CF_3}{\underset{|}{CF}} -$$

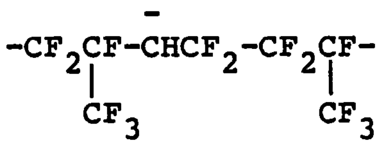
while in (b) the only such site is

$$-CF_2CF_2- CH_2CF_2 - CF_2CF_2-$$

Comparison of the rates of gelation of copolymers (a) and (b), of equal molar ratio $CH_2{=}CF_2$, showed that these sites had approximately equal reactivity. [49]

Consider the stability of the respective carbanions upon removing H^+:

(a)

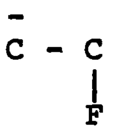


$$-CF_2\underset{CF_3}{\underset{|}{CF}}-\overset{-}{C}HCF_2-CF_2\underset{CF_3}{\underset{|}{CF}}-$$

(b) $-CF_2CF_2-\overset{-}{C}HCF_2-CF_2CF_2-$

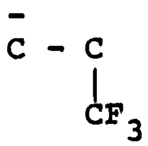
Since a fluorine atom β- to a negative charge centre has been shown to have a similar stabilizing effect to that of a $-CF_3$ group (w.r.t. hydrogen) [83]

e.g. (b)



$$\overset{-}{C} - \underset{F}{\underset{|}{C}}$$

(a)

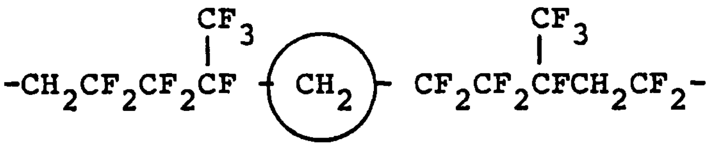


$$\overset{-}{C} - \underset{CF_3}{\underset{|}{C}}$$

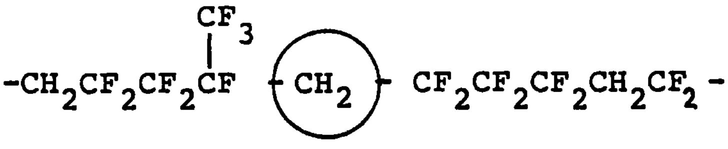
then a similar reactivity would be predicted for HF elimination from each system.

However upon removal of HF from the system (a) there is more relief of crowding than in system (b) [84] which, together with the lower C-F bond strength of tertiary fluorine [85] would indicate that system (a) should be more reactive. On the whole it is therefore surprising that both systems show equal reactivity.

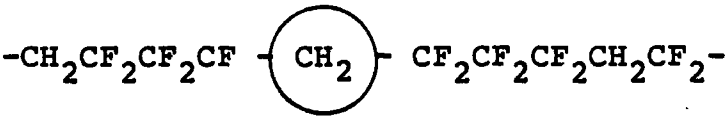
Consideration of the terpolymer system (c) is more complex because there are four possible environments for the $-CH_2-$ group


$-CH_2CF_2CF_2\overset{CF_3}{\overset{|}{C}}F-\boxed{CH_2}-CF_2CF_2\overset{CF_3}{\overset{|}{C}}FCH_2CF_2-$

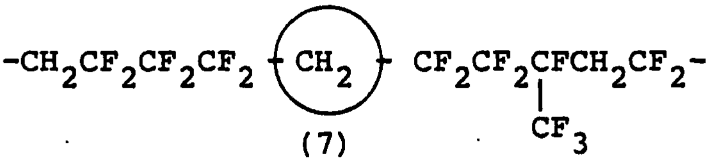
(4)


$-CH_2CF_2CF_2\overset{CF_3}{\overset{|}{C}}F-\boxed{CH_2}-CF_2CF_2CF_2CH_2CF_2-$

(5)


$-CH_2CF_2CF_2CF-\boxed{CH_2}-CF_2CF_2CF_2CH_2CF_2-$

(6)

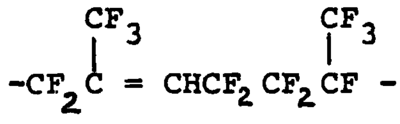

$-CH_2CF_2CF_2CF_2-\boxed{CH_2}-CF_2CF_2\underset{CF_3}{\underset{|}{C}}FCH_2CF_2-$

(7)

Using the earlier comparison of the reactivity of $CH_2=CF_2/CF_3CF=CF_2$ copolymers with $CH_2=CF_2/CF_2=CF_2$ copolymers, it follows that there should be equal reactivity associated with (4) and (6) above. Since, structurally, (4) and (5) are similar and (6) and (7) are also similar, it is understandable that the terpolymer system (c) has similar reactivity towards base (compared with the copolymer systems) (a) and (b).[49]

(ii) Reactivity of Unsaturated Systems towards the Bisphenolate Salt (3)

Again consider the systems (a) $CH_2=CF_2/CF_3CF=CF_2$ (b) $CH_2=CF_2/CF_2=CF_2$ and (c) $CH_2=CF_2/CF_2=CF_2/CF_3CF=CF_2$. Upon removal of HF from the base-sensitive site the relevant structures are (8), (9), (10A) and (10B) respectively:

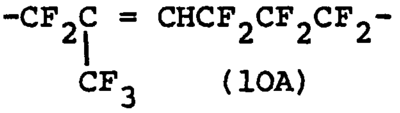


$$-CF_2\overset{CF_3}{\overset{|}{C}} = CHCF_2CF_2\overset{CF_3}{\overset{|}{C}}F -$$

(8)

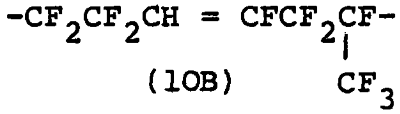
$$-CF_2CF_2CH = CFCF_2CF_2-$$

(9)



$$-CF_2\underset{CF_3}{\underset{|}{C}} = CHCF_2CF_2CF_2-$$

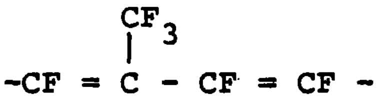
(10A)



$$-CF_2CF_2CH = CFCF_2\underset{CF_3}{\underset{|}{C}}F-$$

(10B)

In the presence of active F^- only the structures (8) and (10A) isomerise with concomitant loss of HF to give conjugated diene systems as described earlier (Section I.D.(ii))[49]



$$-CF = \overset{CF_3}{\overset{|}{C}} - CF = CF -$$

(11)

Solution studies using cyclic amidines, which remove HF but are too hindered to behave as nucleophiles, showed that the bisphenolate salt (3) reacts rapidly with the unsaturated copolymer in comparison to removing HF.[49] Therefore, since HF removal occurs at about the same rate, whatever the system, it is possible to predict the relative reactivities of the systems (a), (b) and (c) in terms of the rate of production of conjugated diene sites(11)(above). In system (a) all initial unsaturated sites lead to dienes whereas in (b) none at all and in (c) only half (*i.e.* only 10A). Therefore the rates of gelation should occur in the following decreasing order

$CH_2{=}CF_2/CF_3CF{=}CF_2 > CH_2{=}CF_2/CF_2{=}CF_2/CF_3CF{=}CF_2 > CH_2{=}CF_2/CF_2{=}CF_2$
(a) (c) (b)

for equal mol-fractions of $CH_2{=}CF_2$. The experimental observations of Smeigel were in accordance with this model.[49]

The later stages of the cross-linking process may well be more complicated. However, solution studies become difficult after gelation has occurred.

(c) Stability Considerations

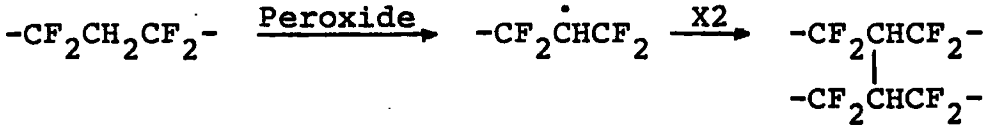
Bisphenol cures have largely replaced amine cures due to their better end-use properties, for example, the storage stability of $CH_2{=}CF_2$ copolymer systems cured with bisphenol AF is excellent[86] and mould-staining and fouling during processing is minimized.

However, aromatic and aliphatic amines, succinimide and succinic esters, steam and aqueous acids degrade the bishphenol cured systems.[26] Model studies directed towards this problem are discussed in Chapter Four.

I.D. (iv) The Use of Cure-Site Comonomers

(a) Introduction

In principle, $CH_2{=}CF_2$ fluoroelastomers can be cross-linked by the action of peroxides alone *via* the abstraction of hydrogen atoms

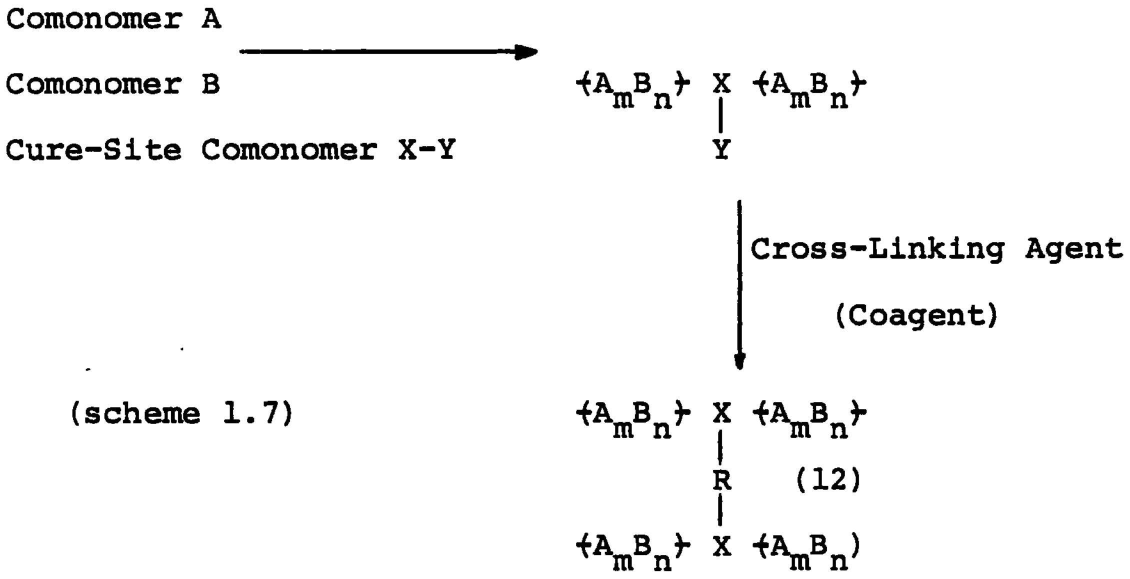


$$-CF_2CH_2CF_2- \xrightarrow{\text{Peroxide}} -CF_2\dot{C}HCF_2 \xrightarrow{X2} \begin{array}{l} -CF_2CHCF_2- \\ \quad\quad\;| \\ -CF_2CHCF_2- \end{array}$$

with the advantage that no heteroatom is involved in the cross-link. In practice, however, this leads to poor cure responses because of the large energy required to abstract $H^{\bullet}$ and the high reactivity of the peroxides needed which causes scorching. An approach is needed, therefore, which enhances response to milder peroxides.

(b) Mechanistic Considerations

In principle the concept of incorporating a cure-site comonomer into a copolymer, in order to promote cross-linking, may be represented by scheme 1.7.



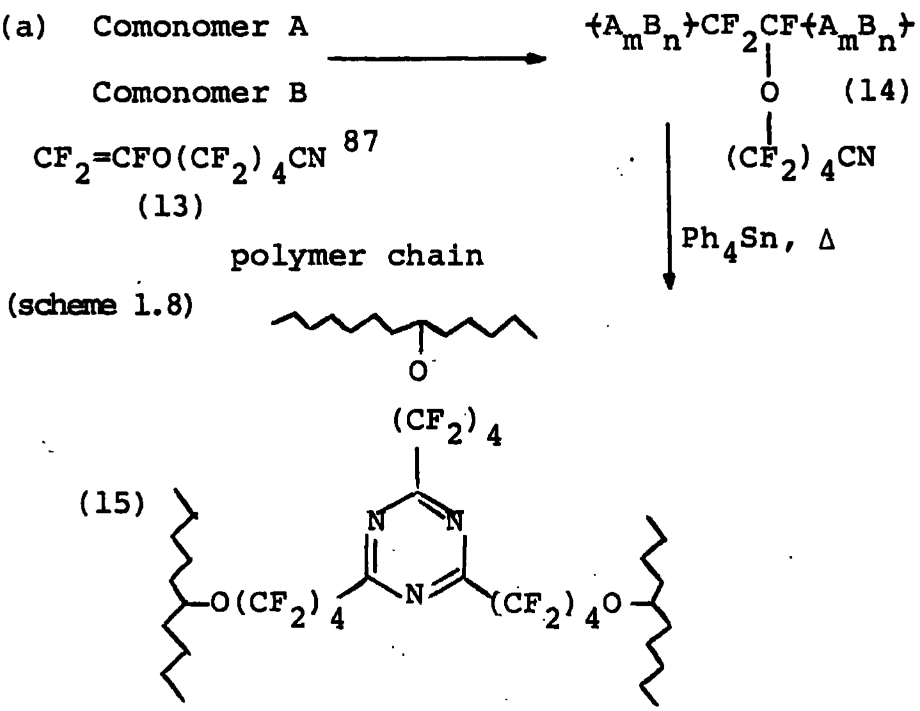
(scheme 1.7)

(12)

The cross-link -R- in (12) may still contain the group -X in either (a) a modified form (scheme 1.8) or (b) not at all.

e.g.

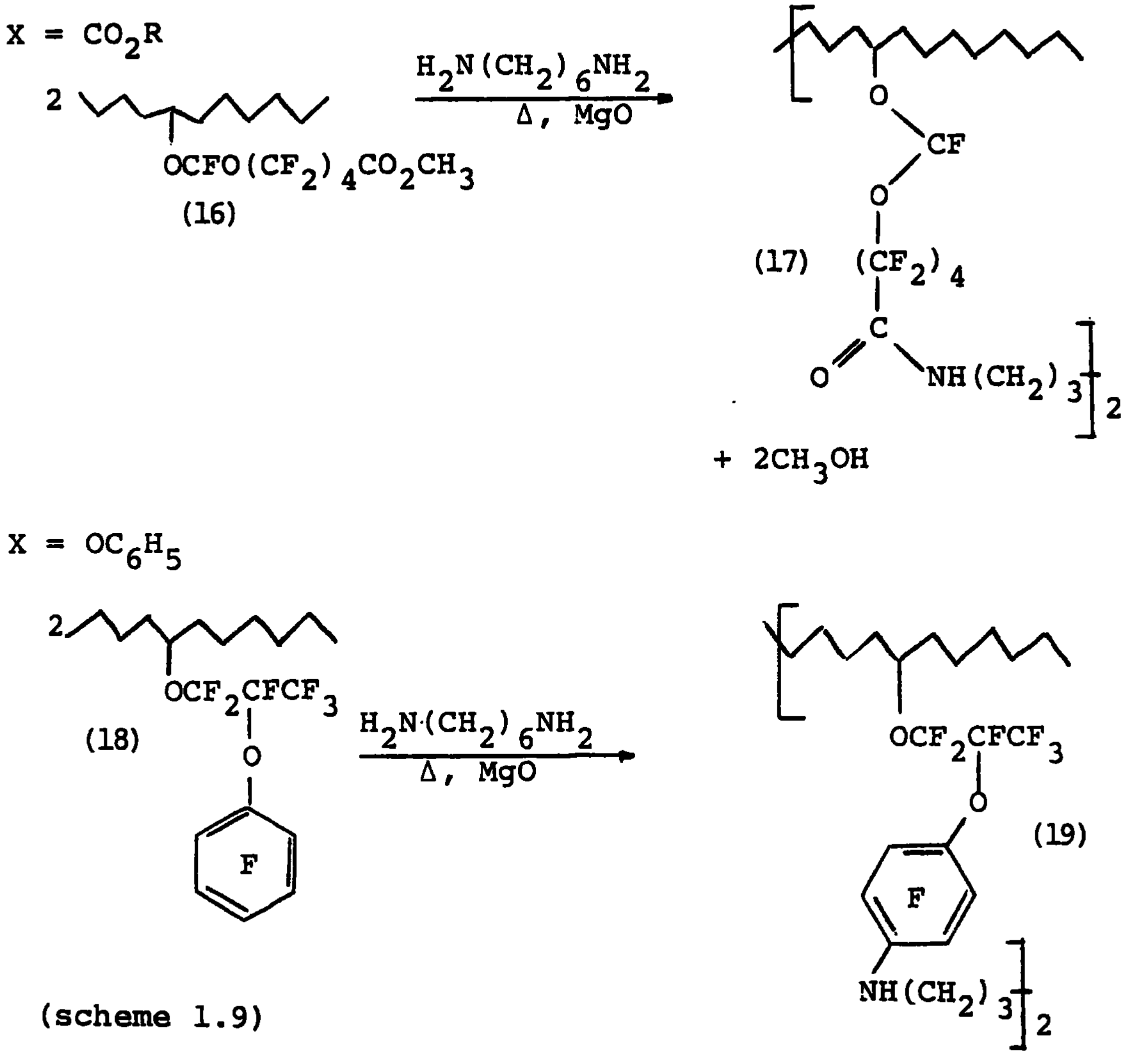
(a)



(b) Incorporation of $CF_2{=}CFBR$ (X-Y) as outlined in Section I.D.(i) scheme 1.4.

Both of the above processes are facile owing to the enhanced reactivity at the cure-site and make practical cure times possible using safe non-scorching initiators.

Clearly the cure-site comonomer should not inhibit the initial copolymerisation process. For example, if it contained two vinyl groups the reactivity of each should be different, *i.e.* one group should be reactive in free-radical polymerisation (*e.g.* $S_2O_8^{2-}/Fe^{2+}$, 40°C) while the other group must provide good cure response at temperatures above 150°C. This is illustrated by the use of perfluorovinyl ethers of the form $CF_2{=}CFOR_FX$ (X=Cn, [see (13) above], CO_2R, OC_6F_5) which are now known to be successful cure-site comonomers. They are easily copolymerised but do not inhibit the copolymerisation process.[87,88] Cross-linking is achieved using poly-functional amines at temperatures above moulding requirements whilst not affecting the performance of the final material. Examples are outlined in scheme 1.9.



(scheme 1.9)

The thermal and chemical stabilities of these systems are excellent, though for X = OC_6F_5 there is some reduction in thermal stability.

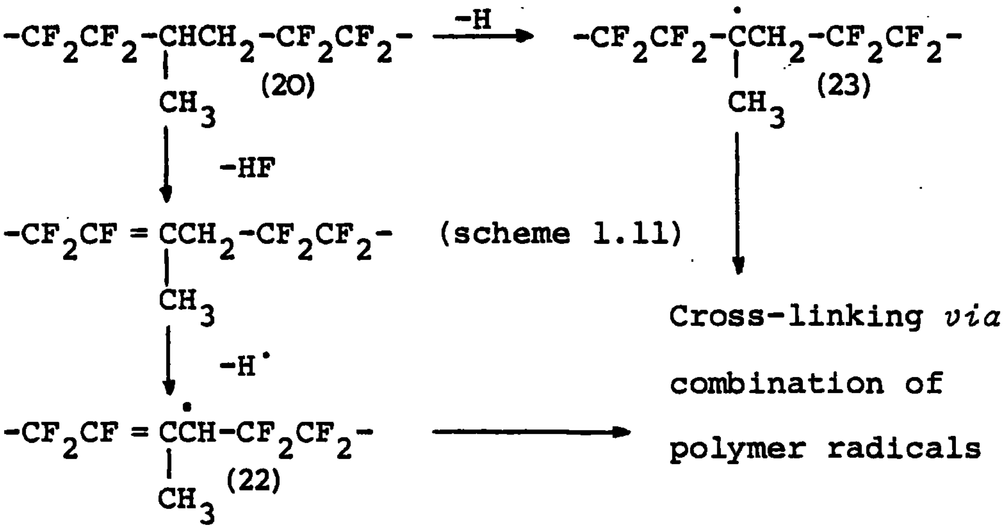
I.D. (v) Other Methods

There are two other important methods for cross-linking copolymers of $CH_2{=}CF_2$; (i) radiation techniques (ii) *via* peroxides alone. Both methods, assumed to produce carbon-carbon cross-links, have rarely attained industrial importance.

(i) Radiation Techniques

Radiation in the form of α-particles, slow neutrons, X or γ-ray photons, liberates secondary electrons upon passing through matter (often the wall of a reaction vessel). These secondary electrons interact directly with organic molecules to form free-radicals.[27] Overall, therefore, the reactions can resemble those brought about by free-radical initiators.

The discovery in 1955 that irradiated PTFE gives a strong e.s.r. signal[89] (attributed to the polymer radical $-CF_2\dot{C}FCF_2-$) prompted extensive research into the radiation treatment of fluorinated polymers. Treatment of the VF_2/HFP copolymer system with β-particles (low energy electrons) results in cross-linking. It is proposed that radicals formed on the copolymer backbone combine to form C-C bonds between polymer chains. This method of cross-linking (or use of cure-site comonomers) has to be used with propene/TFE copolymers, for which polyamines and polyhydroxyphenols are ineffective. Scheme 1.11 shows the mechanisms proposed for this process.[90]


(scheme 1.11)

The presence of HF in the system is considered to have a stabilizing effect upon the polymer radicals formed, thus reducing the rate of cross-linking. This effect can be reduced by the presence of MgO, $Ca(OH)_2$ or KOH.[91]

(ii) Peroxide Curing

The problems encountered with peroxide cures, in the absence of cure-site comonomers, have been described (Section I.D.(iv), *i.e.* highly active peroxides are required to promote the process

$$R_FCXYCH_2R_F \longrightarrow R_FCXY\dot{C}HR_F$$

resulting in scorching.

However, vulcanizates of $CH_2{=}CF_2/CF_3CF{=}CF_2$ and $CH_2{=}CF_2/CF_2{=}CFCl$ copolymers using aromatic peroxides have been reported.[92] These cures, however, are generally poorer than those obtained with amines and bisphenols for two reasons:

(i) The cross-linking density is lower for peroxide formulations.

(ii) Although the degradation effect upon the polymer of peroxide cures is less than that of amine and bisphenol cures, the vulcanizates are thermally much less stable than the raw gums.

I.E. Model Studies Related to Cross-Linking

I.E. (i) Introduction

The amount of definitive information which can be obtained from solution studies about the mechanistic aspects of cross-linking is limited for two reasons:

(i) Structure determination once gelation has occurred is difficult because n.m.r. data is not attainable.

(ii) Actual polymer cures are, in general, carried out in bulk, without solvent interactions.

Model compounds containing structures closely related to those known to occur in the real systems often contain less than ten carbon atoms. The models, and their derivatives, can therefore be characterized fully using the powerful laboratory techniques available. Thus definitive information can be obtained about the chemistry most likely to occur in the real systems.

For example, in order to investigate the peroxide-induced cross-linking of $CH_2{=}CF_2$ copolymers, the following model reactions were attempted, albeit unsuccessfully[76]

$$\underset{(24)}{C_2F_5CF_2CH_2C_3F_7} \xrightarrow{(PhCO_2)_2} \text{No Dimer}$$

$$\underset{(25)}{C_2F_5CF{=}CHC_3F_7} \xrightarrow{(PhCO_2)_2} \text{No Dimer}$$

where a dimer represents a cross-link.

I.E. (ii) Discussion of Results Obtained

Model studies related to the cross-linking of $CH_2{=}CF_2$ elastomers have been carried out in three areas which are discussed below

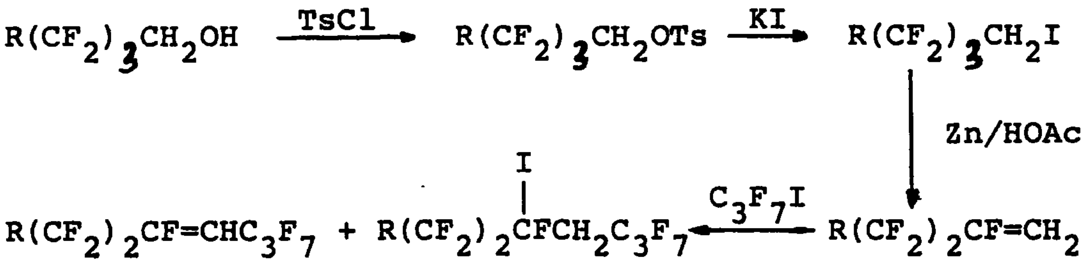
(a) Amine Cross-linking.

(b) The effect of peroxides.

(c) Cross-linking involving $CF_2{=}CFBr$

(a) Amine Cross-Linking

Paciorek and coworkers synthesized the four model compounds (25-28) as shown in scheme 1.10.[93,94]



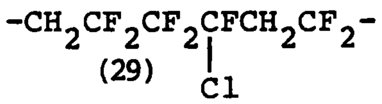
$$\begin{tikzcd} R(CF_2)_3CH_2OH \arrow[r, "TsCl"] & R(CF_2)_3CH_2OTs \arrow[r, "KI"] & R(CF_2)_3CH_2I \arrow[d, "Zn/HOAc"] \\ R(CF_2)_2CF{=}CHC_3F_7 + R(CF_2)_2\overset{\overset{I}{|}}{C}FCH_2C_3F_7 & & R(CF_2)_2CF{=}CH_2 \arrow[ll, "C_3F_7I"'] \end{tikzcd}$$

R = F (25) R = F (27)

R = CF_2H (26) R = CF_2H (28)

Scheme 1.10

Since the HCF_2- group is comparatively inert, these compounds resemble the copolymer system



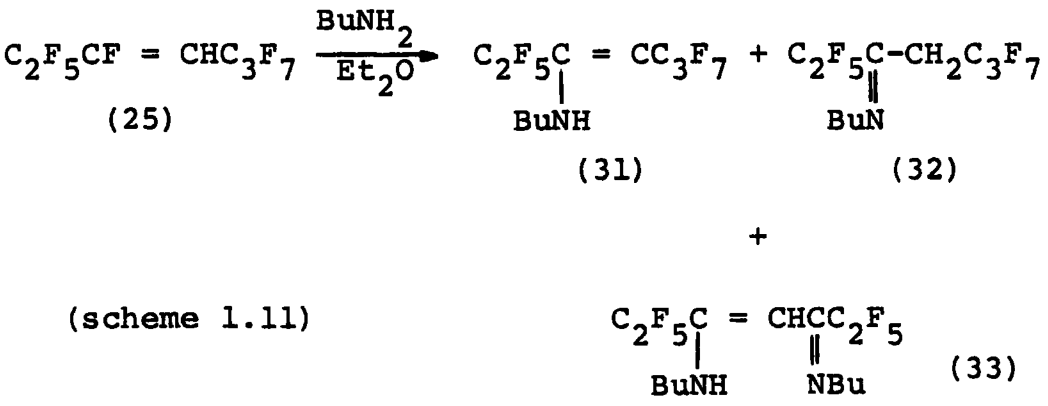
$$-CH_2CF_2CF_2\underset{\underset{Cl}{|}}{C}FCH_2CF_2-$$

(29)

The model (24) and the model $HCF_2(CF_2)_2CF_2CH_2C_3F_7$ (30) were treated with $BuNH_2$, Bu_2NH and NEt_3 with the results that dehydrofluorination was the initial step in all cases to give (25) and (26)

$CF_3CF_2CF = CHCF_2CF_2CF_3$ (25) $HCF_2CF_2CF_2CF = CHCF_2CF_2CF_3$ (26)

Further treatment of (25) with $BuNH_2$ resulted in a mixture of addition-elimination products as outlined in scheme 1.11.

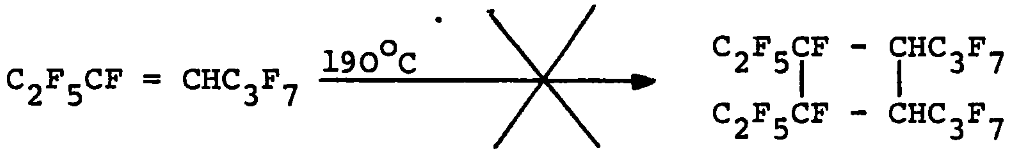


$$\underset{(25)}{C_2F_5CF = CHC_3F_7} \xrightarrow[Et_2O]{BuNH_2} \underset{(31)}{C_2F_5\underset{\underset{BuNH}{|}}{C} = CC_3F_7} + \underset{(32)}{C_2F_5\underset{\underset{BuN}{\|}}{C}-CH_2C_3F_7} + C_2F_5\underset{\underset{BuNH}{|}}{C} = CH\underset{\underset{NBu}{\|}}{C}C_2F_5 \quad (33)$$

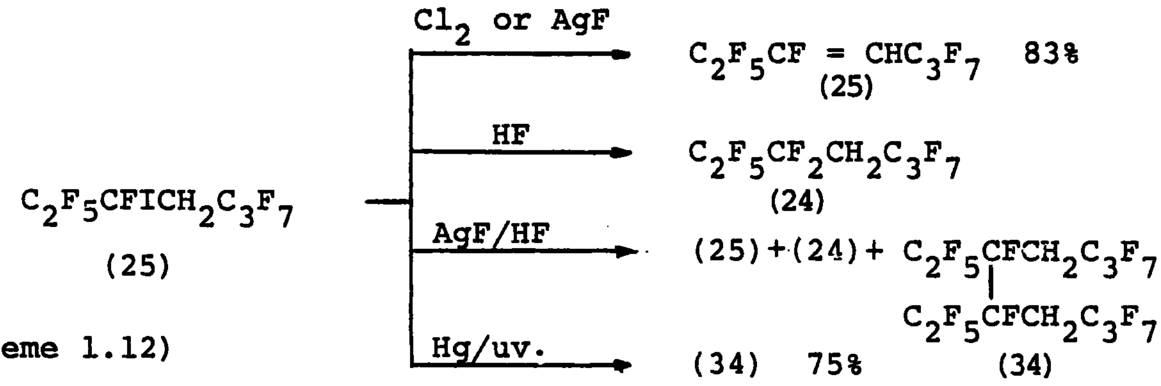
(scheme 1.11)

The infra-red spectrum of the conjugated model (33) resembles most closely that of the cross-linked polymer in the 5-7μ region, which indicates that structures of the type present in (33) may be of major significance.

It is concluded, therefore, that while dehydrohalogenation is the initial step, the cross-links are formed either by addition of the amine to the unsaturated sites or by interaction of the unsaturated sites alone. In order to test the latter case, the model (25) was heated over a prolonged period but found to be unreactive.



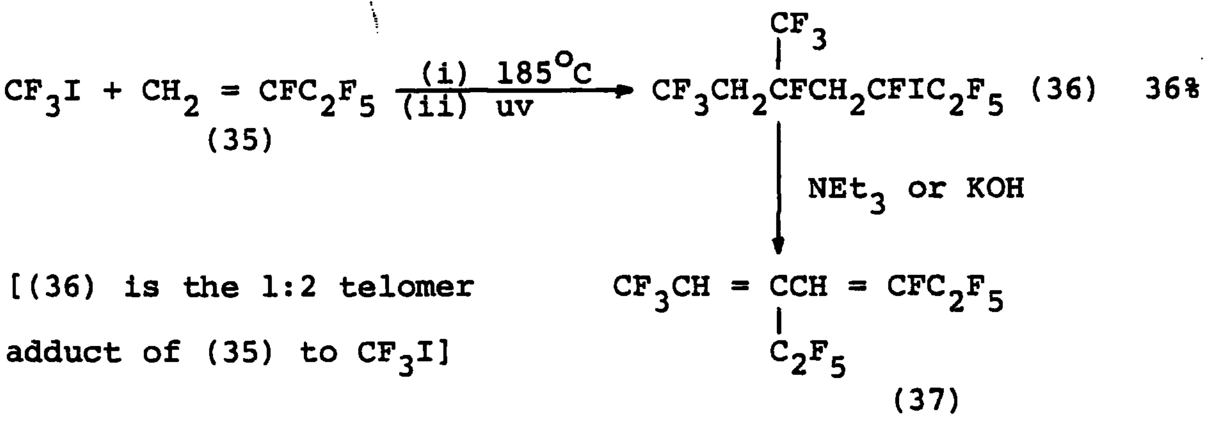
This is in agreement with the findings of Park *et al* that cyclobutane rings are not formed when hydrogen is one of the substituents[95] (Section I.D. (ii)). In order to produce models more closely resembling the CH_2=CF_2/CF_2=CFCl copolymer systems, the reactions outlined in scheme 1.12 were carried out involving the model (25)[94]



(scheme 1.12)

Although replacement of I with Cl was not achieved, the saturated model (24) was useful for peroxide studies. In an effort to produce a conjugated model system related to the

$CH_2=CF_2/CF_3CF=CF_2$ copolymer, the synthesis outlined in scheme 1.13 was attempted.



$$CF_3I + \underset{(35)}{CH_2=CFC_2F_5} \xrightarrow[(ii)\ uv]{(i)\ 185^{o}C} CF_3CH_2\overset{CF_3}{\overset{|}{C}}FCH_2CFIC_2F_5\ (36)\quad 36\%$$

$$\big\downarrow \text{NEt}_3 \text{ or KOH}$$

$$CF_3CH=\underset{C_2F_5}{\underset{|}{C}}H=CFC_2F_5\quad (37)$$

[(36) is the 1:2 telomer adduct of (35) to CF_3I]

(scheme 1.13)

However no model studies involving the diene (37) have been reported.

(b) The Effect of Peroxides

Several mechanisms can be postulated for the peroxide cross-linking of $CH_2=CF_2$ copolymers. Hydrogen abstraction followed by subsequent combination of polymer radicals has been discussed (Section I.D.(iv)(a). However model studies using both $C_2F_5CF=CHC_3F_7$ (25) and $C_2F_5CF_2CH_2C_3F_7$ (24) with benzoyl peroxide failed to produce any dimers. Furthermore, substances known to liberate phenyl radicals (Ph_3Sb, Ph_3As) failed to promote reaction.[76] Yet benzoyl peroxide gives rise to a polymer vulcanizate far superior to that produced by MgO alone.[69]

It is clear therefore that cross-linking must be due to reaction of the polymer chain with benzoyl peroxide or its radicals or *via* other radicals produced during the cure. No study so far carried out has elucidated either the type of cross-link formed or the mechanism by which it is formed.

(c) Cross-Linking Involving $CF_2=CFBr$ (BTFE)

Model studies were carried out related to copolymers incorporating the cure-site comonomer $CF_2=CFBr$[73,74](Section I.D.(i) Scheme 1.4) in order to elucidate the mechanism involved and the final structure of the cross-linked network. The work was based partly on e.s.r. data because it involved production of the model perfluoroalkyl radical (37).

$$CF_3CF_2CFCF_3 \xrightarrow{\text{peroxide}} CF_3CF_2\dot{C}FCF_3$$

(36) (37)

The study of fluorinated alkyl radicals has been well developed[96,98] and therefore provides a powerful tool for this type of study.

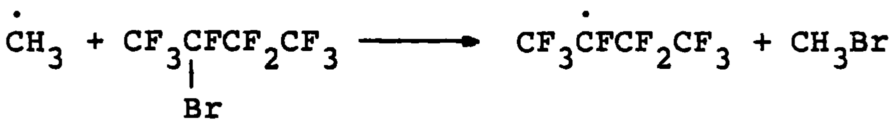
2-Bromooctafluorobutane, a model for the pendant Br atoms of copolymers incorporating $CF_2=CFBr$, was treated initially with di-t-butyl peroxide in cyclopropane. The resulting solution gave an intense e.s.r. signal due to the production of the radical (37).

It is postulated that, after β-scission of the radical (38)

$$(CH_3)_2C\dot{O} \longrightarrow (CH_3)_2C=O + \dot{C}H_3$$

(38)

abstraction of Br is achieved by the resulting $\dot{C}H_3$ radicals



$$\dot{C}H_3 + CF_3\underset{\substack{|\\ Br}}{C}FCF_2CF_3 \longrightarrow CF_3\dot{C}FCF_2CF_3 + CH_3Br$$

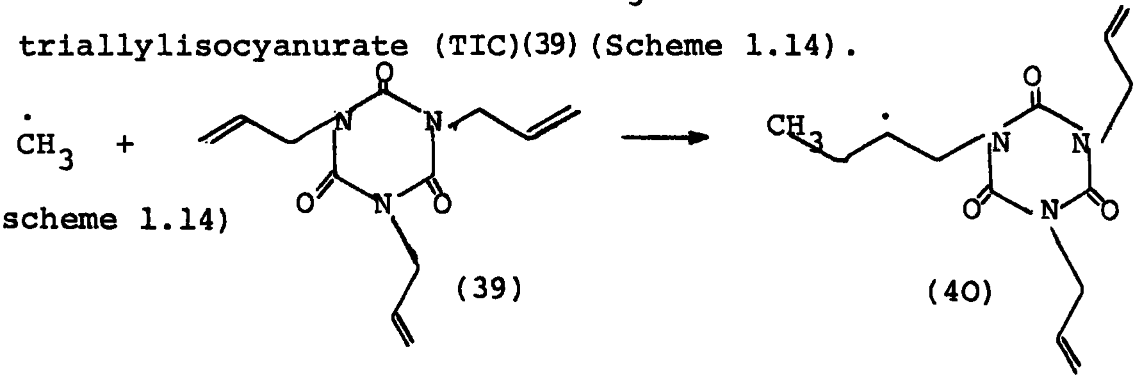
(36) (37)

However when the volatile materials from the actual polymer cure were analysed, very little CH_3Br was detected (Table 1.9).

TABLE 1.9 Volatile Products from Cure Involving $CF_2=CFBr$

Product	Amount Generated (relative)
$(CH_3)_2C=O$	100
$(CH_3)_3COH$	8.1
CH_3Br	1.9
CH_4	28.7

While the relative proportion of acetone to t-butanol is in accordance with β-scission of the radical, (38) the relatively low amounts of CH_3Br and CH_4 produced have been explained in terms of the rapid addition of $\dot{C}H_3$ radicals to the radical trap triallylisocyanurate (TIC)(39) (Scheme 1.14).



(scheme 1.14)

(39)

(40)

Abstraction of $Br^{\bullet}$ from the polymer is thought mainly to be by the radical, (40) with the polymer radicals (resulting from abstraction of $Br^{\bullet}$) then adding across the double bonds of TIC to give a cross-linked network (Scheme 1.15).

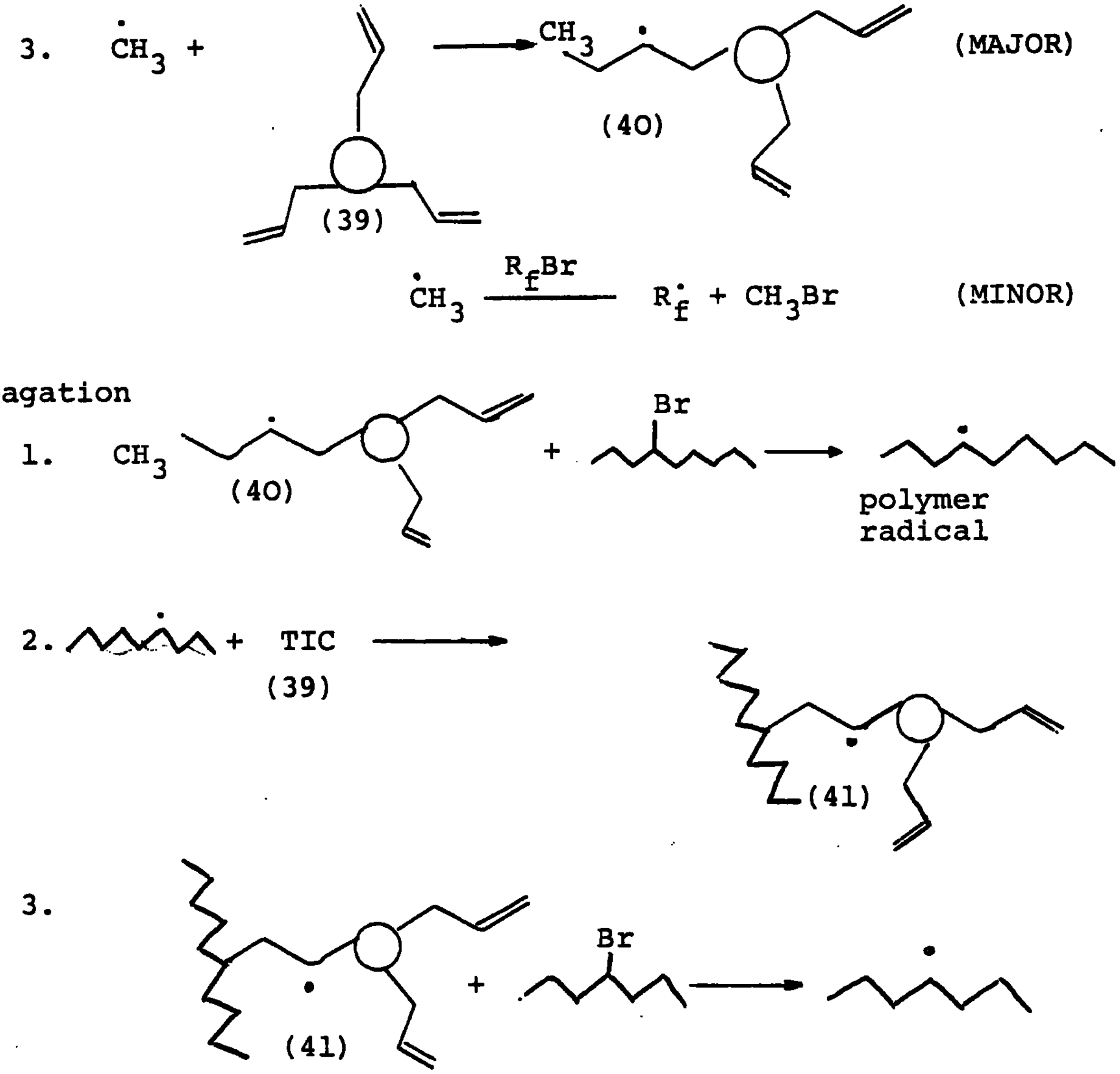
The mechanism may be viewed as a chain reaction. The driving force during the propagation step appears to be the transfer of $Br^{\bullet}$ from the electron-poor fluoropolymer to the electron-rich hydrocarbon radical.

Initiation

1. $(CH_3(_3COOC(CH_3)_3 \longrightarrow (CH_3)_3CO^{\bullet}$ (38) (MAJOR)

2. $(CH_3)_3CO^{\bullet}$ (38) $\longrightarrow \dot{C}H_3 + (CH_3)_2C{=}O$ (MAJOR)

$(CH_3)_3CO^{\bullet}$ (38) $\longrightarrow (CH_3)_3COH + R^{\bullet}$ (MINOR)



(scheme 1.15)

I.E. (iii) Conclusions

The mechanisms involved in the cross-linking by amines is well understood. However it is thought that post-cure heating of the cross-linked polymers results in the formation of a certain amount of new cross-links, the nature of which is not fully understood. There have been no model studies directed towards investigating this effect.

The bisphenol cross-linking process has not been studied using model systems. Such a study could give more information as to the significance of post-cure heating and might also verify the postulates of Smeigel[49] (Section I.D.(iii)). Furthermore, model studies should be carried out to establish the stability of bisphenol cross-links.

While model studies could give more definitive information about the other systems discussed above, their excellent physical properties and stability have not yet necessitated this type of investigation.

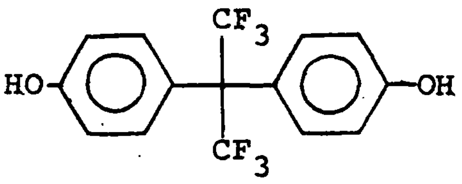
CHAPTER TWO

SYNTHESIS AND EXAMINATION OF SATURATED MODEL COMPOUNDS

2A. Introduction - Research Objectives

The objectives of this research are to synthesize and explore the chemistry of model compounds related to the cross-linking of copolymers of $CH_2=CF_2$ and $CF_3CF=CF_2$.

Initially this involves an investigation into the mechanism of cross-linking involving bisphenol AF (2) and the stability of such cross-links.



(2)

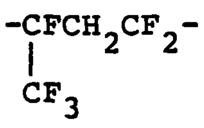
The general chemistry of the model compounds is investigated both to provide a broader background as to the reactivity of the copolymer systems and an opportunity to explore some novel reactions of fluorohydrocarbon systems.

2B. Choice of Model Compounds and Strategy

The important structural features of the $CH_2=CF_2/CF_3CF=CF_2$ copolymer system are the following -[39,80]

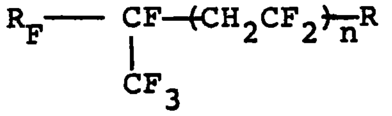
(i) $-CH_2CF_2CH_2-$ (41)

(ii) $-CF_2CH_2CF_2-$ (42)

(iii)  (43)

$-\underset{\displaystyle CF_3}{CF}CH_2CF_2-$

Model compounds of the form[99-102]

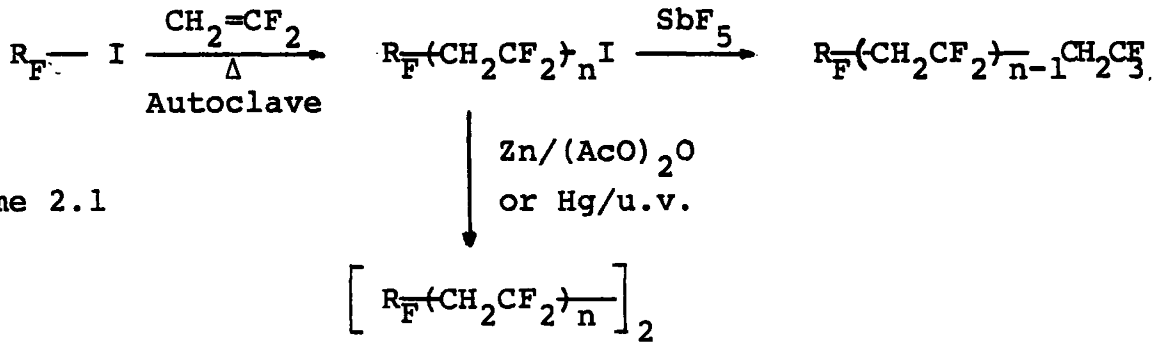


$$R_F\text{—}\underset{\displaystyle CF_3}{CF}\text{—}(CH_2CF_2)_n\text{—}R$$

$n = 1,2$ $R_F = F, CF_3$

$R = F$, Coupled.

contain all of these structures and may be obtained in good yields, *via* two-step syntheses, from perfluoroiodoalkanes. This approach is outlined in scheme 2.1.



Scheme 2.1

These reactions and the synthesis of $(CF_3)_2CFI$ (44) are discussed below.

2C. Synthesis of Model Compounds

2C (i) Synthesis of 2-Iodoheptafluoropropane (44)

There are many reports in the literature about the synthesis and chemistry of perfluoroiodoalkanes.[103-107] 2-Iodoheptafluoropropane $(CF_3)_2CFI$ (44) was prepared in excellent yields using the method of Chambers *et al.* This involves the addition of "I-F" to $CF_3CF{=}CF_2$ under autogenous pressure[108]

$$CF_3CF = CF_2 \xrightarrow[\substack{150^{\circ}C \\ \text{Autoclave}}]{I_2, IF_5} \underset{(44)}{(CF_3)_2CFI} \quad 99\%$$

2C (ii) Telomerization Reactions[109,110]

(a) $(CF_3)_2CFI/CH_2{=}CF_2$ Telomers[101]

When $(CF_3)_2CFI$ (44) is used as a chain transfer agent (*e.g.* in the reaction with $CH_2{=}CF_2$, Scheme 2.2) it is a useful source of tertiary fluorine.

Initiation $$\underset{(44)}{(CF_3)_2CFI} \xrightarrow{\Delta} \underset{(45)}{(CF_3)_2\dot{C}F} + I^{\bullet}$$

Propagation $$(CF_3)_2\dot{C}F + n\ CH_2{=}CF_2 \longrightarrow (CF_3)_2CF(CH_2CF_2)_n^{\bullet}$$

Chain Transfer $$\underset{(46)}{(CF_3)_2CF(CH_2CF_2)_n^{\bullet}} \xrightarrow{(CF_3)_2CFI} \underset{(47)}{(CF_3)_2CF(CH_2CF_2)_nI} + \underset{(45)}{(CF_3)_2\dot{C}F}$$

Scheme 2.2

The reactions were carried out in an autoclave without free-radical initiators at 185°C for 24h. The maximum yield of 2H, 2H-1-iodononafluoro-3-methylbutane (n=1), $(CF_3)_2CFCH_2CF_2I$ (48) was 75% using a 1:1 molar ratio of $CH_2{=}CF_2$ to (44).

In order to increase the yields of the higher telomers ($n>1$) the proportion of $CH_2{=}CF_2$ was raised and the reaction carried out at 220°C for 36h. The results are shown in Table 2.1.

TABLE 2.1 The Yields of Higher Telomers. $n\geq2$.

Ratio of Reactants	Approx. % Composition of (47)				
	n=1	n=2	n=3	n=4	n=5
$(CF_3)_2CFI$: $CH_2{=}CF_2$ 1 : 3	5	30	30	20	10

These results are in accordance with those of Chambers *et al.*[101]

(b) $C_2F_5I/CH_2=CF_2$ Telomers

This reaction was carried out at 180°C for 24h using a 1:1 molar ratio of $CH_2=CF_2$ and C_2F_5I (48) together with a trace (1%) of the free-radical initiator cumene hydroperoxide. However the yield of 2H,2H-1-iodoheptafluorobutane (n=1), $C_2F_5CH_2CF_2I$ (49) was only 40% under these conditions.

$$\underset{(48)}{C_2F_5I} \xrightarrow[180^{\circ}C \quad 24h]{CH_2=CF_2} \underset{(49)}{C_2F_5CH_2CF_2I} \quad 40\% + \text{Higher Telomers}$$

(c) $(CF_3)_2CFI/CHF=CF_2$ Telomers

This reaction was carried out at 185°C for 24h also using a 1:1 molar ratio of reactants. No free-radical initiator was necessary. The yield of 2H-1-iododecafluoro-3-methylbutane (n=1), $(CF_3)_2CFCFHCF_2I$ (50) was lowered to *ca.* 50% because of the production of the regioisomer (51) as well as the n=2 telomers (52).

$$\underset{(44)}{(CF_3)_2CFI} \xrightarrow[180^{\circ}C,24h.]{CHF=CF_2} \underset{\substack{(50)\\ ca.\ 50\%}}{(CF_3)_2CFCFHCF_2I} + \underset{\substack{(51)\\ ca.\ 10\%}}{(CF_3)_2CFCF_2CFHI.}$$

$$+ \underset{\substack{(52)\\ ca.\ 20\%.}}{(CF_3)_2CF(CFHCF_2)_2I}$$

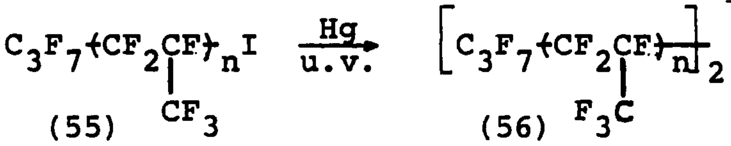
2C (iii) Coupling Reactions

(a) Introduction

The coupling of fluoroiodoalkanes has been achieved using mercury and ultra-violet light. For example

$$\mathrm{CClF_2CFClI} \xrightarrow[\text{u.v.}]{\text{Hg}} \left[\mathrm{CClF_2CFCl}\right]_2 \quad {}^{111}$$

(53) (54)



$$\mathrm{C_3F_7(CF_2\underset{CF_3}{\underset{|}{C}F})_nI} \xrightarrow[\text{u.v.}]{\text{Hg}} \left[\mathrm{C_3F_7(CF_2\underset{F_3C}{\underset{|}{C}F})_n}\right]_2 \quad {}^{112}$$

(55) (56)

$$\mathrm{CF_3CF_2CH_2CF_2I} \xrightarrow[\text{u.v.}]{\text{Hg}} \left[\mathrm{CF_3CF_2CH_2CF_2}\right]_2 \qquad 70\%$$

(49) (57)

These reactions are believed to proceed the formation of the mercurials R_FHgI which decompose upon further irradiation to give the coupled products R_F-R_F.

Fluoroiodoalkanes are also coupled by reaction with zinc in dioxane[113] or in $(CH_3CO)_2O/CH_2Cl_2$.[114] For example Henne and coworkers report the following

$$\mathrm{CF_2Cl\text{-}CFClI} \xrightarrow[(\mathrm{CH_3CO})_2\mathrm{O}]{\text{Zn}} \left[\mathrm{CF_2Cl\text{-}CFCl}\right]_2 \quad {}^{115}$$

(53) (54)

However[114] the iodide (58) did not couple.

$$\mathrm{CF_3(CF_2)_3CFICF_3} \xrightarrow[(\mathrm{CH_3CO})_2\mathrm{O},\mathrm{CH_2Cl_2}]{\text{Zn}} \mathrm{CF_3(CF_2)_3CF{=}CF_2}$$

(58) (59)

+

$$\mathrm{CF_3(CF_2)_2CF{=}CFCF_3}$$

(60)

There appears therefore to be a degree of uncertainty when the $(CH_3CO)_2O$, Zn/CH_2Cl_2 system is used.

(b) $(CF_3)_2CFCH_2CF_2I$ (48)

Chambers *et al* observed the following[101]

$$\underset{(48)}{(CF_3)_2CFCH_2CF_2I} \xrightarrow[\text{7 days}]{\text{Hg, u.v.}} \underset{(61)}{\left[(CF_3)_2CFCH_2CF_2\right]_2} \qquad 75\%$$

$$\xrightarrow[CH_2Cl_2]{Zn,\ (CH_3CO)_2O} (61) \qquad 45\%.$$

During the course of the present work it was found that 80% isolated yields of the coupled product (61) could be obtained when CH_2Cl_2 was excluded and the reaction carried out at 50°C. Vacuum-line techniques were used to purify the product.

(c) $(CF_3)_2CF(CH_2CF_2)_2I$ (62)

When (62) was treated with Zn, $(CH_3CO)_2O$ at 50°C only 40% yields of the coupled model (63) could be obtained.

$$\underset{(62)}{(CF_3)_2CFCH_2CF_2CH_2CF_2I} \xrightarrow[(CH_3CO)_2O]{Zn} \underset{(63)}{\left[(CF_3)_2CFCH_2CF_2CH_2CF_2\right]_2} \quad 40\%$$

$$(50\%)$$

$$+$$

$$\underset{(63A)}{(CF_3)_2CFCH_2CF_2CH_2CF_2H} \quad \textit{ca. } 20\%$$

(d) $CF_3CF_2CH_2CF_2I$ (49) and $(CF_3)_2CFCFHCF_2I$ (50)

2H,2H-1-iodoheptafluorobutane (49) and 2H-1-iododecafluoro-3-methylbutane (50) were both coupled in excellent yields using the Hg/u.v. method.

$$CF_3CF_2CH_2CF_2I \xrightarrow[\text{7 days}]{\text{Hg, u.v.}} \left[CF_3CF_2CH_2CF_2\right]_2 \qquad 90\%$$

(49) (57)

$$(CF_3)_2CFCFHCF_2I \xrightarrow[\text{7 days}]{\text{Hg, u.v.}} \left[(CF_3)_2CFCFHCF_2\right]_2 \qquad 75\%$$

(50) (64)

2C. (iv) Fluorination of the Telomer Iodides

(a) Introduction

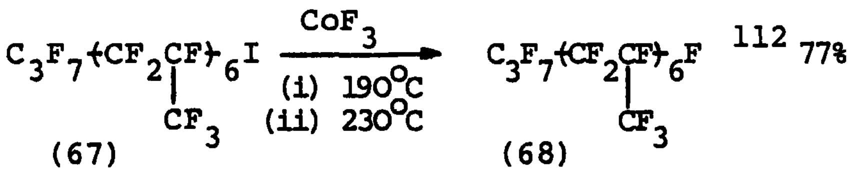
The C-I bond of iodofluoroalkanes may be converted to a C-F bond by reaction with SbF_3Cl_2,[116] HF,[94] CoF_3[112] and Hg_2F_2 [117] as exemplified below

$$C_3F_7CH_2CF_2I \xrightarrow{SbF_3Cl_2} C_3F_7CH_2CF_3 \quad ^{116}$$

(65) (66)

$$C_2F_5CFICH_2C_3F_7 \xrightarrow{HF} C_2F_5CF_2CH_2C_3F_7 \quad ^{94}$$

(25) (24)



$$C_3F_7(CF_2\underset{CF_3}{\underset{|}{C}F})_6I \xrightarrow[\substack{\text{(i) } 190^\circ C \\ \text{(ii) } 230^\circ C}]{CoF_3} C_3F_7(CF_2\underset{CF_3}{\underset{|}{C}F})_6F \quad ^{112} \; 77\%$$

(67) (68)

$$C_2F_5CH_2CF_2I \xrightarrow{Hg_2F_2} C_2F_5CH_2CF_3 \quad ^{117}$$

(49) (69)

SbF_5 has also been used for similar reactions[118] and was found to work very well at 0°C with the fluorinations described below.

(b) $(CF_3)_2CF(CH_2CF_2)_nI$. Telomers (n=1-5)

The telomer iodides $(CF_3)_2CF(CH_2CF_2)I$ (n=1→5) were each fluorinated using SbF_5 at 0°C in $CF_2ClCFCl_2$ to yield the fluorohydrocarbons $(CF_3)_2CF(CH_2CF_2)_nF$ in good yields.

In an earlier experiment the iodide (62) was sealed with a 2:1 excess of SbF_5 in an evacuated tube. The fluorination reaction is exothermic and caused the temperature to exceed 100°C resulting in an unexpected product (71).

$$\underset{(62)}{(CF_3)_2CF(CH_2CF_2)_2I} \xrightarrow[100^{\circ}C]{SbF_5} \underset{(70)}{(CF_3)_2CF(CH_2CF_2)_2F} \quad 30\%$$

$$+$$

$$\underset{(71)}{(CF_3)_2C{=}CHCF_2CH_2CF_3} \quad 65\%$$

This was rationalized as a Lewis acid catalysed elimination of HF and is discussed in Chapter Three, Section C.

(c) $(CF_3)_2CF(CFHCF_2)_2I$ (52)

Fluorination of (52) was also achieved using SbF_5 at 0°C in $CF_2ClCFCl_2$ to give the diasteromer mixture (72)

$$\underset{(52)}{(CF_3)_2CF\overset{*}{C}FHCF_2\overset{*}{C}FHCF_2I} \xrightarrow[0^{\circ}C]{SbF_5} \underset{(72)}{(CF_3)_2CF\overset{*}{C}FHCF_2\overset{*}{C}FHCF_3} \quad 90\%$$

2D. Examination of the Saturated Model Compounds

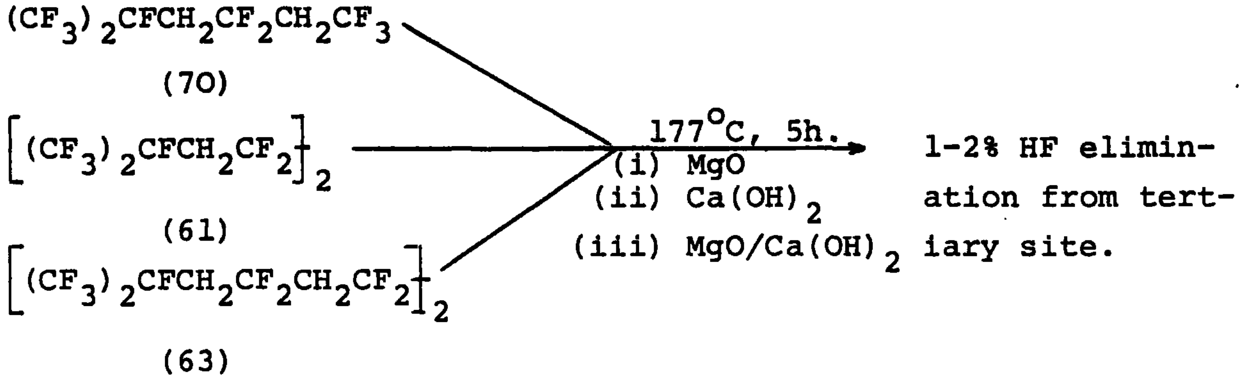
2D (i) Introduction

The ingredients used in a typical bisphenol cure of $CH_2{=}CF_2/CF_3CF{=}CF_2$ copolymers were outlined in Chapter One, ID(iii).[49] In order to discover the mechanism of the bisphenol cure each saturated model was heated to the cure temperature 177°C (and higher, for extended times with a variety of the curing agents.

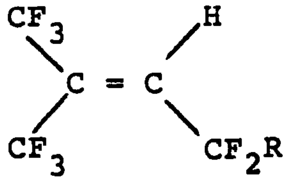
2D (ii) Response to the Curing Agents

(a) Inorganic Acid-Acceptors MgO, $Ca(OH)_2$

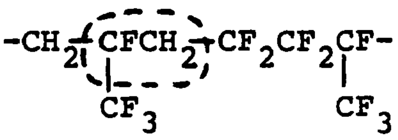
Treatment of the models (70), (61) and (63) with MgO and $Ca(OH)_2$ at 177°C resulted in only 1-2% unsaturation, (Scheme 2.2).



Elimination of HF occurred preferentially at tertiary sites to yield products of the form (in low yields)



which are easily identified by ^{19}F, ^{1}H nmr spectroscopy. This supports the postulate of Smeigel that the sensitive site in $CH_2{=}CF_2/CF_3CF{=}CF_2$ copolymers is



$$-CH_2\underset{\substack{|\\CF_3}}{CF}CH_2CF_2CF_2\underset{\substack{|\\CF_3}}{CF}-$$

(b) Bisphenol AF

When the model (61) was treated with bisphenol AF (2) at 200°C for 3h. there was no reaction.

$$\left[(CF_3)_2CFCH_2CF_2\right]_2 \xrightarrow[200^{\circ}C,\ 3h.]{\text{Bisphenol AF(2)}} \text{No Reaction}$$

(61)

(c) Phosphonium Accelerators

When the model (61) was treated with

(i) Tetraphenylphosphonium Chloride, $Ph_4P^+Cl^-$

(ii) Benzyltriphenylphosphonium Chloride, $Ph_3(PhCH_2)P^+Cl^-$

at 190°C for 18h. there was no reaction.

$$\left[(CF_3)_2CFCH_2CF_2\right]_2 \xrightarrow[(i),\ (ii)]{190^{\circ}C,\ 18h} \text{No Reaction}$$

(61)

(d) Combinations of the Curing Agents

Table 2.2 summarizes the experiments which were carried out. The temperature in each case was 177°C unless stated, and maintained over 5h., with the reactants stirred or shaken in sealed tubes. In each case there was no reaction.

TABLE 2.2 Combinations of the Curing Agents

Models	Curing Agents
$\left[(CF_3)_2CFCH_2CF_2\right]_2$ (61)	Bisphenol Af, $Ca(OH)_2$, MgO
$\left[(CF_3)_2CFCH_2CF_2CH_2CF_2\right]_2$ (63)	Bisphenol Af, $Ca(OH)_2$, MgO
$\left[(CF_3)_2CFCH_2CF_2\right]_2$ (61) $\left[(CF_3)_2CFCH_2CF_2CH_2CF_2\right]_2$ (63)	Bisphenol Af $PPh_4^+\ Cl^-$ 190°, 18h.
$\left|(CF_3)_2CFCH_2CF_2\right|_2$ (61)	Bisphenol Af, MgO, $Ca(OH)_2$, $PPh_4^+Cl^-$

In addition the following experiment was also tried

$$\left[(CF_3)_2CFCH_2CF_2\right]_2 \xrightarrow[K_2CO_3,177^{o}C,2h]{\text{Bisphenol AF}} \text{No Reaction}$$

(61)

2E. Attempts to Incorporate Bromine

It is an accepted principle that the inductive effect of fluorine lowers the reactivity of hydrogen in fluorohydrocarbons to radical abstraction by chlorine [31,119] and bromine.[120] However photochemical bromination [121,122] and thermal brominations (above $400^{o}C$) have been reported. [123]

When the models (61) and (63) were irradiated with a ^{60}Co -source at $300^{o}C$ in the presence of Br_2, no incorporation of Br was detected.

$$\left[(CF_3)_2CF\left(CH_2CF_2\right)_{n}\right]_2 \xrightarrow[300^{o}C]{Br_2} \text{No Reaction}$$

n = 1 (61) γ-ray

n = 2 (63) 3 days

2F. Conclusions

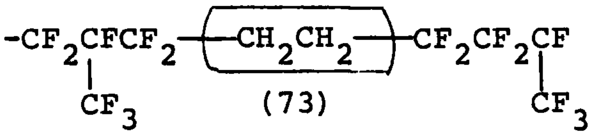
The amount of unsaturation generated in the model compounds (61), (63) and (70) during reactions analogous to the curing processes is very low (*ca.* 1%) even at temperatures above $177^{o}C$ over extended periods.

On the assumption that cross-linking must occur at double bonds, the low reactivity of the models leads to either of two conclusions:

(i) The copolymer system, for reasons which are not clear, is much more reactive than the models (61), (63) and (70) despite the exactly analogous structural features,

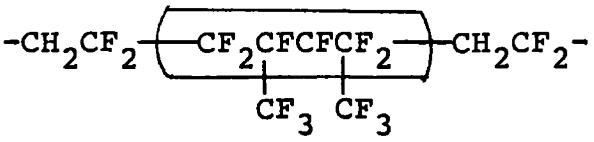
(ii) Very little unsaturation is involved in the curing process.

In the first case the presence in the copolymer cures of significant levels of impurities (*e.g.* F^-) or structural irregularities,*e.g.* (73) or (74) may be important



$-CF_2\underset{CF_3}{CF}CF_2-(CH_2CH_2)-CF_2CF_2\underset{CF_3}{CF}$

(73)



$-CH_2CF_2-(CF_2\underset{CF_3}{CF}\underset{CF_3}{CF}CF_2)-CH_2CF_2-$

(74)

Model reactions involving unsaturated sites is discussed in Chapter Four.

CHAPTER THREE

SYNTHESIS OF UNSATURATED MODELS

3A. Introduction

Elimination of HF from saturated fluorohydrocarbons provides a general route to unsaturated model compounds.[90,100] The systems $(CF_3)_2CFCH_2CF_2R$, [R=F (66), $R=CH_2CF_3$ (70) and R = -coupled (61)] were investigated.

3B. Base-Catalysed Elimination of HF

3B.(i) Using KOH [100]

Treatment of $[(CF_3)_2CFCH_2CF_2\dagger_2$, (61) with KOH at 80°C without a solvent caused tarring, although *ca*. 5% removal of HF occurred. Elimination occurred preferentially at tertiary sites, since the ^{19}F nmr spectrum showed clearly the presence of the $(CF_3)_2C=$ group.[124,125] However both refluxing (61) over KOH at 130°C and passing the vapour of (61) in N_2 through KOH at 180°C resulted in extensive decomposition and tar.

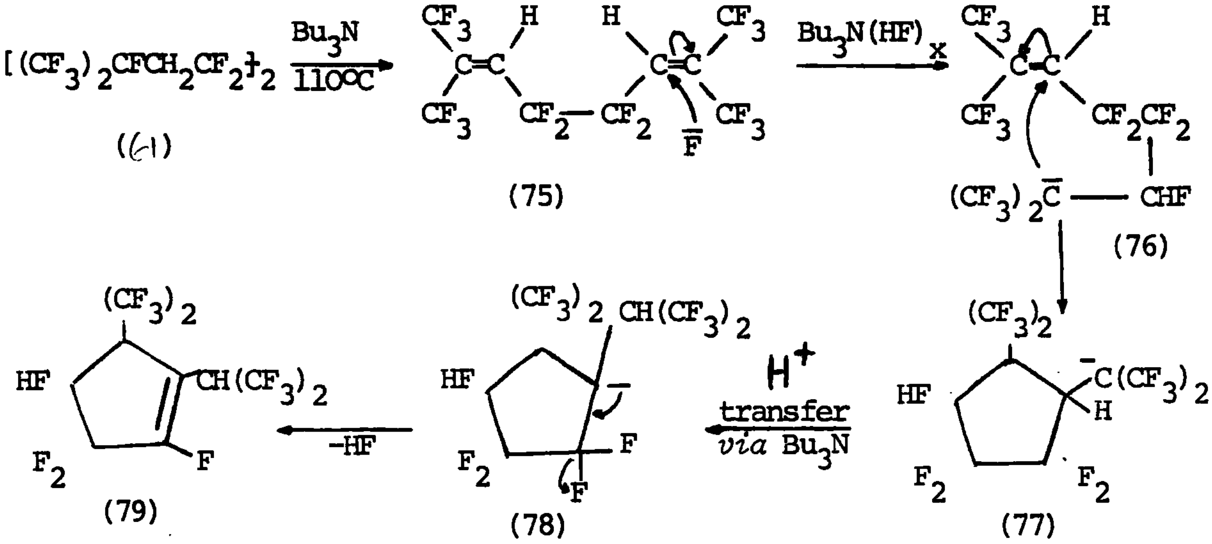
3B. (ii) Using Lithium Alkyls

Treatment of $[(CF_3)_2CFCH_2CF_2\dagger_2$, (61) with (i) CH_3Li and (ii) $^nC_4H_9Li$ at -78°C resulted in vigorous decomposition.

It was concluded that the lithium alkyls were acting as powerful nucleophiles to any unsaturated sites despite the fact that the lithiation of hydrofluoroalkenes is well known.[126]

B. (iii) Using Nitrogen Bases

Treatment of $[(CF_3)_2CFCH_2CF_2\dagger_2$, (61) with $(C_4H_9)_3N$ at 110°C resulted in the single cyclic product 1-(2H-hexafluoroisopropyl)-3-hydrodecafluoro-2,2-dimethylcyclopentene, (79).[100] The most likely mechanism for this reaction is shown in Scheme 3.1.



Scheme 3.1

The cyclisation step to produce the intermediate (77) is surprising in view of the steric crowding of the system[127] and provides evidence that large amine hydrofluorides are a source of active F^-.[128,129] When the reaction was repeated under milder conditions (NBu_3, 100°C, 1h) the monoalkene $(CF_3)_2C{=}CHCF_2CF_2CH_2CF(CF_3)_2$, (80) together with (79) were the only products.

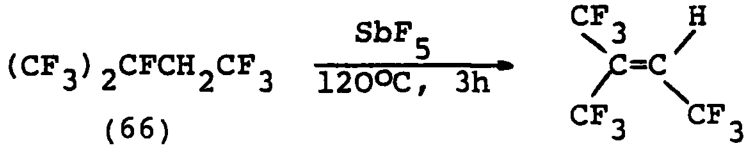
Further chemistry of the product (79) is discussed in Chapter Seven.

When the saturated model $[(CF_3)_2CFCH_2CF_2\dagger_2$, (61) was treated with the hindered nitrogen base lithium diisopropylamide (L.D.A.), $[(CH_3)_2CH]_2NLi$ at -78°C there was vigorous tarring.

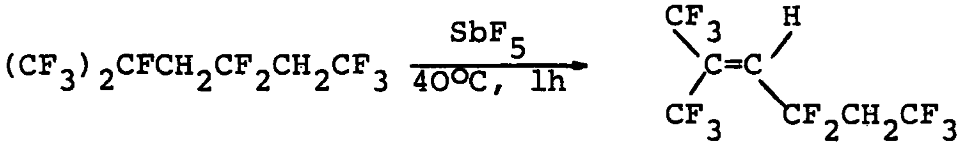
3C. Lewis-Acid Catalysed Eliminations of HF

3C. (i) Use of Antimony Pentafluoride

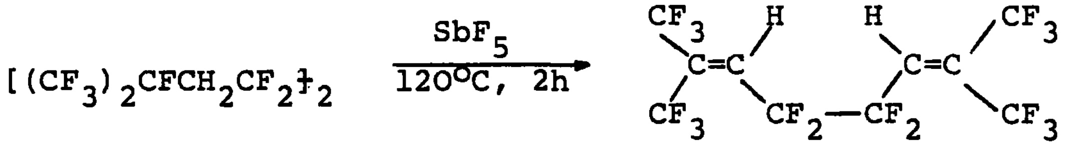
Eliminations of HF from the saturated models (66), (70) and (61) were achieved in excellent yields to give the single products 2H-nonafluoro-3-methylbut-2-ene (81), 2,2,4-trihydroundecafluoro-5-methylhex-4-ene (71), and 3,6-dihydrohexadecafluoro-2,7-dimethyl-2,6-octadiene (75) respectively.



(66) (81) (Quant.)



(70) (71) (Quant.)



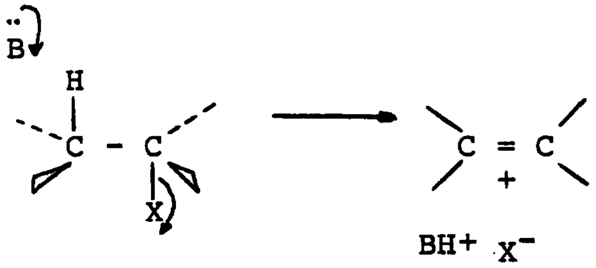
(61) (75) (Quant.)

These eliminations represent an entirely novel approach to the synthesis of fluorinated alkenes, *i.e.* *via* Lewis acid-catalysed elimination of HF.

3C. (ii) Mechanistic Considerations

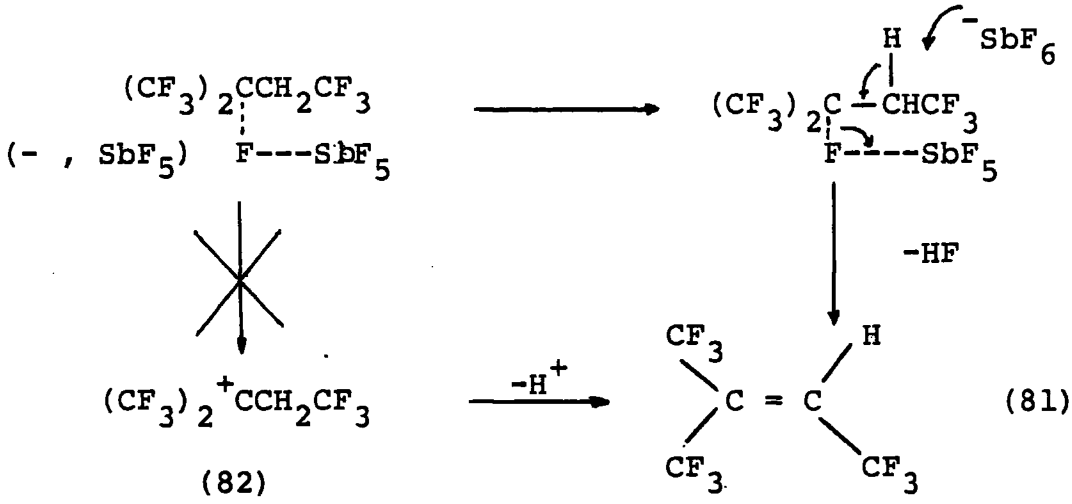
The mechanistic aspects of base-catalysed elimination of HX (X=F, Cl, Br, I) *via* either E1 or E2 routes is well understood.[130]

e.g. E2



However rarely have Lewis acids been used to form alkenes (*e.g.* biproducts during Friedel-Crafts reactions[131]). The use of SbF_5 to form fluorinated alkenes is therefore of great interest since, (a) the yields obtained were quantitative and (b) the resulting fluoroalkenes are quite stable to further attack, (*cf.* with NBu_3 the diene (75) is cyclised by a nucleophilic process).

It is expected that the acid-catalysed route is concerted since the production of an intermediate carbocation (82) would be unlikely due to the presence of $-CF_3$ groups at the charge-centre (Scheme 3.2), *e.g.*



In order to determine whether the presence of superacid SbF_5,HF (a strong protic acid) was not responsible, the model $[(CF_3)_2CFCH_2CF_2]_2$, (61) was treated with a solution of SbF_5 in excess HF under autogenous pressure at 120°C. Only a trace of unsaturation resulted (*cf.* Quant. using SbF_5).

i.e. $$[(CF_3)_2CFCH_2CF_2]_2 \quad \cancel{\xrightarrow[120^{\circ}C,\ 3h]{SbF_5/HF}} \quad [(CF_3)_2C{=}CHCF_2]_2$$

(61) (75)

Furthermore the rates of the elimination reactions involving SbF_5 did not increase as they proceeded (monitored using ^{19}F

nmr. techniques) which would be expected if $SbF_5.HF$ was responsible, and when a deficiency of SbF_5 was used, the reactions did not go to completion.

3D. Other Routes to Unsaturated Models

3D. (i) Synthesis of 2H-heptafluorobut-2-ene (83)

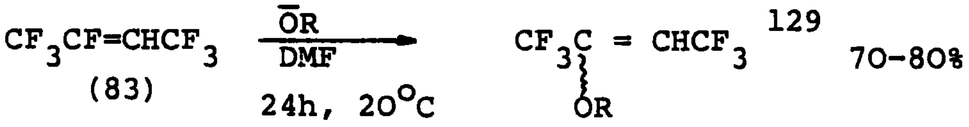
$CF_3CF{=}CHCF_3$, (83) was synthesized in good yield using the reaction [132,133]

$$\underset{(84)}{Cl_2C{=}CCl{-}CCl{=}CCl_2} \xrightarrow[\text{Sulpholane}\ 200^{o}C]{KF} \underset{(83)}{CF_3CF{=}CHCF_3}$$

(95% *trans*)

3D. (ii) Reactions of (83) with Sodium Alkoxides

A series of model compounds, which relate to the proposed structure of the bisphenol-cured $CH_2{=}CF_2/CF_3CF{=}CF_2$ copolymers, [49] were synthesized by nucleophilic displacement of vinyl fluorine from (83) by the sodium alkoxides Na^+Ro^- (R=Ph, CH_3, CH_2CH_3).



$$\underset{(83)}{CF_3CF{=}CHCF_3} \xrightarrow[\text{DMF}\ 24h,\ 20^{o}C]{\bar{O}R} CF_3\underset{\substack{\wr \\ OR}}{C} = CHCF_3 \quad ^{129} \quad 70\text{–}80\%$$

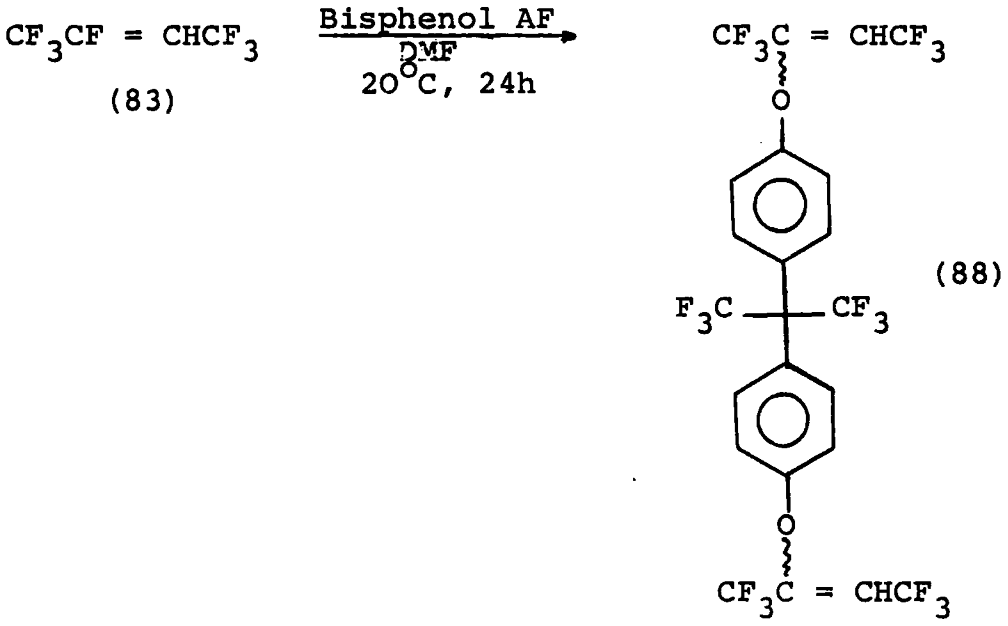
(95% *trans*)

R = Ph, 75% *trans*, (85)

R = CH_3, 95% *trans*, (86)

R = CH_2CH_3, 95% *trans*, (87)

The model (83) was also treated with bisphenol AF (2) in DMF in the presence of K_2CO_3 to form the model cross-link (88).



