Free-radical approaches to new fluorocarbon derivatives

Alan Peter Swales

FREE-RADICAL APPROACHES TO NEW FLUOROCARBON DERIVATIVES

by

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To Mum and Dad

MEMORANDUM

The work described in this thesis was carried out at the Universities of Durham, United Kingdom and Duisburg, West Germany between October 1985 and December 1988. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

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ABSTRACT

This thesis is concerned with the free-radical addition of nitrogen, silicon and oxygen containing compounds to fluoroalkenes and the chemistry of some of the adducts produced.

Free-radical adducts of many amines cannot be produced directly since nucleophilic attack on the fluoroalkene is often the preferred reaction pathway. An alternative route to primary and secondary mono-amine adducts via N-trimethylsilylamines has been developed. An alternative synthesis of di-amine adducts via amides has met with some success.

Free-radical additions of organosilicon compounds to fluoroalkenes have produced a variety of fluorosilicon adducts. The chemistry of some of these adducts has been investigated.

Work with mono- and di-oxygen functional compounds has provided information on the scope and limitations of this type of free-radical addition reaction.

The dehydrofluorination of ether/hexafluoropropene mono- and di-adducts has been investigated and some novel dienes have been produced.

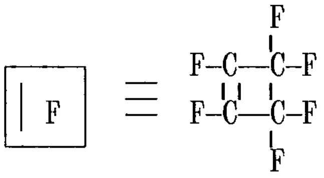
Polymers containing amide or ether groups added to hexafluoropropene under free-radical conditions. The use of a solvent dramatically increased the degree of this incorporation.

The electrochemical fluorination of cyclic ether/hexafluoropropene di-adducts has been investigated. Good recoveries of highly fluorinated products were obtained, indicating that these types of adducts are good starting materials for electrochemical fluorination.

NOMENCLATURE

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

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



CONTENTS

INTRODUCTION

EXPERIMENTAL

CHAPTER ONE

THE CARBON-HYDROGEN BOND AS A FUNCTIONAL GROUP IN FREE-RADICAL ADDITIONS TO FLUORINATED ALKENES

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THE CARBON-HYDROGEN BOND AS A FUNCTIONAL GROUP IN FREE-RADICAL ADDITIONS TO FLUORINATED ALKENES

A. Introduction

Replacement of hydrogen by fluorine in organic molecules can lead to compounds which display unique physical and chemical properties. These properties result from a variety of factors, notably (a) the small size of fluorine (Van der Waals radius, 1.35Å), (b) the high electronegativity of fluorine (Pauling Scale, 4.0[1]), (c) the presence of unshared electron pairs on fluorine and (d) the high bond strength of C-F (116 kcal/mole[2]). Properties such as high thermal and chemical stability, high water and oil repellency, and biological activity have resulted in a diversity of applications for organic fluorine compounds. At present, organic fluorine compounds are used in a wide variety of applications including use as lubricants, elastomers, sealants, protective coatings, pharmaceutical intermediates, textile treating agents, propellants and fire extinguishing agents. Clearly development of techniques for the introduction of fluorine or fluorocarbon groups into organic molecules is of great significance.

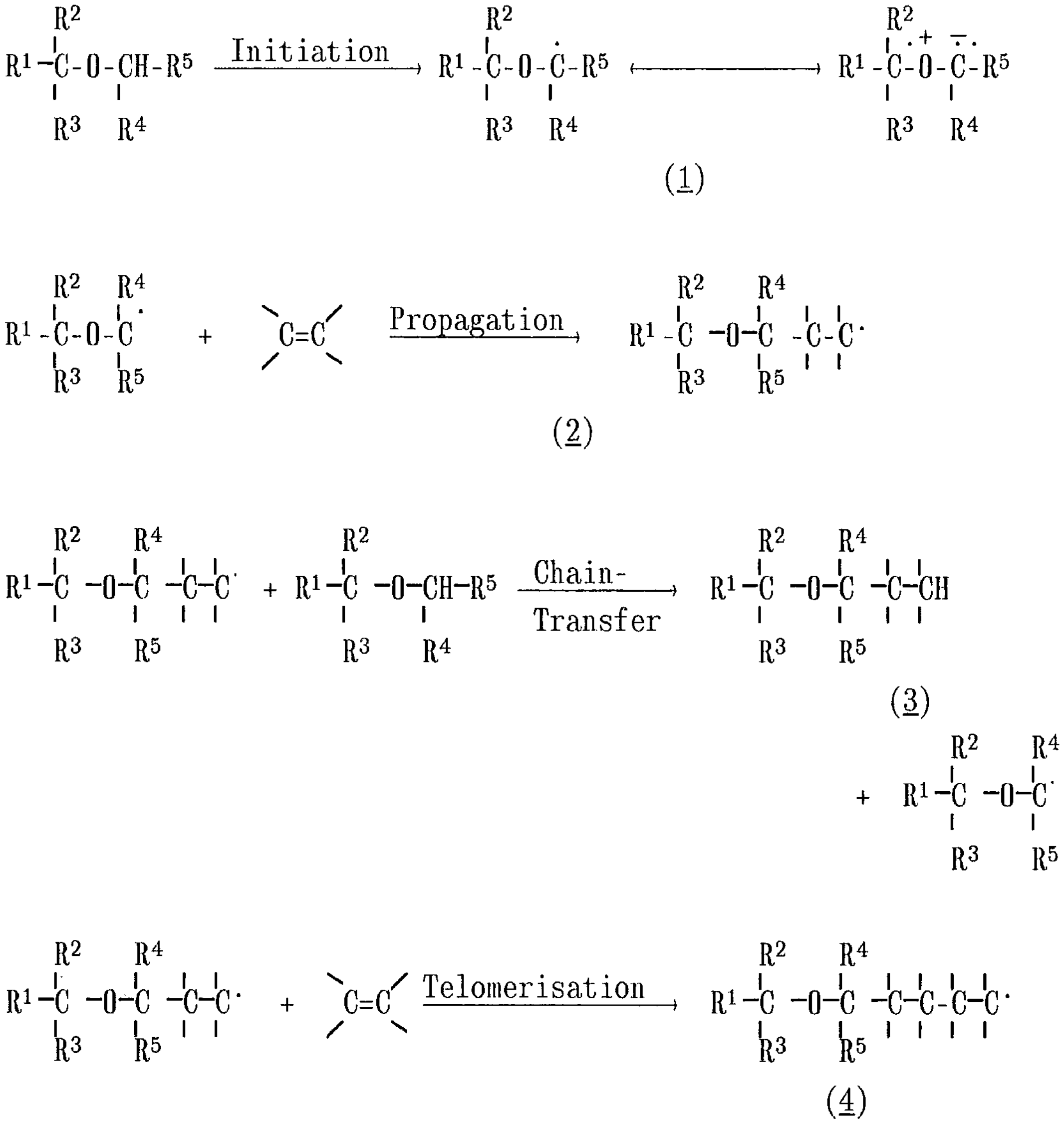
B. Free-Radical Additions To Fluorinated Alkenes

In this laboratory we have a continuing interest in free-radical addition reactions of carbon centred radicals to fluorinated alkenes.[3-5] Radicals stabilised by an adjacent oxygen (e.g. ethers, alcohols), or nitrogen (e.g. amines, amides) are nucleophilic in character and are therefore ideally set up to react with electrophilic fluorinated alkenes. Thus, such reactions in effect utilize a carbon-hydrogen bond as a functional group.

1. Mechanism of Free-Radical Addition

The free-radical addition reactions referred to above are typical radical chain reactions. Scheme 1 below uses the free-radical addition of an ether to an alkene to illustrate the mechanistic steps involved.

SCHEME 1



(i) Initiation methods available include chemical initiators, photochemical irradiation and high energy radiation, e.g. gamma-rays. The initiation step involves abstraction of a hydrogen atom from the ether to give a stabilised radical(1).

(ii) Propagation involves the addition of radical (1) to an alkene molecule, forming a new single bond and generating a new adduct radical (2). Several subsequent reactions of adduct radical (2) are available, leading to a variety of possible products.

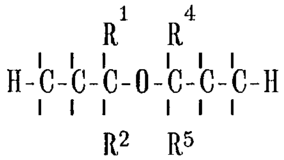
(iii) Chain-Transfer involves abstraction of a hydrogen atom from the ether substrate by the adduct radical (2), leading to a mono-adduct of ether and alkene. This step also regenerates the initial stabilised ether radical (1).

(iv) Telomerisation is an alternative to chain-transfer. Here, the adduct radical (2) adds to another alkene molecule. Similar successive additions are possible, leading to a series of telomeric products. The alkene/ether ratio and the nature of the alkene are important in determining the balance between chain-transfer and telomerisation. Telomerisation is favoured by excess alkene and/or easily telomerisable alkenes, e.g. tetrafluoroethene.

(v) Chain-Termination can occur by a variety of reactions, including radical dimerisations or disproportionations. Only at high radical concentrations or in short chain-length reactions are chain-termination products important.

If the ether contains more than one easily abstractable hydrogen atom then the production of higher adducts is potentially possible.

e.g. If R^3=H then di-adduct (5) could be formed.



$$\mathrm{H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{R^1}{\underset{R^2}{C}}-O-\overset{R^4}{\underset{R^5}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H}$$

(5)

2. Rate and Orientation of Addition

A number of publications dealing with the rate and orientation of free-radical addition to alkenes are available.[6-15] Notable amongst these are several reviews by Tedder and Walton[6-11] who conclude that a combination of polarity, resonance effects and steric hindrance is required in order to rationalize experimental observations.[7] Of these competing factors they consider those affecting bond formation to be more important than intermediate radical stability. The free-radical addition of carbon centred radicals to fluorinated alkenes illustrates well this often complex interplay of competing factors.

The orientation ratios for addition of a series of alkyl radicals to fluoroethene, 1,1-difluoroethene and trifluoroethene are shown in Table 1.

TABLE 1[6]

Orientation Ratios (α:β) for the Addition of Alkyl Radicals to Fluoroethene, 1,1-Difluoroethene and Trifluoroethene at 150°C

Radical	α β CH_2=CHF	α β CH_2=CF_2	α β CHF=CF_2
$CF_3^{\cdot}$	1:0.09	1:0.03	1:0.50
$CHF_2^{\cdot}$	1:0.19	1:0.15	1:0.95
$CH_2F^{\cdot}$	1:0.30	1:0.44	1:2.04
$CH_3^{\cdot}$	1:0.20		1:2.10

For both fluoroethene and 1,1-difluoroethene all radicals add preferentially to the unsubstituted site. This suggests that delocalisation of the unpaired electron in the adduct radical is important in determining the orientation of addition to these alkenes. Delocalisation, however, is not the only factor to be considered. A closer look at the orientation ratios reveals a polar effect: the proportion of attack at the more substituted end of the alkenes decreasing as the radical becomes more 'electrophilic'.

For trifluoroethene, this polar effect becomes dominant, leading to a reversal of orientation within the series of alkyl radicals. The fluorine atoms in trifluoroethene enhance the rate of attack by the 'nucleophilic' methyl radicals, but retard attack by the 'electrophilic' trifluoromethyl radicals (Table 2), thus leading to the observed orientation ratios.

TABLE 2[6]

Relative Rates of Addition of Radicals to Trifluoroethene[a]

Alkene[b]	$CF_3^\cdot$	$CHF_2^\cdot$	$CH_2F^\cdot$	$CH_3^\cdot$
$^*CH_2=CH_2$	1.00	1.00	1.00	1.00
$^*CHF=CF_2$	0.031	0.15		1.00
$^*CF_2=CHF$	0.016	0.14		1.90

a Measurements from gas-phase reactions at 164°C

b * indicates site of addition

The importance of polarity can be further illustrated by looking at the relative rates of addition of radicals $CH_3^\cdot$, $CH_2F^\cdot$, $CHF_2^\cdot$ and $CF_3^\cdot$ to ethene and tetrafluoroethene (Table 3).

TABLE 3[8]

The Ratio of Radical Addition Rates $CF_2=CF_2/CH_2=CH_2$

Radical	$k_{C_2F_4}/k_{C_2H_4}$ (164°C)
$CH_3^\cdot$	9.5
$CH_2F^\cdot$	3.4
$CHF_2^\cdot$	1.1
$CF_3^\cdot$	0.1

By analogy with the polar effects observed within the fluoromethyl radical series, replacement of F in the attacking radical by the less electronegative Br should lead to a small increase in the proportion of attack at the more substituted β- position. The orientation ratios given in Table 4 for addition to fluoroethene and trifluoroethene show that β- addition in fact decreases, thus illustrating the importance of steric effects.

TABLE 4[8]

Orientation Ratios (α:β) for the Addition of Fluorobromomethyl Radicals to Fluoroethene and Trifluoroethene (164°C)

Radical	$\overset{\alpha}{CH_2}=\overset{\beta}{CHF}$	$\overset{\alpha}{CHF}=\overset{\beta}{CF_2}$
$CF_3^\cdot$	1:0.094	1:0.5
$CF_2Br^\cdot$	1:0.089	1:0.47
$CFBr_2^\cdot$	1:0.085	1:0.36
$CBr_3^\cdot$	1:0.040	1:0.24

Stronger evidence for classical steric hindrance comes from the radical series $CF_3^\cdot$, $CF_3CF_2^\cdot$, $(CF_3)_2CF^\cdot$ and $(CF_3)_3C^\cdot$ (Table 5).

TABLE 5[8]

Orientation Ratios for the Addition of Branched Chain Radicals to Fluoroethene (164^{o}C)

Radical	$\overset{\alpha}{C}H_2=\overset{\beta}{C}HF$	
	$\alpha:\beta$	$2k_{\alpha}/k_{e}$
$CF_3\cdot$	1:0.1	0.5
$CF_3CF_2\cdot$	1:0.06	0.6
$(CF_3)_2CF\cdot$	1:0.02	0.5
$(CF_3)_3C\cdot$	1:0.005	0.5

(k_e = the rate of addition to ethene)

The similarity of the $2k_{\alpha}/k_{e}$ values, where k_e is the rate of addition to ethene, confirms that the large variation in orientation ratios ($\alpha:\beta$) is due to specific hindrance to attack at the β-position.

Although the aforegoing results have only scratched the surface, they serve to illustrate that a combination of factors must be addressed when considering the rate and orientation of free-radical addition to alkenes.

3. Review of Recent Literature (1985-1988)

(a) Introduction

Several recent papers have been published concerning the free-radical addition of carbon centred radicals stabilised by an adjacent functional group to fluoroalkenes. The following section aims to bring together these contributions into a single review.

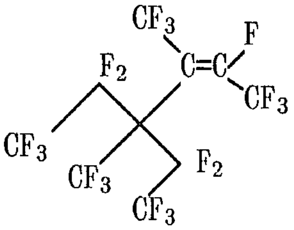
(b) Free-Radical Additions of Oxygen-Functional Substrates to Fluoroalkenes

Free-radical addition reactions of ethers, alcohols and aldehydes etc. to fluorinated alkenes have been well documented in the past.[16] Recent work has provided useful information on the effects of structure, substitution, conformation and reaction conditions in free-radical reactions. Although these effects are all inter-related, it was felt meaningful to separate steric effects from substitution and conformation effects.

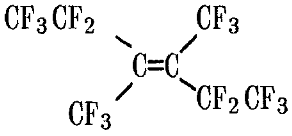
(i) Structural Effects in Free-Radical Additions

Studies of structural effects in free-radical reactions have been directed at both the alkene and the substrate.

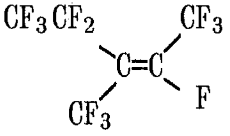
Chambers et al[17] have systematically studied γ-ray induced additions of oxolane to a series of fluorinated alkenes. Fluorinated alkenes such as hexafluoropropene and perfluorocyclopentene reacted well with oxolane but as the substitution at the double bond increased a trend to lower reactivity was observed. Hence perfluoro-3,4-dimethyl-4-ethylhex-2-ene (6) gave only 10% conversion to products and no observable product was obtained from perfluoro-3,4-dimethylhex-3-ene (7).



(6)



(7) (E + Z isomers)

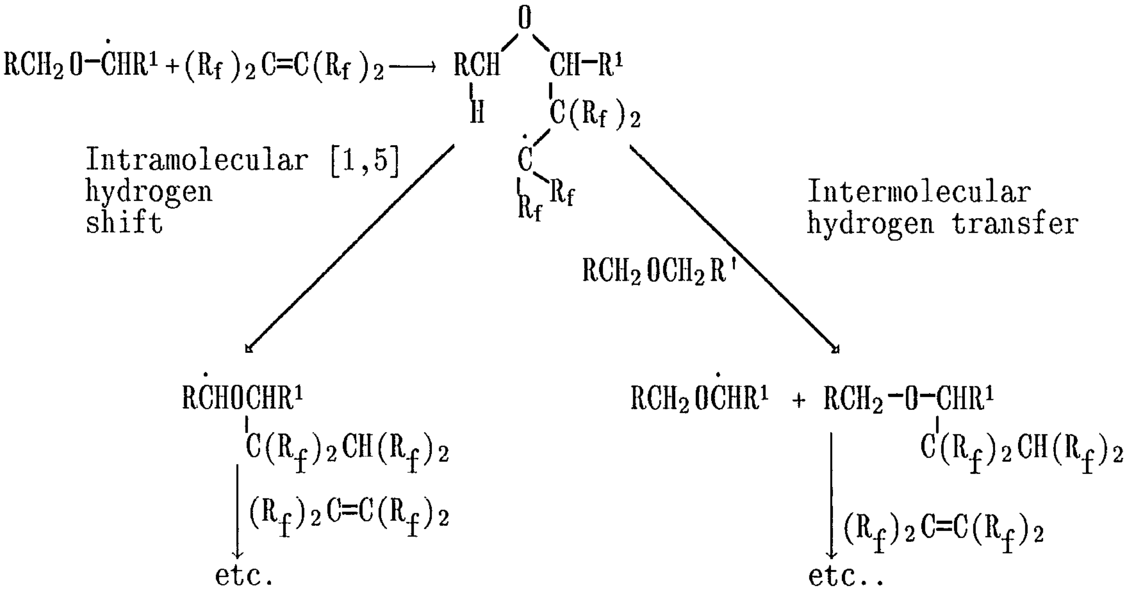


(8)

These results pointed to the importance of steric effects in determining the outcome of free-radical additions. A further significant point reported in the same paper was that, of all the <u>reactive</u> fluoroalkenes studied, only perfluoro-3-methylpent-2-ene (<u>8</u>) gave significant amounts of di-addition product. Comparison of the alkene structures led Chambers et al[17] to conclude that steric effects were again responsible for this result. They suggested that steric inhibition of bimolecular hydrogen transfer was allowing an intramolecular hydrogen shift to compete.

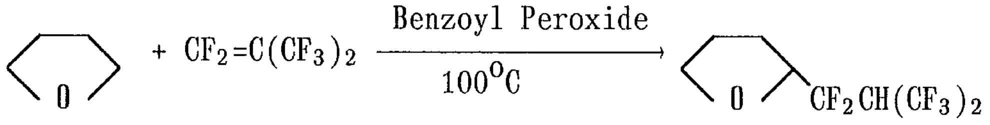
It was Muramatsu and co-workers[18] who originally suggested that the chain-transfer step of a free-radical addition reaction (Scheme 1) could occur via an intramolecular rearrangement as well as via the more accepted intermolecular route (Scheme 2). Evidence was provided by the reaction of diethyl ether with hexafluoropropene. Here, significant proportions of di-addition product were produced even though reaction of the mono-adduct with hexafluoropropene could only yield minor quantities of the di-adduct.

SCHEME 2

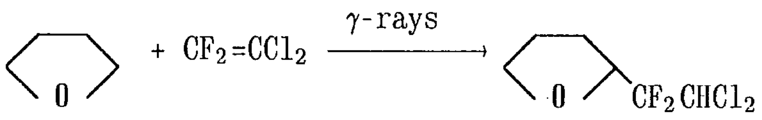


Muramatsu and co-workers[18] and, more recently, Modena and co-workers[19] explained the absence of any di-adduct in reactions with oxolane by referring to its rigid structure. They suggested that this would inhibit formation of an intermediate cyclic structure, so preventing the intramolecular pathway from competing effectively with the intermolecular process. With this in mind, the earlier steric argument outlined by Chambers et al takes on even greater significance.

Other work concerned with the effect of alkene structure on free-radical addition reactions has been performed by Jones.[5] In this work the effects of chlorine verses trifluoromethyl substitution on the reactivity of an alkene were compared. The similarity in steric bulk of a chlorine atom and a trifluoromethyl group was used to explain the similarity in the reactions of perfluoroisobutene and 1,1-dichlorodifluoroethene with oxolane. For both alkenes the intermolecular hydrogen transfer dominates, thus leading exclusively to the mono-adducts (9) and (10) respectively.

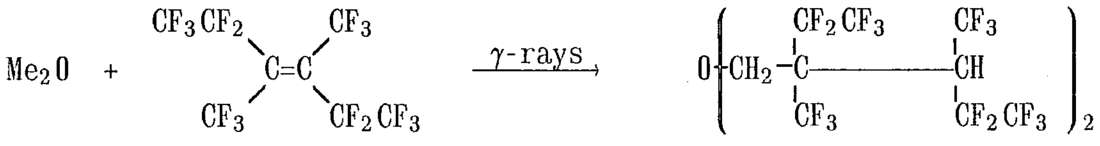


(9) 48%

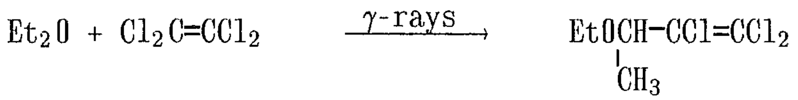


(10) 36%

However, for perfluoro-3,4-dimethyl-3-hexene (7) and tetrachloroethene the steric bulk of the intermediate radical, although similar for both cases, leads to a difference in product composition. For (7) this steric bulk allowed the intramolecular hydrogen transfer process to compete, leading to a di-addition product (11), whereas the steric bulk in the chlorinated intermediate radical favoured elimination of a chlorine atom in the propagation step to give (12).



(7) (11) 28%

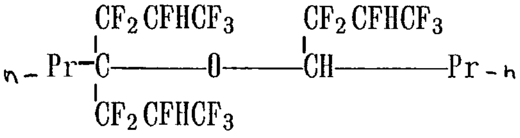


$$Et_2O + Cl_2C{=}CCl_2 \xrightarrow{\gamma\text{-rays}} EtO\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}CCl{=}CCl_2$$

(12) 20%

The author concluded that, even though different types of products were sometimes observed, the steric effect of a chlorine atom and a trifluoromethyl group were similar in these free-radical addition reactions.

The effect of substrate structure in free-radical addition reactions has been addressed by several authors.[5,19-21] In the preceding paragraphs attention was drawn to the work of Muramatsu et al[18] who suggested that the low reactivity of mono-adducts towards fluorinated alkenes was strong evidence that the formation of di-adducts occurs via an intramolecular hydrogen transfer process. Further support for such a mechanism has since been provided by Chambers and co-workers[20] who observed the formation of a tri-adduct (13) as a major product in a γ-ray initiated reaction between dibutyl ether and hexafluoropropene - even in the presence of remaining dibutyl ether.

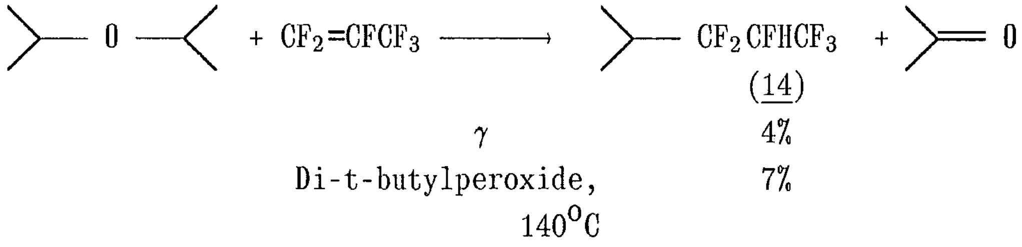


$$n\text{-}Pr{-}\overset{\displaystyle CF_2CFHCF_3}{\underset{\displaystyle CF_2CFHCF_3}{C}}{-}O{-}\overset{\displaystyle CF_2CFHCF_3}{C}H{-}Pr\text{-}n$$

(13)

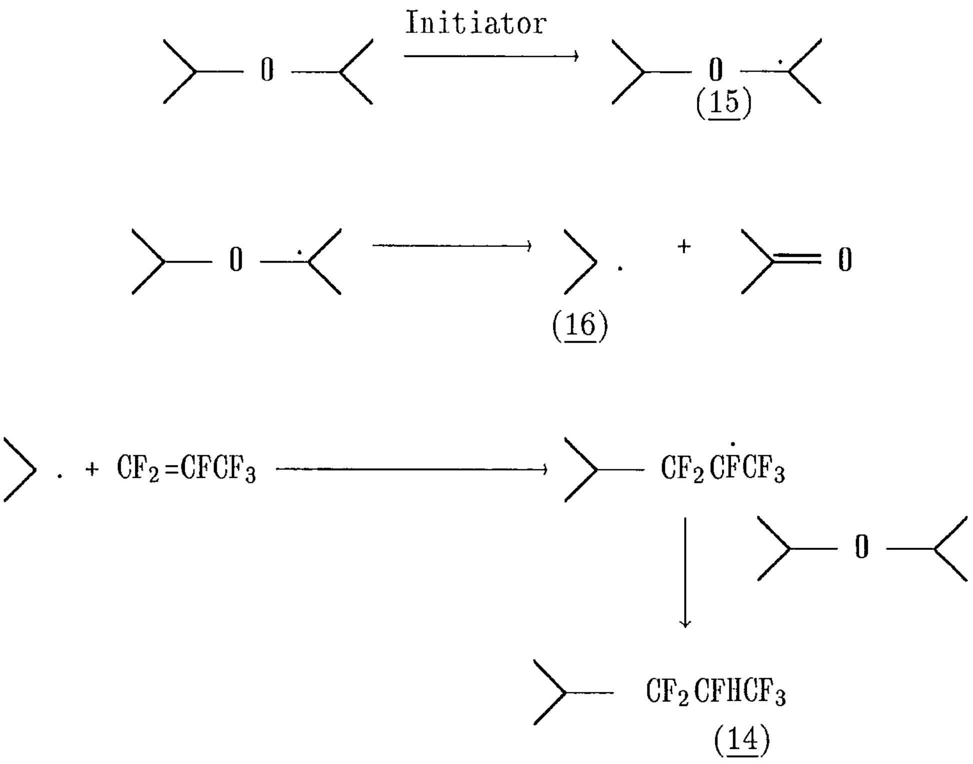
The intermolecular hydrogen transfer step leading to the mono-adduct is obviously impeded in some way in this ether, thus allowing the intramolecular hydrogen transfer to compete more effectively. The authors[20] suggested that the sterically demanding alkyl chains were responsible for this inhibition, a view supported by their observance of a trend to greater di-addition within the acyclic ether series dimethyl ether, diethyl ether and dipropyl ether. They further proposed that increasing the alkyl chain length probably favoured conformations of the intermediate radical which assisted the intramolecular hydrogen transfer step.

Within the same paper,[20] Chambers et al observed a very low conversion to unidentified products for the γ-ray initiated reaction of di-isopropyl ether with hexafluoropropene. Similarly, Modena and co-workers[19] obtained no products from the peroxide initiated addition of di-isopropyl ether to 1,1-dichlorodifluoroethene. Both sets of authors attributed this surprising lack of reactivity to steric hindrance at the reaction centre. Subsequent to these communications, the free-radical reaction of di-isopropyl ether with hexafluoropropene was re-investigated using both γ-ray and peroxide initiation.[5]

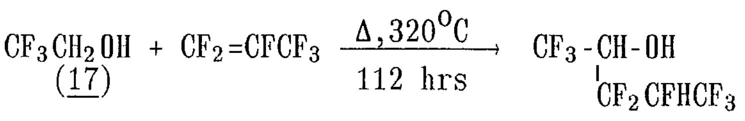


In both cases small amounts of acetone and 1,1,1,2,3,3-hexafluoro-4-methylpentane (<u>14</u>) were detected. These findings led the author to suspect the intermediacy of an isopropyl radical (<u>16</u>). Such a radical could result from rearrangement of the original di-isopropylether radical (<u>15</u>), leading to both acetone and an isopropyl radical (Scheme 3).

<u>SCHEME 3</u>



A further example of the importance of steric effects in free-radical addition reactions was provided by Haszeldine and co-workers[21] during a study into the reactions of a number of alcohols with hexafluoropropene. They obtained a high yield of mono-adduct from the thermal reaction of hexafluoropropene with 2,2,2-trifluoroethanol (<u>17</u>), but a similar reaction between hexafluoropropene and 2,2,3,4,4,4-hexafluorobutan-1-ol (<u>18</u>) proved unsuccessful.



$$\underset{(\underline{17})}{CF_3CH_2OH} + CF_2{=}CFCF_3 \xrightarrow[112\text{ hrs}]{\Delta, 320^{\circ}C} \underset{CF_2CFHCF_3}{CF_3\text{-}\underset{|}{C}H\text{-}OH} \qquad 95\%$$

$$\underset{(\underline{18})}{CF_3CFHCF_2CH_2OH} + CF_2{=}CFCF_3 \; \not\xrightarrow[120\text{ hrs}]{\Delta, 355^{\circ}C}$$

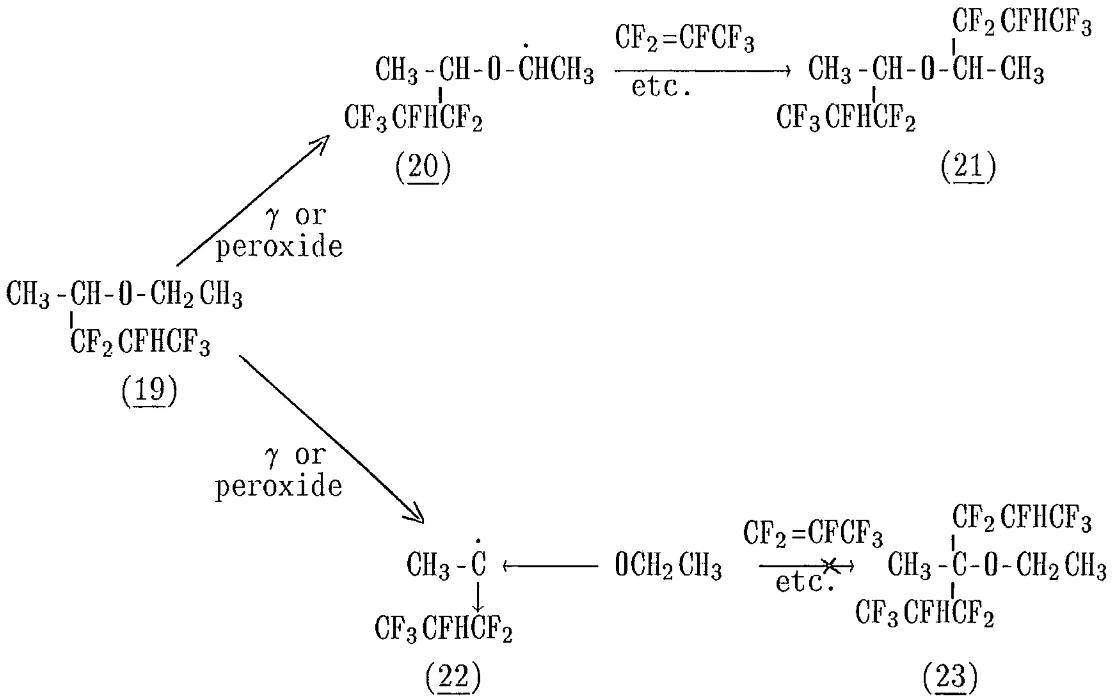
In order to explain these results, Haszeldine et al[21] suggested that the more bulky CF_3CFHCF_2 group was sterically hindering abstraction of an α-hydrogen atom, so preventing adduct formation.

The above examples illustrate quite clearly that the size of substituents in both the alkene and the substrate play a significant role in determining the outcome of many free-radical addition reactions.

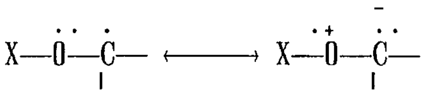
(ii) Substituent Effects in Free-Radical Additions

Katritzky and co-workers[22] and Viehe and co-workers[23] have emphasised the stablilizing effect of a combination of donor and acceptor groups attached to a radical centre. This 'capto-dative' effect has been well illustrated for compounds which incorporate a conjugatively electron-withdrawing group.[23] Chambers et al[20] reasoned that the free-radical addition reaction between diethyl ether/hexafluoropropene mono-adduct (19) and hexafluoropropene would be a good test of the applicability of this concept to compounds containing inductively electron-withdrawing groups. Thus, the reaction should proceed via radical (22), which has the opportunity of capto-dative stabilisation, rather than via radical (20) (Scheme 4). Like Muramatsu and co-workers[18] before them, they found extreme difficulty in producing any di-adduct at all and, when analysed, the product proved to be of structure (21). This led the authors[20] to suggest that capto-dative effects were unimportant for systems with inductively electron-withdrawing groups.

SCHEME 4



In the same paper Chambers et al reported the results of a study into the free-radical addition reactions of ethers, of general structure X-O-Me, with hexafluoropropene.[20] Using γ-ray initiation at room temperature they found negligible conversion to products for all cases where X was electron-withdrawing. Representing the stabilising effect of an ether oxygen on an adjacent radical by (24), they suggested that their observations could be explained by a reduced ability to donate, as represented by (24b), when X was electron-withdrawing.



(24a) (24b)

Such an effect would reduce both the nucleophilic character and stability of the radical and could therefore manifest itself in either the addition (eqn. 1) or chain-transfer (eqn. 2) steps of the addition reaction.

$$X\text{—}O\text{—}\dot{C}H_2 \; + \; CF_2{=}CFCF_3 \longrightarrow X\text{—}O\text{—}CH_2\text{—}CF_2\dot{C}FCF_3$$

eqn.1

$$X\text{—}O\text{—}CH_2CF_2\dot{C}FCF_3 + X\text{—}OMe \longrightarrow X\text{—}O\text{—}CH_2CF_2CFHCF_3 + XO\dot{C}H_2$$

eqn.2

Further information was sought by measuring acetone-t-butylalcohol ratios[24] for the decomposition of di-t-butylperoxide in the presence of several of the X-O-Me derivatives.[20] In this technique the di-t-butylperoxide decomposes to tertiarybutoxy radicals (25) which undergo a β-scission reaction at a constant rate (k_2) to give acetone and a methyl radical. In competition with this β-scission is the tertiarybutoxy radical abstraction of a hydrogen atom from the X-O-Me substrate. The rate of this hydrogen abstraction (k_1) is dependent on the ease of production of a radical from the substrate. Tertiarybutanol is produced as a side product and so the relative

$$^{t}BuO\text{-}O^{t}Bu \longrightarrow \underset{(25)}{2\,^{t}BuO^{\cdot}}$$

$$^{t}BuO^{\cdot} + R\text{-}H \xrightarrow{k_1} {}^{t}BuOH + R^{\cdot}$$

$$^{t}BuO^{\cdot} \xrightarrow{k_2} CH_3COCH_3 + Me^{\cdot}$$

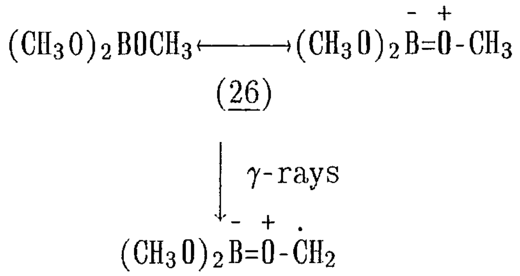
rates of the two reactions can be found from the ratio of acetone and t-butanol formed in the reaction.

$$\frac{k_2}{k_1} \; \alpha \; \frac{\left[CH_3COCH_3\right]}{\left[{}^{t}BuOH\right]}$$

Chambers and co-workers found a clear relationship between these ratios and reactivity towards hexafluoropropene for the X-OMe series of derivatives. From this they concluded that the substituent effects that they had observed were related to the ease of hydrogen abstraction, as outlined in eqn. 2.

A similar study into the effect of varying substituent R in aldehydes of general structure RCHO was carried out by another worker.[5] In both acetone-t-butylalcohol ratios and reactivity towards hexafluoropropene, the results matched those for ethers.[20] Interestingly, when Jones extended his investigation to include unsaturated substituents such as phenyl or allyl then, although the acetone-t-butylalcohol ratios suggested that radicals were being produced, no products were observed in reactions with hexafluoropropene. To explain these apparently anomalous results the author suggested that the radicals formed in these cases were extensively delocalised by interaction with electrons in the oxygen lone-pair and the double bonds, thus rendering them too stable to undergo addition.

In connection with their work on the general ether series X-O-Me, Chambers et al[20] looked at the room temperature γ-ray initiated reaction of trimethyl borate with hexafluoropropene. Here X was the very powerful conjugatively electron-withdrawing group $(MeO)_2B$ and , as such, was expected to greatly inhibit the reaction. In practice the addition proceeded smoothly to give a good yield of tri-adduct. Further reactions with a series of cyclic fluoroalkenes also proceeded readily to give analogous products. After eliminating the possibility that minute traces of methanol were providing an alternative route to the observed products, the authors were left with the conclusion that boron was promoting, rather than inhibiting, the production of a radical at the attached alkoxy site. They proposed that the boron was participating in a pseudo-allylic system (26), leading to the radical (27) in which the unpaired electron was in an orbital extending to include B-O-C.



$$(CH_3O)_2BOCH_3 \longleftrightarrow (CH_3O)_2\overset{-}{B}=\overset{+}{O}-CH_3$$

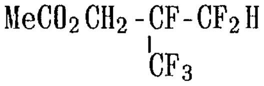
(26)

$$\Big\downarrow \gamma\text{-rays}$$

$$(CH_3O)_2\overset{-}{B}=\overset{+}{O}-\dot{C}H_2$$

(27)

In the same paper[20] it was reported that, despite giving negligible amounts of products when reacted at room temperature, the ethers X-O-Me, where X = HCO,MeCO and MeOCO, reacted reasonably well with hexafluoropropene at elevated temperatures. The important point to arise from these experiments was that, for the ethers that could produce more than one possible radical ,the major product was formed by addition of the $-O\dot{C}H_2$ radical to hexafluoropropene. In the reaction of methyl acetate a small amount of product (28) resulting from radical attack on the central carbon of hexafluoropropene was observed.



$$MeCO_2CH_2-\underset{\displaystyle CF_3}{\underset{|}{C}}F-CF_2H$$

(28)

This type of product has been previously observed for other radicals with electron-withdrawing substituents[25] and is perhaps understandable in the light of the polarity of hexafluoropropene $(\overset{\delta+}{C}F_2=\overset{\delta-}{C}FCF_3)$. A similar product was also reported to be a minor adduct in the free-radical addition of methanol to hexafluoropropene.[21] The authors did not observe any corresponding products in the reactions of longer alkyl chain length alcohols with hexafluoropropene. They therefore cited the greater steric bulk and lower electrophilicity of the intermediate radicals formed from these higher alcohols to explain this lack of attack on the central hexafluoropropene carbon atom.

(iii) Conformational Effects in Free-Radical Additions

An excellent series of papers[26-29] reporting the results of investigations into the rates of hydrogen atom abstraction from a series of ethers, 1,3-dioxanes and amines appeared in the early 1980's. The authors reported pronounced stereoelectronic effects similar to those observed earlier in heterolytic chemistry by Deslongchamps et al.[30]

For cyclic ether systems of different sizes Maletesta and Scaiano[27] found that the absolute rate constants for hydrogen abstraction by t-butoxy radicals decreased along the series in the order 5>7>4>6>3. Given that the activating influence of oxygen on the formation of a radical at an adjacent site can be represented by (29), the interaction of an electron-pair on oxygen with the orbital

$$-\ddot{O}-\dot{C}H- \longleftrightarrow -\overset{+}{\dot{O}}-\overset{-}{\ddot{C}}H-$$

(29a) (29b)

containing the odd-electron is crucial. It has been established by photoelectron spectroscopy that the two lone-pairs of electrons on oxygen are not equivalent.[31] One is roughly an s-type orbital and the other is essentially a higher energy p-type orbital. Since the p-type orbital is of similar energy to that of the unpaired electron in a radical, this alone should be the crucial interaction.[26] Malatesta and Scaiano[27] attributed the observed rate constants for cyclic ethers to a combination of ring-strain relief and the energy requirement for each ring system to produce an essentially eclipsing interaction between this p-type orbital on oxygen and the breaking carbon-hydrogen bond.

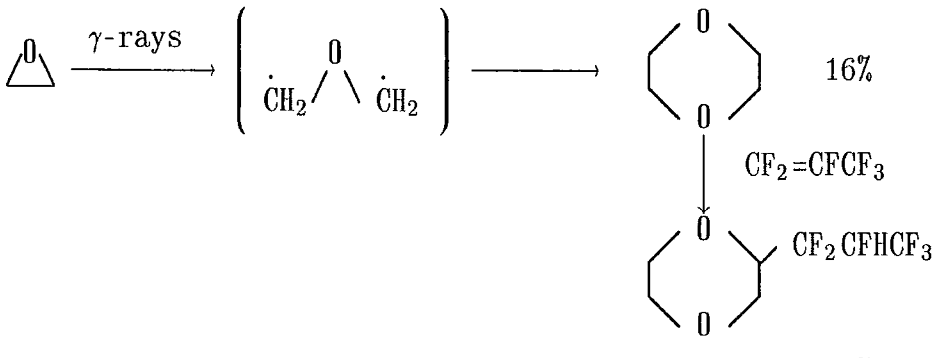
In a more recent publication,[17] Chambers and Grievson reported the results of a study into the additions of a series of cyclic ethers to some fluoroalkenes. For reactions with perfluoro-2-butene (<u>30</u>) they observed a reduction in reactivity in the order oxolane > oxepane > oxane.

$CF_3CF{=}CFCF_3$

(<u>30</u>)

By performing a series of competition reactions for a deficiency of perfluoroalkene they were able to confirm this observed reactivity order. The authors noted that this order was the same as that reported by Malatesta and Scaiano[27] for the rate constants for hydrogen abstraction by t-butoxy radicals and invoked the same conformational explanation. Thus they suggested that the greater reactivity of oxolane reflected the lower energy-barrier to attainment of the favourable eclipsing interaction in comparison with other ring systems. Similarly, the higher conformational mobility of the seven-membered ring accounted for the greater reactivity of oxepane over oxane.

In the same paper, oxirane was found to give only products arising from ring opening, (<u>31</u>), when reacted with hexafluoropropene.



(<u>31</u>) 5%

In addition, free-radical reactions of 12-crown-4 and 18-crown-6 polyethers to hexafluoropropene proved to be unsuccessful. The authors concluded that the crown ethers adopted conformations which were very unfavourable to interaction of electron-pairs on oxygen with the adjacent radical site.

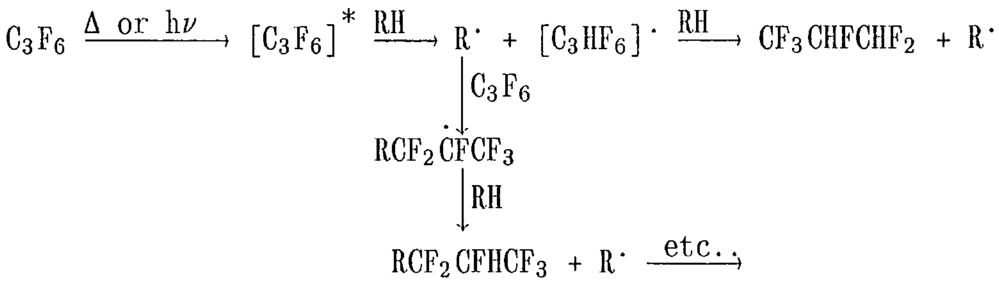
(iv) The Effect of Reaction Conditions on Free-Radical Additions

This section will address both the effects of using different modes of initiation and the effects of varying the conditions, within a single initiation type, on free-radical addition reactions.

In a recent publication by Haszeldine et al[21] the results of a series of reactions between hexafluoropropene and various alcohols were reported. Many of the reactions were carried out under thermal, photochemical (no added photoinitiator) and peroxide-initiated conditions, thus enabling comparisons to be drawn. For methanol, ethanol and isopropanol only mono-adducts were observed and, in each case, photoinitiation gave the highest yields and thermal initiation the lowest. For isobutanol only thermal and photochemical initiation were examined with the photochemcial route again leading to the highest product yield. In all the reactions high product yields were reported, regardless of the mode of initiation.

A radical-chain mechanism initiated by excited hexafluoropropene was proposed for the essentially 'uninitiated' thermal and photochemical reactions (Scheme 5).

SCHEME 5



$$\begin{tikzcd}
C_3F_6 \arrow[r, "\Delta \text{ or } h\nu"] & {[C_3F_6]^*} \arrow[r, "RH"] & R^{\cdot} \arrow[d, "C_3F_6"] & + [C_3HF_6]^{\cdot} \arrow[r, "RH"] & CF_3CHFCHF_2 + R^{\cdot} \\
 & & RCF_2\dot{C}FCF_3 \arrow[d, "RH"] & & \\
 & & RCF_2CFHCF_3 + R^{\cdot} \arrow[r, "etc."] & {} &
\end{tikzcd}$$

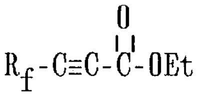
This mechanism was supported by the detection of the hexafluoropropane, $CF_3CHFCHF_2$ in the products of reactions so initiated. An alternative mechanism proceeding via the same type of radical intermediates but involving charge-transfer complexes has been proposed in the past[32] for similarly initiated free-radical reactions.

Other recent work[5] on uninitiated free-radical additions has led to the observation that both oxolane and N-methylpyrrolidine add to hexafluoropropene at room temperature in the dark to produce excellent yields of the corresponding mono-adducts. The failure of a series of other ethers and amines to add to hexafluoropropene under the same conditions led the author to suggest that the high stability of the radicals in the five-membered ring was a driving force for the reaction. Similar uninitiated additions to chlorotrifluoroethene and 1,1-dichlorodifluoroethene proved unsuccessful even with oxolane and N-methylpyrrolidine at elevated temperatures.

Another recent investigation into uninitiated free-radical addition reactions has involved the thermal additions of oxolane to several F-alkylethenes (32), F-alkylethynes (33) and ethyl 3-F-alkyl propynoates (34).[33]

R_f-$CH{=}CH_2$ (32)

R_f-$C{\equiv}CH$ (33)



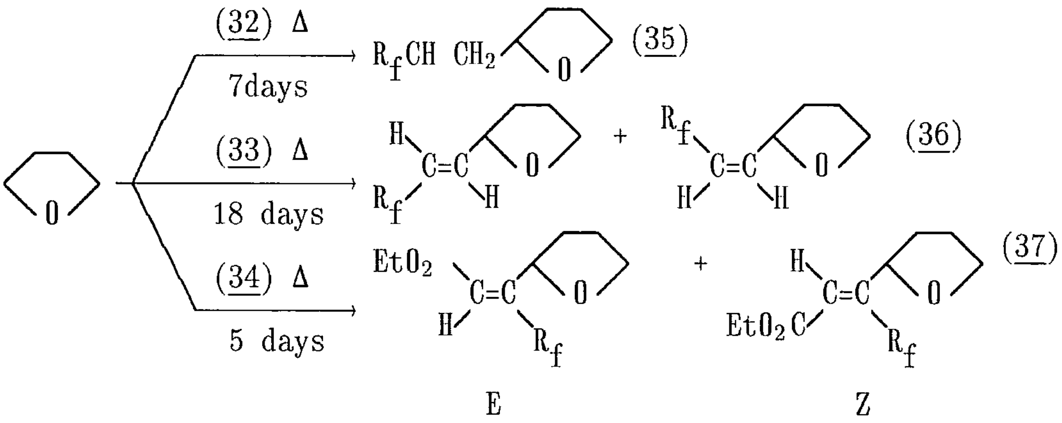
$R_f\text{-}C{\equiv}C\text{-}\overset{O}{\overset{\|}{C}}\text{-}OEt$

(34)

where R_f = n-C_4F_9; n-C_6F_{13}; n-C_8F_{17}

No reaction occurred at temperatures below -10°C and at 20°C only the ethyl 3-F-alkyl propynoates (34) reacted. Even in this case the products, (37), were produced at a very slow rate. At reflux, however, all the reactions proceeded to completion according to Scheme 6, with the ethyl 3-F-alkyl propynoates (34) requiring the shortest reaction time.

SCHEME 6



Analysis of the products revealed the F-alkylethenes (32) and F-alkylethynes (33) produced adducts resulting from attack at the unsaturated terminal carbon, while oxolane added to the F-alkyl site in the ethyl 3-F-alkyl propynoates. For additions to both (33) and (34) the E-isomer was most abundant in the products.

In contrast, Modena and co-workers[19,34] have concentrated on the effects of altering the type and concentration of peroxide in free-radical addition reactions. Their work centred on the additions of alcohols, esters and ethers to 1,2-dichlorodifluoroethene, some of which were previously investigated using γ-ray initiation by Muramatsu et al.[16b,16c]

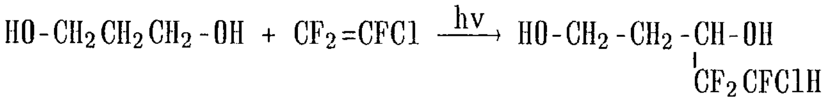
Normally in this type of free-radical addition reaction a small amount of peroxide is used but, for these reactions, the authors achieved higher conversion to products as the peroxide concentration was increased (up to 50% mol based on the alkene). Even employing these high peroxide concentrations the conversions still didn't approach those observed for similar reactions with other fluoroalkenes. The authors attributed this to the steric influence of the bulky chlorine atoms in 1,2-dichlorodifluoroethene.

Modena et al[19] also investigated the effect of different types of peroxide on the additions of oxolane, isopropanol and ethyl acetate to 1,2-dichlorodifluoroethene. They chose standard sets of conditions and interpreted their results as showing that conversions in ether and ester additions were independent of the kind of peroxide, while conversions in alcohol additions were strongly dependent on the peroxide used.

(v) Addition of Di-Functional Compounds to Fluoroalkenes

The majority of recent work concerning oxygen-functional substrates has been directed at mono-functional compounds. Work on di-functional compounds has centred on di-alcohols and so this will be reviewed.

Dedek and Hemer[35] have investigated the photochemically initiated reactions of chlorotrifluoroethene with the diols, 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol and 1,3-butanediol. The reaction between chlorotrifluoroethene and 1,3-propanediol proceeded smoothly in the absence of a photoinitiator to give a good yield of the mono-adduct (<u>38</u>). By using acetone as a photoinitiator, an increase in the yield of about one half was observed.



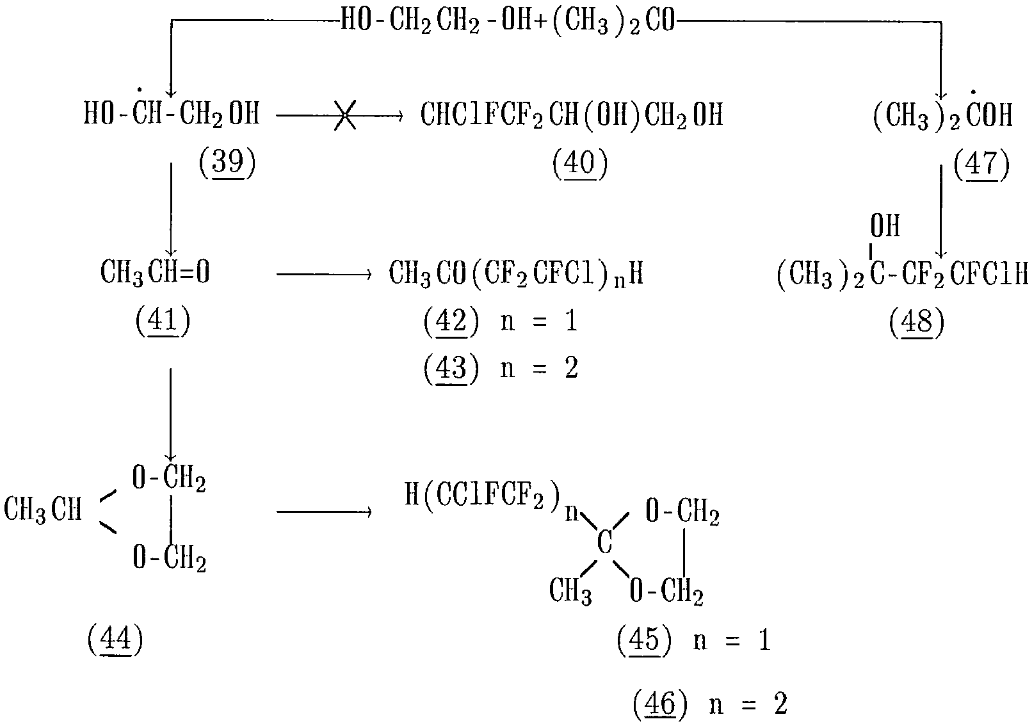
$$HO\text{-}CH_2CH_2CH_2\text{-}OH + CF_2\text{=}CFCl \xrightarrow{hv} HO\text{-}CH_2\text{-}CH_2\text{-}\underset{\overset{|}{CF_2CFClH}}{CH}\text{-}OH$$

(<u>38</u>)

In the absence of a photoinitiator the reactions of 1,4-butanediol and 1,3-butanediol gave significant amounts of di-addition products, together with the products of mono-substitution. In these di-addition products the chlorotrifluoroethyl groups were located on each of the hydroxyl-bearing carbon atoms. No telomeric products were isolated. In both cases the use of acetone as a photoinitiator led to greater proportions of di-addition products, leading the authors to conclude that the acetone was supporting intramolecular hydrogen transfer in the radical intermediates.

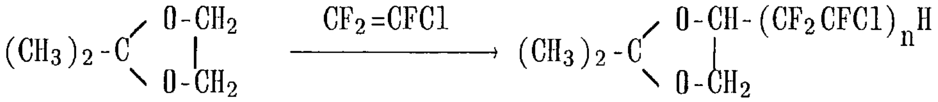
Unlike the other diols, 1,2-ethanediol only reacted satisfactorily with chlorotrifluoroethene after the introduction of acetone as a photoinitiator. Additionally, the products arising from this reaction proved to be very different from those observed for the other diols. The major product was identified as

SCHEME 7



2-(2-chloro-1,1,2-trifluoroethyl)-2-methyl-1,3-dioxolane (45). Several minor species were also detected and analysis of these led the authors to propose the above reaction scheme (Scheme 7). They suggested that the initially formed 1,2-dihydroxyethyl radical (39) was preferentially cleaved to give acetaldehyde and water without reacting with chlorotrifluoroethene. This acetaldehyde could either add to chlorotrifluoroethene or be acetalised with 1,2-ethanediol to give (44) and hence the addition products (45) and (46). They also suggested that the alcohol adduct (48) could be formed via the 1-methyl-1-hydroxyethyl radical (47), produced by reduction of acetone.

The expected mono-addition product of 1,2-ethanediol and chlorotrifluoroethene, 4-chloro-3,3,4-trifluoro-1,2-butanediol (40), was realised by reaction of 2,2-dimethyl-1,3-dioxolane (49) with chlorotrifluoroethene followed by hydrolysis.



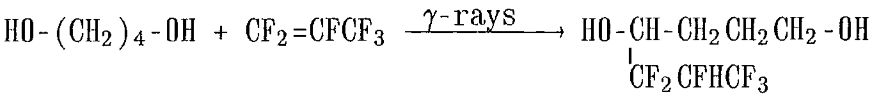
(49)

(50) n = 1

(51) n = 2

$$(\underline{50}) \xrightarrow[\text{dil. HCl}]{\text{Hydrolysis}} CHClFCF_2CH(OH)CH_2OH \; (\underline{40})$$

In contrast to Dedek and Hemer, Jones[5] observed only a low yield of mono-adduct (52) from a γ-ray reaction of 1,4-butanediol and hexafluoropropene. An alternative route to the same product via reduction of a mono-adduct, (53), of γ-butyrolactone and hexafluoropropene proved equally low yielding.



$$HO\text{-}(CH_2)_4\text{-}OH + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} HO\text{-}\underset{CF_2CFHCF_3}{\underset{|}{CH}}\text{-}CH_2CH_2CH_2\text{-}OH$$

(52) 7%

(53)

(52) 8%

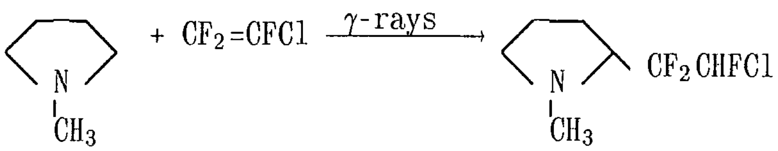
(c) Free-Radical Additions of Nitrogen-Functional Substrates to Fluoroalkenes

The majority of recent work on free-radical addition reactions of functional compounds to fluoroalkenes has concentrated on oxygen-functional substrates. Some useful work involving nitrogen-functional substrates has however been performed.[5,36]

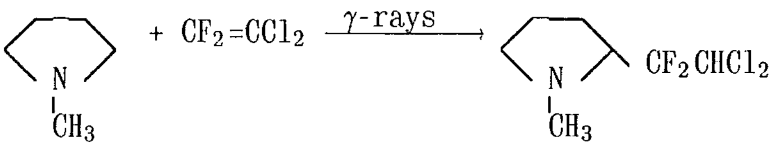
(i) Structural Effects in Free-Radical Additions

Free-radical additions of tertiary amines to a variety of fluoroalkenes have highlighted several interesting structural effects.[5]

The γ-ray initiated additions of N-methylpyrrolidine to chlorotrifluoroethene and 1,1-dichlorodifluoroethene gave modest yields of the mono-adducts (54) and (55) respectively, along with some unidentified nucleophilic products.



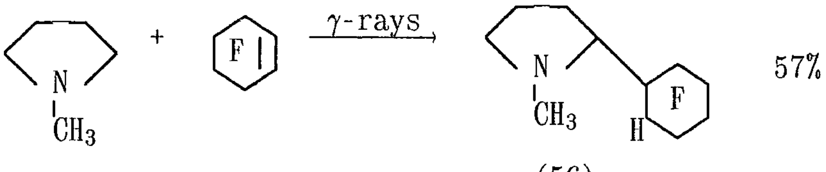
(54) 37%



(55) 55%

In both cases reaction occurred at the less hindered CF_2 group due to the large steric requirement of chlorine.

The addition of N-methylpyrrolidine to perfluorocyclobutene and perfluorocyclopentene gave unidentified nucleophilic products. In contrast, a similar γ-ray addition to perfluorocyclohexene proceeded to a mono-adduct, (56), in good yield. The author proposed that rapid nucleophilic attack on the smaller rings was promoted by the accompanying reduction in ring strain. The lower ring strain of perfluorocyclohexene meant that the nucleophilic reaction was slower and hence the free-radical reaction was allowed to compete.



(56)

Reactions of N-methylpiperidine and triethylamine with hexafluoropropene gave greater proportions of multiple adducts than equivalent reactions with tetrafluoroethene. The author[5] suggested that the lower steric requirement of the primary adduct radicals involving tetrafluoroethene would cause both the inter- and intramolecular hydrogen transfer reactions to proceed more rapidly. He further suggested that the effect on the rate of the intermolecular mechanism would be greater, hence favouring mono-adduct formation.

(ii) Substituent Effects in Free-Radical Additions

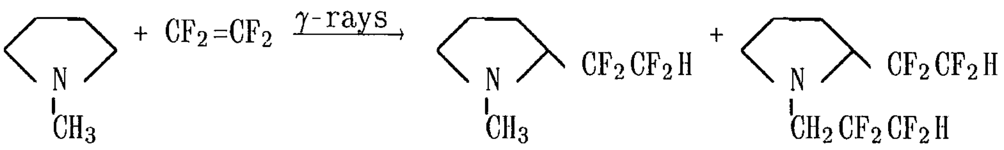
Jones[5] has investigated the relative abilities of oxygen and nitrogen to stabilise an adjacent radical and has also considered how the introduction of a carbonyl group next to nitrogen would affect radical stability.

The acetone-t-butylalcohol ratios for amines were lower than those for ethers and similarly the amide ratios were lower than the ratios for esters. This demonstrated that nitrogen is more effective at stabilising an adjacent radical than oxygen. This was illustrated nicely by the higher yields obtained in the free-radical additions of amides to fluoroalkenes with respect to the corresponding esters. Although both ethers and amines reacted well with fluoroalkenes the greater reactivity of amines was demonstrated by competition reactions for a deficiency of alkene.

A comparison of acetone-t-butylalcohol ratios for amines and amides revealed the expected reduced ability of amides to stabilise an adjacent radical.

(iii) Conformational Effects in Free-Radical Additions

Some initial studies on hydrogen abstraction from amines with butoxy radicals[29] and carbonate radicals[37] have highlighted the importance of a stereoelectronic effect, as observed for ethers[17,26,27] and 1,3-dioxanes.[28] More recently Jones[5] investigated how this stereoelectronic effect would manifest itself in the reactivity of a series of cyclic tertiary amines with fluoroalkenes. Competition reactions, similar to those performed to determine the order of reactivity of cyclic ethers,[17] were complicated by the appearance of di-adducts, e.g. (<u>58</u>) in equation 3.

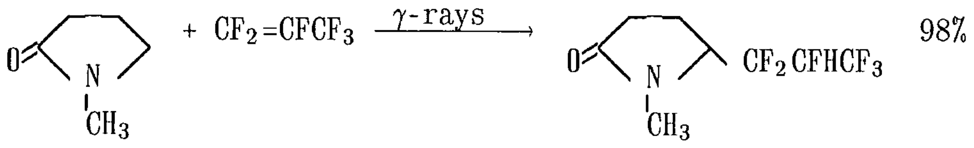


(<u>57</u>) 90%　　(<u>58</u>) 8%

(eqn. 3)

As an alternative, Jones suggested that the order of reactivity of cyclic amines could be derived from the proportions of mono- and di-adducts formed in their reactions with fluoroalkenes. He proposed that the rate of intramolecular hydrogen transfer, leading to di-adduct formation, would be essentially independent of the amine structure within an analogous cyclic series provided that the hydrogen involved was not sterically hindered. The rate of intermolecular hydrogen transfer, leading to mono-adduct formation would however be dependent on the ease of hydrogen abstraction from the amine and would thus determine the product ratio. Hence, a high proportion of mono-adduct should result from a highly reactive cyclic amine. Using this strategy, the author determined the order or reactivity for 5,6 and 7-membered cyclic tertiary amines to be the same as that observed previously for the analogous cyclic ethers.[17]

In contrast to cyclic amines, cyclic tertiary amides with the carbonyl group incorporated in the ring, only gave mono-adducts when reacted with hexafluoropropene,[5] e.g. (<u>59</u>) in equation 4.

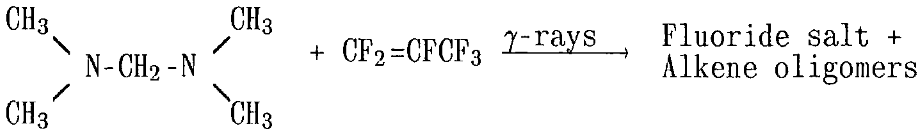


(<u>59</u>) (eqn. 4)

In all cases reaction occurred exclusively in the ring and thus the relative reactivity order with change in ring size could be determined from the amounts of products produced. Jones reported a decrease in reactivity in the order 5>6>7, which was different to that observed for amines[5] and ethers.[17] This reactivity order was confirmed by a series of competition experiments for a deficiency of alkene.[5] From a study of the relative ring conformations within the cyclic amide series the author suggested that this change in reactivity order, with respect to ethers and amines, was mainly due to an increase in the reactivity of the 6-membered ring. This, in turn, resulted from an alteration in conformation caused by the carbonyl group.

