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A THESIS  
entitled

NOVEL FLUORINATED CYCLIC DIENES  
AND THEIR CHEMISTRY

submitted by

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(St. Mary's College)

A candidate for the degree of Doctor of Philosophy

1992



- 8 SEP 1992

**To Emi, our parents,  
my friends, and  
Daikin Industries**

## ACKNOWLEDGEMENTS

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Finally, I should like to thank Daikin Industries for their financial support and encouragement to absorb everything I have experienced in Europe.

## MEMORANDUM

The work described in this thesis was carried out in the University of Durham between April 1989 and March 1992. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

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

M.W. Briscoe, R.D. Chambers, S.J. Mullins, T. Nakamura, and F.G. Drakesmith, *J. Chem. Soc., Chem. Commun.*, 1990, 1127

and has been presented by the author at:

15th Fluorine Chemistry Meeting, Kudan-Kaikan, Tokyo, Japan; October 1990.

13th International Symposium, Ruhr University, Bochum, Germany; September 1991.

NOMENCLATURE

Throughout this thesis as "F" in the centre of a ring is used to denote that all unmarked bonds are attached to fluorines unless stated.

## ABSTRACT

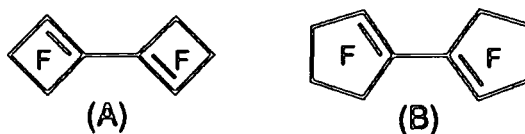
NOVEL FLUORINATED CYCLIC DIENES AND THEIR CHEMISTRY

by

Takayuki Nakamura

The work described in this thesis is concerned with three areas which are synthesis, nucleophilic reactions, and cycloaddition reactions of novel fluorinated cyclic dienes.

1 Sodium amalgam has been investigated as an electromimetic medium to reduce various fluorinated alkenes. It has been found that this can act as a single electron transfer reagent and defluorinate a series of cyclic alkenes to yield their corresponding dienes in good yield and conversion. Tetrakis(dimethylamino) ethylene (TDAE) has also been found to be a suitable reagent. The chemistry of these dienes, in particular (A) and (B), is then discussed.



2 A number of reactions with nucleophiles has been studied employing novel dienes (A) and (B). Basically vinylic fluorine has been replaced to yield a range of mono- or di-substituted products.

Reactions of fluoride ion sources with (A) and (B) have been studied. Addition of fluoride ion sources to these dienes in a solvent forms their carbanionic intermediates. That of (A) is very unstable and reacts further with (A) to give its oligomers. However it can lead to the observable carbanion by reaction of the precursor of (A) with TDAE. On the other hand, the carbanionic

intermediate of (B) is very stable, being observed by  $^{19}\text{F}$ -NMR. These carbanions have been characterised by various methods.

- 3 Numerous cycloaddition reactions have been attempted. Dienes (A) and (B) did not undergo Diels-Alder reaction as diene because of their extremely electron-deficient double bonds and their specific conformations. Diene (A) has reacted as a dienophile with hydrocarbon dienes to yield the corresponding cycloadducts. Addition of an excess of diazomethane to dienes (A) and (B) has given rise to 1,3-dipole cycloaddition reactions forming their corresponding diadducts, which have been identified as  $\Delta^2$ -dihydropyrazole derivatives.

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## CHAPTER ONE



# 1 INTRODUCTION

## 1.1 General Introduction

The history of fluorine chemistry is considerably more recent than that of the other halogens. In the 1930's, there was a significant breakthrough with the application of fluorinated compounds as refrigerants. This discovery gave impetus to research into the preparation of organic fluorine compounds<sup>1</sup>. In the following years the notorious "Manhattan Project" was set up and in the USA, another epochal discovery, polytetrafluoroethylene (PTFE), was made. Fluorine chemistry is increasingly explored and applied in such widely differing fields as polymers, medicine and agricultural chemistry.

Fluorine is the only element which can, in principle, replace any number of hydrogen atoms in a molecule because the van-der Waals radius of fluorine is the closest to that of a hydrogen, and the C-F bond is one of the most stable bonds including carbon-carbon bond. The development of numerous fluorination techniques has enabled one to synthesise a large variety of compounds<sup>2</sup>.

Perfluoro organic compounds often have widely different physical properties and certainly a quite different chemistry from the corresponding hydrocarbon compounds. Remarkably, fluorocarbons have very similar volatility to the corresponding hydrocarbons in spite of the increased molecular weight. Their effects may be attributed to lower interaction between molecules. Reactions of unsaturated fluorocarbons have been widely investigated. The chemistry has been compared with that of hydrocarbons and so called 'mirror image' relationship has been exploited<sup>3</sup>. However, there are not many reports concerning the reaction of fluorinated dienes. Most of them deal with the reactions of perfluorohexa-1,3-diene, perfluorocyclopentadiene, and perfluorocycloheptadiene, and particularly cycloaddition reactions<sup>1,4</sup>. In fact there have not been many suitable methods to synthesise fluorinated dienes.

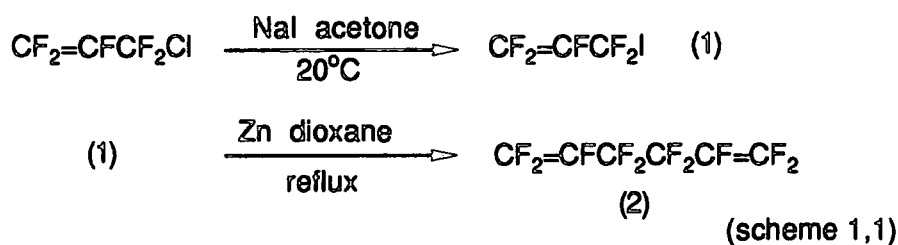
This thesis will be concerned with a study of the synthesis of novel perfluorinated dienes, a variety of nucleophilic reactions, some attempted cycloaddition reactions and will compare the results with other systems that have been reported. In the following review, the synthesis, structure and reactions of fluorinated dienes will be discussed.

## 1.2 Synthesis of Fluorinated Dienes

### 1.2.1 Intermolecular dehalogenation

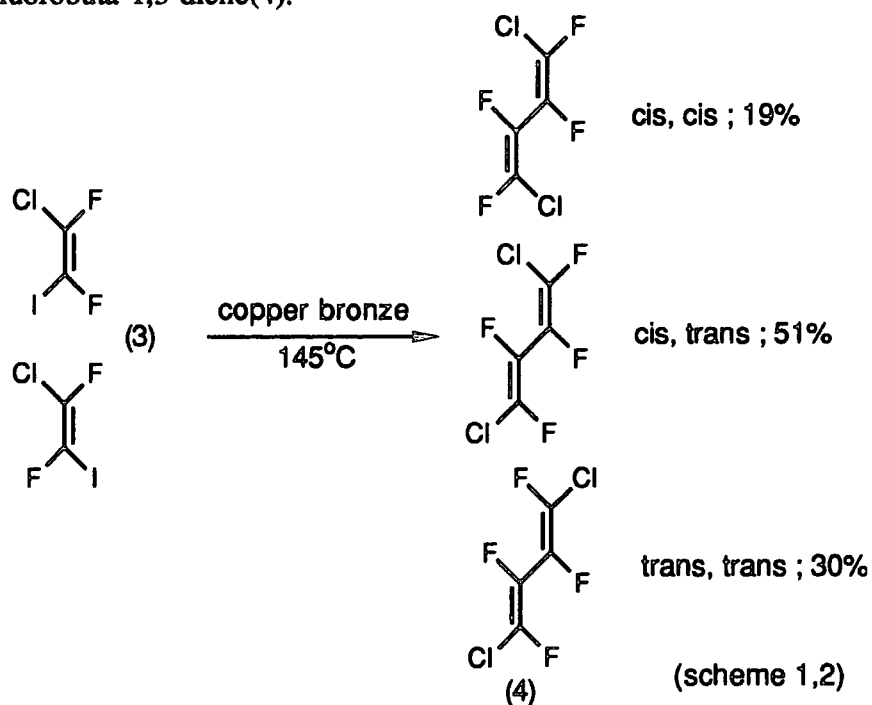
#### 1.2.1.1 Metal induced coupling of fluorinated alkenes

Intermolecular dehalogenation of perfluoroalkyl and alkenyl halides has been reported using zinc in various solvents by several workers. For example, perfluoroallyliodide (1) was coupled in dioxane by zinc to give perfluorohexa-1,5-diene(2)<sup>5</sup>.

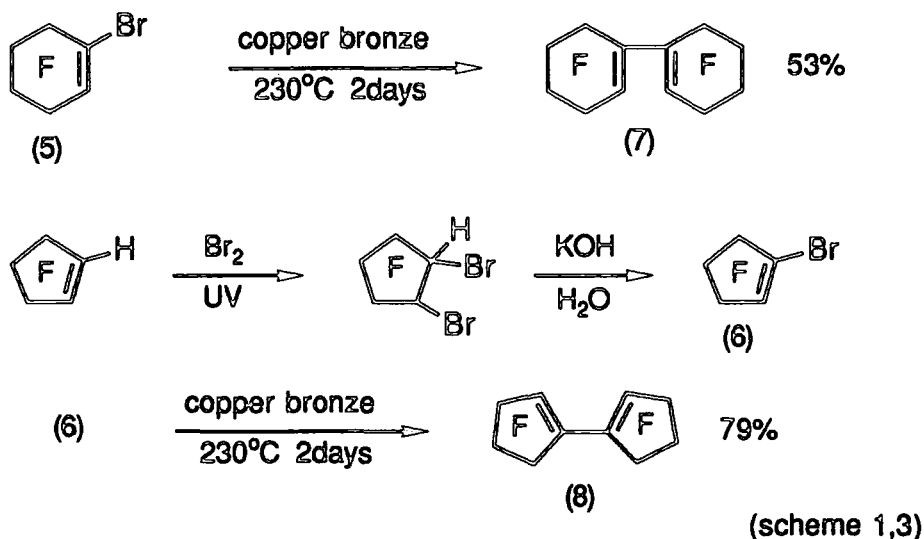


Later it was reported that copper or mercury under UV irradiation also couple (1), giving diene (2) in better yield<sup>6</sup>.

Camaggi and coworkers<sup>7</sup> reported that 1-chloro-1,2-difluoro iodoethylene (3) underwent a reductive coupling reaction when heated with copper bronze to yield 1,4-dichloro-tetrafluorobuta-1,3-diene(4).

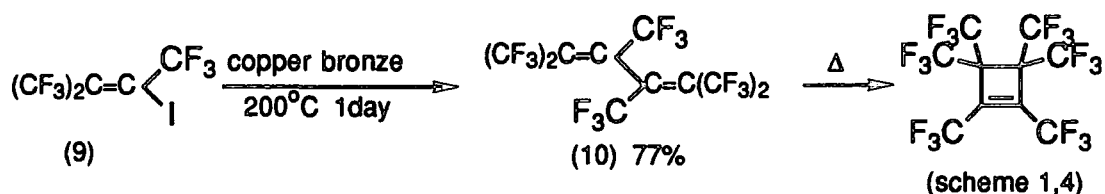


They further reported<sup>8</sup> that two perfluorinated cyclic alkenyl bromides 1-Bromononafluorocyclohexene (5) and 1-bromoheptafluorocyclopentene (6) also reacted with copper bronze to give the corresponding coupled dienes (7) and (8) respectively.

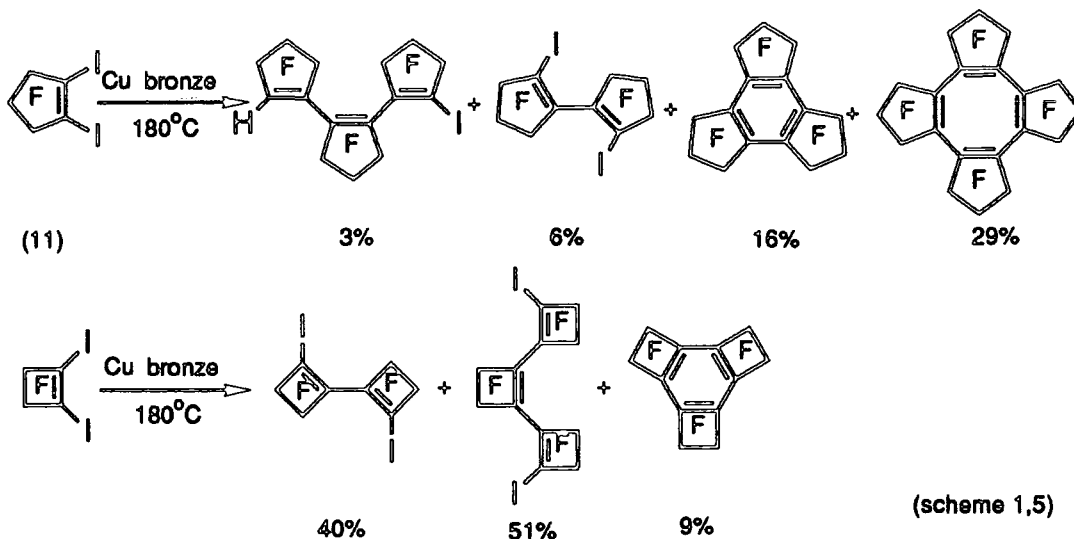


These reactions are analogous to the facile Ullmann reactions of electron deficient aryl bromides and iodides.

When 2-iodoperfluoro-3-methyl-2-butene (9) was heated with copper bronze, the highly hindered diene (10) was formed in good yield<sup>9</sup> but the interconversion of (10) to its cyclobutene cannot be completely avoided.

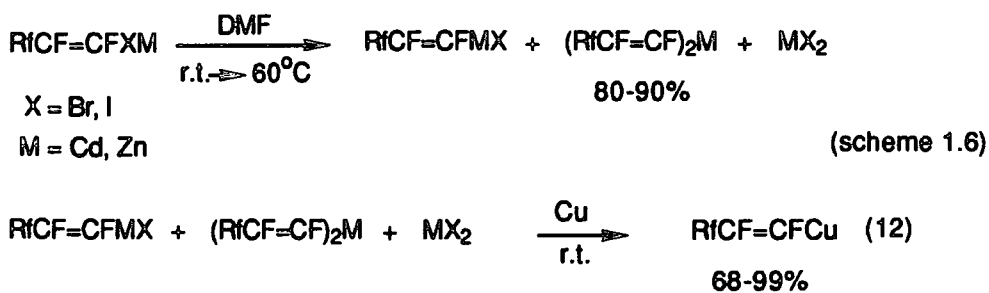


The copper bronze induced coupling reactions of 1,2-diiodoperfluorocycloalkenes (11) were demonstrated by Camaggi<sup>10</sup>, yielding not only linearly coupled cyclic dienes, but intramolecularly cyclised trienes and tetraenes (Scheme 1,5).



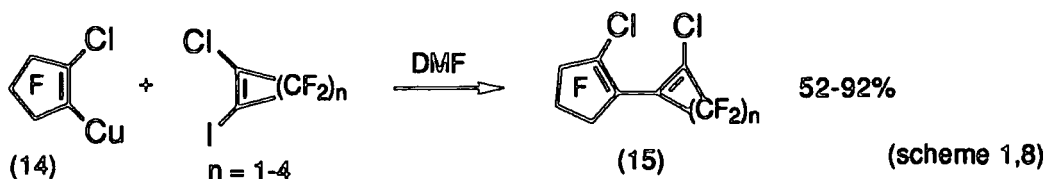
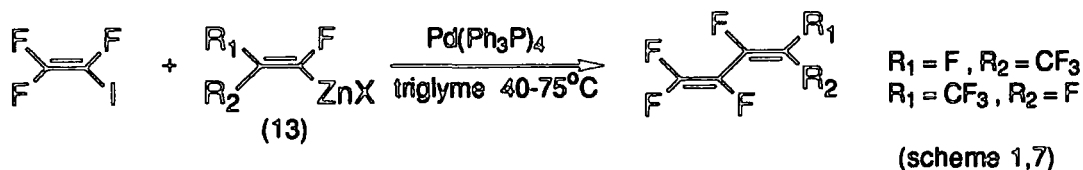
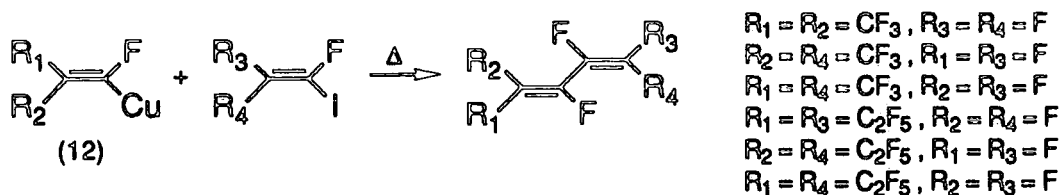
The yield in each case, however, was not good because intermolecular coupling was more favoured. Soulen and coworkers<sup>11</sup> claimed that cyclic trimer and tetramer were predominantly obtained in greater yield when a trace of *N,N*-dimethylformamide (DMF) was added.

Recently, Burton and coworkers<sup>12-15</sup> have successfully synthesised the stable polyfluorinated vinyl zinc, cadmium, and copper reagents.



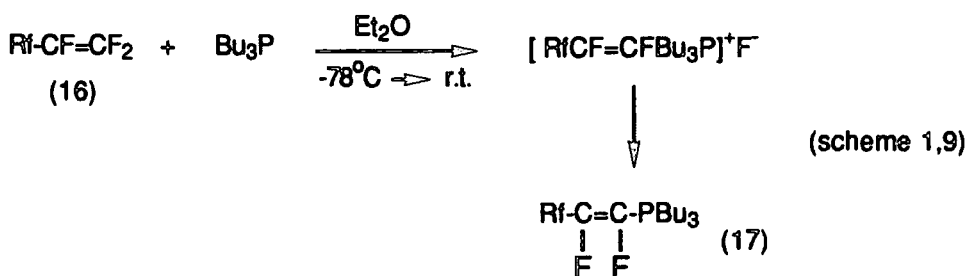
These vinyl copper and zinc reagents, (12) and (13), can react with polyfluorinated alkenyl iodides to give a variety of poly- or per-fluorinated dienes (scheme 1,6)<sup>16-18</sup>.

More recently it has been claimed<sup>19</sup> that polyfluorinated cyclo-pentenyl copper reagent (14) reacts with iodopolyfluorinated cycloalkenes to yield cyclic dienes (15) (scheme 1,8).

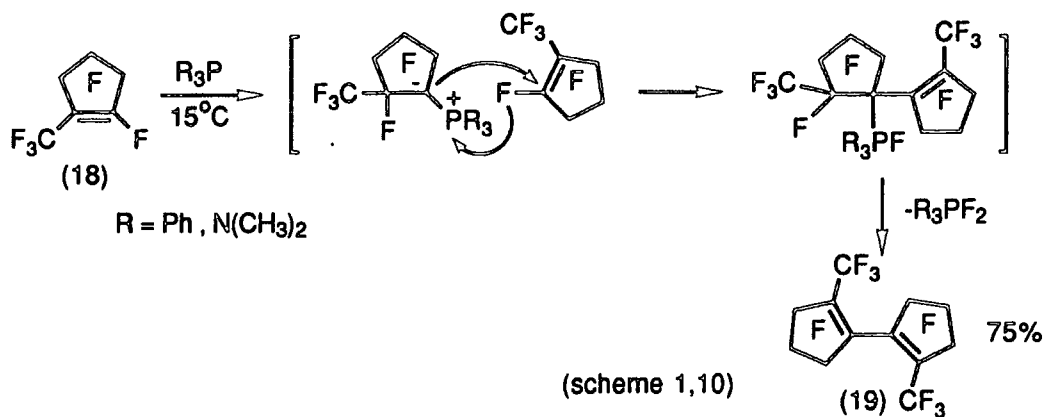


### 1.2.1.2 Phosphine induced reductive coupling of fluorinated alkenes

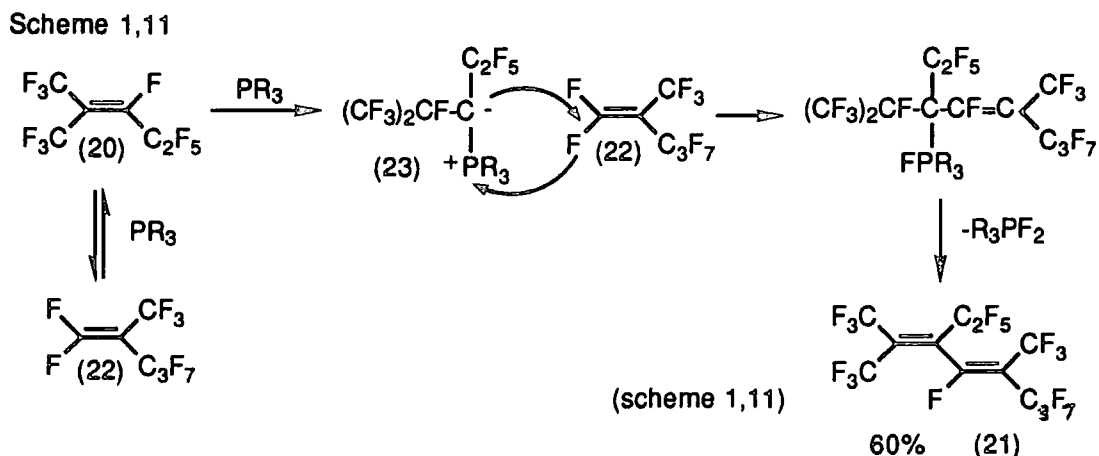
Fluorinated alkenes react readily with tertiary phosphine to form various products, depending on the position of the double bond in the molecule. Internal olefins, such as perfluorocyclobutene and 2-perfluorobutene allow phosphine to attack at the double bond and form the stable ylides<sup>20</sup>. Terminal fluorinated alkenes (16) under the same condition lead to the corresponding fluorinated vinyl phosphoranes (17)<sup>21</sup>.



An increase in electrophilicity of the double bond in internal fluorinated alkenes is proportional to the number of perfluoroalkyl groups at the double bond, and changes the reactivity with tertiary phosphine. Stepanov and coworkers<sup>22,23</sup> reported that alkenes containing three perfluoroalkyl groups at the double bond undergo a unique reductive coupling in the presence of tertiary phosphines.

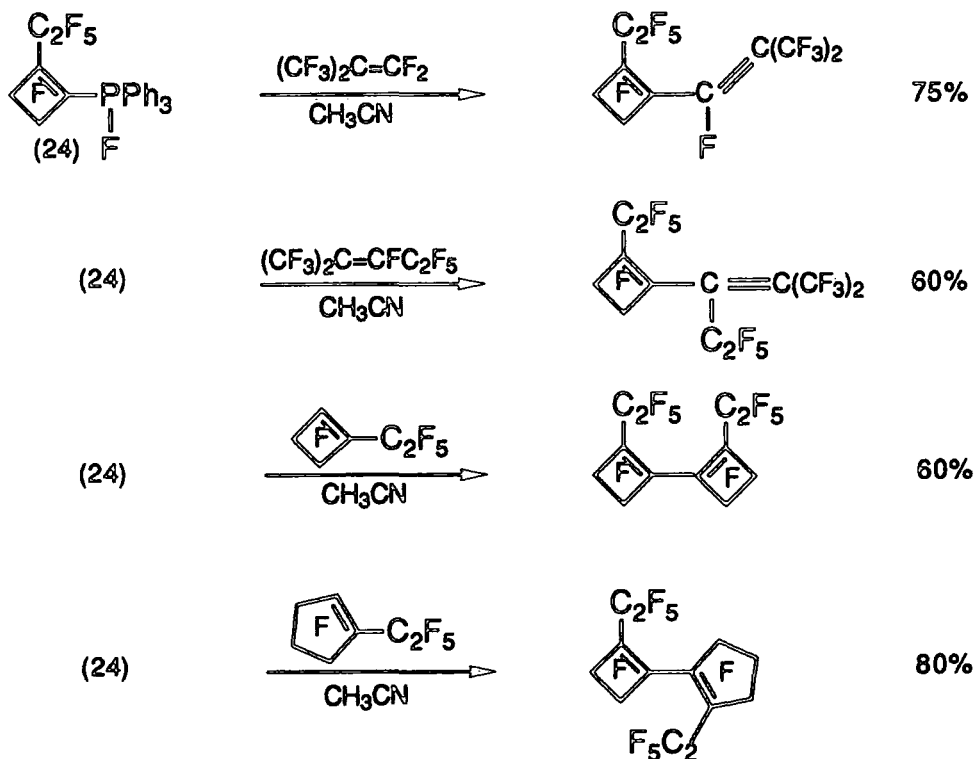


Compound(18) reacts with phosphines to give (19) in good yield. Reactions of thermodynamic dimers of hexafluoropropene (20) with phosphines lead to perfluoro-2,5-dimethyl-3-ethyl-hexa-2,4-diene (21). Isomerisation of (20) to the corresponding terminal alkene (22) occurs in the presence of phosphine (base), which is then attacked by ylide (23) to give (21).



They<sup>24</sup> subsequently studied the reactions of various perfluoroalkenyl-phosphoranes. For example, perfluoro-2-methyl-1-cyclobutenyl triphenyl-fluorophosphorane (24) reacts with perfluoroalkenes to yield conjugated dienes. Several reactions are illustrated in Table 1,1.

Table 1.1. Reactions of fluorophosphorane(24) with various fluoroalkenes

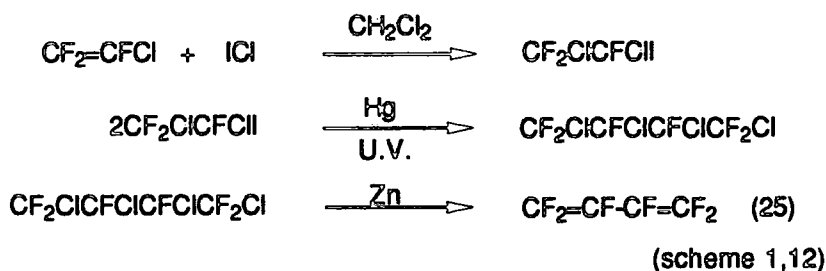


However, it should be noted that compounds containing P-F bond have great toxicity, and therefore they must be treated very carefully.

## 1.2.2 Intramolecular Dehalogenation



### 1.2.2.1 Zinc induced dehalogenation

Elimination of two halogen atoms from two adjacent carbon atoms results in the formation of fluorinated alkenes<sup>1</sup>. Dehalogenation of polyhalogenated alkenes with zinc has been used extensively in the preparation of fluorinated alkenes. Haszeldine<sup>25</sup> reported the synthesis of perfluorobut-1,3-diene (25) by dechlorination with zinc.



In the same year, the synthesis of perfluorocyclohexa-1,3-diene by dechlorination with zinc was also reported<sup>26</sup>. Some syntheses of fluorinated dienes are illustrated in Table 1,2.

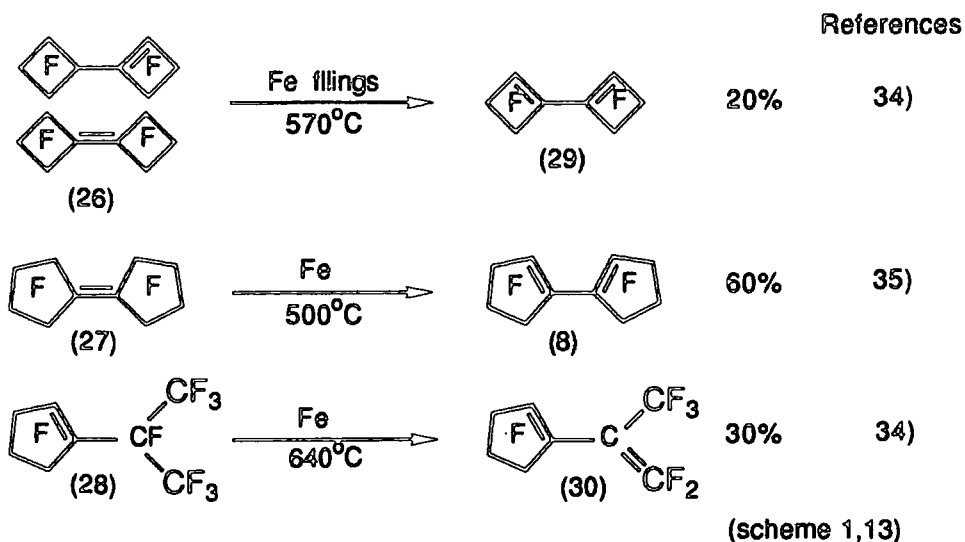
Table 1,2. Dehalogenation of various fluorocompounds by zinc

			References
	$\xrightarrow[\text{dioxane}]{\text{Zn}}$		27)
(CF <sub>3</sub> ) <sub>2</sub> C=CFCFCICFCI	$\xrightarrow[\text{diglyme}]{\text{Zn}}$	CF <sub>2</sub> =CF-CF=CF <sub>2</sub>	28)
CF <sub>2</sub> BrCFCICFCICF <sub>2</sub> Br	$\xrightarrow[\text{EtOH}]{\text{Zn}}$	(25) 80%	29)
CFCI <sub>2</sub> CFCICFCICF <sub>2</sub> I	$\xrightarrow[\text{ROH}]{\text{Zn}}$	CIFC=CF-CF=CF <sub>2</sub>	30)
CF <sub>2</sub> BrCFCICFCICF <sub>2</sub> CFCICF <sub>2</sub> Br	$\xrightarrow[\text{EtOH}]{\text{Zn}}$	CF <sub>2</sub> =CFCFCICF <sub>2</sub> CF=CF <sub>2</sub> 35% CF <sub>2</sub> =CF-CF=CFCF=CF <sub>2</sub> 65%	31)

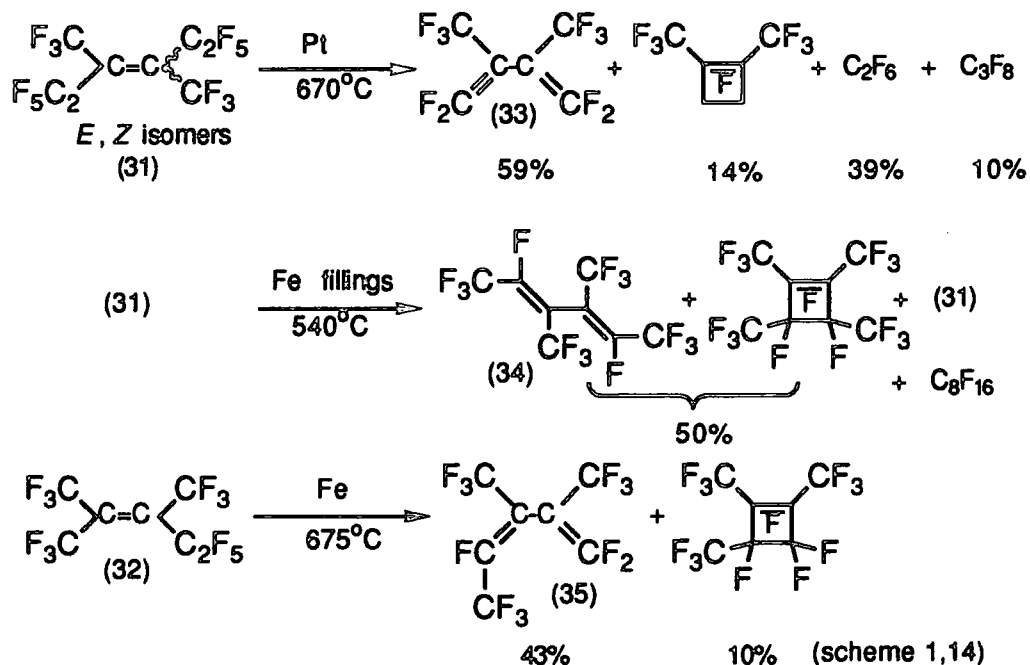
### 1.2.2.2 Defluorination

a) Thermal defluorination - thermolytic reactions have formed many applications in organic fluorine chemistry<sup>32,33</sup>. Passage of fluorinated cyclic alkenes (26-28) over iron at high temperature leads to the corresponding dienes (29), (8) and (30) respectively.

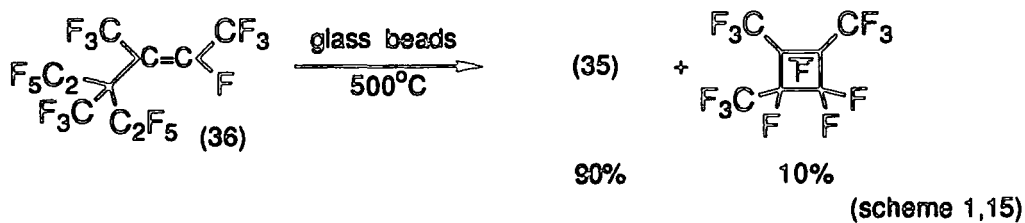




Chambers and coworkers<sup>36</sup> reported that a smooth fragmentation occurs when perfluorinated alkenes (31) and (32) were passed through a platinum lined tube or fresh iron fillings at 540-700°C, giving diene (33), (34) and (35).

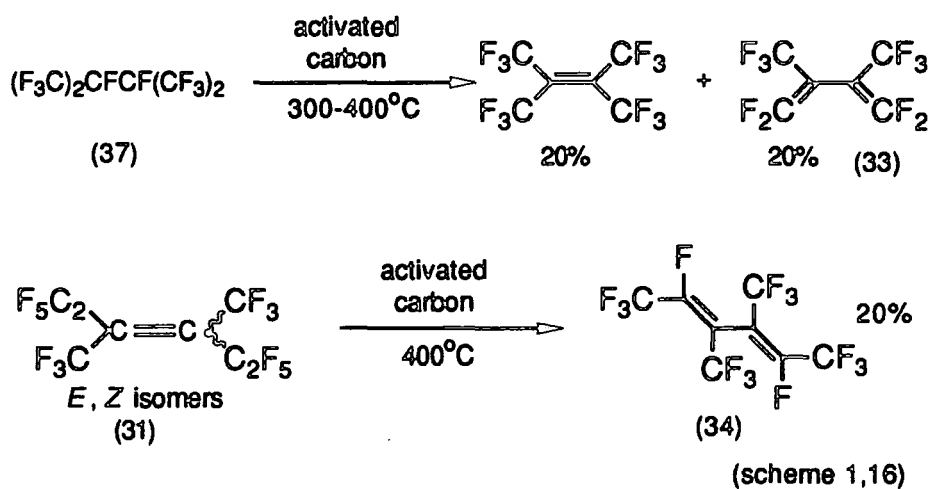


Coe and coworkers<sup>37</sup> demonstrated that the pyrolysis of perfluoro-4-ethyl-3,4-dimethylhexa-2-ene (pentamer of TFE) (36) over glass beads at 500°C gave perfluoro-2,3-dimethyl penta-1,3-diene (35) and its cyclised product.

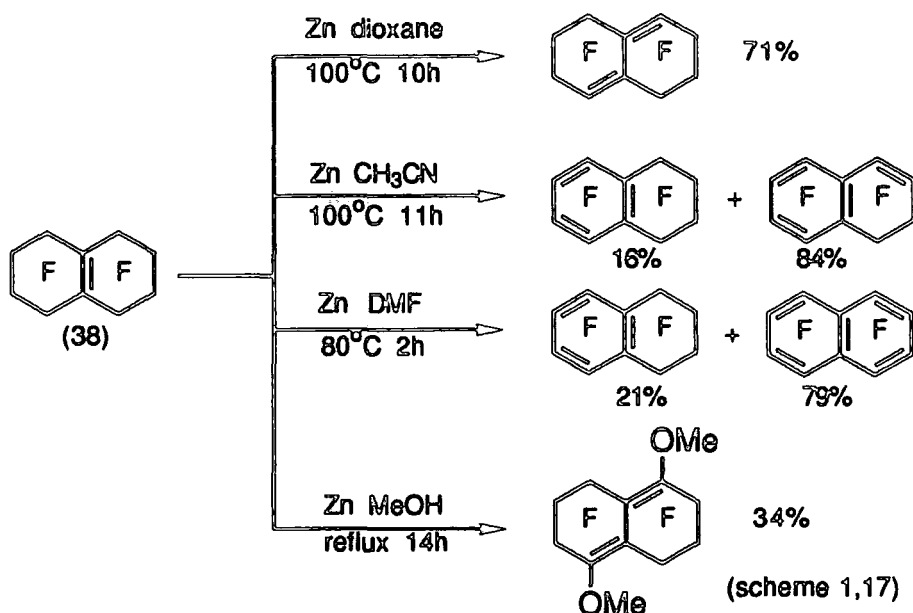


They have recently claimed flash vacuum thermolysis of (36) at 500°C led to the same products in a different ratio<sup>38</sup>.

Defluorination of fluorinated alkanes and alkenes over activated carbon at high temperature has been claimed by Du Pont<sup>39,40</sup>, providing their corresponding dienes. When perfluoro-2,3-dimethylbutane (37) and (31) were heated at 300-400°C with activated carbon, an amorphous carbon having high absorptivity for gases, vapours and colloidal solids, diene (33) and (34) were obtained as the main products.

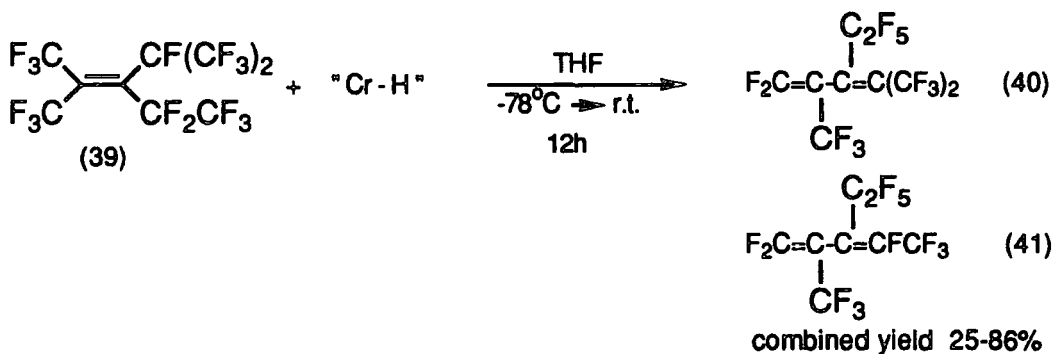


b) Defluorination by zinc - as described before, dechlorination by zinc has been largely studied. However, defluorination by zinc has been rarely demonstrated. Recently the defluorination of hexafluorobicyclo [4,4,0] deca-1-ene (38) by activated zinc powder has been carried out in various solvents by Chinese researchers<sup>41</sup>.



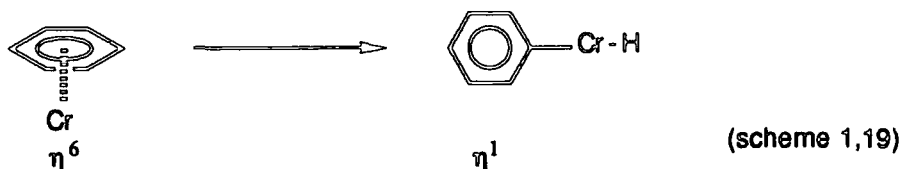
The fact that perfluorodecalin could not be defluorinated under the same condition may imply that at least one preexisting double bond is necessary for the defluorination.

c) Defluorination by organometallic compounds - it was reported<sup>42</sup> that bis( $\eta^6$ -arene) chromium (0) could oligomerise perfluoropropene catalytically at room temperature to give two dimers, two trimers, and the corresponding two defluorinated trimers. When one of the trimers obtained, perfluoro-3-ethyl-2,4-dimethylpent-2-ene(39), was treated with "Cr-H" species which was derived from  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CrCl}_2(\text{THF})_3/\text{NaH}$  or  $\text{C}_6\text{H}_5\text{CrCl}_2(\text{THF})_3$ , the corresponding defluorinated dienes (40) and (41) were formed<sup>43</sup>.

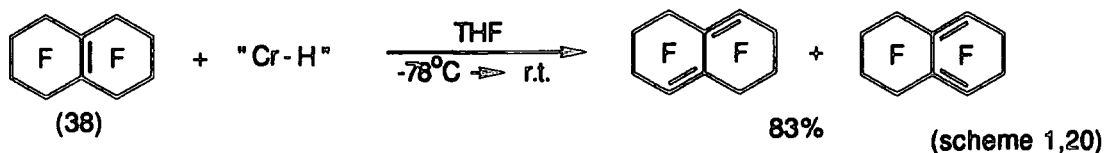


(scheme 1,18)

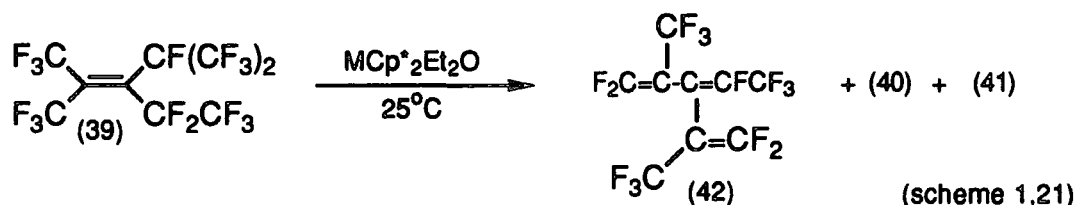
It was suggested that the hydrogenation of (39) occurred as the first step, being followed by spontaneous elimination of two molecular proportions of HF to give the dienes. It was also demonstrated that the hydrogen source for reductive defluorination of (39) was to be considered in the ligand of the catalyst through  $\eta^6$ - $\eta^1$  rearrangement.



This "Cr-H" species was used for defluorination of perfluoro- $\Delta^9(10)$  decalin [hexafluorobicyclo[4,4,0]deca-1-ene (38)] into the corresponding dienes<sup>43</sup>.



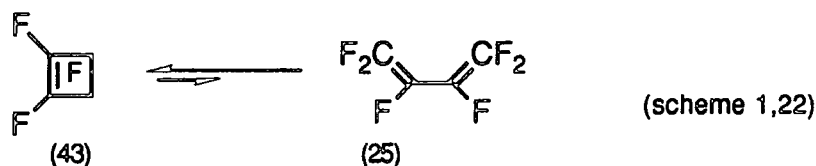
More recently, the researchers in Du Pont<sup>44</sup> have reported that divalent lanthanoid complexes  $\text{MCp}_2^*\text{L}$  ( $\text{M} = \text{Yb}, \text{Eu}, \text{Sm}$ ;  $\text{L} = \text{Et}_2\text{O}$  or  $\text{THF}$ ,  $\text{Cp}^* = \eta^5$ -methylcyclopentadienyl,  $\text{L} = \text{THF}$ ) rapidly defluorinate a variety of fluorinated alkenes. Each of the lanthanoid complexes  $\text{MCp}_2^*\text{OEt}_2$  ( $\text{M} = \text{Yb}, \text{Sm}, \text{Eu}$ ) and  $\text{YbCp}_2^*\text{OEt}_2$  reacted with a trimer of hexafluoropropene (39) on its isomer in toluene at  $25^\circ\text{C}$ , yielding dienes (40), (41) and triene (42).



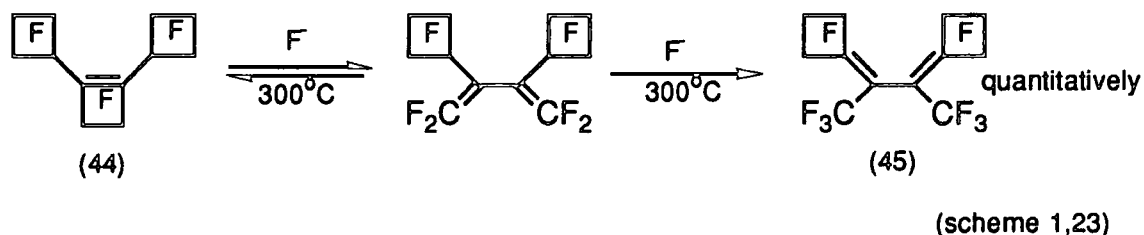
The driving forces for such reactions should be a negative reduction potential of the metal ions, augmented by the formation of a very strong lanthanoid-fluorine bond.

1.2.3 By fluoride ion induced isomerisation

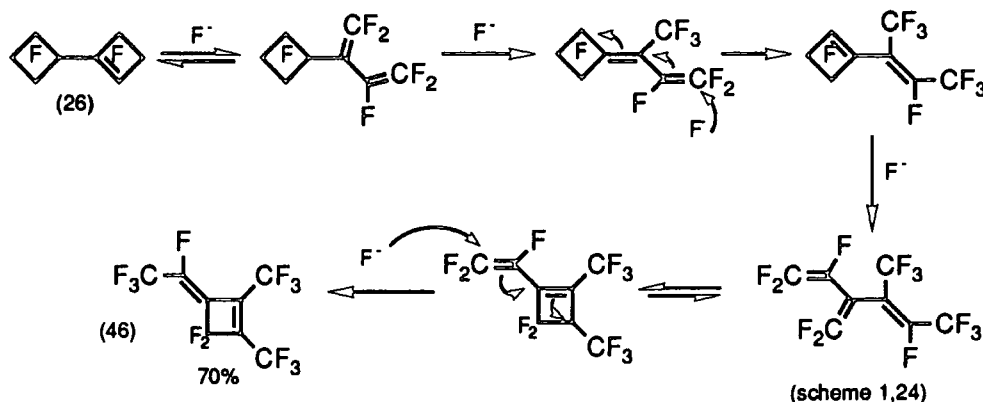
Thermal equilibrium exists between perfluorocyclobutene (43) and perfluorobute-1,3-diene (25), as it does with the hydrocarbon analogues but is predominantly on the side of perfluorocyclobutene, which is opposite to the case of the hydrocarbons<sup>45,46</sup>.



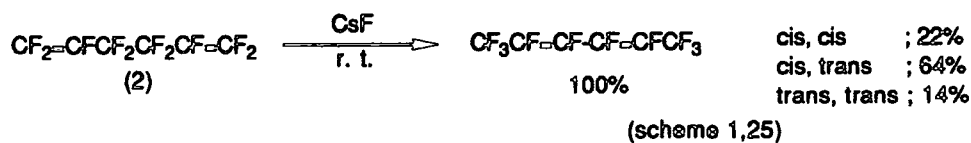
When caesium or potassium fluoride are used at moderate temperature, perfluorocyclobutene (43) is converted into perfluoro-3-butyne<sup>47</sup>. Heating trimer of hexafluorobutene<sup>48</sup>(44) with caesium or potassium fluoride at 300°C gives the corresponding isomer (45) quantitatively<sup>49</sup>.



More interestingly, passage of dimer (26) over potassium fluoride at 510°C gives (46) in ca. 70% yield<sup>49</sup>.

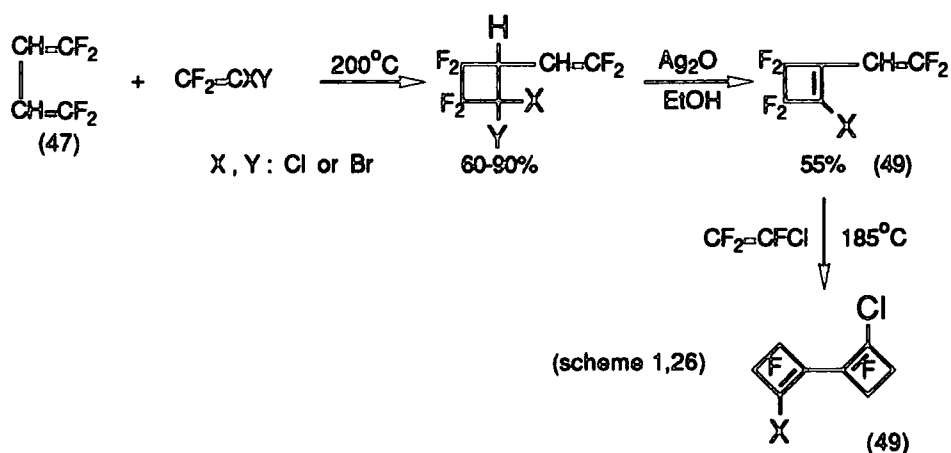


Perfluorohexa-1,5-diene(2) is readily isomerised by caesium fluoride at room temperature to give perfluorohexa-2,4-diene quantitatively<sup>50</sup>.



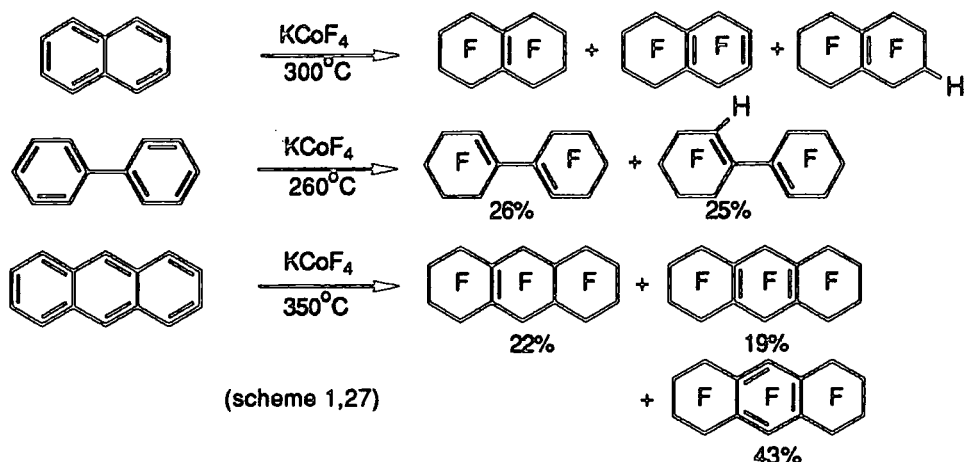
#### 1.2.4 By cycloaddition

The thermal cycloaddition of 1,1,4,4-tetrafluoro-but-1,3-diene (47) with tetrahaloethylene lead to the 1:1 adduct. Dehydrohalogenation was carried out with  $\text{Ag}_2\text{O}$  in EtOH to give (48), which further reacted with chlorotrifluoroethylene at  $185^\circ\text{C}$ , yielding fluorinated bicyclobutenyl derivatives (49)<sup>51</sup>.



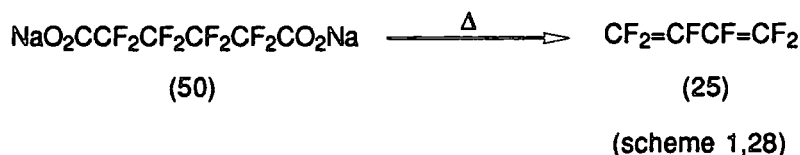
#### 1.2.5 By fluorination of hydrocarbons

Potassium tetrafluoro cobalt is milder than cobalt trifluoride for fluorination of benzene and some aliphatic compounds<sup>52</sup>. Coe and coworkers<sup>53,54</sup> reported a variety of methods for the fluorination of hydrocarbon aromatics by  $\text{KCoF}_4$ , which led to some unsaturated fluorocarbons, including dienes.



### 1.2.6 By decarboxylation

Haszeldine<sup>55</sup> reported that pyrolysis of anhydrous disodium octafluoro adipates (50) gave a perfluoro-but-1,3-diene (25).



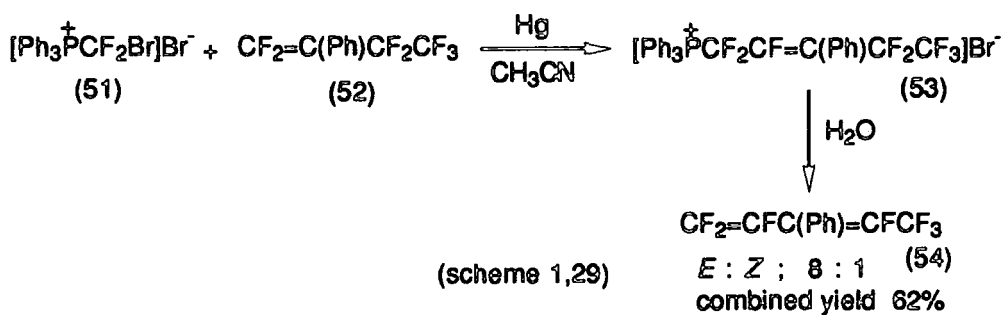
This method has been applied to the synthesis of perfluorovinylethers and divinylethers<sup>56</sup>, which are nowadays very important for fluoropolymer industries.

### 1.2.7 By chain-extension reaction

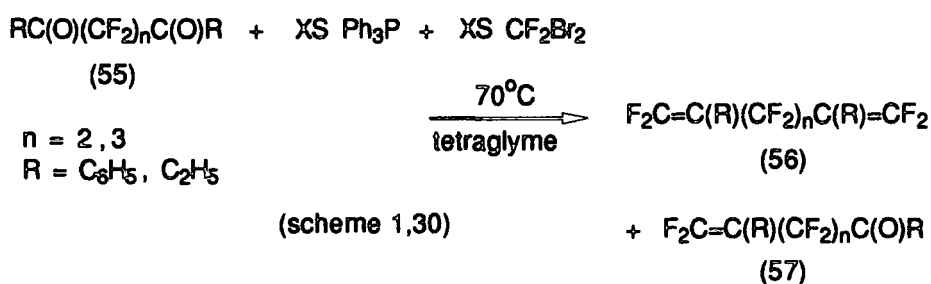
Chain-extension or hemolongation reactions are widely demonstrated in organic synthesis. Burton and coworkers<sup>57,58</sup> have claimed the first example of a difluoromethylene (CF<sub>2</sub>) chain-extension reaction that retains the precursor functionality to give fluorinated dienes.

When bromodifluoromethyl triphenyl phosphonium bromide (51), which is formed by the reaction of dibromo-difluoromethane and triphenyl phosphine<sup>59</sup>, is treated with 2-phenyl fluorobutene (52) in the presence of mercury, the chain-extended phosphonium salt (53) is formed in good yield. Subsequent hydrolysis of (53) with H<sub>2</sub>O gives mainly 3-phenyl-perfluoropenta-1,3-diene (54).

Scheme 1,29



Furthermore, they have applied this idea to another synthesis of fluorinated dienes via an analogs of the Wittig Reaction<sup>60</sup>. Fluorinated dienes (55) reacted with an excess of triphenyl-phosphine and dibromo-difluoromethane to give the respective diene (56) and enones (57).



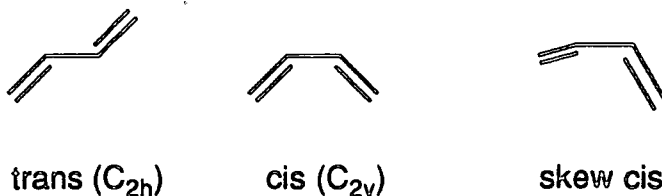
### 1.3 Structure of Fluorinated Dienes

Perfluorobuta-1,3-diene (25) is the simplest fluorocarbon having a conjugated double bond and is a model of linear perfluoro conjugated oligomers and polymers. Therefore the structure of this diene has been investigated for many years<sup>61-69</sup>, being compared with that of buta-1,3-diene, which has two energy minima - a trans form and a skew cis form with torsion angle 30-40°, (s-cis is defined as 0° and s-trans as 180°)<sup>61,62</sup>.

The first report of vibrational studies<sup>63</sup> concerning diene(25) implied that the trans form does not exist, but was not able to observe the difference between the s-cis and skew-cis form. Brundle and Robin<sup>64</sup> suggested their photoelectron and UV spectra supported a nonplanar structure and predicted a torsion angle of  $42^\circ \pm 15^\circ$  (C=C-C=C dihedral angle). An electron diffraction study by Bauer and coworkers<sup>65</sup> was also consistent with a skew structure and the dihedral angle was calculated to be  $47.4^\circ \pm 2.4^\circ$ .



Recently, the vibrational spectrum of (25) has been assigned and is consistent with gauche structure (skew cis structure)<sup>66</sup>.



The structure of (25) has also been examined by theoretical calculations<sup>67-69</sup>. Most of their results are consistent with those by spectroscopic studies.

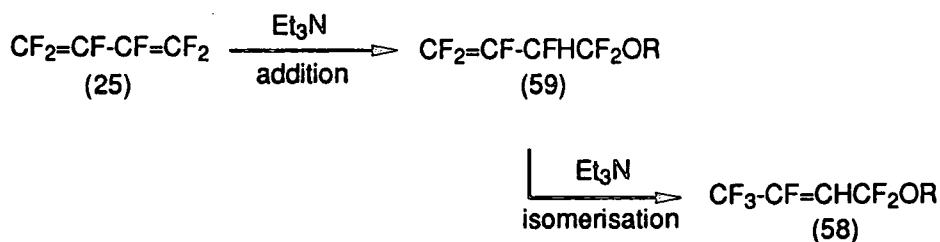
#### 1.4 Reaction of Fluorinated Dienes

Reactions of nucleophiles with fluorinated alkenes are among the most important reactions in organic fluorine chemistry and they have been extensively investigated<sup>1,3</sup>. In contrast, those of fluorinated dienes have not been investigated thoroughly.