85% *trans, trans*

CHAPTER FOUR

REACTIONS OF UNSATURATED MODEL COMPOUNDS

4A. Introduction

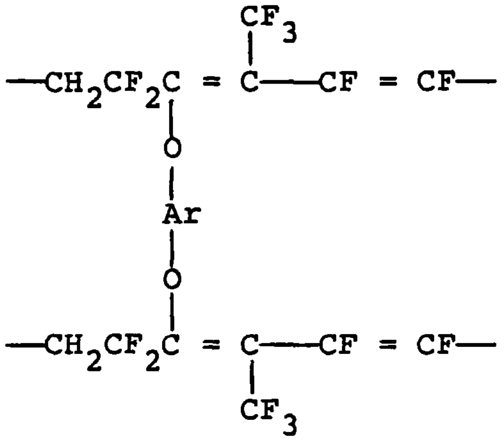
Copolymers of $CF_3CF{=}CF_2$ and $CH_2{=}CF_2$ cured with bisphenol AF are degraded when subjected to hydrolytic conditions (*e.g.* steam, aqueous alkali) and amines over a prolonged period.[26] This proves a serious disadvantage when these materials are employed in coolant systems.

At the outset of this research the reasons for this instability were by no means clear and it was believed that the bisphenol cross-link was the source of the instability.[26] However a definitive study of this problem had not been carried out despite much speculation.

A study of the unsaturated model systems was therefore carried out in order to establish the reactivity of the bisphenol cross-links (89) and other unsaturated systems related to the $CF_3CF{=}CF_2/CH_2{=}CF_2$ copolymer system.

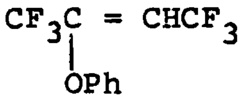
e.g.

(89)



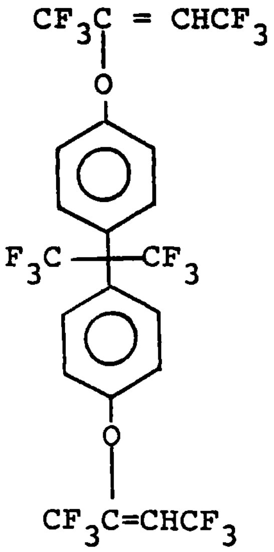
4B. The Hydrolytic Stability of the Model Compounds

The stabilities of 2H-3-phenoxyhexafluorobut-2-ene (85) and 2,2-bis-(4-[2H-hexafluorobut-2-en-oxy-phenol) hexafluorobutane (88) were investigated in the presence of hot water, succinimide and amines.



$$\mathrm{CF_3\underset{\displaystyle |\atop OPh}{C} = CHCF_3}$$

(85)



(88)

The conditions employed in the tests were very aggressive and carried out in sealed tubes. Reagents and conditions are summarized in Table 4.1. The systems involving the solvent N,N-dimethylformamide (DMF) were homogeneous whereas those involving steam, inorganic acid acceptors (MgO, $Ca(OH)_2$) and KOH were heterogeneous.

In each case there was no detectable chemical change in the models (85) and (88). We have therefore been unable to demonstrate any hydrolytic instability attributable to the bisphenol cross-link.

Consequently unsaturated sites generated in the copolymer system which remain unconverted to cross-links may contribute to the lower stability. Therefore the reactivity of the unsaturated model compounds was examined.

TABLE 4.1 The Hydrolytic Stability of Model Aryl-Ether Cross-links

Model System(s)	Conditions
(85), (88)	30% Aqueous KOH 100°C, 3h
(85), (88)	MgO, $Ca(OH)_2$ 177°C, 3h
(88)	H_2O 250°C, 60h
(88)	5% Succinimide DMF 140°C, 36h
(88)	5% NEt_3 DMF 140°C, 60h
(88)	5% $PhNH_2$ DMF 140°C, 60h

4C. The Reactivity of Model Compounds containing the Group $(CF_3)_2C{=}CH-$

(i) Under Typical Cure Conditions

The unsaturated model $(CF_3)_2C{=}CHCF_2CH_2CF_3$, (71) was subjected to conditions typical of the bisphenol curing process.[49] These are summarized in Table 4.2.

TABLE 4.2 Reactivity of $(CF_3)_2C{=}CHCF_2CH_2CF_3$ (71) under Typical Cure Conditions

Components	Conditions
(71) MgO, $Ca(OH)_2$ $PPh_4^+Cl^-$, PhOH	180°C, 24h
(71) MgO, $Ca(OH)_2$ PhOH	180°C, 24h
(71) MgO, $Ca(OH)_2$ Bisphenol AF(2) $PPh_4^+Cl^-$	200°C, 18h

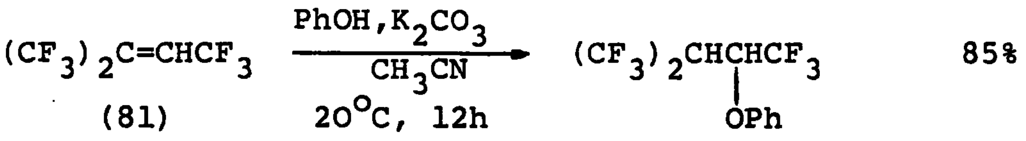
----

The model (71) was unchanged under these conditions even over the prolonged periods shown. This stability is very remarkable in the light of the extreme reactivity towards nucleophiles of these model compounds described below.

4C. (ii) Towards Phenoxide, Hydroxide and Fluoride

(a) $(CF_3)_2C{=}CHCF_3$

When 2H-nonafluoro-3-methylbut-2-ene (81) was treated with PhOH in CH_3CN at 20°C in the presence of base (K_2CO_3) the single nucleophilic adduct 2-phenoxy-2H,3H,3-trifluoromethylhexafluorobutane (90) was obtained in good yield.



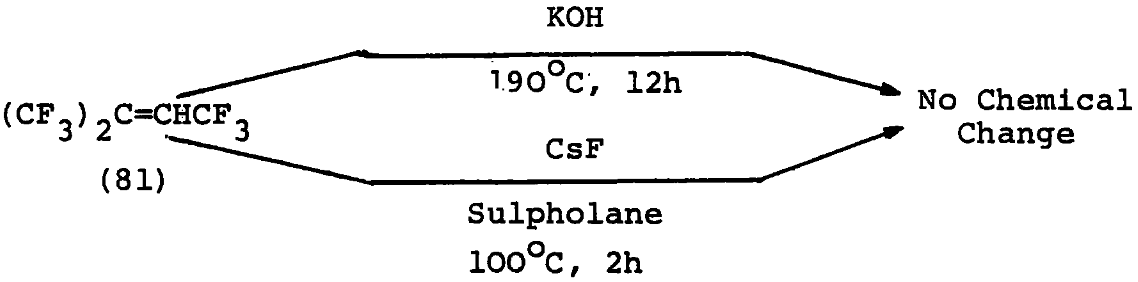
$$(CF_3)_2C{=}CHCF_3 \xrightarrow[\substack{CH_3CN \\ 20^\circ C,\ 12h}]{PhOH, K_2CO_3} (CF_3)_2CH\underset{\displaystyle OPh}{C}HCF_3 \quad 85\%$$

(81)

(90)

This result demonstrates that this type of unsaturated site is highly susceptible to nucleophilic attack under very mild conditions.

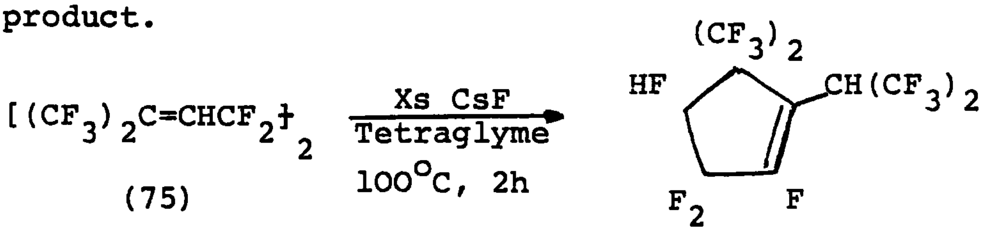
In complete contrast however the model (81) was wholly unchanged when treated with solid powdered KOH at 190°C for 12h. When treated with CsF in sulpholane at 100°C for 2h there was also no chemical change.



(81)

(b) $(CF_3)_2C{=}CHCF_2CF_2CH{=}C(CF_3)_2$

When the model 2,7-bistrifluoromethyl-3,6-dihydrodecafluoroocta-2,7-diene (75) was treated with CsF in tetraglyme at 100°C the cyclopentene derivative (79) was obtained as the only product.



(75)

(79)

The product (79) is identical to that which was obtained when the saturated model $[(CF_3)_2CFCH_2CF_2]_2$ (61) was treated with NBu_3. This result is particularly important because it again demonstrates the susceptibility of this type of unsaturated site to nucleophilic attack. Furthermore, however, it provides support for the mechanism proposed for the reaction involving the saturated model (61) and NBu_3 (Scheme 3.1) which suggests that $NBu_3(HF)_x$ is a source of active fluoride ion. This is particularly apparent since the cyclisation step is achieved in each reaction over the same period of time (2h, 100°C) even though excess CsF was used in the reaction involving (75).

Treatment of $[(CF_3)_2C{=}CHCF_2]_2$ (75) with PhOH (3:1 excess), again under very mild conditions (K_2CO_3, 20°C), resulted in a complex misture of products which were not separable. Analysis by ^1H and ^{19}F nmr techniques[134] showed the presence of unsaturated products containing vinyl fluorine[135] as well as saturated products. Analysis by mass spectrometry using capillary column gas chromatography showed that the products included nucleophilic diadducts (Molecular weight 614) as well as products from nucleophilic substitution.

$$\underset{\text{(75)}}{[(CF_3)_2C{=}CHCF_2]_2} \xrightarrow[\substack{CH_3CN \\ 20^{\circ}C,\ 12h}]{PhOH,\ K_2CO_3}$$

Products of Masses
614 (Diadduct)
594, 574, 554.

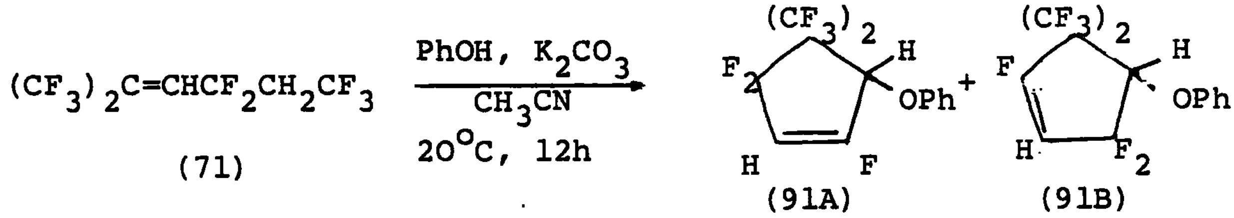
Molecular Wt.
426

At the time of writing these products had not been fully characterized but further work in the laboratory is proceeding.

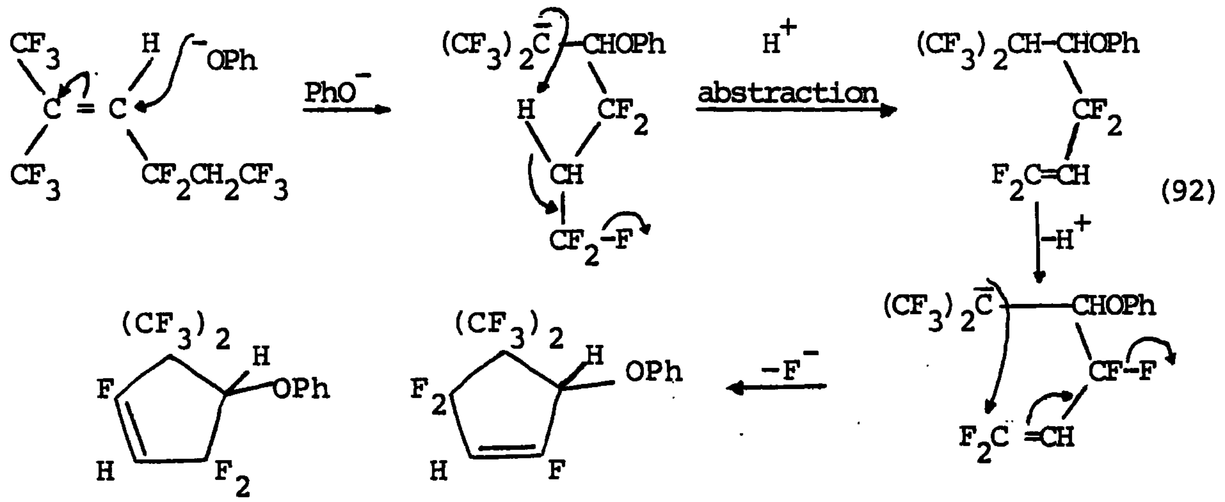
This result again demonstrates a high susceptibility to nucleophilic attack associated with the models.

(c) $(CF_3)_2C{=}CHCF_2CH_2CF_3$

When 2H,2H,4H-undecafluoro-5-methylhex-4-end (71) was treated with PhOH under very mild conditions, identical to those used for (75) and (81) above, the unusual products (91A) and (91B) were obtained.



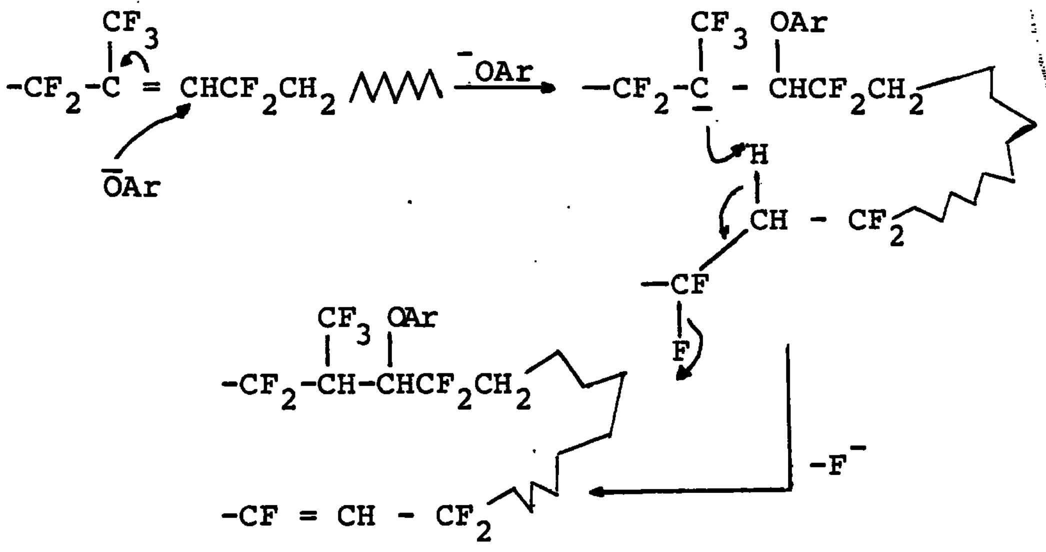
This result presents an interesting mechanistic problem, which may be very relevant to the cross-linking process. The pathway proposed for this reaction is outlined in Scheme 4.1.



Scheme 4.1

When this type of process is considered in the context of the copolymer system the analogous intramolecular abstraction of H^+ by a copolymer anion (93) could give rise to further unsaturated sites of the form (94) as exemplified by Scheme 4.2.

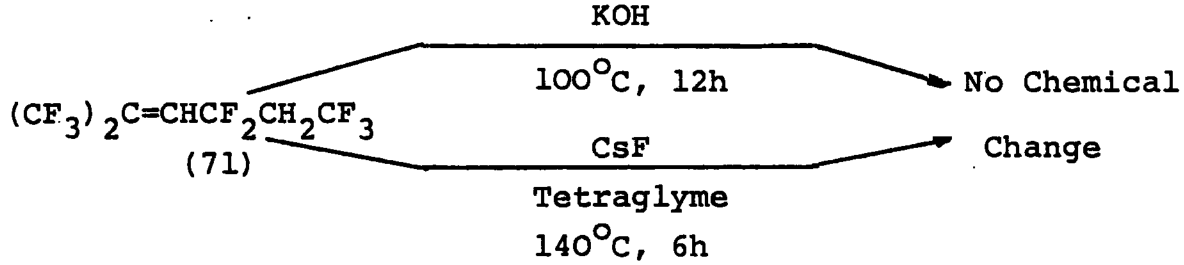
Scheme 4.2



(94)

Alternatively abstraction of H^+ could possibly take place between copolymer chains if they were in suitably close proximity in the solid.

In stark contrast the model (71) was found to be completely unchanged by CsF and KOH under very forcing conditions.



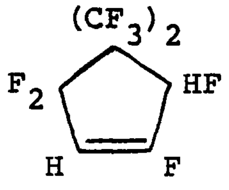
Only after 72h at 150°C did some tarring of (71) occur in the presence of KOH.

The stability of (71) in the presence of CsF at 140°C is very surprising for two reasons:

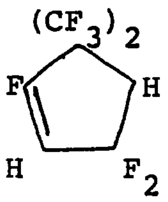
(i) The high reactivity of (71) to PhOH under mild conditions.

(ii) The cyclisation of $[(CF_3)_2C=CHCF_2 \}_2$ (75) in the presence of CsF at 100°C indicates that (71) might also be susceptible to attack.

However the expected derivatives (95) and (96) (by analogy to Scheme 4.1) were not obtained.



(95)



(96)

4D. Conclusions

(i) Relevance of Results Obtained

Summary

The important observations are summarized by points (a)-(f):

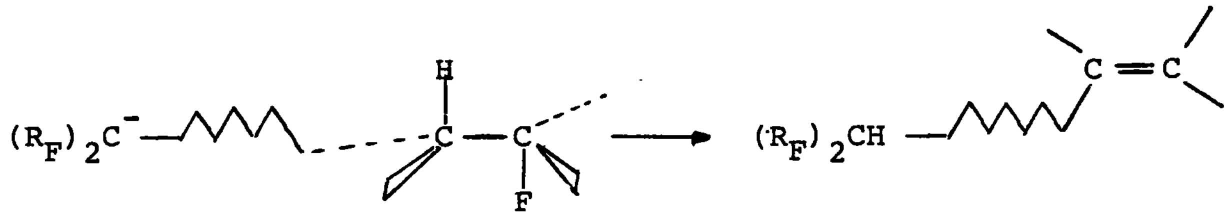
(a) The model aryl-ether cross-links (85) and (88) are stable under extremely aggressive conditions.

(b) Under typical cure conditions [49] the model $(CF_3)_2C=CHCF_2CH_2CF_3$ (71) showed no tendency to react with bisphenol AF.

(c) Under very forcing conditions the models (71) and $(CF_3)_2C=CHCF_3$ (81) were unchanged in the presence of KOH (no solvent) and CsF (solvent).

(d) In complete contrast the models (71), (81) and $[CF_3)_2C=CHCF_2]_2$ (75) undergo nucleophilic attack in the presence of PhOh (with solvent) under very mild conditions.

(e) The reaction of (71) with PhOH clearly demonstrates the feasibility of $H^{+\cdot}$ abstractions from saturated sites in the copolymer *via* carbanionic sites, *e.g.*:

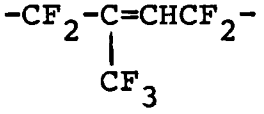


(This may be an intramolecular or intermolecular process).

(f) The model (75) is susceptible to nucleophilic attack by F$^-$ (with solvent).

Remarks

It was shown in Chapter Two that elimination of HF by base occurs preferentially at tertiary sites resulting in double bonds of the form (97)

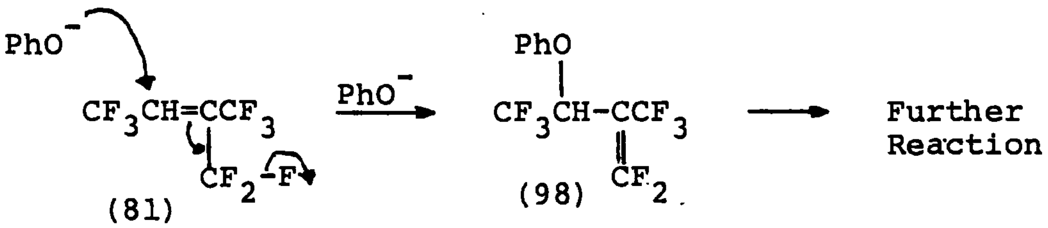


$$-CF_2-\underset{\displaystyle CF_3}{\underset{|}{C}}=CHCF_2-$$

(97)

We have now shown that this structure is highly susceptible to nucleophilic attack under mild conditions.

It is worth emphasizing that no products were obtained from nucleophilic attack which involve allylic displacement of F$^-$ (Scheme 4.3) as postulated by Schneigel for the co-polymer.[49]



Scheme 4.3

The unsaturated models, however, show surprising resistance to KOH although this may be due to a lack of phase contact in this system.

4D. (ii) Implications for the Copolymer Systems

The stability of the model cross-links (85) and (88) demonstrate clearly that the aryl-ether cross-link (89) in the bisphenol cured copolymer is not the source of instability in this system.

The high susceptibility of the unsaturated models to nucleophilic attack demonstrates that residual unsaturated sites in the cured copolymer will be a source of instability in hydrolytically aggressive environments. Furthermore the number of residual sites may be higher than expected due to H^+ abstraction processes as outlined in Scheme 4.2. Therefore any cross-linking process which employs nucleophilic attack under basic conditions results in a loss of stability under hydrolytically aggressive conditions.

We have now put on a firm basis the reactivity of copolymer sites which previously was a source of much speculation.

Further work in this area is currently being conducted in the laboratory.

CHAPTER FIVE

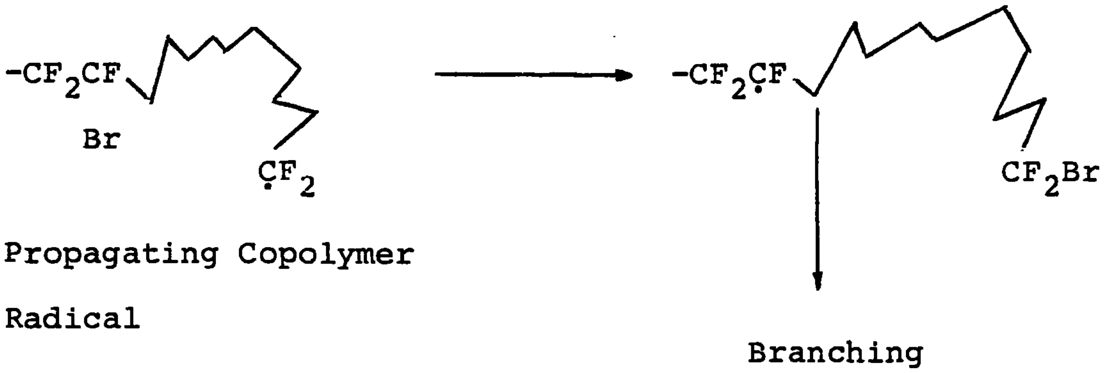
AN APPROACH TO A NEW FREE-RADICAL CROSS-LINKING PROCESS

In the previous chapter it was shown that the cross-linking of $CH_2=CF_2/CF_3CF=CF_2$ copolymers using bisnucleophiles, *e.g.* bisphenol AF (2) results in a considerable reduction of the chemical stability of the system. In this chapter an entirely novel approach to cross-linking is discussed. This approach involves the production of free-radical sites in the copolymer promoted by the incorporation of special sterically crowded comonomers.

5A Introduction

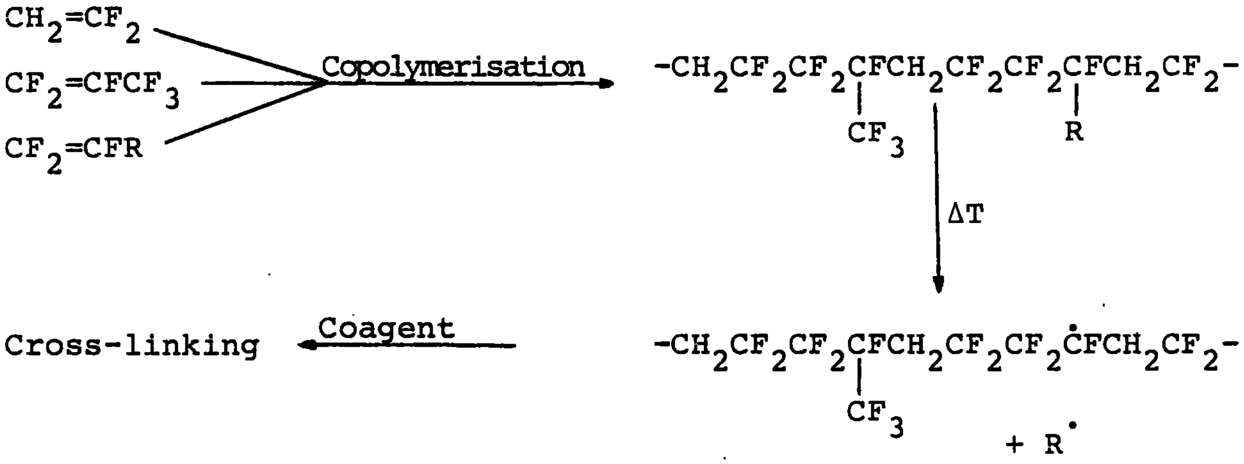
In Chapter One (Scheme 1.4) the use of bromine-containing comonomers was shown to promote cross-linking *via* scission of pendant polymer C-Br bonds and reaction of the subsequent polymer radical sites with the coagent triallyl isocyanurate (TIC).$^{72-74}$

However, the use of bromine containing comonomers does result in some inhibition of the copolymerisation process^{26} (Scheme 5.1) and loss of active C-Br sites:



Scheme 5.1

Our objective therefore was to synthesize copolymers which did not involve the incorporation of C-Br bonds but which, on heating, gave rise to copolymer radical sites. These sites would be active towards cross-linking in the presence of a suitable coagent (*e.g.* TIC). This objective was achieved by incorporating into the polymer system a varying amount of a third comonomer containing a large, sterically demanding vinyl group. In general this approach is illustrated by Scheme 5.2.



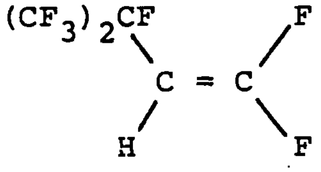
Scheme 5.2

When the group R is large the bond C-R in the copolymer is considerably weakened due to steric crowding and on heating undergoes facile thermolysis giving rise to copolymer radical sites.

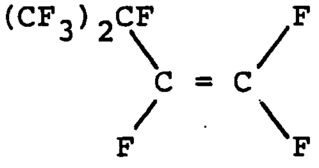
We have successfully synthesized and made a preliminary study of copolymer systems incorporating sterically crowded comonomers using vacuum pyrolysis and differential scanning calorimetric techniques.

5B Synthesis of Crowded Comonomers

The two crowded alkenes chosen for study initially were 2H-nonafluoro-3-methylbut-1-ene (99) and perfluoro-3-methylbut-1-ene (100).

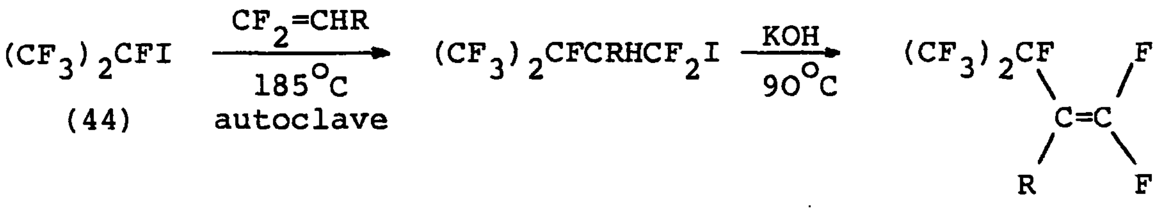


(99)



(100)

The syntheses of the alkenes (99) and (100) were achieved in excellent yields using the routes outlined in Scheme 5.3.



R = H (99) (quant.)

R = F (100) (quant.)[136]

Scheme 5.3

The alkenes (99) and (100) are low-boiling liquids (b.pts. 30°C and 32°C resp.) and easily stored and handled using vacuum-line techniques. These properties render them particularly suited to copolymerisation with $CH_2=CF_2$ and $CF_3CF=CF_2$ in sealed glass ampoules in the presence of γ-radiation.

5C Synthesis of Copolymers Incorporating the Crowded Comonomers

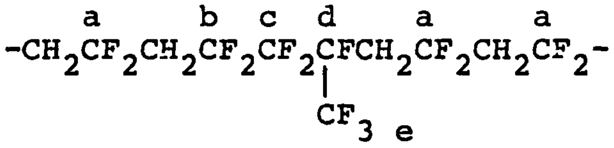
The copolymerisations described below were carried out (in sealed evacuated glass tubes) in the presence of a ^{60}Co γ-source. This method of initiation is advantageous because it excludes impurities, *e.g.* initiators, H_2O *etc.* which remain in the copolymer when aqueous emulsion methods are used.[5,6] Good samples of pure copolymers were therefore easily obtained using this technique.

(i) $CH_2=CF_2$ Homopolymer

Samples of poly-1,1-difluoroethene were obtained after γ-irradiation of $CH_2=CF_2$ for 3 days at 20°C.

(ii) $CH_2=CF_2/CF_3CF=CF_2$ Copolymers

When a 1:1 molar mixture of $CH_2=CF_2$ and $CF_3CF=CF_2$ was irradiated for 3 days at 20°C a copolymer was obtained which was determined using ^{19}F nmr studies (in solution inDMAC) to have molar composition 70:30 in favour of $CH_2=CF_2$. Analysis of the spectra showed that the structure



$$-CH_2\overset{a}{CF_2}CH_2\overset{b}{CF_2}\overset{c}{CF_2}\underset{\underset{CF_3\ e}{|}}{\overset{d}{C}}FCH_2\overset{a}{CF_2}CH_2\overset{a}{CF_2}-$$

accounts for >95% of the $CF_3CF=CF_2$ monomer units, which result is in agreement with the findings of Ferguson.[39] The ^{19}F nmr data are summarized in Table 5.1 relating to the above structure. Assignment of these chemical shift data was greatly facilitated by using that of model compounds which contained similar structures (see Appendix).

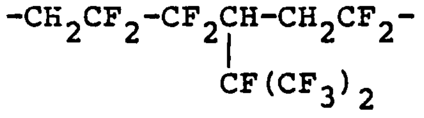
TABLE 5.1 ^{19}F nmr Data for 70:30 $CH_2{=}CF_2/CF_3CF{=}CF_2$ Copolymer

δ $CFCl_3$ 0 ppm.

Chemical Shift ppm.	Relative Intensity	Assignment
- 75.9	9	e $-CF_3$
- 94.0	10	a $-CF_2$
-109.5	4	b $-CF_2$
-118.1	6	c $-CF_2$
-183.8	3	d $-CF$

(iii) $CH_2{=}CF_2/(CF_3)_2CFCH{=}CF_2$ Copolymers

When a 3:2 molar mixture of $CH_2{=}CF_2$ and $(CF_3)_2CFCH{=}CF_2$ (99) respectively was irradiated at 20°C for 24 hours a copolymer was obtained which gave a surprisingly complex ^{19}F nmr spectrum (in solution in DMAC). It is clear from resonances observed in the range -60 to -75 ppm that incorporation of the comonomer (99) had taken place, however, the structure of the resulting copolymer is not (101) as expected, but a complex mixture of structures



$$-CH_2CF_2-CF_2\underset{CF(CF_3)_2}{\underset{|}{CH}}-CH_2CF_2-$$

(101)

which could not be resolved using nmr techniques.

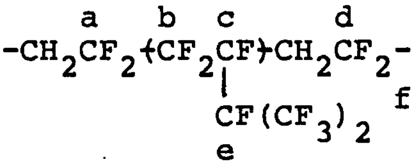
(iv) $CH_2{=}CF_2/(CF_3)_2CFCF{=}CF_2$ Copolymers

A range of copolymers of $CH_2{=}CF_2$ and the crowded comonomer $(CF_3)_2CFCF{=}CF_2$ (100) were synthesized which varied in composition. These are summarized in Table 5.2. The percentage incorporation of the comonomer (100) by moles was determined by ^{19}F nmr spectral analysis (in solution in DMAC).

TABLE 5.2 Molar Compositions of Copolymers of $CH_2{=}CF_2/(CF_3)_2CFCF{=}CF_2$ (100)

Molar Ratio of Comonomer Mixture		Conditions (γ-Irradiation)	% Molar Incorporation of (100)
$CH_2{=}CF_2$:	$(CF_3)_2CFCF{=}CF_2$		
9	1	72h, 20°C	7%
8	3	72h, 20°C	10%
9	6	168h, 20°C	17%

The ^{19}F nmr spectra were consistent with the structure (102) accounting for >98% of the comonomer (100).



$$-CH_2\overset{a}{CF_2}\left(\overset{b}{CF_2}\underset{\underset{e}{CF}(CF_3)_2\ f}{\overset{c}{CF}}\right)CH_2\overset{d}{CF_2}-$$

(102)

However it is notable that the chemical shifts of the ^{19}F atoms present in the structure (102) are moved to lower field as the % incorporation of the crowded comonomer (100) increases. This trend is summarized in Table 5.3.

This trend could be correlated with chronic steric repulsion resulting in a weakening of the structure (102) and a perturbation of the electron density. This effect could result in a deshielding of certain ^{19}F nuclei. In the more crowded case there is evidence for restricted

TABLE 5.3 The Dependence of Chemical Shift Data from $CH_2=CF_2/(CF_3)_2CFCF=CF_2$ Copolymers upon Composition

δ $CFCl_3$ 0 ppm

Chemical Shifts/ppm			Assignment
Molar % (100)	7	17	
	- 72.6	- 67.6, -69.6	f $-CF_3$'s
	- 91.4	- 91.4	d $-CF_2$
	-108.2	-109.5	a $-CF_2$
	-116.0	-111.8	b $-CF_2$
	-186.6	-173.6	e $-CF$
	-197.0	-180.8	c $-CF$

rotation about the $CF-CF(CF_3)_2$ bond since the $-CF_3$ groups are inequivalent.

(v) Terpolymer Systems

Terpolymers of $CH_2=CF_2/CF_3CF=CF_2$ and $(CF_3)_2CFCR=CF_2$ (R=H(99), R=F(100)) were also synthesized using γ-irradiation. The resulting terpolymer compositions, as estimated by ^{19}F nmr techniques are summarized in Table 5.4.

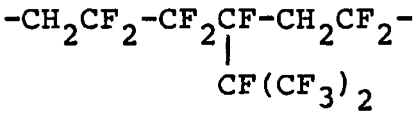
TABLE 5.4 Terpolymer Compositions

Molar Ratio of Comonomers				Conditions	% Molar Composition of Termpolymers		
	$CH_2=CF_2$	$CF_3CF=CF_2$	$C_3F_7CR=CF_3$		$CH_2=CF_2$	$CF_3CF=CF_2$	$C_3F_7CR-CF_2$
R=H	4 :	3 :	2	72h	70	27	*ca.* 3
R=F	6 :	4 :	1	20°C	85	14	*ca.* 1

5D Vacuum Pyrolysis of $CH_2=CF_2/(CF_3)_2CFCF=CF_2$ Copolymers

The thermal decomposition of copolymers of $CH_2=CF_2$ and $(CF_3)_2CFCF=CF_2$ (100) shown in Table 5.2 were studied over the temperature range 20°-220°C. Volatile decomposition products were collected in liquid-air-cooled traps using vacuum line techniques. In this way definitive information about the ease of fragmentation of these materials in relation to steric strain was obtained.

When the copolymer containing 7% molar concentration of the structure (102) was heated to 90°C under vacuum a bright orange-red colouration appeared in the cold-trap.



$$-CH_2CF_2-CF_2\underset{\displaystyle CF(CF_3)_2}{\underset{|}{C}}F-CH_2CF_2-$$

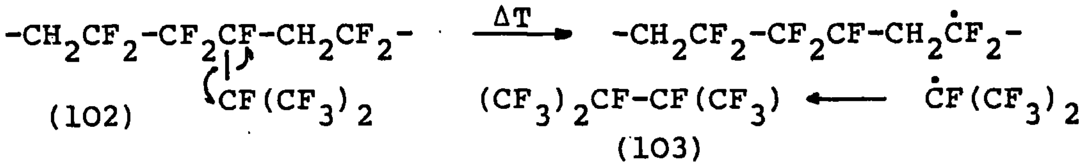
(102)

After prolonged heating at 120°C the contents of the cold-trap were examined. This consisted of the single product perfluoro-2,3-dimethylbutane (103) and provides clear evidence for the production of the free-radical $(CF_3)_2CF^{\bullet}$.

$$(CF_3)_2CF-CF(CF_3)_2$$

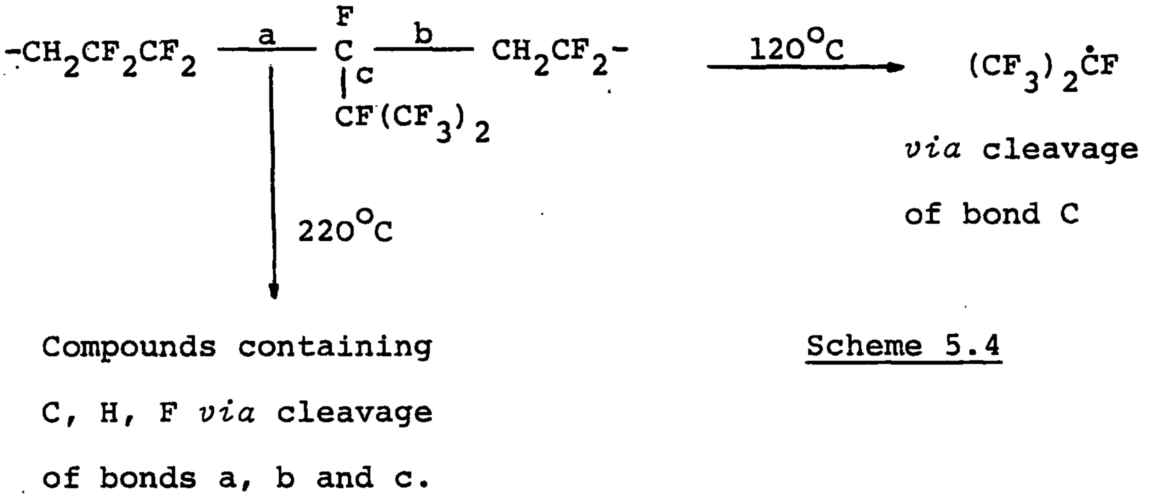
(103)

When a portion of the copolymer residue was redissolved in DMAC a ^{19}F nmr spectrum was obtained which showed that the % molar concentration of the structure (102) had fallen to 5.8%. Further heating of the copolymer residue resulted in a further reduction to 3.8%. This result demonstrates clearly that selective homolytic cleavage takes place in the copolymer as follows:



(102) (103)

On further heating of the copolymer to 220°C a high-boiling liquid mixture was obtained which contained $-CH_2-$ groups (^1H nmr). This provides evidence that at higher temperatures the bond-cleavage is less selective (Scheme 5.4).

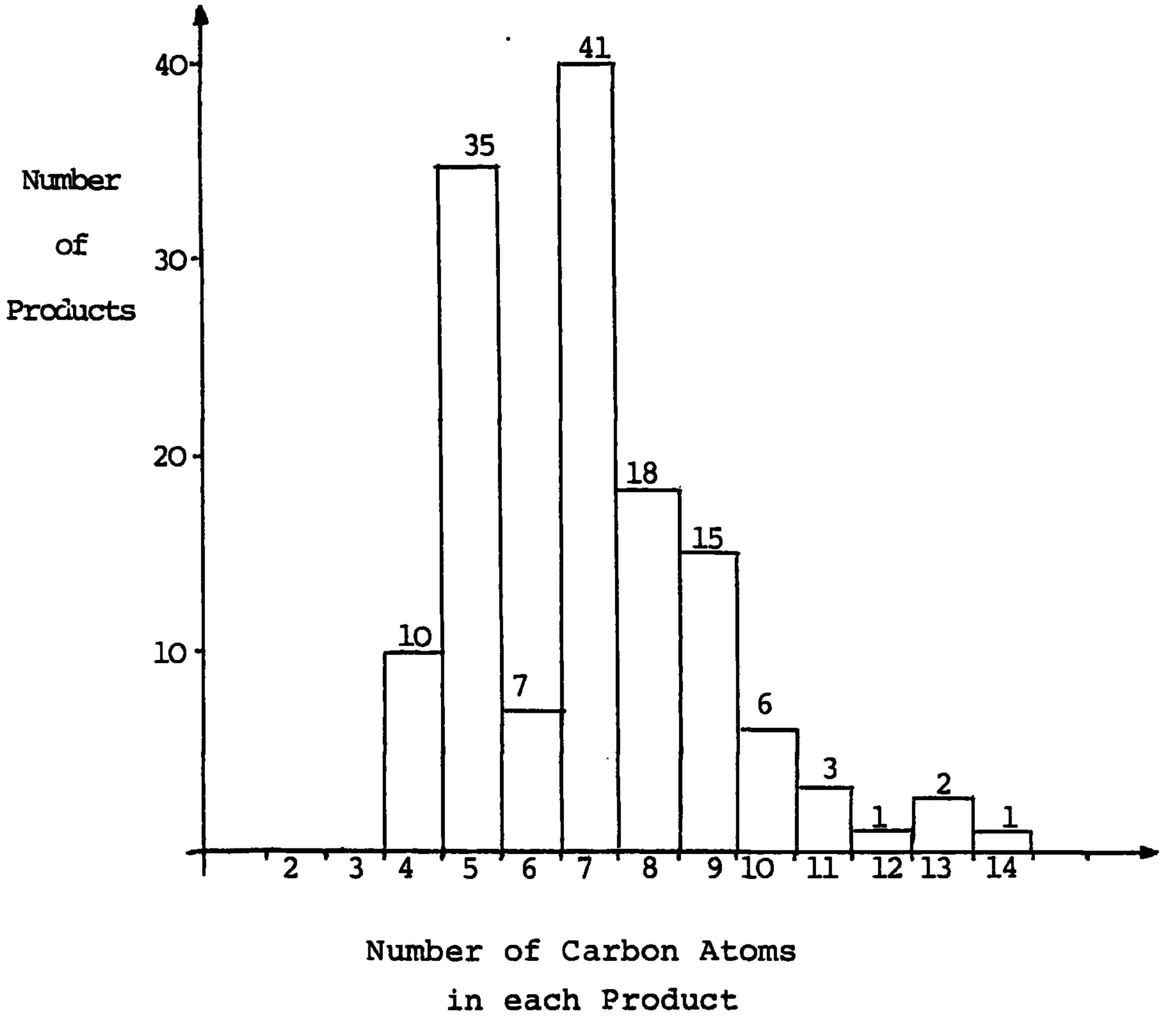


Scheme 5.4

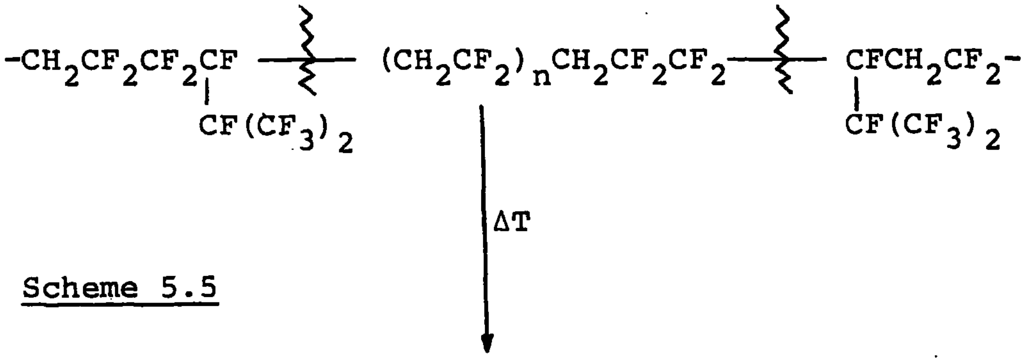
When the copolymer containing 17% molar concentration of the structure (102) was heated at 90°C for 6h a complex mixture of products was obtained containing C, F and H. These products were analysed by mass-spectrometry using capillary column gas chromatography. 140 products were resolved of mass-range 200-700 mass units. Using the approximate empirical formula C_nF_{2n} it is possible to estimate the number of carbon atoms in each product. The distribution of carbon numbers is represented in Figure 5.1.

It is notable that products containing 5 and 7 carbon atoms are preferred. This is easily rationalized by considering the structure of the copolymer. It may be assumed that no two $(CF_3)_2CFCF=CF_2$ (100) can occur consecutively on

FIGURE 5.1 Approximate Molecular Weight Distribution of the Thermal Decomposition Products of $CH_2=CF_2/(CF_3)_2CF=CF_2$(17%) Copolymer



the basis that if $CF_3CF=CF_2$ does not homopolymerise easily[34] due to steric effects (see Chapter One) then it is even less feasible that (100) will do so. Therefore the shortest product fragments from thermal bond-scission will contain either 5 or 7 carbon atoms as shown by Scheme 5.5.



$$-CH_2CF_2CF_2\underset{CF(CF_3)_2}{C}F \wr (CH_2CF_2)_nCH_2CF_2CF_2 \wr \underset{CF(CF_3)_2}{C}FCH_2CF_2- \xrightarrow{\Delta T}$$

Scheme 5.5

Product fragments
containing (2n+3)
carbon atoms n = 0, 1, 2 ....

5E Differential Scanning Calorimetry Studies

The technique of differential scanning calorimetry (DSC) involves the slow heating of sample materials over a given temperature range to observe variations in the specific heat capacity. Thus endo- and exo-thermic processes can be observed as increases and decreases in the specific heat capacity respectively. In this way DSC techniques may be used qualitatively to identify chemical changes in the crowded copolymer systems which occur as a result of bond-breaking and bond-forming. For example the ejection of $(CF_3)_2\dot{C}F$ radicals by $CH_2=CF_2/(CF_3)_2CFCF=CF_2$ (100) copolymers to give $(CF_3)_2CFCF(CF_3)_2$ (103) is expected to be an exothermic process on account of the weak sterically crowded bonds in the copolymer.

(i) $CH_2=CF_2$ Homopolymer and $CH_2=CF_2/CF_3CF=CF_2$ Copolymer

When a sample of the $CH_2=CF_2$ homopolymer (produced by γ-irradiation of $CH_2=CF_2$) was investigated no exothermic processes could be identified below 400°C. A sample of the copolymer of $CH_2=CF_2/CF_3CF=CF_2$ containing 30% $CF_3CF=CF_2$ did not exhibit any exothermic behaviour below 330°C. Above this temperature a steady exotherm of increasing magnitude occurred which was attributed to decomposition.

(ii) $CH_2=CF_2/(CF_3)_2CFCF=CF_2$ Copolymers

A sample of the $CH_2=CF_2/(CF_3)_2CFCF=CF_2$ (100) copolymer containing 7% molar concentration of (100) was studied using DSC techniques over the temperature range 20°-330°C. A sharp endothermic melting point was observed at 174°C which was reversible and became sharper on cooling and repeating the experiment. However when the copolymer was heated over the temperature range 280°C-330°C an exothermic process occurred which was not reversible. Furthermore on cooling to 20°C and repeating over the full temperature range no melting point was observed. When the cooled residue was examined it had become brittle and dark brown in appearance in contrast to the soft white plastic appearance of the starting material. These observations are consistent with the formation of a cross-linked network following bond-breaking at the weak sterically crowded sites.

When the copolymer with 17% incorporation of the crowded comonomer (100) was examined a steady and increasing exotherm was observed over the temperature range 90°-200°C. No melting point was observed. This result is again best explained by exothermic cross-link formation, the rate of which increases with the applied temperature.

5E (iii) $CH_2=CF_2/(CF_3)_2CFCH=CF_2$ Copolymer

When a sample of a $CH_2=CF_2/(CF_3)_2CFCH=CF_2$ (99) copolymer containing 5% of the crowded comonomer (99) was studied over the temperature range 20°C-200°C a weak exotherm was observed between 110° and 150°C.

(iv) $CH_2=CF_2/CF_3CF=CF_2/(CF_3)_2CR=CF_2$, (R=H,F) Terpolymers

A sample of a $CH_2=CF_2/CF_3CF=CF_2/(CF_3)_2CFCH=CF_2$ (99) containing respective mole-fractions 70%/25%/5% showed clear exotherms at 140°C and 170°C. Another sample of this system, of similar composition, was synthesized and studied by Dr. Alberto Fontana (Montefluos SPA). This sample underwent a clear exothermic process at 165°C[137] as shown by Figure 5.2. When the terpolymer system $CH_2=CF_2/CF_3CF=CF_2/(CF_3)_2CFCF=CF_2$ (100) of molar composition 85%/14%/1% respectively was examined a weak exothermic feature was observed at 175°C.

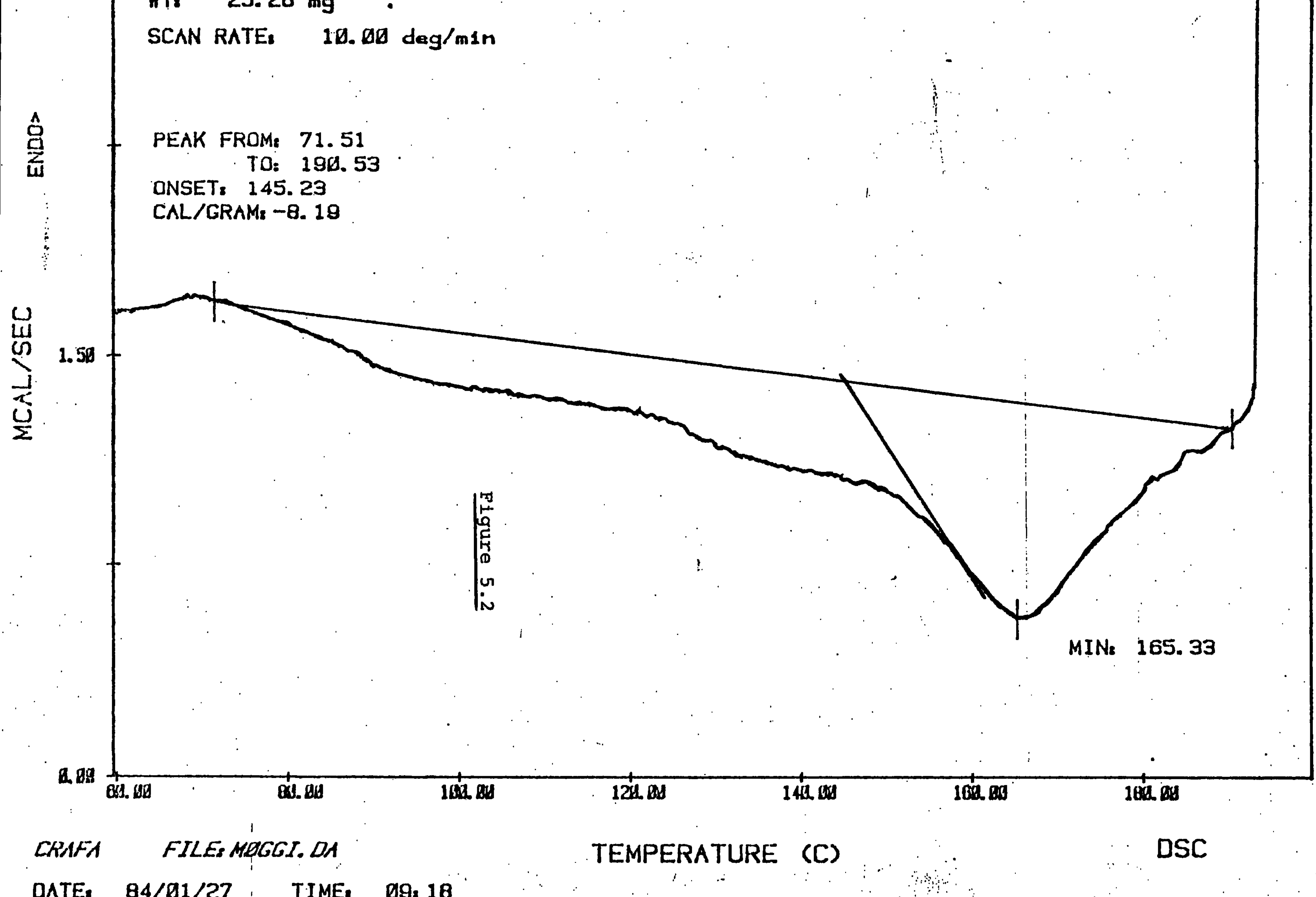
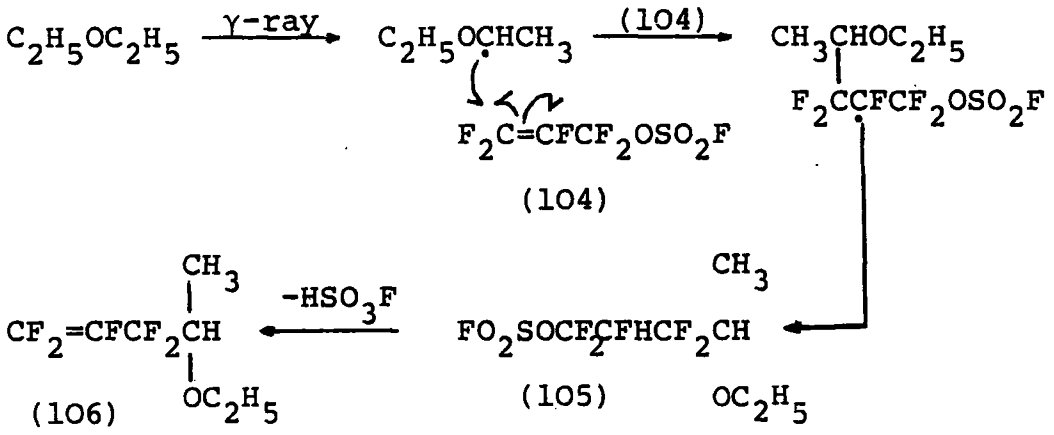

WT: 25.26 mg
SCAN RATE: 10.00 deg/min
PEAK FROM: 71.51
TO: 190.53
ONSET: 145.23
CAL/GRAM: -8.19
MIN: 165.33
ENDO>
MCAL/SEC
1.50
0.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
TEMPERATURE (C)
DSC
CRAFA
FILE: MØGGI. DA
DATE: 84/01/27
TIME: 09:18

Figure 5.2

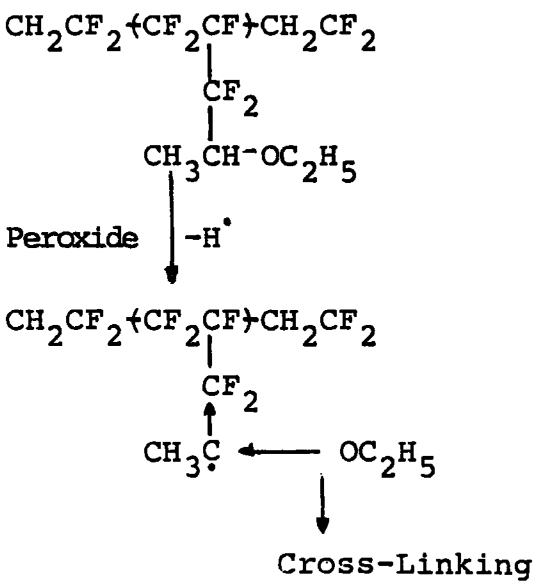
5F Attempted Synthesis of a Comonomer to Promote Capto-Dative Free-Radical Stabilization

Scheme 5.6 outlines an approach to the synthesis of 2-ethoxy-3,3,4,5,5-pentafluoropent-4-ene (106).



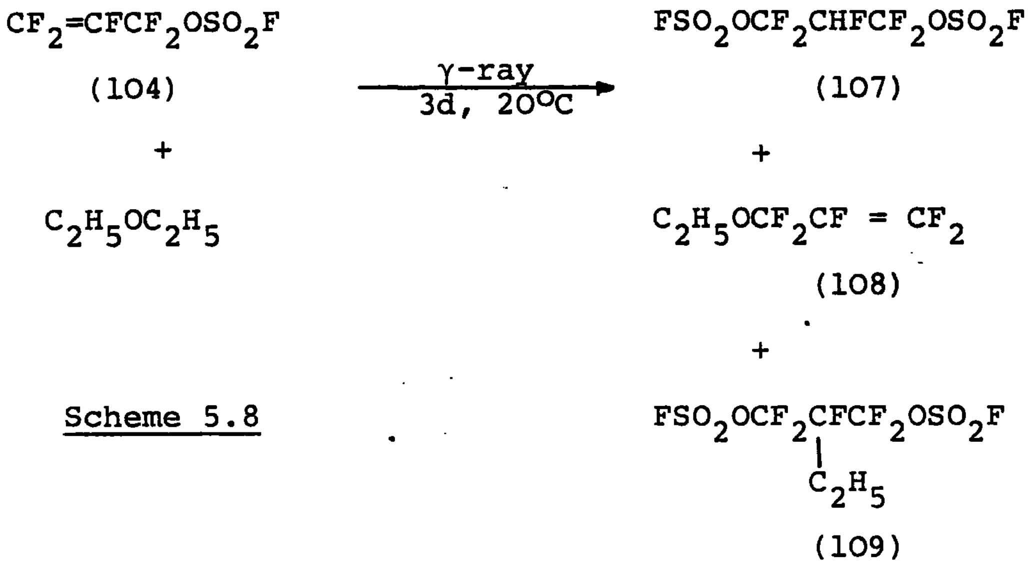
Scheme 5.6

The alkene (106) on incorporation into the $CH_2{=}CF_2/CF_3CF{=}CF_2$ system was thought likely to promote free-radical processes assisted by capto-dative free-radical stabilization (Scheme 5.7)



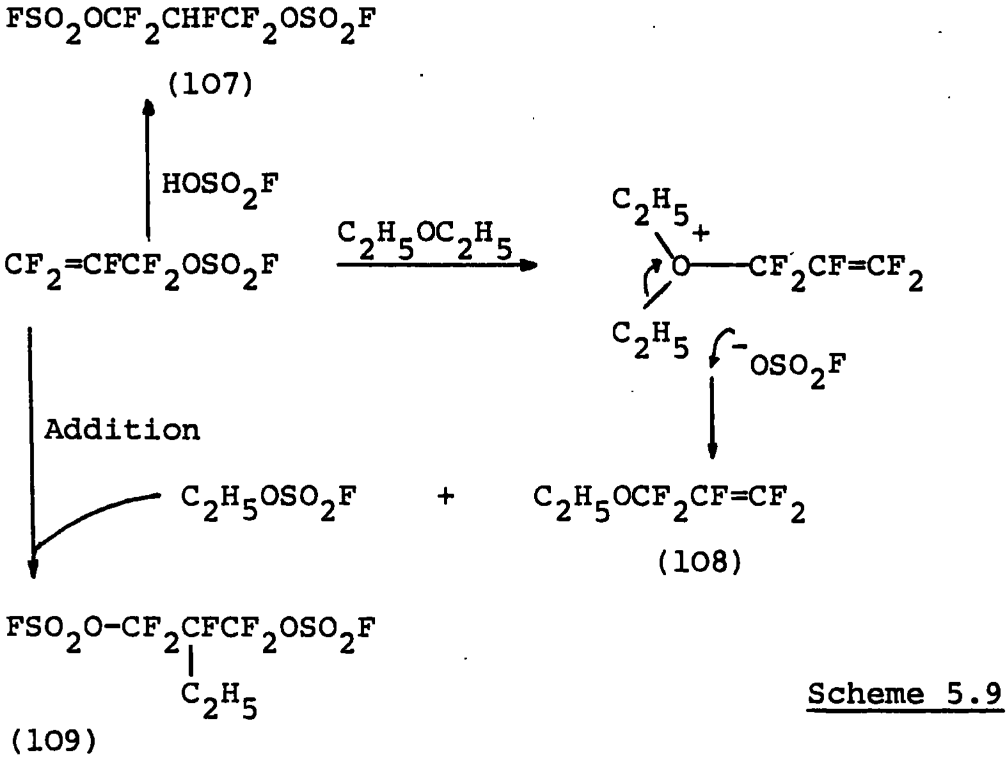
Scheme 5.7

The synthesis of the alkene (106) was however not successful using the approach outlined in Scheme 5.6, the only products isolated from the reaction between $(C_2H_5)_2O$ and (104) being (107), (108) and (109) as shown in Scheme 5.8.



Scheme 5.8

The products (107-109) are rationalized by the ionic processes outlined in Scheme 5.9.



Scheme 5.9

This approach was not further developed.

5G Conclusions

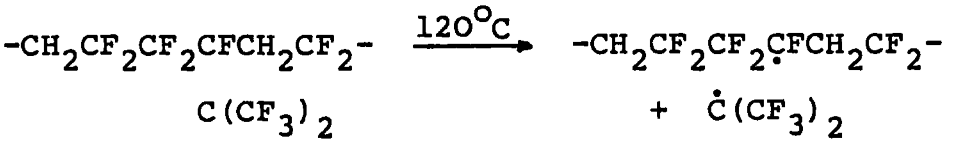
(i) A summary of Results obtained

(a) The comonomers $(CF_3)_2CFCH=CF_2$ (99) and $(CF_3)_2CFCF=CF_2$ (100) are easily synthesized in excellent yields from available precursors and are easily handled using vacuum-line techniques.

(b) These crowded comonomers are each easily incorporated into the $CH_2=CF_2$ and $CH_2=CF_2/CF_3CF=CF_2$ polymer system using γ-ray initiation. Furthermore the amount of incorporation can be controlled to a large extent by varying the proportions of the comonomers used.

(c) When $CH_2=CF_2/(CF_3)_2CFCF=CF_2$ (100) copolymers are heated bond-scissions occur due to steric overcrowding. At 120°C this process occurs selectively for 7% incorporation of (100) to give $\dot{C}F(CF_3)_2$ and polymer radicals.

e.g.



$$-CH_2CF_2CF_2\underset{C(CF_3)_2}{CF}CH_2CF_2- \xrightarrow{120^{\circ}C} -CH_2CF_2CF_2\underset{\bullet}{C}FCH_2CF_2- \; + \; \dot{C}(CF_3)_2$$

At higher temperatures, *e.g.* 220°C bond-scissions occur less selectively and fragmentation of the polymer backbone takes place. When the concentration of the comonomer was increased to 17% the temperature at which bond-scission occurred was lower *ca.* 90°C and, from analysis of the products of decomposition, appeared to be completely non-selective involving fragmentation of the polymer backbone.

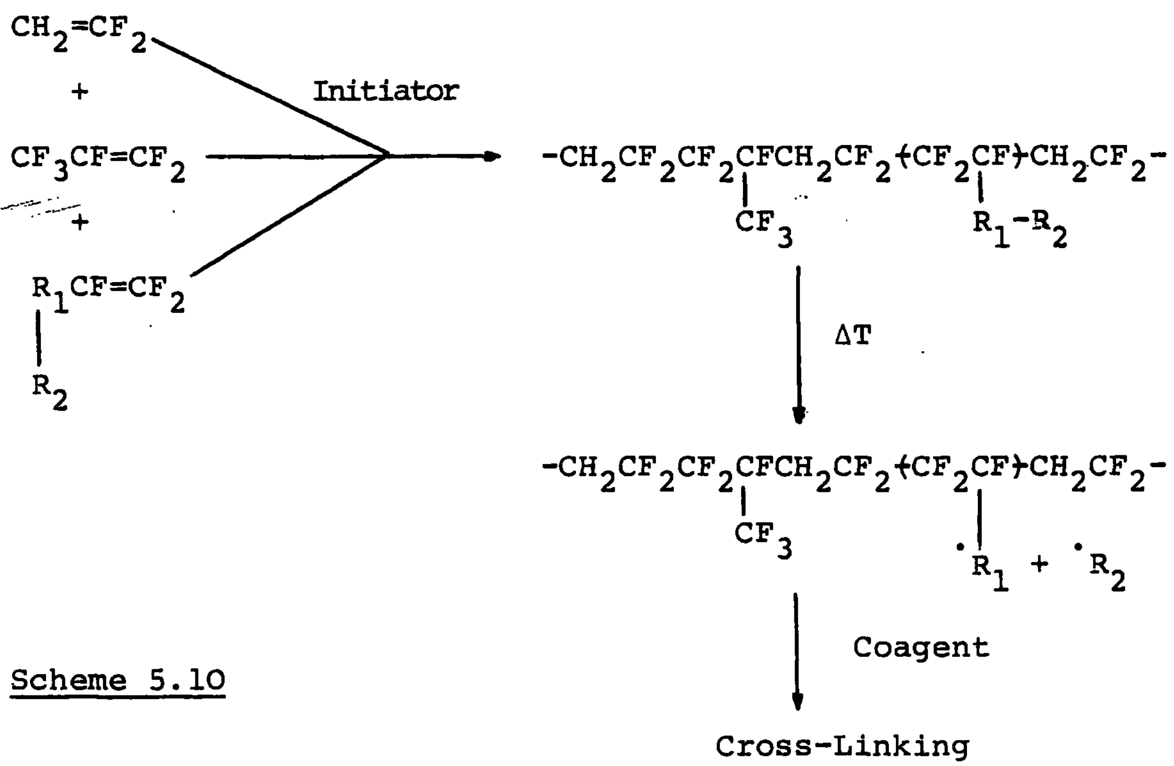
(d) When differential scanning calorimetric (DSC) methods were used to study the thermal behaviour of $CH_2=CF_2$

and $CH_2=CF_2/CF_3CF=CF_2$ copolymers incorporating the special comonomers (99) and (100), exothermic processes were identified which did not occur when the special comonomers were excluded. The DSC study of the $CH_2=CF_2/CF_3CF=CF_2/(CF_3)_2CFCH=CF_2$ (99) was particularly promising, showing clear exothermic non-reversible processes between 140°C and 170°C.

(ii) Implications for Cross-Linking

The results discussed in this chapter provide an excellent basis for an entirely novel approach to the cross-linking of $CH_2=CF_2/CF_3CF=CF_2$ copolymers. In principle this approach involves the inclusion into the copolymerisation mixture of a special third comonomer alkene containing a large sterically demanding group. The resulting polymer therefore contains built-in sites of instability due to steric crowding which may undergo thermolysis to give polymer radical sites. Cross-linking may then take place *via* combination of these radical sites with a suitable coagent (*e.g.* TIC). We have demonstrated that the generation of polymer radicals by this approach is very feasible (Scheme 5.2).

Research is also currently being carried out in order to synthesize comonomers containing sterically crowded sites which are remote from the site of copolymerisation. This study will also be extended to include non-fluorinated crowded comonomers. This approach is illustrated by Scheme 5.10.



Scheme 5.10

Here the incorporation into the copolymerisation mixture of an alkene containing a group R_2 which is sterically demanding, *e.g.* $(CF_3)_2CF-$, results in a weakening of the bond R_1-R_2 in the copolymer and facile thermal homolytic cleavage to form radical sites remote from the polymer backbone. Cross-linking achieved using this approach should result in very little loss of chemical and thermal stability in comparison with the raw $CH_2=CF_2/CF_3CF=CF_2$ copolymer.

Thus we have provided an alternative approach to the curing of $CH_2=CF_2/CF_3CF=CF_2$ copolymers not involving dehydrohalogenation, which we now believe to be a major source of instability generated during the bisphenol cure.

CHAPTER SIX

NOVEL CHEMISTRY INVOLVING ANTIMONY PENTAFLUORIDE

During investigations into the general chemistry of the model compounds related to $CH_2=CF_2/CF_3CF=CF_2$ copolymers it became clear at an early stage that treatment with antimony pentafluoride in many cases resulted in reactions which were both fundamentally novel in nature and had potential relevance to fluoropolymers. Therefore the chemistry of these systems was pursued and developed providing the content of this chapter.

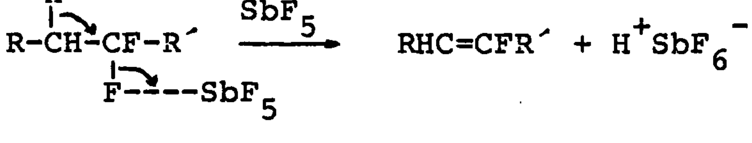
6A Introduction: An Unusual Discovery

In Chapter Three the elimination of HF from the saturated model $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (70) in the presence of SbF_5 to give $(CF_3)_2C=CHCF_2CH_2CF_3$ (71) was discussed. This reaction represents a Lewis acid-catalysed elimination process of a kind, which to our knowledge, has not previously been exploited. This reaction, together with the following are essentially quantitative and, in principle, provides a simple route to fluoroalkenes and polyenes.

$$\underset{(66)}{(CF_3)_2CFCH_2CF_3} \xrightarrow[120^{o}C,\ 3h]{SbF_5} \underset{(81)}{(CF_3)_2C=CHCF_3} \quad \text{quant.}$$

$$\underset{(61)}{[(CF_3)_2CFCH_2CF_2]_2} \xrightarrow[120^{o}C,\ 2h]{SbF_5} \underset{(75)}{[(CF_3)_2C=CHCF_2]_2} \quad \text{quant.}$$

The general mechanism proposed for this process is as follows:



$$R\text{-}\overset{H}{C}H\text{-}\underset{F\text{---}SbF_5}{C}F\text{-}R' \xrightarrow{SbF_5} RHC=CFR' + H^{+}SbF_6^{-}$$

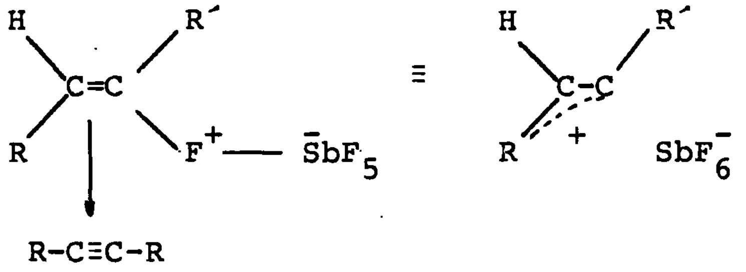
Therefore in order to investigate the feasibility of further elimination of HF from fluorohydroalkenes to form fluoroallenes or fluoroalkynes, the unsaturated models $(CF_3)_2CFCH=CF_2$ (99) and $CF_3CH=CFCF_3$ (83) were treated with SbF_5.

When (83) was heated with SbF_5 in a sealed system at 120°C for 12h a small amount of HF elimination occurred to give $CF_3C\equiv CCF_3$ (108) which was identified by mass spectrometry and ^{19}F nmr techniques

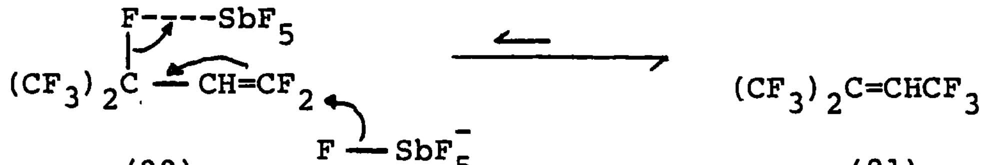
$$CF_3CH=CFCF \xrightarrow[120^{o}C,\ 12h]{SbF_5} CF_3C\equiv CCF_3 \quad 5\%$$

(83) (108)

This observation demonstrates that complexation of SbF_5 to vinyl fluorine can result in elimination to give alkynes:



When $(CF_3)_2CFCH=CF_2$ (99) was treated at 20°C with SbF_5, quantitative isomerisation to the product $(CF_3)_2C=CHCF_3$ (81) occurred over *ca.* 10 min and no elimination products were obtained. This observation is readily explained by the strong complexation of SbF_5 to the tertiary fluorine atom of (99). Subsequent isomerisation of the C=C bond in the presence of SbF_6^- is then preferable to elimination of a molecule of HF:

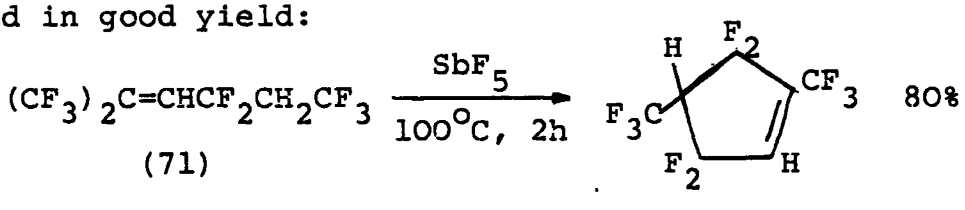


(99) (81)

6B Some Novel Elimination Reactions

(i) A Novel 1,5-Elimination of Hydrogen Fluoride

When the unsaturated model $(CF_3)_2C{=}CHCF_2CH_2CF_3$ (71) was treated with SbF_5 at 110°C for 2h, the product 1H-2,4-bistrifluoromethyl-4H-tetrafluorocyclopentene (109) was obtained in good yield:

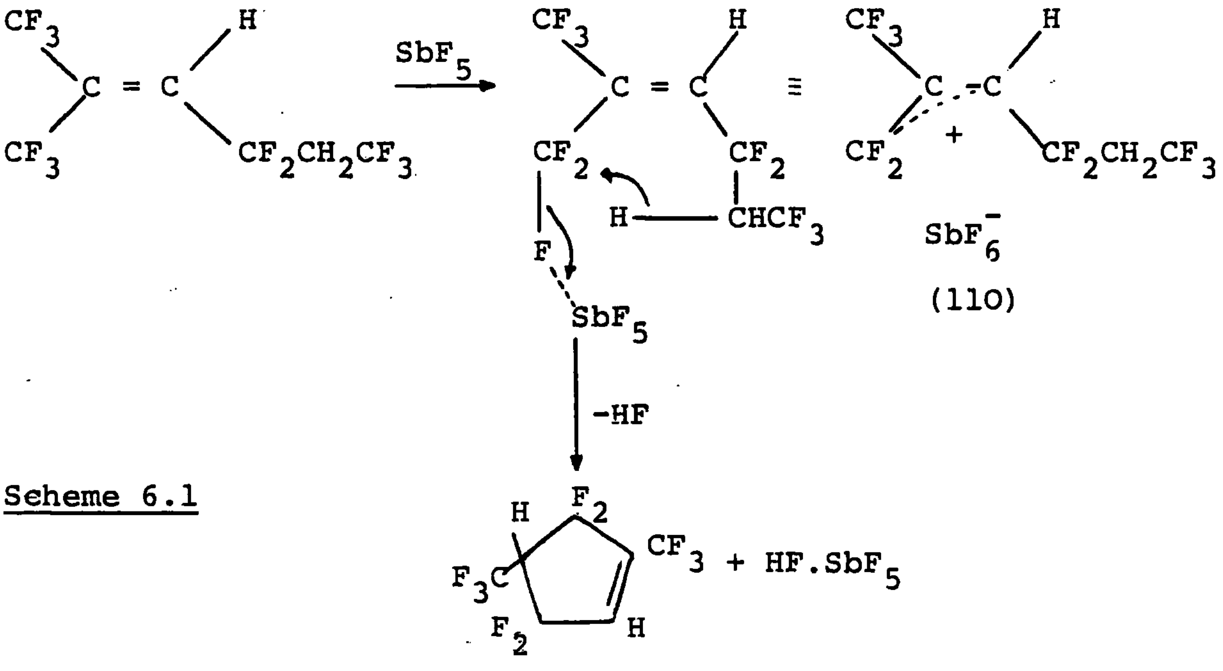


(71)

(109)

Other products were not characterized.

This reaction represents an entirely novel intramolecular 1,5-elimination of HF. The mechanism proposed for this reaction is shown in Scheme 6.1.



(110)

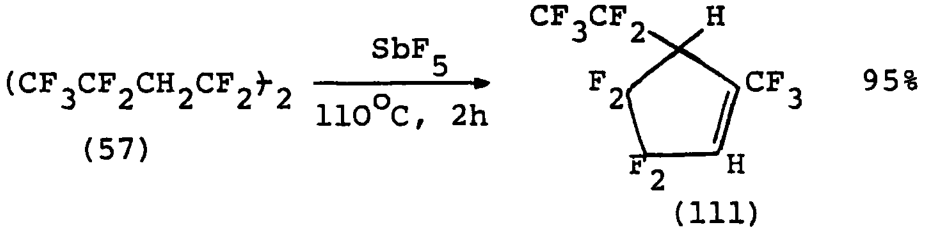
Scheme 6.1

(109)

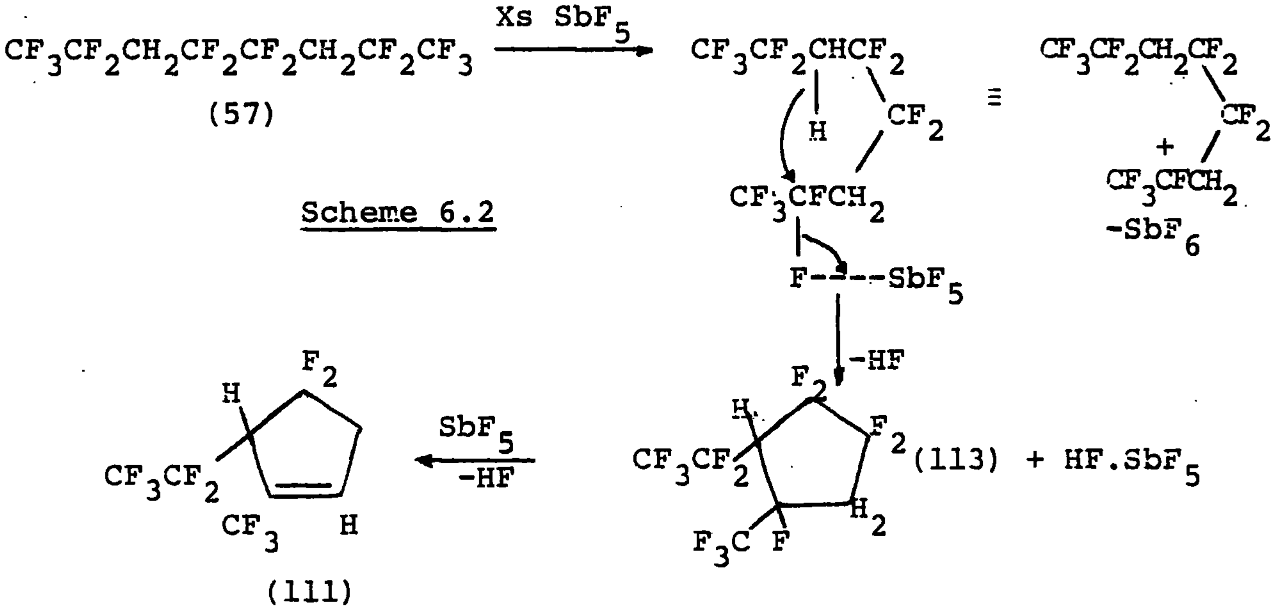
This mechanism involves nucleophilic attack by a saturated C-H bond on a saturated C-F bond complexed to SbF_5 and has not previously been reported. This result therefore represents an area of potentially fundamental interest to mechanistic organic chemistry.

6B (ii) Cyclisation of a Saturated Fluorohydrocarbon

When the saturated model compound $(CF_3CF_2CH_2CF_2)_2$ (57) was treated with SbF_5 at 110°C for 2h the product 1H-2-trifluoromethyl-3H-3-pentafluoroethyltetrafluorocyclopentene (111) was obtained in excellent yield.



The mechanism proposed for this reaction involves again the nucleophilic attack by a saturated C-H bond at a saturated C-F bond. This pathway is illustrated by Scheme 6.2.



Scheme 6.2

The saturated cyclic intermediate (113) could not be isolated or observed by ^{19}F nmr spectroscopy and it was concluded that, under the conditions employed, the final elimination step to give the product (111) takes place very rapidly.

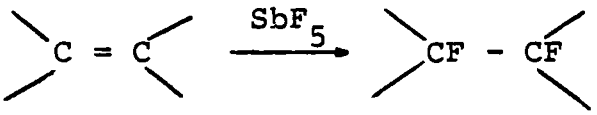
In an attempt to reproduce this reaction mechanism the model compound ${}^{n}C_8F_{17}CH_2CF_3$ (116) was synthesized using the route outlined below:

$$\underset{(114)}{n\text{-}C_8F_{17}I} \xrightarrow[185^{o}C,24h]{CH_2=CF_2} \underset{(115)}{{}^{n}C_8F_{17}CH_2CF_2I} \xrightarrow[0^{o}C]{SbF_5} \underset{(116)}{n\text{=}C_8F_{17}CH_2CF_3}$$

If the model (116) cyclised in the presence of SbF_5 it would support the mechanism proposed in Scheme 6.2, and indicate the preferred ring size for the process. However no reaction between (116) and SbF_5 occurred below 190°C. After 12h at this temperature the following products were identified:

$${}^{n}C_8F_{17}CH_2CF_3 \xrightarrow[190^{o}C,12h]{SbF_5} C_8F_{16},\ C_9F_{18},\ C_{10}F_{20} + \underset{n\ >\ 10}{C_nF_{2n}}$$

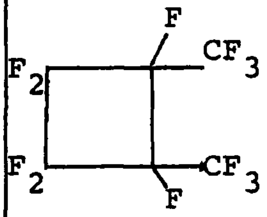
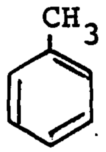
These products suggest that fragmentation processes have taken place, however so far we are unable to advance a satisfactory explanation for the formation of these products. It would appear that dehydrofluorination has taken place as expected, but the overall substitutions of F for H in each product suggest that SbF_5 is acting as a fluorinating agent towards the resulting alkenes, which is a known process.[138]



(iii) Attempts to Promote Related Inter-Molecular Reactions

In order to determine whether the mechanisms proposed for the above two intramolecular reactions (Schemes 6.1 and 6.2) could be extended to include intermolecular processes the systems outlined in Table 6.1 were investigated.