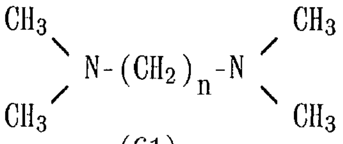
(iv) Addition of Di-Functional Amines to Fluoroalkenes

Unlike many mono-functional tertiary amines, preliminary work[4] on di-functional tertiary amines yielded no free-radical addition products. Thus, in the γ-ray initiated addition of N,N,N',N'-tetramethyldiaminomethane (60) to hexafluoropropene, only products typical of a nucleophilic reaction were observed.



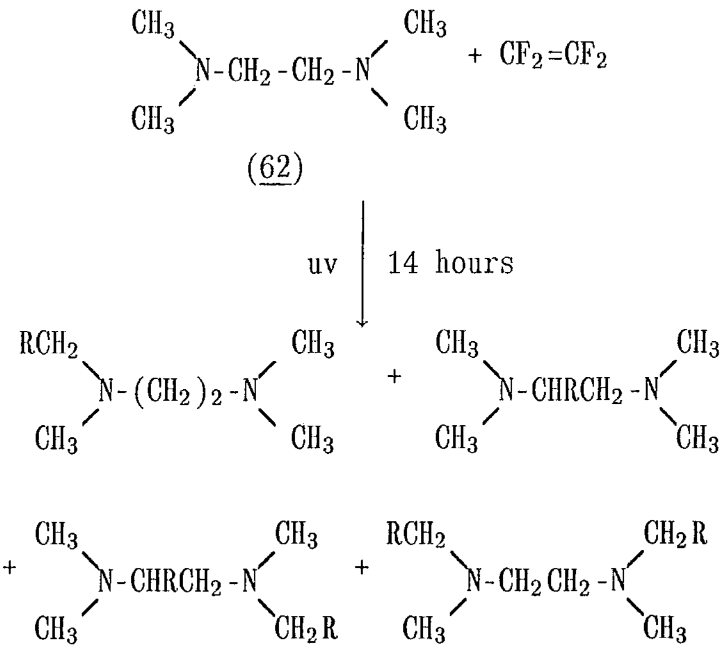
(60)

However, in a recent publication,[36] Dedek and co-workers have reported the production of adducts resulting from photoinitiated free-radical addition of tertiary di-amines to C_2-C_4 fluoroalkenes or chlorofluoroalkenes. The di-amines were of general structure (61) and tended to yield both mono-adduct and di-adducts. Thus addition of N,N,N',N'-tetramethyldiaminoethane (62) to tetrafluoroethene gave a mixture of four adducts.



where n = 2-10

(61)



(62)

(where R = CF_2CF_2H)

(d) Free-Radical Additions of Silicon Compounds to Fluoroalkenes

α-Silyl radicals can be produced by hydrogen abstraction with acyl radicals, giving high enough concentrations to be detected by e.s.r.[38] A series of compounds was studied and some examples are included in Table 6.

TABLE 6 Hydrogen Abstraction by $CH_3\overset{O}{\overset{\|}{C}}\cdot$

Substrate	Product detected by e.s.r.
Me_4Si	$Me_3Si\dot{C}H_2$
$Me_3SiOSiMe_3$	$Me_3SiOSi(Me_2)\dot{C}H_2$
Me_3SiOCH_3	$Me_3SiO\dot{C}H_2$

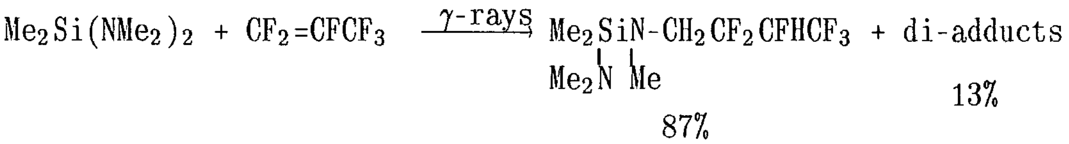
The radicals were formed α to silicon except in the cases where an alkoxy group was present, thus illustrating that stabilisation by an

α-oxy group is greater than by an α-silyl group. E.s.r. studies of the substituted methoxy radicals showed a restricted Si-O bond rotation, indicating the presence of some bonding between the silicon and oxygen atoms. In connection with this, Jones[5] observed that the acetone-t-butylalcohol ratio for dimethyldiethoxysilane was higher than that for diethyl ether and therefore concluded that the presence of a silicon atom reduces the availability of the oxygen lone-pair for radical stabilisation by overlap of the oxygen p-orbital and a silicon d-orbital. He also suggested that the same overlap leads to an increase in the ability of a silicon atom to stabilise an adjacent radical. This was illustrated by the lower acetone-t-butylalcohol ratio for hexamethyldisiloxane compared to tetramethylsilane.

In agreement with the hydrogen abstraction studies,[38] addition of methoxytrimethylsilane to hexafluoropropene was shown to occur preferentially via the α-oxy radical[3] (eqn. 5). Since then Jones[5]

$$Me_3SiOCH_3 + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} \underset{62\%}{Me_3SiOCH_2CF_2CFHCF_3} \quad \text{(eqn. 5)}$$

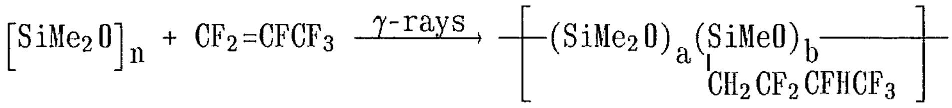
has also shown that addition of bisdimethylaminodimethylsilane to hexafluoropropene occurs exclusively at the position α to the nitrogen atom (eqn. 6).



$$Me_2Si(NMe_2)_2 + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} \underset{87\%}{Me_2\underset{Me_2N}{Si}\underset{Me}{N}\text{-}CH_2CF_2CFHCF_3} + \underset{13\%}{\text{di-adducts}}$$

(eqn. 6)

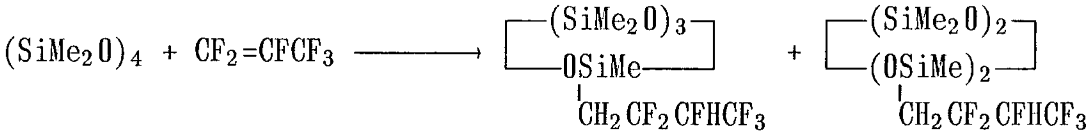
A number of publications concerned with peroxide initiated free-radical addition of organosilicon compounds, and especially polysiloxanes, to fluoroalkenes are available.[39-43] In a more recent survey, Jones[5] achieved reasonable incorporation of hexafluoropropene into silicon oil using γ-ray initiation (eqn. 7).



$$[SiMe_2O]_n + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} [(SiMe_2O)_a(SiMeO(CH_2CF_2CFHCF_3))_b]$$

49% a/b = 4.8 (eqn.7)

In the same survey high yields of adducts in γ-ray and peroxide initiated additions of hexamethyldisiloxane and octamethylcyclotetrasiloxane to hexafluoropropene were achieved (e.g. eqn. 8).



γ	33%	—
Di-t-butylperoxide, 140^{o}C	84%	16%

(eqn. 8)

Under similar conditions tetramethylsilane and hexafluoropropene were found to give corresponding products, although in lower yield (eqn. 9).

$$SiMe_4 + CF_2{=}CFCF_3 \longrightarrow Me_3SiCH_2CF_2CFHCF_3 + Me_2Si(CH_2CF_2CFHCF_3)_2$$

γ	14%	—
Di-t-butylperoxide, 140^{o}C	89%	11%

(eqn. 9)

This reduction in yield is consistent with the higher acetone-t-butyl-alcohol ratio for tetramethylsilane.

CHAPTER TWO

SYNTHESIS AND CHEMISTRY OF FLUOROCARBON DERIVATIVES OF AMINES AND RELATED COMPOUNDS

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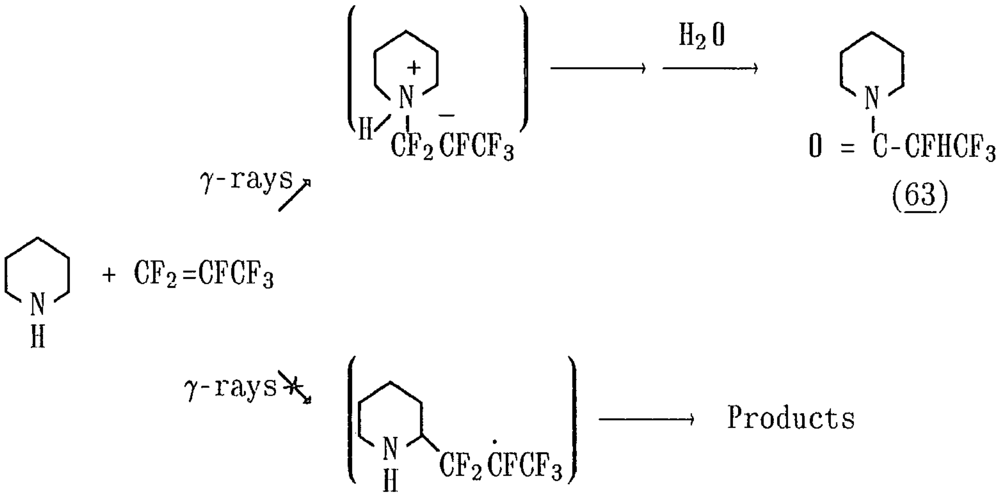
SYNTHESIS AND CHEMISTRY OF FLUOROCARBON DERIVATIVES OF AMINES AND RELATED COMPOUNDS

A. Introduction

The free-radical addition of amines to fluoroalkenes is potentially a direct route to fluorocarbon amines. However, the base strength of amines is high[44] and the possibility of alternative nucleophilic reactions exists. Primary and secondary amines react readily with fluoroalkenes by nucleophilic addition[45,46] and thus the free-radical route is unlikely to compete. This is pointedly illustrated by the γ-ray initiated reaction of piperidine and hexafluoropropene which yielded only products of nucleophilic attack, (63).[4]

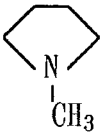
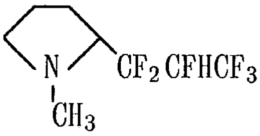
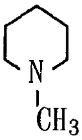
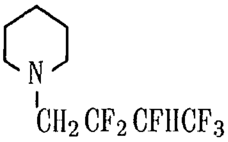
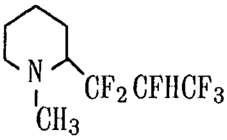
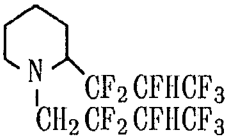
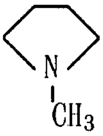
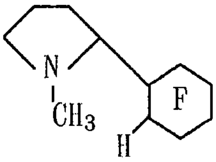


(63)

However, a number of free-radical additions of tertiary amines to fluoroalkenes are known.[4,5,47,48] A few illustrative examples are included in Table 7.

Despite these successes, the problem of synthesising adducts of primary and secondary amines still exists.

TABLE 7 Addition of Tertiary Amines to Fluoroalkenes

Fluoroalkene	Amine	Reaction Conditions	Products	Ref
CF_2=CFCl	Me_3N	γ	$ClCHFCF_2CH_2NMe_2$; $(ClCHFCF_2CH_2)_2NMe$; $ClCHFCF_2CClFCF_2CH_2NMe_2$; $ClCHFCONMe_2$	47
CF_2=CFCl	Me_2CHNMe_2	γ (or UV light)	$HCClFCF_2CH_2NMeCHMe_2$; $HCClFCF_2CMe_2NMe_2$; $HCClFCF_2CMe_2NMeCH_2CF_2CClFH$	48
CF_2=$CFCF_3$		γ		5
CF_2=$CFCF_3$		γ	 ;  ; 	4
		γ		5

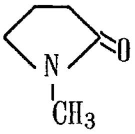
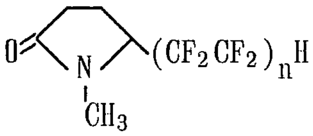
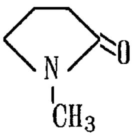
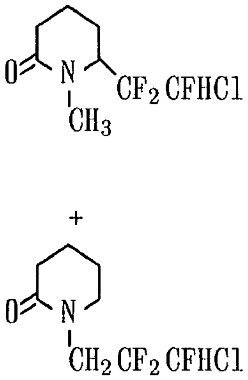
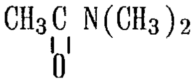
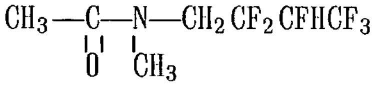
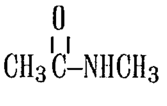
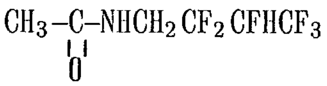
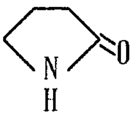
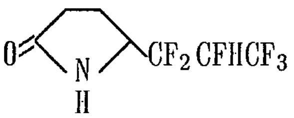
B. Alternative Routes to Mono-Amine Adducts

1. Amide Approach

Amides are much less basic than amines[44] and thus the possibility of competing nucleophilic reactions is reduced.

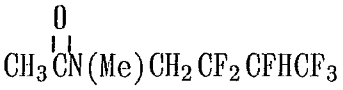
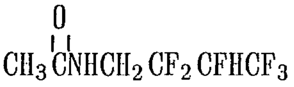
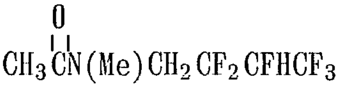
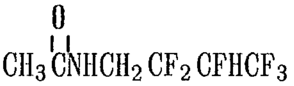
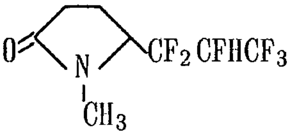
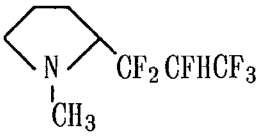
Unfortunately, the introduction of an electron-withdrawing carbonyl group also leads to a reduction in the stability and nucleophilic character of radicals formed *α* to nitrogen. Despite this, however, various free-radical additions between amides and fluoroalkenes have been reported[4,5,49,50] and a few examples are included in Table 8.

TABLE 8 Addition of Amides to Fluoroalkenes

Alkene	Amide	Initiation	Products	Ref.
$CF_2{=}CF_2$		$(^tBuO)_2$		49
$CF_2{=}CFCl$		u.v. acetone		50
$CF_3{=}CFCF_3$	 $CH_3C(=O)N(CH_3)_2$	γ	 $CH_3-C(=O)-N(CH_3)-CH_2CF_2CFHCF_3$	4
$CF_2{=}CFCF_3$	 $CH_3C(=O)-NHCH_3$	γ	 $CH_3-C(=O)-NHCH_2CF_2CFHCF_3$	5
$CF_2{=}CFCF_3$		$(^tBuO)_2$		49

Wide applicability of this route to the production of fluorocarbon amides has been illustrated and a range of fluorocarbon amines has been synthesised by hydrolysis or reduction of these adducts[5] (Table 9).

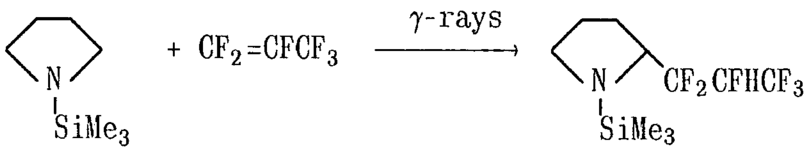
TABLE 9 Synthesis of Amines by Hydrolysis or Reduction of Amide Adducts

Amide	Conditions	Product	Yield
 $CH_3\overset{O}{\overset{\|}{C}}N(Me)CH_2CF_2CFHCF_3$	H_2SO_4/H_2O	$CH_3NHCH_2CF_2CFHCF_3$	26%
 $CH_3\overset{O}{\overset{\|}{C}}NHCH_2CF_2CFHCF_3$	H_2SO_4/H_2O	$H_2NCH_2CF_2CFHCF_3$	26%
 $CH_3\overset{O}{\overset{\|}{C}}N(Me)CH_2CF_2CFHCF_3$	$LiAlH_4$	$CH_3CH_2N(CH_3)CH_2CF_2CFHCF_3$	26%
 $CH_3\overset{O}{\overset{\|}{C}}NHCH_2CF_2CFHCF_3$	$LiAlH_4$	$CH_3CH_2NHCH_2CF_2CFHCF_3$	47%
	$LiAlH_4$		55%

2. Silicon Protecting Group Approach

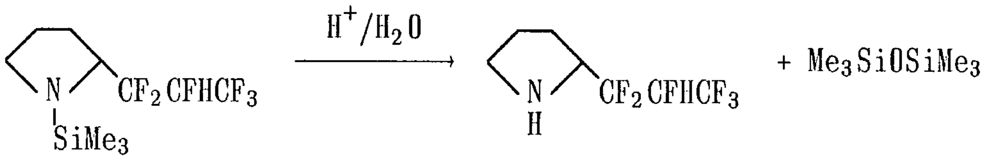
As illustrated above, many tertiary amines undergo smooth free-radical addition to fluoroalkenes and, clearly, the increased crowding around the nitrogen with respect to primary and secondary amines hinders the nucleophilic reaction, thus allowing the free-radical route to compete. By protecting primary and secondary amines with silyl groups, compounds structurally more akin to tertiary amines can be obtained and, provided that these groups have no adverse affect on the free-radical reaction, such compounds should offer a potential route to amine adducts.

Pyrrolidine was silylated using chlorotrimethylsilane and the resulting N-trimethylsilylpyrrolidine (64) was exposed to γ-rays in the presence of a deficiency of hexafluoropropene. [For the purpose of this study most of the experimental conditions used for free-radical addition reactions involved a deficiency of the alkene, which favours mono-adduct formation[4,5]]. The mono-adduct (65) was formed in good yield and acid hydrolysis of (65) gave the corresponding secondary amine adduct (66) as the sole nitrogen



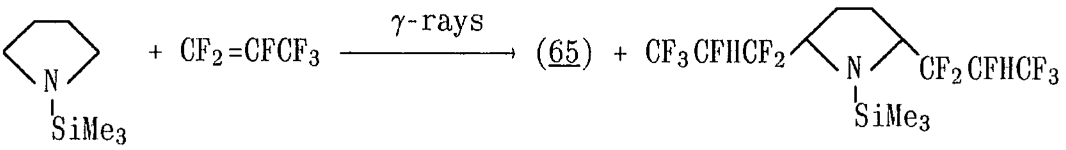
(64) (65) 62%

containing product, thus illustrating the applicability of this strategy to the production of fluorocarbon amines.



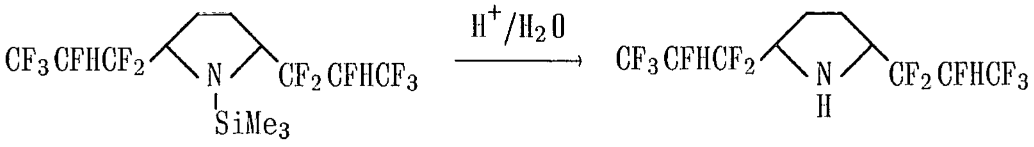
(65) (66) 53%

A γ-ray initiated reaction of (64) with an excess of hexafluoropropene gave a mixture of mono- (65) and di-adducts (67)



(64) 21% (67) 40%

Acid hydrolysis of (67) gave the corresponding amine di-adduct (68).



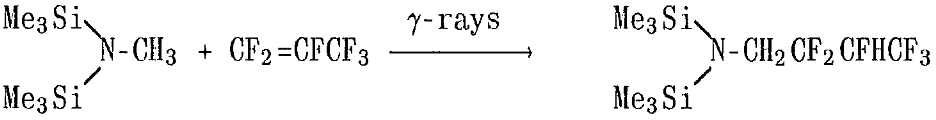
(<u>67</u>) (<u>68</u>) 75%

+ $Me_3SiOSiMe_3$

For comparison, only a brown tarry material was obtained from a γ-ray initiated reaction of dimethylamine, i.e. a secondary amine, with hexafluoropropene.

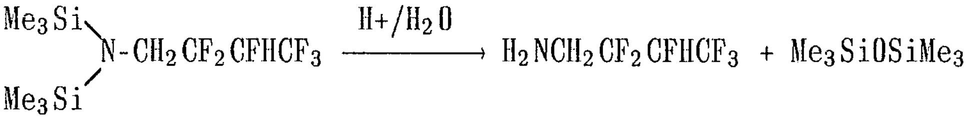
$$Me_2NH + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} \text{Brown Tarry Material}$$

Primary fluorocarbon amines can also be readily produced via their silyated analogues. Thus N,N-bis(trimethylsilyl)methylamine gave the mono-adduct (<u>69</u>) when reacted with hexafluoropropene. The corresponding primary amine adduct, (<u>70</u>), was obtained by acid hydrolysis of (<u>69</u>).



$$(Me_3Si)_2N\text{-}CH_3 + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} (Me_3Si)_2N\text{-}CH_2CF_2CFHCF_3$$

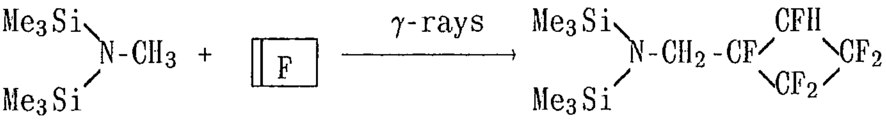
(<u>69</u>) 86% (by g.l.c.)



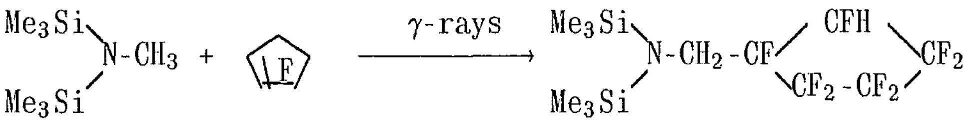
$$(Me_3Si)_2N\text{-}CH_2CF_2CFHCF_3 \xrightarrow{H+/H_2O} H_2NCH_2CF_2CFHCF_3 + Me_3SiOSiMe_3$$

(<u>69</u>) (<u>70</u>) 30% (combined yield for 2-step synthesis)

Additional reactions of N,N-bis(trimethylsilyl)methylamine with perfluorocyclobutene and perfluorocyclopentene also led to the expected free-radical addition products in good yields.



(<u>71</u>) 90% (by g.l.c.)



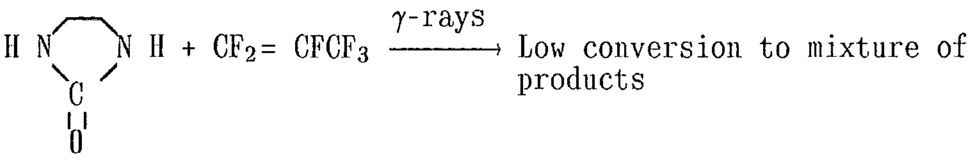
(72) 58% (from recovered alkene)

Several practical methods for the introduction[51–53] and removal[54] of silyl groups into and from primary and secondary amines are available, thus confirming the wide applicability of this method for the production of fluorocarbon amines.

C. Routes to Di-Amine Adducts

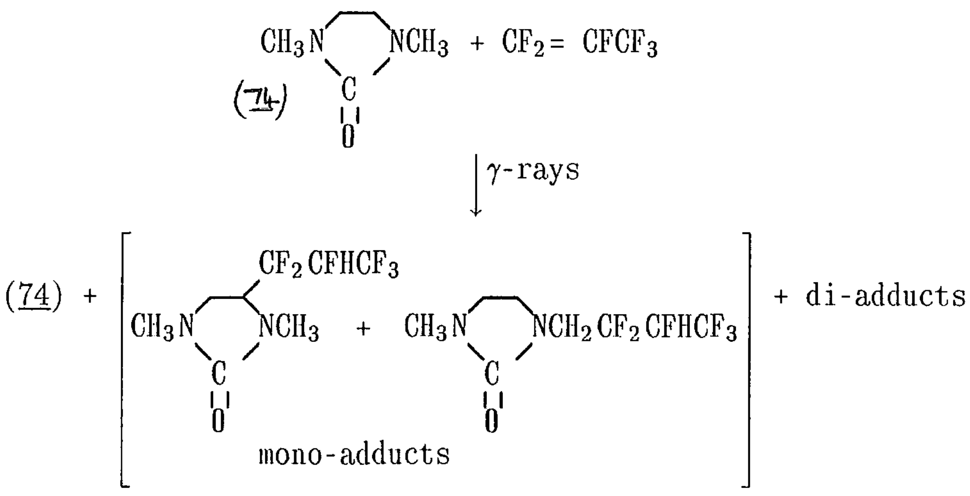
The free-radical addition of tertiary di-amines to fluoroalkenes has been dealt with by other workers with mixed success[4,36] (see Chapter 1). For primary and secondary di-amines competing nucleophilic reactions still present problems. A potential alternative approach to the required fluorocarbon adducts involves the use of amides.

1,2-Diaminoethane can be produced by hydrolysis of 2-imidazolidinone (73), a cyclic amide. It was envisaged that introduction of a fluorocarbon group into 2-imidazolidinone prior to hydrolysis would present an excellent route to the corresponding fluorocarbon di-amine. However, a γ-ray initiated reaction involving (73) and hexafluoropropene gave only very low conversion to a mixture of products. [Mass spectrum, chemical ionisation, m/z 387 (M+1 for di-adduct, 0.5%), 237 (M+1 for mono-adduct, 100), 87 (M+1 for 2-imidazolidinone, 23). Elemental analysis closest to a mono-adduct, found: C, 31.2; H, 2.4; N, 11.2; F, 47.3%. Di-adduct requires C, 28.0; H, 1.6; N, 7.3; F, 59.1%. Mono-adduct requires C, 30.5; H, 2.5; N, 11.9; F, 48.3%. 2-imidazolidinone requires C, 41.9; H, 7.0; N, 32.6%.]. Due to the very low yield this material was not analysed further.

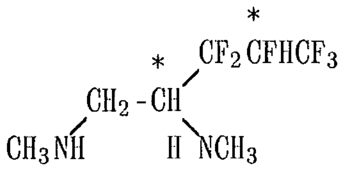


(73)

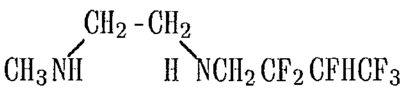
Using di-t-butylperoxide at 140^{0}C as an initiator a brown tarry solid was obtained, from which only starting material could be recovered. In view of the low yields involved, no hydrolysis reactions were performed. As 2-imidazolidinone is a solid, the low yield in the γ-ray reaction could be attributed to a phase problem and so attention was switched to the use of 1,3-dimethyl-2-imidazolidinone (74), as a liquid reagent. A γ-ray initiated reaction of (74) with hexafluoropropene proceeded smoothly to give a viscous liquid (75) which was assigned as a mixture of (74), mono- and di-adducts by g.l.c.-mass spectroscopy [Electron impact, mono-adduct, m/z 264 (M+, 1.7%), 113 (35.6, M-CF_2CFHCF_3). Di-adduct, m/z 414 (M+, 1.3 %), 263 (12.3, M-CF_2CFHCF_3)].



The product mixture, (75), was hydrolysed under acidic conditions without further separation but, under the conditions used, (75) remained largely unchanged. However, small amounts of three ring-opened mono-amine adducts were obtained and it was possible to separate these amine adducts from the reaction mixture but not from each other. Probable structures for these adducts are (76) (2 isomers) and (77).



(76)



(77)

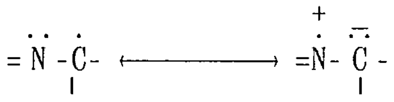
Although the yields are low, the observance of these secondary di-amine adducts is encouraging and indicates that with optimum conditions this could be made into a viable synthetic pathway.

D. Routes to Isocyanate Adducts

1. Mono-Isocyanates

When nitrogen is involved in a double bond it retains its lone pair of electrons which is thus available for stabilisation of an adjacent radical site.

i.e.

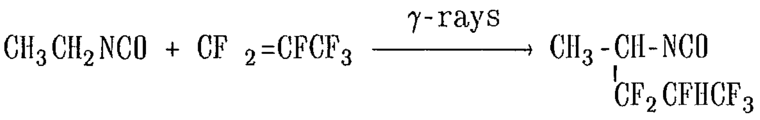


$$=\ddot{N}-\dot{C}- \longleftrightarrow =\overset{+}{\dot{N}}-\overset{-}{\ddot{C}}-$$

or

$$-\ddot{N}=\dot{C}- \longleftrightarrow -\overset{+}{\dot{N}}=\overset{-}{\ddot{C}}-$$

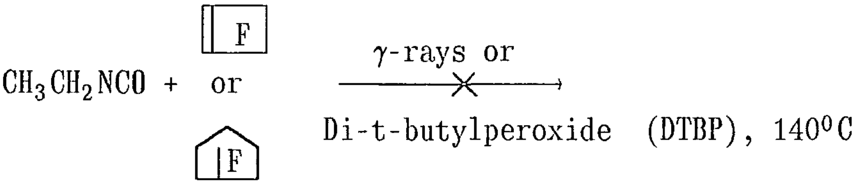
In a previous study[5] imines were found to be too basic to give free-radical addition products with fluoroalkenes and so the less basic isocyanates were considered. In a preliminary reaction ethyl isocyanate added to hexafluoropropene via γ-ray initiation to give a moderate yield of mono-adduct (78).



$$CH_3CH_2NCO + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} CH_3\text{-}\underset{\displaystyle CF_2CFHCF_3}{CH}\text{-}NCO$$

(<u>78</u>) 25%

In the present work however, no products were obtained from either γ-ray or peroxide initiated reactions of ethyl isocyanate with perfluorocyclobutene or perfluorocyclopentene.



2. <u>Di-isocyanates</u>

Di- and tri-isocyanates are important precursors to a variety of industrially important polymers[55] and introduction of fluorocarbon groups into such isocyanates could provide potential precursors to corresponding fluorine containing polymers.

To test the first stage of this strategy, 1,6-diisocyanatohexane was reacted with hexafluoropropene via peroxide initiation. 54% of the hexafluoropropene reacted with the isocyanate to give a viscous liquid product (<u>79</u>).

$$OCN\ (CH_2)_6NCO + CF_2{=}CFCF_3 \xrightarrow[140^{o}C]{DTBP} \text{Viscous liquid}$$

(<u>79</u>)

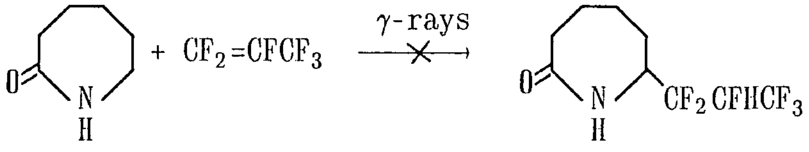
Even small amounts of fluorine in polymers can lead to desirable properties and so incorporation of 54% of the hexafluoropropene is very encouraging.

E. Additions of Miscellaneous Nitrogen Compounds

1. ε-Caprolactam

ε-Caprolactam, a cyclic secondary amide, has been shown to add to fluoroalkenes via peroxide initiation.[49] Since ε-caprolactam can be polymerised to give nylon 6, these products represent potential precursors to fluorine-containing nylon 6.

Only starting materials were recovered from a γ-ray initiated reaction of ε-caprolactam and hexafluoropropene. A similar reaction initiated by di-t-butylperoxide at 140°C gave a brown tarry solid, from which no products could be recovered. Since the lack of addition in the γ-ray initiated reaction could be due to a phase problem, the reaction was repeated using a solvent. No adduct was obtained but a small amount of polymeric material (81) with a high fluorine content (49%) was isolated. From i.r. (broad amide, carbonyl and fluorocarbon absorbances) and n.m.r. data (multiple resonances in CF_3, CF_2 and CFH regions of the spectrum [cf Chapter 5 on polymer modification]) it seems probable that (81) is nylon 6 modified by incorporation of a large number of hexafluoropropyl groups.

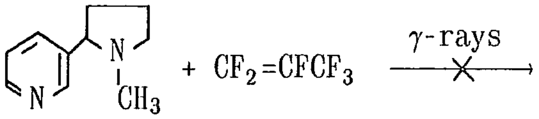


(80)

2. L-Nicotine

The introduction of fluorine or fluorocarbon groups into biologically important molecules can lead to improvements in their pharmacological properties.[56] One of the major reasons for this is the higher lipid solubility of the fluorine containing compounds which enhances the rates of absorption and transport of drugs *in vivo*.

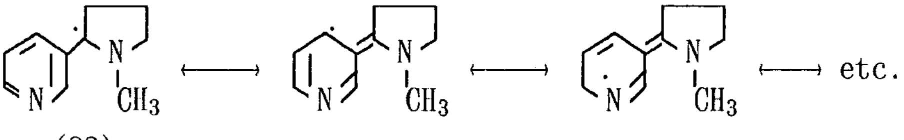
Free-radical addition to fluoroalkenes provides a potential way of introducing fluorocarbon groups into compounds of biological importance. Nicotine (82), a stimulant for striated muscle,[57] should be a good candidate since it is a derivative of N-methylpyrrolidine, a compound which adds readily to fluoroalkenes under free-radical conditions.[5] However, only starting materials were recovered from a γ-ray initiated reaction between L-nicotine and hexafluoropropene even when a solvent was used to improve reagent contact.



(82)

A possible explanation for this surprising observation can be derived by consideration of the stability of any radicals generated from nicotine. Within nicotine the most likely site for radical generation is at the tertiary carbon α to nitrogen in the pyrrolidine ring to give (83). This radical would be highly stabilised by both the adjacent nitrogen atom and by delocalisation into the pyridine ring, (Scheme 8). Loss of this extra stabilisation energy will make the subsequent addition step less exothermic and hence less likely.

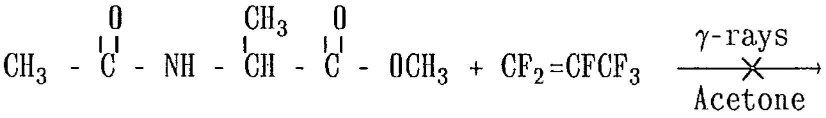
SCHEME 8



(83)

3. Amino Acids

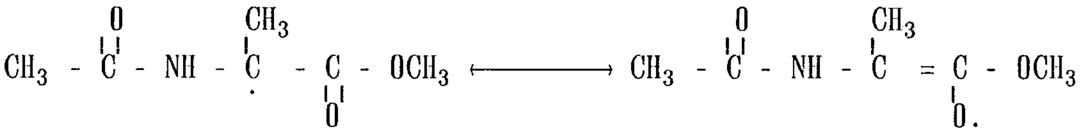
New amino acids, and particularly those containing fluorine,[58] are of great interest to chemists and the presence of an amine function makes amino acids potential reagents for free-radical addition to fluoroalkenes. To investigate this possibility (84), a derivative of alanine, was chosen for reaction with hexafluoropropene. The amide derivative was chosen to reduce the likelihood of competing nucleophilic reactions and a solvent was used to improve contact between the reagents but only starting materials were recovered from a γ-ray initiated reaction.



$$CH_3-\overset{O}{\overset{\|}{C}}-NH-\overset{CH_3}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-OCH_3+CF_2{=}CFCF_3\;\cancel{\xrightarrow[\text{Acetone}]{\gamma\text{-rays}}}$$

(84)

To find a possible explanation for this observation it is again necessary to look at the intermediate radical, (85). Delocalisation of this radical onto the carbonyl oxygen to give (86) is possible



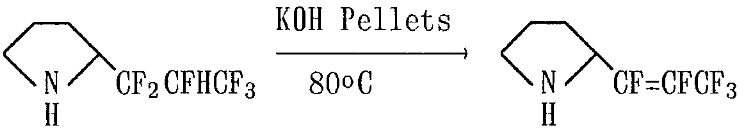
$$CH_3-\overset{O}{\overset{\|}{C}}-NH-\underset{\cdot}{\overset{CH_3}{\overset{|}{C}}}-\underset{\underset{O}{\|}}{C}-OCH_3\longleftrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH-\overset{CH_3}{\overset{|}{C}}=\underset{\underset{O\cdot}{|}}{C}-OCH_3$$

(85) (86)

and a combination of this increased radical stability together with the accompanying reduction in the nucleophilic character of the intermediate radical would disfavour the subsequent addition step.

F. Conclusions

In many cases the free-radical addition of amines to fluoroalkenes is masked by a competing nucleophilic reaction. This problem can now be overcome by using amide or silyamine precursors, making a whole range of previously inaccessible fluorocarbon amines available and investigation of the chemistry of these amines is now possible. A preliminary dehydrofluorination reaction of 2-(2H-hexafluoropropyl)pyrrolidine (66) has been performed, yielding alkene (87) as the sole product.



(66) (87) 40%

The amide and silylamine methodology should now be applied to the synthesis of di-amine adducts since these compounds could be used as polymer precursors. Preliminary work with cyclic amides has yielded some encouraging results, although further work is still needed in this area.

The ability of nitrogen to stabilise an adjacent α-radical presents opportunities for free-radical addition of many other nitrogen -containing species to fluoroalkenes. These reactions and, especially those involving more complex molecules, should provide both interesting new products and invaluable information to expand our knowledge of free-radical chemistry.

CHAPTER THREE

SYNTHESIS AND CHEMISTRY OF FLUOROSILICON COMPOUNDS

CHAPTER THREE

SYNTHESIS AND CHEMISTRY OF FLUOROSILICON COMPOUNDS

A. Introduction

The ablity of silicon to stabilise an α-carbon radical, as demonstrated by e.s.r. measurements,[38] has led to intense industrial interest in the free-radical additions of a variety of organosilicon compounds to fluoroalkenes.[39-43] Particular attention has been paid to the modification of polysiloxanes by this route since it is claimed that the products show improvements in properties when compared with the already widely used unmodified materials.

Despite this industrial interest there is a dearth of information concerning the free-radical synthesis and accompanying chemistry of simple fluorosilicon adducts. Consequently, recent work in this laboratory has focused on the free-radical additions of simple organosilicon compounds to hexafluoropropene.[5] In continuation of this work, the additions of similar organosilicon compounds to other fluoroalkenes and some further chemistry of simple fluorosilicon adducts will now be described.

B. Synthesis of Simple Fluorosilicon Adducts

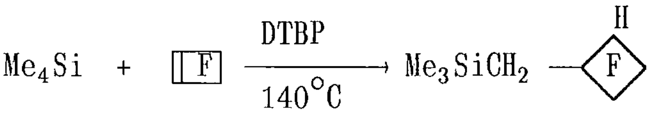
1. Silanes

Previous work in this laboratory showed that tetramethylsilane adds to hexafluoropropene via γ-ray initiation to give a low yield of mono-adduct (<u>88</u>). The corresponding peroxide initiated reaction gave a high yield of this mono-adduct along with some di-adduct, (<u>89</u>).

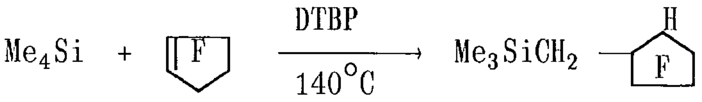
$$\mathrm{Me_4Si + CF_2{=}CFCF_3 \longrightarrow \underset{(88)}{Me_3SiCH_2CF_2CFHCF_3} + \underset{(89)}{Me_2Si(CH_2CF_2CFHCF_3)_2}}$$

	(88)	(89)
γ-rays	14%	—
Di-t-butylperoxide(DTBP),140°C	89%	11%

In this study only starting materials were recovered from γ-ray initiated reactions of tetramethylsilane with perfluorocyclobutene and perfluorocyclopentene. Even using more forcing conditions the corresponding mono-adducts, (90) and (91), were only produced in amounts sufficient for g.l.c.-mass spectral indentification.



(90) Trace

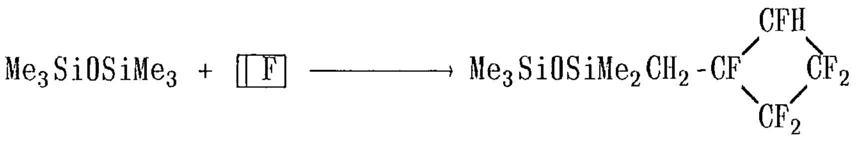


(91) Trace

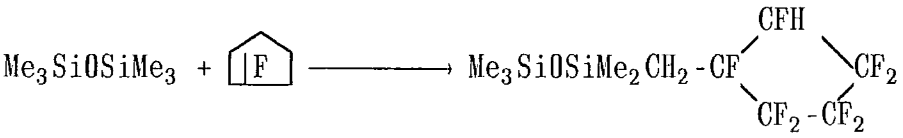
2. Siloxanes

In the previous study,[5] siloxanes were found to add to hexafluoropropene in higher yields than tetramethylsilane and so the reactions of siloxanes with perfluorocyclobutene and perfluorocyclopentene were investigated.

γ-ray initiated reactions of hexamethyldisiloxane with perfluorocyclobutene and perfluorocyclopentene gave only trace amounts of mono-adducts (92) and (93) respectively. However, by using a peroxide initiator, better yields of these mono-adducts were obtained.

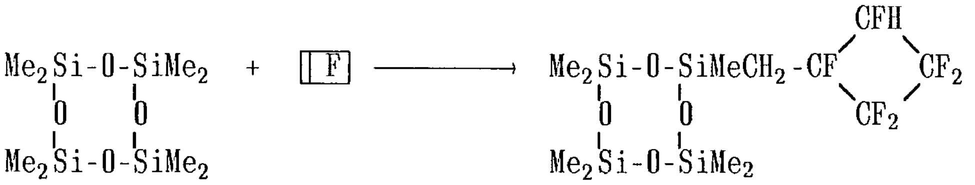

(92)

γ-rays	trace
DTBP,140°C	14%

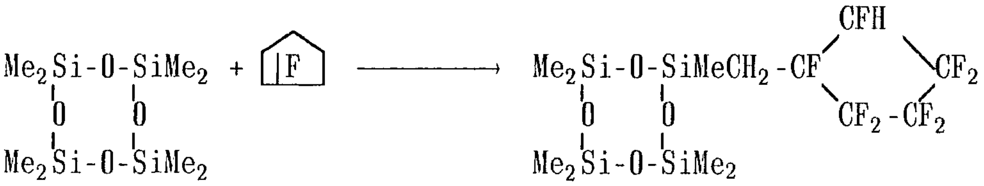

(93)

γ-rays	trace
DTBP,140°C	12%

Similarly, γ-ray initiated reactions of octamethylcyclotetrasiloxane with perfluorocyclobutene and perfluorocyclopentene gave only trace amounts of mono-adducts (94) and (95) respectively, while better yields of these mono-adducts were obtained by using a peroxide initiator.


(94)

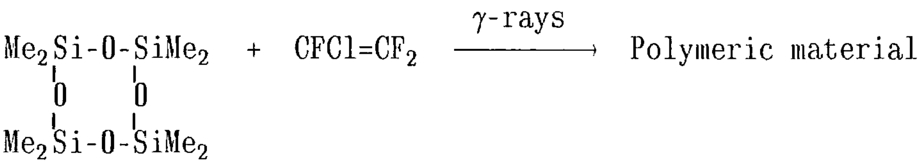
γ-rays	trace
DTBP,140°C	17%


(95)

γ-rays	trace
DTBP,140°C	17%

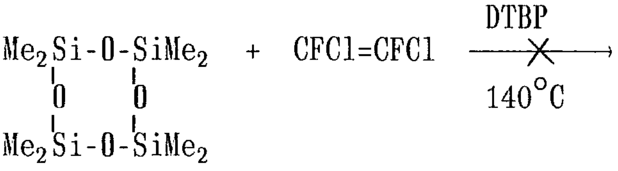
The higher yields in these siloxane reactions compared with those in the corresponding silane reactions lends support to the theory that oxygen donates through silicon[5] (see Chapter 1 for a fuller explanation).

Because of the encouraging results obtained from the siloxane reactions, further reactions of octamethylcyclotetrasiloxane with other fluoroalkenes were investigated. Only polymeric material and unreacted siloxane were recovered from a γ-ray initiated reaction of octamethylcyclotetrasiloxane with chlorotrifluoroethene.



$$\begin{array}{ccc} Me_2Si & -O- & SiMe_2 \\ | & & | \\ O & & O \\ | & & | \\ Me_2Si & -O- & SiMe_2 \end{array} + CFCl{=}CF_2 \xrightarrow{\gamma\text{-rays}} \text{Polymeric material}$$

This indicates that polymerisation of the alkene occurs at a much faster rate than free-radical addition of the siloxane to chlorotrifluoroethene. To increase the likelihood of free-radical addition, octamethylcyclotetrasiloxane was reacted with 1,2-dichlorodifluoroethene, a less readily polymerised alkene, at elevated temperature. Only starting materials were recovered from this reaction, suggesting that the large steric requirement of the chlorine atoms is preventing addition.



$$\begin{array}{ccc} Me_2Si & -O- & SiMe_2 \\ | & & | \\ O & & O \\ | & & | \\ Me_2Si & -O- & SiMe_2 \end{array} + CFCl{=}CFCl \;\cancel{\xrightarrow[140^{\circ}C]{DTBP}}$$

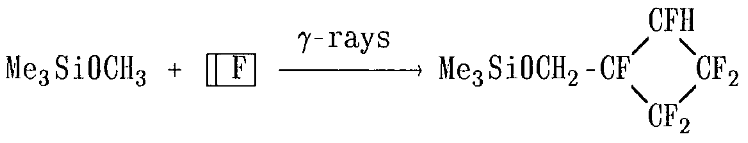
3. Alkoxysilanes

Methoxytrimethylsilane has been shown to add to hexafluoropropene to give the mono-adduct (96) in good yield.[3] As discussed in the introduction, addition occurs preferentially via the α-oxy radical.

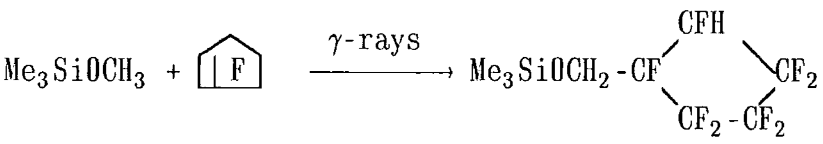
$$Me_3SiOCH_3 + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} Me_3SiOCH_2CF_2CFHCF_3$$

(96) 62%

In this study methoxytrimethylsilane was found to give low yields of the corresponding mono-adducts when reacted with perfluorocyclobutene and perfluorocyclopentene.



(97) 16%



(98) 8%

4. Stereochemistry

In all the successful reactions of siloxanes and methoxytrimethylsilane with the cyclic fluoroalkenes, products were isolated as mixtures of geometric isomers. These isomers, which result from cis and trans addition to the alkene, are illustrated for a general case in Figure 1.

FIGURE 1

cis-derivative trans-derivative

From work by Chambers and co-workers[59,60] on similar acetaldehyde, methanol and dimethyl ether adducts it was proposed that ^{19}F n.m.r. resonances for the CFR and CFH positions of a trans-isomer appear at lower field from the corresponding resonances of the cis-isomer and this was therefore advanced as a method of assigning such geometric isomers.

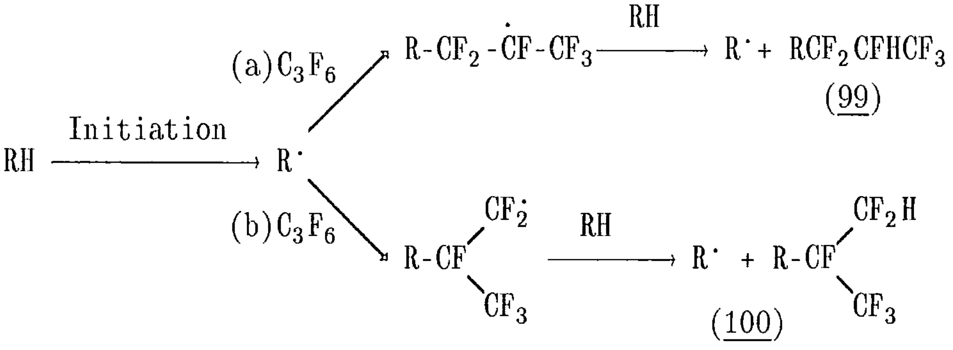
The geometric isomers obtained from these siloxane and methoxytrimethylsilane reactions were all assigned using this ^{19}F n.m.r. chemical shift method. These assignments show that for all siloxane additions to perfluorocyclobutene the products are formed in a 10:1, trans:cis ratio, while similar additions to perfluorocyclopentene realised products in a 2.5:1, trans:cis ratio. For additions of methoxytrimethylsilane to perfluorocyclobutene and perfluorocyclopentene these ratios were 8:1 and 1.5:1, trans:cis respectively. This corresponds well with the results of Chambers and co-workers,[59,60] who also found that the proportion of the cis-isomer increased with increasing fluoroalkene ring size.

C. Reactions of Fluorosilicon Adducts

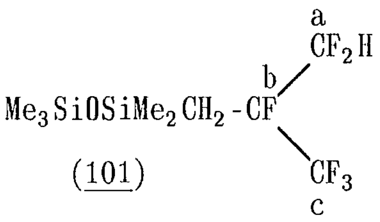
1. Introduction

In preparation for these reactions, the earlier syntheses of silane and siloxane adducts with hexafluoropropene[5] were repeated. In each case the product was found to be inseparable from a small quantity of another species of very similar g.l.c. retention time. From n.m.r. analyses these compounds were assigned as mono-adducts, (<u>100</u>), resulting from radical addition to the central carbon atom of hexafluoropropene (Scheme 9, route (b)).

<u>SCHEME 9</u>



e.g. For (<u>101</u>)



$Me_3SiOSiMe_2CH_2\text{-}CF(CF_2H)(CF_3)$

(<u>101</u>)

Shift(ppm)	Fine Structure	Relative Intensity	Assignment
^1H			
5.97	T of D J_{HF} = 55 Hz J_{ab} = 4.5 Hz		a
^{19}F			
79.4	S	3	c
131.1 134.3	AB of D J_{AB} = 300 Hz J_{HF} = 53 Hz	2	a
172.7	Broad S	1	b

This type of unsymmetrical addition to hexafluoropropene has been observed in cases where the nucleophilic character of a radical has been reduced by attached electron-withdrawing substituents.[20,25] By extrapolation, the observance of unsymmetrical adducts in the additions of silanes and siloxanes to hexafluoropropene is an indication that the intermediate silicon stabilised radicals are less nucleophilic than corresponding oxygen or nitrogen stabilised radicals, probably due to electron backdonation from the radical p-orbital to an empty silicon d-orbital.

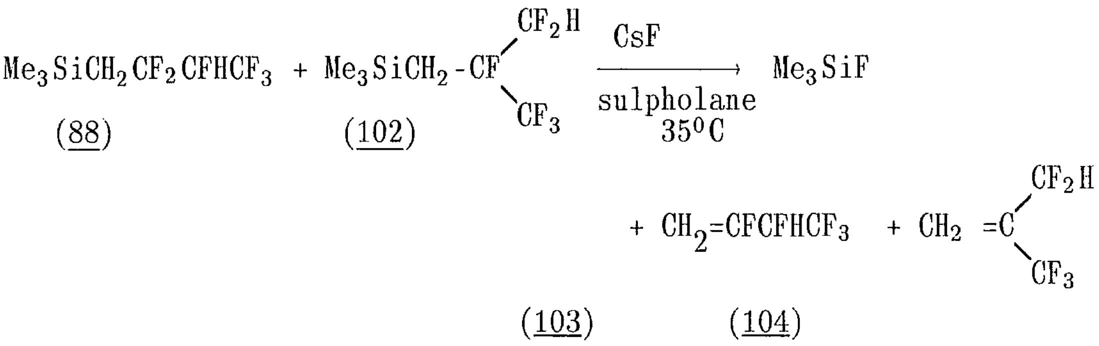
2. Action of Fluoride Ion

Given the strong affinity of silicon for fluoride ion,[61] and the tendency of fluorosilicon compounds to eliminate fluorine from positions α or β to silicon,[62] action of fluoride ion on the simple fluorosilicon adducts described in the preceeding sections should provide a potential route to a range of novel alkenes

viz

where R_f = perfluoroalkyl and R_f' = F or perfluoroalkyl

Accordingly the mono-adduct mixture obtained from addition of tetramethylsilane to hexafluoropropene was reacted with caesium fluoride in sulpholane and quantitative conversion to the expected gaseous alkenes, (103) and (104), was obtained.

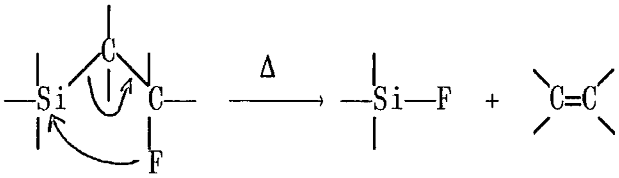


$$\underset{(88)}{Me_3SiCH_2CF_2CFHCF_3} + \underset{(102)}{Me_3SiCH_2\text{-}CF(CF_2H)(CF_3)} \xrightarrow[\text{sulpholane, } 35^{0}C]{CsF} Me_3SiF + \underset{(103)}{CH_2{=}CFCFHCF_3} + \underset{(104)}{CH_2{=}C(CF_2H)(CF_3)}$$

3. Thermal Studies

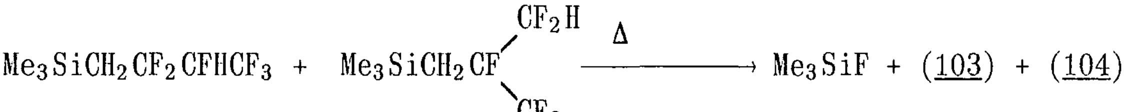
Haszeldine and co-workers have examined the thermal stability of β-fluorosilanes[63] and siloxanes[64]. They found that decomposition by unimolecular transfer of fluorine to silicon occurred at relatively low temperatures, often below $200^{0}C$, to give alkenes.

viz



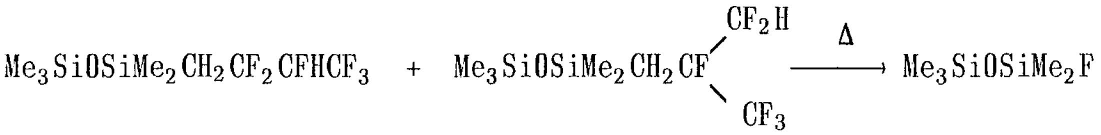
By extrapolation to our simple fluorosilicon adducts, thermolysis should provide an alternative route to the products available from the fluoride ion reactions. Accordingly, thermal studies were performed on a variety of these adducts.

As expected, all the silane and siloxane adducts investigated gave the predicted alkenes. The siloxane adducts proved to be slightly more stable than the silane adducts:



$$\underset{(88)}{Me_3SiCH_2CF_2CFHCF_3} + \underset{(102)}{Me_3SiCH_2CF(CF_2H)(CF_3)} \xrightarrow{\Delta} Me_3SiF + (103) + (104)$$

$150^{0}C$,24 hrs	0%
$180^{0}C$,24 hrs	80%
$200^{0}C$,24 hrs	95%

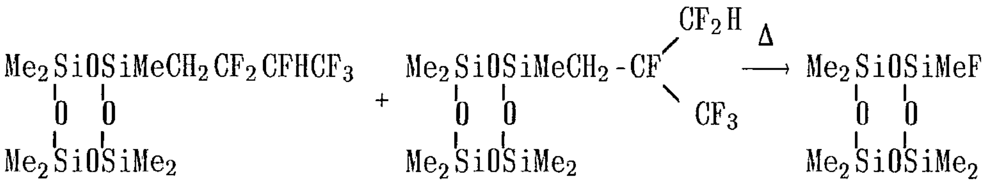


$Me_3SiOSiMe_2CH_2CF_2CFHCF_3 + Me_3SiOSiMe_2CH_2CF(CF_2H)(CF_3) \xrightarrow{\Delta} Me_3SiOSiMe_2F$

(105) (101) + (103) + (104)

200°C,24 hrs 0%

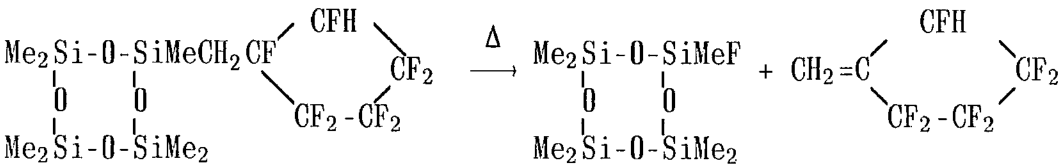
250°C,24 hrs 70%



(106) (107) + (103) + (104)

200°C,24 hrs 0%

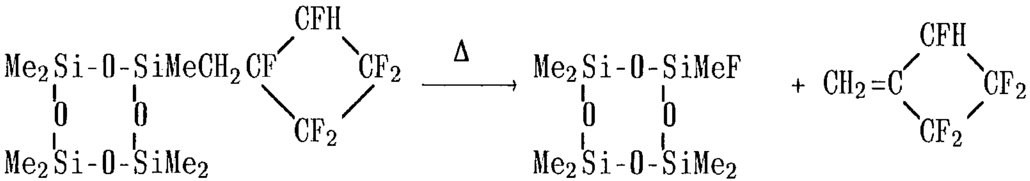
250°C,24 hrs 60%



(108)

(95) 250°C, 2 hrs 30%

250°C, 6 hrs 85%



(109)

(94) 250°C, 2 hrs 0%

300°C, 2.5 hrs 90%

The free-radical synthesis of these simple fluorosilicon adducts coupled with their pronounced thermal lability towards β-elimination provides for a highly novel synthesis of some alkenes by adding effectively one carbon unit to a fluorinated alkene.

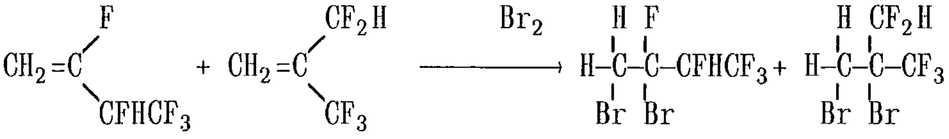
In contrast to the silane and siloxane adducts, the methoxytrimethylsilane adducts have no β-fluorines. In fact, all fluorines are at least as far from silicon as the γ-position. Although structurally different to these methoxytrimethylsilane adducts, Haszeldine and co-workers observed high thermal stabilities for silanes and siloxanes in which fluorine had been removed to the γ-position or beyond.[63b,64-66] A preliminary investigation into the thermal stability of the methoxytrimethylsilane adduct with hexafluoropropene, (96), showed that it was stable to at least $250^{0}C$.

$$\underset{(96)}{Me_3SiOCH_2CF_2CFHCF_3} \not\xrightarrow{250^{0}C,24\ hrs}$$

D. Conclusions

Free-radical addition reactions of the type described provide an excellent method for the introduction of fluorocarbon groups into silicon compounds. This methodology has been used to produce fluorosilicon polymers, although a limiting feature is the tendency to eliminate fluorine from positions α or β to silicon. The situation is different for fluorine in the γ position or beyond and so reactions of silicon polymers with fluoroalkenes such as 1,1-difluoroethene are more promising.

Silicon often mediates in the conversion of a silicon-free precursor into a silicon-free product. A good example of this is the addition of a silicon compound to a fluoroalkene, followed by treatment with fluoride ion or heat. Effectively this adds a one carbon unit to a fluoroalkene, producing some very interesting products which have a whole new chemistry of their own. A preliminary reaction of the alkenes (103) and (104) with bromine has been performed, addition of bromine across the double bonds occuring readily to give products (110) and (111).



(103) (104) (110) (111)

80%

Many other reactions of these alkenes and of the original fluorosilicon adducts remain to be tried. The reactions described here just give a flavour of the new and interesting chemistry available from these compounds.

CHAPTER FOUR

SYNTHESIS AND CHEMISTRY OF FLUOROCARBON DERIVATIVES OF OXYGEN-FUNCTIONAL COMPOUNDS

CHAPTER FOUR

SYNTHESIS AND CHEMISTRY OF FLUOROCARBON DERIVATIVES OF OXYGEN-FUNCTIONAL COMPOUNDS

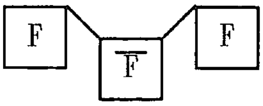
A. Introduction

Free-radical addition reactions of ethers, alcohols and aldehydes etc. to fluoroalkenes are well documented[16,67] and are of continuing interest in this laboratory.[3-5] Reactions of the resulting adducts have also been addressed,[3-5,60,68-74] often as a means of elucidating the original adduct structure.[16a,75-77] The work in this study is directed at both the synthesis and chemistry of oxygen-functional adducts and is meant to supplement previous work in this laboratory.

B. Synthesis

1. Free-Radical Additions of Mono-Oxygen Functional Compounds to Fluoroalkenes

Despite the interest in free-radical additions of mono-oxygen functional compounds to fluoroalkenes, a previous worker in this laboratory[3] noted that additions to non-terminal fluoroalkenes, other than polyfluorocycloalkenes, remained largely unexplored. Consequently he undertook a study into the reactions of methanol, acetaldehyde and dimethyl ether with a variety of non-terminal fluoroalkenes. Most reactions proceeded well, although those involving perfluoro-1,2-bis(cyclobutyl)cyclobutene (112) were notable exceptions.

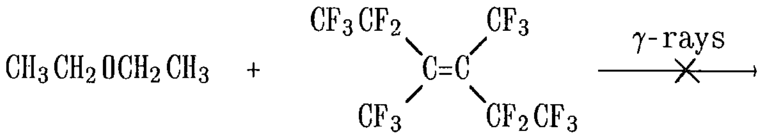


(112)

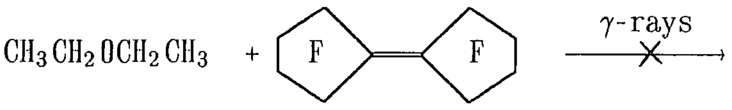
It was suggested that in these perfluoro-1,2-bis(cyclobutyl)-cyclobutene reactions, the perfluorocyclobutyl substituents in the alkene were sterically hindering approach of the α-oxy radical and were therefore preventing addition.

A similar lack of reaction was observed when the study was extended to include reactions of ethanol and cyclohexanol with perfluoro-3,4-dimethyl-3-hexene (7). This was attributed to unfavourable interactions of the bulky hydroxyalkyl radicals with the perfluoroalkyl substituents on the alkene. These observations provide valuable information on the steric limits which prevail in free-radical addition reactions of this kind.

In a continuation of this study, γ-ray initiated reactions of diethyl ether with perfluoro-3,4-dimethyl-3-hexene (7) and perfluorobicyclopentylidene (113) were investigated. In both cases only starting materials were recovered.

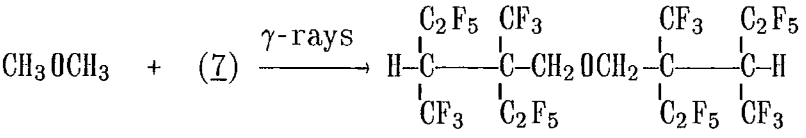


(7)



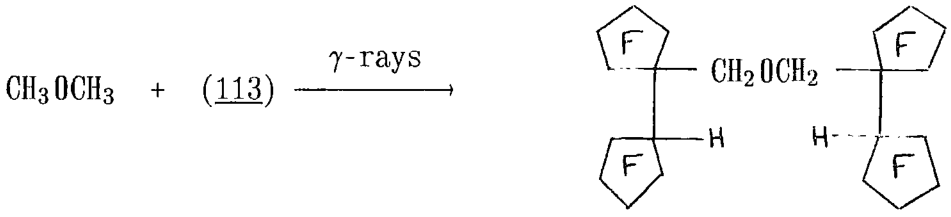
(113)

By contrast, in the earlier study,[3] γ-ray reactions of dimethyl ether with (7) and (113) gave di-adducts in reasonable yield.



$$CH_3OCH_3 \;+\; (7) \xrightarrow{\gamma\text{-rays}} H\!-\!\underset{CF_3}{\overset{C_2F_5}{C}}\!-\!\underset{C_2F_5}{\overset{CF_3}{C}}\!-\!CH_2OCH_2\!-\!\underset{C_2F_5}{\overset{CF_3}{C}}\!-\!\underset{CF_3}{\overset{C_2F_5}{C}}\!-\!H$$

(11) 28%



(<u>114</u>) 61%

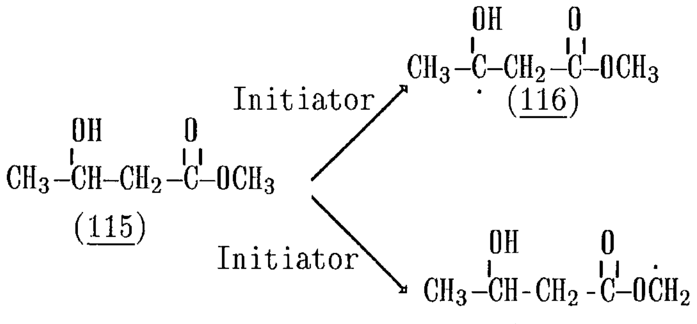
This again pointedly illustrates that only the least sterically demanding α-oxy radicals will add to crowded fluoroalkenes.