In this section, some illustrative examples of reactions of fluorinated 'cyclic' and 'acyclic' dienes will be described.

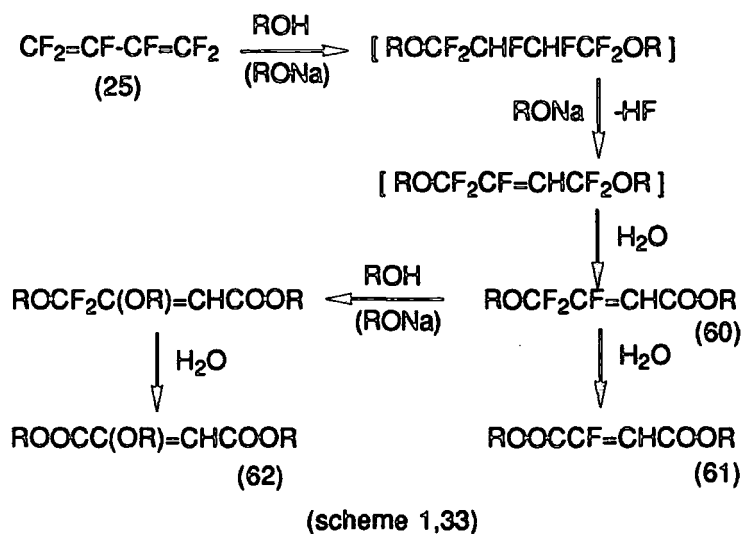
##### 1.4.1 Reactions with oxygen-containing nucleophiles

Nucleophilic addition of primary alcohols to perfluorobut-1,3-diene(25) were reported for the first time by Knunyants and coworkers<sup>70</sup>, who reported that, for example, the addition of ethanol to (25) in the presence of catalytic amount of triethylamine afforded 1-ethoxy-1,1,3,4,4,4-hexafluoro-but-2-ene (58) (1,2-addition)<sup>71</sup>. They assumed that triethyl-amine not only catalyses the addition of alcohol to (25) as base, but causes isomerisation of the original product (59) into (58).



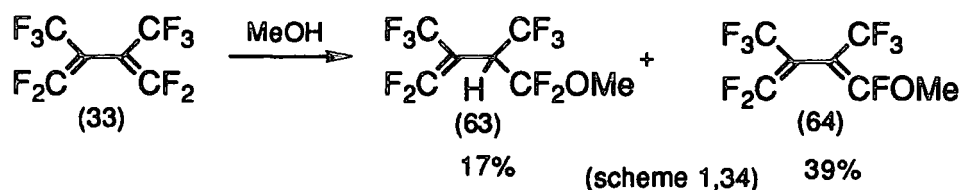
(scheme 1,32)

Recently, however, Dêdek and coworkers<sup>72</sup> demonstrated that the addition of ethanol to (25) was more complicated in the presence of sodium alkoxide as a catalyst. According to their study, the nucleophilic addition of ethanol to (25) gave a mixture of ethyl-4-ethoxy-3,4,4-trifluoro-2-butenoate (60);43%, diethyl-2-fluorofumarate (61); 18%, and diethyl-2-ethoxy-2-butenedioate (62);32%. Similar products were obtained by the addition of methanol to (25), catalysed with sodium methoxide.



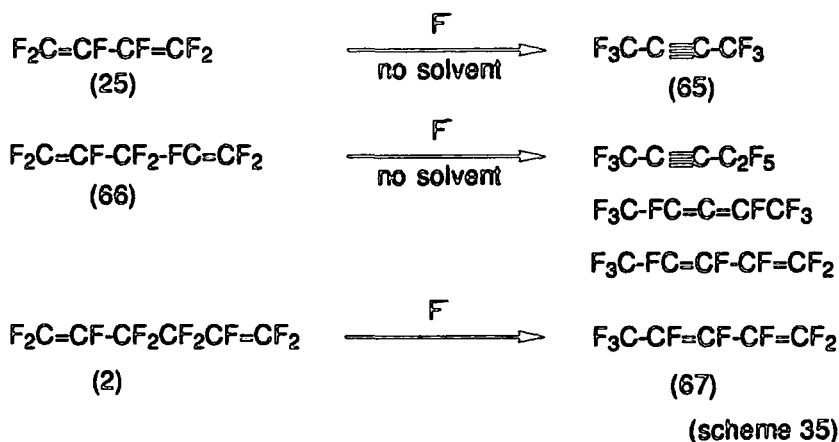
The reactions consist of the sequence addition, elimination and hydrolysis. They also studied the nucleophilic reactions of non-conjugated fluorinated diene and triene with various oxygen containing nucleophiles<sup>73</sup>.

Perfluoro-2,3-dimethylbuta-1,3-diene (33) reacted with an excess of methanol to give a 1,2-addition product (63);17%, and a substitution product (64);39%<sup>74</sup>.



#### 1.4.2 Reactions with fluoride ion

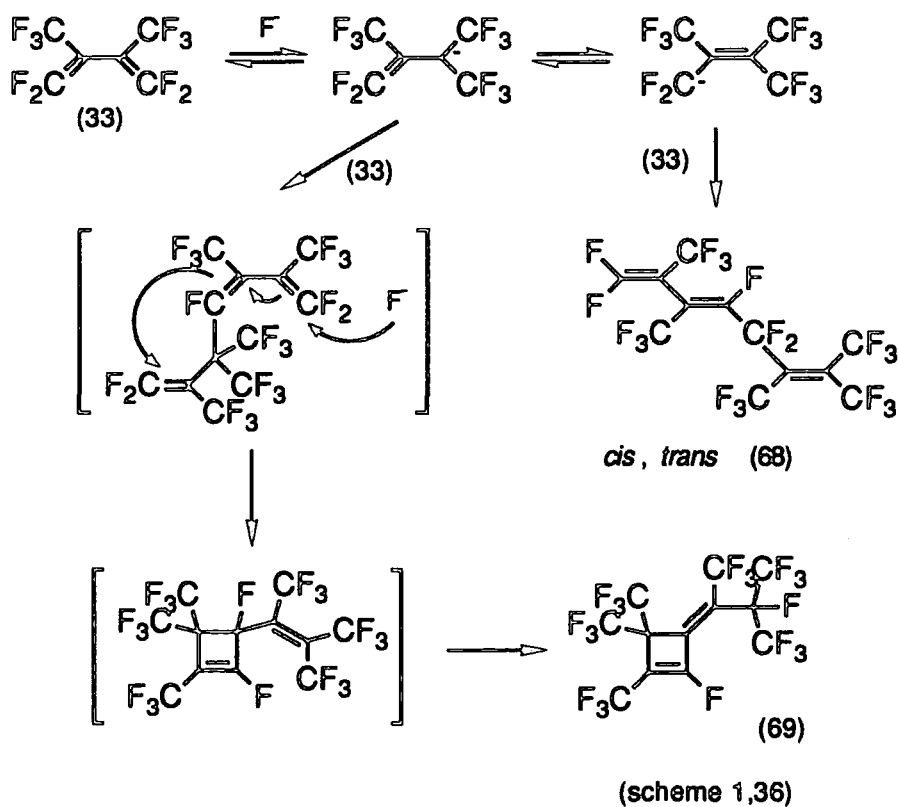
Perfluorobut-1,3-diene (25) is readily isomerised by fluoride ion to hexafluorobutene. Similarly, perfluoro-penta-1,4-diene(66) is converted into the corresponding internal isomer<sup>75</sup>.



Perfluoro-hexa-2,4-diene (67) can be obtained quantitatively by the fluoride ion induced isomerisation of perfluorohexa-1,5-diene (2)<sup>76</sup>.

In the case of perfluoro-2,3-dimethylbuta-1,3-diene (33), however, dimerisation occurs very readily in the presence of caesium fluoride, giving dimers (68) and (69)<sup>77</sup>.

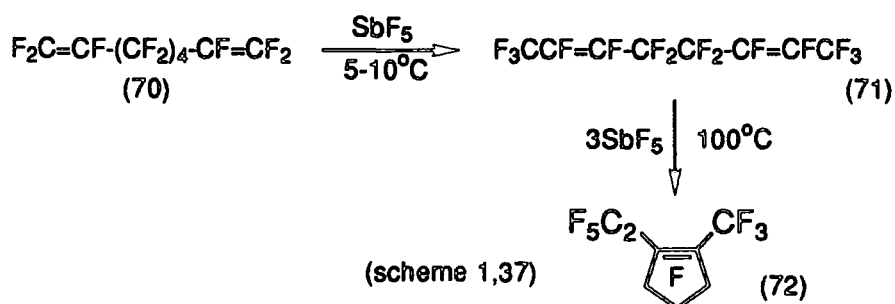
The ratio of (68) and (69) is temperature dependent.



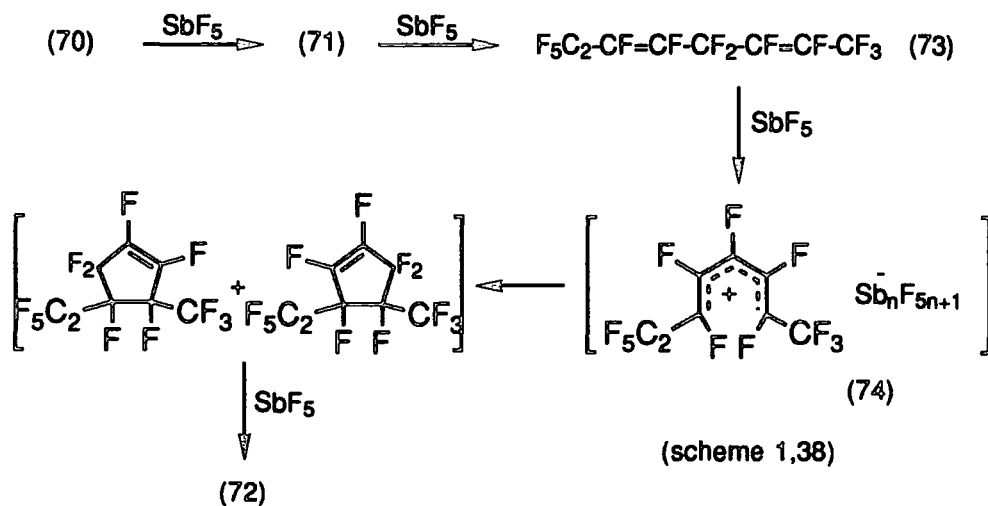
### 1.4.3 Reactions with antimony pentafluoride

It was reported by Russian workers<sup>78</sup> that the double bond in higher perfluoroalkenes is readily shifted from position 1 to 2 in the presence of antimony pentafluoride. In the same manner, perfluoroocta-1,7-diene (70) isomerises quantitatively at lower temperature to perfluoroocta-2,6-diene (71), with the preferred trans-trans structure<sup>78</sup>.

When (71) is heated with three molar equivalents of antimony pentafluoride at 90-100°C, (71) is internally cyclised to give (72).

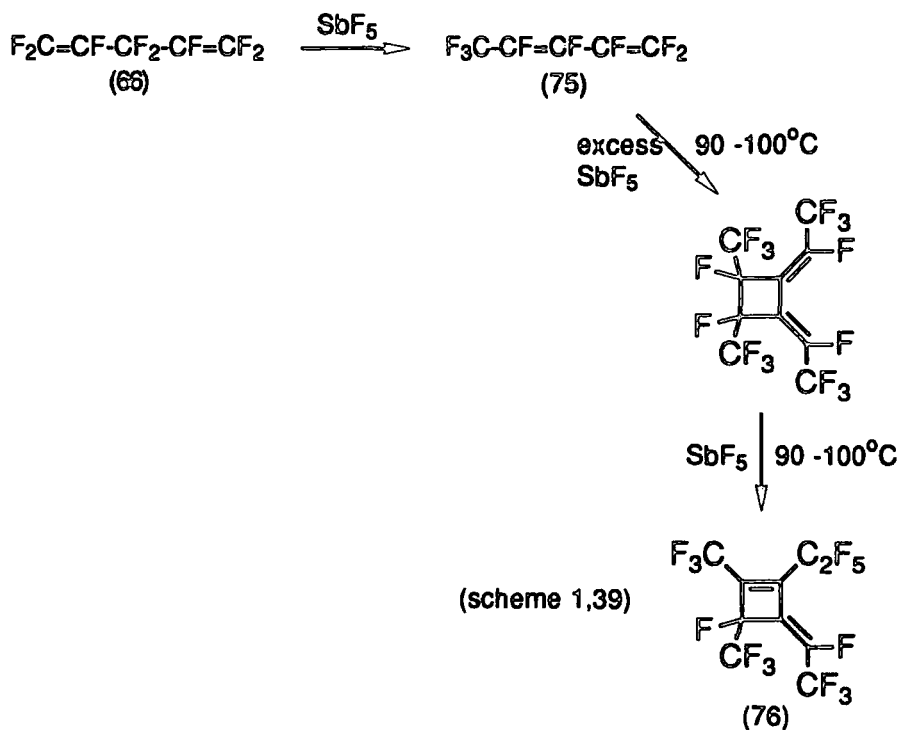


They subsequently reported that a variety of perfluorodienes underwent the same isomerisation and intramolecular cyclisation on heating with  $\text{SbF}_5$ <sup>80</sup>. They proposed the reaction mechanism of these reactions as follows:



The first and second stages are clearly the isomerisation of (70) into (73). At the next stage, the perfluoropentadienyl cation (74) is generated by an excess of  $\text{SbF}_5$ , followed by 1,5-cyclisation and another isomerisation giving (72)<sup>80</sup>.

When perfluoropenta-1,3-diene (75), which is obtained by the isomerisation of perfluoropenta-1,4-diene (66) by  $\text{SbF}_5$ , is heated with an excess of  $\text{SbF}_5$ , it does not afford intramolecular cyclisation but cyclodimerises<sup>80</sup> to give (76).



## CHAPTER TWO

## 2 THE SYNTHESIS OF FLUORINATED DIENES

### 2.1 Introduction

#### 2.1.1 Oligomerisation of fluorinated alkenes

Fluoride ion induced reactions of fluorinated alkenes have been extensively investigated<sup>1</sup> because:

- (a) These reactions form an analogy with reactions between protons and unsaturated hydrocarbons.
- (b) A carbanion is generated during these reactions which was first established by Miller and coworkers<sup>81</sup>, and was later shown as a very good method to build up carbon-carbon bonds.

For example, tetrafluoroethylene is readily oligomerised in the presence of fluoride ion to give a range of oligomers<sup>82,83</sup>. The system is quite complex, as illustrated in Scheme 2,1.

Hexafluoropropene is also oligomerised by fluoride ions to yield a variety of oligomers<sup>84,85</sup>.


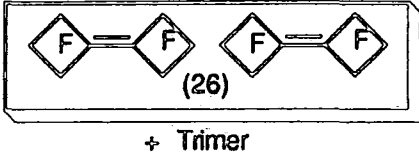

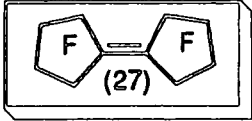

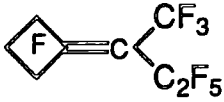


Chambers and coworkers<sup>86-88</sup> have demonstrated a variety of reactions of fluorinated cycloalkenes induced by fluoride ion, *e.g.* oligomerisation and co-oligomerisation of fluorinated cycloalkenes, giving very interesting fluorinated alkenes. Table 1 illustrates some of their studies.

Among them, dimers of perfluorocyclobutene(43) and its isomer (26) are particularly interesting because of their angle strain and susceptibility to nucleophilic attack. Dimer of perfluorocyclopentene (27) can be considered to have less angle strain than (26). This part describes the synthesis of some fluorinated cyclic alkenes as the precursor for diene synthesis.





Table 1. Oligomerisations Of Various Fluorinated Alkenes

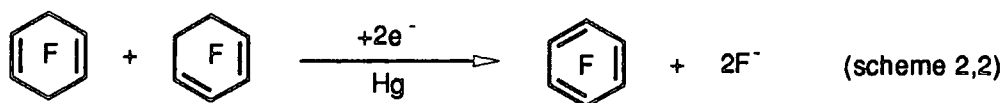
Substrate	Conditions	Products	Reference
	CsF, r. t.		34)
	CsF, 125°C sulpholane		88)
 + CF <sub>3</sub> CF=CFCF <sub>3</sub>	CsF, r. t. DMF		34)
	CsF, 150°C DMF		34)

### 2.1.2 Reductive defluorination

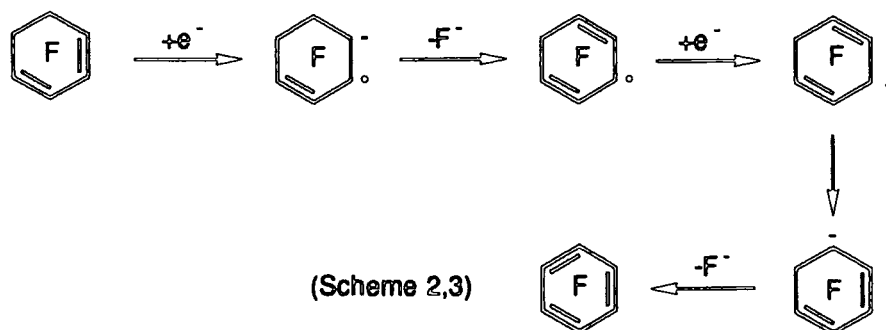
The double bond of the fluorinated alkenes is extremely electron poor, therefore it would not be very difficult to accept an electron on the anti-bonding orbital of the double bond. For example, an electron transfer may take place at the cathode on electrochemical reduction or on contact with an electron donating reagent<sup>23</sup>. Both of these applications have been explored in the present work as a possible route to dienes by defluorination.

#### 2.1.2.1 Electrochemical defluorination

Pedler and coworkers<sup>89</sup> reported that perfluorocyclohexa-1,3- and -1,4-dienes can be defluorinated by electrolytic reduction at a mercury cathode to give hexafluorobenzene in high yield.



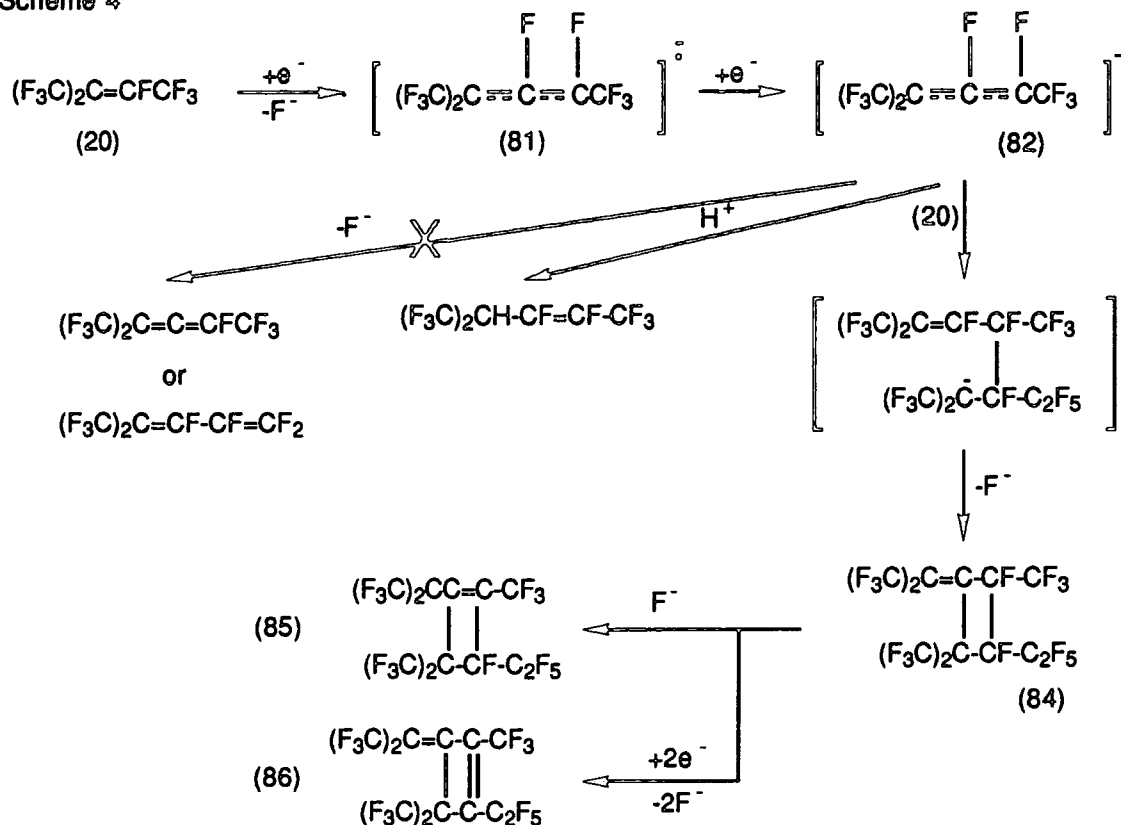
They suggested the following mechanism for the reactions involving a series of one-electron transfer steps.



Knunyants and coworkers<sup>23</sup> claimed that cathodic reduction of perfluoro-2-methyl-2-pentene (20) leads to 2-hydro-perfluoro-2-methyl-3-pentene (79) in a proton donating medium or to the reductive coupling dimerisation to give two products (81) and (82). The proposed reaction mechanism includes (i) a transfer of an electron to (20), (ii) the simultaneous elimination of fluoride ion giving the radical (77), and (iii) another transfer of an electron, generating the allylic carbanion (78).

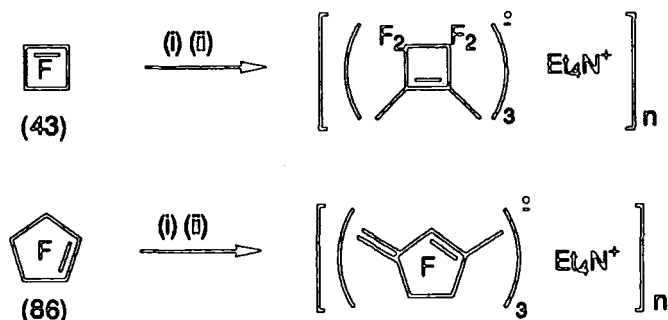
In order to stabilise (78), either a proton may be abstracted from the solvent to give (79), or (78) may be attacked by the starting alkene in aprotic solvent accompanying an internal nucleophilic substitution reaction to give (80). Compound (80) is further isomerised by fluoride ion or defluorinated, yielding (81) and (82) respectively.

Scheme 4



No further defluorination of (78) occurred to give the corresponding diene or allene.

Electrochemical reactions of fluorinated compounds have also been studied in this laboratory<sup>90,91</sup>. It should be noted that lustrous blue-black polymers were obtained by the electrochemical reactions of perfluorocyclobutene(43) or pentene(86), and mechanisms involving electrochemical defluorination have been suggested<sup>92</sup>. Also low yields of diene (34) were obtained in the electrochemical reduction of the tetramer (31). It is extremely difficult to control the reaction conditions accurately and perform preparative-scale electrochemistry, therefore we have explored chemical methods for defluorination that would 'mimic' electrochemistry involving electron transfer processes.



(i) Pt or Hg cathode, divided cell, CH<sub>3</sub>CN or DMF. Et<sub>4</sub>NBF<sub>4</sub>

(ii) -1.9V(saturated calomel electrode)

(scheme 2,5)

### 2.1.2.2 Defluorination by electron donating reagents

Russian researchers<sup>23</sup> have shown that sodium-naphthalene, defluorinates and dimerises (20) in monoglyme to give the same product (81) and (82) (see Scheme 2,4). Recently Chinese researchers<sup>41</sup> have claimed that activated zinc can defluorinate some fluorinated cycloalkenes to give the corresponding defluorinated products. These reagents probably donate electrons to fluorinated substrates, causing defluorination. We have explored the pyrolytic defluorination of cycloalkene derivatives (26) and (27)<sup>34,35</sup> (see Chapter 1), but this approach can be limited on scale-up, more seriously accompanied by fragmentation and isomerisation.

Following, however, is an effective electro-mimetic procedure to synthesise fluorinated dienes using sodium amalgam<sup>91,93</sup>.

## 2.2 Discussion

### 2.2.1 Preparation of the diene precursor

#### 2.2.2.1 Oligomerisation of perfluorocyclobutene

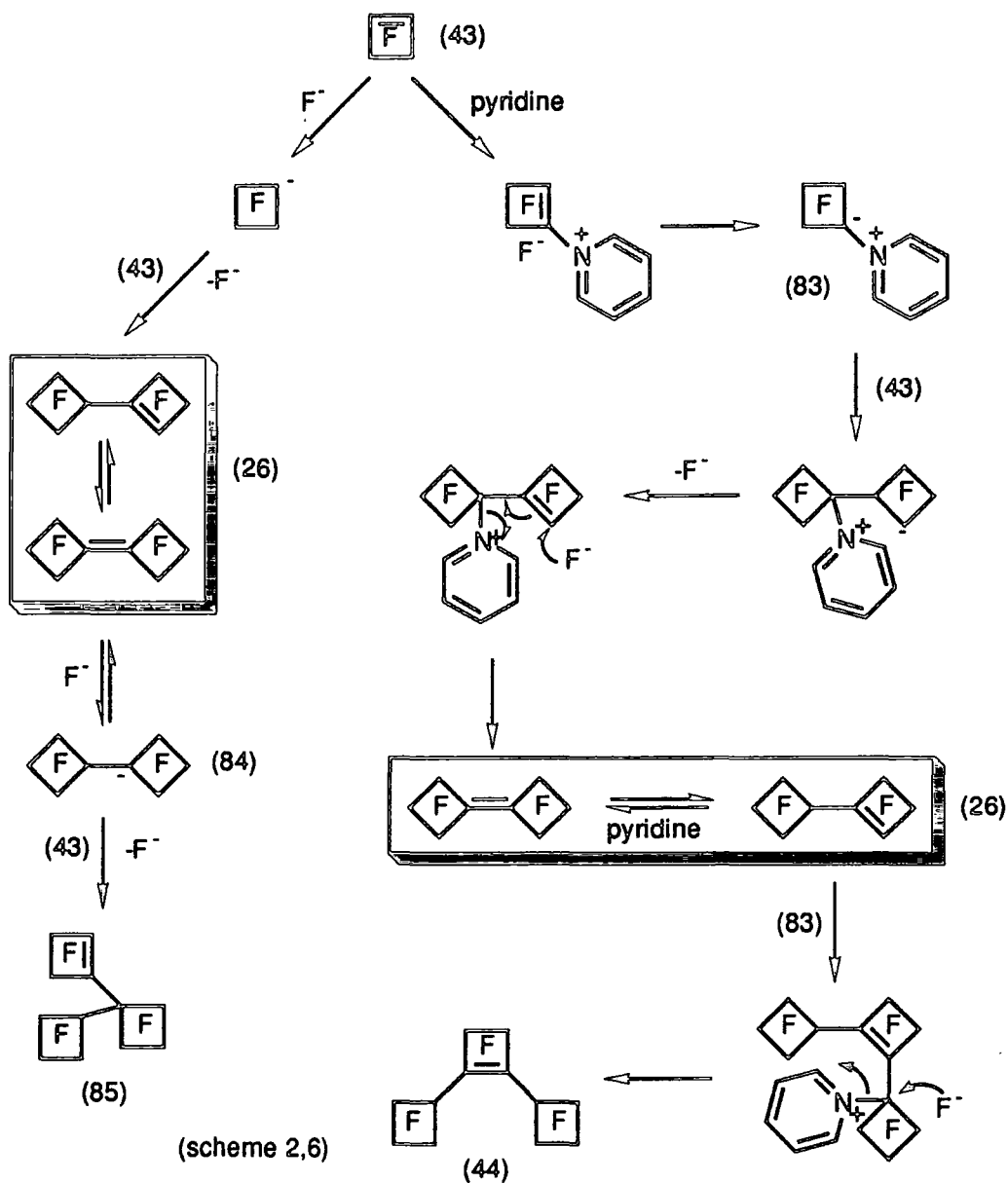
There are two reactions to provide the diene (26); either with caesium fluoride or with pyridine from perfluoro cyclobutene(43)<sup>34,86,87</sup>. As reported previously, pyridine-induced oligomerisation gave dimers (26) in better yield than fluoride ion. The mechanism of pyridine and fluoride ion induced oligomerisation is shown in Scheme 2,<sup>34,86,88</sup>.

The reason the pyridine induced oligomerisation gives the dimers (26) in better yield can be explained as follows:

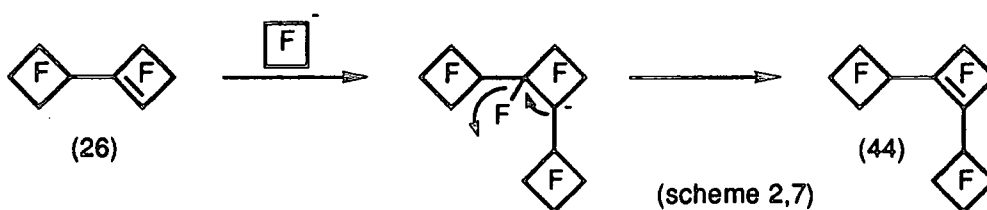
(i) The reaction rate between the ylide (83) and the dimer (26) can be limited by steric hindrance; therefore the reaction rate of generating trimer (44) is fairly slow.

(ii) The carbanion (84) is readily generated by fluoride ion and is very stable. This can be observed by <sup>19</sup>F-NMR at room temperature<sup>94</sup>. Therefore (84) readily reacts with perfluorocyclobutene to give trimer (85). It should be pointed out that each system gives a different trimer. It was reported that fluoride ion induced oligomerisation of (43) leads to trimer (85) and a small amount of its isomer which had not been fully characterised (87). In the present work this was separated by preparative gas chromatography and characterised by <sup>19</sup>F-NMR as trimer (44). It was probably produced via the following pathway (scheme 2,7).

The ratio of trimer (44) and (85) by fluoride ion is dependent on the reaction conditions.



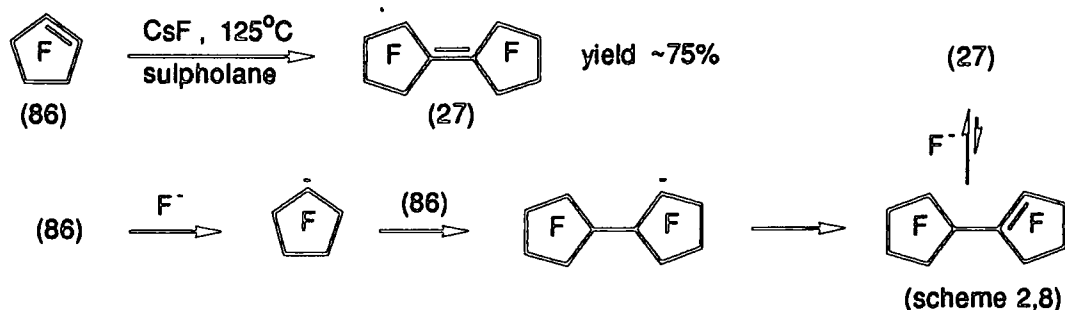
Scheme 2,7



### 2.2.1.2 Dimerisation of perfluorocyclopentene

According to the literature<sup>88</sup>, perfluorocyclopentene (86) is dimerised in sulpholane at 125°C to give perfluoro-bicyclopentylidene (27) in high yield (~ 80%).

Indeed, the reaction proceeded very well if it was done using a Carius tube and an oil bath rotation system (yield ~ 75%).



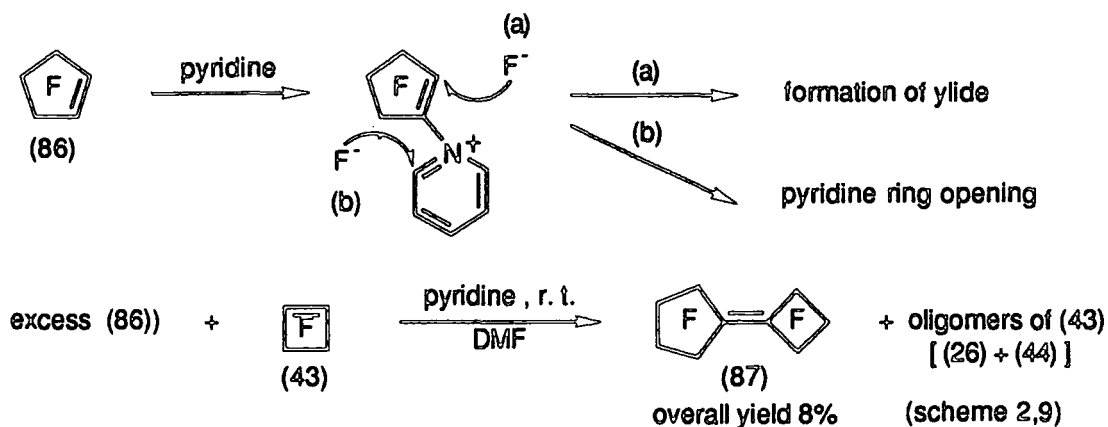
However, when the reaction was scaled up using an autoclave under the same conditions, the yield was very poor (less than 30%) in spite of using dry caesium fluoride and dry sulpholane.

The reason was probably inadequate agitation. In the rocking system good agitation could not be achieved.

### 2.2.1.3 Co-oligomerisation of perfluorocyclobutene and perfluorocyclopentene

Perfluorocyclopentene (86) does not form oligomers with pyridine<sup>34,87</sup> because the fluoride ion which is produced could either lead to ylide formation or may also attack a carbon adjacent to nitrogen causing ring opening of the pyridine ring to mainly give a black tar. However, a mixture of (86) and other perfluoroalkenes in DMF using pyridine gives a range of oligomers<sup>34,87</sup>. As reported previously pyridine induced reaction of (86) with perfluorocyclobutene (43) at room temperature to give (87) and oligomers of (43).

The isolation of (87) was attempted by distillation from the reaction mixture but it has not been very successful (no more than 83% pure).



This product would be expected to be intermediate in reactivity compared with compounds (26) and (27). It would, perhaps, be interesting to confirm this.

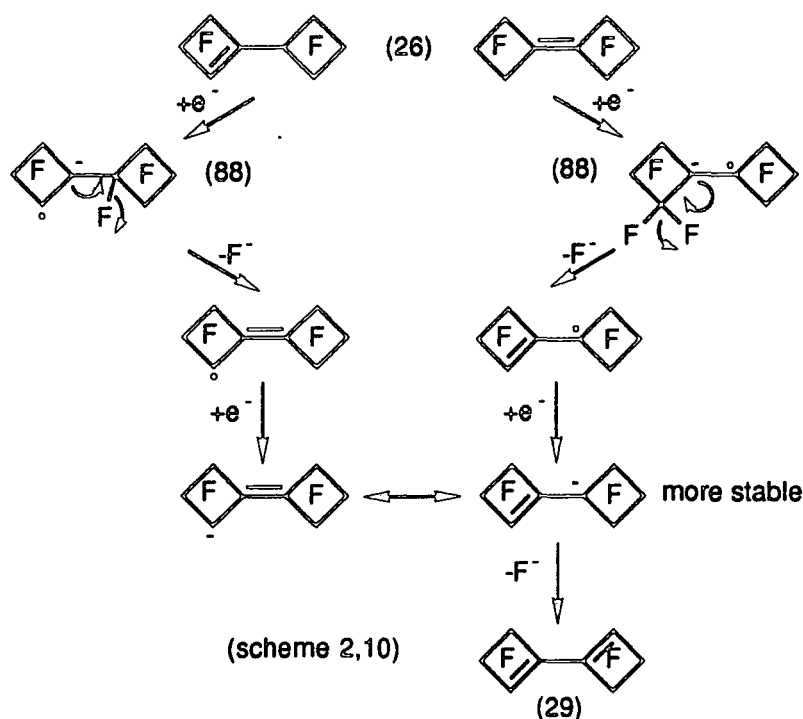
## 2.2.2 Attempted defluorination

### 2.2.2.1 Sodium amalgam system

It was reported<sup>91</sup> that potassium amalgam is able to reduce fluorinated cycloalkenes such as (43) and (86) to give blue-black coloured polymer in the same manner as those demonstrated electrochemically. We have recently developed a new defluorination system using sodium amalgam<sup>91,94,95</sup>. This Chapter describes more investigation of this system and some other attempted defluorinations of fluorinated alkenes which have been described in 2.2.1.

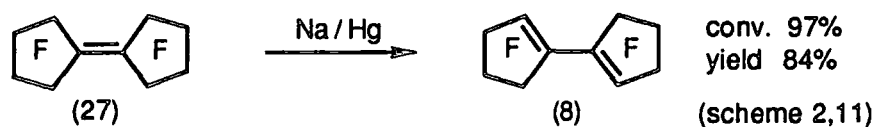
a) Reduction of perfluorobicyclobutylidene and perfluoro-1-cyclobutylcyclobutylidene (26) - reduction of (26) with sodium amalgam caused defluorination to give perfluorobicyclobut-1,1'-enyl (29) in 83% yield, 98% conversion. The reaction was extremely exothermic. The mechanism for this reaction is shown in Scheme 2,10.





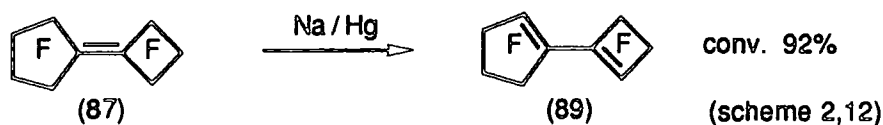
One electron transfer from sodium amalgam to (26) may produce the radical anion (88) and, simultaneously, a fluoride ion is eliminated. Another electron donation causes one more elimination of a fluoride ion to give (29). When the reaction was completed, a fine black solid was produced on the top of the mercury layer. This would probably be a mixture of sodium fluoride, mercury and the carbon black which was produced by further defluorination of a small amount of (29). The same black solid was obtained by defluorination of other alkenes.

b) Reduction of perfluorobicyclopentylidene (27) - compound (27) was defluorinated by sodium amalgam to give perfluorobicyclopent-1,1'-enyl (8) as the only product.



The reaction may proceed in the same manner as that of (29).

c) Reduction of perfluoro-1-cyclobutylidene-cyclopentene (87) - a mixture of 80% (87) and 20% (26) underwent defluorination with sodium amalgam to yield a mixture of perfluoro-1-cyclobutenyl-1-cyclopentene (89) and (29).

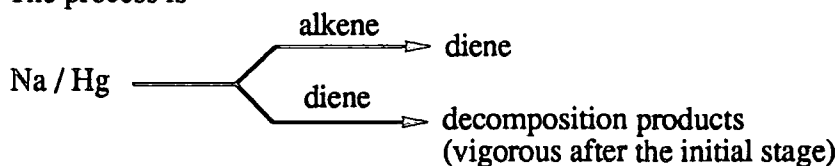


d) Reaction conditions - in order to optimise the yield of dienes, a series of experiments was carried out, altering the reaction conditions. The ratio of sodium to mercury was kept at 0.49-0.60 w/w % which has been shown to be the optimum ratio<sup>95</sup>.

When the ratio of sodium to fluorinated alkenes (26) or (27) was in the range of 2.5:1 - 2.8:1, both the yield and the conversion seemed to be maximised. In addition the following should be taken into account.

- (i) There is a 1 V difference of reduction potential between alkenes (26), (27) and the corresponding diene (29), (8)<sup>91</sup>.
- (ii) The dienes themselves will react further with sodium amalgam if an excess is present.
- (iii) The selectivity is remarkable because, in principle, we would not anticipate isolating such high yields of the dienes.

(iv) The process is



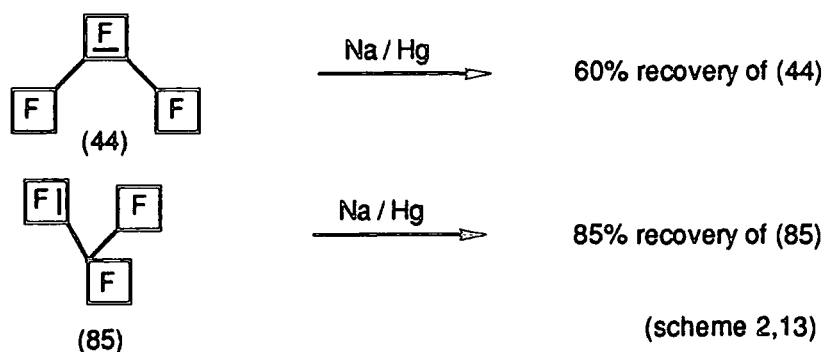
Therefore an excess of alkene present over diene is essential.

- (v) The points indicated above explain why it is necessary to add the alkene all at once to the Na/Hg. This severely restricts the scale of the process for safety reasons.

e) Purification of the dienes - the dienes (29) and (8) have been purified by preparative gas chromatography but this method is very inefficient and very time

consuming. Interestingly, it was found that the dienes (29) and (8) have their melting points at ca. 0°C and 5°C respectively. Their precursors have lower melting points (less than -10°C). Therefore, (29) and (8) can be readily purified by cooling down in either a refrigerator or a freezer. For example, the mixture of (27) and (8) (ratio 52:48) was cooled down to -15°C and kept for ca. 2 hours. Compound (8) gradually crystallised and was isolated by filtration at lower temperatures (5:95). Compound (29) was also purified by the same procedure.

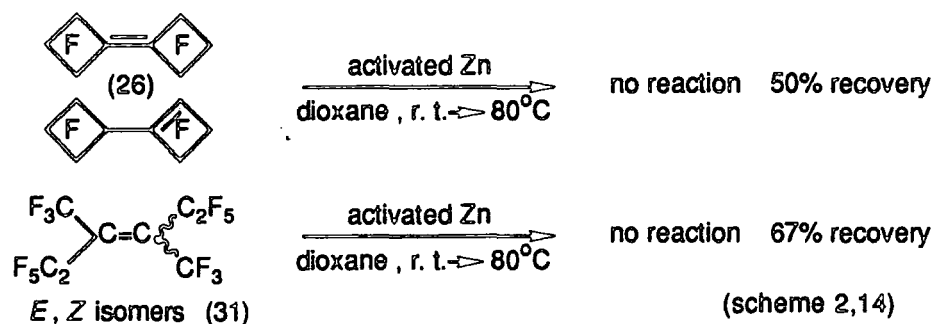
f) Reduction of other fluorinated cycloalkenes - reduction of other fluorinated alkenes such as (44) and (85) with sodium amalgam was attempted. In each case only starting material was recovered. The reaction itself was exothermic and a black solid was produced. A small amounts of the substrates would be defluorinated first and subsequently further reduction must have occurred to finally give a carbon black. These two alkenes have higher reduction potentials than (26) and (27)<sup>91</sup>, and therefore it is more difficult to do defluorination.



#### 2.2.2.2 Zinc induced defluorination

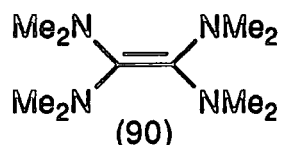
As described before, it has been reported<sup>41</sup> that activated zinc can be used to defluorinate perfluorobicyclo[4.4.0]dec-1(b)-ene (38) to give a variety of the defluorinated products. Zinc plays a role as an electron donating reagent.

Zinc induced reduction of (26) and (31) was attempted using dioxane as solvent. Zinc was activated by HCl/acetone before use. At room temperature and 80°C no reaction occurred.

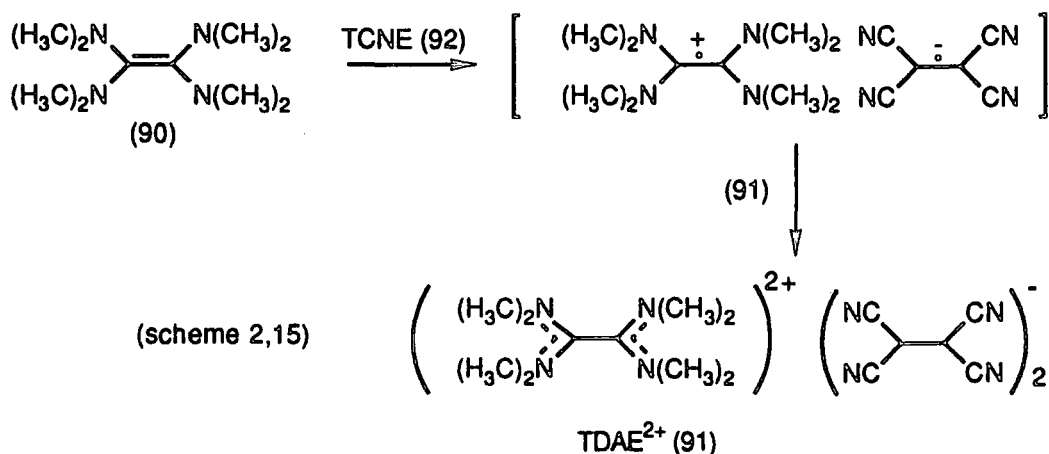


### 2.2.2.3 The tetrakis(dimethylamino)ethylene(TDAE) system

Tetrakis(dimethylamino)ethylene (TDAE) (90) and its analogs are known as strong electron donating agents<sup>97,98</sup>. Therefore, the chemistry of these compounds is dominated by redox reactions. They give up some of their electrons to an oxidising agent.



Oxidising agents such as halogen<sup>96,99</sup>, silver<sup>100</sup>, carbon tetrachloride<sup>99</sup>, and tetracyanoethylene<sup>99</sup> (TCNE) withdraw two electrons from TDAE (90). TDAE (90) is then converted into the corresponding dication TDAE<sup>2+</sup> (91), the octamethyl-oxamidinium ion. For example, when TDAE (90) and TCNE (92) are mixed in acetonitrile at 0°C, octamethyl-oxamidinium bis(tetracyanoethylenide) is formed<sup>99</sup>.

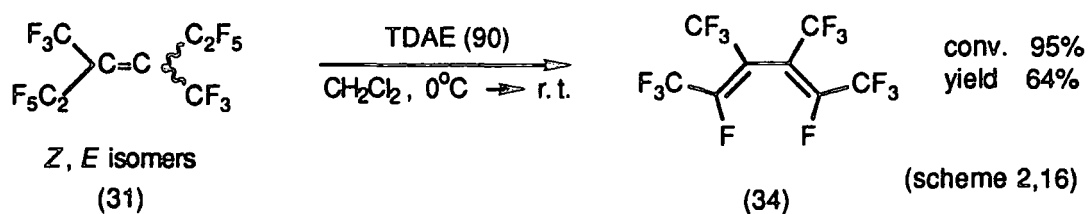


It was also reported<sup>101</sup> that TDAE (90) reacts with polyhalogenated compounds either by replacing a single halogen atom with a hydrogen atom or by removing two vicinal halogens to form the corresponding alkene. Dechlorination of perchloroethane takes place in the analogous manner to the sodium amalgam system; two sets of electron transfer and subsequent elimination of chloride ion. The relative ease of halogen removal appears to be in the order of I > Br > Cl > F and increases with the number of halogens attached to a given carbon<sup>97</sup>.

This analogy prompted us to study if TDAE (90) can defluorinate fluorinated alkenes or even fluorinated alkanes.

#### 2.2.2.4 Reduction by TDAE (90)

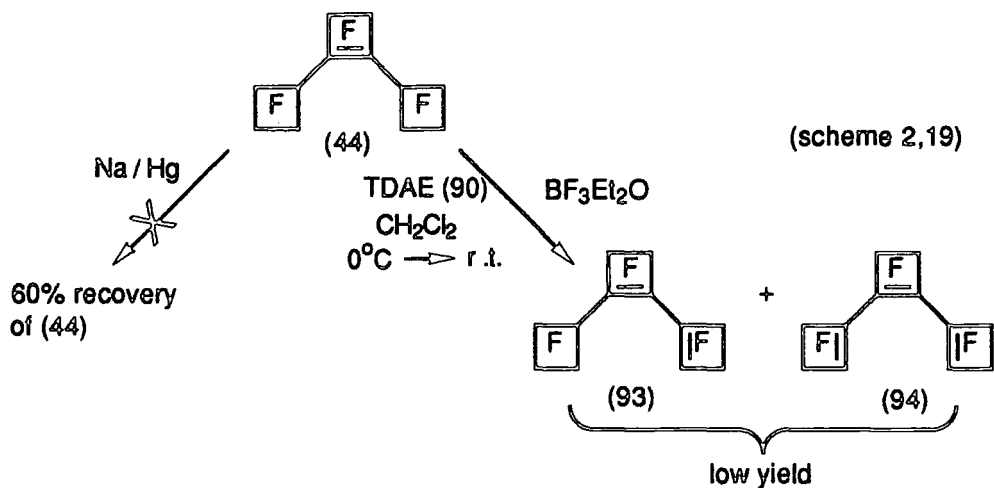
(a) Reduction of perfluoro-3,4-dimethyl-hex-3-ene (31) - compound (31) can be defluorinated by sodium amalgam to give the corresponding diene (34) in 70% yield<sup>91,93,95</sup>. Remarkably, TDAE (90) defluorinated (31) in dichloromethane at 0°C to give (34) in 64% yield. The addition of TDAE to (31) in CH<sub>2</sub>Cl<sub>2</sub> caused an immediate colour change to dark red. When the solution was allowed to stand at room temperature the colour gradually turned to orange. More interestingly (34) was separated as a bottom layer and was readily collected.



The mechanism for this reaction is outlined in Scheme 2,17.

The one electron transfer from TDAE (90) to (31) causes almost simultaneous elimination of fluoride ion and, subsequently, another electron transfer and fluoride ion elimination takes place to yield (34) and octamethyl-oxamidinium difluoride (92), which will be discussed in detail later.

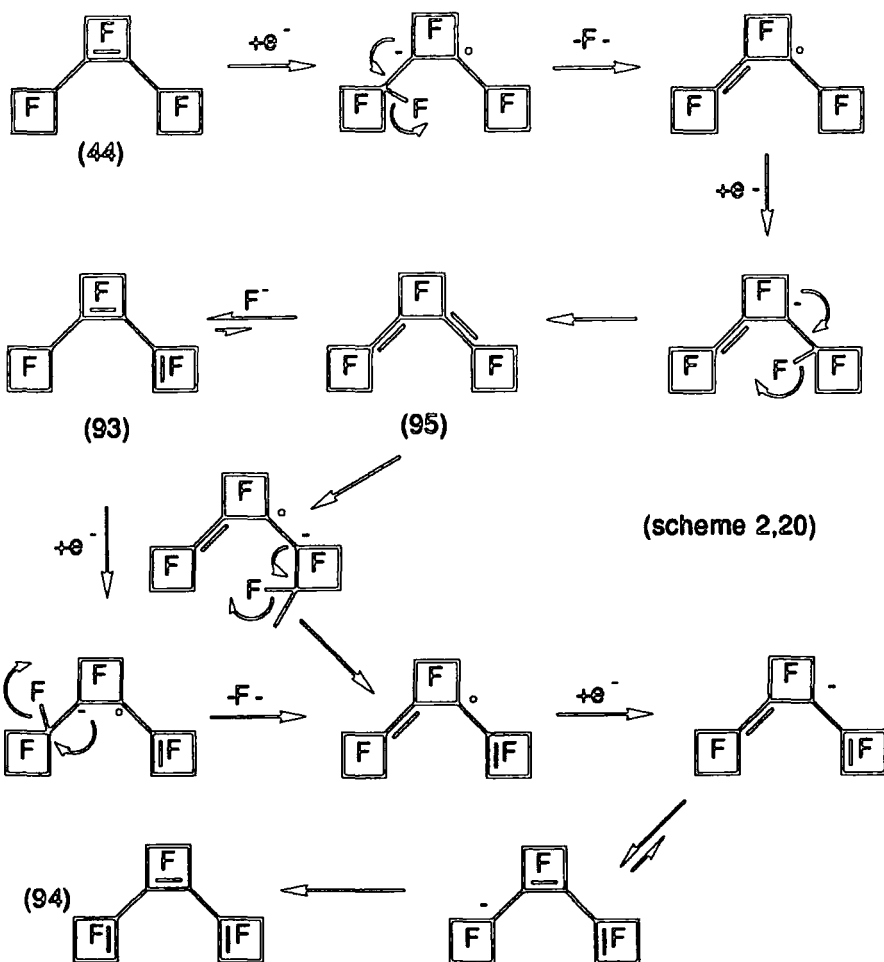




As shown in Scheme 2,20 trimer (44) is defluorinated to give (95) which is readily isomerised by fluoride ion to (93). Then these dienes are further reduced to triene (94).  $\text{BF}_3\text{OEt}_2$  was added to this solution after the completion of the reaction in order to recover diene (93) and triene (94) since the carbanions of (93) and (94) were considered to be readily produced by fluoride ion in the solution. The yield of (93) and (94) was quite low (less than 20%). They are only observed as a mixture by  $^{19}\text{F}$ -NMR. It has not yet been possible to isolate them. Trimer (44) is more viscous than other fluorinated alkenes such as (26) and (27). Therefore, it is more difficult to disperse it homogeneously into sodium amalgam by shaking. As a result only part of (44) can contact sodium amalgam to undergo defluorination, giving carbon black (completely defluorinated) and the starting trimer (44).

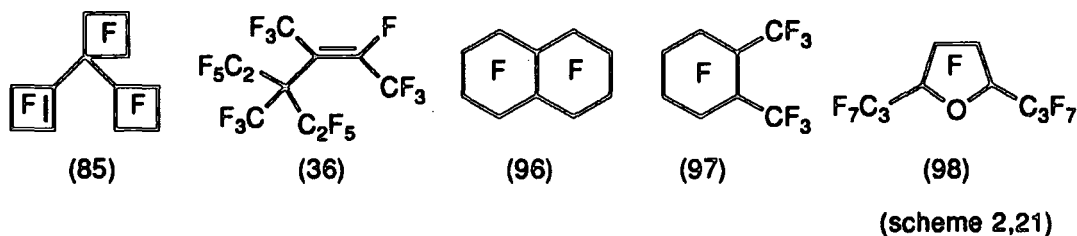
On the other hand reduction with TDAE (90) is carried out in  $\text{CH}_2\text{Cl}_2$  in spite of trimer (44) being insoluble in  $\text{CH}_2\text{Cl}_2$ . Trimer(44) and TDAE (90) can contact each other more readily. Furthermore, the defluorinated products may either react with  $\text{TDAE}^{2+} + 2\text{F}^-$  (92) to give the corresponding stable carbanion, or react with TDAE (90) itself to possibly yield a further product.

The neat reaction of (44) with TDAE (90) was attempted, however the volatile recovered was found to be the starting material (44).



### 2.2.2.5 Reduction of other fluorinated alkenes and alkanes

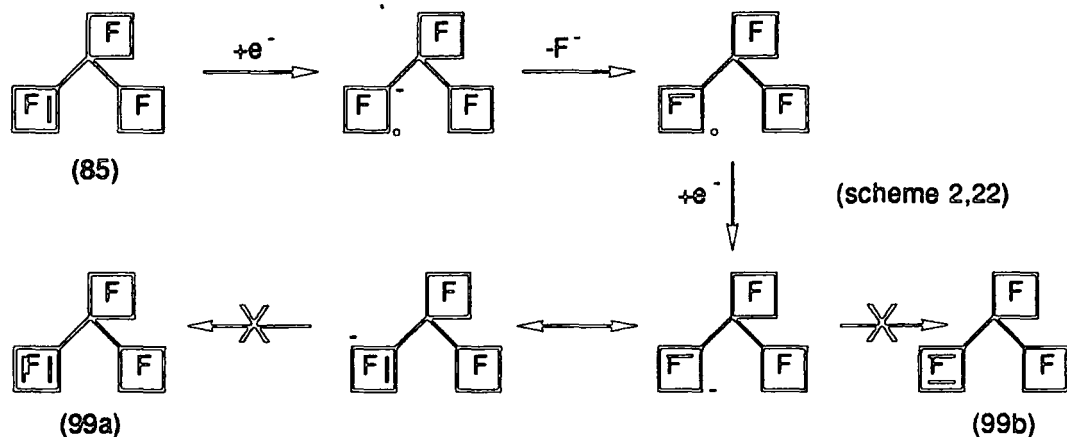
Defluorination of fluorinated alkenes (85) and (36) and alkanes (96)-(98) was attempted under the same conditions. However, only the starting material was observed by  $^{19}\text{F}$ -NMR in each case.



Each alkene has a double bond to hold an electron which is given by TDAE (90). Compound (36) does not have any allyl fluorines to be eliminated. Trimer (85) does have



them, therefore, it could have been defluorinated but the expected structure of the corresponding diene (99) would have great angle strain and be extremely unstable.