TABLE 6.1 Intermolecular Systems Related to Observed Intramolecular Displacement of C-F by C-H

C-F Substrate	C - H Nucleophile	Conditions
 (118)	$CF_3CF_2CH_2CF_3$	Xs SbF_5, 150°C, 12h
$(CF_3)_2CF\text{-}CF(CF_3)_2$ (103)	$CF_3CF_2CH_2CF_3$ (119)	Xs SBF_5, 180°C, 12h
$(CF_3)_2C{=}CHCF_3$ (81)	$CF_3CF_2CH_2CF_3$ (119)	Xs SbF_5, 150°C, 12h
$(CF_3)_2C{=}CHCF_3$ (81)		Xs SbF_5, -78°C, 2h

In each case, however, no chemical change took place. Furthermore variable temperature ^{19}F nmr studies of the systems SbF_5/(118) and SbF_5/(81) over the range -70°C to +100°C showed no occurrence of stable complexes or ions.

6C The Formation of Some Remarkably Stable Fluorinated Cations and their Chemistry

The results discussed so far show clearly that elimination of HF from simple fluorohydrocarbon systems, *e.g.* $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (70) is achieved easily in the presence of SbF_5 to form the corresponding mono- and di-alkenes *e.g.*

$(CF_3)_2C{=}CHCF_2CH_2CF_2$ (71). A study was therefore carried out involving the higher homologues $(CF_3)_2CF(CH_2CF_2)_nF$ [n=3 (120), n=4 (121)]. These models were synthesized as follows (Scheme 6.3):

$$\underset{(44)}{(CF_3)_2CFI} \xrightarrow[220^\circ C,\ 36h]{Xs\ CH_2{=}CF_2} (CF_3)_2CF(CH_2CF_2)_nI \xrightarrow[0^\circ C]{SbF_5} (CF_3)_2CF(CH_2CF_2)_nF$$

n=3 (122) 30% n=3 (120) 75%

n=4 (123) 20% n=4 (121) 60%

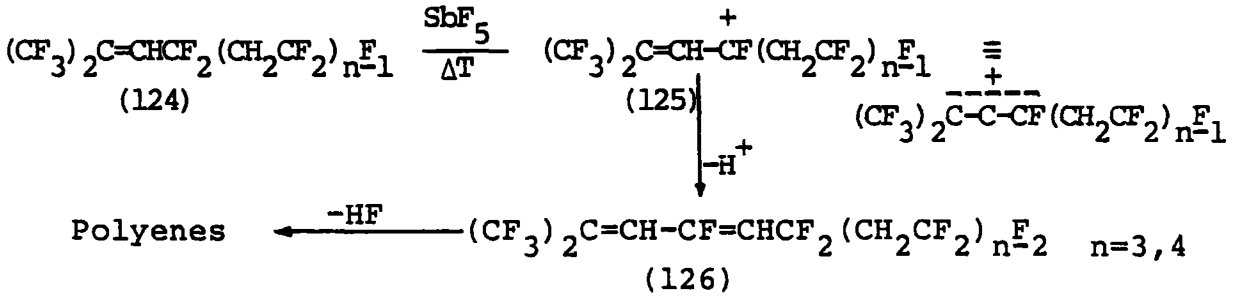
(i) Observations

It was expected that, after preferential elimination of HF from the tertiary sites of (120) and (121) to yield alkenes of the form (124)

$$(CF_3)_2C{=}CHCF_2(CH_2CF_2)_{n-1}F \qquad n = 3,4$$

(124)

further removal of HF from the allylic sites of (124,n=3,4) would be favoured since removal of F^- by SbF_5 from these sites would result in carbocations stabilized by the double bond (Scheme 6.4).



$$\underset{(124)}{(CF_3)_2C{=}CHCF_2(CH_2CF_2)_{n-1}F} \xrightarrow[\Delta T]{SbF_5} \underset{(125)}{(CF_3)_2C{=}CH{-}\overset{+}{C}F(CH_2CF_2)_{n-1}F} \equiv (CF_3)_2\overset{+}{C}{\cdots}C{\cdots}CF(CH_2CF_2)_{n-1}F$$

$$(125) \xrightarrow{-H^+} \underset{(126)}{(CF_3)_2C{=}CH{-}CF{=}CHCF_2(CH_2CF_2)_{n-2}F} \quad n=3,4$$

$$\text{Polyenes} \xleftarrow{-HF} (126)$$

Scheme 6.4

However when the saturated models (120) and (121) were dissolved in 5:1 excess SbF_5 at 20°C the remarkably stable fluorinated carbocations (127) and (128) were formed in quantitative yields.

$$(CF_3)_2CF(CH_2CF_2)_3F \xrightarrow[20^{o}C]{Xs\ SbF_5} (CF_3)_2CFCH_2\text{-}\overset{+}{\overline{CFCHCF}}\text{-}CH_2CF_3 \quad SbF_6^-$$

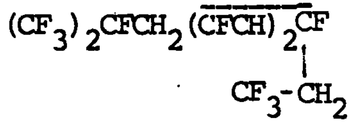
(122) (127)

$$(CF_3)_2CF(CH_2CF_2)_4F \xrightarrow[20^{o}C]{Xs\ SbF_5} (CF_3)_2CFCH_2\text{-}\overset{+}{\overline{CFCHCFCHCF}}\text{-}CH_2CF_3 \quad \bar{S}bF_6$$

(123) (128)

These carbocations persist over several weeks and, using ^{19}F nmr techniques, no chemical change is observed over this period of time. It is also remarkable that elimination of HF in each case occurred from $-CH_2CF_2-$ sites and under extremely mild conditions (20°C) prior to the formation of the allylic cations (127) and (128). This is in stark contrast to the observed reactivity of the smaller homologues (n = 1,2) towards SbF_5. The range of reactivity of the saturated model systems is now summarized fully in Table 6.2.

TABLE 6.2 <u>Comparison of the Reactivity of the Saturated Models towards SbF_5</u>

Model Compound	Preferred Site for elimination	Conditions employed	Products
$(CF_3)_2CFCH_2CF_3$ (66)	$>CFCH_2-$	120°C, 3h	$(CF_3)_2C{=}CHCF_3$ (81)
$[(CF_3)_2CFCH_2CF_2]_2$ (61)	$>CFCH_2-$	120°C, 2h	$[(CF_3)_2C{=}CHCF_2]_2$ (75)
$(CF_3)_2CF(CH_2CF_2)_2F$ (70)	$>CFCH_2-$	40°C, 1/3h	$(CF_3)_2C{=}CHCF_2CH_2CF_3$ (71)
$(CF_3)_2CF(CH_2CF_2)_3F$ (120)	$-CF_2CH_2-$	20°C,Inst.	$(CF_3)_2CFCH_2\overset{+}{\overline{CFCHCF}}CH_2CF_3$ (127)
$(CF_3)_2CF(CH_2CF_2)_4F$ (121)	$-CF_2CH_2-$	20°C,Inst.	 $(CF_3)_2CFCH_2\overset{+}{\overline{(CFCH)}}_2\underset{CF_3\text{-}CH_2}{CF}$ (128)

Using the above data the following trend in the reactivity of the models (66), (61) and (70) towards elimination of HF from the tertiary site is apparent.

$$(CF_3)_2CFCH_2\text{-}R \qquad R = \underset{(70)}{-CH_2CF_2-} > \underset{(61)}{-CF_2CF_2-} > \underset{(66)}{-F}$$

Clearly the order of reactivity is determined by the electron withdrawing ability of the group R. However the extreme reactivity of the higher homologues (120) and (121) towards elimination from secondary sites $-CF_2CH_2-$ is not explained.

6C (ii) Interpretation of NMR Spectra

The ^{19}F, ^1H and ^{13}C nmr spectra of the cations (127) and (128) were recorded in solution in SbF_5 at 20°C. With reference to the many reports in the literature of stable fluorinated carbocations[139-144] and ^{19}F nmr studies involving SbF_5,[144] the carbocations (127) and (128) were easily characterized. The important ^{19}F and ^1H nmr data are shown in Table 6.3. (See Appendix for full analysis including ^{13}C data)

TABLE 6.3 Diagnostic Resonances in ^1H, ^{19}F nmr Spectra of the Cations (127) and (128)

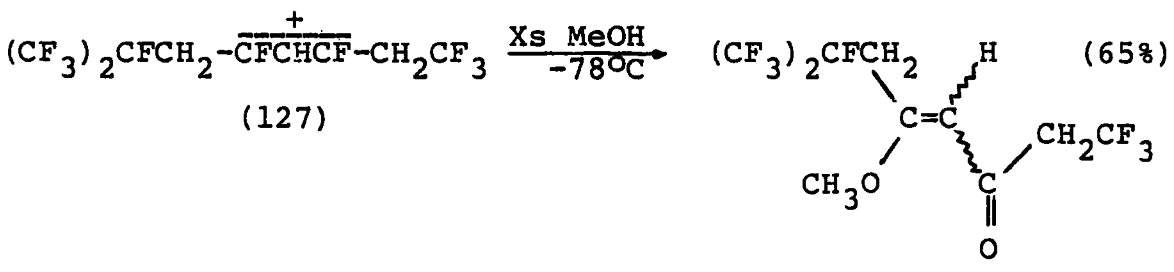
Cation	^1H shifts/ppm TMS δ 0.0	^{19}F shifts/ppm $CFCl_3$ δ 0.0
$(CF_3)_2CFCH_2\overset{+}{\overline{CFCHCF}}CH_2CF_3$ a b c d e f g h (127)	-4.5 to -5.0 c,g -8.2 e	-180.5 b - 76.9 a - 61.4 h + 68.1 d,f
$(CF_3)_2CFCH_2\overset{+}{\overline{CFCHCFCHCF}}CH_2CF_3$ a b c d e f g h i j	-4.0 to -4.5 c,i -6.5 to -7.0 e,g	-181.0 b - 76.9 a - 62.4 j + 7.0 to 0 d,f,h

Recording these spectra at +20°C gives rise to considerable broadening of the resonances due to exchanging processes. Current studies are taking place in order to obtain data from spectra run on solutions of (127) and (128) in SbF_5/SO_2ClF at -80°C. The ^{19}F nmr resonances observed at +68.1 ppm for the cation (127) are consistent with extensive deshielding expected for nuclei close to the positive charge centre. It is notable that the corresponding ^{19}F nuclei in the cation (128) are deshielded to a lesser extent (δ +7 to 0 ppm) due to greater delocalization of formal charge. The same trend is also observed for the ^{1}H nuclei of (127) and (128) near to the charge centre which came into resonance at -8.2 and -6.5 to -7.0 ppm respectively.

Further confirmation of the production of the cation (127) was obtained by the quenching experiments described below.

(iii) Reaction of the Stable Carbocation (127) with Methanol

A solution of the carbocation (127) in SbF_5 was quenched with excess methanol at -78°C. The major product (65%) isolated was the α,β-unsaturated ketone (129)

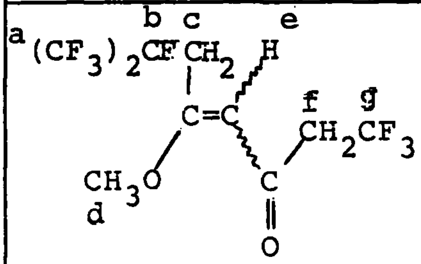


(127)

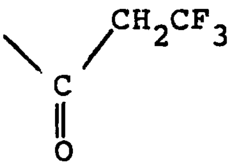
(129)

The structure of the product (129) was determined by mass spectrometry (M^+ 350), infra-red spectrophotometry (strong bands 1600 cm^{-1} and 1700 cm^{-1} characteristic of conjugated unsaturated ketone) and the ^{1}H and ^{19}F nmr data summarized in Table 6.4.

TABLE 6.4 ^{1}H and ^{19}F nmr Data for Structure Confirmation of the Product (129)

Structure	^{1}H shifts/ppm TMS δ 0	^{19}F shifts/ppm $CFCl_3$ δ 0
 (129)	-3.2 (q) f -3.6 (s) d -5.6 (s) e	-65.0 (t) g -78.5 (d) a -182.8 (m) b

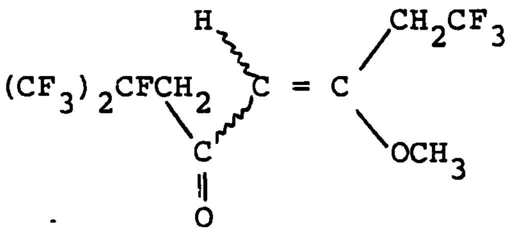
The structure of (129) was finally uniquely determined by mass-spectrometry due to the high intensity peak of 111 mass units arising from the fragment (130)



Mol wt 111

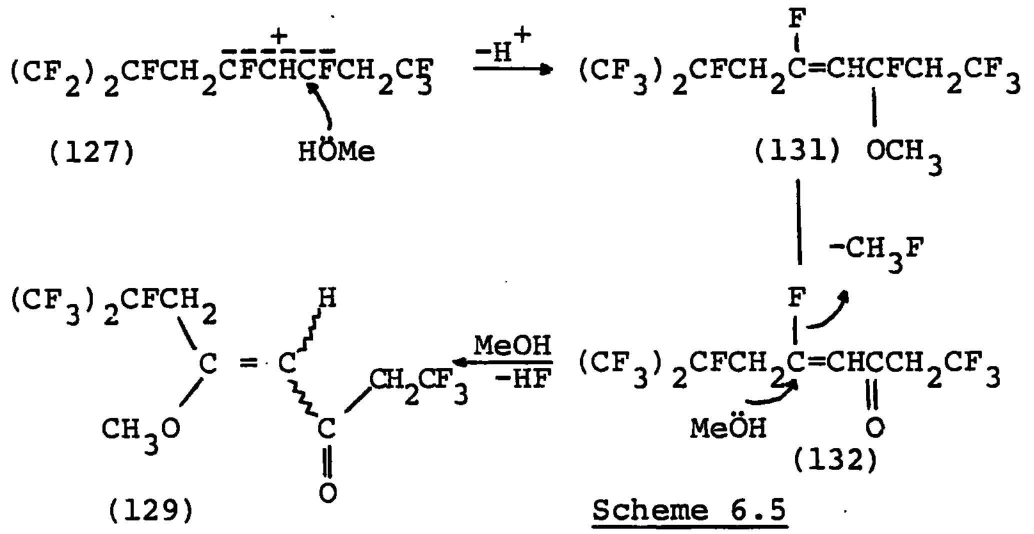
(130)

This observation distinguishes the product from the possible isomer (129a)



(129a)

The simple mechanistic pathway outlined in Scheme 6.5 for the quenching of the cation (127) with methanol to give (129) therefore provides further support for the structure of (127).

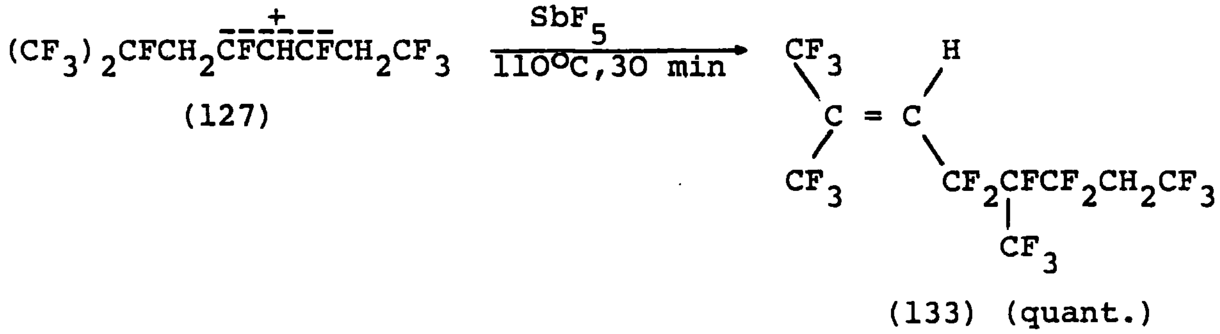


Scheme 6.5

The loss of CH_3F from the intermediate (131) to form (132) is in accordance with the findings of England *et al* which relate very closely to this step of the mechanism.

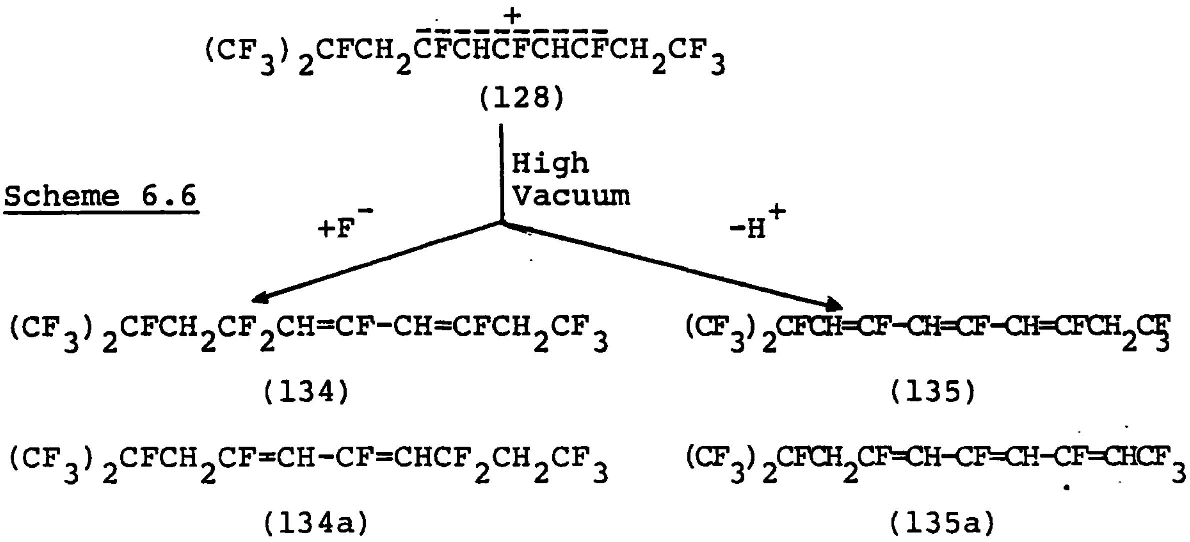
(iv) Other Reactions

When a solution of the cation (127) in SbF_5 was heated to 110°C for ½h the unexpected product 2,5-bistrifluoromethyl-3H,7H,7H-undecafluorooct-2-ene (133) was obtained in essentially quantitative yield.



The structure of the product (133) was established using ^{19}F and ^{1}H nmr spectrometry (see appendix), mass spectrometry (M^+-19, 427) and infra-red spectrophotometry ($\nu_{C=C}$ 1680 cm^{-1}). We have not been able to explain this result satisfactorily and work is currently being carried out.

An attempt was made using vacuum-line techniques to isolate polyenes from a solution of the cation (128) in SbF_5 as outlined in Scheme 6.6.



$(CF_3)_2CFCH_2\overset{+}{\overline{CFCHCFCHCF}}CH_2CF_3$

(128)

Scheme 6.6

$(CF_3)_2CFCH_2CF_2CH{=}CF{-}CH{=}CFCH_2CF_3$

(134)

$(CF_3)_2CFCH{=}CF{-}CH{=}CF{-}CH{=}CFCH_2CF_3$

(135)

$(CF_3)_2CFCH_2CF{=}CH{-}CF{=}CHCF_2CH_2CF_3$

(134a)

$(CF_3)_2CFCH_2CF{=}CH{-}CF{=}CH{-}CF{=}CHCF_3$

(135a)

The separation of product material from the solution of (128) in SbF_5 was achieved by vacuum transfer onto dry NaF and subsequent molecular distillation under high vacuum (10^{-5} torr) from the NaF/$NaSbF_6$ residue. However the products obtained were not the expected polyenes as outlined in Scheme 6.6, but a complex mixture of lower molecular weight materials. It is thought that decomposition may have been promoted by NaF.

The reactivities of the fluorohydrocarbons $(CF_3)_2CF(CHFCF_2)_nR$ [R=F n=2 (72) n=3 (136) and R= -coupled n=1 (64)] towards SbF_5 were investigated in an attempt to produce the corresponding mono- and di-alkenes. It is remarkable however that these compounds showed no susceptibility to Lewis acid catalyzed elimination of HF at 150°C over a period of 6h. This is in complete contrast to the extreme susceptibility of the compounds containing the structures $>CFCH_2-$ and $-CH_2(CF_2CH_2)_nCF_2-$ discussed earlier.

6D Treatment of Fluorohydrocarbon Polymers with SbF_5: A Route to Fluorinated Polyacetylenes

(i) Introduction

The results described in this chapter have demonstrated clearly that model compounds related to $CH_2{=}CF_2/CF_3CF{=}CF_2$ copolymers and the $CH_2{=}CF_2$ homopolymer are highly susceptible to elimination of HF in the presence of the powerful Lewis-acid SbF_5. Furthermore the resulting unsaturated systems are stable to SbF_5 under the conditions used to promote elimination. In principle therefore this property should also extend to the polymer systems themselves where extensive elimination of HF would lead to highly unsaturated polymers. Indeed, in the case of poly,1,1-difluoroethene, $\leftarrow CH_2CF_2 \rightarrow_n$, this process could result in a potentially conducting polymer (137)

e.g. $\leftarrow CH_2CF_2CH_2CF_2 \rightarrow_n \xrightarrow{SbF_5} \leftarrow CH{=}CF{-}CH{=}CF \rightarrow_n$

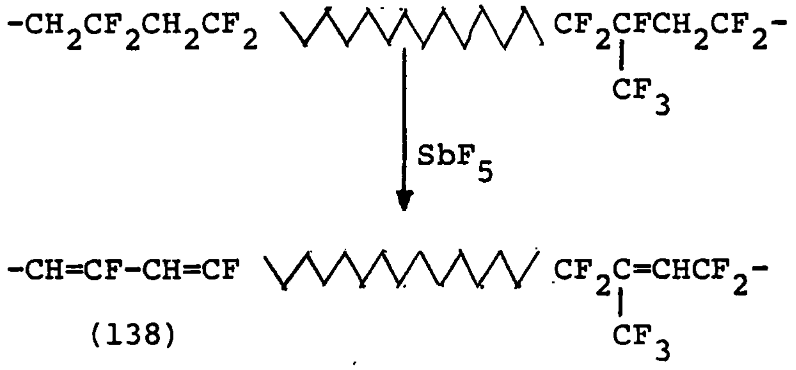
(137)

A study of the reactivity of a series of polymer systems towards SbF_5 was therefore carried out.

(ii) $CH_2{=}CF_2/CF_3CF{=}CF_2$ Copolymer Systems

When a sample of finely divided $CH_2{=}CF_2/CF_3CF{=}CF_2$ copolymer (70:30) was exposed to SbF_5 vapour over a prolonged period using vacuum-line techniques, an intensely coloured powder was obtained. Analysis of this material was examined using advanced infra-red techniques (Nicolet 60 SX photo-acoustic infra-red spectrophotometer, which does not require any modification of the material for sampling) a broad intense - band was observed in the region 1600-1650 cm^{-1}. This band is not present in the infra-red spectrum of the saturated starting material and is likely to be due to the presence of structures of the forms (138) and (139):

e.g.



(138)

(139)

No other analytical techniques were available for further study of this system.

(iii) <u>Homopolymer Systems</u>

The study of potentially conducting polymers is of major importance to industry[146] with particular interest in the synthesis of polyacetylene (140)

$$\left(CH=CH-CH=CH\right)_n$$

(140)

However this material is susceptible to air-oxidation. Therefore polydifluoroacetylene (141) and polymonofluoroacetylene (137) are materials most desirable for synthesis and study. In this field however there has been only very limited success.[147]

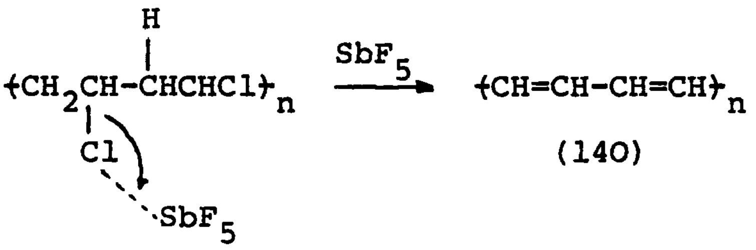
$\left(CF=CF-CF=CF\right)_n$ (141)

$\left(CH=CF-CH=CF\right)_n$ (137)

A novel approach to the synthesis of this mateial was therefore undertaken using Lewis-acid catalysed elimination of HF from saturated precursors in the presence of SbF_5.

(a) Polychloroethene

When a thin film of polychloroethene (PVC) was exposed to SbF_5 an instantaneous and intense colouration occurred. Ultrasonic infra-red studies of the resulting material in the absence of air yielded a spectrum which was altogether different from that of PVC. Furthermore on exposure to air the infra-red spectrum obtained was wholly changed and contained a strong band at 1700 cm^{-1} indicative of C=O functionality. When a solid-state ^1H nmr spectrum was obtained on the unoxidized material a single resonance was observed at *ca.* -6.3 ppm (δ TMS 0 ppm). These observations are consistent with extensive elimination of HCl by SbF_5 resulting in a material which we believe to be a polyconjugated system (140) doped with SbF_5.



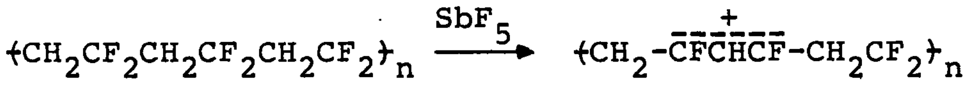
$$\leftarrow CH_2\underset{\underset{\cdot\cdot SbF_5}{Cl}}{CH}-\overset{H}{C}HCl\rightarrow_n \xrightarrow{SbF_5} \leftarrow CH=CH-CH=CH\rightarrow_n$$

(140)

(b) Poly-1,1-difluoroethene and Polytrifluoroethene

When a thin film of poly-1,1-difluoroethene was exposed to SbF_5 vapour an intensely coloured material was obtained. Infra-red studies of this product showed a strong bond in the region *ca.* 1600-1700 cm^{-1} which is indicative of extensive unsaturation. However when a thin film of polytrifluoroethene was treated under identical conditions the film became coloured only slowly. The film was then further treated with liquid SbF_5 at 60°C whereupon a strong colouration was achieved. Infra-red studies of this material again showed evidence of unsaturation.

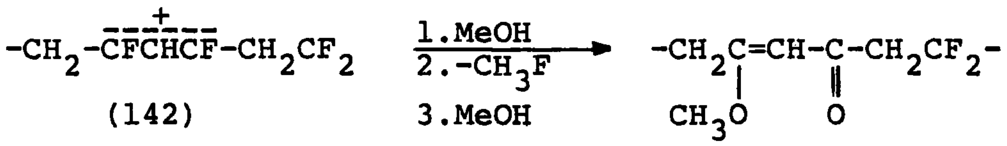
These results clearly demonstrate a successful new approach to highly unsaturated polymer systems. From the results obtained using the model systems it is reasonable to assume that the polymers after treatment with SbF_5 contain residual charged sites, *e.g.* of the form (142)



$$\left(CH_2CF_2CH_2CF_2CH_2CF_2 \right)_n \xrightarrow{SbF_5} \left(CH_2\text{-}\overset{+}{\overline{CFCHCF}}\text{-}CH_2CF_2 \right)_n$$

(142)

Therefore, in principle, functionalisation of the saturated polymers is now possible using, for example, (i) SbF_5, (ii) MeOH resulting in materials of great potential for industrial applications, *e.g.* :



$$\text{-}CH_2\text{-}\overset{+}{\overline{CFCHCF}}\text{-}CH_2CF_2 \xrightarrow[\substack{2.\text{-}CH_3F \\ 3.MeOH}]{1.MeOH} \text{-}CH_2\underset{\substack{| \\ CH_3O}}{C}{=}CH\text{-}\underset{\substack{\| \\ O}}{C}\text{-}CH_2CF_2\text{-}$$

(142) (143)

Further studies of these systems are currently being developed.

6E Conclusions

We have shown that Lewis-acid catalyzed eliminations of HF from fluorohydrocarbon systems by SbF_5 provides an excellent and entirely novel route to fluorinated mono- and di-enes and a potential route to fluorinated polyenes. Furthermore treatment of the unsaturated products with SbF_5

under more forcing conditions can lead to some highly unusual reactions which are of fundamental importance to organic chemistry in their own right.

When this approach is applied to fluorohydrocarbon polymer systems it is clear from model studies that extensive elimination of HF can occur to yield highly unsaturated and potentially conducting polymers, *e.g.* systems related to polyacetylene, polymonofluoroacetylene and polydifluoroacetylene most probably containing stable charged sites.

It is also probable that these sites can be functionalized,*e.g.* with methanol to yield new materials for industry.

CHAPTER SEVEN

THE GENERAL CHEMISTRY OF THE MODEL COMPOUNDS

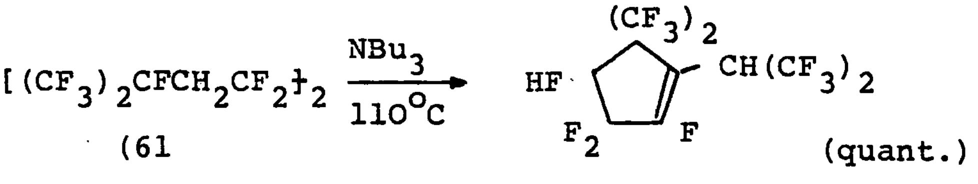
7A Introduction

The objectives of this research include primarily the discovery of definitive information about the chemistry involved in the cross-linking of $CH_2=CH_2/CF_3CF=CF_2$ copolymers. The results obtained in this area have been discussed in detail together with their implications in Chapters Two to Five. In the previous chapter it was shown that the model chemistry performed in achieving these results gave rise to some highly novel and fundamentally important chemistry involving antimony pentafluoride.

Therefore in order to extend our understanding of the chemistry of these systems a wider variety of experiments was carried out in some of the more important areas, *e.g.* nucleophilic attack, free-radical addition, addition of 1,3-dipoles and the formation of some stable long-lived carbanions, *etc.* The results of this study are discussed in this chapter.

7B Chemistry Involving 2-(2H-hexafluoro-2-propyl)-4-hydro decafluoro-3,3-dimethylcyclopentene (79)

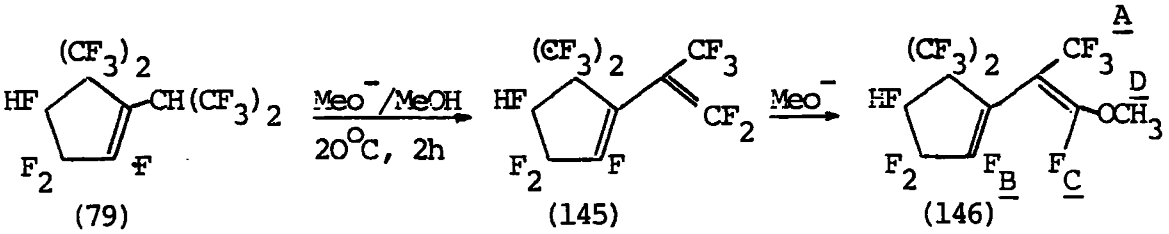
The cyclopentene derivative (79) was obtained in quantitative yield by the following reaction (Ch.3B(iii))



(79)

7B(i) Reaction with Sodium Methoxide

When the cyclic product (79) was treated with sodium methoxide in methanol using very mild conditions a mixture of two components was obtained and separated using preparative scale gas chromatography. The components were identified as starting material (79) and the trans-methoxy-derivative (146) in 70% yield:

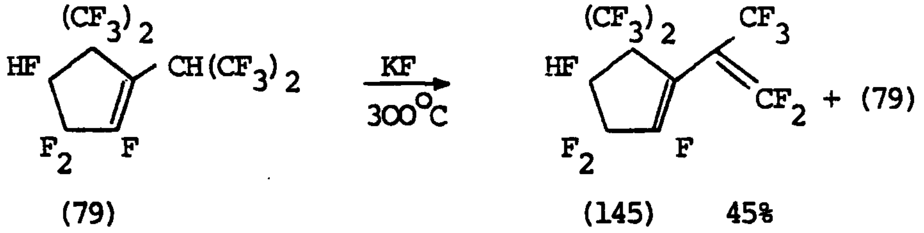


The structure of the product was established using ^{19}F and ^{1}H nmr spectroscopy wherein the chemical shifts and coupling of the ring atoms resemble strongly those of the established compound (79). In addition the ^{19}F nmr spectrum of (146) contained resonances at -57.8 ppm (3 F, s, A-CF_3), -71.0 ppm (1 F, d, J 12.5, C-F) and -119.8 ppm (1 F, d, J_{BC} 12.5, B-F) and the ^{1}H nmr spectrum showed a resonance at -3.8 ppm (3 H, s, D-OCH_3). The *trans*-stereochemistry was indicated by the large through-space coupling between the F-atoms B and C. Infra-red spectrophotometry showed an intense broad absorption (ν_{max} 1650 cm^{-1}) which is characteristic of a conjugated diene. Mass spectrometry gave a strong molecular ion peak at 418 mass units.

This result demonstrates that the hydrogen atom of the hexafluoro-2-propyl group, $-CH(CF_3)_2$, of (79) is the selectivity base-sensitive site of this molecule in preference to the ring hydrogen. However when (79) was treated separately with D_2O, $(CD_3)_2C{=}O$ and CH_3OD, and the ^1H spectrum of each system recorded, there was no decrease in the intensity of the $-CH(CF_3)_2$ ^1H resonance (δ-4.25 ppm) indicating that no H/D exchange had taken place.

(ii) Pyrolysis Experiments

The result described above indicated that production of the conjugated diene (145) by base-catalysed elimination of HF from (79) in solution is not feasible due to subsequent nucleophilic attack at the $=CF_2$ group of this molecule. Therefore the compound (79) was passed through a pyrolysis tube containing hot potassium fluoride using vacuum-line techniques. When the temperature of the KF was 300°C conversion to the diene (145) was achieved in 45% yield.

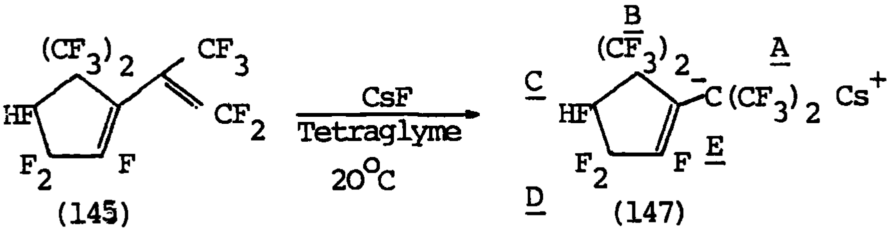


Some decomposition (*ca.* 15%) occurred in the pyrolysis tube.

In an attempt to promote "cracking" processes the cyclo-pentene derivative (79) was passed over hot iron at temperatures ranging from 300°C, which resulted in no chemical change, to 500°C which caused total decomposition.

(iii) Reaction of 2-(pentafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (145) with Cesium Fluoride; Formation of a Stable Carbanion

When the diene (145) was added to a solution of CsF in tetraglyme an intense red colouration was observed. The immediate ^{19}F nmr spectrum of the resulting system showed complete change from that of the starting material (145). Most notably a new resonance signal appeared at δ_F -45.5 ppm which is indicative of the formation of the carbanion (147) [148]



The ^{19}F nmr data recorded for the anion (147) is summarized in Table 7.1. After a period of several hours the ^{19}F nmr spectrum of the solution became complex and the low-field resonance (-45.5 ppm) associated with the anion (147) vanished.

TABLE 7.1 ^{19}F NMR Data for the Stable Carbanion (147)

δ $CFCl_3$ 0 ppm.

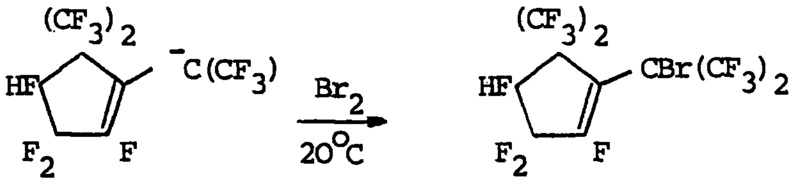
Chemical Shift/ppm	Intensity	Assignment
-45.5	6	A $-CF_3$
-61.0, -62.4	6	B $-CF_3$
-109.0	1	E -CF
-122.6	2	D $-CF_2-$
-210.8	1	C -CF-

This observation indicates that decomposition of the anion occurs over this period. On repeating this experiment an attempt was made to trap the anion (147) using Br_2. After the addition of Br_2 the resultant solution was added to water and a fluorocarbon layer was recovered which was resolved into 2 components of highest masses 426 and 487 using analytical gas chromatography/mass spectroscopy. The lower molecular weight component was deduced to be (79) by ^1H nmr spectroscopy (δ_H-$CH(CF_3)_2$ -4.25 ppm, sept). The higher molecular weight product was not, however, isolable using preparative scale gas chromatography due to thermal decomposition (attributable to the longer retention times experienced with this technique). The mass spectrum obtained from the resolved product mixture, however, provides sufficient evidence for production of the bromo-derivative (148) *via* successful trapping of the carbanion (147). This evidence is summarized as follows:

(i) M^+ -19, 487 observed.

(ii) M+2 Monobromosubstituted pattern observed.

(iii) High intensity peaks which correspond to loss of $-CF_3$ (69) and -Br (79,81) from the sterically crowded $-CBr(CF_3)_2$ group[148] of (148).



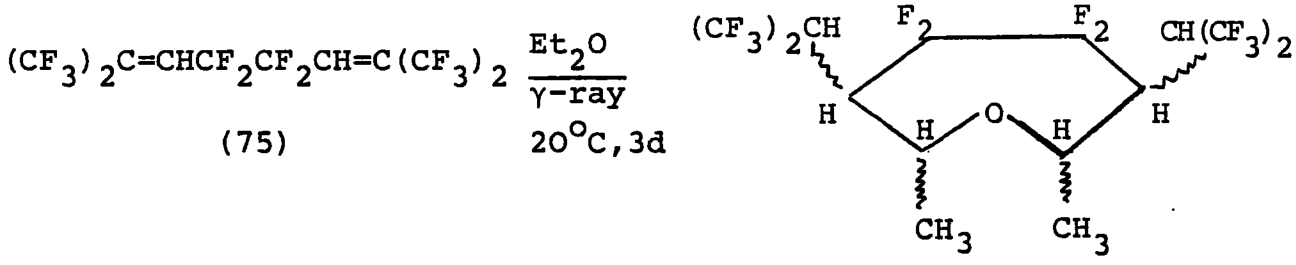
(147) (148)

7C Chemistry involving 3,6-Dihydrohexadecafluoro-2,7-dimethylocta-2,6-diene (75) and 2H-nonafluoro-3-methylbut-2-ene (81)

$[(CF_3)_2C{=}CHCF_2]_2$ (75) was synthesized in excellent yields by the reaction of $[(CF_3)_2CFCH_2CF_2]_2$ (61) with SbF_5 at 120°C, and $(CF_3)_2C{=}CHCF_3$ (81) by reaction of $(CF_3)_2CFCH_2CF_3$ (66) with SbF_5 at 130°C. The reactivities of (75) and (81) towards F^-, $\bar{O}H$ and PhO^- have been discussed in Chapter Four.

(i) Free-Radical Additions

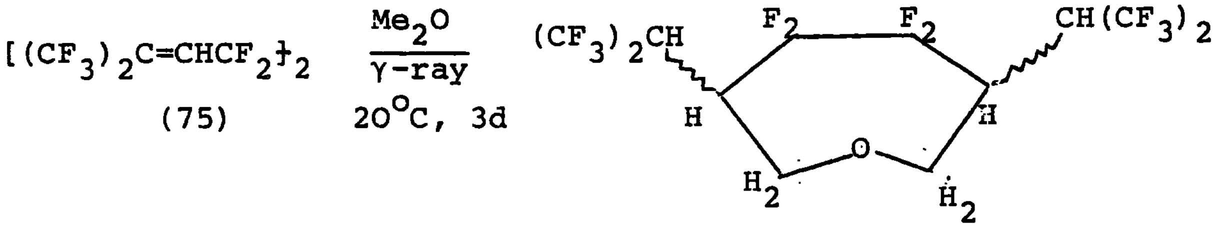
When the diene $[(CF_3)_2C{=}CHCF_2]_2$ (75) was irradiated with γ-rays in the presence of diethyl ether (2:1 excess) a mixture of the product (149) and involatile material was obtained. The oxepane derivative (149) was isolated as an isomeric mixture.



(149) 50%

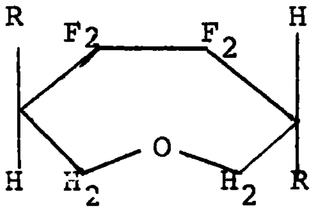
The structure of the product (149) was determined using mass spectrometry (M^+ 500), infra-red and raman spectrophotometry ($\nu_{C=C}$ absent) and nmr spectroscopy (see Appendix).

When the diene (75) was treated with dimethyl ether (1:1) in the presence of γ-rays the product (150) was obtained in good yield.

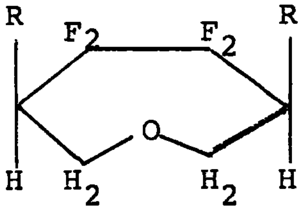


(75) (150) 60%

The structure of the product (150) was determined using mass spectrometry (M^+ 472 and loss of $-CH(CF_3)_2$ fragment of mol.wt. 151) and infra-red spectrophotometry ($\nu_{C=C}$ absent). The ^{19}F nmr spectrum recorded for the product (150) was consistent with the presence of two isomeric forms (150A) and (150B):



(150A)
transoid



(150B)
cisoid

R = $-CH(CF_3)_2$

The transoidal isomer (150A) comprises a pair of enantiomers which are nmr equivalent. The ^{19}F nmr spectrum is, however, further complicated by the prochirality of the $-CF_3$ groups which results in two separate resonances for each $-CF_3$ group. Full assignment of the chemical shift data has consequently not been achieved, however the available data is summarized in Table 7.2.

TABLE 7.2 NMR Data for the Oxepane Product (150)

^{19}F nmr Data δ $CFCl_3$ 0 ppm.

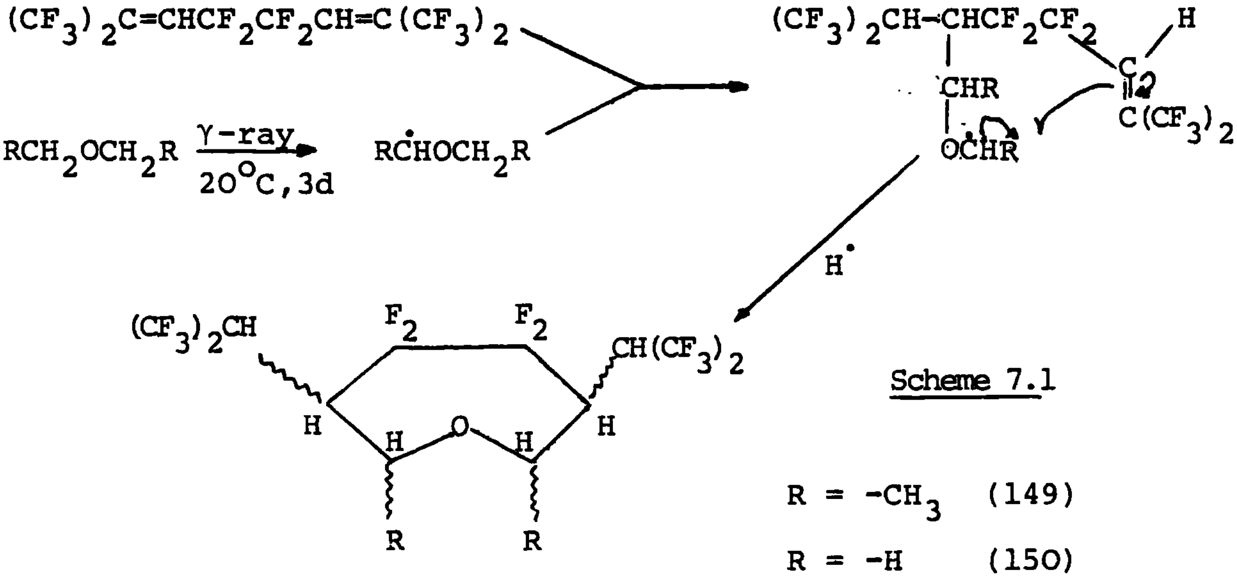
Shift	Intensity	Coupling	Assignment
-60.0	12	Complex Multiplets	$-CF_3$
-60.7			
-68.0			
-68.8			
-112.4	2	AB J_{AB}=271 Hz	$-CF_2-$
-122.2	2	AB J_{AB}=262 Hz	

^1H nmr Data δ TMS 0 ppm.

-4.3 to -3.2	-	complex	-

^{13}C data on the product (150) together with high-field ^{19}F and ^1H data are awaited.

The two results described above represent a novel route to seven membered polyfluorocyclic ethers and the mechanism proposed is outlined by Scheme 7.1.

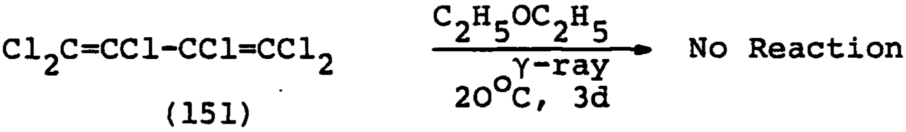


Scheme 7.1

R = $-CH_3$ (149)

R = -H (150)

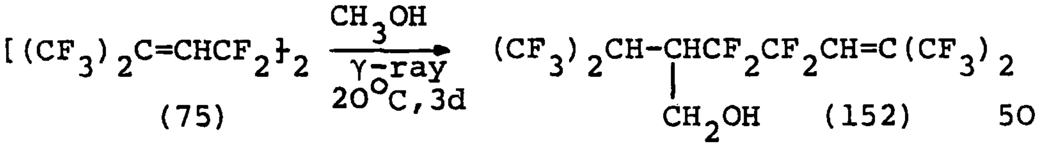
The addition of ethers to (75) is facilitated by the electrophilic nature of this molecule (see Chapter I.B(ii)). Therefore hexachlorobuta-1,3-diene (151) was irradiated by a ^{60}Co γ-source in the presence of diethyl ether in order to investigate whether perchloroalkenes are active towards free-radical attack. However after 3 days at 20°C no chemical change had occurred.



$$Cl_2C{=}CCl{-}CCl{=}CCl_2 \xrightarrow[\substack{\gamma\text{-ray}\\ 20^{\circ}C,\ 3d}]{C_2H_5OC_2H_5} \text{No Reaction}$$

(151)

When a 1:1 molar ratio mixture of (75) and MeOH was irradiated by γ-rays the solid monoadduct (152) was obtained in moderate yield.



$$[(CF_3)_2C{=}CHCF_2]_2 \xrightarrow[\substack{\gamma\text{-ray}\\ 20^{\circ}C,3d}]{CH_3OH} (CF_3)_2CH{-}\underset{\substack{|\\ CH_2OH}}{C}HCF_2CF_2CH{=}C(CF_3)_2$$

(75) (152) 50%

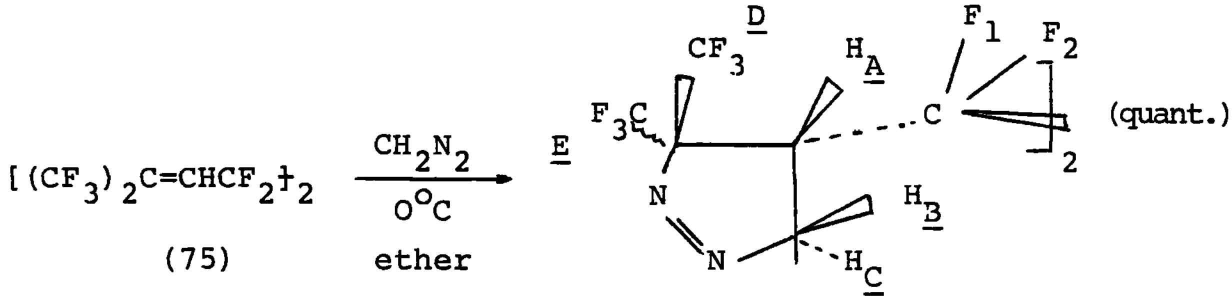
The structure of (152) was established using mass spectrometry (M^+ 458) and infra-red spectraphotometry ($\nu_{C=C}$ 1695 cm^{-1} weak, ν_{OH} 3600-3000 cm^{-1} broad strong). ^{19}F and ^{1}H nmr data summarized in the Appendix.

These simple addition reactions demonstrate clearly that the unsaturated model compounds are highly susceptible to free-radical attack by species of the form $RO\dot{C}H\,R$. Contrastingly, no addition of Br_2 to the diene (75) was achieved under very forcing conditions, *i.e.* 300°C, 3d in the presence of γ-radiation.

(ii) Addition of Diazomethane

The addition of the 1,3-dipole diazomethane CH_2N_2 to fluorinated alkenes has been the subject of much study.[150,151] Therefore this reaction was investigated using the novel unsaturated systems which we have produced. Diazomethane was synthesized in the laboratory using the method of Boer and Backer.[152]

Treatment of (75) with diazomethane in ether gave the di-Δ^1-pyrazoline derivative (153)



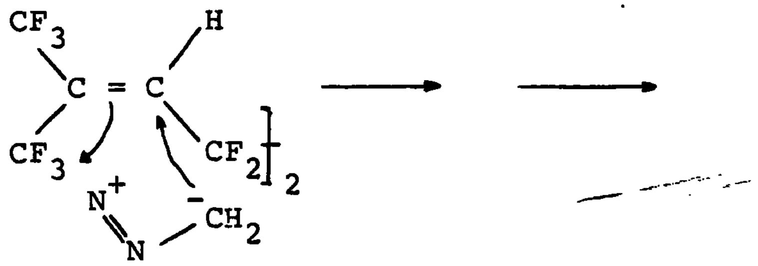
$$[(CF_3)_2C{=}CHCF_2\frac{}{}]_2 \xrightarrow[0^{o}C \text{ ether}]{CH_2N_2}$$

(153)

No Δ^2-pyrazoline derivatives were obtained in contrast to the observations of Bryce *et al.*[151]

The structure of the product (153) was established using mass spectrometry (diadduct M^+ 510 with rapid loss of 28 and 56 due to -N=N-) infra-red spectrophotometry ($\nu_{C=N}$ (Δ^2-) absent, ν_{N-H} (Δ^2-) absent) and the ^1H and ^{19}F nmr data summarized in Table 7.3.

The regiochemistry of addition was deduced by noting the coupling between the *cis* hydrogen atoms H_A and H_B (J-9Hz). This is in accordance with the postulate of Bryce *et al.* that the addition mechanism has an appreciable degree of nucleophilic character since the expected site for nucleophilic attack is at the carbon bearing hydrogen:



(153)

TABLE 7.3 NMR Data for Identification of Di-Δ^1-pyrazoline(153)

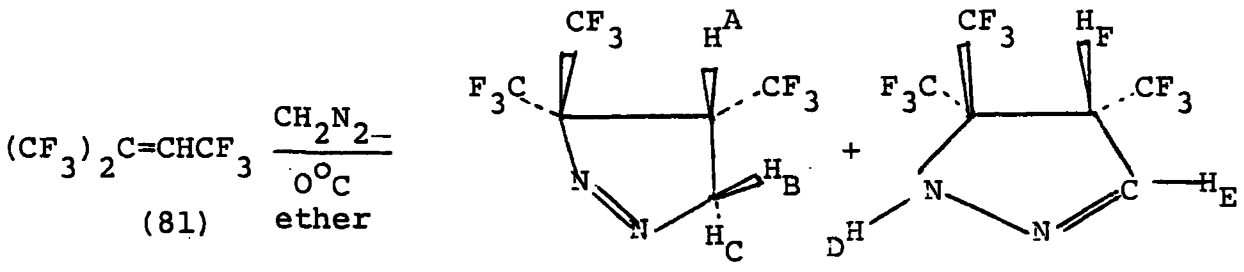
^1H Data δ TMS 0 ppm.

Shift/ppm	Coupling	Intensity	Assignment
-3.2	d,d,d J_{AB} = 9Hz J_{AC} = 9Hz J_{AF_1} = 9Hz	1	H_A
-4.4 -5.3	AB,d J_{BC} =18Hz J_{BA} = 9Hz J_{CA} = 9Hz	2	H_B, H_C

^{19}F Data δ $CFCl_3$ 0 ppm.

-65.0	M	3	$-CF_3$D,E
-69.0	M	3	
-109.7	AB $J_{F_1F_2}$ =280Hz	2	$-CF_2-F_1F_2$

When the monoalkene (81) was treated with CH_2N_2 at 0°C in ether a mixture of the Δ^1 (154) and Δ^2- (155) pyrazoline derivatives was obtained in the ratio 3:5.



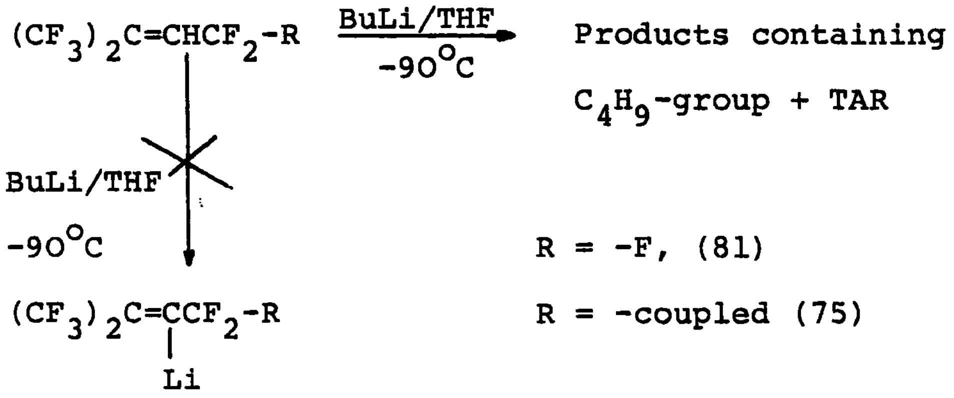
(154) Δ^1- 37%

(155) Δ^2- 63%

The product mixture was resolved using analytical scale gas chromatography/mass spectrometry (M^+ 274 for each component) and characterized using ^1H nmr (δH_B, H_C (154) -4.8 ppm, δH_D (155) -7.8 ppm, δH_E (155) -6.6 ppm). The regiochemistry of addition was determined for the Δ^1-isomer (154) by the observation of the coupling constant J_{AB} = 25Hz and for the Δ^2-isomer (155) by the loss of the fragment $-C(CF_3)_2NH-$ (M^+ 164 18% of base peak) in the mass spectrum of (155).

(iii) Attempted Metallations using Butyl Lithium

Hahnfield and Burton reported successful lithiation of a range of fluoroalkenes at vinyl hydrogen sites using solutions of butyl lithium in THF at -90°C.[126] However when the alkenes $[(CF_3)_2C=CHCF_2]_2$ (75) and $(CF_3)_2C=CHCF_3$ (81) were treated with BuLi under these conditions only complex mixtures of nucleophilic products were obtained in low yield with considerable tarring.

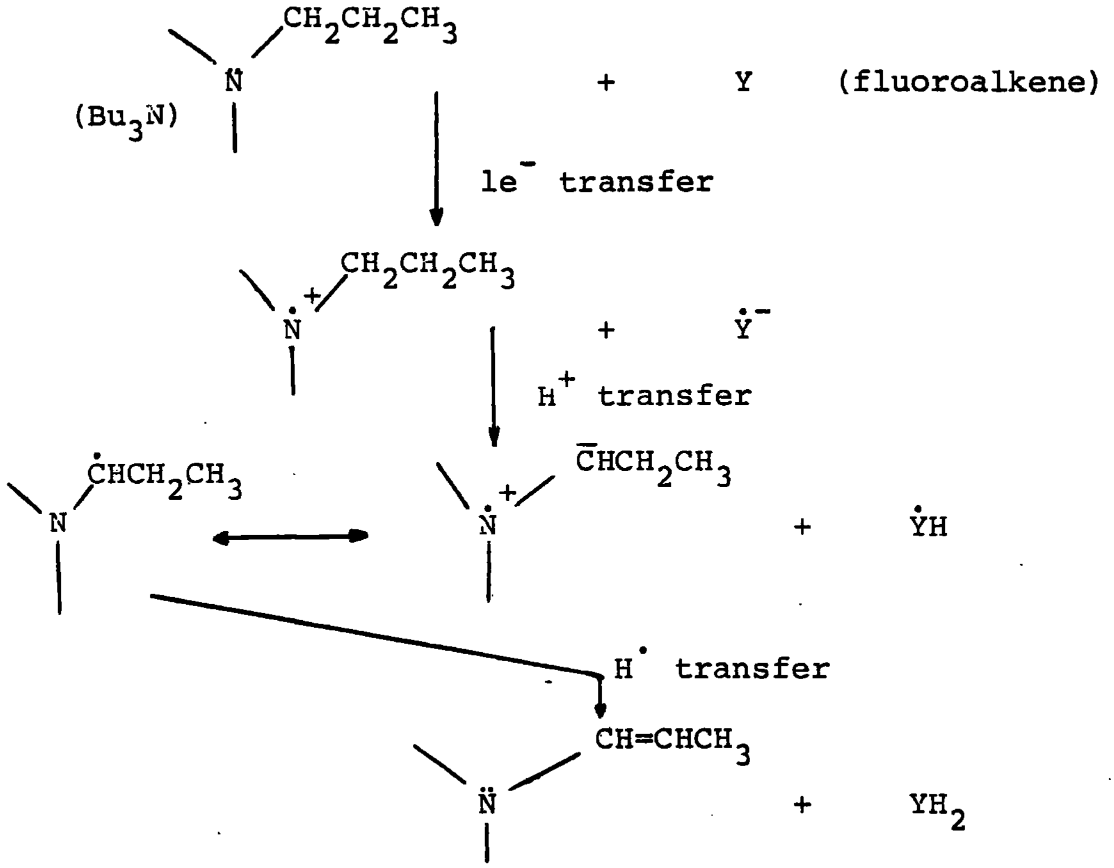


7D One Electron Transfer Reactions involving Tri-n-butylamine

One electron-transfer is now well established as a common occurrence in mechanism and may, in most general terms, be expressed[153]

$$\ddot{X} + Y \longrightarrow \dot{X}^{+} + \dot{Y}^{-}$$

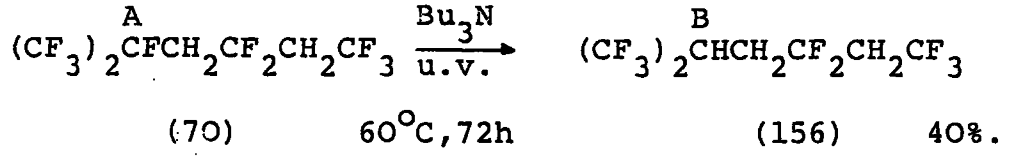
In the case of $(Bu)_3N$ reduction of double bonds is feasible *via* one electron transfer, particularly if the double bond has electron-withdrawing substituents. This process is expressed generally by Scheme 7.2 which will be used to explain the results described thereafter.



<u>Scheme 7.2</u>

7D (i) <u>2,2,4,4-Tetrahydrododecafluoro-5-methylhexane (70) and Tri-n-butylamine</u>

When $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (70) was treated with NBu_3 at 60°C for 72h in the presence of ultra-violet light there was 40% conversion to the reduced product (156).



$$\overset{A}{(CF_3)_2CF}CH_2CF_2CH_2CF_3 \xrightarrow[u.v.]{Bu_3N} \overset{B}{(CF_3)_2CH}CH_2CF_2CH_2CF_3$$

(70) 60°C,72h (156) 40%.

The structure of the product (156) was determined using mass spectrometry (M^+ 298), ^1H nmr (δH_B sept -3.0 ppm) and ^{19}F nmr spectroscopy (δ F_A absent).

The above result is explained by the following mechanism (Scheme 7.3) which uses the reduction process described earlier.

$$\begin{tikzcd} \underset{(70)}{(CF_3)_2CFCH_2CF_2CH_2CF_3} \arrow[r, "NBu_3", "-HF"'] & \underset{(71)}{(CF_3)_2C{=}CHCF_2CH_2CF_3} \arrow[d, "1e^e \text{ transfer reduction (Scheme 7.2)}"] \\ & \underset{(156)\quad 40\%}{(CF_3)_2CHCH_2CF_2CH_2CF_3} \end{tikzcd}$$

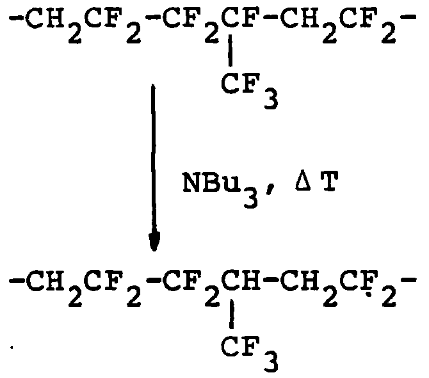
Scheme 7.3

In order to verify the second step of this mechanism the unsaturated model (71) was treated separately with Bu_3N under the following conditions:

(i) UV 60°C, 72h (photochemical)

(ii) 130°C, 12h (thermal)

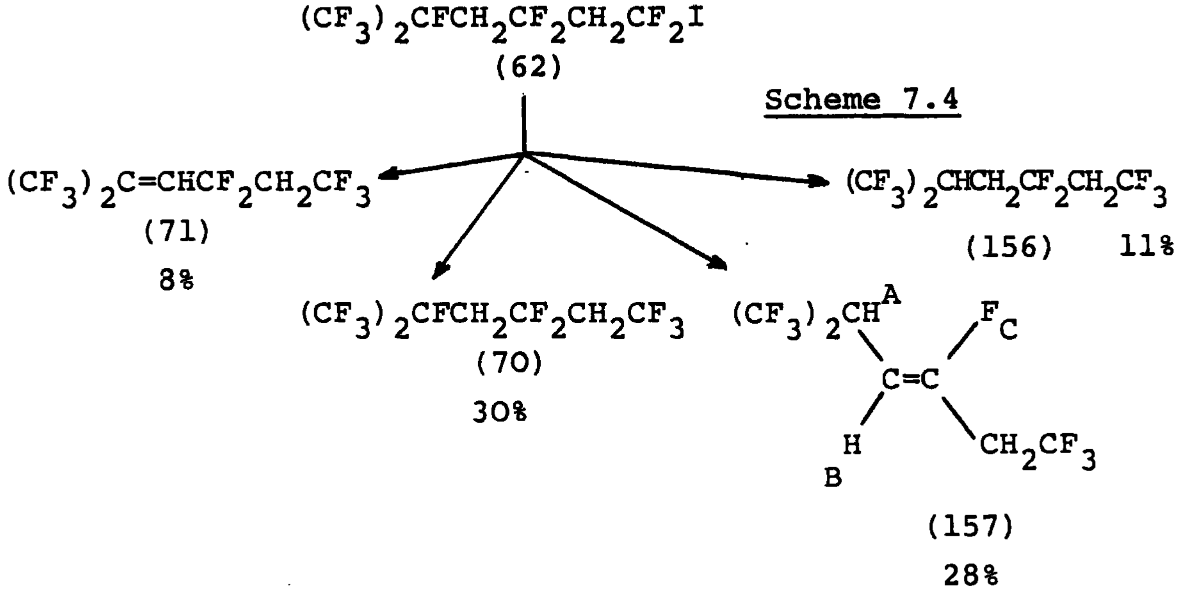
In each case a good yield of the reduced product $(CF_3)_2CHCH_2CF_2CH_2CF_3$ (156) was obtained ((i) 50% (ii) 90%). We have therefore established that structures of the form $-CF(CF_3)CH_2-$, as are present in $CH_2{=}CF_2/CF_3CF{=}CF_2$ copolymers, are susceptible to reduction in the presence of large tertiary amines at elevated temperatures. The reduction process comprices two separate steps which are (i) dehydrofluorination (ii) 1 electron transfer at the resultant $-C(CF_3){=}CH-$ site and concomitant reduction to give $-CH(CF_3)_2CH_2-$. It is therefore highly likely that these reduced structures are present in $CH_2=CF_2/CF_3CF=CF_2$ which have come into contact with amines at elevated temperatures and that they are contributors to the overall susceptibility of these copolymers to amines:



$$\text{-}CH_2CF_2\text{-}CF_2\underset{CF_3}{\underset{|}{C}}F\text{-}CH_2CF_2\text{-} \xrightarrow{NBu_3,\ \Delta T} \text{-}CH_2CF_2\text{-}CF_2\underset{CF_3}{\underset{|}{C}}H\text{-}CH_2CF_2\text{-}$$

(ii) <u>1-Iodo-2,2,4,4-tetrahydroundecafluoro-5-methylhexane(62) and Tri-n-butylamine</u>

When the telomer iodide $(CF_3)_2CFCH_2CF_2CH_2CF_2I$ (62) was treated with NBu_3 (2:1 excess) at 120°C for 12h four products were obtained in moderate yields. These products were isolated using preparative scale gas chromatography and are shown below (Scheme 7.4).



Scheme 7.4

The structure of the product (157) was determined using mass spectrometry (M^+ 278), infra-red spectrophotometry ($\nu_{C=C}$

1650 cm^{-1} weak), ^1H and ^{19}F nmr spectroscopy in which the coupling constant of the vinyl H_B (δ -4.9 ppm) and vinyl F_C (δ -100.0 ppm) was observed to be 30 Hz which is characteristic of a *trans* H,F system. The H_A atom was observed at δ -4.0 ppm as a septet (J=6 Hz). Clearly conversion of the $-CH_2CF_2I$ group of (62) to $-CH_2CF_3$ has occurred in each case. However this conversion cannot occur primarily because there is no source of fluorine until appreciable elimination of HF from (62) has occurred. Therefore the first step in the mechanism must be elimination of HI by the amine acting as a base, which is a known reaction.[100,115]

$$\underset{(62)}{(CF_3)_2CFCH_2CF_2CH_2CF_2I} \xrightarrow{NBu_3} \underset{(158)}{(CF_3)_2CFCH_2CF_2CH{=}CF_2}$$

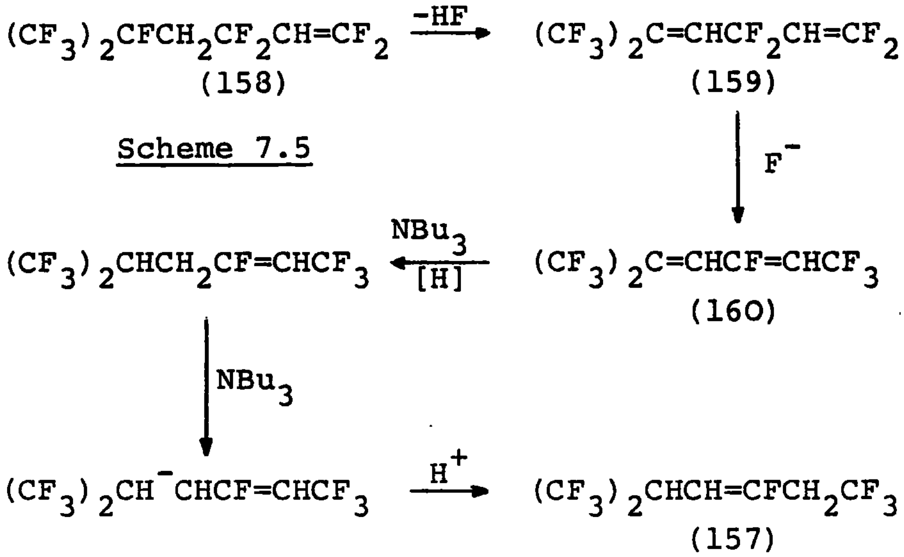
Elimination of HF from (158) at the tertiary site is then expected under the conditions employed (120°C). However any $(Bu)_3N.HF$ thus generated, being a source of active fluoride ion (Chapter Three B(iii)), is expected to react rapidly with the terminal $=CF_2$ group of (158) resulting in addition of HF to give (70) and (71)

i.e.

$$\underset{(158)}{(CF_3)_2CFCH_2CF_2CH{=}CF_2} \xrightarrow[\text{(ii) } NBu_3.HF]{\text{(i) } NBu_3} \underset{(70)}{(CF_3)_2CFCH_2CF_2CH_2CF_3} + \underset{(71)}{(CF_3)_2C{=}CHCF_2CH_2CF_3}$$

At some stage during the equilibration of the system the diene (159) is likely to be produced by removal of HF from (158). In the presence of F^- (159) can undergo isomerisation to give the conjugated diene (160) which, on reduction by

NBu_3 involving one electron transfer and subsequent base catalysed isomerisation, provides a route to the product (157) as outlined in Scheme 7.5.



$$\begin{tikzcd}
\underset{(158)}{(CF_3)_2CFCH_2CF_2CH{=}CF_2} \arrow[r, "-HF"] & \underset{(159)}{(CF_3)_2C{=}CHCF_2CH{=}CF_2} \arrow[d, "F^-"] \\
(CF_3)_2CHCH_2CF{=}CHCF_3 \arrow[d, "NBu_3"] & \underset{(160)}{(CF_3)_2C{=}CHCF{=}CHCF_3} \arrow[l, "NBu_3"', "{[H]}"] \\
(CF_3)_2CH^-CHCF{=}CHCF_3 \arrow[r, "H^+"] & \underset{(157)}{(CF_3)_2CHCH{=}CFCH_2CF_3}
\end{tikzcd}$$

Scheme 7.5

The product (156) arises simply from reduction of (71) by NBu_3 as previously described.

The products obtained provide further evidence for the one-electron reduction process described earlier.

7E Further Chemistry resulting from 7-Iodo-2-hydrodecafluoro-3-methyl butane (50)

The synthesis of $(CF_3)_2CFCFHCF_2I$ (50) was described in Chapter Two C.

(i) Synthesis of Perfluoro-2-methylbut-2-ene (161)

Perfluoro-2-methylbut-2-ene $(CF_3)_2C{=}CFCF_3$ (161) synthesized in excellent yields using the approach outlined below (Scheme 7.6).

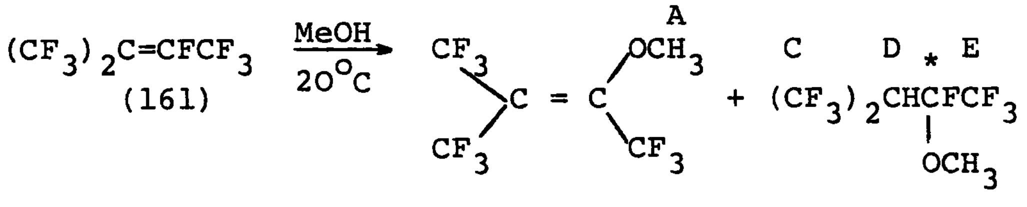
$$\underset{(50)}{(CF_3)_2CFCFHCF_2I} \xrightarrow[90^{o}C,2h]{KOH} \underset{\substack{(100)\\(quant.)}}{(CF_3)_2CFCF{=}CF_2} \xrightarrow[100^{o}C,2h]{\substack{CsF\\sulpholane}} \underset{\substack{(161)\\(quant.)}}{(CF_3)_2C{=}CFCF_3}$$

Scheme 7.6

Both reactions were carried out using sealed glass ampoules.

(ii) Chemistry of Perfluoro-3-methylbut-2-ene (161)

When the monoalkene (161) was treated with excess neutral methanol at 20^{o}C a mixture of two products was obtained which were identified as (162) and (163) in approximately 1:1 ratio.



(162) (163)

The structure of the product (162) was established using the following data:

(i) M^{+} 262 corresponding to addition of MeOH with loss of HF

(ii) δ_{3H} $-OCH_3$ at -4.0 ppm together with vinyl $-CF_3$ groups at δ_{6F} -60 to -64 ppm.

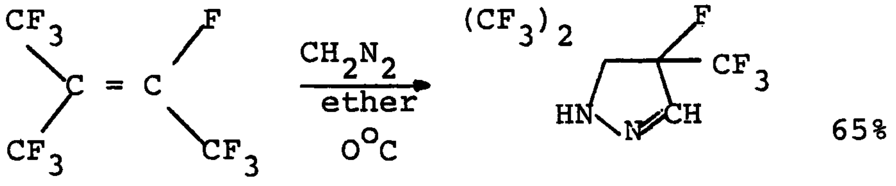
while the structure of (163) was deduced using the data:

(i) M^{+} 282, *i.e.* 1:1 MeOH adduct

(ii) δ_{3H} $-OCH_3$ at -3.7 ppm, δ_H $-CH(CF_3)_2$ at -3.6 ppm (septet) and δ_F -128.3 ppm (tertiary fluorine), $_{6F}$ -60.0 and -64.7 ppm (prochiral) attributable to the $-CH(CF_3)_2$ group.

This result demonstrates that the perfluoroalkene (161) is exceedingly susceptible to nucleophilic attack and merits comparison with perfluorobut-2-ene $(CF_3)_2C{=}CF_2$ which is also attacked by neutral MeOH. [83] Removal of HF from (163) to give the second product (162) is facilitated by the seven fluorine atoms β -to the proton D -CH of (164), which results in enhanced acidity, [83] together with relief of steric crowding.

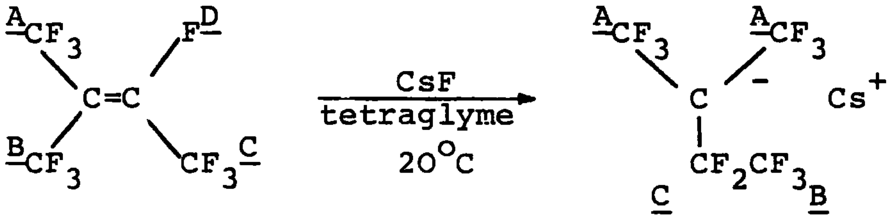
When $(CF_3)_2C{=}CFCF_3$ (161) was treated with CH_2N_2 at 0°C in ether instantaneous addition occurred and the product (164) was isolated.



(161) (164)

The regiochemistry of addition was determined using mass spectrometry in which the fragment $-NHC(CF_3)_2-$ (M^+ 165) occurs. This fragment can only arise from the regio adduct shown. The product (164) was further identified as the Δ^2-pyrazoline derivative using ^1H nmr spectroscopy (δ TMS 0 ppm, δ -NH -7.4 ppm, δ -CH -6.8 ppm).

When (161) was stirred with excess CsF in tetraglyme a dark red solution was obtained. The ^{19}F nmr spectrum recorded using this solution is consistent with the formation of the carbanion (165).



(161) (165)

The ^{19}F nmr data recorded for the carbanion (165) are summarized in Table 7.4 together with that for the alkene (161).

TABLE 7.4 ^{19}F nmr Data recorded for the Alkene (161) and Carbanion (165)

δ $CFCl_3$ 0 ppm. (165) Carbanion

Shift/ppm.	Intensity	Assignment
-42.0	6	A $-CF_3$'s
-85.7	3	B $-CF_3$
-95.0	2	C $-CF_2$

(161) Alkene

Shift/ppm.	Intensity	Assignment
-60.4	3	A $-CF_3$
-61.7	3	B $-CF_3$
-69.0	3	C $-CF_3$
-100.3	1	D $-CF$

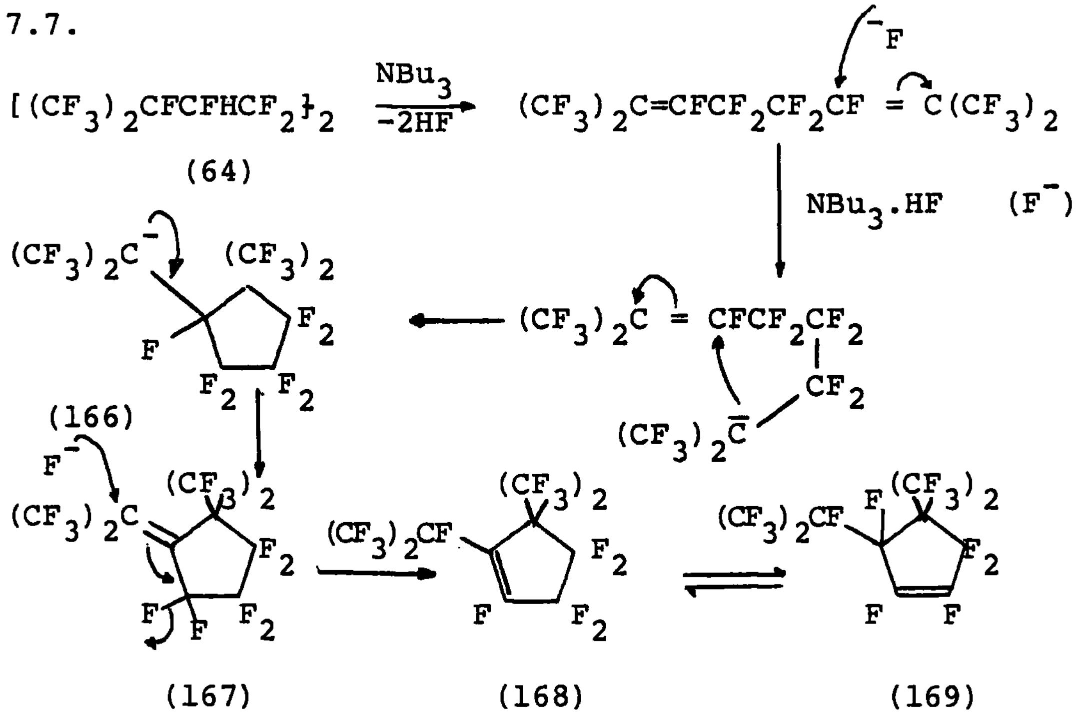
When a mixture of (161) with diethyl ether (1:1) was irradiated by γ-rays no chemical change occurred after 72h. This is in contrast to the facile addition of diethyl ether to the diene (75) and is most feasibly explained in terms of steric repulsion.

7F Chemistry of 3,6-Dihydroeicosafluoro-2,7-dimethyloctane (64)

The title compound $[(CF_3)_2CFCFHCF_2]_2$ (64) was prepared in excellent yield by coupling $(CF_3)_2CFCFHCF_2I$ (50) in the presence of Hg and u.v. light.

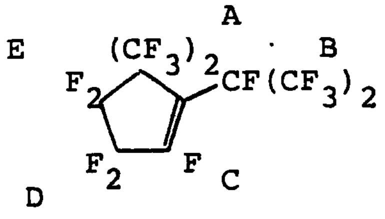
(i) Reaction with Tri-n-butylamine

This system was investigated in an attempt to produce perfluoroalkenes by elimination of hydrogen fluoride. When $[(CF_3)_2CFCFHCF_2]_2$ (64) was stirred with NBu_3 at 125°C for 12h two products were obtained and isolated using preparative scale gas chromatography. The products were the cyclic olefins (168) and (169). This result, together with the mechanism proposed for this reaction, is outlined in Scheme 7.7.

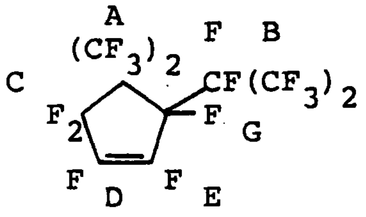


Scheme 7.7

The products (168) and (169) were identified using the ^{19}F nmr spectroscopy data shown in Tables 7.5 and 7.6.



(168)



(169)

TABLE 7.5 ^{19}F NMR Data used for identification of (168)

δ $CFCl_3$ 0 ppm.

Shift/ppm.	Intensity	Assignment
-65.7	6	A $-CF_3$
-75.7	6	B $-CF_3$
-107.3	1	C $-CF$
-122.3	4	D,E $-CF_2$
-181.2	1	F $-CF$

The intermediate cyclic olefin (167) was not isolated. This result is somewhat surprising because (167) is the least sterically crowded molecule shown in the scheme and should be the thermodynamically favoured product.

TABLE 7.6 ^{19}F NMR Data used for identification of (168)

δ $CFCl_3$ 0 ppm.