2. <u>Free-Radical Additions of Di-Oxygen Functional Compounds to Fluoroalkenes</u>

To gain further information on the scope and limitations of these free-radical addition reactions, several γ-ray initiated reactions of di-oxygen functional compounds with hexafluoropropene were investigated.

(a) <u>Methyl 3-hydroxybutanoate</u>

It is possible to produce two stabilised radicals, (<u>116</u>) and (<u>117</u>), by abstraction of a hydrogen atom from methyl 3-hydroxybutanoate (<u>115</u>).



$CH_3-CH(OH)-CH_2-C(=O)-OCH_3$ (<u>115</u>)

$CH_3-\dot{C}(OH)-CH_2-C(=O)-OCH_3$ (<u>116</u>)

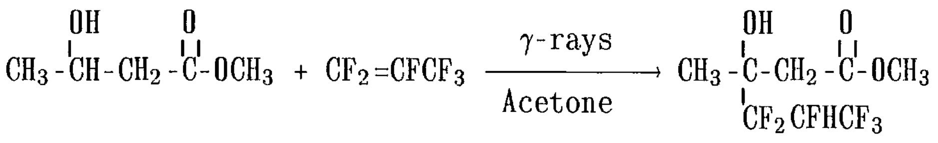
$CH_3-CH(OH)-CH_2-C(=O)-O\dot{C}H_2$ (<u>117</u>)

However, a γ-ray initiated reaction of (<u>115</u>) with an excess of hexafluoropropene yielded only one product as a mixture of diastereomers. Spectroscopic analysis of this product revealed several salient features which point to (<u>118</u>) as its structure.

(i) mass spectrum, chemical ionisation, $^{m}/z$ 269 (M + 1 for a mono-adduct, 100%)

(ii) i.r absorptions, ν_{max} 3460 br (OH), 1720 (C=O), and 1200 s (C-O stretching of an ester)

(iii) n.m.r. data, δ_H, $-O\underline{CH_3}$ still present at δ 3.68 as a singlet, $-\overset{|}{\underline{CH}}-OH$ not present, and $-\underline{CFH}-$ present at δ 5.21 as a multiplet.



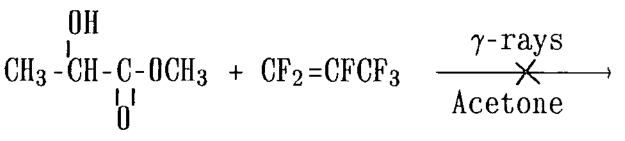
$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 + CF_2{=}CFCF_3 \xrightarrow[\text{Acetone}]{\gamma\text{-rays}} CH_3-\underset{\underset{\displaystyle CF_2CFHCF_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$$

(<u>115</u>) (<u>118</u>) 42%

This result indicates that addition via the tertiary radical *α* to the hydroxy function, (<u>116</u>), is much more favourable than addition via the secondary methyl radical, (<u>117</u>).

(b) <u>Methyl 2-hydroxypropanoate</u>

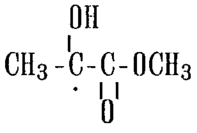
In contrast to the methyl 3-hydroxybutanoate reaction, only starting materials were recovered from a *γ*-ray initiated reaction between methyl 2-hydroxypropanoate (<u>119</u>) and hexafluoropropene.



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-\underset{\underset{\displaystyle O}{\|}}{C}-OCH_3 + CF_2{=}CFCF_3 \overset{\gamma\text{-rays}}{\underset{\text{Acetone}}{\not\longrightarrow}}$$

(<u>119</u>)

From evidence provided by the previous reaction involving methyl 3-hydroxybutanoate, the most likely site for radical generation in (<u>119</u>) is *α* to the hydroxy function, to give (<u>120</u>).



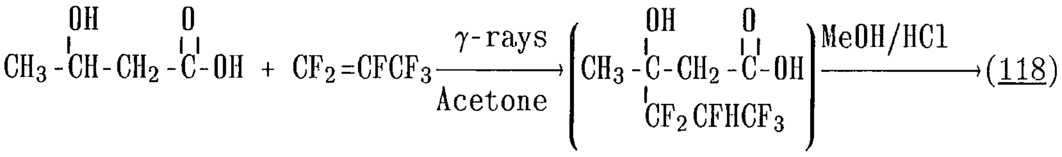
$$CH_3\text{-}\underset{\cdot}{\overset{OH}{C}}\text{-}\underset{O}{C}\text{-}OCH_3$$

(120)

However, the electron-withdrawing ester group in (120) is one carbon atom closer to the radical centre than in the corresponding methyl 3-hydroxybutanoate intermediate radical (116) and thus (120) is likely to be less nucleophilic and hence less reactive towards electrophilic fluoralkenes than (116).

(c) 3-Hydroxybutanoic Acid

By exposing a mixture of 3-hydroxybutanoic acid (121) and hexafluoropropene to γ-rays and esterifying the product by reaction with methanol and hydrogen chloride, methyl 3-hydroxybutanoate and adduct (118) were obtained as the major products.



$$CH_3\text{-}\overset{OH}{CH}\text{-}CH_2\text{-}\overset{O}{C}\text{-}OH + CF_2{=}CFCF_3 \xrightarrow[\text{Acetone}]{\gamma\text{-rays}} \left(CH_3\text{-}\underset{CF_2CFHCF_3}{\overset{OH}{C}}\text{-}CH_2\text{-}\overset{O}{C}\text{-}OH\right) \xrightarrow{MeOH/HCl} (118)$$

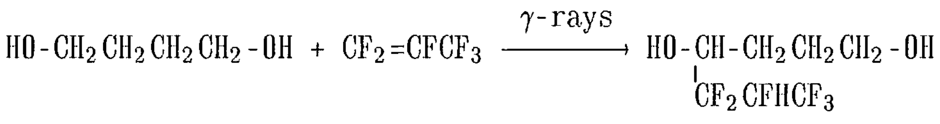
(121) (122)

By extrapolation, the observance of (118) points to adduct (122) as the major product of the free-radical step of this reaction, demonstrating that a whole variety of carboxylic acid containing compounds could be modified via free-radical additions to fluoroalkenes.

(d) 1,4-Butanediol

A previous worker in this laboratory[5] obtained only a low yield of mono-adduct (52) from a γ-ray initiated reaction of

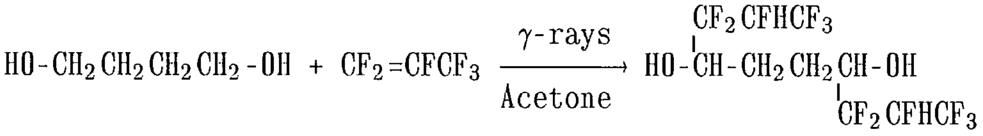
1,4-butanediol with hexafluoropropene.



$$HO\text{-}CH_2CH_2CH_2CH_2\text{-}OH + CF_2{=}CFCF_3 \xrightarrow{\gamma\text{-rays}} HO\text{-}\underset{\displaystyle CF_2CFHCF_3}{CH}\text{-}CH_2CH_2CH_2\text{-}OH$$

(52) 7%

1,4-Butanediol is a viscous material and so this experiment was repeated using an acetone solvent to improve contact between the reagents. A high yield of the di-adduct (123) was obtained, emphasizing the value of using solvents in these free-radical addition reactions.



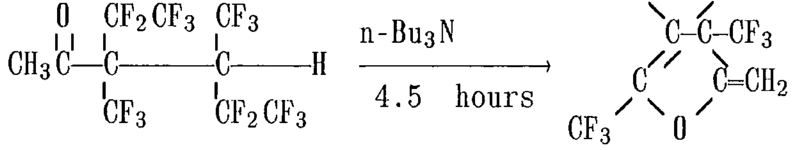
$$HO\text{-}CH_2CH_2CH_2CH_2\text{-}OH + CF_2{=}CFCF_3 \xrightarrow[\text{Acetone}]{\gamma\text{-rays}} HO\text{-}\overset{\displaystyle CF_2CFHCF_3}{CH}\text{-}CH_2CH_2\underset{\displaystyle CF_2CFHCF_3}{CH}\text{-}OH$$

(123) 61%

C. Reactions

1. Aldehyde Adducts

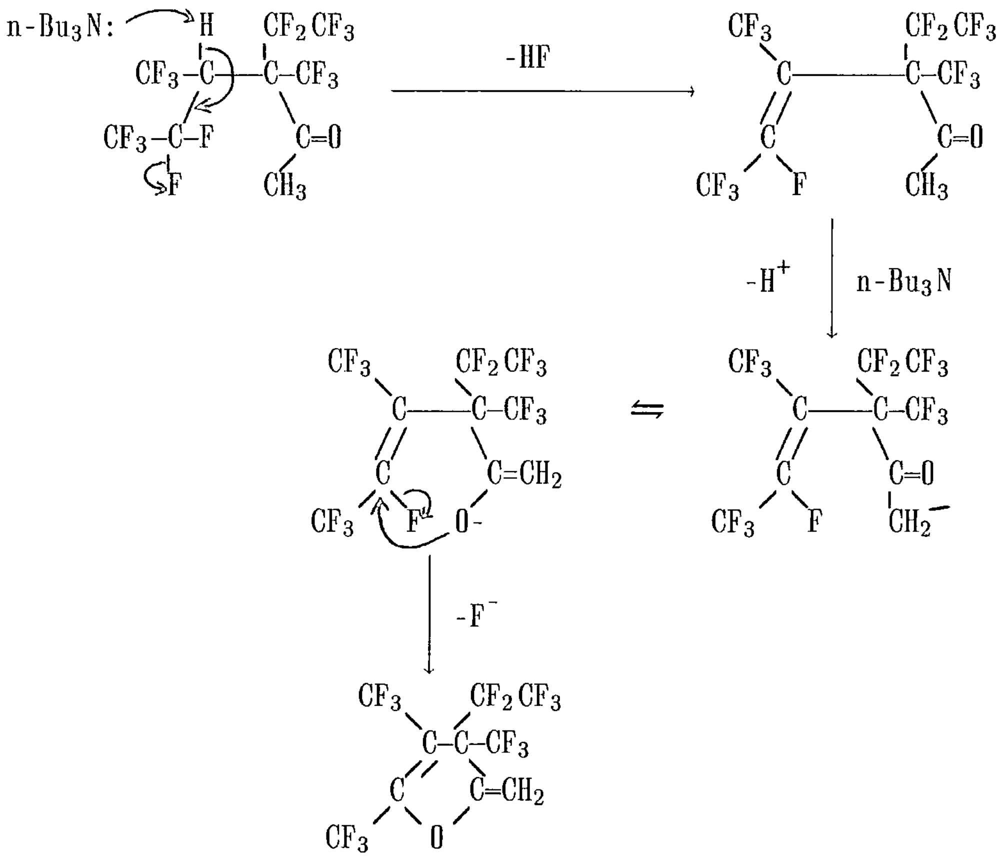
A previous worker in this laboratory[3] observed a fascinating cyclisation when the mono-adduct of acetaldehyde and perfluoro-3,4-dimethyl-3-hexene, (124), was treated with tri-n-butylamine.



(124) (125) 83%

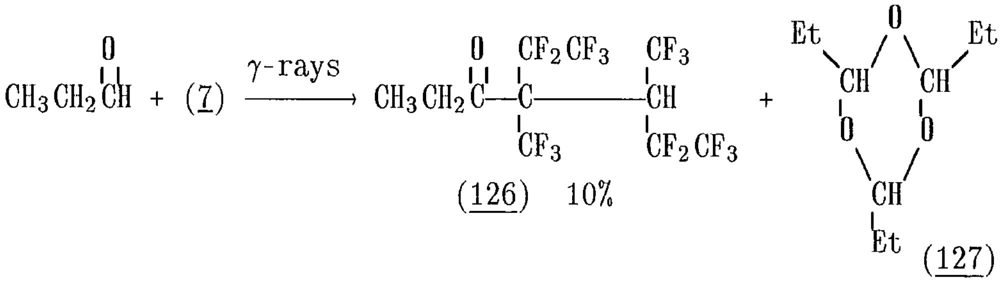
The mechanism proposed to account for the formation of (125) is illustrated in Scheme 10.

SCHEME 10



(125)

In order to repeat this cyclisation on a different analogue, propionaldehyde and perfluoro-3,4-dimethyl-3-hexene (7) were reacted with a view to forming the corresponding mono-adduct, (126). This adduct was formed, although in low yield, along with a trimer of propionaldehyde, (127).



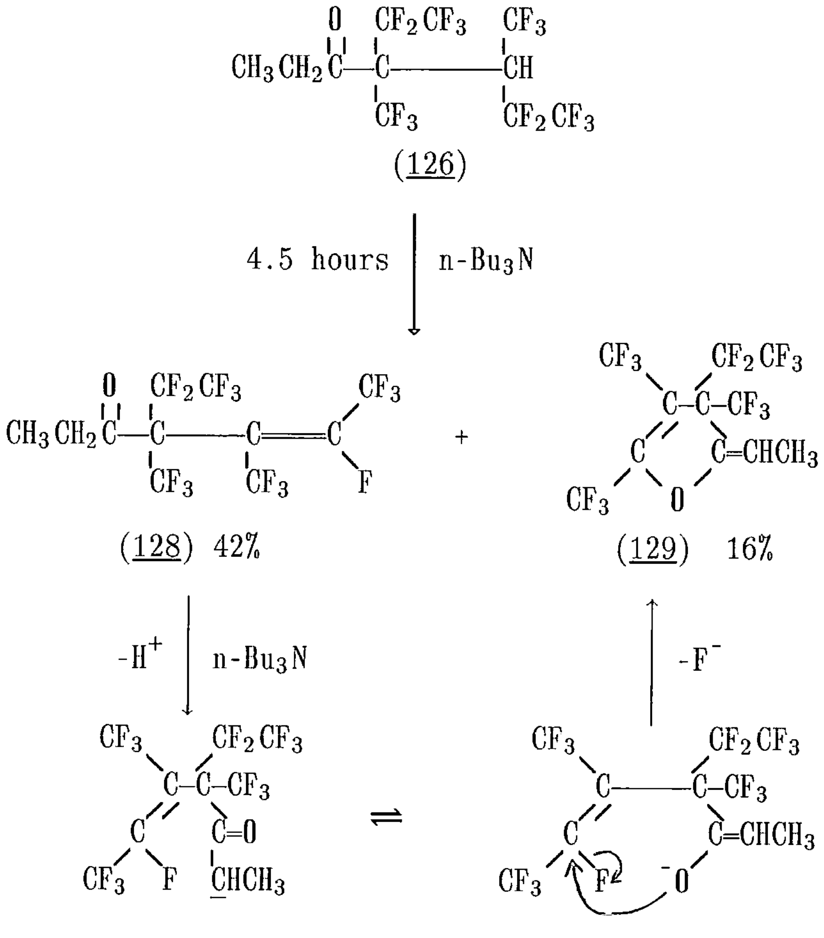
(126) 10%

(127)

Reaction of propionaldehyde with acid can lead to formation of

(127)[78] and so it is likely that some hydrogen fluoride is being produced during this reaction.

Treatment of the mono-adduct (126) with tri-n-butylamine yielded, not only the expected cyclic product (129) but also the singly de-hydrofluorinated product (128).

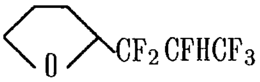
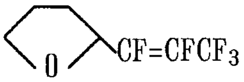
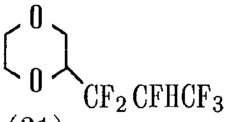
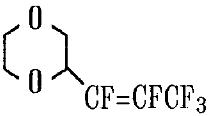
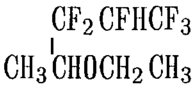
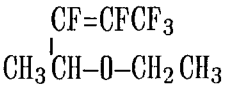


By treating (128) with tri-n-butylamine for 24 hours, 78% conversion to the cyclic product (129) was obtained, thus demonstrating that (128) is an intermediate in the conversion of (126) to (129) and thereby providing evidence in support of the earlier proposed[3] cyclisation mechanism (Scheme 10).

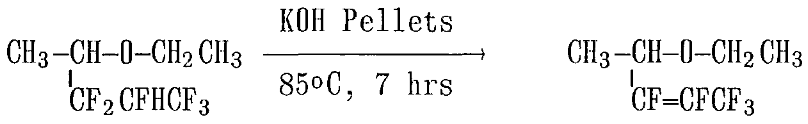
2. Dehydrofluorinations

The dehydrofluorination of simple ether/hexafluoropropene mono-adducts has been addressed by several authors[5,71,76] with varying success (Table 10).

TABLE 10

Adduct	Product	Conditions	Yield	Ref.
 (130)	 (131)	KOH Powder, 150°C, 7.5 hrs	47%	76
(130)	(131)	KOH Powder, reflux, 2 hrs	75%	5
(130)	(131)	KOH Powder diglyme, 120°C, 8 hrs	75%	71
(130)	(131)	Sodium/ t-butylalcohol, 25°C, 7 hrs	71% (88% pure)	71
 (31)	 (132)	KOH Powder, 150°C, 7.5 hrs	21%	76
 $CH_3\overset{CF_2CFHCF_3}{\overset{\mid}{C}}HOCH_2CH_3$ (19)	 $CH_3\overset{CF=CFCF_3}{\overset{\mid}{C}}H\text{–}O\text{–}CH_2CH_3$ (133)	KOH Powder, 150°C, 7.5 hrs	54%	76
(19)	(133)	KOH Powder, reflux, 2 hrs	47%	5
$CH_3OCH_2CF_2CFHCF_3$ (134)	$CH_3OCH_2CF=CFCF_3$ (135)	KOH Powder, reflux, 3 hrs	24%	5

In this study a substantially improved yield of dehydrofluorinated adduct (133) was obtained by heating the diethylether/hexafluoropropene mono-adduct (19) with potassium hydroxide pellets in a sealed system. In addition, unlike previous dehydrofluorination experiments, no further purification of the product was required, making this an attractive route to these alkenes.



$$\underset{CF_2CFHCF_3}{CH_3\text{-}CH\text{-}O\text{-}CH_2CH_3} \xrightarrow[85^{o}C,\ 7\ hrs]{KOH\ Pellets} \underset{CF{=}CFCF_3}{CH_3\text{-}CH\text{-}O\text{-}CH_2CH_3}$$

(19) (133) 78%

In contrast, other attempts to dehydrofluorinate (19) using triethylamine and tri-n-butylamine proved unsuccessful, even at elevated temperatures.

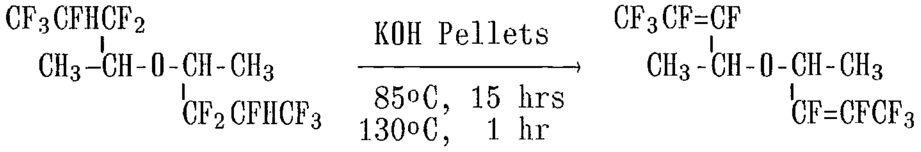
$$(\underline{19}) \quad \overset{Et_3N}{\underset{80^{o}C,\ 5\ hrs}{\nrightarrow}}$$

$$(\underline{19}) \quad \overset{n\text{-}Bu_3N}{\underset{175^{o}C,\ 3\ hrs}{\nrightarrow}}$$

Dehydrofluorination of di-adducts would provide very interesting dienes with potential uses in areas such as polymer cross-linking and so the above potassium hydroxide sealed system methodology was applied to some ether/hexafluoropropene di-adducts.

Although requiring harsher conditions, the diethylether/hexafluoropropene di-adduct (21) gave the diene (136) in good yield. The product was complicated by the appearance of several isomers but these all gave similar mass spectra. As in the corresponding mono-adduct reaction, no further purification of

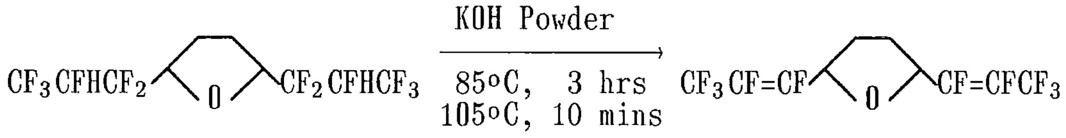
(136) was required.



$$\underset{\underset{CF_2CFHCF_3}{|}}{\overset{\overset{CF_3CFHCF_2}{|}}{CH_3-CH}-O-CH-CH_3}} \xrightarrow[\substack{85^oC,\ 15\ hrs \\ 130^oC,\ 1\ hr}]{\text{KOH Pellets}} \overset{\overset{CF_3CF=CF}{|}}{CH_3-CH}-O-\underset{\underset{CF=CFCF_3}{|}}{CH}-CH_3$$

(21) (136) 60%

The di-adduct of oxolane and hexafluoropropene, (137), proved to be still more difficult to dehydrofluorinate, powdered potassium hydroxide being necessary to effect complete dehydrofluorination. The diene, (138), was again obtained in high purity, although the yield was somewhat lower. Like diene (136), the product contained several isomers which gave similar mass spectra.



(137) (138) 25%

D. Conclusions

The free-radical addition of ethers, alcohols, aldehydes etc. to fluorinated alkenes provides an excellent route to functional fluorocarbons. For simple molecules yields are high but, as the reaction centres become more crowded, steric inhibition of addition occurs. The reactions of di-functional compounds with fluoroalkenes provide useful information on the scope and limitations of these free-radical additions. The adducts produced from these reactions can be converted into novel and interesting products with a whole new chemistry of their own.

CHAPTER FIVE

POLYMER MODIFICATION VIA FREE-RADICAL ADDITION TO FLUOROALKENES

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POLYMER MODIFICATION VIA FREE-RADICAL ADDITION TO FLUOROALKENES

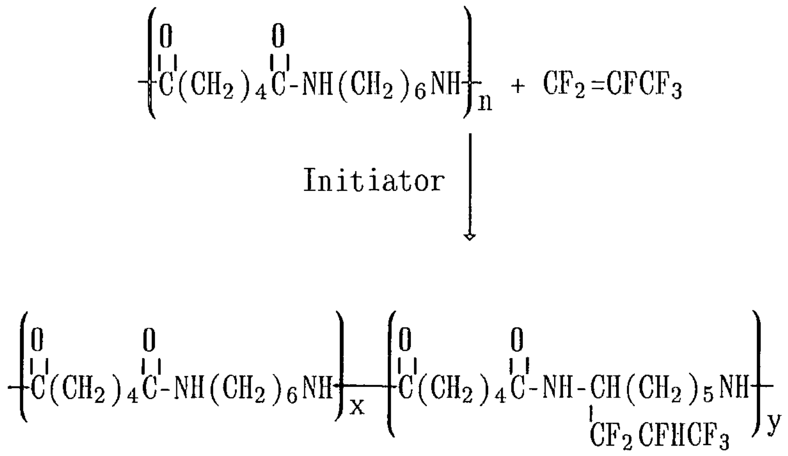
A. Introduction

In the preceding chapters, various free-radical additions of simple nitrogen, silicon and oxygen containing compounds to fluoroalkenes have been illustrated. Extension of this methodology to suitable polymeric materials would be of great value since fluorine-containing polymers often show improved properties over their hydrocarbon analogues.[79] Indeed, organosilicon polymers modified in this way have already generated industrial interest.[39-43] (See Chapter 3)

B. Nylon 66

For suitable monomeric amides, abstraction of a hydrogen atom from the carbon adjacent to the amide nitrogen, followed by addition of the resultant radical to a fluoroalkene, provides an excellent route to fluorocarbon amides.[4,5,49,50] (See Chapters 1 and 2) By extrapolation, nylons, i.e. polyamides, possessing such a hydrogen bearing α-carbon should be ideally set-up for modification via free-radical addition to fluoroalkenes.

e.g. For reaction of nylon 66 with hexafluoropropene,



$$\left[-\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-NH(CH_2)_6NH-\right]_n + CF_2{=}CFCF_3 \xrightarrow{\text{Initiator}} \left[-\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-NH(CH_2)_6NH-\right]_x \left[-\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-NH-\underset{CF_2CFHCF_3}{\underset{|}{CH}}(CH_2)_5NH-\right]_y$$

In fact e.s.r. studies have demonstrated that radicals are produced in such nylons exposed to high-energy radiation in vacuo and have confirmed that the predominant free-radical species is formed by abstraction of a hydrogen atom from the carbon adjacent to the amide nitrogen.[80] Although reactions of these nylon radicals can lead to cross-linking and degradation of the nylon,[80,81] if a fluoroalkene is present, addition of a nylon radical to a fluoroalkene molecule may occur at a much greater rate than this cross-linking or degradation in the regions where the polymer is in contact with the fluoroalkene.

Grafting of a variety of hydrocarbon materials onto nylons by reaction with nylon radicals has been described[80] but work involving fluoroalkenes has been restricted to <u>photochemical</u> insertion of hexafluoropropene into a nylon 6 film.[82] In the present study, γ-ray initiated reactions of nylon 66 with hexafluoropropene were investigated. Solution phase reactions were targeted to facilitate good contact between the reagents.

From the solvents available for nylons,[83] 2,2,2-trifluoroethanol (<u>17</u>) was chosen for use in this study since, unlike many of the other common nylon solvents, aliphatic fluorinated alcohols are reported not to cause polymer aggregation, hydrolytic breakage of the amide groups, or degradation on dissolution of the polyamide.[84] To determine whether 2,2,2-trifluoroethanol could be effectively removed from nylon 66, a sample of nylon 66 was dissolved in 2,2,2-trifluoroethanol and the solvent was then removed under reduced pressure. Elemental analysis data for the resulting polymer film (139) is given in Table 11 along with data for a stock nylon 66 sample for comparison.

TABLE 11

	% C	% H	% N
Required for nylon 66	63.7	9.7	12.4
Stock nylon 66	62.7	9.9	11.4
(139)	61.8 61.0	10.2 9.9	11.2 10.7

The discrepancy between the data for the stock material and the calculated values for nylon 66 demonstrates that the elemental analysis date for nylon 66 materials cannot be regarded as totally reliable. However, the values obtained for (139) are not sufficiently different from the stock nylon 66 values to suggest that a significant amount of 2,2,2-trifluoroethanol remains in the film. Since abstraction of a hydrogen atom from 2,2,2-trifluoroethanol to produce (140), a stabilised radical, is probable under the proposed reaction conditions, a series of control experiments was performed to determine whether 2,2,2-trifluoroethanol would react with either hexafluoropropene or nylon 66 when exposed to γ-rays.

$$CF_3\text{-}\dot{C}H\text{-}OH$$

(140)

Starting materials were recovered from a γ-ray initiated reaction between 2,2,2-trifluoroethanol and hexafluoropropene, indicating that the electron-withdrawing trifluoromethyl group in 2,2,2-trifluoroethanol makes radical (140) too electrophilic to react with hexafluoropropene.

$$\underset{(17)}{CF_3CH_2OH} + CF_2{=}CFCF_3 \overset{\gamma\text{-rays}}{\not\longrightarrow}$$

Exposure of a solution of nylon 66 in 2,2,2-trifluoroethanol to γ-rays, followed by removal of the solvent, gave a polymer film (141). Elemental analysis data for (141) is given in Table 12, along with data for a nylon 66 film irradiated in vacuo for comparison.

TABLE 12

	% C	% H	% N
(141)	57.3	8.9	9.2
	56.7	9.1	9.4
Irradiated nylon 66 film	56.5	9.1	10.4

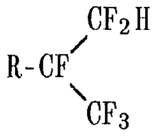
Although the elemental analysis data for (141) varies significantly from the elemental analysis data for the non-irradiated nylons (Table 11), its similarity to the elemental analysis data for the nylon film irradiated in vacuo suggests that it is perhaps some effect of the γ-rays, rather than incorporation of 2,2,2-trifluoroethanol, which is causing this difference. As the percentages of carbon, hydrogen and nitrogen in the irradiated nylons are all lower than in the non-irradiated nylons, incomplete combustion due to cross-linking could explain the difference in analysis values between these materials. However, incorporation of 2,2,2-trifluoroethanol would also result in a reduction in the carbon, hydrogen and nitrogen values for nylon 66 and so the possibility that (141) contains some 2,2,2-trifluoroethanol cannot be discounted. Despite this possibility, γ-ray initiated solution phase reactions of nylon 66 with hexafluoropropene using 2,2,2-trifluoroethanol as the solvent were still investigated.

In a preliminary experiment, introduction of hexafluoropropene into a reaction vessel containing a solution of nylon 66 in 2,2,2-trifluoroethanol caused precipitation of the nylon, presumably due to its lower solubility in hexafluoropropene. Assuming that each repeat unit of the polymer has only one site available for addition to hexafluoropropene, the amount of hexafluoropropene used in this reaction represents a 40 times excess over the nylon 66. (NB This assumption has been made in order to give an indication of reactant proportions. Similar assumptions will be made in subsequent cases for the same reason). The heterogeneous mixture was irradiated with γ-rays and after removal of excess hexafluoropropene the nylon 66 re-dissolved in the 2,2,2-trifluoroethanol solvent. Removal of this 2,2,2-trifluoroethanol gave a yellowy coloured polymer film (142) which contained 36% fluorine (by elemental analysis).

By using a large 2,2,2-trifluoroethanol to nylon 66 ratio it was possible to maintain complete solubility of a nylon 66 sample when hexafluoropropene (140 times excess over nylon 66) was introduced. Irradiation of this solution then gave, after removal of excess hexafluoropropene and the solvent, a viscous yellow liquid (143) which contained 57% fluorine (by elemental analysis). Although unable to dissolve nylon 66, acetone was found to be a suitable solvent for (143) and so ^{19}F n.m.r. spectroscopic analysis was performed on this material using d_6-acetone as the n.m.r. solvent. The spectrum obtained showed a multiplicity of resonances in four distinct regions: 67 to 74 ppm (region A); 101 to 131 ppm (region B); 174 to 185 ppm (region C) and ; 210 to 214 ppm (region D). The resonances in regions A (CF_3), B (CF_2) and C (CFH) are consistent with a product containing hexafluoropropyl groups which result from addition to the terminal carbon of hexafluoropropene i.e. (99).

$R\text{-}CF_2\text{-}CFH\text{-}CF_3$

(99)



$R\text{-}CF(CF_2H)(CF_3)$

(100)

The resonances in region C (tertiary fluorine) suggest that addition to the central carbon atom of hexafluoropropene may have occurred, i.e. (100). Addition of 2,2,2-trifluoroethanol to the n.m.r. sample demonstrated that there was no contribution from 2,2,2-trifluoroethanol in the spectrum of (143). However, if (143) contained only fluorocarbon groups resulting from addition to hexafluoropropene, the integration of region A should be equal to the combined integrations of the other regions, but comparison of these integrations revealed that the contribution from region A (CF_3) was almost twice the expected value. Although integrations of the broad resonances associated with polymers cannot be compared with total confidence, the high contribution to the CF_3 resonances in (<u>143</u>) is significant and suggests that perhaps some reaction of nylon 66 with 2,2,2-trifluoroethanol has occurred. It should be noted however, that addition of each repeat unit of nylon 66 to more than four hexafluoropropene and/or 2,2,2-trifluoroethanol molecules would be required to give a product like (<u>143</u>) which contains 57% fluorine. This is obviously unrealistic and suggests that addition of nylon 66 to either hexafluoropropene or hexafluoropropene and 2,2,2-trifluoroethanol is not the whole story.

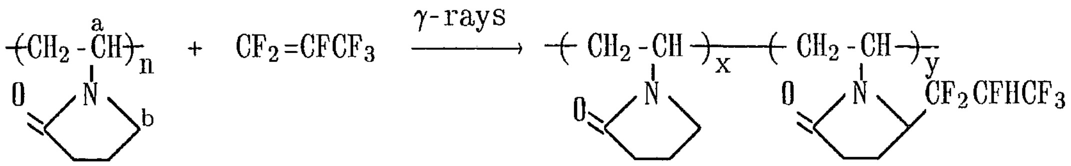
For comparison, a ^{19}F n.m.r. spectrum of the polymeric nylon product (<u>81</u>), obtained from the γ-ray initiated reaction involving ϵ-caprolactam and hexafluoropropene in an acetone solvent (Chapter 2), contained no evidence for addition to the central carbon atom of hexafluoropropene and gave the correct integrations for each series of resonances.

Despite the obvious complexity of the solution state nylon 66 reaction, the ^{19}F n.m.r. spectrum of (<u>143</u>) suggests that addition of nylon 66 to hexafluoropropene is significant. Some of this contribution could arise from nucleophilic rather than free-radical addition to hexafluoropropene and so a control experiment was performed to investigate this possibility. Nylon 66, 2,2,2-trifluoroethanol and hexafluoropropene were mixed in the same ratio as in the initial experiment and the resulting solution was allowed to stand in the dark, in the absence of γ-rays, for 96 hours (<u>cf</u> 96 hours exposure to γ-rays for the initial experiment). Removal of hexafluoropropene and 2,2,2-trifluoroethanol gave a polymer film (<u>144</u>); (Found:C, 63.0; H, 10.7; N, 11.7%) Comparison of the elemental analysis data for (<u>144</u>) with the elemental analysis data for the unreacted nylon 66 materials (Table 11) suggests that nucleophilic addition to hexafluoropropene has not occurred.

C. <u>Poly-N-vinylpyrrolidone</u>

Previous work in this laboratory[4] has shown that poly-N-vinylpyrrolidone (<u>145</u>), a solid polyamide substrate, will add to hexafluoropropene when irradiated with γ-rays to a high dose (100 Mrads), despite the poor contact between reagents. In the present study we have shown that significant improvements to systems occur by the use of solvents and therefore this work was repeated for comparison with an analogous <u>solution</u> phase reaction.

A reaction without solvent (3 times excess of hexafluoropropene over poly-N-vinylpyrrolidone) was irradiated to a total dose of 100 Mrad, while a solution phase reaction (2,2,2-trifluoroethanol solvent, 3.5 times excess of hexafluoropropene over poly-N-vinylpyrrolidone) was subject to a 20 Mrad dose. In both instances the final product obtained was a yellow solid. A ^{19}F n.m.r. spectrum of the product obtained from the solution state reaction was recorded using methanol as the n.m.r. solvent and the spectrum showed a multiplicity of resonances in the CF_3, CF_2, and CFH regions which integrated to 3:2:1. In contrast to the nylon 66 reactions described above, there was no evidence for addition to the central carbon atom of hexafluoropropene. Elemental analysis data for the products is given in Table 13 along with various calculated values for comparison.



(<u>145</u>)

Without solvent (<u>146</u>)

2,2,2-Trifluoroethanol solvent (<u>147</u>) (eqn. 10)

TABLE 13

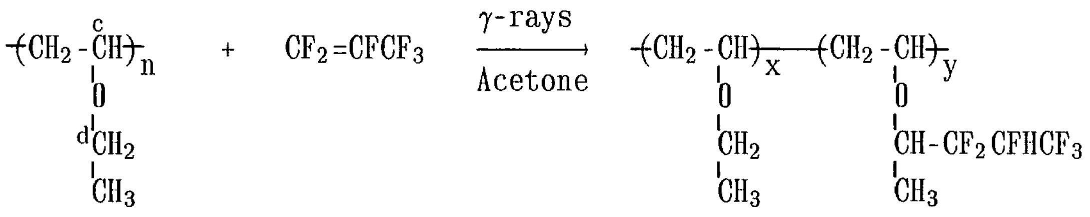
	% C	% H	% N	% F
(<u>146</u>)	50.7	6.5	8.3	19.4
(<u>147</u>)	42.2	4.3	5.8	37.4
Calc. for x:y = 0	64.9	8.1	12.6	-
Calc. for x:y = 100:35	51.7	5.5	8.6	24.4
Calc. for x:y = 2:1	48.4	4.8	7.5	30.6
Calc. for x:y = 3:2	44.3	4.0	6.3	38.3

Consideration of the structure of poly-N-vinylpyrrolidone (<u>145</u>) indicates that there are two probable positions for radical generation and subsequent addition to hexafluoropropene within each repeat unit, i.e. **a** and **b**. However, despite the fact that the intermediate radical formed at carbon **a** would be a tertiary radical while the intermediate radical formed at carbon **b** would be a secondary radical, the favourable stereoelectonic effect in the 5-membered amide ring[5] (see Chapter 1), coupled with the lower steric requirement for addition at carbon **b**, should favour addition at the ring site. Since the elemental analysis data indicates that the products contain less than one hexafluoropropyl group per repeat unit of poly-N-vinylpyrrolidone, it seems likely that the structure of the product is as represented in equation 10 above.

Comparison of the elemental analysis data in Table 13 shows quite clearly that, although hexafluoropropene incorporation can be achieved by reaction with a solid polymeric material, <u>much greater</u> incorporation can be obtained at very much lower irradiation doses if a solvent is used.

D. <u>Poly(vinyl ethyl ether)</u>

Poly(vinyl ethyl ether) (<u>148</u>), a polymer containing pendant ether linkages, was subject to γ-radiation in the presence of hexafluoropropene (3 times excess over poly(vinyl ethyl ether)). From the amount of recovered hexafluoropropene, alkene incorporation into the polymer was calculated to be less than one unit in every eight repeat units of the polymer. Since poly(vinyl ethyl ether) is a viscous liquid, the low hexafluoropropene incorporation could be due to a contact problem and so the reaction was repeated using an acetone solvent. In this reaction a 2.5 times excess of hexafluoropropene over poly(vinyl ethyl ether) was used. A ^{19}F n.m.r. spectrum of the viscous liquid product (<u>149</u>) contained a multiplicity of resonances in the CF_3, CF_2 and CFH regions of the spectrum which integrated to 3:2:1. There was no evidence for addition to the central carbon atom of hexafluoropropene. Elemental analysis data for (<u>149</u>) is given in Table 14 along with some calculated values for comparison.



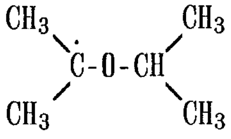
$$\left(CH_2-\underset{\substack{|\\O\\|\\{}^{d}CH_2\\|\\CH_3}}{\overset{c}{C}H}\right)_n + CF_2=CFCF_3 \xrightarrow[\text{Acetone}]{\gamma\text{-rays}} \left(CH_2-\underset{\substack{|\\O\\|\\CH_2\\|\\CH_3}}{CH}\right)_x\!\!-\!\!\left(CH_2-\underset{\substack{|\\O\\|\\CH-CF_2CFHCF_3\\|\\CH_3}}{CH}\right)_y$$

(<u>148</u>) (<u>149</u>) (eqn. 11)

TABLE 14

	% C	% H	% F
(149)	49.6	6.7	29.4
Calc. for x:y = 0	66.7	11.1	-
Calc. for x:y = 3:1	49.2	6.6	31.1
Calc. for x:y = 2:1	44.9	5.4	38.8

Like poly-N-vinylpyrrolidone, poly(vinyl ethyl ether) (148) has two possible sites for addition to hexafluoropropene, i.e. **c** and **d**. An intermediate radical formed by abstraction of a hydrogen atom from carbon **c** would be a tertiary radical while addition via carbon **d** would involve a secondary radical. However, work with monomeric ethers has emphasized the importance of steric effects in free-radical reactions, e.g. the methyl groups in di-isopropylether prevent addition of the tertiary radical (15) to hexafluoropropene,[20] and thus addition at the sterically less demanding carbon **d** is probably more likely. Since the elemental analysis data indicates that product (149) contains less than one hexafluoropropyl group per repeat unit of poly(vinyl ethyl ether), it is probable that the structure of this product is as represented in equation 11 above.



(15)

Comparison of the elemental analysis data for (149) in Table 14 with the calculated values indicates that approximately one alkene unit was incorporated into every three repeat units of the polymer, demonstrating again the advantage of using a solvent.

E. Conclusions

The results presented show that the free-radical addition of polymers to fluoroalkenes provides a good route to partially fluorinated polymers. Although fluoroalkene incorporation into polymers can be achieved by reaction without a solvent, there is often a contact problem and the use of a solvent dramatically increases the degree of this incorporation.

CHAPTER SIX

ELECTROCHEMICAL FLUORINATION OF ETHER ADDUCTS

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ELECTROCHEMICAL FLUORINATION OF ETHER ADDUCTS

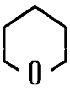
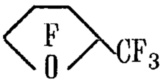
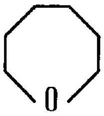
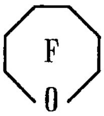
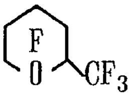
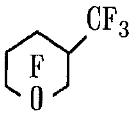
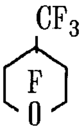
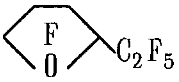
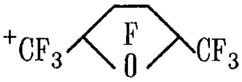
A. Introduction

Electrochemical fluorination is one of the most widely use techniques for the synthesis of perfluorinated compounds.[85–91] In general, this technique involves the electrolysis of a solution or suspension of a substrate in anhydrous hydrogen fluoride by application of a direct current at low voltage (usually 5-6 V). If necessary an electrolyte such as potassium fluoride is added to render the solution conducting. Nickel anodes are essential but the cathodes can be either nickel or steel. At this low voltage no free fluorine is generated but perfluorinated compounds are produced at the anodes and hydrogen is evolved at the cathodes.

Despite low yields and often complex product mixtures, perfluoroethers, a class of compound of considerable industrial importance,[92,93] are usually prepared using this technique. Either hydrocarbon ethers[90,91,94–99] or alkane carboxylic acids (or suitable derivatives) [97,100–102] are used as starting materials, the latter producing cyclic perfluoroethers as side-products via an intramolecular cyclisation reaction (see Table 15 for examples). Consequently, ways of improving perfluoroether yields in these electrochemical fluorination reactions would prove very valuable.

TABLE 15a

Electrochemical Fluorination of Hydrocarbon Ethers

Ether	Product (% yield)	Ref.
$(C_2H_5)_2O$	$(C_2F_5)_2O$ (32) + CF_3COF (36) + C_2F_6	90
$(C_3H_7)_2O$	$(C_3F_7)_2O$ (26) + C_2F_5COF (21)	91
$(n\text{-}C_4H_9)_2O$	$(n\text{-}C_4F_9)_2O$ (15) + $n\text{-}C_3F_7COF$ (20) + C_2F_5COF (3) + CF_3COF	90
$n\text{-}C_4H_9OC_5H_{11}\text{-}n$	$n\text{-}C_4F_9OC_5F_{11}\text{-}n$ (14)	94
$n\text{-}C_4H_9OC_6H_{13}\text{-}n$	$n\text{-}C_4F_9OC_6F_{13}\text{-}n$ (10)	94
$C_2H_5OCH_2CH_2OCH_2CH_2OC_2H_5$	$C_2F_5OCF_2CF_2OCF_2CF_2OC_2F_5$ (4)	95
	 (42)	96
	 (35)	96
	 (16) +  (7) +  (2)	97
	 (11) +  (7) +  (5) +  (5) +  (11) +  (1) + $n\text{-}C_4F_9OC_2F_5$ (2)	98

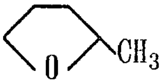
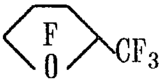
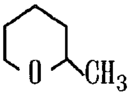
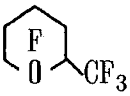
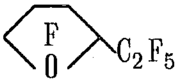
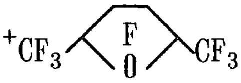
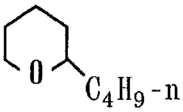
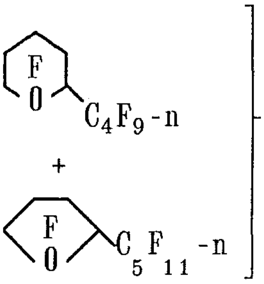
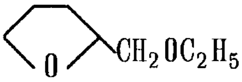
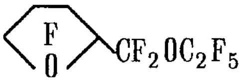
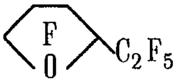
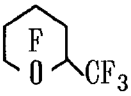
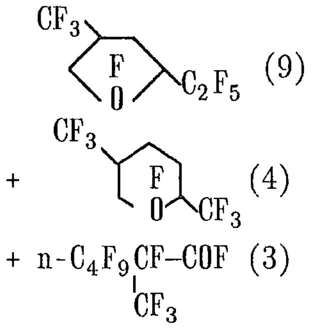
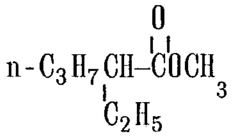
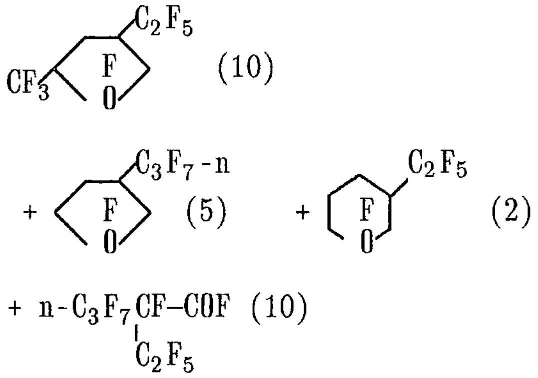
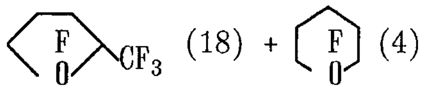
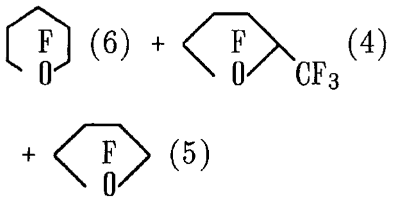
	 (36) +  (9)	97
	 (28) +  (10) +  (3) +  (3) + n-$C_4F_9OC_2F_5$ (6)	98
	 (30) +  (12) + n-$C_4F_9OC_5F_{11}$-n (4)	94
	 (42)	99

TABLE 15b

Electrochemical Fluorination of Carboxylic Acids and Derivatives

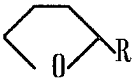
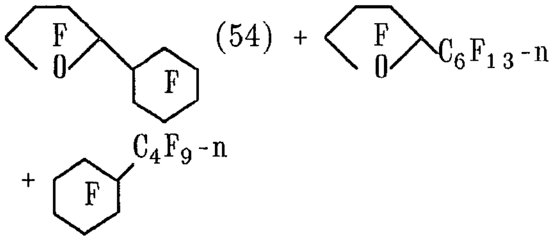
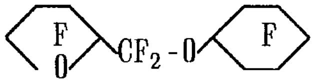
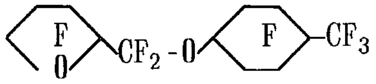
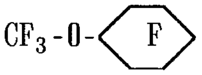
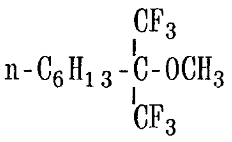
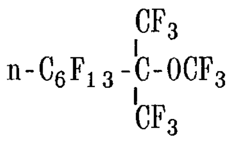
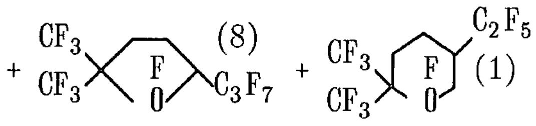
Substrate	Product (% yield)	Ref.
$CH_3(CH_2)_4COOH$	 + 	100

n-$C_4H_9CH(CH_3)COCl$	 (9) + (4) + n-$C_4F_9CF(CF_3)$–COF (3)	101
 n-$C_3H_7CH(C_2H_5)$–$C(=O)OCH_3$	 (10) + (5) + (2) + n-$C_3F_7CF(C_2F_5)$–COF (10)	101
CH_3-$(CH_2)_4$-OH	 (18) + (4)	102
HO-$(CH_2)_5$-OH	 (6) + (4) + (5)	97

Work in this laboratory has shown that simple ether/fluoroalkene adducts can be exhaustively fluorinated using cobalt trifluoride[5,69] or direct fluorination[103] techniques in much higher yields than analogous hydrocarbon ethers. Also, there is some precedent for improved yields and reduced fragmentation in the electrochemical fluorination of partially fluorinated ethers[104,105] (Table 16) and so it would be valuable to investigate the fluorination of simple ether/fluoroalkene adducts using this technique.

TABLE 16

Electrochemical Fluorination of Partially Fluorinated Ethers

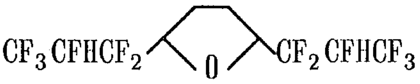
Substrate	Product (% yield)	Ref.
		
R = C_6F_5	 (54)	104
R = $CH_2OC_6F_5$	 (75)	104
R = $CH_2OC_6F_4CF_3$-p	 (71)	104
$CH_3-O-C_6F_5$	 (36, 93% pure)	104
 $n\text{-}C_6H_{13}\text{-}C(CF_3)_2\text{-}OCH_3$	 $n\text{-}C_6F_{13}\text{-}C(CF_3)_2\text{-}OCF_3$ (27)  (8) (1)	105

B. Discussion

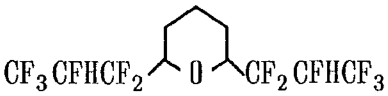
The electrochemical fluorination experiments described below were carried out in the laboratories of Professor P. Sartori at the University of Duisburg, West Germany and also in collaboration with Mr. R.W. Fuss.

1. Starting Materials

Generally cyclic ethers give higher yields of perfluoroethers than acyclic ethers (see Table 15) and so the substrates chosen for electrochemical fluorination were 2,5-bis-(2H-hexafluoropropyl)oxolane (137) and 2,6-bis-(2H-hexafluoropropyl)oxane (150). Di-adducts were targeted to maximize any stabilizing effect arising from the presence of fluorine in the ether starting materials.



(137)



(150)

2. Electrochemical Fluorination Conditions

Within a given electrochemical fluorination cell with a fixed electrode arrangement the major variables are cell voltage, cell temperature and substrate concentration. Each substrate requires a unique set of conditions for optimum fluorination. Conditions described in the literature are diverse, however, preferred cell voltage, cell temperature and substrate concentration tend to be within the ranges 5-6 V,[90] 0-20°C[90] and < 15%[88] respectively. Therefore, for these preliminary experiments, conditions within these ranges were chosen.

3. Electrochemical Fluorination of 2,5-Bis-(2H- hexafluoropropyl)oxolane (137)

The electrochemical fluorination of (137) was performed using the conditions outlined in Table 17. The cell temperature was the only variable.

TABLE 17

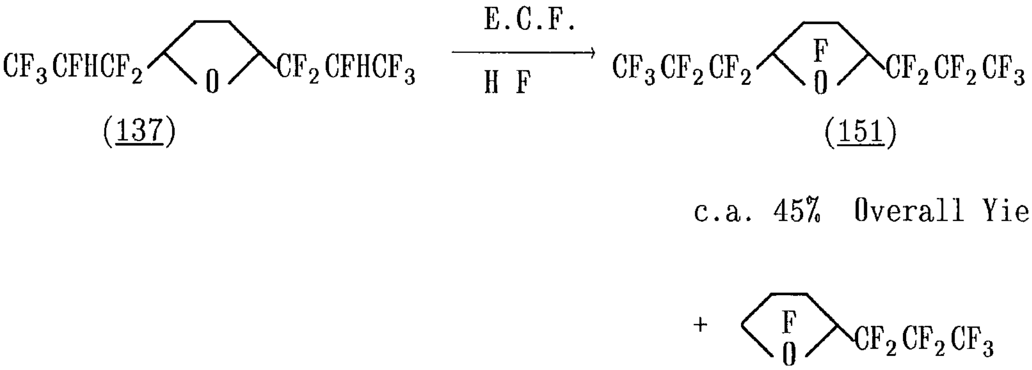
Run	Concentration of (137) in 800 g HF	Cell Voltage	Cell Temp.	Weight of Recovered Organic Material
I	12.5% by weight	5.5 V	5-6^{0}C	70.0 g
II	12.5% by weight	5.5 V	0^{0}C	82.7 g

Volatile products were trapped at acetone/dry ice temperature (-78^{0}C) but since, in both instances, the amounts involved were negligible (< 0.5 g), no further investigation of these materials was performed. On completion of the electrolysis, organic material which separated from the hydrogen fluoride was run off from the bottom of the cell and treated with anhydrous potassium fluoride. The higher weight of recovered organic material obtained from run II (Table 17) cannot be regarded as significant since both runs were performed using the same hydrogen fluoride and so a saturation effect cannot be discounted.

Initial g.l.c. analysis of these organic materials showed them to be of very similar composition and so they were combined. Further g.l.c. analysis (capillary g.l.c., 40^{o}C, isothermal) of this combined material showed that it was composed of one major species (85% by g.l.c.) and several minor species. The major species gave m/z 497 as the highest mass when analysed by electron impact g.l.c.-mass spectroscopy, i.e. M - 19 for the perfluorinated di-adduct (151). A negative ion g.l.c.-mass spectrum of this species gave m/z 516 as the highest mass, i.e. M^- for (151). Some very minor species with similar electron impact mass spectra but differing negative ion mass spectra breakdown patterns to the major species and to each other were also detected but were not investigated further.

The major species was separated by preparative g.l.c. and gave correct elemental analysis for (151). A ^{19}F n.m.r. spectrum of this material was complicated but showed the expected CF_3:CF_2/CF integration although this does not definitely confirm (151) as its structure. The observed integration does however exclude the possibility that the product contains i-propyl groups resulting from side-chain rearrangement. In addition, no distinctive $OC\underline{F_2}$ resonance ($\delta \sim$ 73-93 ppm) was observed, eliminating the possibility of any side-chain migration. I.r. analysis of this material showed no carbonyl absorption, indicating that the product is not a ring-opened isomer of (151). No strong evidence for ring-expanded or ring-contracted isomers of (151) could be observed in the mass spectra of this material (electron impact, m/z 447 (M-CF_3, 0.2%), 397 (M-CF_2CF_3, 0.4), 297(M-$CF_2CF_2CF_2CF_3$, 0.1) but 347 (M-$CF_2CF_2CF_3$, 30); negative ion, m/z 447 (M-CF_3, 0.1%), 397 (M-CF_2CF_3, 1.9), 297 (M-$CF_2CF_2CF_2CF_3$, 0) but 347 (M-$CF_2CF_2CF_3$, 8.5)) and so it seems likely that (151) is the structure of this major product.

Of the other products detected in the organic material recovered from the electrochemical fluorination, only the perfluorinated mono-adduct (152) could be positively identified by g.l.c.-mass spectroscopy.



(137)

(151)

c.a. 45% Overall Yield

(152)

4. Electrochemical Fluorination of 2,6-Bis-(2H-hexafluoropropyl)oxane (150)

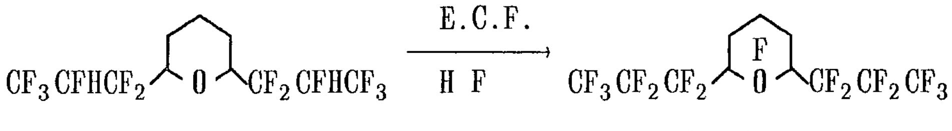
The electrochemical fluorination of (150) was performed using the conditions outlined in Table 18.

TABLE 18

Concentration of (150) in 800 g HF	Cell Voltage	Cell Temp.	Weight of Recovered Organic Material
6% by weight	5.5 V	$0^{0}C$	30.5 g

Volatile products were not collected in this instance. The work-up procedure was as detailed in the previous section. Capillary g.l.c. analysis of the recovered organic material showed that it contained a number of major and minor components. G.l.c.-mass spectroscopic analysis of this material suggested that these species were highly fluorinated materials, composed to a large extent of the required perfluorinated di-adduct (153) and/or isomers (electron impact, highest mass m/z 547, M-19 for (153); negative ion, highest mass m/z 566, M^- for (153)).

Isolation of the perfluorinated di-adduct species by preparative g.l.c. proved unsuccessful, although a simplified mixture of products was obtained. Despite the fact that a number of the species in this simplified mixture didn't give mass spectra consistent with (153) or isomers, the mixture gave correct elemental analysis for (153) and/or isomers. A ^{19}F n.m.r. spectrum of this mixture was complex, showing CF_3 and/or CF_2 adjacent to oxygen, CF_2 and/or CF adjacent to oxygen and CF(minor) resonances. At present further work is underway to gain more information on the product composition of the organic material recovered from this reaction.


(150) (153)

C. Conclusions

Although these are only preliminary experiments carried out under non-optimized conditions, electrochemical fluorination of the cyclic ether di-adducts (137) and (150) gave good recoveries of highly fluorinated products, indicating that these types of adducts are good starting materials for electrochemical fluorination. Work is currently being conducted to further investigate the nature of the products recovered from the electrochemical fluorination of (150) and to investigate the electrochemical fluorination of a more diverse range of adducts. Since a whole range of ether, amine etc. adducts are available via high yielding free-radical reactions,[3-5] this methodology could be potentially very wide-ranging.

INSTRUMENTATION AND REAGENTS

INSTRUMENTATION

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

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

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

Carbon, hydrogen and nitrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba 1106 Elemental Analyser. Analysis for halogens was performed as described in the literature.[106]

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

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

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

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

REAGENTS

In general all chemicals were used as received from suppliers.

Sulpholane was purified by distillation under reduced pressure, the middle fraction being collected over dried molecular sieve (type 4A) and stored under dry nitrogen. Tetraglyme was purified by distillation under vacuum from sodium metal, the middle fraction being collected over dried molecular sieve (type 4A) and stored under dry nitrogen. Diethyl ether was dried over sodium wire. 2,2,2-Trifluoroethanol was gold label and was stored under dry nitrogen.

Caesium fluoride was dried by heating at 180°C under high vacuum for several days, grinding under a dry nitrogen atmosphere, followed by further heating under high vacuum. The dry powder was stored under dry nitrogen.

Fluoroalkenes were either available within this laboratory or were prepared by technical staff.

CHAPTER SEVEN

EXPERIMENTAL TO CHAPTER TWO

CHAPTER SEVEN

EXPERIMENTAL TO CHAPTER TWO

A. GENERAL PROCEDURE

1. γ-Ray Initiated Reactions

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

2. Peroxide Initiated Reactions

Carius tubes were prepared as described above for γ-ray initiated reactions except that di-t-butylperoxide was included as an initiator. The sealed tube was placed in a metal sleeve and was then heated at the required temperature in a thermostatically controlled furnace. The tube was opened while the contents were frozen (liquid air) and any gaseous species were transferred under vacuum.

B. SILICON PROTECTING GROUP APPROACH TO SYNTHESIS OF FLUOROCARBON AMINES

1. 2-(2H-Hexafluoropropyl)pyrrolidine (66)

(a) Addition of N-Trimethylsilylpyrrolidine (64) to Hexafluoropropene

A mixture of N-trimethylsilylpyrrolidine (64) (4.3 g, 30 mmol) and hexafluoropropene (2.0 g, 13 mmol) was irradiated with γ-rays. The product was exposed to a partial vacuum (100mm Hg) but no alkene was recovered and a liquid (6.1 g) remained. This liquid was distilled *in vacuo* to give *2-(2H-hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine* (65), (2.4 g, 62%); b.p. 86°C at 24 mm Hg; (Found: C, 40.9; H, 5.6; N, 4.6; F, 38.4. $C_{10}H_{17}F_6NSi$ requires C, 40.9; H, 5.8; N, 4.8; F, 38.9%); i.r. spectrum 1; n.m.r. spectrum 1; mass spectrum 1.

(b) *Hydrolysis of (65)*

Distilled water (57 ml , 3.2 mol) was gradually added to compound (65) (5.1 g, 17 mmol). A lower fluorocarbon layer formed and therefore the liquids were vigorously stirred for one hour. When the stirring was discontinued a lower fluorocarbon layer again formed. This lower layer was analysed as recovered (65). Concentrated hydrochloric acid (5 ml , 50 mmol) was added to the mixture of (65) and water and the resulting solution was vigorously stirred for one hour. When the stirring was discontinued no lower fluorocarbon layer separated, but an upper hydrocarbon layer was observed which was separated and analysed as hexamethyldisiloxane (0.9 g, 6 mmol) (identified by comparison of spectra with those of an authentic sample). The remaining solution was neutralised with sodium carbonate to give a lower fluorocarbon layer which was separated, dried ($MgSO_4$), transferred under vacuum and analysed as *2-(2H-hexafluoropropyl)pyrrolidine* (66), (1.9 g, 53%); b.p. 156°C (Siwoloboff); (Found: C, 38.2; H, 4.3; N, 6.3; F, 51.1. $C_7H_9F_6N$ requires C, 38.0; H, 4.1; N, 6.3; F, 51.6%); i.r. spectrum 2; n.m.r. spectrum 2; mass spectrum 2.

2. 2,5-Bis-(2H-hexafluoropropyl)pyrrolidine (68)

(a) Addition of N-Trimethylsilylpyrrolidine (64) to an Excess of Hexafluoropropene

A mixture of N-trimethylsilylpyrrolidine (64) (9.6 g, 67 mmol) and hexafluoropropene (31.0 g, 207 mmol) was irradiated with γ-rays. Excess alkene (15.6 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (21.0 g) and a solid (1.2 g). The liquid was distilled *in vacuo* to give (65), (4.1 g, 21%) and 2,5-bis-(2H-hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine (67), (10.6 g, 36%); b.p. 73°C at 2 mm Hg; (Found: C, 35.0; H, 3.6; N, 3.5; F, 51.4. $C_{13}H_{17}F_{12}NSi$ requires C, 35.2; H, 3.8; N, 3.2; F, 51.5%); i.r. spectrum 3; n.m.r. spectrum 3; mass spectrum 3. The solid was identified as (67) (1.2 g, 4%) by comparison with spectra of the distilled material.

(b) Hydrolysis of (67)

A mixture of compound (67) (7.1 g, 16 mmol), distilled water (100 ml , 5.6 mol) and concentrated hydrochloric acid (40 ml , 400mmol) was stirred vigorously for one hour. When stirring was discontinued an upper hydrocarbon layer was observed. This upper layer was separated and analysed as hexamethyldisiloxane (identified by comparison of spectra with those of an authentic sample). The remaining solution was neutralised with sodium carbonate to give a lower fluorocarbon layer which was separated, dried ($MgSO_4$), transferred under vacuum and analysed as 2,5-bis-(2H-hexafluoropropyl)pyrrolidine (68), (4.3 g, 75%); (Found: C, 32.1; H, 2.2; N, 3.6; F, 61.0. $C_{10}H_9F_{12}N$ requires C, 32.3; H, 2.4; N, 3.8; F, 61.5%); i.r. spectrum 4; n.m.r. spectrum 4; mass spectrum 4.

3. Attempted Addition of Dimethylamine to Hexafluoropropene

A mixture of dimethylamine (6.1 g, 136 mmol) and hexafluoropropene (7.2 g, 48 mmol) was irradiated with γ-rays. Excess alkene (0.8 g) was removed by transfer under vacuum (100mm Hg) to leave a brown tar which was not investigated further.

4. 2,2,3,4,4,4-Hexafluorobutylamine (70)

(a) Addition of N,N-Bis(trimethylsilyl)methylamine to Hexafluoropropene

A mixture of N,N-bis(trimethylsilyl)methylamine (4.8 g, 27 mmol) and hexafluoropropene (2.3g, 15 mmol) was irradiated with γ-rays. The product was exposed to a partial vacuum (100mm Hg) but no alkene was recovered and a liquid (7.1 g) remained. This liquid was distilled *in vacuo* to give 2,2,3,4,4,4-hexafluoro-N,N-bis(trimethylsilyl)butylamine (69), (86% by g.l.c., column K, 140^{o}C); b.p. 70^{o}C at 6 mm Hg; (Found: C, 37.2; H, 6.2; N, 4.2; F, 34.8. $C_{10}H_{21}F_6NSi_2$ requires C, 36.9; H, 6.5; N, 4.3; F, 35.1%); i.r. spectrum 5; n.m.r. spectrum 5; mass spectrum 5.