Fluorinated alkanes (96)-(98) do not have double bonds but tertial fluorines which seem to be more readily eliminated than other C-F bonds. Despite heating the mixture of each alkene and TDAE in a sealed tube up to 100°C, no reactions took place.

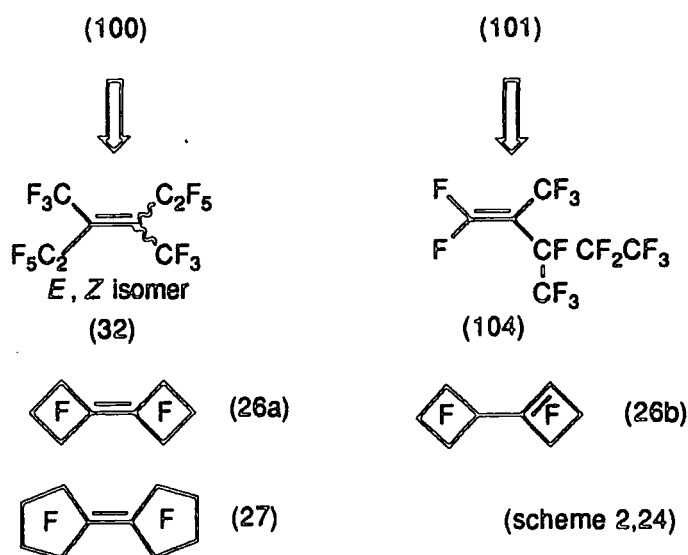
#### 2.2.2.6 The preferable structure for defluorination

Let us consider the possible structures that would allow defluorination to be effected by either sodium amalgam or TDAE. From the results above two kinds of structures, (100) and (101), can be proposed as suitable compounds.

(100) and (101) can be defluorinated to give the corresponding dienes (102) and (103) respectively. The simplest compounds with each structure would be perfluoro-2,3-dimethyl-hex-1-ene (104) and perfluoro-3,4-dimethyl-hex-3-ene (31).

The analogues of (100) are (26a) and (27) and the analogues of (101) can be (26b).

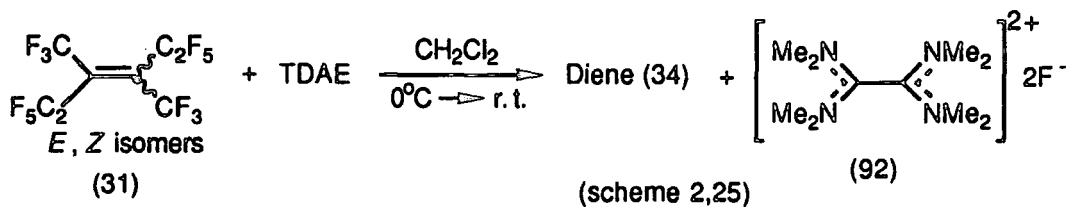




### 2.2.2.7 Attempt to isolate octamethyl oxamidinium difluoride (92)

The TDAE salts, octamethyl oximidinium salts  $[\text{TDAE}]^{2+} \text{X}^-_2$  are obtained by oxidation of TDAE<sup>98</sup>, e.g. with halogen  $\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ )<sup>99</sup>,  $\text{CX}_4$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ )<sup>99,101</sup>,  $\text{Co}_2(\text{CO})_8$ <sup>102</sup> in organic solvents or by metathetic reaction from  $[\text{TDAE}]^{2+} \text{X}^-_2$  ( $\text{X}^- = \text{Cl}, \text{Br}, \text{I}$ ). Surprisingly, the fluoride salt has not been previously characterised.

However, during the reduction of (31) with TDAE (90), octamethyl oxamidinium difluoride must have been produced.



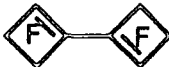
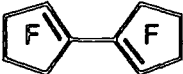
In fact, a solid was precipitated during the reaction. This solid was filtered and washed with  $\text{CH}_2\text{Cl}_2$  to give a white solid, which was soluble in  $\text{D}_2\text{O}$ .  $^1\text{H-NMR}$  spectrum of  $\text{D}_2\text{O}$  solution of this solid showed two signals of equal intensity ( $\delta = 3.30$  ppm, 3.58 ppm). This is consistent with the literature data<sup>99</sup> that also shows the same spectrum (2.90 ppm, 3.18 ppm, acetonitrile) of  $\text{TDAE}^{2+}$ , whereas TDAE (90) gives only one sharp signal at  $\delta = 2.55$  ppm<sup>104</sup>. The dimethylamino groups can evidently rotate about the C-N bond in TDAE (90) and this rotation is rapid on the NMR scale. However this rotation can be interrupted in  $\text{TDAE}^{2+}$  due to the high C-N bond order<sup>97,98</sup>.

$^{19}\text{F}$ -NMR spectrum showed one sharp signal at  $-130.3\text{ppm}$ . Caesium fluoride and  $\text{tert-nBu}_4\text{N}^+\text{F}^-$  in water have sharp signals at  $-116.9\text{ ppm}$ ,  $-119.6\text{ ppm}$  respectively. From these results probably octamethyloxamidinium difluoride (92) could be produced during the defluorination reaction. Elemental analysis of (92) was unsatisfactory because (92) is very hygroscopic. This is the first example of the isolation of octamethyloximidinium difluoride (92).

2.3 Structures of dienes (29) and (8)

Table 2,3 shows C=C stretching vibrations in IR spectra for various dienes.

Table 2,3. IR C=C stretching vibrations for dienes

Compound	Frequency( $\text{cm}^{-1}$ )	Reference
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	1600	106)
$\text{CH}_2=\text{CH}-\text{CH}=\text{CHCH}_3$	1650 1600	106)
$\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ (25)	1795 1765	66)
 (29)	1750 1670	
 (8)	1720 1660	

The olefinic bond stretching vibration in conjugated dienes without a centre of symmetry, such as penta-1,3-diene, give two C=C stretching bands.<sup>105</sup>


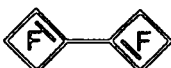
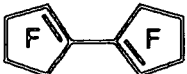
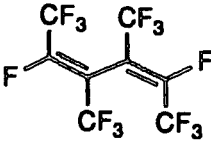
As described in Chapter 1, perfluorobut-1,3-diene (25) has the skew cis structure and the two C=C stretching bands account for the fact that (25) is an unsymmetrical diene. Both spectra of (29) and (8) show the two C=C stretching bands, which may indicate that they are unsymmetrical.

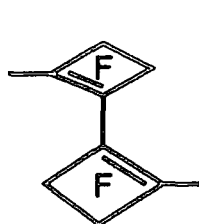
Table 2,4 displays UV absorption data for various conjugated dienes. It is known that buta-1,3-diene has the s-trans-planar conformation with the minimum energy level.<sup>67</sup> Therefore the  $\pi$ -orbitals are effectively overlapped. High molar absorptivity can account for this fact. As expected (25) has a considerably lower molar absorptivity since the overlap of the  $\pi$ -orbitals is partially destroyed due to its skew-cis structure. However (29) and (8) are characterised by high molar absorptivities, 18,800 and 10,900 respectively. These results therefore suggest that (29) has nearly either the s-cis planar or s-trans planar conformation. Theoretical calculation shows that (29) may have both conformations without interaction between 2 vinylic fluorines and, more importantly,

(29) may keep the eight carbon atom skeleton planar. In contrast it is assumed by theoretical calculation that (8) may have the skew-cis conformation with a torsional angle of  $65^\circ$ , which is in fair agreement with the significantly lower molar absorptivity.

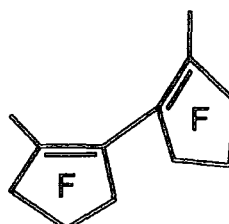
Therefore, from both IR and UV analysis, we conclude that (29) has a coplanar s-trans conformation, whereas (8) has a slightly distorted skew-cis conformation shown below.

Table 2.4. UV absorption data for various conjugated dienes

Compound	$\pi \rightarrow \pi^*$ Transition		Reference
	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$	
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	217	21,000	66)
	256	8,000	66)
$\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ (25)	206 215	2,800 1,350	25)
	277	18,800	
	278	10,900	
	234	272	



s trans  
(29)



skew cis  
(8)

## 2.4 Summary

We have shown that the sodium amalgam system is a very useful method of synthesising some cyclic and acyclic fluorinated dienes in moderate yield and conversion from fluorinated alkenes. However, there is still some limitation by this method.

Tetrakis(dimethylamino)ethylene TDAE (90) has also been shown to be a useful reagent for synthesising, in particular, diene (34) in good yield. The reaction procedure is so simple and easy to manipulate that it can be readily scaled up. The factors affecting efficient defluorination to give dienes, has been explored, but further investigation is necessary to establish the limit of the processes.

## CHAPTER THREE



### 3 REACTIONS OF FLUORINATED DIENES WITH VARIOUS NUCLEOPHILES

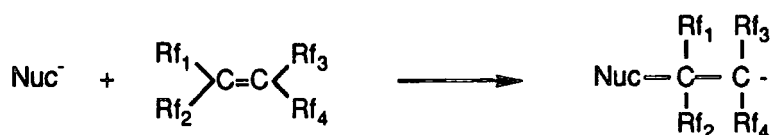
#### 3.1 Introduction

The reactions of a variety of nucleophiles with fluorinated alkenes have been reported<sup>1-3,106</sup>. We have previously reported the synthesis of novel fluorinated alkenes (see Chapter 2) and studied a range of nucleophilic reactions of them<sup>84,107</sup> which we intend to investigate. Before discussing nucleophilic reactions of fluorinated dienes, it is important and useful to again summarise nucleophilic attack on fluorinated alkenes because it would be anticipated that nucleophilic reactions of fluorinated dienes should obey the same rules.

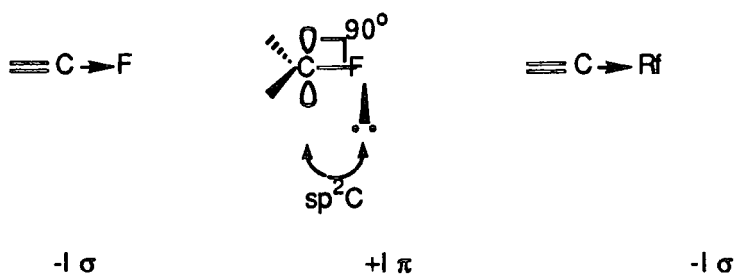
#### 3.1.1 Nucleophilic attack on fluorinated alkenes

##### 3.1.1.1 Reactivity and orientation<sup>1,3,108</sup>

There are two factors to be taken into account, one of which is how fluorine or perfluorinated alkyl group (Rf) influences the double bonds of fluorinated alkenes, the other is the effect on the carbanionic intermediates which can be generated by attack of nucleophiles on fluorinated alkenes.



Despite the great electro-negativity of fluorine (inductive  $-\text{I}\sigma$  effect), when fluorine is directly attached to a carbanionic centre the electron-pair repulsion ( $+\text{I}\pi$ ) can affect inductive electron withdrawal (*i.e.* stabilisation). In contrast, perfluoroalkyl groups evidently show only the inductive stabilisation ( $-\text{I}\sigma$ ).



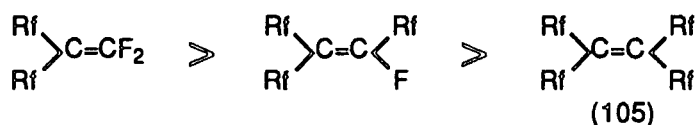


An alternative approach<sup>111</sup> to understand these different reactivities is to consider Frontier Orbitals. This approach implies that HOMO-LUMO interaction between nucleophile and fluorinated alkene respectively would be very important and electro-negative perfluoroalkyl groups would lower the LUMO energy (the effect of the fluorine atom still remains ambiguous). Reducing LUMO energy, with increase of the number of perfluoroalkyl groups, increases reactivity,

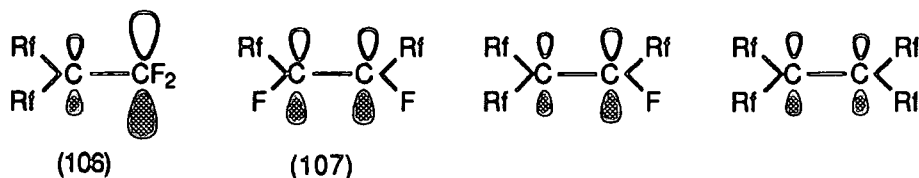


Nevertheless, reactivity towards nucleophiles is not simply dependent upon the number of perfluoroalkyl groups present, because structures such as (105) are the least reactive among the corresponding isomers, towards nucleophiles<sup>112</sup>. Therefore, the coefficients should be important<sup>111</sup>.

Relative reactivity order toward nucleophiles



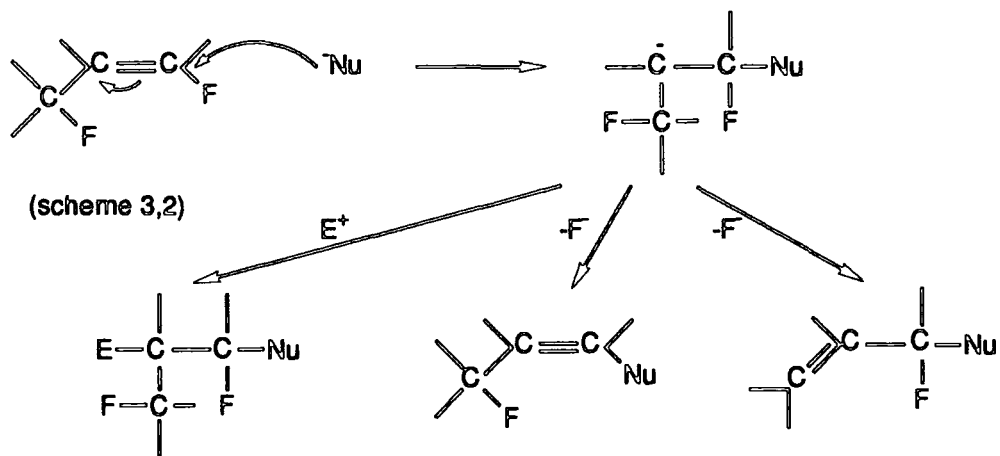
Introduction of a fluoroalkyl group increases the coefficient in the LUMO at the opposite carbon<sup>111</sup>. The effects of perfluoroalkyl groups on the same side of a double bond enhance each other in the structure (106), but offset each other in the structure (107). This may be attributed to the greater reactivity of (106) than (107).



It is now possible to rationalise the reactivity and orientation of fluorinated alkenes towards nucleophiles.

3.1.1.2 Possible products formed

This carbanionic intermediate may further react in mainly three ways, such as



- 1 proton abstraction from the media, abstraction of a suitable electrophile, or combination with it, giving the additional product,
- 2 elimination of fluoride ion, which has been attached to a vinyl site to yield the substitution product,
- 3 elimination of fluoride ion accompanied by allylic rearrangement ( $S_N2'$ ) to give the other substitution product.

However, it should be noted that these systems are dependent on many factors, such as the nature of the electrophile, solvent effects, steric hindrance, and, more importantly, the stability of the carbanionic intermediate.

In the following discussion we shall consider whether various nucleophilic reactions of the fluorinated dienes (29) or (8) obey the rules described above.

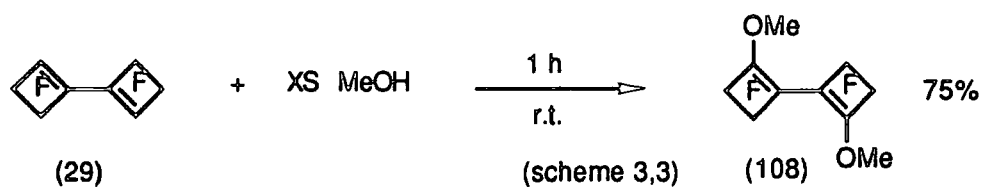
## 3.2 Discussion

The results described in this Chapter are the chemistry of perfluorobicyclobut-1,1'-enyl (29) and perfluoro-bicyclopent-1,1'-enyl (8) with various nucleophiles. Some of them will be compared with those of perfluoro-3,4-dimethylhexa-2,4-diene (34).

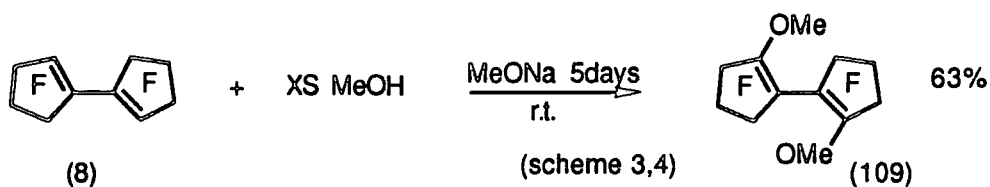
### 3.2.1 Oxygen nucleophiles

#### 3.2.1.1 Reactions with alcohols

a). Diene (29) with methanol. - the addition of an excess of methanol to diene (29) led to an exothermic reaction. In one hour a white crystalline solid was precipitated and identified as dimethoxy derivatives (108).



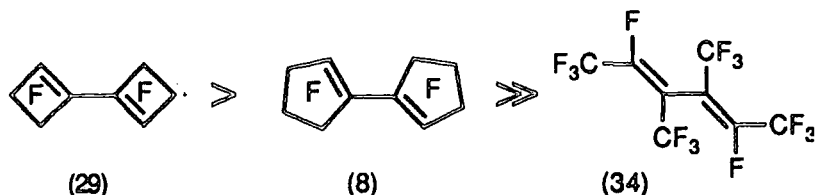
b). Diene (8) with methanol. - the reaction of diene (8) with an excess methanol and a small amount of sodium methoxide afforded the dimethoxyderivative (109). However, it took 5 days to complete the reaction.



These two reactions are merely nucleophilic substitution of fluoride ion by methoxide ion. No addition nor  $S_N2'$  rearrangement substitution product was observed. It has been reported<sup>91,93</sup> that perfluoro-3,4-dimethyl-hexa-2,4-diene (34) reacted with methanol under basic conditions (an excess of sodium carbonate) to give a mixture of mono- and di-substituted products. The reaction did not proceed with neutral methanol.

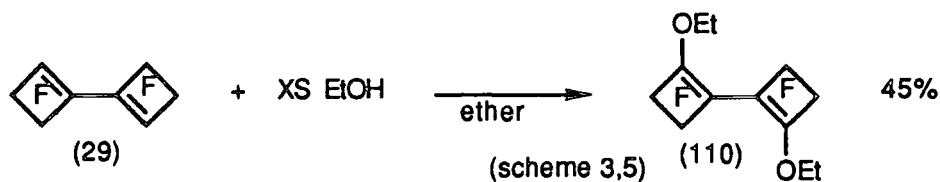
These results illustrate a large difference in the relative reactivity of dienes (29), (8), and (34), as indicated below.

Relative reactivity order toward nucleophiles

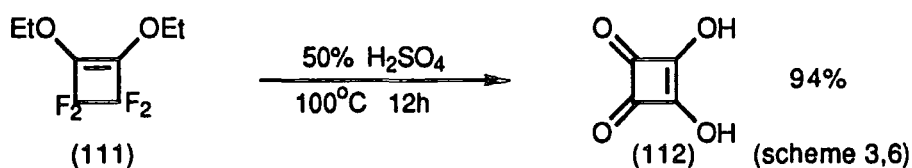


Electronically these systems are very similar; therefore these dramatic differences provide a clear illustration of the effect of angle strain on nucleophilic attack at unsaturated carbon<sup>93</sup>.

c). Diene (29) with ethanol - the addition of an excess of ethanol to diene (29) in dry ether afforded a slightly exothermic reaction and yielded the diethoxy derivatives (110).



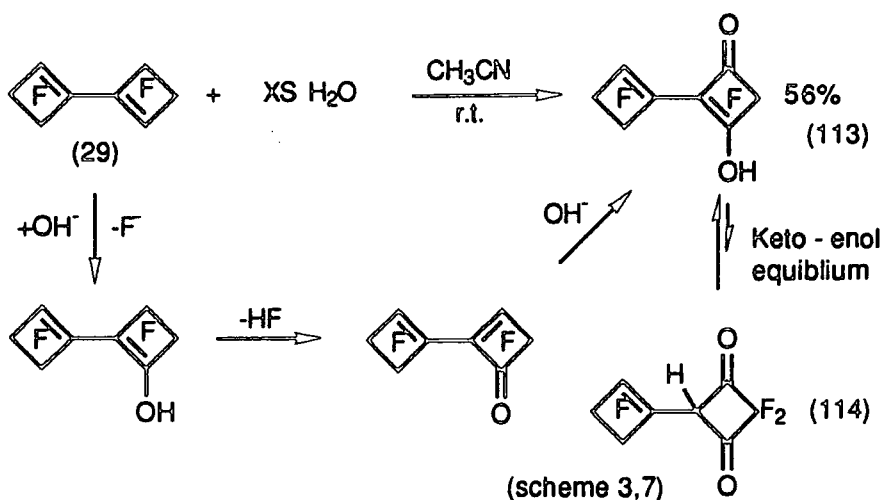
d). Attempted hydrolysis of (108)-(110) - 1,2-Diethoxy-3,3,4,4-tetrafluorocyclobutene (111) is hydrolysed by 50% sulphuric acid to give diketo-cyclobutene-diol (112), squaric acid, in high yield<sup>113</sup>. The chemistry of oxocarbon such as (112) has been studied<sup>114</sup>



Hydrolysis of (108)-(110) were attempted under the same conditions as that of (111). In each case, however, only starting material was recovered.

### 3.2.1.2. Reactions with water.

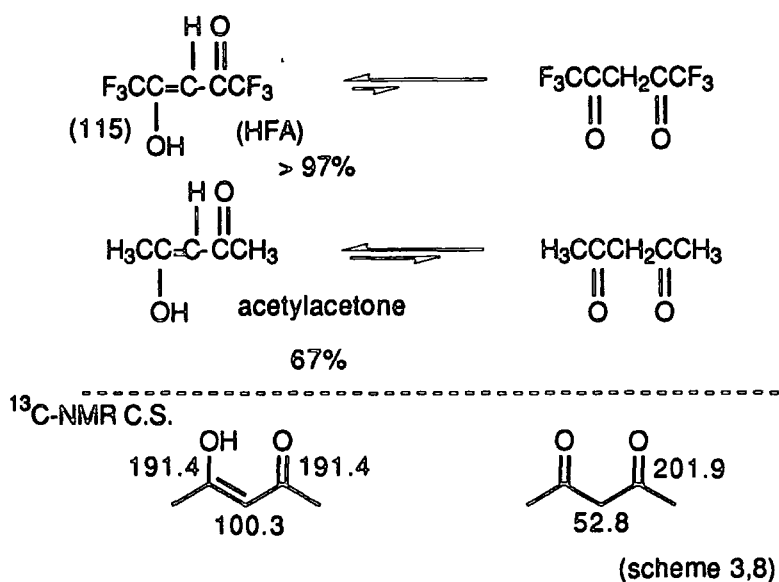
a) Diene (29) - diene (29) reacted exothermically with an excess of water in acetonitrile to give a white solid.



Mass spectrum data of the product gave a parent molecular ion  $M^+$ , 262, for  $C_8H_1F_7O_2$ .  $^{19}F$ -NMR spectrum showed four resonances, one of which can be assigned to a vinylic fluorine in comparison to that of diene (29). Other three resonances were observed with the same intensity in typical region of  $CF_2$  groups. Although  $^{13}C$ -NMR showed a rather complicated spectrum, it showed the presence of seven different carbon atoms which include one kind of carbonyl group, a vinylic carbon attached to a fluorine, and a  $CF_2$  group which does not have any other F-F couplings.

These results may suggest two possible structures, the enol (113) and its keto isomer (114). It has been reported<sup>115,116</sup> that 1,1,1,5,5,5-hexafluoro-acetylacetone is overwhelmingly present as the enol form (115) (> 97% in DMSO, >99.5% in  $CDCl_3$ ), whereas acetylacetone is 67% in the enol form (scheme 3,8).

Keto - enol equilibrium of Hexafluoro-acetylacetone  
(HFA) and acetylacetone



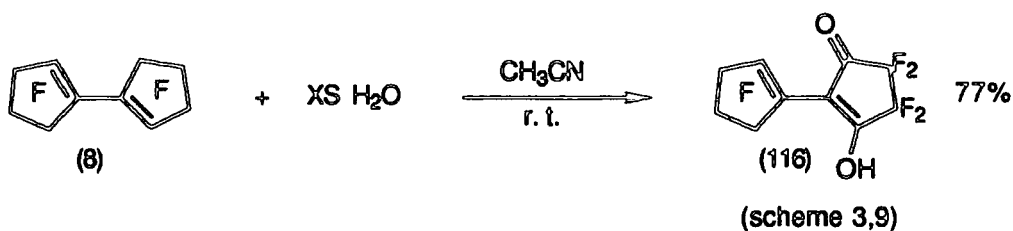
<sup>13</sup>C-NMR chemical shifts of the enol keto isomer of acetylacetone (see scheme 3,8) may indicate that if the keto isomer (114) were present, one resonance due to OC-CH-CO should be observed around 50 ppm<sup>105</sup>. The absence of this resonance and predominant presence of the enol (115), therefore, can suggest that the product is favoured to have the enol form (113).

IR spectrum showed C=O absorption at 1640 cm<sup>-1</sup>, which is more intense than normal carbonyl one and three bands around 1720 ~ 1800 cm<sup>-1</sup>. Two of them may be attributed to C=C-C=C. We are not able to explain what the other is responsible for.

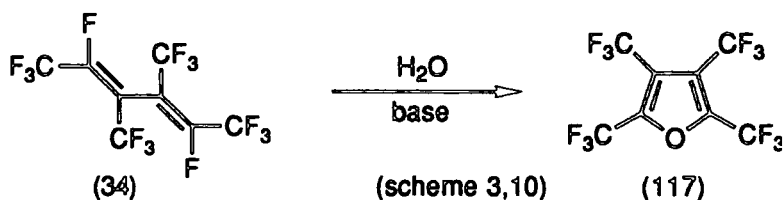
<sup>1</sup>H-NMR did not show any resonances (due to C=C-OH). The product (113) is very hygroscopic and probably hydrogen may be solvated by even a trace of water atoms (this phenomenon often occurs to alcohol in organic solvent, with a trace of water).

b) Diene (8) - addition of diene (8) to acetonitrile with water afforded the analogous enolic derivative (116). Spectroscopic data were examined and consistent with the structure.

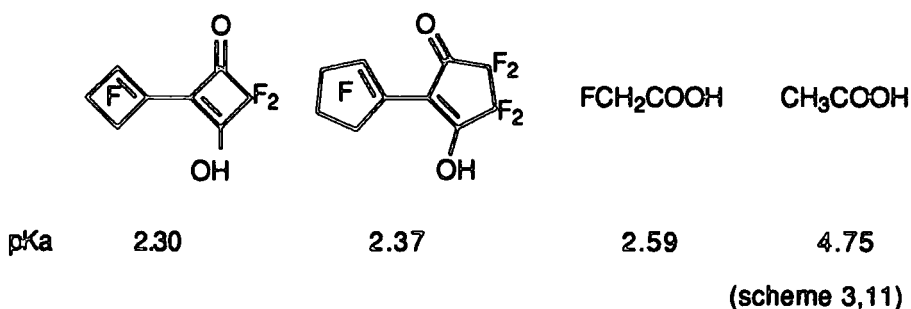




On the contrary, acyclic diene (34) does not react with neutral water, but reacts under basic conditions to yield a furan derivative (117)<sup>91,93,95</sup>.

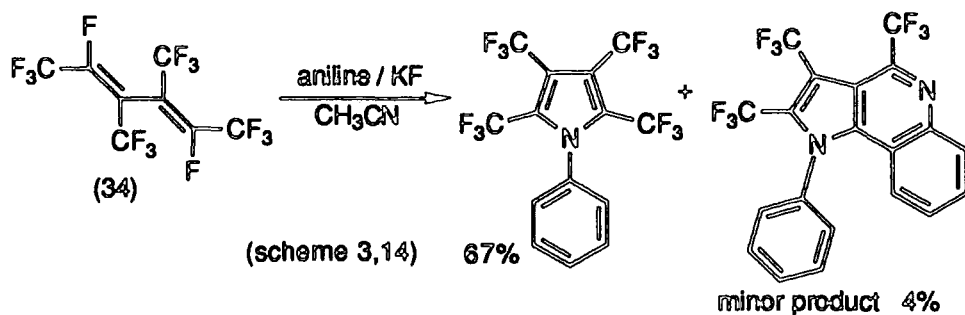


c) Acidity of the enol derivatives - both (113) and (116) are completely soluble in water and show strong acidity. pK<sub>a</sub> of both products are shown below and compared with those of other acids.



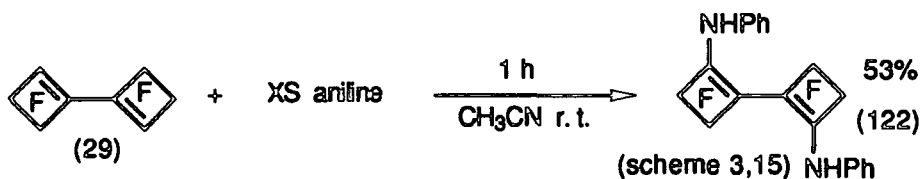
d) Salts of (113) and (116) - the enol derivatives (113) and (116) were neutralised with aqueous sodium hydroxide to form yellowish and whitish solids respectively, after evaporation of water.



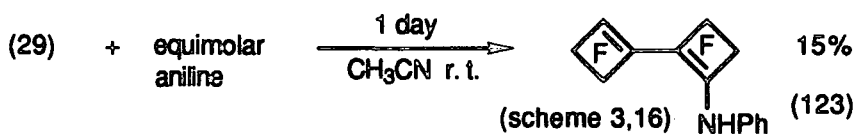


### 3.2.2.1 Reactions with aniline

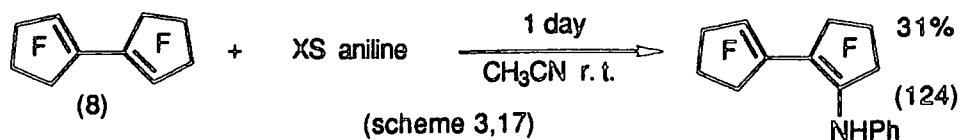
a) Diene (29) - the addition of an excess of aniline to diene (29) in acetonitrile caused an immediate exothermic reaction and afforded the corresponding diamine derivative (122). The  $^{19}\text{F}$ -NMR spectrum of (122) showed two  $\text{CF}_2$  groups and the IR spectrum showed a weak absorption at  $3400\text{ cm}^{-1}$  due to N-H stretch, consistent with a secondary aromatic amine. Other analytical data confirmed the structure of (122).



When an equivalent of aniline was added to diene (29), a viscous brown liquid was obtained. The sublimation of this liquid gave a white needle-like crystal which has been characterised as the mono amine derivative (123).



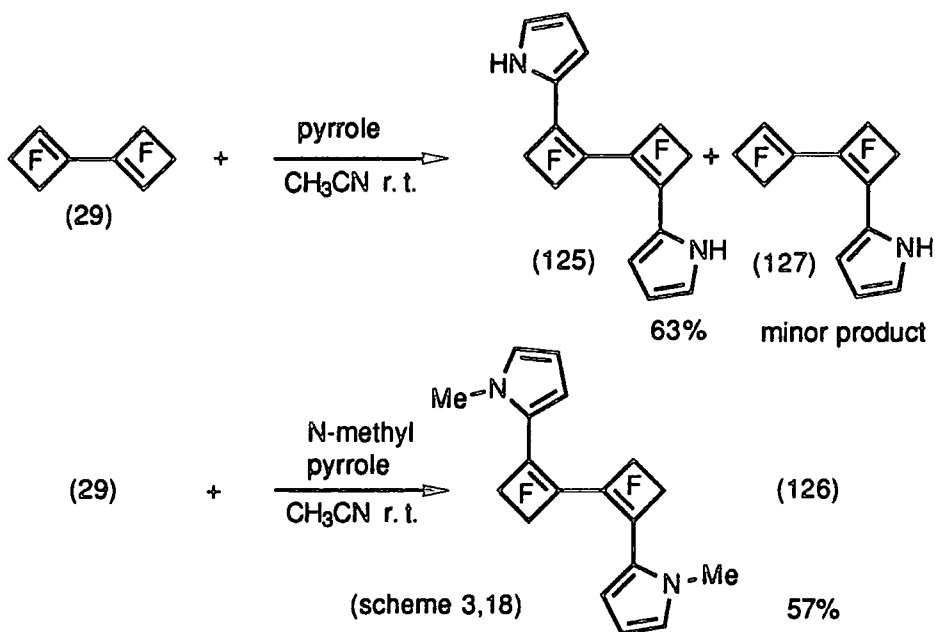
b) Diene (8) - the reaction of (8) with an excess of aniline in acetonitrile at room temperature gave the mono amine derivative (124). No diamino derivative was obtained, because the lower reactivity of (8) than that of (29) and steric hindrance.



### 3.2.2.2 Reactions with pyrrole and N-methylpyrrole

Pyrrole and its derivatives readily react with a wide range of electrophiles because of their electron-rich character, giving the corresponding substituted compounds<sup>119</sup>. They do not normally undergo Diels-Alder reactions and only a few exceptions are known<sup>120</sup>.

a) Diene (29) - pyrrole and N-methyl pyrrole reacted with diene (29) in acetonitrile to form electrophilic di-substitution products (125) and (126) respectively in moderate yield. In the reaction with pyrrole, a mono-substituted product was obtained as minor product (127). The products were purified by vacuum sublimation.



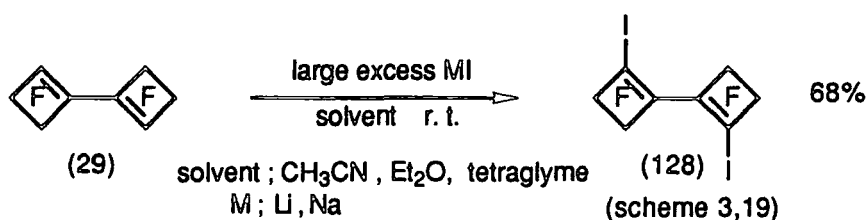
b) Diene (8) - no reaction occurred when the mixture of diene (8) and pyrrole was refluxed in ether for one day. Refluxing in acetonitrile did give a dark green viscous liquid, which showed many signals in <sup>19</sup>F-NMR but no substitution products were detected.

### 3.2.3 Iodide ion as nucleophile

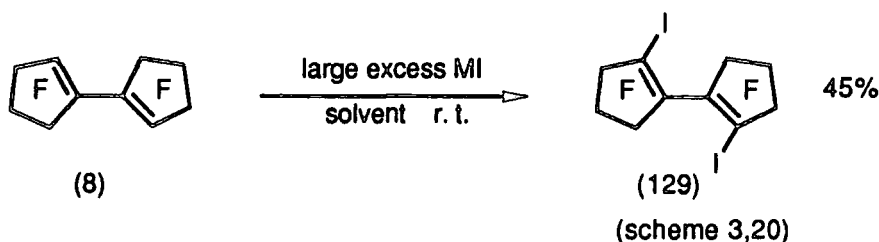
Perfluorinated alkyl or alkenyl iodide compounds are useful functional derivatives as the precursors for coupling reactions using copper or zinc and, for generation of organometallic reagents<sup>121</sup>. In the following part, the synthesis of the iodo-substituted compounds from (29) and (8) under mild conditions and the preliminary work using the products obtained, *i.e.* the coupling reaction with copper, will be discussed.

#### 3.2.3.1 Reaction with sodium ( lithium ) iodide

a). Diene (29) - remarkably, diene(29) reacted with sodium or lithium iodide in ether, tetraglyme, or acetonitrile at room temperature to give the corresponding diiodo-substituted product (128) in good yield.



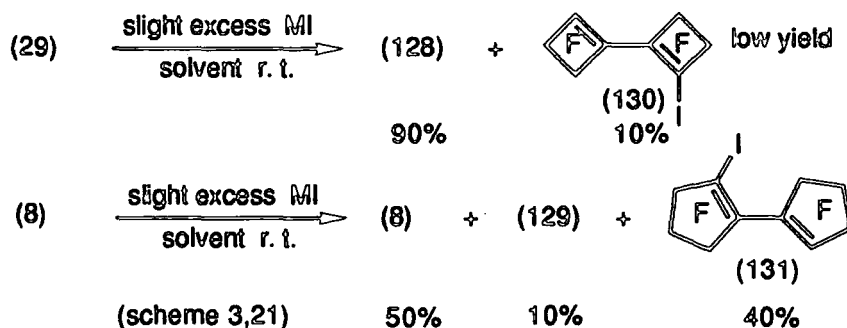
b). Diene (8) - the addition of diene (8) to sodium (lithium) iodide in acetonitrile or ether also afforded the di-iodo derivative (129). This product is a liquid at room temperature and was purified by preparative g.l.c..



c). Diene (34) - the mixture of diene (34) and an excess of lithium iodide was stirred in acetonitrile at room temperature for 3 days, but no reaction took place.

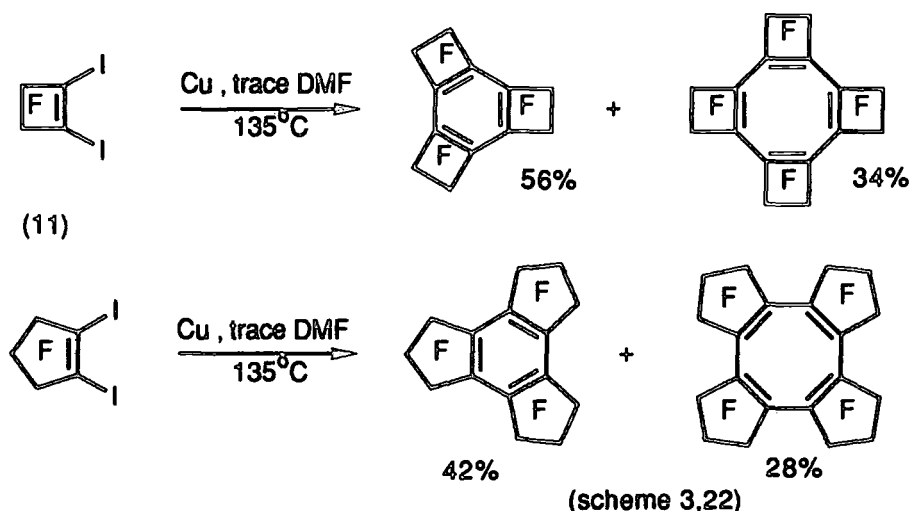
d). Attempt to synthesise mono iodo-derivatives - to synthesise di-iodide derivative, a large excess of iodide salt was employed because the reaction system is heterogeneous.

heterogeneous. When a slight excess of iodide salt was used, a mixture of mono-iodo derivatives (130) and (131) and di-iodide derivatives were obtained in low yield.  $^{19}\text{F}$ -NMR spectra and mass spectra of the products proved the existence of mono-iodide derivatives, though it has not yet been possible to isolate them.



### 3.2.3.2 Attempted coupling reaction

As described in Chapter 1, copper has been used for coupling reactions to synthesise fluorinated dienes. Interestingly, 1,2-diiodoperfluorocycloalkenes such as (11) were coupled by copper at  $135^\circ\text{C}$  in the presence of a small amount of DMF to give predominantly the corresponding cyclic trimer and tetramer<sup>11</sup>.



It was reported<sup>10</sup> that 2,2'-diiodoperfluorobicyclobut-1,1'-enyl (128) did not afford any coupling products as volatiles using copper bronze. The copper-coupling reactions of (128) and (129) using DMF at  $135^\circ\text{C}$  were attempted. Volatiles were recovered by sublimation in vacuum.



Table 3.1. IR and UV data of (128) and (129)

	(128)	(129)
IR( $\text{cm}^{-1}$ )	1530(m)	1590(s) 1660(s)
UV <sup>a)</sup>	271 ( $\epsilon = 12900$ )	224 ( $\epsilon = 8750$ )
$\lambda_{\text{max}}$ (nm)	280 ( $\epsilon = 14900$ )	252 ( $\epsilon = 8000$ )
$\epsilon_{\text{max}}$	301 ( $\epsilon = 18200$ )	315 ( $\epsilon = 18000$ )

a) ; reference 10)

$^{19}\text{F}$ -NMR spectra of (128) and (129) were very interesting. The spectrum of (128) showed two multiplet signals due to  $\text{CF}_2$  groups, whereas that of (129) showed two very broad signals at room temperature. Variable temperature measurement by  $^{19}\text{F}$ -NMR spectroscopy of (129) was carried out in the range of  $-40 \sim 40^\circ\text{C}$ . Some of them are illustrated in Figure 3.1.

At  $-40 \sim -20^\circ\text{C}$ , the spectra showed the typical AB type coupled signals because the rotation between  $\text{C}_1\text{-C}_2$  bond was restricted and the two geminal fluorines were non-equivalent in each  $\text{CF}_2$  group. The couplings between vicinal fluorines were so small that they could not be observed. Figure 3.2 illustrates the approximate relationship between the relative energy level of (129) and the torsional angle of two double bonds. As the temperature is elevated, the probability of transition between A and C becomes greater in spite of passing a higher energy level B. At  $10^\circ\text{C}$  the transition rate is already greater than the NMR time scale. Therefore the coupling can no longer be observed and signals begin to be completely eclipsed. At  $40^\circ\text{C}$  only two broad signals can be observed. The signal at  $-108$  ppm should be split into two at higher temperature and eventually, three single signals would be observed.



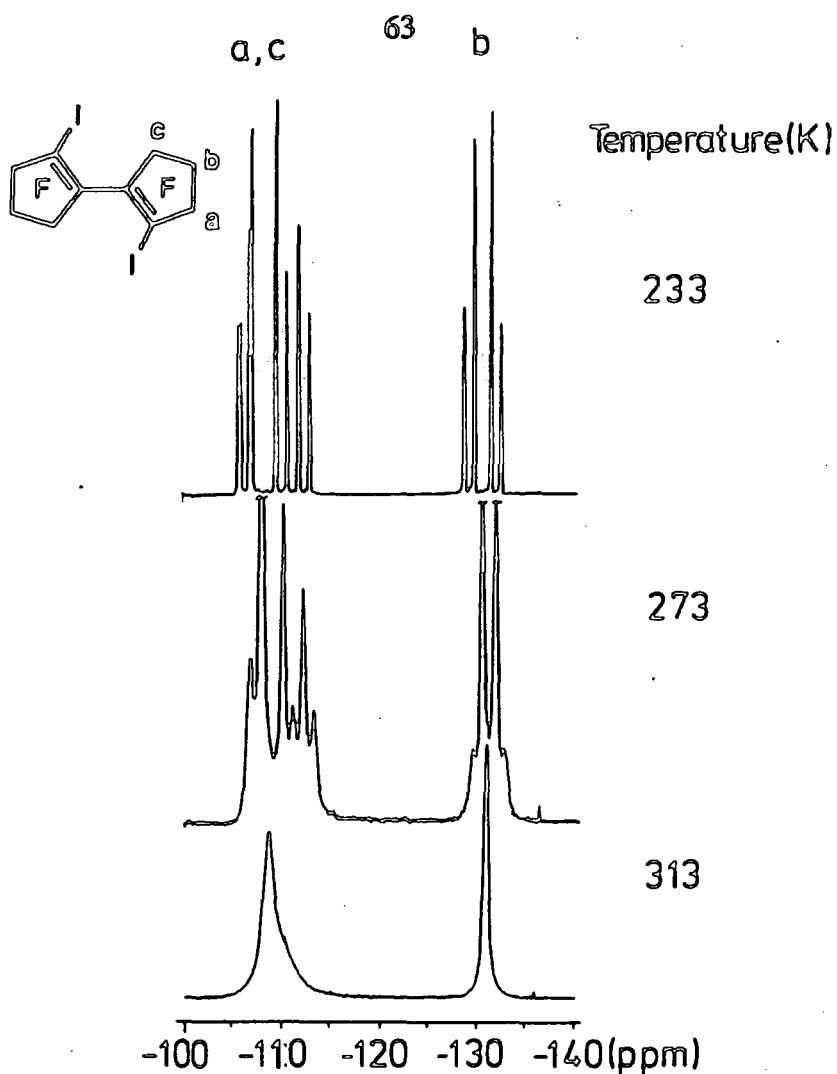


Figure 3.1  $^{19}\text{F}$ -NMR spectra of diiodo derivative (129) at various temperature solvent:  $(\text{CD}_3)_2\text{CO}$

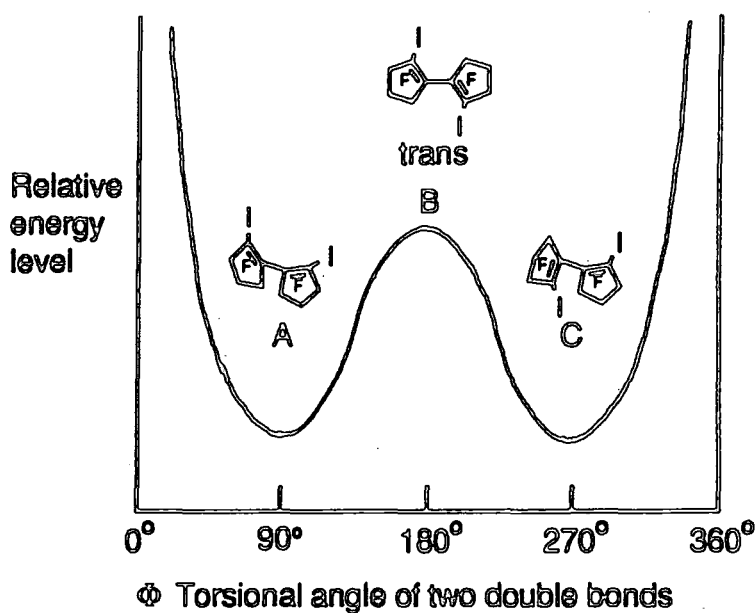


Figure 3.2 The relationship between relative energy level and torsional angle of double bonds

### 3.2.4 Bifunctional nucleophiles

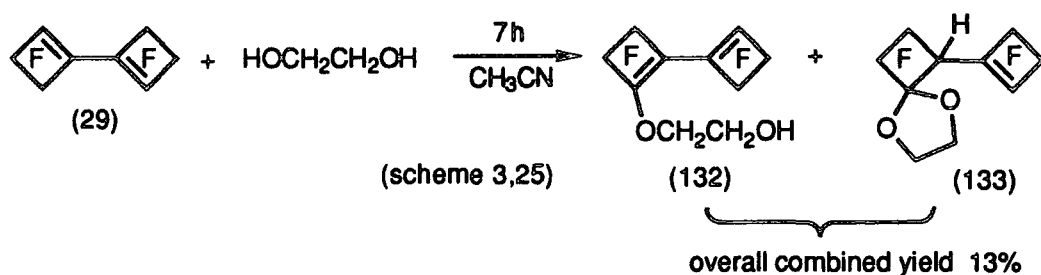
The reactions of fluorinated alkenes with bifunctional nucleophiles such as ethylene glycol<sup>122-125</sup> and a range of aromatic bifunctional nucleophiles<sup>126</sup> have been studied. Possible mechanistic pathways for such reactions were proposed<sup>126</sup>, which are illustrated in Scheme 3,24.

However, the reactions of fluorinated dienes with bifunctional nucleophiles have not been fully investigated. Basically there are two possibilities of reaction behaviour when fluorinated dienes react with bifunctional nucleophiles; intermolecular and intramolecular reactions. Of course the reactions are affected by reaction conditions, the structures of substrates, their reactivities, etc.

In this part the reactions of dienes (29) and (8) with ethylene glycol are discussed as an introductory study.

#### 3.2.4.1 Diene (29) with ethylene glycol

Diene (29) reacted with ethylene glycol in acetonitrile at room temperature to give mainly two products. Mass spectra of both products showed a parent molecular ion  $M^+$ , 328, for  $C_{10}H_5F_9O_2$ . They were then separated by preparative g.l.c..

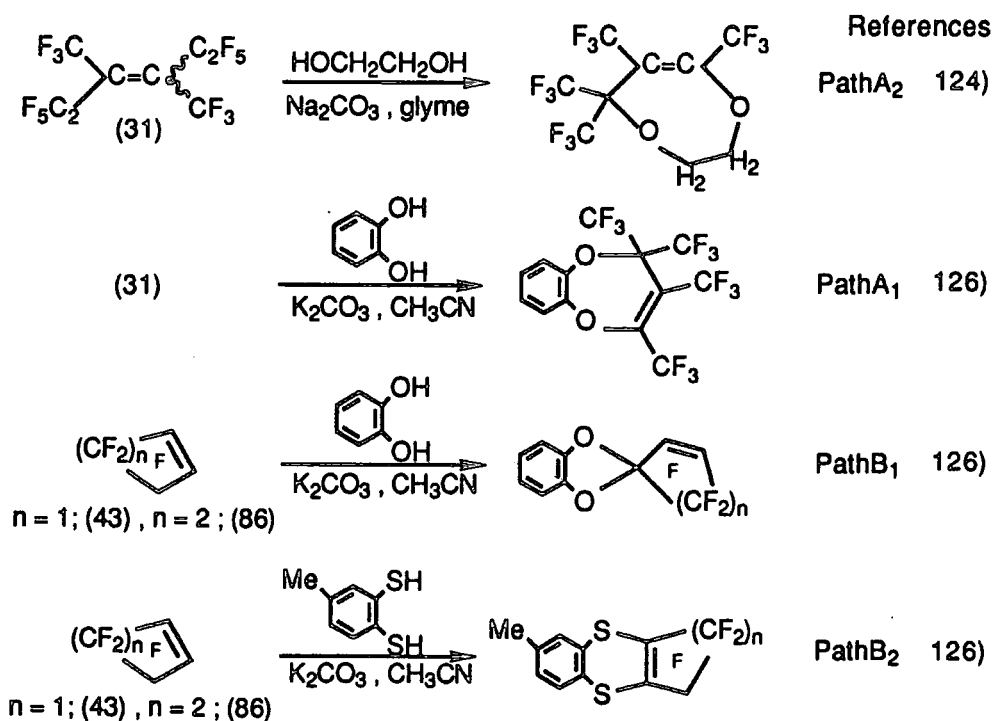
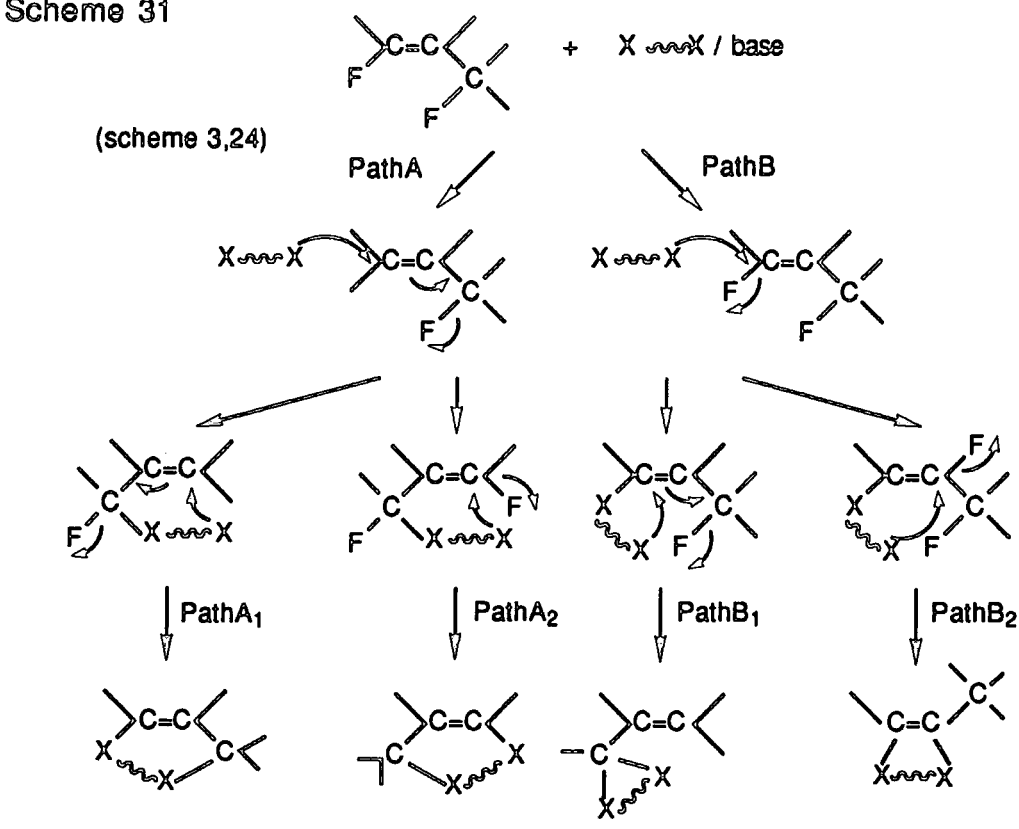


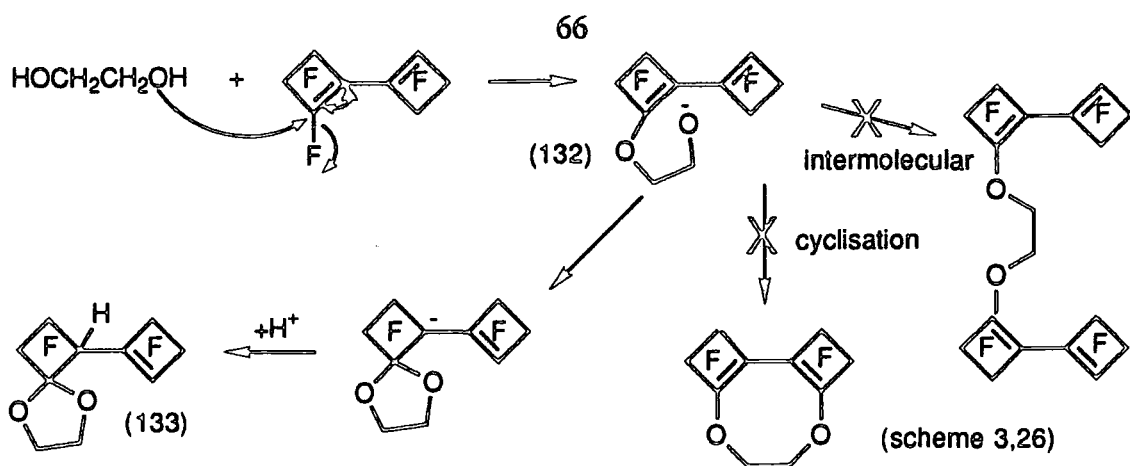
<sup>19</sup>F-NMR spectrum of one of them showed the presence of four different CF<sub>2</sub> groups and one vinylic fluorine. <sup>1</sup>H-NMR spectrum indicated the presence of two -CH<sub>2</sub>O- groups and a broad OH signal. The IR spectrum still showed the existence of the conjugation. On the other hand, <sup>19</sup>F-NMR spectrum of the other was more complicated. It showed the typical two AB type CF<sub>2</sub> groups signals, of which the coupling constants are consistent with those of perfluorocyclobutyl-cyclobut-1-ene (26b). <sup>1</sup>H-NMR

spectrum showed two different  $-\text{CH}_2\text{O}-$  groups and a broad multiplet signal at 4.5 ppm, which probably derived from a tertiary hydrogen. We, therefore, consider that these products have the structures such as (132) and (133).

The possible mechanism of this spiro acetal derivative (133) is shown in Scheme 3,26.

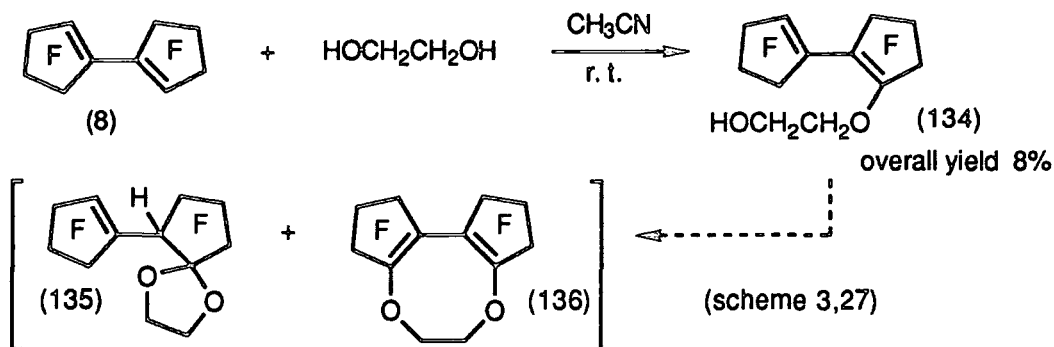
Scheme 31





### 3.2.4.2 Diene (8) with ethylene glycol

The reaction of diene (8) with ethylene glycol in acetonitrile afforded only one product (134).  $^{19}\text{F}$ -NMR spectrum showed clearly four  $\text{CF}_2$  groups and one vinylic fluoroine. Mass spectrum displayed the parent molecular ion  $\text{M}^+$ , 428 for  $\text{C}_{12}\text{H}_5\text{F}_{13}\text{O}_2$ . IR spectrum showed the evidence of the conjugated double bond.  $^1\text{H}$ -NMR spectrum showed the same signals as those of (132)(Scheme 3,27).