Shift/ppm.	Intensity	Assignment
-74.6	6	A $-CF_3$
-74.8, -77.8	6	B $-CF_3$ (prochiral)
-118.6	2	C $-CF_2$
-122.2, -124.4	2	D,E $-CF$
-188.1, -188.5	2	F,G $-CF$

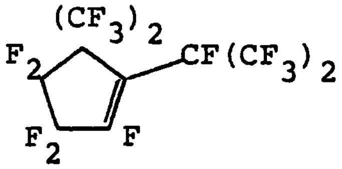
Excellent molecular ion peaks (M^- 462) were obtained for each of the isomers (168) and (169) using negative ion mass spectrometry.[154]

(ii) Reaction with Cesium Fluoride

In order to determine the preferred thermodynamic product from the reaction between NBu_3 and $[(CF_3)_2CFCFHCF_2]_2$ (64) an experiment was tried using CsF alone under forcing conditions. At elevated temperatures CsF acts as a base towards acidic protons [149] and therefore should behave entirely analogously to NBu_3.

When $[(CF_3)_2CFCFHCF_2]_2$ (64) was stirred at 140°C in a solution of CsF in sulpholane, and the reaction followed using ^{19}F nmr techniques, complete conversion to the cyclic product (168) was observed after 3h.

$$\underset{(64)}{[(CF_3)_2CFCFHCF_2]_2} \xrightarrow[\text{sulpholane}]{\text{CsF}} \quad 140^{\circ}C,\ 3h$$



(168)

The isomers (167) and (169) were not present in detectable amount (<1% by nmr).

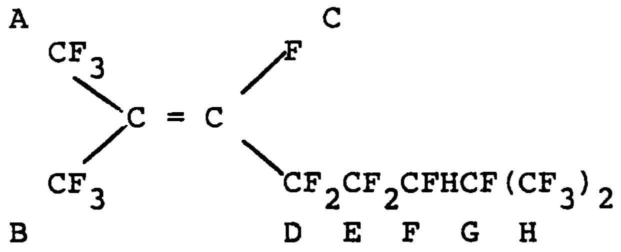
(iii) Pyrolysis over Potassium Fluoride

In an attempt to isolate acyclic alkenes *via* removal of HF from $[(CF_3)_2CFCFHCF_2]_2$ (64) this compound was passed over hot KF using vacuum-line techniques. The experiment was conducted over a range of temperatures as outlined in Table 7.7 together with the products obtained.

TABLE 7.7 Products obtained from the Pyrolysis of $[(CF_3)_2CFCFHCF_2]_2$ (64) over KF

Temperature	Materials isolated
400°C	(64)
470°C	$(CF_3)_2C{=}CFCF_2CF_2CFHCF(CF_3)_2$ (170 + (64)
500°C	(168) + (169)
520°C	At least 15 products which were not separated

The monoalkene 6H-nonadecafluoro-2,7-dimethyloct-2-ene (170) was identified using the ^1H and ^{19}F nmr data shown in Table 7.8.



(170)

Notably the diene $[(CF_3)_2C{=}CFCF_2]_2$[155] (171) could not be isolated under these conditions. Therefore, upon removal of a second unit of HF from the monoalkene (170) to produce (171), cyclisation of (171) takes place rapidly.

The monoalkene $(CF_3)_2C{=}CFCF_2CF_2CFHCF(CF_3)_2$ (170) was stirred with CsF in tetraglyme in an attempt to form the corresponding carbanion $(CF_3)_2CFCFHCF_2CF_2CF_2\bar{C}(CF_3)_2\ Cs^+$ (170A). However the ^{19}F nmr spectrum was recorded for the resulting solution and was highly complex. It was concluded

TABLE 7.8 ^{1}H and ^{19}F nmr Data for $(CF_3)_2C{=}CFCF_2CF_2CFHCF(CF_3)_2$
(171)

^{19}F nmr Data: δ $CFCl_3$ 0 ppm

Shift/ppm	Coupling	Intensity	Assignment
-58.3	m	3	B $-CF_3$
-61.3	d,q J_{AC}=32Hz J_{AB}=10Hz	3	A $-CF_3$
-74.3, -77.3	m	6	H $-CF_3$ (prochiral)
-96.0	m	1	C $=CF$
-115.3	t J_{DE}=17Hz	2	D $-CF_2$
-122.6	AB J = 280Hz	2	E $-CF_2$
-187.3	m	1	G $-CF$
-210.1	m	1	F $-CF$

^{1}H nmr Data : δ TMS 0 ppm

-5.6	d J_{FF} = 46Hz	-	F $-CH$

that the presence of H destabilizes the anion (170A) and leads to a series of further reactions.

(iv) Reaction with Potassium Hydroxide

When $[(CF_3)_2CFCFHCF_2\frac{1}{2}_2$ (64) was stirred with KOH in acetone no reaction occurred until the temperature was raised to 90°C whereupon tar was produced and only (64) was isolated from the system. Treatment of (64) with dry KOH gave similar results at 90°-100°C.

7G Chemistry of 2,4-Dihydrotetradecafluoro-5-methylhexane (72)

The title compound (72) was synthesized using the following route (Chapter Two, B).

$$\underset{(44)}{(CF_3)_2CFI} \xrightarrow[185^{\circ}C]{CFH=CF_2} \underset{(52)\quad 20\%}{(CF_3)_2CFCFHCF_2CFHCF_2I} \xrightarrow[0^{\circ}C]{SbF_5} \underset{(72)\quad \text{quant.}}{(CF_3)_2CFCFHCF_2CFHCF_3}$$

(i) Interpretation of ^{19}F NMR Spectrum

2,4-Dihydrotetradecafluoro-5-methylhexane (72) contains two chiral centres:

$$(CF_3)_2CF\overset{*}{C}FHCF_2\overset{*}{C}FHCF_3$$

(72)

This property gives rise to two diastereoisomers. Each diastereoisomer consists of a further pair of enantiomers which are ^{19}F nmr equivalent.

The diastereoisomers were separated on a polar column using preparative scale gas chromatography.

The ^{19}F nmr spectra of 1:1 mixtures of the diastereoisomers were recorded both neat and in solution in acetone. On separating the diastereoisomers the ^{19}F nmr spectrum of each was again recorded neat and in solution in acetone. Comparison of the spectra obtained made apparent some unusual solvent effects concerning the central $-CF_2-$ group of the molecule. These observations are summarized in Table 7.9.

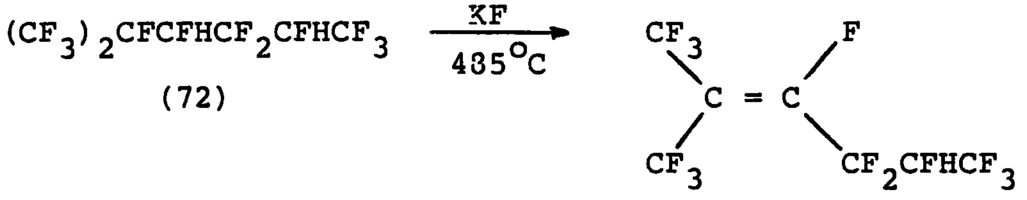
TABLE 7.9 Solvent effects upon ^{19}F nmr signal of $-CF_2-$ group of $(CF_3)_2CFCFHCF_2CFHCF_3$

System observed	Observation
1:1 Mixture neat	Both $-CF_2-$ resonances were singlets δ 121.5 and 122.7 ppm.
1:1 Mixture in Acetone	One AB - CF_2- resonance δ_{AB} -121.0 ppm, J_{AB}=177Hz. One singlet $-CF_2-$ resonance δ_S -122.4 ppm.
Each Diastereomer (isolated) neat	Both $-CF_2-$ resonances were singlets *ca.* δ -122.0 ppm.
Each Diastereomer (isolated in solution in Acetone	One AB $-CF_2-$ resonance δ_{AB} -122.0 ppm J_{AB}=180Hz. One singlet $-CF_2-$ resonance δ_S - 122.5 ppm.

Clearly interaction between the two diastereoisomers cannot give rise to inequivalence of the F atoms since the signals obtained from the neat mixture were both singlets. Therefore this effect must be attributed to the solvation of one of the diastereoisomers by acetone. It is however unusual that this effect should be observed for only one of the diastereoisomers and not both. We have not been able to determine which of the diastereoisomers (72, RR+SS) or (72, SR+RS) is active in this way.

(ii) Pyrolysis over Potassium Fluoride

When $(CF_3)_2CFCFHCF_2CFHCF_3$ (72) was passed over KF at 485°C, conversion to the monoalkene 2H-terdecafluoro-5-methylhex-4-ene (172) was achieved.



(72) (172) 20%

The alkene (172) was identified using mass spectrometry (M^+ 332), ^{19}F nmr spectroscopy (δ $CFCl_3$ 0 ppm δ_F C=CF -96.7 ppm) and infra-red spectrophotometry ($\nu_{C=C}$ 1690 cm^{-1}).

EXPERIMENTAL

SECTION

INSTRUMENTATION

Infrared spectra, unless stated, were recorded on a Perkin-Elmer 577 Infrared Spectrophotometer. Solid samples were recorded as KBr discs, liquids as contact films between KBr plates and volatile samples in a cylindrical cell with KBr windows.

^{1}H and ^{19}F n.m.r. spectra were recorded on a Varian EM360L spectrometer operating at 60 and 56.4 MHz respectively at the ambient probe temperature (40°C) and on a Brüker HK90 with Fourier Transform facility at elevated temperatures. Chemical shifts are quoted in ppm relative to TMS and $CFCl_3$. Carbon (^{13}C) spectra were recorded on a Brüker WH-360 operating at 90.6 MHz. Chemical shifts are quoted in ppm relative to TMS.

Mass spectra were recorded on a Varian Associates 77E spectrometer equipped with electron-impact, negative ion (NH_3 gas)[154] and chemical ionization ($^iC_4H_8$)[154] facilities together with a capilliary column gas chromatograph. Spectra were also recorded on a VG Micromass 12B Spectrometer fitted with a Pye 104 Gas Chromatograph.

Gas liquid chromatographic analyses were carried out on Varian Aerograph Model 920 or Pye Unicam GCD chromatographs using columns packed with diisodecylphthalate (10% and 20%) on chromasorb P (column A), 20% Krytox (perfluoropolyoxypolylene) on chromasorb P (column K) and Silicon elastomer (5%, 10% and 20%) on chromasorb P (column O). Preparative scale gas liquid chromatography was performed on a Varian Aerograph Model 920 using Columns A, K and O.

Fractional distillations of product mixtures were carried out using a Fischer-Spaltrohr MMM202 system and other packed columns.

Carbon, hydrogen and nitrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyzer. Analyses for halogens were performed as described in the literature.[156]

Boiling points and melting points were determined at atmospheric pressure and are uncorrected.

Reagents

Hexafluoropropene, 1,1-difluoroethene, perfluoroallylfluorosulphate (F.A.F.S.), antimony pentafluoride, iodine pentafluoride and bisphenol AF (2) were obtained from the Montedison Company (Montefluos SPA, Milan).

CsF and KF were obtained dry by repeatedly heating under high vacuum (10^{-5} torr) and grinding in a glove-bag under dry N_2. Solvents sulpholane, N,N-dimethylformamide and tetraglyme were purified by vacuum distillation and subsequent storage over molecular sieve type 4A.

CHAPTER EIGHT

EXPERIMENTAL FOR CHAPTER TWO - SYNTHESIS AND EXAMINATION OF SATURATED MODEL COMPOUNDS

8A. Synthesis of Saturated Model Compounds

(i) Synthesis of Iodofluoroalkanes[47-50,52,62]

Perfluoro-2-iodopropane (44).[108]

A mixture containing hexafluoropropene (120g, 0.80 mole), iodine pentafluoride (35.4g, 0.16 mole) and iodine (80.4g, 0.64 mole), in a sealed stainless steel autoclave (1175 ml capacity) was rocked under autogenous pressure at 150°C for 24 h. On opening the autoclave hexafluoropropene (approx. 1g) was recovered. Further material (228g) transferred from the autoclave using vacuum line techniques was washed with aqueous alkaline sodium thiosulphate and water. Gas chromatography showed one component. Perfluoro-2-iodopropane, $(CF_3)_2CFI$ (44)[108] (96%) was identified by comparison of the infra red spectrum with that recorded in the literature.[100]

Telomers with 1,1-Difluoroethene[100,101]

A mixture containing perfluoro-2-iodopropane (44) (90.4g, 0.305 mole) and 1,1-difluoroethene (24.0g, 0.375 mole) in a sealed nickel tube (150 ml capacity) was rocked at 185°C for 36 h. under autogenous pressure. On opening the tube after cooling no gaseous products were recovered and a purple liquid (114g) was poured from the tube. Analytical gas chromatography (column O, 120°C) showed the presence of 4 components. Fractional distillation of the mixture using a packed insulated column yielded perfluoro-2-iodopropane (44) (5g, 0.017 mole), b.pt. 38°C; 2H,2H-1-iodonona-fluoro-3-methylbutane[100] (48) (73g, 67%), b.pt. 103°C (lit.100, 105°C) δ_H (60MHz; CCl_4) -2.8 (2H, t, 2-H); δ_F (56.4 MHz; CCl_4) -76.4 (6F, d, 3,4-CF_3), -49.6 (2F, m, 1-F), -184.5 (1F, sept, 3-F); m/z 360 (M^+ 8%) and 233 (M-127, 31%); 2H,2H,4H,4H-1-iodoundecafluoro-5-methylhexane,[100] $(CF_3)_2CF(CH_2CF_2)_2I$ (62) (26g, 20%); b.pt. 157°C; δ_H (60 MHz; CCl_4) -2.8 to -3.2 (4H, m, 2-H, 4-H); δ_F (56.4 MHz; CCl_4) -76.0 (6F, d, 5,6-CF_3), -49.2 (2F, m, 1-F), -93.6 (2F, m, 3-F), -185.0 (1F, sept, 5-F); m/z 424 (M^+, 1%) and 297 (M-127, 15%).

Preparative scale gas liquid chromatography (column O, 200°C) on the distillation residue yielded 2,2,4,4,6,6-hexahydro-1-iodoterdecafluoro-7-methyloctane; $(CF_3)_2CF(CH_2CF_2)_3I$ (47) (1g, 0.6%); δ_H (60 MHz; CCl_4) -2.8 to -3.2 (6H, m, 2-H, 4-H,6-H); δ_F (56.4 MHz; CCl_4) -76.2 (6F, d, 7,8-CF_3), -49.0 (2F, m, 1-F, -90.3 to -92.0 (4F, m, 3,5-F), -185.0 (1F, sept, 7-F); m/z 488.

A mixture containing perfluoro-2-iodopropane (44) (66.5g, 0.22 mole) and 1,1-difluoroethene (43.0g, 0.66 mole) was sealed in a nickel tube which was then rocked under autogenous pressure at 220°C for 36 hr. On opening the tube a purple liquid (98g) was poured out. Temperature programmed analytical gas chromatography (column O, 100°C to 250°C) showed 5 components. Fractional distillation yielded (48) (4.3g, 5.4 mole) and (62) (25.0g, 26%). Preparative scale gas liquid chromatography (30% column O, 250°C) yielded the higher telomers $(CF_3)_2CF-(CH_2CF_2)_nI$, n=3 (47)[100] (2g) and n=4, 2,2,4,4,6,6,8,8-octahydropentadecafluoro-1-iodo-9-methyldecane[100] (1g); δ_F (56.4 MHz; CCl_4) -49.0 (2F, m, 1-F); m/z 552.

A mixture containing perfluoroiodoethane (69g, 0.28 mole) 1,1-difluoroethene (16.4g, 0.26 mole) and cumene hydroperoxide (2g) was sealed in a nickel tube which was then rocked under autogenous pressure at 180°C for 24 h. On opening the tube a purple liquid (70g) was poured out and washed with aqueous alkaline sodium thiosulphate and water. Gas liquid chromatography (5% column O, 105°C) showed 5 components. Mass spectrometry of these components showed highest masses 146, 210, 210, 274 and 274 corresponding to $C_2F_5(C_2H_2F_2)_nI$, n=0, 1,1,2,2. Fractional distillation yielded 2H,2H-1-iodoheptafluorobutane, $C_2F_5CH_2CF_2I$[100] (50) (21 g, 24%), b.pt. 88°C; identified by comparison of infra-red spectrum with that of an authentic sample.[100] The other fractions and residue (*ca* 40g) were not fully characterized.

Telomers with Trifluoroethene[100]

A mixture of perfluoro-2-iodopropane (44) (50g, 0.17 mole) and trifluoroethene (13g, 0.16 mole) was sealed in a nickel tube (150 ml capacity) and rocked at 200°C for 24 h under autogenous pressure. On opening the cooled tube no gaseous products were recovered. A purple liquid (60g) was poured from the tube which was observed to consist of 4 major components using analytical gas chromatography (column K, 110°C). Fractional distillation using a Fischer-Spaltrohr column yielded 4 fractions in 95% purity (column K, 110°C) as summarized below (Table 8.1).

A pure sample of each of the 2 middle fractions was isolated using preparative scale gas chromatography (column K, 120°C). Fraction II yielded 2H-1-iododecafluoro-3-methylbutane (50) (*ca* 1g), b.pt. 101°C;[100] δ_H (60 MHz; Neat) -5.1 (1H, d d t, J 42, 10 and 10 Hz, 2-H); δ_F (56.4 Mz; Neat) -55.0 (2F, br, 1-F),

TABLE 8.1 Fractions Obtained from the Reaction of $(CF_3)_2CFI$ (44) and $CF_2{=}CFH$

B. pt.	No.	Amount Obtained
35-50°C	I	10 g
98-103°C	II	16 g
150-155°C	III	20 g
180-185°C	IV	8 g

-74.0 and -77.7 (6F, br, 2,3-CF_3, prochiral), -213.6 (1F, br, 2-F); m/z 378. Identification of (50) was also facilitated by comparison of infrared spectra with that given in the literature.[100] Fraction III yielded 2H,4H-1-iodododeca-fluoro-5-methylhexane, $(CF_3)_2CFCFHCF_2CFHCF_2I$ (52), b.pt.151°C; δ_H (60 MHz; neat) -5.1 (2H, br m, 2,4-H); δ_F -54.1 (2 F, br m, 1-F), -73.0 and -76.4 (6 F, br, 5,6-CF_3 prochiral), -121.9 (2 F, br, 3-F), -211.9 (2 F, br, 2,4-F); m/z 460.

Relatively small amounts of the regioisomers $(CF_3)_2CFCF_2CFHI$ and $(CF_3)_2CFCFHCF_2CF_2CFHI$ were identified in the crude product mixture using ^1H nmr spectroscopy δ_H *ca.* -6.1. The fractions I, b.pt. 35-40°C and IV, b.pt. 180-185°C were not fully characterized.

(ii) Coupling Reactions (63,64)

$(CF_3)_2CFCH_2CF_2I$ (48)[100,101]

A mixture of $(CF_3)_2CFCH_2CF_2I$ (48) (40 g, 0.086 mole), acetic anhydride (25 ml) and zinc metal (25 g) was stirred mechanically in a 3-necked glass vessel at 50°C for 4 h.[100]

Volatile products were transferred to a fresh flask, using vacuum line techniques, and stirred with aqueous HCl (100 ml, 0.05M) for 1 h and then washed with water (2 x 50 ml). The fluorocarbon layer was removed and dried ($MgSO_4$), filtered, and then stored over molecular sieve (type 4A). Analytical gas chromatography showed the product to be (>95% 3H,3H,6H,6H-octadecafluoro-2,7-dimethyloctane, $[(CF_3)_2CFCH_2CF_2\frac{1}{2}_2$ (61)[100] (15.0g, 75%); m/z 466. The product was identified by comparison of infra-red spectra with that of an authentic sample.[100]

$(CF_3)_2CF(CH_2CF_2)_2I$, (62)

A mixture of $(CF_3)_2CF(CH_2CF_2)_2I$ (62) (33.5g, 79 mmol), acetic anhydride (30 ml) and zinc metal was stirred mechanically at 60°C for 2h. Volatile materials were transferred to a fresh flask using vacuum line techniques, stirred with aqueous HCl (50 ml, 0.05M) and then washed with water (100 ml). The fluorocarbon layer was separated and dried over $MgSO_4$. Analytical gas chromatography showed 1 major and 3 minor components. Distillation of the products removed a forefraction refluxing in the range 80-100° (13g). The residue was distilled under reduced pressure collecting the fraction b.pt. 130-135°C (3mm Hg). Analytical gas chromatography (column K, 175°C) showed this fraction to be >95% pure and was identified as $[(CF_3)_2CFCH_2CF_2CH_2CF_2\frac{1}{2}_2$ (63) (9.5g, 40%); variable analysis; δ_H -2.9 to -3.1 (br m); δ_F -76.2 (12 F, br, 4-CF_3), -94.5 (4 F, br, 2-F), -108.5 (4 F, br, 1-F), -184.6 (2 F, br, 3-F); m/z 594. The volatile products were not fully characterized.

$(CF_3)_2CFCFHCF_2I$ (50)

A sealed glass ampoule containing $(CF_3)_2CFCFHCF_2I$, (50) (10g, 26 mmol) and mercury (10 ml) was irradiated using a 1 KW ultra-violet lamp at *ca*. 60°C for 7 d. Volatile material transferred from the glass ampoule using vacuum line techniques was shown to be (> 95% purity) by analytical gas chromatography (column A, 80°C) 3,6-dihydroeicosafluoro-2,7-dimethyloctane, $[(CF_3)_2CFCFHCF_2]_2$ (64) (5.8g, 89%); (Found: C, 23.1; H, 0.6; F, 75.1. $C_{10}H_2F_{20}$ requires C, 23.90; H, 0.40; F, 75.70%); δ_H -5.1 (d, J 40 Hz, 3,6-H); δ_F -74.0 and -77.7 (12 F, br, 2,7-CF_3, prochiral), -114.8 (4 F, br, 4,5-F), -216.0 (2 F, br, 2,7-F); m/z 483 (M^+ - 19).

A glass ampoule containing $CF_3CF_2CH_2CF_2I$ (49) (5g, 16 mmol) and mercury (10 ml) was irradiated using a 1 KW ultra-violet lamp at 60°C for 5d. Volatile material transferred from the tube using vacuum line techniques was found by gas chromatography (column O, 120°C) to be one component (>95% purity). The product was 3,3,6,6-tetrahydrotetradecafluorooctane, $[CF_3CF_2CH_2CF_2]_2$ (57);[100] δ_H -3.0 (m, 3,6-H); δ_F -87.1 (6 F, s, 2,7-CF_3), -114.5 (4 F, br, 4,5-F), -117.8 (4 F, m, 2,7-F); m/z 366. Further identification was provided by comparison of infrared spectra with that given in the literature.[100]

(iii) Fluorination of the Telomer Iodides (70,72,122)

$(CF_3)_2CF(CH_2CF_2)_nI$

A mixture of the telomer iodies $(CF_3)_2CF(CH_2CF_2)_nI$ (36g) of approximate molar composition n=1 40%, n=2 30% and n=3 10%, dissolved in $CF_2ClCFCl_2$ (100 ml), was stirred mechanically in a 3-necked glass vessel. The temperature in the flask was maintained at 0°C using an ice bath while a solution of antimony pentafluoride (40 g, 0.19 mole) in $CF_2ClCFCl_2$ (50 ml) was added over a period of 0.5 h. The contents of the flask which became viscous and intensely coloured due to the deposition of iodine, were stirred for a further 0.5 h after the addition was complete. After this time further $CF_2ClCFCl_2$ (50 ml) was added and the resulting mixture filtered to remove solid material. The solid residue was washed with $CFCl_2CF_2Cl$ (30 ml) and the washings added to the initial filtrate. The resulting solution was then washed with water (250 ml) and neutralised by addition of solid $NaHCO_3$ until effervescence ceased. The fluorocarbon layer was separated and $CFCl_2CF_2Cl$ removed by distillation to leave a pale yellow liquid (16 g). Distillation of this liquid resulted in 3 fractions; I b.pt. 50-55°C, II b.pt. 80-85°C and III 120-130°C. Analytical gas chromatography (column O, 70-110°C) showed that the separation was not complete. Therefore the major component of each fraction was isolated using preparative scale gas chromatography (30% column O, 100°C). The first component was identified as $(CF_3)_2CFCH_2CF_3$[100,101] (66); m/z 252 and by comparison of the infrared spectrum that of an authentic sample.[100] The second component was <u>2H,2H,4H,4H-dodecafluoro-5-methylhexane</u> $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (70), (Found: C, 26.8; H, 1.1; F, 71.7; $C_7H_4F_{12}$ requires C, 26.58; H, 1.23; F, 72.15%); δ_H -3.0 to -3.2 (br m, 2,4-H); δ_F -63.0 (3 F, t, J 14Hz, 1-CF_3) -77.9 (6 F, dt, J t and 7 Hz, 5,6-CF_3) -90.8 (2 F, br m, 3-F) -185.8 (1 F, br m, 5-F); m/z 297 (M^+ -19). The third component was <u>2,2,4,4,6,6-hexahydrotetradecafluoro-7-methyloctane</u> $(CF_3)_2CFCH_2CF_2CH_2CF_2CH_2CF_3$ (122)*; δ_H -3.0 to -3.2 (br m, 2,4,6-H); δ_F -64.3 (3 F, t, J 13 Hz), 1-CF_3 -79.3 (6 F, d, J 8 Hz, 7,8-CF_3) -91.1 (2 F, br.m, 5-F) -92.7 (2 F, br m, 3-F) -187.3 (1 F, br m, 7-F); m/z 371 (M^+ -19).

* variable analysis.

When the residue from the distillation was examined using analytical gas chromatography (column O, 180°C) two major components were resolved. These components were isolated using preparative scale gas chromatography (column O, 200°C) and were identified as the n=4 and n=5 telomers $(CF_3)_2CF(CH_2CF_2)_nF$; m/z (n=4) 435 (M^+ -19) and (n=5) 599 (M^+ -19).

$(CF_3)_2CFCFHCF_2CFHCF_2I$

A mixture of $(CF_3)_2CF(CFHCF_2)_2I$ (52) (42g, 0.08 mole) and antimony pentafluoride (20g, 0.1 mole) was sealed in a glass ampoule under vacuum at -196°C and allowed to warm up to 0°C using an ice-bath. The mixture was then shaken gently over a period of 0.5 h during which time the contents of the tube turned black due to deposition of iodine. The products were then transferred onto NaF in order to remove antimony pentafluoride and finally transferred from the NaF to a fresh glass vessel, washed with aqueous alkaline $Na_2S_2O_3$, water, dried over $MgSO_4$ and filtered to leave a colourless liquid. The product was examined using analytical gas chromatography and found to be (>95% purity) 2H,4H-tetradecafluoro-5-methylhexane, $(CF_3)_2CFCFHCF_2CFHCF_3$ (72) (21g, 75%); (Found: C, 23.6; H, 0.4; F, 75.0; $C_7H_2F_{14}$ requires C, 23.86; H, 0.57; F, 75.57%); δ_H (60 MHz; Neat) -5.4 (M, 2,4-H); δ_F -73.9 and 77.5 (6 F, br m, 5,6-CF_3, prochiral), -75.9 (3 F, br m, 1-CF_3), -121.5 (2 F, br, 3-F), -185.0 (1 F, br, 5-F), -211.2 (2 F, br, 2,4-F); m/z 333 (M^+ -19).

8B Examination of the Saturated Model Compounds

Response to the Curing Agents, General Procedure - In each experiment a sample of the saturated model was sealed under vacuum in a small glass ampoule (equipped with a "Rotoflo" tap for use with vacuum-lines) with one or a combination of the curing agents. The mixture was then shaken and heated to the temperature indicated. Products were then transferred from the tube by vacuum line techniques and characterized. Solid residues remaining in the glass ampoule were extracted with CH_2Cl_2 and examined using ^{19}F nmr spectroscopy.

(i) Response to MgO and $Ca(OH)_2$

When a mixture of $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (70) (2g, 0.o63 mole) and MgO (2g, 0.05 mole) was heated to 177°C for 5 h a colourless liquid was obtained (1.9g) which was examined using analytical gas chromatography (column A, 80°C) and found to be (>95% purity) one component with a trace component. ^{19}F nmr spectroscopy confirmed that the major component was (70) and that the minor component contained the $(CF_3)_2C{=}CH-$ group (δ_F -61.0 and -68.4 ppm). When the experiment was repeated under identical conditions with $Ca(OH)_2$ a similar result was obtained. The residue did not contain fluorinated material.

Treatment of the models $[(CF_3)_2CFCH_2CF_2]_2$ (61) and $[(CF_3)_2CF(CH_2CF_2)_2]_2$ (63) under conditions identical to those described above also produced a similar result.

(ii) Response to Bisphenol AF

When a mixture of $[(CF_3)_2CFCH_2CF_2-]_2$(2g, 0.043 mole) and bisphenol AF (2) (1g, 0.03 mole) was heated to 200°C for 3 hr a colourless liquid was obtained which was identified as pure (61). When the residue was extracted with CH_2Cl_2 and examined using ^{19}F nmr spectroscopy only (2) was detected.

(iii) Response to Phosphonium Salts

When a mixture of the model (61) (1.5g, 0.028 mole) and $Ph_4P^+cl^-$ (1g, 0.027 mole) was heated to 190°C for 18 h a colourless liquid was obtained which was identified as pure (61). The residue did not contain fluorinated material. When the experiment was repeated under identical conditions using $PhCH_2(Ph)_2P^+Cl^-$ there was also no reaction.

(iv) Combinations of the Curing Agents

Table 8.2 summarizes the experimental conditions used. In each experiment which included the inorganic acid-acceptors, $Ca(OH)_2$ and MgO, a trace of unsaturation was detected using ^{19}F nmr spectroscopy. In all other experiments no detectable chemical change occurred.

TABLE 3.2 Combinations of the Curing Agents

Saturated Model (2g)	Curing Agents (1 g)	Conditions
(61)	bisphenol AF $Ca(OH)_2$ MgO	177°C, 5 h
(63)	bisphenol AF $Ca(OH)_2$ MgO	177°C, 5 h
(61)	bisphenol AF $PPh_4{}^+Cl^-$	190°C, 18 h
(63)	bisphenol AF $PPh_4{}^+Cl^-$	190°C, 18 h
(61)	bisphenol AF $PPh_4{}^+Cl^-$ MgO $Ca(OH)_2$	177°C, 6 h
(61)	bisphenol AF K_2CO_3	177°C, 2 h

8C Attempts to Incorporate Bromine

$[(CF_3)_2CFCH_2CF_2\dagger_2$ (0.53 g, 1.1 mmol) and Br_2 (0.65 g, 4 mmol) were sealed in a glass tube and heated under autogenous pressure to 300°C for 72 h while under the influence of γ-radiation. When the tube was opened a brown liquid (*ca.*1 g) was recovered using avacuum-line techniques. Examination of this liquid using ^{19}F and ^{1}H nmr techniques showed it to be pure (61).

When a mixture of $[(CF_3)_2CF(CH_2CF_2)_2\dagger_2$ (63) (0.40 g, 6.7 mmol) and Br_2 (0.60 g, 3.7 mmol) was treated under conditions identical to those described above there was also no reaction.

CHAPTER NINE

EXPERIMENTAL FOR CHAPTER THREE - SYNTHESIS OF UNSATURATED MODELS

9A. Treatment of $[(CF_3)_2CFCH_2CF_2]_2$ with Bases (79,80)

Potassium Hydroxide

A mixture of $[(CF_3)_2CFCH_2CF_2]_2$ (61) (8g, 0.017 mole) and anhydrous KOH (3g, 0.05 mole), sealed in a pyrex Carius tube using vacuum line techniques, was shaken at 20°C for 5 h. On opening the tube a colourless liquid (7 g) was recovered which consisted of one component (gas chromatography, column O, 150°C). The liquid was identified as (61) using infrared and nmr techniques.

A mixture of (61) (8g, 0.017 mole) and anhydrous KOH (5.5g, 0.1 mole), sealed in a pyrex Carius tube was rotated at 80°C for 18 h. On opening the tube a colourless liquid (5.3 g) was recovered using vacuum line techniques. Analytical gas chromatography (carbowax, 105°C) showed one major and one minor component. Mass spectroscopy indicated molecular weights 466 (M^+ -19) and 446 (M^+ -19) respectively. Gas-phase infrared spectroscopy of the products showed ν_{max} 1730 cm^{-1} (C=C). ^{19}F nmr spectroscopy was consistent with a mixture of (61) and 3H,6H,6H-heptadecafluoro-8-methyloct-2-ene (80) in 10:1 ratio (δ_F -61.0 ppm, 2-CF_3(z); -67.9 ppm, 1-CF_3(E)).

$[(CF_3)_2CFCH_2CF_2]_2$ (61) (5g, 0.011 mole) was refluxed over anhydrous KOH (5g) using glass apparatus at 130°C for 2 h. During this time the mixture became black and no material was recovered.

$[(CF_3)_2CFCH_2CF_2]_2$ (61) (3g, 6mmol) was heated to 100°C and swept by a flow of N_2 through a glass tube containing KOH pellets. The temperature of the glass tube was maintained at 180°C by an oil-bath and the contact time between (61) and KOH was estimated at *c.a.* 1 second. The reaction tube was backed by a second glass tube cooled to -196°C and a drying tube containing H_2SO_4. The experiment was continued until all of the starting material had evaporated (2 h). During the experiment the KOH became black and no material condensed in the cold-trap. When the KOH had cooled it was extracted with CH_2Cl_2 (30 ml). The ^{19}F nmr spectrum of the CH_2Cl_2 extract showed no resonances.

Stirring with aqueous KOH (30%) at 20°C resulted in no reaction.

Lithium Alkyls - General Procedure

$[(CF_3)_2CFCH_2CF_2]_2$ (61) was stirred using a magnetic stirrer in a 50 ml glass flask fitted with a rubber septum and under an atmosphere of dry N_2. The temperature of the flask was then maintained at -78°C using an acetone/solid CO_2 slush bath. A solution of the lithium alkyl in hexane was then added slowly through the rubber septum using a dry syringe. After the addition the contents of the flask were stirred at -78°C for 1 h and allowed to warm to +20°C by removing the slush bath.

The results using CH_3Li and $^nC_4H_9Li$ are tabulated below (Table 9.1).

TABLE 9.1 Treatment of (61) with Lithium Alkyls)

Lithium Alkyl (1.55 M in hexane)	Moles (61)	Result
$LiCH_3$, 0.03 mol	0.01 mol	Vigorous reaction and tarring. No products isolable
$Li^nC_4H_9$, 0.03 mol	0.01 mol	

Tri-n-butylamine

A mixture of (61) (5g, 0.011 mol) and NBu_3 (3.5g, 0.024 mol) was stirred using a magnet stirrer in a 50 ml flask fitted with a reflux condenser at 110°C for 5 h. The products were transferred from the flask using vacuum line techniques and washed with water (10 ml) to leave a pale yellow liquid (3.5 g). Analysis by gas chromatography showed this liquid to be >95% one component. A small sample of this component was isolated using preparative scale gas chromatography (column A, 130°C) and identified as 1-(2H-hexafluoro-2-propyl)-3-hydrodecafluoro-2,2-dimethylcyclopentene (79) (3.5g, 74%), (Found: C, 28.0; H, 0.5; F, 71.6; $C_{10}H_2F_{16}$ requires C, 28.16; H, 0.47; F, 71.37%); ν_{max} 1695 cm^{-1} (C=C); δ_H (Neat, capill) -3.9 (1 H, sept, J 7.2 Hz, 2-H), -5.5 (1 H, ddd, J 4.2, 12.3 and 48.0 Hz, 3-H); δ_F -63.0 (3F, m, 2-CF_3), -64.6 (3F, m, 2-CF_3), -68.6 (6 F, d, m, 2-$C(CF_3)_2$), -111.6 (1 F, sept, J 16 Hz, 5-F), -112.0 (2 F, AB, J 265 Hz, 4-F), -212.0 (1 F, d, J 48.0 Hz, 3-F), δ_C -47.4 (1 C, sept, J 33 Hz, 1-CH), -59.5 (1 C, sept, J 36 Hz, 2-C), -86.6 (1 C, ddd, J 13, 34 and 223 Hz, 3-C), -106.6 (1 C, s, 1-C), -117.5 (1 C, t, J 260 Hz, 4-C), -121.9 to -122.9 (1 C, q, J 285 Hz, 2-$(CF_3)_2$ and 3-$(CF_3)_2$), -159.2 (1 C, dt, J 27 and 309 Hz, 5-C); m/z 426 (M^+, 5%) and 275 (M^+ -151, 17%).

The above reaction was repeated as described above except at the lower temperature of 100°C for 1 h. The product obtained consisted of three components (gas chromatography; column A, 100°C). The three components were isolated using preparative scale gas chromatography (column A, 130°C) and identified as (61), (79) and 3H,6H,6H-heptadecafluoro-7-methyloct-2-ene, $(CF_3)_2C{=}CHCF_2CF_2CH_2CF(CF_3)_2$ (80), (Found: C, 27.15; H, 0.40; $C_{10}H_3F_{17}$ requires C, 26.60; H, 0.44%; ν_{max} 1655 cm^{-1} (C=C); δ_H -6.8 (1 H, t, J 14 Hz, 3-H), -2.9 (2 H, t, J 17.3 Hz, 6-H); δ_F -61.0 (3 F, br, 2-CF_3 (z)), -68.0 (3 F, q, J 8Hz, 2-CF_3 (E)), -79.0 (6 F, dt, J 6.8 and 6.8 Hz, 7 and 8-CF_3), -111.3 (2 F, t, J 14 Hz, 4-F), -113.3 (2 F, br, 5-F), -185.6 (1 F, br, 7-F); m/z 427 (M^+ -18).

9B. Reactions Involving SbF_5 (71, 75, 81)

A mixture of (61) (5g, 10.7 mmol) and SbF_5 (3.3 g, 15 mmol) was stirred in a 50 ml glass flask using a magnetic stirrer and under an atmosphere of dry N_2. The temperature of the flask was maintained at 120°C for 2 h using an oil-bath after which time the product was transferred onto dry NaF (10g) using vacuum line techniques. The product remained in contact with NaF for 0.5 h and was then transferred to a fresh flask using vacuum line techniques, washed with water (15 ml) and aq. $NaHCO_3$solution (15 ml) and dried over $MgSO_4$ to yield a colourless liquid (3.9g) identified as 3H,6H-hexadecafluoro-2,7-dimethyloct-2,6-diene, $(CF_3)_2C{=}CHCF_2CF_2CH{=}C(CF_3)_2$ (75) (3.9g, 86%); (Found: C, 28.1- H, 0.1- F, 71.7. $C_{10}H_2F_{16}$ requires requires C, 28.17; H, 0.47; F, 71.36%); ν_{max} 1680 cm^{-1} (C=C); δ_H -6.7 (2 H, t, J 14 Hz, 3,6-H); δ_F -60.8 (6 F, m, 2,6-CF_3 (z)), -68.2 (6 F, q, J 8.8 Hz, 1,8-CF_3(E)), -111.0 (4 F, t, J 15 Hz, 4,5-F); δ_C -112.7 (1 C, tt, J 37 and 256 Hz, 4,5-C), -118.9 (2 C, q, J 277 Hz, 2,7-CF_3(z)), -120.1 (2 C q, J 275 Hz, 1,8-CF_3(E)), -128.9 (2 C, t, J 26 Hz, 3,6-C), -132.5 (2 C, sept, J 34 Hz, 2,7-C); m/z 426 (M^+).

Elimination of HF from $(CF_3)_2CFCH_2CF_3$ (66) and $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (70), General Procedure

A mixture of the saturated model and SbF_5 was sealed in a glass ampoule and heated using an oil-bath. Products were transferred onto NaF using vacuum line techniques and then into a fresh flask, washed with water and aq- NaHCO3 and the fluorocarbon layer separated and dried over $MgSO_4$.

A mixture of (66) (6.3g, 27 mmol) and SbF_5 (8.7 g, 40 mmol) was heated to 120°C for 3 h. Analysis of the product by gas chromatography (column A, 20°C) showed a single component in >95% purity. The product was identitied as 2H-nonafluoro-3-methylbut-2-ene, $(CF_3)_2C{=}CHCF_3$ (81) (5 g, 80%); δ_H -6.7 (1 H, q, J 8.0 Hz, 2-H); δ_F -61.0 (3 F, q, J 8.1 Hz, 3-CF_3(z)), -62.0 (3 F, q, J 8.1 Hz, 4-CF_4(E)), -67.6 (3 F, m, 1-CF_3); δ_C -127.8 (1 C, sept, J 30 Hz, 3-C), -118.8 -118.0 and -117.0 (3 C, q, K 275 Hz, 1,3,4-CF_3), δ_C for 3-C not observed.

A mixture of (70) (14.8g, 0.05 mol) and SbF_5 (15 g, 0.08 mol) was heated to 40°C for 20 min. Analysis of the product by gas chromatography (column A, 60°C) showed a single component in >95% purity which was identified as 2H,2H,4H-undecafluoro-5-methylhex-4-ene, $(CF_3)_2C{=}CHCF_2CH_2CF_3$ (71) (11g, 74%); (Found: C, 28.1; H, 0.9; F, 71.1. $C_7H_3F_{11}$ requires: C, 28.38; H, 1.01; F, 70.61%); ν_{max} 1674 cm^{-1} (C=C); δ_H -2.8 (2 H, m, 2-H); -5.6 (1 H, t, J 13.5 Hz, 4-H); δ_F -61.0 (3 F, m, 1-CF_3(Z)), -64.0 (3 F, t, J 9.0 Hz, 6-CF_3), 167.0 (3F, q, J 7.5 Hz, 5-CF_3(E)), -92.0 (2 F, m, 4-F; m/z 277 (M^+ -19).

9C. Unsaturated Models (87,88) Derived from $CF_3CF=CHCF_3$

Synthesis of $CF_3CF=CFCF_3$ (83)

A 5 l three-necked flask was charged with sulpholane (1900 ml) and KF (670 g) and stirred mechanically. The temperature inside the flask was maintained at 200°C using an oil-bath. Hexachlorobuta-1,3-diene (84) (334 g, 1.28 mole) was added dropwise over a period of 3 h and stirred for a further 2 h. The products were collected in liquid air-cooled florentine flasks (2 x 250 ml capacity) using a gentle sweep of dry N_2. In all 140 g of material was collected and distilled to yield 2H-heptafluorobut-2-ene,[132,133] $CF_3CF=CHCF_3$ (83) (95% trans) (122 g, 52%), b.pt. 6°C. The product (83) was identified using mass spectroscopy (m/z 182) and comparison of infra-red spectra with that of an authentic sample.[129]

Reactions Involving $CF_3CF=CHCF_3$ (83)

Preparation of $CF_3C(OR)=CHCF_3$, General Procedure - A mixture of (83), NaOR (R = Ph, CH_3, CH_3CH_2) and N,N-dimethylformamide (20 ml) was sealed in a glass tube and shaken at room temperature for 6 h. On opening the tube, (83) was recovered using vacuum line techniques before the products were poured into water (100 ml) and extracted with CH_2Cl_2 (2 x 30 ml). Removal of the CH_2Cl_2 yielded a mixture of *cis* and *trans* $CF_3C(OR)=CHCF_3$ in >95% purity (gas chromatography, column O, 40-100°C). Variations on this procedure are detailed where applicable. The quantities used and yields obtained are summarized in Table 9.2.

TABLE 9.2 Preparations of $CF_3C(OR)=CHCF_3$

Quantities of Reactants	Ult of Products obtained	Yield
(83) (3.65g, 0.02 mole) $NaOCH_3$ (1.08g, 0.02 mole)	(83) (0.8g, 4.4 mmol) $CF_3C(OCH_3)C=CCF_3$ (86)[129] (3 g, 0.016 mole)	80%
(83) 5.46g, 0.03 mole) $NaOC_2H_5$ (2g, 0.03mole)	(83) (1.2 g, 6.6mmol) $CF_3C(OC_2H_5)C=CCF_3$ (87), (4 g, 0.02 mole)	65%
(83) (3.64 g, 0.02 mole) NaOPh (2.32g, 0.02 mole)	(83) (1.3g, 7.1 mmol) $CF_3C(OPh)C=CCF_3$ (85)[129] (3.1 g, 12 mmol)	61%

The product (86) was obtained by direct transfer under vacuum from the reaction tube.

The products (85) and (86) were identified using mass-spectroscopy (m/z 256 and 194 resp.) and comparison of infra-red spectra with those of authentic samples.[129]

Characterization of <u>2H-3-ethoxyhexafluorobut-2-ene</u>, $CF_3C(OC_2H_5)=CHCF_3$ (87) was achieved as follows: (Found: C, 35.52; H, 2.44. $C_6H_6F_6O$ requires C, 34.61; H, 2.88%); ν_{max} 1660 cm^{-1} (c=C); δ_H (capill.) -1.2 (3 H, t, J 7Hz, 3-CH_3), -3.4 (2 H, q, J 7Hz, 3-CH_2), -6.3 (1 H, q, J 7.5 Hz, 2-H); δ_F -59.3 (3 F, d, J 7.5 Hz, 1-F (*trans*)), -72.0 (3 F, s, 4-F (*trans*))- m/z 206.

A mixture of bisphenol AF (2), (6.72 g, 0.02 mole), (83) (5.7 g, 0.05 mole), K_2CO_3 (5 g) and DMF (30 ml) was sealed in a glass tube and shaken at room temperature for 24 h. On opening the tube (83) (0.6g, 3.3 mmol) was recovered using vacuum line techniques. The products were poured into water (150 ml) and extracted with CH_2Cl_2 (2x20 ml). The extract was dried ($MgSO_4$), filtered and evaporated to leave a colourless oil (10.2g) which was dissolved in n-hexane and eluted down a short column packed with Al_2O_3 to yield 2,2-bis-(4-[3H-hexafluorobut-3-en-2-oxy]phenyl)hexafluoropropane, (88) (9.8g, 74%); (Found: F, 52.40. $C_{23}H_{10}F_{18}O_2$ requires: F, 51.82%); δ_H (d6-acetone) -6.3 (2 H, q, J 7 Hz, 2-H); -7.1 to -7.7 (10 H, AA′XX′ coupling,[157] ring-H); δ_F -59.7 (6 F, d, J 7Hz, $=CHCF_3$ (*trans*)), -63.7 (6 F, s, 1,3-F), -69.6 (6 F, s, $=C(OR)CF_3$ (*trans*)); m/z 660.

CHAPTER TEN

EXPERIMENTAL FOR CHAPTER FOUR - REACTIONS OF UNSATURATED MODEL COMPOUNDS

10A. The Hydrolytic Stability of the Model Cross-Links

A mixture of (85) (0.3 g, 1.2 mmol) and aqueous KOH (10 ml, 30% solution) was stirred magnetically in a 25 ml glass flask equipped with a reflux condenser. The temperature of the flask was maintained at 100°C for 3 h using an oil-bath. After cooling the products were extracted with diethyl ether (10 ml), dried ($MgSO_4$) and the extract evaporated to leave a colourless liquid (0.2g) identified as (85) by infra red techniques.

When the above procedure was repeated using a mixture of (88) (2g, 3mmol) and aqueous KOH (10 ml, 30% solution) no chemical change took place and (88) (1.5g) was recovered and identified using infra-red and ^{19}F nmr techniques.

Sealed Tube Experiments with MgO, $Ca(OH)_2$. General Procedure

The models (85) and (88) were each separately sealed in glass tubes with a mixture of $Ca(OH)_2$ and MgO using vacuum line techniques. The tubes were rotated in a stirred oil-bath at 177°C for 3 h. After cooling, the tubes were opened and no volatile material recovered. The products were extracted with CH_2Cl_2 (10 ml) and the CH_2Cl_2 evaporated in each case to leave unchanged (85) and (88) respectively. The quantities used and recovered are summarized in Table 9.3.

Material recovered was identified using infra red and ^{19}F nmr techniques.

TABLE 10.1 Treatment of (85) and (88) with $MgO/Ca(OH)_2$ Mixture

Amount of Model used	Amount of Model Recovered	Amount of $MgO/Ca/OH)_2$
(85) (1 g, 4 mmol)	(85) (0.5 g, 2 mmol)	1 g, 50:50
(88) (2 g, 3 mmol)	(88) (1.5 g, 2.2 mmol)	1 g, 50:50

Sealed Tube Experiments - General Procedure - Mixtures of (88) with each of water, succinimide, triethylamine and aniline were sealed in nmr sample tubes using vacuum line techniques and heated using a stirred oil-bath. On cooling, ^{19}F nmr spectra were recorded for each mixture in order to detect chemical changes. The quantities of reagents and conditions are summarized in Table 10.2.

TABLE 10.2 Treatment of (88) with H_2O, Succinimide,NEt_3 and $PhNH_2$

Quantities used	Conditions	^{19}F nmr Observations
(88) (0.3g, 0.4 mmol) H_2O (0.6g, 33 mmol)	250°C, 60 h	No change in spectrum from that of (88)
(88) (0.3g, 0.4 mmol) Succinimide, 5% soln. in DMF, (0.6 g)	140°C, 36 h	
(88) (0.3g, 0.4 mmol) NEt_3, 5% soln. in DMF, (0.6g)	140°C 60 h	
(88) (0.3g, 0.4 mmol) $PhNH_2$, 5% soln. in DMF, (0.6g)	140°C, 60 h	

10B. Reactivity of Unsaturated Models (90, 91A and 91B)

Experiments Involving $(CF_3)_2C{=}CHCF_2CH_2CF_3$ (71)

(71) was sealed separately in glass tubes with each of the mixtures outlined in Table 10.3 using vacuum line techniques. The tubes were then subjected to the conditions summarized by Table 10.3, after which volatile material was recovered using vacuum line techniques and the residue extracted with CH_2Cl_2 (20 ml) and examined using ^{19}F nmr techniques.

TABLE 10.3 Response of (71) to Typical Cure Conditions

Quantity of (71) Used	Composition of Cure-type Mixture	Volatile Material Recovered
3g, 10 mmol	$MgO/Ca(OH)_2$, 1g, 50:50, phOH (0.94g, 10 mmol)	(71)
3g, 10 mmol	$MgO/Ca(OH)_2$, 1g, 50:50, PhOH (0.94g, 10 mmol), $PPh_4{}^+Cl^-$ (0.1g, 2.6 mmol)	(71)
3g, 10 mmol	$MgO/Ca(OH)_2$, 1g, 50:50, Bisphenol AF (3g, 10 mmol) $PPh_4{}^+Cl^-$ (0.1g, 2.6 mmol)	(71)

In each case examination of the CH_2Cl_2 extract by ^{19}F nmr techniques indicated (71) as the only fluorinated material present.

A mixture of (71) (2.50g, 8.4 mmol), phenol (0.6g, 6.4 mmol), K_2CO_3 (0.88g, 6.4 mmol) and CH_3CN (1 ml) was stirred magnetically in a 50 ml flask fitted with a reflux condenser at 40°C for 12 h. The products were then added to water (30 ml) and extracted with diethyl ether (2x10 ml) and evaporated to leave a colourless oil (2.5g). After molecular distillation of this oil, using vacuum line techniques, analytical gas chromatography (capillary column O, 190°C) showed the presence of two components with similar retention times. Separation of these components by preparative scale gas chromatography was not possible and therefore a sample of the mixture was isolated (30% column O, 200°C) and identified as <u>1H,3H,3- phenoxynonafluoro-4,4-dimethylcyclopentene</u> (91A) and <u>1H,4H,4-phenoxynonafluoro-3,3-dimethylcyclopentene</u> (91B) (50:50 mixture) (2.5g, 85%); variable analysis; ν_{max} 1645 cm^{-1} (C=C); δ_H -7.7 to -7.0 (10H, br m, ring-H), -5.7 (2 H, m, 1-H), -3.5 to -3.0 (2 H, m, 3,4-H); δ_F -62.7 and -63.7 (6 F, m, 3,4-CF_3), -67.6 (6 F, m, 3,4-CF_3); m/z 350.

A mixture of (71) (0.3g, 1 mmol) and KOH (0.2g), sealed in a nmr tube using vacuum line techniques, was heated to 100°C for 12 h, during which time the contents of the tube turned black. When the ^{19}F nmr spectrum was recorded, (71) was identified as the only fluorocarbon present.

Experiments Involving $(CF_3)_2C=CHCF_3$ (81)

A mixture of (81) (5.0g, 21.5 mmol), PhOH (2.0g, 21.5 mmol), K_2CO_3 (4.0 g, 28 mmol) and CH_3CN (10 ml), sealed in a glass tube fitted with a "Rotaflo" tap using vacuum line techniques, was shaken at 20°C for 12 h. The products were then added to water (150 ml), extracted with CH_2Cl_2 (10 ml), dried ($MgSO_4$), filtered and distilled to leave a colourless liquid (4.5g) which was shown by gas chromatography (column A, 100°C) to consist of one component (>95% purity) identified as 2H,2-phenoxy-3-hydrohexafluoro-3-methylbutane, $(CF_3)_2CHCH(OPh)CF_3$, (90) (68%), (Found: C, 40.2; H, 1.85; F, 52.18. $C_{11}H_7F_9O$ requires C, 40.49; H, 2.15- F, 52.45%); δ_H -3.3 (1 H, sept, J 8 Hz, 3-H), -4.9 (1 H, q, J 7 Hz, 2-H), -7.0 (5 H, m, ring-H); δ_F -62.4 and -67.6 (6 F, m, 3 prochiral), -76.2 (3 F, m, 1-F); m/z 326.

A mixture of (81) (0.3g, 1.3 mmol) and KOH (0.1g), sealed in a nmr tube using vacuum line techniques, was heated for 12 h. When the ^{19}F nmr spectrum was recorded (81) was identified as the only fluorocarbon present.

A mixture of (81) (0.3g, 1.3 mmol), sulpholane (0.5 ml) and CsF (0.1g), sealed in a nmr tube using vacuum line techniques, was heated to 100°C for 2 h. When the ^{19}F nmr spectrum was recorded (81) was identified as the only fluorocarbon present.

Experiments Involving $[(CF_3)_2C{=}CHCF_2]_2$ (75)

A mixture of (75) (0.3g, 0.7 mmol), tetraglyme (0.5 ml) and CsF (0.1g), sealed in an nmr tube using vacuum line techniques, was heated to 100°C for 2 h. When the ^{19}F nmr spectrum was recorded (79) was identified as the only fluorocarbon present.

A mixture of (75) (2g, 5 mmol), PhOH (1 g, 10 mmol), K_2CO_3 (2g, 10 mmol) and CH_3CN (2 ml) was stirred magnetically at 30°C for 12 h. The products were added to water (50 ml), extracted with CH_2Cl_2 (20 ml), dried ($MgSO_4$) and distilled to leave a colourless liquid (1.5g). Capillary column gas chromatography (column O, 180°C) showed 4 major components, which were not isolable using preparative scale gas chromatography. Mass spectroscopy showed highest masses of 614, 594, 574 and 554 and all components showed high intensity (M^+ -77) and (M^+ -93) mass peaks.

CHAPTER ELEVEN

EXPERIMENTAL FOR CHAPTER FIVE - AN APPROACH TO A NEW FREE-RADICAL CROSS-LINKING PROCESS

11A. Synthesis of Crowded Comonomers

Synthesis of $(CF_3)_2CFCR{=}CF_2$ (R=H, 99; R=F, 100) - General Procedure

Separate mixtures of $(CF_3)_2CFCHRCF_2I$ (R=H(48), F(50)) with KOH pellets, were sealed in glass tubes fitted with "Rotaflo" taps using vacuum line techniques and heated to 90°C for 3 h. Volatile material was then transferred from the tubes and distilled using a short packed column. The quantities used are summarized in Table 11.1.

TABLE 11.1 Synthesis of $(CF_3)_2CFR{=}CF_2$ (99,100)

Wt of Iodide	Wt. of KOH	Wt of Alkene	Yield
(48) (30g, 0.08 mol)	(15g, 0.25 mol)	(100) (15g, 0.06 mol)	75%
(50) (45g, 0.12 mol)	(20g, 0.34 mol)	(99) (23g, 0.1 mol)	83%

The alkenes (99) [100,101] and (100) [136] were characterized using analytical data available in the literature.

11B. Synthesis of Polymer Samples

General Procedure - Mixtures of monomer alkenes were sealed in glass tubes using vacuum line techniques and irradiated by a ^{60}Co γ-ray source at 20°C for 3-7 days. The tubes were then opened and volatile material recovered using high-vacuum (10^{-4} torr) at 20°C.

The quantities and proportions of comonomers used are summarized in Table 11.2. The structures of the copolymers have been discussed in detail in Chapter Five, together with ^{19}F nmr analysis of these products.

TABLE 11.2 Synthesis of Special Copolymers

Comonomers	Quantity Used	Volatile Material Recovered
(i) $CH_2{=}CF_2$	20g, 0.31 mol	None
(ii) $CH_2{=}CF_2$ $CF_3CF{=}CF_2$	1.8g, 0.03 mol 6.0g, 0.04 mol	$CF_3CF{=}CF_2$ (4.1g)
(iii) $CH_2{=}CF_2$ (99)	1.3g, 0.02 mol 7.4g, 0.03 mol	(99) (7g)
(iv) $CH_2{=}CF_2$ (100)	7.7g, 0.12 mol 3.2g, 14 mmol	(100) (*ca.* 2g)
(v) $CH_2{=}CF_2$ (100)	5.0g, 0.08 mol 7.2g, 0.03 mol	(100) (*ca.* 6g)
(vi) $CH_2{=}CF_2$ (100)	5.7g, 0.09 mol 16.6g, 0.06 mol	(100) (*ca.* 13g)
(vii) $CH_2{=}CF_2$ $CF_3CF{=}CF_2$ (99)	2.0g, 0.03 mol 6.0g, 0.04 mol 5.0g, 0.02 mol	$CF_3CF{=}CF_2$/99 Mixture (9 g)

$(CF_3)_2CFCF{=}CF_2$ (100) $(CF_3)_2CFCH{=}CF_2$ (99)

11C. Vacuum Pyrolysis of $CH_2{=}CF_2/(CF_3)_2CFCF{=}CF_2$ Copolymers

General Procedure - Samples of the copolymers were heated under high vacuum in a 100 ml glass flask backed by a cold trap (-196°C). When no more volatile material could be condensed into the cold-trap, it was removed and a molecular distillation bucket fitted to the 100 ml flask. On raising the temperature further material was collected in the molecular distillation bucket.

The polymer samples are referenced below using Table 11.2.

Sample (iv) (3.0g) was heated to 90°C for 1 h during which time a bright orange colouration appeared in the cold-trap. After further heating to 120°C for 1 h a colourless liquid (<0.1g) was collected in the cold-trap and identified as perfluoro-2,3-dimethylbutane (103) (lit.100) by infra-red and ^{19}F nmr techniques.[100] The molecular distillation bucket was fitted and the sample heated to 180°C for 1 h. The sample was observed to melt and become discoloured. After heating to 220°C for 1 h a trace of involatile material was condensed into the molecular distillation bucket. The ^{19}F nmr spectrum recorded on this material was very complex and the ^{1}H nmr spectrum showed the presence of $-CH_2-$ groups (δ_H -3.1 ppm). After each stage of heating a small portion of the copolymer residue was dissolved in DMAC and the ^{19}F nmr spectrum recorded. The proportion of units derived from (100) remaining in the copolymer was calculated using the intensity of the resonance of the pendant $-CF_3$ groups. The results are shown in Table 11.3.

TABLE 11.3 % of Comonomer Units Derived from (100) Remaining in the Copolymer (iv) at Each Stage after Vacuum Pyrolysis

Conditions	% Incorporation
Initial	7.0
120°C, 1 h	5.8
180°C, 1 h	3.8

Sample (vi) (5.0g) was heated to 160°C for 2h. A colourless liquid (0.3g) was obtained using molecular distillation apparatus, dissolved in $CF_2ClCFCl_2$ (0.3 ml) and found to contain *ca*. 140 products by analytical gas chromatography (capill. column O, 150°C), of mass range 200-800. The ^1H nmr spectrum recorded on this solution showed the presence of $-CH_2-$ groups (δ_H -3.0 ppm), (see Figure 5.1, Chapter Five).

11D. Differential Scanning Calorimetry Studies - General Procedure

Two samples of each copolymer (*ca*. 0.02g) studied were heated slowly under argon from 20°C to temperatures above 300°C. Six thermograms, obtained using differential scanning calorimetry, are represented qualitatively by Figure 11.1 with reference to Table 11.2.

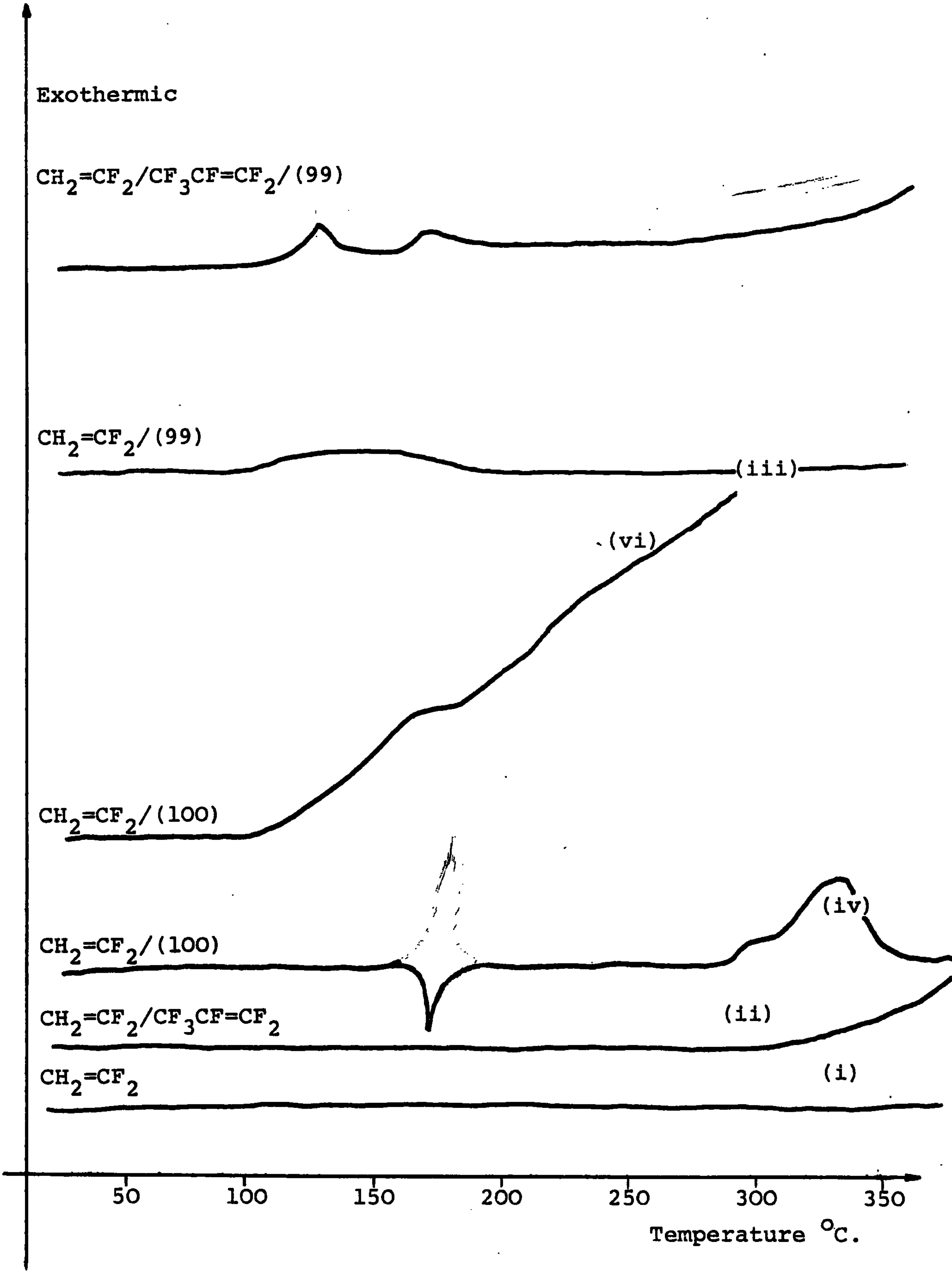


FIGURE 11.1 Differential Thermograms for Copolymers Incorporating Crowded Comonomers

11E. Perfluoroallylfluorosulphate/Diethyl Ether Experiment

A mixture of perfluoroallylfluorosulphate (104) (19.8g, 86 mmol) and diethyl ether (20g, 0.27 mole), sealed in a glass ampoule using vacuum line techniques was irradiated by γ-rays at 20°C for 4 d. A second tube containing (104) (20g, 87 mmol) was also irradiated under the same conditions as a control. On opening the first tube a colourless liquid (38g) was obtained and shown by analytical gas chromatography (column O, 100°C) to consist of 3 main components. A small sample of each main component was isolated (>90% purity) by preparative scale gas chromatography and partially characterized as $FSO_2OCF_2CHFCF_2OSO_2F$ (107); δ_H -4.0 (1 H, 2-H)- δ_H +8.0 (2 F, 1-SO_3F); m/z 330- $C_2H_5OCF_2CF{=}CF_2$ (108); ν_{max} 1695 cm^{-1} (C=C); m/z 176; $FSO_2OCF_2CF(C_2H_5)CF_2OSO_2F$ (109); δ_F+ 8.0 (2 F, 1,3-SO_3F), -185.0 (1 F, 2-F); m/z 358. On opening the control tube no chemical change was observed.

CHAPTER TWELVE

EXPERIMENTAL FOR CHAPTER SIX - NOVEL CHEMISTRY INVOLVING ANTIMONY PENTAFLUORIDE

12A. Cyclisation Reactions (109,111)

A mixture of $(CF_3)_2C{=}CHCF_2CH_2CF_3$ (71) (2g, 67 mmol) and SbF_5 (2 g, 100 mmol) in a 50 ml round bottomed flask was stirred magnetically at 100°C for 2 h. Volatile material (1.8 g) was then transferred from the flask using vacuum-line techniques, washed with water (10 ml) and shown by analytical gas chromatography (column A, 75°C) to consist of one major component (>95% purity). A small sample was then isolated by preparative scale gas chromatography (column A, 100°C) and characterized as 1H-2,4-bistrifluoromethyl-4H-tetrafluorocyclopentene (109) (1.8g, 97%). (Found: C, 30.1; H, 0.4. $C_7H_2F_{10}$ requires C, 30.43; H, 0.72%); ν_{max} 1690 cm^{-1} (C=C); δ_H -3.2 (1 H, tq, J 4 and 8 Hz, 1-H); -6.4 (1 H, br, 4-H); δ_F -67.0 (3 F, br, 4-CF_3), -67.5 (3 F, br, 2-CF_3), -100.0 (2 F, AB, J 282 Hz) and -100.5 (2 F, AB J 269 Hz) (3 and 5-CF_2); δ_C -57.1 (br m, 4-C), -122.1 (q, J 250 Hz) and -125.0 (q, J 279 Hz) (2 and 4-CF_3), -120.6 and -120.7 (2 C, t, J 257 Hz, 3 and 5-C), -137.4 (t, J 31 Hz, 1-C), -138 (br m, 2-C)- m/z 276 (M^+, 36%) and 257 (M^+ -19, 79%).

A mixture of $(CF_3CF_2CH_2CF_2)_2$ (57) (4 g, 11 mmol) and SbF_5 (5 g, 25 mmol), sealed in a glass ampoule using vacuum line techniques, was stirred magnetically at 110°C for 2 h. Volatile material was transferred onto NaF (2.0 g) and then, after 30 min, to a fresh flask to yield a colourless liquid (3g) shown by analytical gas chromatography (column A, 120°C) to consist of one component (>95% purity) characterized as <u>1H-2-trifluoromethyl-3H,3-pentafluoroethyltetrafluorocyclopentene</u> (111) (2.5g, 70%), (Found: C, 29.5; H, 0.6; F, 69.5 $C_8H_2F_{12}$ requires C, 29.45; H, 0.61; F, 69.91%; δ_H -3.8 (1 H, t, J 20 Hz, 3-H), -6.6 (1 H, br, 1-H); δ_F -69.0 (3 F, d, J 60 Hz, 2-CF_3), -85.0 (3 F, d, J 20 Hz, 3-$CF_2\underline{CF_3}$), -115.0 (2 F, AB, J 245 Hz, 4-F), -115.6 (2 F, br, 3-$\underline{CF_2}CF_3$); -117.0 (2 F, AB, J 273 Hz, 5-F); δ_C -51.7 (m, 3-C), -114.0, -119.0, -122.0 (3 C, br m, 4,5-C and 3-$\underline{CF_2}CF_3$), -119.5 (q, J 272 Hz) and -120.6 (q, J 280 Hz) (2-CF_3 and 3-$CF_2\underline{CF_3}$), -134.4 (t, J 17 Hz, 1-C), -138.1 (q, J 39 Hz, 2-C); m/z 326 (M^+, 2%) and 207 (M^+ -119, 11%).

Isomerisation of $(CF_3)_2CFCH=CF_2$ (99)

A mixture of (99) (0.5 g, 2.1 mmol) and SbF_5 (0.6, 3 mmol) was sealed in an nmr tube and shaken at 20°C for 1 h. When ^{19}F and ^1H nmr spectra were recorded $(CF_3)_2C=CHCF_3$ (81) was identified as the only product; δ_F -61.0 (3 F), -62.0 (3 F) and -67.6 (3 F); δ_H -6.7 (1 H, q, J 8.0 Hz).

12B. Attempts at Related Reactions (115, 116)

Synthesis of $C_8F_{17}CH_2CF_3$ (116)

A mixture of 1-iodoperfluorooctane (114) (120 g, 0.2 mole) and 1,1-difluoroethene (9.9 g, 0.15 mole), in a sealed nickel tube (150 ml capacity) was rocked under autogenous pressure at 185°C for 36 h. On opening the tube the solid products (122 g) were removed by shaking with CH_2Cl_2 (100 ml) and distillation at room temperature. Distillation at 18 mm Hg afforded a fraction boiling at 75°C which was (114) (23 g) and one at 110°C to yield 1-iodo-2,2-dihydrononadecafluorodecane, $C_8F_{17}CH_2CF_2I$ (115) (66g, 54%), (Found: C, 18.0; H, 0.20; F, 58.3; I, 20.25. $C_{10}H_2F_{19}I$ requires C, 19.60; H, 0.33; F, 59.18; I, 20.89%); δ_H -3.0 (2 H, tt, J 15 and 15 Hz, 2-H); δ_F -38.3 (2 F, m, 1-F), -80.5 (3 F, t, J 16 Hz, 10-F); 113.3 (2 F, br, 9-F), -123 (10 F, br, 4,5,6,7,8-F), -127.1 (2 F, br, 3-F); m/z 610 (M^+, 5%) and 483 (M^+ -127, 44%).

A solution of (115), (55g, 85 mmol) in $CF_2ClCFCl_2$ (50 ml) was stirred mechanically in a 1 ℓ round bottomed 3-necked flask equipped with a reflux condenser and a supply of dry N_2. A solution of SbF_5 (25g, 0.12 mole) in $CF_2ClCFCl_2$ (50 ml) was added with caution over a period of 1 h and the temperature in the flask maintained at 0-5°C using an ice-bath. After stirring for a further 30 min the products were added to water (300 ml) and then washed with aqueous Na_2HCO_3 (300 ml). The fluorocarbon layer was separated, filtered and distilled at room temperature to obtain a pale yellow liquid (38g) which was shown to consist of one component (>95% purity) by analytical gas chromatography (column O, 150°C). Distillation under hard vacuum yielded 2H,2H-eicosafluorodecane, $C_8F_{17}CH_2CF_3$ (116) (32g, 75%) (Found: C, 23.4; H, 0.2; F, 75.3. $C_{10}H_2F_{20}$ requires C, 23.90; H, 0.40; F, 75.70%); δ_H -3.1 (2 H, tq, J 15 and 15 Hz, 2-H); δ_F -62.0 (3 F, t, J 17 Hz, 1-F), -78.5 (3 F, t, J 20 Hz, 10-F), -113.0 (2 F, br, 9-F), -123.0 (10 F, br, 4,5,6,7,8-F), -128.5 (2 F, br, 3-F); m/z 483 (M^+ -19, 17%).

Attempted Cyclisation of (116)

A mixture of (116) (38g, 76 mmol) and SbF_5 (32.8g, 0.15 mol), sealed in a glass ampoule, was stirred magnetically under autogenous pressure at 190°C for 12 h, during which time the

the contents of the tube turned bright orange/red. Volatile material (20 g) was then transferred to a fresh tube using vacuum line techniques, by which it was found to have a very high vapour pressure. SiF_4 was identified as a component using gas phase infra-red techniques; ν_{max} 1029 and 388 cm^{-1},[158] and vented cautiously from the tube. The products were then washed with water (2x30 ml) and shown by analytical gas chromatography (column K, 80°C) to consist of three main components (*ca.* 80%) and less volatile material (*ca.* 20%). ^1H nmr studies on the products showed no resonances. A sample of each of the three main components was isolated (>95% purity) using preparative scale gas chromatography (column A, 50°C) identified as C_nF_{2n} (n=8-10) using the data summarized in Table 12.1

TABLE 12.1 Volatile Products from Reaction between (116) and SbF_5

n	^{19}F nmr Data	Neg.Ion m/z
8	-82.5 (6 F, t, J 18 Hz) -113 to -127 (10 F, complex)	400
9	-83.0 (6 F, t, J 18 Hz) -113 to -127 (12 F, complex)	450
10	-83.0 (6 F, t, J 18 Hz) -113 to -127 (14 F, complex)	500

Other Reactions Attempted - General Procedure

The reactant mixtures summarized in Table 12.2 were each sealed with SbF_5 in glass ampoules and subjected to the conditions stated. Volatile material was then transferred into an nmr tube and sealed using vacuum line techniques and products identified using nmr spectroscopy. Variations on this procedure are detailed where applicable.

TABLE 12.2 Attempted Inter-Molecular Reactions involving Antimony Pentafluoride

Reactants	Conditions	Observations
(118) (3.0g, 10 mmol) (119) (2.0g, 10 mmol) SbF_5 (2.0g, 9 mmol)	150°C, 12 h	No Reaction
(109) (5.8g, 14.2 mmol) (119) (3.5g, 10 mmol) SbF_5 (3.7g, 16 mmol)	190°C, 12 h	
(81) (3.0g, 12.9 mmol) (119) (3.5g, 18 mmol) SbF_5 (6.8g, 31.5 mmol)	150°C, 12 h	
(118) (0.3g, 1 mmol) SbF_5 (0.3g, 1.5 mmol)	Sealed in nmr tube, -50°C to + 20°C	
Toluene (5g, 54 mmol) (118) (3g, 10 mmol) SbF_5 (3g, 14 mmol)	Soln. of (118) in SbF_5 added drop-wise to toluene at -78°C	Vigorous tarring

12C. Elimination Reactions and the Formation of Stable Carbocations (127, 128, 129, 133)

Synthesis of Cations (127) and (128)

Separate mixtures of $(CF_3)_2CF(CH_2CF_2)_nF$, n=3 (122) (0.3g, 0.8 mmol) and n=4 (123) (0.3g, 0.7 mmol), with SbF_5 (1.0g, 5.0 mmol) were sealed in nmr tubes using vacuum line techniques. ^1H and ^{19}F nmr spectra were recorded at 40°C and the stable cations (127) and (128) characterized using the data which is summarized fully in Table 6.3.

Quenching of the Cation (127) with MeOH

A mixture of (122), (1.0g, 2.7 mmol) and SbF_5 (3g, 14 mmol) stirred magnetically in a 50 ml round-bottomed flask under an atmosphere of dry N_2, was cooled to -78°C using an acetone dry-ice bath and MeOH (3g, 0.1 mol) added slowly over a period of 30 min. Stirring was then continued for a further 1 h when the products were allowed to warm to 20°C, poured into water (200 ml), extracted with CH_2Cl_2 (2x30 ml), washed with water (100 ml), dried ($MgSO_4$) and distilled at room temperature to obtain a yellow oil (0.8g). Molecular distillation at high vacuum followed by chromatography on silica gel with diethyl ether-light petroleum (b.p. 60-80°C) (1:3) yielded 3,3,5,7,7-pentahydro-4-methoxydecafluoro-2-methyloct-4-enone, $(CF_3)_2CFCH_2C(OCH_3){=}CHCOCH_2CF_3$ (129) (0.5g, 53%);*;ν_{max} 1600 and 1700 cm^{-1} (α,β-unsaturated ketone); δ_H -3.2 (2 H, q, J 10.6 Hz,7-H), -3.6 (3H, s, 4-OMe), -3.7 (2 H, d, J 22 Hz, 3-H), -5.6 (1 H, s, 5-H); δ_F -65.0 (3 F, t,J 10.6 Hz, 8-F), -78.5 (6 F, d, J 7 Hz, 2-CF_3), -182.8 (1 F, m, 2-F); m/z 350 (M^+, 8%). and 111 (M^+ -239, 29%).

* variable analysis.

Reaction of the Cation (127) with SbF_5

A mixture of (122) (5.1g, 13.4 mmol) and SbF_5 (9.0g, 41 mmol) was stirred magnetically in a 50 ml round-bottomed flask at 20°C under an atmosphere of dry N_2. A small sample was removed after 5 min and a ^{19}F nmr spectrum recorded which showed the presence of the cation (127). The temperature in the flask was then maintained at 110°C for 30 min using an oil-bath after which time the temperature was lowered to 0°C and water (50 ml) added with caution. The fluorocarbon layer was washed with weak aqueous $NaHCO_3$ (200 ml) to leave a yellow liquid (2.55g) shown by analytical gas chromatography (capill. column O, 80°C), to consist of one main component (>90% purity). A sample of this component was isolated (>95% purity) using preparative scale gas chromatography and characterized as 2,5-bistrifluoromethyl-3H,7H-undecafluorooct-2-ene, $(CF_3)_2C{=}CHCF_2CF(CF_3)CF_2CH_2CF_3$ (133) (approx. 40%); ν_{max} 1680 cm^{-1} (C=C); variable analysis; δ_H -3.0 (2 H, m, 7-H), -6.8 (1 H, t, J 14 Hz, 3-H); δ_F -61.0 (3 F, br, 2-CF_3 (z)), -62.5 (3 F, br, 8-F), -68.3 (3 F, br, 2-CF_3 (E)), -78.2 (3 F, br, 5-CF_3), -110.9 (2 F, br, 6-F), -120.1 (2 F, br, 4-F), -185.5 (1 F, br, 5-F); m/z 427 (M^+ -19, 6%) and 163 (M^+ -283, 82%).

Isolation of Polyenes from the Cation (128)

A mixture of $(CF_3)_2CF(CH_2CF_2)_4F$ (123) (2.8g, 6.3 mmol) and SbF_5 (7 g, 33 mmol) was stirred magnetically in a 50 ml round-bottomed flask at 20°C for 30 min. A small sample was removed and a ^{19}F nmr spectrum recorded which showed the presence of the cation (128). The mixture was then transferred dropwise into a 500 ml round-bottomed flask containing NaF (20g) maintained at 0-5°C by an ice-bath. After 1 h a molecular distillation bucket was fitted to the flask which was evacuated and heated to 60°C for 2 h. An orange liquid (1.5g) was collected and shown by gas chromatography (column K, 130°C) to consist of many components of masses in the range 200-350 mass units. The products were not isolated.

Treatment of $(CF_3)_2CF(CHFCF_2)_nR$ with SbF_5

Separate mixtures of (64), (72) and (136) with SbF_5, sealed in nmr tubes using vacuum line techniques, were subjected to the conditions outlined in Table 12.3. ^{19}F nmr spectra were then recorded and no chemical change detected in each system.

TABLE 12.3 Treatment of $(CF_3)_2CF(CHFCF_2)_nR$ with SbF_5

Substrate	Conditions
$[(CF_3)_2CFCHFCF_2]_2$ (0.3g, 0.6 mmol) (64)	SbF_5 (0.3g, 1.5 mmol) 150°C, 12 h.
$(CF_3)_2CF(CHFCF_2)_2F$ (0.3g, 0.8 mmol) (72)	
$(CF_3)_2CF(CHFCF_2)_3F$ (0.3g, 0.75 mmol) (136)	

12D. Dehydrohalogenation of Polymers by SbF_5

General Procedure - Samples of the polymers summarized in Table 12.4 were dissolved in the specified solvent, filtered and cast into thin films by slow evaporation of the solvent using vacuum line techniques. After continued removal of the solvent under high vacuum (10^{-5} torr) the films were exposed to SbF_5 vapour. The treated films were then handled in a dry glove-box in order to prepare samples for ^1H nmr and infra-red analyses.