(b) Synthesis of 2,2,3,4,4,4-Hexafluorobutylamine (70)

A mixture of N,N-bis(trimethylsilyl)methylamine (9.8 g, 56 mmol) and hexafluoropropene (4.9 g, 33 mmol) was irradiated with γ-rays. The product was exposed to a partial vacuum (100mm Hg) but no alkene was recovered and a liquid (13.1 g) remained. Comparison of g.l.c. retention times showed this liquid to consist of N,N-bis(trimethylsilyl)methylamine and (69). Distilled water (40 ml , 2.2 mol) and concentrated hydrochloric acid (28 ml , 280 mmol) were added to the liquid and the resulting solution was stirred for three hours. When stirring was discontinued an upper hydrocarbon layer was observed. This hydrocarbon layer was analysed as hexamethyldisiloxane (identified by comparison of spectra with those of an authentic sample). The solution was neutralised with sodium carbonate to give a lower fluorocarbon layer which was separated, dried ($MgSO_4$), transferred under vacuum and analysed as 2,2,3,4,4,4-hexafluoro-butylamine (70), (1.9 g, 30% overall yield) (identified by comparison of spectra with those of an authentic sample[5]).

5. Addition of N,N-Bis(trimethylsilyl)methylamine to Perfluorocyclobutene

A mixture of N,N-bis(trimethylsilyl)methylamine (2.3 g, 13 mmol) and perfluorocyclobutene (0.8 g, 5 mmol) was irradiated with γ-rays. The product was exposed to a partial vacuum (100mm Hg) but no alkene was recovered and a liquid (2.9 g) remained. Preparative g.l.c. (column PEG20M, 150°C) of the liquid gave (2H-hexafluorocyclobutyl)-N,N-bis(trimethylsilyl)methylamine (71), (90% by g.l.c., column PEG20M, 130°C); (Found: C, 39.0; H, 6.5; N, 4.4; F, 33.3. $C_{11}H_{21}F_6NSi_2$ requires C, 39.1; H, 6.2; N, 4.2; F, 33.8%); i.r. spectrum 6; n.m.r. spectrum 6; mass spectrum 6.

6. Addition of N,N-Bis(trimethylsilyl)methylamine to Perfluorocyclopentene

A mixture of N,N-bis(trimethylsilyl)methylamine (2.1 g, 12 mmol) and perfluorocyclopentene (1.2 g, 6 mmol) was irradiated with γ-rays. Excess alkene (0.5 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (2.5 g). Preparative g.l.c. (column PEG20M, 130°C) of the liquid gave (2H-octafluorocyclopentyl)-N,N-bis(trimethylsilyl)methylamine (72), (58% from recovered perfluorocyclopentene); (Found: F, 38.6. $C_{12}H_{21}F_8NSi_2$ requires F, 39.3%); i.r. spectrum 7; n.m.r. spectrum 7; mass spectrum 7, chemical ionisation, m/z 388 (M +1, 21%).

C. Routes to Di-amine Adducts

1. Addition of 2-Imidazolidinone (73) to Hexafluoropropene

(a) γ-Ray Initiation

A mixture of 2-Imidazolidinone (73) (7.0 g, 81 mmol) and hexafluoropropene (4.7 g, 31 mmol) was irradiated with γ-rays. Excess alkene (4.4 g) was removed by transfer under vacuum to leave a white solid. This solid was washed with water to leave 0.16 g of an insoluble white solid which was dried in vacuo. Mass spectroscopy and elemental analysis of this material indicated that it was a mixture of compounds; (Found: C, 31.2; H, 2.4; N, 11.2; F, 47.3. Di-adduct requires C, 28.0; H, 1.6; N, 7.3; F, 59.1%. Mono-adduct requires C, 30.5; H, 2.5; N, 11.9; F, 48.3%. 2-Imidazolidinone requires C, 41.9; H, 7.0; N, 32.6%); mass spectrum 8, chemical ionisation, m/z 387 (M + 1 for di-adduct, 0.5%), 237 (M + 1 for mono-adduct, 100), 87 (M + 1 for 2-imidazolidinone, 23). Due to the low yield this material was not analysed further.

(b) Peroxide Initiation

A mixture of 2-imidazolidinone (73) (4.2 g, 49 mmol), hexafluoropropene (4.1 g, 27 mmol) and di-t-butylperoxide (0.1 g) was heated at 140°C for 24 hours. Excess alkene (3.2 g) was removed by transfer under vacuum to leave a brown tarry solid. Fractional crystallisation of this solid gave only 2-imidazolidinone.

2. Addition of 1,3-Dimethyl-2-imidazolidinone (74) to Hexafluoropropene

A mixture of 1,3-dimethyl-2-imidazolidinone (74) (3.4 g, 30 mmol) and hexafluoropropene (4.8 g, 32 mmol) was irradiated with γ-rays. The product was exposed to a vacuum but no alkene was recovered and a viscous liquid (7.4 g) remained. This liquid was assigned as a mixture, (75), of starting material, mono- and di-adducts by g.l.c.-mass spectroscopy; mono-adduct, mass spectrum 9, electron impact, m/z 264 (M^+ , 1.7%), 113 (35.6, M-CF_2CFHCF_3); di-adduct, mass spectrum 10, electron impact, m/z 414 (M^+, 1.3%), 263 (12.3, M-CF_2CFHCF_3).

3. Hydrolysis of (75)

A mixture of (75) (3.6 g) and 70% sulphuric acid (25 ml , 175 mmol) was heated to 145°C for 65 hours. The solution was cooled, neutralised with sodium carbonate and extracted with diethyl ether. The diethyl ether aliquots were combined, dried ($MgSO_4$) and distilled to give 0.1 g of a liquid which was tentatively assigned as a mixture of di-amine mono-adducts (76) and (77); (Found: C, 34.8; H, 5.1; N, 12.4. $C_7H_{12}F_6N_2$ requires C, 35.3; H, 5.0; N, 11.8%); i.r. spectrum 8; n.m.r. spectrum 8; mass spectrum 11, chemical ionisation, m/z 239
(M + 1, 100%) for all species.

D. Routes to Isocyanate Adducts

1. Ethyl isocyanate

(a) Addition of Ethyl isocyanate to Perfluorocyclobutene

(i) γ-Ray Initiation

A mixture of ethyl isocyanate (4.9 g, 69 mmol) and perfluorocyclobutene (5.1 g, 31 mmol) was irradiated with γ-rays. Excess alkene (3.1 g) was removed by transfer under vacuum (100 mm Hg) to leave a liquid (6.0 g). This liquid was shown to contain only starting materials by g.l.c.

(ii) Peroxide Initiation

A mixture of ethyl isocyanate (2.3 g, 32 mmol), perfluorocyclobutene (2.6 g, 16 mmol) and di-t-butylperoxide (0.2 g) was heated at 140°C for 24 hours. Excess alkene (1.7 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (2.7 g). The liquid was shown to contain only starting materials by g.l.c.

(b) Addition of Ethyl isocyanate to Perfluorocyclopentene

(i) γ-Ray Initiation

A mixture of ethyl isocyanate (5.0 g, 70 mmol) and perfluorocyclopentene (5.9 g, 28 mmol) was irradiated with γ-rays. The product was shown to contain only starting materials by g.l.c.

(ii) Peroxide Initiation

A mixture of ethyl isocyanate (2.6 g, 37 mmol), perfluorocyclopentene (4.9 g, 23 mmol) and di-t-butylperoxide (0.2 g) was heated at 140°C for 24 hours. The product was shown to contain only starting materials by g.l.c.

2. Addition of 1,6-Diisocyanatohexane to Hexafluoropropene

A mixture of 1,6-diisocyanatohexane (3.0 g, 18 mmol), hexafluoropropene (1.3 g, 9 mmol) and di-t-butylperoxide (0.1 g) was heated at 140°C for 48 hours. Excess alkene (0.6 g) was removed by transfer under vacuum to leave a viscous yellow liquid (79), (3.3 g). The liquid was shown to contain fluorocarbon groups by ^{19}F n.m.r. No further analysis was performed on this liquid.

E. Additions of Miscellaneous Nitrogen Compounds

1. Attempted Addition of ϵ-Caprolactam to Hexafluoropropene

(a) γ-Ray Initiation

(i) Without Solvent

A mixture of ϵ-caprolactam (8.0 g, 71 mmol) and hexafluoropropene (4.2 g, 28 mmol) was irradiated with γ-rays. Excess alkene (3.9 g) was removed by transfer under vacuum to leave a white solid. This solid was washed with water but no fluorocarbon material was obtained.

(ii) In Acetone

A mixture of ϵ-caprolactam (1.1 g, 10 mmol), hexafluoropropene (6.3 g, 42 mmol) and acetone (7.4 g) was irradiated with γ-rays. Excess alkene (5.4 g) was removed by transfer under vacuum (100 mm Hg) to leave a liquid (8.6 g). Acetone was removed under reduced pressure to leave a solid (1.2 g). A ^{19}F n.m.r. spectrum of this material ($CDCl_3$ solvent) showed multiple resonances in the CF_3, CF_2 and CFH regions of the spectrum and so the n.m.r. solvent was removed under reduced pressure and the resulting solid was washed with water. The remaining solid was dissolved in diethyl ether, washed with further aliquots of water and then dried ($MgSO_4$). The ether was removed under reduced pressure to leave a viscous yellow polymer (<u>81</u>), (0.1 g) with a high fluorine content which gave a ^{19}F n.m.r. spectrum comparable to the preliminary spectrum; (Found: C, 37.4; H, 3.2; N, 3.6; F, 48.8%); i.r. spectrum 9; n.m.r. spectrum 9.

(b) Peroxide Initiation

A mixture of ϵ-caprolactam (5.4 g, 48 mmol), hexafluoropropene (3.8 g, 25 mmol) and di-t-butylperoxide (0.1 g) was heated at 140^{0}C for 24 hours. Excess alkene (2.0 g) was removed by transfer under vacuum to leave a brown tarry solid. Extraction of this solid with various solvents failed to produce any fluorocarbon material.

2. Attempted Addition of L-Nicotine (82) to Hexafluoropropene

(a) Without Solvent

A mixture of L-nicotine (82) (1.1 g, 7 mmol) and hexafluoropropene (4.5 g, 30 mmol) was irradiated with γ-rays. Excess alkene (3.7 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (1.1 g). The liquid was shown to contain only starting material by g.l.c.

(b) In Acetone

A mixture of L-nicotine (82) (1.6 g, 10 mmol), hexafluoropropene (13.3 g, 89 mmol) and acetone (10.7 g) was irradiated with γ-rays. Excess alkene was transferred under vacuum to leave a liquid which was shown to contain only starting materials by g.l.c.

3. Attempted Addition of Protected Amino Acid (84) to Hexafluoropropene

A mixture of the protected amino acid (84)(0.4 g, 3 mmol), hexafluoropropene (4.9 g, 33 mmol) and acetone (3.3 g) was irradiated with γ-rays. Excess alkene (4.5 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (3.9 g). The liquid was shown to contain only starting materials by g.l.c.

F. Dehydrofluorination of 2-(2H-Hexafluoropropyl)pyrrolidine (66)

A mixture of 2-(2H-hexafluoropropyl)pyrrolidine (66) (1.0 g, 5 mmol) and potassium hydroxide pellets (19.8 g, 404 mmol) was heated at 80^{o}C for 4 hours. A liquid was obtained by vacuum transfer which was dried ($MgSO_4$) and analysed as 2-(pentafluoro-1-propenyl)-pyrrolidine (87), (0.4 g, 40%); (Found: C, 41.5; H, 4.1; N, 6.9; F, 47.1. $C_7H_8F_5N$ requires C, 41.8; H, 4.0; N, 7.0; F, 47.3%); i.r. spectrum 10; n.m.r. spectrum 10; mass spectrum 12.

CHAPTER EIGHT

EXPERIMENTAL TO CHAPTER THREE

CHAPTER EIGHT

EXPERIMENTAL TO CHAPTER THREE

A. GENERAL PROCEDURE

1. γ-Ray Initiated Reactions

γ-ray initiated reactions were carried out using the method detailed in Chapter 7.

2. Peroxide Initiated Reactions

Unless otherwise stated, liquid and gaseous reagents were introduced into a nickel tube (ca. 150 ml) which was then sealed with the reagents frozen (liquid air) and under vacuum. The tube was heated at the required temperature in a thermostatically controlled rocking furnace. The tube was opened while the contents were frozen (liquid air) and any gaseous species were transferred under vacuum.

B. SYNTHESIS OF SIMPLE FLUOROSILICON ADDUCTS

1. Silanes

(a) Addition of Tetramethylsilane to Perfluorocyclobutene

(i) γ-Ray Initiation

A mixture of tetramethylsilane (5.0 g, 57 mmol) and perfluorocyclobutene(3.5 g, 22 mmol) was irradiated with γ-rays. The product was shown to contain only starting materials by g.l.c.

(ii) Peroxide Initiation

(Carius tube reaction, prepared and worked-up according to the method detailed in Chapter 7).

A mixture of tetramethylsilane (1.8 g, 20 mmol), perfluorocyclobutene (2.4 g, 15 mmol) and di-t-butylperoxide (0.2 g) was heated at 140°C in a thermostatically controlled rocking furnace for 24 hours. The product was shown to contain starting materials and a very small amount of [(2H-hexafluorocyclobutyl)methyl]trimethylsilane (90) by g.l.c.-mass spectroscopy; mass spectrum 13.

(b) Addition of Tetramethylsilane to Perfluorocyclopentene

(i) γ-Ray Initiation

A mixture of tetramethylsilane (5.2 g, 59 mmol) and perfluorocyclopentene (5.2 g, 25 mmol) was irradiated with γ-rays. The product was shown to contain only starting materials by g.l.c.

(ii) Peroxide Initiation

(Carius tube reaction, prepared and worked-up according to the method detailed in Chapter 7).

A mixture of tetramethylsilane (1.4 g, 16 mmol), perfluorocyclopentene (1.7 g, 8 mmol) and di-t-butylperoxide (0.1 g) was heated at 140°C in a thermostatically controlled furnace for 24 hours. The product was shown to contain starting materials and a very small amount of [(2H-octafluorocyclopentyl)methyl]trimethylsilane (91) by g.l.c.-mass spectroscopy; mass spectrum 14.

2. Siloxanes

(a) Addition of Hexamethyldisiloxane to Perfluorocyclobutene

(i) Peroxide Initiation

A mixture of hexamethyldisiloxane (24.9 g, 154 mmol), perfluorocyclobutene (9.9 g, 61 mmol) and di-t-butylperoxide (0.8 g) was heated at 140°C in a rocking furnace for 24 hours. Excess alkene (6.9 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (26.1 g), which was distilled in vacuo to give [(2H-hexafluorocyclobutyl)methyl]pentamethyldisiloxane (92), (2.7 g, 14%); b.p. 53-54°C at 6 mm Hg; (Found: C, 36.8; H, 5.6; F, 34.7. $C_{10}H_{18}F_6Si_2O$ requires C, 37.0; H, 5.6; F, 35.2%); i.r. spectrum 11; n.m.r. spectrum 11; mass spectrum 15.

(ii) γ-Ray Initiation

A mixture of hexamethyldisiloxane (9.0 g, 56 mmol) and perfluorocyclobutene (3.4 g, 21 mmol) was irradiated with γ-rays. Excess alkene (3.0 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (9.1 g). The liquid was shown to contain starting materials and a trace of (92) by g.l.c.

(b) Addition of Hexamethyldisiloxane to Perfluorocyclopentene

(i) Peroxide Initiation

A mixture of hexamethyldisiloxane (28.1 g, 173 mmol), perfluorocyclopentene (20.2 g, 95 mmol) and di-t-butylperoxide (1.5 g) was heated at 140°C in a rocking furnace for 24 hours. Excess alkene (2.7 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (45.7 g), which was distilled in vacuo to give [(2H-octafluorocyclopentyl)methyl]pentamethyldisiloxane (93), (4.4 g, 12%); b.p. 55-56°C at 3 mm Hg; (Found: C, 35.1; H, 4.8; F, 41.0. $C_{11}H_{18}F_8Si_2O$ requires C,35.3; H, 4.8; F, 40.6%); i.r. spectrum 12; n.m.r. spectrum 12; mass spectrum 16.

(ii) γ-Ray Initiation

A mixture of hexamethyldisiloxane (9.0 g, 55 mmol) and perfluorocyclopentene (4.6 g, 22 mmol) was irradiated with γ-rays. Excess alkene (3.6 g) was removed by transfer under vacuum (100mm

Hg) to leave a liquid (9.5 g). The liquid was shown to contain starting materials and a trace of (93) by g.l.c.

(c) Addition of Octamethylcyclotetrasiloxane to Perfluorocyclobutene

(i) Peroxide Initiation

A mixture of octamethylcyclotetrasiloxane (32.2 g, 109 mmol), perfluorocyclobutene (9.6 g, 59 mmol) and di-t-butylperoxide (0.9 g) was heated at 140° C in a rocking furnace for 24 hours. Excess alkene (2.8 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (38.3 g), which was distilled *in vacuo* to give [(2H-hexafluorocyclobutyl)methyl]heptamethylcyclotetrasiloxane (94), (4.6 g, 17%); b.p. 76-77°C at 0.95 mm Hg; (Found: C, 31.6; H, 5.3; F, 25.0. $C_{12}H_{24}F_6Si_4O_4$ requires C, 31.4; H, 5.2; F, 24.9%); i.r. spectrum 13; n.m.r. spectrum 13; mass spectrum 17.

(ii) γ-Ray Initiation

A mixture of octamethylcyclotetrasiloxane (14.3 g, 48 mmol) and perfluorocyclobutene (3.0 g, 19 mmol) was irradiated with γ-rays. Excess alkene (2.3 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (14.6 g). The liquid was shown to contain starting materials and a trace of (94) by g.l.c.

(d) Addition of Octamethylcyclotetrasiloxane to perfluorocyclopentene

(i) Peroxide Initiation

A mixture of octamethylcyclotetrasiloxane (32.2 g, 109 mmol), perfluorocyclopentene (12.9 g, 61 mmol) and di-t-butylperoxide (0.9 g) was heated at 140° C in a rocking furnace for 24 hours. Excess alkene (1.5 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (43.1 g), which was distilled in vacuo to give [(2H-Octafluorocyclopentyl)methyl]heptamethylcyclotetrasiloxane (95), (5.4 g, 17%); b.p. 81-82^{o}C at 0.8 mm Hg; (Found: C, 30.6; H, 4.8; F, 30.5. $C_{13}H_{24}F_8Si_4O_4$ requires C, 30.7; H, 4.7; F, 29.9%); i.r. spectrum 14; n.m.r. spectrum 14; mass spectrum 18.

(ii) γ-Ray Initiation

A mixture of octamethylcyclotetrasiloxane (14.0 g, 47 mmol) and perfluorocyclopentene (4.0 g, 19 mmol) was irradiated with γ-rays. Excess alkene (2.9 g) was removed by transfer under vacuum (100 mm Hg) to leave a liquid (14.6 g). The liquid was shown to contain starting materials and a trace of (95) by g.l.c.

(e) Addition of Octamethylcyclotetrasiloxane to Chlorotrifluoroethene

A mixture of octamethylcyclotetrasiloxane (14.1 g, 48 mmol) and chlorotrifluoroethene (2.2 g, 19 mmol) was irradiated with γ-rays. The product contained only polymeric material and octamethylcyclotetrasiloxane (by g.l.c.).

(f) Addition of Octamethylcyclotetrasiloxane to 1,2-Dichlorodifluoroethene

A mixture of octamethylcyclotetrasiloxane (32.1 g, 108 mmol), 1,2-dichlorodifluoroethene (8.4 g, 63 mmol) and di-t-butylperoxide (1.0 g) was heated at 140^{o}C in a rocking furnace for 24 hours. Excess alkene (0.9 g) was removed by transfer under vacuum (100 mm Hg) to leave a liquid (38.7 g). The liquid was shown to contain only starting materials by g.l.c.

3. Alkoxysilanes

(a) Addition of Methoxytrimethylsilane to Perfluorocyclobutene

A mixture of methoxytrimethylsilane (7.9 g, 76 mmol) and perfluorocyclobutene (6.6 g, 41 mmol) was irradiated with γ-rays. The product was exposed to a partial vacuum (100mm Hg) but no alkene was recovered and a liquid (14.2 g) remained. This liquid was distilled in vacuo to give [(2H-hexafluorocyclobutyl)methoxy]trimethylsilane (97), (1.7 g, 16%); b.p. 68-69°C at 68 mm Hg; (Found: C, 36.0; H, 4.7; F, 43.4. $C_8H_{12}F_6SiO$ requires C, 36.1; H, 4.5; F, 42.8%); i.r. spectrum 15; n.m.r. spectrum 15; mass spectrum 19.

(b) Addition of Methoxytrimethylsilane to Perfluorocyclopentene

A mixture of methoxytrimethylsilane (9.2 g, 88 mmol) and perfluorocyclopentene (9.0 g, 42 mmol) was irradiated with γ-rays. The product was exposed to a partial vacuum (100mm Hg) but no alkene was recovered and a liquid (17.6 g) remained. This liquid was distilled in vacuo to give [(2H-octafluorocyclopentyl)-methoxy]trimethylsilane (98), (1.1 g, 8%); b.p. 76-77°C at 47 mm Hg; (Found: C, 34.5; H, 3.5; F, 48.1. $C_9H_{12}F_8SiO$ requires C, 34.2; H, 3.8; F, 48.1%); i.r. spectrum 16; n.m.r. spectrum 16; mass spectrum 20.

C. Reactions of Fluorosilicon Adducts

1. Reaction of Tetramethylsilane/Hexafluoropropene Mono-Adducts (88) and (102) with Caesium Fluoride

The tetramethylsilane/hexafluoropropene mono-adduct mixture, (88) and (102), (2.0 g, 8 mmol) was added to a solution of caesium fluoride (2.0 g, 13 mmol) in sulpholane (5 ml). The mixture was stirred at 35°C for 3 hours, gaseous products being trapped at liquid air temperature in a stream of nitrogen. The contents of the trap were transferred under vacuum to give a mixture of 2,3,4,4,4-pentafluoro-1-butene (<u>103</u>), 2-difluoromethyl-3,3,3-trifluoro-1-propene (<u>104</u>) and fluorotrimethylsilane (2.0 g, 100%); i.r. spectrum 17, n.m.r. spectrum 17.

2. <u>Thermal Studies</u>

(a) <u>Tetramethylsilane/Hexafluoropropene Mono-Adducts (88) and (102)</u>

A sealed 4 mm glass tube containing tetramethylsilane/hexafluoropropene mono-adducts (<u>88</u>) and (<u>102</u>) was heated to 150°C for 24 hours, 180°C for 24 hours and 200°C for 24 hours in turn. N.m.r. spectra were recorded after each period of heating.

(b) <u>Hexamethyldisiloxane/Hexafluoropropene Mono-Adducts (105) and (101)</u>

A sealed 4 mm glass tube containing hexamethyldisiloxane/hexafluoropropene mono-adducts (<u>105</u>) and (<u>101</u>) was heated to 150°C for 24 hours, 180°C for 24 hours, 200°C for 24 hours and 250°C for 24 hours in turn. N.m.r. spectra were recorded after each period of heating.

(c) <u>Octamethylcyclotetrasiloxane /Hexafluoropropene Mono-Adducts (106) and (107)</u>

A sealed 4 mm glass tube containing octamethylcyclotetrasiloxane/hexafluoropropene mono-adducts (<u>106</u>) and (<u>107</u>) was heated to 150°C for 24 hours, 180°C for 24 hours, 200°C for 24 hours and 250°C for 24 hours in turn. N.m.r. spectra were recorded after each period of heating.

(d) [(2H-Octafluorocyclopentyl)methyl]heptamethylcyclotetrasiloxane (95)

A sealed 4 mm glass tube containing [(2H-octafluorocyclopentyl)methyl]heptamethylcyclotetrasiloxane (95) was heated to 250°C for 2 hours, followed by a further 6 hours at 250°C. N.m.r. spectra were recorded after each period of heating. After the final period of heating the volatile material in the tube was removed under vacuum to give 2,2,3,3,4,4,5-heptafluoro-1-methylenecyclopentane (108); i.r. spectrum 18; n.m.r. spectrum 18, mass spectrum 21.

(e) [(2H-Hexafluorocyclobutyl)methyl]heptamethylcyclotetrasiloxane (94)

A sealed 4 mm glass tube containing [(2H-hexafluorocyclobutyl)-methyl]heptamethylcyclotetrasiloxane (94) was heated to 250°C for 2 hours, followed by 2.5 hours at 300°C. N.m.r. spectra were recorded after each period of heating. After the final period of heating the volatile material in the tube was removed under vacuum to give 2,2,3,3,4-pentafluoro-1-methylenecyclobutane (109); i.r. spectrum 19; n.m.r. spctrum 19; mass spectrum 22.

(f) 2,2,3,4,4,4-Hexafluorobutoxytrimethylsilane (96)

A sealed 4 mm glass tube containing 2,2,3,4,4,4-hexafluorobutoxytrimethylsilane (96) was heated to 250°C for 24 hours. N.m.r. spectra showed that no reaction had taken place.

D. Bromination of Alkenes (103) and (104)

The alkene mixture of (103) and (104) (2.2 g, 15 mmol) was transferred under vacuum into a rotaflo containing bromine (3.7 g, 46 mmol). The resulting mixture was shaken for 10 minutes and then transferred under vacuum into a series of traps at liquid air temperature and ice/salt temperature (-20^{o}C). The contents of the trap at ice/salt temperature were transferred under vacuum to give a mixture of 1,2-dibromo-2,3,4,4,4-pentafluorobutane (110) and 1,2-dibromo-2-difluoromethyl-3,3,3-trifluoropropane (111) (3.7 g, 80%); (Found: C, 16.0; H, 1.0; F, 30.1; Br, 52.4. $C_4H_3F_5Br_2$ requires C, 15.7; H, 1.0; F, 31.1; Br, 52.3%); i.r. spectrum 20; n.m.r. spectrum 20; mass spectra 23 (for (110)) and 24 (for (111)).

CHPATER NINE

EXPERIMENTAL TO CHAPTER FOUR

CHAPTER NINE

EXPERIMENTAL TO CHAPTER FOUR

A. General Procedure

1. γ-Ray Initiated reactions

γ-ray initiated reactions were carried out using the method detailed in chapter 7.

B. Synthesis

1. Free-Radical Additions of Mono-Oxygen Functional Compounds to Fluoroalkenes

(a) Attempted Addition of Diethyl ether to Perfluoro-3,4-dimethyl-3-hexene (7)

A mixture of diethyl ether (9.5 g, 128 mmol) and perfluoro-3,4-dimethyl-3-hexene (7) (20.6 g, 52 mmol) was irradiated with γ-rays. The product (29.3 g) was shown to contain only starting materials by g.l.c.

(b) Attempted Addition of Diethyl ether to Perfluorobicyclopentylidene (113)

A mixture of diethyl ether (1.3 g, 18 mmol) and perfluorobicyclopentylidene (113) (2.9 g, 7 mmol) was irradiated with γ-rays. The product (3.9 g) was shown to contain only starting materials by g.l.c.

2. Free-Radical Additions of Di-Oxygen Functional Compounds to Fluoroalkenes

(a) Addition of Methyl 3-hydroxybutanoate (115) to Hexafluoropropene

A mixture of methyl 3-hydroxybutanoate (115) (0.3 g, 3 mmol), hexafluoropropene (4.0 g, 27 mmol) and acetone (2.9 g) was irradiated with γ-rays. Excess alkene (3.5 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (3.0 g). Acetone was removed from this liquid under reduced pressure to leave a yellow liquid (0.4 g). Preparative g.l.c. (column 10% SE30, 140°C) gave methyl-4,4,5,6,6,6-hexafluoro-3-hydroxy-3-methylhexanoate (118) (42% by g.l.c.); i.r spectrum 21, n.m.r. spectrum 21, mass spectrum 25, chemical ionisation, m/z 269 (M+1, 100%).

(b) Attempted Addition of Methyl 2-hydroxypropanoate (119) to Hexafluoropropene

A mixture of methyl 2-hydroxypropanoate (119) (0.3 g, 3 mmol), hexafluoropropene (5.0 g, 33 mmol) and acetone (3.0 g) was irradiated with γ-rays. Excess alkene (4.6 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (3.0 g). The liquid was shown to contain only starting materials by g.l.c.

(c) Addition of 3-Hydroxybutanoic Acid (121) to Hexafluoropropene

A mixture of 3-hydroxybutanoic acid (121) (0.2 g, 2 mmol), hexafluoropropene (3.0 g, 20 mmol) and acetone (2.3 g) was irradiated with γ-rays. Excess alkene (2.6 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (2.4 g). Acetone was removed from this liquid under reduced pressure to leave a yellow liquid (0.2 g). Hydrogen chloride was bubbled through a solution of this liquid in methanol (4.5 ml) and the resulting solution stirred for 24 hours. Excess methanol and hydrogen chloride were removed under reduced pressure to leave a liquid which was shown to contain mainly methyl 3-hydroxybutanoate (115) and (118). (Identified by comparison of g.l.c.-mass spectrum with that obtained in (a)).

(d) Addition of 1,4-Butanediol to Hexafluoropropene

A mixture of 1,4-butanediol (1.0 g, 11 mmol), hexafluoropropene (6.6 g, 44 mmol) and acetone (8.3 g) was irradiated with γ-rays. Excess alkene (3.5 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (12.0 g). Acetone was removed from this liquid under reduced pressure to leave 3.9 g of another liquid. This liquid was distilled in vacuo to give 1,1,1,2,3,3,8,8,9,10,10,10-dodecafluoro-4,7-decanediol (123), (2.6 g, 61%); b.p. 70°C at 0.15 mm Hg; (Found: C,31.1; H, 2.7; F, 58.7. $C_{10}H_{10}F_{12}O_2$ requires C, 30.8; H, 2.6; F, 58.5%); i.r. spectrum 22, n.m.r. spectrum 22, mass spectrum 26, chemical ionisation, m/z 391 (M+1, 9%).

C. Reactions

1. Aldehyde Adducts

(a) Addition of Propionaldehyde to Perfluoro-3,4-dimethyl-3-hexene (7)

A mixture of propionaldehyde (8.8 g, 152 mmol) and perfluoro-3,4-dimethyl-3-hexene (7) (22.2 g, 56 mmol) was irradiated with γ-rays. The product (30.8 g) was distilled in vacuo to give 6,6,7,7,7-pentafluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-3-heptanone (126), (2.6 g, 10%); b.p. 41°C at 6 mm Hg; (Found: C,28.9; H, 1.7; F, 65.9. $C_{11}H_6F_{16}O$ requires C, 28.8; H, 1.3; F, 66.4%); i.r. spectrum 23, n.m.r. spectrum 23, mass spectrum 27. Another product, propionaldehyde trimer (127) (identified by g.l.c.-mass spectroscopy and comparison of n.m.r. spectrum with that of an authentic sample[107]) depolymerised on distillation.[108]

(b) Reaction of (126) with Tri-n-butylamine

Compound (126) (2.0 g, 4 mmol) was added to tri-n-butylamine (2.7 g, 15 mmol) dissolved in tetraglyme (3 ml) and the mixture stirred at room temperature for 4.5 hours. Excess dilute hydrochloric acid was added and the fluorocarbon lower layer separated, washed with water, separated, dried ($MgSO_4$) and filtered. Preparative g.l.c. (column A, 70°C) of the resulting liquid (1.0 g) gave 6,7,7,7-tetrafluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-5-heptene-3-one (128), (42% by g.l.c., column A, 75°C); (Found: C,30.0; H, 1.3; F, 65.3. $C_{11}H_5F_{15}O$ requires C, 30.1; H, 1.1; F, 65.1%); i.r. spectrum 24, n.m.r. spectrum 24, mass spectrum 28, and 5-ethylidene-4-pentafluoroethyl-2,3,4-tris(trifluoromethyl)-dihydrofuran (129), (16% by g.l.c., column A, 75°C); (Found: C,31.7; H, 0.9; F, 64.1. $C_{11}H_4F_{14}O$ requires C, 31.6; H, 1.0; F, 63.6%); i.r. spectrum 25, n.m.r. spectrum 25, mass spectrum 29.

(c) Reaction of (128) with Tri-n-butylamine

Compound (128) (0.14 g, 0.3 mmol) was added to tri-n-butylamine (0.5 g, 2.7 mmol) dissolved in tetraglyme (1 ml) and the mixture stirred at room temperature for 24 hours. Excess dilute hydrochloric acid was added and the fluorocarbon lower layer separated, washed with water and separated. This material was shown to contain 78% (129) and 22% (128) by g.l.c. (column A, 75°C).

2. Dehydrofluorinations

(a) Diethyl ether/Hexafluoropropene Mono-Adduct (19)

(i) Using Potassium Hydroxide

A mixture of 4-ethoxy-1,1,1,2,3,3-hexafluoropentane (19) (2.0 g, 9 mmol) and potassium hydroxide pellets (8.7 g, 155 mmol) was heated in a sealed rotaflo for 7 hours at 85°C. Volatile material in the rotaflo was transferred under vacuum to give 4-ethoxy-1,1,1,2,3-pentafluoro-2-pentene (133), (1.5 g, 78%).

(Identified by comparison of spectra with those of an authentic sample[5]).

(ii) Using Triethylamine

A mixture of 4-ethoxy-1,1,1,2,3,3-hexafluoropentane (19) (2.5 g, 11 mmol) and triethylamine (5.0 g, 50 mmol) was stirred at room temperature for 15 hours but the resulting liquid was shown to contain only starting materials by g.l.c. In addition, only starting materials were recovered after heating the reactants to 65°C for 80 hours and 80°C for 5 hours in a sealed rotaflo (shown by g.l.c.).

(iii) Using Tri-n-butylamine

A mixture of 4-ethoxy-1,1,1,2,3,3-hexafluoropentane (19) (2.2 g, 10 mmol) and tri-n-butylamine (6.0 g, 32 mmol) was stirred at room temperature for 24 hours but the resulting liquid was shown to contain only starting materials by g.l.c. In addition, only starting materials were recovered after heating the reactants to 65°C for 4 hours, 105°C for 19 hours, 130°C for 4 hours and 175°C for 3 hours in a sealed rotaflo (shown by g.l.c.).

(b) Diethyl ether/Hexafluoropropene Di-Adduct (21)

A mixture of bis-(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether (21) (3.7 g, 10 mmol) and potassium hydroxide pellets (13.9 g, 248 mmol) was heated in a sealed rotaflo for 15 hours at 85°C followed by 1 hour at 130°C. Volatile material in the rotaflo was transferred under vacuum, dried ($MgSO_4$) and filtered to give bis-(2,3,4,4,4-pentafluoro-1-methyl-2-butenyl) ether (136), (1.9 g, 60%) as a mixture of isomers; (Found: C, 35.7; H, 2.5; F, 56.5. $C_{10}H_8F_{10}O$ requires C, 35.9; H, 2.4; F, 56.9%); i.r. spectrum 26, n.m.r. spectrum 26, mass spectrum 30.

(c) Oxolane/Hexafluoropropene Di-Adduct (137)

A mixture of 2,4-bis-(2H-hexafluoropropyl)oxolane (137) (3.0 g, 8 mmol) and potassium hydroxide powder (6.0g, 107 mmol) was heated in a sealed rotaflo for 3 hours at 85°C followed by 10 minutes at 105°C. Volatile material in the rotaflo was transferred under vacuum, dried ($MgSO_4$) and filtered to give 2,5-bis(pentafluoro-1-propenyl)oxolane (138), (0.8 g, 25%) as a mixture of isomers; (Found: C,35.9; H, 1.9; F, 57.0. $C_{10}H_6F_{10}O$ requires C, 36.1; H, 1.8; F, 57.2%); i.r. spectrum 27, n.m.r. spectrum 27, mass spectrum 31.

CHAPTER TEN

EXPERIMENTAL TO CHAPTER FIVE

CHAPTER TEN

EXPERIMENTAL TO CHAPTER FIVE

A. General Procedure

1. γ-Ray Initiated Reactions

γ-ray initiated reactions were carried out using the method detailed in Chapter 7.

2. Reactant Ratios

For reactions between a polymer and hexafluoropropene an indication of the relative reactant proportions has been included. These values are based on the assumption that each repeat unit of the polymer has only one site available for addition to hexafluoropropene and are thus a guide only.

B. Addition of Nylon 66 to Hexafluoropropene

1. Control Reactions

(a) Reaction of 2,2,2-trifluoroethanol (17) with Hexafluoropropene

A mixture of 2,2,2-trifluoroethanol (17) (6.7 g, 67 mmol) and hexafluoropropene (12.8 g, 85 mmol) was irradiated with γ-rays. Excess alkene (12.2 g) was removed by transfer under vacuum (100 mm Hg) to leave a liquid (6.9 g). This liquid was shown to contain only starting materials by g.l.c.

(b) Reaction of Nylon 66 with 2,2,2-trifluoroethanol (17)

A mixture of nylon 66 (0.26 g) and 2,2,2-trifluoroethanol (17) (7.9 g, 79 mmol) was irradiated with γ-rays. The resulting solution was filtered to remove foreign particles acquired during work-up (e.g. rubber, glass etc.) and then 2,2,2-trifluoroethanol was removed under reduced pressure to leave a polymer film (141), (0.17 g); (Found: C, 57.3; H, 8.9; N, 9.2 and C, 56.7; H, 9.1; N, 9.4%).

(c) Irradiation of a Nylon 66 Film in Vacuo

A nylon 66 thin film (0.0044 g) was irradiated *in vacuo* with γ-rays to give a yellowy coloured film (0.0031 g); (Found: C, 56.5; H, 9.1; N, 10.4%).

(d) Reaction of a Nylon 66 Solution with Hexafluoropropene in the Absence of γ-Rays

Hexafluoropropene (6.4 g, 43 mmol, 140 times excess over nylon 66) was introduced into a Carius tube containing a solution of nylon 66 (0.07 g) in 2,2,2-trifluoroethanol (23.5 g). The resulting solution was left in the dark in the absence of γ-rays for 96 hours. Excess alkene (5.7 g) was removed by transfer under vacuum (100 mm Hg) to leave a liquid (23.0 g). This liquid was filtered to remove foreign particles acquired during work-up and then 2,2,2-trifluoroethanol was removed under reduced pressure to leave a polymer film (144), (0.06 g); (Found: C, 63.0; H, 10.7; N, 11.7%).

2. Reaction of a Heterogeneous Nylon 66/2,2,2-trifluoroethanol/ Hexafluoropropene Mixture

Hexafluoropropene (12.4 g, 83 mmol, 40 times excess over nylon 66) was introduced into a Carius tube containing a solution of nylon 66 (0.46 g) in 2,2,2-trifluoroethanol (6.7 g). This caused precipitation of the nylon 66 but the resulting heterogeneous mixture was irradiated with γ-rays. Excess alkene (11.9 g) was removed by transfer under vacuum (100mm Hg) causing the nylon 66 to re-dissolve in the 2,2,2-trifluoroethanol. The resulting liquid (7.1 g) was filtered to remove foreign particles acquired during work-up and then 2,2,2-trifluoroethanol was removed under reduced pressure to leave a yellowy coloured polymer film (142); (Found: C, 40.7; H, 4.8; N, 5.4; F, 36.5 and C, 41.6; H, 4.7; N, 5.1%).

3. Reaction of a Nylon 66 Solution with Hexafluoropropene

Hexafluoropropene (3.7 g, 25 mmol, 140 times excess over nylon 66) was introduced into a Carius tube containing a solution of nylon 66 (0.04 g) in 2,2,2-trifluoroethanol (13.3 g) and the resulting solution was irradiated with γ-rays. Excess alkene (2.55 g) was removed by transfer under vacuum (100mm Hg) to leave a liquid (13.7 g). This liquid was filtered to remove foreign particles acquired during work-up and then 2,2,2-trifluoroethanol was removed under reduced pressure to leave a viscous yellow liquid (143); (Found: C, 30.6; H, 2.2; N, 1.1; F, 57.3 and C, 30.5; H, 2.3; N, 1.0%); n.m.r. spectrum 28.

C. Addition of Poly-N-vinylpyrrolidone (145) to Hexafluoropropene

1. Without Solvent

Hexafluoropropene (6.5 g, 43 mmol, 3 times excess over poly-N-vinylpyrrolidone (145)) was introduced into a Carius tube containing poly-N-vinylpyrrolidone (145) (1.5 g) and the resulting heterogeneous mixture was irradiated with γ-rays to a total dose of 100 Mrad. Excess alkene (5.6 g) was removed by transfer under vacuum to leave a yellow solid (146), (1.7 g); (Found: C, 50.7; H, 6.5; N, 8.3; F, 19.4%).

2. In a 2,2,2-trifluoroethanol Solvent

Hexafluoropropene (7.3 g, 49 mmol, 3.5 times excess over poly-N-vinylpyrrolidone (145)) was introduced into a Carius tube containing a solution of poly-N-vinylpyrrolidone (145) (1.5 g) in

2,2,2-trifluoroethanol (30.7 g) and the resulting solution was irradiated with γ-rays to a total dose of 20 Mrad. Excess alkene (5.6.g) was removed by transfer under vacuum (100mm Hg) to leave a liquid. This liquid was filtered to remove foreign particles acquired during work-up and then 2,2,2-trifluoroethanol was removed under reduced pressure to leave a yellow solid (147), (2.2 g); (Found: C, 42.2; H, 4.3; N, 5.8; F, 37.4%); n.m.r. spectrum 29.

D. Addition of Poly(vinyl ethyl ether) (148) to Hexafluoropropene

1. Without Solvent

A mixture of poly(vinyl ethyl ether) (148) (3.6 g) and hexafluoropropene (23.3 g, 155 mmol, 3 times excess over poly(vinyl ethyl ether) (148)) was irradiated with γ-rays. Excess alkene (22.4 g) was removed by transfer under vacuum to leave a liquid (3.7 g). Due to the small amount of reaction this liquid was not investigated further.

2. In an Acetone Solvent

Hexafluoropropene (7.1g, 47 mmol, 2.5 times excess over poly(vinyl ethyl ether) (148)) was introduced into a Carius tube containing a solution of poly(vinyl ethyl ether) (148) (1.4 g) in acetone (17.4 g) and the resulting solution was irradiated with γ-rays. Excess alkene was removed by transfer under vacuum (100mm Hg) to leave a liquid. This liquid was filtered to remove foreign particles acquired during work-up and then acetone was removed under reduced pressure to leave a viscous liquid (149); (Found: C, 49.6; H, 6.7; F, 29.4%); n.m.r. spectrum 30.

CHAPTER ELEVEN

EXPERIMENTAL TO CHAPTER SIX

CHAPTER ELEVEN

EXPERIMENTAL TO CHAPTER SIX

The electrochemical fluorination experiments described below were carried out in the laboratories of Professor P. Sartori at the University of Duisburg, West Germany and also in collaboration with Mr. R.W. Fuss.

A. General Procedure

Electrochemical fluorination experiments were performed in a 1170 ml steel cell equipped with nickel anodes and cathodes of total surface area 3588 cm^2 (Diagram 1). Commercial anhydrous hydrogen fluoride was charged into the cell under a stream of argon and further dried electrochemically. The substrate was introduced into the cell under a stream of argon. Electrolysis was maintained until approximately 130% of the calculated current necessary for complete fluorination had been passed. Volatile products were collected in traps at acetone/dry ice temperature (-78^{o}C). Organic material which separated from the hydrogen fluoride (cell drainings) was run off from the base of the cell and treated with anhydrous potassium fluoride before further analysis.

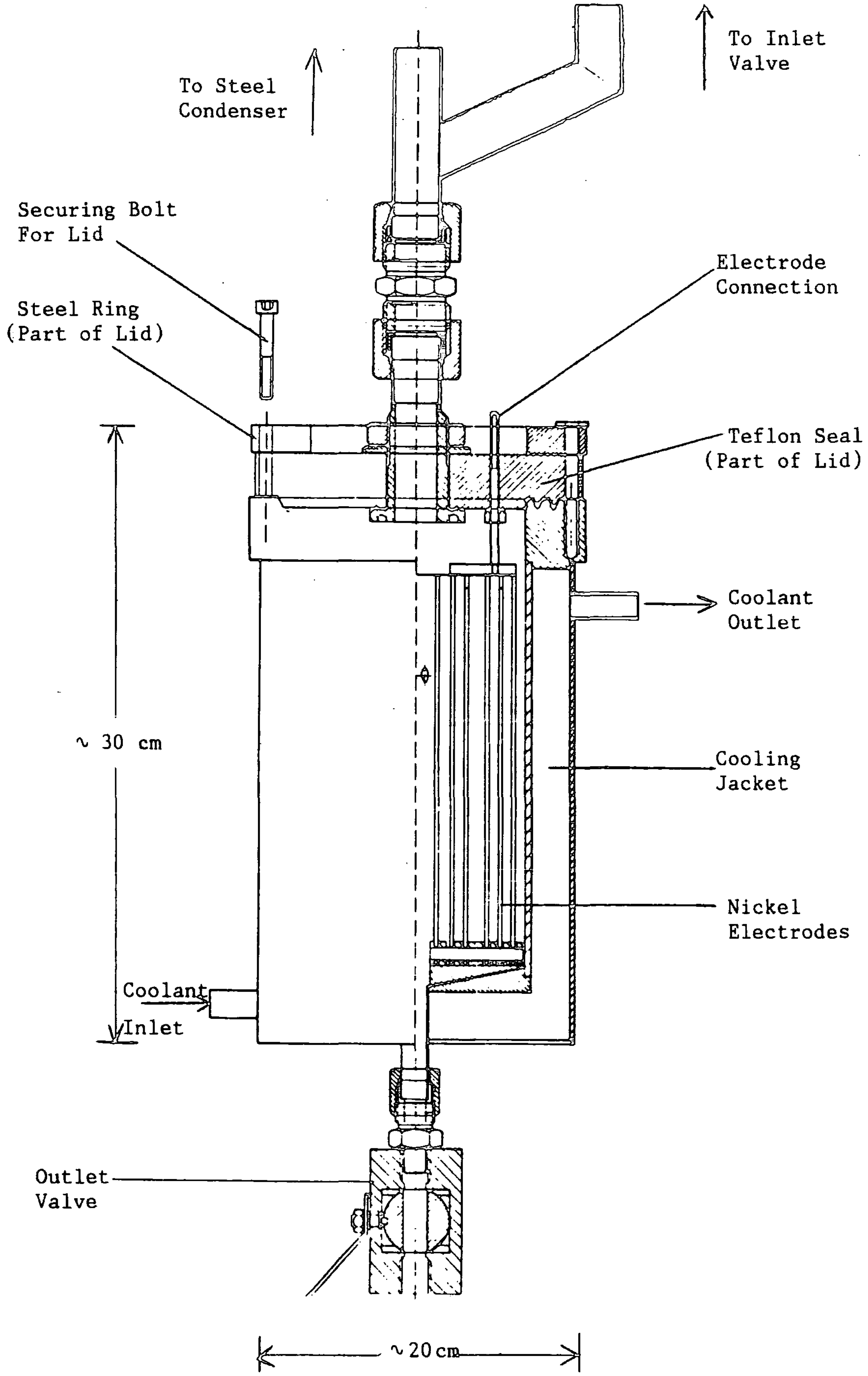
B. Electrochemical Fluorination of 2,5-Bis-(2H-hexafluoropropyl)oxolane (137)

1. Run I

A solution of (137) (100 g, 269 mmol) in dry hydrogen fluoride (800 g) was electrolysed by application of a cell voltage of 5.5V at a cell temperature of 0^{o}C. Volatile products were minor (< 0.5 g) and so were not investigated further. Initial g.l.c. analysis of the cell drainings (70.0 g) showed them to be of very similar

DIAGRAM 1

Electrochemical Fluorination Cell



composition to the cell drainings obtained from run II and so these materials were combined before further analysis.

2. Run II

A solution of (137) (100 g, 269 mmol) in dry hydrogen fluoride (800 g) was electrolysed by application of a cell voltage of 5.5V at a cell temperature of 5-6°C. Volatile products were minor (< 0.5 g) and so were not investigated further. Initial g.l.c. analysis of the cell drainings (82.7 g) showed them to be of very similar composition to the cell drainings obtained from run I and so these materials were combined before further analysis. Preparative g.l.c. (column 10% SE30, 130°C) of this combined material gave perfluoro-2,5-dipropyloxolane (151), (85% of recovered organic material by g.l.c.); (Found: C, 23.5; F, 73.9. $C_{10}F_{20}O$ requires C, 23.3; F, 73.6%); i.r. spectrum 28, n.m.r. spectrum 31, mass spectrum 32. Several other minor products were detected by g.l.c. but only perfluoro-2-propyloxolane (152) could be positively identified by g.l.c.-mass spectroscopy (by comparison with the mass spectrum of an authentic sample[5]).

C. Electrochemical Fluorination of 2,6-Bis-(2H-hexafluoropropyl)oxane (150)

A solution of (150) (50 g, 130 mmol) in dry hydrogen fluoride (800 g) was electrolysed by application of a cell voltage of 5.5V at a cell temperature of 0°C. Volatile products were not collected in this instance. Preparative g.l.c. (column 10% SE30, 130°C) of the cell drainings (30.5 g) gave a mixture of species which were mainly perfluoro-2,6-dipropyloxane (153) and/or isomers (by g.l.c.-mass spectroscopy); (Found: C, 23.0; F, 74.4. $C_{11}F_{22}O$ requires C, 23.3; F, 73.9%); i.r. spectrum 29, n.m.r. spectrum 32, mass spectrum 33.

At present further work is underway to gain more information on the product composition of the organic material recovered from this reaction.

APPENDIX 1

N.M.R. SPECTRA

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N.M.R. SPECTRA

1 2-(2H-Hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine (65)

2 2-(2H-Hexafluoropropyl)pyrrolidine (66)

3 2,5-Bis-(2H-hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine (67)

4 2,5-Bis-(2H-hexafluoropropyl)pyrrolidine (68)

5 2,2,3,4,4,4-Hexafluoro-N,N-bis(trimethylsilyl)butylamine (69)

6 (2H-Hexafluorocyclobutyl)-N,N-bis(trimethylsilyl)methylamine (71)

7 (2H-Octafluorocyclopentyl)-N,N-bis(trimethylsilyl)methylamine (72)

8 Mixture of Di-Amine Mono-Adducts (76) and (77)

9 ε-Caprolactam/Hexafluoropropene Polymer (81)

10 2-(Pentafluoro-1-propenyl)pyrrolidine (87)

11 [(2H-Hexafluorocyclobutyl)methyl]pentamethyldisiloxane (92)

12 [(2H-Octafluorocyclopentyl)methyl]pentamethyldisiloxane (93)

13 [(2H-Hexafluorocyclobutyl)methyl]heptamethylcyclotetrasiloxane (94)

14 [(2H-Octafluorocyclopentyl)methyl]heptamethylcyclotetrasiloxane (95)

15 [(2H-Hexafluorocyclobutyl)methoxy]trimethylsilane (97)

16 [(2H-Octafluorocyclopentyl)methoxy]trimethylsilane (98)

17 2,3,4,4,4-Pentafluoro-1-butene (103), 2-Difluoromethyl-3,3,3-trifluoro-1-propene (104), Fluorotrimethylsilane Mixture

18 2,2,3,3,4,4,5-Heptafluoro-1-methylenecyclopentane (108)

19 2,2,3,3,4-Pentafluoro-1-methylenecyclobutane (109)

20 1,2-Dibromo-2,3,4,4,4-pentafluorobutane (110), 1,2-Dibromo-2-difluoromethyl-3,3,3-trifluoropropane (111) Mixture

21 Methyl 4,4,5,6,6,6-hexafluoro-3-hydroxy-3-methylhexanoate (118)

22 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluoro-4,7-decanediol (123)

23 6,6,7,7,7-Pentafluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-3-heptanone (126)

24 6,7,7,7-Tetrafluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-5-heptene-3-one (128)

25 5-Ethylidene-4-pentafluoroethyl-2,3,4-tris(trifluoromethyl)-dihydrofuran (129)

26 Bis-(2,3,4,4,4-pentafluoro-1-methyl-2-butenyl) ether (136)

27 2,5-Bis(pentafluoro-1-propenyl)oxolane (138)

28 Nylon 66/Hexafluoropropene Polymer (143)

29 Poly-N-vinylpyrrolidone/Hexafluoropropene Polymer (147)

30 Poly(vinyl ethyl ether)/Hexafluoropropene Polymer (149)

31 Perfluoro-2,5-dipropyloxolane (151)

32 Mixture of Highly Fluorinated Compounds Composed Mainly of Perfluoro-2,6-dipropyloxane (153) and/or Isomers

Unless otherwise stated, spectra were recorded of samples in solution in deuterochloroform ($CDCl_3$).

For proton spectra, chemical shifts are quoted in ppm relative to external tetramethylsilane with downfield shifts positive. For fluorine spectra, chemical shifts are quoted in ppm relative to external trichlorofluoromethane with upfield shifts positive.

For the splitting patterns of the n.m.r. resonances the following abbreviations are used:

S = singlet

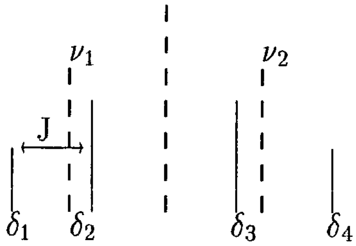
D = doublet

T = triplet

Q = quartet

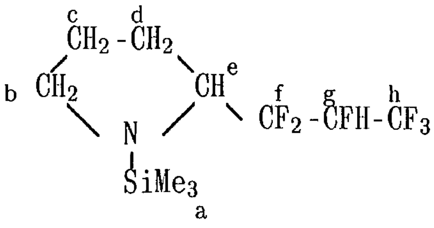
For an AB system, chemical shifts are quoted as the 'centre of gravity' or ± $\Delta\nu/2$ from the mid-point of the pattern, calculated from:

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



No.1 2-(2H-Hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine (65)

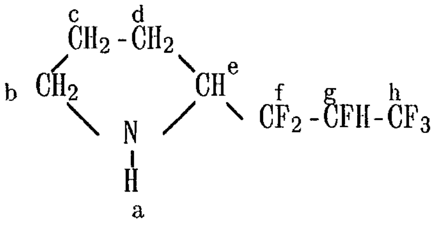
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
0.17	S	9	a
2.00	M(broad)	4	c,d
3.02	M	2	b
3.23	M		
3.86	M	1	e
4.93	D of M, J_{HF} = 45	1	g
^{19}F			
74.7	S	3	h
116.6	S	2	f
121.8 124.6	AB, J_{AB} = 271		
210.6	D, J_{HF} = 42	1	g
211.7	D, J_{HF} = 38		



(65)

No.2 2-(2H-Hexafluoropropyl)pyrrolidine (66)

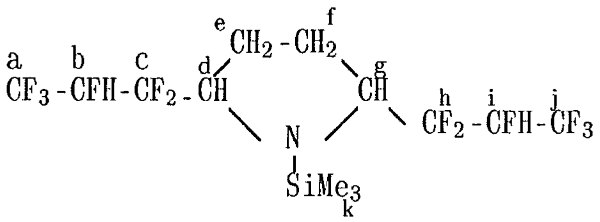
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
1.89	M (Broad)	5	c,d,a
2.85	M	2	b
3.58	M	1	e
5.28	D of M, J_{HF} = 44	1	g
^{19}F			
75.5	S	3	h
75.7	S		
118.2 123.4	AB, J_{AB} = 265	2	f
123.2 129.6	AB, J_{AB} = 262		
214.7	D, J_{HF} = 35	1	g
218.3	D, J_{HF} = 40		



(66)

No.3 2,5-Bis-(2H-hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine (67)

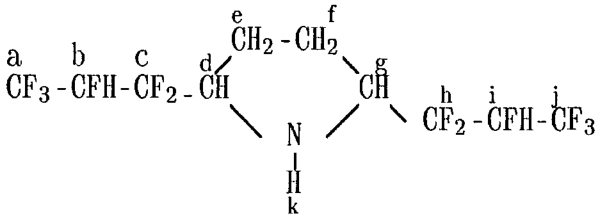
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
0.21	S	9	k
2.11	M	4	e,f
3.59 to 3.90	M	2	d,g
4.03	M (major isomer)		
4.66 to 5.31	M	2	b,i
4.94	D of M, J_{HF} = 44 (major isomer)		
^{19}F			
74.8	S (major isomer)	3	a,j
75.0	S		
113.4 119.4	AB, J_{AB} = 274 (major isomer)	2	c,h
Series of peaks between 110.4 and 125.9	Unassigned		
211.0	D, J_{HF} = 40 (major isomer)	1	b,i
211.6	D		
212.4	D, J_{HF} = 37		



(67)

No.4 2,5-Bis-(2H-hexafluoropropyl)pyrrolidine (68)

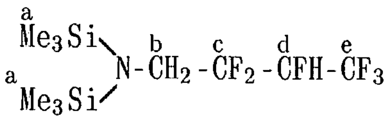
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
2.12	M	5	e,f,k
3.82	M	2	d,g
5.08	D of M, J_{HF} = 44	2	b,i
^{19}F			
74.6	S	3	a,j
117.2 121.8	AB, J_{AB} = 269 (major isomer)	2	c,h
Series of peaks between 120.7 and 127.5	Unassigned		
212.9	D, J_{HF} = 43	1	b,i
214.1	D, J_{HF} = 44		
215.2	D, J_{HF} = 41 (major isomer)		



(68)

No.5 2,2,3,4,4,4-Hexafluoro-N,N-bis(trimethylsilyl)butylamine (69)

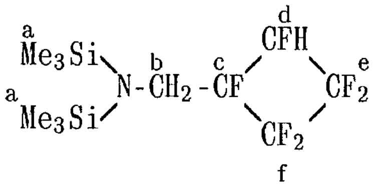
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
0.18	S	18	a
3.42	M	2	b
4.73	D of M, $J_{HF} = 44$	1	d
^{19}F			
74.3	S	3	e
109.6	AB, $J_{AB} = 268$	2	c
115.0			
210.9	D, $J_{HF} = 42$	1	d



(69)

No.6 (2H-Hexafluorocyclobutyl)-N,N-bis(trimethylsilyl)methylamine (71)

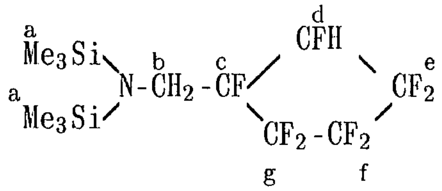
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
0.15	S	18	a
3.48	S	2	b
3.56	S		
5.05	D of M, J_{HF} = 51	1	d
^{19}F			
121.9	AB, J_{AB} = 229	2	e
134.1			
127.0	AB, J_{AB} = 228	2	f
130.6			
168.9	S	1	c
215.5	D, J_{HF} = 47	1	d



(71)

No.7 (2H-Octafluorocyclopentyl)-N,N-bis(trimethylsilyl)methylamine (72)

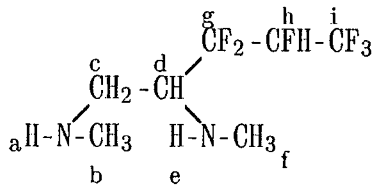
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
0.18	S	18	a
3.55	M	2	b
4.93	D of M, J_{HF} = 47	1	d
^{19}F			
Series of peaks between 113.5 and 138.2	Overlapping AB's	6	e,f,g
179.1	S	1	c (trans)
185.9	S		c (cis)
204.2	D of M, J_{HF} = 47	1	d (trans)
221.1	D of M, J_{HF} = 47		d (cis)



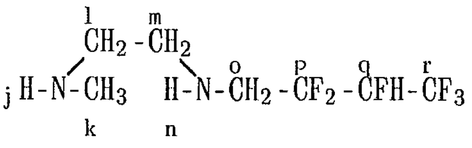
(72)

No.8 Mixture of Di-Amine Mono-Adducts (76) and (77)

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
1.88	S (Broad)		a,e,j,n
2.50	S		b,f,k
2.52	S		
2.55	S		
2.58	S		
2.92	M (Broad)		c,d,l,m,o
5.59	M (Broad)		h,q
^{19}F			
75.3	S	3	i,r
75.7	S		
115.4	AB, J_{AB} = 274	2	g,p
121.0			
117.3	AB, J_{AB} = 280		
118.9			
122.9	AB, J_{AB} = 267		
126.1			
213.1	D, J_{HF} = 40	1	h,q
215.5	D, J_{HF} = 40		
216.0	D, J_{HF} = 40		



(76)



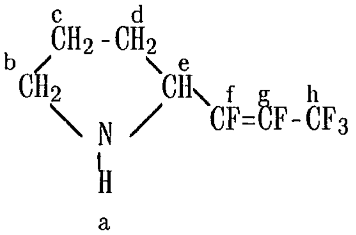
(77)

No.9 ε-Caprolactam/Hexafluoropropene Polymer (81)

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{19}F			
74 to 76	Many Peaks	3	CF_3
114 to 128	Many Peaks	2	CF_2
211 to 215	Many Peaks	1	CFH

No.10 2-(Pentafluoro-1-propenyl)pyrrolidine (87)

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
1.91	M	5	a,c,d
3.04	M	2	b
4.14 4.26	Overlapping D of M's, J_{ef} ~ 30	1	e
^{19}F			
Cis Isomer			
65.9	S	3	h
138.6	D, J_{ef} = 33	1	f
157.9	M	1	g
Trans Isomer			
68.4	S	3	h
154.8	D of D of Q, J_{fg} = 133 J_{ef} = 25 J_{fh} = 22	1	f
175.3	D of M, J_{fg} = 131	1	g

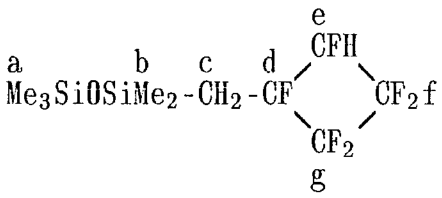


[cis:trans = 4:1]

(87)

No.11 [(2H-Hexafluorocyclobutyl)methyl]pentamethyldisiloxane (92)

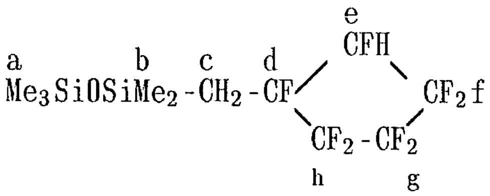
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
0.12	S	9	a
0.23	S	6	b
1.31	M	2	c
5.04	M (Broad)	1	e
^{19}F			
Series of peaks between 117.3 and 135.3	Overlapping AB's	4	f,g
161.2	S	1	d (trans)
182.6	S		d (cis)
211.2	D, J_{HF} = 52	1	e (trans)
216.1	D, J_{HF} = 50		e (cis)



(92)

No.12 [(2H-Octafluorocyclopentyl)methyl]pentamethyldisiloxane (93)

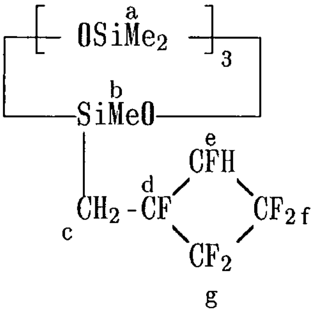
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
0.25	S	9	a
0.36	S	6	b
1.44	M	2	c
5.02	M (Broad)	1	e
^{19}F			
Series of peaks between 113.2 and 140.3	Overlapping AB's	6	f,g,h
165.9	S	1	d (trans)
175.5	S		d (cis)
203.8	D, J_{HF} = 47	1	e (trans)
223.1	D, J_{HF} = 48		e (cis)



(93)

No.13 [(2H-Hexafluorocyclobutyl)methyl]heptamethylcyclotetrasiloxane (94)