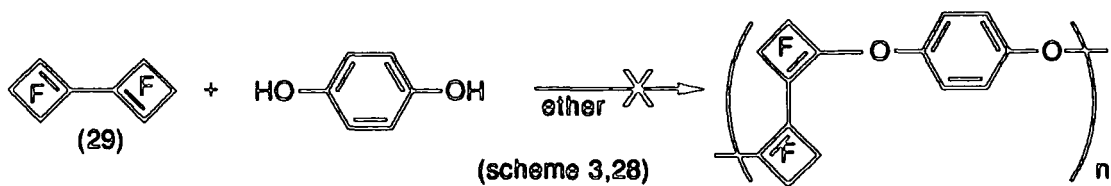


It has been reported<sup>91</sup> that the stirring of the mixture of diene (8) and ethylene glycol in dry ether for 14 days gave two products (135) and (136), while the reaction time of the formation of (134) was 2 days. Probably compound (134) is a product which may further react intramolecularly to form (135) and (136).

### 3.2.4.3 Diene (29) with hydroquinone

If the more rigid bifunctional oxygen nucleophile is employed, it might be possible to undergo inter-molecular reaction rather than intra-molecular. The mixture of diene (29) and hydroquinone in dry ether was stirred at room temperature for 2 days.

However, no reaction took place. The lone pair electrons of oxygens are likely to be delocalised over the benzene ring. Therefore, the reactivity towards diene (29) may decrease.



### 3.3 Summary

We have shown that dienes (29) and (8) are very susceptible to nucleophiles due to their extremely electron-poor conjugated double bond and also (29) is more reactive than (8) because of angle strain.

All reactions demonstrated here are initiated by attack of nucleophile at vinylic carbon and proceed by replacing a fluoroine; that is nucleophilic substitution reaction ( $S_N2$ ). In the reaction of (29) and (8) with water, the vinyl alcohol intermediates are still reactive and further reactions readily take place to give enol derivatives. They showed fairly strong acidity.

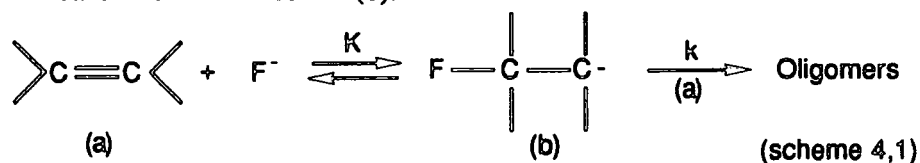
Bifunctional nucleophile such as ethylene glycol reacted with diene (29) and (8) to give a substituted product and an unexpected spiro-acetal product for (29).

## CHAPTER FOUR

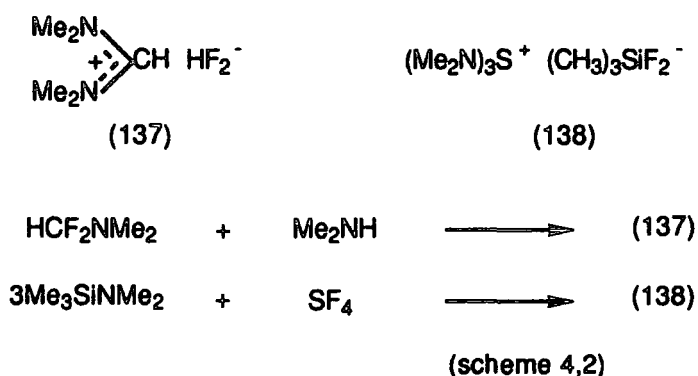
## 4. FLUORIDE ION INDUCED REACTIONS

4.1 Introduction4.1.1 Fluorocarbanions4.1.1.1 Observable carbanions

Fluorinated carbanions play a significant role in the chemistry of fluorinated alkenes.<sup>3,126</sup> Basically, they can be generated by the reactions of fluorinated alkenes with fluoride ion, but one difficulty lies in the tendency of fluorinated alkenes to undergo oligomerisation with fluoride ion (Scheme 1). When  $K$  is large, or the rate constant for oligomerisation  $k$  is small, obviously there will be a long-lived and observable carbanion intermediate (b).<sup>128</sup>



Indeed, observable carbanions have been generated by Chambers and coworkers<sup>94,128,129</sup>, Russian researchers<sup>130-133</sup>, and researchers in Du Pont.<sup>134-137</sup> It is notable that they have employed caesium fluoride, N,N,N',N'-tetramethylform-amidinium bifluoride (137)<sup>131</sup> and tris(dimethylamino)sulfonium trimethyl difluorosiliconate (TAS-F) (138)<sup>134,138</sup> respectively, as a fluoride ion source.



Various observable carbanions are tabulated in Table 4,1<sup>108,135,137</sup>.

The typical examples of generating the carbanion(140) from perfluoroisobutene (139), using three different fluoride ion sources, are illustrated in Scheme 4,3.



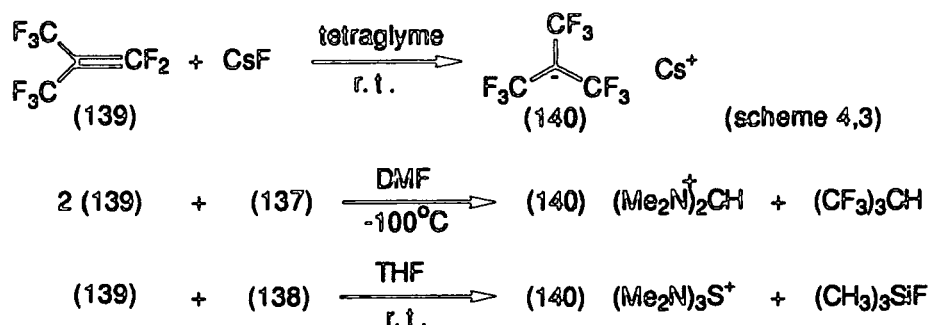
Table 4.1. Observable Fluorinated Carbanions

Alkene Precursor	Counter Ion	Anion	Reference
$(CF_3)_2C=CF_2$	A, B, C	$(CF_3)_3C^-$	94), 129), 131), 135)
$(CF_3)_2C=CFCF_3$	B	$C_2F_5\dot{C}(CF_3)_2^-$	135)
$C_2F_5(CF_3)C=CF(CF_3)$	A	$C_2F_5(CF_3)\dot{C}C_2F_5$	129)
$(CF_3)_2C=CFC_2F_5$	A, B, C	$C_3F_7\dot{C}(CF_3)_2^-$	129), 131), 135)
$C_2F_5(CF_3)C=C(CF_3)C_2F_5$	B	$C_2F_5(\dot{C}F_3)CFC(CF_3)C_2F_5^-$	135)
$C_3F_7(CF_3)C=CFC_2F_5$	C	$C_3F_7(CF_3)\dot{C}C_3F_7$	131)
$(CF_3)_2C=C(C_2F_5)_2$	B	$(CF_3)_2\dot{C}CF(C_2F_5)_2^-$	135)
$(CF_3)_2C=C=C(CF_3)_2$	A, B	$(CF_3)_2C=C=C(CF_3)_2^-$	130), 136)
-----			
	C		132)
	C		132)
	B		137)
	C		132)
	A, B		94), 129), 135)
	B		135)
	A		129)
	A		94)
	B		135)

A; Cs<sup>+</sup> B; (Me<sub>2</sub>N)<sub>3</sub>S<sup>+</sup> C; [(Me<sub>2</sub>N)<sub>2</sub>CH]<sup>+</sup>

The isolable anions are marked with °

Compound (137) reacts with (139) by both addition of fluoride ion and hydrogen fluoride to the double bond. The resulting mixture contains the corresponding carbanion(140) and  $(\text{CF}_3)_3\text{CH}$ . TAS-F (138) reacts with (139) to give the carbanion(140) and  $(\text{CH}_3)_3\text{SiF}$  as a byproduct.



It should be noted that some of these carbanions have been isolated as their TAS-salts<sup>135,136</sup> and, more interestingly, their crystal structures have been determined by X-ray diffraction.<sup>135-137</sup> The insoluble carbanions are marked with an asterisk in Table 4.1.

#### 4.1.1.2 NMR spectra of the carbanion solutions

$^{13}\text{C}$ -,  $^{19}\text{F}$ -NMR chemical shifts<sup>129,139</sup> of the carbanion derived from hexafluoropropene dimer (20) and its bromo derivative are shown below (Table 4,2).

Table 4,2 . NMR spectra data(chemical shift , ppm) of an observable carbanion

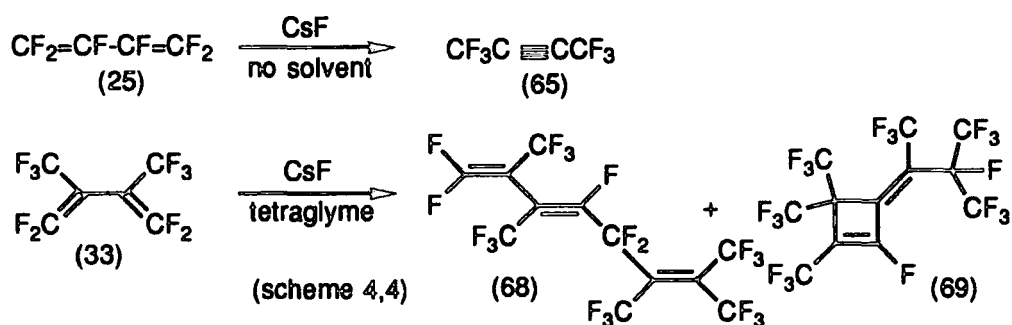
	$^{19}\text{F}$ -NMR	$^{19}\text{F}$ -NMR	$^{13}\text{C}$ -NMR	$^{19}\text{F}$ -NMR	$^{13}\text{C}$ -NMR
a	-62.8	-42.4	128.4	-66.4	119.5
b	-60.2	-42.4	128.4	-66.4	119.5
c	-	-	37.0	-	57.5
d	-100.5	-81.1	118.0	-106.8	112.1
e	-119.6	-126.2	107.5	-123.7	108.3
f	-86.4	-81.1	116.6	-82.3	116.7

The remarkable phenomena<sup>94,108,128,129,139</sup> are that the <sup>13</sup>C-NMR chemical shift associated with the carbon (c) bearing the negative charge is shift upfield as expected from an appropriate model compound (the bromo derivative), but the carbon atoms (a,b, and d) adjacent to the negative charge are associated with a downfield shift. This is also reflected in the <sup>19</sup>F-NMR spectra for the sites adjacent to the charge. The analogous changes of the chemical shifts are observed on other carbanion systems.

It has been demonstrated<sup>140</sup> that the basic theory of substituted chemical shifts does not necessarily apply to all the cases and increased electron density may be associated with shifts to lowfield for positions removed from the electron withdrawing substituent. Therefore, it is reasonable that chemical shifts of the carbons (a,b, and d) (Table 4.2) adjacent to the negative charge could be shifted downfield in spite of increased electron density.

#### 4.1.2 Reactions of fluorinated dienes with fluoride ion

Not many reactions have been reported concerning fluorinated dienes with fluoride ion. Perfluorobuta-1,3-diene (25) leads to perfluorobut-2-yne (65).<sup>75</sup> Perfluoro-2,3-dimethyl-buta-1,3-diene (33) gives the two corresponding dimers (68) and (69) (Scheme 4,4, or see Chapter 1). The carbanions appear to be generated as intermediates which are not stable enough to be observed spectroscopically.



In this Chapter, reactions of perfluoro-bicyclo-but-1,1'-enyl (29) and -pent-1,1'-enyl (8) with a variety of fluoride ion sources are discussed.

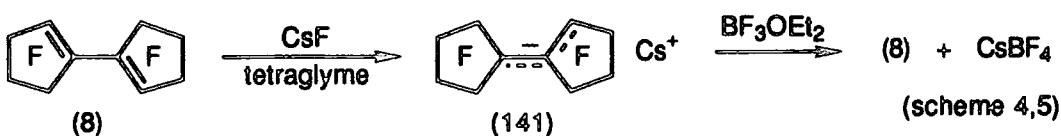
## 4.2 Discussion

### 4.2.1 Perfluorobicyclopent-1,1'-enyl (8)

#### 4.2.1.1 Generation of a carbanion

Remarkably, diene (8) reacted with some of the fluoride ion sources in various solvents to form the corresponding carbanion (141). The spectroscopic evidence and some trapping reactions of (141) will be discussed later.

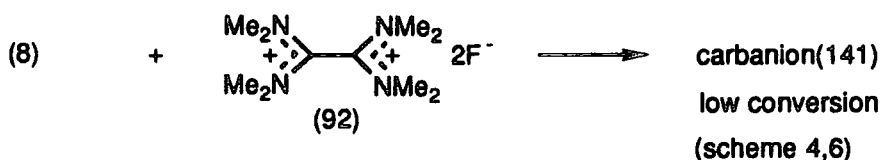
a) With caesium fluoride - an equimolar amount of caesium fluoride, dissolved in a mixture of (8) and tetraglyme, gave a violet homogeneous solution. The  $^{19}\text{F}$ -NMR spectrum showed six fairly sharp signals, one of which appeared at -85 ppm (Fig. 4,1). Signals derived from (8) were not observed. Addition of  $\text{BF}_3\text{OEt}_2$  gave a separated lower layer, which was identified as diene (8).



b) With other alkali metal fluorides - although potassium fluoride is a poorer fluoride ion donor than caesium fluoride, it also gave the carbanion (141) with sharp signals on  $^{19}\text{F}$ -NMR since diene (8) is very reactive. The reactions with sodium and lithium fluoride did not lead to (141).

c) With TAS-F - TAS-F (138) gave the carbanion (141) in acetonitrile. The comparison between caesium fluoride and the TAS-F system will be described later.

d) With  $\text{TDAE}^{2+}2\text{F}^-$  (92) -  $\text{TDAE}^{2+}2\text{F}^-$  (92) is obtained as a byproduct by the defluorination of tetramer (31) (see Chapter 2). Generation of the carbanion (141) was attempted using this new fluoride ion source in acetonitrile.



$^{19}\text{F}$ -NMR showed the broad signals based on (141) with low intensity, however, those of diene (8) and several new signals were also observed. It can be concluded that  $\text{TDAE}^2+2\text{F}^-$  (92) acts as a novel fluoride ion source, but no further study has been attempted.

e) With potassium iodide - lithium or sodium iodide reacted with diene (8) to give iodo substituted derivatives (see Chapter 3). Surprisingly, addition of potassium iodide to diene(8) in tetraglyme gave mono iodo substituted diene (131) together with the carbanion (141). Clearly, potassium iodide first reacts with (8) to form (131) and potassium fluoride, which reacts with diene (8) to give the carbanion (141).  $^{19}\text{F}$ -NMR showed a mixture of (131) and the carbanion(141) in a 1:1 ratio.

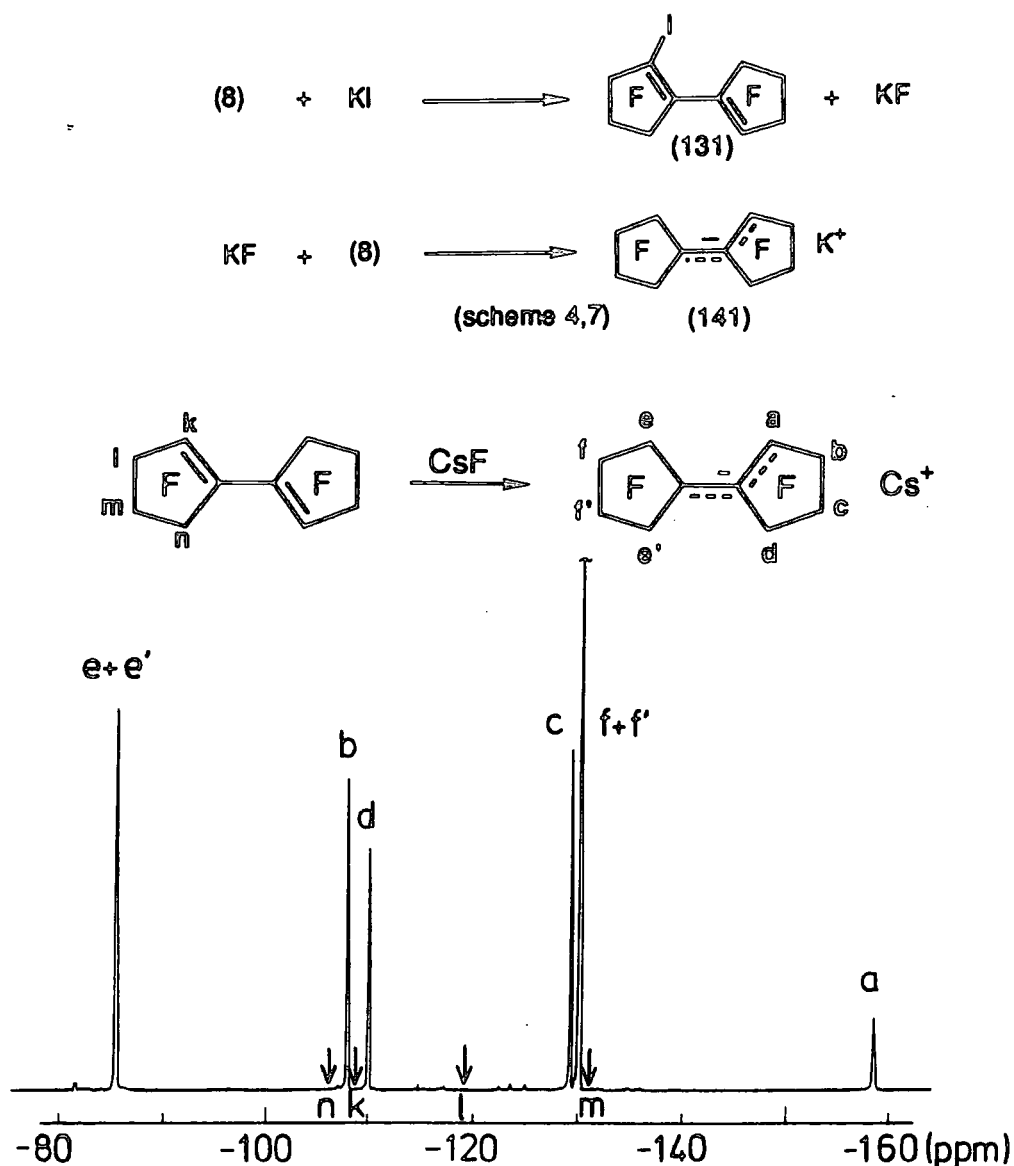


Figure 4.1.  $^{19}\text{F}$ -NMR spectrum of the carbanion(141) with CsF in tetraglyme relative intensity ; a : b : c : d : e + e' : f + f' = 1 : 2 : 2 : 2 : 4 : 4

4.2.1.2 NMR of the carbanion (141)

a) Chemical shifts -  $^{19}\text{F}$ -NMR spectrum of the carbanion (141) is shown in Fig. 4,1. No F-F coupling is evident and the signals are remarkably sharp. Assignments are made on the following basis:

- (i) assuming that the carbon a bears the negative charge, the signal should be shifted considerably upfield from vinylic fluorine;
- (ii) the carbon d is at an allylic node, therefore the signal can be less affected;
- (iii) the carbons c, f, and f' will not be affected;
- (iv) the carbons b, e, and e' are adjacent to the negative charge and should be shifted downfield. However, one puzzling feature remains that signals e and e' are almost identical (see later discussion).

Therefore it can be concluded that the carbanion (141) is conjugated.  $^{13}\text{C}$ -NMR spectrum of the carbanion (141) also supported this conclusion since two signals derived from the carbons with the charge were shifted upfield (Fig. 4,2).

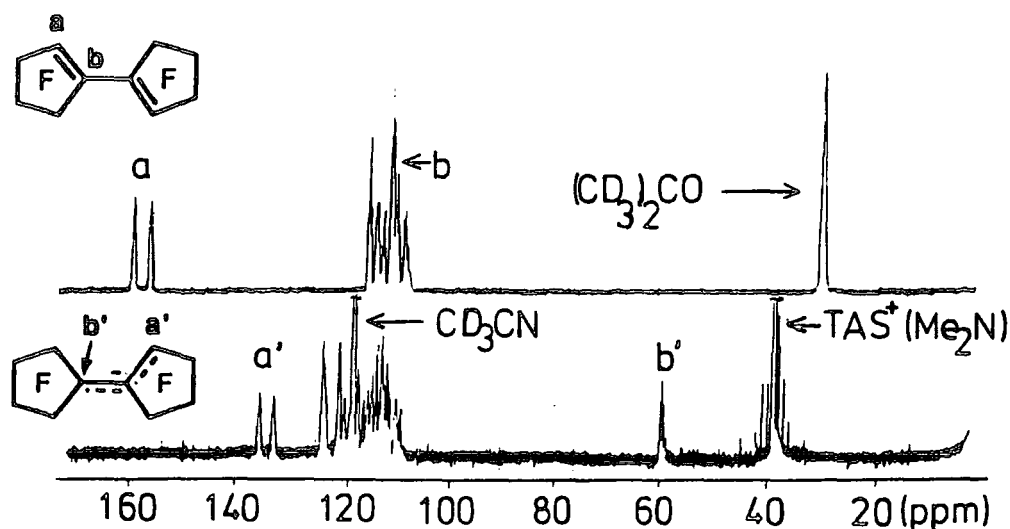


Figure 4,2.  $^{13}\text{C}$ -NMR spectra of diene(8) and its carbanion(141)

b) Counter ion dependence -  $^{19}\text{F}$ -NMR spectra of the carbanions with  $\text{K}^+$ ,  $\text{Cs}^+$ , and  $\text{TAS}^+$  cations were compared, under conditions of excess of fluoride ion sources. Fig.4,3 shows the  $^{19}\text{F}$ -NMR spectra of the carbanion (141) with different counter ions. All of the corresponding signals are almost identical in terms of their sharpness and their chemical shifts can hardly be distinguished.

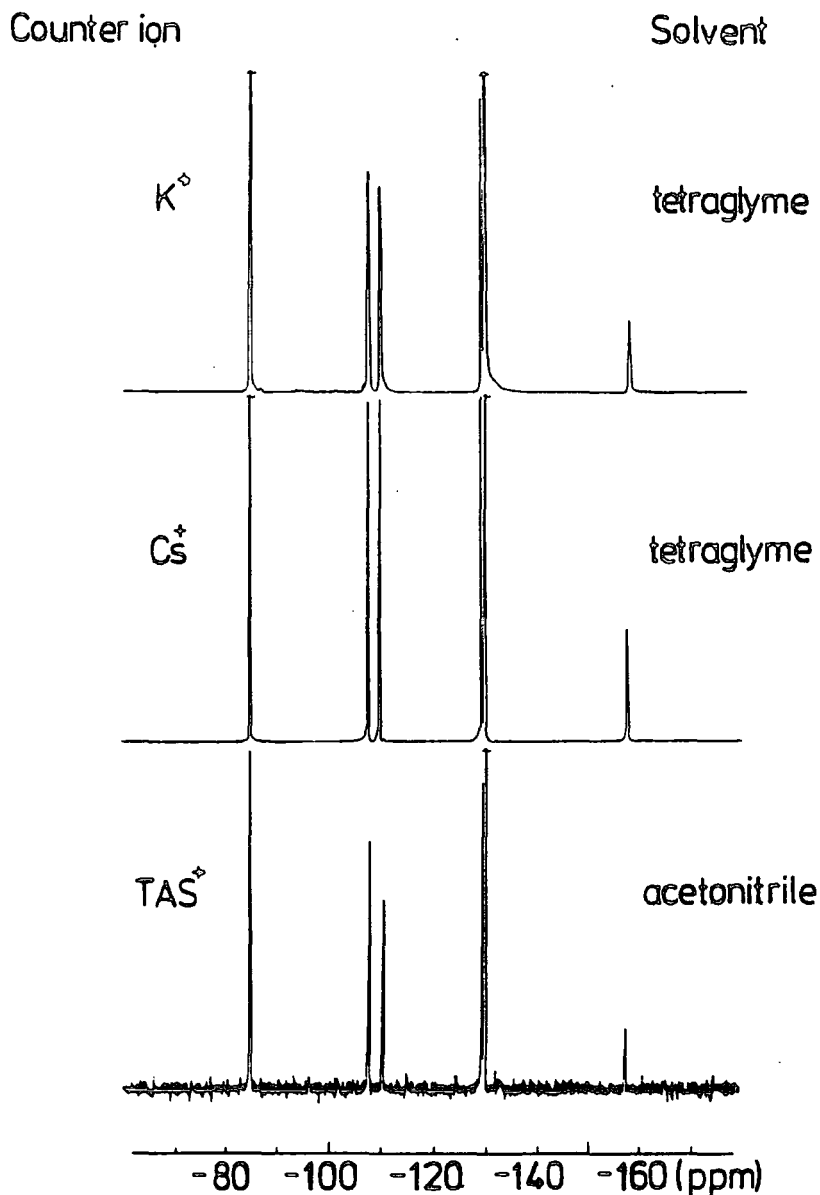
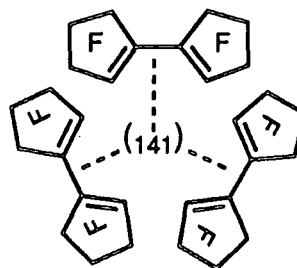


Figure 4.3.  $^{19}\text{F}$ -NMR spectra of the carbanion(141) with various counter ions

c) Solvent dependence - under the conditions of excess of the fluoride ion source, there seems to be a close similarity between the  $^{19}\text{F}$ -NMR spectra of the carbanions (141) in various solvents, such as tetraglyme, dimethylsulphoxide (DMSO), and N,N-dimethylformamide (DMF).

When acetonitrile was used as a solvent, however, the carbanions (141) with  $\text{K}^+$  and  $\text{Cs}^+$  gave broader  $^{19}\text{F}$ -NMR signals in comparison with those in tetraglyme, whereas  $\text{TAS}^+$  cation showed sharp signals in acetonitrile.  $\text{TAS}^+$  cation is an organic molecule.  $\text{K}^+$  and  $\text{Cs}^+$  are more solvated in tetraglyme than in acetonitrile since the former has the ability of binding metal cations.

d) Diene (8)/F<sup>-</sup> ratio dependence - it has been reported<sup>129</sup> that  $\text{TAS-F}(138)$  takes into solution more than one molar equivalent of a fluorinated alkene and leads to the considerable line-broadening of  $^{19}\text{F}$ -NMR signals associated with fluorine atoms at carbons that are adjacent to the negative charge. This fact indicates that if an excess of a fluorinated alkene is present in solution, then rapid fluoride ion exchange occurs between fluorinated alkenes and the corresponding carbanion.<sup>129</sup> This is also the case with diene (8) under the same conditions. An excess of diene (8) completely dissolved in acetonitrile with  $\text{TAS-F}$  and the  $^{19}\text{F}$ -NMR spectrum showed very broad signals derived from the carbanion (141) and diene (8). Evidently, the fluoride ion exchange occurs on the NMR time-scale (Fig.4,4). Fluoride ion is able to interact, on average, with more than one equivalent of diene (8) and this interaction is sufficiently significant to take into account, otherwise insoluble diene (8) would remain in the solution. The nature of this average interaction may be described below; as if fluoride ion can do the negative equivalent of hydrogen-bonding, which may be partial.



$^{19}\text{F}$ -NMR measurements were attempted, altering the ratio of diene (8) to caesium fluoride in acetonitrile. Fig. 4,5 shows some of the  $^{19}\text{F}$ -NMR spectra of each carbanion solution. In the presence of an excess of diene (8), the signals are broader than those



with an excess of caesium fluoride. However, no signals of diene (8) were observed and some diene (8) remained in the bottom layer. This result may indicate that the interaction between fluoride ion and diene (8) is not as strong as in the case of TAS-F, in spite of fluoride ion exchange.

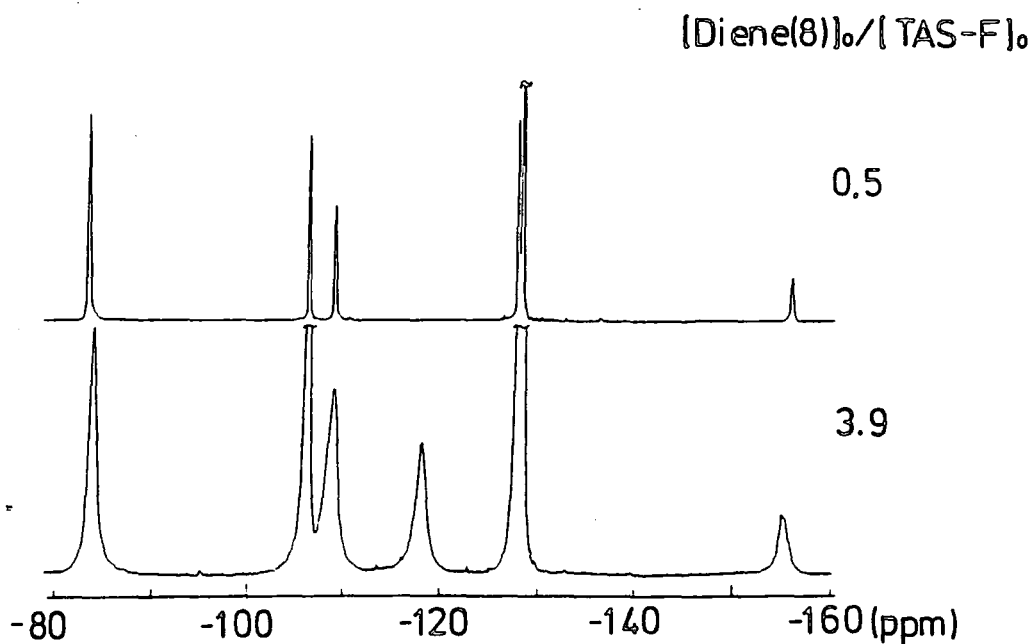


Figure 4.4.  $^{19}\text{F}$ -NMR spectra of the carbanion(141) with TAS-F in  $\text{CH}_3\text{CN}$

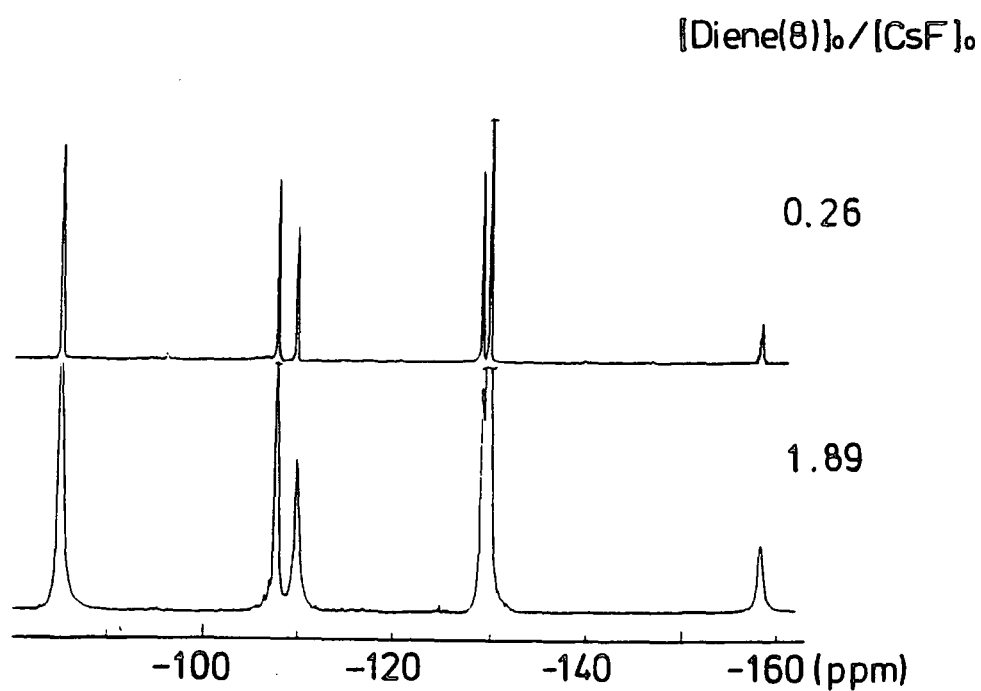


Figure 4.5.  $^{19}\text{F}$ -NMR spectra of the carbanion(141) with CsF in tetraglyme

e) Variable temperature behaviour - at room temperature, the carbanion (141) gave sharp signals without couplings if appropriate solvent and fluoride ion source were chosen. As described earlier, two  $^{19}\text{F}$ -NMR signals (e, e') for the sides, which are adjacent to the carbon with the charge, are identical. It may be considered that the bond between the carbon 1 and 2 is rotating freely at room temperature.

A solution of carbanion (141) has been studied by  $^{19}\text{F}$ -NMR spectroscopy at various temperatures in the range of  $-40 \sim 80^\circ\text{C}$ . Surprisingly, no dramatic changes were observed either with  $\text{Cs}^+$  or  $\text{TAS}^+$  as a cation. The signals retain their sharpness and signals e and e' were still identical at  $-40^\circ\text{C}$  (Fig. 4,6).

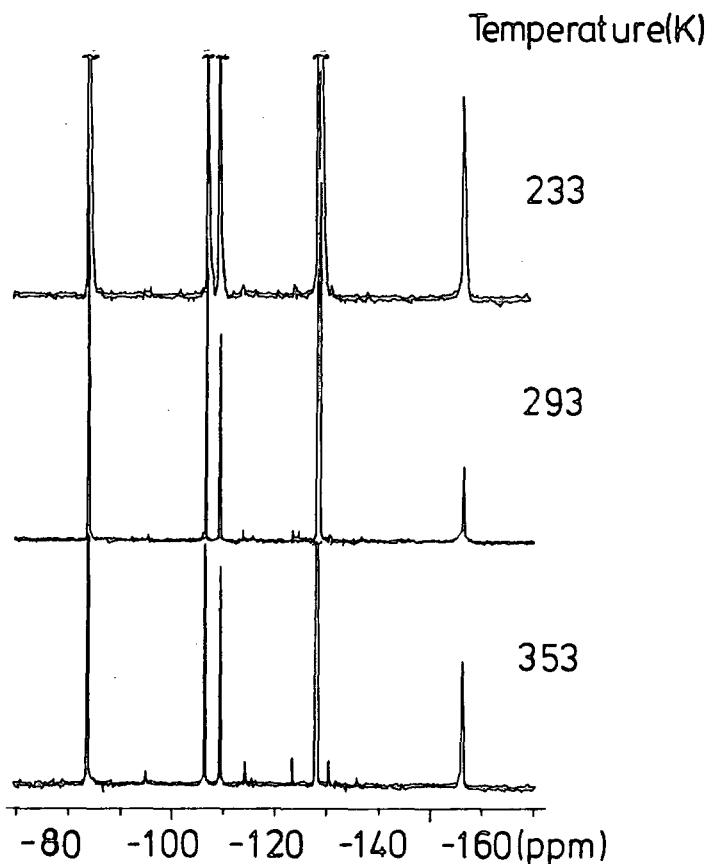
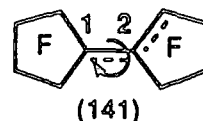


Figure 4,6.  $^{19}\text{F}$ -NMR spectra of the carbanion(141) at various temperature. Solvent :  $\text{CD}_3\text{CN}$

It has been reported<sup>129</sup> that increasing temperature of solutions of various carbanion salts causes line-broadening of the signals due to fluoride ion exchange. However, such a line-broadening was not observed even at 80°C in this case.

It can be concluded, therefore, that the carbanion (141) is remarkably stable and has an extremely low rotation barrier on the C<sub>1</sub>-C<sub>2</sub> bond.

#### 4.2.1.3 Attempt to isolate the carbanion salt (141)

Researchers in Du Pont<sup>136,137</sup> have isolated several fluorinated carbanion TAS salts (see Table 4,1). The isolation of the caesium salts has also been attempted in our laboratories<sup>129,139</sup>. However, only perfluoro-*t*-butyl caesium has been isolated<sup>129</sup>. Evaporating the solvent in vacuum normally gave caesium fluoride and starting fluorinated alkenes<sup>139</sup>.

The TAS salt of (141) can be isolated simply by removing the solvent in vacuum to give a brown solid, which was completely redissolved in acetonitrile. The <sup>19</sup>F-NMR spectrum showed only the presence of the carbanion (141). It has not been possible to isolate the caesium salt.

Recrystallisation of (141) salts has been attempted using various solvents but without success in attempts to obtain samples of crystallographic quality.

#### 4.2.1.4 Reactions of the carbanion (141)

Fluorinated carbanions are obviously strong nucleophiles and are likely to react with suitable electrophiles to form the corresponding adducts<sup>94,129,135,139</sup>. Several trapping reactions of the carbanion (141) have been attempted. Methyl iodide and allyl bromide did not react with (141).

Bromine was expected to form the corresponding bromo derivatives but, instead, diene (8) and its precursor (27) were obtained. Bromo derivatives produced were readily attacked by fluoride ion, which had probably been derived from the carbanion (141), to yield the precursor alkene (27).



can be attributed to  $-\text{CF}_2$  groups. IR spectrum did not show a great absorption according to the conjugated double bond. Probably (142) has a distorted non-planar structure and this may partially destroy the conjugation.

Potassium and sodium fluoride are poorer fluoride ion sources than caesium fluoride, but the great susceptibility of (29) aids in the dimerisation.

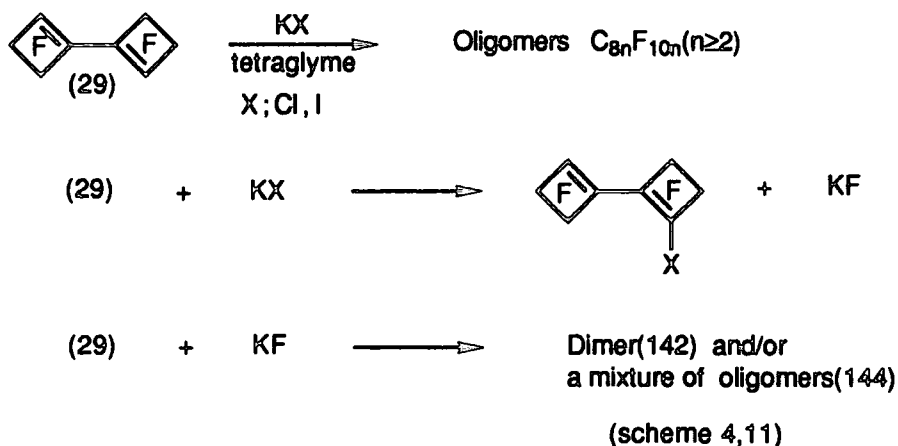
#### 4.2.2.2 With a deficiency of fluoride ion

Dimer (142) and an insoluble solid (144) were obtained and elemental analysis of the latter suggested the formula  $\text{C}_{8n}\text{F}_{10n}$ . Mass spectrum shows peaks such as 858, 958, 1055, 1144, etc. IR spectrum of (144) is different from that of (142) and showed a medium absorption at  $1720\text{ cm}^{-1}$  which was not observed on dimer (142).

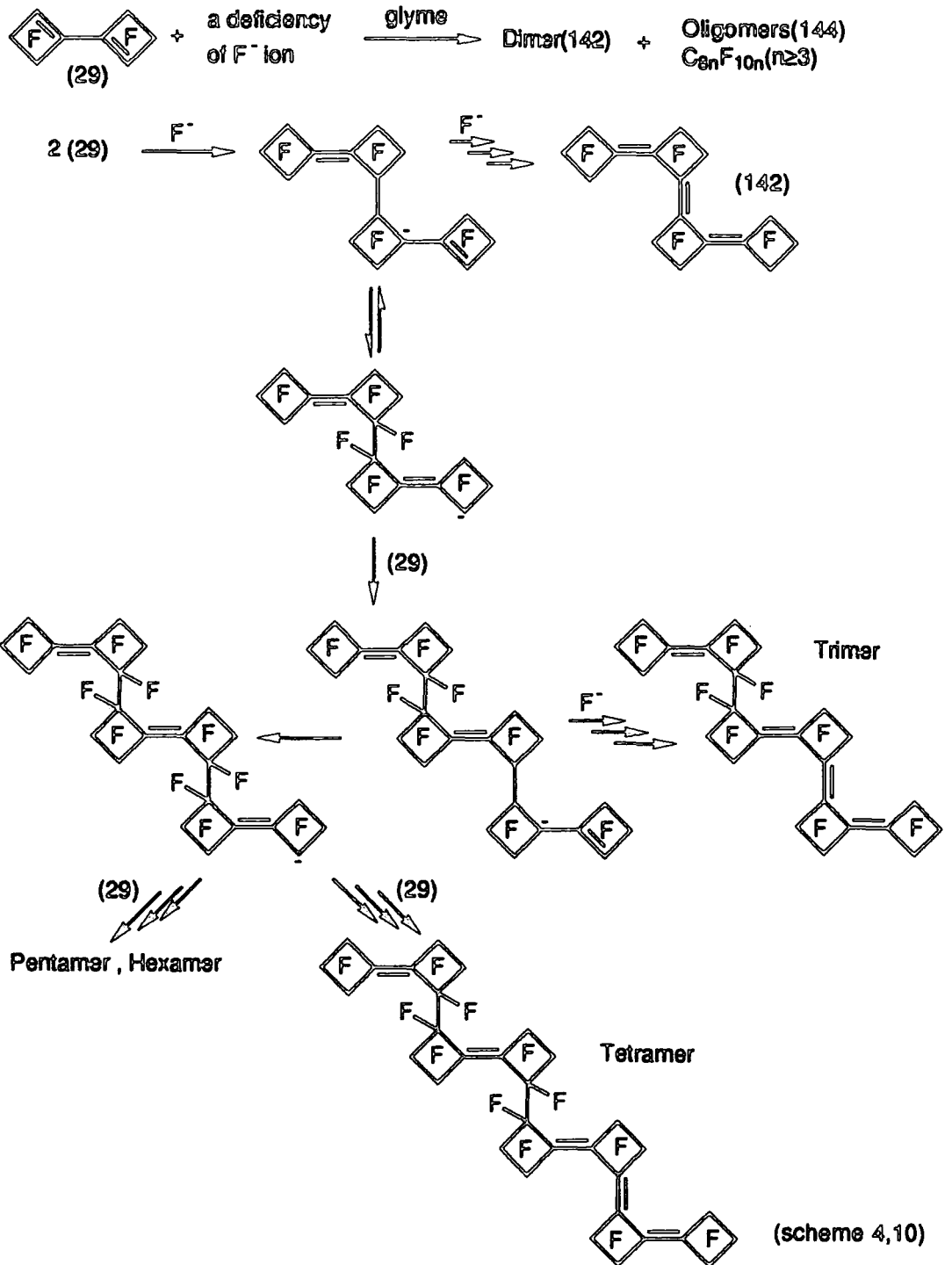
These results suggest that (144) can be a mixture of oligomers ( $\text{C}_{8n}\text{F}_{10n}$ ,  $n \geq 3$ ). The probable reaction mechanism is shown in Scheme 4,10.

#### 4.2.2.3 With other halide ions

Surprisingly, chloride or iodide ions can react with diene (29) to yield oligomers. For example, an equimolar amount of potassium iodide gave the dimer (142), and an equimolar amount of potassium chloride gave a mixture of oligomers ( $\text{C}_{8n}\text{F}_{10n}$ ,  $n = 2,3,4,\dots$ )(144). Chloride or iodide ions attack diene (29), forming chloro or iodo substituted compounds, and potassium fluoride induces the oligomerisation. Only a small amount of potassium fluoride can induce oligomerisation and the substituted products were not obtained.



Scheme 4,10



4.2.2.4 With the carbanion (141)

Fluorinated carbanions can act as fluoride ion sources.<sup>129</sup> Diene (29) was added to the carbanion (141) solution and the reaction was followed by <sup>19</sup>F-NMR spectrometry. Intensity of the signals for (141) decreased, however, only the original carbanion signals were observed in solution, at the end of the reaction. During the reaction, a solid was precipitated, which was characterised as dimer (142). The <sup>19</sup>F-NMR spectra are illustrated in Fig.4,7. This is a good example of how the carbanion (141) solution can play a role as a catalytic fluoride ion source.

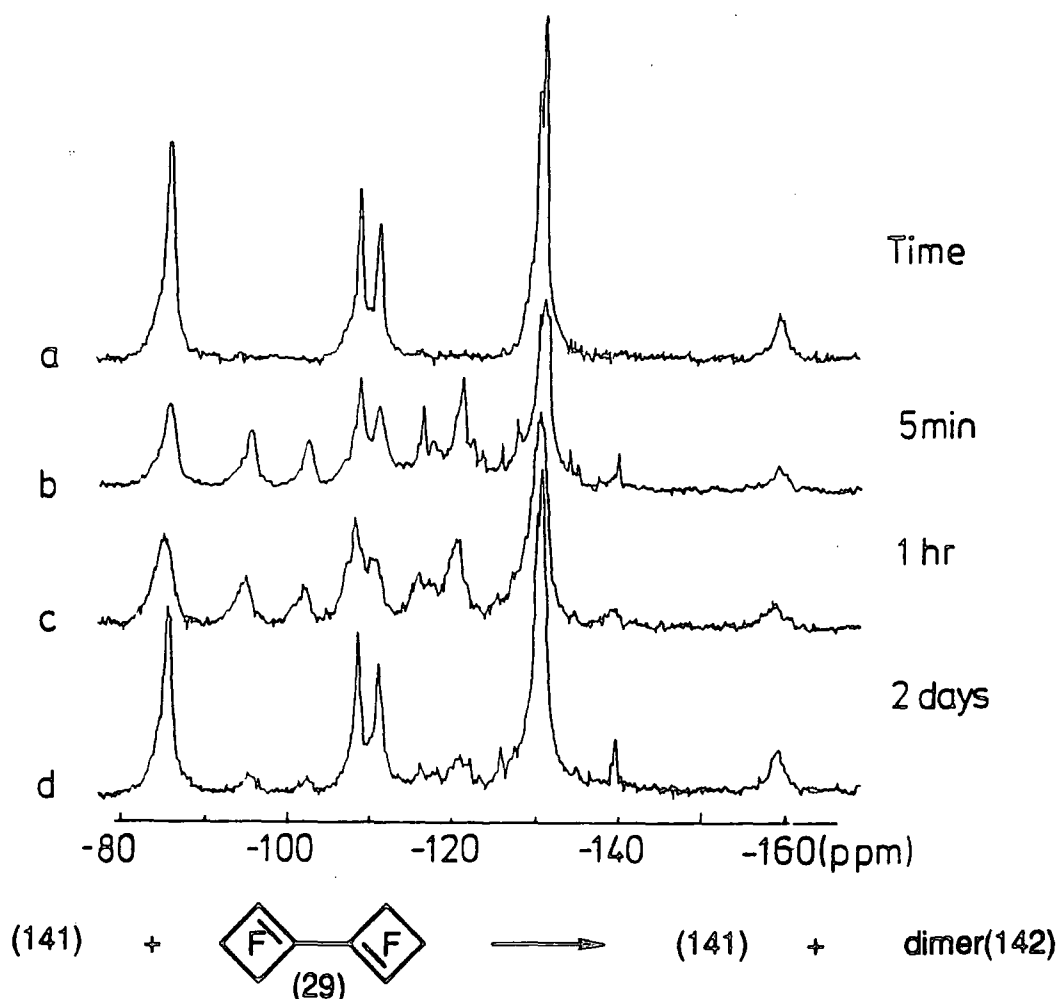


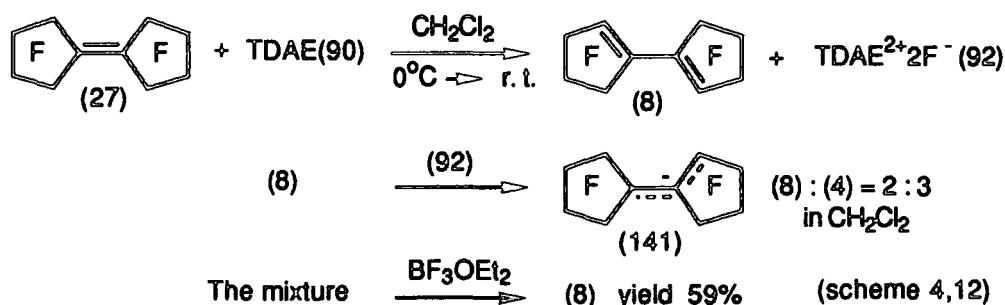
Figure 4,7. <sup>19</sup>F-NMR spectra for the reaction of the carbanion(141) with diene(29)

#### 4.2.3 Reactions of perfluorobicyclobutylidene (26) and perfluorobicyclopentylidene (27) with TDAE (90)

TDAE (90) can defluorinate perfluoro-3,4-dimethyl-hex-3-ene (31) to form the diene (34) (see Chapter 2). Defluorination of (26) and (27) was attempted using TDAE (90).

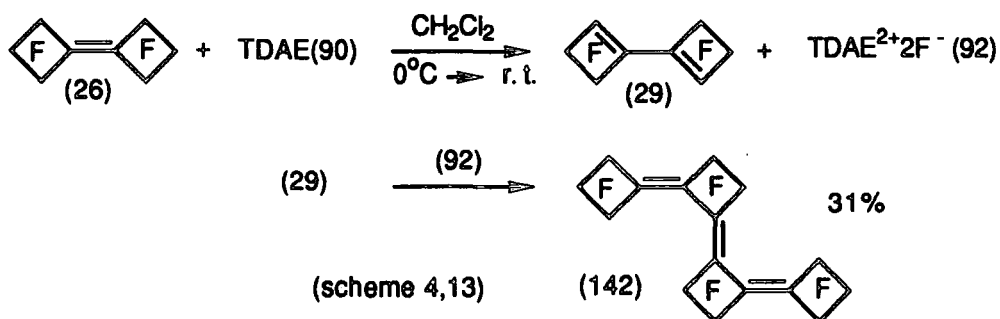
##### 4.2.3.1 With (27)

As expected (27) was defluorinated in TDAE to give diene (8). However, the byproduct  $\text{TDAE}^{2+}2\text{F}^-$  (92) is a potential fluoride ion source and, in fact, donated a fluoride ion to the part of the diene (8) produced, generating the carbanion (141) (Scheme 4,12). When acetonitrile was used, which is more polar than dichloromethane, all diene (8) was converted into the carbanion (141). Addition of  $\text{BF}_3\text{OEt}_2$  to the carbanion solution formed diene (8).



##### 4.2.3.2 With (26)

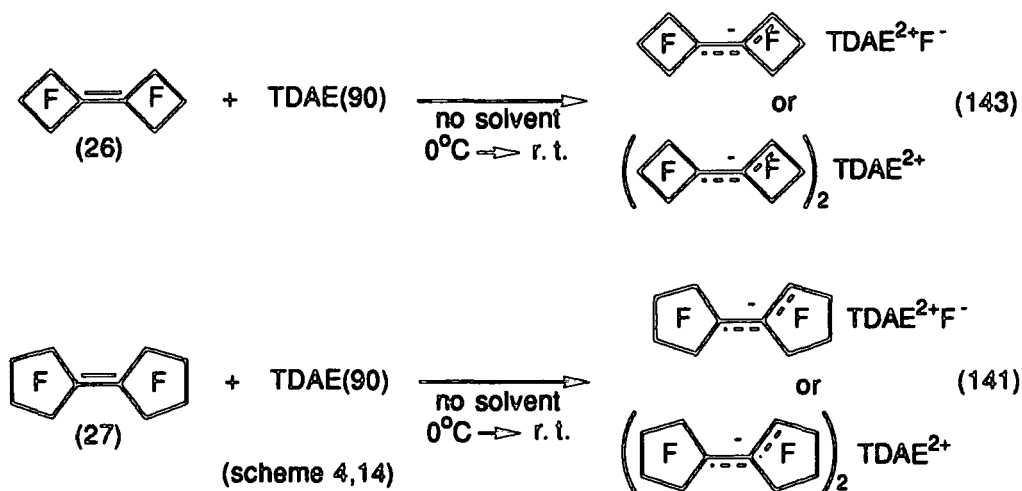
Diene (29) was produced by defluorination. However, this diene reacted with  $\text{TDAE}^{2+}2\text{F}^-$  immediately to give dimer (142).  $\text{BF}_3\text{OEt}_2$  cannot be used with TDAE at the same time since  $\text{BF}_3\text{OEt}_2$  reacts with  $\text{TDAE}^{98}$ .





4.2.3.3 Reactions with (26) and (27) without solvent

Direct addition of TDAE to (26) caused an exothermic reaction. The colour changed to brown red and then further to dark brown, finally giving a brown solid. This solid was partially soluble in acetonitrile. The  $^{19}\text{F}$ -NMR spectrum showed mainly five resonances at -88.5, -107.0, -113.0, 121.7, and 142.2 ppm (Fig. 4,8). These resonances were compared with those of the carbanion (141) and it is reasonable to consider that the carbanion(143) was generated. Assignments were made in the manner described earlier (see 4.2.1.2). Signals  $d$  and  $d'$  are identical and it suggested free rotation between  $\text{C}_1$  and  $\text{C}_2$  at room temperature. This carbanion is also considered to be conjugated. Addition of  $\text{BF}_3\text{OEt}_2$  to the solution gave the diene (29) as the main product. This result suggests that the carbanion (143) can be generated by neat reaction with TDAE and it may be isolated. This is the first example of the generation of the unstable carbanion (143) which has been unsuccessful using TAS-F(138) or caesium fluoride.



The carbanion salt (141) with  $\text{TDAE}^{2+}$  can also be generated by the same procedure using (27) and TDAE(90). As described above, in the course of these reactions the acetonitrile-insoluble solid was obtained. This solid was soluble in  $\text{D}_2\text{O}$  and characterised as  $\text{TDAE}^{2+}2\text{F}^-$ (92).

There could be two alternatives for the carbanion salts, which are illustrated in Scheme 4,14.

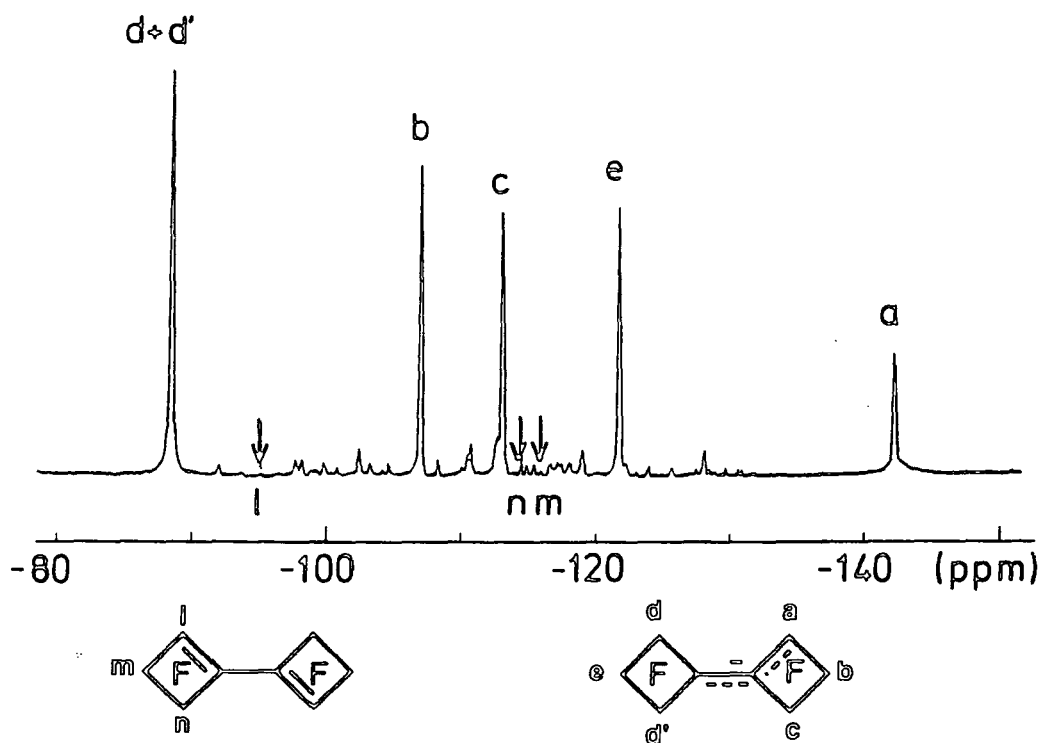


Figure 4.8.  $^{19}\text{F}$ -NMR spectrum of the carbanion(143) in  $\text{CD}_3\text{CN}$   
 relative intensity ;  $a : b : c : d + d' : e = 1 : 2 : 2 : 4 : 2$

## 4.2.4 Ylides

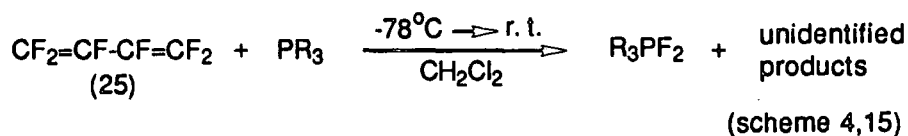
It was reported<sup>141</sup> that perfluorocyclobutene (43) reacted with triphenylphosphine to give the 1:1 adduct. Burton and coworkers<sup>142</sup> have characterised this adduct as 2,2,3,3,4,4-hexafluoro(triphenylphosphoranylidene)cyclobutene (145). This ylide is a rare example of an insoluble fluorinated carbanion. The overlap of the phosphorus d-orbitals with the ylide carbon p-orbitals and the strong inductive effect of the adjacent CF<sub>2</sub> lead to remarkable stability.<sup>142</sup>

They subsequently claimed<sup>20</sup> the formation of trialkylammonium ylides by the reaction of (43) with trialkyl-amines. These ylides are stabilised only by inductive effects. Various fluorinated ylides<sup>20,21,142,143</sup> are illustrated in Table 4,3.