TABLE 12.4 Treatment of Polymers with SbF_5

Polymer	Solvent	Observation	Analytical Data from Treated Film
$(CH_2{=}CF_2/CF_3CF{=}CF_2$	-	Instantaneous intense colouration	i.r. 1600-1650 cm^{-1} (C=C
$\leftarrow CH_2CHCl \rightarrow_n$	Acetone	"	i.r. 1700 cm^{-1}(C=C) ^1H nmr δ_H -6.3 ppm
$\leftarrow CH_2CF_2 \rightarrow_n$	DMF	"	i.r. 1600-1700 cm^{-1} (C=C)
$\leftarrow CHFCF_2 \rightarrow_n$	DMAC	Became dark only after prolonged contact at 60°C	i.r. 1600-1700 cm^{-1} (C=C

CHAPTER THIRTEEN

EXPERIMENTAL FOR CHAPTER SEVEN -
THE GENERAL CHEMISTRY OF THE MODEL COMPOUNDS

13A. Reactions Involving 1-(2H-hexafluoro-2-propyl)-3-hydrodecafluoro-2,2-dimethylcyclopentene (79) (145-148)

Reaction of (79) with Methoxide

Freshly cut sodium (0.1g, 5 mmol) was added to dry MeOH (5 ml) and stirred at 20°C for 1 h under dry N_2. (79) (2g, 4 mmol) was then added over a period of 10 min with further stirring. After washing with water (2 x 10 ml) a fluorocarbon layer was separated, distilled under hard vacuum to obtain a colourless liquid (1.4g) and shown by gas chromatography (column O, 150°C) to consist of 2 main components. A sample of each component was isolated (>95% purity) using preparative scale gas chromatography (column O, 150°C) and identified as (79) and 1-(2-methoxytetrafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (146); (Found: C, 31.8; H, 0.8; F, 63.6. $C_{11}H_4F_{14}O$ requires C, 31.58, H, 0.96; F, 63.64%); ν_{max} 1650-1700 cm^{-1} (conjugated diene); δ_H -3.8 (3 H, s, 2-OCH_3), -5.4 (1 H, dd, J 15 and 48 Hz, 3-H), δ_F -57.8 (3 F, m, vinyl-CF_3), -65.3 and -70.o (6 F, br, 2-CF_3), -71.0 (1 F, d, J 12.5 Hz, acyclic vinyl-F), -111.9 (2 F, AB, J 261 Hz, 4-F), -119.8 (1 F, d, J 12.5 Hz, 5-F), -210.9 (1 F, m, 3-F); m/z 418 (M^+, 100%) and 315 (M^+ -103, 29.8%).

Pyrolysis over Potassium Fluoride

(79) (2 g, 4.7 mmol) in the vapour phase was passed through a glass tube packed with KF heated to 300°C by a furnace, and backed by a cold trap (-196°C), using vacuum line techniques. A colourless liquid (1.8g) was obtained

and shown by gas chromatography (column A, 95°C) to consist of 2 main components. A sample of each component was isolated (>95% purity) using preparative scale gas chromatography and identified as (79) and <u>1-(pentafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene</u> (145); (Found: C, 29.3; requires C, 29.56%); ν_{max} 1700-1750 cm^{-1} (conjugated diene); δ_H -5.0 (1 H, ddd, J 5, 12 and 48 Hz); δ_F -60.0 (3 F, br, vinyl-CF_3), -66.7 and -71.0 (6 F, br, 2-$(CF_3)_2$), -68.3 (2 F, m, Acyclic Vinyl-F), -113.2 (2 F, AB, K 261 Hz, 4-F), -117.2 (1 F, t, J 14.0 Hz, 5-F), -211.6 (1 F, m, 3-F); m/z 406 (M^+, 20%) and 249 (M^+ -157, 21%).

Reaction of (145) with Caesium Fluoride

(145) (1.0 g, 2.5 mmol) was added dropwise to a stirred suspension of CsF (0.5g) in tetraglyme (2 ml). After stirring for a further 10 min a small sample was removed, the ^{19}F nmr spectrum recorded, and the stable carbanion (148) identified using the data summarized in Chapter Seven, Table 7.1. Bromine (*ca*. 0.5 g, 3.3 mmol) was then added to the stirred solution. After stirring for a further 1 h. water (5 ml) was added and a fluorocarbon layer isolated which was shown by gas chromatography (column A, 125°C) to consist of two main components identified as a mixture of (79) and <u>1-(2-bromohexafluoro-2-propyl)-3-hydrodecafluoro-2,2-dimethylcyclopentene</u> (148); m/z 487 (M^+ -19) and 425 (M^+ -81, 9%).

13B. Reactions involving 3,6-Dihydrohexadecafluoro-2,7-dimethylocta-2,6-diene (75) and 2H-nonafluoro-3-methylbut-2-ene (81) (149,150,152-155)

Free-Radical Additions - General Procedure

Binary mixtures of (75) with $[CH_3(CH_2)_n]_2O$ (n=0,1) and methanol, sealed in glass ampoules using vacuum line techniques, were irradiated with γ-rays under the conditions summarized in Table 13.1

TABLE 13.1 Free-Radicals Additions to (75) and (81)

Substrate	Addend	Conditions (γ-ray)
(75) (3.0g, 7 mmol)	$(C_2H_5)_2O$ (0.5g, 7 mmol)	20°C, 3 d
(1.9g, 4.5 mmol)	MeOH (0.3g, 10 mmol)	
(1.3g, 3.1 mmol)	$(CH_3)_2O$ (0.3g, 6 mmol)	
Hexachlorobuta-1,3-diene, (151) (7.3g, 28 mmol)	$(C_2H_5)_2$ (2.1g, 28 mmol)	20°C, 8 d

Diethyl ether/(75)

On opening the tube a colourless liquid (3.0 g) was distilled from polymeric residue (0.5g) using vacuum line techniques. Gas chromatography (carbowax, 140°C) on the volatile material showed the presence of two main components one of which had a short retention time equal to that of diethyl ether. A sample of the less volatile component was isolated (>95% purity) using preparative scale gas chromatography (column Z, 180°C) and identified as 2,7-dimethyl-3,6-bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluorooxepane (149) (Found: C, 33.7; H, 2.1; F, 61.3. $C_{14}H_{12}F_{16}O$ requires C, 33.6; H, 2.4; F, 60.8%); ν_{max} (C=C) absent; δ_H -3.9 (2 H, sept, J 8 Hz, 3,6-$CH(CF_3)_2$), -3.3 (2 H, m, 2,7-H), -1.3 to

-1.7 (6 H, s, 2,7-Me), -1.6 (2 H, m, 3,6-H); δ_F -60.7 and -63.7 to -67.3 (12 F, m, 3,6-CH$(CF_3)_2$), -120.5 (2 F, s) and -123.1 (2 F, AB, J 242 Hz), (4,4,5,5-F); m/z (CI) 501 (M^+, 33%) and (EI) 249 (M^+ -151, 8%).

Methanol/(75)

On opening the tube, water (5 ml) was added and a white solid precipitate (1.0 g) separated. Recrystallisation to constant melting point from CH_2Cl_2 yielded 3-hydroxymethylhexafluoro-2,7-dimethyloct-6-ene (152) (0.5 g, 24%), m.p. 73.5°C (Found: C, 29.5; H, 1.1. $C_{11}H_6F_{16}O$ requires C, 28.82; H, 1.31%); ν_{max} 1680 cm^{-1}; δ_H -5.9 (2 H, s, 3-CH_2), -3.2 (1 H, m, 3-H); δ_F -61.0 (3 F, br, 7-CF_3 (z)), -65.3 to -67.3 (3 F, br, 8-F(E)) and (6 F, br, 1,2-CF_3 (prochiral)). -124.3 (4 F, br, 4,5-CF_2); m/z (CI) 459 (M^+, 9%).

Dimethyl Ether/(75)

On opening the tube, a colourless liquid (1.3g) was obtained using vacuum line techniques and shown by gas chromatography (column O, 65°C) to consist of 2 major components, one of which had a very short retention time. A sample of the less volatile component was isolated (>95% purity) using preparative scale gas chromatography (column O, 90°C) and identified as 3,6-bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluorooxepane (150); variable analysis; ν_{max} (C=C) absent; δ_H -4.0 to -3.3 (broad); δ_F -60.0 to -63.8 (12 F, br, 3,6-CH$(CF_3)_2$), -112.4 (2 F, AB, J 271 Hz) and 122.2 (2 F, AB, J 262 Hz) (4,5-CF_2); m/z (CI) 473 (M^+, 2%).

Diethyl Ether/Hexachlorobuta-1,3-diene

On opening the tube a small sample was withdrawn and the ^1H nmr spectrum recorded showed diethyl ether (>99% purity) as the only hydrocarbon present.

Addition of Diazomethane - General Procedure

Diazomethane was prepared using the method of Boer and Backer[152]. Separate solutions of (75) and (81), stirred in 50 ml round-bottomed flasks and cooled to 0°C, were treated with a solution of CH_2N_2 in diethyl ether until the yellow colouration of CH_2N_2 persisted. On warming to 20°C the ether was removed by distillation at room temperature to obtain the crude products which were purified by vacuum transfer.

CH_2N_2/(75)

Compound (75) (1.0g, 2.2 mmol) and diazomethane yielded a white solid (1.1g), recrystallized from $CH_2Cl_2$and identified as 1,2-di(5,5-bistrifluoromethyl-4,5-dihydro-3H-4-pyrazolo)-tetrafluoroethane (153) (80%), (Found: C, 28.4; H, 0.8; N, 11.2; F, 59.9. $C_{12}H_6N_4F_{16}$ requires C, 28.24; H, 1.18; N, 10.98; F, 59.61%); ν_{max} (C=N), (N-H) absent; δ_H -3.2 (2 H, ddd, J 9, 9 and 9 Hz, 4-H), -4.4 to -5.3 (4 H, AB d, J 18 and 9 Hz, 3-H); δ_F -65.0 and -69.0 (6 F, m, 5-CF_3), -109.7 (4 F, AB, J 290 Hz, 1,2-F); m/z (CI) 511 (M^+, 73%) and 483 (M^+ -28, 16%).

CH_2N_2/(81)

Compound (81) (5.0 g, 22 mmol) and diazomethane yielded a colourless liquid (5.0 g) shown by gas chromatography (column A, 50°C) to consist of 2 components with very similar retention times identified as 4,5,5-tris(trifluoromethyl)-4,5-dihydro-3H-pyrazole (154); variable analysis; δ_H -4.8 (2 H, AB, J 20 Hz, 3-H), -5.0 (1 H, m, 4-H); δ_F -60.7 (3 F, m, 4-CF_3), -71.9 and -72.9 (6 F, m, 5,5-CF_3); m/z 274 (M^+, 55%) and 266 (M^+ -28, 21%); and 4,5,5-tris(trifluoromethyl)-4,5-dihydro-1H-pyrazole (155); variable analysis; δ_H -7.8 (1 H, br, N-H), -6.6 (1 H, br, 3-H), -5.0 (1 H, m, 4-H); δ_F -60.7 (3 F, m, 4-CF_3), -71.9 and -72.9 (6 F, m, 5,5-CF_3); m/z 274 (M^+, 65%) and 164 (M^+ -110, 18%).

13C. One Electron Transfer Reactions[156,157]

Reduction of (70) by Tri-n-butylamine

A mixture of (70) (1.5g, 4.7 mmol) and tri-n-butylamine (2.0g, 14 mmol), sealed in a small glass ampoule using vacuum line techniques was irradiated using a 1 KW high pressure ultra-violet lamp for 3 d. The temperature in the region of the tube was *ca.* 60°C. On opening the tube a colourless liquid (1.0g) was distilled out and shown by gas chromatography (column A, 95°C) to consist of 2 main components, one of which had a retention time identical to that of (70). A sample of the second component was isolated (>95% purity) using preparative scale gas chromatography (column A, 120°C) and identified as 2,3,3,4,4-pentahydro undecafluoro-2-methylhexane (156) (Found: C, 28.1; H, 1.6; F, 69.6. $C_7H_5F_{11}$ requires C, 28.19; H, 1.68; F, 70.13%); ν_{max} (C=C) absent; δ_H -3.0 (1 H, sept, J 8 Hz), -2.5 to 1.9 (4 H, m, 3,5-H); δ_F -62.5 (3 F, dt, J 9 and 9 Hz, 6-F), -69.2 (6 F, m, 2-CF_3); m/z 298 (M^+) and 133 (M^+ -165, 100%).

Reaction of (62) with Tri-n-butylamine

A mixture of (62) (5.0g, 11.8 mmol) and tri-n-butylamine (3.4 g, 23.6 mmol) was stirred magnetically in a 50 ml round-bottomed flask, equipped with a reflux condenser and drying tube ($CaCl_2$), at 120°C for 12 h. Volatile material (3.6g) was then transferred from the flask using vacuum line techniques and shown by gas chromatography (column A, 80°C) to consist of four main components. Separation of the mixture by preparative scale gas chromatography (column A, 100°C) yielded (95% purity) $(CF_3)_2C{=}CHCF_2CH_2CF_3$ (71) (0.2g), $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (70) (1.0g), $(CF_3)_2CHCH_2CF_2CH_2CF_3$ (156) (0.3g) and <u>2,3,5,5-tetrahydrodecafluoro-2-methylhex-3-ene</u> (*trans*) (157) (1.1g, 33%); variable analysis; ν_{max} 1650 cm^{-1} (C=C); δ_H -4.9 (1 H, dd, J 10 and 30 Hz, 3-H)- -3.9 (1 H, d.sept, J 8 and 10 Hz, 2-H), -2.9 (2 H, dq, J 10 and 10 Hz, 5-H); δ_F -67.0 (3 F, dt, J 6 and 10 Hz, 6-F), -70.0 (6 F, dd, J 3 and 8 Hz, $2-CF_3$), -100.0 (1 F, br, 4-F); m/z 278 (M^+, 16%) and 127 (M^+ -151, 11%).

13D. Reactions involving Perfluoro-2-methylbut-2-ene (161)[161,165]

Synthesis of (161)

A mixture of (100) (5.0g, 20 mmol), CsF (0.5g) and sulpholane (10 ml), sealed in a glass ampoule using vacuum line techniques, was heated to 100°C for 2 h with occasional shaking. After cooling to 20°C the tube was opened and a colourless liquid (4.5g) transferred to a fresh flask using vacuum line techniques. Gas chromatography (column A, 20°C) showed this liquid to consist of one component (>95% purity) identified as perfluoro-2-methylbut-2-ene (161) (4.5 g, 90%), b.pt. 29^{o}C; variable analysis; ν_{max} 1690 cm^{-1} (C=C, weak) δ_F -60.4 (3 F, qd, J 10 and 4 Hz, 2-CF_3 (Z)), -61.7 (3 F, dq, J 30 and 10 Hz, 3-CF_3 (Z)), -69.0 (3 F, q, J 10 Hz, 2-CF_3 (E)), -100.3 (1 F, qqq, J 4, 10 and 30 Hz, 3-F); m/z 250 (M^+).

Reaction of (161) with MeOH

A mixture of (161) (1.8g, 7.2 mmol) and methanol (0.7g, 21.6 mmol), sealed in a glass ampoule using vacuum line techniques, was shaken at 20^{o}C for 6 h. On opening the tube a colourless liquid (2.5g) was removed using a pipette and shown by gas chromatography (column K, 50^{o}C) to consist of three main components, one of which had a retention time identical to that of methanol. The remaining two components were isolated as a mixture using preparative scale gas chromatography (column K, 80^{o}C) and identified as a 1:1 mixture of 2-methoxynonafluoro-3-methylbut-2-ene (162); δ_H -4.0 (3 H, s, 2-OMe); δ_F -60.0 - 64.0 (9 F, br m, 2,3-CF_3); m/z 262; and 2H-3-methoxydecafluoro-2-methylbutane (163); δ_H -3.7 (3 H, s, 3-OMe), -3.6 (1 H, sept, J 7 Hz, 2-H); δ_F -60.0 and -64.7 (6 F, br, 2-CF_3 (prochiral)), -77.5 (3 F, d, J 8 Hz, 3-CF_3), -130.6 (1 F, q, J 8 Hz, 3-F); m/z 282 (M^+).

Reaction of (161) with CH_2N_2

A solution of (161) (1.8g, 7.2 mmol) in diethyl ether (2 ml), stirred in a 50 ml round-bottomed flask cooled to 0^{o}C, was treated with a solution of diazomethane in diethyl ether until the yellow colouration of CH_2N_2 persisted. On warming to 20^{o}C the ether was removed by distillation at room temperature to obtain a colourless liquid (1.5 g) shown by gas chromatography (column A, 50°C) to consist of one main component (>95% purity) and identified as 4,5,5-tris(trifluoromethyl)-4-fluoro-4,5-dihydro-1H-pyrazole (164); variable analysis; ν_{max} 1600 cm^{-1} (C=N); δ_H -6.8 (1 H, br, C-H), -7.5 (1H, br, N-H)- δ_F -68.3 to -71.0 (6 F, br m, 5,5-CF_3), -75.2 (3 F, dd, J 14 and 14 Hz, 4-CF_3), -163.7 (1 F, m, 4-F); m/z (CI) 292 (M^+, 17%), 204 (M^+ -88, 14%) and 165 (M^+ -127, 1%).

Reaction of (161) with CsF

The alkene (161) (1.0g, 4 mmol) was added dropwise to a stirred suspension of CsF (0.5g) in tetraglyme (2 ml). After stirring for a further 1 h a small sample was removed, the ^{19}F nmr spectrum recorded, and the stable carbanion (161) identified using the chemical shift data summarized in Chapter Seven, Table 7.4.

13E. Reactions of Models derived from 1-Iodo-2-Hydrodecafluoro-3-methylbutane (50) (168-170,172)

Reaction of (64) with Tri-n-butylamine

A mixture of (64) (1.0 g, 2 mmol) and tri-n-butylamine (0.8g, 5.6 mmol), stirred in a 10 ml round-bottomed flask equipped with a reflux condenser, was heated to 125°C for 12 h. Volatile material (1.5g) was then recovered using vacuum line techniques and shown by gas chromatography (column F, 130°C) to consist of two main components in approximately equal ratio. The two components were then isolated (>95% purity) using preparative scale gas chromatography (Column F, 130°C) and identified as perfluoro-2-(prop-2-yl)-3,3-dimethylcyclopentene (168); ν_{max} 1695 cm^{-1} (C=C); δ_F -65.7 (6 F, br, 3-CF_3), -75.7 (6 F, dq, J 24 and 5 Hz, 2-C$(CF_3)_2$), -107.3 (1 F, m, 5-F), 122.3 (4 F, br m, 3,4-F), -181.2 (1 F, sept sept, J 5 and 24 Hz, 2-CF); m/z (neg. ion) 462 (M^-, 11%) and 293 (M^- -169, 12%); and perfluoro-3-(prop-2-yl)-4,4-dimethylcyclopentene (169); δ_F -74.6 (6 F, br, 4-CF_3), -75.0 and -77.8 (6 F, br, 3-C$(CF_3)_2$ (prochiral)), -118.6 (2 F, br, 5-F), -123.3 (2F, br, 1,2-F), 188.3 (2 F, br, 3-F and 2-CF); m/z (neg.ion) 462 (M^-, 33%) and 262 (M^- -200, 100%).

Reaction of (64) with CsF

A mixture of (64) (0.3 g, 0.6 mmol), CsF (0.1 g) and sulpholane (0.3 ml), sealed in an nmr tube using vacuum line techniques, was heated to 140°C for 3 h. The ^{19}F nmr spectrum was then recorded and (168) identified as a single product using the chemical shift data summarized above.

Pyrolysis of (64) over Potassium Fluoride - General Procedure

(64), in the vapour phase, was passed through a tube containing KF using vacuum line techniques. Product material was condensed into a cold trap (-196°C), allowed to warm to room temperature and separated into component products using preparative scale gas chromatography (column A, 70°C). The quantities and conditions used are summarized in Table 13.2.

TABLE 13.2 Pyrolysis of (64) over Potassium Fluoride

Starting Material	Temperature	Products Isolated
(64) (1.5g, 3 mmol)	400°C	(64)
(64) (10g, 20 mmol)	470°C	(170) + (64)
(64) (4g, 8 mmol)	500°C	(168) + (169)
(64) (2g, 4 mmol)	520°C	Complex Mixture not separable

6H-Nonadecafluoro-2,7-dimethyloct-2-ene

$(CF_3)_2C{=}CFCF_2CF_2CFHCF(CF_3)_2$ (170); variable analysis; ν_{max} 1680 cm^{-1} (C=C); δ_H -5.5 (1 H, d, J 46 Hz, 6-H); δ_F -58.3 (3 F, m, 2-CF_3 (Z)), -61.3 (3 F, dq, J 32 and 12 Hz, 2-CF_3(E)), -74.3 and -77.3 (6 F, br, 7-CF_3 (prochiral)), -96.0 (1 F, m, 3-F), -115.3 (2 F, m, 4-F), -122.6 (2 F, AB, J 248 Hz, 5-F), -187.3 (1 F, br, 7-F), -211.1 (1 F, br, 6-F); m/z 463 (M^+ -19, 1%).

Pyrolysis of (72) over Potassium Fluoride

Using the general procedure described above (72) (8g, 23 mmol) yielded a colourless liquid (6.0g) which was shown by gas chromatography (column A, 60°C) to consist of 2 main components one of which had a retention time identical to that of (72). A sample of the second component was isolated (>95% purity) using preparative scale gas chromatography (column A, 60°C) and identified as 2H-terdecafluoro-5-methyl-hex-4-ene (172) (Found: C, 25.4; H, 0.1; F, 74.1. C_7HF_{13} requires C, 25.30; H, 0.30; F, 74.40%); ν_{max} 1690 cm^{-1} (C=C); δ_H -5.3 (1 H, d, J 45 Hz); δ_F -58.7 (3 F, m, 5-CF_3 (Z)), -60.2 (3 F, dq, J 28 and 11 Hz, 5-CF_3(E)), -76.6 (3 F, br, 1-F), -96.7 (1 F, m, 4-F), -114.8 (2 F, AB, J 254 Hz, 3-F), -216.6 (1 F, d, J 45 Hz, 2-F); m/z 332 (M^+, 9%).

APPENDIX ONE

N.M.R. Spectra

1. 2H,2H,4H,4H-dodecafluoro-5-methylhexane (70)
2. 2,2,4,4,6,6-Hexahydrotetradecafluoro-7-methyloctane (122)
3. 2,3,3,5,5-Pentahydro undecafluoro-2-methyl hexane (156)
4. 1-Iodo-2,2-dihydrononadecafluorodecane (115)
5. 2H,2H-eicosafluorodecane (116)
6. 3,5-Dihydroeicosafluoro-2,7-dimethyloctane (64)
7. 2H,4H-tetradecafluoro-5-methylhexane (72)
8. 2H,2H,4H-undecafluoro-5-methylhex-4-ene (71)
9. 3H,6H,6H-heptadecafluoro-7-methyloct-2-ene (80)
10. 3H,6H-hexadecafluoro-2,7-dimethyloct-2,6-diene (75)
11. 6H-nonadecafluoro-2,7-dimethyloct-2-ene (170)
12. 2H-terdecafluoro-5-methylhex-4-ene (172)
13. 2,3,5,5-Tetrahydrodecafluoro-2-methylhex-3-ene (157)
14. 2,5-Bis(trifluoromethyl)-3H,7H,7H-undecafluorooct-2-ene (133)
15. 2-Methoxynonafluoro-3-methylbut-2-ene (162)
16. 3-Hydroxymethylhexadecafluoro-2,7-dimethyloct-6-ene (152)
17. 2H-3-ethoxyhexafluorobut-2-ene (87)
18. 2H,2-phenoxy-3-hydrohexafluoro-3-methylbutane (90)
19. 1H,3H,3-phenoxynonafluoro-4,4-dimethylcyclopentene (91A)
20. 1H,4H,4-phenoxynonafluoro-3,3-dimethylcyclopentene (91B)
21. 1-(2H-hexafluoro-2-propyl)-3-hydrodecafluoro-2,2-dimethylcyclopentene (79)
22. 1-(Pentafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (146)
23. 1-(2-Methoxytetrafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (146)
24. 1H-2,4-bis(trifluoromethyl)-4H-tetrafluorocyclopentene (109)
25. 1H-2-trifluoromethyl-3H,3-pentafluoroethyltetrafluorocyclopentene (111)

26. Perfluoro-2-(prop-2-yl)-3,3-dimethylcyclopentene (168)
27. Perfluoro-3-(prop-2-yl)-4,4-dimethylcyclopentene (169)
28. 4,5,5-Tris(trifluoromethyl)-4,5-dihydro-3H-pyrazole (154)
29. 4,5,5-Tris(trifluoromethyl)-4,5-dihydro-1H-pyrazole (155)
30. 1,2-Di(5,5-bis(trifluoromethyl)-4,5-dihydro-3H-4-pyrazolo)tetrafluoroethane (153)
31. 4,5,5-Tris(trifluoromethyl)-4-fluoro-4,5-dihydro-1H-pyrazole (164)
32. Stable Carbocation (127)
33. Stable Carbocation (128)
34. 3,3,5,7,7-Pentahydro-4-methoxydecafluoro-2-methyloct-4-enone (129)
35. 2,7-Dimethyl-3,6-bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluorooxepane (149)
36. 3,6-Bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluoro-oxepane (150)
37. Perfluoro-2-methylbut-2-ene (161)
38. 2H-3-methoxydecafluoro-2-methylbutane (163)
39. 2,2-Bis-(4-[2H-hexafluorobut-2-enoxy]phenyl)hexafluoropropane (88)

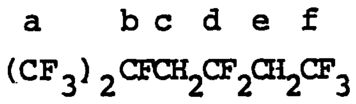
The following abbreviations are used in this appendix: S, singlet; D, doublet; T, triplet- Q, quartet; Sept, septet; M, complex multiplet.

Unless otherwise stated the spectra were recorded at 40°C in $CDCl_3$, or CCl_4.

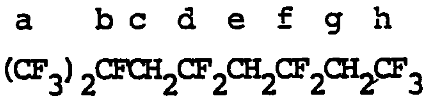
$CFCl_3$, TMS and TMS were used as reference for ^{19}F, ^{1}H and ^{13}C spectra respectively.

For ^{1}H spectra downfield chemical shifts are quoted as positive whilst for ^{19}F spectra, upfield shifts are quoted as positive. For ^{13}C spectra "downfield" shifts are quoted as positive where downfield is the direction of increasing the absolute values.

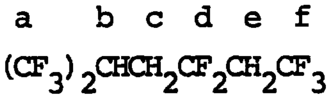
Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
1. 2H,2H,4H,4H-dodecafluoro-5-methylhexane (70)			
^{19}F Spectrum: (capill. neat)			
63.0	T (J = 14)	3	f-CF_3
77.9	D (J = 7) of T (J = 7)	6	a-CF_3
90.8	M	2	d-CF_2
185.8	M	1	b-CF
^{1}H Spectrum: (capill. heat)			
3.0 to 3.2	M	4	c,e-CH_2
2. 2,2,4,4,6,6-Hexahydrotetradecafluoro-7-methyloctane (122)			
^{19}F Spectrum: (capill. neat)			
64.3	T (J = 13)	3	h-CF_3
79.3	D (J = 8)	6	a-CF_3
91.1	M	2	d-CF_2
92.7	M	2	f-CF_2
187.3	M	1	b-CF
^{1}H Spectrum: (capill. neat)			
3.0 to 3.2	M	6	c,e,g -CH_2


$\overset{a}{(CF_3)_2}\overset{b}{CF}\overset{c}{CH_2}\overset{d}{CF_2}\overset{e}{CH_2}\overset{f}{CF_3}$

(70)


$\overset{a}{(CF_3)_2}\overset{b}{CF}\overset{c}{CH_2}\overset{d}{CF_2}\overset{e}{CH_2}\overset{f}{CF_2}\overset{g}{CH_2}\overset{h}{CF_3}$

(122)


$\overset{a}{(CF_3)_2}\overset{b}{CH}\overset{c}{CH_2}\overset{d}{CF_2}\overset{e}{CH_2}\overset{f}{CF_3}$

(156)

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
3. 2,3,3,5,5-Pentahydroundecafluoro-2-methylhexane (156)			
^{19}F Spectrum: (capill. neat)			
62.5	D (J = 9) of T (J = 9)	3	f-CF_3
69.2	M	6	a-CF_3
98.5	M	2	d-CF_2
^{1}H Spectrum:			
3.0	Sept (J = 8)	1	b-CH
1.9 to 2.5	M	4	c,3-CH_2

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
4. <u>1-Iodo-2,2-dihydrononadecafluorodecane</u> (115)			
^{19}F Spectrum:			
38.3	M	2	f-CF_2
80.5	T(J = 16)	3	a-CF_3
113.3	M	2	b-CF_2
123.0	M	10	c-CF_2
127.1	M	2	d-CF_2
^{1}H Spectrum:			
3.0	T(J = 15) of T(J = 15)	2	e-CH_2
5. <u>2H,2H-eicosafluorodecane</u> (116)			
^{19}F Spectrum:			
62.0	T (J = 17)	3	f-CF_3
78.5	T (J = 20)	3	a-CF_3
113.0	M	2	b-CF_2
123.0	M	10	c-CF_2
128.5	M	2	d-CF
^{1}H Spectrum:			
3.1	T(J = 15) of Q(J = 15)	2	e-CH_2

a b c d e f
$CF_3CF_2(CF_2)_5CF_2CH_2CF_2I$
(115)

a b c d e f
$CF_3CF_2(CF_2)_5CF_2CH_2CF_3$
(116)

a b c d
$[(CF_3)_2CFCFHCF_2]_2$
(64)

6. <u>3,6-Dihydroeicosafluoro-2,7-dimethyloctane</u> (64)			
^{19}F Spectrum:			
74.0	M	6	a-CF_3
77.7	M	6	
114.8	M	4	d-CF_2
186.0	M	2	b-CF
216.0	M	2	c-CF
^{1}H Spectrum:			
5.1	D (J = 40)	-	c-CH

7. 2H,4H-tetradecafluoro-5-methylhexane (72) (neat, diastereomer mixture)

^{19}F Spectrum:

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
73.9	M	3)	a-CF_3
77.5	M	3)	
75.9	M	3	f-CF_3
121.5	M	2	d-CF_2
185.0	M	1	b-CF
211.2	M	1	c-CF

^{1}H Spectrum:

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
5.4	M		c,2-CH

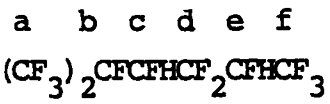
8. 2H,2H,4H-undecafluoro-5-methylhex-4-ene (71)

^{19}F Spectrum:

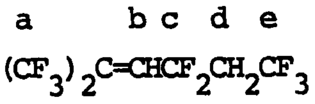
Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
61.0	M	3	a-CF_3 (z)
64.0	T (J = 9)	3	e-CF_3
67.0	Q (J = 7.5)	3	a-CF_3 (E)
92.0	M	2	c-CF_2

^{1}H Spectrum:

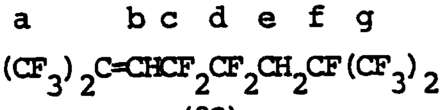
Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
2.8	M	2	d-CH_2
6.6	T (J = 13.5)	1	b-CH


$\overset{a}{(CF_3)_2}\overset{b}{CF}\overset{c}{CFH}\overset{d}{CF_2}\overset{e}{CFH}\overset{f}{CF_3}$

(72)


$\overset{a}{(CF_3)_2}\overset{b}{C{=}CH}\overset{c}{CF_2}\overset{d}{CH_2}\overset{e}{CF_3}$

(71)


$\overset{a}{(CF_3)_2}\overset{b}{C{=}CH}\overset{c}{CF_2}\overset{d}{CF_2}\overset{e}{CH_2}\overset{f}{CF}\overset{g}{(CF_3)_2}$

(80)

9. 3H,6H,6H-heptadecafluoro-8-methyloct-2-ene (80)

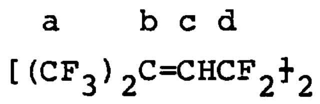
^{19}F Spectrum:

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
61.0	M	3	a-CF_3 (z)
68.0	Q (J = 8)	3	a-CF_3 (E)
79.0	D (J=6.8) of T(J=6.8)	6	g-CF_3
111.3	T (J = 14)	2	c-CF_2
113.3	M	2	d-CF_2
185.6	M	7	f-CF

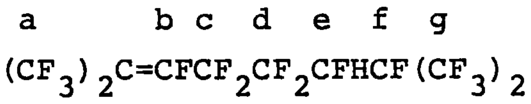
^{1}H Spectrum:

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
2.9	T (J = 17)	2	e-CH_2
6.8	T (J = 14)	1	b-CH

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
10. <u>3H,6H-hexadecafluoro-2,7-dimethyloct-2,6-diene</u> (75)			
^{19}F Spectrum:			
60.8	M	6	a-CF_3 (z)
68.2	Q (J = 9)	6	a-CF_3 (E)
111.0		4	d-CF_2
^{1}H Spectrum:			
6.7	T (J = 14)	-	c-CH
^{13}C Spectrum:			
112.7	T(J=256) of T(J=37)	-	d-C
118.9	Q(J=277)	-	a-C (z)
120.1	Q(J=275)	-	a-C (E)
128.9	T(J=26)	-	c-C
132.5	Sept (J=34)	-	b-C


$$\overset{a}{[(CF_3)_2}\overset{b}{C}=\overset{c}{C}H\overset{d}{C}F_2]_2$$

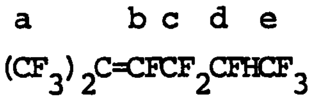
(35)


$$\overset{a}{(CF_3)_2}\overset{b}{C}=\overset{c}{C}F\overset{d}{C}F_2\overset{e}{C}F_2\overset{f}{C}FH\overset{g}{C}F(CF_3)_2$$

(170)

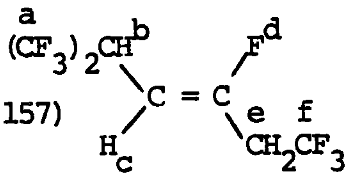
Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
11. <u>6H-nonadecafluoro-2,7-dimethyloct-2-ene</u> (170)			
^{19}F Spectrum:			
58.3	M	3	a-CF_3 (z)
61.3	D(J=32) of Q(J=12)	3	a-CF_3 (E)
74.3	M	3	g-CF_3
77.3	M	3	
96.0	M	1	b-CF
115.3	M	2	c-CF_2
122.6	AB (J = 248)	2	d-CF_2
187.3	M	1	f-CF
211.1	M	1	e-CF
^{1}H Spectrum:			
5.5	D (J = 46)	-	e-CH

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
12. 2H-terdecafluoro-5-methylhex-4-ene (172) (neat. capill.)			
^{19}F Spectrum:			
58.7	M	3	a-CF_3 (z)
60.2	D(J=28) of Q(J=11)	3	a-CF_3 (E)
76.6	M	3	e-CF_3
96.7	M	1	b-CF
114.8	AB (J = 254)	2	c-CF_2
216.6	D (J = 45)	1	d-CF
^{1}H Spectrum:			
5.3	D (J = 45)	-	d-CH
13. 2,3,5,5-Tetrahydrodecafluoro-2-methylhex-3-ene (157)			
^{19}F Spectrum:			
67.0	D (J=10) of T(J=6)	3	f-CF_3
70.0	D (J=2) of D(J=8)	6	a-CF_3
100.0	M	1	d-CF
^{1}H Spectrum:			
2.9	D(J=10) of Q(J=10)	2	e-CH_2
3.9	d(J=8) of Sept (J=10)	1	b-CH
4.9	D(J=10) of D(J=30)	1	c-CH

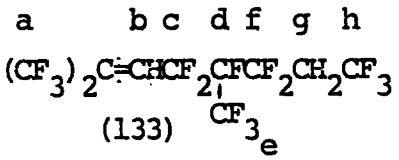


$(CF_3)_2C{=}CFCF_2CFHCF_3$

(172)



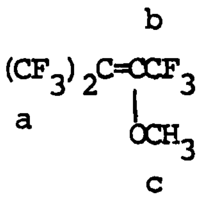
(157)



(133)

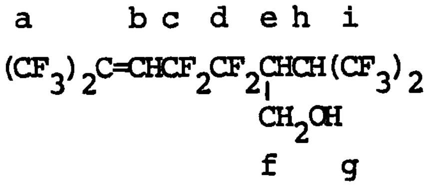
Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
14. 2,5-Bis(trifluoromethyl)-3H,7H,7H-undecafluorooct-2-ene (133)			
^{19}F Spectrum			
61.0	M	3	a-CF_3 (z)
62.5	M	3	h-CF_3
68.3	M	3	a-CF_3 (E)
78.2	M	3	e-CF_3
110.9	M	2	f-CF_2
120.1	M	2	c-CF_2
185.5	M	1	d-CF
^{1}H Spectrum:			
3.0	M	2	g-CH_2
6.8	T (J = 14)	1	b-CH

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
15. <u>2-Methoxynonafluoro-3-methylbut-2-ene</u> (162) (neat capill.)			
^{19}F Spectrum:			
60.0 to 64.0	M	-	a,b - CF_3
^{1}H Spectrum:			
4.0	S	-	c-OCH_3
16. <u>3-Hydromethylhexadecafluoro-2,7-dimethyloct-6-ene</u> (152)			
^{19}F Spectrum:			
61.0	M	3	a-CF_3 (z)
65.3 to 67.3	M	9	a,i -CF_3
124.3	M	4	c,d -CF_2
^{1}H Spectrum:			
3.2	M	1	e-CH
3.4	S	2	f-CH_2
4.0	M	1	h-CH
5.9	T (J = 13)	1	b-CH



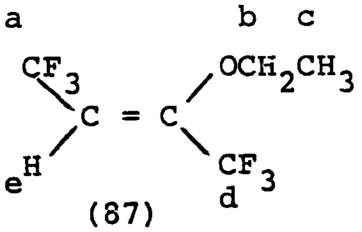
$(CF_3)_2C{=}C(CF_3)OCH_3$

(162)



$(CF_3)_2C{=}CHCF_2CF_2CH(CH_2OH)CH(CF_3)_2$

(152)



$(CF_3)HC{=}C(OCH_2CH_3)CF_3$

(87)

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
17. <u>2H-3-ethoxyhexafluorobut-2-ene</u> (87)			
^{19}F Spectrum:			
59.3	D (J = 7.5)	3	a-CF_3
72.0	S	3	d-CF_3
^{1}H Spectrum:			
1.2	T (J = 7.0)	3	c-CH_3
3.4	Q (J = 7.0)	2	b-CH_2
6.3	Q (J = 7.5)	1	e -CH

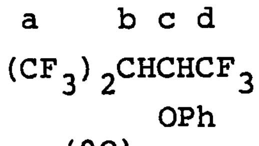
18. <u>2H-2-phenoxy-3-hydrohexafluoro-3-methylbutane</u> (90)

^{19}F Spectrum:

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
62.4	M	3)	a-CF_3
		)	
67.6	M	3)	
76.2	M	3	d-CF_3

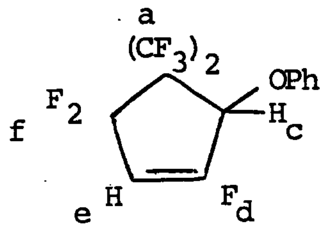
^{1}H Spectrum:

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
3.3	Sept (J = 8)	1	b-CH
4.9	Q (J = 7)	1	c-CH
7.0	M	5	ring-H

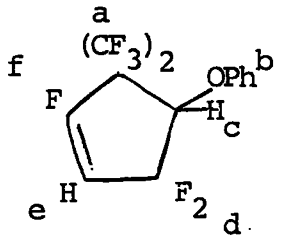


$\overset{a}{(CF_3)_2}\overset{b}{C}H\overset{c}{C}H\overset{d}{CF_3}$ with $\underset{OPh}{}$ on c: $(CF_3)_2CH\underset{OPh}{C}HCF_3$

(90)



(91A)



(91B)

19 and 20. <u>Mixture (50:50) of 1H,3H-3-phenoxynonafluoro-4,4-dimethylcyclopentene (91A) and 1H,4H-4-phenoxynonafluoro-3,3-dimethylcyclopentene (91B)</u>

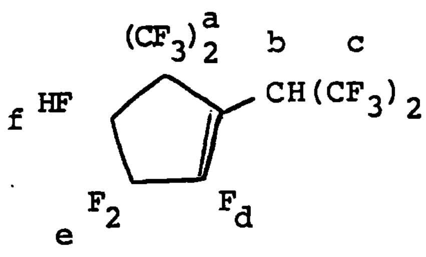
^{19}F Spectrum:

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
62.7	M	3)	a-CF_3
		)	
63.7	M	3)	
		)	
67.6	M	6)	
115 to 120	M	3	d,f-CF

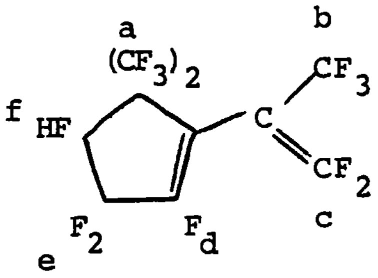
^{1}H Spectrum

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
3.0 to 3.5	M	1	c-CH
5.7	M	1	e-CH
7.0 to 7.7	M	5	ring-H

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
21. 1-(2H-hexafluoro-2-propyl)-3H-decafluoro-2,2-dimethylcyclopentene (79)			
^{19}F Spectrum:			
63.0 to 64.6	M	6	a-CF_3
68.6	D	6	c-CF_3
111.6	Sept (J = 16)	1	d-CF
112.0	AB (J = 265)	2	e-CF_2
212.0	D (J = 48)	1	f-CF
^{1}H Spectrum:			
3.9	Sept (J = 7)	1	b-CH
5.5	D(J=4) of D(J=12) of D(J=48)	1	f-CH
22. 1-(Pentafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (145)			
^{19}F Spectrum:			
6.0	M	3	b-CF_3
66.7 and 71.0	M	6	a-CF_3
68.3	M	2	c-CF_2
113.2	AB (J = 261)	2	e-CF_2
117.2	T (J = 14)	1	d-CF
211.6	M	1	f-CF
^{1}H Spectrum:			
5.0	D(J=5) of D(J=12) of D(J=48)	1	f-CH

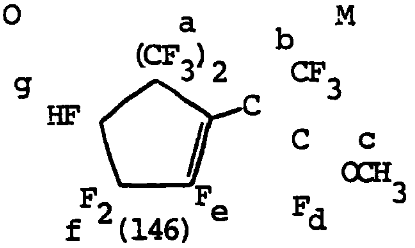


(79)

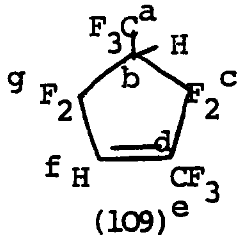


(145)

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
23. 1-(2-Methoxytetrafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (146)			
^{19}F Spectrum:			
57.8	M	3	b-CF_3
65.3 and 70.0	M	6	a-CF_3
71.0	D (J = 12.5)	1	d-CF
111.9	AB (J = 261)	2	f-CF_2
119.8	D (J = 12.5)	1	e-CF
210.9	M	1	g-CF
^{1}H Spectrum:			
3.8	S	3	c-OCH_3
5.4	D(J=48) of D(J=15)	1	g-CH
24. 1H-2,4-bis(trifluoromethyl)-4H1tetrafluorocyclopentene (109)			
^{19}F Spectrum:			
67.0	M	3	a,e-CF_3
67.5	M	3	
100.0	AB (J = 260)	2	c,g-CF_2
100.5	AB (J = 282)	2	
^{1}H Spectrum:			
3.2	T (J = 8) of Q (J = 4)	1	b-CH
6.4	M	1	f-CH
^{13}C Spectrum:			
57.1	M	1	b-C
120.6 and 120.7	T(J = 257)	2	c,g-CF_2
122.1	Q(J = 250)	1	a,e-CF_3
125.0	Q(J = 279)	1	
137.4	T(J = 31)	1	f-CH
138.0	M	1	d-C

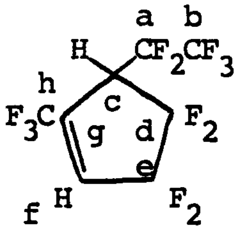


(146)



(109)

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
25. 1H-2-trifluoromethyl-3H,3-pentafluoroethyltetrafluorocyclopentene (111)			
^{19}F Spectrum:			
69.0	D (J = 20)	3	h-CF_3
85.0	D (J = 20)	3	b-CF_3
115.0	AB (J = 245)	2	d-CF_2
115.6	M	2	a-CF_2
117.0	AB (J = 273)	2	e-CF_2
^1H Spectrum:			
3.8	T (J = 20)	1	c-CH
6.6	M	1	f-CH
^{13}C Spectrum:			
51.7	M	1	c-C
114.0	M	3	c,d,e-CF_2
122.0	M		
119.5	Q (J = 272)	1	b,h-CF_3
120.6	Q (J = 280)	1	
134.4	T (J = 17)	1	f-CH
138.1	Q (J = 39)	1	g-C



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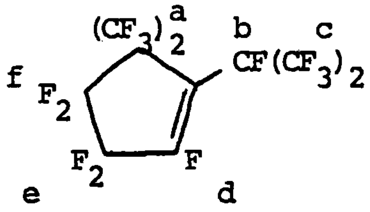
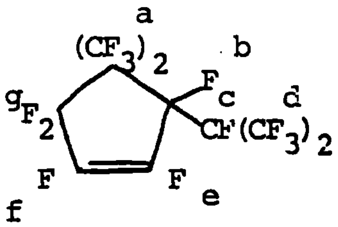


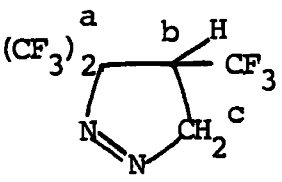
(168)



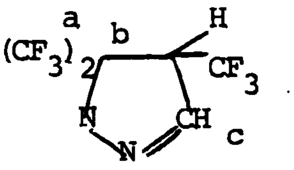
(169)

26. Perfluoro-2-(prop-2-yl)-3,3-dimethylcyclopentene (168)			
^{19}F Spectrum:			
65.7	M	6	a-CF_3
75.7	D(J = 24) of Q(J = 5)	6	c-CF_3
107.3	M	1	d-CF
122.3	M	2	f-CF_2
181.3	M	1	b-CF

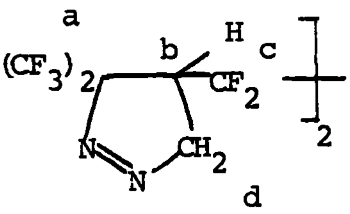
Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
27. Perfluoro-3-(prop-2-yl)-4,4-dimethylcyclopentene (169)			
^{19}F Spectrum:			
74.6	M	6	a-CF_3
75.0 and 77.8	M	6	d-CF_3
118.6	M	2	g-CF_2
123.3	M	2	3,f-CF
188.3	M	1	c-CF
28. 4,5,5-Tris(trifluoromethyl)-4,5-dihydro-3H-pyrazole (154)			
^{19}F Spectrum:			
60.7	M	3	b-CF_3
71.9 and 72.9	M	6	a-CF_3
^{1}H Spectrum:			
4.8	AB (J = 20)	1	b-CH
5.0	M	1	b-CH
29. 4,5,5-Tris(trifluoromethyl)-4,5-dihydro-1H-pyrazole (155)			
^{19}F Spectrum:			
60.7	M	3	b-CF_3
71.9 and 72.9	M	6	a-CF_3
^{1}H Spectrum:			
5.0	M	1	b-CH
6.6	M	1	c-CH
7.8	M	1	d-NH



(154)

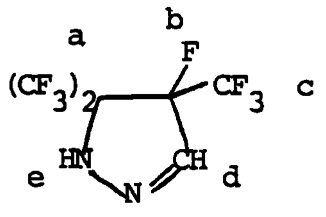


(155)



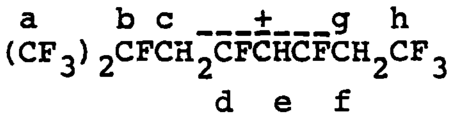
(153)

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
30. <u>1,2-Di(5,5-bis(trifluoromethyl)-4,5-dihydro-3H-4-pyrazolo)tetrafluoroethane</u> (153)			
^{19}F Spectrum:			
65.0	M		a-CF_3
69.0	M		
109.7	AB (J = 280)	4	c-CF_2
^{1}H Spectrum:			
3.2	D(J=9) of D(J=9) of D(J=9)	2	b-CH
4.4 to 5.3	AB (J = 18) of D(J = 9)	4	d-CH_2
31. <u>4,5,5-Tris(trifluoromethyl)-4-fluoro-4,5-dihydro-1H-pyrazole</u> (164)			
^{19}F Spectrum:			
68.3 to 71.0	M	6	a-CF_3
75.2	D (J=14) of D(J = 14)	3	c-CF_3
163.7	M	1	b-CF
^{1}H Spectrum:			
6.8	br	1	d-CH
7.5	br	1	e-NH



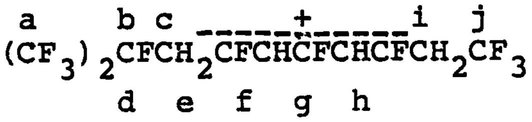
(164)

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
32. Stable Carbocation (127) (Soln. in SbF_5)			
^{19}F Spectrum:			
-68.1	br M	2	d,f-CF
61.4		3	h-CF_3
76.9		6	a-CF_3
180.9		1	b-CF
^{1}H Spectrum:			
4.5 to 5.0	br M	4	c,g-CH_2
8.2		1	e-CH
33. Stable Carbocation (128) (Soln. in SbF_5)			
^{19}F Spectrum:			
-7.0 to 0.0	br M	3	d.f.h-CF
62.4		3	-CF_3
76.9		6	a-CF_3
181.0		1	b-CF
^{1}H Spectrum:			
4.0 to 4.5	br M	4	c,i-CH_2
6.5 to 7.0		2	e,g-CH



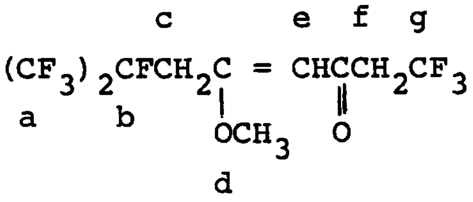
$\overset{a}{(CF_3)_2}\overset{b}{C}F\overset{c}{CH_2}\overbrace{\underset{d}{CF}\overset{+}{\underset{e}{CH}}\underset{f}{CF}}\overset{g}{CH_2}\overset{h}{CF_3}$

(127)



$\overset{a}{(CF_3)_2}\overset{b}{C}F\overset{c}{CH_2}\overbrace{\underset{d}{CF}\underset{e}{CH}\overset{+}{\underset{f}{CF}}\underset{g}{CH}\underset{h}{CF}}\overset{i}{CH_2}\overset{j}{CF_3}$

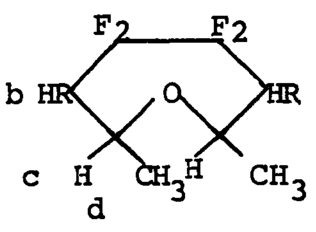
(128)



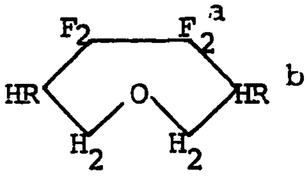
$\underset{a}{(CF_3)_2}\underset{b}{CF}\overset{c}{CH_2}\underset{\underset{d}{OCH_3}}{C}=\overset{e}{CH}\overset{f}{\underset{\underset{O}{\|}}{C}}\overset{g}{CH_2}CF_3$

(129)

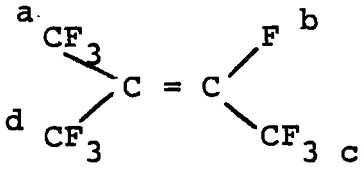
Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
34. 3,3,5,7,7-Pentahydro-4-methoxydecafluoro-2-methyloct-4-enone (129)			
^{19}F Spectrum:			
65.0	T (J = 10.6)	3	g-CF_3
78.5	D (J = 7.0)	6	a-CF_3
182.5	M	1	b-CF
^1H Spectrum:			
3.2	Q (J = 10.6)	2	f-CH_2
3.6	S	3	d-OCH_3
3.7	D (J = 22.0)	2	c-CH_2
5.6	S	1	e-CH
35. 2,7-Dimethyl-3,6-bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluorooxepane (149)			
^{19}F Spectrum:			
60.7	M	12	b-CF_3
63.7 to 67.3	M		
120.5	S	2	a-CF_2
123.1	AB (J = 242)	2	
^1H Spectrum:			
1.3 to 1.7	S	6	d-CH_3
1.6	M	2	b-CH
3.3	M	2	c-CH
3.9	Sept (J = 8)	2	e-CH
36. 3,6-Bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluoro-oxepane (150			
^{19}F Spectrum:			
60.0 to 60.8	M	12	
112.4	AB (J = 271)	2	
122.2	AB (J = 262)	2	
^1H Spectrum:			
3.3 to 4.0	br M	-	



(149) e
(R= $-CH(CF_3)_2$)

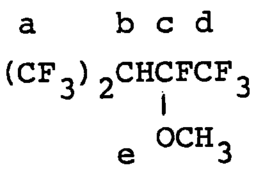


(150)



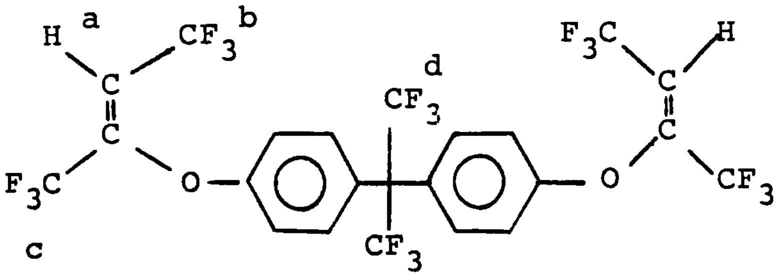
(161)

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
37. Perfluoro-2-methylbut-2-ene (161)			
^{19}F Spectrum:			
60.4	Q (J = 10) of D (J = 4)	3	d-CF_3
61.7	D (J = 30) of Q (J = 10)	3	c-CF_3
69.0	Q (J = 10)	3	a-CF_3
100.3	Q (J = 30) of Q(J=10) of Q(J=4)	1	b-CF
38. 2H-3-methoxydecafluoro-2-methylbutane (163)			
^{19}F Spectrum:			
60.0	br M	3	a-CF_3
64.7	Br M	3	
77.5	D (J = 8)	3	d-CF_3
130.6	Q (J = 8)	1	c-CF
^{1}H Spectrum:			
3.6	Sept (J = 7)	1	b-CH
3.7	S	3	e-OCH_3



$$\overset{a}{(CF_3)_2}\overset{b}{C}H\overset{c}{C}F\overset{d}{C}F_3 \quad \text{e } OCH_3$$

(163)



(88)

39. 2,2-Bis-(4-[2H-hexafluorobut-2-enoxy]phenyl)hexafluoropropane (88)			
^{19}F Spectrum:	(d6-acetone)		
59.7	D (J = 7.0)	6	b-CF_3
63.7		6	d-CF_3
69.6		6	c-CF_3
^{1}H Spectrum:	(d6-acetone)		
6.3	Q (J = 7.0	2	a-CH
7.1 to 7.7	AA´XX´ pattern	8	ring-H

APPENDIX TWO

Infra Red Spectra

1. 1-(2H-hexafluoro-2-propyl)-3H-decafluoro-2,2-dimethylcyclopentene (79)
2. 1-(Pentafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (145)
3. 1-(2-Methoxytetrafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (146)
4. Perfluoro-2-(prop-2-yl)-3,3-dimethylcyclopentene (168)
5. Perfluoro-3-(prop-2-yl)-4,4-dimethylcyclopentene (169)
6. 1H-2-trifluoromethyl-3H,3-pentafluoroethyltetrafluorocyclopentene (111)
7. 1H-2,4-bis(trifluoromethyl)-4H-tetrafluorocyclopentene (109)
8. 1H,3H,3-phenoxynonafluoro-4,4-dimethylcyclopentene (91A) and 1H,4H,4-phenoxynonafluoro-3,3-dimethylcyclopentene (91B) (Mixture)
9. 2H,2-phenoxy-3H-hexafluoro-3-methylbutane (90)
10. 2H-3-methoxydecafluoro-2-methylbutane (163) and 2-Methoxynonafluoro-3-methylbut-2-ene (162 (Mixture)
11. 2,3,5,5-Tetrahydrodecafluoro-2-methylhex-3-ene (157)
12. 3H,6H,6H-heptadecafluoro-7-methyloct-2-ene (80)
13. 2H,2H,4H-undecafluoro-5-methylhex-4-ene (71)
14. 2H-terdecafluoro-5-methylhex-4-ene (172)
15. 2,5-Bis(trifluoromethyl)-3H,7H,7H-undecafluorooct-2-ene (133)
16. 3H,6H-hexadecafluoro-2,7-dimethyloct-2,6-diene (75)
17. 3-Hydroxymethylhexadecafluoro-2,7-dimethyloct-6-ene (152)
18. 1-Iodo-2H,2H-nonadecafluorodecane (115)
19. 2H,2H-eicosafluorodecane (116)
20. 2H,2H-octafluorobutane (119)
21. 2,3,3,5,5-Pentahydroundecafluoro-2-methylhexane (156)
22. 2H,4H-tetradecafluoro-5-methylhexane (72)
23. 3H,6H-eicosafluoro-2,7-dimethyloctane (64)

24. 2,2-Bis-(41[2H-hexafluorobut-2-enoxy]phenyl)hexafluoropropane (88)

25. 2,2-Bis-(4-methoxyphenyl)hexafluoropropane (88A)

26. 2,2-Bis-(4-[pentafluoropyridino]phenyl)hexafluoropropane (88B)

27. 4,5,5-Tris(trifluoromethyl)-4,5-dihydro-1H-pyrazole (155)

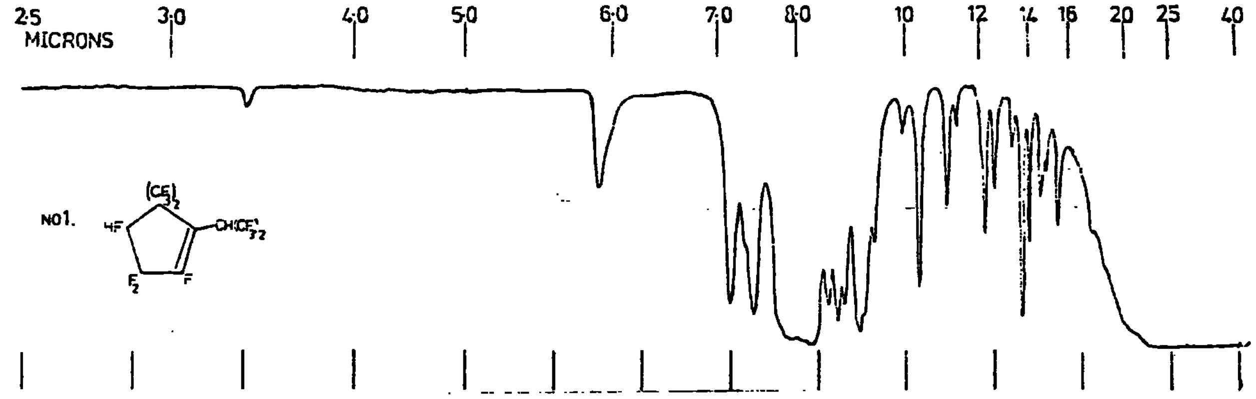
28. 4,5,5-Tris(trifluoromethyl)-4-fluoro-4,5-dihydro-1H-pyrazole (164)

29. 1,2-Di(5,5-bis(trifluoromethyl)-4,5-dihydro-3H,4-pyrazolo)-tetrafluoroethane (153)

30. 3,6-Bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluorooxepane (150)

31. 2,7-Dimethyl-3,6-bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluorooxepane (149)

32. 3,3,5,7,7-Pentahydro-4-methoxydecafluoro-2-methyloct-4-enone (129)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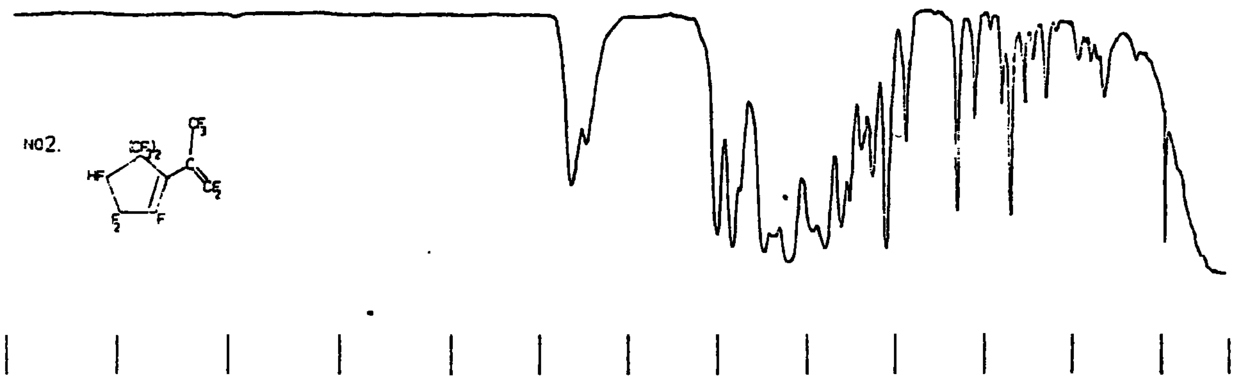
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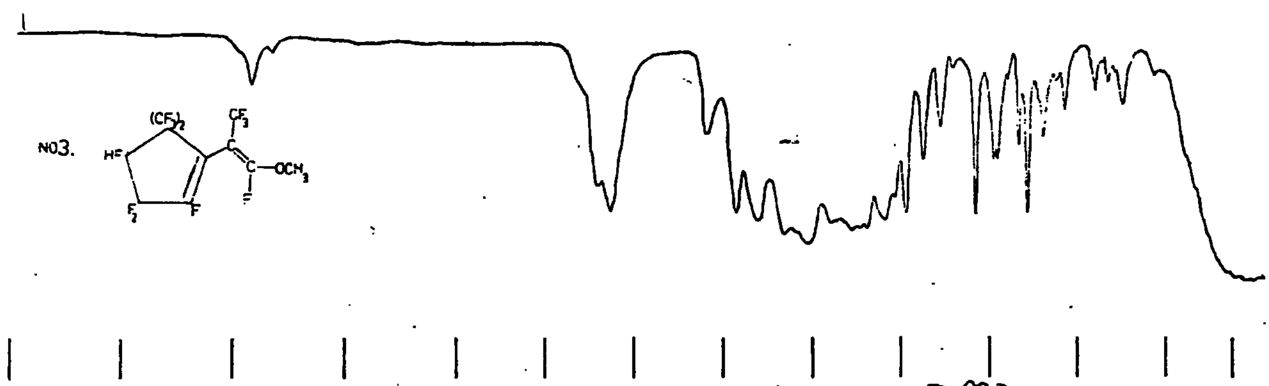
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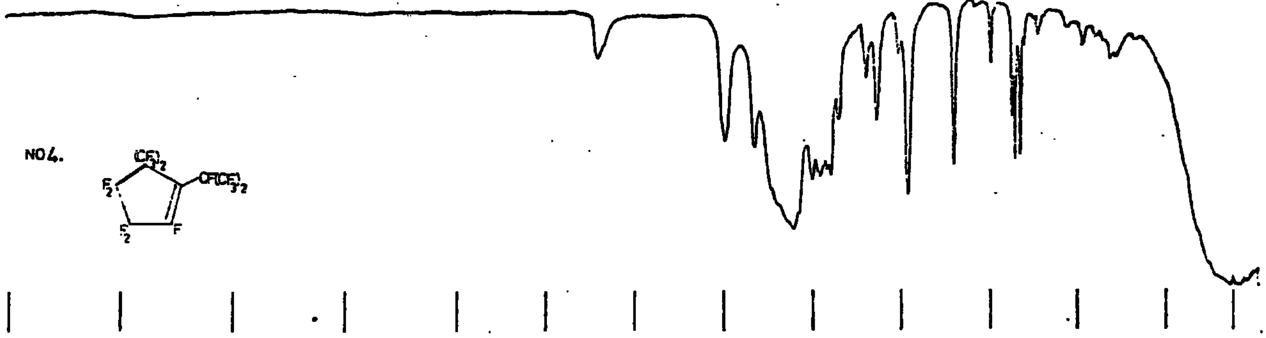
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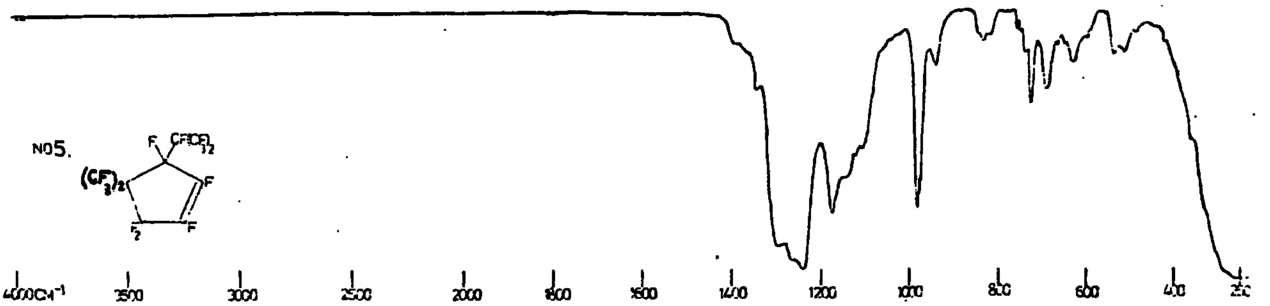
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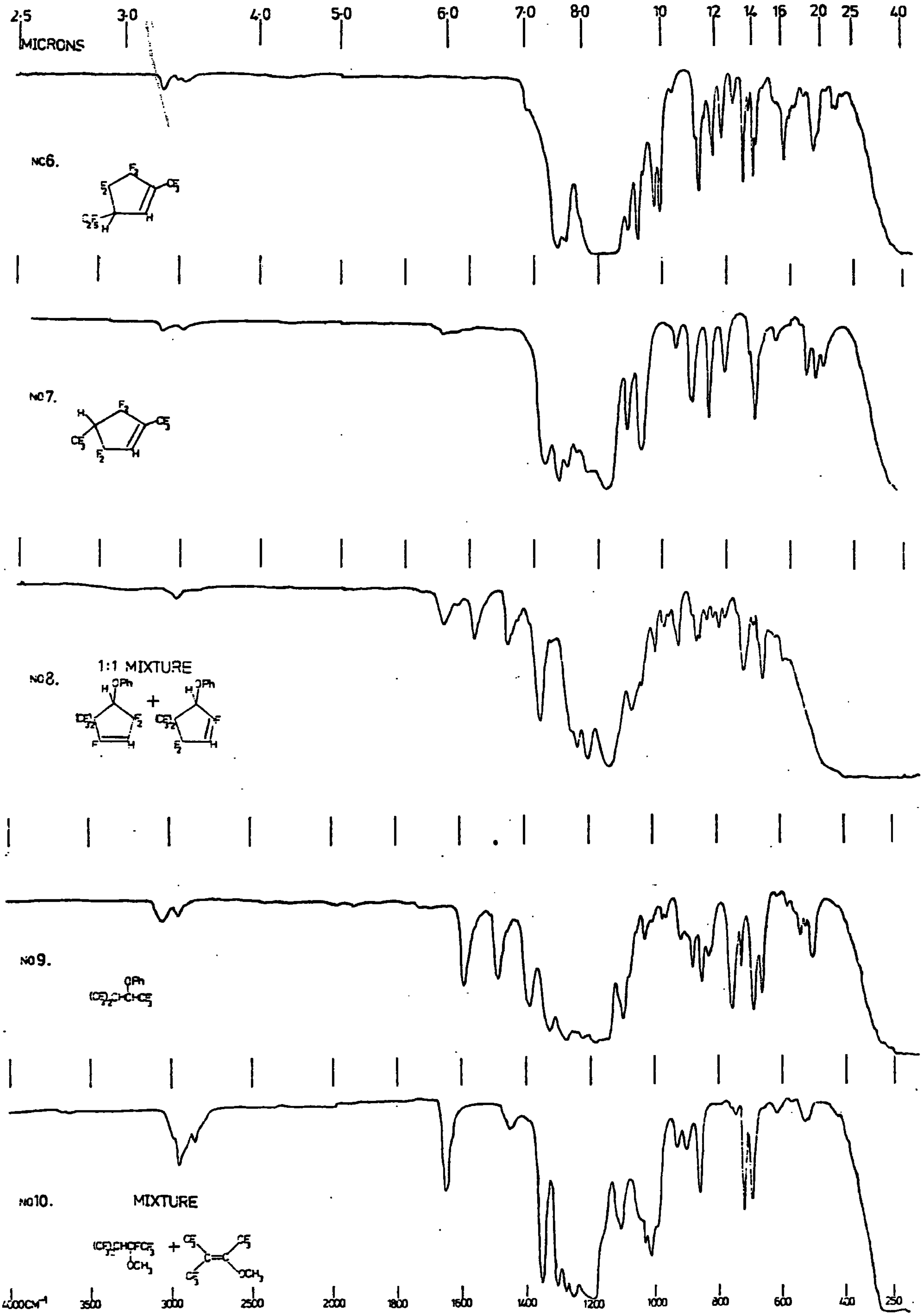
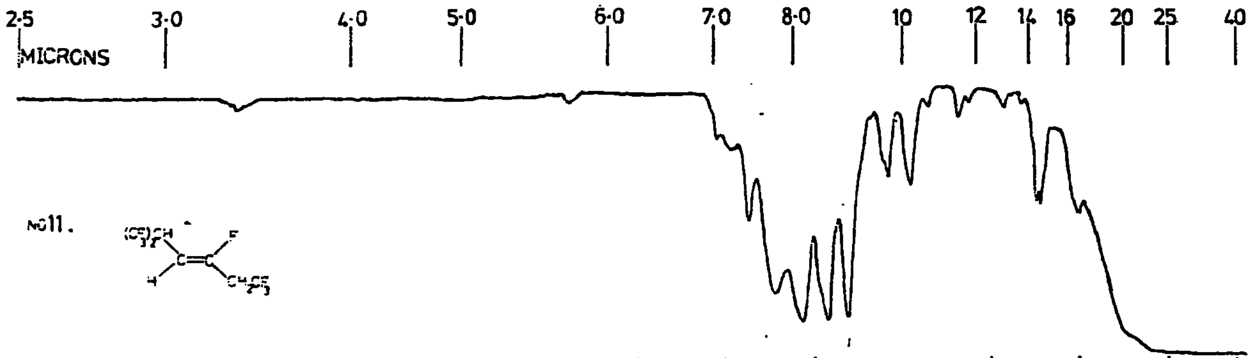
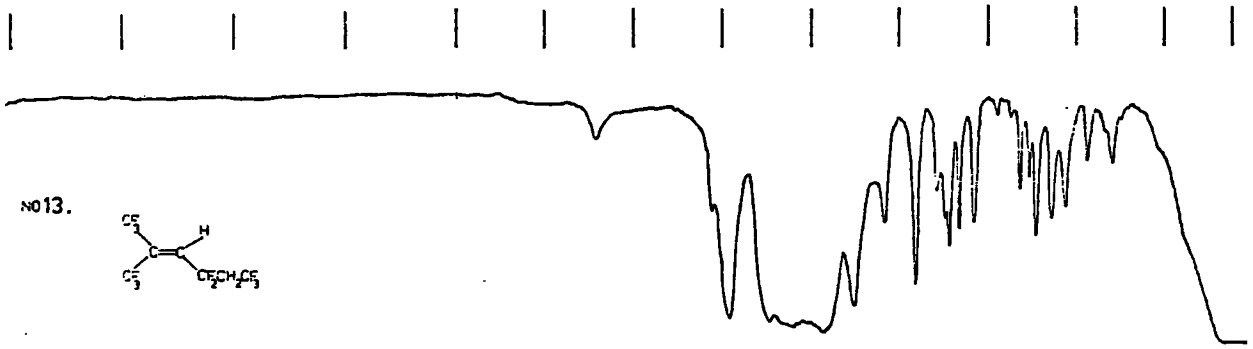

2·5
MICRONS
3·0
4·0
5·0
6·0
7·0
8·0
10
12
14
16
20
25
40
No6.
No7.
No8.
1:1 MIXTURE
No9.
No10.
MIXTURE
4000CM⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

NO11.



NO12.

NO13.



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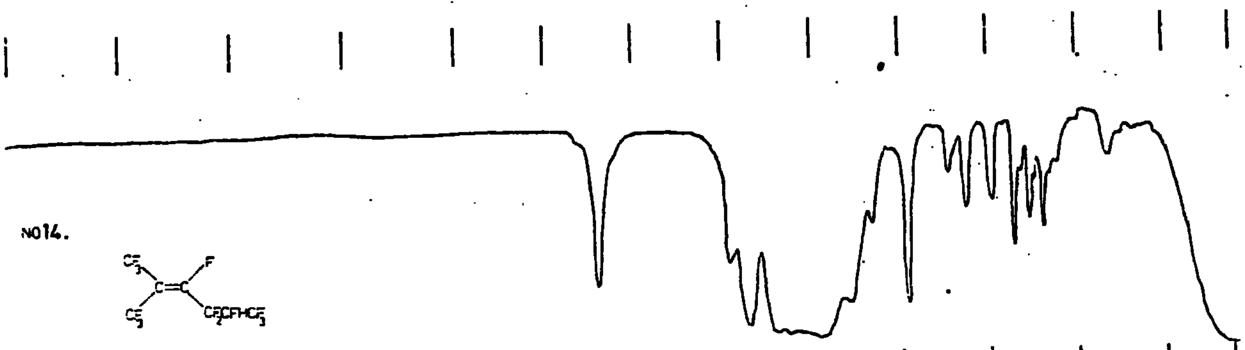

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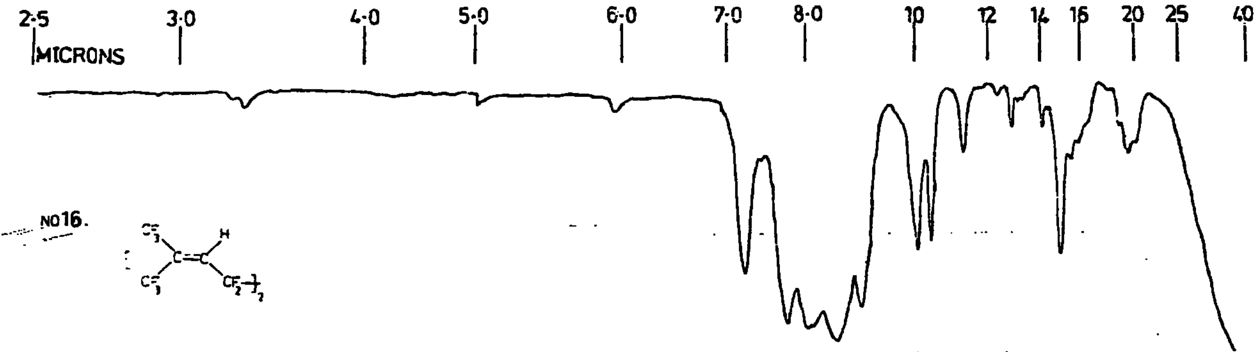
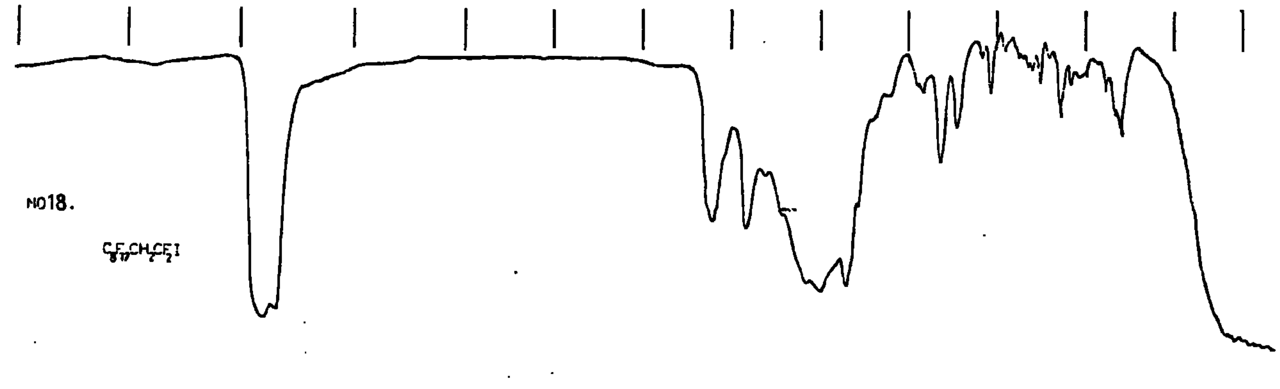


NO 16.

NO 17.

$(CF_3)_2CHCHCF_2CF_2CH{=}C(CF_3)_2$ with CH_2CH below the second CH

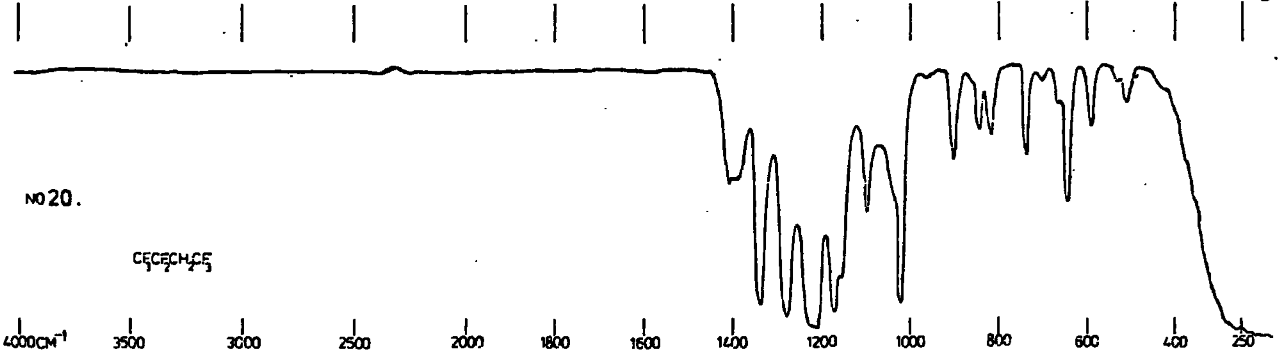


NO 18.

$C_8F_{17}CH_2CF_2I$

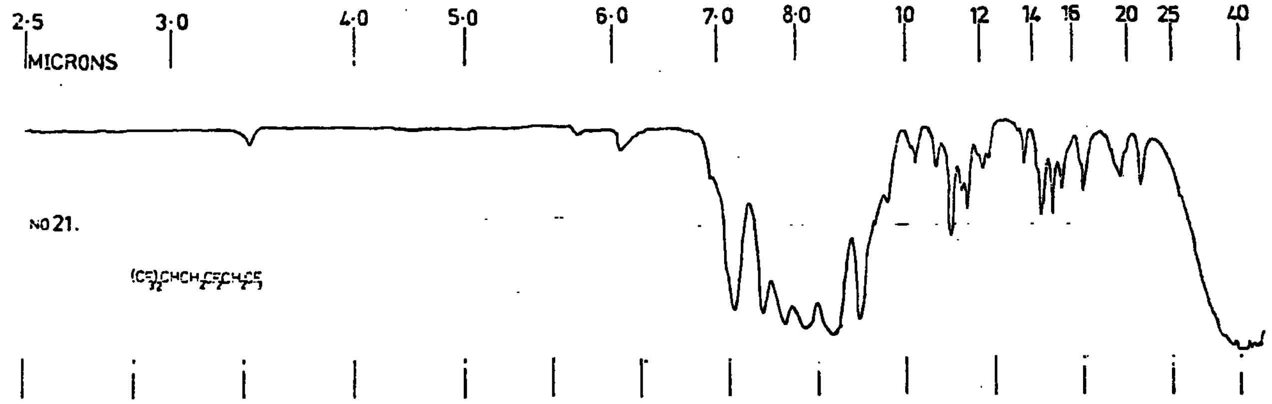
NO 19.

$C_8F_{17}CH_2CF_3$



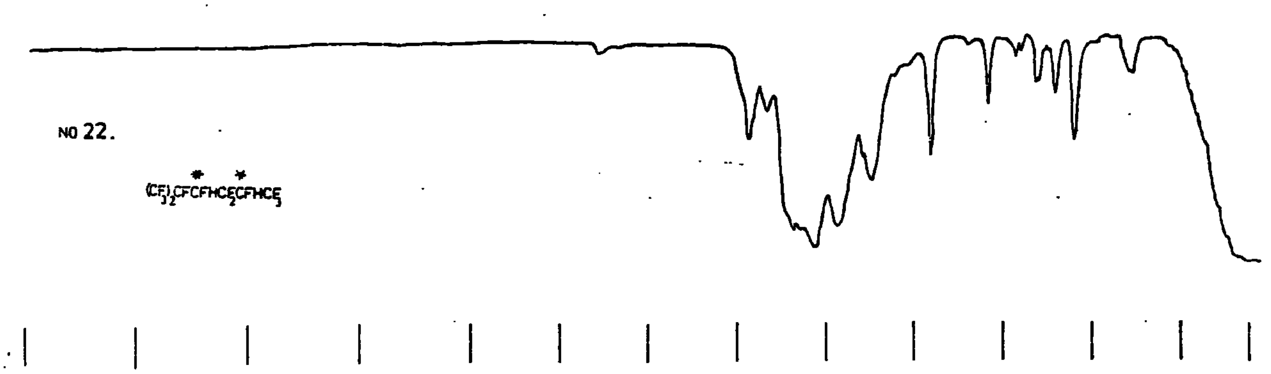
NO 20.