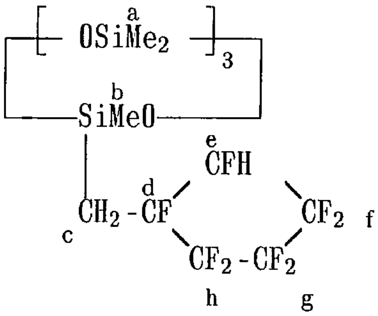
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
0.24	S	18	a
0.35	S	3	b
1.41	M	2	c
5.27	M (Broad)	1	e
^{19}F			
Series of peaks between 117.4 and 135.4	Overlapping AB's	4	f,g
161.7	S	1	d (trans)
182.8	S		d (cis)
211.4	D, J_{HF} = 51	1	e (trans)
216.4	D, J_{HF} = 50		e (cis)



(94)

No. 14 [(2H-Octafluorocyclopentyl)methyl]heptamethylcyclotetrasiloxane (95)

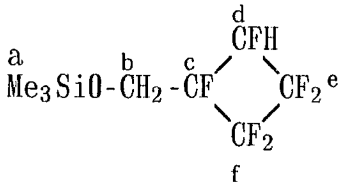
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
0.13	S	18	a
0.26	S	3	b
1.38	M	2	c
5.02	M (Broad)	1	e
^{19}F			
Series of peaks between 109.0 and 136.0	Overlapping AB's	6	f,g,h
162.6	M	1	d (trans)
170.5	S		d (cis)
199.5	D	1	e (trans)
219.3	D		e (cis)



(95)

No.15 [(2H-Hexafluorocyclobutyl)methoxy]trimethylsilane (97)

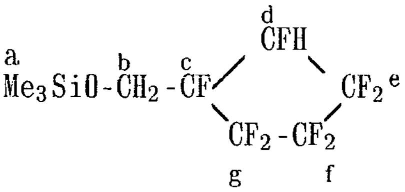
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
0.16	S	9	a
4.01	M	2	b
5.17	M (Broad)	1	d
^{19}F			
Series of peaks between 118.6 and 135.4	Overlapping AB's	4	e,f
179.9	S	1	c (trans)
196.9	S		c (cis)
218.3	D, J_{HF} = 48	1	d (trans)
220.4	D, J_{HF} = 55		d (cis)



(97)

No.16 [(2H-Octafluorocyclopentyl)methoxy]trimethylsilane (98)

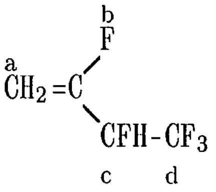
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
0.10	S	9	a
3.97	M	2	b
5.11	M (Broad)	1	d
^{19}F			
Series of peaks between 117.6 and 133.5	Overlapping AB's	6	e,f,g
181.2	S	1	c (trans)
192.8	S		c (cis)
211.5	D, $J_{HF} = 46$	1	d (trans)
225.9	D, $J_{HF} = 47$		d (cis)



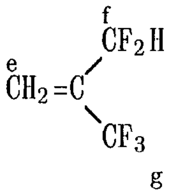
(98)

No.17 2,3,4,4,4-Pentafluoro-1-butene (103), 2-Difluoromethyl-3,3,3-trifluoro-1-propene (104), Fluorotrimethylsilane Mixture (Neat Sample)

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Assignment
^1H		
0.18	D, J_{hi} = 7	h
4.99	M (Broad)	a,c
6.02	S	e
6.09	S	
6.21	T, J_{HF} = 54	f
^{19}F		
66.1	S	g
78.5	S	d
113.6	S	b
118.6	D, J_{HF} = 47	f
157.6	S	i
202.1	S	c



(103)

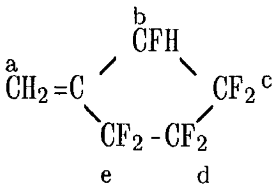


(104)

$\overset{h}{Me_3}Si\overset{i}{F}$

No.18 2,2,3,3,4,4,5-Heptafluoro-1-methylenecyclopentane (108)

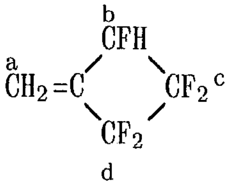
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
5.33	D of M, J_{HF} = 52	1	b
6.24	S (Broad)	2	a
6.40	S (Broad)		
^{19}F			
110.4 114.2	AB, J_{AB} = 260	2	e
124.6 134.8	AB, J_{AB} = 258	2	c
133.9 136.3	AB, J_{AB} = 249	2	d
191.5	D, J_{HF} = 55	1	b



(108)

No.19 2,2,3,3,4-Pentafluoro-1-methylenecyclobutane (109)

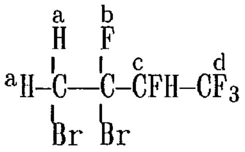
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
5.45	D of M, J_{HF} = 55	1	b
6.08 6.21	M M	2	a
^{19}F			
113.8 114.8	AB, J_{AB} = 234	2	d
119.9 134.5	AB, J_{AB} = 223	2	c
194.5	D, J_{HF} = 56	1	b



(109)

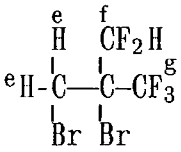
No.20 1,2-Dibromo-2,3,4,4,4-pentafluorobutane (110), 1,2-Dibromo-2-difluoromethyl-3,3,3-trifluoropropane (111) Mixture

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
4.02	M	2	a,e
5.22	D of M, J_{HF} = 43	1	c
6.14	T, J_{HF} = 54		f
^{19}F			
67.5	S		g
72.0	S	3	d
72.3	S		
118.2	S	2	b
122.8	S		
124.5	AB of D, J_{AB} = 281 J_{HF} = 62		f
128.1			
198.6	D, J_{HF} = 41		c
200.0	S		



$$\begin{array}{c} \overset{a}{H}\;\;\overset{b}{F} \\ {}^{a}H-C-C-\overset{c}{C}FH-\overset{d}{C}F_3 \\ Br\;\;Br \end{array}$$

(110)

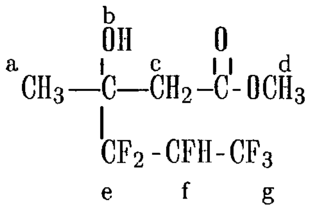


$$\begin{array}{c} \overset{e}{H}\;\;\overset{f}{C}F_2H \\ {}^{e}H-C-C-\overset{g}{C}F_3 \\ Br\;\;Br \end{array}$$

(111)

No.21 Methyl 4,4,5,6,6,6-hexafluoro-3-hydroxy-3-methylhexanoate (118)

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
1.31	M	3	a
1.35	M		
1.48	S	1	b
2.42	AB, J_{AB} = 17	2	c
2.80			
2.49	AB, J_{AB} = 16		
2.77			
3.68	S	3	d
5.21	D of M, J_{HF} = 40	1	f
^{19}F			
74.3	S	3	g
122.6	AB, J_{AB} = 278	2	e
127.0			
122.9	AB, J_{AB} = 273		
126.5			
207.8	D, J_{HF} = 41	1	f
208.4	D, J_{HF} = 41		

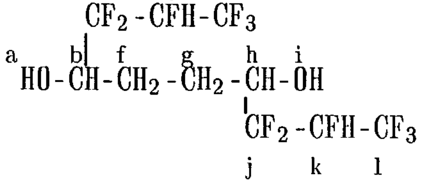


$$\overset{a}{CH_3}-\overset{\overset{b}{OH}}{\underset{\underset{e}{CF_2}-\underset{f}{CFH}-\underset{g}{CF_3}}{C}}-\overset{c}{CH_2}-\overset{O}{\overset{\|}{C}}-O\overset{d}{CH_3}$$

(118)

No. 22 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluoro-4,7-decanediol (123)

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
1.88	M	2	f,g
3.00	S (Broad)	1	a,i
3.52	S (Broad)		
4.02	M	1	b,h
5.13	D of M, J_{HF} = 43	1	d,k
^{19}F			
74.3	S	3	e,l
74.6	S		
Series of peaks between 119.3 and 130.2	Overlapping AB's	2	c,j
Series of peaks between 213.2 and 215.1	Unassigned	1	d,k

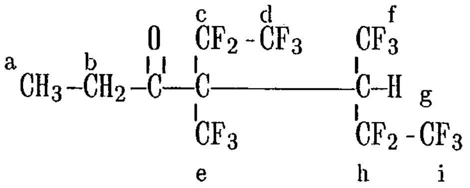


$$\overset{a}{HO}-\overset{\overset{\overset{c}{CF_2}-\overset{d}{CFH}-\overset{e}{CF_3}}{|}}{\overset{b}{CH}}-\overset{f}{CH_2}-\overset{g}{CH_2}-\underset{\underset{\underset{j}{CF_2}-\underset{k}{CFH}-\underset{l}{CF_3}}{|}}{\overset{h}{CH}}-\overset{i}{OH}$$

(123)

No. 23 6,6,7,7,7-Pentafluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-3-heptanone (126)

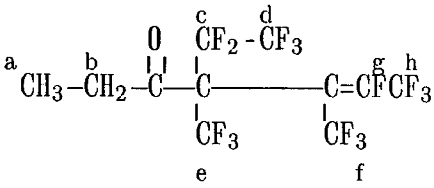
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
1.16	T, J_{ab} = 7	3	a
1.18	T, J_{ab} =7		
2.87	M	2	b
4.84	M	1	g
^{19}F			
54.9	S	3	e,f
56.6	S		
58.2	S	3	
58.8	S		
75.6	S	3	d,i
82.3	S	3	
82.8	S		
Series of peaks between 101.9 and 113.8	Unassigned	4	c,h



(126)

No.24 6,7,7,7-Tetrafluoro-4-pentafluoroethyl-4,5-bis(trfluoromethyl)-5-heptene-3-one(128)

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
1.20	T, J_{ab} = 7	3	a
2.83	M	2	b
^{19}F			
51.3	S	3	f
52.0	S		
58.4	S	3	e
58.9	S		
67.2	S	3	h
67.6	S		
77.5	S	3	d
78.5	S		
87.5	S (Broad)	1	g
94.0	S (Broad)		
Series of peaks between 106.2 and 110.9	Unassigned	2	c

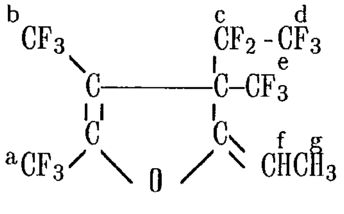


$$\overset{a}{\mathrm{CH_3}}-\overset{b}{\mathrm{CH_2}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\underset{e}{\mathrm{CF_3}}}{\overset{\overset{c\qquad d}{\mathrm{CF_2-CF_3}}}{\mathrm{C}}}-\underset{\underset{f}{\mathrm{CF_3}}}{\mathrm{C}}=\overset{g}{\mathrm{CF}}\overset{h}{\mathrm{CF_3}}$$

(128)

No.25 5-Ethylidene-4-pentafluoroethyl-2,3,4-tris(trifluoromethyl)dihydrofuran (129)

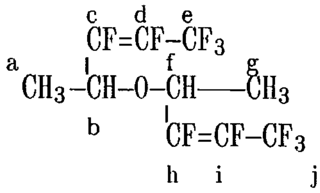
Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
1.87	D, J_{fg} = 7	3	g
5.68	M	1	f
^{19}F			
54.7	M	3	b
65.7	Q, J_{ab} = 10	3	a
68.1	M	3	e
80.3	S	3	d
115.4 118.8	AB, J_{AB} = 272	2	c



(129)

No.26 Bis-(2,3,4,4,4-pentafluoro-1-methyl-2-butenyl) ether (136)

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^{1}H			
2.91	D, J_{ab} (J_{fg}) = 7	3	a,g
4.44	M	1	b,f
^{19}F			
66.2	S		e,j (cis)
66.6	S		
68.3	S		e,j (trans)
68.6	S		
139.5	S		c,h (cis)
140.1	S		
140.7	S		
153.2	S		d,i (cis)
153.9			
154.5	S		
Series of peaks between 155.7 and 157.6	Unassigned		c,h (trans)
Series of peaks between 170.5 and 171.4	Unassigned		d,i (trans)



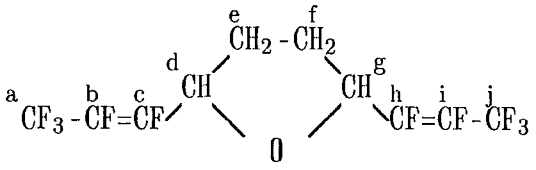
$$\overset{a}{CH_3}-\underset{b}{\overset{\overset{c\quad d\quad e}{CF=CF-CF_3}}{CH}}-O-\overset{f}{\underset{\underset{h\quad i\quad j}{CF=CF-CF_3}}{CH}}-\overset{g}{CH_3}$$

(136)

[Complex mixture of geometric and stereoisomers, overall cis double bond:trans double bond = 9:2]

No.27 2,5-Bis(pentafluoro-1-propenyl)oxolane (138)

Shift(ppm)	Fine Structure Coupling Constants(Hz)	Relative Intensity	Assignment
^1H			
2.30	M	2	e,f
5.11	M	1	d,g
^{19}F			
65.8	M		a,j (cis)
68.3	M		a,j (trans)
141.0	M		c,h (cis)
141.4	M		
152.7	M		b,i (cis)
153.3	M		
Series of peaks between 157.0 and 157.9	Unassigned		c,h (trans)
Series of peaks between 170.7 and 171.6	Unassigned		d,i (trans)



(138)

[Complex mixture of geometric and stereoisomers, overall cis double bond:trans double bond = 2:1]

No.28 Nylon 66/Hexafluoropropene Polymer (143) (d_6-acetone n.m.r. solvent)

Shift (ppm)	Fine Structure	Relative Intensity	Assignment
^{19}F			
67 to 74	Many Peaks	16	CF_3
101 to 131	Many Peaks	6	CF_2,CF_2H
174 to 185	Many Peaks	2	CF
210 to 214	Many Peaks	1	CFH

No.29 Poly-N-vinylpyrrolidone/Hexafluoropropene Polymer (147) (methanol n.m.r. solvent)

Shift (ppm)	Fine Structure	Relative Intensity	Assignment
75 to 76	Many Peaks	3	CF_3
107 to 137	Many Peaks	2	CF_2
211 to 216	Many Peaks	1	CFH

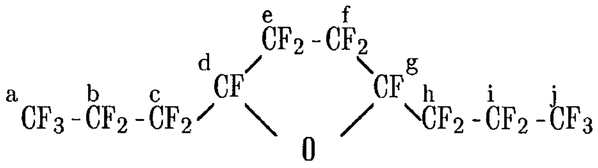
No.30 Poly(vinyl ethyl ether)/Hexafluoropropene Polymer (149)

(d_6-acetone n.m.r. solvent)

Shift (ppm)	Fine Structure	Relative Intensity	Assignment
^{19}F			
74 to 75	Many Peaks	3	CF_3
110 to 133	Many Peaks	2	CF_2
208 to 217	Many Peaks	1	CFH

No.31 Perfluoro-2,5-dipropyloxolane (151)

Shift (ppm)	Fine Structure	Relative Intensity	Assignment
^{19}F			
84.0	S	3	a,j
Series of peaks between 121.8 and 135.9	Unassigned	7	b,c,d,e,f g,h,i



(151)

No.32 Mixture of Highly Fluorinated Compounds Composed mainly of Perfluoro-2,6-dipropyloxane (153) and/or Isomers

Shift (ppm)	Fine Structure	Relative Intensity	Assignment
^{19}F			
Series of peaks between 72.7 and 83.4	Unassigned (minor)	~ 3	CF_3 and/or CF_2O
83.8	S(major)		
Series of peaks between 115.3 and 144.3	Unassigned (major)	~ 8	CF_2 and/or CFO
Series of peaks between 179.1 and 190.0	Unassigned (minor)		CF

APPENDIX 2

INFRARED SPECTRA

APPENDIX 2

INFRARED SPECTRA

1 2-(2H-Hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine (65)

2 2-(2H-Hexafluoropropyl)pyrrolidine (66)

3 2,5-Bis-(2H-hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine (67)

4 2,5-Bis-(2H-hexafluoropropyl)pyrrolidine (68)

5 2,2,3,4,4,4-Hexafluoro-N,N-bis(trimethylsilyl)butylamine (69)

6 (2H-Hexafluorocyclobutyl)-N,N-bis(trimethylsilyl)methylamine (71)

7 (2H-Octafluorocyclopentyl)-N,N-bis(trimethylsilyl)methylamine (72)

8 Mixture of Di-Amine Mono-Adducts (76) and (77)

9 ε-Caprolactam/Hexafluoropropene Polymer (81)

10 2-(Pentafluoro-1-propenyl)pyrrolidine (87)

11 [(2H-Hexafluorocyclobutyl)methyl]pentamethyldisiloxane (92)

12 [(2H-Octafluorocyclopentyl)methyl]pentamethyldisiloxane (93)

13 [(2H-Hexafluorocyclobutyl)methyl]heptamethylcyclotetrasiloxane (94)

14 [(2H-Octafluorocyclopentyl)methyl]heptamethylcyclotetrasiloxane (95)

15 [(2H-Hexafluorocyclobutyl)methoxy]trimethylsilane (97)

16 [(2H-Octafluorocyclopentyl)methoxy]trimethylsilane (98)

17 2,3,4,4,4-Pentafluoro-1-butene (103), 2-Difluoromethyl-3,3,3-trifluoro-1-propene (104), Fluorotrimethylsilane Mixture

18 2,2,3,3,4,4,5-Heptafluoro-1-methylenecyclopentane (108)

19 2,2,3,3,4-Pentafluoro-1-methylenecyclobutane (109)

20 1,2-Dibromo-2,3,4,4,4-pentafluorobutane (110), 1,2-Dibromo-2-difluoromethyl-3,3,3-trifluoropropane (111) Mixture

21 Methyl 4,4,5,6,6,6-hexafluoro-3-hydroxy-3-methylhexanoate (118)

22 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluoro-4,7-decanediol (123)

23 6,6,7,7,7-Pentafluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-3-heptanone (126)

24 6,7,7,7-Tetrafluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-5-heptene-3-one (128)

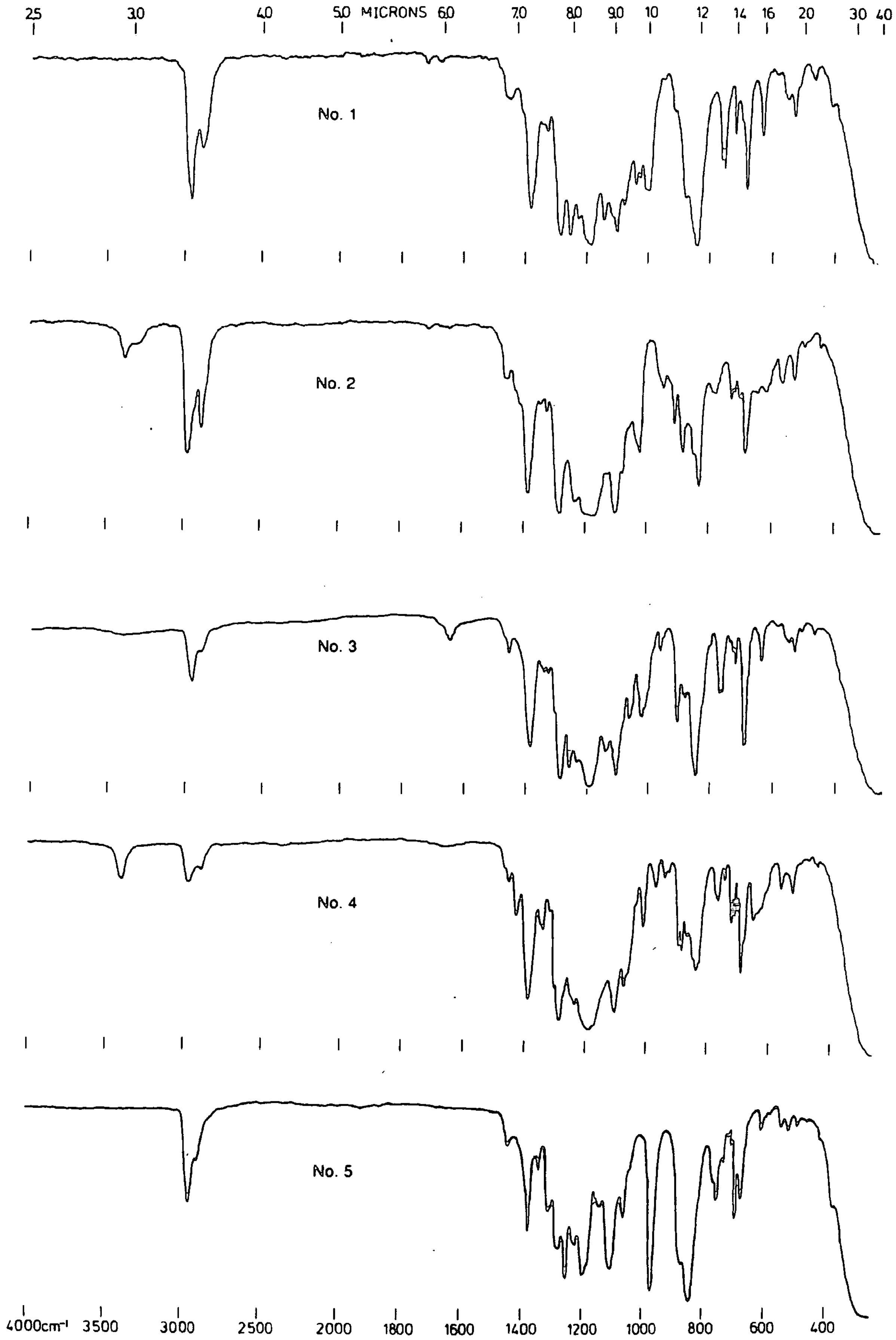
25 5-Ethylidene-4-pentafluoroethyl-2,3,4-tris(trifluoromethyl)-dihydrofuran (129)

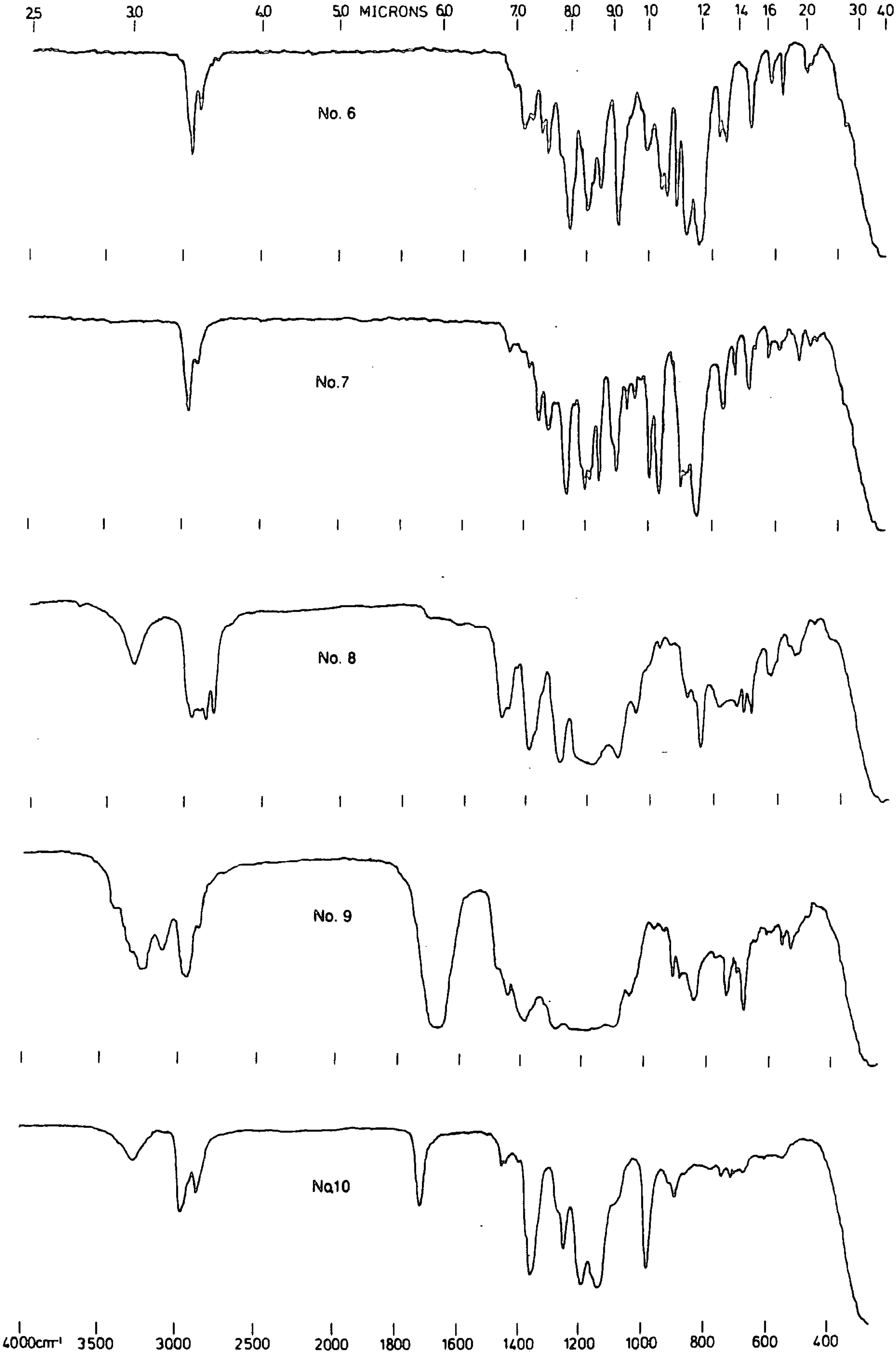
26 Bis-(2,3,4,4,4-pentafluoro-1-methyl-2-butenyl) ether (136)

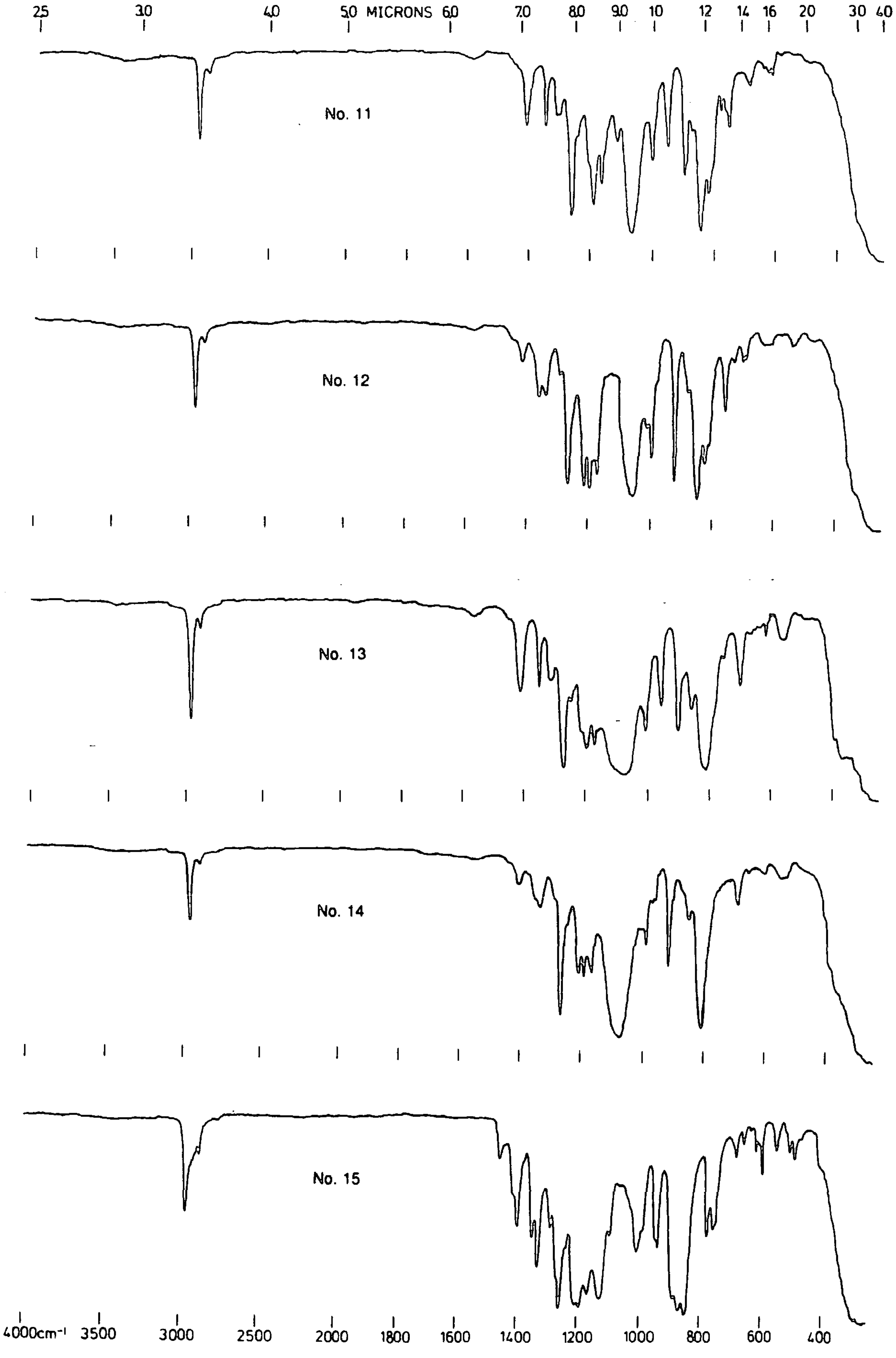
27 2,5-Bis(pentafluoro-1-propenyl)oxolane (138)

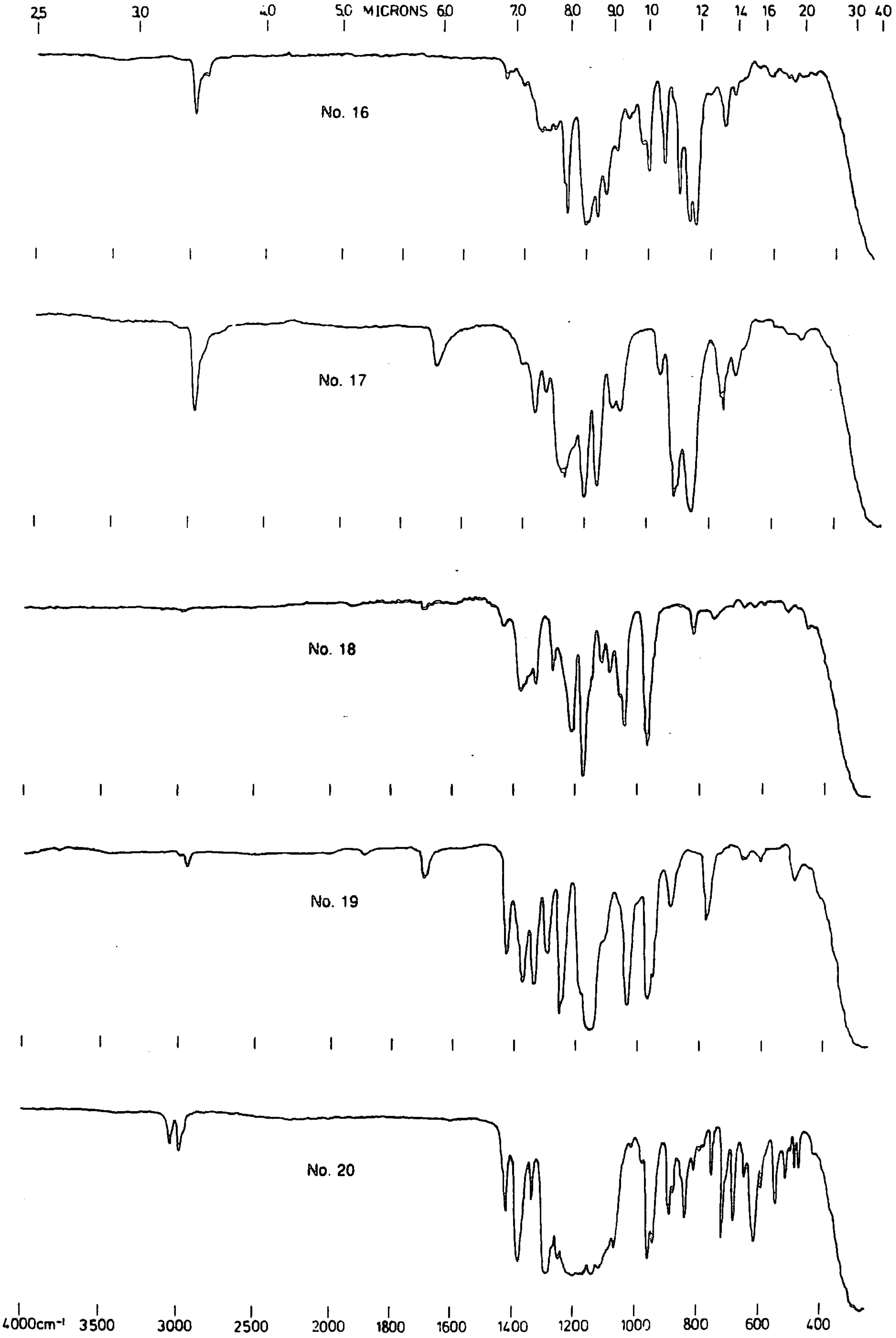
28 Perfluoro-2,5-dipropyloxolane (151)

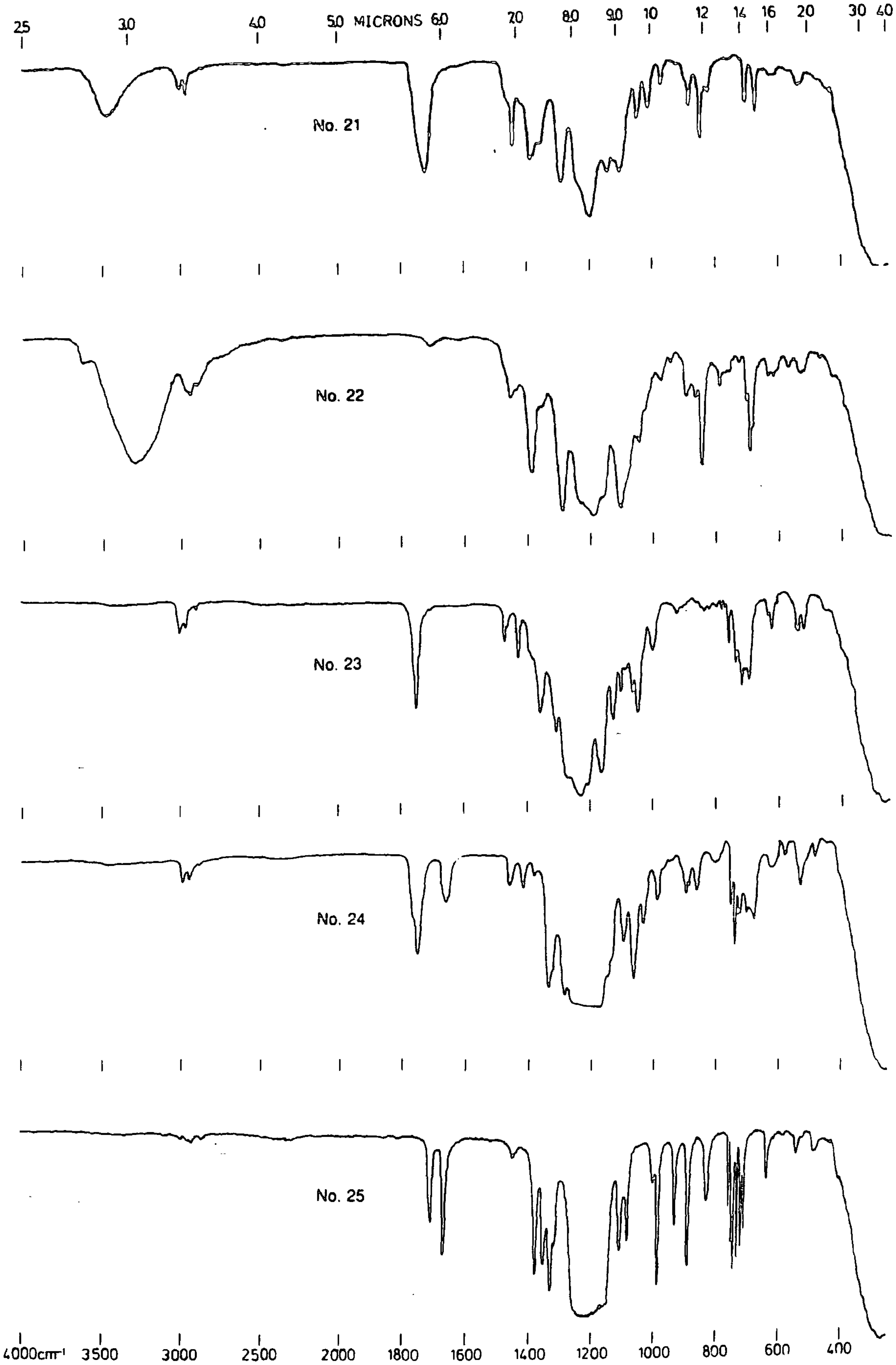
29 Mixture of Highly Fluorinated Compounds Composed Mainly of Perfluoro-2,6-dipropyloxane (153) and/or Isomers

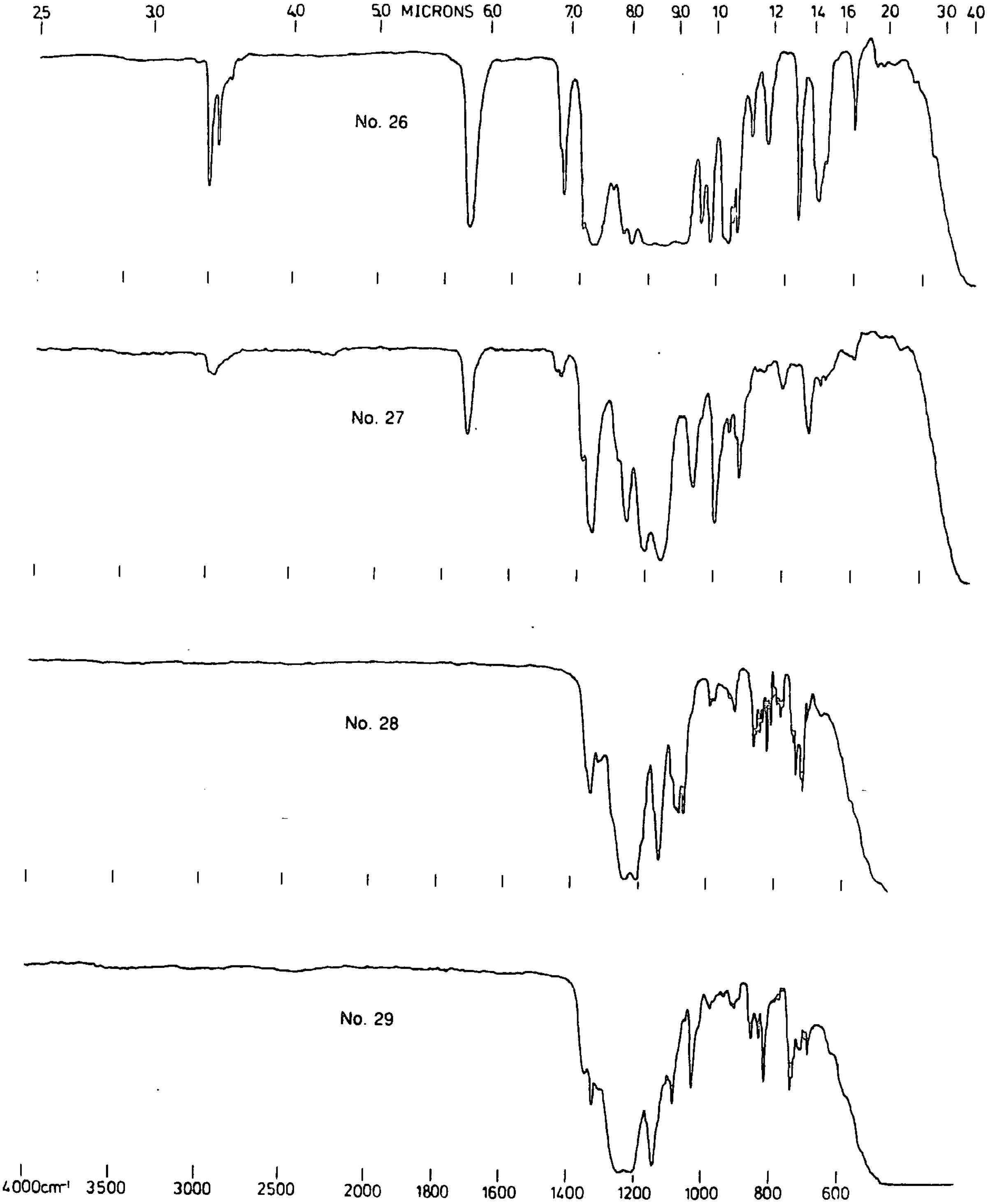

2.5
3.0
4.0
5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
16
20
30
40
No. 1
No. 2
No. 3
No. 4
No. 5
4000cm⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


2.5
3.0
4.0
5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
16
20
30
40
No. 6
No.7
No. 8
No. 9
No.10
4000cm⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


2.5
3.0
4.0
5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
16
20
30
40
No. 11
No. 12
No. 13
No. 14
No. 15
4000cm⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


2.5
3.0
4.0
5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
16
20
30
40
No. 16
No. 17
No. 18
No. 19
No. 20
4000cm⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


2.5
3.0
4.0
5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
16
20
30
40
No. 21
No. 22
No. 23
No. 24
No. 25
4000cm⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


2.5
3.0
4.0
5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
16
20
30
40
No. 26
No. 27
No. 28
No. 29
4000cm⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600

APPENDIX 3

MASS SPECTRA

APPENDIX 3

MASS SPECTRA

1 2-(2H-Hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine (65)

2 2-(2H-Hexafluoropropyl)pyrrolidine (66)

3 2,5-Bis-(2H-hexafluoropropyl)-N-(trimethylsilyl)pyrrolidine (67)

4 2,5-Bis-(2H-hexafluoropropyl)pyrrolidine (68)

5 2,2,3,4,4,4-Hexafluoro-N,N-bis(trimethylsilyl)butylamine (69)

6 (2H-Hexafluorocyclobutyl)-N,N-bis(trimethylsilyl)methylamine (71)

7a Trans-(2H-octafluorocyclopentyl)-N,N-bis(trimethylsilyl)methylamine (72)

7b Cis-(2H-octafluorocyclopentyl)-N,N-bis(trimethylsilyl)methylamine (72)

8 2-Imidazolidinone, 2-Imidazolidinone/Hexafluoropropene Mono- and Di-Adduct Mixture

9 1,3-Dimethyl-2-imidazolidinone/Hexafluoropropene Mono-Adduct

10 1,3-Dimethyl-2-imidazolidinone/Hexafluoropropene Di-Adduct

11a
11b Di-Amine Mono-Adducts (76) and (77)
11c

12 2-(Pentafluoro-1-propenyl)pyrrolidine (87)

13a Trans-[(2H-hexafluorocyclobutyl)methyl]trimethylsilane (90)

13b Cis-[(2H-hexafluorocyclobutyl)methyl]trimethylsilane (90)

14a Trans-[(2H-octafluorocyclopentyl)methyl]trimethylsilane (91)

14b Cis-[(2H-octafluorocyclopentyl)methyl]trimethylsilane (91)

15a Trans-[(2H-hexafluorocyclobutyl)methyl]pentamethyldisiloxane (92)

15b Cis-[(2H-hexafluorocyclobutyl)methyl]pentamethyldisiloxane (92)

16a Trans-[(2H-octafluorocyclopentyl)methyl]pentamethyldisiloxane (93)

16b Cis-[(2H-octafluorocyclopentyl)methyl]pentamethyldisiloxane (93)

17a Trans-[(2H-hexafluorocyclobutyl)methyl]heptamethylcyclotetrasiloxane (94)

17b Cis-[(2H-hexafluorocyclobutyl)methyl]heptamethylcyclotetrasiloxane (94)

18a Trans-[(2H-octafluorocyclopentyl)methyl]heptamethylcyclotetrasiloxane (95)

18b Cis-[(2H-octafluorocyclopentyl)methyl]heptamethylcyclotetrasiloxane (95)

19a Trans-[(2H-hexafluorocyclobutyl)methoxy]trimethylsilane (97)

19b Cis-[(2H-hexafluorocyclobutyl)methoxy]trimethylsilane (97)

20a Trans-[(2H-octafluorocyclopentyl)methoxy]trimethylsilane (98)

20b Cis-[(2H-octafluorocyclopentyl)methoxy]trimethylsilane (98)

21 2,2,3,3,4,4,5-Heptafluoro-1-methylenecyclopentane (108)

22 2,2,3,3,4-Pentafluoro-1-methylenecyclobutane (109)

23 1,2-Dibromo-2,3,4,4,4-pentafluorobutane (110)

24 1,2-Dibromo-2-difluoromethyl-3,3,3-trifluoropropane (111)

25 Methyl 4,4,5,6,6,6-hexafluoro-3-hydroxy-3-methylhexanoate (118)

26 1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluoro-4,7-decanediol (123)

27 6,6,7,7,7-Pentafluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-3-heptanone (126)

28 6,7,7,7-Tetrafluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-5-heptene-3-one (128)

29 5-Ethylidene-4-pentafluoroethyl-2,3,4-tris(trifluoromethyl)-dihydrofuran (129)

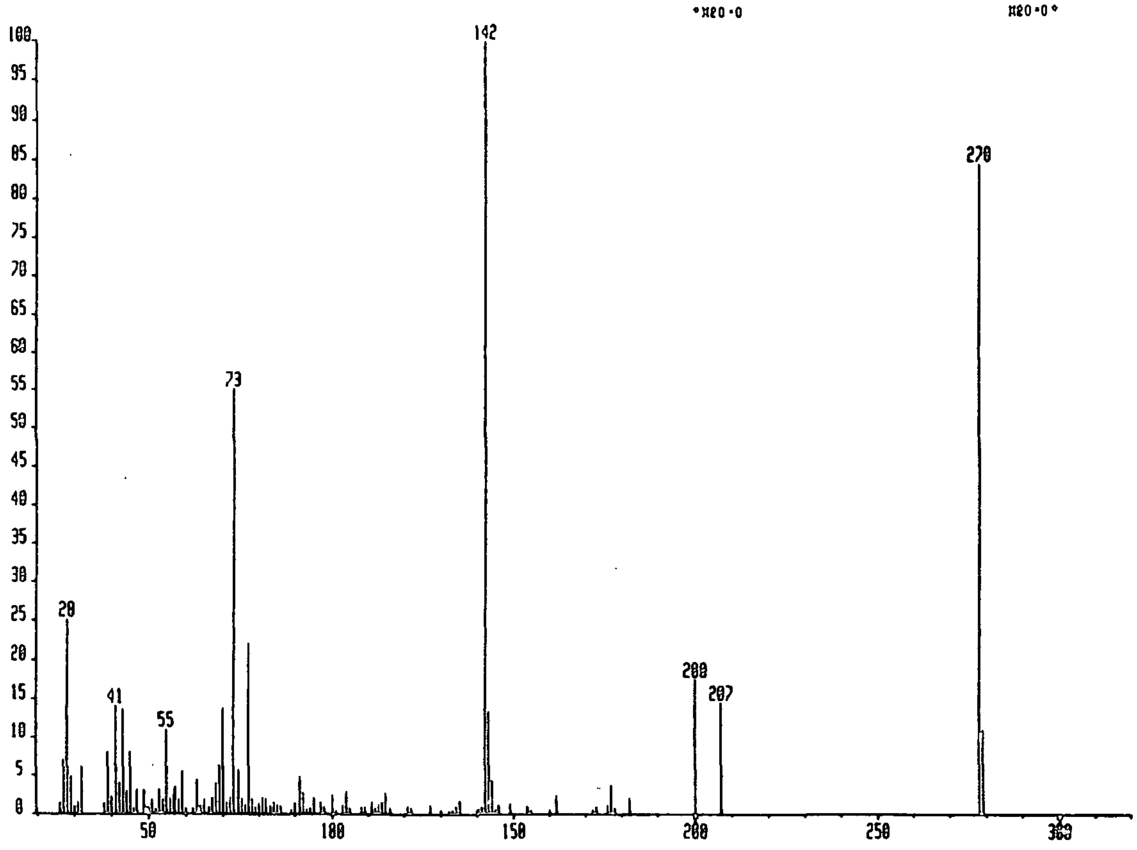
30 Bis-(2,3,4,4,4-pentafluoro-1-methyl-2-butenyl) ether (136)

31 2,5-Bis(pentafluoro-1-propenyl)oxolane (138)

32 Perfluoro-2,5-dipropyloxolane (151)

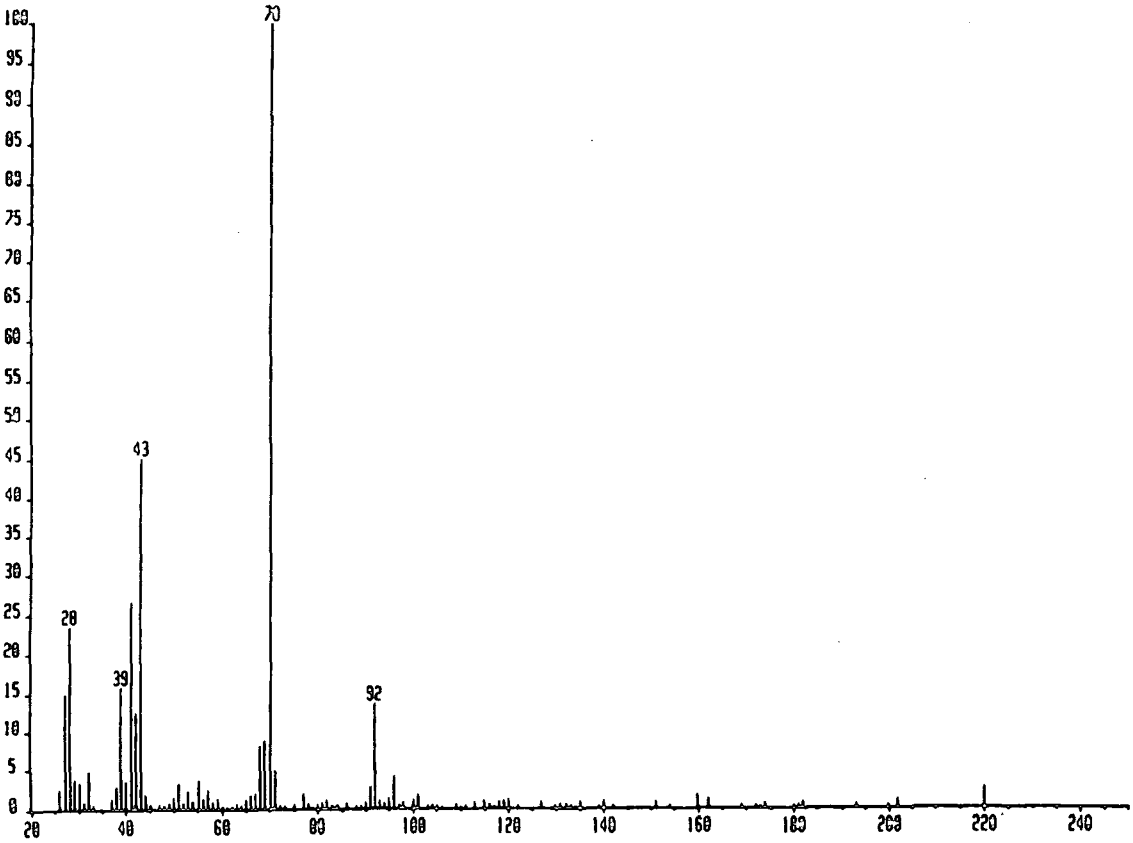
33 Perfluoro-2,6-dipropyloxane (153)/or Isomer

EI⁺ M.Wt. 293 No. 1



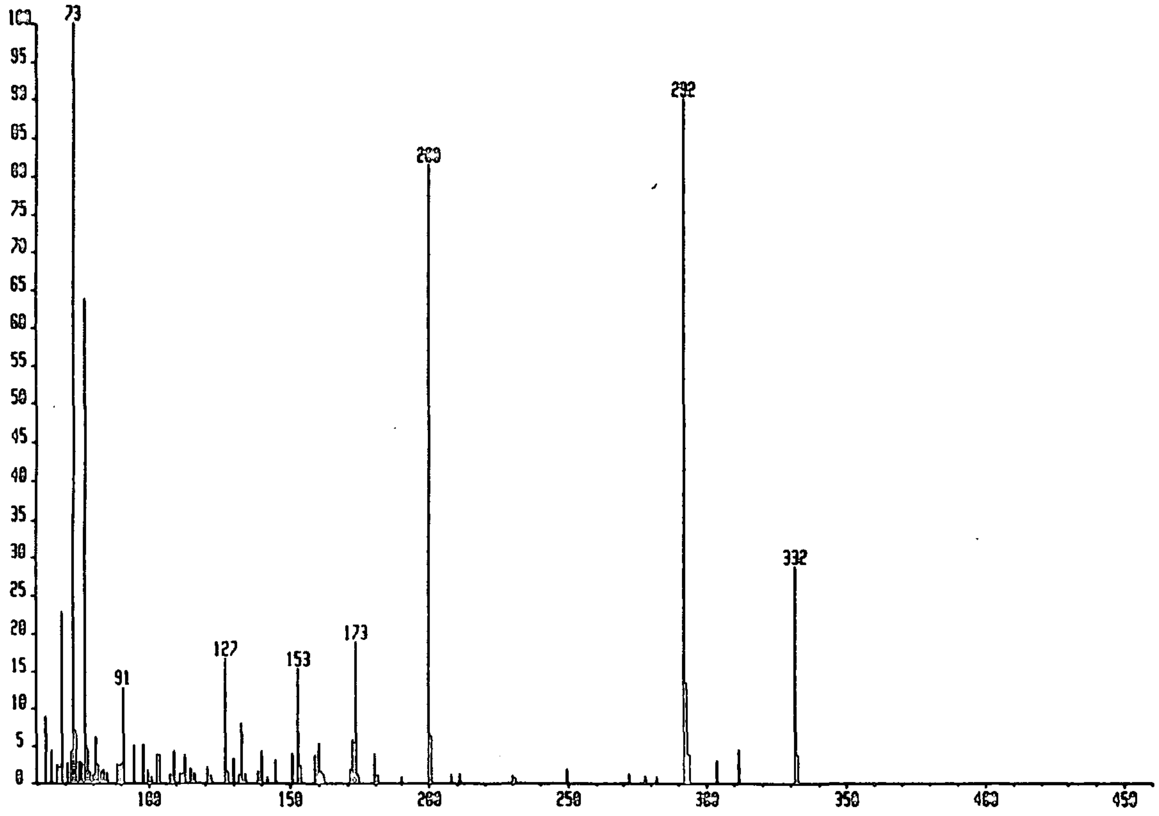
Mass	% Base
26.00	1.34
27.01	6.97
27.96	0.40
27.99	24.96 F
28.00	6.36 F
28.97	1.93
28.99	0.55
29.02	4.70
30.02	0.89
30.98	1.34
31.00	0.74
31.97	6.01
38.00	1.11
39.01	7.94
39.94	2.13
40.01	1.01
41.02	14.01
41.98	0.73
42.02	3.77
42.98	5.95
43.03	13.58
43.98	2.73
44.96	0.50
44.99	8.06
46.00	0.65
46.96	2.88
47.01	1.18
48.97	2.90
50.99	1.66
52.01	0.49
53.02	2.90
54.02	1.67
54.98	0.83
55.04	10.85
55.88	0.89
56.04	1.77
57.00	2.23
57.05	3.31
58.01	1.58
58.06	0.47
59.01	5.39
62.99	4.29
63.52	0.74
63.99	0.83
65.01	1.56
66.02	0.71
67.03	1.84
68.03	3.80
68.97	6.23
69.05	1.75
70.00	0.58
70.05	13.69
71.01	1.25
71.06	1.24
72.02	1.88
73.03	54.94
74.03	5.53
75.02	1.73
75.99	1.07
77.00	22.03
78.00	1.76
79.00	0.69
80.03	1.18
80.98	1.98
81.04	1.04
82.01	1.80
83.01	0.76
83.07	0.91
84.01	1.25
84.07	0.95
85.02	1.00
90.00	1.16
91.03	4.71
92.03	2.54
94.99	1.93
95.06	0.86
96.99	1.27
100.04	2.21
101.04	0.26
103.02	1.07
104.01	2.85
111.03	1.38
112.04	0.61
112.98	0.97
113.05	0.99
114.05	1.27
115.02	2.44
116.02	0.64
121.01	0.93
122.01	0.56
127.00	1.08
130.03	0.42
132.04	0.34
133.01	0.47
134.01	0.86
135.03	1.59
140.00	0.43
140.07	0.48
141.08	0.70
142.09	100.00
143.09	13.28
144.09	4.25
145.09	0.48
146.06	1.03
149.01	1.11
154.01	0.90
155.04	0.32
160.02	0.43
162.04	2.16
172.02	0.38
173.02	0.75
176.06	0.99
177.07	3.49
178.07	0.62
182.05	1.98
200.05	0.87
207.04	0.72
278.10	4.23
279.09	0.54

EI$^+$ M.Wt. 221 No. 2



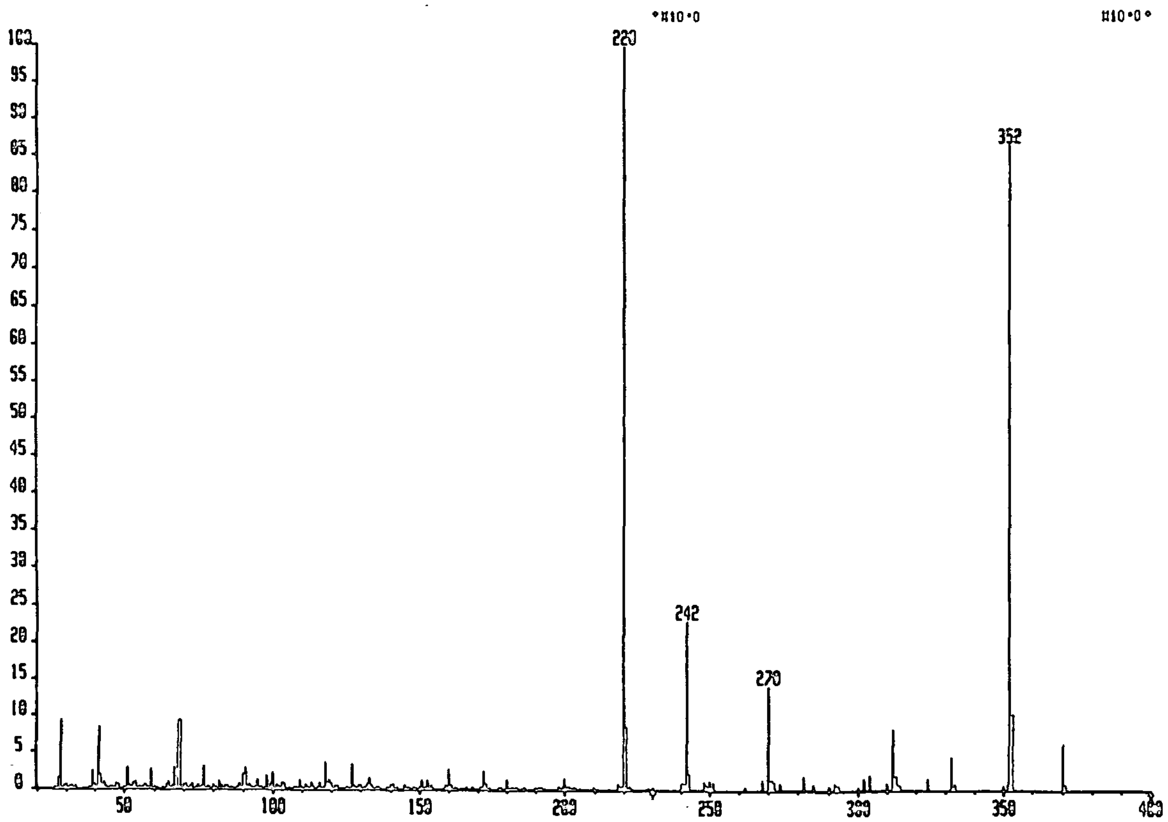
Mass	% Base	
26.00	2.27	
27.01	14.81	
27.99	20.14	F
28.00	23.50	F
28.01	2.22	F
28.98	0.96	
29.01	1.13	F
29.02	3.56	F
30.02	3.14	
30.98	0.75	
31.00	0.31	
31.97	4.58	
33.00	0.44	
36.99	1.09	
38.00	2.66	
39.00	15.66	
39.94	1.70	
40.01	3.27	
41.02	26.55	
41.99	0.57	
42.02	12.43	
43.03	45.10	
43.96	0.86	
44.03	1.62	
49.98	1.30	
50.97	3.07	F
50.99	1.64	F
51.99	0.61	
53.00	2.16	
54.00	0.87	
55.02	3.39	
56.02	1.08	
56.98	0.92	
57.03	2.12	
57.98	0.10	
58.04	0.67	
58.99	1.09	
65.00	1.02	
66.00	1.61	
67.00	1.74	
67.98	4.34	F
68.01	7.88	F
68.95	8.70	
69.02	2.91	
70.02	100.00	
70.98	0.23	
71.02	4.78	
71.98	0.32	
73.00	0.32	
74.96	0.50	
76.97	1.73	
90.99	2.53	
91.96	13.56	F
92.00	1.59	F
92.93	0.14	
92.97	0.83	
93.01	0.19	
93.98	0.54	
94.95	1.16	
95.02	0.33	
95.96	3.91	
96.96	0.25	
97.04	0.24	
97.97	0.70	
99.93	0.31	
99.99	0.94	
100.94	0.30	
101.00	1.64	
119.98	1.01	
121.95	0.26	
126.93	0.69	
129.95	0.23	
130.91	0.49	
131.97	0.37	
132.94	0.23	
134.02	0.12	
134.95	0.66	
138.93	0.15	
139.92	0.82	
141.95	0.32	
150.89	0.75	
153.92	0.29	
159.91	1.62	
161.94	1.03	
168.88	0.26	
171.90	0.36	
172.92	0.19	
173.91	0.50	
179.91	0.33	
180.86	0.34	
181.93	0.77	
192.89	0.45	
199.90	0.33	
201.92	1.07	
219.90	2.33	