Table 4,3. Fluorinated Ylides

Precursor	Reactant	Ylide	Reference
$\boxed{\text{F}}^-$ (43)	PPh <sub>3</sub>	$\boxed{\text{F}}^- \text{---} \overset{+}{\text{P}}\text{Ph}_3$ (145)	142
(43)	NR <sub>3</sub> (R = Et, Bu)	$\boxed{\text{F}}^- \text{---} \overset{+}{\text{N}}\text{R}_3$	20
(43)	AsBu <sub>3</sub>	$\boxed{\text{F}}^- \text{---} \overset{+}{\text{As}}\text{Bu}_3$	143
CF <sub>3</sub> CF=CFCF <sub>3</sub>	PBu <sub>3</sub>	$\text{CF}_3\text{CF}_2\overset{-}{\text{C}}\text{---}\overset{+}{\text{P}}\text{Bu}_3$   CF <sub>3</sub>	21

Reactions of perfluorobuta-1,3-diene (25) with a variety of trivalent phosphorus compounds have been studied.<sup>144</sup> Unstable products are formed and they usually decompose to difluorophosphoranes; R<sub>3</sub>PF<sub>2</sub> and unidentified products.



4.2.4.1 Attempt to generate the conjugated ylides of diene (29) and (8)

a) Reactions with triphenyl phosphine - diene (29) reacted with triphenylphosphine in dry ether or acetonitrile at room temperature. Removal of the solvent in vacuum gave a brown solid. Mass spectrometry gave a parent molecular ion,  $M^+548$ , for  $C_{26}H_{15}F_{10}P$  and elemental analysis supported this formula. The  $^{19}F$ -NMR spectrum is shown in Figure 4,9.

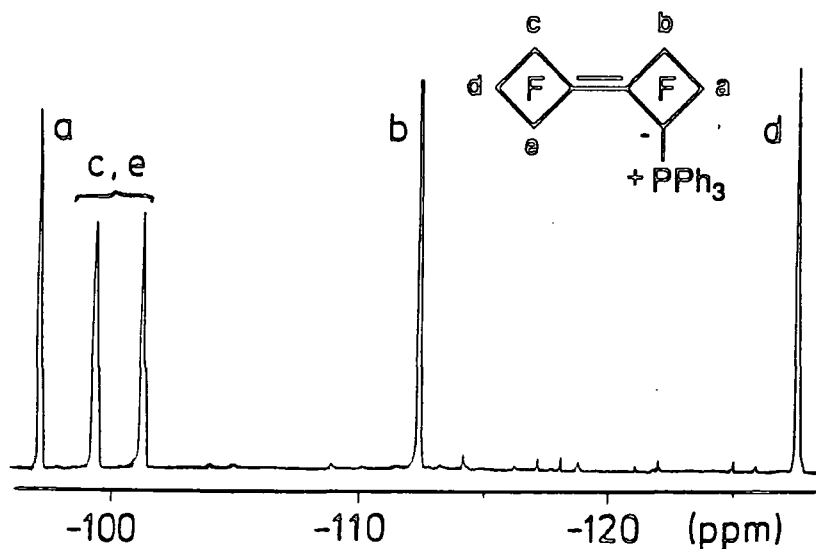
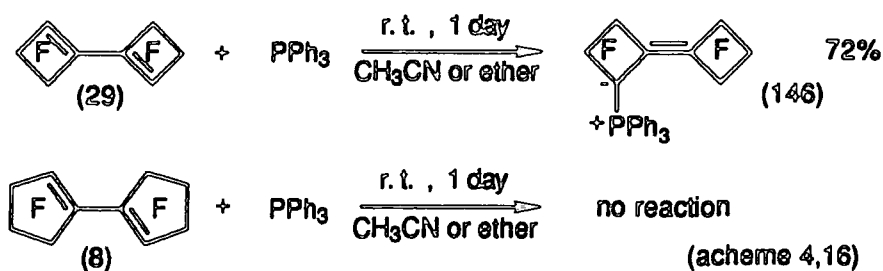
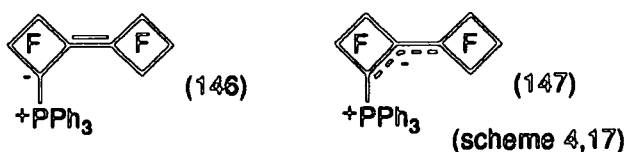


Figure 4,9.  $^{19}F$ -NMR spectrum of the phosphonium ylide(146) of diene(29)  
relative intensity;  $a : b : c : d : e = 1 : 1 : 1 : 1 : 1$

There are five broad signals with equal intensity, which are significantly different from those of the conjugated carbanion (143). The results from mass spectrum, elemental analysis and  $^{19}F$ -NMR suggest the presence of five  $CF_2$  groups in different environments. Signal **a** is shifted downfield and this can be attributed to the site that is adjacent to the carbon bearing the charge. Signals **c** and **e** are also shifted downfield, but

not as much as signal a. It can be considered that three  $\text{CF}_2$  groups are affected by the neighbouring negative charge.

There could be two possible structures: non-conjugated ylide (146) and the conjugated one (147). If the negative charge was delocalised, like the carbanion (143), only four  $^{19}\text{F}$ -NMR signals should be observed.

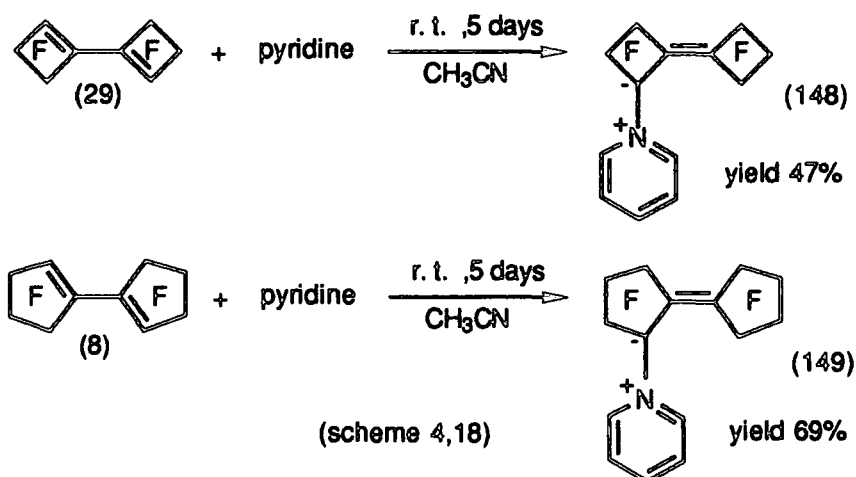


$^{19}\text{F}$ -NMR data indicate the bond rotation between  $\text{C}_1$  and  $\text{C}_2$  may be restricted. Moreover, IR spectrum showed the absorption at  $1720\text{ cm}^{-1}$  which can be attributed to  $\text{C}=\text{C}$  bond attached to  $\text{R}_f$  or  $\text{F}$ .

Therefore, we conclude that the product has structure (146). It is reasonable to think that the negative charge has great interaction with the phosphonium and this interaction disturbs the delocalisation. However, to confirm this non-conjugated structure, it would be necessary to study its X-ray crystal structure.

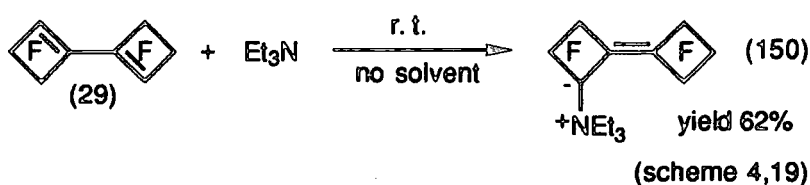
Diene (8) and (34) did not form their phosphonium salts with  $\text{PPh}_3$ .

b) Reactions with pyridine - both diene (29) and (8) reacted with pyridine in acetonitrile at room temperature to afford a yellow and a brown solid respectively.



The  $^{19}\text{F}$ -NMR spectrum of the former in acetonitrile showed five signals with equal intensity, and seven signals for the latter. In both cases three signals are shifted downfield. The IR spectrum of each solid gave absorptions at 1700 and 1720  $\text{cm}^{-1}$  respectively, based on  $(\text{Rf})_2\text{C}=\text{C}(\text{Rf})_2$ . Mass spectroscopic data and elemental analysis did not give the expected results, due to the unstable structure. However, in comparison with the phosphonium ylide (146) these two solids may also be considered to have non-conjugated ylide structures such as (148) and (149).

c) Reaction with triethylamine - the reaction of diene (29) with triethylamine without solvent afforded the corresponding ylide (150). Spectroscopic data were compared with other ylides and consistent with the non-conjugated structure .



### 4.3 Summary

We have demonstrated the generation of the conjugated carbanion (141) by the reactions of diene (8) with a variety of fluoride ion sources. The carbanionic intermediate (143) is normally unstable and reacts further with diene (29) to give the corresponding oligomers. However, TDAE (90) defluorinates fluorinated cyclic alkenes (26) to form diene (29), which reacts with TDAE<sup>2+</sup>2F<sup>-</sup> (92) without solvent, providing the observable carbanion (143).

Diene (29) and (30) react with electron donating reagents, such as triphenylphosphine, pyridine, and triethylamine to yield the ylide derivatives. These ylides have been assumed to be non-conjugated.

Nevertheless, in order to confirm the structures of these carbanionic species, further investigations are necessary, *i.e.* X-ray crystal structure.

## CHAPTER FIVE



## 5 CYCLOADDITION REACTIONS OF FLUORINATED DIENES

### 5.1 Introduction

In this part, attempted Diels-Alder reactions and 1,3-dipole cycloaddition reactions of fluorinated dienes are mainly described.

#### 5.1.1 Diels-Alder reactions of fluorinated dienes

A large number of Diels-Alder reactions of unsaturated fluorinated compounds have been reported.<sup>1,145</sup> In general, fluorinated dienes are less reactive in the Diels-Alder reaction than their hydrocarbon equivalent, due to electron-withdrawing property of fluorine or fluorinated alkyl groups. Fluorinated dienophiles, on the contrary, are more reactive than their hydrocarbon equivalent.

Perfluorocyclopenta-1,3-diene (151) and hexa-1,3-diene (152) have *s-cis* conformation and may undergo the Diels-Alder reaction as a diene. Several examples are shown in Table 5.1.

Perfluorobuta-1,3-diene (25) has a distorted skew-*cis* conformation (see Chapter 1) and was considered to exclude the possibility of the formation of its [2 + 4] cycloadducts with dienophiles.<sup>147</sup> Nevertheless, cyclisation<sup>151,152</sup> and [2 + 2] cycloaddition<sup>153</sup> reactions of (25) have been reported.

Recently, Russian workers<sup>154-159</sup> have claimed that (25) reacts with electron-rich dienophiles such as *para*-substituted styrenes,  $\alpha$ -substituted styrene, and phenylacetylene to give both [2 + 2]- and [2 + 4]-cycloadducts. These systems (diene-acceptor, dienophile-donor) are opposite to classic Diels-Alder reaction (diene-donor, dienophile-acceptor). Some reactions of (25) are listed in Table 5.2.

In our laboratory the reactions of fluorinated diene (8) and (34) with various dienophiles have been attempted<sup>35,91</sup>. However, only starting material was recovered in each case.

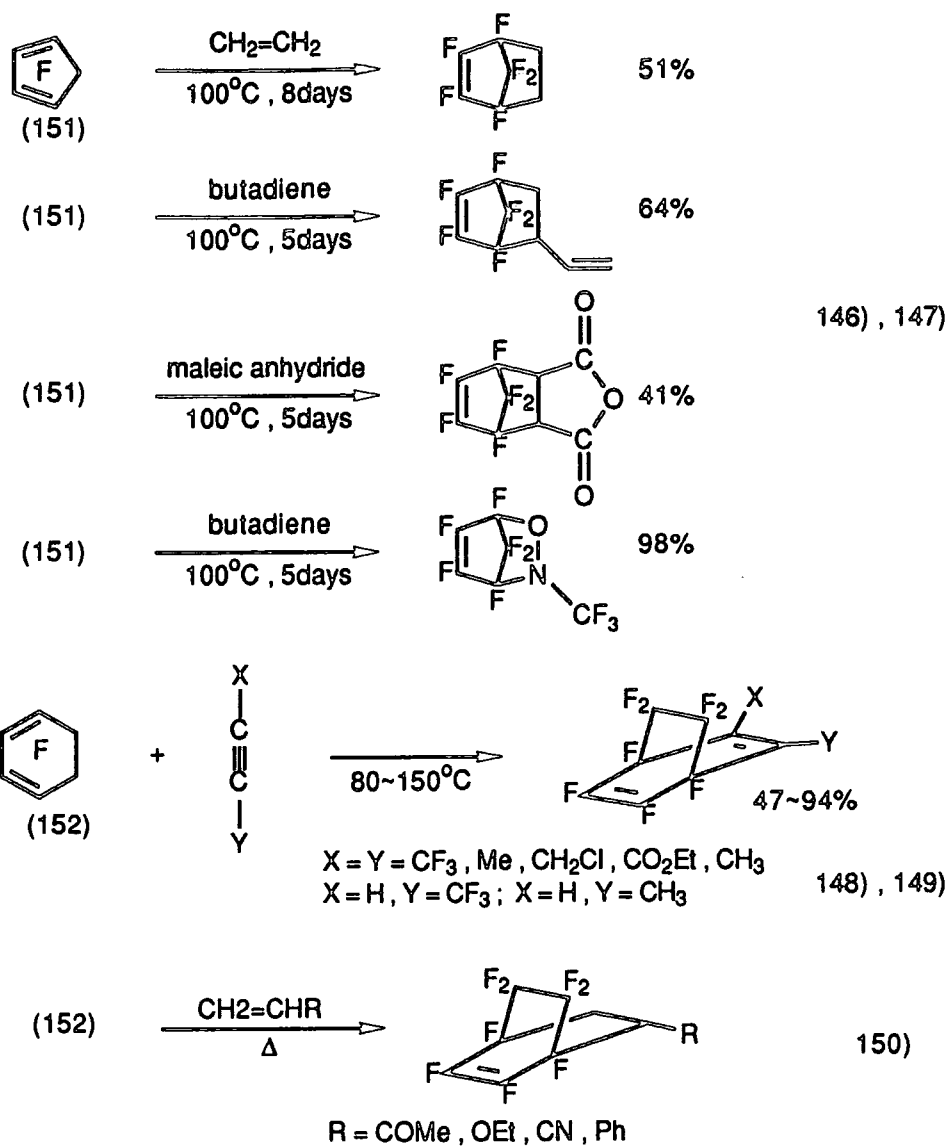
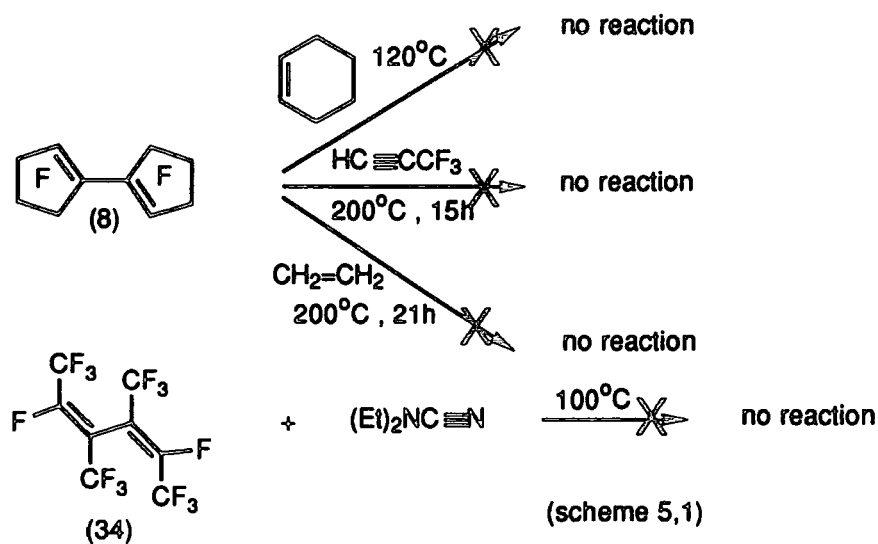
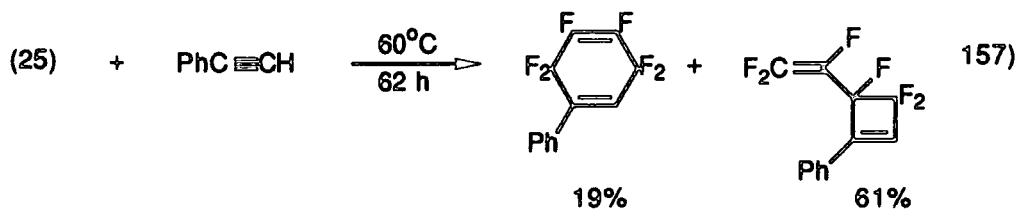
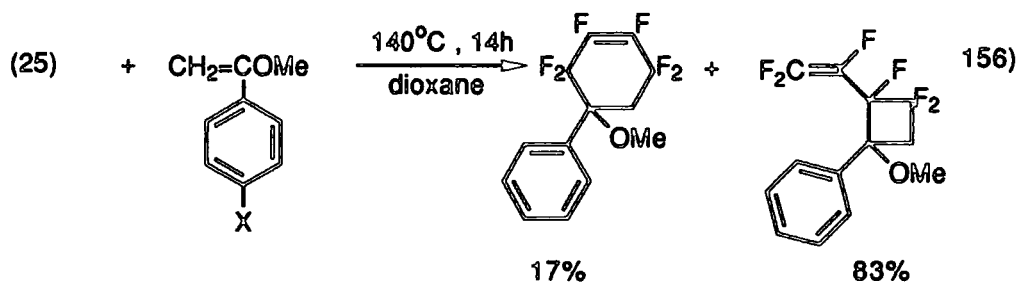
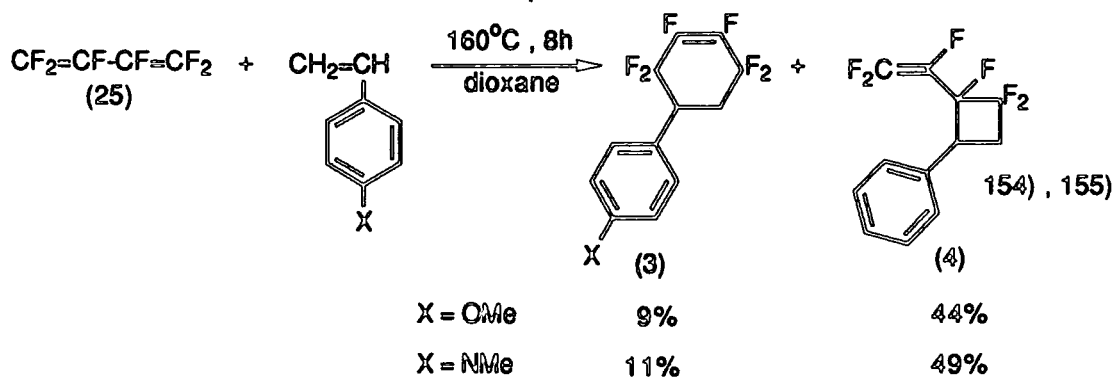
Table 5.1. Diels-Alder Reactions of (151) and (152) Reference

Table 5.2. Diels-Alder Reactions of Perfluorobuta-1,3-diene(25) with Various Dienophiles Reference

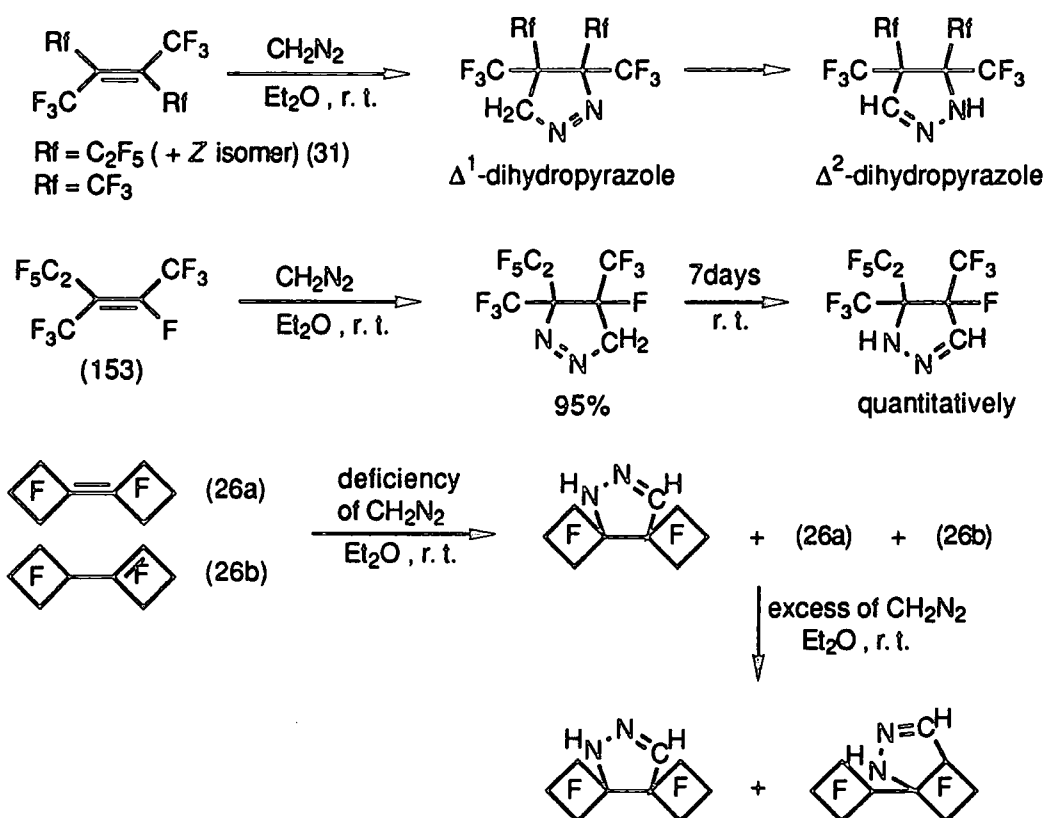


### 5.1.2 1,3-Dipole Cycloaddition Reactions of Fluorinated Dienes

There are only a few reports of reactions involving addition of diazomethane to fluorinated alkenes.<sup>160-163</sup> We have also reported<sup>164</sup> additions of diazomethane to a variety of perfluorinated alkenes and rationalised their reactivity and, furthermore, their reactivity towards general nucleophilic attack, based on considering frontier orbitals (F.O.)<sup>164</sup> (see details in Chapter 3). Several reactions are illustrated in Table 5,3.

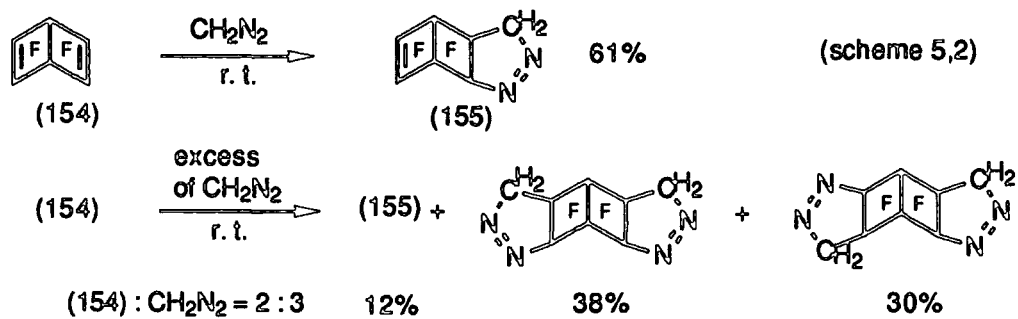
It should be noted<sup>164</sup> that during these reactions  $\Delta^1$ -dihydropyrazole derivatives are presumably produced as an intermediate and are very susceptible towards traces of acid or base to give  $\Delta^2$ -dihydropyrazole. Alkene (153) afforded the corresponding  $\Delta^1$ -dihydropyrazole as an isolable solid, which isomerised quantitatively to its  $\Delta^2$ -dihydropyrazol.

Table 5,3. Addition of diazomethane to various perfluorinated alkenes



As far as fluorinated dienes are concerned, only one report<sup>165</sup> has appeared in the course of our literature search. Hexafluorobicyclo[2,2,0]hexa-2,5 diene (154), which is readily

prepared by the photo chemical isomerisation of hexafluorobenzene, reacted with diazomethane to form the corresponding adducts (Scheme 5,2).



## 5.2 Discussion

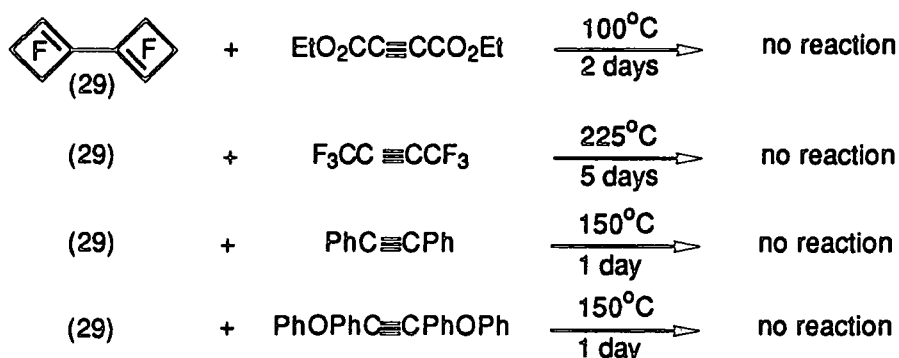
### 5.2.1 Diels-Alder Reactions of Diene (29) and (30)

#### 5.2.1.1 With various acetylene derivatives (as diene)

A series of reactions of diene (29) with acetylenes has been attempted. However, only starting material was recovered. These reactions are summarised in Table 5.4. Relatively electron-rich acetylenes, such as diphenylbut-2-yne and bis(paraphenoxyphenyl)but-2-yne did not undergo a [2 + 4] cycloaddition reaction. Their bulky aromatic groups might have affected the overlap of  $\pi$  orbitals.

Table 5.4

Table 5.4. Attempted Diels-Alder Reactions of Diene(29) with Various Acetylene Derivatives



#### 5.2.1.2 With various hydrocarbon olefins (as diene)

It has been reported<sup>166</sup> that cyclohexa-1,3-diene and propene reacted with perfluorobicyclobutylidene (26a) to afford the products (156) and the 'ene' product (157) respectively. Propene and  $\alpha$ -methylstyrene did not undergo the expected reactions with diene (29) and (8).

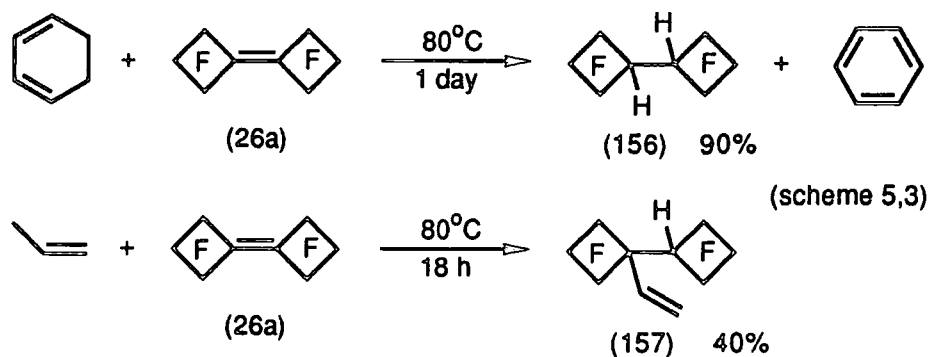
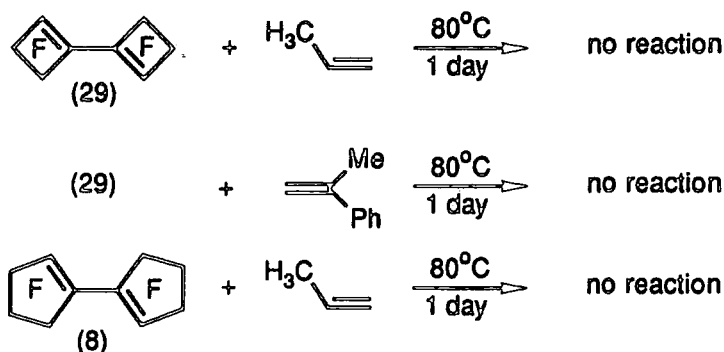


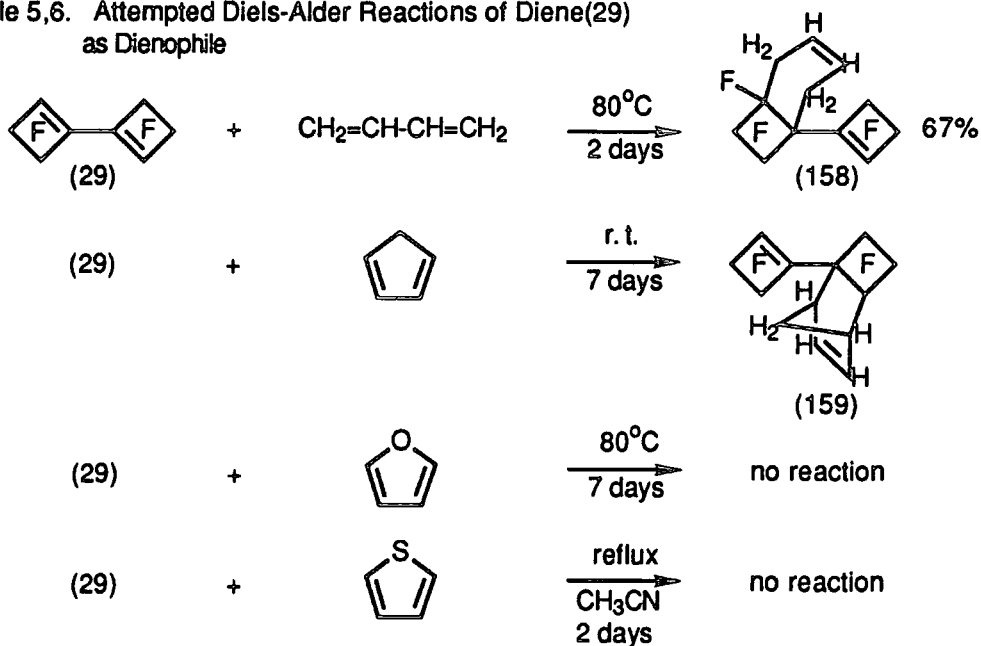
Table 5.5. Attempted 'ene' and Diels-Alder Reactions of Dienes (29) and (8)



### 5.2.1.3 With various hydrocarbon diene derivatives

Various hydrocarbon dienes have been employed for the reactions of diene (29). Diene (29) reacted with butadiene and cyclopentadiene as dienophile to give the [2 + 4] cycloadducts (158) and (159) respectively.

Table 5.6. Attempted Diels-Alder Reactions of Diene(29) as Dienophile



Mass spectrum data of (158) gave a parent molecular ion, M<sup>+</sup> 340 for C<sub>12</sub>H<sub>6</sub>F<sub>10</sub>. <sup>19</sup>F- and <sup>1</sup>H-NMR spectra were consistent with the structure. IR spectrum showed -FC=C< stretching vibration at 1720 cm<sup>-1</sup> and a very weak vibration due to -CH=CH- stretching. The product (158) has two enantiomers.

Mass spectrum data of (159) gave a parent molecular ion,  $M^+$  352, for  $C_{13}H_6F_{10}$ .  $^{19}F$ -NMR spectrum was also consistent with the structure given. The reaction was carried out with an excess of diene (29), but cyclopentadiene can readily dimerise at room temperature and this dimer and the product (159) could not be separated. The  $^1H$ -NMR spectrum confirmed this mixture. The reaction of a cyclic diene with a dienophile yields predominantly the endo product (Alder-Stein Rules) which has two enantiomers, as described above.

Diene (29) did not afford [2 + 4] cycloadduct by reactions with cyclohexadiene and heterocyclic dienes such as furan and thiophene.

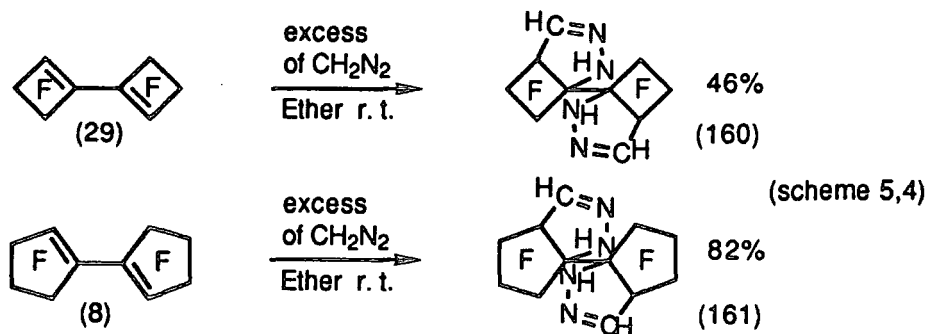
A range of reactions of diene (8) has also been attempted but no cycloadducts were obtained.

These results may suggest that the higher reactivity of diene (29) than diene (8) towards hydrocarbon dienes can be attributed to the effect of angle strain in (29) since the geometries of (29) and (8) are quite similar, in spite of a slightly distorted structure in (8). The greater reactivity of (26a) than (29) can also be attributed to more angle strain in (26a) than (29), which is not necessarily the case in nucleophilic reactions of these two compounds.

## 5.2.2 Addition of Diazomethane to Diene (29) and (8)

### 5.2.2.1 Addition to diene (29)

Diene (29) reacted with an excess of diazomethane in ether at room temperature to form a yellowish solid.





Mass spectral data gave a parent molecular ion  $M^+$  370 for  $C_{10}H_4F_{10}N_4$ , which was supported by elemental analysis. IR spectrum showed a broad absorption at  $3380\text{ cm}^{-1}$  due to N-H stretch, a broad absorption at  $1550\text{ cm}^{-1}$  due to  $>C=N-$ . However,  $^{19}F$ -NMR spectrum gave a great number of signals, which have not yet been assigned.  $^1H$ -NMR spectrum gave one signal for  $-CH=N-$  at 5.8 ppm ( $J_{HF}$ :17.5 Hz) but  $-NH-$  signal was not observed. As described above (see Table 5.3), its  $\Delta^1$ -dihydropyrazole derivative must have been produced first, but isomerised to  $\Delta^2$ -dihydropyrazole. This can be explained by the absence of  $^1H$ -NMR signal for  $-CH_2-N=N-$ .

Therefore, it is reasonable to conclude that the product has the structure (160). Nevertheless, the product should have several isomers and the complicated  $^{19}F$ -NMR spectrum accounts for this fact.

#### 5.2.2.2 Addition of diene (8)

A white solid was obtained by addition of diazomethane to diene (8). Mass spectrum and elemental analysis gave a chemical formula,  $C_{12}H_4F_{14}N_4$ . IR spectrum showed N-H stretch absorption at  $3260\text{ cm}^{-1}$  and  $>C=N-$  stretch absorption at  $1600\text{ cm}^{-1}$ .  $^1H$ - and  $^{19}F$ -NMR spectra were too complicated to be assigned, but we assume that the diadduct has the structure (161), and there are also several isomers.

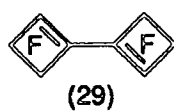
#### 5.2.3 Attempted UV irradiation of dienes

Surprisingly, diene (29) was irradiated with UV to form an insoluble solid. Elemental analysis gave the formula  $C_{8n}F_{10n}$ . Mass spectrum showed several high molecular ions at 572 ( $n = 2$ ), 858 ( $n = 3$ ), 1144 ( $n = 4$ ), etc. IR spectrum showed very broad absorption in all regions. There are two possibilities of explaining this result :

- (i) UV irradiation initiated the radical oligomerisation of diene (29);
- (ii)  $[2 + 2]$  cycloaddition reaction occurred between several molecules to give oligomers.

However we have not yet reached a conclusion. Dienes (8) and (34) did not react when subjected to UV irradiation. Angle strain in (29) probably excites the electronic state of the conjugated double bond and induces the reaction.



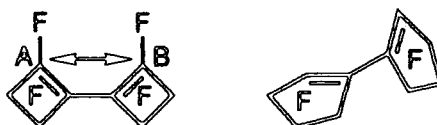


UV irradiation  
5 days

Oligomers  $C_{2n}F_{10n}$   
(scheme 5,5)

### 5.3 Summary

Dienes (29) and (8) did not undergo the Diels-Alder reaction with dienophiles. Diene (29) could have a *s-cis* conformation, however, the spacial separation between carbons A and B is wider than would be expected due to an additional angle strain of the four membered ring. Diene (8) is not coplanar and it is difficult to hold *s-cis* conformation. More importantly, these dienes are extremely electron poor.



Diene (29) led to monoadducts by reactions with butadiene and cyclopentadiene. Diene (29) played a role as an electron-poor dienophile. Diene (8) did not react even as a dienophile, probably because of its steric hindrance.

Addition of diazomethane to dienes (29) and (8) gave diadducts, which consisted of several stereo isomers.

Diene (29) was oligomerised by UV irradiation and this remarkable phenomenon may be attributed to the excited state due to angle strain.

## CHAPTER SIX

## INSTRUMENTATION

### Gas Liquid Chromatographic Analysis

Quantitative analysis was obtained using a Hewlett Packard 5890A gas liquid chromatograph equipped with a 25 m cross-linked methyl silicone capillary column.

Preparative g.l.c. was performed on a Varian Aerograph Model 920 (catharometer detector) gas liquid chromatograph with packed columns, which was mainly a 3 m 10% SE 30.

### Elemental Analysis

Carbon, hydrogen, and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or Carlo Erba Strumentazione 1106 Elemental Analyser. Analysis for halogens was performed as described in the literature<sup>168</sup>

### NMR spectra

<sup>1</sup>H-NMR spectra were recorded on an Hitachi Perkin-Elmer R-24B (60 MHz), a Bruker AC 250 (250 MHz), and a Varian VXR400S (400 MHz) NMR spectrometer.

<sup>19</sup>F-NMR spectra were recorded on a Varian EM3601 (56 MHz), the Bruker AC 250 (235 MHz), and the Varian VXR400S (376 MHz) NMR spectrometer.

<sup>13</sup>C-NMR spectra were recorded on the Bruker AC 250 (63 MHz) and the Varian VXR400S (101 MHz) NMR spectrometer.

### Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer 457 or 577 Grating spectrometer using KBr discs (for solid samples) or thin films between two KBr plates (for liquid samples). Gaseous samples were condensed into a cylindrical cell fitted with KBr plates.

### Mass spectra

Mass spectra of solid samples were recorded on a VG 7070E spectrometer. G.l.c. mass spectra were recorded on the VG 7070E spectrometer linked to the Hewlett Packard 5790A gas chromatograph fitted with a 25 m cross-linked methyl silicone capillary column.

#### Ultraviolet spectra

Ultraviolet spectra were recorded on a Philips PU8720 UV/Vis scanning spectrometer.

#### Distillation

Fractional distillation of product mixtures was carried out using a Fischer Spahltröh MMS255 small concentric tube apparatus. Boiling points were recorded during the distillation.

#### Melting Points

Melting points were carried out at atmospheric pressure and are uncorrected.

#### Reagents and Solvent

Unless otherwise stated, reagents were used as supplied. Solvents were dried by standard methods and stored over a molecular sieve (type 4A).

## 6 EXPERIMENTAL TO CHAPTER 2

6.1 Oligomerisation of Fluorinated Alkenes6.1.1 Oligomerisation of perfluorocyclobutene (43) with pyridine

Perfluorocyclobutene (90) (73.5 g, 465 mmole) was transferred *in vacuo* to a Carius tube cooled in liquid air, which was precharged with pyridine (1.9 g, 24 mmole), and sealed. This tube was then rotated at room temperature for 5 days. Volatile material (56.5 g) was transferred *in vacuo* to a cold trap, washed with water (50 ml x 2), dried over P<sub>2</sub>O<sub>5</sub>, and further transferred *in vacuo* to a cold trap. Distillation gave dimers (26a) and (26b) (25 g, 34%), b.p. 75-82°C and the trimer (44) (30 g, 41%), b.p. 147-148°C. Their mass spectra, IR spectra [number 1 for (26)], and <sup>19</sup>F-NMR [number 7 for (44)] were consistent with literature data<sup>86</sup>.

6.1.2 Oligomerisation of perfluorocyclobutene (43) with caesium fluoride in dimethylformamide (DMF)

A Carius tube was charged with dry caesium fluoride (9.1 g, 60 mmole) and N,N'-dimethylformamide (30ml) and degassed under vacuum. Perfluorocyclobutene (43) (45.7 g, 282 mmole) was transferred *in vacuo* to the tube, and cooled down in liquid air. The tube was sealed and rotated in a rotating machine at room temperature for 65 h. The solution changed in colour to yellow and then gradually to red-yellow. Volatile material (38.4 g) was transferred *in vacuo* to a cold trap, washed with water (50 ml x 2), dried over P<sub>2</sub>O<sub>5</sub>, and once again transferred *in vacuo* to a cold trap. Distillation afforded the dimers (26a) and (26b) (10 g, 22%) and the mixture of trimer (85) and its isomer (30 g, 66%), the ratio 9:1, b.p. 141-147°C. The latter was separated by preparative g.l.c. and was identified as (44). The spectroscopic data were compared with literature data<sup>86,88</sup>.

6.1.3 Dimerisation of perfluorocyclopentene (86)6.1.3.1 In a Carius tube

A Carius tube (quartz) was charged with dry caesium fluoride (16 g, 105 mmole) and sulpholane (30 ml) and degassed *in vacuo*. Perfluorocyclopentene (86)(36 g, 170 mmole) was transferred *in vacuo* to the tube cooled in liquid air. The tube was

then sealed and agitated at 120°C for 60 hr. After that the tube was opened and the two layers of liquid were subsequently distilled to give perfluorobicyclobutylidene (27) (25 g, 71%), b.p. 124.5°C ; IR spectrum number 2. Other spectroscopic data were consistent with those in literature<sup>88</sup>.

#### 6.1.3.2 In an auto clave

Typically, perfluorocyclopentene (86) (72.2 g, 341 mmole) was transferred *in vacuo* to a 250 ml autoclave, cooled in liquid air and precharged with dry caesium fluoride (25.1 g, 165 mmole) and sulpholane (130 ml). the mixture was then heated at 125°C, with agitation, in a rocking furnace for 48 hr. Volatile material (68.1 g) was transferred *in vacuo* to a cold trap and distillation afforded the starting material (86) (42.7 g, 59%), b.p. 26.9°C and the corresponding dimer (27) (22.5 g, 31%).

This dimerisation was carried out many times under the same condition but in most cases the yield of (27) was lower than that obtained by carrying out the reaction on a smaller scale, in a Carius tube.

#### 6.1.4 Co-oligomerisation of perfluorocyclobutene (43) and perfluorocyclopentene (86) with pyridine

A Carius tube was charged with pyridine (1.5 g, 19 mmole), cooled in liquid air, and degassed *in vacuo* . Perfluorocyclobutene (46) (12.4 g, 77 mmole) and perfluorocyclopentene (86) (25.2 g, 119 mmole) were transferred *in vacuo* to the tube and sealed. The tube was agitated in a rotating arm at room temperature for 6 days and then opened with volatile materials being transferred *in vacuo* to a cold trap. The resultant liquid (30.1 g) was washed with water (50 ml x 2), dried over P<sub>2</sub>O<sub>5</sub> and transferred *in vacuo* to a cold trap again. This liquid was distilled to yield the starting material (86) (16 g), perfluorocyclobutene dimers (26a) and (26b) (3 g, 24%), b.p. 75-80°C, and co-dimer, perfluorocyclobutyldienecyclopentene (87) [4 g, 80% purity as a mixture with (26), the ratio 8:1]. Mass spectrum and <sup>19</sup>F-NMR spectrum were compared with literature data<sup>87</sup>.



## 6.2 Defluorination by Sodium Amalgam System

### 6.2.1 General procedure

Basically, sodium was allowed to stand in dry ether to remove paraffin and then cut into small pieces. These pieces were added to a Schlenk tube, equipped with a stop-cock, which was precharged with mercury. The Schlenk was gently shaken to dissolve the sodium in the mercury, to produce an amalgam. This procedure was carried out under dry nitrogen and was repeated until the concentration of the amalgam reached *c.a.* 0.5 w/w %. Making the amalgam was so exothermic that the Schlenk had to be constantly cooled with running water.

The reactant, which was *c.a.* 0.4 equimolar with respect to sodium, was carefully added to the amalgam in the Schlenk under dry nitrogen. The top of the Schlenk was sealed with a rubber 'Suba-seal' to release the developed pressure.

The Schlenk was then shaken vigorously whilst being cooled with running water. During the reaction the appearance of the mixture drastically changed into a metallic mercury coloured, very viscous solid. Completion of the reaction was implied by the reformation of elemental mercury and the formation of a dark grey fine dust on the mercury. The product was obtained by transferring *in vacuo* to a cold trap.

**Caution:** the reaction was carried out in a sealed system and was extremely exothermic; therefore shaking was done behind a blast screen whilst wearing gloves.

### 6.2.2 Reduction of Perfluorobicyclobutylidene (26a) and its Isomer (26b)

Perfluorobicyclobutylidene (26a) and its isomer (26b) (9.5 g, 29.3 mmole) was added to a 0.55 w/w % sodium amalgam (Na:1.7 g, 74 mmole, Hg: 311.4 g). The Schlenk was sealed and then shaken, following the general procedure. The volatile fraction (7.3 g) was obtained by transferring *in vacuo* to a cold trap. The subsequent g.l.c. analysis showed one product (purity 95%), which was identified as perfluorobicyclobut-1,1'-enyl (29) (6.9 g, 83%). (Found: C, 33.8; F, 66.1. C<sub>8</sub>F<sub>10</sub> requires C, 33.6; F, 66.4%); *m/z* 286 (M<sup>+</sup>, 32%); <sup>19</sup>F-NMR spectrum number 1; IR spectrum number 3; mass spectrum number 1.

Many such reductions were carried out and some of them are detailed below.

(26)		Na		Hg	Yield (29)	Conversion
g	mmole	g	mmole	g	%	%
9.6	29.8	1.8	78.3	304.6	81	95
9.5	29.3	1.7	73.9	306.5	72	95
7.7	23.7	1.5	65.2	290.0	71	90
9.0	27.8	1.8	78.3	286.8	68	95
11.3	34.8	2.0	87.0	340.5	81	92
11.8	36.4	1.9	82.6	339.4	66	88
12.0	37.0	1.8	78.3	342.6	75	93

### 6.2.3 Reduction of perfluorobicyclopentylidene (27)

Perfluorobicyclopentylidene (27) (12.0 g, 28.3 mmole) was added to a 0.54 w/w % sodium amalgam (Na: 1.7 g, 73.9 mmole; Hg: 312.2 g) as described in the general procedure. On completion of the reaction the volatile fraction (9.4 g) was recovered by transferring *in vacuo* to a cold trap. The g.l.c. analysis showed only one product (purity 97%) which was identified as perfluorobicyclopent-1,1'-enyl (8) (9.2 g, 84%): (Found: C, 31.3; F, 68.6. C<sub>10</sub>F<sub>14</sub> requires C, 31.1; F, 68.9); *m/z* 386 (M<sup>+</sup>, 61%); <sup>19</sup>F-NMR spectrum number 2; IR spectrum number 4; mass spectrum number 2.

A series of these reductions were carried out and the results are tabulated below.

(27)		Na		Hg	Yield(8)	Conversion
g	mmole	g	mmole	g	%	%
12.8	30.1	1.9	82.6	319.3	83	98
10.1	23.8	1.4	60.9	268.0	49	63
13.3	31.4	1.8	78.3	341.2	66	87
13.5	31.8	2.0	87.0	369.0	79	94
11.9	28.0	1.6	70.0	276.3	52	81

#### 6.2.4 Reduction of perfluoro-1-cyclobutylidene-cyclopentene (87)

The mixture of perfluoro-1-cyclobutylidene-cyclopentene (87) and dimer (26) [2.5 g, (87):(26) = 78:22] was added to a 0.42 w/w % sodium amalgam (Na: 0.5 g, 22 mmole, Hg: 113.8 g). The reaction was carried out as described in the general procedure. The volatile fraction (1.62 g) was recovered by transferring *in vacuo* to a cold trap. Analysis by g.l.c. showed mainly two products, one of which was perfluorobicyclobut-1,1"-enyl (29) and the other was identified as perfluoro-1-cyclobutenyl-1-cyclopentene (89) (conv. 92%);  $m/z$  336 ( $M^+$ , 100%);  $^{19}\text{F}$ -NMR spectrum number 3; mass spectrum number 3.

#### 6.2.5 Reduction of other fluorinated alkenes

Reduction of perfluoro-1,2-dicyclobutylcyclobutene (44) and perfluoro-1-cyclobutyl-1-cyclobutenyl-cyclobutene (85) with sodium amalgam was carried out as described in the general procedure. Both reductions failed to yield any dienes. Only starting materials were recovered. The details are described below.

Substrate		Na		Hg	Recovery of Substrate
g	mmole	g	mmole	g	%
(46)					
7.3	15.0	1.7	73.9	344.2	60
(89)					
4.0	8.0	0.7	30.4	150.1	85

### 6.3 Zinc Induced Defluorination

#### 6.3.1 Attempted reduction of perfluorobicyclobutylidene (26a) and its isomer (26b)

A mixture of perfluorobicyclobutylidene (26a) and its isomer (26b) (2.0 g, 6.9 mmole) was added dropwise to refluxing dioxane (10 ml) with zinc (4.6 g, 71 mmole), which had been activated by washing with hydrochloric acid-acetone solution and then with dry acetone and finally dried under vacuum. The mixture was then allowed to stand under reflux for 10 h. Zinc was then removed by filtration. The filtrate was distilled to recover (26a) and (26b) (1.0 g)

$^{19}\text{F}$ -NMR spectrum of the dioxane solution showed a number of peaks, but they have not yet been assigned.

#### 6.3.2. Attempted reduction of perfluoro-3,4-dimethyl-hex-3-ene (31)

Perfluoro-3,4-dimethyl-hex-3-ene (31) (4.0 g, 10 mmole) was added dropwise to dioxane (15 ml) with activated zinc (4.5 g, 68 mmole) under reflux and the mixture was stirred for 2 h. Then the mixture was filtered to remove zinc dust. The filtrate consisted of two layers, the bottom layer was identified as starting material (31) (2.97 g, 66%).  $^{19}\text{F}$ -NMR spectrum of the upper dioxane solution showed several peaks which were different from those of (31), but have not been identified.

#### 6.4 Tetrakis(dimethylamino)ethylene (TDAE) (90) System

##### 6.4.1. General procedure

Typically fluorinated substrate and dichloro-methane were precharged into a two-neck flask equipped with a pressure-equalising dropping funnel. TDAE-dichloromethane solution was added dropwise with stirring, whilst cooling the vessel in an ice-bath. On completion of the addition the mixture was stirred for half an hour. During the reaction the colour of the solution changed and a white solid was precipitated. The ice bath was then removed and the reaction mixture allowed to warm up to room temperature. Stirring was continued for 1 h. The mixture was filtered if necessary to separate the solid from the solution. Analysis was done by means of  $^{19}\text{F}$ -NMR, to check the formation of diene.

##### 6.4.2. Reduction of perfluoro-3,4-dimethyl-hex-3-ene (31)

Perfluoro-3,4-dimethyl-hex-3-ene (31) (12.1 g, 30.3 mmole) and dichloromethane (30 ml) were charged into the flask and TDAE (6.1 g, 30.3 mmole) in dichloromethane (15 ml) was added slowly at  $0^\circ\text{C}$ . The solution turned dark red in colour immediately and a whitish solid was gradually precipitated. As the temperature increased to room temperature, the colour of the solution changed to orange and, surprisingly, a transparent layer separated at the bottom again. Although (31) was not soluble in dichloromethane, the addition of TDAE made the mixture homogeneous. The bottom layer (7.0 g) was collected by pipette. Subsequent analysis of  $^{19}\text{F}$ -NMR and g.l.c. showed only one product, which was identified as perfluoro-3,4-dimethyl-hexa-2,4-diene (34) (7.0 g, 64%);  $m/z$  362 ( $M^+$ , 1%), ( $M-19$ , 26%);  $^{19}\text{F}$ -NMR spectrum number 6; IR spectrum number 5; mass spectrum number 4.

A series of these reductions was carried out. The details are as below.

(32)		TDAE (94)		CH <sub>2</sub> Cl <sub>2</sub>	Yield	Conversion
g	mmole	g	mmole	ml	%	%
8.0	20.0	4.0	20.0	35	44	78
12.2	30.6	6.0	29.9	40	65	95
4.5	11.3	2.2	11.0	20	58	85

#### 6.4.3 Reduction of (31) without solvent (with J Vaughan)

TDAE (5.03 g, 25.2 mmole) was added dropwise to stirred tetramer (31) (11.15 g, 27.9 mmole) at 0°C, under nitrogen. A dark red solid was produced immediately and increased in amount. The solid was then allowed to warm up to room temperature. Heating it to 80°C under vacuum isolated a volatile in a cold trap. The liquid was identified as (34) (8.3 g, 82%).

#### 6.4.4 Reduction of perfluoro-1,2-dicyclobutylcyclo-butene (46)

TDAE (1.5 g, 7.6 mmole) in dichloromethane (10 ml) was added to perfluoro-1,2-dicyclobutyl-cyclobutene (44) (1.9 g, 3.9 mmole) in dichloromethane (10 ml) as described previously. During the reaction the solution turned from orange to brown. The mixture was filtered under nitrogen to yield a brown solid and a brown liquid. Borontrifluorideetherate BF<sub>3</sub>OEt<sub>2</sub> (1.2 g, 5.5 mmole) was then added to this liquid to give a further brown liquid and brown solid. A colourless liquid was obtained by transferring this brown liquid *in vacuo* to a cold trap. Analysis by g.l.c. showed that this dichloromethane solution contained two products: (i) (6%), and (ii) (6%). There was not enough products to be separated, however, mass spectra and <sup>19</sup>F-NMR spectra of this mixture indicated the presence of the following compounds:

- (i) perfluoro-2-cyclobutyl-bicyclobut-1,1'-enyl (93)  
mass spectrum number 5;  $^{19}\text{F}$ -NMR spectrum number 8
- (ii) perfluoro-2-cyclobutenyl-biucyclobut-1,1'-enyl (94)  
mass spectrum number 6;  $^{19}\text{F}$ -NMR spectrum number 9

#### 6.4.5 Attempted reduction of other fluorinated alkenes and alkanes

The table below summarises attempted reductions of various fluorinated alkenes and alkanes. They did not lead to any defluorinated products.