$CF_3CF_2CH_2CF_3$



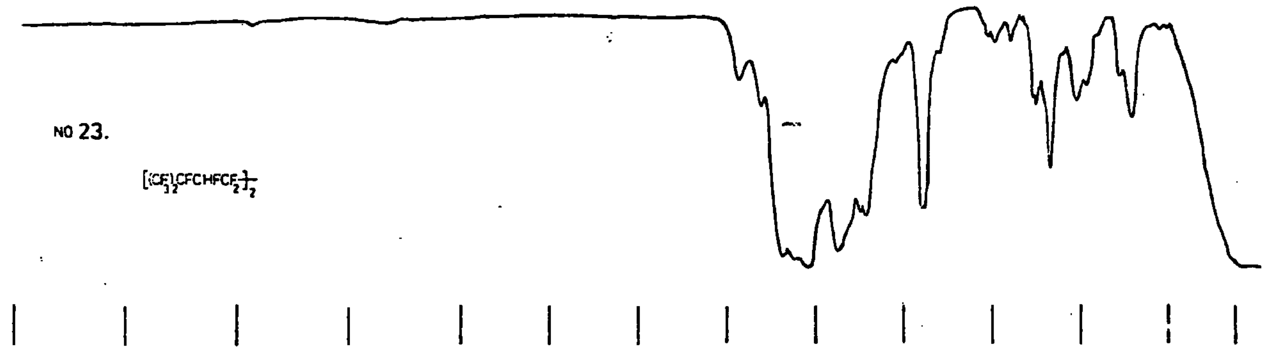
NO 21.

$(CF_3)_2CHCH_2CF_2CH_2CF_3$



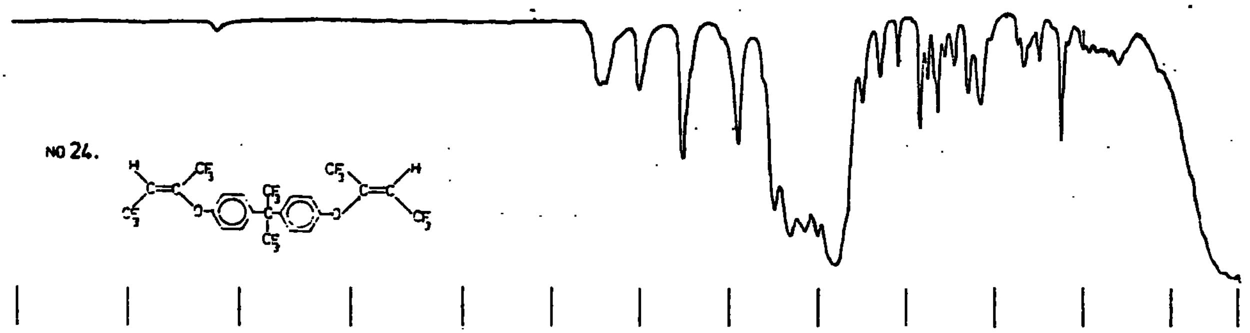
NO 22.

$(CF_3)_2CF\overset{*}{C}FHCF_2\overset{*}{C}FHCF_3$



NO 23.

$[(CF_3)_2CFCHFCF_2\text{—}]_2$



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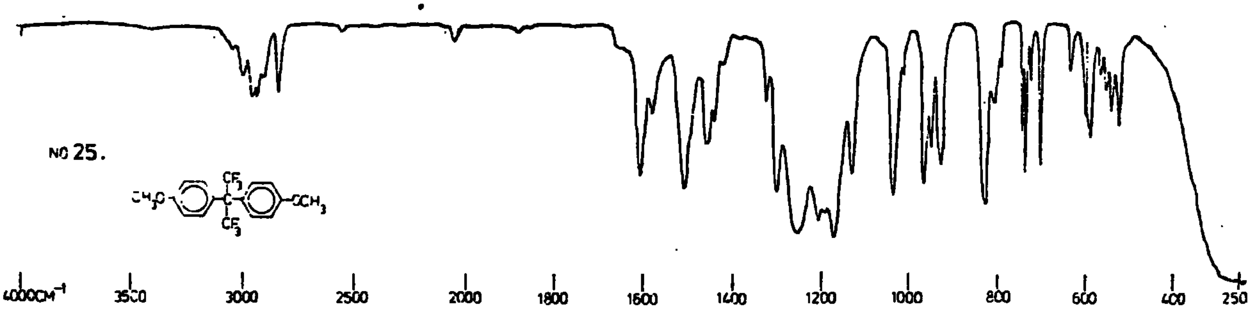

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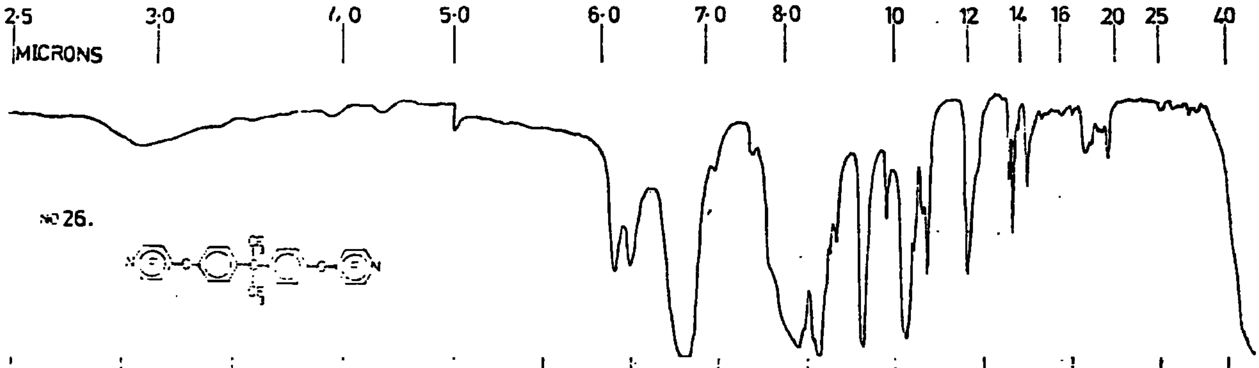

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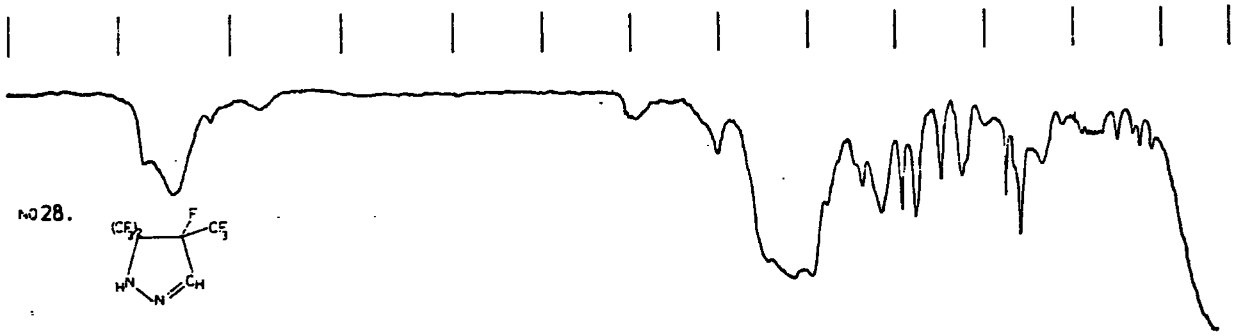
No 27.



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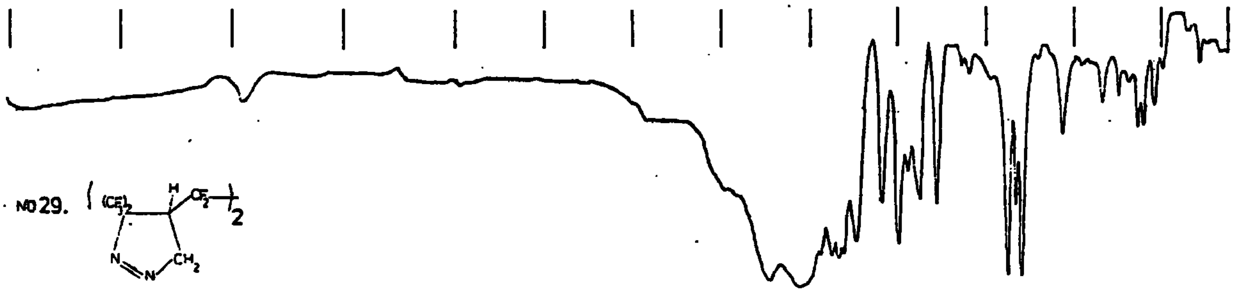

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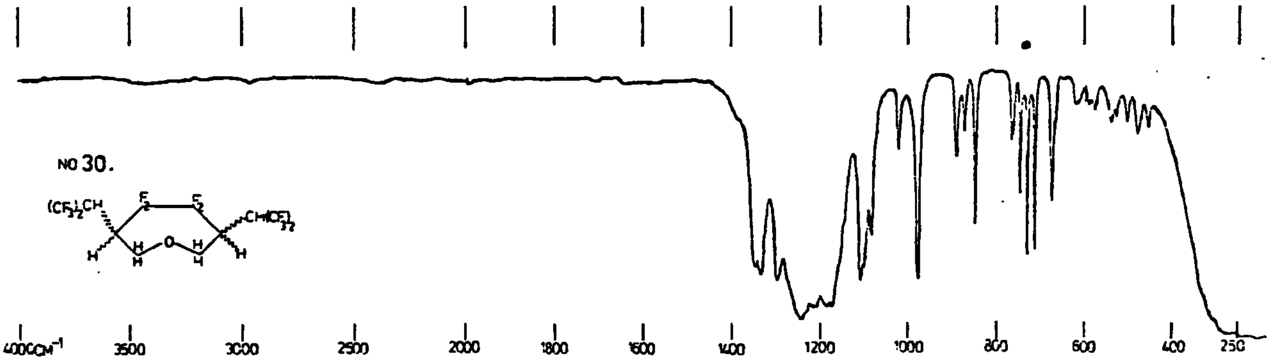

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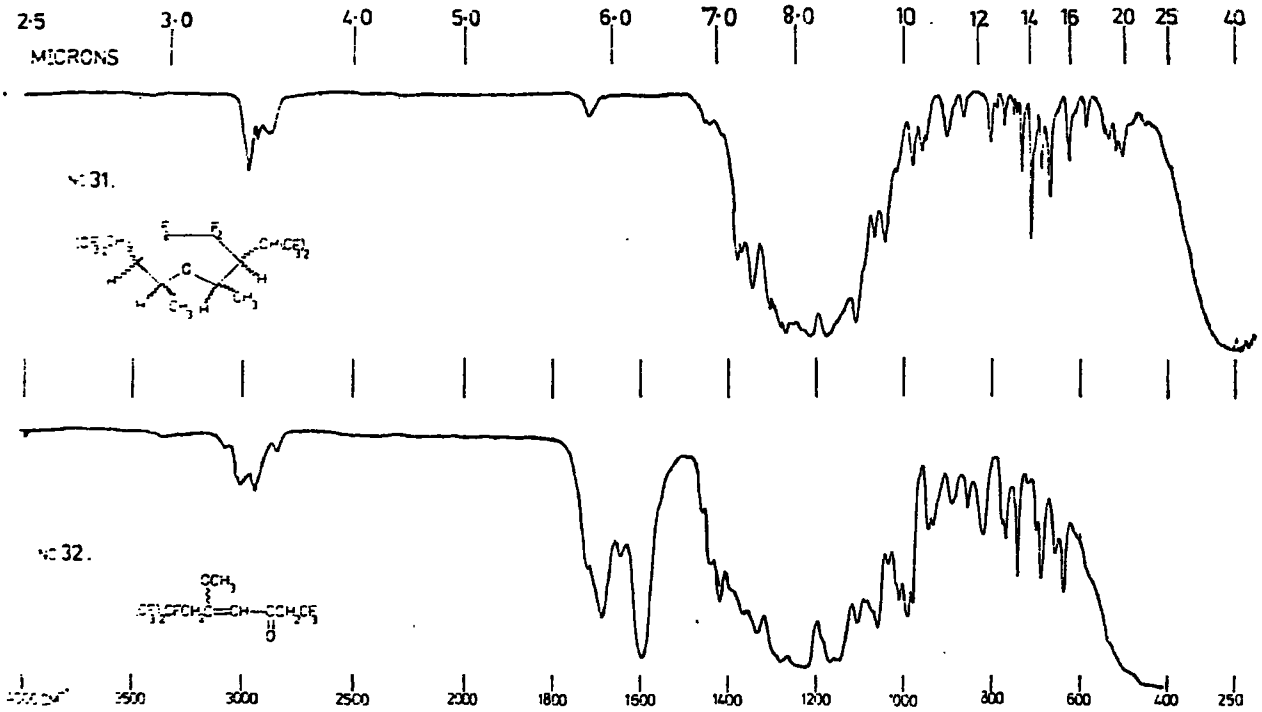

2·5
3·0
4·0
5·0
6·0
7·0
8·0
10
12
14
16
20
25
40
MICRONS
No 31.
F
F2
(CF3)2CF2
CH(CF3)2
O
H
CH3
H
CH3
H
No 32.
OCH3
(CF3)2CFCH2C=CH—CCH2CF3
O
4000 CM⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

APPENDIX THREE

Mass Spectra

The following abbreviations are used in this appendix:

NEG - Negative Ion ^{410} (NH_3 or $^{i}C_4H_{10}$)

EI - Electron Impact

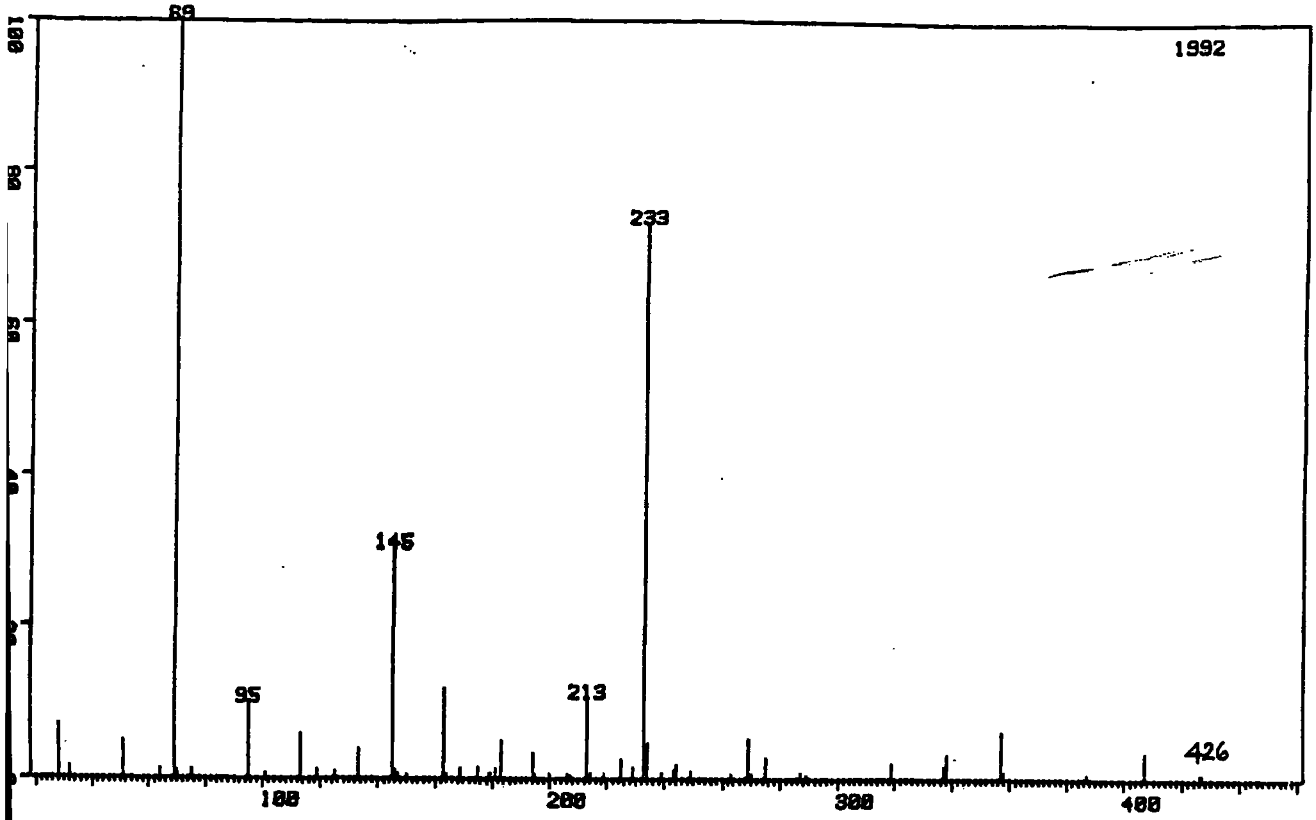
CI - Chemical Ionization

1. EI/1-(2H-hexafluoro-2-propyl)-3H-decafluoro-2,2-dimethylcyclopentene (79)
2. EI/1-(Pentafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (145)
3. EI/1-(2-Bromohexafluoro-2-propyl)-3H-decafluoro-2,2-dimethylcyclopentene (148)
4. EI/1-(2-Methoxytetrafluoroprop-2-enyl)-3H-decafluoro-2,2-dimethylcyclopentene (146)
5. NEG/Perfluoro-2-(prop-2-yl)-3,3-dimethylcyclopentene (168)
6. NEG/Perfluoro-3-(prop-2-yl)-4,4-dimethylcyclopentene (169)
7. EI/1H-2-trifluoromethyl-3H,3-pentafluoroethyltetrafluorocyclopentene (111)
8. NEG/ (111)
9. EI/1H-2,4-bis(trifluoromethyl)-4H-tetrafluorocyclopentene (109)
10. CI/1H,3H,3-phenoxynonafluoro-4,4-dimethylcyclopentene(91A) and 1H,4H,4-phenoxynonafluoro-3,3-dimethylcyclopentene (91B) (Mixture
11. EI/2H,2-phenoxy-3H-hexafluoro-3-methylbutane (90)
12. CI/2-Methoxynonafluoro-3-methylbut-2-ene (162)
13. CI/2H-3-methoxydecafluoro-2-methylbutane (163)
14. EI/2,3,5,5-Tetrahydrodecafluoro-2-methylhex-3-ene (157)
15. CI/3H,6H,6H-heptadecafluoro-7-methyloct-2-ene (80)
16. EI/2H,2H,4H-undecafluoro-5-methylhex-4-ene (71)
17. EI/2H-terdecafluoro-5-methylhex-4-ene (172)
18. EI/6H-nonadecafluoro-2,7-dimethyloct-2-ene (170)
19. EI/2,5-Bis(trifluoromethyl)-3H,7H,7H-undecafluorooct-2-ene(133)
20. EI/3H,6H-hexadecafluoro-2,7-dimethyloct-2,6-diene (75)
21. NEG/ (75)

22. CI/3-Hydroxymethylhexadecafluoro-2,7-dimethyloct-6-ene (152)
23. NEG/ (152)
24. EI/1-Iodo-2H,2H-nonadecafluorodecane (115)
25. EI/eH,2H-eicosafluorodecane (116)
26. EI/2,3,3,5,5-Pentahydroundecafluoro-2-methylhexane (156)
27. EI/2H,4H-tetradecafluoro-5-methylhexane (72)
28. NEG/3H,6H-eicosafluoro-2,7-dimethyloctane (64)
29. EI/2,2-Bis-(4-[2H-hexafluorobut-2-enoxy]phenyl)hexafluoropropane (88)
30. NEG/ (88)
31. EI/2,2-Bis-(4-methoxyphenyl)hexafluoropropane (88A)
32. EI/2,2-Bis-(4-[pentafluoropyridino]phenyl)hexafluoropropane (88B)
33. EI/4,5,5-Tris(trifluoromethyl)-4,5-dihydro-1H-pyrazole (155)
34. CI/4,5,5-Tris(trifluoromethyl)-4-fluoro-4,5-dihydro-1H-pyrazole (164)
35. NEG/ (164)
36. CI/1,2-Di(5,5-bis(trifluoromethyl)-4,5-dihydro-3H,4-pyrazolo)tetrafluoroethane (153)
37. NEG/ (153)
38. CI/3,6-Bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluorooxepane (150)
39. NEG/ (150)
40. CI/2,7-Dimethyl-3,6-bis(2H-hexafluoro-2-propyl)-4,4,5,5-tetrafluorooxepane (149)
41. NEG/ (149)
42. EI/3,3,5,7,7-Pentahydro-4-methoxydecafluoro-2-methyloct-4-enone (129)
43. CI/ (129)

MJS271 28
CAL:CALMS

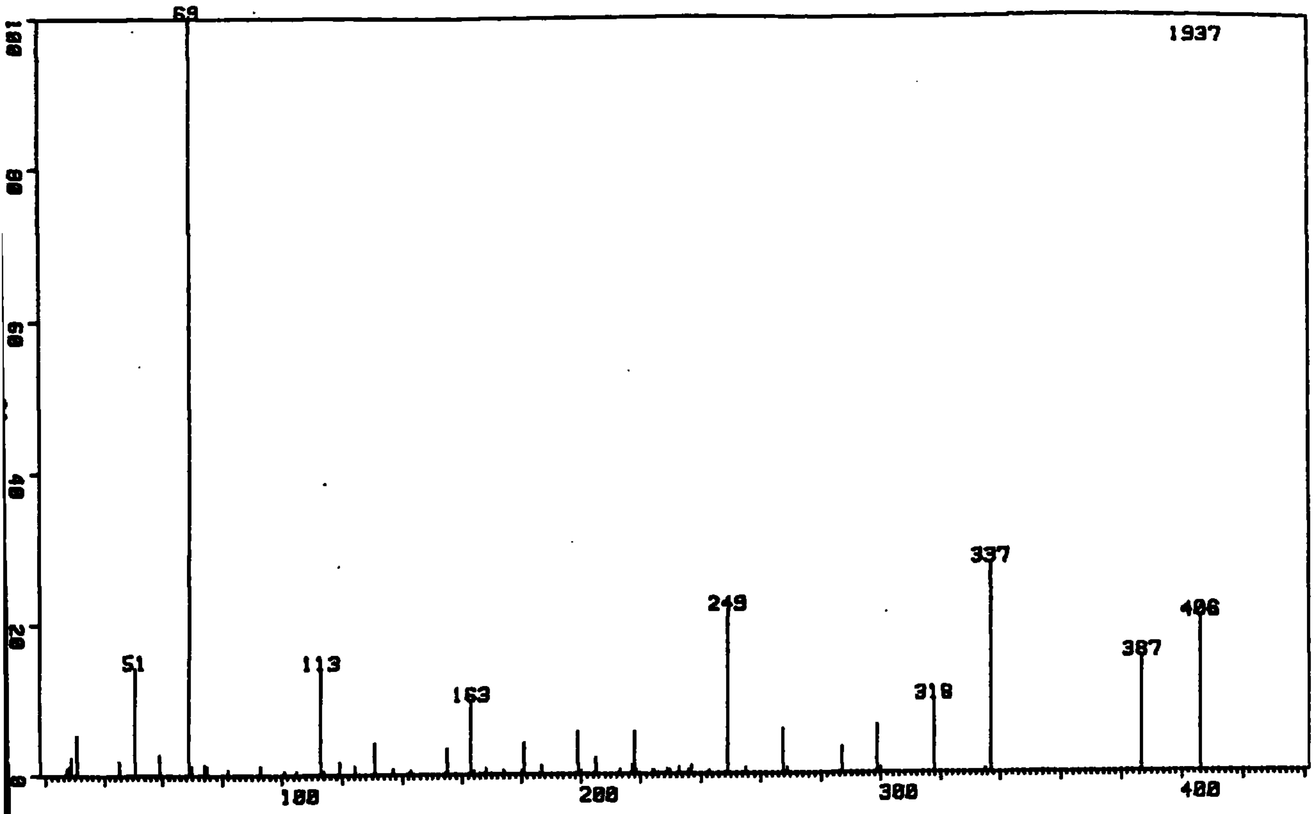
13-FEB-84
4:56



PEAK NO.	MASS	%HT. BASE
1	28.12	5.10
2	30.91	0.49
3	32.00	0.88
4	43.11	0.59
5	49.87	0.27
6	50.94	23.30
7	52.03	0.42*
8	58.08	0.29
9	68.95	100.00*
0	69.13	2.32*
1	69.86	1.90
2	75.04	0.68*
3	81.96	0.61*
4	93.03	0.24
5	95.02	0.78
6	100.94	0.39*
7	106.04	0.46*
8	112.01	0.22*
9	113.00	7.89*
0	114.00	0.32*
1	118.94	2.34*
2	124.99	0.46
3	130.89	1.20*
4	131.97	0.34*
5	136.98	1.44
6	142.95	0.42
7	144.98	0.32
8	149.91	1.15*
[illegible]	[illegible]	[illegible]
30	155.97	0.83*
31	156.97	0.37
32	162.96	2.44*
33	167.96	0.61*
34	168.94	0.81*
35	174.97	2.12*
36	180.90	3.54*
37	181.93	0.32
38	186.09	0.37*
39	186.91	2.42*
40	187.94	0.42*
41	198.88	1.64*
42	199.90	3.49*
43	200.95	0.44*
44	204.93	1.12*
45	205.93	2.44
46	206.97	0.46*
47	213.00	0.29
48	213.69	0.27*
49	217.94	1.95*
50	218.92	2.49*
51	219.94	0.24
52	223.93	0.39*
53	224.91	13.55*
54	225.94	0.95
55	230.92	1.03
56	231.95	0.27*
57	236.91	0.76*
58	237.90	0.46*
59	242.89	0.44*
60	248.89	4.47*
61	249.87	1.76*
62	250.96	0.27
63	255.00	0.39*
64	256.97	0.27
65	266.83	1.10*
66	268.89	28.64*
67	269.86	4.03*
68	274.97	16.87*
69	275.71	4.91*
70	287.03	4.62*
71	288.09	0.71
72	293.02	0.24
73	299.01	1.10*
74	300.10	0.29*
75	307.07	0.76
76	318.76	8.11*
77	319.72	4.18*
78	337.08	8.25*
79	338.08	19.02*
80	338.98	2.91
81	357.00	42.52*
82	358.06	4.42
83	387.03	1.78
84	387.93	0.27
85	406.96	17.97*
86	407.89	2.71
87	426.08	5.01*

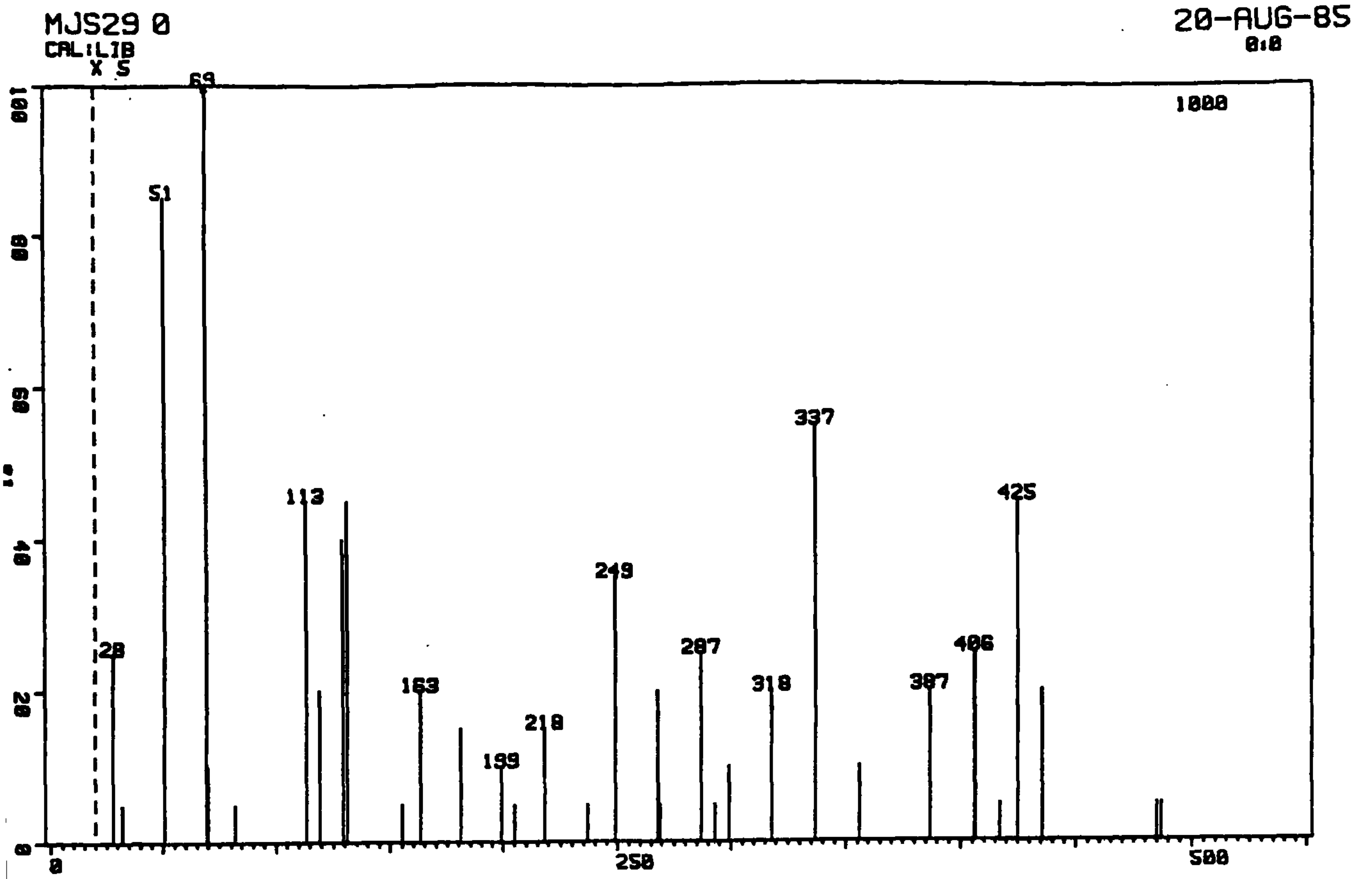
MJS238 15
CAL:CALM25

25-SEP-84
2:45



2

PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.17	0.93	36	217.93	5.52
2	28.06	1.24	37	218.91	0.52
3	28.96	2.43	38	223.94	0.62
4	30.85	5.21	39	224.97	0.46
5	45.15	1.86	40	228.90	0.67
6	50.94	14.20	41	229.96	0.52
7	59.01	2.68	42	232.93	0.98
8	68.96	100.00	43	235.89	0.62
9	69.91	1.34	44	236.95	1.19
10	74.14	1.39	45	242.92	0.46
11	75.05	1.24	46	248.96	21.73
12	81.97	0.72	47	254.95	0.88
13	93.00	1.19	48	267.37	5.89
14	100.91	0.57	49	268.93	0.77
15	104.99	0.62	50	286.93	3.41
16	112.96	14.04	51	298.75	6.30
17	113.99	0.46	52	299.90	0.72
18	118.92	1.76	53	317.83	9.65
19	124.00	1.19	54	335.15	0.46
20	130.92	4.08	55	337.06	27.88
21	136.97	0.83	56	386.93	15.28
22	142.94	0.52	57	406.00	20.55
23	154.98	3.36			
24	162.97	9.65			
25	164.00	0.52			
26	167.96	0.83			
27	174.01	0.57			
28	179.93	0.57			
29	180.93	4.08			
30	186.97	1.19			
31	198.91	5.63			
32	199.96	0.52			

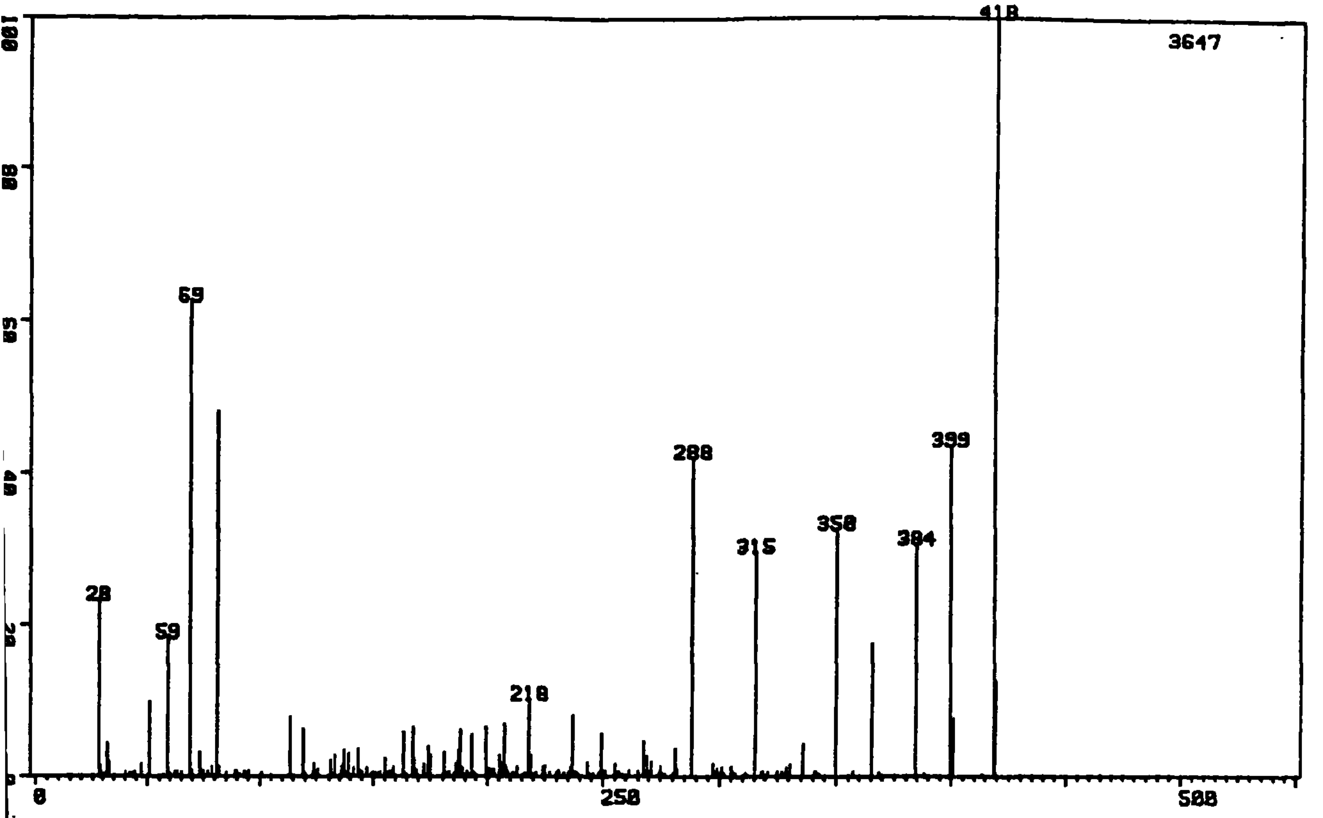


3

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
44.10	0.85	175.08	0.34	297.02	0.32
45.15	0.37	178.98	0.51	298.06	0.51
49.87	0.24	181.01	3.37	299.05	2.03
50.94	16.78	182.04	0.32	300.04	0.32
68.98	100.00	186.07	0.27	303.00	0.37
69.47	0.22	187.07	0.95	305.04	0.63
69.91	1.61	193.06	0.29	306.06	0.34
75.06	0.76	199.02	2.30	317.87	3.59
78.88	0.29	200.01	0.39	325.13	0.37
80.84	0.56	205.06	1.20	337.11	10.70
82.01	0.95	206.09	0.29	339.04	0.39
85.05	0.27	213.05	0.39	342.97	0.27
93.05	0.66	217.07	0.81	346.94	0.76
95.11	0.37	218.05	2.98	348.95	0.88
99.97	0.37	219.02	0.66	352.94	0.37
101.02	0.49	224.05	0.66	356.02	1.83
105.07	0.24	225.08	0.71	366.02	0.27
110.93	0.66	229.05	0.63	367.00	0.39
113.06	9.21	231.03	0.42	368.03	0.32
114.10	0.29	236.03	0.42	375.07	0.37
119.01	3.69	237.06	1.15	385.04	0.51
124.07	0.61	243.08	0.68	387.03	3.98
128.95	8.47	248.97	7.16	396.93	0.56
130.95	8.99	250.00	0.83	398.94	0.66
132.06	0.44	255.06	0.56	405.88	5.30
137.08	0.51	267.58	4.32	416.74	1.20
143.09	0.42	269.01	1.39	419.05	0.32
145.09	0.34	275.06	0.83	425.17	9.13
149.09	0.22	281.00	0.27	436.05	3.76
155.08	1.34	286.91	4.66	485.02	0.88
163.07	4.40	288.07	0.49	486.94	0.90

MS210X 28
CAL:CALM17

21-SEP-84
S:4

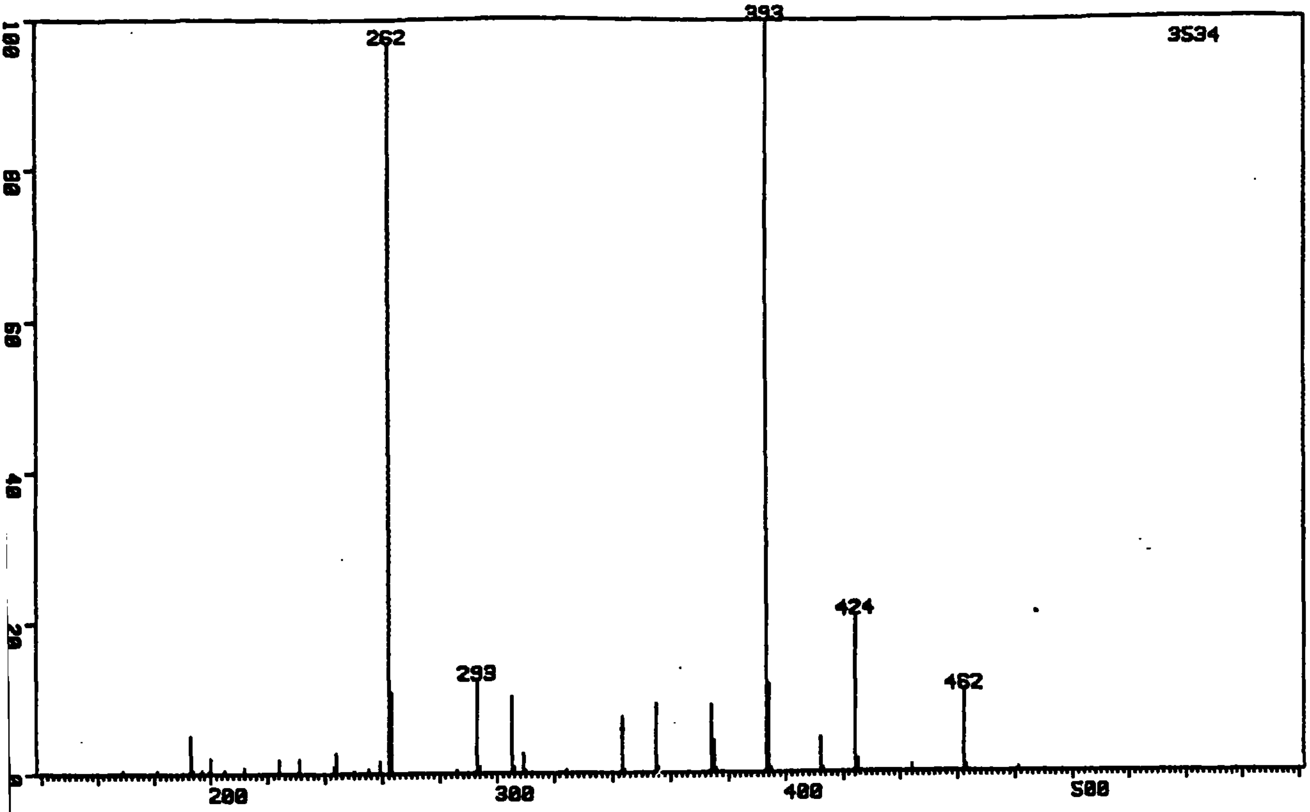


4

PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
112	233.10	0.44	147	300.09	0.30
113	235.11	0.47	148	301.17	1.32
114	236.10	1.15	149	302.10	0.41
115	237.09	8.20	150	305.07	1.32
116	238.08	0.85	151	306.10	0.63
117	239.06	0.41	152	307.12	0.33
118	243.09	1.89	153	311.06	0.44
119	244.12	0.27	154	312.01	0.27
120	245.11	0.30	155	315.22	29.78
121	246.14	0.38	156	318.01	0.44
122	248.13	0.44	157	319.06	0.58
123	249.08	5.68	158	321.05	0.58
124	250.08	0.77	159	325.05	0.58
125	251.12	0.80	160	326.99	0.58
126	255.08	1.54	161	327.97	0.30
127	256.11	0.47	162	328.99	1.18
128	257.09	0.71	163	330.67	1.62
129	258.43	0.25	164	335.87	4.36
130	261.19	0.82	165	341.19	0.77
131	265.07	0.66	166	342.19	0.33
132	267.57	4.61	167	343.11	0.25
133	269.04	2.69	168	349.71	32.77
134	270.04	0.74	169	357.24	0.52
135	271.06	1.97	170	365.30	17.63
136	274.07	0.41	171	368.15	0.38
137	275.09	1.40	172	384.33	30.68
138	276.11	0.33	173	388.22	0.36
139	277.12	0.36	174	399.16	43.62
140	280.11	0.36	175	400.69	7.70
141	281.12	3.67	176	413.46	0.27
142	282.15	1.01	177	418.12	100.00
143	287.83	42.20	178	419.30	12.67

MS992N 39
CAL:CALN16

24-MAY-85
1:59

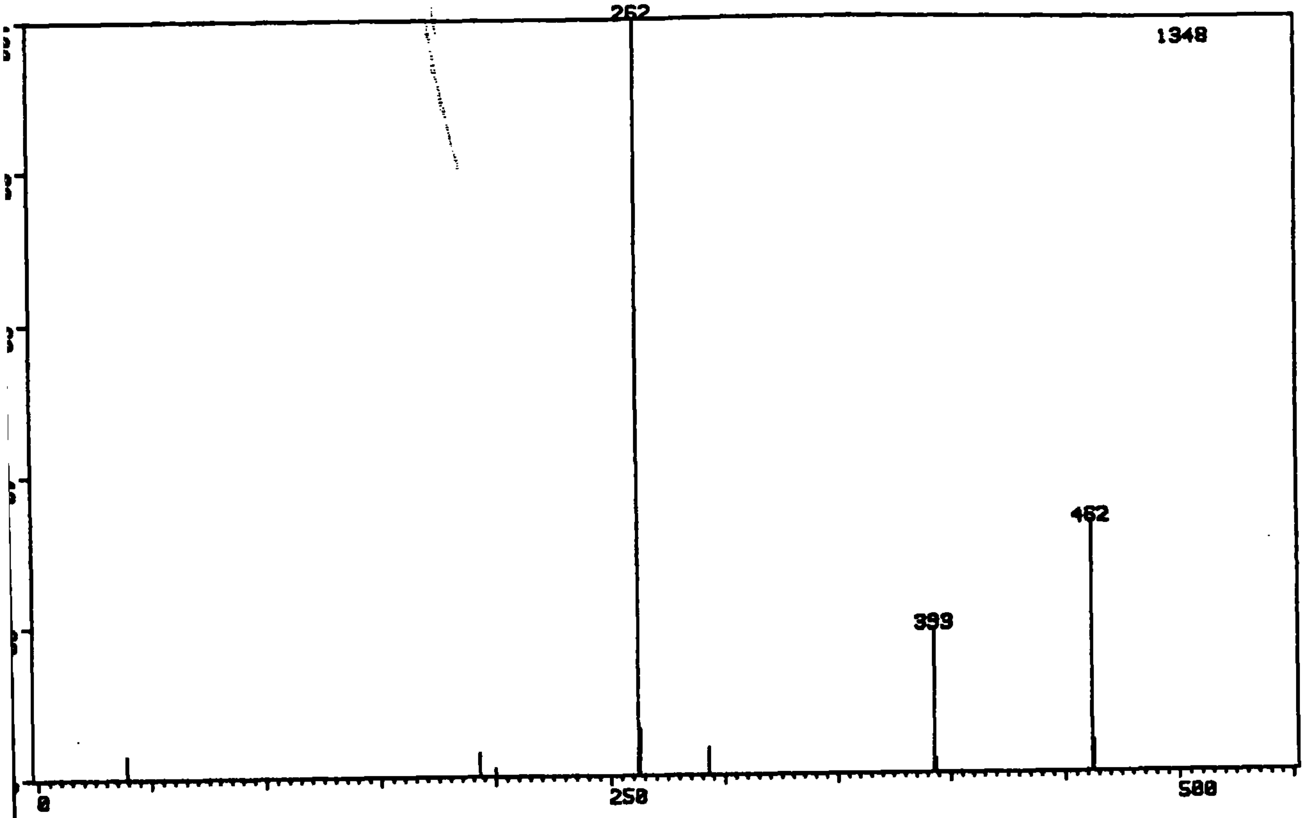


5

MASS	%HT. BASE
196.97	0.40
199.96	2.01
205.04	0.40
212.02	0.82
224.04	1.87
231.00	1.95
243.04	0.88
244.06	2.66
250.05	0.31
255.09	0.54
259.01	1.61
262.02	96.86
263.05	10.72
286.06	0.37
293.05	12.37
294.05	0.93
305.04	10.13
306.04	0.88
309.03	2.57
310.00	0.31
324.09	0.37
343.10	7.50
344.10	0.42
355.10	9.20
356.07	0.76
374.10	8.97
375.06	4.24
376.07	0.57
393.04	100.00
394.07	11.74
395.06	0.65
412.07	4.58
413.03	0.59
424.06	20.97
425.09	1.75
444.07	0.88
462.10	10.84
463.13	0.85

MS79NX 52
CAL:CALN16

02-JUL-85
2:38

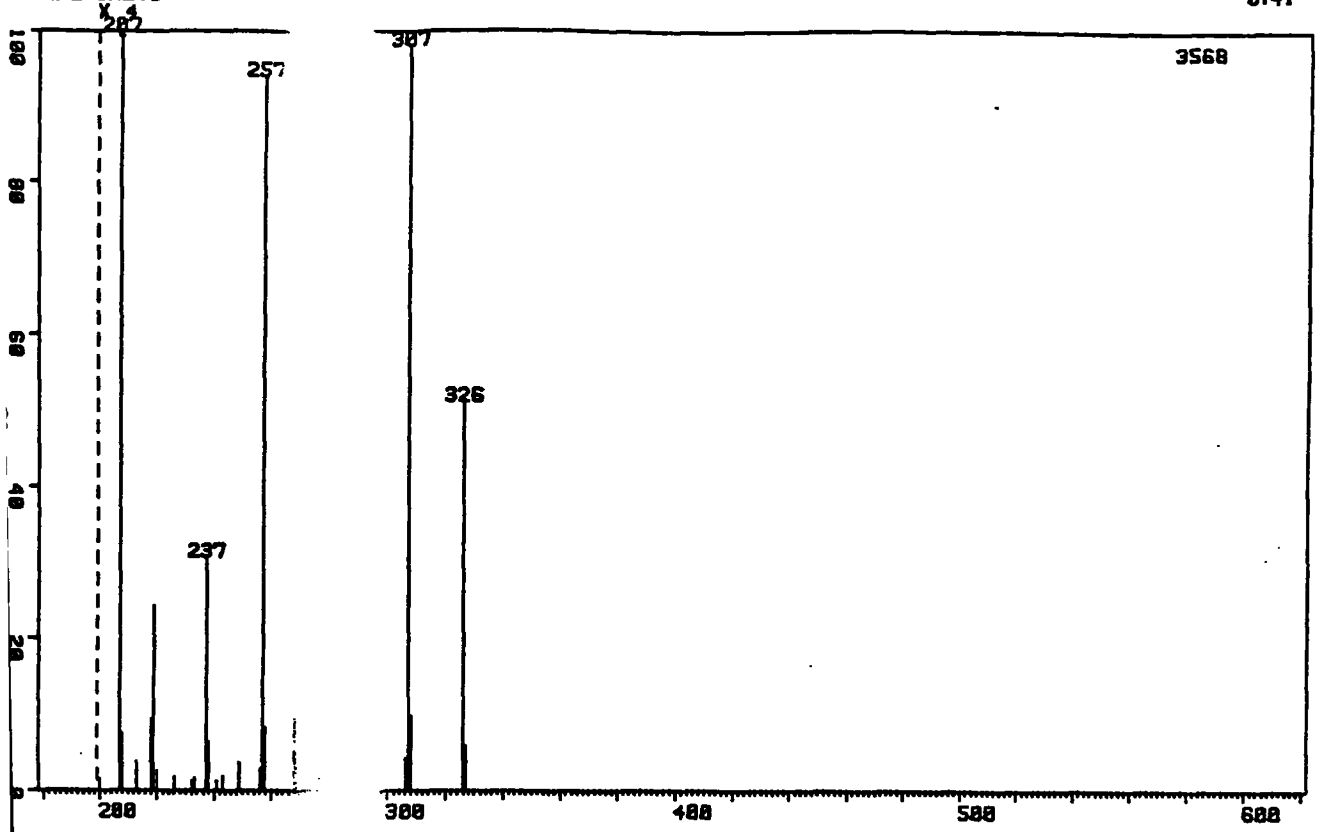


6

MASS	%HT. BASE
39.00	3.04
193.02	3.19
199.96	1.11
261.97	100.00
263.00	6.16
293.00	3.71
392.98	19.07
394.01	1.85
461.97	33.16
462.96	4.08

MS234X 4
CAL:CALTS

21-SEP-84
8:41



7

PE N	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
[illegible]	60.93	1.11	60	149.97	1.59
[illegible]	62.00	0.52	61	157.03	8.71
[illegible]	63.03	0.66	62	158.02	0.66
[illegible]	64.06	1.21	63	168.00	1.87
[illegible]	68.02	2.39	64	168.98	4.53
[illegible]	68.96	100.00	65	183.01	1.42
[illegible]	69.91	1.28	66	187.02	1.63
[illegible]	74.06	1.90	67	188.01	1.80
[illegible]	75.07	20.71	68	207.02	11.07
[illegible]	76.07	1.11	69	208.00	1.11
[illegible]	78.97	0.80	70	218.99	4.39
[illegible]	79.92	2.32	71	237.01	1.00
[illegible]	80.97	2.63	72	257.03	5.95
[illegible]	82.00	0.45	73	258.02	0.93
[illegible]	87.03	2.21	74	286.99	0.80
[illegible]	88.01	8.02	75	307.02	2.84
[illegible]	88.98	0.59	76	326.01	1.59
[illegible]	93.02	4.50			
[illegible]	94.04	1.45			
[illegible]	95.06	6.60			
[illegible]	98.97	5.19			
[illegible]	99.92	3.53			
[illegible]	06.04	1.28			
[illegible]	07.03	0.66			
[illegible]	13.02	10.13			
[illegible]	14.03	0.38			
[illegible]	17.02	1.42			
[illegible]	18.00	0.93			
[illegible]	18.97	18.64			
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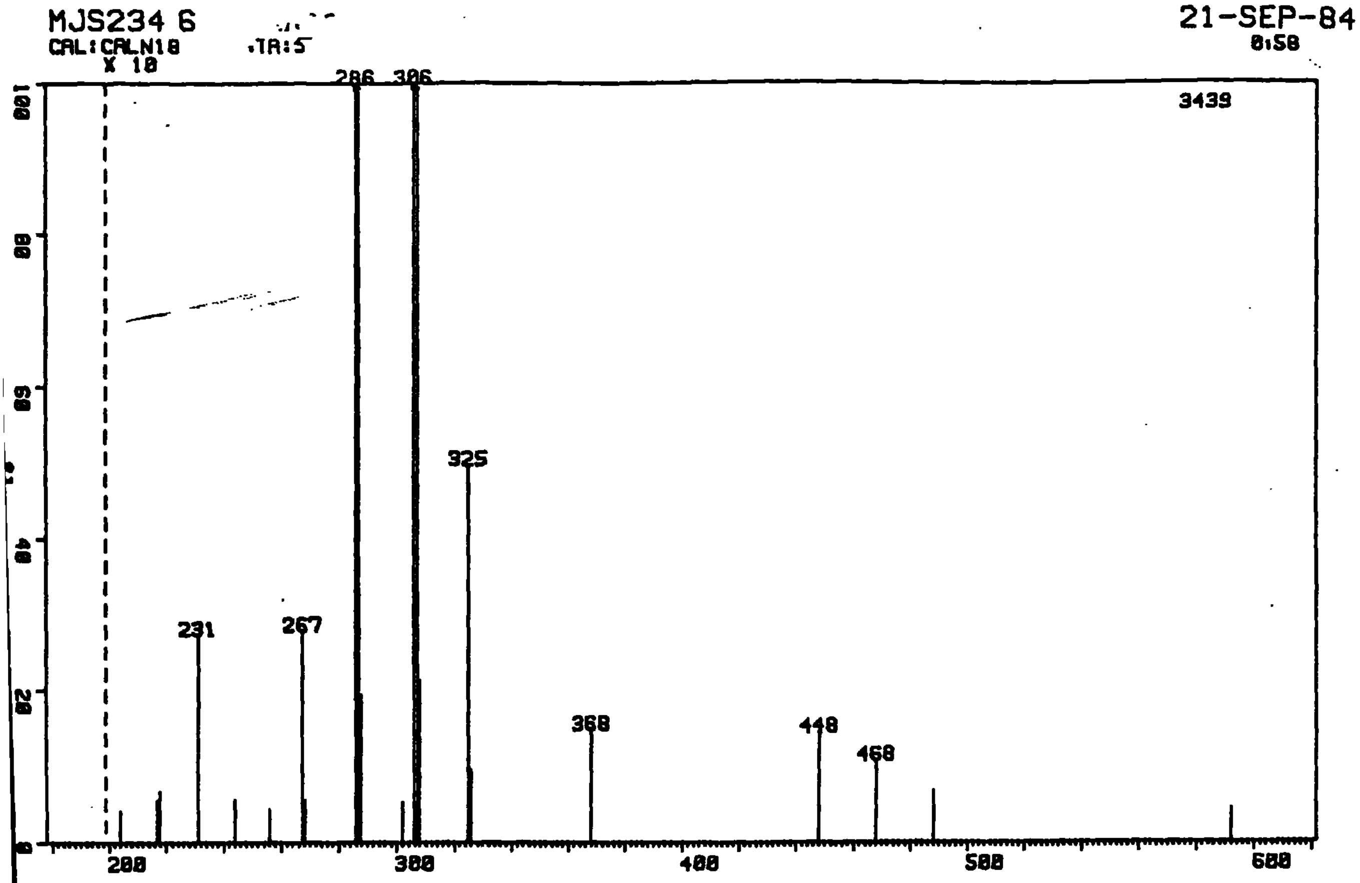
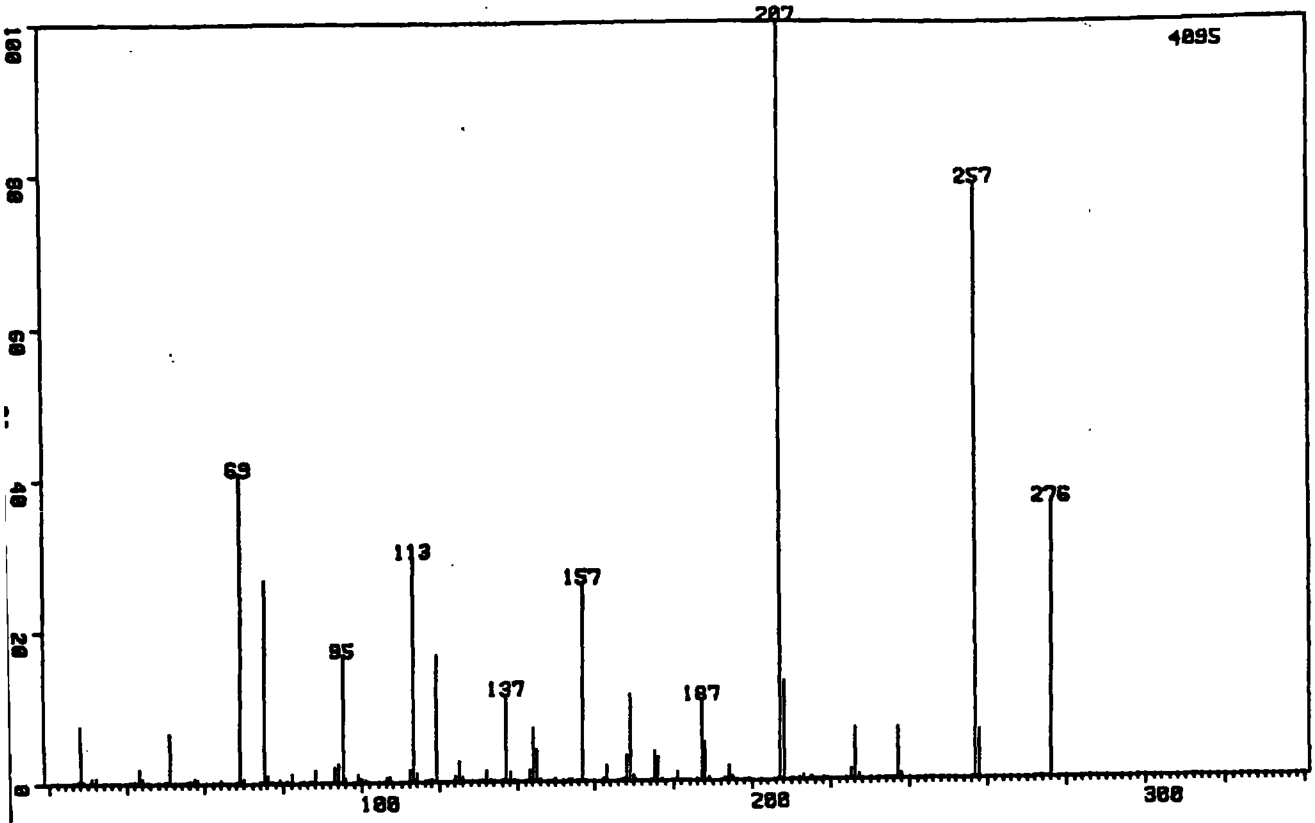


8

MASS	%HT. BASE
167.09	0.73
184.06	0.85
187.05	0.56
188.02	0.50
193.01	100.00
194.01	8.43
203.94	0.50
216.97	0.68
217.95	0.41
231.10	2.85
244.09	0.56
267.47	3.14
268.63	0.41
286.09	97.91
287.09	36.97
288.09	2.09
306.05	97.30
307.09	46.87
308.07	2.29
317.06	0.35
325.09	4.91
326.11	0.56
333.09	0.62
368.06	1.82
448.11	1.38
468.19	1.18
488.07	0.79
592.08	0.56

MJS48 30
CAL:CALM2S

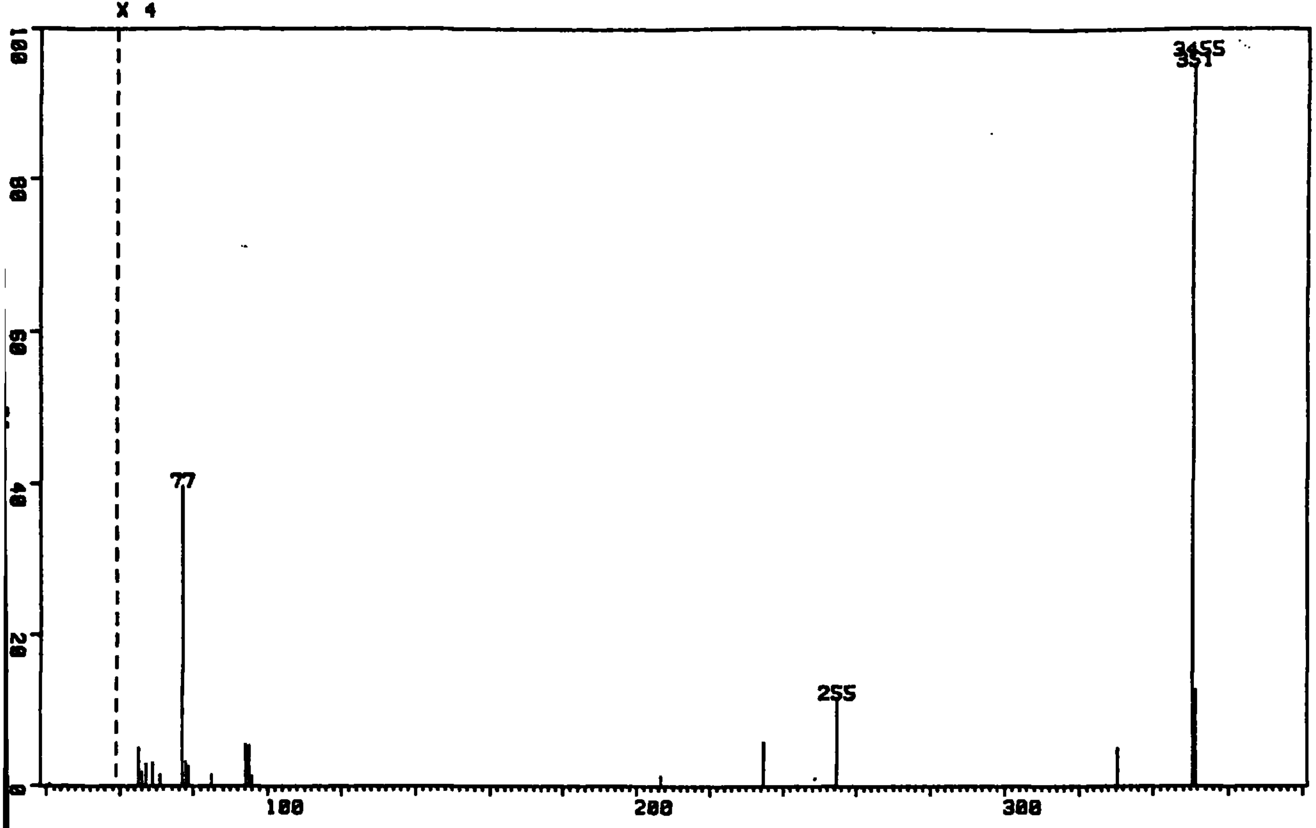
02-NOV-84
4:27



9

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
31.95	0.85	112.05	1.73	170.06	0.93
40.97	0.24	112.43	0.24	175.10	3.88
42.03	0.27	113.07	29.67	176.08	3.20
43.09	1.88	113.57	0.22	177.05	0.32
44.10	0.73	114.09	1.17	181.00	1.15
45.14	0.22	117.05	0.22	186.04	0.24
49.88	0.29	118.09	0.32	187.03	10.67
50.95	6.57	119.07	16.65	187.88	5.13
55.16	0.27	124.06	0.85	189.10	0.46
56.13	0.39	125.09	2.64	193.12	0.37
57.10	0.76	126.08	0.73	194.10	1.95
58.07	0.61	131.04	0.27	195.09	0.61
64.10	0.46	132.07	1.47	199.03	0.32
68.67	0.22	133.09	0.32	202.50	0.22
68.99	40.71	136.09	0.22	206.97	100.00
69.94	0.51	136.61	0.20	208.07	13.14
74.09	0.22	137.07	11.36	209.91	0.22
75.10	26.67	138.07	1.34	210.63	0.22
76.10	1.00	139.05	0.22	212.04	0.27
77.09	0.24	143.07	1.44	213.09	0.56
79.00	0.37	144.07	7.06	215.09	0.44
81.01	0.29	145.10	4.25	217.04	0.27
82.03	1.17	146.10	0.27	218.13	0.37
85.06	0.29	150.02	0.37	219.04	0.27
87.07	0.27	153.11	0.22	225.07	1.39
88.04	1.56	153.99	0.22	226.10	6.81
93.06	2.05	154.23	0.24	227.13	0.66
94.07	2.54	156.94	26.01	237.06	6.81
95.10	16.61	162.06	0.39	238.05	0.78
96.10	0.66	163.09	2.12	256.95	78.68
99.01	1.07	167.05	0.24	276.13	36.48

MS662C 139 24-MAY-85
CAL:CALT23 6:57

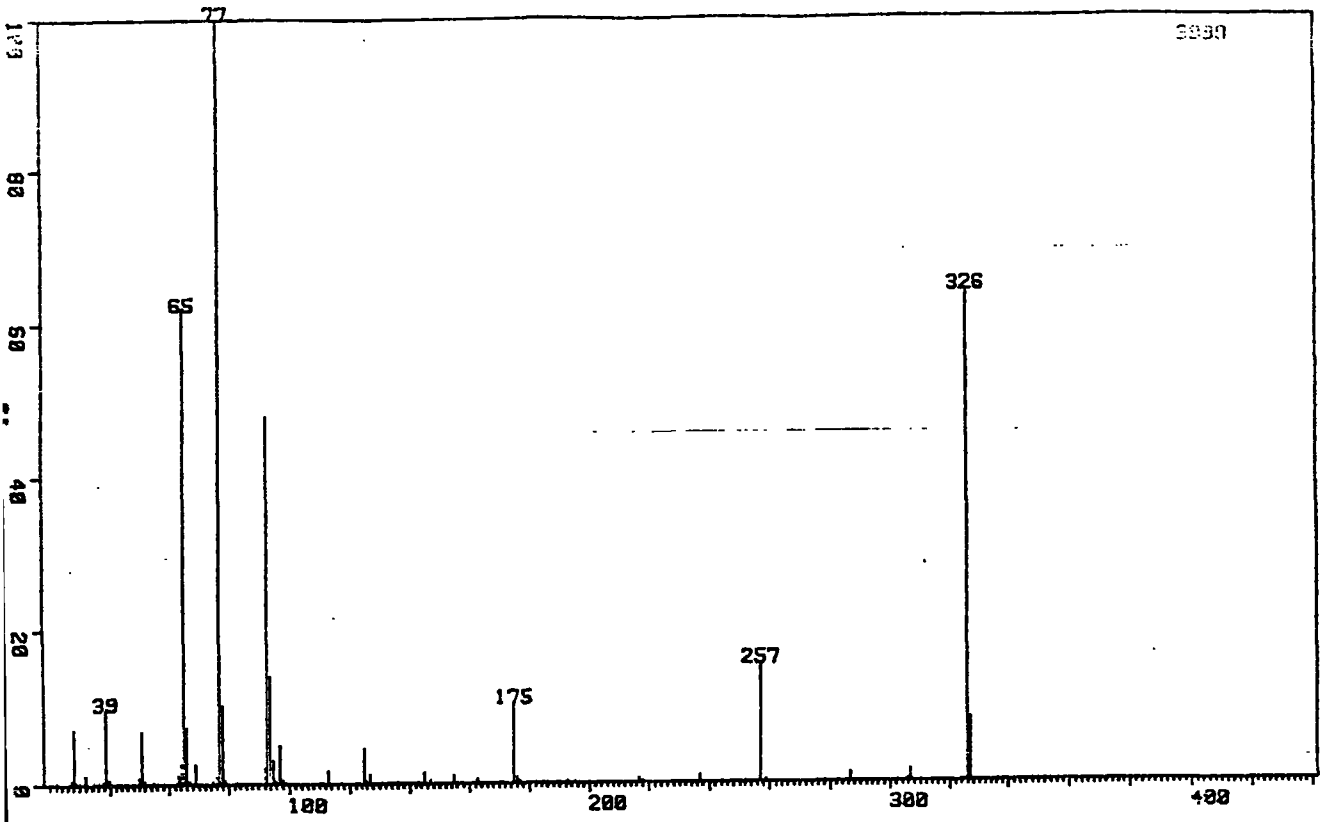


10

MASS	%HT. BASE
65.02	1.13
66.03	0.43
67.01	0.67
68.93	0.69
70.94	0.35
76.97	8.91
77.94	0.75
78.92	0.61
85.04	0.35
93.95	1.24
94.96	1.22
95.95	0.32
206.70	0.32
234.69	1.33
254.65	2.60
330.55	1.13
350.51	21.39
351.54	2.87

MS10SX 68
CAL:CALM30

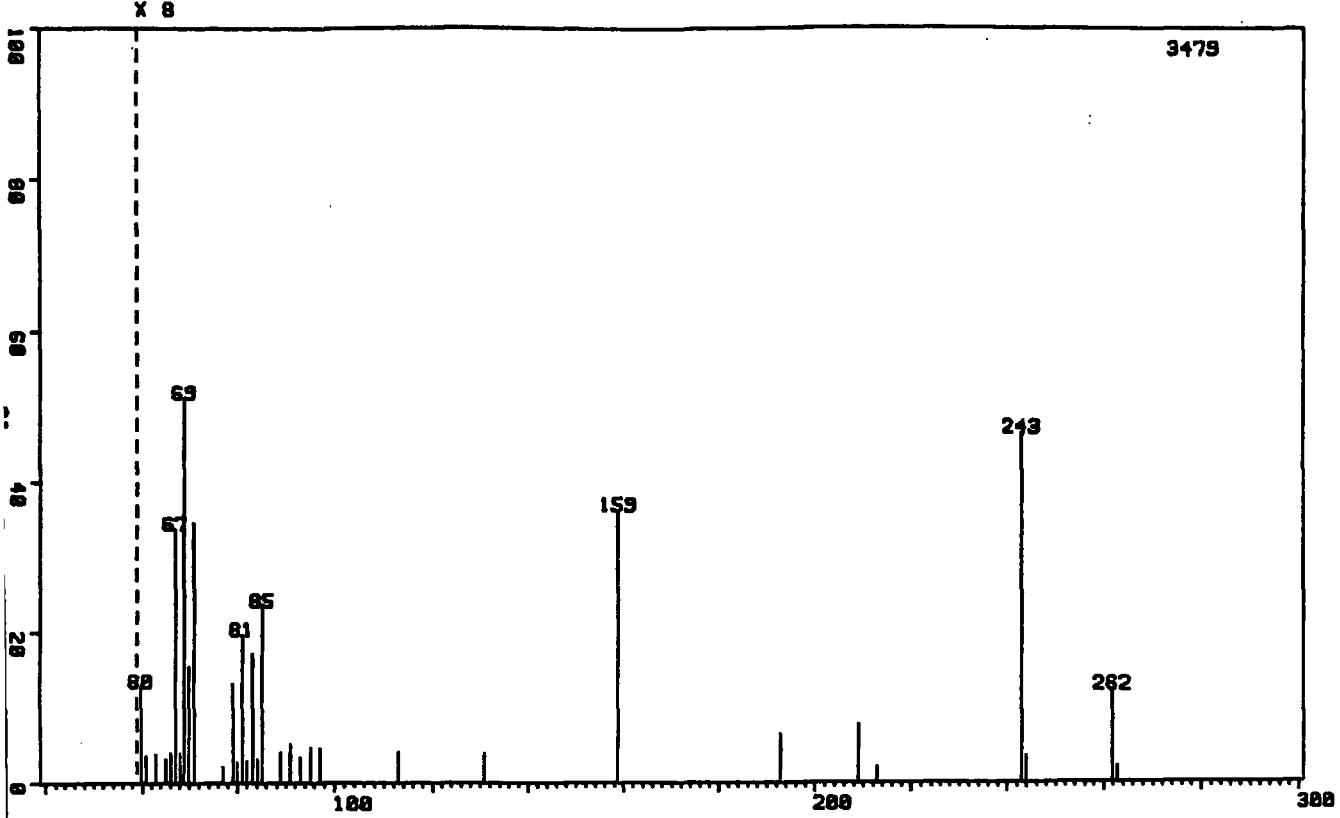
26-JUN-85
11:16



MASS	%HT. BASE
28.13	7.18
28.99	0.28
32.01	1.20
38.08	0.38
39.00	9.60
39.89	0.60
49.89	1.05
50.96	6.93
52.04	0.48
55.11	0.30
63.06	1.25
64.10	2.65
65.09	61.79
66.08	7.40
67.08	0.38
68.93	2.63
75.05	0.58
76.07	1.08
77.05	100.00
77.46	0.25
77.61	0.23
77.69	0.23
78.03	10.35
78.98	0.50
83.03	0.28
91.98	2.20
92.99	47.94
94.01	14.03
95.01	3.13
96.01	0.35
97.00	5.05
122.92	0.23
124.96	4.55
125.95	0.43
126.96	1.28
135.96	0.23
142.93	0.28
144.93	1.45
146.94	0.48
154.93	1.13
162.84	0.48
170.80	0.25
174.91	10.38
175.92	0.93
176.90	0.23
192.84	0.28
216.85	0.65
236.85	0.98
256.96	15.43
258.81	0.33
286.80	1.15
305.81	0.33
306.83	1.58
325.79	64.07
326.99	8.28

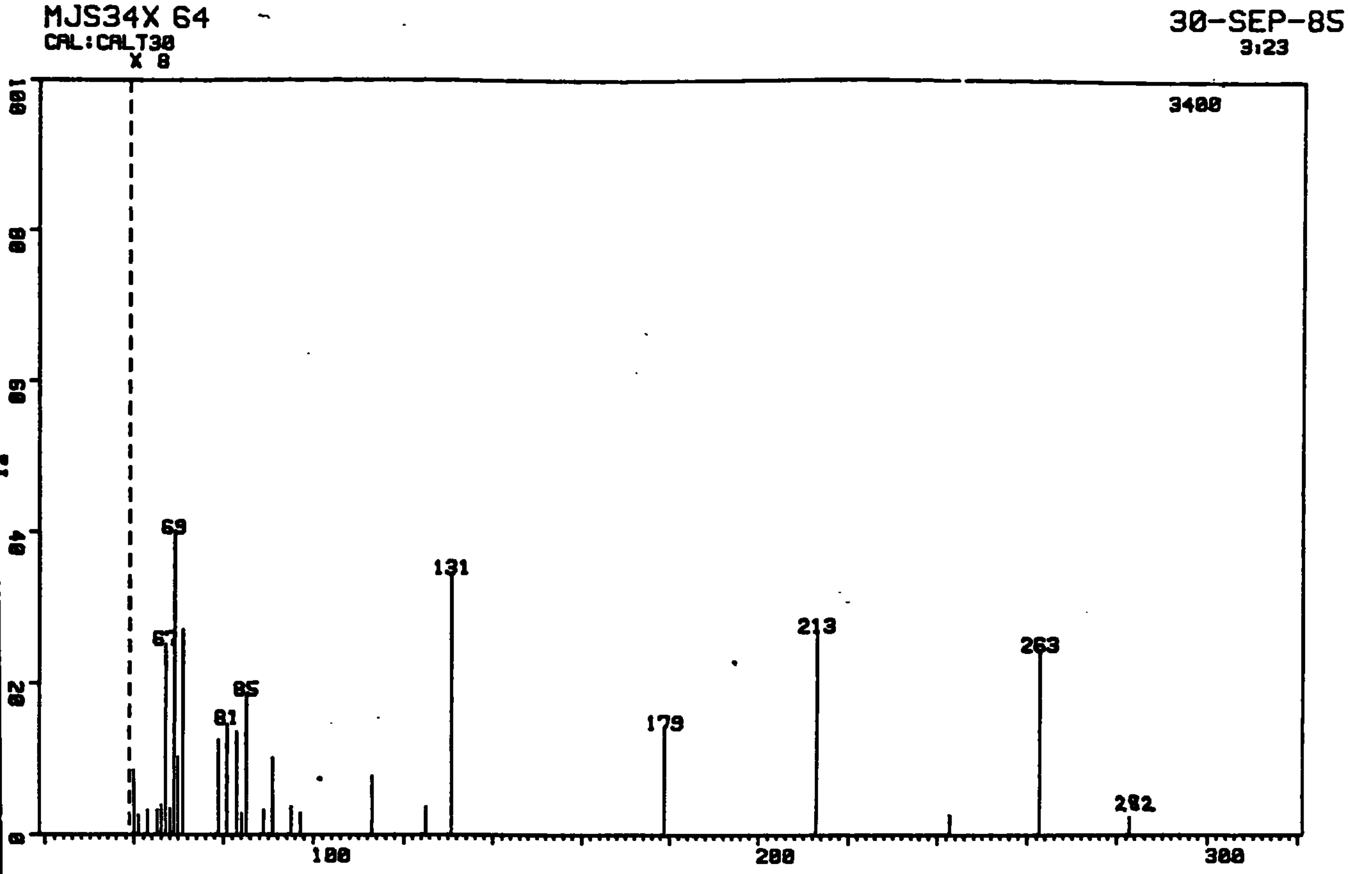
MJS34X 63
CAL:CALT30

30-SEP-85
3:20



12

MASS	%HT. BASE
67.02	4.51
67.99	0.55
68.88	0.32
68.95	6.81
69.89	2.07
70.97	4.63
77.01	0.29
78.95	1.75
79.90	0.37
80.94	2.62
82.00	0.40
83.03	2.30
84.06	0.43
85.07	3.13
88.94	0.55
90.86	0.69
90.96	0.60
93.03	0.46
95.07	0.63
97.06	0.60
112.93	0.55
130.87	0.52
158.83	4.83
192.88	0.86
208.84	1.03
212.92	0.29
242.88	6.18
243.89	0.49
261.83	1.64
262.85	0.29

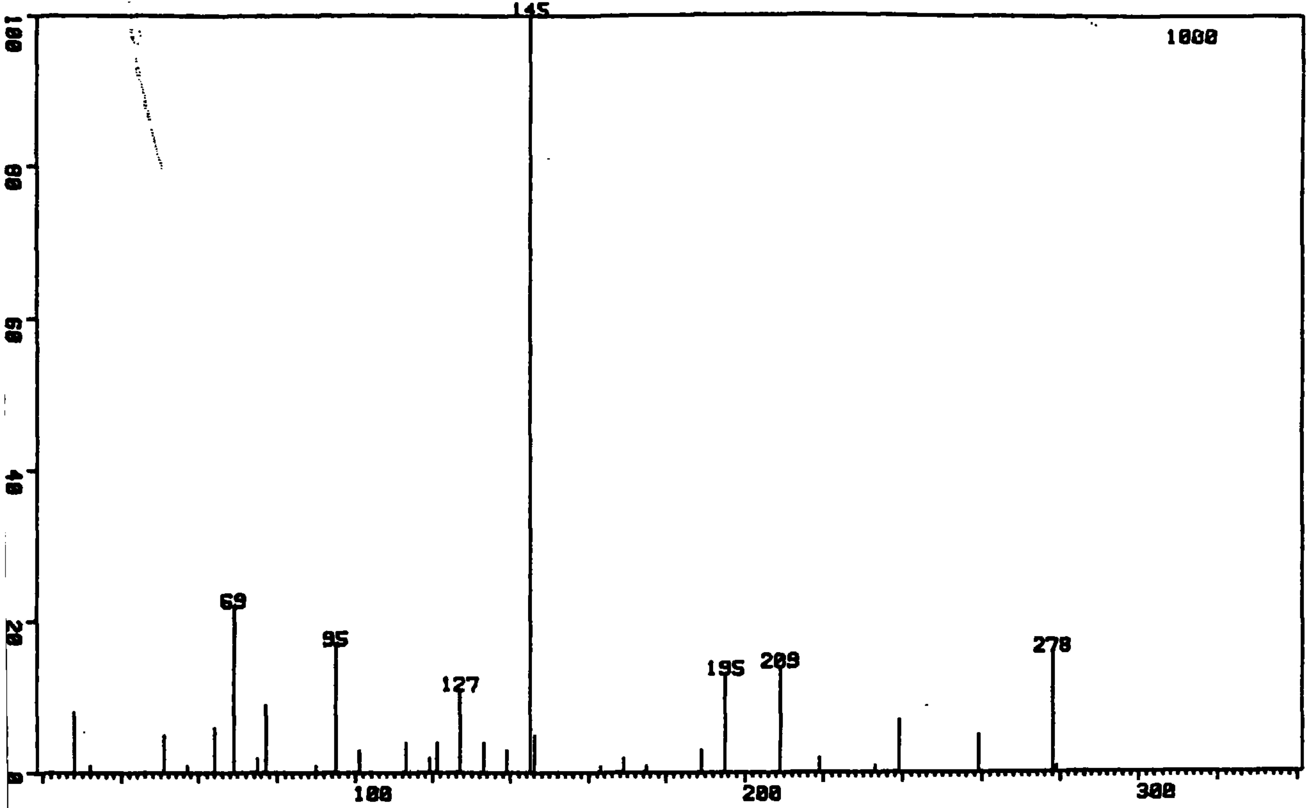


13

MASS	%HT. BASE
60.92	0.35
62.98	0.44
65.03	0.44
66.03	0.53
67.01	3.35
67.98	0.47
68.88	0.35
68.94	5.32
69.89	1.38
70.97	3.62
78.94	1.68
80.91	1.97
83.02	1.82
84.05	0.38
85.07	2.47
88.94	0.44
90.85	1.35
90.95	0.56
95.07	0.50
97.06	0.38
112.92	1.03
124.95	0.50
130.85	4.62
178.82	1.88
212.84	3.59
242.83	0.35
262.82	3.26
282.82	0.32