EI⁺ M.Wt. 443 No. 3



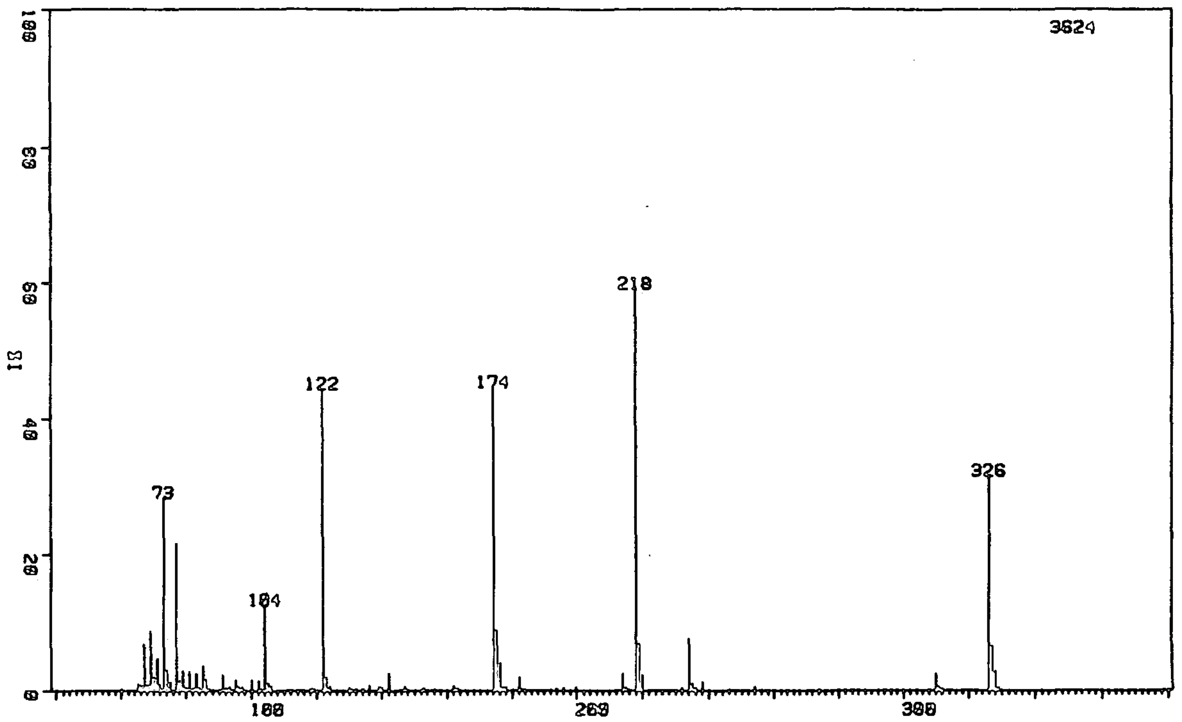
Mass	% Base
62.97	8.89
64.98	4.34
67.00	2.52
68.01	2.11
68.95	22.82
70.99	2.72
71.99	4.34
73.00	100.00
74.00	7.02
74.96	1.14
75.00	2.76
75.97	2.72
76.97	63.91
77.97	4.59
78.97	1.46
80.01	1.02
80.95	6.29
81.95	2.44
82.98	1.46
83.98	1.79
84.99	1.30
88.96	2.52
89.96	2.48
90.97	12.71
94.95	5.08
97.98	5.20
99.99	1.71
100.95	0.73
102.97	3.90
103.97	3.65
107.94	1.14
108.95	4.30
110.98	1.22
111.98	1.22
112.93	3.69
114.95	1.87
115.94	1.18
120.92	2.07
121.92	0.93
126.91	16.61
127.91	1.46
129.94	3.25
131.91	1.06
132.92	8.04
133.93	1.18
138.92	1.54
139.97	4.30
141.95	0.81
144.92	3.13
150.91	4.02
152.93	15.23
153.93	2.15
158.92	3.65
159.92	5.32
160.94	1.50
161.95	1.10
170.90	1.83
171.89	5.81
172.91	18.88
173.93	1.10
179.91	3.86
180.92	0.97
189.97	0.81
199.93	81.53
200.93	6.17
207.96	1.06
210.92	1.26
229.91	0.89
230.91	0.57
249.91	1.83
271.86	1.18
277.84	0.89
281.91	0.73
291.92	90.01
292.91	13.28
293.92	3.65
303.85	2.92
311.87	4.38
331.86	28.70
332.87	3.65

EI^{+} M.Wt. 371 No. 4



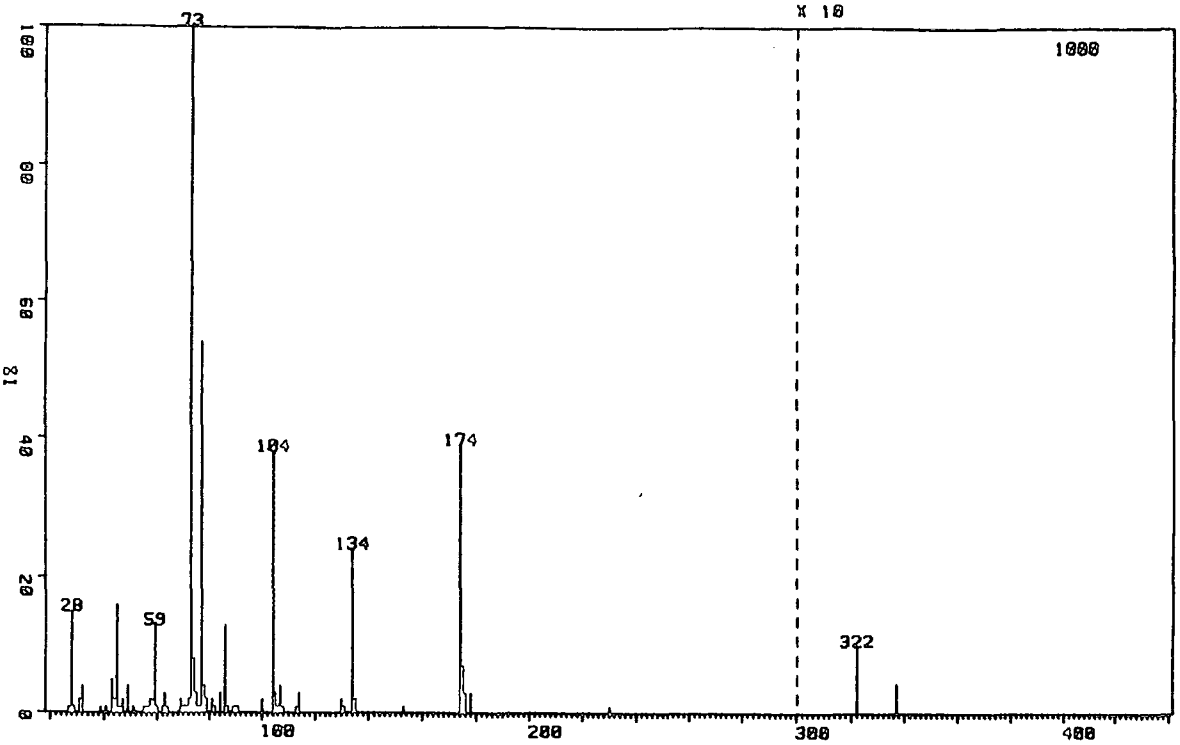
Mass	% Base
28.00	9.22
39.01	2.31
41.02	8.35
42.02	1.68
50.99	2.74
59.01	2.40
67.02	2.76
68.03	9.22
68.97	7.50 F
69.03	9.20 F
76.99	2.83
89.98	1.88
90.99	2.73
94.97	1.04
98.00	1.66
100.02	2.13
118.01	3.51
126.97	3.25
132.98	1.36
150.96	1.03
152.98	1.13
159.98	2.64
171.98	2.32
179.99	1.16
199.98	1.42
220.01	100.00
220.36	0.04
220.43	0.08
220.63	0.05
221.01	8.30
222.00	0.36
222.97	0.06
227.99	0.05
229.01	0.05
229.99	0.09
239.97	0.08
240.98	0.08
241.97	2.28
242.98	0.20
247.98	0.09
248.99	0.05
250.00	0.11
251.00	0.09
262.01	0.04
268.00	0.12
270.00	1.40
271.01	0.12
271.98	0.09
274.00	0.08
282.01	0.16
284.96	0.05
285.00	0.06
289.99	0.05
291.98	0.08
292.80	0.05
293.56	0.05
299.98	0.04
302.00	0.14
303.98	0.18
309.97	0.08
311.99	0.80
312.62	0.04
312.74	0.07
313.15	0.16
313.79	0.06
313.90	0.03
314.32	0.04
323.98	0.14
332.00	0.43
333.01	0.07
349.98	0.05
351.58	0.06
352.00	8.67
352.51	0.04
353.01	1.02
369.99	0.61
371.01	0.07

CI (*i*- butane) M.Wt. 325 No. 5



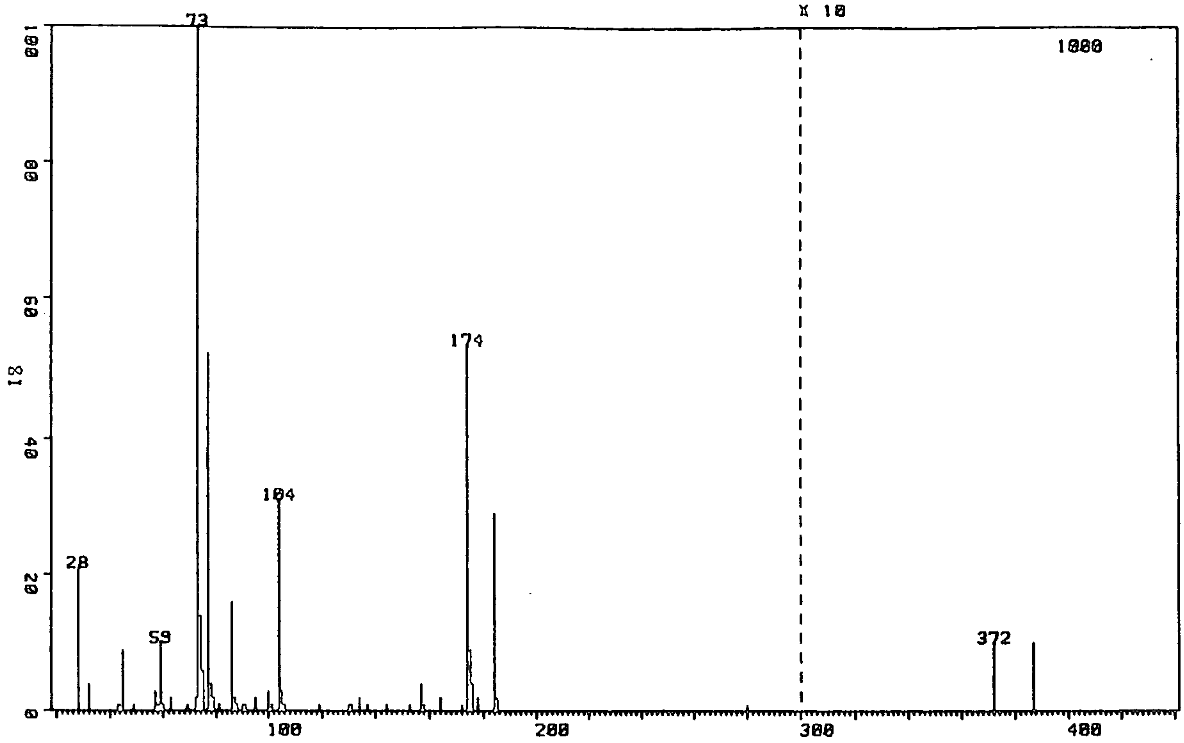
MASS	%HT. BASE
65.08	1.02
66.08	0.88
67.07	6.93
68.04	0.97
68.93	0.33
69.00	8.83
69.94	2.01
71.00	4.83
71.99	0.97
72.05	0.47
73.04	28.48
74.06	3.09
75.05	1.24
77.02	21.61
77.98	1.49
78.96	2.87
79.91	0.50
80.97	2.73
82.01	0.41
83.06	2.57
84.08	0.52
85.09	3.67
86.03	1.60
86.08	0.30
87.01	0.30
90.94	2.35
91.98	0.44
93.02	0.50
95.01	1.68
95.98	0.63
97.05	0.52
99.91	1.71
101.98	1.52
103.02	0.33
104.00	12.67
105.00	1.16
106.00	0.66
117.99	0.30
118.98	0.30
121.94	44.40
122.96	2.01
123.99	0.61
129.91	0.55
130.95	0.25
131.97	0.33
133.97	0.41
135.99	0.86
138.99	0.63
139.87	0.55
141.95	2.62
147.02	0.58
152.98	0.30
161.94	0.75
163.03	0.41
174.03	44.78
175.02	9.05
176.02	4.03
177.01	0.63
177.97	0.52
181.92	1.99
199.86	0.61
213.96	2.57
214.95	0.41
217.91	59.16
218.91	7.01
219.88	2.29
231.94	0.41
233.97	7.78
234.96	1.13
235.95	0.47
237.91	1.27
253.92	0.63
273.91	0.28
307.93	0.25
309.86	2.54
310.91	0.55
311.91	0.28
325.96	31.65
326.95	6.59
327.95	2.84
328.95	0.44

EI^{+} M.Wt. 337 No. 6



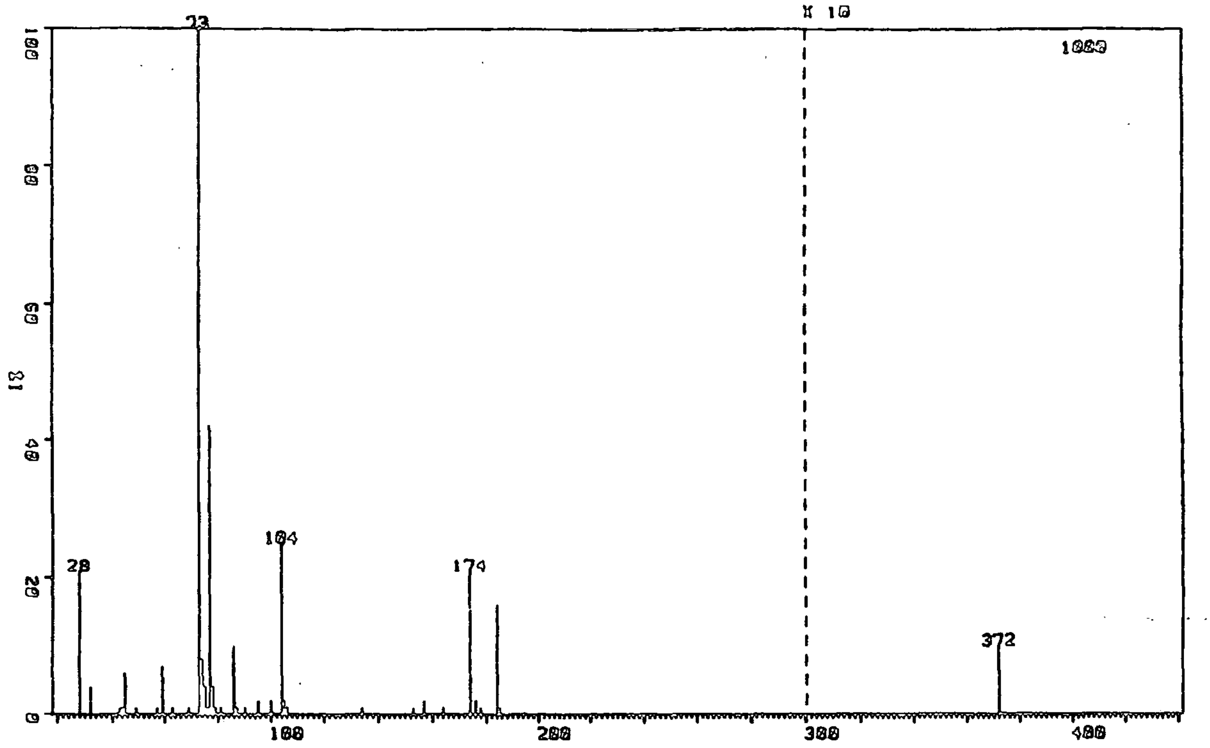
MASS	%HT. BASE
27.21	0.75
28.09	14.91
28.94	1.46
30.85	1.74
31.96	3.52
38.96	1.03
40.95	0.53
42.03	0.39
43.06	4.51
43.11	0.78
44.10	2.10
45.12	15.59
46.12	1.07
47.05	1.67
47.08	0.53
48.95	4.15
50.94	0.71
55.10	0.64
56.09	0.85
57.08	2.38
58.04	1.67
59.00	13.28
59.92	1.28
60.98	0.53
62.02	0.50
63.06	3.41
64.09	0.39
68.98	1.60
69.88	0.50
69.93	0.43
71.01	0.64
72.06	1.88
73.09	100.00
74.12	7.74
75.08	3.20
76.06	1.03
77.04	53.94
78.01	3.84
78.96	1.88
80.93	2.45
81.97	0.71
84.05	2.98
86.06	13.03
87.05	1.42
88.03	0.46
88.97	0.89
89.91	0.71
90.98	0.50
99.93	1.95
100.96	0.39
104.04	38.21
105.04	2.81
106.03	1.21
107.01	4.23
107.99	0.92
113.01	0.57
114.03	2.66
118.97	0.39
129.96	1.95
131.01	0.71
134.02	23.54
135.03	1.99
153.02	1.24
158.05	0.43
174.08	39.20
175.10	7.07
176.08	3.20
177.08	0.39
178.04	2.77
179.97	0.46
229.95	1.31
322.00	0.89
337.03	0.43

EI$^+$ M.Wt. 387 No. 7a



MASS	%HT. BASE
28.05	21.10
30.83	0.37
31.94	3.83
39.80	0.24
43.06	0.71
44.11	1.05
45.13	8.94
46.13	0.37
47.07	0.27
48.95	0.90
50.92	0.34
57.06	2.76
58.04	0.56
58.98	10.48
59.90	0.66
60.96	0.32
63.03	1.71
68.94	1.07
72.03	2.17
73.05	100.00
73.71	0.29
74.06	14.24
75.08	5.98
76.05	0.46
77.03	52.11
78.00	4.00
78.95	1.54
80.90	1.20
86.04	15.80
87.05	1.51
88.01	0.54
88.94	0.32
89.89	0.81
90.99	0.54
95.04	2.15
96.04	0.24
99.96	3.49
100.99	0.56
102.05	0.29
104.05	30.57
105.07	2.61
106.05	1.05
108.01	0.27
118.98	0.71
129.94	0.78
130.99	0.93
133.99	1.83
135.04	0.42
136.98	0.59
143.97	0.63
152.97	1.44
156.92	3.57
158.00	0.85
163.93	1.93
172.03	0.54
172.47	0.27
174.01	53.11
174.91	9.47
176.04	4.22
177.06	0.44
177.99	1.66
183.92	28.60
184.94	1.71
279.80	1.00
371.82	0.22
386.81	0.22

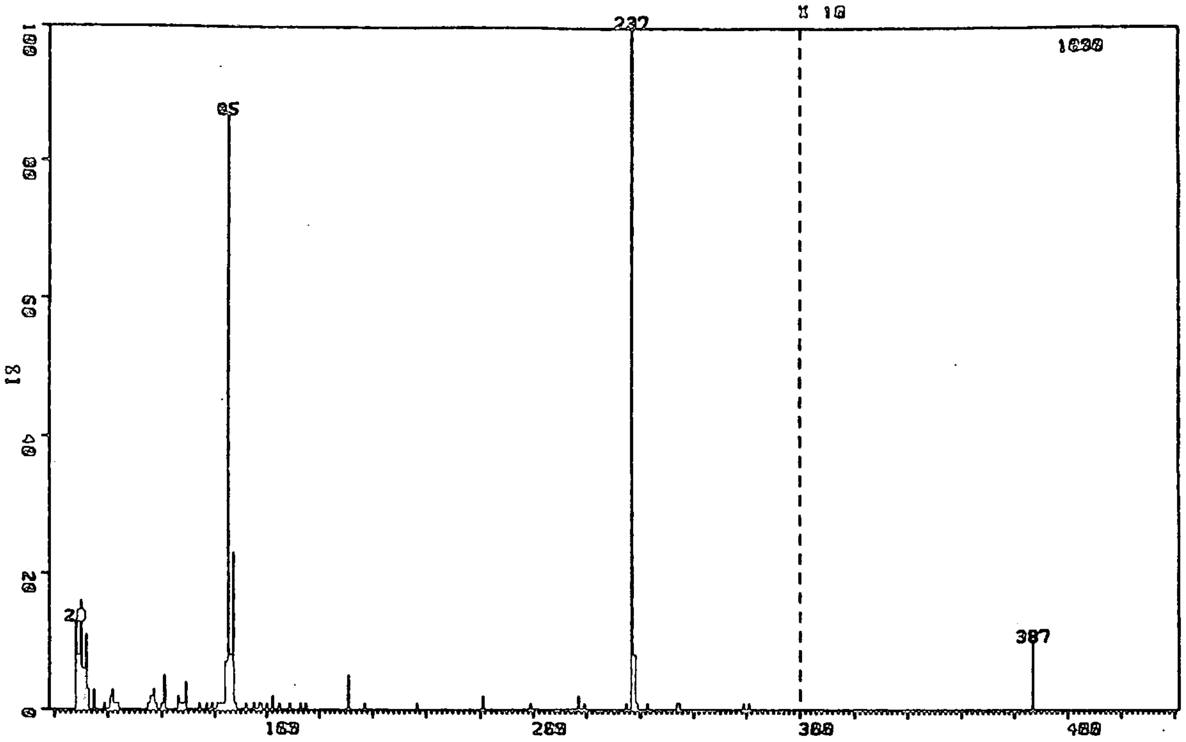
EI$^+$ M.Wt. 387 No. 7b



MASS	%HT. BASE
28.05	21.28
28.92	0.28
30.83	0.28
31.94	3.83
39.80	0.39
43.06	0.54
44.11	0.74
45.13	6.34
46.13	0.33
47.06	0.36
48.94	0.62
50.93	0.28
57.06	0.51
58.04	0.41
58.97	7.14
59.89	0.41
63.03	1.16
68.94	0.62
71.48	0.39
71.59	0.23
72.99	100.00
73.74	7.83
75.13	3.54
76.09	0.62
76.26	0.31
77.05	42.18
77.78	0.26
78.02	3.67
78.98	1.26
80.94	1.16
86.08	9.53
87.06	0.74
89.92	0.56
91.00	0.44
95.05	1.57
99.97	1.75
100.98	0.26
102.04	0.33
103.35	0.28
104.04	25.19
105.06	2.11
106.06	0.90
118.97	0.28
131.00	0.44
133.99	1.23
136.97	0.49
153.01	0.90
156.93	2.44
158.01	0.39
163.93	1.39
174.07	20.77
175.53	0.26
175.67	0.28
176.02	1.82
177.97	0.62
183.87	16.02
184.94	1.16
371.74	0.44

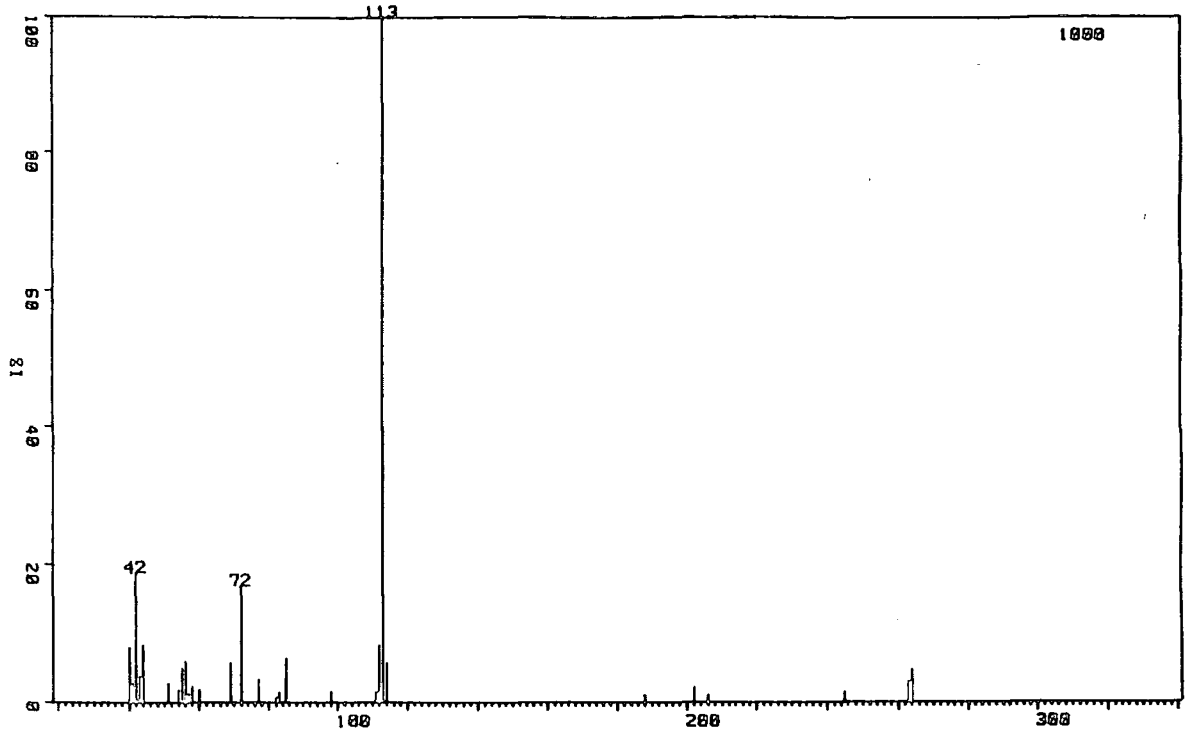
CI (NH$_3$)

No. 8



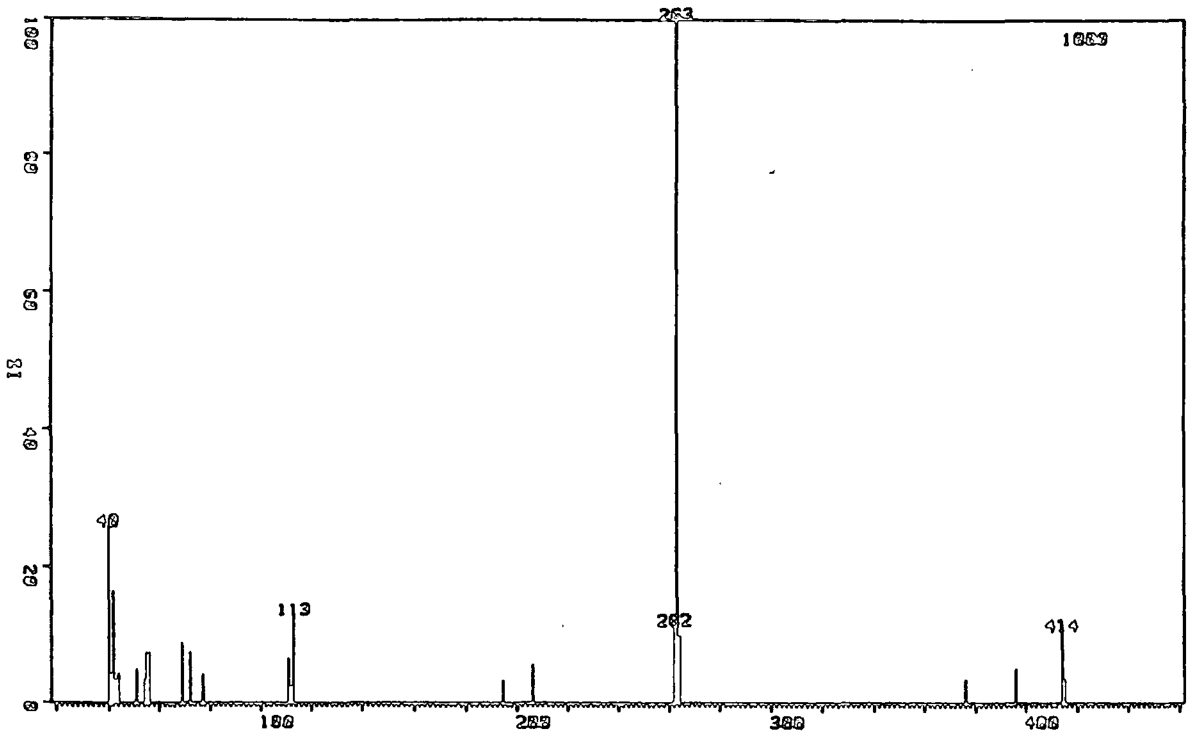
MASS	%HT. BASE
27.22	0.34
28.11	12.70
28.98	8.39
29.82	16.30
30.89	6.45
31.97	2.48
32.02	11.48
33.11	3.17
35.10	0.29
35.19	2.80
36.10	0.34
38.96	1.00
39.80	0.31
40.94	2.23
42.03	2.51
43.09	1.08
44.08	0.31
44.11	0.37
44.15	1.34
45.16	0.34
46.16	0.49
54.13	0.43
55.14	0.80
56.12	1.60
57.12	2.71
58.09	1.31
59.01	0.29
59.95	0.60
61.01	5.22
65.14	0.26
66.12	1.94
67.10	0.54
68.07	0.54
68.96	3.65
69.03	1.46
69.97	0.43
71.04	0.40
72.07	0.26
73.09	0.40
74.09	0.54
75.07	0.49
77.06	0.86
78.03	0.43
78.99	0.54
79.96	0.29
81.02	1.46
82.05	0.54
83.10	0.74
84.06	6.65
85.06	87.27
86.06	7.68
87.06	23.15
88.04	1.06
90.98	0.49
92.00	0.71
92.99	0.37
93.06	0.43
94.07	0.49
95.08	0.94
96.10	0.43
97.08	0.54
98.06	0.71
99.01	0.43
99.96	1.23
102.05	1.91
104.06	0.37
105.09	0.54
107.10	0.29
109.06	0.60
110.03	0.37
111.07	0.29
112.09	0.34
113.03	0.94
113.11	0.31
114.12	0.37
115.11	0.83
116.05	0.31
117.09	0.34
117.99	0.37
119.03	0.49
121.06	0.43
123.12	0.40
129.98	0.37
130.96	4.82
133.04	0.37
134.14	0.26
135.15	0.31
136.15	0.31
137.13	0.54
139.05	0.46
145.09	0.29
148.99	0.34
155.05	0.23
156.02	0.26
157.01	0.77
163.13	0.49
174.03	0.43
177.03	0.29
180.95	1.60
194.05	0.31
199.02	1.31
205.07	0.49
217.07	2.08
218.06	0.31
219.06	0.57
231.01	0.31
235.06	0.69
237.07	100.00
238.06	7.79
239.05	0.49
243.01	0.26
254.10	1.20
255.08	0.26
279.20	0.31
281.03	0.40
387.27	0.49

EI$^+$ M.Wt. 264 No. 9



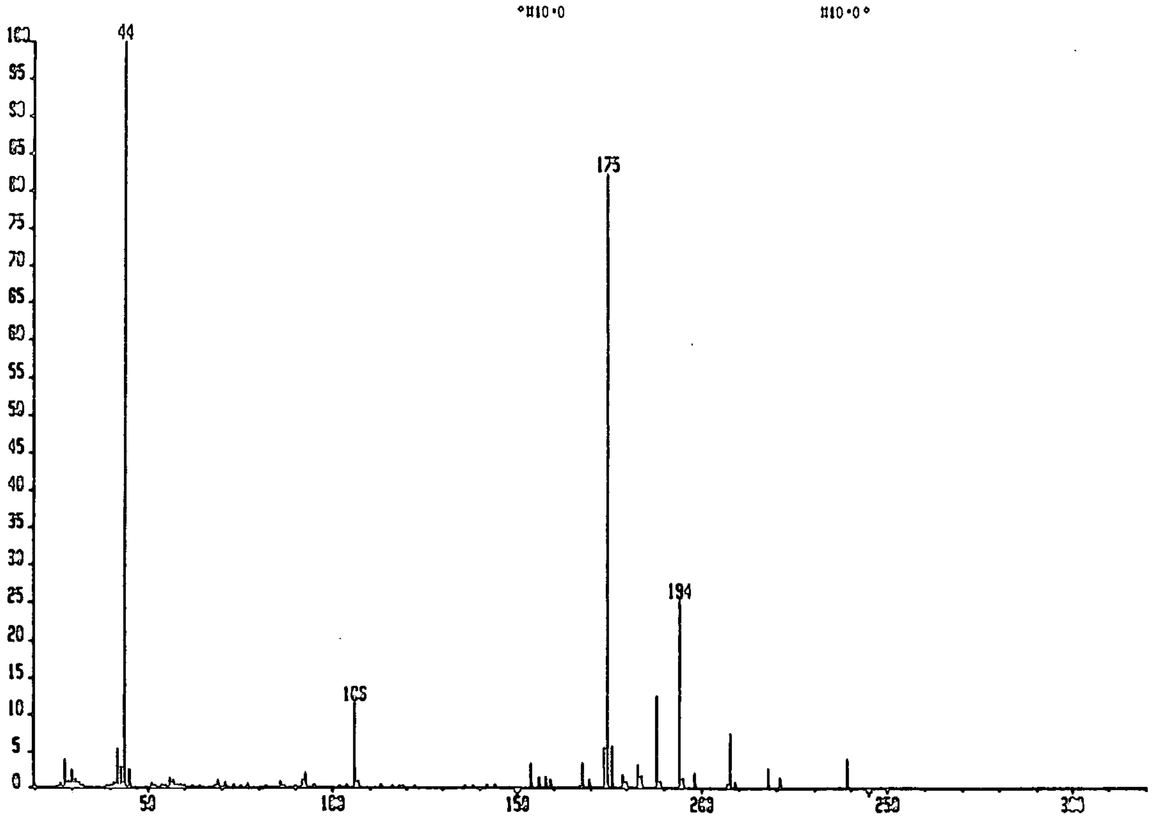
MASS	%HT. BASE
27.22	0.84
28.10	100.00
28.96	1.13
28.99	0.61
29.82	0.67
31.97	33.95
39.82	2.87
39.87	0.32
40.96	0.98
42.05	6.69
43.12	1.36
44.11	0.46
44.16	3.01
50.96	1.01
54.15	0.67
55.17	1.79
56.16	2.23
57.12	0.49
58.09	0.93
59.96	0.69
69.02	2.14
72.12	5.90
77.10	1.22
82.04	0.29
83.12	0.61
85.13	2.34
98.04	0.61
111.05	0.61
112.08	3.04
113.12	35.63
114.11	2.05
188.16	0.43
202.19	0.81
206.19	0.35
245.30	0.58
263.23	1.07
264.23	1.65

EI^+ M.Wt. 414 No. 10



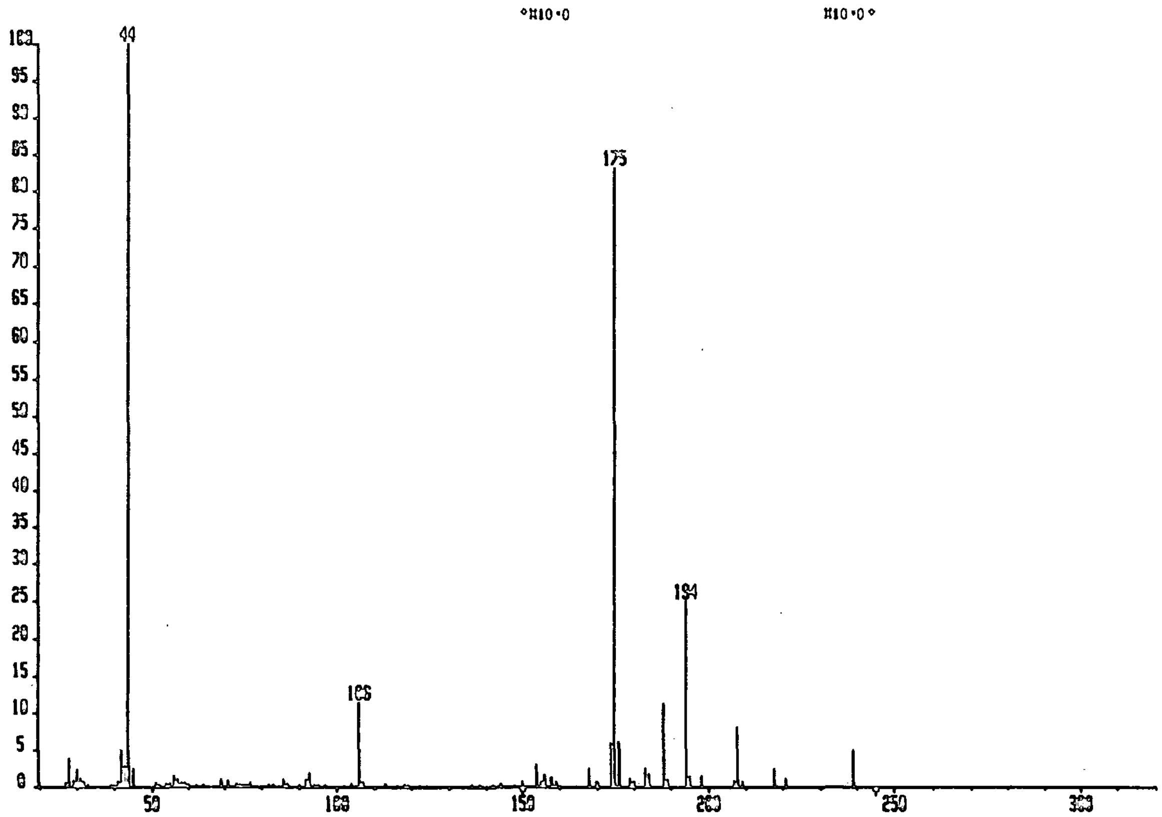
MASS	%HT. BASE
28.10	100.00
28.96	1.05
31.97	34.34
39.82	3.22
40.96	0.45
42.05	2.04
43.12	0.36
44.11	0.42
44.17	0.45
50.97	0.57
54.15	0.39
55.17	0.93
56.16	0.90
69.02	1.11
72.12	0.90
77.10	0.51
111.12	0.81
112.13	0.30
113.15	1.62
194.25	0.36
206.29	0.69
262.37	1.41
263.36	12.26
264.39	1.23
375.72	0.36
395.80	0.63
413.91	1.32
414.91	0.36

EI^{+} M.Wt. 238 No. 11a



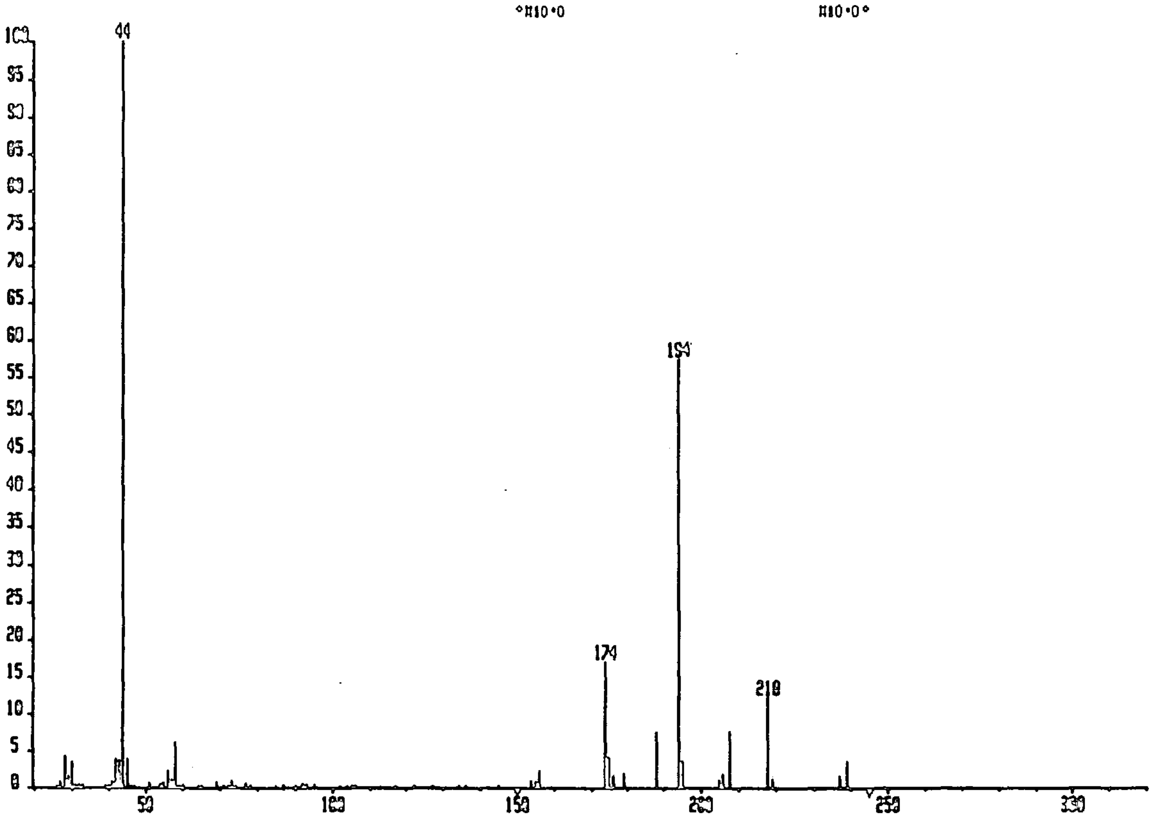
Mass	% Base
28.01	3.86
30.02	2.24
31.03	1.10
42.02	5.36
43.02	2.69
44.03	100.00
45.03	2.49
56.03	1.22
93.01	1.95
102.00	0.08
104.00	0.33
106.01	11.42
107.01	0.68
112.96	0.23
116.00	0.09
118.01	0.17
119.02	0.09
119.04	0.07
121.98	0.12
135.99	0.17
138.01	0.19
141.98	0.27
144.00	0.29
147.99	0.07
153.97	0.33
156.00	0.13
158.00	0.14
159.02	0.10
167.98	0.34
169.99	0.11
173.96	0.54
174.97	8.26
175.99	0.56
179.03	0.16
179.98	0.07
183.00	0.31
184.01	0.16
187.99	1.24
188.99	0.07
193.98	2.51
194.98	0.12
198.02	0.20
206.96	0.04
207.99	0.74
209.00	0.07
218.02	0.26
220.99	0.14
239.03	0.39

EI$^+$ M.Wt. 238 No. 11b



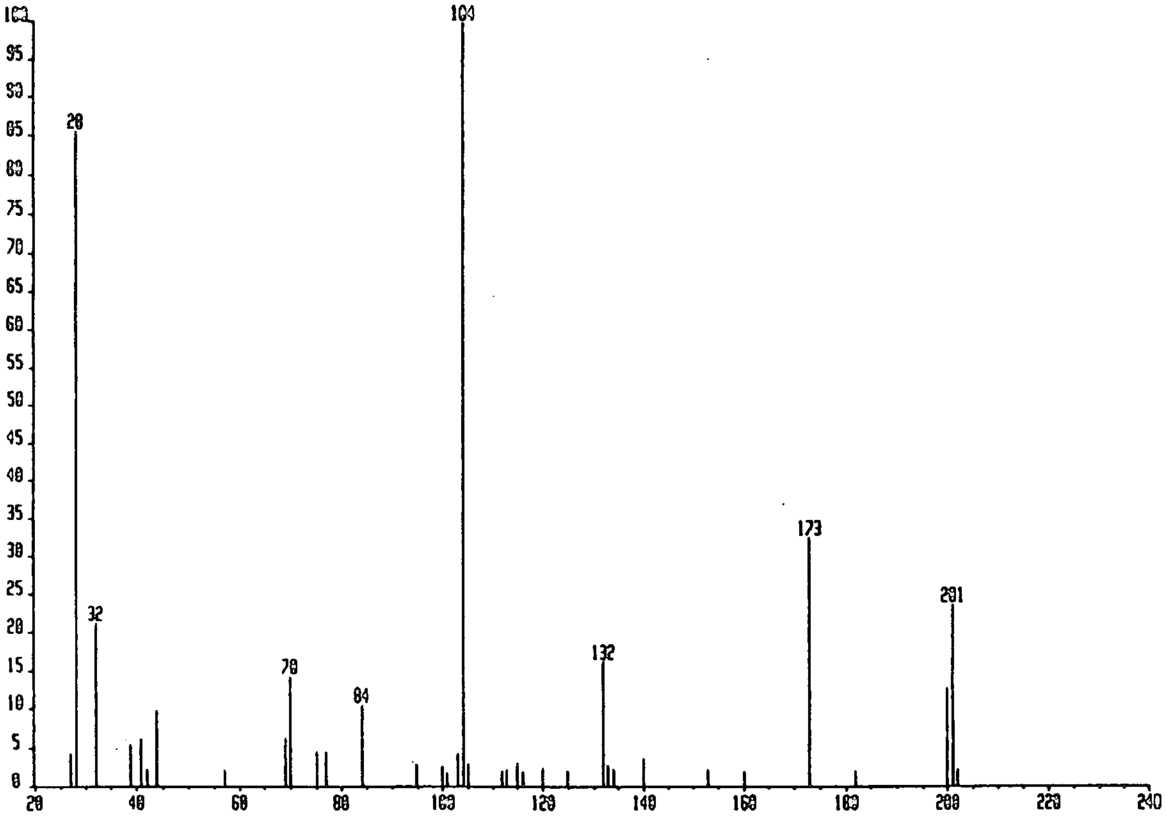
Mass	% Base
28.01	3.80
30.02	2.33
31.03	1.01
42.02	5.07
43.02	2.68
44.03	100.00
45.03	2.47
56.03	1.39
93.01	1.88
101.99	0.05
104.00	0.32
105.00	0.06
105.02	0.05
106.01	11.42
107.01	0.60
112.97	0.23
115.98	0.04
116.00	0.06
118.01	0.26
119.01	0.11
121.98	0.07
122.00	0.06
124.00	0.05
135.99	0.17
138.01	0.13
141.98	0.16
143.99	0.24
147.98	0.06
150.02	0.06
153.97	0.30
154.97	0.06
155.99	0.15
158.01	0.12
159.02	0.07
167.98	0.24
169.99	0.06
170.01	0.07
173.98	0.60
174.98	8.35
175.99	0.60
179.02	0.11
179.98	0.06
183.00	0.24
184.00	0.16
187.99	1.11
188.99	0.09
193.98	2.49
194.97	0.14
198.02	0.14
206.98	0.07
207.99	0.80
209.00	0.06
218.01	0.25
220.98	0.11
239.03	0.49

EI$^+$ M.Wt. 238 No. 11c



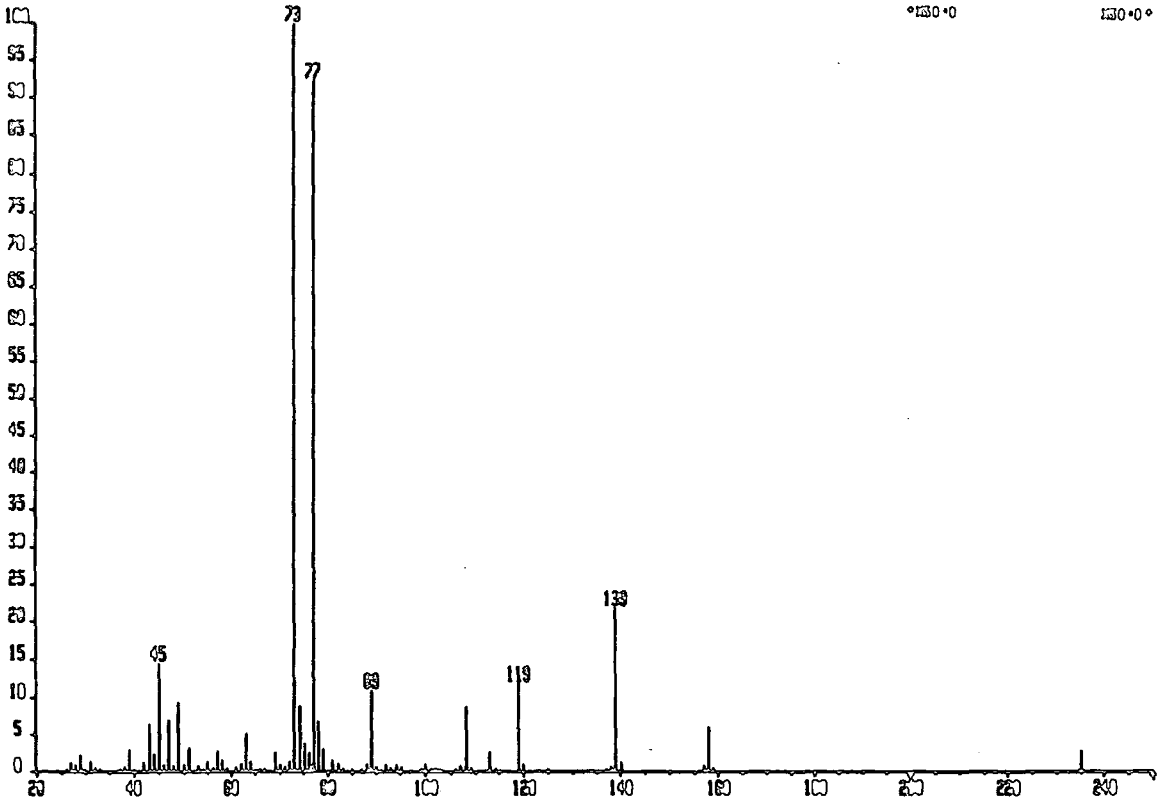
Mass	% Base
28.01	4.18
29.02	1.56
30.02	3.55
42.02	3.76
43.03	3.65
44.03	100.00
45.03	3.81
56.03	2.28
57.04	1.09
58.05	6.09
101.98	0.11
104.00	0.09
105.01	0.09
106.02	0.18
112.97	0.07
117.05	0.09
121.99	0.13
126.99	0.09
133.99	0.09
134.00	0.07
135.99	0.11
144.95	0.15
153.97	0.09
154.98	0.08
155.99	0.22
173.98	1.70
174.99	0.41
176.00	0.15
179.03	0.18
187.99	0.74
193.98	5.76
194.99	0.34
204.98	0.09
205.98	0.18
207.99	0.75
218.03	1.22
219.03	0.11
237.02	0.15
239.04	0.35
249.01	0.07

EI$^+$ M.Wt. 201 No. 12



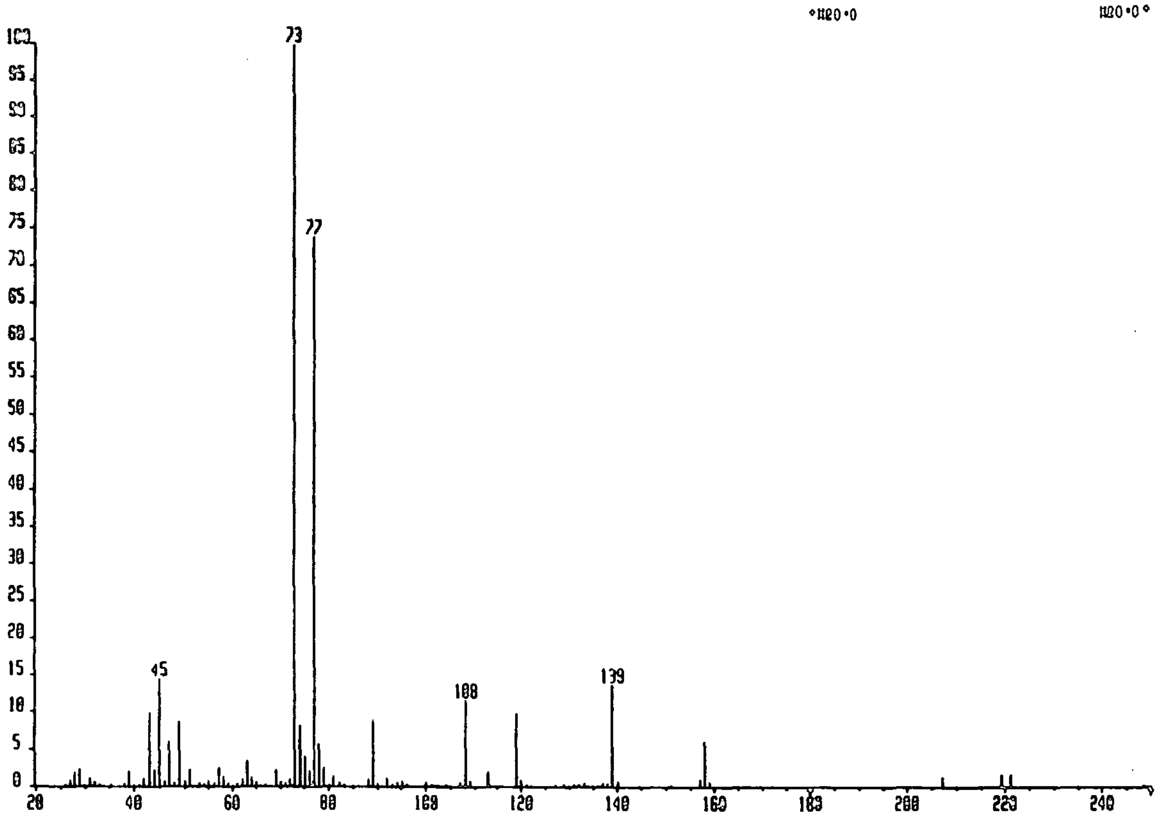
Mass	% Base	
27.00	4.11	
27.98	85.44	F
28.00	22.47	F
31.97	20.97	
39.00	5.38	
41.00	6.09	
42.01	2.06	
43.96	9.65	
56.98	2.14	
68.96	6.25	
70.03	14.00	
74.96	4.51	
76.98	4.51	
83.98	10.44	
94.96	2.85	
100.00	2.53	
100.96	1.66	
102.97	4.19	
103.97	100.00	
104.98	2.77	
112.00	1.98	
112.94	2.06	
114.97	3.01	
115.96	1.74	
119.91	2.22	
124.91	1.98	
131.96	15.98	
132.93	2.61	
133.93	2.22	
139.93	3.56	
152.93	2.06	
159.95	1.74	
172.91	32.28	
181.95	1.98	
199.95	12.66	
200.95	23.42	
201.96	2.06	

EI$^+$ M.Wt. 250 No. 13a



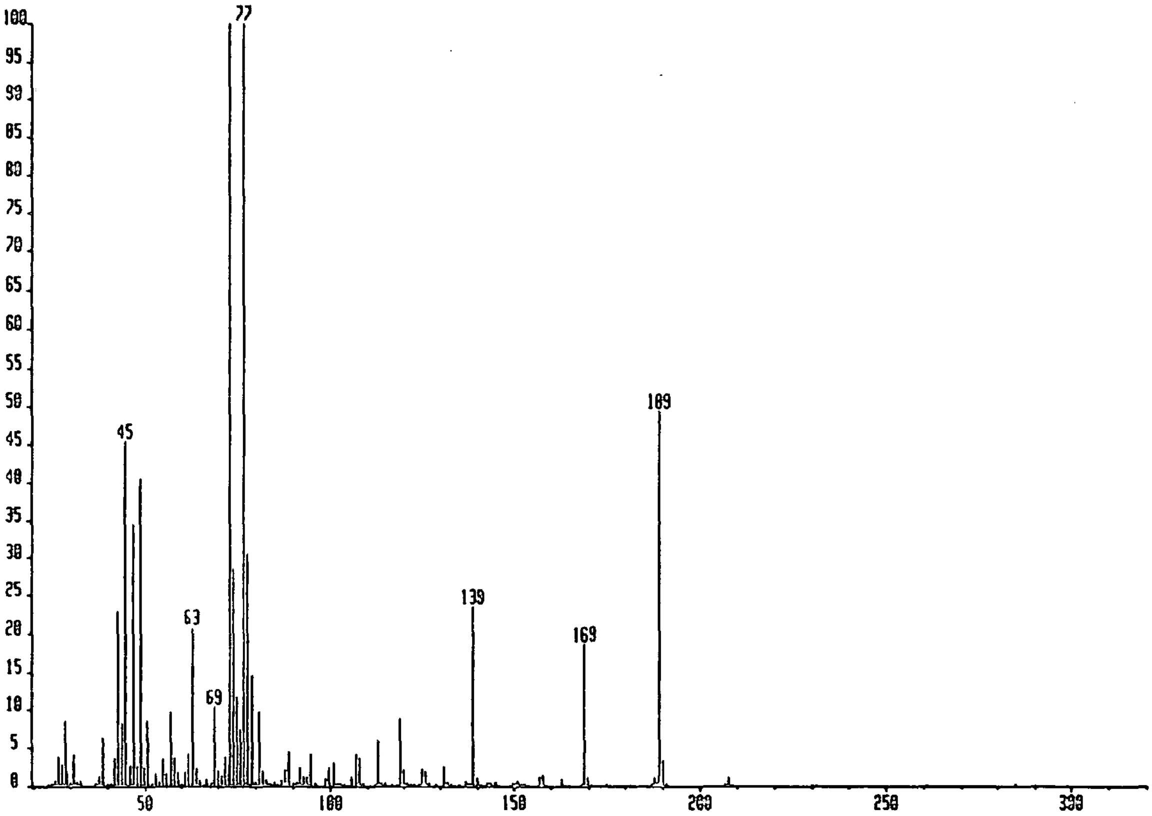
Mass	% Base
28.98	2.07
39.03	2.72
43.02	6.25
44.02	2.17
45.03	14.28
46.99	6.82 F
49.01	9.26
51.03	2.98
57.04	2.62
63.04	5.05
69.03	2.39
73.08	100.00
74.08	8.80
75.03	2.06 F
75.08	3.68 F
76.05	2.37
77.06	92.44
78.06	6.66
79.05	2.81
89.07	10.75
100.05	0.74
101.07	0.18
101.27	0.04
101.43	0.05
101.68	0.06
101.85	0.09
101.98	0.09
102.04	0.07
102.07	0.06
102.11	0.05
102.19	0.10
102.32	0.06
102.37	0.05
102.53	0.04
102.55	0.04
102.77	0.06
103.09	0.05
106.05	0.11
107.06	0.56
107.97	0.07
108.07	8.58
109.07	0.33
112.04	0.07
113.05	2.43
114.05	0.09
115.09	0.06
118.95	0.09
119.06	11.72
120.06	0.74
121.09	0.07
123.04	0.06
125.05	0.08
130.94	0.04
130.97	0.04
132.05	0.04
133.97	0.06
137.07	0.08
138.06	0.40
138.57	0.04
138.78	0.08
138.93	0.18
139.07	21.61
139.19	0.06
140.07	1.12
157.06	0.61
157.83	0.06
157.93	0.05
158.07	5.93
159.07	0.26
235.09	0.05

EI$^+$ M.Wt. 250 No. 13b



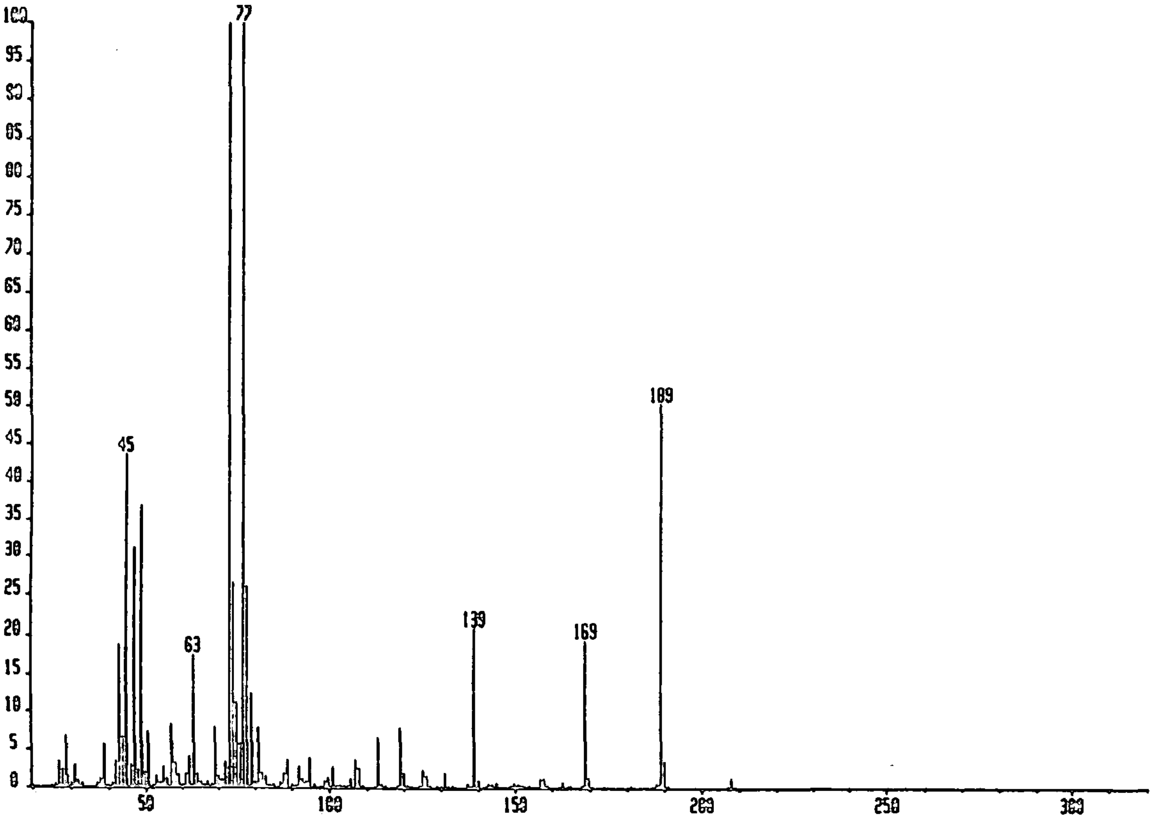
Mass	% Base	
28.00	1.76	
28.98	2.07	
39.03	1.98	
43.03	9.86	
44.02	2.16	
45.03	14.23	
46.99	5.93	F
49.01	8.50	
51.03	2.10	
57.04	2.44	
58.05	1.19	
63.04	3.33	
64.04	1.13	
69.03	2.13	
73.08	100.00	
74.08	8.10	
75.04	1.60	F
75.08	3.99	F
76.05	1.95	
77.05	73.98	
78.06	5.54	
79.05	2.40	
81.03	1.23	
89.07	8.80	
92.11	1.09	
100.05	0.47	
101.07	0.18	
101.47	0.06	
102.08	0.07	
102.62	0.04	
104.09	0.09	
107.06	0.51	
107.97	0.11	
108.07	11.39	
109.07	0.58	
113.04	1.76	
118.95	0.09	
119.06	9.76	
120.06	0.69	
121.07	0.09	
122.10	0.06	
126.06	0.05	
127.07	0.21	
128.95	0.14	
130.96	0.11	
131.96	0.11	
133.09	0.26	
135.97	0.06	
137.07	0.25	
138.06	0.33	
138.93	0.11	
139.07	13.53	
140.07	0.65	
151.07	0.06	
157.07	0.70	
158.07	5.96	
159.07	0.42	
207.11	0.06	
219.08	0.07	
221.09	0.07	

EI$^+$ M.Wt. 300 No. 14a



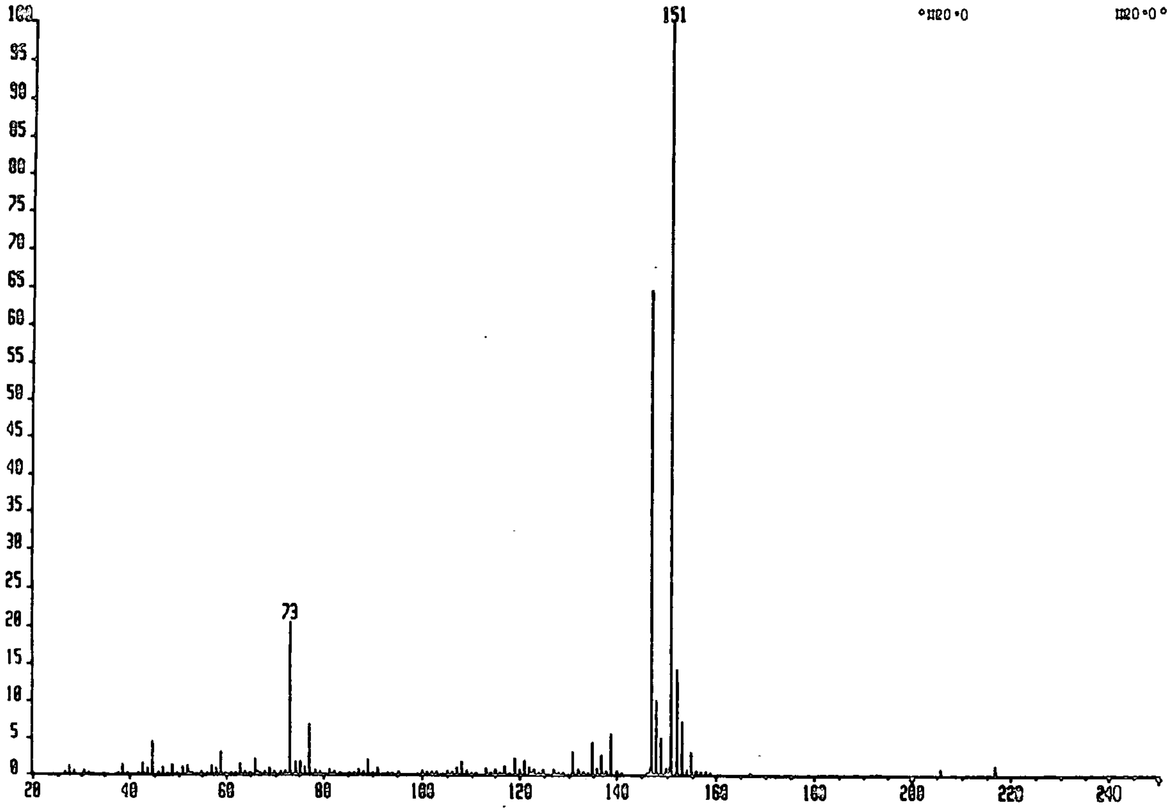
Mass	% Base	
26.98	3.69	
27.93	2.62	F
27.96	1.93	F
28.94	8.45	
28.99	1.73	
30.94	3.95	
37.95	1.22	
38.96	6.44	
41.93	3.60	
42.93	22.80	
43.94	8.11	
44.95	45.55	
45.95	2.60	
46.91	34.33	F
46.95	1.57	F
47.91	2.45	
48.92	40.47	
49.92	2.43	F
50.93	8.56	
52.92	1.61	
54.93	3.50	
55.93	1.44	
56.94	9.75	
57.95	3.73	
58.96	1.82	
60.92	1.93	
61.92	4.31	
62.93	20.70	
63.93	2.20	
68.92	10.43	
69.94	1.99	
70.95	1.27	
71.95	3.92	
72.89	2.69	
72.96	100.00	0
73.96	28.64	
74.91	6.01	F
74.96	11.71	F
75.93	7.46	F
76.86	2.87	F
76.93	100.00	0
77.93	30.46	
78.93	14.47	
80.90	9.82	
81.91	1.94	F
87.92	2.08	
88.93	4.47	
91.95	2.37	
92.91	1.21	
93.91	1.16	
94.91	4.20	
99.90	2.37	
100.91	3.01	
105.90	1.23	
106.90	4.21	
107.91	3.51	
112.89	5.91	
118.90	8.78	
119.90	2.00	
124.88	2.23	
125.89	1.77	
130.87	2.57	
138.89	23.55	
139.89	1.10	
156.88	1.08	
157.88	1.32	
168.87	18.61	
169.88	1.05	
188.85	49.66	
189.85	3.23	
206.86	0.10	
207.87	1.08	
208.86	0.06	
225.84	0.05	
284.88	0.11	