Substrate		TDAE		$\text{CH}_2\text{Cl}_2$	Recovery of Substrate
g	mmole	g	mmole	ml	%
(85)					
5.0	10.2	2.0	10.0	20	60
(36)					
5.2	10.4	2.1	10.5	25	65
(96)					
4.6	10.0	2.1	10.5	25	*
(97)					
4.0	10.0	2.0	10.2	25	65
(98)					
0.2	0.4	0.1	0.5	-	90

\* (96) is partially soluble in  $\text{CH}_2\text{Cl}_2$

#### 6.4.6 Attempted synthesis of octamethyloximidinium difluoride (92)

As detailed in 6.4.2, a white solid (0.6 g) was obtained by filtration of the reaction mixture followed by washing with dichloromethane (5 ml x 2). It was slightly soluble in acetonitrile and soluble in water. Analysis by  $^1\text{H}$ ,  $^{19}\text{F}$ -NMR spectra indicated the presence of octamethyloxamidinium difluoride (92).  $^1\text{H}$ -,  $^{19}\text{F}$ -NMR spectra number 5; Elemental analysis did not afford the expected figures because this solid (92) was proved to be very hygroscopic.

## CHAPTER SEVEN



## 7 EXPERIMENTAL TO CHAPTER 3

7.1 Oxygen Nucleophiles7.1.1 Reactions with alcohols7.1.1.1 Diene (29) with methanol

Diene (29) (1.27 g, 4.4 mmole) was added to an excess of methanol (0.64 g, 20 mmole) in ether (10 ml). An exothermic reaction took place and a white solid was precipitated within an hour. The solution was then evaporated to give a white solid. Vacuum sublimation yielded 2,2-dimethoxy-perfluorobicyclobut-1,1'-enyl (108) (0.47 g, 75%);  $m/z$  310 ( $M^+$ , 100%); (Found: C, 38.5; H, 1.9; F, 49.4.  $C_{10}H_6O_2F_8$  requires C, 38.7; H, 1.94; F, 49.0%);  $m/z$  310 ( $M^+$ , 100%);  $^1H$ -,  $^{19}F$ -NMR spectrum number 10; IR spectrum number 6; mass spectrum number 7.

7.1.1.2 Diene (8) with methanol

The addition of diene (30) (1.64 g, 4.2 mmole) to an excess of methanol (1.12 g, 35 mmole) with a catalytic amount of sodium methoxide in ether (10 ml) caused an exothermic reaction to take place. The mixture was stirred for 5 days at room temperature. The solvent was then removed to yield a white solid. Purification by vacuum sublimation gave 2,2-dimethoxy-perfluorobicyclopent-1,1'-enyl (109) (0.2 g, 63%); (Found: C, 35.1; H, 1.8; F, 55.2.  $C_{12}H_6F_{12}O_2$  requires C, 35.1; H, 1.6, F, 55.6%);  $m/z$  410 ( $M^+$ , 100%);  $^1H$ -,  $^{19}F$ -NMR spectrum number 11; IR spectrum number 7; mass spectrum number 8

7.1.1.3 Diene (29) with ethanol

The mixture of diene (29) (1.33 g, 4.7 mmole) and ethanol (0.92 g, 20 mmole) was stirred in ether(10ml) for 2 days at room temperature. The removal of the solvent afforded a viscous liquid. The liquid was purified by molecular distillation. This has been identified as 2,2-diethoxy-perfluorobicyclobut-1,1'-enyl (110) (0.52 g, 45%); (Found: C, 42.2; H, 2.7; F, 44.9.  $C_{12}H_{10}O_2F_8$  requires C, 42.6; H, 3.0; F, 45.0%);  $m/z$  338 ( $M^+$ , 42%);  $^1H$ -,  $^{19}F$ -NMR spectrum number 12; IR spectrum number 8; mass spectrum number 9.

7.1.1.4 Attempted hydrolysis of (108)-(110)

Typically the alkoxy derivatives were added to 50% aqueous sulphuric acid solution and then heated at 100°C for 12 hours. In each case a white solid was filtered off and found to be starting material.

Substrate	Recovery (%)
(108)	75
(109)	67
(110)	62

7.1.2 Reactions of water7.1.2.1 With diene (29)

Diene (29) (1.15 g, 4 mmole) was added to acetonitrile (7 ml) containing water (1.33 g, 74 mmole) and was stirred at room temperature for 1 day. Then evaporation of the solution gave a brown solid as a residue. Vacuum sublimation of this solid yielded a white hygroscopic solid, which has been identified as 1-(2',3',3',4',4'-pentafluoro)cyclobut-1'-enyl-2-hydroxy-3,3-difluoro-but-4-ene (113) (0.8 g, 76%); (Found: C, 36.2; H, 0.8; F, 53.2. C<sub>8</sub>H<sub>1</sub>F<sub>7</sub>O<sub>2</sub> requires C, 36.6; H, 0.4; F, 53.8%); *m/z* 262 (M<sup>+</sup>, 14%); <sup>19</sup>F-NMR spectrum number 13; IR spectrum number 9; mass spectrum number 10.

7.1.2.2 With diene (8)

The mixture diene (8) (0.7 g, 1.8 mmole), water (1.05 g, 58.3 mmole), and acetonitrile (7 ml) was stirred at room temperature for 3 days. Evaporation of the solvent gave a brown solid which was then sublimed in vacuum and identified as 1-(2',3',3',4',4',5',5'-heptafluoro)cyclopent-1'-enyl-2-hydroxy-3,3,4,4-tetrafluorocyclopent-5-enone(116) (0.5 g, 77%); (Found: C, 33.0; H, 0.3; F, 53.0. C<sub>10</sub>H<sub>1</sub>F<sub>11</sub>O<sub>2</sub> requires C, 32.5; H, 0.3; F, 53.7%); *m/z* 362 (M<sup>+</sup>, 14%); <sup>19</sup>F-NMR spectrum number 14; IR spectrum number 10; mass spectrum number 11.

### 7.1.2.3 Synthesis of the sodium salts from (113) and (116)

The aqueous solution of (113) (0.242 g, 0.92 mmole) was neutralised with 0.1M NaOH solution. The molar concentration of (113) calculated by titration, was fairly consistent with its original value (0.92 : 1.02 mmole). Then water was evaporated in vacuum to give an orange solid, which has been identified as the sodium salt (118) (0.15 g, 58%);  $^{19}\text{F}$ -NMR spectrum number 15; IR spectrum number 11; mass spectrum number 12.

In the same procedure, the neutralisation of (116) with NaOH solution gave the corresponding salt, which has been identified as the sodium salt (119) (0.19 g, 70%);  $^{19}\text{F}$ -NMR spectrum number 16; IR spectrum number 12; mass spectrum number 13.

## 7.2 Nitrogen Nucleophiles

### 7.2.1 Reactions of aniline

#### 7.2.1.1 Diene (29) with aniline

Aniline (0.89 g, 9.6 mmole) was added slowly to diene (29) (1.12 g, 3.92 mmole) in acetonitrile (10 ml) at room temperature. An exothermic reaction took place immediately and the solution turned yellow. The stirring continued for 1 hour. The solvent and the unreacted aniline were removed in high vacuum to give a yellow solid, which was washed with pentane (10 ml x 2) and has been identified as 2,2'-bis(phenylamino)perfluorobicyclobut-1,1'-enyl (122) (0.89 g, 53%); (Found: C, 55.5; H, 2.6; N, 6.2; F, 34.8.  $\text{C}_{20}\text{H}_{10}\text{N}_2\text{F}_8$  requires C, 55.8; H, 2.3; N, 6.5; F, 35.4%);  $m/z$  432 ( $\text{M}^+$ , 6%);  $^1\text{H}$ -,  $^{19}\text{F}$ -NMR spectra number 17; IR spectrum number 13; mass spectrum number 14.

#### 7.2.1.2 Diene (29) with an equimolar amount of aniline

The mixture of aniline (0.58 g, 6.3 mmole) and diene (29) (1.79 g, 6.3 mmole) was stirred in acetonitrile (7 ml) at room temperature for 1 day. The solvent was then evaporated in vacuum to give a brown viscous liquid. The sublimation of this liquid in vacuum gave white needle-like crystals which have been identified as 2-(phenylamino)perfluorobicyclobut-1,1'-enyl (123) (0.35 g, 15%); (Found: C, 47.0; H, 1.7; N, 3.8;

F, 47.2.  $C_{14}H_6N_1F_8$  requires C, 46.8; H, 1.4; N, 3.9; F, 47.6%);  $m/z$  359 ( $M^+$ , 100%);  $^1H$ -,  $^{19}F$ -NMR spectra number 18; IR spectrum number 14; mass spectrum number 15.

### 7.2.1.3 With diene (8)

The addition of aniline (0.21 g, 2.26 mmole) to diene (8) (1.05 g, 2.72 mmole) in acetonitrile caused an exothermic reaction and a colour change to green. The mixture was stirred for 1 day. Then the liquid was evaporated to give a yellow solid. This solid was recrystallised from acetonitrile in a freezer (at  $-15^\circ C$ ) and has been identified as 2-(phenylamino)-perfluorobicyclo-pent-1,1'-enyl (124) (0.38 g, 31%); (Found: C, 41.5; H, 1.2; N, 3.6; F, 54.7.  $C_{16}H_6N_1F_{13}$  requires C, 41.8; H, 1.3; N, 3.1; F, 54.7%);  $m/z$  459 ( $M^+$ , 16%);  $^1H$ -,  $^{19}F$ -NMR spectra number 19; IR spectrum number 19; mass spectrum number 16.

## 7.2.2 Reaction of pyrroles

### 7.2.2.1 Diene (29) with pyrrole

Pyrrole (0.28 g, 4.2 mmole) in acetonitrile (5 ml) was added to diene (29) (0.68 g, 2.5 mmole) in acetonitrile (5 ml) and the mixture was then stirred at room temperature. An exothermic reaction took place immediately. After 1 day,  $^{19}F$ -NMR spectrum of the mixture no longer showed the presence of diene (29). The removal of the solvent gave a brown-red solid (0.75 g) and sublimation of this solid afforded a yellow-red solid as the first fraction (0.13 g) and a yellow solid as the second one. The second one has been identified as 2,2'-bis(pyrrol-2-yl)-perfluorobicyclo-but-1,1'-enyl (125) (0.55 g, 63%); (Found: C, 50.1; H, 2.1; N, 7.4; F, 40.4.  $C_{16}H_8N_2F_8$  requires C, 50.5; H, 2.1; N, 7.4; F, 40.0%);  $m/z$  380 ( $M^+$ , 3%);  $^1H$ -,  $^{19}F$ -NMR spectra number 20; IR spectrum number 16; mass spectrum number 17.

The first one has been identified as a mixture of (125) as the main component and 2-(pyrrol-2-yl)-perfluoro-bicyclobut-1,1'-enyl (127) by  $^{19}F$ -NMR (number 21).

### 7.2.2.2 Diene (29) with N-methylpyrrole

The mixture of N-methylpyrrole (0.52 g, 6.4 mmole) and diene (29) (0.62 g, 2.2 mmole) was refluxed in acetonitrile (10 ml) for 3 days. The removal of the solution gave a brown yellow solid. This solid was purified by vacuum sublimation to give a yellow solid, which has been identified as 2,2'-bis(N-methylpyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl (126) (0.51 g, 57%); (Found: C, 52.6; H, 2.9; N, 6.8; F, 37.1.  $C_{18}H_{12}N_2F_8$  requires C, 52.4; H, 2.9; N, 6.9; F, 37.3%);  $m/z$  408 ( $M^+$ , 21%);  $^1H$ -,  $^{19}F$ -NMR spectra number 22; IR spectrum number 17; mass spectrum number 18.

### 7.2.2.3 Diene (8) with pyrrole

The mixture of diene(8) (0.62 g, 1.6 mmole) and pyrrole (0.42 g, 6.3 mmole) was refluxed in ether for 2 days, but no reaction occurred.

## 7.3 Iodide ion as nucleophile

### 7.3.1 Synthesis of the di-iodo substituted product of (29)

Diene (29) (1.24 g, 4.33 mmole) was simply added to an excess of lithium iodide (2.48 g, 18.5 mmole) in tetralyglyme (10 ml) and the mixture was stirred at room temperature for 2 days. The solution became homogeneous, because lithium iodide is soluble in tetraglyme. Then the addition of water (50 ml) precipitated a yellow solid, which was then dried in vacuum and purified by vacuum sublimation. This has been identified as 2,2'-diiodo-perfluorobicyclobut-1,1'-enyl (128) (1.34 g, 68%); (Found C, 19.0; I, 50.2.  $C_8I_2F_8$  requires C, 19.1; I, 50.6%);  $m/z$  502 ( $M^+$ , 56%);  $^{19}F$ -NMR spectrum number 23; IR spectrum number 18); mass spectrum number 19.

Sodium iodide can be used as iodide source and solvents such as ether and acetonitrile can also be useful for the synthesis.

### 7.3.2 Synthesis of the di-iodo substituted product from (8)

Diene (8) (2.22 g, 5.8 mmole) was added to an excess of sodium iodide (4.13 g, 27.5 mmole) in acetonitrile (30 ml) and was then stirred at room temperature for

1 day. The solvent was removed in vacuum and subsequently purified by molecular distillation in high vacuum to yield an orange viscous liquid. This has been identified as 2,2'-diiodo-perfluorobicyclopent-1,1'-enyl (129) (1.57 g, 45%); (Found: C, 20.2; I, 41.7.  $C_{10}I_2F_{12}$  requires C, 19.9; I, 42.2%);  $m/z$  602 ( $M^+$ , 100%);  $^{19}F$ -NMR spectrum (at  $-40^\circ C$ ) number 25; IR spectrum number 19; mass spectrum number 20.

### 7.3.3 Attempted synthesis of the mono-iodo substituted products

#### 7.3.3.1 With diene (29)

The mixture of diene (29) (2.45 g, 8.6 mmole), sodium iodide (1.59 g, 10.6 mmole), and acetonitrile (10 ml) was stirred at room temperature for 7 days. Then ether (20 ml) was added to the mixture, which was filtered to remove NaI and NaF precipitated. The ether filtrate was evaporated to give a small amount of solid ( $< 0.15$  g). This solid has been identified as a mixture of (128) (9%) and 1-iodo-perfluoro-bicyclobut-1,1'-enyl (130) (90%);  $^{19}F$ -NMR spectrum number 24.

#### 7.3.3.2 With diene (8)

The mixture of diene (8) (1.90 g, 4.9 mmole) sodium iodide (0.81 g, 5.4 mmole), and acetonitrile (7 ml) was stirred at room temperature for 3 weeks. Then ether (20 ml) was added and filtered to remove the salts. Evaporation of the filtrate gave a very viscous liquid (0.25 g). GC analysis showed that this liquid consisted of three components, which have been identified as the starting diene (8) (50%), di-iodo derivatives (129) (10%), and 1-iodo perfluorobicyclopent-1,1'-enyl (131) (40%);  $m/z$  494 ( $M^+$ , 100%);  $^{19}F$ -NMR spectrum number 26; mass spectrum number 21

### 7.3.4 Attempted coupling reactions of the di-iodo derivatives (128) and (129)

The products (128) or (129), copper powder, and a trace of DMF were charged in a small Carius tube, which was then sealed and heated at  $130-200^\circ C$ . The colour of the mixture changed to black immediately in each case. The tube was opened and the mixture was sublimed in vacuum. In all cases, only a small amount of (128) or (129) was recovered.

A series of reactions was carried out, altering the conditions. Some are tabulated below.

	Substrate g	mmole	Cu g	mmole	Temp °C	Time hrs
(128)	0.50	1	1.0	15.7	150	17
(activated)						
(128)	0.50	1	0.93	14.6	135	20
(non-activated)						
(128)	0.3	0.6	0.07	1.1	135	5
(non-activated)						
(129)	0.2	0.3	1.0	15.7	135	7
(non-activated)						

### 7.3.5 Variable temperature NMR study of (129) in acetonitrile

A homogeneous acetonitrile solution of di-iodo substituted compound (129) was examined by a Bruker AC250 ( $^{19}\text{F}$ , 235 Hz) NMR spectrometer and the temperature was decreased to  $-40^\circ\text{C}$ . The measurement was carried out at  $10^\circ\text{C}$  intervals up to  $40^\circ\text{C}$ .

## 7.4 Bifunctional Nucleophiles

### 7.4.1 Diene (29) with ethylene glycol

Diene (29) (2.09 g, 7.31 mmole) was placed in a round bottomed flask with dry ether (10 ml) and ethylene glycol (0.65 g, 10.5 mmole). Acetonitrile (8 ml) was added slowly. The mixture was then stirred at room temperature for 7 hours. Evaporation of the solution gave a viscous liquid (1.96 g). GC analysis showed that this liquid consisted of two components, which were separated by preparative g.l.c. and have been identified as:

- (i) 2-(2-hydroxyethoxy)perfluorobicyclobut-1,1'-enyl (132) (0.13 g, 5 %);  
(Found: C, 36.3; H, 1.6; F, 51.8.  $\text{C}_{10}\text{H}_5\text{F}_9\text{O}_2$  requires C, 36.6; H, 1.5; F, 52.1%);

$m/z$  328 ( $M^+$ , 17%);  $^1H$ -,  $^{19}F$ -NMR spectra number 28; IR spectrum number 21; mass spectrum number 23.

(ii) 6-(pentafluorocyclobut-1'-enyl)-7,7,8,8 tetrafluoro-1,4-dioxaspiro-(5,4)-octane (133) (0.15 g, 6%); (Found: C, 36.4; H, 1.9; F, 51.7.  $C_{10}H_5O_2F_9$  requires C, 36.6; H, 1.5; F, 52.1%);  $m/z$  328 ( $M-20$ , 42%);  $^1H$ -,  $^{19}F$ -NMR spectra number 27; IR spectrum number 20; mass spectrum number 22.

#### 7.4.2 Diene (8) with ethylene glycol

Ethylene glycol (0.37 g, 5.97 mmole) in acetonitrile (5 ml) was added dropwise to diene (8) (1.50 g, 3.89 mmole) in acetonitrile (5 ml). The mixture was stirred at room temperature for 2 days. The solvent was evaporated to give a viscous liquid (0.92 g). GC analysis of the acetonitrile solution of this solution showed only two products. One of them was found to be diene (8) The other was separated by preparative g.l.c. and has been identified as 2-(2-hydroxyethoxy)perfluorobicyclopent-1,1'-enyl (134) (0.13 g, 7.8%); (Found: C, 33.5; H, 1.3; F, 57.2.  $C_{12}H_5F_{13}O_2$  requires C, 33.6; H, 1.2; F, 57.7%);  $m/z$  428 ( $M^+$ , 2%);  $^1H$ -,  $^{19}F$ -NMR spectra number 29; IR spectrum number 22; mass spectrum number 24.

#### 7.4.3 Diene (29) with hydroquinone

The mixture of diene (29) (1.09 g, 3.8 mmole) and hydroquinone (0.30 g, 2.7 mmole) in ether (15 ml) was stirred at room temperature for 2 days.  $^{19}F$ -NMR spectrum of this solution showed only starting diene (29).

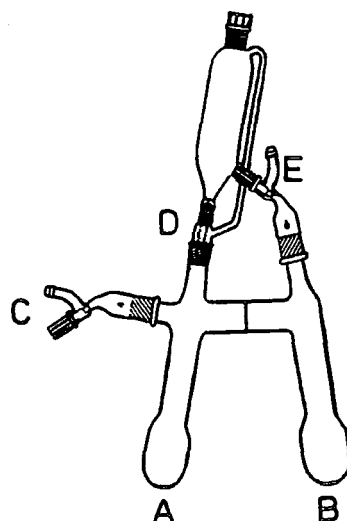


## CHAPTER EIGHT

## 8. EXPERIMENTAL TO CHAPTER 4

8.1 Synthesis of tris(dimethylamino)sulphonium trimethyl-difluorosilicate (138)

A 1 l 'rotaflo' flask was evacuated and SF<sub>4</sub> (5.4 g, 50 mmole) was transferred to this flask, taking care to exclude moisture. Ether (100 ml), which had been distilled over CaH<sub>2</sub> and stored over Na wire, was added to the A side of a Schlenk under N<sub>2</sub> (see below). Then the Schlenk was cooled down in liquid air and evacuated (through E). SF<sub>4</sub> was transferred to the Schlenk through C. Liquid air was replaced by acetone-dry ice bath and allowed to warm up to -78°C. N,N-dimethyltrimethylsilylamine (20.5 g, 17.5 mmole) was added dropwise to ether SF<sub>4</sub> solution, using a dropping funnel with a pressure equalising arm, the temperature was maintained at -78°C (for 30 mins) under N<sub>2</sub>. The acetone dryice bath was then removed and the mixture was allowed to warm up to room temperature and stirred for 3 days. After several hours a white solid began to precipitate. 2 days later the Schlenk was full with a white solid and stirring was difficult. More dry ether (20 ml) was added to the Schlenk. After a total of 3 days the reaction mixture was filtered from A to B in vacuum (through E). A white solid in the side A was washed with dry ether (25 ml x 2) and the mixture was filtered in vacuum again. The white solid was dried in vacuum for a while and then stored under dry N<sub>2</sub> (yield 11 g, 81%). This was found to be the desired product (138), by a comparison of <sup>19</sup>F-NMR spectrum (number 30) in the literature.<sup>14</sup>



## 8.2 Generation of the carbanion (141) from diene (8) with various fluoride ion sources

### 8.2.1 General Procedure

Simply, various fluoride ion sources were added to the required solvent and the mixture was stirred vigorously for a while. The diene (8) was added to this mixture under dry N<sub>2</sub>. The system was continuously stirred normally for 1 day. Before examination by NMR, the mixture was allowed to stand for ten minutes and the upper layer(if there were two layers) was collected carefully under N<sub>2</sub> as an NMR sample.

### 8.2.2 With caesium fluoride

Diene (8) (1.2 g, 3.1 mmole) was added to caesium fluoride (0.5 g, 3.3 mmole) in tetraglyme (5 ml). The solution turned to violet in colour immediately. After 2 hours, a homogeneous solution was obtained. <sup>19</sup>F-NMR spectrum (number 31) confirmed that the carbanion (141) had been generated. A slight excess of BF<sub>3</sub>OEt<sub>2</sub> (0.47 g, 3.3 mmole) was added to the mixture to form two layers. The bottom layer was found to be diene (8) (1.0 g, 83%).

### 8.2.3 With other alkali metal fluorides



Diene (8)		Fluoride ion source			Solvent	Time	the carbanion (141)
g	mmole	g	mmole	ml	days		
0.3	0.77	KF 0.5	8.6	4	1	formed	
0.4	1.0	NaF 0.7	16.7	4	14	not formed	
0.3	0.77	LiF 1.2	46.3	5	14	not formed	

#### 8.2.4 With TAS-F(138)

Diene (8) (0.7 g, 1.8 mmole) and TAS-F(138) (0.56 g, 2.0 mmole) with acetonitrile (5 ml) gave the carbanion (141) solution.

#### 8.2.5 With TDAE<sup>2+</sup>2F<sup>-</sup> (92)

Diene (8) (0.2 g, 0.5 mmole) and the salt (92) (0.2 g, 0.8 mmole) with acetonitrile (4 ml) gave a mixture of the carbanion (141) and starting diene (8).

#### 8.2.6 With potassium iodide

Diene (8) (1.2 g, 3.1 mmole) was added to potassium iodide (1.0 g, 6.0 mmole) in tetraglyme (5 ml) and a colour change to dark red occurred. <sup>19</sup>F-NMR spectrum showed the presence of carbanion (141) and 1-iodo-perfluorobicyclopent,1,1'-enyl (131) by a comparison of the results in Chapter 3.

### 8.3 Generation of the carbanion (141) in various solvents

Diene (8)		F <sup>-</sup> Source			Solvent	
g	mmole		g	mmole		ml
0.6	1.6	CsF	0.4	2.6	CH <sub>3</sub> CN	5
0.7	1.8	KF	0.2	3.5	CH <sub>3</sub> CN	5
0.6	1.6	CsF	0.5	3.3	DMSO	7

#### 8.4 Diene (8) / F<sup>-</sup> ratio dependence

Diene (8)		Fluoride ion source			Solvent		Ratio (8) / (F <sup>-</sup> )
g	mmole	g	mmole	ml			
1.0	2.7	TAS-F	0.2	0.7	CH <sub>3</sub> CN	3	3.9
1.0	2.6	TAS-F	1.5	5.5	CH <sub>3</sub> CN	3	0.5
0.18	0.47	CsF	0.28	1.8	tetraglyme	4	0.26
1.34	3.50	CsF	0.28	1.8	tetraglyme	4	1.9

#### 8.5 Variable temperature NMR studies

A homogeneous carbanion solution was examined by Bruker AC250 (235 Hz) NMR spectrometer and the temperature was decreased to -40°C. The measurement was carried out at 10°C intervals up to 80°C.

#### 8.6 Attempt to isolate the carbanion salt

##### 8.6.1 Caesium salt

The carbanion (141) solution obtained from diene (8)(0.5 g, 1.3 mmole) and caesium fluoride (0.19, 1.25 mmole) in acetonitrile (3 ml) was cooled down to -15°C but no solid was precipitated. The solution was evaporated in vacuum to give a yellowish solid. This solid was not soluble in acetonitrile. The condensed volatile material formed two layers and the lower one was found to be diene (8).

##### 8.6.2 TAS salt

The carbanion (141) solution generated by diene (0.7 g, 1.8 mmole) and TAS-F (0.46 g, 1.7 mmole) in acetonitrile (4 ml) was cooled to -15°C but no recrystallisation

occurred. Evaporation of the solvent produced a brown solid (0.73 g, 72%). This solid was redissolved completely in acetonitrile.  $^{19}\text{F}$ -NMR still showed only the signals corresponding to the carbanion (141).

### 8.7 Reactions of the carbanion(141)

The carbanion solution obtained by diene (8) (1.1 g, 2.8 mmole) and caesium fluoride (0.6 g, 3.9 mmole) in tetraglyme (5 ml) was used for the following reactions.

#### 8.7.1 With methyl iodide

Methyl iodide (0.3 g, 2.1 mmole) was added to the carbanion (141) solution (1 ml) and the mixture was stirred at room temperature for 1 week. Only carbanion (4) was detected by  $^{19}\text{F}$ -NMR.

#### 8.7.2 With allylbromide

Allylbromide (0.25 g, 2.1 mmole) was added to the carbanion (141) solution and the mixture was stirred at room temperature for 1 day.  $^{19}\text{F}$ -NMR spectrum still showed the signals for the carbanion (141).

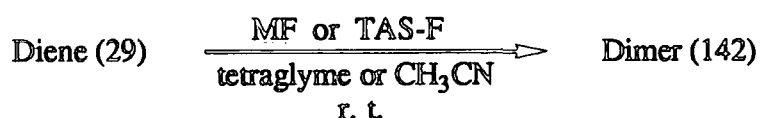
#### 8.7.3 With bromine

Bromine (0.35 g, 3.2 mmole) was added to the carbanion (141) solution (2 ml) and the mixture was stirred at room temperature for 1 week to give two layers. The lower layer was found to be a mixture of diene (8) (44%) and perfluorobicyclopentylidene (27) (56%) by  $^{19}\text{F}$ -NMR.

### 8.8 Reactions of diene (29) (Oligomerisation)

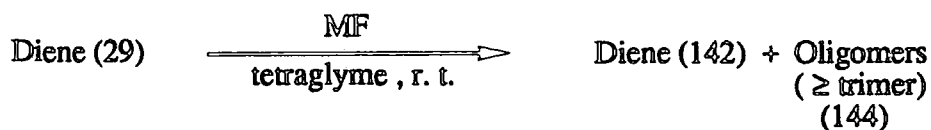
#### 8.8.1 General procedure

Basically, diene (29) was added to the solution with fluoride ion sources or metal halide. The mixture was stirred for a certain period. Addition of water precipitated a yellowish or brownish solid. Vacuum sublimation afforded a white solid.

8.8.2 With an equimolar or excess of fluoride ion

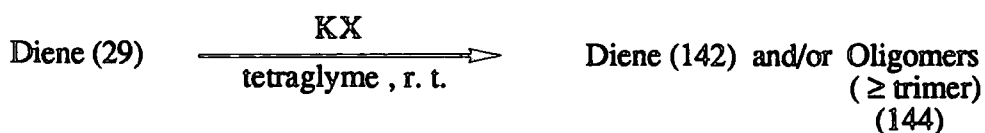
Diene (29)		Solvent	F-source	Time		Yield (142)	
g	mmole			g	mmole		day
1.6	5.6	tetraglyme	CsF	0.84	5.5	1	76
2.3	8.0	tetraglyme	KF	0.58	10.0	1	65
1.3	4.5	tetraglyme	NaF	0.85	20.0	7	68
3.2	11.2	acetonitrile	CsF	1.10	7.2	2	82
2.1	7.3	acetonitrile	TAS-F	2.20	8.0	1	65

A white solid was identified as perfluoro-2,4'-di-(1-cyclo-butylidene)-bicyclobutylidene (142); m.p. 127-129°C; (Found: C, 33.4; F, 66.9. C<sub>10</sub>F<sub>20</sub> requires C, 33.6; F, 66.4%); *m/z* 572 (M<sup>+</sup>, 7%); <sup>19</sup>F-NMR spectrum number 32; IR spectrum number 23; mass spectrum number 25.

8.8.3 With a deficiency of fluoride ion

Diene (29)		F-source		Time	Yield		
g	mmole	g	mmole	day	(142) %	(144) %	
0.9	3.2	CsF	0.02	0.13	6	43	39
0.8	2.8	CsF	0.05	0.31	5	34	24
1.3	4.5	KF	0.11	1.90	5	26	45
2.2	7.7	NaF	0.11	1.90	5	26	47

An insoluble solid was identified as oligomer (C<sub>8n</sub>F<sub>10n</sub>, n ≥ 3) (144):  
 m.p. 74-78°C; (Found: C, 33.7; F, 66.6. C<sub>8n</sub>F<sub>10n</sub> requires C, 33.6; F, 66.4%); IR  
 spectrum number 24; mass spectrum number 26.

8.8.4 With other halide ions

Diene (29)		Halide ion source		Time	Yield		
g	mmole	X	g	mmole	day	(142) %	(144) %
1.5	5.2	I	0.91	5.5	14	68	-
1.9	6.6	Cl	0.50	6.7	2	12	36



### 8.8.5 With the carbanion (141)

Diene (29) (0.5 g, 1.7 mmole) was added to the carbanion (4) solution that was generated by diene (80) (1.1 g, 2.8 mmole) and caesium fluoride (0.45 g, 2.96 mmole) in acetonitrile (10 ml). The reaction was monitored by  $^{19}\text{F}$ -NMR spectrometer. The mixture was stirred at room temperature for 2 days then filtered under  $\text{N}_2$  to give a whitish solid and a violet solution.  $^{19}\text{F}$ -NMR spectrum of this solution showed signals for the carbanion(141) and the solid was found to be dimer (142) (0.28 g, 56%).

## 8.9 Reactions of perfluorobicyclobutylidene (26) and perfluoro-bicyclopentylidene (27) with TDAE (90)

### 8.9.1 Alkene (27) in $\text{CH}_2\text{Cl}_2$

TDAE (90)(1.41 g, 7.1 mmole) in  $\text{CH}_2\text{Cl}_2$  (20 ml) was added dropwise to alkene (27) (3.1 g, 7.3 mmole) in  $\text{CH}_2\text{Cl}_2$  (20 ml), cooling down at  $0^\circ\text{C}$ . The solution turned to orange. The mixture was then allowed to warm up to room temperature. The solution turned from orange to cream yellow. A white solid was precipitated during the reaction. The mixture was filtered under  $\text{N}_2$  to afford a white solid and an orange solution. The  $^{19}\text{F}$ -NMR spectrum of this solution showed the presence of diene (8) and the carbanion (141) in the ratio of 3:2. No alkene (27) was detected. Addition of  $\text{BF}_3\text{OEt}_2$  (1.05 g, 7.4 mmole) gave two layers. This was found to be diene (8), (1.66 g, 59%).

### 8.9.2 Alkene (27) in $\text{CH}_3\text{CN}$

TDAE (90)(0.97 g, 4.9 mmole) in  $\text{CH}_3\text{CN}$  (3 ml) was added to alkene (27) (2.02 g, 4.8 mmole) in  $\text{CH}_3\text{CN}$  (3 ml) at room temperature. The solution turned to yellow and a white solid was precipitated. The mixture was filtered under  $\text{N}_2$  to give a white solid and a yellow solution. The  $^{19}\text{F}$ -NMR of this solution showed only carbanion (141). Addition of  $\text{BF}_3\text{OEt}_2$  (0.7 g, 5.0 mmole) gave two layers and the bottom one was found to be diene (8). (1.5 g, 81%).

### 8.9.3 Alkene (26) in CH<sub>2</sub>Cl<sub>2</sub>

TDAE (90)(2.0 g, 120 mmole) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was added to alkene (26) (3.5 g, 10.8 mmole) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) at 0°C. A yellowish solid was precipitated immediately. The mixture was filtered under N<sub>2</sub> to give a yellowish solid and an orange solution. This solid was washed with water (10 ml) and sublimed in vacuum to give a white solid (1.1 g, 31%), which was identified as dimer (142).

## 8.10 Reactions of (26) and (27) with TDAE (90) without solvent

### 8.10.1 Alkene (26)

TDAE (90)(1.9 g, 9.5 mmole) was added dropwise to alkene (26) (4.06 g, 12.6 mmole) at 0°C. An orange solid was produced immediately. The liquid was transferred in vacuum from the solid and this was found to be alkene (26) by <sup>19</sup>F-NMR. The orange solid was dissolved in CH<sub>3</sub>CN and filtered under N<sub>2</sub> to give a white solid and a brown solution, which has been found to contain the carbanion (143); <sup>19</sup>F-NMR spectrum number 33. BF<sub>3</sub>OEt<sub>2</sub> (2.0 g, 14 mmole) was added to this carbanion solution and filtered under N<sub>2</sub> to give a brown solid and a brown solution. <sup>19</sup>F-NMR of this solution showed the presence of diene (29) as the main product.

### 8.10.2 Alkene (27)

TDAE (90) (1.33 g, 6.7 mmole) was added to alkene (27) (3.07 g, 7.2 mmole) slowly at 0°C. A brown solid was produced immediately. Unreacted alkene (27) was removed from the system and CH<sub>3</sub>CN (10 ml) was added. The solution was then filtered under N<sub>2</sub> to give a white solid and a brown solution, which was found to contain the carbanion (141) by <sup>19</sup>F-NMR. BF<sub>3</sub>OEt<sub>2</sub> (1.1 g, 7.8 mmole) was added to this solution to give diene (8) (1.9 g, 62%) as a separate layer.

## 8.11 Ylides

### 8.11.1 Reaction with triphenylphosphine

#### 8.11.1.1 Diene (29)

Triphenylphosphine (1.17 g, 4.5 mmole) in CH<sub>3</sub>CN (15 ml) was added dropwise to diene (29) (1.50 g, 5.2 mmole) in CH<sub>3</sub>CN (20 ml) at room temperature and left stirring for 1 day. The mixture turned orange in colour. The evaporation of the solvent gave a brown solid. This was washed with dry ether and has been identified as perfluorobicyclobutylidene-2-triphenylphosphonium (146); (2.05 g, 72%); (Found: C, 57.2; H, 2.8; F, 35.0; P, 5.5. C<sub>26</sub>H<sub>15</sub>F<sub>10</sub>P requires C, 56.9; H, 2.7; F, 34.7; P, 5.7%) *m/z* 548 (M<sup>+</sup>, 6%); <sup>19</sup>F-NMR spectrum number 34; IR spectrum number 25; mass spectrum number 27.

#### 8.11.1.2 Diene (8)

The mixture of diene (8) (1.8 g, 4.7 mmole) and triphenylphosphine (1.00 g, 3.8 mmole) was stirred in dry ether (100 ml) for 1 day. <sup>19</sup>F-NMR showed that diene (8) had not reacted at all.

### 8.11.2 Reactions with pyridine

#### 8.11.2.1 Diene (29)

Pyridine (0.67 g, 8.5 mmole) in CH<sub>3</sub>CN (5 ml) was added dropwise to diene (29) (1.96 g, 6.9 mmole) in CH<sub>3</sub>CN (5 ml) at room temperature. The mixture was stirred for 5 days. The evaporation of the solvent gave a yellow solid and this solid was washed with dry ether (10ml). This has been identified as perfluorobicyclobutylidene-2-pyridinium (148) (1.19 g, 47%); <sup>19</sup>F-NMR spectrum number 35; IR spectrum number 26.

#### 8.11.2.2 Diene (8)

Pyridine (0.45 g, 5.7 mmole) in CH<sub>3</sub>CN (5 ml) was added to diene (1.34 g, 3.5 mmole) and the mixture was stirred at room temperature for 5 days. Removal of the solvent gave a brown solid, which was washed with dry ether(10ml). This solid has

been identified as perfluorobicyclopentylidene-2-pyridinium (149) (1.12 g, 69%);  $^{19}\text{F}$ -NMR spectrum number 36; IR spectrum number 27.

### 8.11.3 Reaction of diene (29) with triethylamine

A Carius tube was charged with triethylamine (0.4 g, 4 mmole) and cooled down in liquid air. Then the diene (29) (1.7 g, 6 mmole) was transferred to the tube in vacuum. The tube was sealed and was rotated at room temperature. An exothermic reaction occurred and a brown solid was produced. After 1 day, the tube was opened under  $\text{N}_2$  and the solid was collected, washed with dry ether (10ml), and dried in vacuum. This has been identified as perfluorobicyclobutylidene-2-triethylammonium (150) (1.43 g, 62%); (Found: C, 43.1; H, 3.7; N, 3.4.  $\text{C}_{14}\text{H}_{15}\text{F}_{10}\text{N}_1$  requires C, 43.4; H, 3.9; N, 3.6%);  $^{19}\text{F}$ -NMR spectrum number 37; IR spectrum number 28.

## CHAPTER NINE

## 9. EXPERIMENTAL TO CHAPTER 5

9.1 Diels-Alder Reactions of Diene (29) and (8)9.1.1 General procedure

Basically, preweighed dienes were transferred in vacuum to a small Carius tube, which had been precharged with the reactants, and then sealed. The tube was allowed to stand at the reaction temperature. The products obtained were purified by molecular distillation or preparative g.l.c. if necessary.

9.1.2 Reactions with various acetylenes

Reactant		Diene (29)		Temperature	Time
g	mmole	g	mmole	°C	days
EtO <sub>2</sub> CC≡CCO <sub>2</sub> Et				100	2
0.2	1.1	0.4	1.4		
F <sub>3</sub> CC≡CCF <sub>3</sub>				225	5
0.2	1.2	0.4	1.4		
Ph <sub>3</sub> CC≡CCPh <sub>3</sub>				150	1
0.2	1.1	0.5	1.7		
PhOPhC≡CPhOPh				150	1
0.2	0.5	0.5	1.7		

No reaction occurred in each case.

9.1.3 Reactions with various olefins

Reactant		Diene (29)		Temp	Time	Recovery of diene
g	mmole	g	mmole	°C	days	%
Propene	(29)					
1.2	28.6	2.0	6.9	80	1	83
$\alpha$ -methyl styrene	(29)					
1.1	5.3	1.8	6.3	80	1	79
Propene	(30)					
1.2	28.6	1.9	4.8	80	1	82

No reaction took place in each case.

9.1.4 Reactions with hydrocarbon dienes9.1.4.1 Diene (29) with butadiene

Diene (29) (2.2 g, 7.5 mmole) and butadiene (3.4 g, 62.9 mmole) were heated at 80°C for 5 days. The product mixture was separated by preparative g.l.c. to give the adduct 1-(1-perfluorocyclobutenyl)-6,7,7,8,8-pentafluorobicyclo[4.2.0]oct-3-ene (158) as a colourless liquid (1.6g, 67%); (Found: C, 41.9; H, 2.1; F, 55.5. C<sub>12</sub>H<sub>6</sub>F<sub>10</sub> requires C, 42.4; H, 1.8; F, 55.9%) *m/z* 340 (M<sup>+</sup>, 8%); <sup>1</sup>H-, <sup>19</sup>F-NMR spectra number 38; IR spectrum number 29; mass spectrum number 28.

9.1.4.2 Diene (29) with cyclopentadiene

A mixture of diene (29) (2.47 g, 8.6 mmole) and cyclopentadiene (0.4 g, 6.1 mmole) was left at room temperature for 7 days. Volatile material was transferred under vacuum to yield a translucent liquid, which contained the mono adduct (159) and the dimer of cyclopentadiene. An attempt to separate the adduct was unsuccessful; *m/z* 352 (M<sup>+</sup>, 1%); <sup>19</sup>F-NMR spectrum number 39; mass spectrum number 29.

Other unsuccessful reactions are tabulated below.

Reactant		Diene		Temperature	Time
g	mmole	g	mmole	°C	days
Furan		(29)			
0.33	3.8	0.53	1.9	80	1
Thiophene		(29)			
0.38	4.5	0.50	1.7	Reflux	2*
Cyclohexa-1,3-diene		(29)			
0.29	3.6	0.42	1.1	80	2
Butadiene		(8)			
0.2	0.5	0.5	1.7	80	2
Cyclopentadiene		(8)			
0.10	1.5	0.16	0.4	80	1
cyclohexa-1,3-diene		(8)			
0.12	1.5	0.2	0.5	80	1

\*CH<sub>3</sub>CN was used as solvent

No reaction took place in each reaction.

## 9.2 Addition of Diazomethane to Diene (29) and (8)

### 9.2.1 Alcohol-free ethereal solution of diazomethane

Glass apparatus used must have so-called 'clearfit' joints, otherwise diazomethane might explode because of the rough surface of ground joints. Potassium hydroxide (6 g) in 10 ml of water, diethylene glycol monoethyl ether (35 ml), and ether (10 ml) were charged to a round bottomed flask. *p*-Tolylsulphonylmethyl nitrosamide (21.5 g) was dissolved in ether (125 ml) and added dropwise to the mixture, which was heated at 70-75°C. During the addition of the ether solution, the flask was shaken occasionally and more ether (30 ml) was added. The mixture was distilled until the distillate was colourless. In order to avoid contacting diazomethane with air (moisture), the distillate



was poured into dry ether at 0°C. The ether contained 3.5g of diazomethane, according to the literature<sup>167</sup> (ether 130 ml, diazomethane 3.5 g).

### 9.2.2 Addition to diene (29)

An excess of diazomethane ethereal solution was added dropwise to diene (29) (2.2 g, 7.7 mmole) with stirring until the yellow colour of diazomethane persisted. The mixture was stirred for 1 hour at room temperature. Evaporation of the solvent gave a brown solid, which was purified to yield the di-adduct (160) (1.3 g, 46%). (Found: C, 32.4; H, 1.1; F, 50.9; N, 14.6.  $C_{10}H_4F_{10}N_4$  requires C, 32.4; H, 1.1; F, 51.4; N, 15.1%);  $m/z$  370 ( $M^+$ , 1%); IR spectrum number 30; mass spectrum number 30.

### 9.2.3 Addition to diene (8)

An excess of diazomethane and diene (8) (1.45 g, 3.8 mmole) yielded a white solid, which was purified by vacuum sublimation to yield the di-adduct (161), (1.47 g, 82%). (Found: C, 30.3; H, 0.8; F, 56.2; N, 11.5.  $C_{12}H_4F_{14}N_4$  requires C, 30.6; H, 0.9; F, 56.6; N, 11.9%);  $m/z$  470 ( $M^+$ , 1%); IR spectrum number 31; mass spectrum number 31.

## 9.3 Attempted UV Irradiation of Dienes

### 9.3.1 Diene (29)

Diene (29) (0.6 g, 2.1 mmole) was charged to a quartz tube, which was then sealed and irradiated using a medium pressure mercury discharge tube, for 7 days. A brown solid was produced during the irradiation and most of the diene (29) was consumed. This insoluble brown solid was found to be oligomers of (29). (Found: C, 33.2; F, 66.9.  $C_{8n}F_{10n}$  requires C, 33.6; F, 66.4%); IR spectrum number 32; mass spectrum number 32.

### 9.3.2 Diene (8)

Diene (30) (0.7 g, 1.8 mmole) was sealed in a quartz tube and irradiated with UV for 7 days, but only unchanged diene (8) was recovered.

## APPENDICES

## Appendix One

NMR data

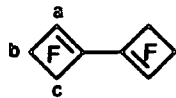
- No.1 perfluorobicyclobut-1,1'-enyl (26)
- No.2 perfluorobicyclopent-1,1'-enyl (8)
- No.3 perfluoro-1-cyclobutenyl-1-cyclopentene (89)
- No.4 tetrakis(dimethylamino)ethylene (90)
- No.5 octaoxamidinium difluoride (92)
- No.6 perfluoro-3,4-dimethyl-hexa-2,4-diene (34)
- No.7 perfluoro-1,2-biscyclobutyl-cyclobutene (44)
- No.8 perfluoro-2-cyclobutyl-bicyclobut-1,1'-enyl (93)
- No.9 perfluoro2-cyclobutenyl-bicyclobut-1,1'-enyl (94)
- No.10 2,2'-dimethyl-perfluorobicyclobut-1,1'-enyl (108)
- No.11 2,2'-dimethyl-perfluorobicyclopent-1,1'-enyl (109)
- No.12 2,2'-diethyl-perfluorobicyclobut-1,1'-enyl (110)
- No.13 1-perfluorocyclobut-1'-enyl-2-hydroxy-3,3-difluoro-cyclobut-3-none (113)
- No.14 1-perfluorocyclopent-1'-enyl-2-hydroxy-3,3,4,4-tetrafluoro-cyclopente-5-none (116)
- No.15 the sodium salt of (113)
- No.16 the sodium salt of (116)
- No.17 2,2'-bis(phenylamino)-perfluorobicyclobut-1,1'-enyl (123)
- No.18 2-phenylamino-perfluorobicyclobut-1,1'-enyl (124)
- No.19 2-phenylamino-perfluorobicyclopent-1,1'-enyl (124)
- No.20 2,2'-bis(pyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl (125)
- No.21 2-(pyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl (127)
- No.22 2,2'-bis(N-methylpyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl (126)
- No.23 2,2'-diiodo-perfluorobicyclobut-1,1'-enyl (128)
- No.24 2-iodo-perfluorobicyclobut-1,1'-enyl (130)
- No.25 2,2'-diiodo-perfluorobicyclopent-1,1'-enyl (129)

- No.26 2-iodo-perfluorobicyclopent-1,1'-enyl (131)
- No.27 6-perfluorocyclobut-1'-enyl-7,7,8,8-tetrafluoro-1,4-dioxaspiro-(5,4)-octane (133)
- No.28 2-(2''-hydroxyethoxy)-perfluorobicyclobut-1,1'-enyl (132)
- No.29 2-(2''-hydroxyethoxy)-perfluorobicyclopent-1,1'-enyl (134)
- No.30 tris(dimethylamino)sulphonium trimethyldifluoro siliconate (138)
- No.31 the carbanion from (8) (141)
- No.32 perfluoro-2,4'-bis(1-cyclobutylidene)-bicyclobutylidene (142)
- No.33 the carbanion from (29) (143)
- No.34 perfluorobicyclobutylidene -2- triphenylphosphine (146)
- No.35 perfluobicyclobutylidene-2-pyridinium (148)
- No.36 perfluobicyclopentylidene-2-pyridinium (149)
- No.37 perfluobicyclobutylidene-2-triethylammonium (150)
- No.38 the mono-adduct by the reaction of diene (29) with butadiene (158)
- No.39 the mono-adduct by the reaction of diene (29) with cyclopentadiene (159)

NMR spectra were recorded in *d*<sub>3</sub>-acetonitrile unless stated. Spectra 5, 15, and 16 and were recorded in D<sub>2</sub>O. Spectra 31 was recorded in tetraglyme. Spectra 1, 2, and 3 were recorded in *d*-chloroform.

No. 1

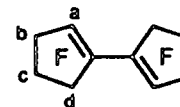
perfluorobicyclobut-1,1'-enyl(29)



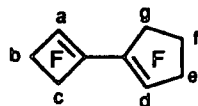
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
-95.7	m		1	a
-115.7	m		2	c
-117.2	m		2	b

No. 2

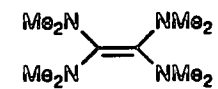
Perfluorobicyclopent-1,1'-enyl(8)



Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
-107.2	m		1	a
-109.1	m		2	d
-119.3	d, $J_{ad} = 19$		2	b
-129.9	m		2	c



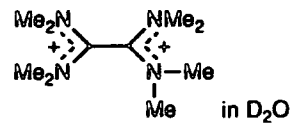
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
-94.2	m	1	a
-109.9	m	2	d
-115.1	d, $J_{ad} = 19$	1	g
-115.7	m	2	c or b
-118.3	m	2	b or c
-120.1	m	2	f
-130.8	m	2	e



Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>1</sup> H 2.5	broad		

No. 5

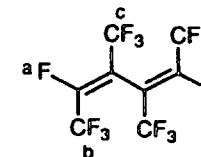
Octaoxamidinium-difluoride(92)



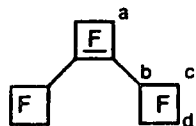
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F -130.3			9	
<sup>1</sup> H 3.3	s, broad		1	
3.6	s, broad		1	

No. 6

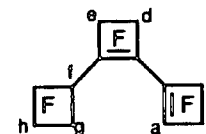
Perfluoro-3,4-dimethyl-hexa-2,4-diene(34)



Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
-60.5	d, J = 19.5		3	c
-72.0	s		3	b
-109.9	s, broad		1	a

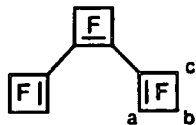


Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
-110.8	s	2	a
-125.2	AB	4	c
-130.7	$J_{FF} = 234$		
-128.2	AB	2	d
-132.0	$J_{FF} = 230$		
-178.5	s	1	b

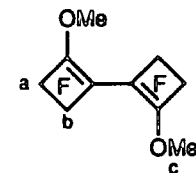


Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
-88.2	m	1	a
-109.7	d ?	2	e
-114.4	s, broad	2	d
-115.9	d ?	2	c
-118.1	m	2	b
-125.9	AB	4	g
-130.2	$J_{FF} = 231$		
-128.2	AB	2	h
-132.2	$J_{FF} = 226$		
-184.5	s, broad	1	b

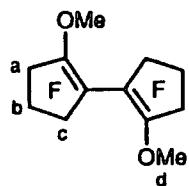




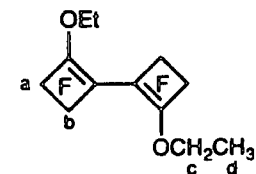
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
-89.1	s , broad		1	a
-113.1	s		2	d
-114.8	s , broad		2	c
-117.7	s , broad		2	d



Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F -111.7	m		1	b
<sup>19</sup> F -114.4	m		1	a
<sup>1</sup> H 4.1	s			c

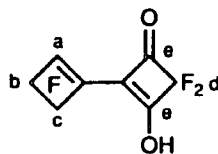


	Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F	-106.0	s		1	c
	-116.4	s		1	a
	-131.3	s		1	b
<sup>1</sup> H	4.1	s			d



	Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F	-110.6	m		1	a
	-113.4	m		1	b
<sup>1</sup> H	1.4	t		3	d
	4.4	q		2	c

No. 13 1-perfluorocyclobut-1'-enyl-2-hydroxy-3,3-difluoro-1-bute-3-none(113)

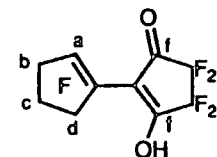


Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F			
-102.8	t	1	a
-113.4	s .broad	2	d.
-115.4	m	2	c
-117.5	m	2	b
<sup>13</sup> C			
125.7	t, J <sub>CF</sub> = 291		d
152.3	t, m, J <sub>CF</sub> = 352.1		a
179.1	t, d, J <sub>CF</sub> = 23.3 J <sub>CF</sub> = 1.9		e

<sup>1</sup>H

The corresponding resonance was not observed due to proton exchange with water.

No. 14 1-perfluorocyclobut-1'-enyl-2-hydroxy-3,3,4,4-tetrafluoro-cyclo-1-pent-3-none(116)

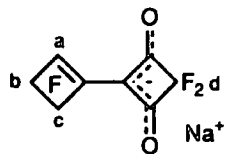


Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F			
-107.9	d, J <sub>FF</sub> = 10.8	2	d
-115.1	m	1	a.
-120.4	d, J <sub>FF</sub> = 14.4	2	b
-125.2	s	4	e
-131.9	s, broad	2	c
<sup>13</sup> C			
109.9	t, t, J <sub>FF</sub> = 263.6 J <sub>CF</sub> = 22.1		e
155.8	d, m, J <sub>CF</sub> = 307.1		a
176.5	t, broad, J <sub>CF</sub> = 25.5		f

<sup>1</sup>H

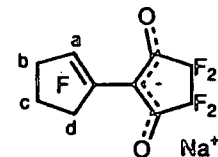
The corresponding resonance was not observed due to proton exchange with water.