MJS 0
CAL:LIB

25-OCT-85
0:0

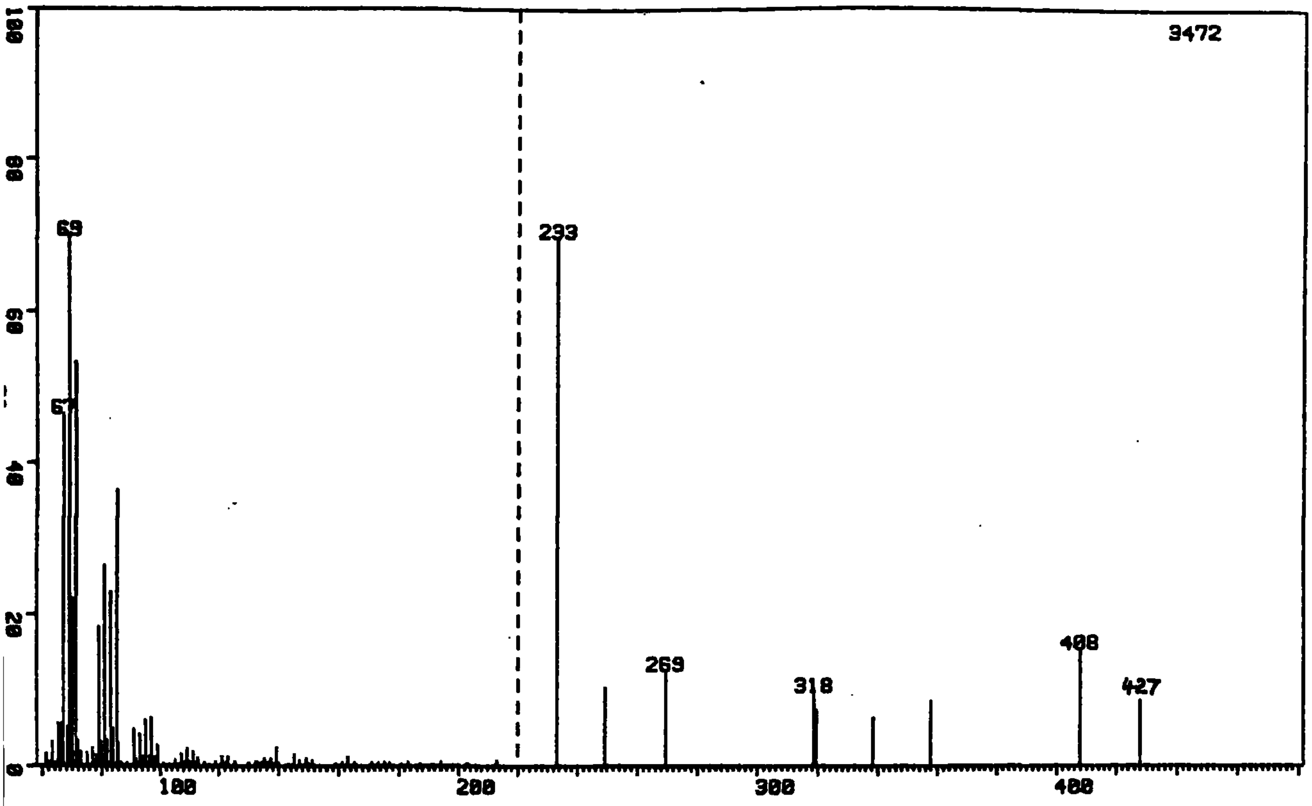


14

MASS	%HT. .BASE
28.00	8.00*
32.00	1.00*
51.00	5.00*
57.00	1.00*
64.00	6.00*
69.00	22.00*
75.00	2.00*
77.00	9.00*
90.00	1.00*
95.00	17.00*
101.00	3.00*
113.00	4.00*
119.00	2.00*
121.00	4.00*
127.00	11.00*
133.00	4.00*
139.00	3.00*
145.00	100.00*
146.00	5.00*
163.00	1.00*
169.00	2.00*
175.00	1.00*
189.00	3.00*
195.00	13.00*
209.00	14.00*
219.00	2.00*
233.00	1.00*
239.00	7.00*
259.00	5.00*
278.00	16.00*
279.00	1.00*

MJS6X 2
CAL:CALT3

11-OCT-85
0:26

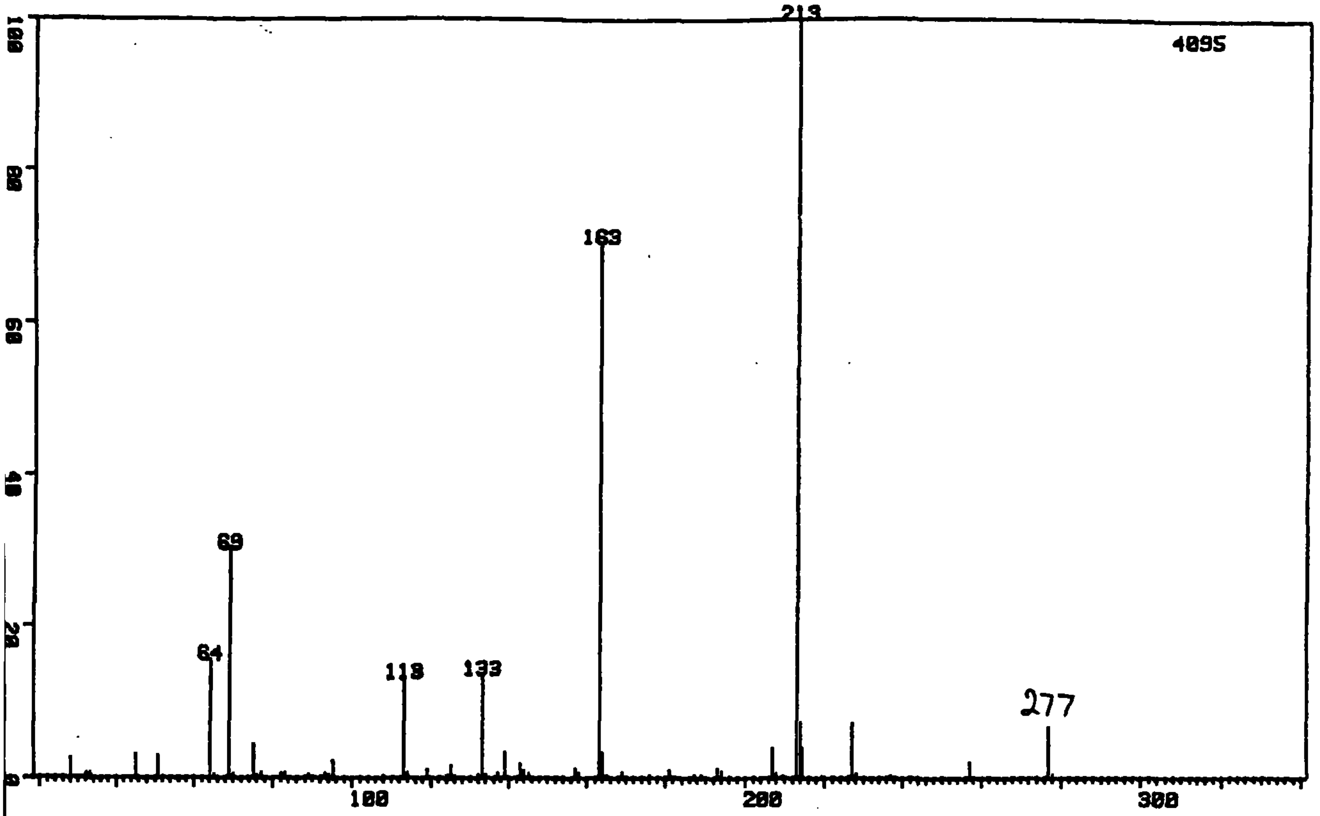


15

MASS	%HT. BASE	MASS	%HT. BASE
67.15	46.63	143.10	0.29
68.13	5.27	145.02	1.53
69.10	70.02	147.11	0.78
70.07	22.09	149.05	1.04
71.14	53.43	150.07	0.40
72.16	3.49	151.10	0.78
73.11	1.93	159.07	0.32
75.13	1.81	161.11	0.52
77.06	2.45	162.97	1.15
78.03	1.44	163.13	0.78
78.99	18.32	165.12	0.43
79.98	3.25	171.03	0.43
81.04	26.47	173.12	0.43
82.09	3.49	175.15	0.55
83.13	22.90	177.11	0.49
84.13	5.04	180.93	0.32
85.11	36.38	183.09	0.52
86.08	3.14	187.10	0.35
86.97	0.40	191.15	0.26
87.02	0.58	194.02	0.63
88.94	0.43	203.19	0.37
90.98	4.87	213.11	0.66
92.03	1.01	233.14	3.49
93.06	4.26	249.13	0.52
94.07	1.30	269.19	0.63
95.08	6.08	318.30	0.49
96.10	1.41	319.30	0.37
97.09	6.39	338.38	0.32
98.07	1.35	357.59	0.43
99.04	2.74	407.68	0.78
101.06	0.43	427.77	0.43

MJS291 20
CAL:CALMG

17-FEB-84
3:33

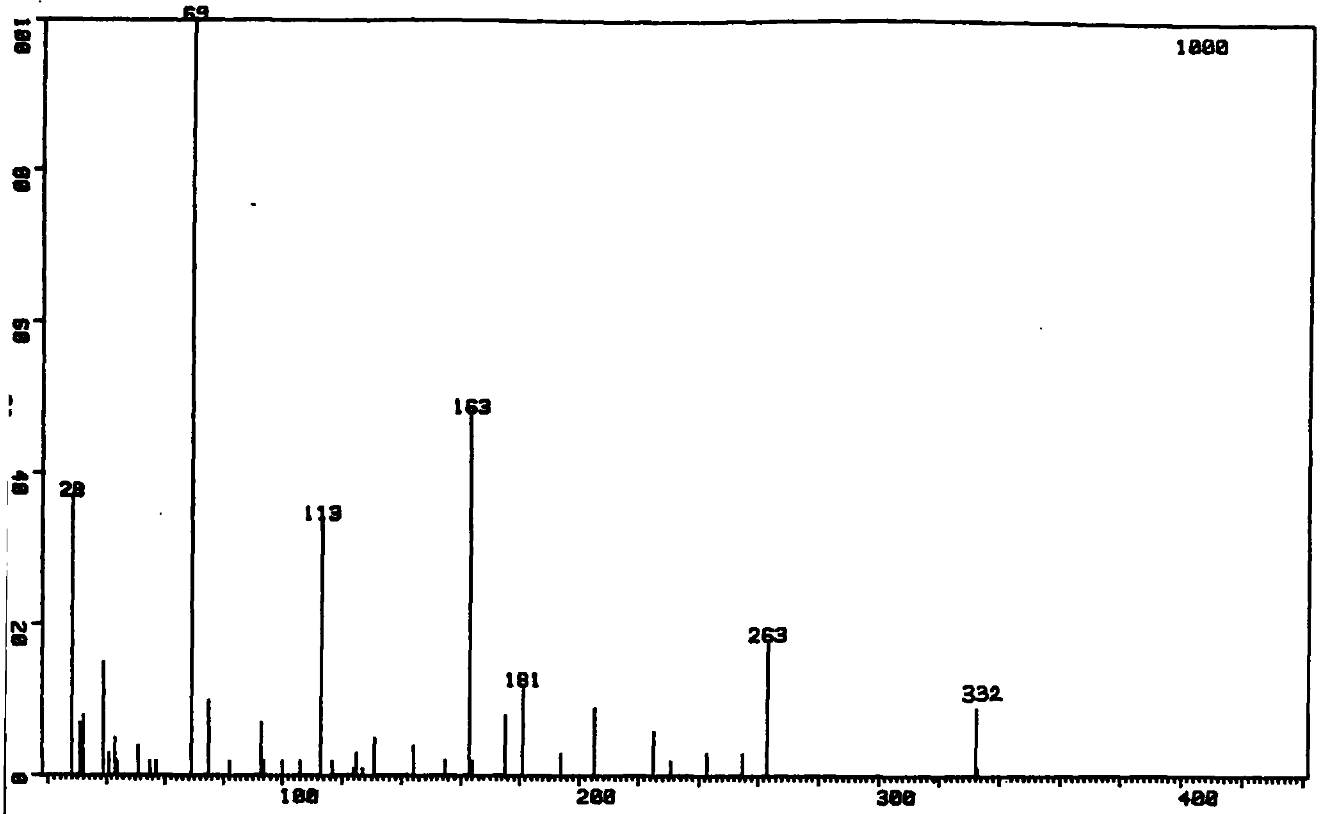


16

MASS	%HT. BASE
28.07	28.80
31.96	5.79
33.07	1.88
45.14	4.49
50.96	5.35
64.11	19.54
68.95	33.14
75.06	8.97
95.04	3.62
113.03	19.39
125.07	1.88
133.04	12.59
138.99	4.78
143.02	2.03
157.06	1.45
163.02	58.47
164.06	2.75
207.08	3.33
213.03	100.00
214.08	6.51
227.07	5.07
257.04	2.17
277.09	4.92

MJS101 0
CAL:LIB

30-SEP-85
0:0

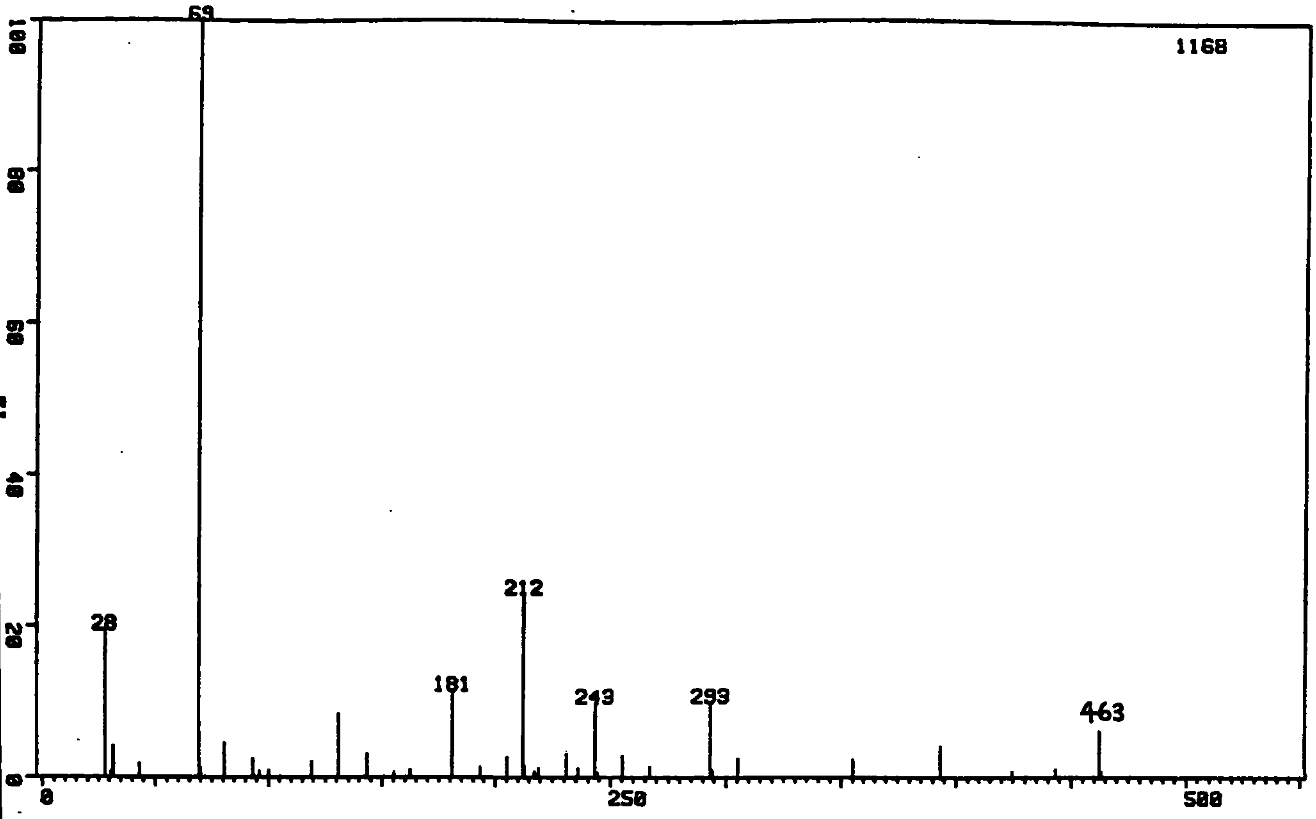


17

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
30.88	7.03	75.08	10.10*	162.91	48.21*
31.99	7.98	76.08	0.42*	163.94	2.09*
37.12	0.64)	77.09	0.31	168.90	0.31*
38.98	1.09	78.98	0.28	173.93	0.33
39.82	15.18	80.96	0.39	174.93	8.29*
39.89	0.36	81.04	0.36	175.94	0.50*
40.97	2.59	82.03	1.48*	180.85	12.14
42.06	0.81	83.13	0.81*	181.93	0.67*
43.12	4.46*	84.11	0.36	185.96	0.33
44.10	2.26	85.13	0.53	192.93	1.31
45.16	0.36	85.99	0.33	193.95	2.76
49.88	0.98	86.98	0.70*	204.91	8.68
50.95	4.05*	90.96	0.50*	205.92	0.78
53.10	0.28	92.96	6.56	211.90	0.36
55.10	0.56*	93.99	2.34*	212.92	1.00
55.15	1.81*	97.06	0.42	224.92	5.64*
56.10	1.20*	97.94	0.25	225.92	0.36*
56.15	0.78*	98.91	0.56*	230.87	2.34
57.14	2.37	99.85	1.70	242.90	3.04
58.07	0.28*	105.04	0.75	243.92	1.03
60.96	0.28*	106.01	2.23*	254.92	2.62*
62.01	0.31	111.95	0.92	262.90	17.94*
63.06	0.45*	112.97	33.59*	263.95	1.03*
65.13	0.42	114.00	1.06*	273.89	1.37*
66.13	0.36*	116.97	2.32	274.95	0.42*
67.12	0.45	118.91	1.40	292.88	0.56
68.03	0.39*	119.00	0.45	293.93	0.25
68.97	100.00*	123.96	1.31	311.89	0.31
69.04	1.31*	124.97	2.96*	312.92	0.47
69.91	1.23	130.90	4.85	331.87	8.90*
69.98	0.78	135.96	1.03	332.90	0.78*

MS31 14
CAL:CALM27

27-AUG-85
2:27

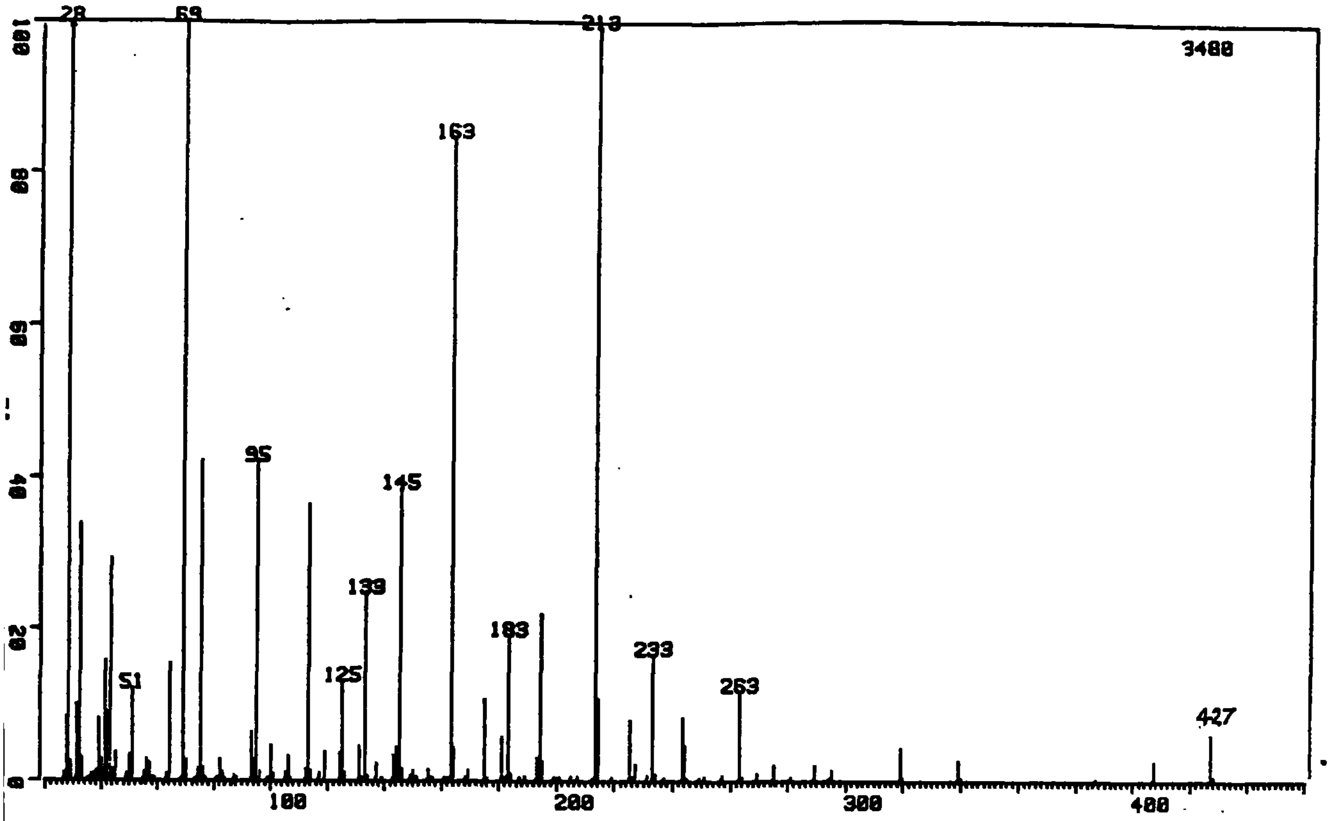


18

MASS	%HT. BASE
27.97	19.61
30.78	0.86
31.92	4.20
43.15	1.80
69.04	100.00
69.99	1.28
80.84	4.54
93.10	2.48
96.21	0.86
100.03	0.94
119.12	2.14
131.14	8.30
143.16	3.08
155.15	0.77
162.08	1.03
181.08	11.56
193.14	1.37
205.16	2.65
212.10	24.32
213.14	1.63
217.09	0.86
219.05	1.28
231.07	3.17
236.12	1.28
243.11	9.93
244.13	0.77
255.06	2.83
267.08	1.46
293.10	10.02
294.12	0.94
305.07	2.57
355.14	2.40
393.20	4.11
424.12	0.86
443.22	1.11
462.19	6.16
463.19	0.86

MJS89X 22
CAL:CAL18

03-JUN-85
1:3

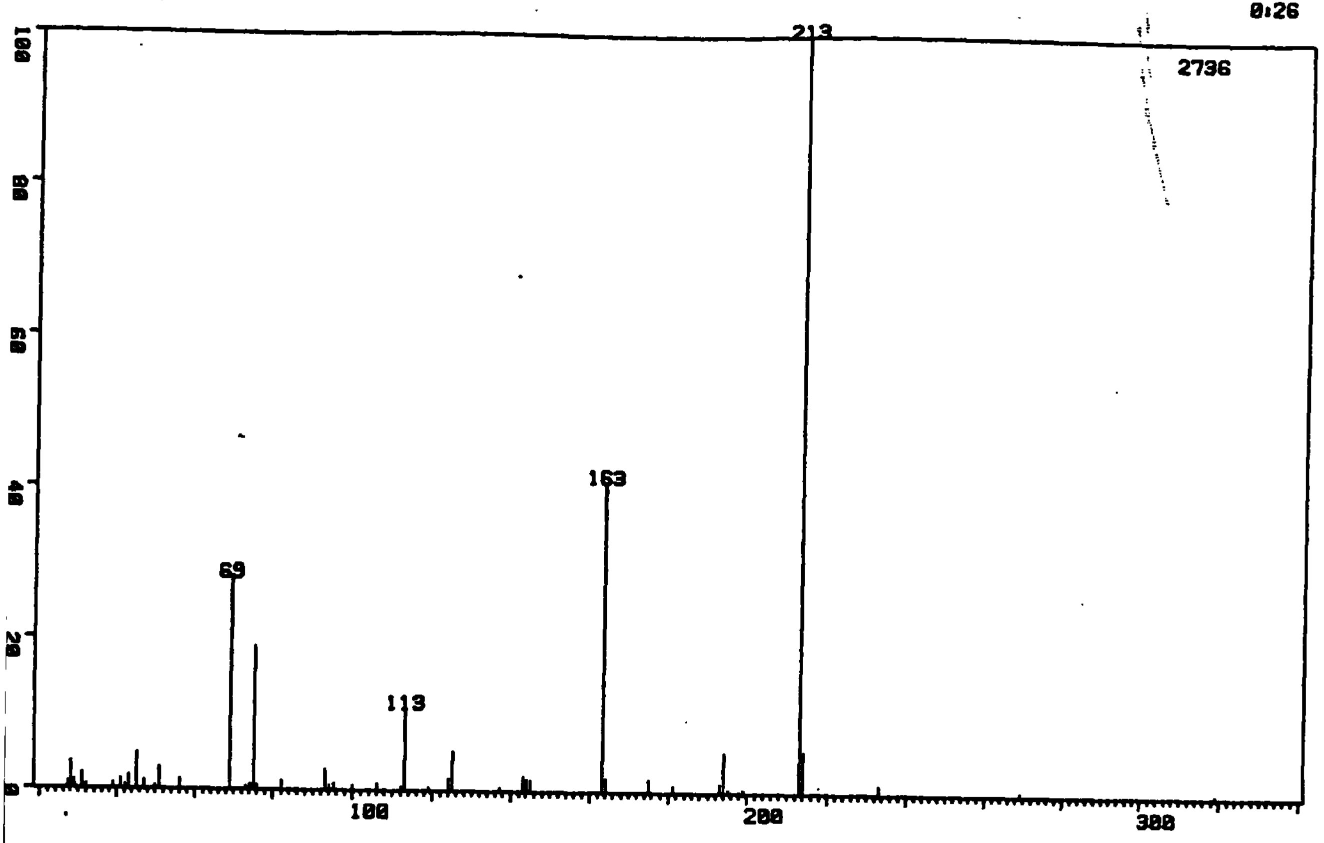


19

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
68.97	97.15	133.03	24.12	213.00	96.48
69.04	0.39	134.05	0.78	214.03	10.58
69.91	2.82	137.03	2.32	218.99	0.39
73.09	0.34	139.01	0.45	225.01	7.84
74.06	1.62	143.01	3.32	226.02	0.50
75.07	41.09	144.03	4.44	227.03	2.18
76.08	1.84	145.03	37.52	230.96	0.78
77.07	0.39	146.04	1.70	233.01	16.28
80.98	0.47	149.01	0.75	234.02	0.98
82.01	2.82	149.96	1.42	237.01	0.39
83.05	1.17	151.00	0.56	242.99	8.15
84.02	0.47	155.03	1.48	244.02	4.72
87.05	0.89	156.04	0.50	245.02	0.36
88.03	0.50	157.04	0.45	248.99	0.36
93.03	6.25	160.99	0.42	250.99	0.50
94.06	2.76	162.01	0.36	257.01	0.81
95.07	40.95	163.02	82.16	263.02	11.59
96.07	1.20	164.03	4.24	264.02	0.53
98.98	0.45	168.02	0.42	268.99	0.98
99.93	4.63	168.99	1.45	275.00	2.04
100.98	1.03	175.02	10.50	280.97	0.36
105.07	1.12	176.04	0.45	289.00	2.04
106.04	3.24	180.98	5.75	294.00	0.34
107.05	0.36	182.00	0.45	295.00	1.42
112.00	1.62	183.03	18.73	318.99	4.27
113.03	35.51	184.06	1.06	319.97	0.50
114.05	1.45	187.02	0.47	339.00	2.65
117.03	1.06	189.00	0.64	340.00	0.36
118.97	3.77	193.01	2.99	386.97	0.34
124.04	3.66	194.02	21.41	406.97	2.60
125.04	12.84	195.02	2.62	426.95	6.03

MJS10X 2
CAL:CALT3

11-OCT-85
0:26

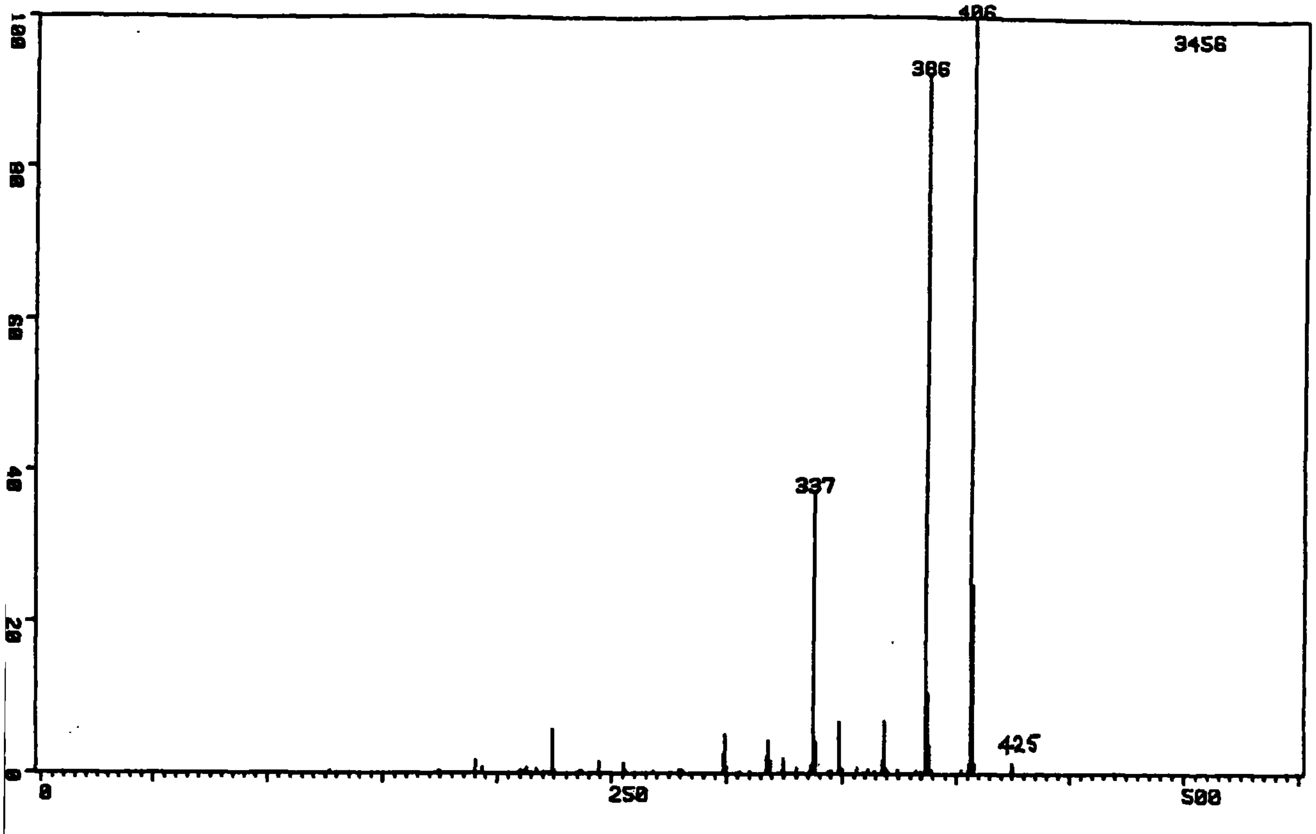


20

MASS	%HT. BASE	MASS	%HT. BASE
27.29	0.99	137.11	0.48
28.17	3.62	143.12	2.12
29.05	1.21	144.11	1.64
30.93	2.01	145.10	1.61
32.03	0.69	163.10	40.94
39.01	0.73	164.12	1.90
41.00	1.35	175.10	1.72
42.09	0.69	181.07	0.95
43.12	1.13	193.10	1.24
43.16	1.90	194.09	5.30
45.18	4.75	195.10	0.48
47.13	1.17	199.04	0.55
49.90	0.48	213.12	100.00
50.98	2.89	214.10	5.52
56.13	1.43	233.12	1.21
69.02	28.03	269.12	0.51
73.18	0.40	319.17	0.37
74.13	0.69		
75.12	18.97		
76.09	0.69		
82.04	1.21		
93.09	2.78		
94.11	0.77		
95.10	0.95		
99.97	0.69		
106.09	0.99		
112.06	0.51		
113.08	10.82		
119.02	0.40		
124.08	1.75		
125.10	5.26		

MJS10X 4
CAL:CALN4

11-OCT-85
0:44

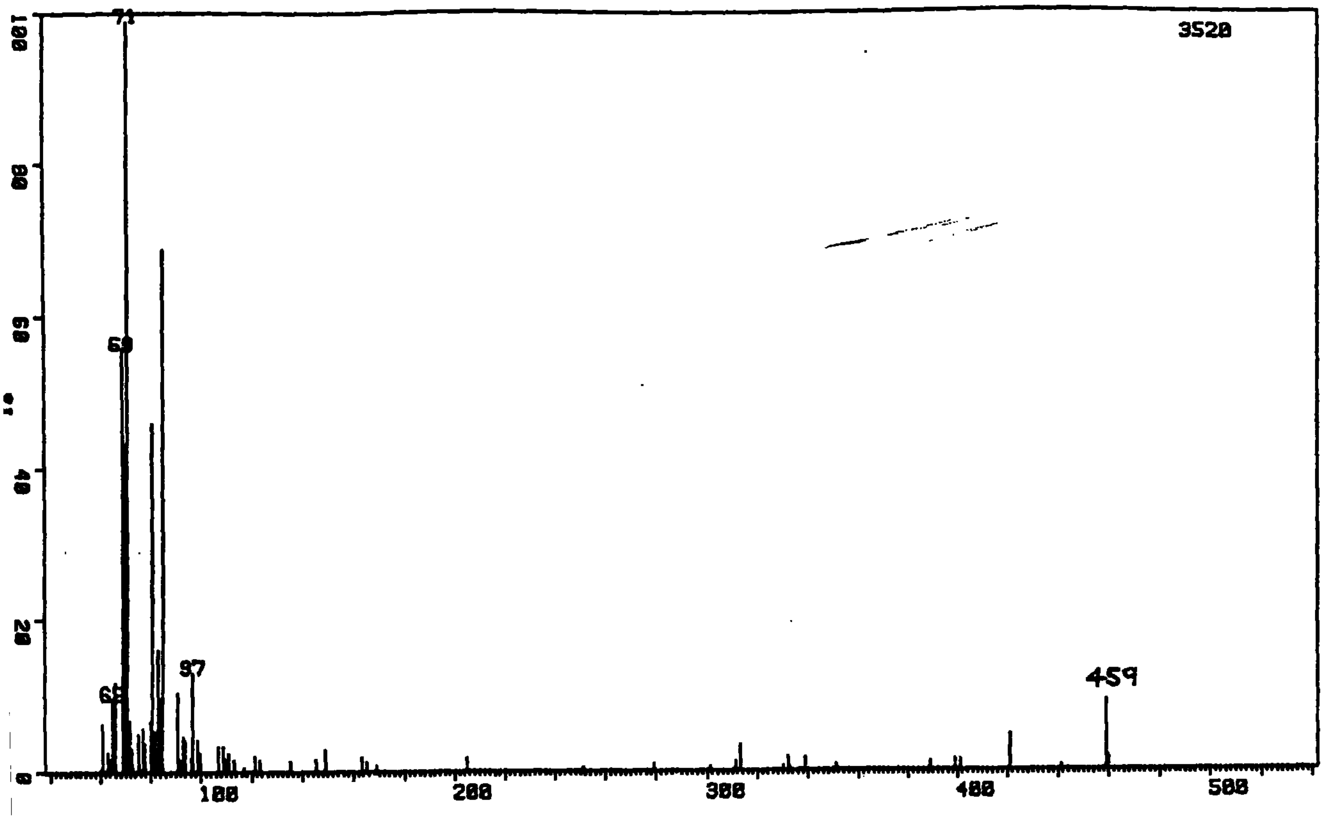


21

MASS	%HT. BASE	MASS	%HT. BASE
174.19	0.38	325.19	0.29
190.15	1.71	330.20	0.78
193.18	0.78	336.19	1.10
210.08	0.49	337.21	37.41
212.11	0.38	338.16	4.22
213.15	0.78	344.21	0.32
217.12	0.41	345.24	0.38
224.13	5.84	348.19	6.83
225.10	0.49	349.18	0.81
236.14	0.32	350.19	0.61
237.11	0.32	356.25	0.81
244.11	1.56	361.23	0.52
255.16	1.36	364.19	0.32
256.17	0.41	367.20	1.65
268.15	0.32	368.17	7.03
279.15	0.61	369.19	0.78
280.16	0.61	370.23	0.38
281.17	0.35	374.22	0.52
298.18	2.58	382.27	0.38
299.18	5.21	384.27	0.32
300.18	0.95	386.26	92.36
306.20	0.26	387.24	10.65
310.16	0.32	388.22	3.79
317.16	2.23	389.21	0.38
318.16	4.37	402.20	0.58
319.19	1.71	405.23	1.42
324.20	1.97	406.25	100.00
		407.25	25.00
		408.25	1.36
		424.27	1.48
		425.27	0.93

2151X 3
CAL:CALT1

24-AUG-84
8:32

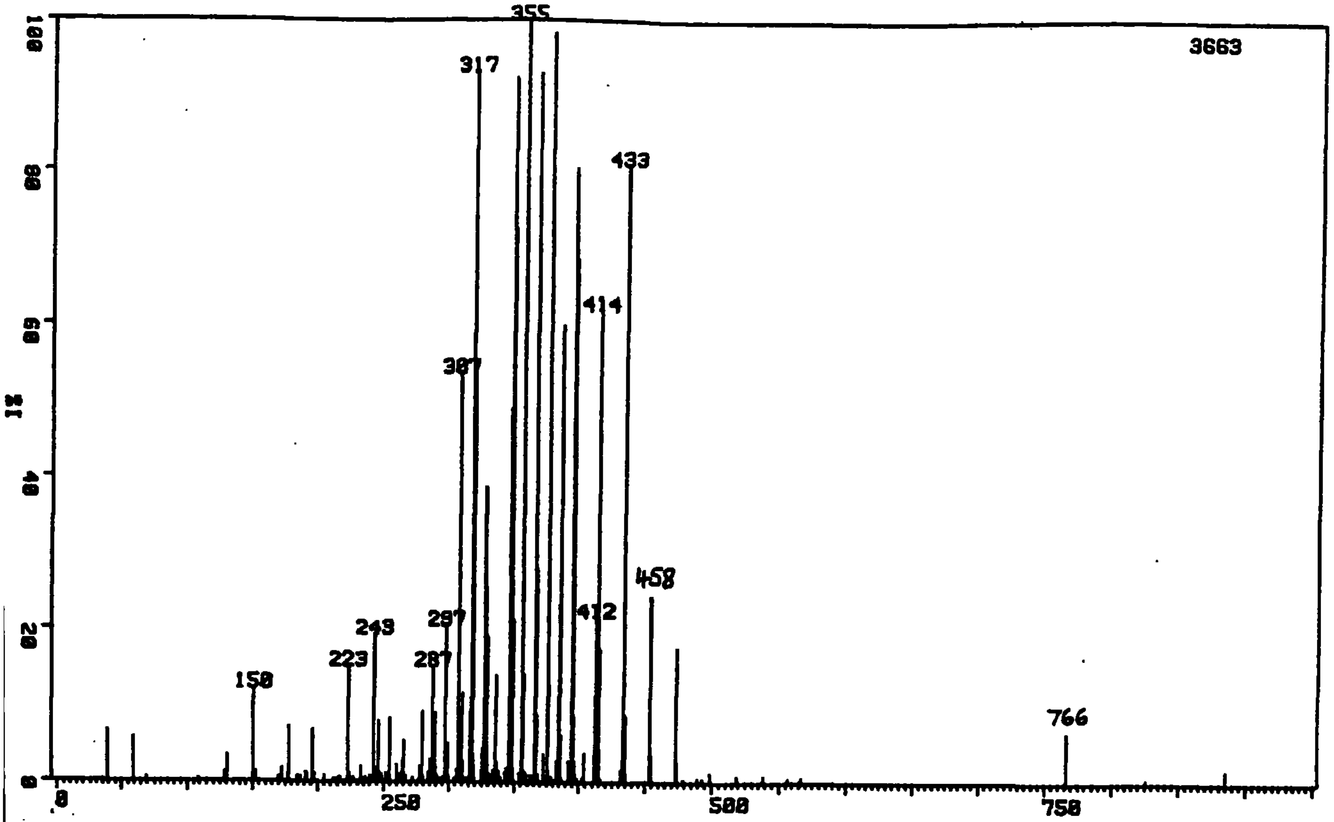


22.

MASS	%HT. BASE .	MASS	%HT. BASE
60.95	6.25	112.94	1.51
63.02	2.59	113.08	1.56
64.06	1.73	117.02	0.54
65.08	9.52	121.01	2.02
66.08	11.79	123.07	1.59
68.94	2.22	135.08	1.36
69.00	55.77	144.98	1.56
69.95	43.30	148.94	2.81
71.02	98.92	149.05	2.16
72.07	7.02	162.96	0.60
73.04	1.59	163.12	1.90
73.08	3.18	165.10	1.25
75.12	5.00	168.90	0.91
77.02	5.88	205.02	1.65
78.00	3.84	250.98	0.48
79.92	6.68	279.09	0.99
80.98	45.99	300.95	0.60
82.02	5.43	310.98	1.19
83.05	16.02	312.99	3.38
84.08	9.74	329.98	0.68
85.10	68.92	331.99	1.79
90.94	10.45	332.93	0.43
91.98	1.56	339.01	1.56
92.96	2.53	350.98	0.82
93.01	4.74	388.99	1.16
94.03	4.18	398.96	1.48
96.05	1.87	401.01	1.45
97.05	13.04	421.02	4.69
98.95	1.19	441.03	0.60
99.00	4.29	459.08	9.09
99.98	2.56	460.09	1.79

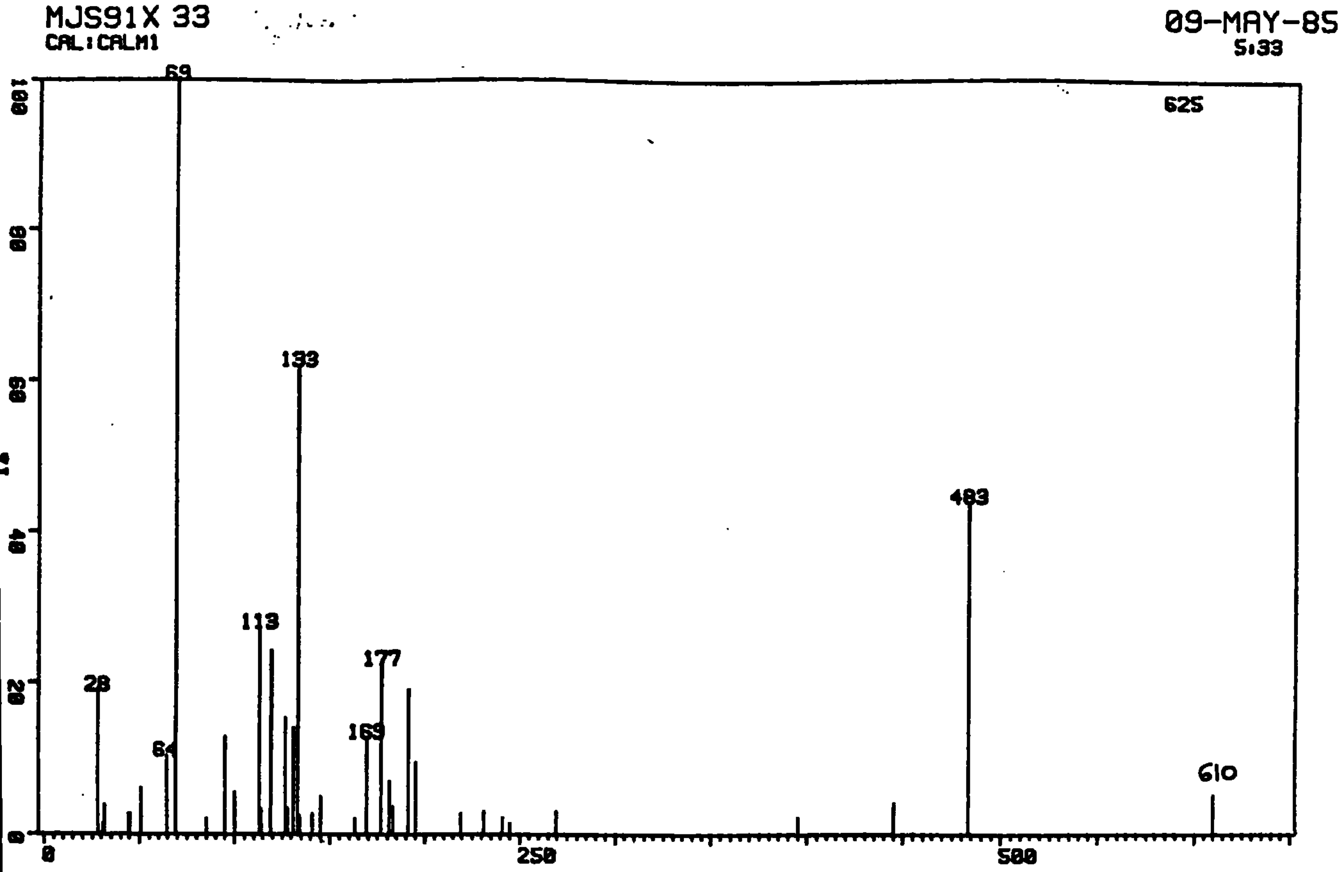
MJS215 6
CAL:CALT2

26-JUL-84
8:57



23

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
305.93	1.50	356.35	14.06	396.87	2.89
306.92	53.70	357.36	1.64	397.83	1.12
307.91	8.87	358.31	1.34	398.88	0.44
308.89	2.48	359.32	1.23	402.84	0.55
309.88	11.68	360.35	0.25	403.77	3.82
310.90	2.70	362.29	0.96	411.66	21.84
312.87	0.38	363.26	1.04	413.65	62.00
313.83	0.33	365.28	92.90	414.68	17.44
314.79	0.57	366.25	27.96	415.71	4.37
315.81	9.17	367.29	9.01	416.66	0.52
316.76	93.26	368.26	1.09	431.49	1.64
317.78	54.14	372.20	3.69	432.48	0.68
318.74	3.69	373.19	0.93	433.47	80.94
319.70	0.60	375.10	98.20	434.46	8.82
324.69	1.50	375.82	0.38	435.54	1.23
325.68	4.45	376.10	12.67	453.22	24.41
326.73	38.66	377.09	1.61	454.26	3.58
327.65	25.55	378.01	0.30	455.22	0.46
328.64	19.19	379.08	0.79	472.97	17.69
329.63	4.45	382.06	0.35	473.96	2.68
330.63	1.23	383.01	2.73	478.92	0.38
331.59	0.60	384.04	23.26	488.89	0.55
345.33	48.92	385.07	59.84	492.80	0.44
346.45	92.30	386.03	6.12	498.60	1.20
347.43	72.48	387.06	0.60	518.53	0.87
348.49	21.38	391.94	2.81	538.26	0.87
349.47	1.88	392.98	1.91	556.95	0.44
353.44	1.23	393.95	80.37	566.81	0.68
355.34	100.00	394.92	68.33	766.81	6.61
355.94	0.38	395.89	8.65	825.94	0.49
				885.00	1.75

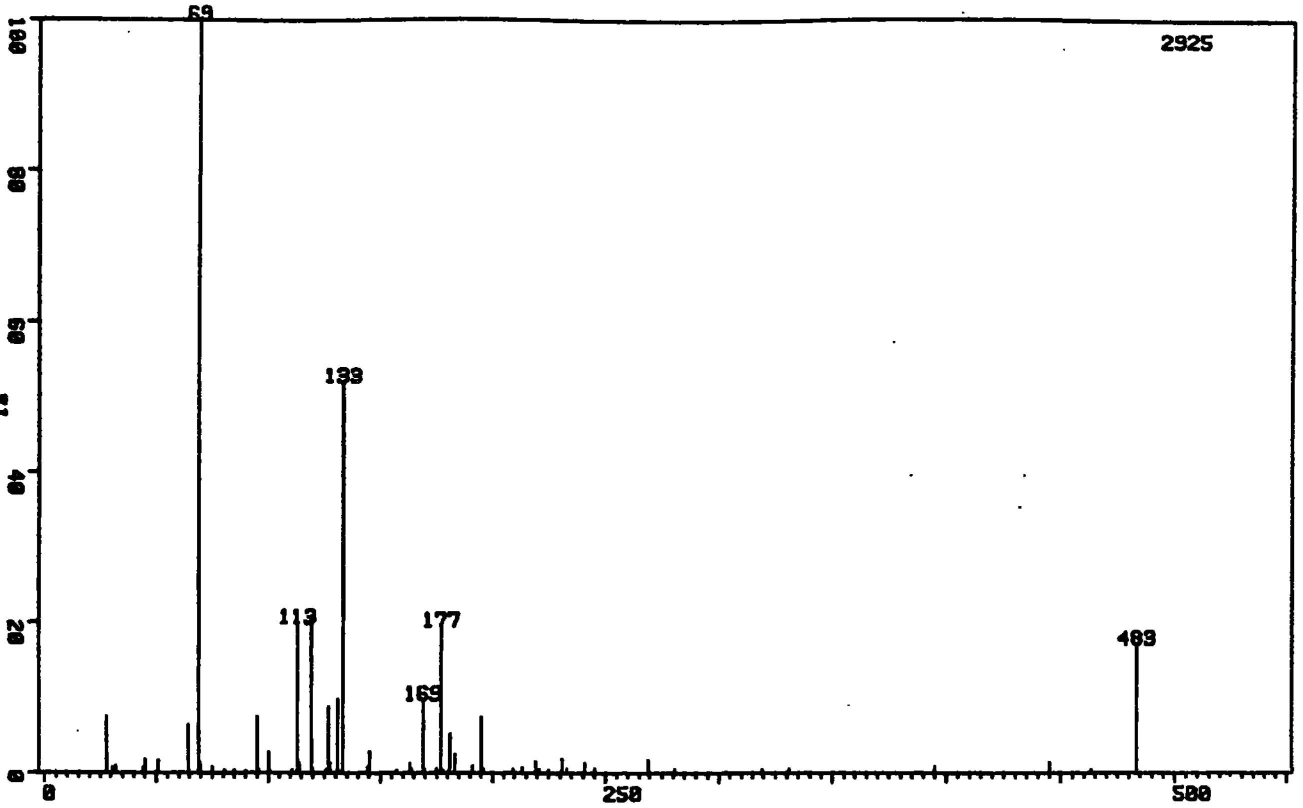


24.

MASS	%HT. BASE	MASS	%HT. BASE
28.06	19.04	245.12	1.44
30.83	1.44	269.08	3.04
31.94	3.84	395.15	2.24
44.11	2.72	445.18	4.16
45.14	2.72	483.24	44.00
50.96	6.08	610.28	5.28
64.11	10.40		
68.96	100.00		
85.01	2.08		
95.07	12.96		
99.96	5.60		
113.07	27.36		
114.07	3.36		
119.00	24.32		
126.98	15.36		
127.97	3.52		
131.04	14.08		
133.08	62.08		
134.11	2.56		
140.94	2.72		
145.09	4.96		
163.06	2.08		
169.02	12.80		
176.99	22.56		
181.07	7.04		
183.12	3.68		
190.97	19.20		
195.08	9.44		
219.04	2.72		
231.10	3.04		
241.03	2.24		

MJS91X 29
CAL:CALM1

09-MAY-85
4:54

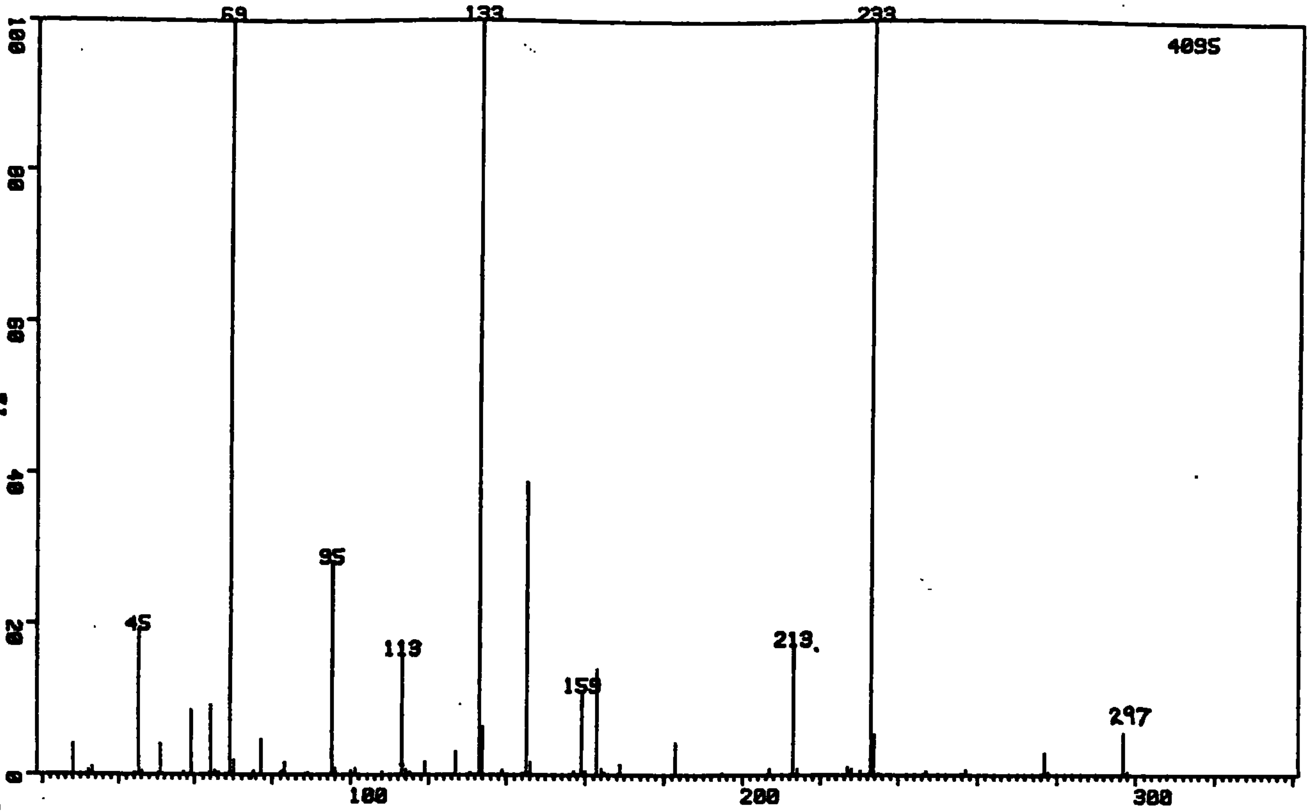


25

MASS	%HT. BASE	MASS	%HT. BASE
45.15	1.81	169.97	0.55
50.96	1.71	175.06	0.58
64.11	6.39	176.96	19.52
68.96	100.00	177.99	0.38
69.47	0.31	181.03	5.16
69.91	1.33	183.09	2.50
75.06	0.75	190.96	0.92
80.92	0.31	195.07	7.38
84.98	0.41	196.06	0.51
89.91	0.34	208.98	0.62
95.07	7.49	213.10	0.75
96.07	0.38	219.04	1.54
99.94	2.70	220.97	0.51
100.98	0.27	225.12	0.34
111.00	0.48	231.05	1.88
113.05	20.00	233.11	0.62
114.07	1.33	240.95	1.40
119.00	20.41	245.08	0.62
119.97	0.62	269.07	1.78
126.08	0.38	281.07	0.58
126.98	8.72	302.98	0.27
127.97	1.33	319.02	0.38
131.02	9.74	331.09	0.44
131.63	0.34	395.11	0.92
133.11	51.97	445.07	1.44
144.07	0.72	463.15	0.44
145.07	2.84	483.17	17.16
157.02	0.31		
163.04	1.33		
164.07	0.44		
169.00	9.74		

MS51X 45
CAL:CALM18

01-SEP-85
6:37

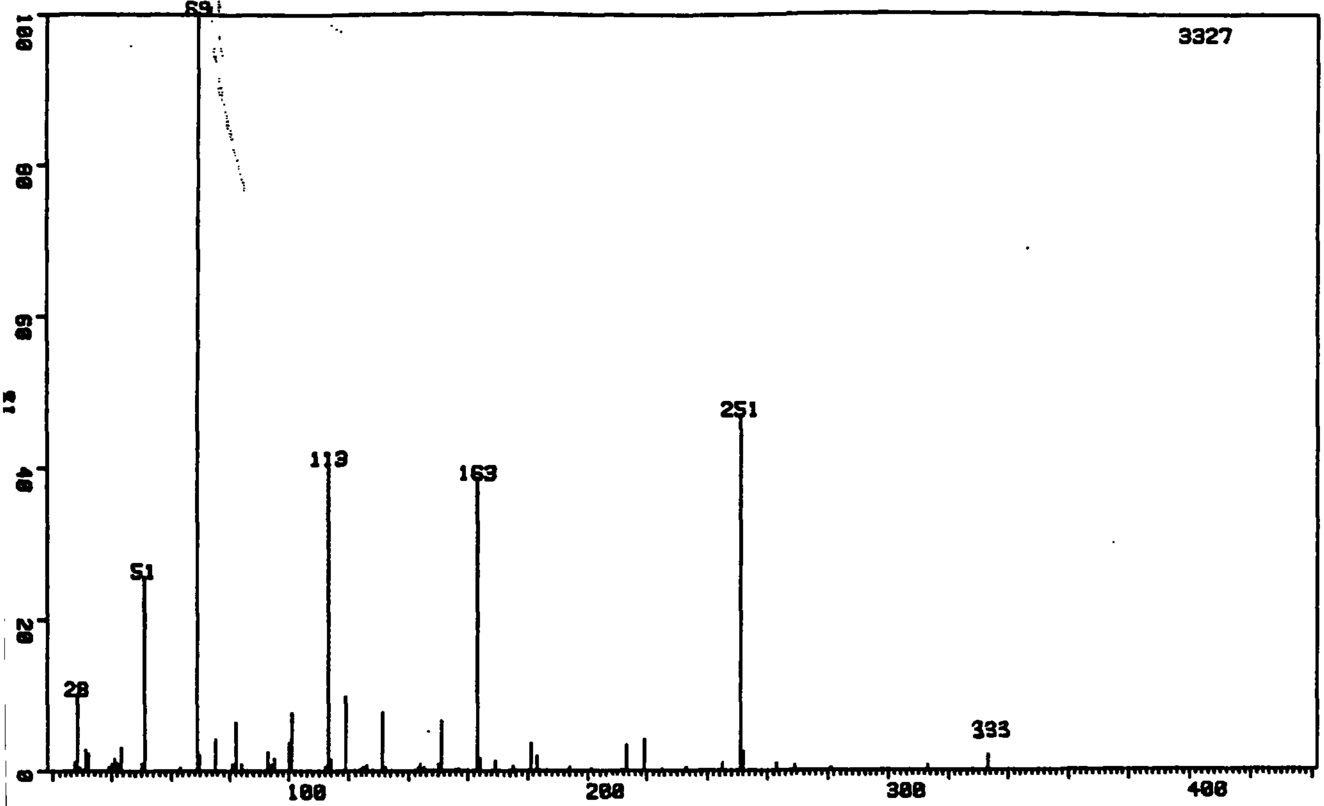


26

MASS	%HT. BASE	MASS	%HT. BASE
28.06	4.05	130.85	0.24
31.94	0.68	132.93	100.00
33.06	1.05	133.75	6.40
44.09	0.24	138.98	0.66
45.12	19.17	144.02	0.22
46.11	0.37	145.00	38.68
50.92	4.00	145.99	1.68
57.07	0.34	156.99	0.42
58.97	8.45	158.94	11.06
64.06	9.18	159.91	0.56
65.08	0.56	162.93	13.94
66.12	0.29	163.96	0.90
68.94	100.00	164.94	0.32
69.24	0.24	168.92	1.39
69.31	0.24	182.95	4.22
69.88	1.93	194.93	0.27
75.09	0.49	206.88	0.81
77.06	4.64	212.88	17.17
81.99	0.46	213.93	0.85
83.02	1.64	226.93	1.00
88.97	0.27	227.91	0.85
95.03	28.01	230.23	0.54
96.03	0.90	232.82	100.00
99.90	0.56	233.77	5.42
100.93	0.90	234.90	0.24
107.99	0.34	246.97	0.39
112.98	15.92	256.93	0.73
114.00	0.78	276.91	2.91
115.01	0.32	277.88	0.34
118.93	1.68	296.83	5.54
126.98	3.00	297.91	0.44

MS30X 4
CAL:CALT3

16-OCT-85
8:44

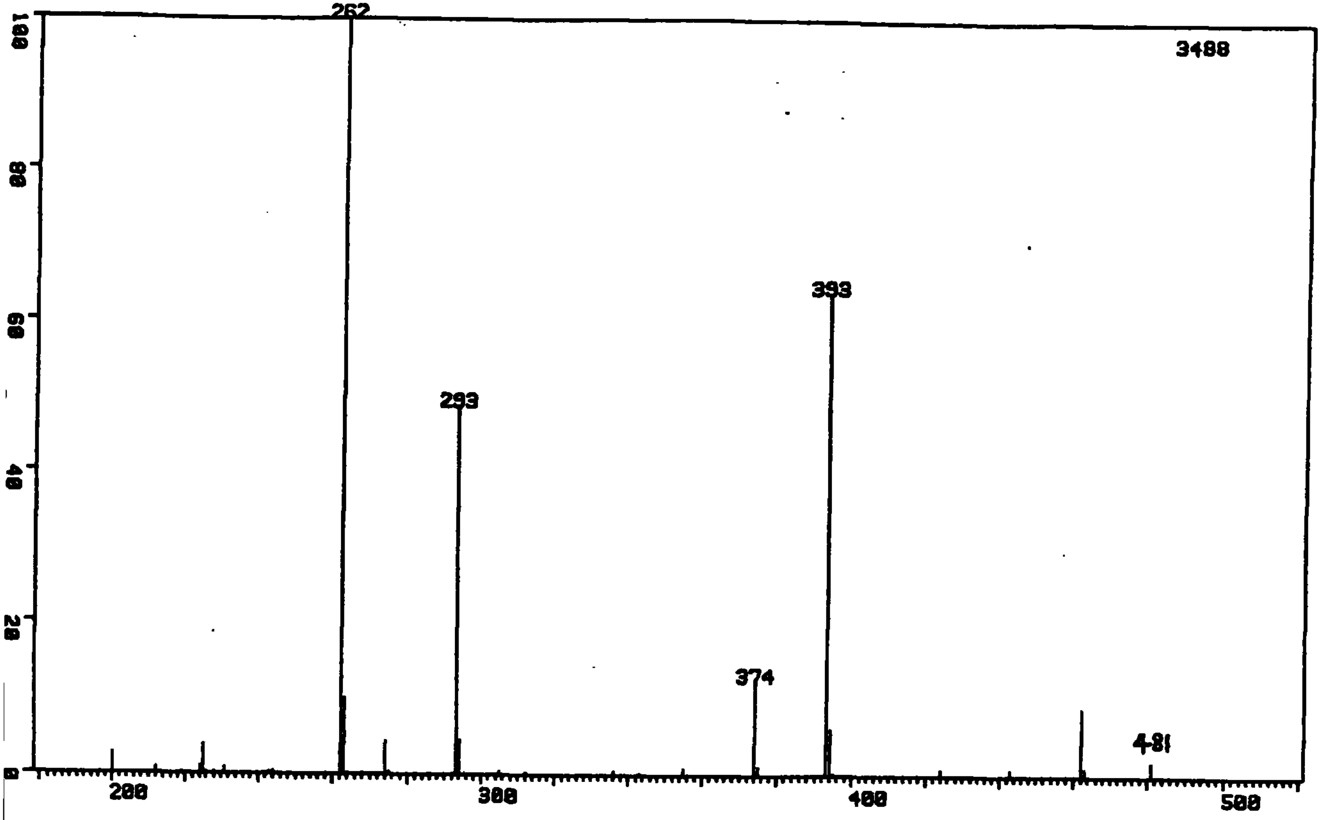


27

MASS	%HT. BASE	MASS	%HT. BASE
27.29	1.11	126.06	0.78
28.17	10.01	130.98	7.78
29.05	0.48	132.03	0.45
30.93	2.80	143.05	0.45
32.03	2.34	144.08	0.99
39.00	0.51	145.09	0.57
39.84	0.93	150.00	0.90
40.98	1.65	151.05	6.64
42.07	1.11	157.08	0.30
43.11	0.87	163.08	38.44
43.14	3.13	164.10	1.71
49.89	1.02	169.05	1.32
50.96	25.70	175.10	0.63
63.08	0.45	181.04	3.70
69.00	100.00	183.09	1.98
69.94	2.19	194.08	0.39
75.12	4.27	201.06	0.39
81.00	0.93	213.10	3.40
82.04	6.49	219.05	4.09
84.18	0.99	225.09	0.33
93.03	2.43	233.12	0.54
94.06	0.90	245.09	1.02
95.07	1.59	251.07	46.86
99.94	3.73	252.09	2.58
100.98	7.69	263.09	0.99
112.01	0.48	269.08	0.78
113.04	40.37	281.07	0.42
114.06	1.56	313.16	0.66
118.98	9.80	333.14	2.04
124.05	0.33		
125.05	0.54		

MS30X 7
CAL:CALN4

16-OCT-85
1:15

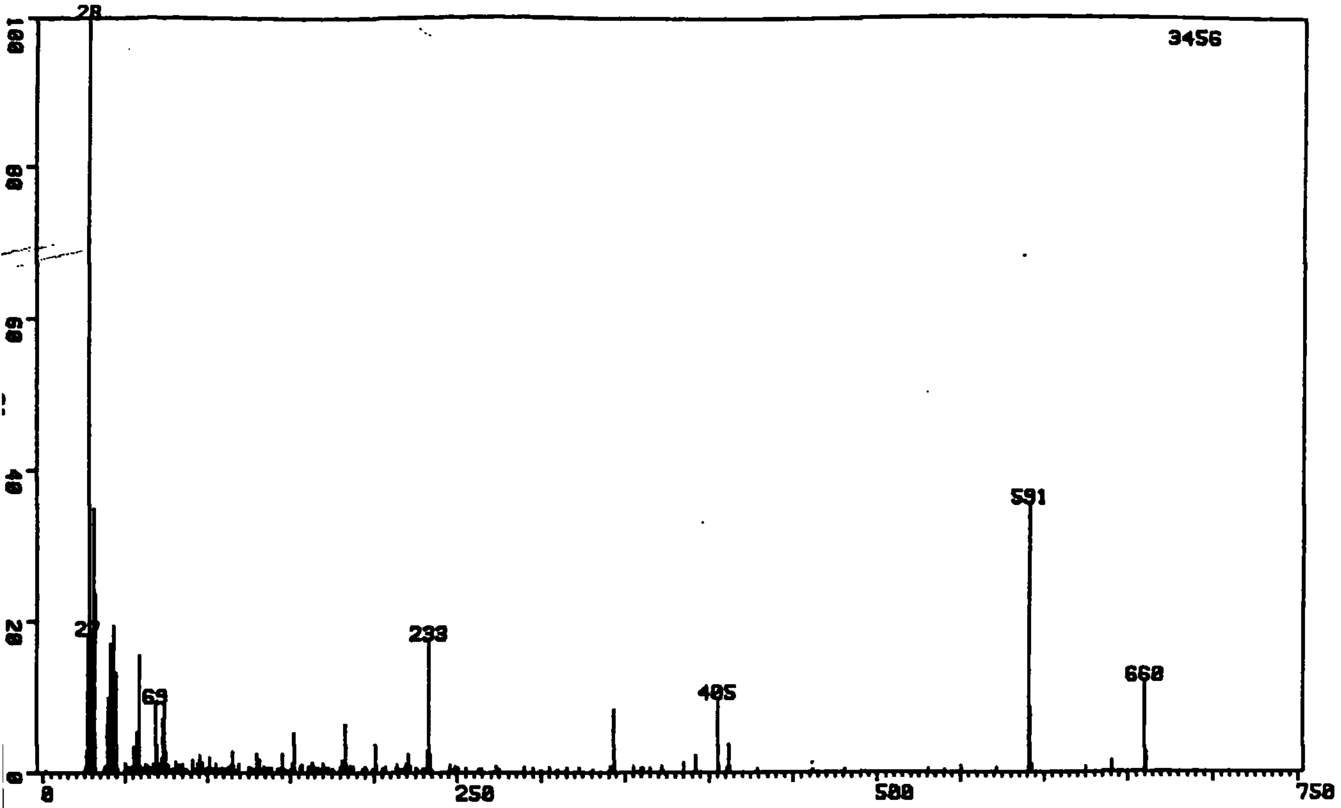


28

MASS	%HT. BASE
39.00	1.26
58.93	0.46
174.03	0.32
193.01	14.54
194.03	1.20
199.96	2.72
211.99	0.80
218.98	0.26
224.01	1.03
225.03	3.84
226.03	0.34
228.00	0.32
230.99	0.86
242.99	0.29
244.03	0.37
262.03	100.00
263.03	10.12
264.05	0.32
274.05	4.33
275.05	0.40
293.04	48.77
294.06	4.59
305.06	0.52
312.05	0.37
336.06	0.52
343.04	0.32
355.07	0.95
374.06	12.47
375.07	1.23
393.05	63.96
394.07	6.16
395.06	0.29
424.10	0.92
443.04	0.89
462.06	8.89
463.04	1.03
481.04	1.92

MJS13X S
CAL:CALT3

04-OCT-85
0:55

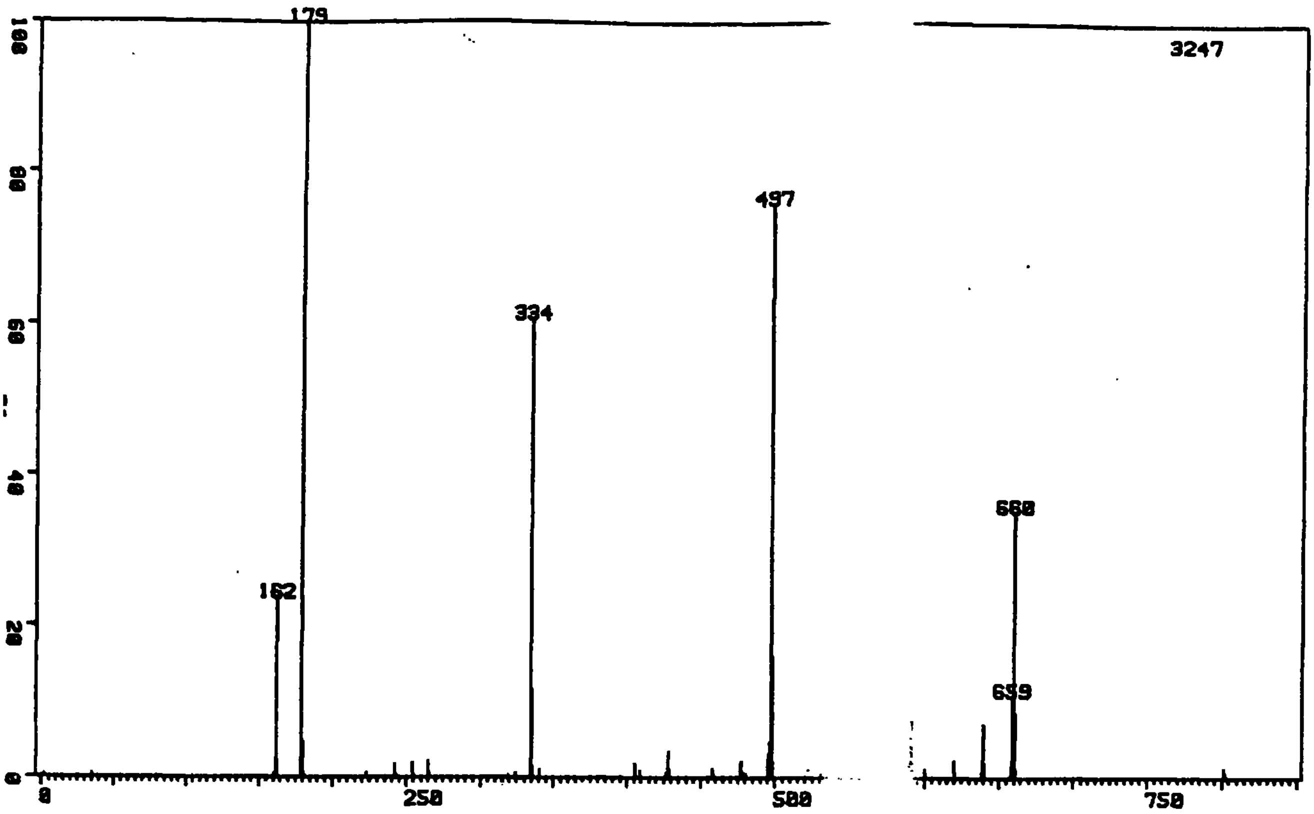


29

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
43.09	15.13	206.93	0.81	342.94	8.36
43.12	19.50	212.92	0.67	343.93	1.56
44.09	1.50	213.97	1.13	354.91	0.93
44.14	1.74	215.01	0.41	358.88	0.49
45.15	13.28	216.02	0.49	360.89	0.67
46.14	0.75	216.95	0.41	364.89	0.61
49.88	1.33	218.91	0.87	371.93	0.95
50.94	0.95	219.90	1.27	372.93	0.32
52.01	0.46	220.91	2.43	384.88	1.36
53.07	0.90	221.93	1.01	391.94	2.34
54.11	0.61	224.91	0.69	392.92	0.46
55.09	0.46	225.93	0.41	404.91	9.81
55.13	3.56	228.92	0.43	405.87	1.19
56.13	2.00	229.89	0.43	410.90	0.72
57.06	0.43	230.90	0.49	411.95	3.85
57.08	0.41	231.91	2.89	412.98	0.98
57.11	5.47	232.93	17.56	428.91	0.46
58.03	0.69	233.96	2.46	461.91	0.38
58.07	0.64	234.91	0.55	480.82	0.43
58.99	15.60	235.90	0.26	530.71	0.49
59.85	0.98	244.91	0.67	540.77	0.35
59.91	0.41	245.95	1.13	550.73	0.90
61.95	0.75	246.96	0.43	571.79	0.61
61.99	0.52	248.91	0.81	590.76	35.62
63.04	1.19	249.90	0.67	591.84	8.65
64.07	1.01	250.92	0.72	592.90	1.13
65.09	0.72	254.90	0.64	624.80	0.72
66.09	0.32	262.88	0.43	640.80	1.53
67.08	1.22	264.91	0.52	641.90	0.35
68.05	0.84	272.90	0.87	659.85	12.09
68.94	9.29	273.95	0.61	660.89	2.75
69.01	3.76				

MJS13X 4
CAL:CALN1

04-OCT-85
8:43

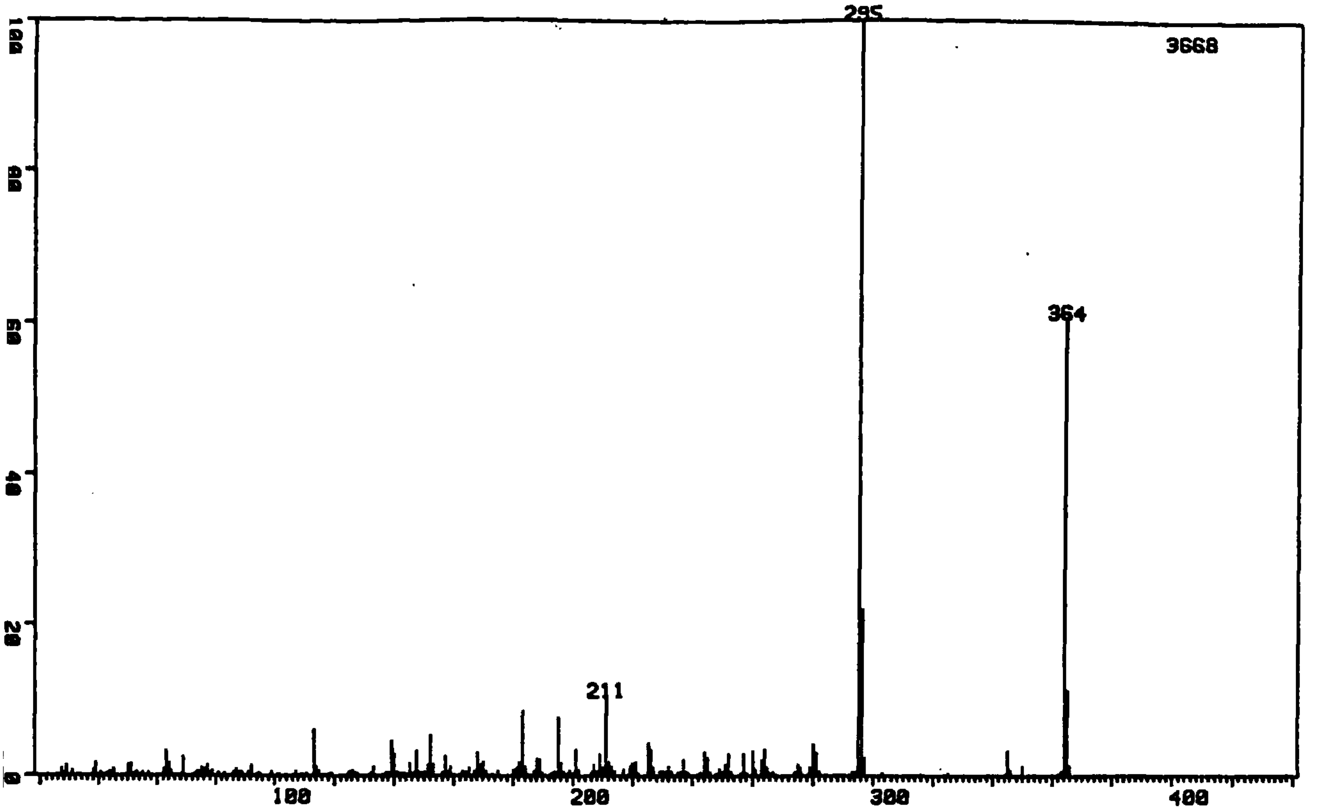


30

MASS	%HT. BASE	MASS	
		476.82	
159.97	0.46	477.86	
162.01	23.78	478.86	
163.03	2.19	479.82	
178.97	100.00	480.88	
179.95	4.65	494.86	
180.96	0.43	495.85	
222.99	0.59	496.84	7
241.98	1.76	497.88	1
242.99	0.34	498.87	
253.98	1.94	530.77	
254.99	0.43	550.79	
265.01	2.13	570.77	
266.03	0.71	571.81	
318.94	0.31	588.77	
323.91	0.65	590.74	
324.90	0.62	591.76	
333.97	60.61	599.71	
334.97	11.58	600.75	
335.96	1.45	619.76	
340.86	1.05	620.78	
404.88	1.88	638.73	
405.85	0.43	639.76	
408.87	0.95	640.73	
426.91	0.46	657.75	
427.89	3.45	658.69	1
428.90	1.08	659.69	3
457.87	1.17	660.70	
458.87	0.49	661.72	
		801.61	
		802.61	