EI$^+$ M.Wt. 300 No. 14b



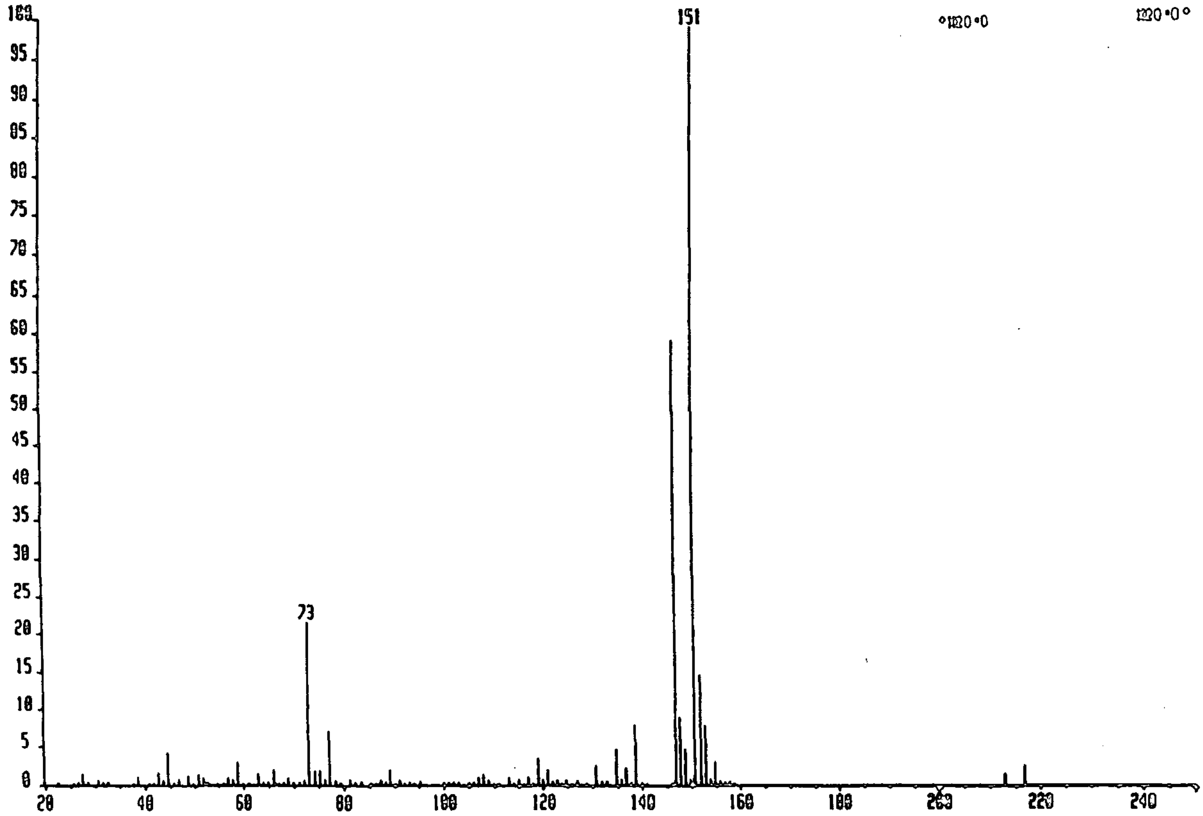
Mass	% Base	
26.99	3.32	
27.93	1.91	F
27.96	2.25	F
28.94	6.61	
28.99	1.39	
30.94	2.81	
38.96	5.58	
41.93	3.35	
42.93	18.75	
43.94	6.56	
44.95	43.48	
45.95	2.79	
46.91	31.13	F
46.95	1.47	F
47.91	2.26	
48.92	36.79	
49.92	1.97	F
50.94	7.22	
52.91	1.30	
54.93	2.55	
55.93	1.00	
56.94	8.20	
57.95	3.16	
58.96	1.45	
60.92	1.66	
61.92	4.06	
62.93	17.36	
63.93	1.59	
68.91	7.92	
69.94	1.38	
71.96	3.31	F
72.90	2.59	F
72.96	100.00	0
73.96	26.39	
74.91	5.39	F
74.95	11.13	F
75.93	5.64	F
76.86	2.69	F
76.93	100.00	0
77.93	25.88	
78.93	12 28	
80 90	7 92	
81.91	1.75	
82.92	1 30	
87.92	1 73	
88 93	3.57	
91 95	2.73	
92 91	1 09	
94.92	3.89	
99.90	1.16	
100.91	2.60	
105.90	1.01	
106.90	3.57	
107.91	2.59	
112.89	6.90	
118.89	7.91	
119.90	1.84	
124.89	2.23	
125.89	1.50	
130.87	1.93	
138.89	20.81	
157.88	1.01	
168.86	19.29	
169.87	1.21	
188.87	50.47	
189.87	3.35	
206.87	0.11	
207.87	1.25	
208.88	0.04	
274.85	0.05	

EI$^+$ M.Wt. 324 No. 15a



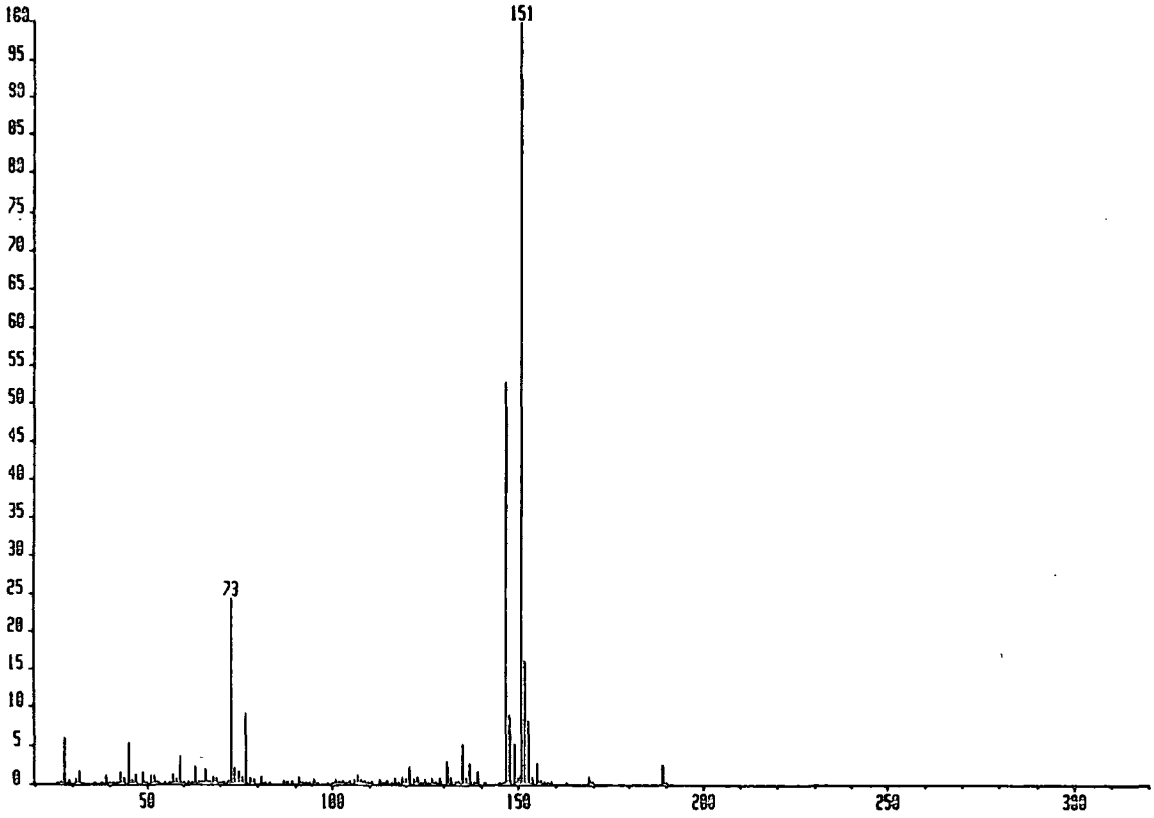
Mass	% Base
27.47	1.06
38.60	1.16
42.62	1.30
44.66	4.51
48.69	1.26
51.73	1.05
58.83	3.07
62.85	1.38
65.90	2.02
73.07	20.40
74.10	1.64
75.10	1.67
77.16	6.85
89.14	1.93
107.94	1.69
116.89	1.10
118.87	2.16
120.86	1.86
130.87	2.97
134.85	4.44
136.86	2.51
138.85	5.61
146.89	64.37
147.89	10.02
148.89	5.07
150.55	0.88 F
150.86	100.00 F
151.70	0.12
151.86	14.25
152.69	0.06
152.86	7.35
153.86	0.66
154.84	3.02
155.83	0.38
156.83	0.30
157.83	0.52
158.80	0.11
166.89	0.10
192.80	0.06
205.79	0.04
216.72	0.05

EI$^+$ M.Wt. 324 No. 15b



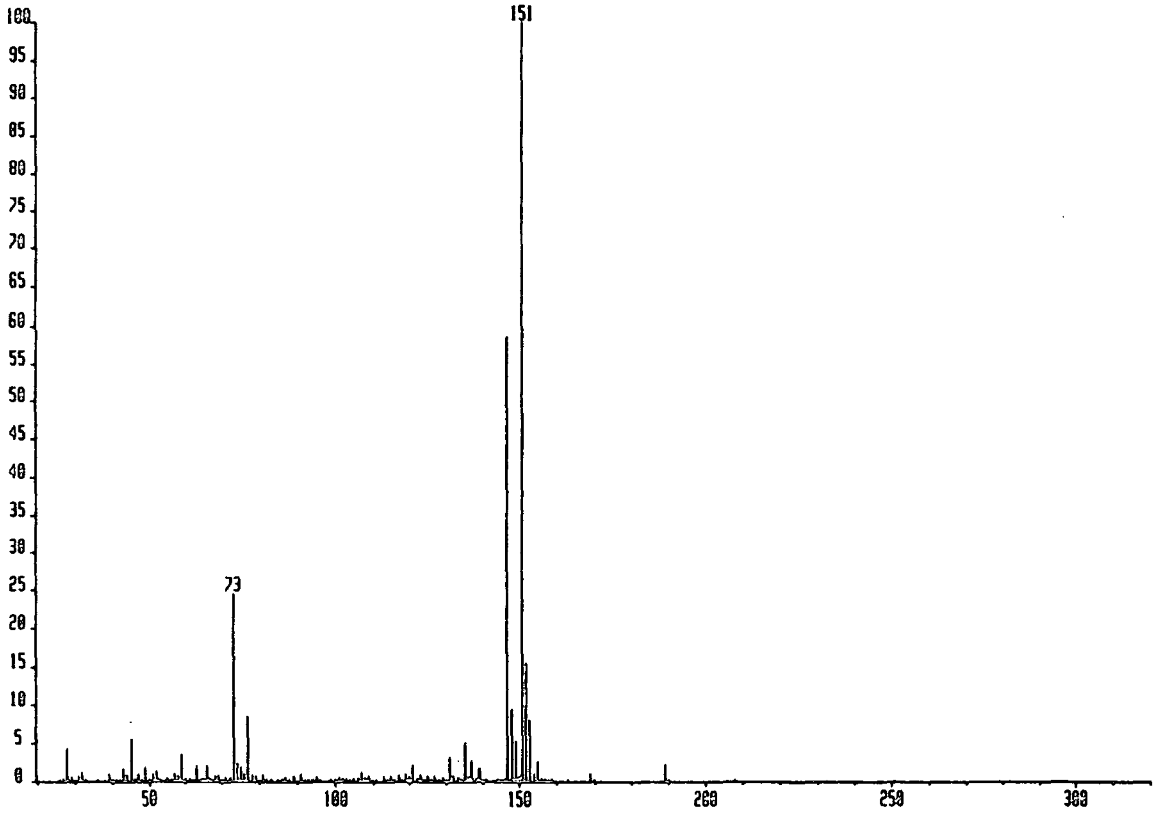
Mass	% Base	
27.47	1.32	
38.60	1.09	
42.63	1.47	
44.66	4.16	
48.69	1.24	
50.73	1.32	
58.83	2.88	
62.85	1.43	
65.90	2.00	
73.07	21.57	
74.10	1.86	
75.09	1.89	F
77.16	6.91	
89.14	2.02	
107.94	1.34	
116.89	1.04	
118.87	3.44	
120.86	1.89	
130.88	2.58	
134.85	4.76	
136.86	2.34	
138.84	7.86	
146.89	59.41	
147.89	8.93	
148.89	4.63	
150.58	0.87	F
150.87	100.00	F
151.71	0.15	
151.87	14.65	
152.86	7.76	
153.86	0.81	
154.83	3.05	
155.84	0.47	
156.82	0.29	
157.82	0.45	
158.82	0.17	
212.81	0.07	
216.75	0.13	

EI^+ M.Wt. 374 No. 16a



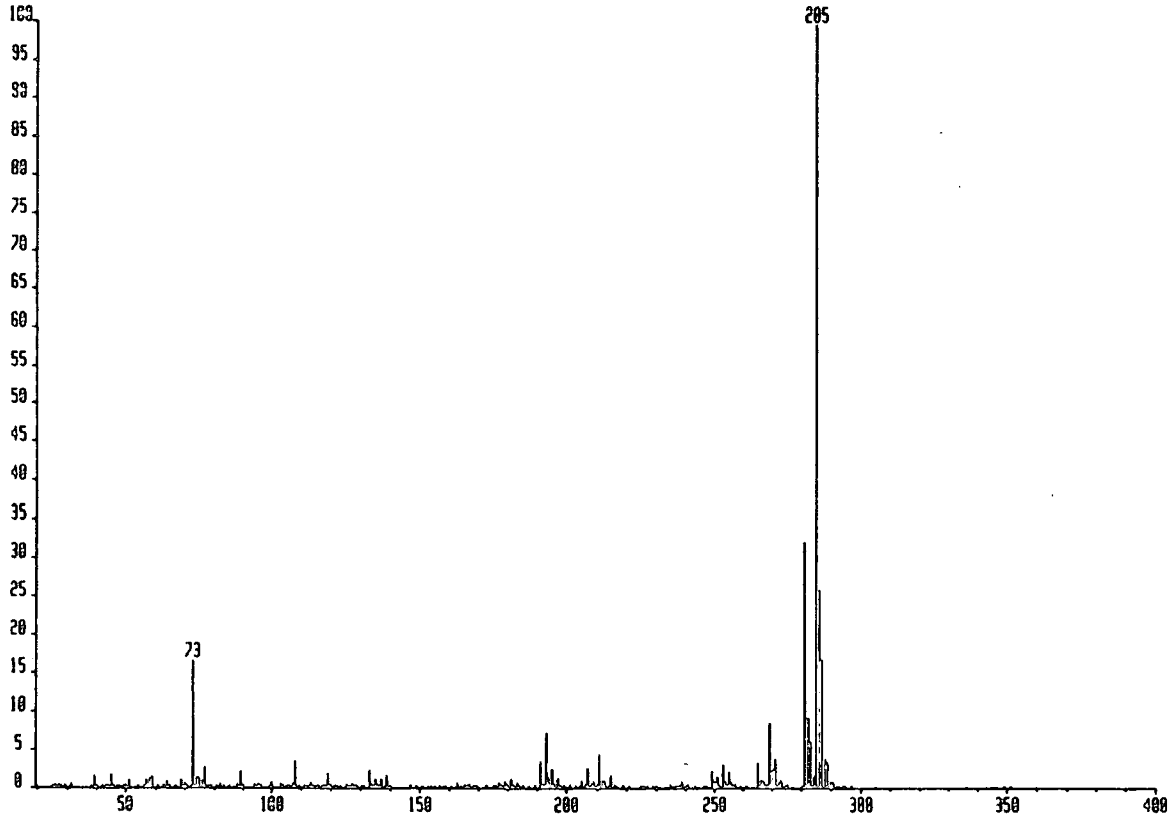
Mass	% Base
28.00	5.85
45.00	5.32
59.02	3.56
62.99	2.22
73.02	24.27
74.02	2.02
77.00	9.03
120.95	2.21
130.96	2.98
134.96	5.32
136.97	2.61
147.01	52.93
148.00	8.89
149.00	5.15
150.98	100.00
151.98	16.06
152.98	8.08
154.96	2.65
188.94	2.45

EI^+ M.Wt. 374 No. 16b



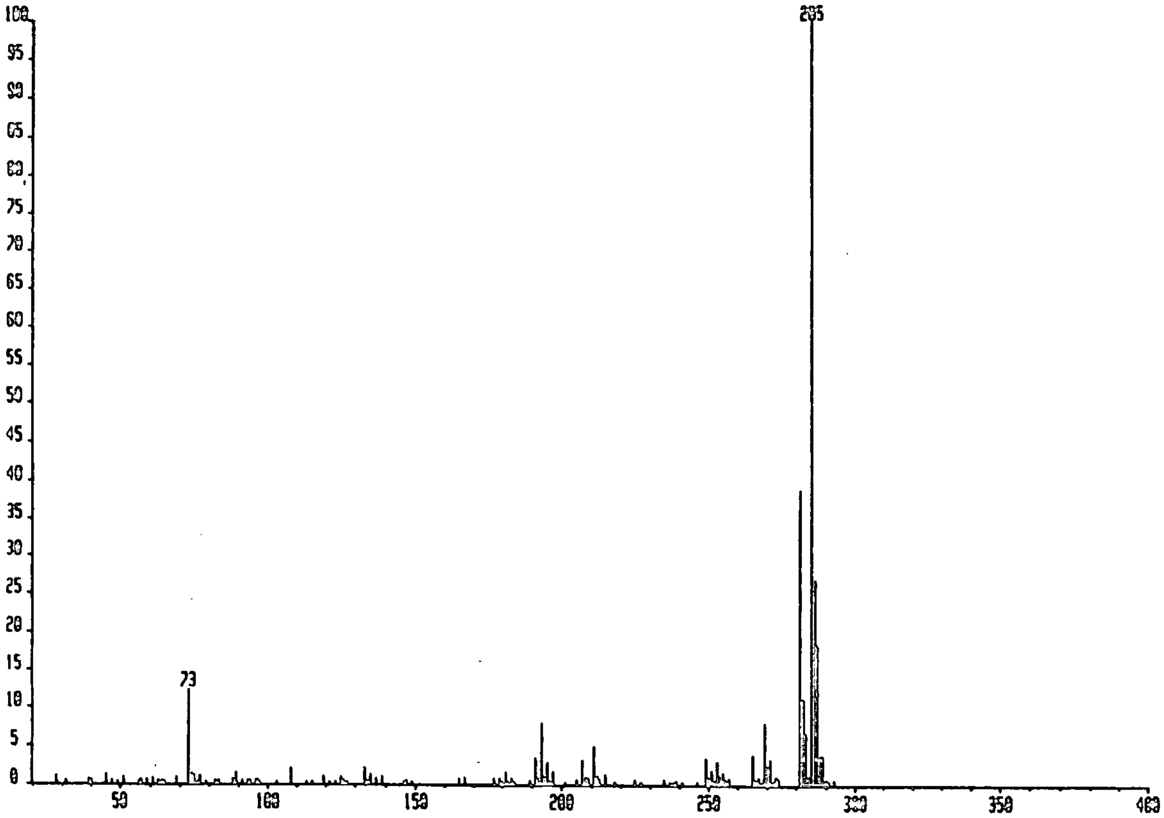
Mass	% Base
28.00	4.33
45.00	5.44
59.02	3.37
73.02	24.43
74.02	2.27
77.00	8.42
120.96	2.00
130.97	3.18
134.97	5.08
136.98	2.62
147.01	58.85
148.01	9.45
149.01	5.12
150.98	100.00
151.98	15.45
152.98	7.98
154.96	2.54
188.95	2.10
207.95	0.07

EI^{+} M.Wt. 458 No. 17a



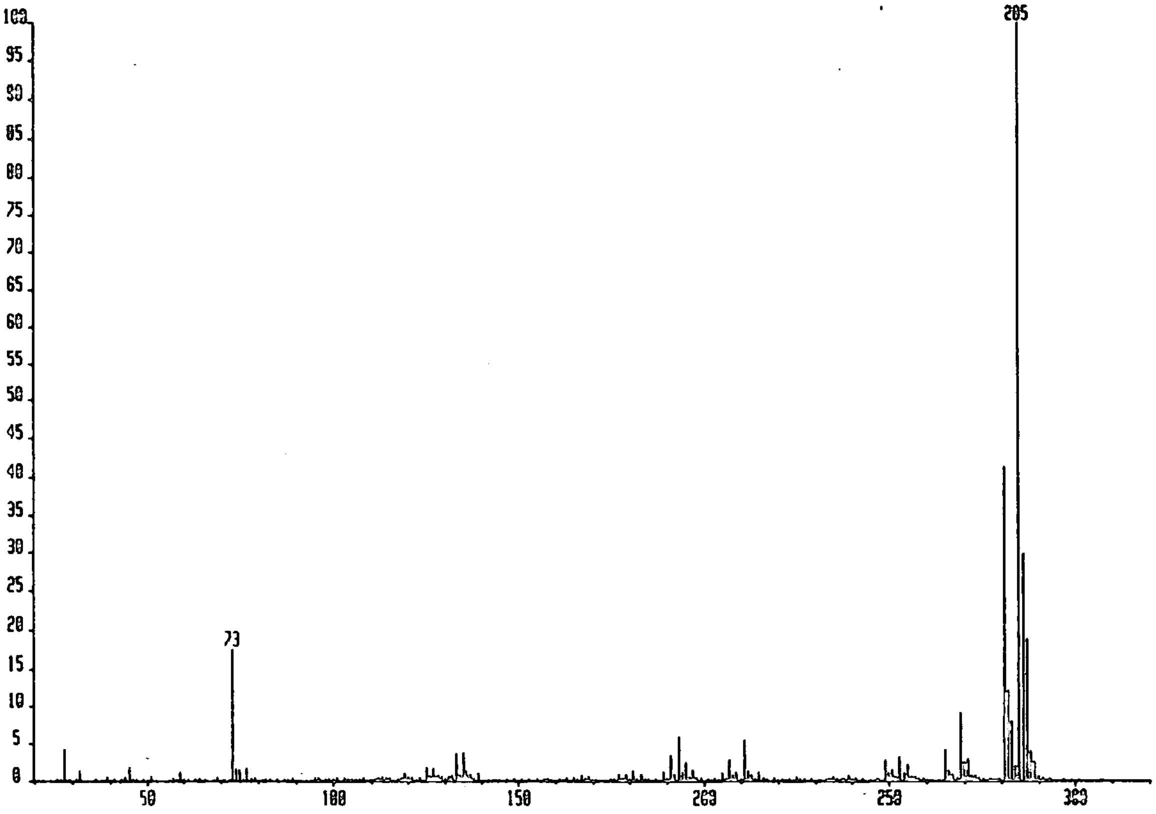
Mass	% Base
39.04	1.43
45.04	1.57
58.06	1.02
59.07	1.34
73.09	16.43
74.09	1.25
75.06	1.20
77.06	2.55
89.07	2.07
108.07	3.39
119.07	1.78
133.07	2.28
135.06	1.03
139.07	1.45
181.03	1.07
191.07	3.38
193.04	7.23
194.04	1.28
195.04	2.35
197.04	1.23
200.03	0.07
201.01	0.23
203.07	0.21
204.40	0.09
205.07	0.87
206.08	0.25
207.10	2.45
207.71	0.07
208.11	0.52
209.08	0.79
210.09	0.33
211.08	4.23
212.09	0.92
213.10	0.74
214.11	0.11
215.06	1.43
249.07	2.08
249.89	0.07
250.06	0.77
250.22	0.10
250.40	0.16
250.87	0.11
251.07	1.29
252.08	0.19
253.05	2.90
253.40	0.10
253.67	0.10
254.07	0.75
254.28	0.11
254.41	0.14
254.55	0.11
254.73	0.22
254.82	0.07
255.06	2.06
256.07	0.63
256.56	0.09
257.06	0.45
259.09	0.11
261.06	0.12
261.09	0.11
265.11	3.20
265.23	0.07
265.27	0.11
265.32	0.11
266.12	0.83
267.11	0.72
268.04	0.09
268.13	0.25
268.51	0.10
269.09	8.46
269.46	0.09
270.09	2.23
270.25	0.11
271.10	3.66
271.49	0.09
272.11	0.61
272.55	0.10
273.07	0.83
274.06	0.09
275.08	0.32
277.11	0.07
280.23	0.10
280.65	0.07
281.14	31.95
282.10	8.75 F
282.19	9.16 F
282.28	0.11
282.75	0.11
283.14	6.00
283.42	0.18
283.55	0.07
284.12	1.34
285.11	100.00
286.02	16.43 F
286.13	25.77 F
286.46	0.09
286.64	0.07
287.11	16.53
288.11	3.65
289.10	3.31
290.10	0.68
291.09	0.63
292.13	0.09
293.10	0.14
294.07	0.14
295.15	0.11
297.05	0.09
305.08	0.07
349.08	0.09
351.04	0.13

EI+ M.Wt. 458 No. 17b



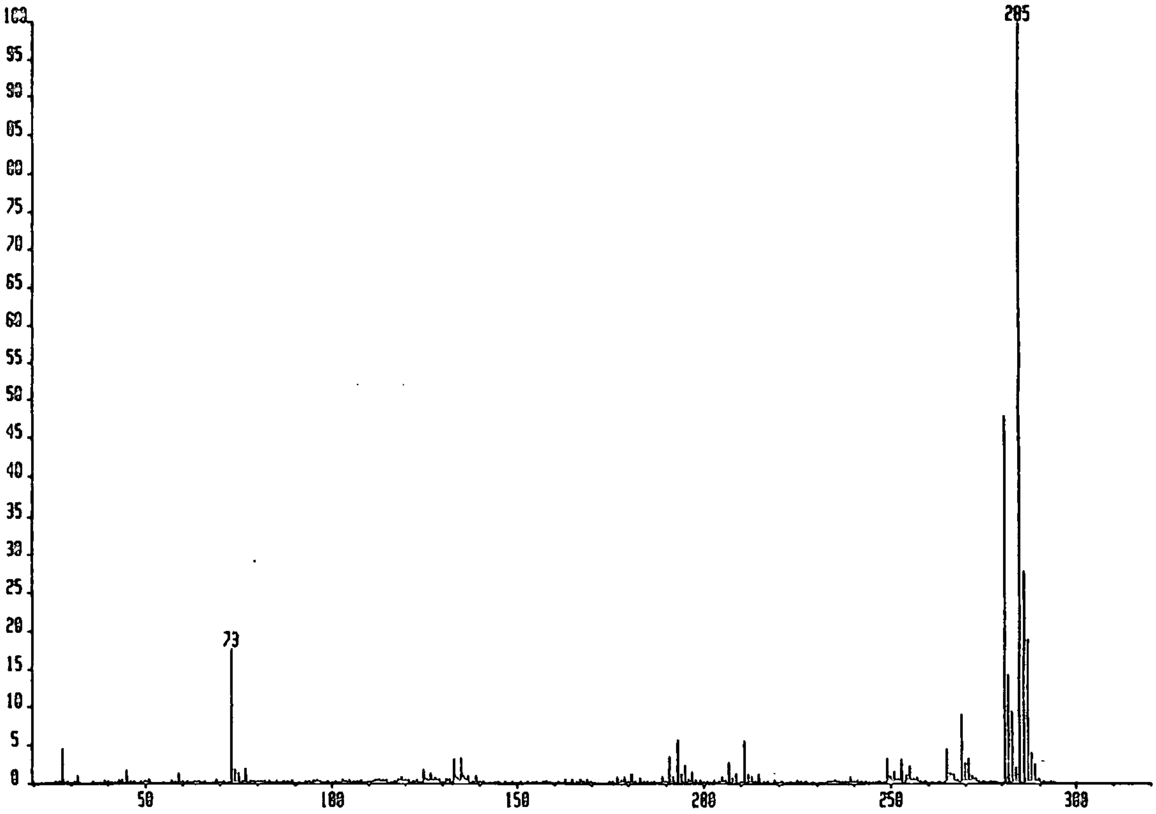
Mass	% Base
28.03	1.11
45.03	1.25
73.08	12.18
74.08	1.27
75.06	1.00
77.06	1.00
89.06	1.54
108.06	2.08
119.06	1.09
133.06	2.14
135.04	1.25
139.07	1.02
181.00	1.64
191.05	3.40
193.02	8.04
194.02	1.09
195.03	2.82
197.04	1.58
201.05	0.34
205.08	0.59
207.10	3.07
208.07	0.92
209.07	0.67
211.07	4.83
212.08	1.11
213.06	0.57
215.04	1.15
218.01	0.32
225.00	0.53
227.00	0.34
235.04	0.59
237.00	0.34
237.91	0.34
237.99	0.33
239.01	0.44
241.03	0.34
245.83	0.34
249.06	3.44
250.06	0.84
251.08	1.74
252.02	0.44
252.53	0.42
253.02	2.99
253.84	0.34
254.05	0.99
255.05	1.49
256.03	0.63
256.81	0.20
257.05	0.67
265.09	3.90
266.07	0.61
267.13	0.86
268.15	0.34
269.08	8.04
270.07	2.43
271.08	3.31
272.10	0.49
273.07	1.09
274.04	0.76
280.85	0.34
281.12	38.84
282.12	11.18
283.12	6.69
283.89	0.26
284.12	1.02
284.48	0.41
284.78	0.91
285.01	60.91 F
285.10	100.00 F
286.09	26.84
287.09	18.22
288.10	3.65
289.08	3.64
290.08	0.66
291.07	0.42
293.04	0.59

EI^{+} M.Wt. 508 No. 18a



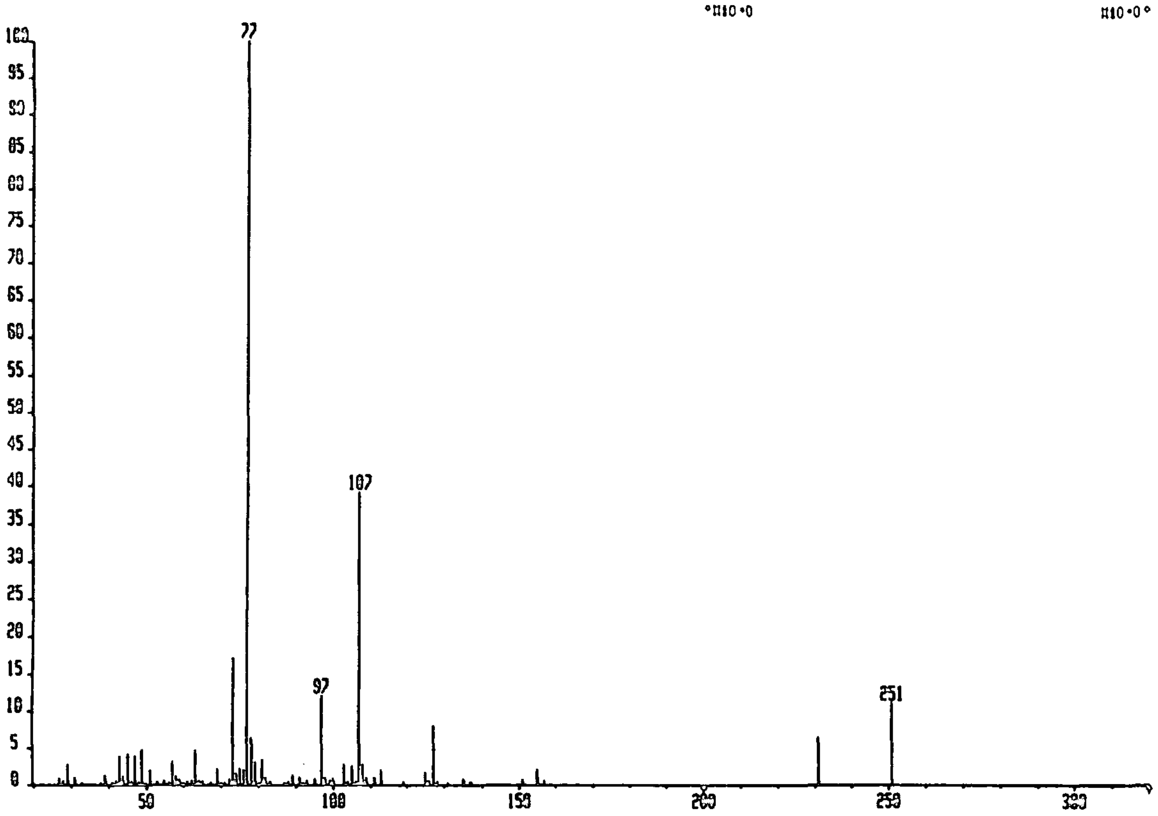
Mass	% Base	
28.00	4.21	
31.98	1.20	
45.01	1.73	
73.03	17.47	
74.03	1.54	
75.01	1.34	
77.01	1.67	
124.97	1.56	
126.95	1.51	
132.98	3.63	
134.97	3.73	
135.47	1.16	
180.91	1.19	
188.96	1.02	
190.95	3.32	
192.93	5.74	
193.93	1.05	
194.92	2.41	
196.93	1.36	
206.97	2.62	
208.94	1.01	
210.94	5.49	
211.94	1.16	
214.91	1.00	
248.94	2.71	
250.95	1.40	
252.92	3.08	
254.90	2.10	F
265.00	3.96	
266.01	1.15	
268.99	9.08	
269.99	2.41	
270.99	2.84	
280.98	41.16	F
281.98	12.04	F
282.98	7.84	F
283.97	1.72	F
284.57	0.89	F
284.95	100.00	F
285.96	29.59	F
286.95	18.68	F
287.27	0.03	
287.58	0.06	
287.70	0.06	
287.96	3.92	
288.62	0.06	
288.95	2.43	
289.95	0.45	
290.95	0.28	
291.94	0.07	
292.91	0.18	
296.89	0.07	
298.98	0.07	
300.92	0.05	
306.99	0.05	

EI^{+} M.Wt. 508 No. 18b



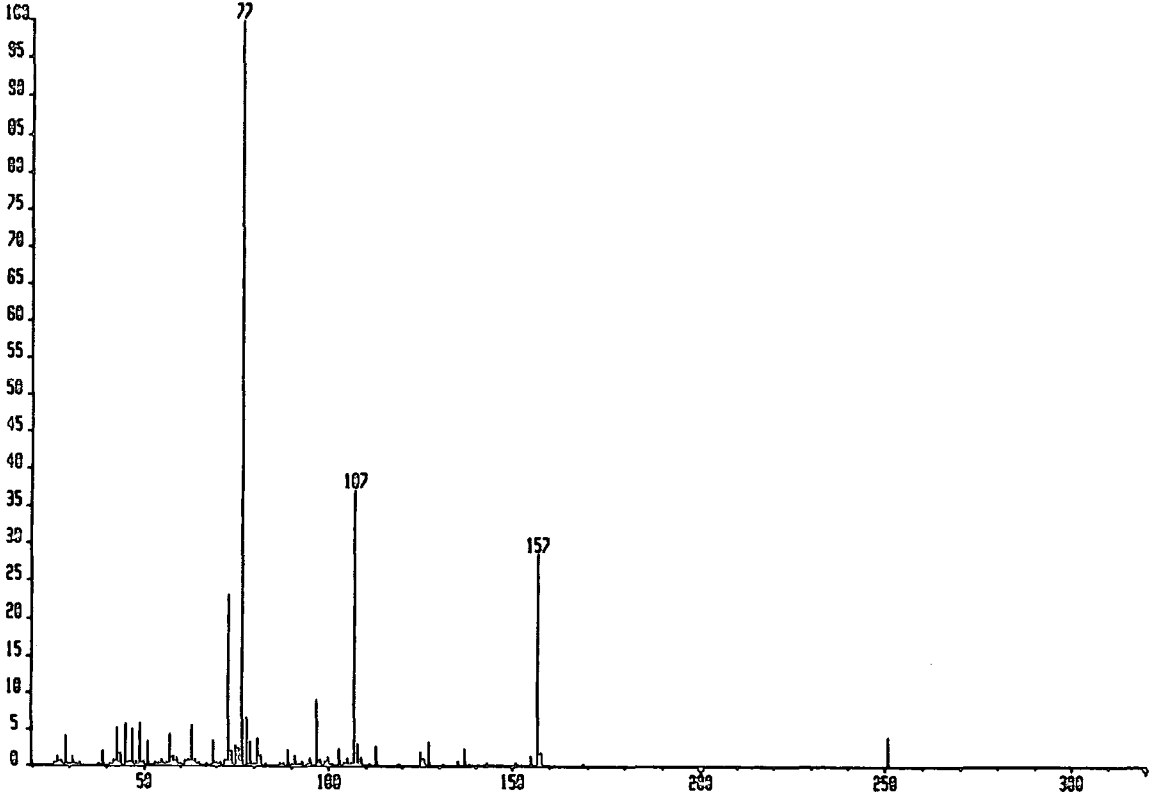
Mass	% Base	
28.00	4.39	
45.01	1.66	
59.03	1.13	
73.03	17.46	
74.03	1.61	
75.01	1.21	
77.01	1.71	
124.97	1.56	
126.95	1.13	
132.98	3.18	
134.97	3.24	
180.91	1.18	
190.95	3.43	
192.93	5.65	
193.93	1.04	
194.92	2.24	
196.93	1.31	
206.97	2.66	
208.95	1.11	
210.94	5.43	
211.94	1.08	
214.92	1.02	
248.94	3.13	
250.94	1.34	
252.93	3.01	F
254.90	2.08	F
265.00	4.25	
266.01	1.24	
267.01	1.00	
268.99	8.86	
269.99	2.48	
270.99	3.10	
280.98	47.89	F
281.98	14.12	F
282.98	9.29	F
283.96	2.00	F
284.58	0.92	F
284.95	100.00	F
285.95	27.89	F
286.95	18.74	F
287.26	0.04	
287.95	3.86	
288.95	2.43	
289.95	0.48	
290.95	0.21	
291.93	0.06	
292.93	0.12	
293.94	0.07	
300.03	0.04	

EI$^+$ M.Wt. 266 No. 19a



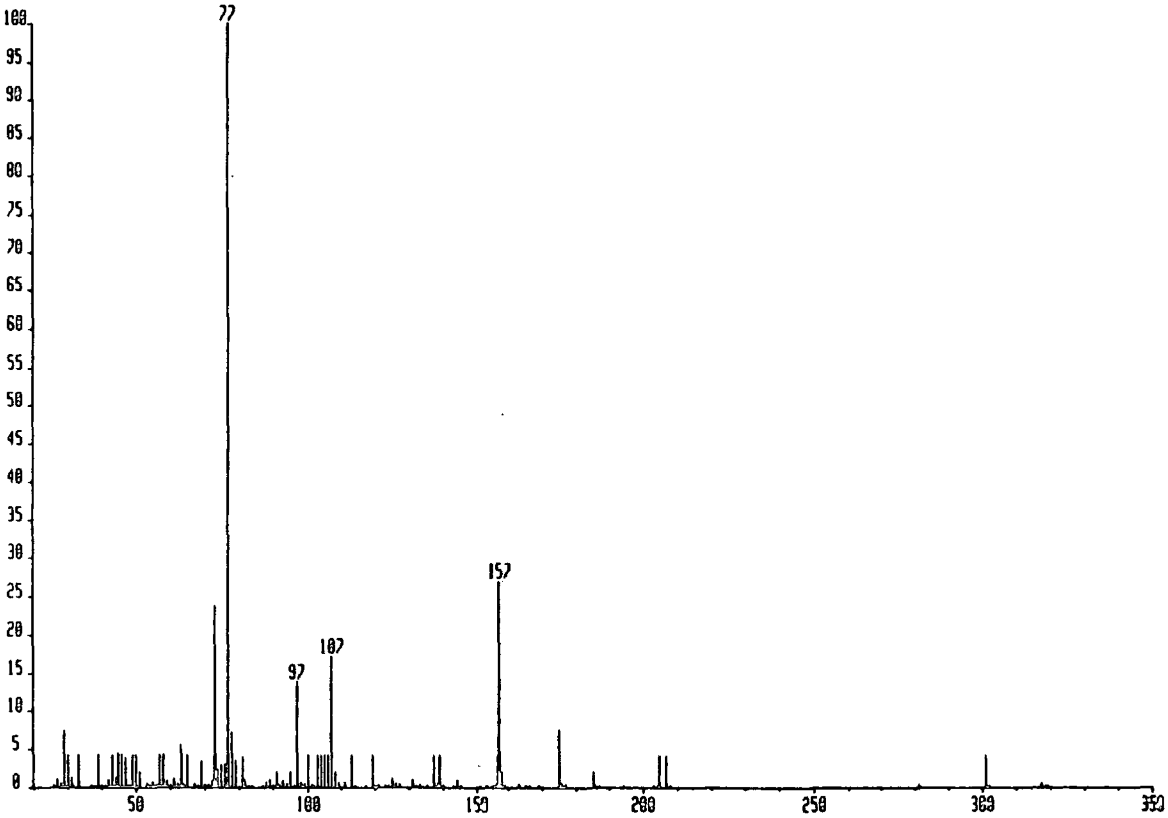
Mass	% Base
28.99	2.80
39.02	1.16
42.99	3.78
43.99	1.13
44.99	4.16
46.97	3.83
48.98	4.72
50.99	1.89
57.00	3.03
58.02	1.04
63.00	4.52
68.99	2.12
73.03	17.15
74.03	1.48
75.00	2.05
76.00	2.02
77.01	100.00
78.01	6.40
79.00	2.99
80.98	3.27
89.00	1.22
97.01	11.91
103.04	2.74
104.99	2.36
107.00	39.13
108.00	2.65
112.98	1.91
124.98	1.67
126.99	8.08
154.97	1.95
230.98	0.65
250.98	1.10

EI$^+$ M.Wt. 266 No. 19b



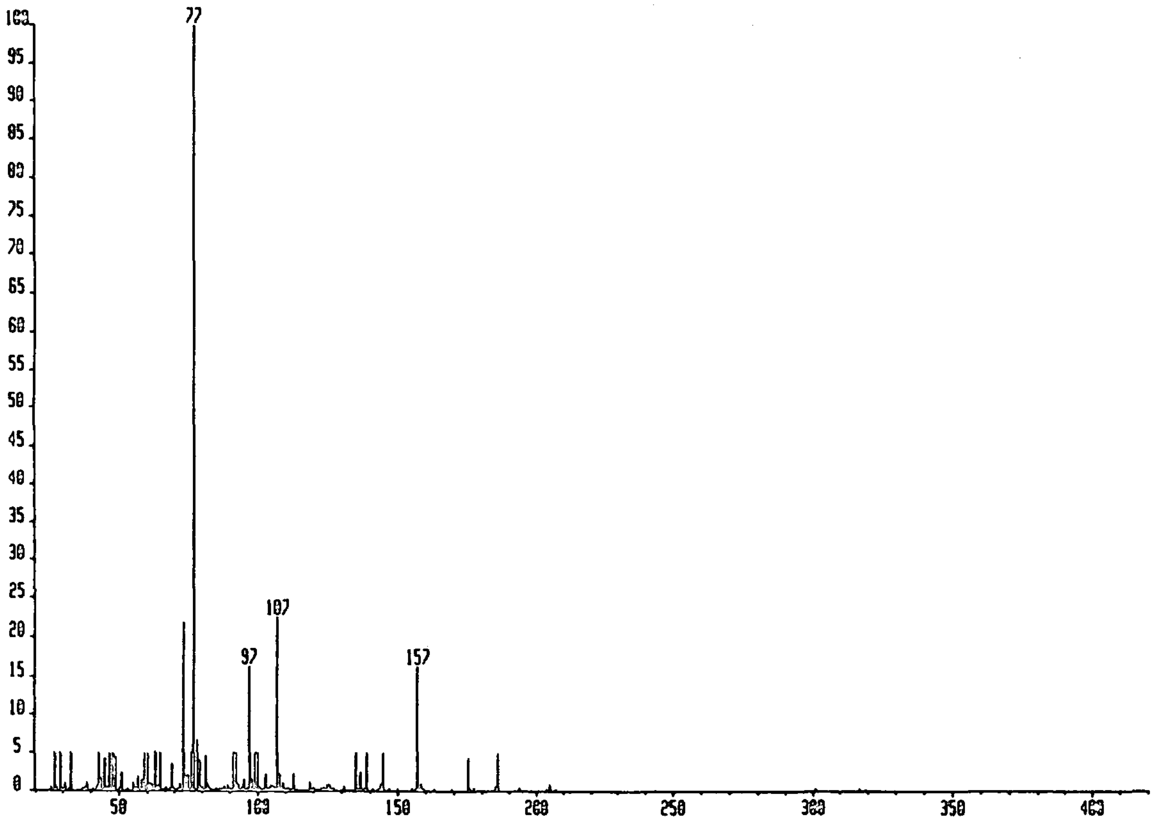
Mass	% Base
27.02	1.26
28.99	4.12
31.00	1.15
39.02	1.90
42.99	5.14
44.00	1.60
44.99	5.81
46.97	4.93
48.98	5.80
51.00	3.14
57.01	4.20
58.02	1.25
63.00	5.45
68.99	3.33
73.04	23.04
74.03	1.95
75.01	2.76
76.01	2.27
77.01	100.00
78.01	6.47
79.00	3.19
80.99	3.56
82.00	1.34
89.01	2.15
91.00	1.29
97.01	8.96
99.99	1.09
103.04	2.23
107.01	36.92
108.01	2.94
109.01	1.01
112.98	2.51
124.99	1.80
127.00	3.20
136.98	2.23
154.98	1.25
156.98	28.32
157.98	1.66
250.99	0.39

EI$^+$ M.Wt. 316 No. 20a



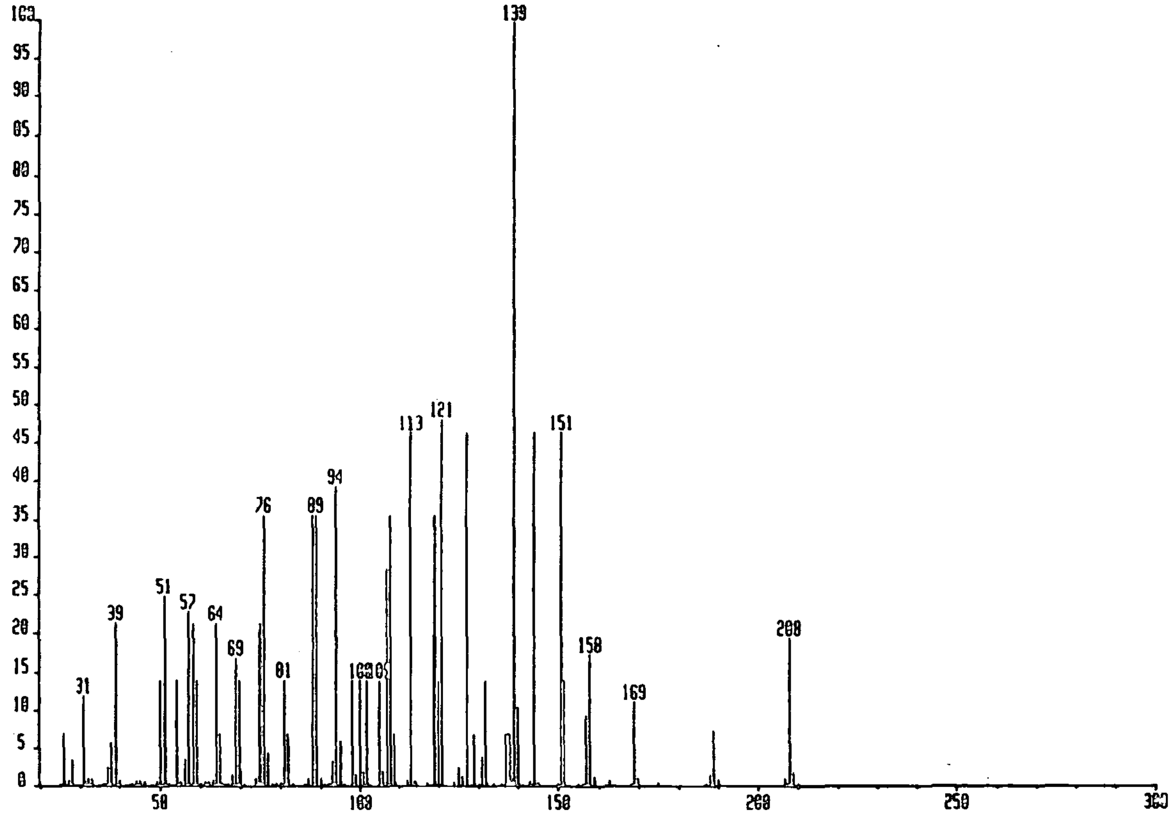
Mass	% Base	
29.01	7.32	F
29.02	7.36	F
30.01	4.18	
31.01	1.25	
33.02	4.18	
39.03	4.18	
43.01	4.11	
44.02	1.18	
44.99	1.66	F
45.03	4.41	F
46.00	4.18	
46.99	3.87	
49.01	4.16	
50.00	4.18	
51.02	1.87	
57.03	4 18	
58.01	4.18	F
58 04	1.39	F
61.03	1.07	
63.03	5.45	
65.03	4.18	
69.02	3.45	
72 99	4.18	
73.06	23.72	F
73.09	7.76	F
74.06	2.24	
75.04	2.86	
76.04	2.96	
76.68	4.18	
77.04	100.00	
78.03	7.21	F
78 05	7.24	F
79.03	3.41	
81.01	4.03	
91.05	1.99	
95.03	2 00	
97.05	13.74	
100.03	4.18	
103.08	4.18	
104 07	4.18	
105.05	4.18	
106.02	4.18	
107 05	17.12	F
107.08	8.21	F
108.05	1 95	
113.02	4.18	
119.03	4.18	
137.02	4.21	
139.04	4.18	
150.04	0.05	
151.06	0.08	
153.04	0.15	
155 04	0 19	
156.03	0.24	
156.69	0.04	
156.81	4.18	
156 87	0 19	
157.03	26.92	
157.46	0.11	
158.03	1 89	
159.02	0.08	
163.02	0.31	
165.00	0.09	
165.04	0.11	
166.04	0.09	
169.05	0.13	
169.99	0.06	
170.01	0.06	
174.84	0.04	
174.99	7.20	F
175.04	7.51	F
176.01	0.39	
177.03	0.31	
185.01	1.89	
186.01	0.17	
187.03	0.10	
194.00	0.16	
203.02	0.08	
204.02	0.10	
205.03	4.18	
207.03	4.18	
208.05	0.10	
281.04	0.43	
301.03	4.18	
302.03	0 12	
317.07	0.38	
318.07	0.07	
319.06	0.07	

EI^{+} M.Wt. 316 No. 20b



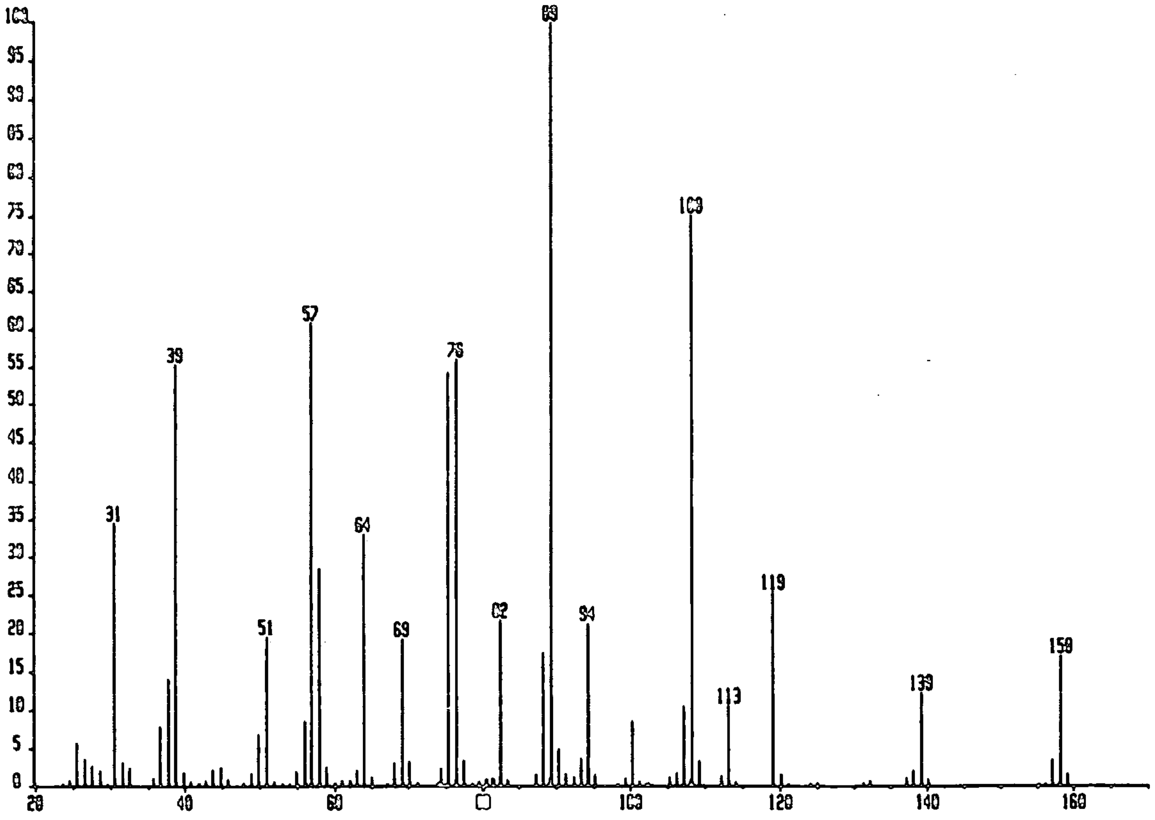
Mass	% Base	
27.04	4.93	
29.01	4.96	
29.05	4.93	
33.01	4.93	
43.01	3.78	
43.07	4.93	
44.02	1.46	
44.99	1.81	F
45.03	4.10	F
46.99	3.50	F
47.01	4.93	F
48.00	4.93	
49.00	4.35	
51.02	2.31	
57.03	1.76	
58.04	1.26	
59.03	4.93	
60.02	4.93	
63.03	4.98	
65.02	4.93	
69.02	3.36	
73.06	21.65	F
73.09	8.98	F
74.06	1.78	
75.03	1.98	
76.03	4.93	
76.77	4.93	
76.95	4.93	
77.04	100.00	
78.04	6.51	
79.03	3.88	
81.01	4.42	
91.04	4.93	
92.02	4.93	
95.04	1.36	
97.04	16.20	F
97.07	8.93	F
98.05	1.27	
99.04	4.93	
100.02	4.93	
103.08	2.12	
107.05	22.44	F
107.08	7.66	F
108.05	2.08	
113.03	2.01	
119.03	1.02	
135.02	4.93	
137.02	2.35	
139.05	4.93	
145.01	4.93	
150.02	0.08	
150.05	0.14	
155.03	0.17	
156.01	0.11	
156.41	0.07	
156.87	0.15	
157.02	16.20	F
157.06	7.57	F
158.03	0.76	
159.01	0.09	
163.01	0.22	
169.02	0.15	
175.01	4.29	
176.00	0.21	
177.01	0.29	
185.01	0.38	
186.03	4.93	
194.01	0.27	
203.99	0.09	
205.03	0.71	
207.07	0.10	
301.05	0.18	
317.06	0.21	
319.07	0.07	

EI$^+$ M.Wt. 208 No. 21



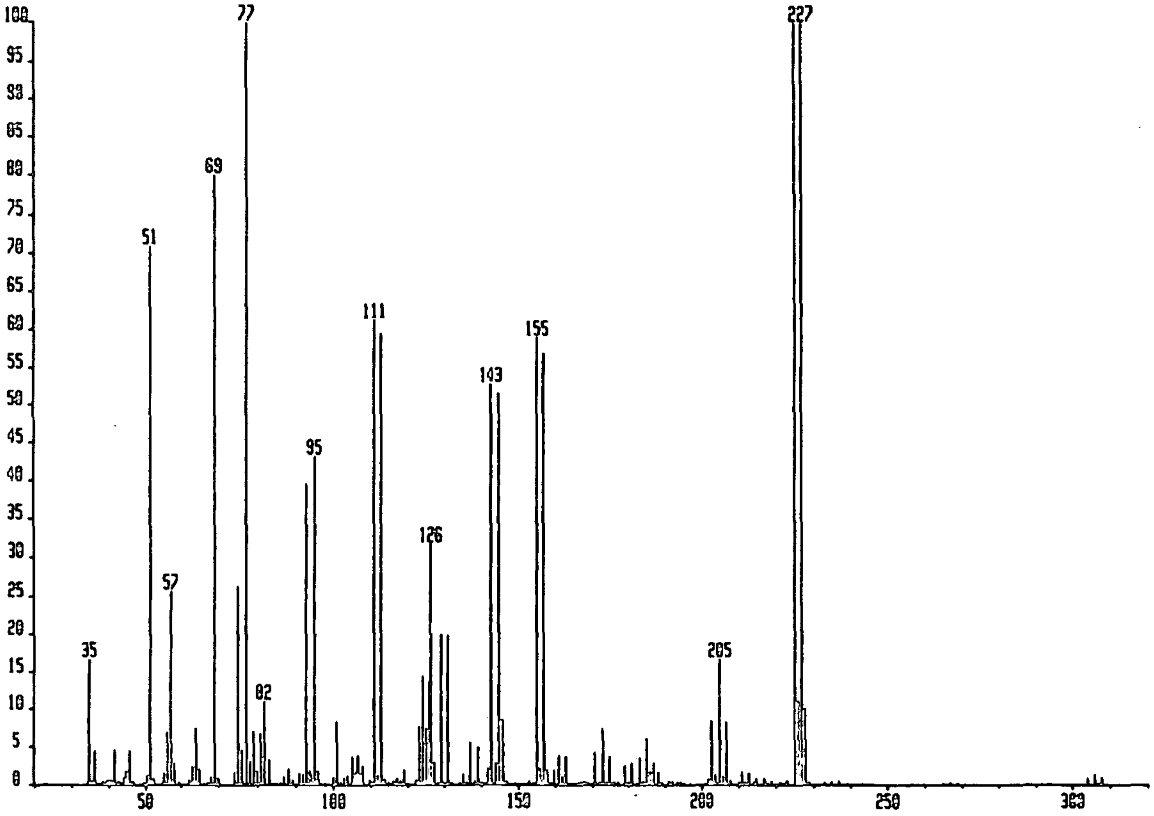
Mass	% Base	
26.00	6.76	
27 99	3.29	
28.00	1.07	
30.98	11.90	
36.99	2.41	
37.00	1.52	
37.99	5.61	
38.01	2.14	
39.01	20.86	F
39.02	21.17	F
49.98	2.16	
50.00	13.96	
50.99	24.77	
51.00	21.17	
51.02	1.01	
54.00	13.96	
55.99	3.41	
57.00	22.65	
57.02	13.96	
58.00	21.17	
59.01	13.96	
63.98	21.17	
64.99	6.76	
67.97	1.43	
68.96	16.80	
69.98	13.96	
69.99	1.88	
74.97	19.95	F
74.99	21.17	F
75.97	35.59	
76.97	4.27	
76.99	3.76	
80.97	13.96	
81.95	5.75	
81.98	6.76	
87.97	35.59	
88.97	18.95	
89.00	35.59	
92.92	3.31	
92.98	1.46	
93.94	13.06	F
93.97	39.19	F
94.96	5.88	
95.00	1.27	
97.94	6.76	
97.97	13.96	
98.94	1.52	
98.97	1.39	
99.94	4.28	
99.99	13.96	
100.96	1.71	
101.82	13.96	
104.94	13.96	
105.94	1.88	
106.96	21.17	
107.00	28.38	
107.95	18.88	F
107.98	35.59	F
108.01	6.76	
108.97	6.76	
112.94	46.40	
118.94	19.53	
118.96	18.68	F
118.98	35.59	F
119.94	2.13	
119.98	13.96	
120.98	48.20	
124.93	2.35	
125.94	1.21	
126.98	46.40	
128.84	6.76	
130.91	3.69	
131.80	13.96	
136.92	6.76	
136.98	1.12	
137.69	6.76	
137.80	6.76	
137.91	1.28	
137.95	1.12	
138.93	78.26	F
138.97	100.00	F
139.92	10.36	
139.96	10.36	
143.90	6.76	
143.94	46.40	
150.74	46.40	
150.77	6.76	
151.24	13.96	
151.39	13.96	
156.90	9.26	
157.92	17.17	
168.92	11.12	
187.90	1.34	
188.91	7.22	
207.89	19.19	
208.89	1.63	