No. 15

The sodium salt of (113)  
(118)

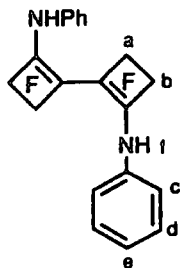
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
-109.4	t	1	a
-114.4	m	2	c
-115.2	s , broad	2	d
-118.4	s , broad	2	b

No. 16

The sodium salt of (116)  
(119)

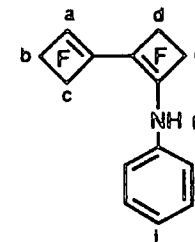
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
-107.9	d , $J_{FF} = 9.6$	2	d
-118.7	d , $J_{FF} = 13.7$	2	b
-120.8	m	1	a
-127.3	s , broad	4	e
-131.0	s , broad	2	c

No. 17 2,2'-bis(phenylamino)-perfluorobicyclobut-1,1'-enyl  
(122)



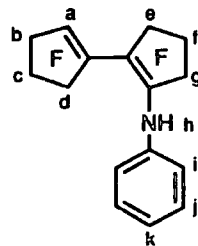
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F			
-106.3	s, broad	1	b
-114.8	s, broad	1	a
<sup>1</sup> H			
6.7	d, broad	2	d
7.1	t	1	e
7.2	t	2	c
9.0	broad	?	f

No. 18 2-phenylamino-perfluorobicyclobut-1,1'-enyl  
(123)



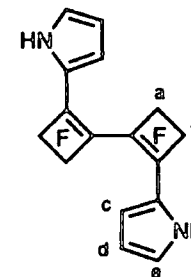
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F			
-107.3	m	2	e
-109.5	s, broad	1	a
-114.4	s, broad	2	d
-115.0	m	2	c
-116.6	m	2	b
<sup>1</sup> H			
7.2	d	2	g
7.3	t	1	i
7.4	t	2	h
8.5	broad	?	f

No. 19 2-phenylamino-perfluorobicyclopent-1,1'-enyl  
(124)



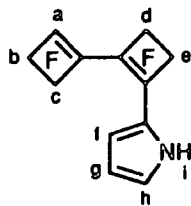
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F				
-100.3	broad		2	g
-107.4	broad		1	a
-115.1	broad		4	d + e
-118.3	broad		2	b
-129.0	broad		2	f or c
-130.2	broad		2	c or f
<sup>1</sup> H				
7.2~7.4	unassigned			

No. 20 2,2'-bis(pyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl  
(125)



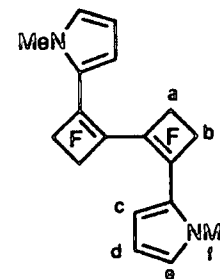
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F				
-106.5	m		1	b
-113.6	m		1	a
<sup>1</sup> H				
6.4~7.3	unassigned			

No. 21 2-(pyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl  
(127)



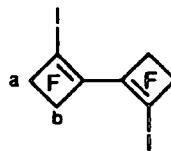
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F -101.4	t		1	a
-111.0	AB	J <sub>FF</sub> = 15.5	2	e
-112.3	m		2	d
-114.1	m		2	c
-115.5	m		2	b

No. 22 2,2'-bis(N-methylpyrrol-2-yl)-perfluorobicyclopent-1,1'-enyl (126)



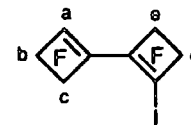
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F -108.4	m		1	b
-109.0	m		1	a
<sup>1</sup> H 3.7	s		3	f
6.1	d		1	e
6.3	AB	J <sub>HH</sub> = 2.2	1	d
6.8	s, broad		1	c

No. 23 2,2 -diiodo-perfluorobicyclobut-1,1'-enyl  
(128)



Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F				
-108.3	m		1	a
-112.0	m		1	b

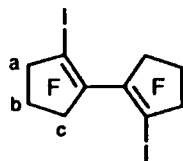
No. 24 2-iodo-perfluorobicyclobut-1,1'-enyl  
(130)



Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F				
-92.1	t		1	a
-111.4	m		2	d
-112.0	m		2	e
-112.4	m		2	c
-116.2	m		2	b

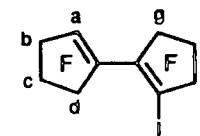


No. 25 2,2-diiodo-perfluorobicyclopent-1,1'-enyl  
(129)



Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F	measured at low temperature(-233K)		
-106.5	AB	1	c or
-110.1	J <sub>FF</sub> = 260.8		
-106.3	AB	1	a or c
-112.3	J <sub>FF</sub> = 259.8		
-129.1	AB	1	b
-131.8	J <sub>FF</sub> = 237.7		

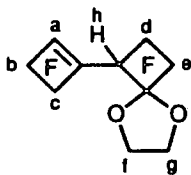
No. 26 2-iodo-perfluorobicyclopent-1,1'-enyl  
(131)



Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F			
-105.9	t	2	e
-106.7	s, broad	2	d or g
-108.2	s, broad	2	g or d
-109.7	s, broad	1	a
-118.2	d, J <sub>FF</sub> = 15.1	2	b
-128.9	s, broad	2	c or f
-129.7	s, broad	2	f or c

No. 27

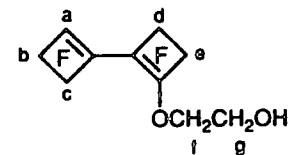
6-pentafluorocyclobut-1'-enyl-7,7,8,8-tetrafluoro-1,4-dioxaspiro-(5,4)-octane (133)



Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F				
-103.0	m		1	a
-114.9	AB, m	J <sub>FF</sub> = 215.4	2	d
-124.6				
-115.6	m		2	c
-119.4	m		2	b
-127.9	AB, m	J <sub>FF</sub> = 217.5	2	e
-133.5				
<sup>1</sup> H				
3.7	t		2	f or g
3.9	t		2	g or f
4.5	broad		1	h

No. 28

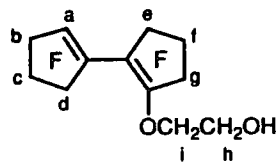
2-(2"-hydroxyethoxy)-perfluorobicyclobut-1,1'-enyl (132)



Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F				
-104.5	t		1	a
-112.3	m		2	d
-115.5	m		2	e
-115.9	m		2	c
-117.5	m		2	b
<sup>1</sup> H				
3.8	t		1	f
4.5	t		1	g

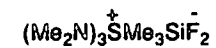
153

No. 29 2-(2"-hydroxyethoxy)-perfluorobicyclopent-1,1'-enyl  
(134)



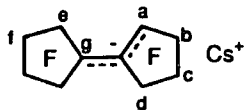
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F			
-105.2	s, broad	2	e
-107.3	s, broad	2	d
-113.1	s, broad	2	g
-113.9	p	1	a
-119.3	d, J <sub>FF</sub> = 16.2	2	b
-130.0	s, broad	2	c or f
-130.5	s, broad	2	f or c
<sup>1</sup> H			
3.8	t	1	h
4.5	t	1	i

No. 30 Tris-(dimethylamino)sulphonium-difluoro-trimethylsiliconate  
(138)



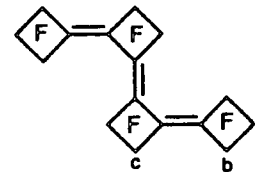
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F			
-59.0	s		

No. 31

The carbanion of diene(8)  
(141)

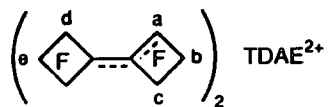
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
-84.6	s , broad		4	e
-107.7	s , broad		2	d
-110.5	s , broad		2	b
-129.2	s , broad		2	c
-129.9	s , broad		4	f
-157.1	s , broad		1	a

No. 32

Perfluoro-2,4'-di(1-cyclobutylidene)-bicyclobutylidene  
(142)

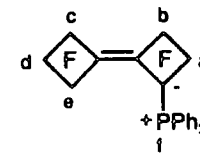
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
-110.1	s		2	c
-117.9	s		2	b
-130.6	s		1	a

No. 33

The carbanion of diene(29)  
(143)

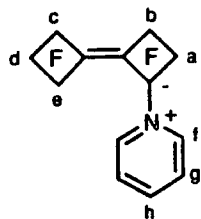
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
-88.5	s , broad	4	d
-107.0	s , broad	2	b
-113.0	d , $J_{FF} = 19.8$	2	c
-121.7	s , broad	2	e
-142.2	s , broad	1	a

No. 34

Perfluorobicyclobutylidene-2-triphenylphosphonium  
(146)

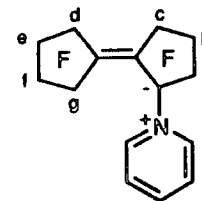
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
-98.0	broad	1	a
-100.3	broad	1	c or e
-102.2	broad	1	e or c
-113.3	d , $J_{FF} = 15.3$	1	b
-128.6	broad	1	d

No. 35

Perfluorobicyclobutylidene-2-pyridinium  
(148)

Chemical Shift (ppm)	Multiplicity	Relative Intensity	Assignment
<sup>19</sup> F			
-91.0	broad	1	a
-96.2	broad	1	c or e
-107.0	broad	1	e or c
-114.6	t?	1	b
-125.8	broad	1	d
<sup>1</sup> H			
8.1	t	2	g
8.4	t	1	h
8.6	d	2	f

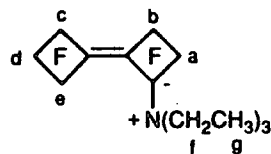
No. 36

Perfluorobicyclopentylidene-2-pyridinium  
(149)

Chemical Shift (ppm)	Multiplicity	Relative Intensity	Assignment
<sup>19</sup> F			
-89.0	broad	1	a
-90.9	broad	1	d or g
-102.6	broad	1	g or d
-109.2	t?	1	c
-129.7	broad	1	b, e or f
-131.6	broad	1	b, e or f
-131.9	broad	1	b, e or f

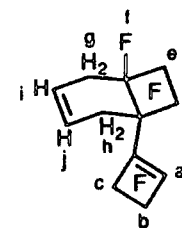
157

No. 37 Perfluorobicyclobutylidene-2-triethylammonium  
(150)



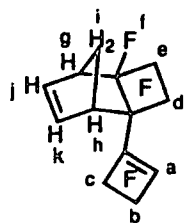
Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F				
-92.1	broad		1	a
-95.1	broad		1	c or e
-99.5	broad		1	e or c
-115.0	t?		1	b
-126.0	m		1	d
<sup>1</sup> H				
1.3	t		3	g
3.6	q		2	f

No. 38 The monoadduct by the reaction of diene(29) with  
butadiene (158)



Chemical Shift (ppm)	Multiplicity	Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F				
-101.1	p		1	a
-113.7	broad		2	c
-119.1	s, broad		2	b
-118.1	AB, J <sub>FF</sub> = 210.6		2	e
-122.7	J <sub>HF</sub> = 19.5			
-127.0	AB, J <sub>FF</sub> = 214.8		2	d
-128.0				
-163.4	s, broad		1	e
<sup>1</sup> H				
2.9	s, broad		2	h
2.6-3.0	m, AB		2	g
6.0	s, broad		1	j

No. 39

The monoadduct by the reaction of diene(8) with  
cyclopentadiene (159)

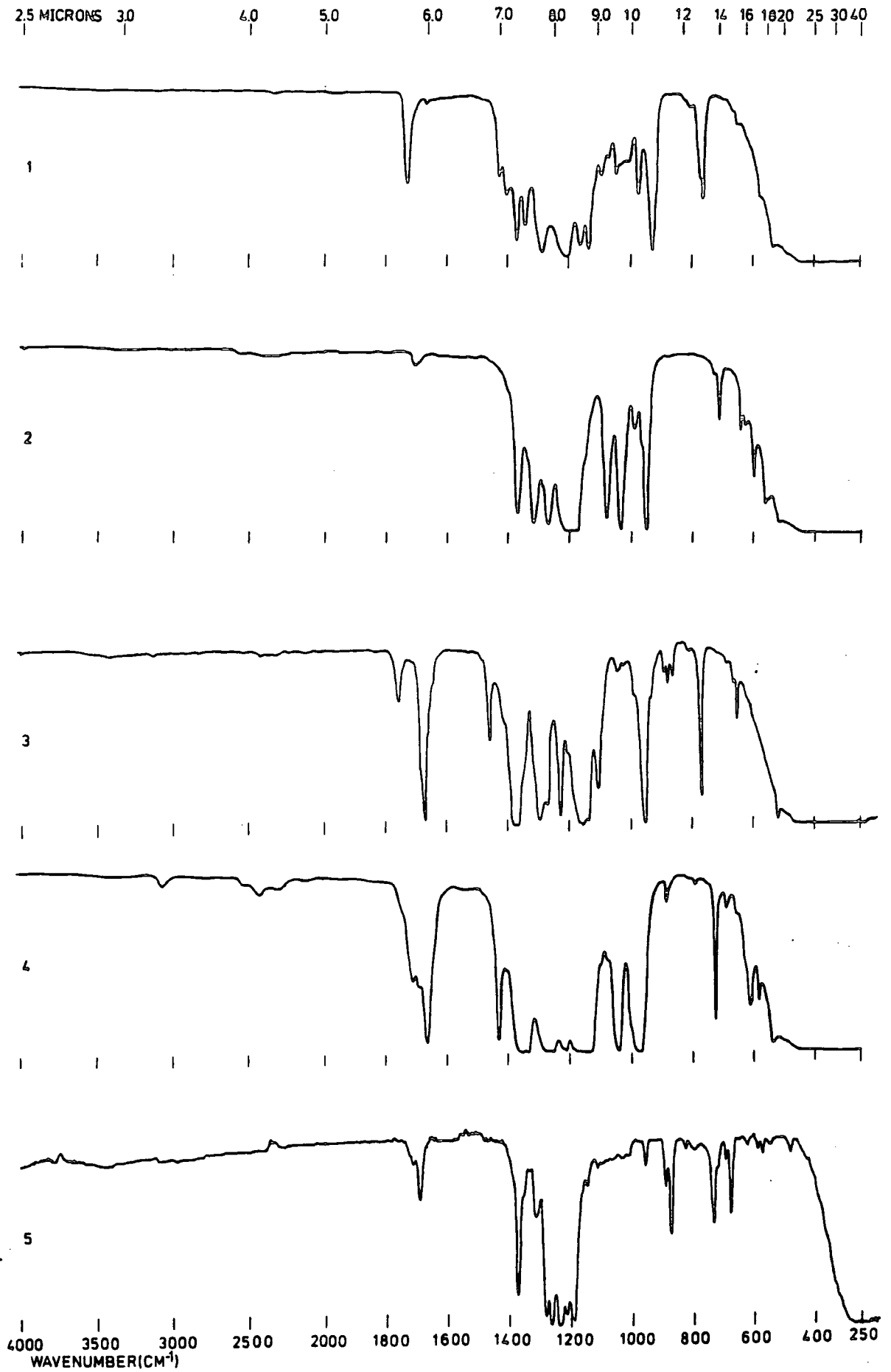
Chemical Shift (ppm)	Multiplicity Coupling Constants(Hz)	Relative Intensity	Assignment
<sup>19</sup> F -102.8	p	1	a
-114.9	broad	2	c
-114.3 -127.1	AB J <sub>FF</sub> = 218.0	2	e
-118.8	t	2	b
-126.7 -128.6	AB J <sub>FF</sub> = 221.2	2	d
-181.9	d, J <sub>HF</sub> = 33.4	1	f

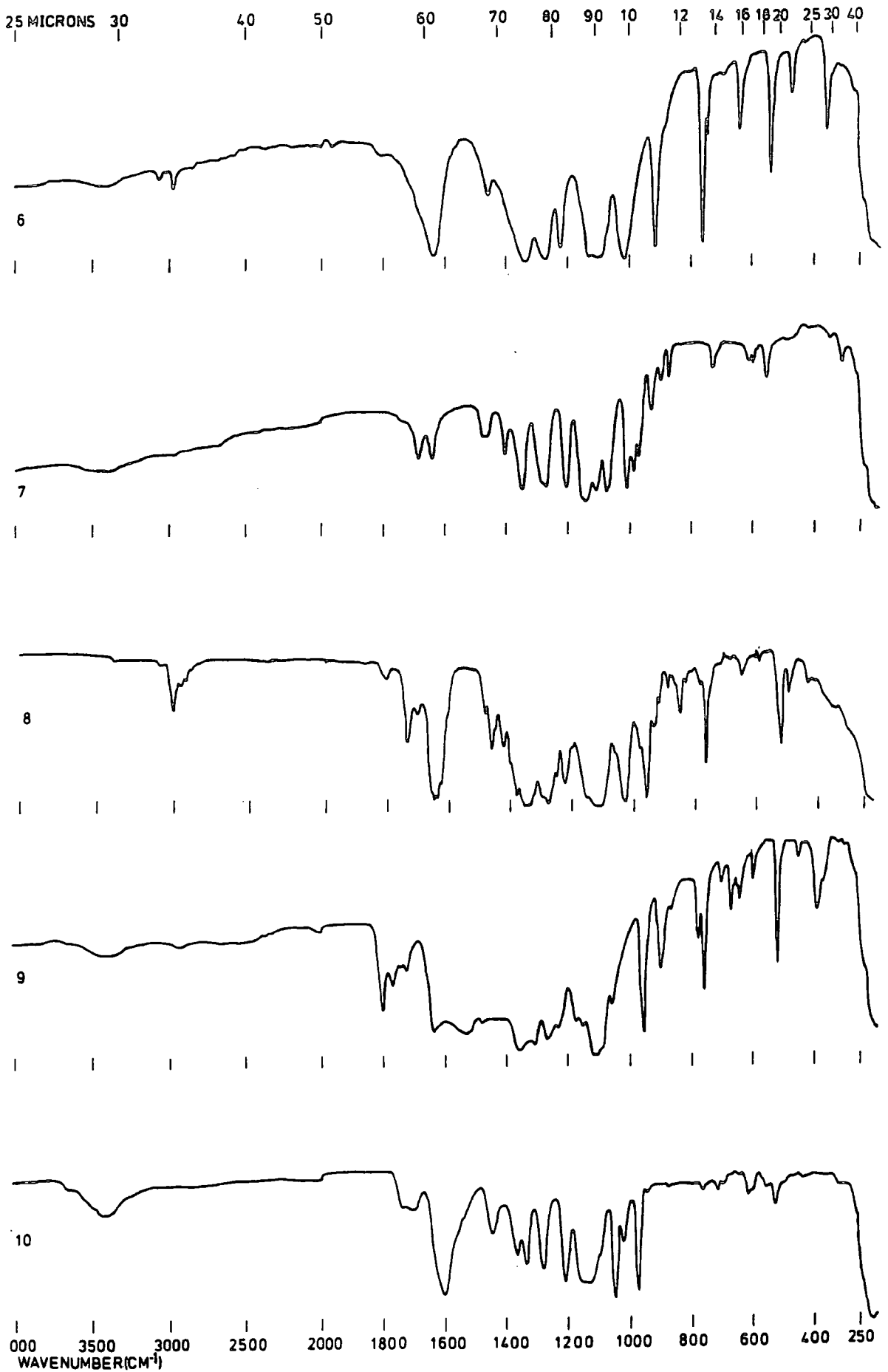


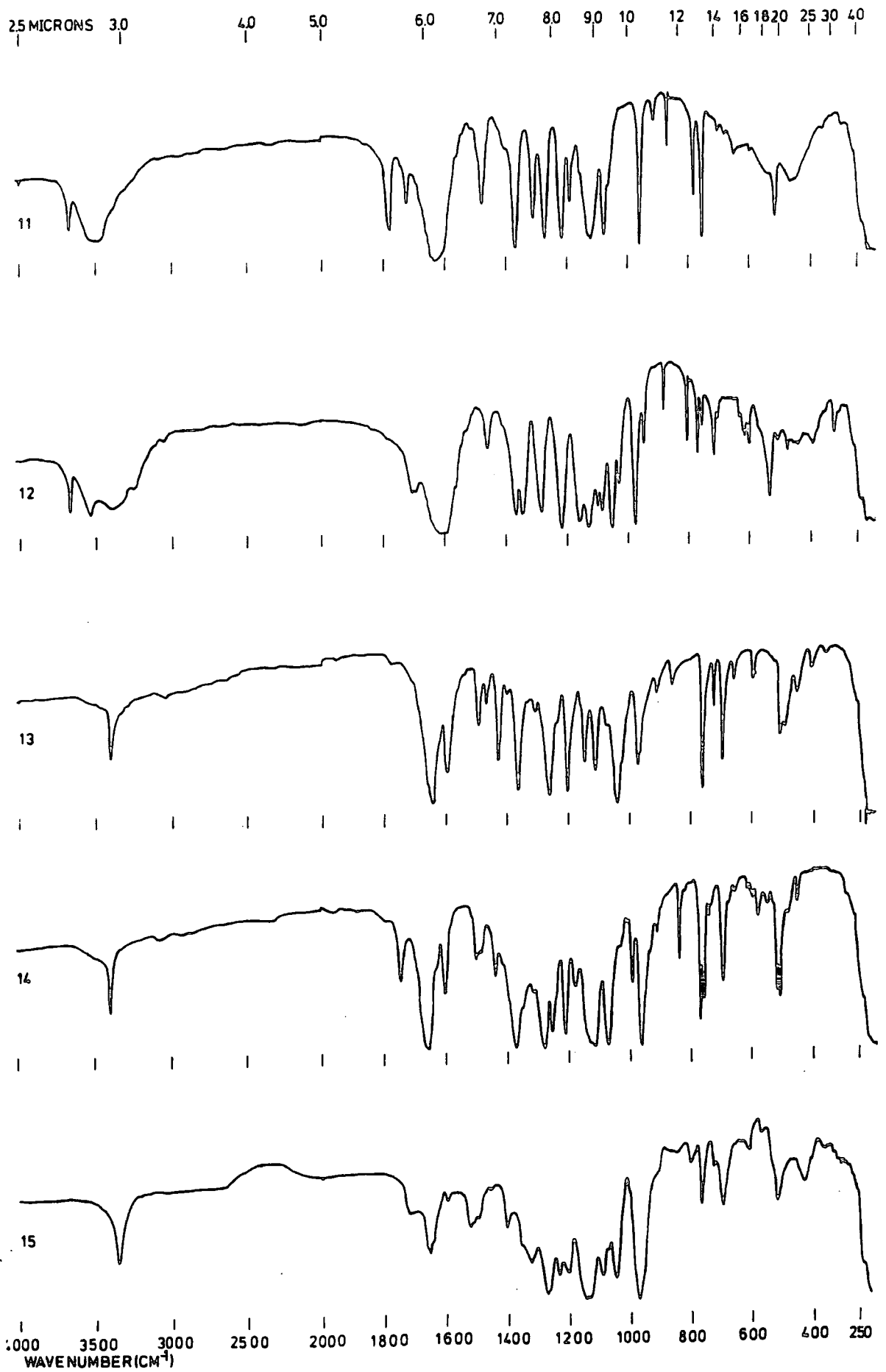
## Appendix Two

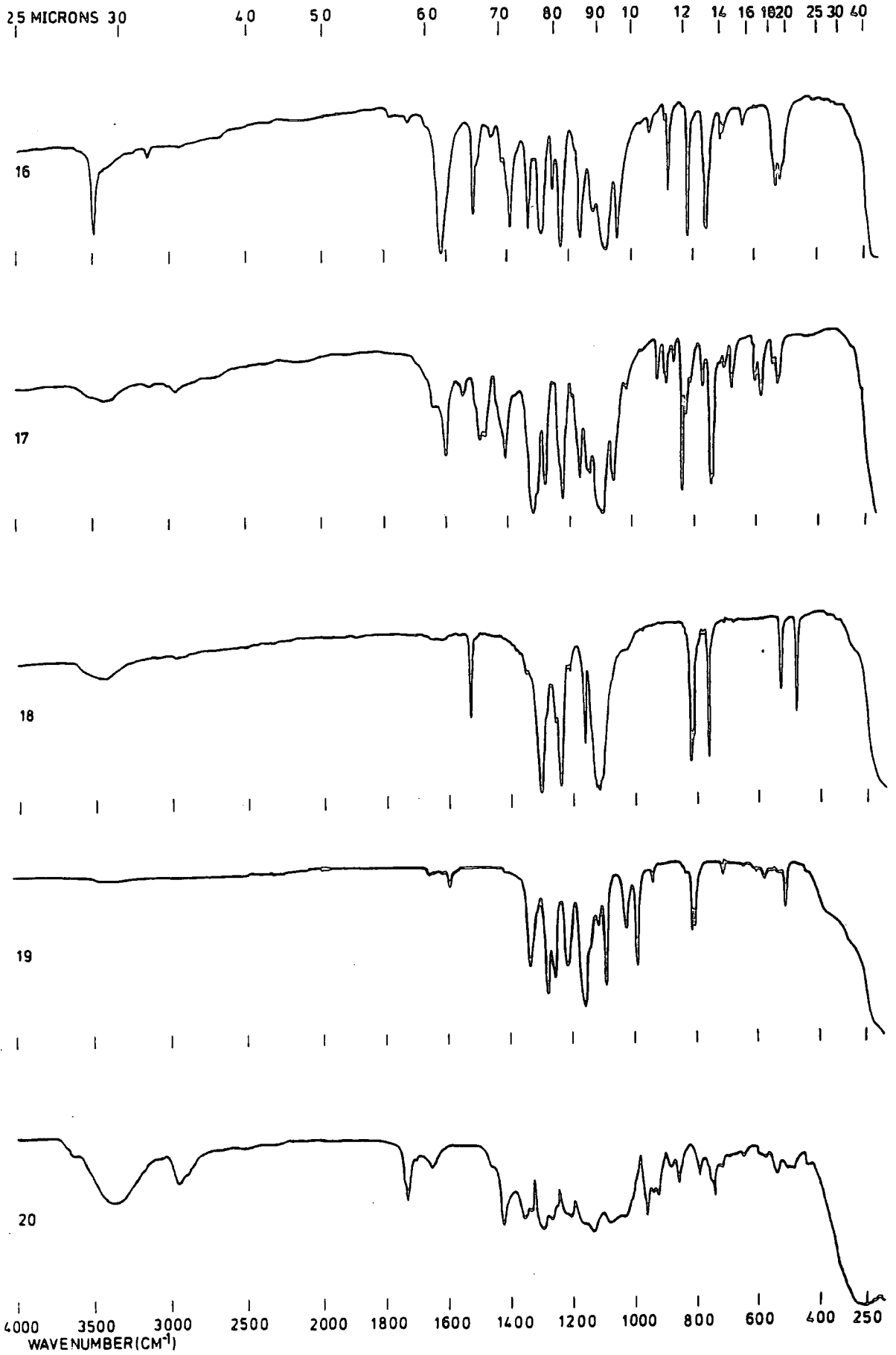
Infra Red Spectra

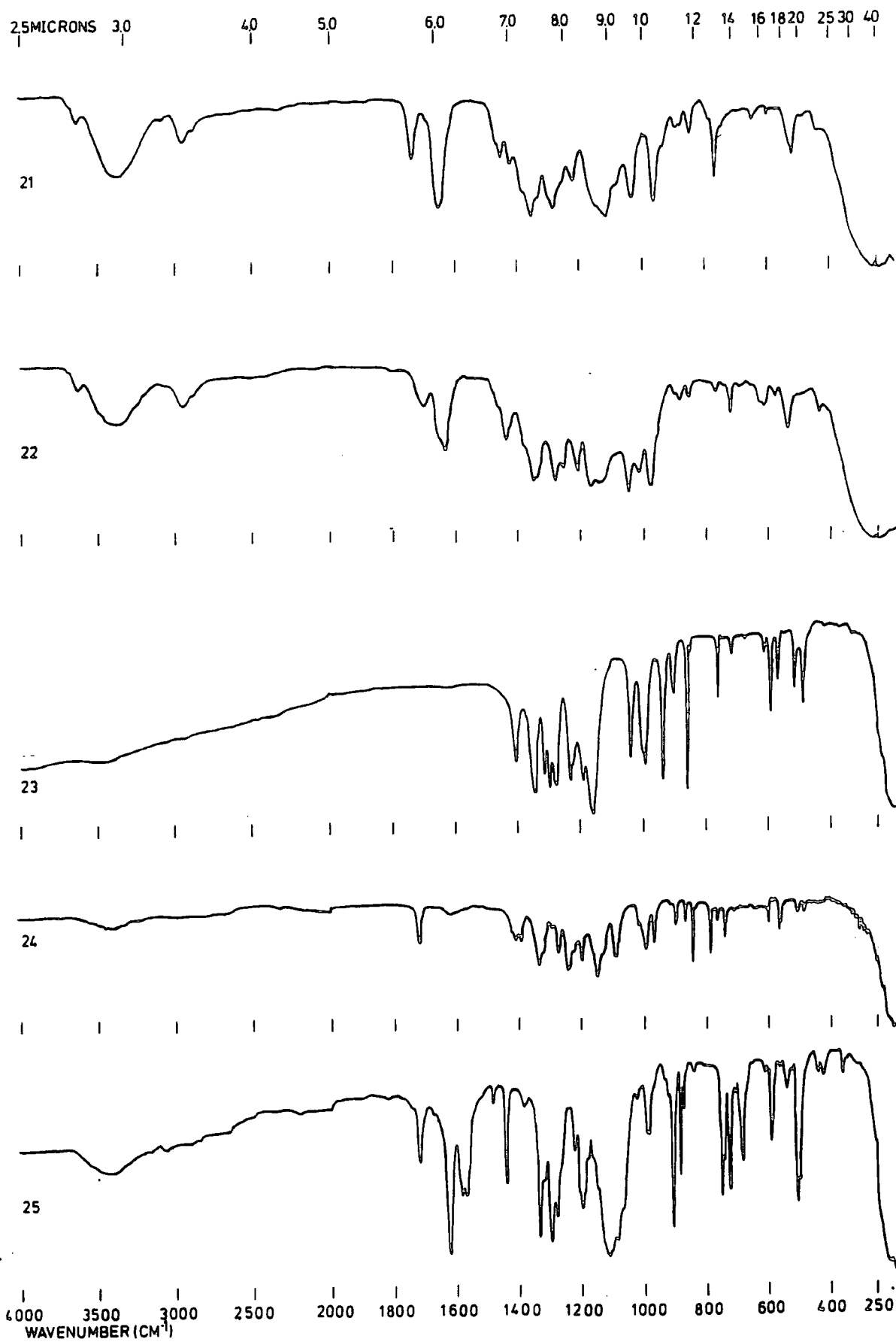
- No.1           perfluorobicyclobutylidene and its isomer (26)
- No.2           perfluorobicyclopentylidene (27)
- No.3           perfluorobicyclobut-1,1'-enyl (26)
- No.4           perfluorobicyclopent-1,1'-enyl (8)
- No.5           perfluoro-3,4-dimethy-hexa-2,4-diene (34)
- No.6           2,2'-dimethyl-perfluorobicyclobut-1,1'-enyl (108)
- No.7           2,2'-dimethyl-perfluorobicyclopent-1,1'-enyl (109)
- No.8           2,2'-diethyl-perfluorobicyclobut-1,1'-enyl (110)
- No.9           1-perfluorocyclobut-1'-enyl-2-hydroxy-3,3-difluoro-cyclobut-3-none (113)
- No.10          1-perfluorocyclopent-1'-enyl-2-hydroxy-3,3,4,4-tetrafluoro-cyclopente-5-none (116)
- No.11          the sodium salt of (113)
- No.12          the sodium salt of (116)
- No.13          2,2'-bis(phenylamino)-perfluorobicyclobut-1,1'-enyl (123)
- No.14          2-phenylamino-perfluorobicyclobut-1,1'-enyl (124)
- No.15          2-phenylamino-perfluorobicyclopent-1,1'-enyl (124)
- No.16          2,2'-bis(pyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl (125)
- No.17          2,2'-bis(N-methylpyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl (126)
- No.18          2,2'-diiodo-perfluorobicyclobut-1,1'-enyl (128)
- No.19          2,2'-diiodo-perfluorobicyclopent-1,1'-enyl (129)
- No.20          6-perfluorocyclobut-1'-enyl-7,7,8,8-tetrafluoro-1,4-dioxa-spirp-(5,4)-octane (133)
- No.21          2-(2''-hydroxyethoxy)-perfluorobicyclobut-1,1'-enyl (132)
- No.22          2-(2''-hydroxyethoxy)-perfluorobicyclopent-1,1'-enyl (134)
- No.23          perfluoro-2,4'-bis(1-cyclobutylidene)-bicyclobutylidene (142)
- No.24          the oligomers of diene (29)
- No.25          perfluorobicyclobutylidene -2- triphenylphosphine (146)
- No.26          perfluobicyclobutylidene-2-pyridinium (148)
- No.27          perfluobicyclopentylidene-2-pyridinium (149)
- No.28          perfluobicyclobutylidene-2-triethylammonium (150)
- No.29          the mono-adduct by the reaction of diene (29) with butadiene (158)
- No.30          the di-adduct by the reaction of diene (29) with diazomethane (160)
- No.31          the di-adduct by the reaction of diene (8) with diazomathane (161)
- No.32          the oligomers of (29) by UV irradiation (162)



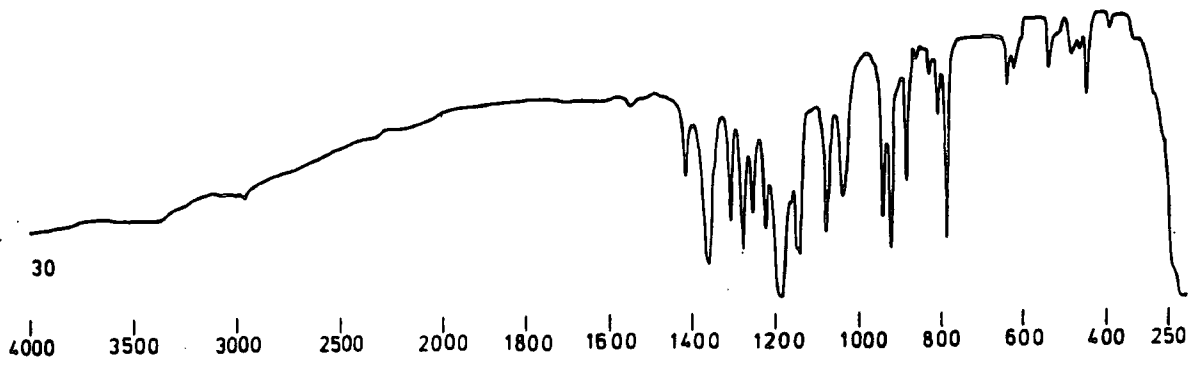
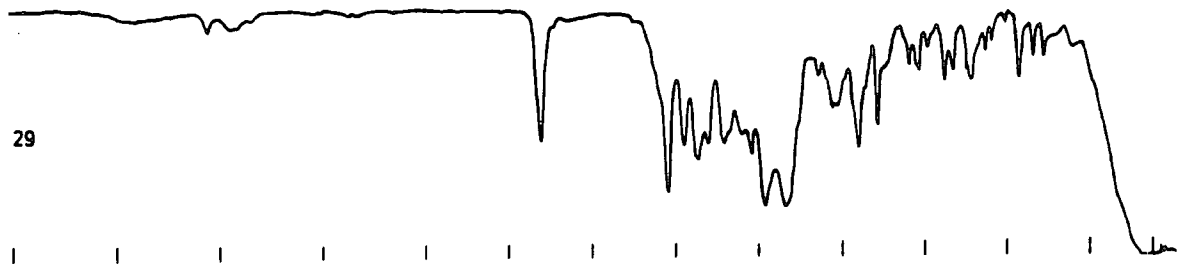
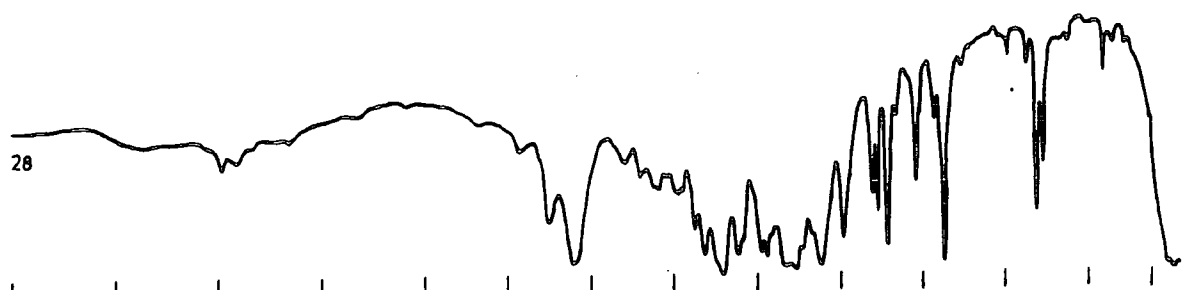
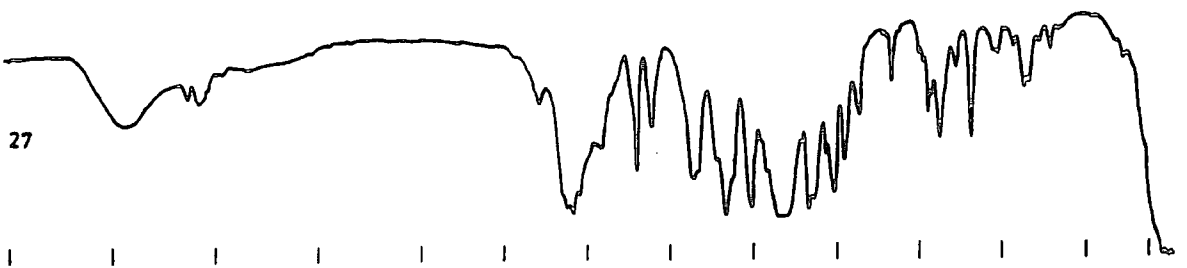
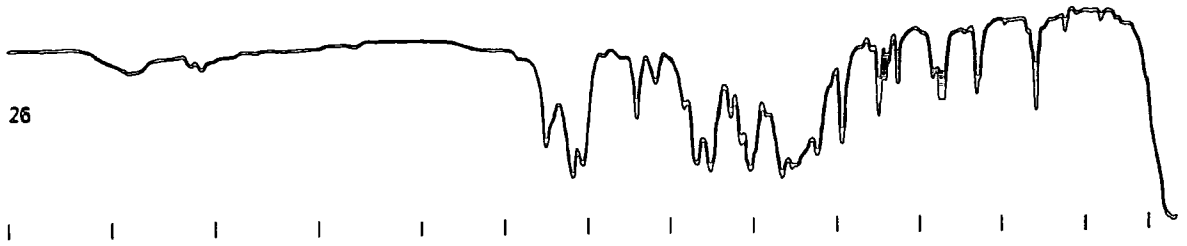


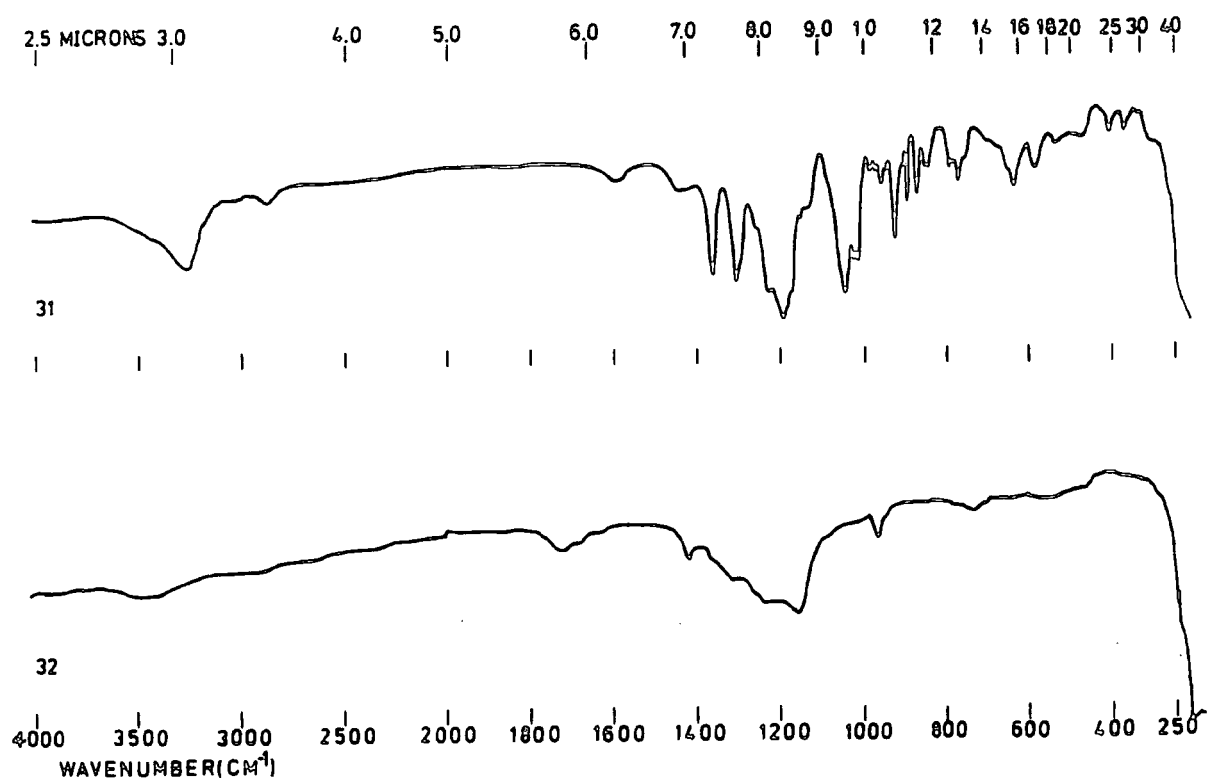






2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 18 20 25 30 40







## Appendix Three

Mass spectra

- |       |  |
|-------|--|
| No.1  | perfluorobicyclobut-1,1'-enyl (26)   |
| No.2  | perfluorobicyclopent-1,1'-enyl (8)   |
| No.3  | perfluoro-1-cyclobutenyl-1-cyclopentene (89)                                       |
| No.4  | perfluoro-3,4-dimethy-hexa-2,4-diene (34)  |
| No.5  | perfluoro-2-cyclobutyl-bicyclobut-1,1'-enyl (93)                                   |
| No.6  | perfluoro-2-cyclobutenyl-bicyclobut-1,1'-enyl (94)                                 |
| No.7  | 2,2'-dimethyl-perfluorobicyclobut-1,1'-enyl (108)                                  |
| No.8  | 2,2'-dimethyl-perfluorobicyclopent-1,1'-enyl (109)                                 |
| No.9  | 2,2'-diethyl-perfluorobicyclobut-1,1'-enyl (110)                                   |
| No.10 | 1-perfluorocyclobut-1'-enyl-2-hydroxy-3,3-difluoro-cyclobut-3-none (113)           |
| No.11 | 1-perfluorocyclopent-1'-enyl-2-hydroxy-3,3,4,4-tetrafluoro-cyclopente-5-none (116) |
| No.12 | the sodium salt of (113)   |
| No.13 | the sodium salt of (116)   |
| No.14 | 2,2'-bis(phenylamino)-perfluorobicyclobut-1,1'-enyl (123)                          |
| No.15 | 2-phenylamino-perfluorobicyclobut-1,1'-enyl (124)                                  |
| No.16 | 2-phenylamino-perfluorobicyclopent-1,1'-enyl (124)                                 |
| No.17 | 2,2'-bis(pyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl (125)                          |
| No.18 | 2,2'-bis(N-methylpyrrol-2-yl)-perfluorobicyclobut-1,1'-enyl (126)                  |
| No.19 | 2,2'-diiodo-perfluorobicyclobut-1,1'-enyl (128)                                    |
| No.20 | 2,2'-diiodo-perfluorobicyclopent-1,1'-enyl (129)                                   |
| No.21 | 2-iodo-perfluorobicyclopent-1,1'-enyl (131)  |
| No.22 | 6-perfluorocyclobut-1'-enyl-7,7,8,8-tetrafluoro-1,4-dioxa-spirp-(5,4)-octane (133) |
| No.23 | 2-(2''-hydroxyethoxy)-perfluorobicyclobut-1,1'-enyl (132)                          |
| No.24 | 2-(2''-hydroxyethoxy)-perfluorobicyclopent-1,1'-enyl (134)                         |
| No.25 | perfluoro-2,4'-bis(1-cyclobutylidene)-bicyclobutylidene (142)                      |
| No.26 | the oligomers of diene (29) (144)  |
| No.27 | perfluorobicyclobutylidene -2- triphenylphosphine (146)                            |
| No.28 | the mono-adduct by the reaction of diene (29) with butadiene (158)                 |
| No.29 | the mono-adduct by the reaction of diene (29) with cyclopentadiene (159)           |
| No.30 | the di-adduct by the reaction of diene (29) with diazomethane (160)                |
| No.31 | the di-adduct by the reaction of diene (8) with diazomethane (161)                 |
| No.32 | the oligomers of diene (29) by UV irradiation (162)                                |

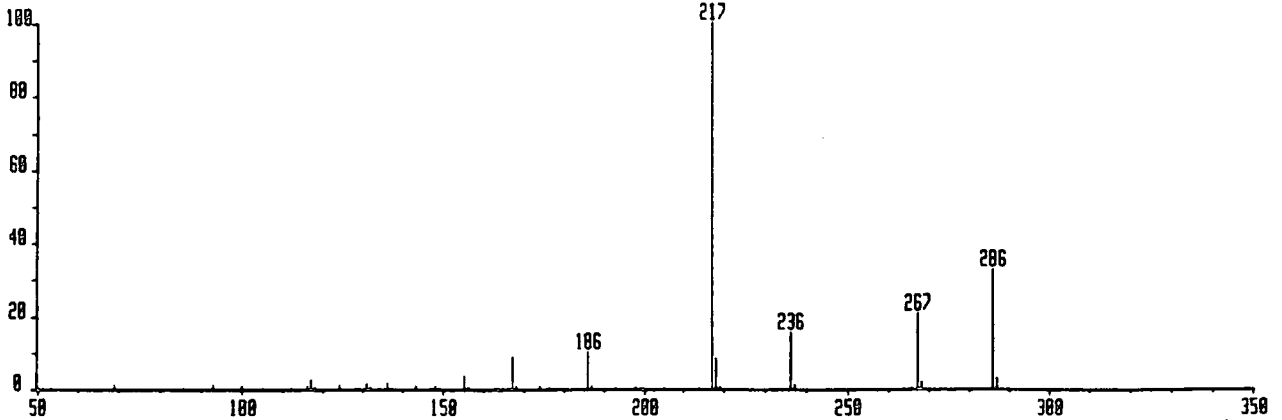
## Spectrum No.1 (EI+ data)

M.W. 286

THF10174o x1 0gd=152 24-FEB-92 18:12:00:09 70E  
 0pA=0 I=7.1v Ha=200 TIC=102611000  
 FA3 0.1A5EC

EI+  
 Acnt: GC= 40° Sys: NAKAFURA  
 Cal: PFKFEB3

HAR: 46592000  
 MASS: 217



Mass	% Base
69.03	1.10
93.05	1.10
100.04	0.55
116.02	0.64
117.05	2.52
118.03	0.38
124.05	1.11
131.05	1.39
136.05	1.21
143.05	0.65
148.05	0.62
155.05	3.30
167.05	8.39
168.06	0.55
174.05	0.55
186.04	10.07
187.05	0.62
217.04	100.00 F
218.05	8.05 F
236.04	15.38
237.05	1.17
267.04	20.43
268.05	1.89
286.02	32.42 F
287.03	2.90 F

## Spectrum No.2 (EI+ data)

M.W. 386

THF28296o x1 Bgd=262 24-FEB-92 11:44:03:40 70E EI-

SpM=0 I=4.9u Ha=387 TIC=116560000

Rcnt:

Sys:NAKAMURA

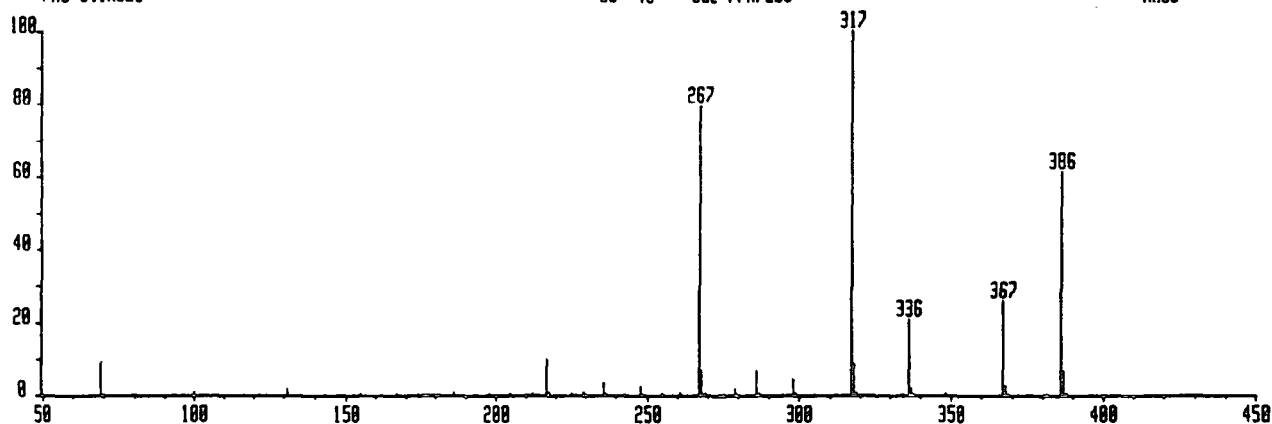
HAR: 32256000

FA3 0.1HSEC

GC= 40°

Cal:PFKFE83

HASS: 317



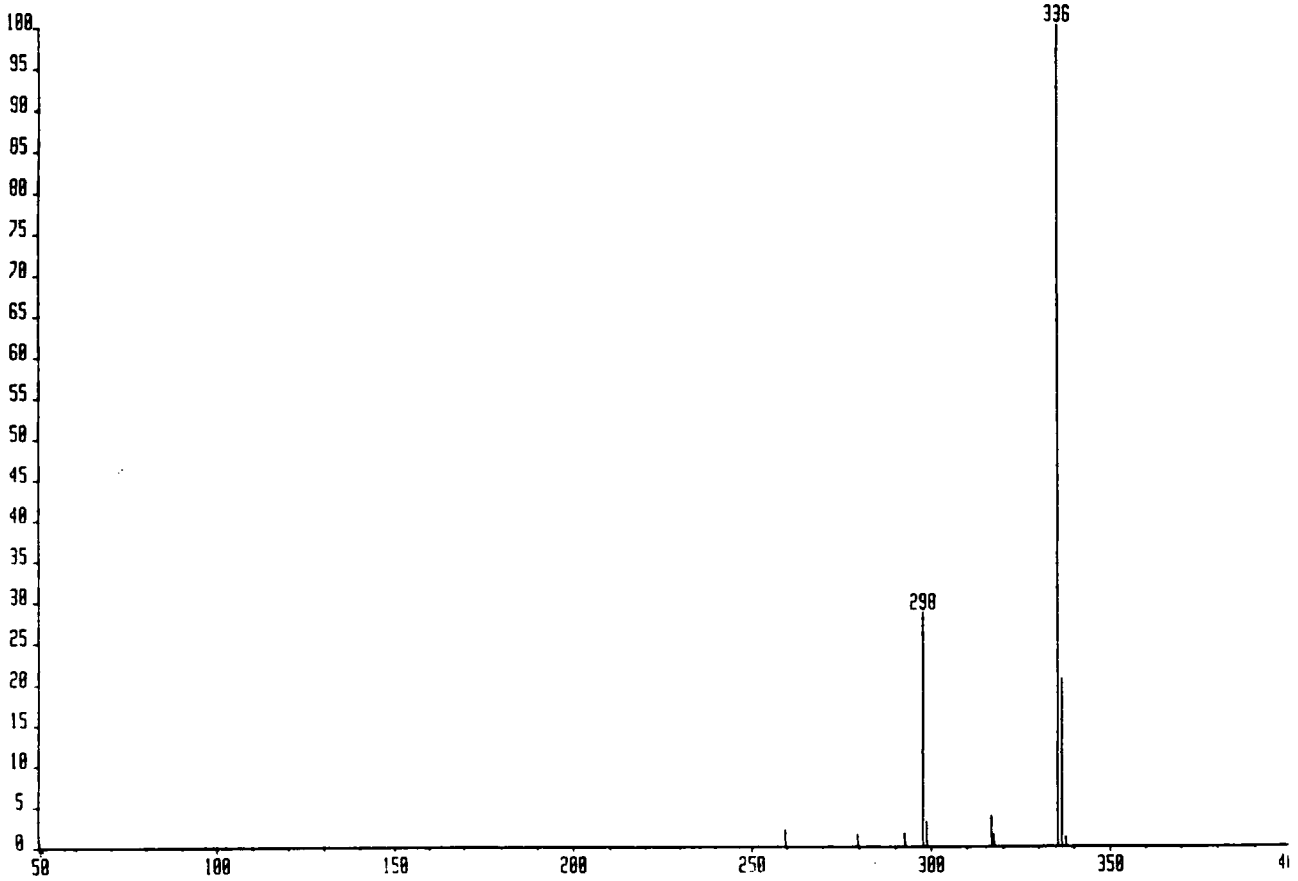
Mass	% Base
69.01	8.91
100.01	0.69
131.01	1.88
186.01	0.79
205.01	0.49
217.01	9.92
218.02	0.79
229.00	0.79
236.00	3.17
248.00	2.38
261.00	0.79
266.98	79.37 F
267.99	6.35 F
278.99	1.73
286.00	6.35
286.99	0.47
298.00	4.05
299.02	0.33
316.99	100.00 F
317.98	8.29 F
318.99	0.33
335.97	20.63 F
336.99	1.75 F
348.00	0.32
366.96	25.60 F
367.98	2.51 F
385.97	61.16 F
386.98	6.35 F

## Spectrum No.3 (Cl- data)

M.W. 336

TN121ND141o x1 8gd=113 9-MAR-98 15 09:01:59 78E Cl-  
 OpR=0 I=10v Ha=634 TIC=111975000 Acnt: Sys NAKAMURA  
 FA3 0.1 RSEC GC= 40° Cal PFK1G.HH

HAR: 65  
 RASS:



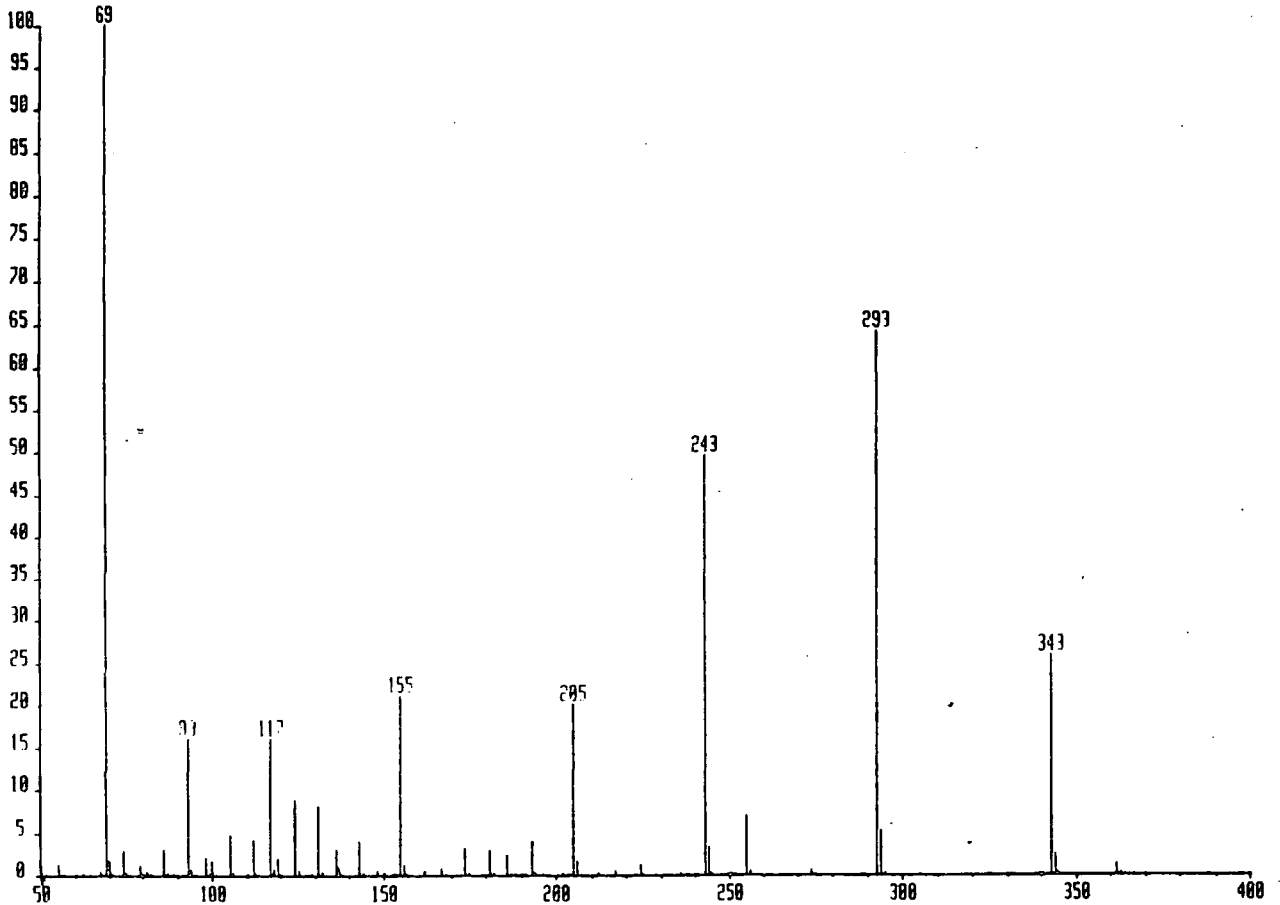
Mass	% Base
235.80	0.16
241.78	0.21
254.73	0.22
259.74	1.90
260.76	0.19
266.74	0.36
273.76	0.10
274.75	0.23
275.74	0.11
278.72	0.36
279.73	1.34
280.74	0.16
285.71	0.24
292.71	1.52
293.71	0.30
294.71	0.11
297.69	28.47
298.69	2.92
299.72	0.25
311.68	0.70
312.68	0.54
313.68	0.73
316.67	3.70
317.69	1.35
323.67	0.11
330.67	0.18
332.21	0.56 F
335.67	100.00 FO
336.63	20.47 F
337.61	1.11

Spectrum No.4 (EI+ data)

M.W. 362

JV101520 x1 Bgd=150 4-OCT-91 11 51-0 01:54 70E EI+  
 BpA=0 I=10v Ho=362 TIC=268425000 Acnt: Sys: VAUGHAN  
 FA3 0.1A5EC GC= 470 Cal: PFK4OCT

NHR: 65534000  
 ARSS: 69



Mass	% Base		
49.98	2.46	161.98	0.40
54.99	1.17	166.97	0.78
61.99	0.22	173.97	3.13
66.99	0.39	174.98	0.17
69.00	100.00	180.97	2.92
69.99	1.65	181.98	0.15
73.99	2.73	185.97	2.36
78.98	0.98	186.97	0.13
80.98	0.25	192.97	3.91
85.98	2.93	193.96	0.23
86.98	0.18	201.61	0.20
92.98	16.02	204.95	20.09
93.98	0.55	205.96	1.56
97.98	2.07	216.96	0.39
98.98	0.14	223.96	1.17
99.98	1.56	235.95	0.18
104.98	4.63	242.97	49.56
105.98	0.23	243.96	3.15
111.98	4.03	254.95	6.82
112.49	0.18	255.97	0.49
116.98	16.08	273.95	0.57
117.98	0.78	292.95	63.98 F
118.98	1.95	293.95	5.09 F
123.98	8.69	294.94	0.13
124.98	0.39		
128.98	0.10	342.92	25.82 F
130.98	7.96	343.95	2.34 F
131.98	0.22	361.94	1.17
135.98	3.13		
136.98	0.85		
142.98	3.91		
143.98	0.12		
147.98	0.39		