MJS12X 6
CAL:CALT3

04-OCT-85
1:1

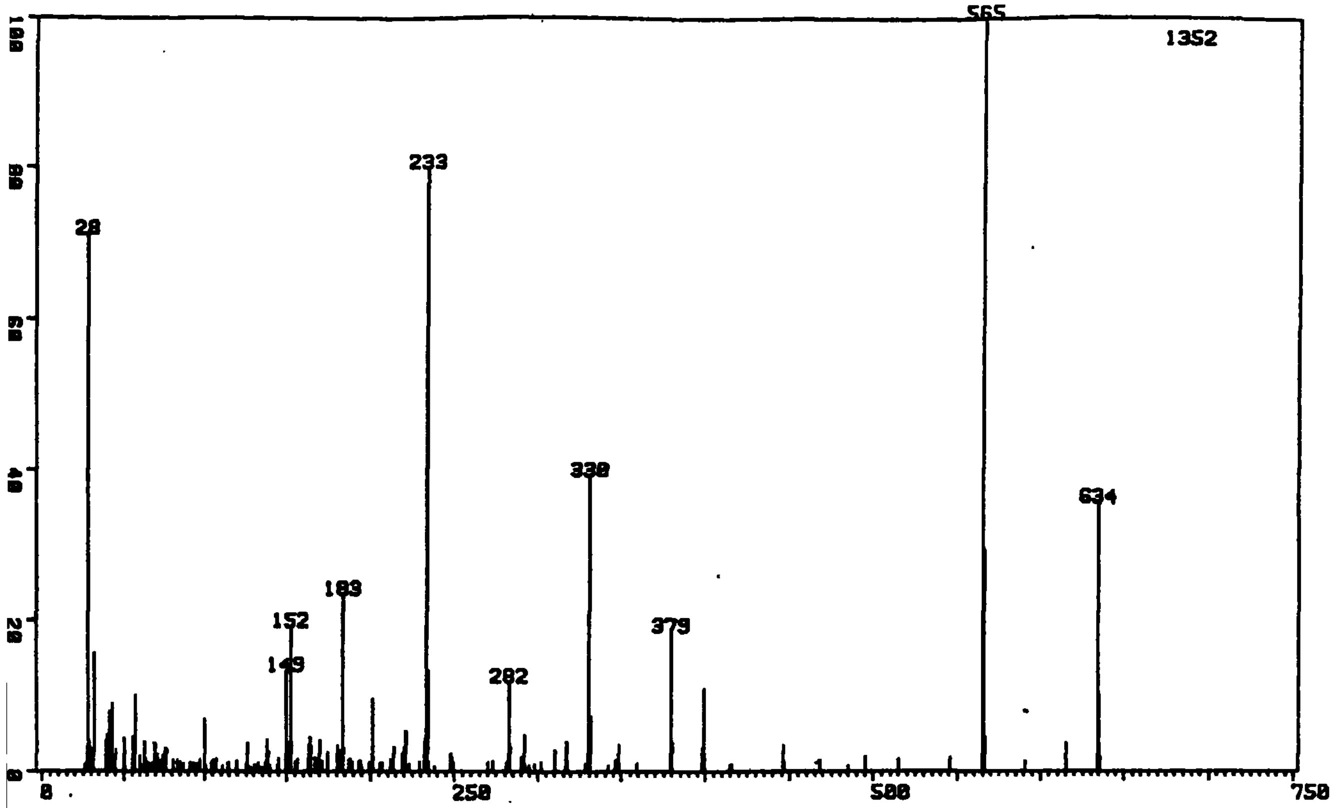


31

MASS	%HT. BASE	MASS	%HT. BASE
209.03	2.89	256.08	0.25
210.02	1.09	257.03	2.86
211.03	10.52	258.03	0.38
212.06	1.91	260.02	3.27
213.05	1.25	261.03	0.93
214.07	0.60	263.06	2.10
217.04	0.87	264.08	3.44
219.01	1.15	265.04	1.09
220.00	1.72	266.06	0.30
221.02	1.88	267.05	0.44
222.04	0.41	274.08	0.46
225.11	4.39	275.08	1.44
226.08	3.49	276.08	1.09
227.07	1.20	279.03	1.06
229.00	0.57	280.03	4.14
230.00	0.68	281.04	3.05
231.02	0.63	282.05	0.57
232.03	1.28	293.09	0.57
233.04	0.71	294.08	0.52
235.05	0.44	295.09	100.00
236.04	0.55	296.11	22.03
237.03	2.18	297.07	2.40
238.02	0.63	303.02	0.41
239.01	0.41	325.06	0.35
242.03	0.27	345.09	3.35
243.04	0.44	346.08	0.74
244.05	3.19	350.04	1.34
245.07	2.45	363.08	0.52
246.08	0.52	364.09	60.61
248.01	0.35	365.10	11.34
249.02	1.01	366.08	1.39

MJS11X 4
CAL:CALT20

03-OCT-85
0:44

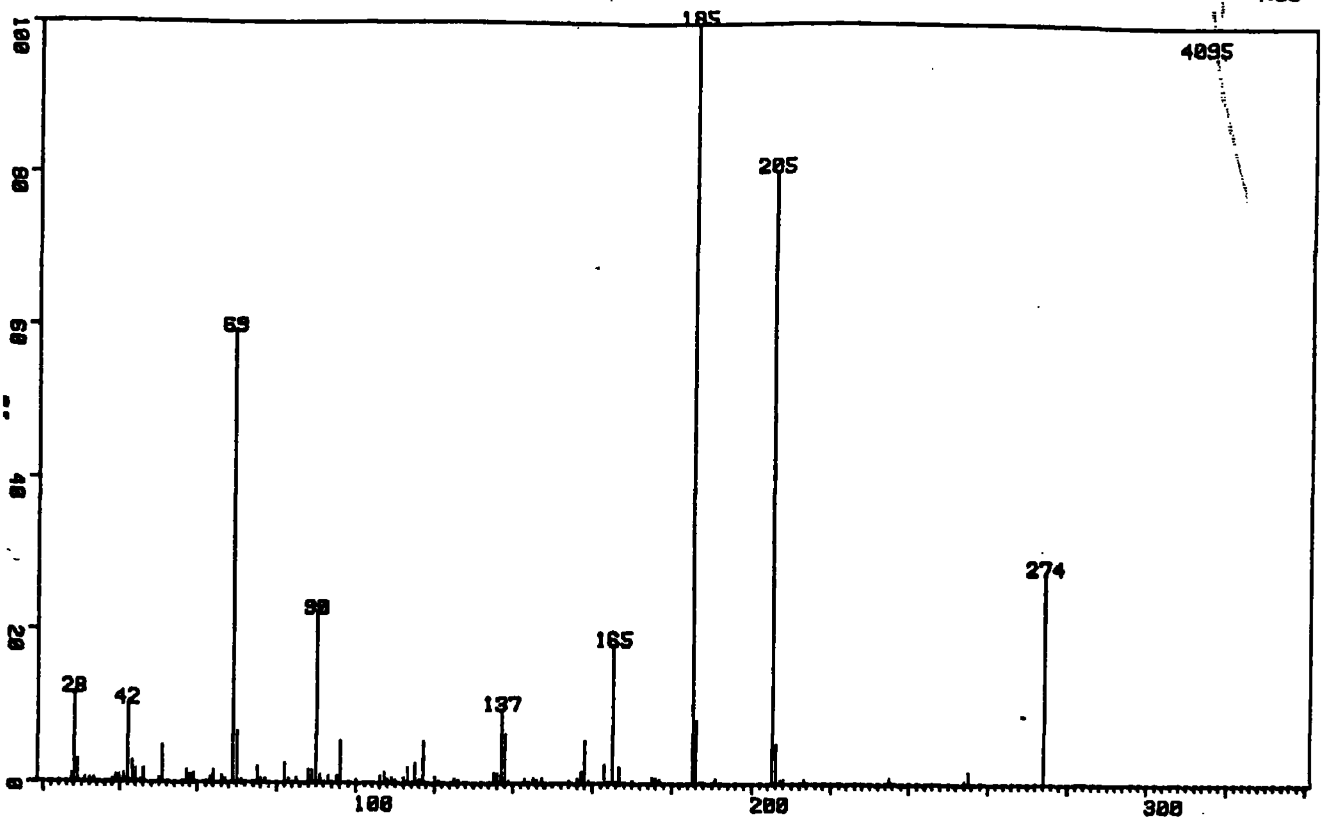


32

MASS	%HT. BASE	MASS	%HT. BASE
211.93	1.70	327.93	1.04
212.95	1.33	328.90	1.04
213.96	3.25	329.95	39.35
218.92	2.37	330.94	7.32
219.91	3.18	341.91	0.81
220.92	5.40	345.96	1.55
222.95	1.04	347.93	3.55
228.91	1.33	348.92	1.11
231.91	4.22	358.94	1.11
232.94	80.03	378.88	18.64
233.94	13.31	379.91	3.92
234.93	1.33	397.93	3.18
237.89	0.74	398.91	10.95
247.90	2.29	399.93	2.29
248.91	1.85	414.94	0.89
249.90	1.18	415.93	0.96
269.91	1.26	446.00	3.48
272.91	1.41	446.97	1.33
280.93	1.18	467.84	1.55
281.91	1.41	484.89	0.74
282.40	11.83	494.89	1.92
282.92	3.33	514.90	1.70
289.90	2.00	545.91	1.85
291.89	4.81	564.83	100.00
292.94	0.96	565.90	29.29
295.00	0.81	566.89	4.51
297.97	0.96	590.92	1.41
301.98	1.33	614.86	3.77
309.94	2.74	615.89	1.48
316.92	4.07	633.87	35.65
317.94	1.33	634.87	10.28
		635.93	2.00

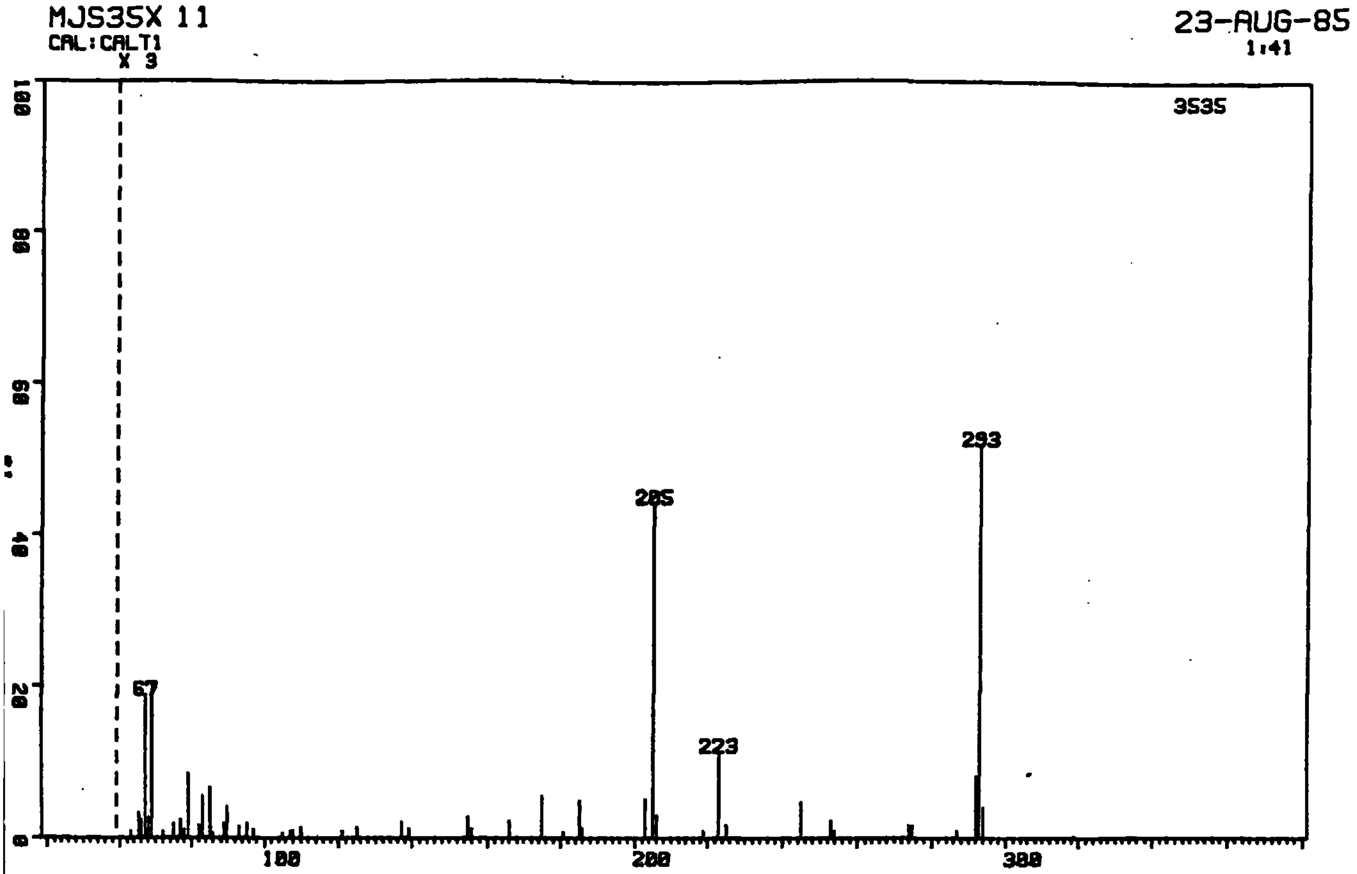
226XI 28
CAL:CALM30

02-AUG-84
4:59



33

MASS	%HT. BASE	MASS	%HT. BASE
33.06	0.51	117.09	5.47
38.04	0.32	119.98	0.88
38.96	1.03	121.03	0.34
39.85	0.95	125.09	0.46
40.93	1.34	126.10	0.39
42.02	10.38	135.11	1.42
43.08	2.91	136.09	1.37
44.09	1.86	137.04	9.67
45.12	0.24	138.02	6.59
46.12	1.83	139.02	0.42
49.87	0.61	143.03	0.51
50.94	4.86	145.06	0.78
57.08	1.71	165.07	18.10
58.06	1.10	166.82	2.08
58.98	1.20	170.05	0.32
63.07	0.76	175.12	0.93
64.10	1.64	176.09	0.85
66.11	0.90	177.09	0.56
67.08	0.54	185.08	100.00
68.95	59.07	185.98	8.42
69.90	6.79	187.08	0.27
71.00	0.27	191.04	0.56
75.07	2.15	205.11	80.37
76.07	0.54	205.98	5.20
77.06	0.46	207.09	0.42
81.98	2.54	208.06	0.63
83.02	0.46	213.08	0.51
85.02	0.71	235.12	0.85
88.01	1.71	254.09	0.42
88.97	1.56	255.08	1.51
89.93	22.20	274.14	27.67

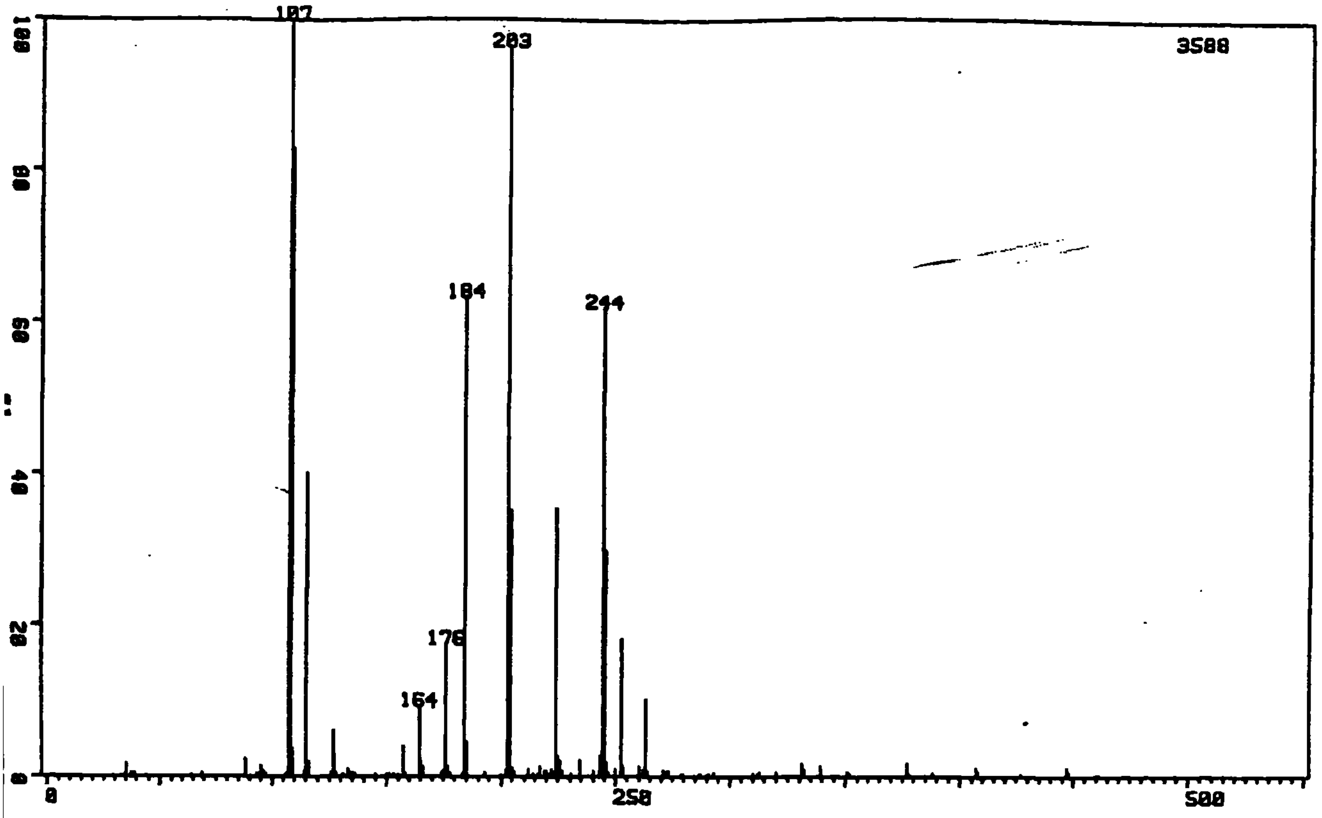


34

MASS	%HT. BASE	MASS	%HT. BASE
26.34	5.04	68.02	0.92
28.17	12.92	68.97	6.77
29.03	100.00	72.03	0.31
29.44	0.22	75.01	0.64
29.48	0.22	77.01	0.81
29.86	2.56	78.00	0.39
37.09	3.09	78.96	2.81
38.04	12.42	82.02	0.56
38.87	0.25	136.92	0.70
38.90	0.33	138.98	0.42
39.17	0.72	154.90	0.92
39.85	65.23	155.91	0.42
42.02	90.23	165.89	0.75
42.76	0.22	174.89	1.84
43.08	92.18	180.85	0.28
44.14	13.89	184.98	1.64
45.13	1.56	185.92	0.45
48.93	0.36	202.83	1.70
49.84	2.26	204.93	14.53
53.04	24.47	205.94	1.03
54.08	5.60	218.91	0.31
55.10	64.00	222.88	3.76
56.10	98.41	224.94	0.58
56.76	0.25	244.94	1.56
57.07	90.87	252.86	0.75
58.04	95.63	253.92	0.33
58.98	3.26	273.86	0.58
63.02	0.31	274.93	0.56
65.06	1.11	286.92	0.33
66.05	0.81	291.87	2.70
67.04	6.21	292.92	17.01

MJS3S 6
CAL:CALN16

22-OCT-85
0:57

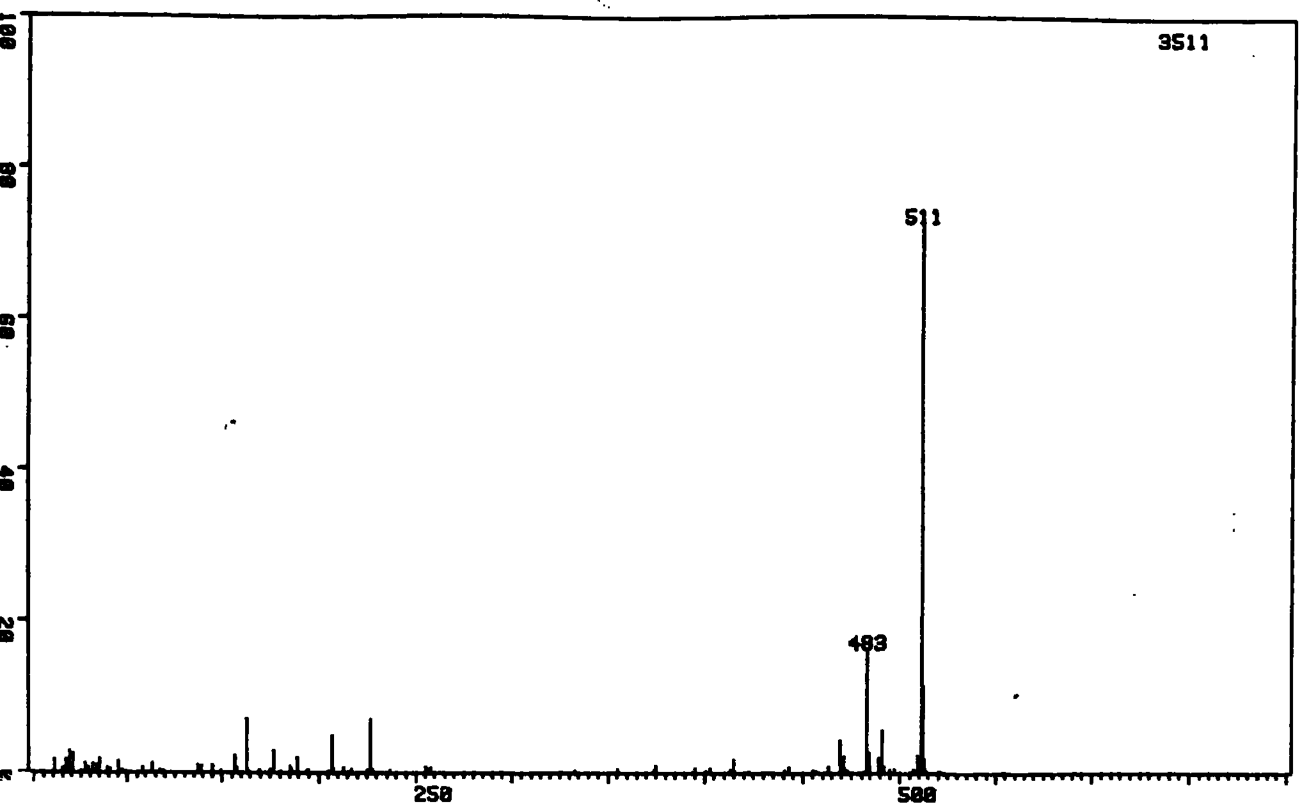


35

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
106.10	0.31	183.07	0.33	253.08	1.48
107.08	100.00	184.08	63.24	260.02	1.31
108.07	82.94	185.08	4.65	261.07	0.28
109.05	3.85	186.09	0.28	262.06	0.86
114.11	0.67	193.07	0.47	263.08	10.26
115.13	40.19	200.02	0.28	264.10	0.72
116.13	2.03	202.06	0.86	271.05	0.86
126.13	0.50	203.07	96.32	272.09	0.53
127.03	6.19	204.08	35.23	273.09	0.81
127.13	2.93	214.07	0.39	279.07	0.36
128.07	0.59	216.10	0.31	287.08	0.36
131.04	0.31	217.10	1.39	291.06	0.36
133.10	1.14	219.05	0.92	293.07	0.56
134.08	0.39	220.05	0.84	310.07	0.47
135.09	0.50	221.06	0.31	312.07	0.33
136.06	0.45	222.06	1.03	313.09	0.59
145.07	0.39	223.08	0.50	320.08	0.50
150.00	0.31	224.07	35.42	331.08	1.76
151.05	0.36	225.07	2.73	332.08	1.03
153.08	0.36	226.08	2.20	339.09	1.39
155.08	0.31	227.08	0.81	351.11	0.67
157.07	4.07	231.05	0.39	352.10	0.36
158.07	0.45	234.08	2.17	377.09	1.84
164.09	9.42	240.01	0.89	378.07	0.31
165.08	2.20	243.05	2.81	388.09	0.47
166.08	1.39	244.07	61.85	407.15	1.20
174.07	0.59	245.08	29.88	408.08	0.81
175.08	0.92	246.07	2.03	427.10	0.36
176.07	17.61	247.06	0.64	447.10	1.25
177.06	1.48	250.04	1.03	448.10	0.64
178.05	0.53	252.05	18.17	461.13	0.31

MJS27X 4
CAL:CALT3

11-OCT-85
0:43

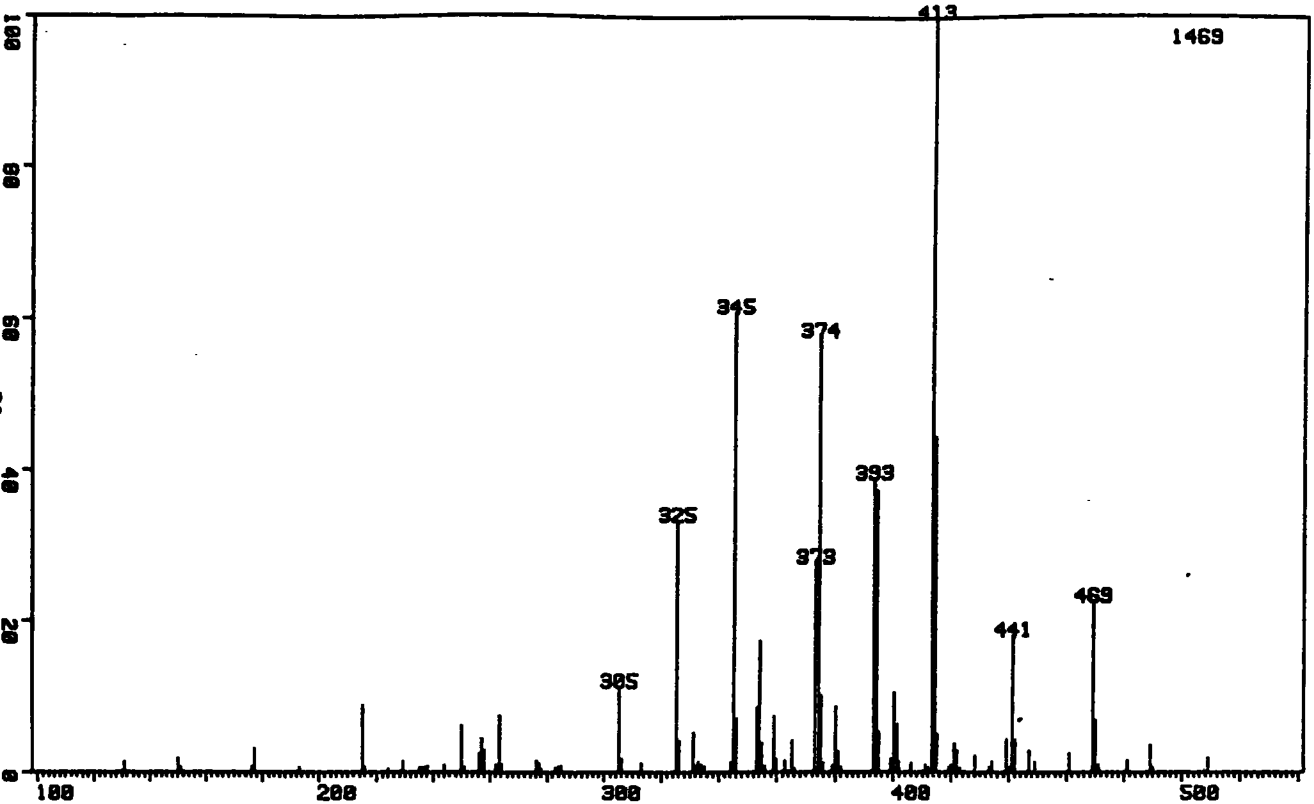


36

MASS	%HT. BASE	MASS	%HT. BASE
112.92	1.28	400.89	0.31
116.95	0.37	402.90	0.71
118.88	0.34	412.89	0.51
136.91	1.08	414.93	1.85
138.89	0.97	415.96	0.26
144.95	1.05	422.90	0.31
145.06	0.26	440.91	0.34
148.92	0.31	442.91	0.83
156.93	2.34	454.95	0.43
157.91	0.66	456.98	0.34
162.90	7.15	462.88	0.94
163.92	0.34	468.89	4.39
168.88	0.48	469.89	0.91
174.91	0.40	470.95	2.34
176.92	2.93	471.94	0.54
180.84	0.31	472.98	0.40
184.90	1.00	481.98	0.23
185.95	0.71	482.95	16.38
186.92	0.28	483.97	2.76
188.86	2.02	484.99	1.05
193.92	0.37	488.93	2.11
194.93	0.37	489.94	0.48
204.94	0.34	490.97	5.67
206.89	4.96	491.96	0.94
207.93	0.60	494.96	0.48
212.91	0.77	496.98	0.60
216.93	0.48	506.90	0.51
224.92	0.37	508.92	2.39
226.93	7.12	509.93	0.88
227.93	0.54	510.90	72.60
236.94	0.37	511.88	11.51

MJS27X 12
CAL:CALN4

11-OCT-85
1:55

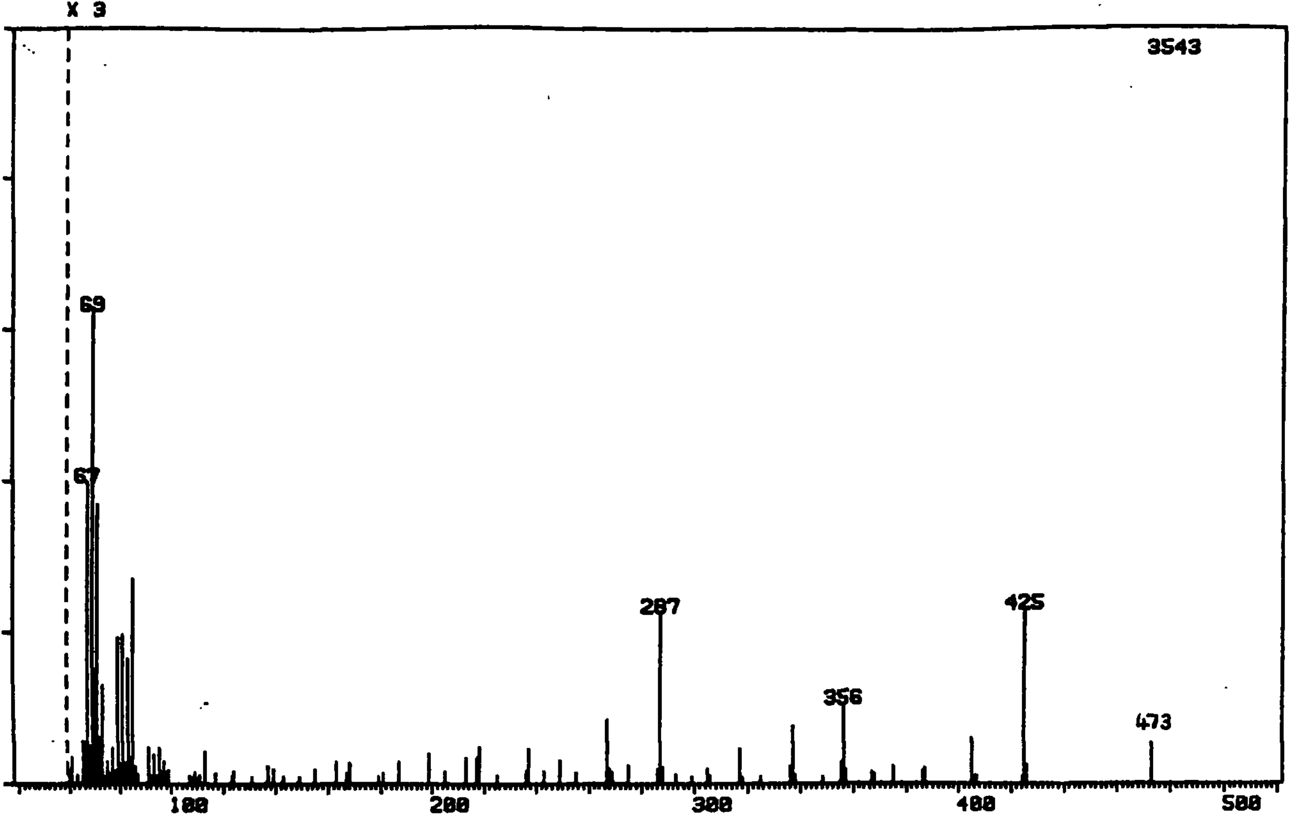


37

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
150.00	1.84	325.10	33.49	400.01	10.55
151.02	0.68	326.07	4.22	401.06	6.33
176.06	0.75	331.04	5.31	402.06	1.43
177.07	3.20	332.07	0.88	406.06	1.23
193.07	0.68	333.09	1.50	411.09	0.95
215.08	8.92	334.08	1.09	412.04	0.61
216.10	0.75	335.08	0.88	413.08	100.00
224.06	0.68	344.09	1.36	414.08	44.38
229.09	1.50	345.08	61.06	415.11	5.11
235.11	0.61	346.08	7.22	419.07	0.75
236.06	0.68	353.08	8.65	420.03	1.02
237.07	0.61	354.07	17.49	421.04	3.81
238.05	0.82	355.05	3.95	422.06	2.86
244.05	0.95	356.07	1.02	423.08	0.61
250.02	6.19	359.03	7.49	428.03	2.18
251.05	0.75	360.02	1.84	433.07	0.75
256.09	2.52	363.06	1.57	434.11	1.43
257.10	4.56	365.09	4.15	439.04	4.42
258.08	3.00	366.07	0.61	440.05	0.75
262.08	1.02	373.08	27.84	441.07	18.18
263.10	7.56	374.09	58.00	442.05	4.29
264.09	1.09	375.10	10.28	447.07	2.93
276.11	1.57	376.07	1.29	449.07	1.36
277.06	1.23	379.09	0.88	461.08	2.52
278.07	0.54	380.07	8.65	469.04	22.74
283.06	0.61	381.06	2.72	470.06	7.01
284.07	0.75	382.09	0.75	471.06	1.02
285.08	0.82	393.09	38.87	481.05	1.57
305.06	11.37	394.11	37.30	489.09	3.61
306.09	1.84	395.06	5.38	490.07	0.75
313.06	1.16	399.02	1.84	509.06	1.97

MS36X 4
CAL:CALP15

16-OCT-85
8:41

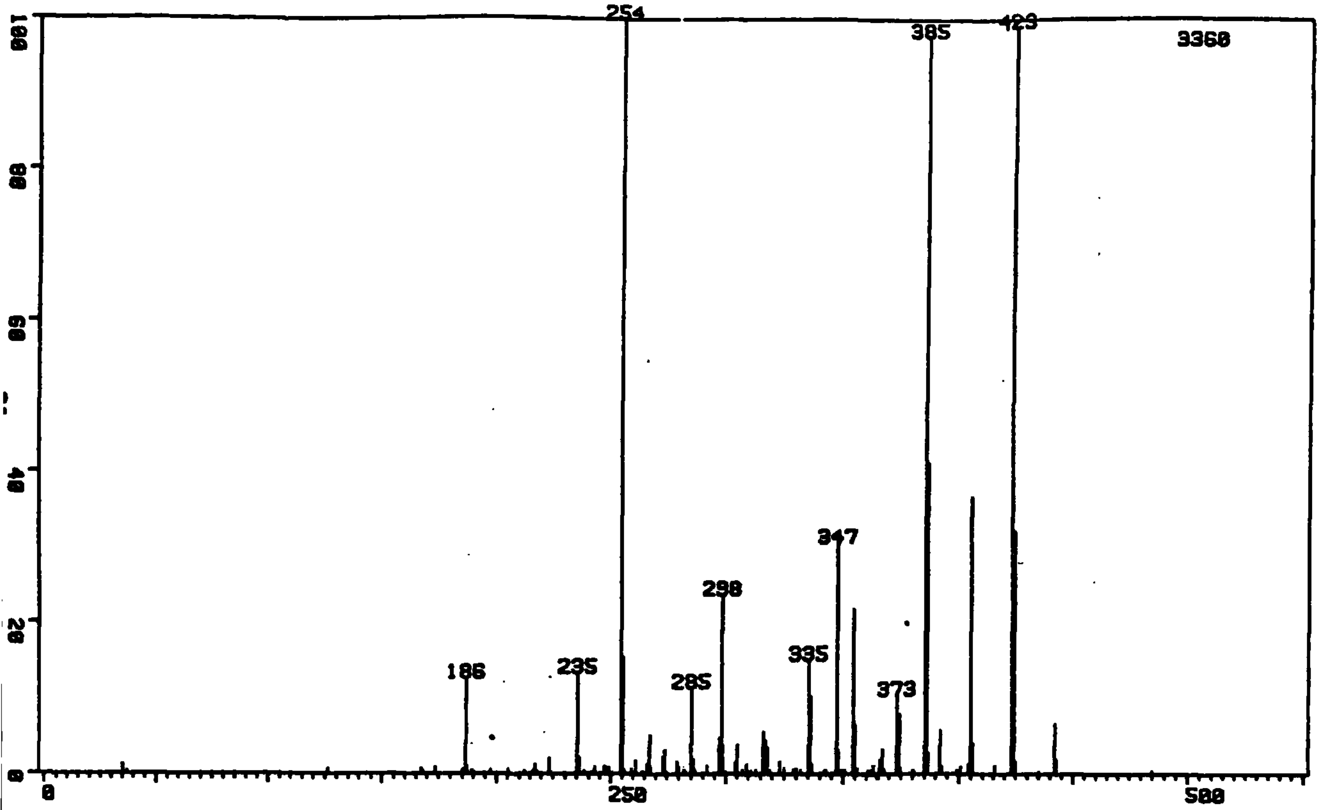


38

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
60.94	1.21	110.97	0.42	268.94	0.54
62.99	0.42	112.92	1.44	274.94	0.82
65.05	1.89	116.91	0.48	285.92	0.65
66.05	1.86	123.03	0.34	286.93	7.59
67.04	13.35	123.93	0.59	287.94	0.76
68.00	1.72	130.85	0.31	292.92	0.42
68.95	20.86	136.90	0.79	298.94	0.34
69.91	5.08	137.02	0.34	304.94	0.68
70.97	12.33	138.98	0.65	305.96	0.37
72.01	2.12	142.88	0.31	316.90	1.55
73.03	4.35	148.96	0.31	317.93	0.31
74.06	0.37	154.89	0.65	324.94	0.34
75.00	0.51	162.91	0.99	335.87	0.76
75.07	1.04	166.90	0.48	336.93	2.54
76.04	0.48	167.89	0.93	337.92	0.42
77.01	1.61	178.89	0.34	347.94	0.31
77.99	0.62	180.85	0.48	354.93	0.93
78.95	6.46	186.90	0.99	355.92	3.53
79.90	0.93	198.89	1.35	356.93	0.65
80.98	6.58	204.96	0.54	366.91	0.51
82.02	1.02	212.93	1.16	367.92	0.45
83.07	5.53	216.92	1.13	374.95	0.76
84.09	1.21	217.93	1.64	385.92	0.56
85.11	9.03	224.94	0.40	386.91	0.71
86.07	0.85	235.93	0.56	404.86	2.00
87.03	0.48	236.92	1.55	405.94	0.37
90.93	1.64	242.90	0.56	406.94	0.40
91.98	0.40	248.93	1.04	423.95	0.31
92.98	1.33	254.92	0.54	424.92	7.71
94.02	0.40	266.91	2.85	425.93	0.85
95.04	1.61	267.90	0.71	472.94	1.81

MS36X 8
CAL:CALN16

16-OCT-85
1:13

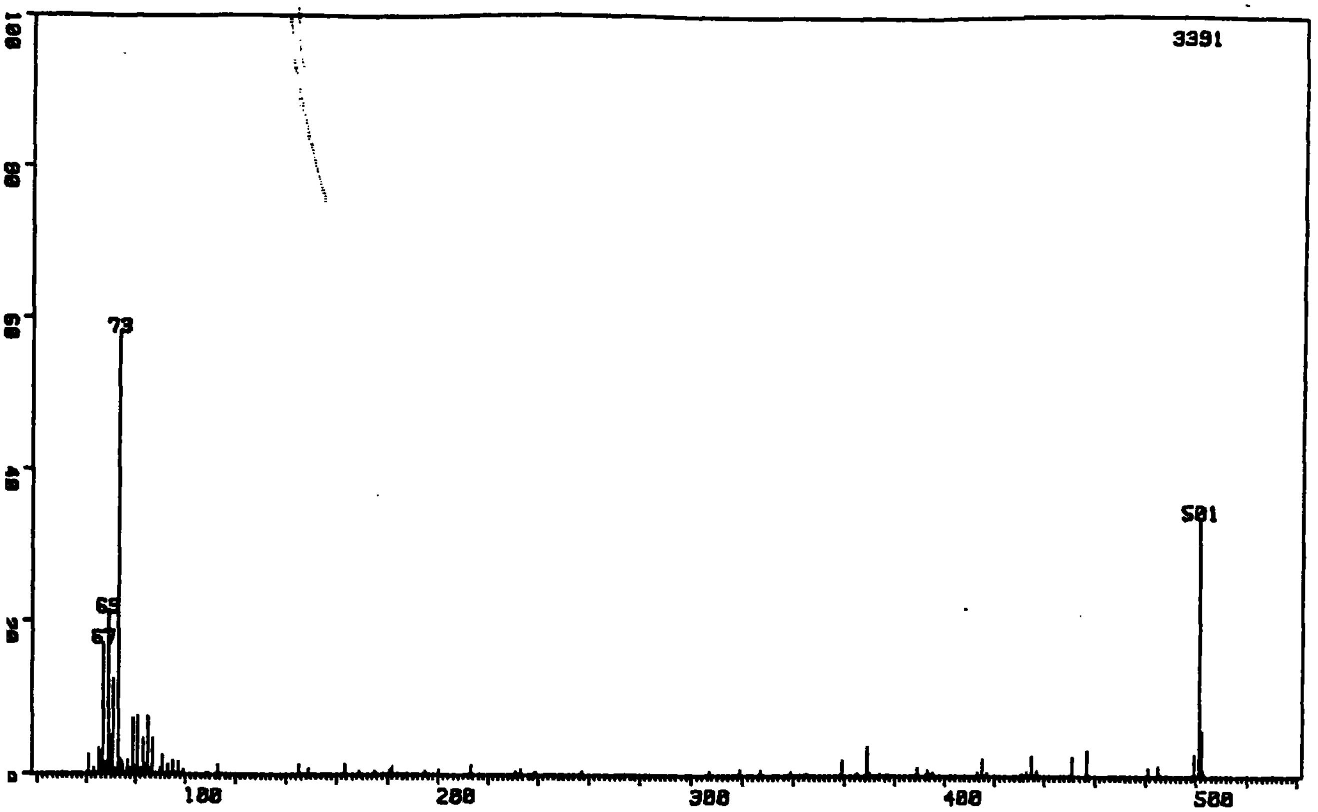


39

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
205.39	0.60	285.99	2.05	350.88	0.62
212.34	0.42	287.00	0.45	353.89	21.90
216.35	0.45	291.95	1.10	354.94	6.64
217.34	1.28	296.95	4.73	355.95	0.74
218.32	0.42	297.97	23.87	360.86	0.51
223.33	2.14	298.96	3.90	361.98	0.39
235.27	13.42	299.93	0.33	362.92	1.19
236.22	2.20	303.94	1.52	365.93	1.93
238.13	0.39	304.96	3.93	366.91	3.30
242.12	0.36	306.95	0.51	367.92	0.51
243.13	0.98	308.91	1.34	372.90	10.54
247.08	1.04	310.90	0.45	373.93	8.07
248.07	0.83	312.93	0.45	374.94	0.77
249.07	0.80	315.88	5.60	379.90	0.51
254.06	100.00	316.94	4.55	380.93	0.39
255.06	15.45	317.94	3.51	384.92	97.74
256.07	0.62	318.94	0.45	385.91	41.28
259.01	0.68	322.92	1.64	386.91	2.89
261.02	1.73	324.92	0.80	391.90	5.80
264.05	0.36	328.87	0.62	392.89	1.07
266.04	1.31	329.90	0.74	398.94	0.57
267.04	5.21	331.90	0.57	400.89	0.98
268.03	0.92	334.95	15.24	403.94	1.31
273.02	2.26	335.94	10.30	404.95	36.64
274.02	3.24	336.94	1.28	405.96	4.08
275.03	0.36	341.92	0.51	415.90	1.07
279.00	1.67	342.91	0.57	422.89	99.05
279.98	0.86	346.92	30.83	423.94	32.02
281.97	0.62	347.91	3.24	424.91	1.73
282.98	0.39	348.90	0.45	434.90	0.36
284.98	11.52	349.90	0.45	441.86	6.64

2172X S
CAL:CALT1

24-AUG-84
8:48

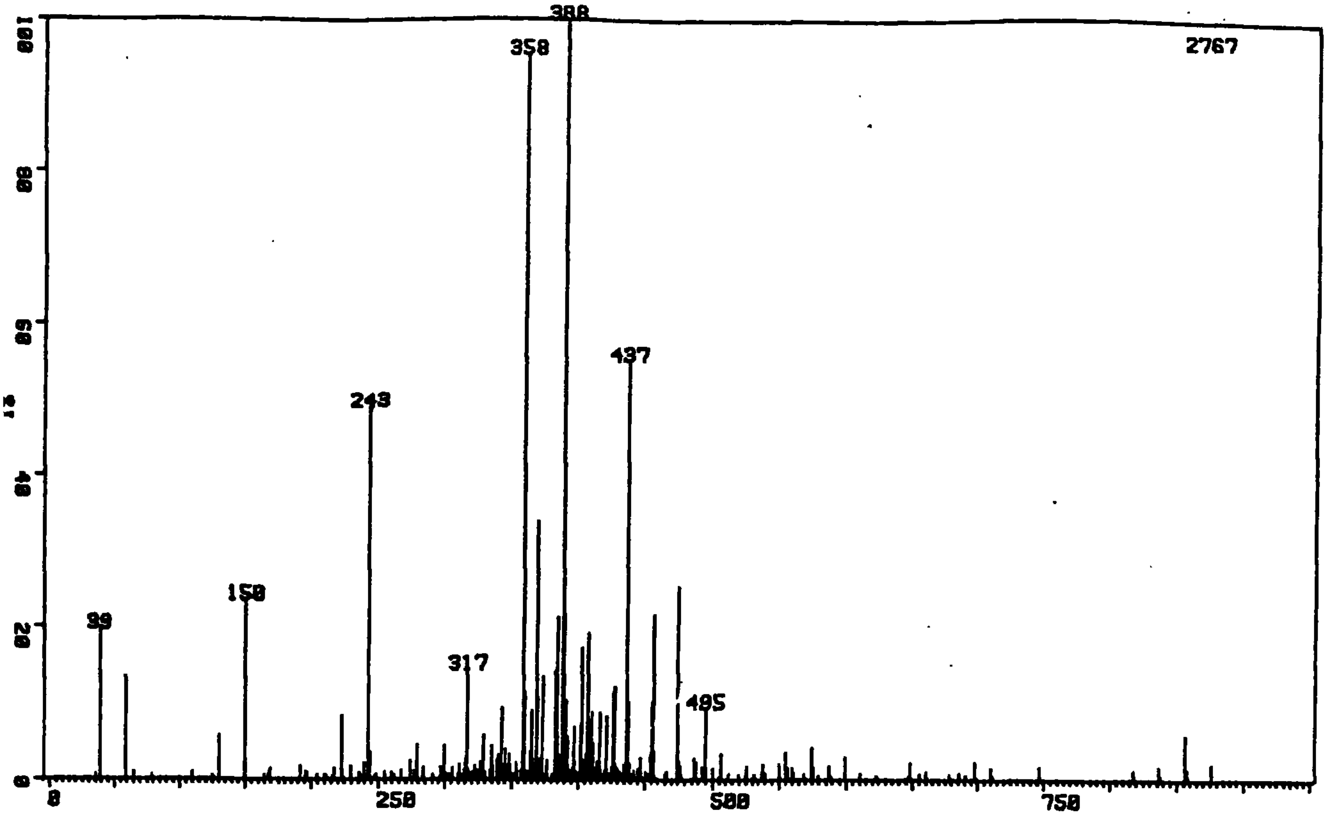


40

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
60.93	2.45	79.90	1.03	256.98	0.44
63.01	0.86	80.96	7.64	306.99	0.59
65.06	3.33	82.01	0.80	318.96	0.86
66.07	2.83	83.05	4.75	326.98	0.77
67.06	17.10	84.08	1.27	338.99	0.47
68.03	1.47	85.08	7.52	345.00	0.32
68.93	2.77	86.09	0.74	359.00	2.12
69.00	21.14	87.05	4.69	365.04	0.41
69.95	5.10	89.88	0.65	368.95	3.83
71.01	12.44	90.96	2.36	369.97	0.44
72.05	0.74	93.00	0.80	374.09	0.35
73.07	58.04	93.06	1.30	376.99	0.29
74.09	2.12	95.02	1.03	388.96	1.09
75.04	0.53	95.09	1.65	392.98	0.88
75.11	1.50	97.09	1.53	394.96	0.47
77.01	1.86	99.05	0.62	413.04	0.56
77.99	0.77	108.95	0.32	415.00	2.27
78.96	7.28	112.97	1.30	417.00	0.44
		145.01	1.33	430.97	0.38
		148.97	0.91	433.03	0.71
		162.98	1.39	435.00	2.60
		168.97	0.47	437.02	0.80
		175.00	0.53	451.02	2.51
		180.94	0.65	457.01	3.30
		182.04	1.09	481.03	1.12
		195.01	0.56	485.05	1.42
		199.98	0.71	485.98	0.29
		212.97	1.24	499.05	2.98
		230.96	0.44	501.07	33.97
		232.99	0.80	502.09	6.05
		238.98	0.44	503.06	0.80

MJS217 11
CAL:CALT2

26-JUL-84
1:39

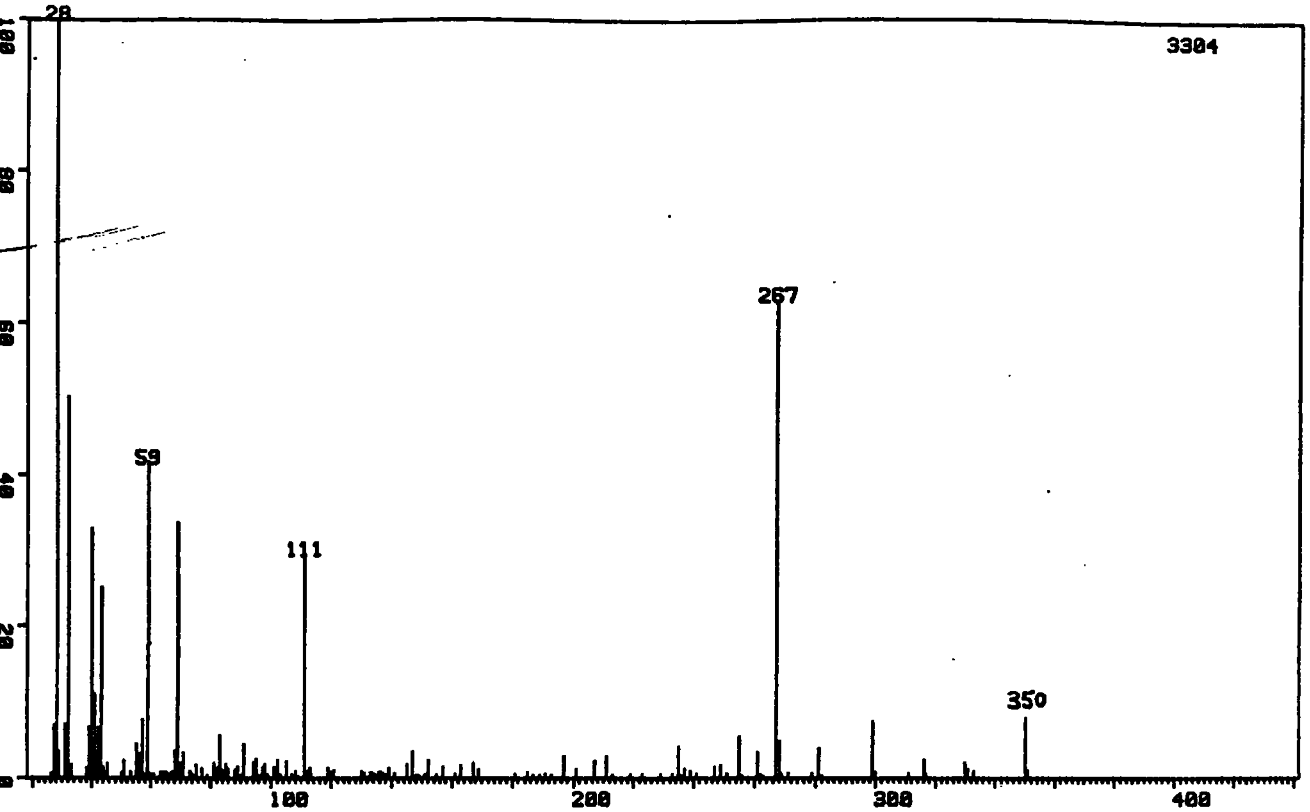


41

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
357.43	1.26	454.26	3.29	554.95	3.51
358.38	95.41	455.30	10.16	556.00	1.12
359.32	11.49	456.26	21.65	557.05	1.52
360.35	4.12	457.30	3.83	560.00	1.48
361.32	1.12	458.26	0.65	561.91	0.90
383.09	14.20	465.17	0.69	568.83	0.83
384.04	21.21	467.10	1.12	574.67	4.26
385.07	5.75	474.05	25.44	575.65	1.59
386.10	2.28	475.04	7.08	579.56	0.51
387.06	3.18	476.04	2.49	587.55	1.84
388.09	100.00	476.94	1.84	588.55	0.69
389.04	21.83	477.93	0.65	599.32	2.96
390.00	3.32	486.85	2.86	611.04	0.90
390.97	10.37	487.87	0.83	622.98	0.47
392.01	5.42	488.79	2.35	647.68	0.47
392.98	5.75	492.80	1.73	648.54	2.28
401.77	7.16	493.74	0.72	655.50	0.72
402.77	17.35	494.86	9.43	660.38	1.05
403.77	2.57	495.79	1.55	678.33	0.69
406.77	7.48	500.58	1.45	686.23	0.90
407.77	19.08	505.67	0.36	691.05	0.47
408.77	7.70	506.63	3.47	698.02	2.35
426.61	11.31	507.59	0.98	709.87	1.63
427.58	12.03	512.55	0.83	711.76	0.47
436.53	55.19	519.41	0.76	747.18	1.73
437.52	10.12	525.34	0.51	817.23	1.26
438.51	1.55	526.34	1.84	836.98	1.70
439.42	2.10	531.22	0.76	837.93	0.76
440.42	0.61	532.35	0.69	856.77	5.96
442.44	1.26	537.24	1.01	857.74	1.37
445.38	1.37	538.26	2.02	876.33	2.20
446.38	0.83				

MJS113 9
CAL:CALT1

25-JUL-85
1:25

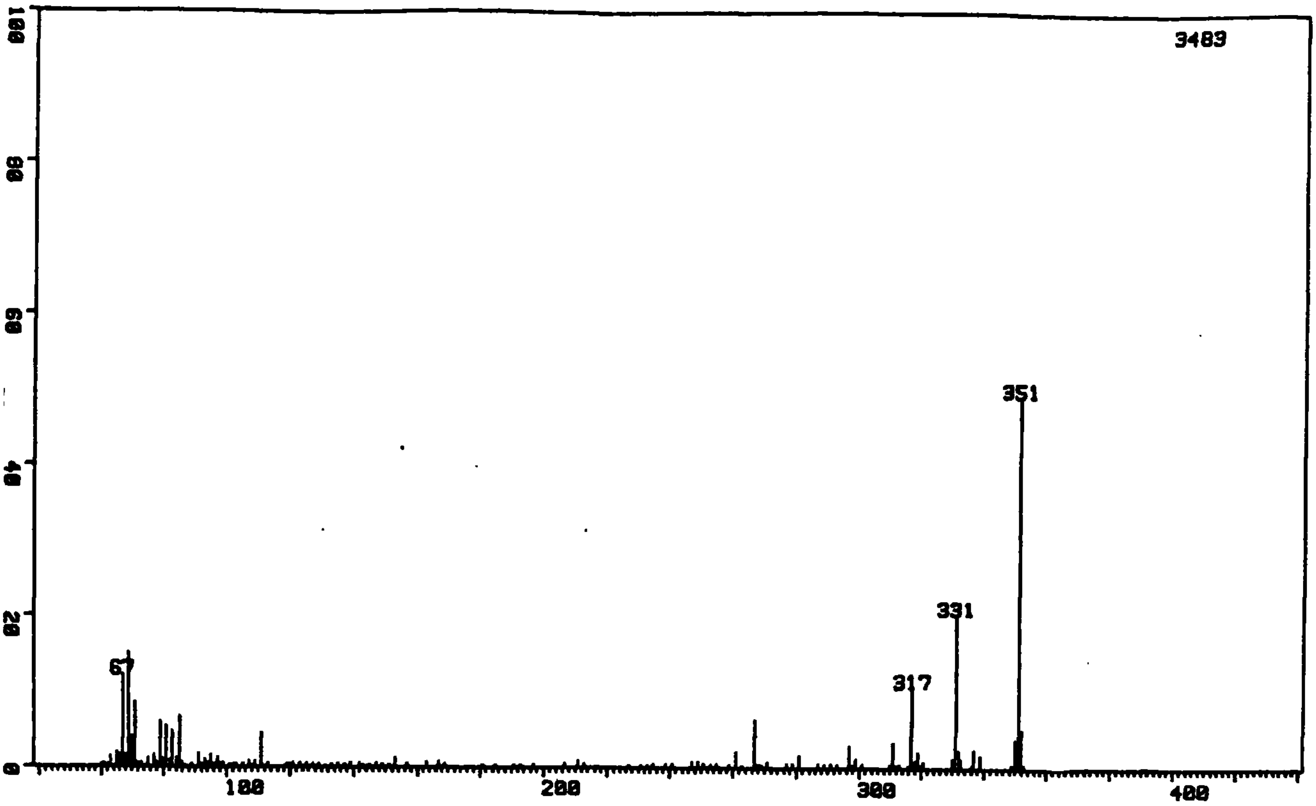


42

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
44.11	0.48	100.93	1.48	234.92	4.15
44.17	0.82	101.97	2.45	235.91	0.42
45.15	2.00	103.00	0.45	236.91	1.30
49.88	0.73	105.04	2.27	238.90	1.06
50.94	2.30	106.97	0.51	240.92	0.61
53.05	0.45	107.95	1.06	246.94	1.54
53.09	0.88	108.99	0.27	248.92	1.76
55.10	2.12	110.89	29.36	250.93	0.61
55.14	4.51	111.03	0.88	254.92	5.48
56.14	3.30	111.95	1.06	255.93	0.42
57.07	2.24	112.07	0.58	260.93	3.48
57.12	7.75	112.96	1.42	261.95	0.48
58.05	0.39	118.91	1.39	262.94	0.33
58.08	0.64	118.98	1.42	266.92	62.92
58.97	41.53	119.94	0.88	267.91	4.96
59.90	0.70	120.91	1.12	268.90	0.64
60.95	0.64	129.88	1.00	270.89	0.67
63.05	0.85	130.94	0.73	278.91	0.70
64.07	0.85	132.98	0.79	280.92	4.00
65.10	0.94	134.08	0.54	281.95	0.33
66.07	0.58	134.98	0.39	298.88	7.45
66.11	0.54	135.99	0.94	299.90	0.88
67.03	0.91	136.97	0.76	310.90	0.70
67.06	0.85	137.95	0.39	315.92	2.42
68.00	3.66	138.93	1.42	316.92	0.51
68.93	33.72	140.91	0.70	329.90	2.06
69.86	0.79	144.98	1.88	330.94	1.24
69.97	2.03	146.97	3.57	332.93	1.00
71.04	3.36	147.96	0.39	349.91	8.05
73.08	1.06	148.93	0.33	350.92	1.09
		150.94	0.54		

MJS113 3
CAL:CALT1

26-JUL-85
0:33



) 43

MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
		180.85	0.34	286.81	0.66
60.91	0.55	184.85	0.32	288.80	0.55
61.94	0.32	190.81	0.32	290.79	0.57
62.99	1.49	192.83	0.26	292.83	0.43
65.03	2.07	196.85	0.43	296.78	2.96
66.03	1.75	206.83	0.57	297.81	0.37
67.01	12.35	210.81	0.86	298.77	1.23
67.98	1.64	212.89	0.49	300.80	0.55
68.93	15.13	226.88	0.32	309.75	0.40
69.88	4.08	230.83	0.32	310.76	3.36
70.97	8.58	232.86	0.32	311.79	0.40
		234.85	0.52	312.79	0.46
128.90	0.32	238.86	0.43	315.75	0.32
130.92	0.26	240.87	0.52	316.78	10.74
132.93	0.37	246.87	0.89	317.78	1.00
135.00	0.49	248.86	0.92	318.77	2.15
137.00	0.40	250.82	0.55	319.75	0.37
138.92	0.66	252.84	0.49	320.76	0.89
141.77	0.43	254.85	0.60	329.73	1.41
142.92	0.34	258.82	0.40	330.75	20.47
144.90	0.32	260.83	2.15	331.78	2.38
146.89	0.60	262.84	0.32	332.77	1.41
148.89	0.34	266.83	6.40	335.78	0.32
148.96	0.34	267.83	0.63	336.74	2.53
150.95	0.29	268.82	0.40	338.73	1.75
152.88	1.23	270.79	0.80	348.72	0.60
156.90	0.40	276.82	0.66	349.72	3.88
162.94	0.78	278.80	0.66	350.73	49.33
166.89	0.80	280.83	1.69	351.75	5.28
168.88	0.40				

COLLOQUIA AND CONFERENCES

COLLOQUIA AND CONFERENCES

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

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

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

(C) details of the postgraduate induction course.

RESEARCH COLLOQUIA, SEMINARS AND LECTURES

A. Lectures and Seminars organised by the Department of Chemistry during the period 1982-1985

13.10.82 * Dr. W.J. Feast (Durham)
"Approaches to the Synthesis of Conjugated Polymers"

14.10.82 Prof. H. Suhr (Tubingen, FRG)
"Preparative Chemistry in Nonequilibrium Plasmas"

27.10.82 Dr. C.E. Housecroft (Oxford High School/Notre Dame)
"Bonding capabilities of butterfly-shaped Fe_4 units. Implications for C-H bond activation in hydrocarbon complexes"

28.10.82 * Prof. M.F. Lappert, FRS (Sussex)
"Approaches to Asymmetric Synthesis and Catalysis using electron-rich olefins and some of their metal complexes"

15.11.82 * Dr G. Bertrand (Toulouse, France)
"Curtius Rearrangement in Organometallic Series: A route for new hybridised species"

24.11.82 Prof. F.R. Hartley (R.M.C.S., Shrivenham)
"Supported Metal-Complex Hydroformulation Catalysts"

24.11.82 * Prof. G.G. Roberts (Applied Physics, Durham)
"Langmuir-Blodgett films: Solid state polymerisation of diacetylenes"

8.12.82 Dr. G. Wooley (Trent)
"Bonds in transition metal-cluster compounds"

12. 1.83 Dr. D.C. Sherrington (Strathclyde)
"Polymer-supported phase transfer catalysts"

9. 2.83 Dr. P. Moore (Warwick)
"Mechanistic studies in solution by stopped flow F.T.-NMR and high pressure NMR line broadening"

21. 2.83 Dr. R. Lynden-Bell (Cambridge)
"Molecular motion in the cubic phase of NaCN"

2. 3.83 * Dr. D. Bloor (Queen Mary College, London)
"The solid-state chemistry of diacetylene monomers and polymers"

8. 3.83 Prof. D.C. Bradley, FRS (Queen Mary College, London)
"Recent Developments in Organo-Imido-Transition Metal Chemistry"

9. 3.83 Dr. D.M.J. Lilley (Dundee)
"DNA, Sequence, Symmetry, Structure and Supercoiling"

11\. 3.83 * Prof. H.G. Viehe (Louvain, Belbium)
"Oxidations on Sulphur" and
"Fluorine substitutions in radicals"
(The W.K.R. Musgrave Lecture)

16\. 3.83 Dr. I. Gosney (Edinburgh)
"New extrusion reactions: Organic synthesis
in a hot-tube"

25\. 3.83 Prof. F.G. Baglin (Nevada, USA)
"Interaction induced Raman Spectroscopy in
Supracritical ethane"

21\. 4.83 Prof. J. Passmore (New Brunswick, Canada)
"Novel selenium-iodine cations"

4\. 5.83 Prof. P.H. Plesch (Keele)
"Binary ionisation equilibria between two ions
and two molecules. What Ostwald never thought of"

10\. 5.83 * Prof. W. Burger (Munich, FRG)
"New reaction pathways from trifluoromethyl-
substituted heterodienes to partially fluorinated
heterocyclic compounds"

11\. 5.83 * Dr. N. Isaacs (Reading)
"The application of high pressures to the theory
and practice of organic chemistry"

13\. 5.83 Dr. R. de Koch (Michigan/Amsterdam)
"Electronic structural calculations in organo-
metallic cobalt cluster molecules. Implications
for metal surfaces"

13\. 5.83 Dr. T.B. Marder (UCLA/Bristol)
"The Chemistry of Metal-carbon and metal-metal
multiple bonds"

16\. 5.83 Prof. R.J. Lagow (Texas, USA)
"The chemistry of polylithium organic compounds.
An unusual class of matter"

18\. 5.83 Dr. D.M. Adams (Leicester)
"Spectroscopy at very high pressures.

25\. 5.83 Dr. J.M. Vernon (York)
"New heterocyclic chemistry involving lead
tetraacetate"

15\. 6.83 Dr. A. Pietrzykowski (Warsaw/Strathclyde)
"Synthesis, structure and properties of Aluminoxanes"

22\. 6.83 Dr. D.W.H. Rankin (Edinburgh)
"Floppy molecules - the influence of phase on
structure"

5\. 7.83 * Prof. J. Miller (Camfinas, Brazil)
"Reactivity in nucleophilic substitution reactions"

5.10.83	Prof. J.P. Maier (Basel, Switzerland) "Recent approaches to spectroscopic characterization of cations"
12.10.83 *	Dr. C.W. McLeland (Port Elizabeth, Australia) "Cyclization of aryl alcohols through the intermediacy of alkoxy radicals and aryl radical cations"
19.10.83	Dr. N.W. Alcock (Warwick) "Aryl tellurium (IV) compounds, patterns of primary and secondary bonding"
26.10.83 *	Dr. R.H. Friend (Cavendish, Cambridge) "Electronic properties of conjugated polymers"
30.11.83	Prof. I.M.G. Cowie (Stirling) "Molecular interpretation of non-relaxation processes in polymer glasses"
2.12.83 *	Dr. G.M. Brooke (Durham) "The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoro-aryl and -heteroaryl systems"
14.12.83	Prof. R.J. Donovan (Edinburgh) "Chemical and physical processes involving the ion-pair states of the halogen molecules"
10. 1.84	Prof. R. Hester (York) "Nanosecond Laser Spectroscopy of Reaction Intermediates"
18. 1.84	Prof. R.K. Harris (UEA) "Multi-nuclear solid state magnetic resonance"
8. 2.84	Dr. B.T. Heaton (Kent) "Multi-nuclear NMR studies"
15. 2.84	Dr. R.M. Paton (Edinburgh) "heterocyclic Syntheses using Nitrile Sulphides"
7. 3.84	Dr. R.T. Walker (Birmingham) "Synthesis and Biological Properties of some 5-substituted Uracic Derivatives; yet another example of serendipity in Anti-viral Chemotherapy"
21. 3.84	Dr. P. Sherwood (Newcastle) "X-ray photoelectron spectroscopic studies of electrode and other surfaces"
21. 3.84	Dr. G. Beamson (Durham/Kratos) "EXAFS: General Principles and Applications"
23. 3.84	Dr. A. Ceulemans (Leuven) "The Development of Field-Type models of the Bonding in Molecular Clusters"
2. 4.84 *	Prof. K. O'Driscoll (Waterloo) "Chain Ending reactions in Free Radical Polymerisation"

3. 4.84	Prof. C.H. Rochester (Dundee) "Infrared Studies of Adsorption at the Solid-Liquid Interface"
25. 4.84	Dr. R.M. Acheson (Biochemistry, Oxford) "Some Heterocyclic Detective Stories"
27. 4.84	Dr. T. Albright (Houston, U.S.A.) "Sigmatropic Rearrangements in Organometallic Chemistry"
14. 5.84 *	Prof. W.R. Dolbier (Florida, USA) "Cycloaddition Reactions of Fluorinated Allenes"
16. 5.84	Dr. P.J. Garratt (UCL) "Synthesis with Dilithiated Vicinal Diesters and Carboximides"
22. 5.84	Prof. F.C. de Schryver (Leuven) "The use of Luminescence in the study of micellar aggregates" and "Configurational and Conformational control in excited state complex formation"
23. 5.84	Prof. M. Tada (Waseda, Japan) "Photochemistry of Dicyanopyrazine Derivatives"
31. 5.84	Dr. A. Haaland (Oslo) "Electron Diffraction Studies of some organometallic compounds"
11. 6.84 *	Dr. J.B. Street (IBM, California) "Conducting Polymers derived from Pyrroles"
19. 9.84 *	Dr. C. Brown, (IBM, California) "New Superbase reactions with organic compounds"
21. 9.84 *	Dr. H.W. Gibson (Signal UOP, Illinois) "Isomerization of Polyacetylene"
19.10.84 *	Dr. A. Germain (Languedoc, Montpellier) "Anodic Oxidation of Perfluoro Organic Compounds in Perfluoroalkane Sulphonic Acids"
24.10.84 *	Prof. R.K. Harris (Durham) "N.M.R. of Solid Polymers"
28.10.84	Dr. R. Snaith (Strathclyde) "Exploring Lithium Chemistry: Novel Structures, Bonding and Reagents"
7.11.84	Prof. W.W. Porterfield (Hampden-Sydney College, USA) "There is no Borane Chemistry (only Geometry)"
7.11.84 *	Dr. H.S. Munro (Durham) "New Information from ESCA Data"
21.11.84	Mr. N. Everall (Durham) "Picosecond Pulsed Laser Raman Spectroscopy"

27.11.84 * Dr. W.J. Feast (Durham)
"A Plain Man's Guide to Polymeric Organic Metals"

28.11.84 Dr. T.A. Stephenson (Edinburgh)
"Some recent studies in Platinum Metal Chemistry"

12.12.84 Dr. K.B. Dillon (Durham)
"^{31}P N.M.R. Studies of some Anionic Phosphorus Complexes"

11. 1.85 Emeritus Prof. H. Suschitzky (Salford)
"Fruitful Fissons of Benzofuroxanes and Isobenzimidazoles (umpolung of o-phenylenediamine)"

13. 2.85 Dr. G.W.J. Flett (Oxford)
"Synthesis of some Alkaloids from Carbohydrates"

19. 2.85 * Dr. D.J. Mincher (Durham)
"Stereoselective Synthesis of some novel Anthracyclinones related to the anti-cancer drug Adriamycin and to the Steffimycin Antibiotics"

27. 2.85 * Dr. R.E. Mulvey (Durham)
"Some unusual Lithium Complexes"

6. 3.85 Dr. P.J. Kocienski (Leeds)
"Some Synthetic Applications of Silicon-Mediated Annulation Reactions"

7. 3.85 Dr. P.J. Rodgers (I.C.I. plc. Agricultural Division, Billingham)
"Industrial Polymers from Bacteria"

12. 3.85 Prof. K.J. Packer (B.P. Ltd./East Anglia)
"N.M.R. Investigations of the Structure of Solid Polymers"

14. 3.85 * Prof. A.R. Katritzky F.R.S. (Florida)
"Some Adventures in Heterocyclic Chemistry"

20. 3.85 Dr. M. Poliakoff (Nottingham)
"New Methods for detecting Organometallic Intermediates in Solution"

28. 3.85 Prof. H. Ringsdorf (Mainz)
"Polymeric Liposomes as Models for Biomembranes and Cells?"

24. 4.85 Dr. M.C. Grossel (Bedford College, London)
"Hydroxypyridone dyes -Bleachable one-dimensional Metals?"

25. 4.85 Major S.A. Shackelford (U.S. Air Force)
"In Situ Mechanistic Studies on Condensed Phase Thermochemical Reaction Processes: Deuterium Isotope Effects in HMX Decomposition, Explosives and Combustion"

1. 5.85 Dr. D. Parker (I.C.I. plc, Petrochemical and Plastics Division, Wilton)
"Applications of Radioisotopes in Industrial Research"

7. 5.85 Prof. G.E. Coates (formerly of University of Wyoming, U.S.A.)
"Chemical Education in England and America: Successes and Deficiencies"

8. 5.85 Prof. D. Tuck (Windsor, Ontario)
"Lower Oxidation State Chemistry of Indium"

8. 5.85 * Prof. G. Williams (U.C.W. Aberystwyth)
"Liquid Crystalline Polymers"

9. 5.85 * Prof. R.K. Harris (Durham)
"Chemistry in a Spin: Nuclear Magnetic Resonance"

14. 5.85 Prof. J. Passmore (New Brunswick, U.S.A.)
"The Synthesis and Characterisation of some Novel Selenium-Iodine Cations, aided by ^{77}Se N.M.R. Spectroscopy"

15. 5.85 Dr. J.E. Packer (Auckland, New Zealand)
"Studies of Free Radical Reactions in squeous solution using Ionising Radiation"

17. 5.85 Prof. I.D. Brown (McMaster University, Canada)
"Bond Valence as a Model for Inorganic Chemistry"

21. 5.85 Dr. D.L.H. Williams (Durham)
"Chemistry in Colour"

22. 5.85 * Dr. M. Hudlicky (Blacksburg, U.S.A.)
"Preferential Elimination of Hydrogen Fluoride from Vicinal Bromofluorocompounds"

22. 5.85 * Dr. R. Grimmett (Otago, New Zealand)
"Some Aspects of Nucleophilic Substitution in Imidazoles"

4. 6.85 Dr. P.S. Belton (Food Research Institute, Norwich)
"Analytical Photoacoustic Spectroscppy"

13. 6.85 Dr. D. Woolins (Imperial College, London)
"Metal - Sulphur - Nitrogen Complexes"

14. 6.85 * Prof. Z. Rappoport (Hebrew University, Jerusalem)
"The Rich Mechanistic World of Nucleophilic Cinylic Substitution"

19. 6.85 Dr. T.N. Mitchell (Dortmund)
"Some Synthetic and NMR - Spectroscopic Studies of Organotin Compounds"

26. 6.85 Prof. G. Shaw (Bradford)
"Synthetic Studies on Imidazole Nucleosides and the Antibiotic Coformycin"

12. 7.85 * Dr. K. Laali (Hydrocarbon Research Institute, University of Southern California)
"Recent Developments in Superacid Chemistry and Mechanistic Considerations in Electrophilic Aromatic Substitutions; a Progress Report"

B. Lectures Organised by Durham University Chemical Society during the period 1982-1985

14.10.82* Mr. F. Shenton (County Analyst, Durham)
"There is death in the pot"

28.10.82 Prof. M.P. Lappert, F.R.S. (Sussex)
"The Chemistry of Some Unusual Subvalent Compounds of the Main Group IV and V Elements"

4.11.82 Dr. D.H. Williams (Cambridge)
"Studies on the Structures and Modes of Action of Antibiotics"

11.11.82 Dr. J. Cramp (I.C.I. plc)
"Lasers in Industry"
(Joint Lecture with the Society of Chemical Industry)

25.11.82 Dr. D.H. Richards, P.E.R.M.E. (Ministry of Defence)
"Terminally Functional Polymers - their Synthesis and Uses"

27. 1.83* Prof. D.W.A. Sharp (Glasgow)
"Some Redox Reactions in Fluorine Chemistry"

3. 2.83 Dr. R. Manning (Dept. Zoology, Durham)
"Molecular Mechanisms of Hormone Action"

10. 2.83 Sir G. Allen, F.R.S. (Unilever Ltd.)
"U.K. Research"

17. 2.83 Prof. A.G. MacDiarmid (Pennsylvania)
"Metallic Covalent Polymers (SN)x and (CH)x and their Derivatives" (R.S.C. Centenary Lecture)

3. 4.83* Prof. A.C.T. North (Leeds)
"The Use of a Computer Display System in Studying Molecular Structures and Interactions"

20.10.83* Prof. R.B. Cundall (Salford)
"Explosives"

3.11.83* Dr. G. Richards (Oxford)
"Quantum Pharmacology"

10.11.83* Prof. J.H. Ridd (U.C.L.)
"Ipso-Attack in Electrophilic Aromatic Substitution"

17.11.83* Dr. J. Harrison (Sterling Organic)
"Applied Chemistry and the Pharmaceutical Industry"
(Joint Lecture with the Society of Chemical Industry)

24.11.83* Prof. D.A. King (Liverpool)
"Chemistry in 2-Dimensions"

1.12.83* Dr. J.D. Coyle (The Open University)
"The Problem with Sunshine"

26. 1.84* Prof. T.L. Blundell (Birkbeck College, London)
"Biological Recognition: Interactions of Macromolecular surfaces"

2. 2.84 *Prof. N.B.H. Jonathan (Southampton)
"Photoelectron Spectroscopy - A Radical Approach"

12. 6.84 *Prof. D. Phillips (The Royal Institution)
"Luminescence and Photochemistry - A Light Entertainment"

23. 2.84 *Prof. F.G.A. Stone F.R.S. (Bristol)
"The Use of Carbene and Carbyne Groups to Synthesise Metal Clusters"
(The Waddington Memorial Lecture)

1. 3.84 * Prof. A.J. Leadbetter (Rutherford Appleton Labs.)
"Liquid Crystals"

8. 3.84 *Prof. D. Chapman (Royal Free Hospital School of Medicine, London
"Phospholipids and Biomembranes, Basic Science and Future Technique"

28. 3.84 *Prof. H. Schmidbaur (Munich, F.R.G.)
"Ylides in Coordination Sphere of Metal: Synthetic, Structural and Theoretical Aspects"
(R.S.C. Centenary Lecture)

18.10.84 Dr. N. Logan (Nottingham)
"N_2O_4 and Rocket Fuels"

23.10.84 *Dr. W.J. Feast (Durham)
"Syntheses of Conjugated Polymers. How and Why?"

8.11.84 Prof. B.J. Aylett (Queen Mary College London)
"Silicon - Dead Common or Refined?"

15.11.84 Prof. B.T. Golding (Newcastle-upon-Tyne)
"The Vitamin B_{12} Mystery"

22.11.84 *Prof. D.T. Clark (I.C.I. New Science Group)
"Structure, Bonding, Reactivity and Synthesis as Revealed by ESCA"
(R.S.C. Tilden Lecture)

29.11.84 Prof. C.J.M. Stirling (University College of North Wales)
"Molecules taking the Strain"

6.12.84 *Prof. R.D. Chambers (Durham)
"The Unusual World of Fluorine"

24. 1.85 Dr. A.K. Covington (Newcastle-upon-Tyne)
"Chemistry with Chips"

31. 1.85 Dr. M.L.H. Green (Oxford)
"Naked Atoms and Negligee Ligands"

7. 2.85 Prof. A. Ledwith (Pilkington Bros.)
"Glass as a High Technology Material"
(Joint Lecture with the Society of Chemical Industry)

14. 2.85 Dr. J.A. Salthouse (Manchester)
"Son et Lumiere"

21. 2.85 Prof. P.M. Maitlis, F.R.S. (Sheffield)
"What Use is Rhodium?"

7. 3.85 Dr. P.W. Atkins (Oxford)
"Magnetic Reactions"

(C) Research Conferences attended

Graduate Symposium, Durham, April 1983

17th Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, 21 December 1983

Graduate Symposium, Durham, April 1984

International Symposium on "Chemistry of Carbanions", University of Durham, 16-20 July 1984

Graduate Symposium, Durham, April 1985

(D) First Year Induction Course, October 1982

This course consists of a series of one hour lectures on the services available in the department.

1. Departmental organisation
2. Safety matters
3. Electrical appliances and infrared spectroscopy
4. Chromatography and Microanalysis
5. Atomic absorptiometry and inorganic analysis
6. Library facilities
7. Mass spectrometry
8. Nuclear magnetic resonance spectroscopy
9. Glassblowing technique.

REFERENCES

REFERENCES

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3. "Preparation, Properties and Industrial Applications of Organofluorine Compounds", M. le Blanc *et al*, ed.R.E.Banks, Ellis Horwood: Chichester, 1982.

4. "Organic Fluorine Chemistry", W.A. Sheppard and C.M. Shorts, Inc., New York, 1969, ch.p.

5. "Organofluorine Chemicals and their Industrial Applications", R.F. Anderson and J.O. Punderson, ed. R.E. Banks, Ellis Horwood: Chichester, 1982.

6. "Preparation, Properties and Industrial Applications of Organofluorine Compounds", S. Smith, ed. R.E. Banks, Ellis Horwood: Chichester, 1979.

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19. F.B. Douning *et al*, U.S.Patent 2,480,560, August 30, 1949.

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