EI$^+$ M.Wt. 158 No. 22



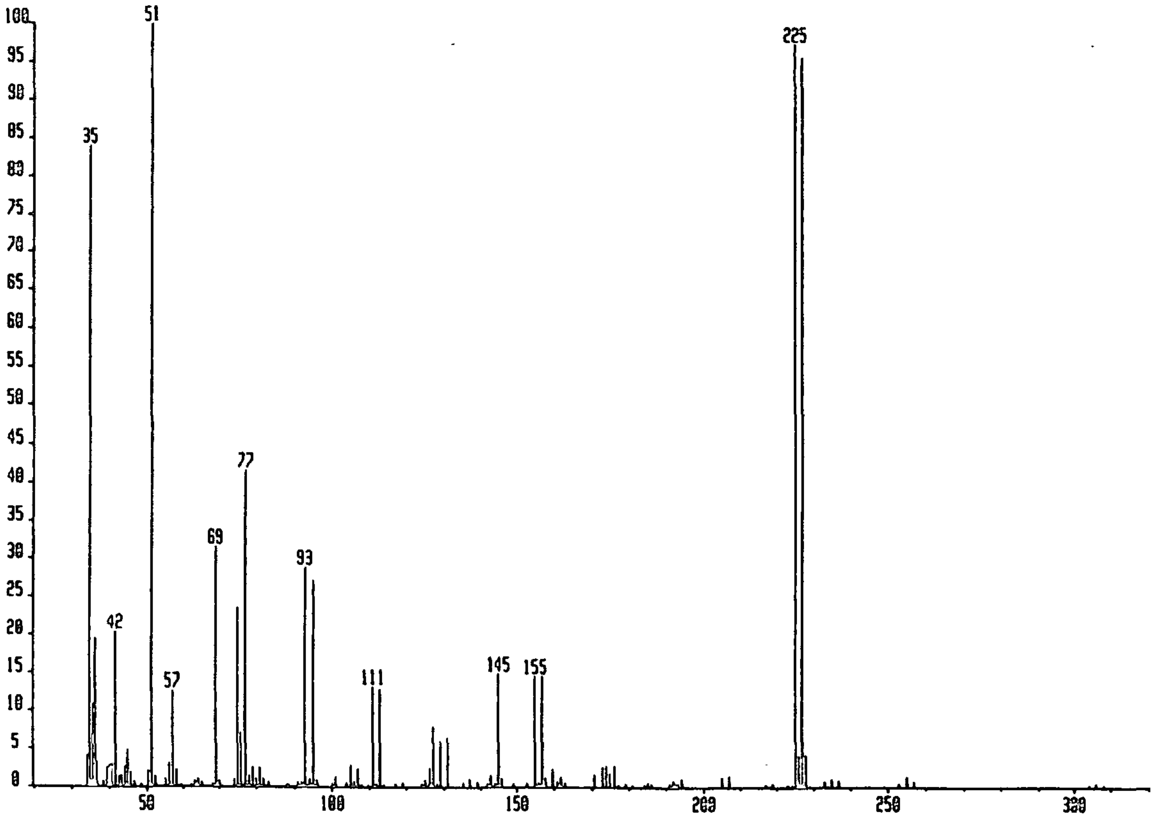
Mass	% Base
25.56	5.58
26.58	3.34
27.57	2.54
28.61	1.93
30.60	34.33
31.62	2.93
32.64	2.25
36.68	7.80
37.71	14.00
38.73	55.20
39.75	1.65
43.79	2.13
44.82	2.36
48.86	1.50
49.88	6.88
50.89	19.45
54.93	1.85
55.95	8.65
56.97	60.82
57.99	28.51
59.02	2.42
63.04	1.90
64.06	32.91
68.11	2.96
69.12	19.17
70.17	3.17
74.30	2.19
75.30	54.26
76.33	56.00
77.37	3.27
82.45	21.59
87.38	1.37
88.38	17.36
89.37	100.00
90.36	4.90
91.38	1.50
92.37	1.02
93.29	3.56
94.29	21.16
95.29	1.40
100.22	8.65
101.23	0.44
102.13	0.14
102.43	0.24
105.23	1.04
106.20	1.60
107.20	10.56
108.02	0.14
108.04	0.15
108.09	0.70
108.20	75.25
109.20	3.20
112.15	1.25
113.16	10.59
114.15	0.44
119.04	0.24
119.16	25.39
120.16	1.55
121.18	0.14
124.15	0.21
125.11	0.30
125.13	0.24
131.14	0.30
132.14	0.59
137.14	0.89
138.16	1.95
139.17	12.08
140.17	0.79
155.21	0.19
156.21	0.19
157.16	3.46
158.01	0.27
158.17	16.85
159.16	1.55

EI$^+$ M.Wt. 306 No. 23



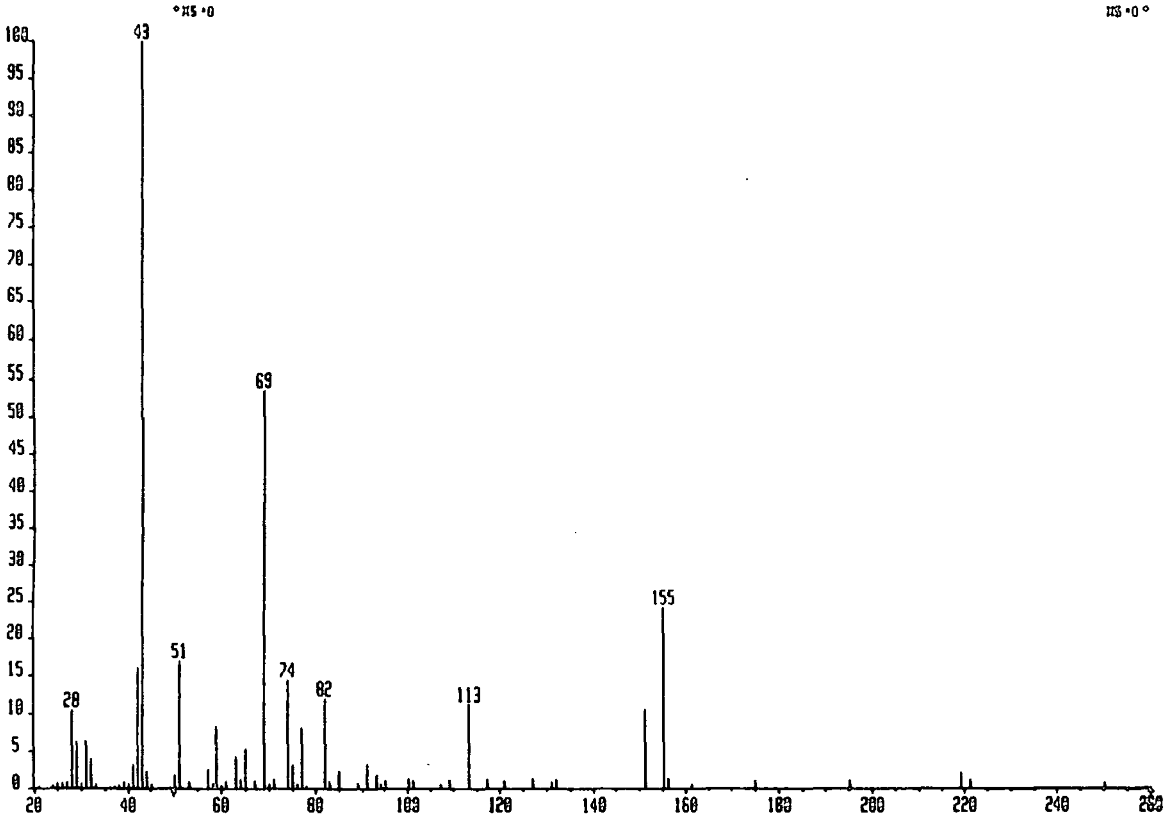
Mass	% Base	
34.65	16.51	
51.35	70.78	
52.31	0.64	
55.19	1.33	
56.17	6.87	
57.15	25.53	
58.14	2.72	
62.07	0.38	
63.07	2.17	
64.06	7.33	
65.06	1.97	
68.05	0.85	
69.03	79.95	
70.03	0.78	
74.02	1.46	
75.02	26.22	
76.03	4.51	
77.03	100.00	0
78.04	2.90	
78.94	6.93	
79.94	1.61	
80.94	6.56	
81.94	1.41	F
82.02	10.76	F
83.03	3.12	
92.97	39.36	
93.96	1.62	F
94.04	1.10	F
94.96	38.42	F
95.05	42.95	F
96.03	1.61	
100.03	0.87	
101.04	8.28	
103.98	0.96	
104.98	3.60	
106.01	1.45	F
106.84	3.76	F
107.18	1.30	F
108.05	2.37	F
109.96	0.45	
110.96	61.18	
111.97	1.09	
112.96	59.46	
119.02	1.78	
121.96	0.50	
122.97	7.52	
123.97	14.20	
124.97	7.31	
125.96	13.45	F
126.05	31.46	F
127.04	2.81	
128.95	19.90	
129.96	0.20	
130.96	19.72	
136.98	5.55	
137.99	0.29	
138.99	4.71	
139.99	0.14	
141.97	1.86	
142.97	52.61	
143.99	2.73	
145.00	51.36	
146.05	8.49	
147.06	0.33	
152.97	0.23	
154.98	58.86	
155.99	1.95	
156.97	56.73	
157.95	1.78	
159.90	1.74	
160.97	3.67	
161.91	0.91	
162.97	3.91	
170.89	3.96	
172.91	7.21	
173.92	0.13	
174.92	3.50	
176.98	0.10	
178.97	2.36	
180.96	2.62	
182.90	3.37	
183.90	0.29	
184.90	5.89	
185.97	1.48	
186.90	2.72	
187.97	1.45	
188.94	0.16	
190.92	0.32	
191.97	0.24	
192.93	0.18	
193.97	0.14	
201.90	0.52	
202.90	8.37	
203.91	1.21	
204.92	16.43	
205.93	0.91	
206.93	8.18	
207.97	0.40	
210.97	1.46	
211.97	0.13	
212.97	1.38	
214.91	0.53	
216.91	0.74	
218.91	0.35	
220.90	0.16	
222.91	0.43	
225.02	100.00	FO
225.98	10.99	F
226.98	100.00	FO
227.99	9.92	F
229.00	0.16	
232.92	0.12	
234.89	0.31	
236.91	0.27	
266.94	0.12	
303.92	0.68	
305.91	1.21	
307.90	0.73	

EI$^+$ M.Wt. 306 No. 24



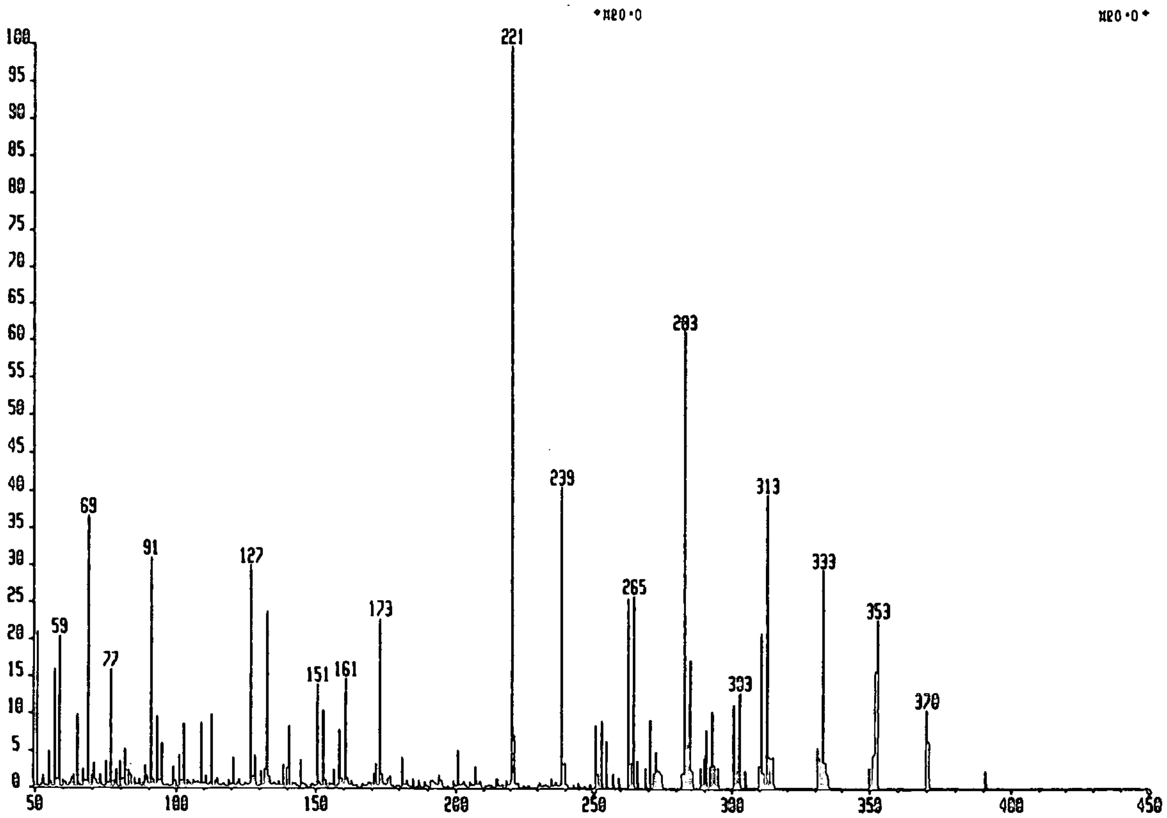
Mass	% Base
34.29	3.93
34.43	2.94
34.64	0.13
34.65	84.05
35.76	10.82
36.25	19.36
36.80	3.08
39.38	2.42
40.11	2.72
40.88	2.84
41.61	20.28
42.47	1.25
43.30	1.36
44.12	0.45
44.16	2.45
44.96	4.78
45.86	1.72
50.41	1.93
51.35	100.00
52.30	1.22
52.33	0.15
55.18	0.93
56.17	2.91
56.22	0.18
57.15	12.47
58.14	2.13
69.03	31.39
75.02	23.34
76.03	6.94
76.95	0.16
77.03	41.43
78.04	1.27
78.93	2.31
79.94	0.89
80.94	2.32
92.98	28.76
93.90	0.11
94.00	0.87
94.97	27.16 F
95.05	14.64 F
101.03	1.11
103.96	0.45
104.97	2.72
106.98	2.24
110.96	13.00
112.96	12.81 F
113.04	5.74 F
126.05	2.44
126.95	0.16
127.06	7.82
128.07	0.30
128.96	5.93
130.95	6.40
142.97	1.29
145.05	14.73
146.06	0.99
149.05	0.23
152.97	0.43
154.98	14.42
155.97	0.48
156.98	14.35
157.92	1.04
159.89	2.21
160.98	0.60
161.88	1.20
162.97	0.49
170.89	1.42
172.92	2.48
173.98	2.60
174.94	1.66
175.97	2.62
178.94	0.30
180.96	0.22
183.90	0.16
184.91	0.43
185.91	0.25
185.99	0.13
190.84	0.18
190.89	0.34
190.99	0.16
191.97	0.77
192.05	0.16
192.84	0.12
192.90	0.26
192.96	0.18
192.99	0.15
193.97	0.89
204.99	1.15
206.99	1.34
216.88	0.16
216.92	0.16
218.89	0.26
222.90	0.15
224.99	97.68
225.84	0.25
225.99	4.07
226.19	0.15
226.29	0.11
226.38	0.19
226.98	95.89
227.99	4.12
232.89	0.59
234.90	0.91
236.88	0.70
252.92	0.36
254.90	1.23
256.89	0.53
303.97	0.11
305.95	0.32
307.91	0.18

EI^{+} M.Wt. 268 No. 25



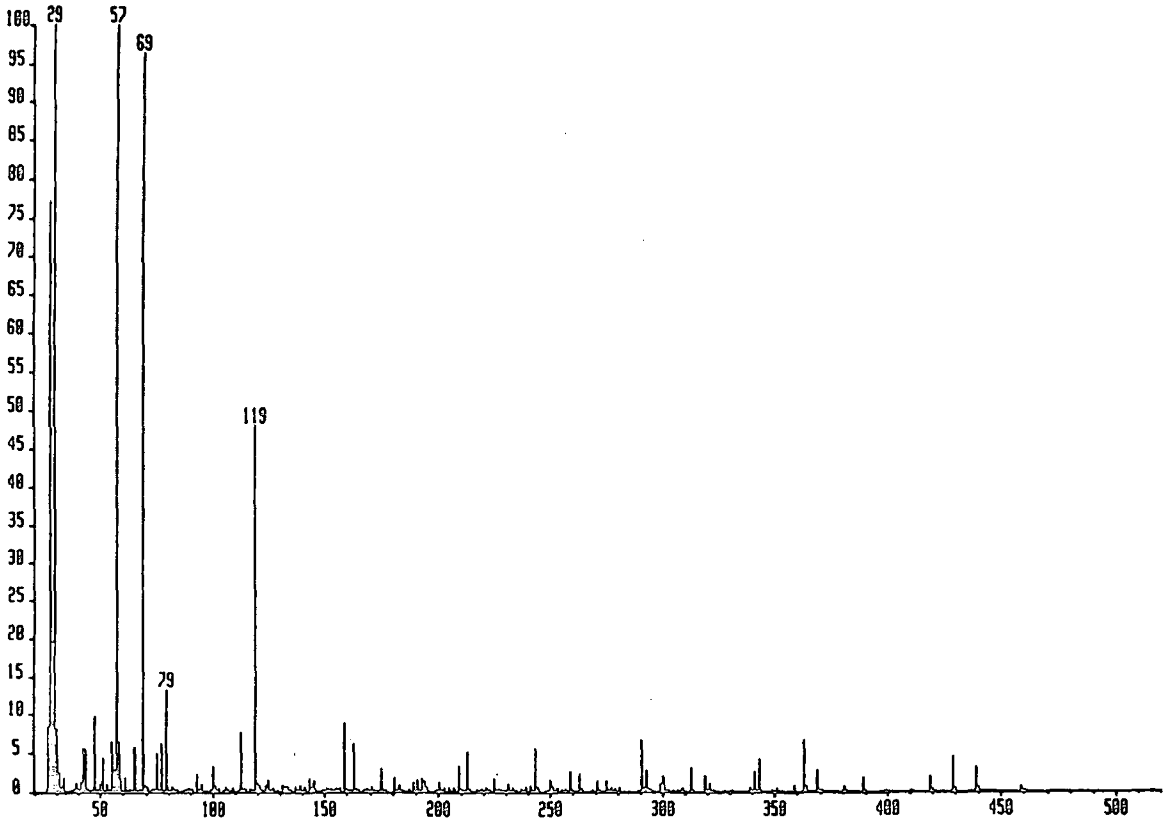
Mass	% Base	
28. 03	10. 29	
29. 03	6. 00	
31. 03	2. 46	F
31. 05	6. 25	F
32. 02	2. 11	F
32. 06	3. 82	F
41. 05	3. 11	
42. 06	15. 94	
43. 07	100. 00	
44. 07	2. 19	
51. 07	3. 37	
59. 07	1. 65	
65. 08	1. 03	
69. 06	10. 71	
74. 11	2. 86	
77. 10	1. 60	
82. 09	2. 38	
100. 10	0. 24	
101. 11	0. 17	
107. 12	0. 09	
109. 14	0. 21	
113. 12	2. 20	
117. 18	0. 21	
121. 13	0. 18	
127. 14	0. 24	
131. 13	0. 14	
132. 14	0. 22	
151. 14	2. 10	
155. 16	4. 82	
156. 16	0. 24	
161. 19	0. 08	
175. 18	0. 18	
195. 21	0. 20	
219. 22	0. 39	
221. 20	0. 21	
250. 25	0. 11	

EI^{+} M.Wt. 390 No. 26



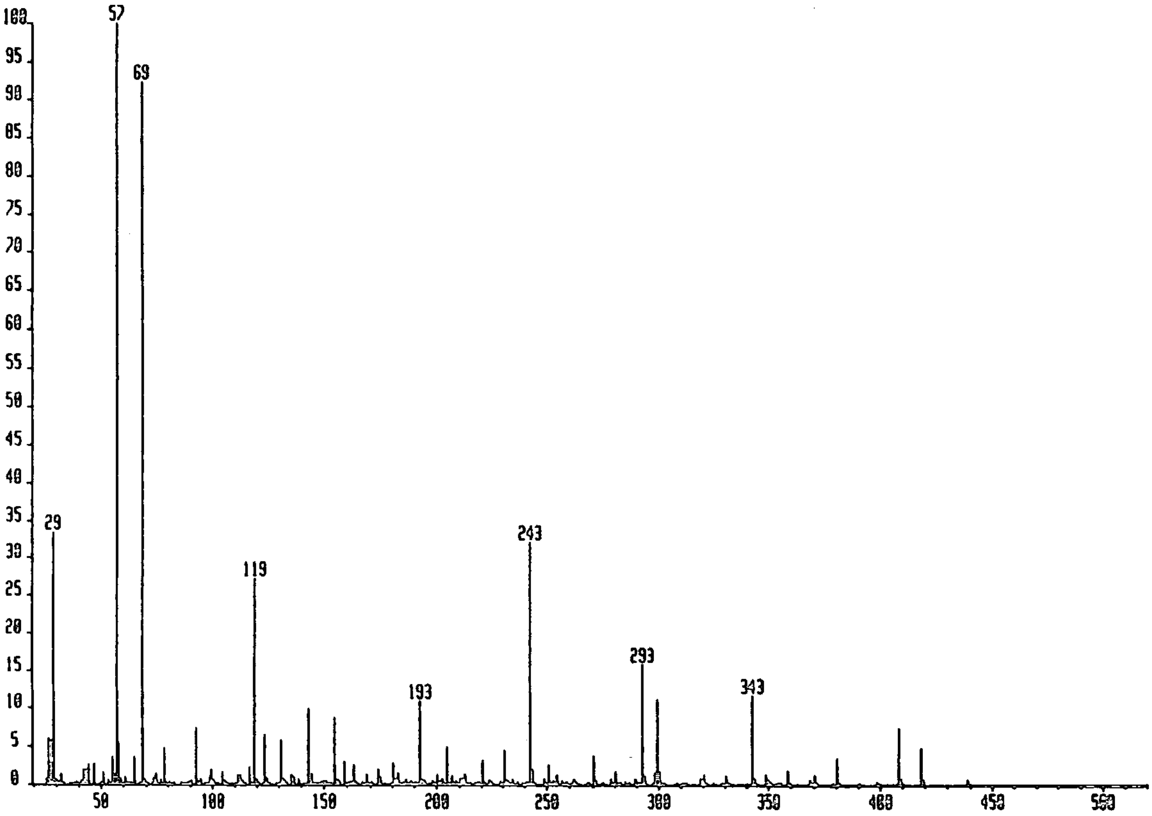
Mass	% Base
50.96	20.94
54.98	4.92
56.99	15.70
58.99	20.33
64.98	9.71
66.96	2.48
68.96	36.44
70.99	3.20
74.97	3.56
76.97	15.81
78.96	2.49
79.95	3.46
81.95	5.09
82.97	2.21
88.97	2.88
90.97	30.89
92.96	9.37
94.95	5.85
98.95	2.70
100.95	4.24
102.97	8.49
108.96	8.62
112.93	9.77
120.96	3.86
126.94	29.86
128.93	4.19
130.93	2.16
131.93	2.38
132.94	23.62
138.94	3.09
139.95	2.58
140.93	8.20
144.93	3.62
150.92	13.80
152.95	10.30
156.94	2.43
158.94	7.72
160.91	14.55
171.95	3.13
172.95	22.80
180.93	4.06
200.95	4.98
206.93	2.74
220.93	100.00
221.94	6.99
238.96	40.43
239.96	3.27
282.95	3.06
300.97	0.55
301.97	0.12
302.95	0.64
304.96	0.12
309.91	0.14
310.94	1.04
311.95	0.10
312.93	1.97
313.95	0.20
314.94	0.20
330.93	0.26
331.94	0.19
332.94	1.46
333.98	0.16
334.38	0.09
334.93	0.08
349.96	0.13
350.95	0.22
351.93	0.78
352.95	1.13
369.94	0.52
370.95	0.31
390.97	0.12

EI$^+$ M.Wt. 458 No. 27



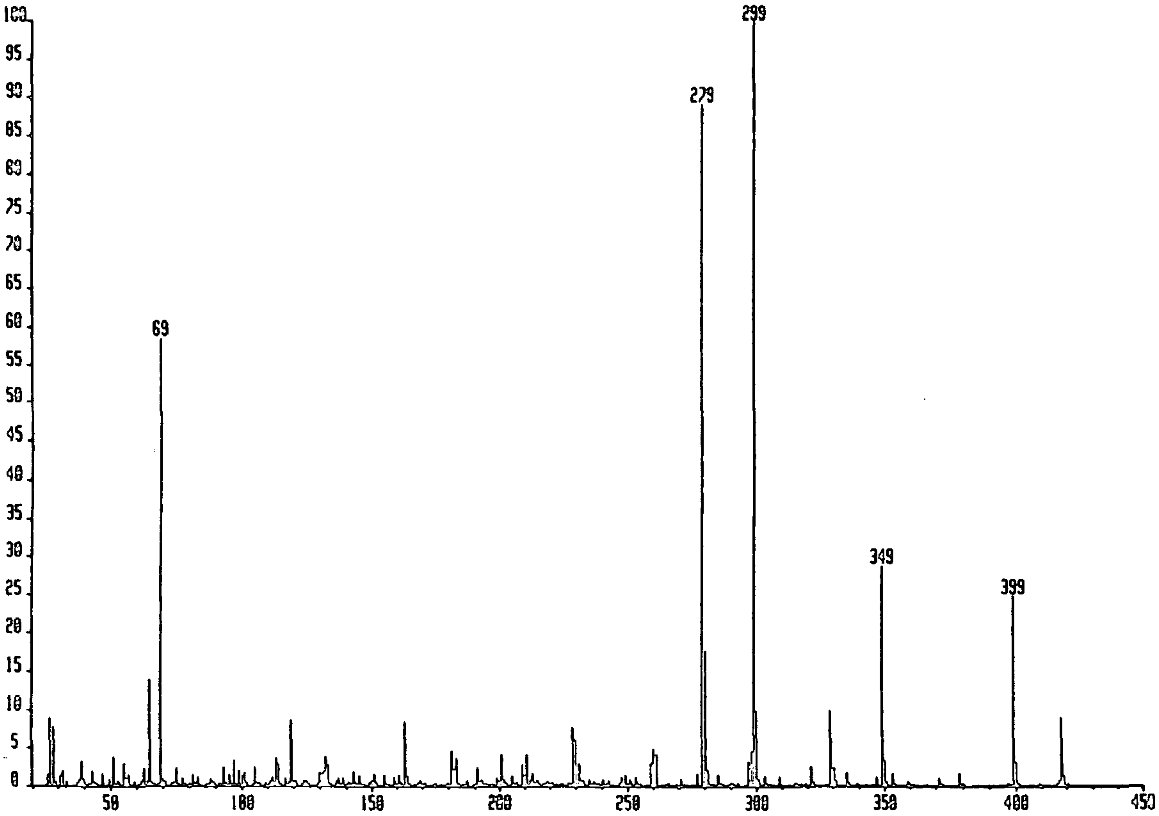
Mass	% Base	
25.98	8.29	
26.99	77.13	
27.96	2.83	
27.99	19.53	
28.96	3.86	
28.99	100.00	0
29.99	8.08	
30.94	2.55	F
32.95	1.83	
38.96	1.08	
40.97	1.12	
41.95	5.53	
42.95	5.37	
46.97	9.57	
50.94	4.35	
54.95	6.44	
55.96	2.79	
56.92	1.54	
56.96	100.00	0
57.97	6.41	
58.96	1.66	
60.94	1.78	F
60.97	1.47	F
64.94	5.68	
68.91	96.55	
74.92	4.91	
76.95	6.00	
78.94	13.25	
92.90	2.28	
99.89	3.31	
112.89	7.48	
118.88	47.96	
124.89	1.47	
142.86	1.67	
144.88	1.27	
158.86	8.73	
162.87	6.06	
174.86	2.99	
180.86	1.78	
188.86	1.14	
190.84	1.52	
192.83	1.60	
193.84	1.32	
200.86	1.17	
208.84	3.26	
212.85	5.08	
224.84	1.67	
242.83	5.55	
249.87	1.42	
258.86	2.53	
262.85	2.20	
270.85	1.38	
274.84	1.40	
290.83	6.57	
292.83	2.71	
299.86	1.94	
300.86	1.69	
312.83	3.05	
318.86	2.02	
320.82	1.08	
340.83	2.58	
342.83	4.09	
362.83	6.50	
368.86	2.71	
388.86	1.71	
410.83	0.13	
418.86	1.91	
419.87	0.29	
428.42	0.05	
428.51	0.06	
428.85	4.45	
429.85	0.45	
438.87	2.89	
439.86	0.39	
458.90	0.66	
459.89	0.08	
460.90	0.03	

EI$^+$ M.Wt. 438 No. 28



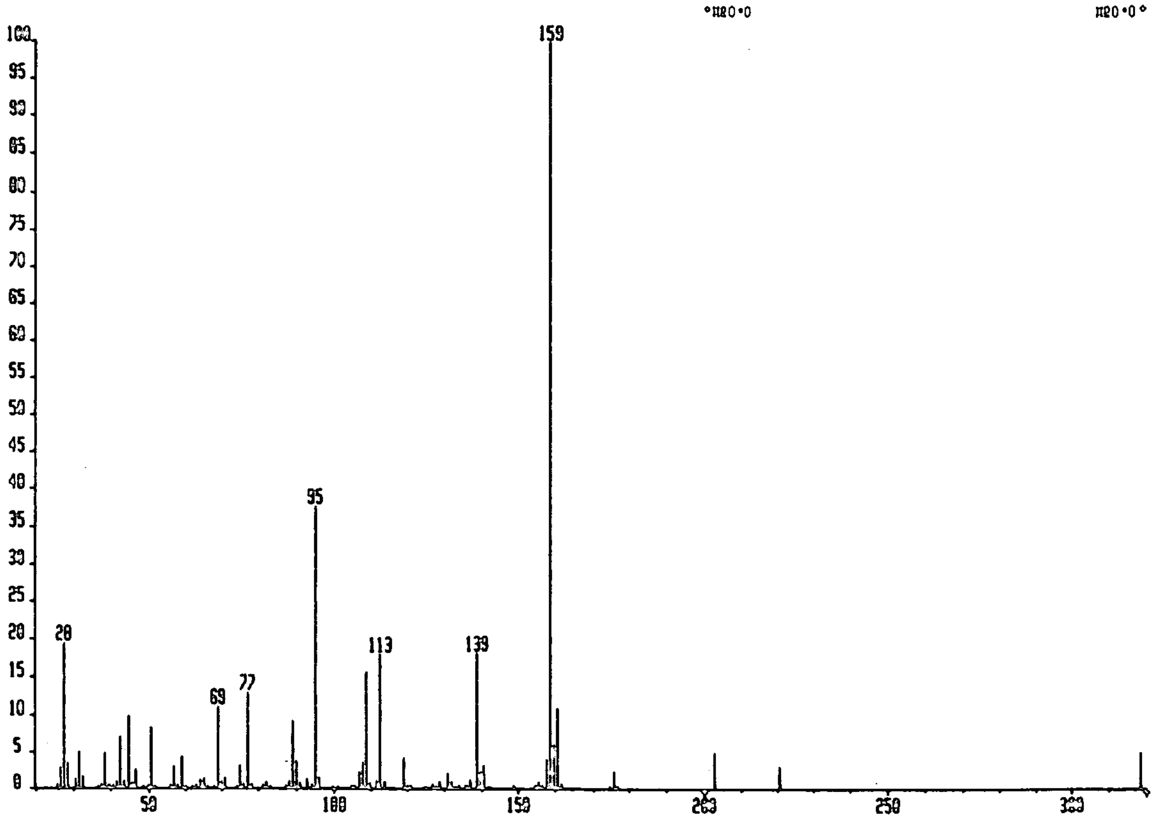
Mass	% Base	
26.97	5.86	
27.94	5.57	F
27.97	1.30	F
28.97	33.39	
31.91	1.33	
41.92	1.91	
42.92	1.99	
43.89	2.57	
46.93	2.73	
50.90	1.64	
54.91	3.60	
55.92	1.35	
56.88	1.40	
56.93	100.00	O
57.93	5.42	
64.90	3.53	
68.87	92.38	
74.88	1.35	
78.89	4.68	
92.84	7.47	
99.83	1.89	
104.83	1.57	
111.82	1.21	
112.83	1.12	
116.81	2.23	
118.81	27.05	
123.80	6.44	
130.80	5.81	
135.79	1.19	
142.78	9.76	
144.80	1.26	
154.77	8.77	
158.76	2.92	
162.79	2.57	
168.76	1.39	
173.75	1.97	
180.74	2.76	
182.76	1.43	
192.74	10.85	
200.76	1.25	
204.74	4.90	
206.75	1.04	
212.75	1.30	
220.73	3.05	
230.74	4.51	
242.71	31.99	
243.71	1.86	
250.73	2.55	
254.70	1.23	
270.71	3.69	
280.73	1.68	
292.68	15.73	
293.69	1.03	
298.70	1.54	
299.71	11.13	
300.71	1.56	
320.67	1.21	
330.70	1.02	
342.67	11.58	
348.70	1.21	
358.66	1.79	
370.66	1.16	
380.65	3.43	
400.26	0.05	
403.31	0.04	
406.06	0.06	
407.21	0.03	
407.74	0.05	
408.19	0.08	
408.63	7.28	
409.64	0.74	
409.93	0.05	
410.67	0.05	
418.34	0.10	
418.68	4.79	
419.69	0.62	
438.33	0.03	
438.68	0.62	
439.71	0.04	

EI$^+$ M.Wt. 418 No. 29



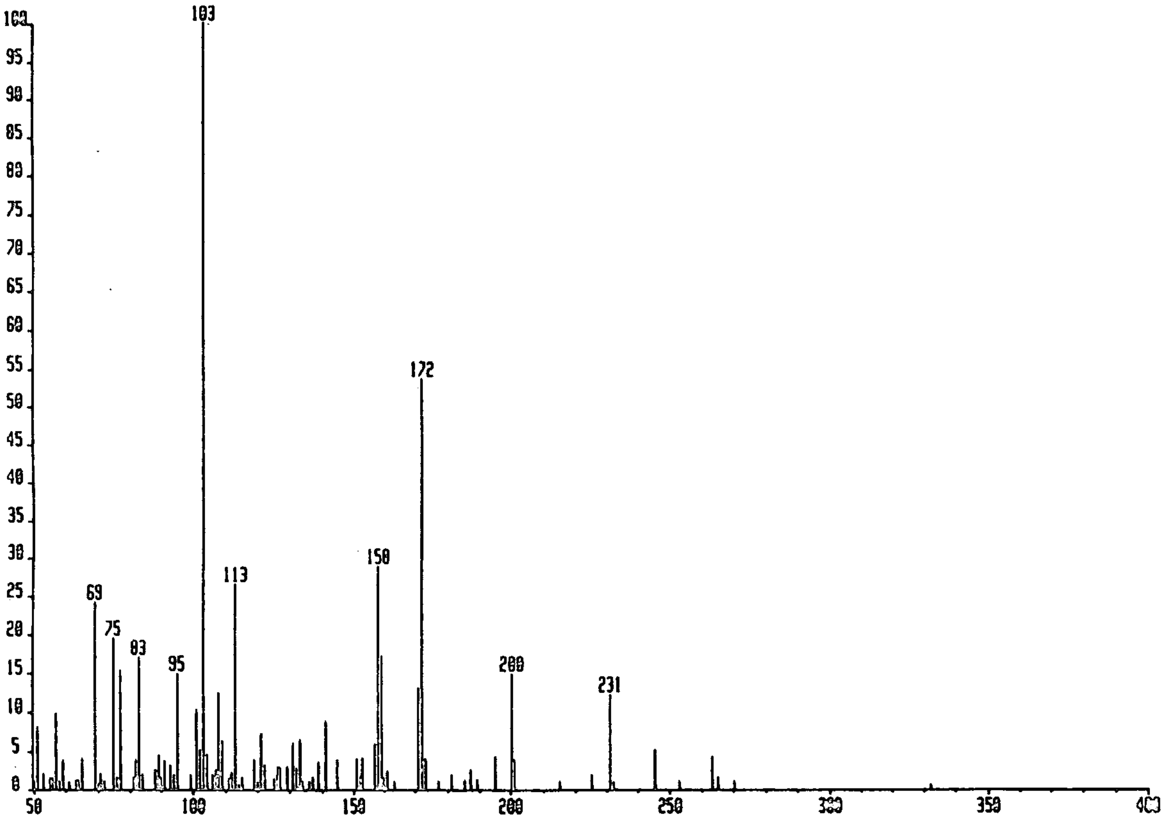
Mass	% Base	
26.94	8.91	
27.92	7.69	F
27.94	3.97	F
38.96	3.11	
50.94	3.67	
54.96	2.84	
62.99	2.24	
64.99	13.76	
68.98	58.31	
75.00	2.24	
93.01	2.32	
97.00	3.32	
105.01	2.34	
113.03	3.54	
114.04	2.69	
119.01	8.61	
132.03	3.78	
133.04	2.73	
163.04	8.43	
181.03	4.58	
182.04	2.15	
183.05	3.48	
191.04	2.22	
201.04	4.06	
209.03	2.71	
211.05	3.93	
229.04	7.76	
230.05	5.95	
231.04	2.77	
259.01	2.88	F
260.14	4.69	F
261.33	4.00	F
279.03	89.21	F
280.04	17.42	F
297.04	3.12	F
298.04	4.40	F
299.04	100.00	F
300.06	9.76	F
321.02	2.38	
329.05	9.83	
330.05	2.22	
349.04	28.62	
350.07	3.12	
399.05	24.53	F
400.07	2.98	F
401.07	0.21	
409.04	0.18	
416.08	0.09	
417.06	0.54	
417.49	0.03	
418.07	8.84	
419.08	1.13	
420.08	0.09	

EI$^+$ M.Wt. 334 No. 30



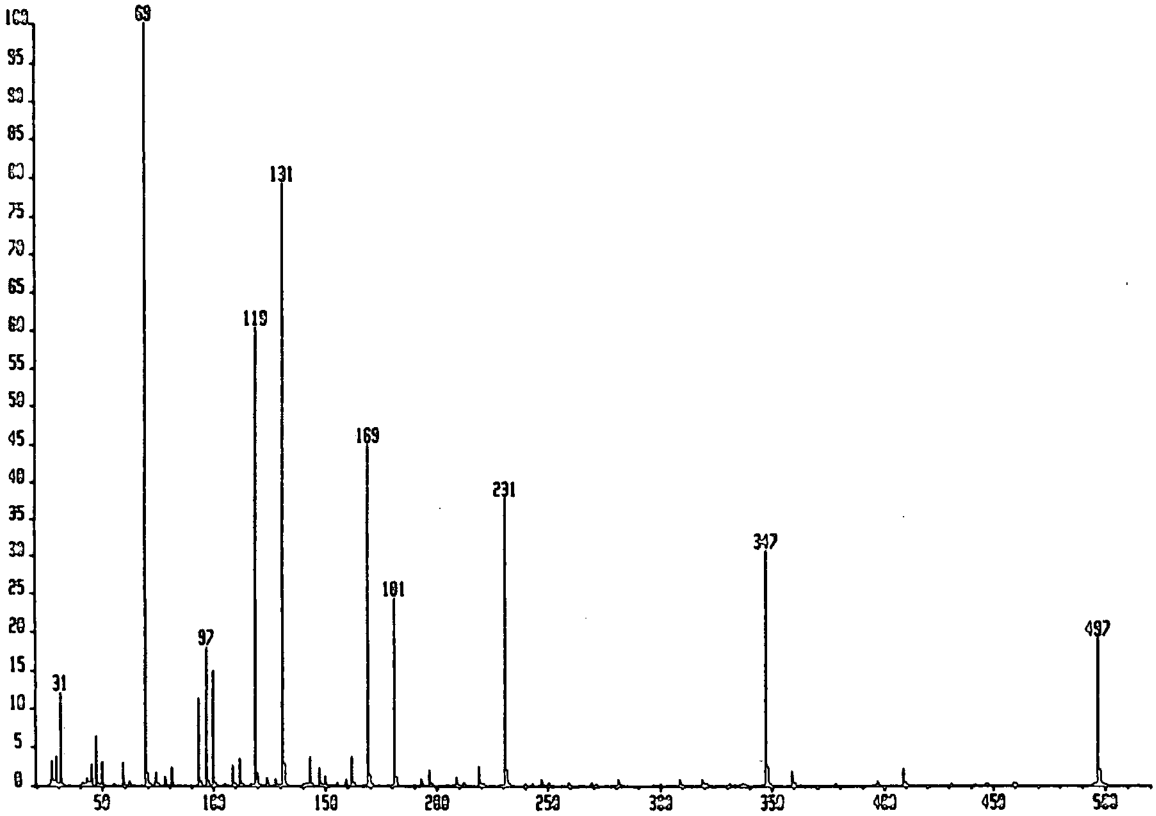
Mass	% Base
25.61	0.41
26.62	2.75
27.60	19.27
28.60	3.39
28.63	0.12
30.60	1 26
31.59	4.90
32.62	1.45
36.62	0.15
37.64	0.50
38.65	4.77
39.59	0.35
39.66	0.33
40.67	0.34
41.65	0.69
41.68	0.17
42.67	7.04
43.65	0.92
44.69	9.77
45.69	0 61
46.66	0.14
46.70	2.45
48.70	0.14
49.71	0.32
50.71	8.15
51.74	0.17
55.75	0.34
56.77	2.93
56.81	0.19
56.83	0.18
57.78	0.33
58.80	4.30
59.81	0.13
61.79	0.19
62.82	0.26
63.84	1.06
64.28	0.19
64.85	1.23
65.80	0.14
67.86	0.15
67.87	0.15
68.87	10.85
69.92	0.79
70.94	1.14
73.97	0.18
75.01	3.05
76.04	0.38
77.07	12.73
78.10	0.51
81.13	0.24
82.13	0.75
83.12	0.14
87.08	0.23
88.07	0.96
89.06	9.13
90.06	3.66
91.04	0.55
92.99	1.22
93.99	0.40
94.98	37.43
95.98	1.36
99.91	0.21
100.93	0.22
104.93	0.29
104.96	0.14
105.88	0.26
106.89	2.13
107.88	3.49
108.88	15.40
109.87	0.61
111.82	0.88
112.82	17.66
113.82	0.72
118.80	4.06
119.81	0.29
120.81	0.29
124.78	0.19
124.82	0.11
126.80	0.42
127.77	0.19
128.68	0.80
130.75	1.94
131.68	0.77
131.77	0.15
132.79	0.16
133.67	0.23
135.68	0.25
135.79	0.27
136.79	1.00
138.79	17.83
139.79	2.05
140.77	3.01
141.76	0.18
148.81	0.29
154.76	0.37
155.76	0.73
156.76	0.34
157.76	4.00
158.47	0.11
158.76	100.00
159.76	5.91
160.74	10.80
161.74	0.49
174.70	0.18
175.72	2.16
176.73	0.14
202.68	0.24
220.67	0.14
318.51	0.24

EI$^+$ M.Wt. 332 No. 31



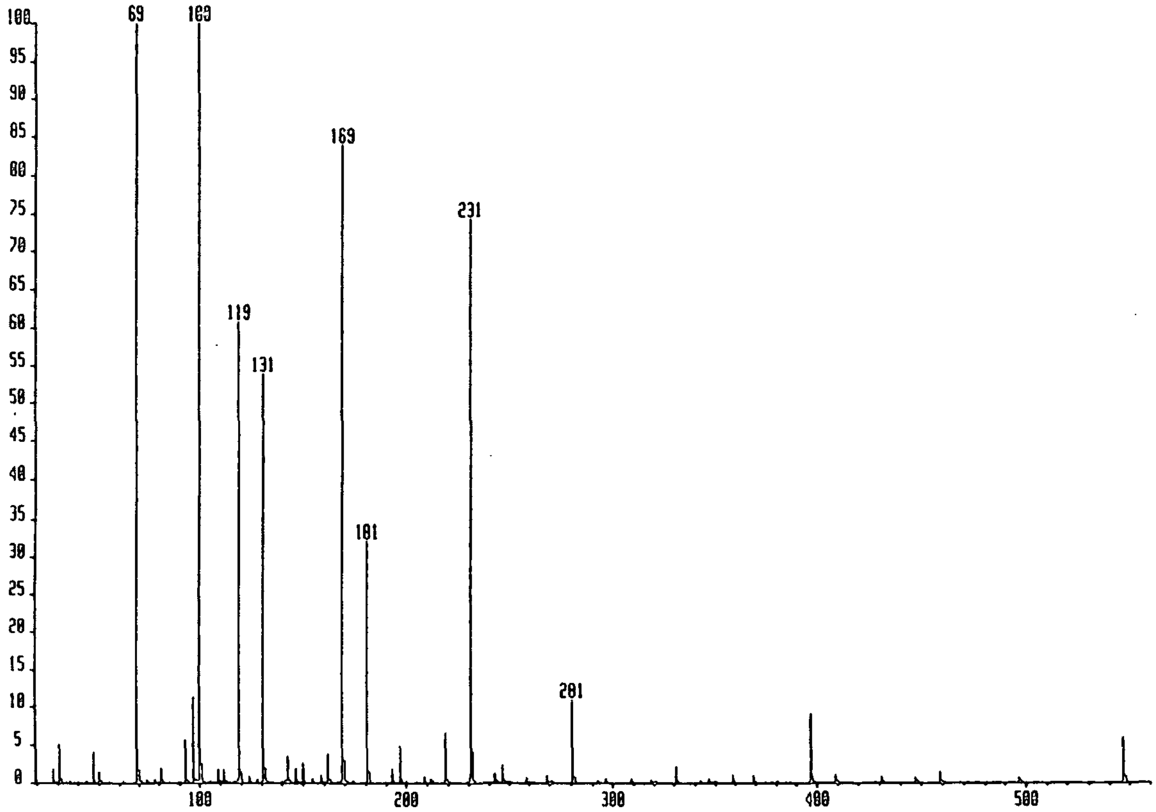
Mass	% Base
50. 05	1. 08
51. 04	8. 22
53. 07	2. 03
55. 05	1. 54
56. 04	1. 54
57. 05	9. 99
58. 06	1. 08
59. 07	3. 82
63. 06	1. 14
64. 05	1. 26
65. 07	4. 17
69. 04	24. 14
71. 07	2. 11
75. 06	19. 35
76. 05	1. 54
76. 07	1. 11
77. 07	15. 24
81. 05	1. 54
82. 05	3. 85
83. 08	16. 84
84. 09	1. 88
88. 07	2. 48
89. 07	4. 51
90. 08	1. 54
91. 06	3. 71
93. 05	3. 14
94. 06	2. 00
95. 07	14. 78
99. 07	1. 94
101. 08	10. 33
102. 08	5. 19
103. 09	100. 00
104. 10	4. 62
106. 07	1. 91
107. 07	2. 48
108. 08	12. 50
109. 06	6. 34
111. 07	1. 43
112. 06	2. 23
113. 07	26. 48
115. 10	1. 43
119. 08	3. 82
121. 09	7. 25
122. 10	3. 14
125. 08	1. 31
126. 09	3. 03
127. 09	2. 80
128. 98	2. 91
130. 99	2. 34
131. 07	6. 11
131. 98	2. 34
132. 09	2. 80
133. 10	6. 56
133. 99	1. 03
136. 00	1. 08
137. 09	1. 66
139. 10	3. 60
141. 08	8. 85
145. 10	3. 82
151. 10	4. 05
152. 11	1. 57
153. 12	4. 17
157. 10	5. 88
158. 11	28. 82
159. 08	17. 24
160. 08	1. 43
161. 09	2. 34
163. 10	1. 08
171. 12	12. 99
172. 13	53. 62
173. 13	4. 05
177. 14	1. 08
181. 13	2. 00
185. 10	1. 20
187. 10	2. 48
189. 12	1. 34
195. 12	4. 28
200. 14	14. 78
201. 14	3. 85
215. 16	1. 00
225. 14	2. 00
231. 15	12. 19
232. 17	0. 91
245. 16	5. 19
253. 16	1. 08
263. 17	4. 28
265. 19	1. 54
270. 17	0. 97
332. 21	0. 63

EI$^+$ M.Wt. 516 No. 32



Mass	% Base	
27.06	3.15	
29.05	1.10	F
29.08	3.71	F
31.05	12.00	
45.09	2.66	
47.05	6.37	
50.06	2.97	
59.12	2.81	
69.09	100.00	0
70.08	1.50	
74.13	1.63	
81.08	2.27	
93.09	11.21	
97.08	17.83	
100.10	14.79	
109.10	2.57	
112.10	3.38	
119.11	60.27	
120.11	1.45	
131.11	79.33	
132.11	2.64	
143.12	3.50	
147.10	2.29	
150.10	1.12	
162.12	3.72	
169.11	44.96	
170.12	1.39	
181.10	24.14	
182.11	1.09	
197.10	1.93	
219.12	2.32	
231.12	37.60	
232.12	1.90	
250.11	0.28	
259.14	0.36	
259.92	0.05	
269.12	0.28	
271.15	0.10	
281.13	0.80	
282.16	0.06	
282.26	0.05	
297.11	0.06	
300.11	0.08	
309.12	0.71	
310.13	0.06	
310.22	0.04	
319.11	0.71	
319.95	0.05	
320.14	0.11	
321.10	0.09	
331.05	0.06	
331.16	0.10	
333.56	0.03	
335.87	0.05	
335.99	0.04	
336.18	0.07	
336.33	0.06	
336.62	0.12	
336.91	0.04	
337.00	0.05	
337.08	0.05	
337.18	0.08	
337.78	0.05	
337.94	0.05	
338.19	0.05	
338.32	0.06	
338.42	0.05	
345.05	0.03	
345.96	0.04	
346.21	0.06	
346.29	0.06	
347.12	30.47	
348.13	2.37	
349.16	0.18	
359.12	1.77	
360.13	0.24	
363.10	0.06	
378.15	0.13	
395.61	0.05	
397.11	0.42	
397.70	0.03	
409.11	2.04	
409.48	0.03	
410.12	0.28	
411.18	0.07	
420.61	0.04	
431.05	0.06	
431.18	0.08	
441.42	0.06	
446.88	0.08	
447.10	0.10	
459.15	0.33	
460.17	0.08	
494.34	0.05	
495.45	0.08	
495.62	0.05	
495.86	0.08	
496.17	0.06	
497.11	18.81	
498.11	1.93	
499.12	0.17	
499.84	0.05	
500.44	0.05	

EI⁺ M.Wt. 566 No. 33



Mass	% Base	
27.93	1.71	
30.92	5.04	
46.89	3.94	
49.90	1.32	
68.80	1.25	
68.86	100.00	0
69.87	1.70	
80.85	1.82	
92.83	5.59	
96.83	11.33	
99.83	100.00	0
100.83	2.41	
108.82	1.69	
111.82	1.61	
118.81	60.72	
119.82	1.28	
130.80	53.80	
131.81	1.79	
142.79	3.35	
146.78	1.81	
149.79	2.58	
161.77	3.72	
168.77	83.96	
169.77	2.77	
180.75	32.01	
181.75	1.45	
192.76	1.83	
196.76	4.79	
218.75	6.54	
230.75	74.44	
231.76	3.99	
242.76	1.12	
246.75	2.29	
280.75	10.87	
330.75	2.13	
396.91	8.99	
458.85	1.27	
546.86	5.96	
547.85	0.76	

APPENDIX 4

COLLOQUIA AND CONFERENCES

APPENDIX 4

(A)

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKER:

1st AUGUST 1985 TO 31st JULY 1986

20.2.86	Dr. C.J.F. Barnard (Johnson Matthey Group) Platinum Anti-Cancer Drug Development
12.3.86	Dr. J.M. Brown Chelater Control in Homogenous Catalysis
28.11.85*	Dr. B.A.J. Clark (Kodak Ltd.) Chemistry and Principles of Colour Photography
29.1.86*	Dr. J.H. Clark (University of York) Novel Fluoride Ion Reagents
28.11.85	Dr. S.G. Davies, (University of Oxford) Chirality Control and Molecular Recognition
24.11.85	Dr. J. Dewing (U.M.I.S.T.) Zeolites - Small Holes, Big Opportunities
7.11.85	Prof. G. Ertl (University of Munich Hetergeneous Catalysis
13.2.86	Prof. R. Grigg (Queens University, Belfast) Thermal Generation of 1,3-Dipoles
27.2.86	Prof. R.K. Harris (University of Durham) The Magic of Solid State NMR
5.3.86	Dr. D. Hathaway (University of Durham) Herbicide Selectivity
6.3.86	Dr. B. Iddon (Univeristy of Salford) The Magic of Chemistry
21.11.85	Prof. K.H. Jack (University of Newcastle) Chemistry of Si-Al-O-N Engineering Ceramics
14.5.86	Dr. P.P.R. Langridge-Smith (Univeristy of Edinburgh) Naked Metal Clusters - Synthesis, Characterisation and Chemistry
23.1.86	Prof. Sir J. Lewis (University of Cambridge) Some more Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls
17.10.85*	Dr. C.J. Ludman (University of Durham) Some Thermochemical Aspects of Explosions
20.11.85	Dr. J.A.H. McBride (Sunderland Polytechnic) A Heterocyclic Tour on a Distorted Tricycle - Biphenylene

5.11.85	Prof. M.J. ODonnell (Indiana-Purdue University) New Methodology for the Synthesis of Amino Acids
13.9.85	Dr. V.S. Parmar (University of Delhi) Enzyme Assisted ERC Synthesis
30.1.86*	Dr. N.J. Phillps (Univeristy fo Technology, Loughborough) Laser Holography
19.2.86	Prof. G. Procter (University of Salford) Approaches to the Synthesis of some Natural Products
9.6.86	Prof. R. Schmultzer (University of Braunschweig) Mixed Valence Diphosphorous Compounds
5.3.86	Dr. M. Schroeder (University of Edinburgh) Studies on Macrocycle Complexes
15.1.86	Prof. N. Sheppard (University of East Anglia) Vibrational and Spectroscopic Determinations of the Structures of Molecules Chemisorbed on Metal Surfaces
12.2.86	Prof. O.S. Tee (Concordia University, Montreal) Bromination of Phenols
26.2.86	Miss C. Till (University of Durham) ESCA and Optical Emission Studies of the Plasma Polymerisation of Perfluoroaromatics
31.10.85*	Dr. P. Timms (University of Bristol) Some Chemistry of Fireworks
28.11.85	Prof. D.J. Waddington (University of York) Resources for the Chemistry Teacher
30.10.85	Dr. S.N. Whittleton (Univeristy of Durham) An investigation of a Reaction Window
23.6.86	Prof. R.E. Wilde (Texas Technical University) Molecular Dynamic Processes from Vibrational Bandshapes
12.2.86	Dr. J. Yarwood (University of Durham) The Strucutre of Water in Liquid Crystals

(B)

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
1st AUGUST 1986 TO 31st JULY 1987

13.11.86*	Prof. Sir G. Allen (Unilever Research) Biotechnology and the Future of the Chemical Industry
6.5.87	Dr. R. Bartsch (University of Sussex) Low Co-ordinated Phosphorus Compounds
27.5.87	Dr. M. Blackburn (University of Sheffield) Phosphonates as Analogues of Biological Phosphate
9.5.87	Prof. F.G. Bordwell (Northeaster University, U.S.A.) Carbon Anions, Radicals, Radical Anions and Radical Cations
26.11.86	Dr. N.D.S. Canning (University of Durham) Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis
11.5.87	Dr. R.D. Cannon (University of East Anglia) Electron Transfer in Polynuclear Complexes
28.1.87	Dr. W. Clegg (University of Newcastle-upon-Tyne) Carboxylate Complexes of Zinc; Charting a Structural Jungle
5.11.86*	Prof. D. Döpp (University of Duisburg) Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes
8.12.86	Prof. T. Dorfmuller (University of Bielefeld) Rotational Dynamics in Liquids and Polymers
12.3.87*	Dr. E.M.Goodger (Cranfield Institute of Technology) Alternative Fuels for Transport
16.10.86	Prof. N.N. Greenwood (University of Leeds) Glorous Gaffes in Chemistry
7.5.87	Dr. M. Harmer (I.C.I. Chemicals and Polymer Group) The Role of Organometallics in Advanced Materials
5.2.87	Dr. P. Hubberstey (University of Nottingham) Demonstration Lecture on Various Aspects of Alkali Metal Chemistry
17.3.87	Prof. R.F. Hudson (University of Kent) Aspects of Organophosphorus Chemistry
15.3.87	Prof. R.F. Hudson (University of Kent) Homolytic Rearrangements of Free Radical Stability
19.2.87	Dr. M. Jarman (Institute of Cancer Research) The Design of Anti Cancer Drugs

26.5.87	Dr. C. Krespan (E.I. Dupont de Nemours) Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry
23.11.86	Prof. H.W. Kroto (University of Sussex) Chemistry in Stars, Between Stars and in the Laboratory
5.3.87	Prof. S.V. Ley (Imperial College) Fact and Fantasy in Organic Synthesis
3.12.86	Dr. J. Miller (Dupont Central Research, U.S.A.) Molecular Ferromagnets; Chemistry and Physical Properties
20.11.86	Dr. A. Milne and Mr. S. Christie (International Paints) Chemical Serendipity - A Real Life Case Study
4.3.87	Dr. R. Newman (University of Oxford) Change and Decay: A Carbon-13 CP/MAS Study of Humification and Coalification Processes
22.1.87	Prof. R.H. Ottewill (University of Bristol) Colloid Science a Challenging Subject
11.5.87	Prof. S. Pasynkiewicz (Technical University, Warsaw) Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium
24.5.87	Prof. S.M. Roberts (University of Exeter) Synthesis of Novel Antiviral Agents
12.2.87	Dr. P.J. Rodgers (I.CI.Billingham) Industrial Polymers from Bacteria
6.11.86	Dr. R.M. Scrowston (University of Hull) From Myth and Magic to Modern Medicine
11.2.87*	Dr. T. Shepherd (University of Durham) Pteridine Natural Products; Synthesis and Use in Chemotherapy
2.2.87	Prof. A. Thompson (University of East Anglia) Metalloproteins and Magnetooptics
27.11.86*	Prof. R.L. Williams (Metropolitan Police Forensic Science) Science and Crime
29.10.86	Prof. E.H. Wong (University Of New Hampshire, U.S.A.) Coordination Chemistry of P-O-P Ligands
17.2.87	Prof. E.H. Wong (University Of New Hampshire, U.S.A.) Symmetrical Shapes from Molecules to Art and Nature

(C)

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS 1st AUGUST 1987 TO 31st JULY 1988

25.4.88	Prof. D. Birchall (I.C.I. Advanced Materials) Environmental Chemistry of Aluminium
18.2.88*	Dr. K. Borer (University of Durham Industrial Research Labs.) The Brighton Bomb - A Forensic Science View
16.3.88	L. Bossons (Durham Chemistry Teacher's Centre) GCSE Practical Assesment
5.11.87	Dr. A.R. Butler (University of St. Andrews) Chinese Alchemy
28.1.88*	Dr. A. Cairns-Smith (Glasgow University) Clay Minerals and the Origin of Life
11.87	Dr. J. Davidson (Herriot-Watt University) Metal Promoted Oligomerisation Reactions of Alkynes
19.4.88*	Graduate Chemists (Northeast Polytechnics and Universities) R.S.C. Graduate Symposium
3.3.88	Prof. W.A.G. Graham (University of Alberta, Canada) Rhodium and Iridium Complexes in the Activiation of Carbon-Hydrogen Bonds
22.10.87*	Prof. G.W. Gray (University of Belfast) Liquid Crystals and their Applications
7.4.88	Prof. M.P. Hartshorn (University of Canterbury, New Zealand) Aspects of Ipso-Nitration
3.11.87	Dr. J. Howard (I.C.I. Wilton) Chemsitry of Non-Equilibrium Processes
29.7.88	Dr. M.E. Jones (Durham Chemistry Teacher's Centre) GCSE Chemistry Post-mortem
29.7.88	Dr. M.E. Jones (Durham Chemistry Teacher's Centre) GCSE Chemistry A Level Post-mortem
6.7.88	Prof. H.F. Koch (Ithaca College, U.S.A.) Does the E2 Mechanism Occur in Solution?
7.3.88	Mr. Lacey (Durham Chemistry Teacher's Centre) Double Award Science
10.12.87*	Dr. C.J. Ludman (University of Durham) Explosives

11.5.88	Dr. W.A. McDonald (I.C.I. Wilton) Liquid Crystal Polymers
8.6.88	Prof. J.-P. Majoral (Universite Paul Sabatier) Stabilisation by Complexation of Short-lived Phosphorus Species
4.11.87	Mrs. Mapletoft ((Durham Chemistry Teacher's Centre) Salter's Chemistry
18.5.88	Prof. C.A. Nieto de Castro (University of Lisbon and Imperial College) Transport Problems of Non-Polar Fluids
29.6.88	Prof. G.A. Olah (University of Southern California) New Aspects of Hydrocarbon Chemistry
21.1.88	Dr. F. Palmer (University of Nottingham) Luminescence (Demonstration Lecture)
28.4.88	Prof. A. Pines (University of California, Berkley, U.S.A) Some Magnetic Moments
27.4.88	Dr. R. Richadson (University of Bristol) X-Ray Diffraction from Spread Monolayers
13.4.88	Mrs. E. Roberts (SASTRO Officer for Sunderland) Talk - Durham Chemistry Teacher's Centre - "Links Between Industry and Schools
27.4.88	Dr. J.A. Robinson (University of Southampton) Aspects of Antibiotic Biosynthesis
29.11.87*	Mrs. van Rose (Geological Museaum) Chemistry of Volcanoes
19.11.87	Prof. P.G. Seebach (E.T.H. Zurich) From Synthetic Methods to Mechanistic Insight
11.5.88	Dr. J. Sodeau (University of East Anglia) Durham Chemistry Teacher's Centre Lecture: "Spray Cans, Smog and Society"
16.12.87	Mr. R.M. Swart (I.C.I.) The Interaction of Chemicals with Lipid Bulayers
11.2.88	Prof. J.J. Turner (University of Nottingham) Catching Organometallic Intermediates
25.2.88*	Prof. A. Underhill (University of Bangor) Molecular Electronics
26.11.87	Dr. D.H. Williams (University of Cambridge) Molecular Recognition
15.10.87*	Dr. M.J. Winter (University of Sheffield) Pyrotechnics (Demonstration Lecture)

(D)

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKER:

6th OCTOBER 1988 TO 14th DECEMBER 1988

6.10.88*	Prof. R. Schmutzler (Technische Universitat Braunschweig) Fluorophosphines Revisited - New Contributions to an Old Theme
18.10.88	Dr. J. Dingwall (Ciba Geigy) Phosphorus-Containing Amino Acids: Biologically Active Natural and Unnatural Products
18.10.88*	Dr. C.J. Ludman (University of Durham) The Energetics of Explosives
18.10.88	Mr. F. Bollen Durham Chemistry Teachers' Centre Lecture About Use of SATIS in the Classroom
21.10.88	Prof. P. Von Racue Schleyer (Universitat Erlangen Nurnberg) The Fruitful Interplay Between Calculation and Experimental Chemistry
27.10.88*	Prof. C.W. Rees (Imperial College, London) Some Very Heterocyclic Compounds (The Musgrave Lecture)
9.11.88	Dr. G. Singh (Teeside Polytechnic) Towards Third Generation Anti-Leukaemics
10.11.88*	Prof. J.I.G. Cadogan (British Petroleum) From Pure Science to Profit
16.11.88	Dr. K.A. McLauchlin (University of Oxford) The Effect of Magnetic Fields on Chemical Reactions
24.11.88	Dr. R.R. Baldwin and Dr. R.W. Walker (Hull University) Combustion: Some Burning Problems
1.12.88	Dr. R. Snaith (Cambridge University) Egyptian Mummies: What, Where, Why and How?
.12.88	Dr. G. Hardgrove (St. Olaf. College, U.S.A.) Polymers in the Physical Chemistry Laboratory
9.12.88	Dr. C. Jäger (Friedrigh-Schiller University) NMR Investigations of Fast Ion Conductors of the NASICON Type (Informal Research Seminar)
14.12.88	Dr. C. Mortimer (Lancashire Polytechnic) The Hindenberg Disaster - An Excuse For Some Experiments Durham Chemistry Teachers' Centre - Schools Christmas Lecture

(E)

RESEARCH CONFERENCES ATTENDED

(* INDICATES POSTER PRESENTATION)

1\. 19th Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, 18 December 1985.

2\. Graduate Symposium,
Durham, 16 April 1986.

3.* International Symposium to celebrate the "Centenary of the Discovery of Fluorine",
Paris, August 1986.
A poster was presented by the author entitled "Free-Radical Additions of Amides and Amines to F-Alkenes".

4\. R.S.C. Perkin Division One-Day Meeting,
Newcastle, 15 September 1987.

5\. 21st Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, 16 December 1987.

6\. Graduate Symposium,
Durham, 19 April 1988.

7.* 12th International Symposium on Fluorine Chemistry,
Santa Cruz, California, U.S.A., August 1988.
A poster was presented by the author entitled "Free-Radical Additions of Silicon Derivatives to F-Alkenes".

(F) FIRST YEAR INDUCTION COURSE OCTOBER 1985

The 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 infra red spectroscopy

(4) Chromotography and microanalysis

(5) Atomic adsorptiometry and inorganic analysis

(6) Library Facilities

(7) Mass Spectroscopy

(8) Nuclear Magnetic Resonance Spectroscopy

(9) Glass blowing techniques

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REFERENCES

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4 B. Grievson, Ph.D. Thesis, University of Durham, 1983.

5 S.L. Jones, Ph.D. Thesis, University of Durham, 1987.

6 J.M. Tedder and J.C. Walton, Acc. Chem. Res., 1976, 9, 183.

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