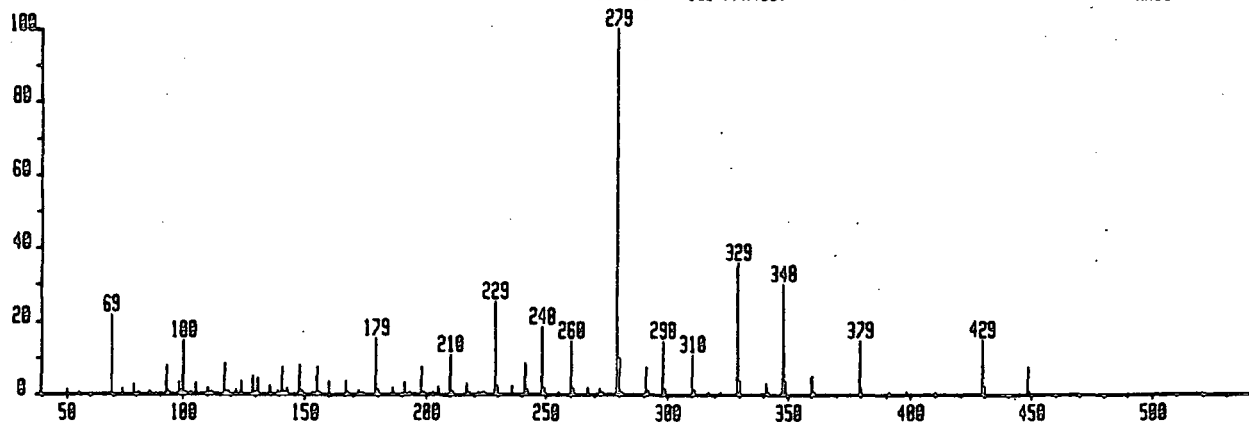
## Spectrum No.5 (EI+ data)

M.W. 448

TN876R0615o x1 Bgd=532 7-OCT-91 15:38:07:39 70E  
 BpA=0 I=1.1v Ha=449 TIC=36407000  
 FAS 0.1ASEC

Acnt: GC= 55°  
 Sys: NAKAURA  
 Cal: PFK4OCT

NRR: 716000  
 MASS: 279



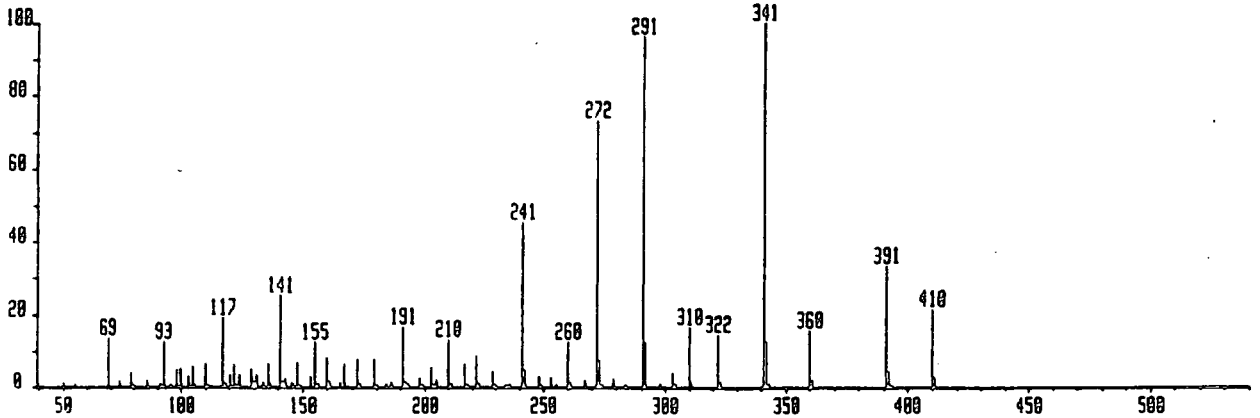
Mass	% Base	Mass	% Base
49.99	1.02	242.02	1.03
55.00	0.28	248.01	18.29
68.99	21.43	249.02	1.42
73.99	1.30	255.03	0.28
79.00	2.40	260.01	14.44
81.00	0.29	261.02	1.33
85.99	0.68	267.02	1.62
92.99	7.62	272.01	1.52
94.00	0.27	273.05	0.21
97.99	3.17	278.43	0.17
99.00	0.53	279.02	100.00
99.99	14.29	280.02	9.53
101.00	0.29	281.04	0.28
102.99	0.22	291.01	7.14
105.00	2.69	292.03	0.63
110.00	1.51	298.02	14.29
112.00	0.33	299.03	1.27
117.00	8.09	310.03	10.71
118.01	0.42	311.04	1.03
119.00	0.73	317.04	0.25
122.00	1.00	322.06	0.28
124.00	3.57	329.03	35.78
129.00	4.67	330.04	3.57
130.01	0.46	341.04	2.65
131.00	3.99	342.08	0.25
136.00	1.93	347.38	0.18
139.51	0.85	348.03	29.91
141.01	7.14	349.04	3.57
142.02	0.40	360.03	4.81
143.01	1.40	361.04	0.42
148.01	7.87	379.04	14.29
149.02	0.60	380.07	1.30
153.02	0.28	391.03	0.33
155.00	7.14	398.06	0.74
156.01	0.24	410.06	0.31
160.00	3.57	429.06	14.75
167.00	3.57	430.07	1.99
168.00	3.29	448.08	7.14
172.01	0.93	449.11	0.63
174.01	0.22		
179.00	15.05		
180.01	1.05		
186.00	1.58		
191.00	2.96		
192.99	0.27		
197.99	7.14		
199.00	0.43		
203.00	0.38		
204.98	1.66		
209.99	10.76		
211.00	0.85		
217.01	2.82		
218.03	0.21		
222.01	0.40		
223.60	0.22		
224.66	0.18		
229.01	29.00		

## Spectrum No.6 (EI+ data)

M.W. 410

TH076R0758o x1 8gd=737 7-OCT-91 15:30:08:19 78E EI+  
 BpA=0 I=627cu Mn=411 TIC=30977000 Rcnt: Sys:NAKAGURA  
 FA3 0.1RSEC GC= 72° Cal:PFK40CT

NAR: 4110000  
 MASS: 341



Mass	% Base	Mass	% Base
49.99	1.12	217.90	0.34
54.99	0.71	218.00	0.49
68.99	13.80	221.99	8.25
73.99	1.58	223.01	0.61
79.00	3.63	229.00	4.04
79.99	0.51	229.99	0.46
86.00	1.58	234.03	0.51
91.00	0.61	236.02	0.61
92.99	12.46	241.01	45.06
95.50	0.51	242.03	4.62
98.00	4.33	248.00	2.60
99.99	4.91	248.93	0.49
103.00	2.65	253.02	2.51
104.99	5.38	254.99	0.34
105.49	0.46	260.01	12.46
110.00	6.23	261.02	1.12
111.00	0.49	267.03	1.87
117.00	18.78	272.02	72.90
118.01	1.05	273.02	7.15
120.50	3.04	274.02	0.41
122.00	5.82	279.03	1.90
123.02	0.32	284.04	0.49
124.00	2.99	291.02	96.40
129.00	4.65	292.03	12.46
130.01	1.27	298.06	0.61
131.00	3.07	303.03	3.87
134.01	0.97	304.05	0.54
136.01	6.23	310.02	16.50
136.51	0.73	311.02	1.53
141.01	24.91	322.04	14.23
142.02	1.29	323.04	1.29
143.00	2.12	340.42	0.39
145.52	1.09	341.03	100.00
146.02	0.46	342.03	12.46
148.01	6.42	343.05	0.56
149.01	0.41	360.04	15.30
153.01	2.60	361.04	1.61
155.00	12.46	391.05	33.09
156.01	0.63	392.07	4.11
160.00	7.96	393.09	0.39
161.00	1.27	410.04	21.31
165.00	1.14	411.05	2.55
167.01	6.23		
172.00	7.37		
173.00	0.61		
179.00	7.66		
180.01	0.44		
184.01	0.66		
186.02	1.29		
191.00	16.30		
192.01	1.34		
193.00	0.66		
198.01	2.48		
199.04	0.41		
203.01	5.16		
204.02	0.54		
209.01	1.82		
209.99	13.09		
211.01	0.66		
216.00	6.23		

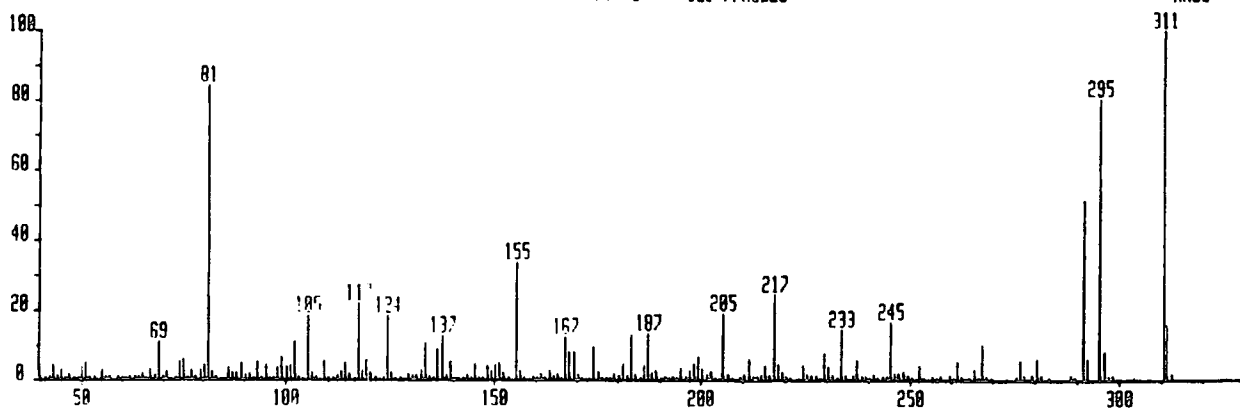
Spectrum No.7 (EI+ data)

M.W. 310

TMB2011o x1 Bgd=1 22-JUN-98 12:38:00 01 04 78C  
 BpR=0 I=10v Na=338 TIC=667982976 Acnt

EI+  
 Sys:ACE  
 PT= 0° Cal:PFK0DEC

HRR:  
 RASS:

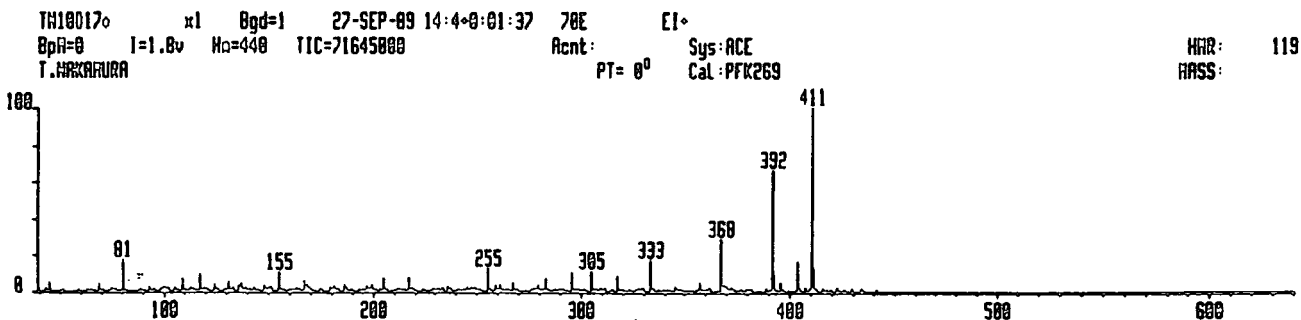
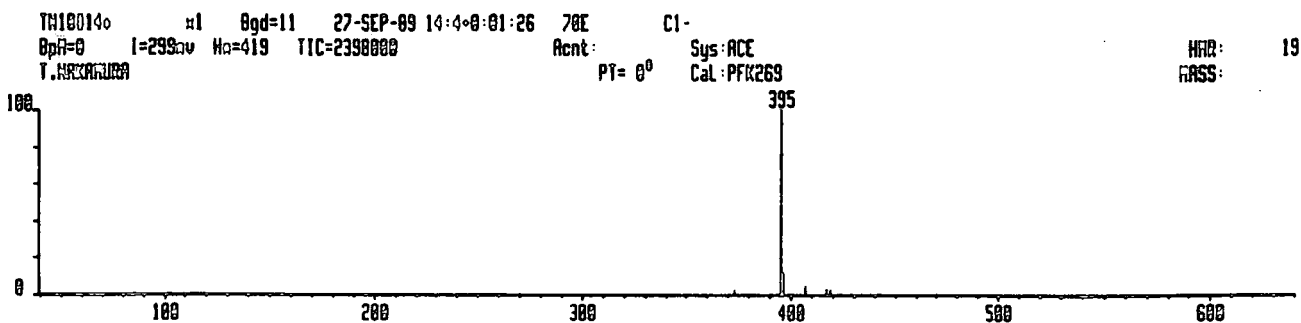


Mass	% Base									
20	33	1.38	86.16	3.19	146.27	0.48	207.37	0.37	268.47	0.87
24	29	0.14	87.17	1.83	147.28	0.47	208.37	0.11	269.49	0.27
25	29	0.13	88.18	1.93	148.26	3.84	209.37	0.81	273.48	0.13
26	28	0.56	89.19	4.59	149.27	2.53	210.38	1.59	275.48	0.62
27	28	0.97	90.17	1.03	150.28	3.93	211.37	5.83	276.48	5.36
28	24	9.12	91.17	1.35	151.29	4.80	212.38	0.83	277.49	0.90
29	23	5.57	92.18	0.25	152.27	1.83	213.39	0.78	278.49	0.11
30	23	1.22	93.17	5.08	153.28	0.42	214.37	1.26	279.49	1.47 F
31	20	10.13	94.18	0.38	155.26	33.49	215.37	3.77	280.48	5.77 F
32	22	0.70	95.18	3.90	156.27	2.58	216.38	1.11	281.49	1.01 F
33	19	2.12	96.19	0.27	157.29	0.52	217.37	24.36	283.47	0.32
34	18	0.12	97.20	0.35	158.30	0.13	218.38	4.32	288.52	1.19
36	14	0.27	98.19	3.24	159.28	0.66	219.39	2.24	289.52	0.24
37	13	0.75	99.19	6.30	160.29	0.33	220.40	0.71	291.48	91.39 F
38	13	0.74	100.19	3.46	161.28	1.37	221.41	0.35	292.53	5.61 F
39	13	3.79	101.21	4.07	162.29	0.52	223.39	0.17	295.46	80.44 F
40	11	0.17	102.18	11.03	163.30	2.48	224.38	4.08	296.51	7.84 F
41	12	0.51	103.19	0.62	164.28	0.98	225.39	1.27	297.52	0.76
42	09	0.74	104.20	0.16	165.29	1.36	226.40	0.90	298.52	0.92
43	09	4.07	105.20	18.05	166.29	0.46	227.39	1.02	299.53	0.13
44	07	1.23	106.20	1.99	167.29	12.07	228.40	0.37	303.57	0.20
45	09	2.39	107.22	0.58	168.29	7.86	229.41	7.39	310.64	100.00 FO
46	09	0.21	108.22	0.15	169.30	7.69	230.40	3.60	311.56	15.87 F
47	06	1.36	109.19	5.46	170.30	1.50	231.41	1.56	312.57	1.32
48	07	0.21	110.20	0.51	171.30	0.35	232.42	0.51		
49	07	0.32	111.20	0.36	172.30	0.11	233.38	14.38		
50	07	3.59	112.21	0.89	173.31	0.11	234.39	1.24		
51	07	5.09	113.21	2.28	174.29	9.18	235.41	0.13		
52	07	0.81	114.20	4.53	175.30	2.09	236.40	1.10		
53	08	0.61	115.21	1.29	176.31	0.27	237.40	5.46		
55	08	2.40	116.22	0.17	177.31	0.44	238.41	0.60		
56	10	0.68	117.20	21.93	178.31	0.49	239.43	0.86		
57	12	0.86	118.20	2.57	179.32	1.66	240.43	0.23		
59	11	0.76	119.21	5.86	180.32	1.07	241.45	1.32		
60	12	0.41	120.22	1.64	181.32	4.32	242.43	0.33		
61	11	0.54	121.21	0.84	182.33	0.94	243.41	0.58		
62	11	0.55	122.21	0.16	183.31	12.90	244.42	0.54		
63	12	0.89	123.22	0.25	184.32	1.30	245.42	16.44		
64	11	0.72	124.20	18.22	185.33	0.24	246.43	1.92		
65	13	1.84	125.21	1.92	186.31	4.07	247.43	1.63		
66	12	0.47	126.22	0.38	187.32	13.34	248.43	2.24		
67	13	3.02	127.23	0.53	188.33	1.74	249.43	0.98		
68	13	1.05	128.23	0.10	189.34	2.45	250.43	0.25		
69	12	10.61	129.22	1.60	190.33	0.29	251.45	0.16		
70	15	0.63	130.22	0.97	191.33	0.72	252.42	4.07		
71	13	2.23	131.23	1.08	192.32	0.22	253.43	0.39		
72	15	0.13	132.24	2.40	193.32	0.72	254.46	0.11		
73	16	0.21	133.22	10.22	194.35	0.34	255.42	0.73		
74	13	5.00	134.23	0.64	195.34	3.10	256.43	0.19		
75	15	5.97	135.26	0.20	196.34	0.73	257.45	1.02		
76	15	0.43	136.23	8.41	197.35	2.39	258.45	0.17		
77	16	2.39	137.24	12.58	198.35	4.67	259.46	0.92		
78	15	0.97	138.25	1.21	199.34	6.43	260.47	0.49		
79	15	2.44	139.26	4.85	200.35	2.69	261.43	5.14		
80	15	3.81	140.27	0.33	201.36	1.47	262.45	0.70		
81	16	83.77	141.26	0.50	202.34	1.99	263.48	0.14		
82	18	2.11	142.26	0.18	203.36	0.40	264.44	0.51		
93	17	0.54	143.26	1.47	204.17	0.13	265.45	3.02		
94	22	0.10	144.28	0.25	205.34	19.03	266.45	0.48		
95	24	0.15	145.27	4.17	206.35	1.55	267.46	9.95		



Spectrum No.8 (EI+ data)

M.W. 410



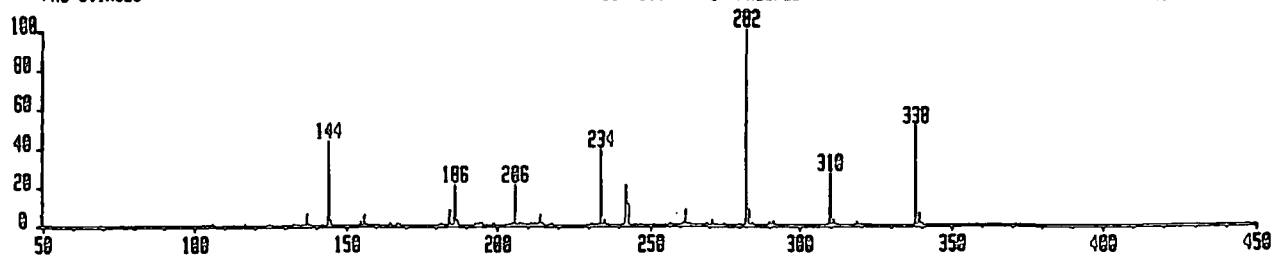
Mass	% Base				
29.04	2.66	139.20	1.16	259.34	12.22
30.04	0.26	141.19	0.54	256.35	0.98
31.04	1.23	143.20	1.47	259.38	3.29
33.06	1.08	148.20	2.82	260.38	1.00
39.07	0.94	149.21	0.83	261.35	3.12
43.07	1.06	150.22	1.92	262.37	0.49
45.09	4.61	151.22	1.86	263.38	0.23
50.06	0.29	155.20	10.27	291.43	0.41
51.07	1.01	156.21	0.60	293.41	10.15
59.08	0.70	159.22	0.27	296.41	0.97
63.10	1.00	160.23	0.21	297.42	0.73
65.10	0.99	161.22	0.74	298.42	0.58
69.07	4.08	162.24	0.20	299.42	0.93
71.08	0.49	163.24	1.15	301.43	0.62
74.08	0.26	164.22	0.34	302.42	0.22
75.10	1.13	167.22	5.10	305.41	10.90
76.13	0.44	168.23	3.37	306.41	0.91
77.12	0.98	169.24	1.89	329.47	2.21
81.12	16.79	170.25	0.47	330.47	0.33
82.13	0.28	174.24	0.44	333.49	17.04
88.13	0.22	175.25	0.48	334.45	1.54
89.14	0.98	179.24	1.86	335.46	0.22
91.12	0.26	180.25	0.93	337.46	0.68
93.13	1.71	181.26	2.39	338.47	0.23
95.13	0.96	182.27	0.74	357.50	4.73
98.13	0.60	183.24	0.71	358.50	0.64
99.14	1.62	186.25	3.31	359.51	0.46
100.13	2.14	187.26	2.17	360.52	0.87
101.16	1.29	189.28	0.75	361.49	1.83
102.13	1.83	193.27	0.47	362.52	0.20
105.14	1.09	195.27	0.71	365.50	0.29
107.17	0.32	197.28	2.70	367.51	28.50
109.14	6.65	198.28	1.34	368.52	3.22
110.15	0.23	199.28	3.10	369.53	2.80
112.16	0.64	200.28	0.93	370.53	1.54
113.15	1.23	201.30	0.86	371.54	0.47
114.15	0.49	203.28	0.63	390.57	0.39
117.15	8.90	205.27	6.95	391.57	66.42
118.15	0.80	206.28	0.41	392.57	8.64
119.16	1.40	209.29	0.23	393.58	0.74
120.17	0.47	210.30	0.24	395.59	5.01
124.16	3.19	211.29	0.73	396.56	0.51
125.17	0.35	212.31	0.36	399.58	0.32
129.17	0.90	213.31	0.46	403.61	15.89
130.17	0.30	214.29	0.29	404.61	2.25
131.17	5.02	215.29	0.34	407.60	2.14
132.19	0.74	217.29	7.11	408.61	0.21
133.17	1.38	218.30	1.35	409.60	1.59
136.18	2.59	219.31	1.50	410.60	100.00
137.19	3.72	224.30	0.36	411.61	13.00
138.21	0.61	225.32	0.28	412.61	1.08
		227.31	0.25		

## Spectrum No.9 (EI+ data)

M.W. 338

IN457018680 x1 Bgd=1854 26-FEB-92 09:37:0:13:11 78E EI+  
 BpA=0 I=1.5v Ma=340 TIC=42147000 Acnt: Sys:NAKAGURA  
 FA3 0.1RSEC GC= 160° Cal: PFK25FEB

HR: 1006  
 HRSS:



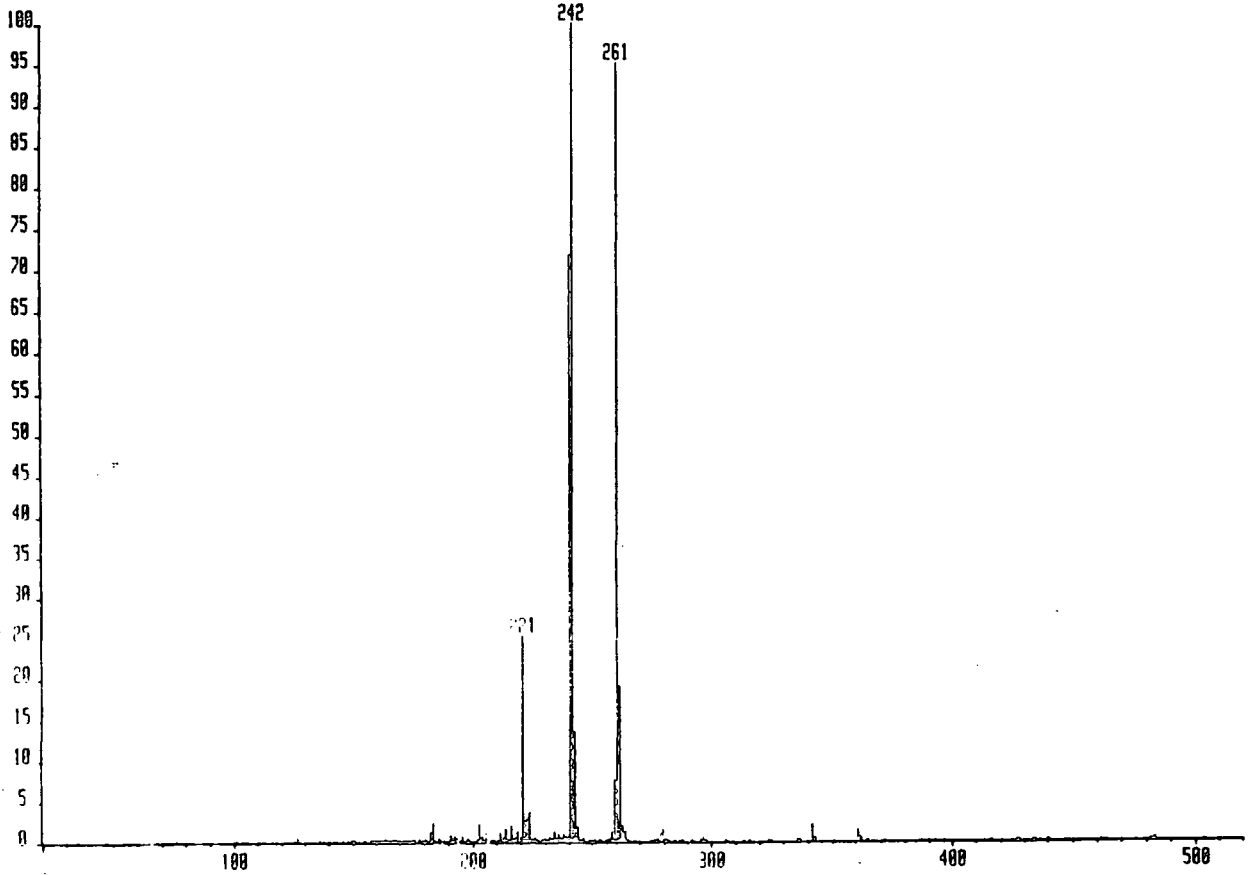
m/z	% Base
116.97	0.39
123.97	0.30
132.96	0.66
136.96	6.82
137.96	0.44
143.99	58.87
144.99	2.76
154.93	1.17
159.93	4.06
164.99	2.09
167.99	0.47
181.67	0.56
183.92	8.12
184.92	0.56
189.91	20.78
186.91	2.28
192.92	0.97
194.92	1.28
198.99	0.44
204.92	1.17
209.93	24.73
206.98	2.03
210.93	0.65
211.94	0.40
213.92	9.98
214.92	1.09
233.91	44.66
234.91	4.06
238.89	0.31
241.90	23.06
243.01	10.45
256.45	0.75
260.90	0.39
261.89	6.37
262.91	0.63
268.93	1.01
270.93	2.71
271.92	0.31
274.89	0.42
281.87	100.00 F
282.89	9.03 F
284.21	1.00
289.94	1.06
290.93	2.03
309.90	24.77
310.92	4.06
318.99	1.09
337.91	41.77 F
338.93	6.09 F
339.99	0.43

Spectrum No.10 (Cl- data)

M.W.262

TH147017o x1 8gd=5 15-MAY-98 14:52:08.01 28 78E Cl-  
 BpA=0 I=10v Hn=522 TIC=263862888 Acnt: Sys: ACE  
 TAKA 15-MAY-98 PT= 0° Cal: PFK10RAY  
 \*x1.0

HAR:  
 RASS:



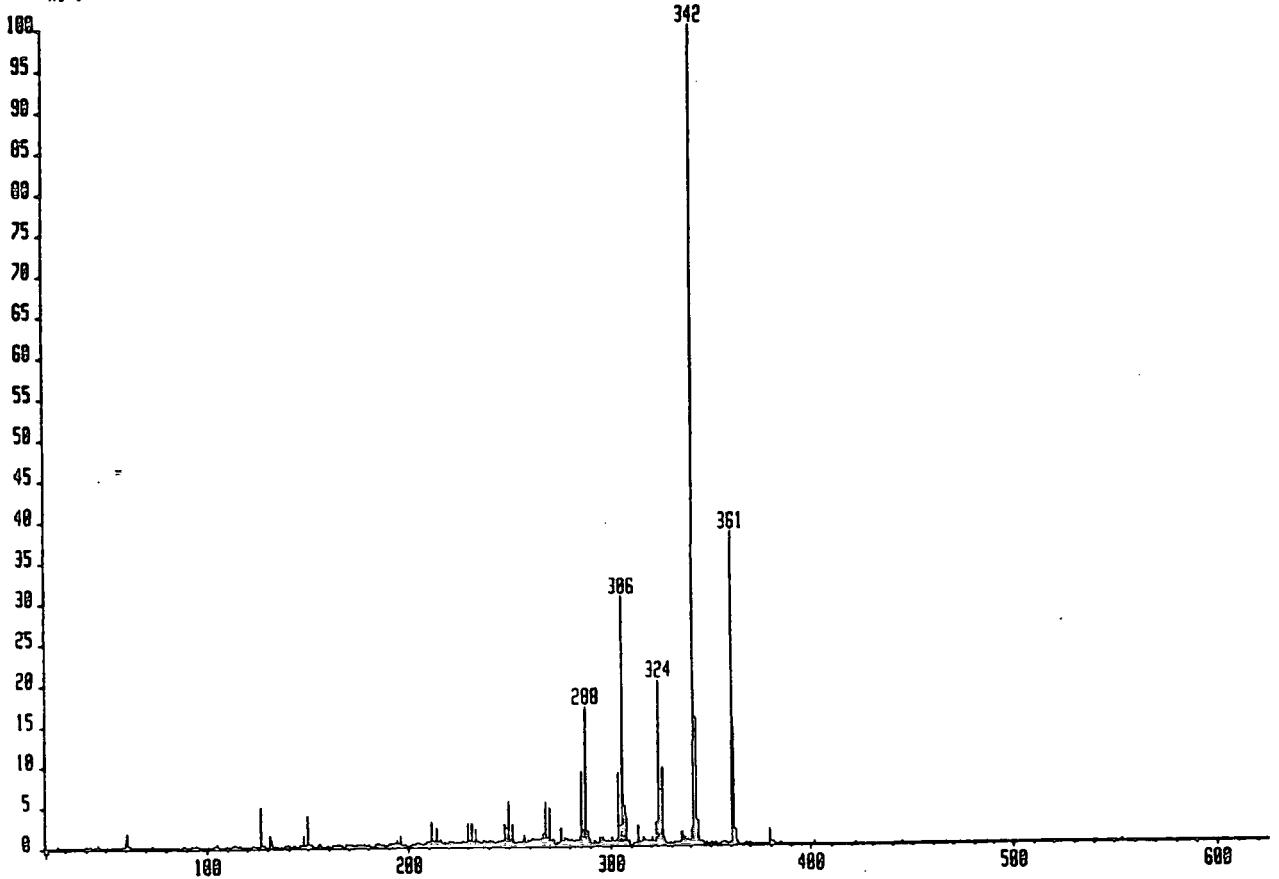
Mass	% Base
182.81	0.40
183.82	1.74
195.81	0.44
202.82	0.87
203.81	0.37
208.81	0.67
213.78	1.11
215.81	1.28
218.80	0.36
220.78	10.62
221.78	0.85
222.79	1.08
223.78	2.93
233.78	0.85
238.78	0.49
240.78	28.92
241.76	100.00
242.77	9.82
243.77	1.37
259.76	2.26
260.74	67.93
261.75	13.87
282.75	1.19

Spectrum No.11 (Cl- data)

M.W.362

TH1480180 x1 Bgd=6 15-MAY-90 15:13:00:32 78E Cl-  
 ApA=0 I=6.7v Ha=553 TIC=184515888 Acnt: Sys:ACE  
 TAKA 15-MAY-90 PT= 0° Cal: PFK18RAY  
 \*RT\*0

HAR:  
 MASS:



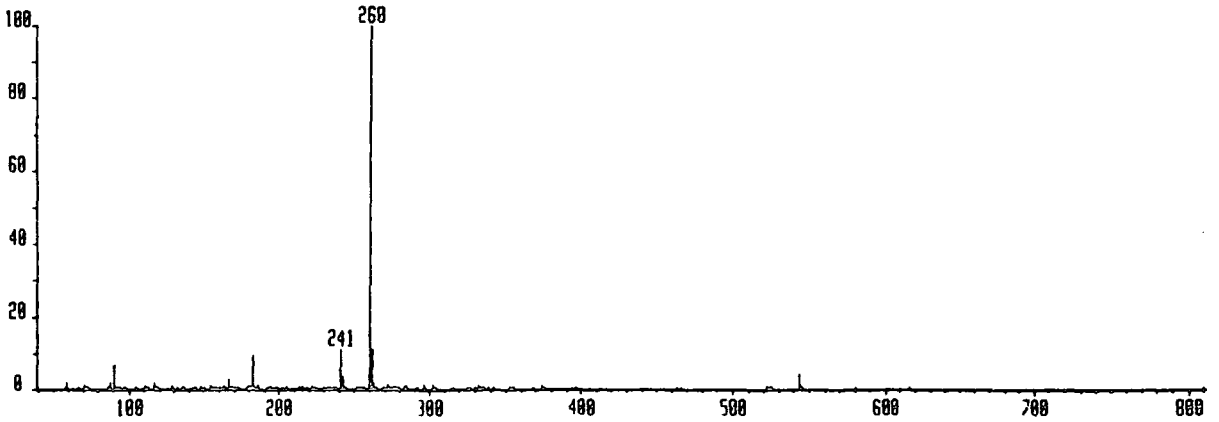
161.79	0.92	303.70	8.84
162.76	0.73	304.71	2.32
163.90	0.77	305.72	30.81
164.78	0.83	306.72	4.71
165.73	0.96	307.74	3.27
166.76	1.51	308.73	0.44
167.75	5.35	313.70	2.21
168.75	1.04	315.73	0.93
169.77	4.57	316.72	0.59
170.77	0.51	317.71	0.47
171.78	0.69	318.72	0.52
175.75	2.15	319.71	0.35
176.76	0.53	320.70	0.66
177.77	0.89	321.72	0.34
178.79	0.80	322.69	2.72
179.79	0.52	323.69	20.12
180.77	0.72	324.70	6.69
181.78	0.38	325.71	9.37
182.76	0.60	326.72	0.95
183.78	0.52	335.72	1.51
184.75	1.05	336.72	0.96
185.74	8.86	337.70	0.41
186.75	1.77	338.70	0.59
187.75	16.95	339.71	0.44
188.76	1.73	340.68	1.90 F
189.74	0.79	341.67	100.00 F
191.73	0.42	342.68	15.66
194.72	0.94	343.68	2.88
195.73	0.97	344.70	0.33
196.72	0.49	360.66	38.35
197.74	0.52	361.67	14.44
198.71	0.45	362.67	1.78
199.74	0.37	363.69	0.35
300.72	0.92		
301.72	0.42		
302.74	0.83		

## Spectrum No.12 (FB- data)

M.W.284

TH433107o x1 8gd=6 7-NOV-91 12 00:0 01:14 70C FB-  
 8pA=0 1=2.7v Ha=009 TIC=36254000 Acnt Sys: FAB  
 TAKR PT= 0° Cal: PFK140CT

HRR:  
 RASS:



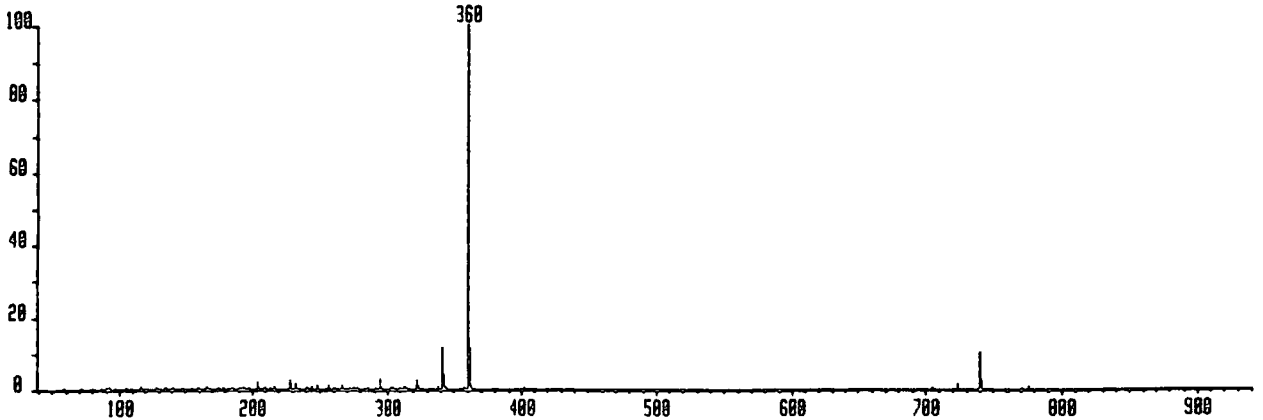
Mass	% Base
58.75	1.74
70.76	1.01
88.75	1.59
90.76	6.43
116.66	1.82
154.59	1.16
163.58	1.11
166.57	2.89
182.56	9.10
185.54	1.13
241.43	10.95
242.43	3.37
260.41	100.00
261.41	11.02
262.41	1.69
272.39	1.43
296.36	1.42
302.35	1.47
332.34	1.02
374.31	1.01
522.16	0.65
523.16	0.29
525.16	0.77
526.18	0.34
544.14	3.99

## Spectrum No.13 (FB- data)

M.W.384

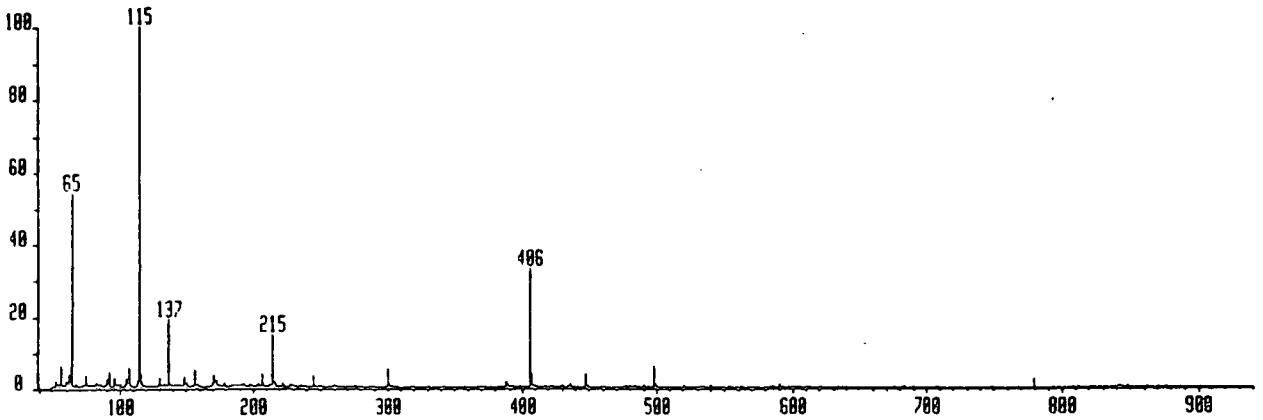
IN4332012o x1 Bgd=6 7-NOV-91 12:09:00 01:00 70E FB-  
 8pA=0 I=4.3v Ha=276 TIC=49893000 Acnt: Sys: FAB  
 TAKA PT= 0° Cal: PFK140CT

HAR: 283  
 MASS:



IN4332012o x1 Bgd=2 7-NOV-91 12:09:00 01:51 70E FB+  
 8pA=0 I=9.7v Ha=076 TIC=273531000 Acnt: Sys: FAB  
 TAKA PT= 0° Cal: PFK140CT

HAR: 635  
 MASS:



Mass	% Base
204.39	2.13
228.53	2.50
232.50	1.25
247.31	1.07
294.19	2.77
322.13	2.52
341.09	11.47
342.11	3.61
360.06	100.00 F
361.07	11.27 F
362.05	1.19
643.53	0.13
705.32	0.20
720.40	0.14
723.44	1.23
740.38	9.95 F
741.39	2.41 F
771.02	0.19
776.01	0.57

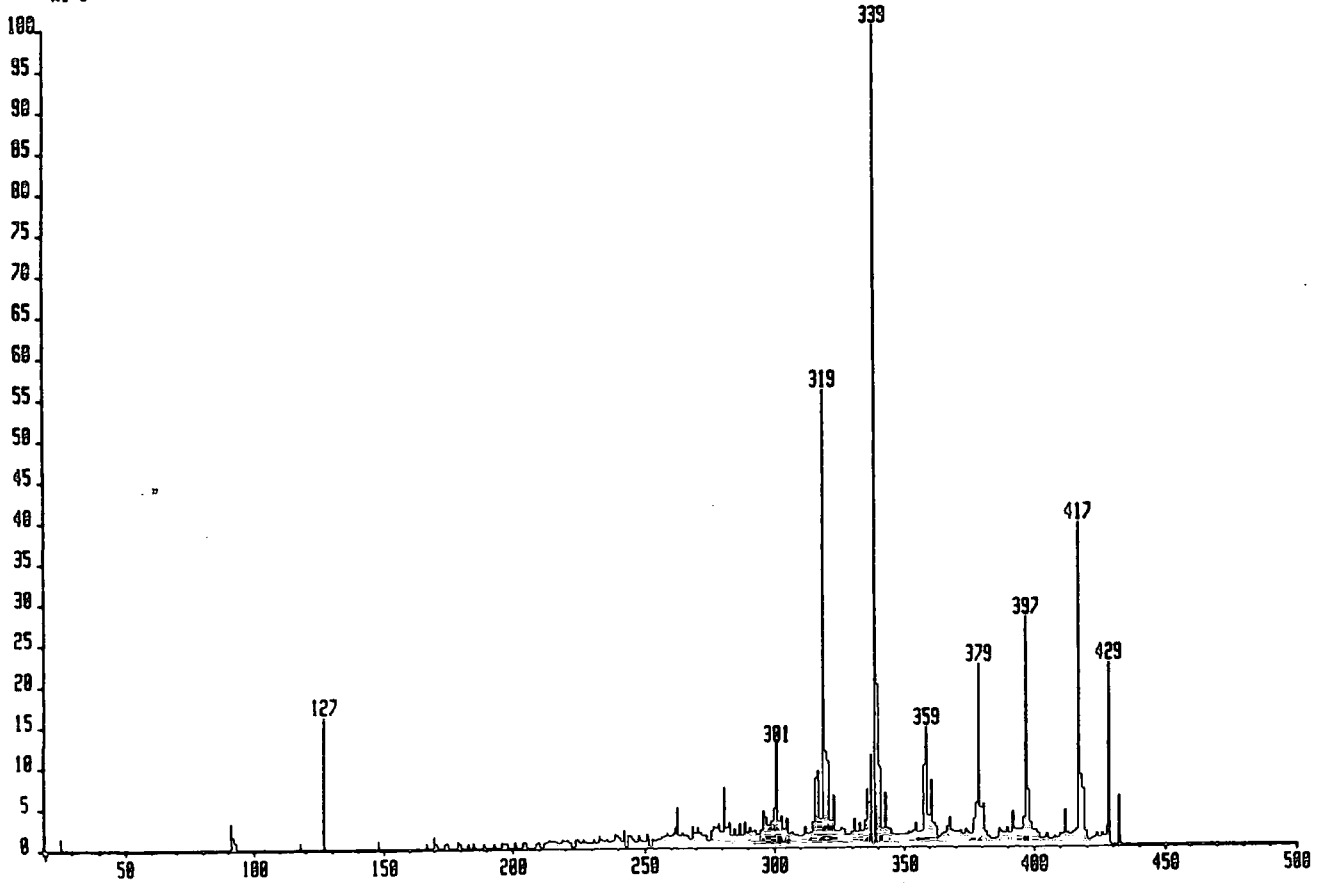
Spectrum No.14 (Cl- data)

M.W.432

TN225SR0150 x1 Bgd=14 20-NOV-90 09:59:00:01:21 70E  
 BpA=0 I=2.9v Ma=400 TIC=168440000 Acnt:  
 TAKA °H1=0

CI-  
 Sys:ACE  
 Cal:PFK26NOV  
 PT= 0°

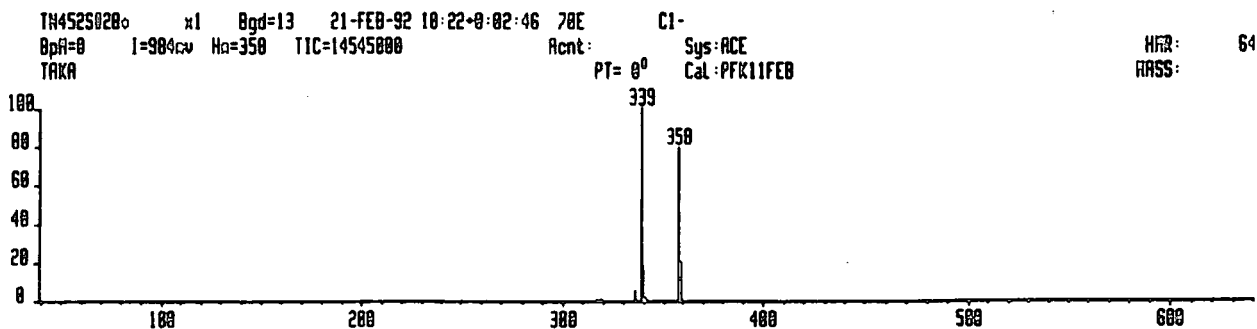
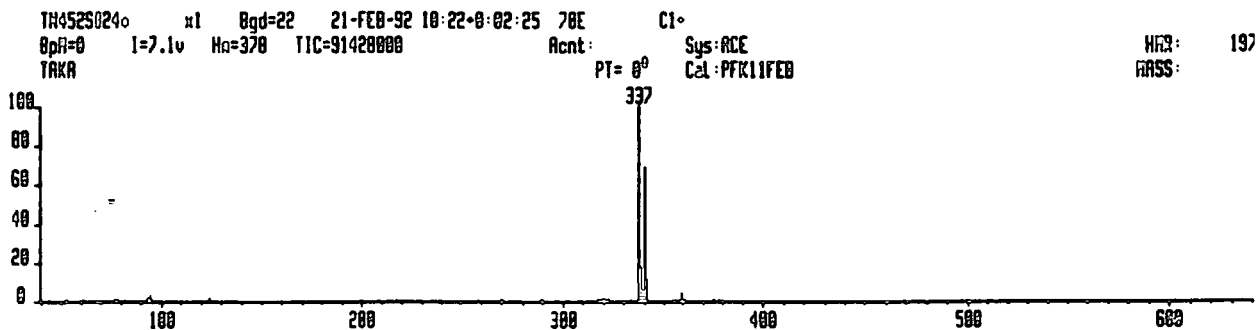
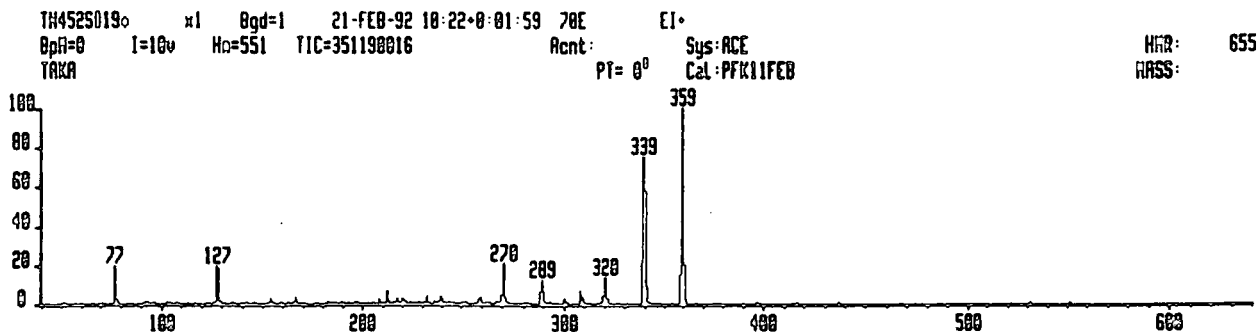
NR2: 10765  
 GRSS:



Mass	% Base
90.97	3.05
91.98	1.41
92.97	0.75
117.95	0.70
126.82	16.13
299.94	4.47
300.95	12.36
316.96	9.06
317.92	3.36
318.93	55.82
319.94	11.53
320.95	10.37
321.96	3.10
322.97	6.10
323.98	1.81
337.32	0.38
337.87	10.99 F
338.94	100.00 F
339.99	19.63
340.95	9.55
427.89	1.52
428.02	2.21
428.15	1.53
428.28	1.53
428.42	2.15
428.66	22.23
432.68	5.90

Spectrum No.15 (EI+ data)

M.W.359



Mz	% Base				
51.04	0.39	208.10	2.33	299.11	2.34
77.06	19.55	209.10	0.78	299.12	3.52
78.06	2.12	212.05	6.28	260.12	0.49
92.07	0.49	213.07	1.17	262.09	0.47
93.08	1.17	215.10	0.78	263.11	0.39
96.06	0.42	216.10	0.39	267.07	1.30
103.07	0.78	217.09	2.73	269.04	4.78 F
104.08	0.78	218.06	0.39	270.11	20.53 F
108.07	0.78	219.09	0.35	271.12	3.52 F
126.07	0.78	220.10	2.83	272.13	0.39
127.07	19.21	221.11	1.17	281.12	0.39
128.08	17.71	224.08	0.39	288.09	9.67 F
129.08	1.30	228.11	0.39	289.11	12.11 F
135.09	0.38	231.10	0.48	290.13	5.57 F
142.08	0.78	232.07	3.91	291.14	0.78
146.08	0.47	233.08	0.39	293.12	0.39
153.08	0.75	236.06	1.17	299.98	2.73 F
154.10	2.34	238.10	1.57	301.99	0.78 F
159.07	0.47	239.11	3.65	308.08	6.95 F
159.09	0.39	240.11	2.34	309.14	3.46 F
162.04	0.78	241.12	0.39	310.14	0.49
165.09	0.39	243.09	0.78	318.11	0.78 F
166.09	3.13	244.10	0.35	319.11	4.08 F
167.08	0.42	246.11	0.39	320.12	13.67 F
182.07	1.23	250.10	0.85	321.26	2.73 F
184.09	0.78	251.11	0.78	338.08	20.71 F
186.05	0.89	252.12	0.39	339.13	75.01 F
189.09	0.78			340.14	97.91 F
190.10	0.94			341.16	8.24 F
193.07	0.39			342.19	0.78 F
196.09	0.78			358.06	14.84 F
197.10	0.78			359.17	100.00 F0
205.05	0.39			360.19	19.63 F

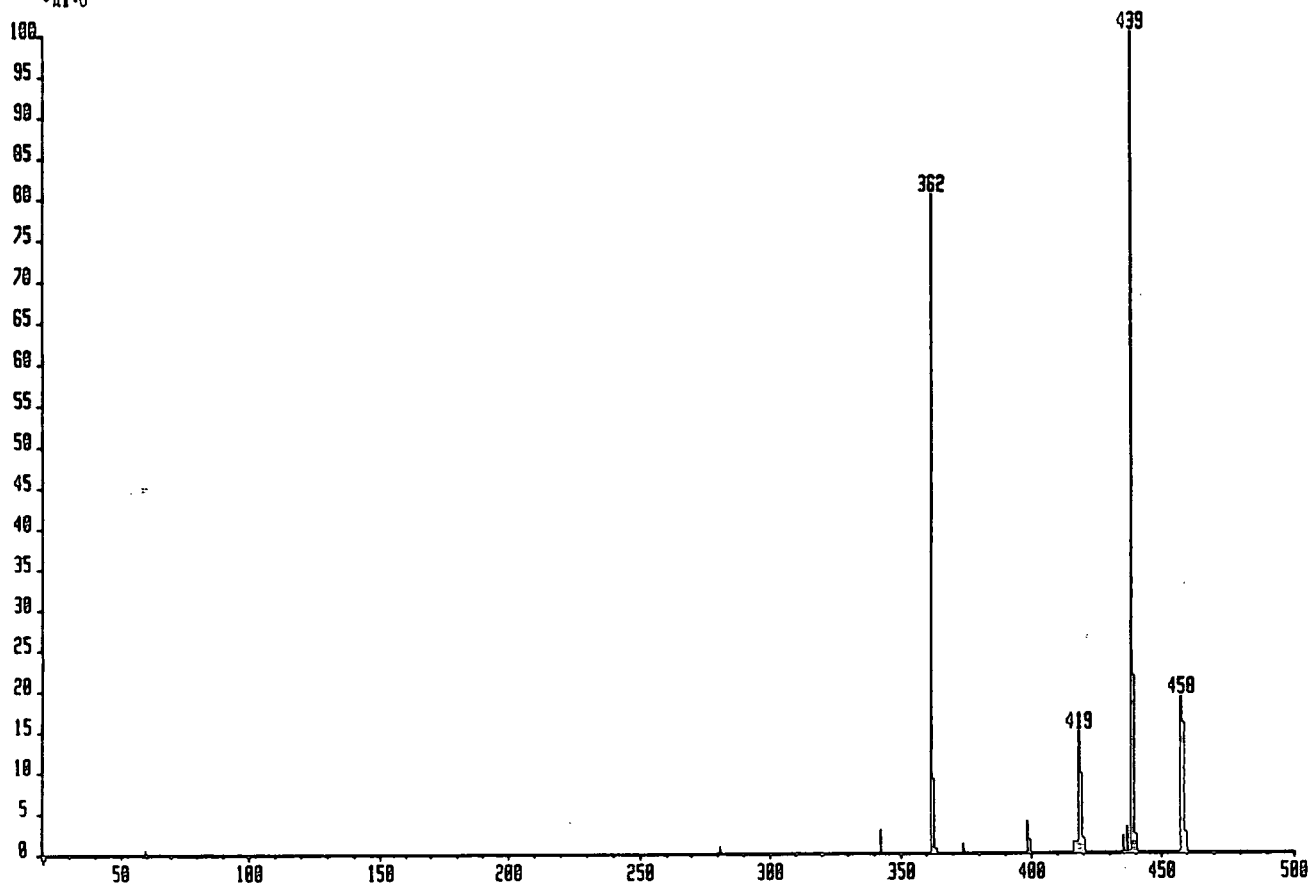


## Spectrum No.16 (Cl- data)

M.W.459

TH226SR050 x1 0gd=1 20-NOV-90 10:14:00:41 78E Cl-  
 BpA=0 I=9.9v M0=464 TIC=192964000 Acnt: Sys:ACE  
 TAKA PT= 0° Cal: PFK2040V

HMR: 64674  
 MASS:

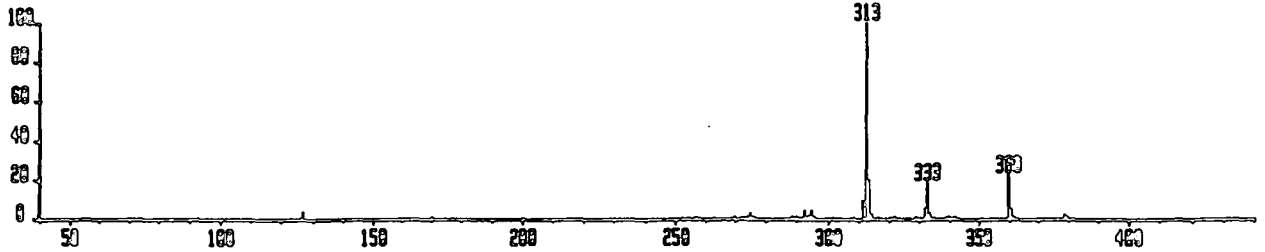


Mass	% Base
59.82	0.43
280.64	0.79
342.60	2.67
343.60	0.32
361.56	80.17 F
362.59	8.96 F
363.59	0.47
373.62	1.11
398.58	3.83 F
399.59	1.59 F
416.61	1.20
417.58	1.19
418.59	14.72 F
419.58	9.30 F
420.59	1.63 F
435.59	1.98
437.32	2.98 F
438.59	100.00 F
439.59	21.44 F
440.60	2.14 F
457.59	19.00 F
458.61	19.83 F
459.61	2.41

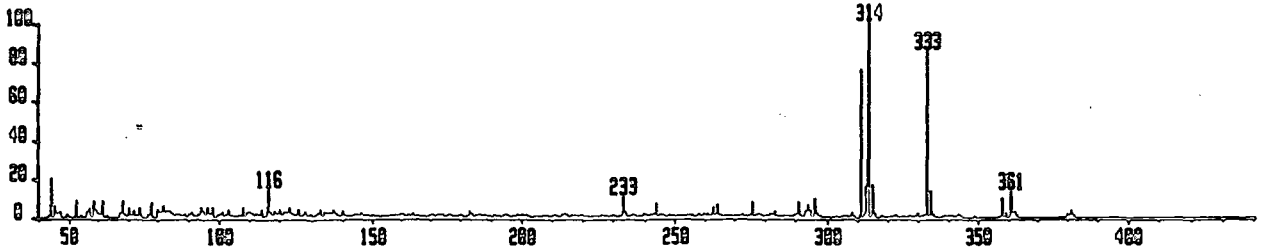
Spectrum No.17 (EI+ data)

M.W.380

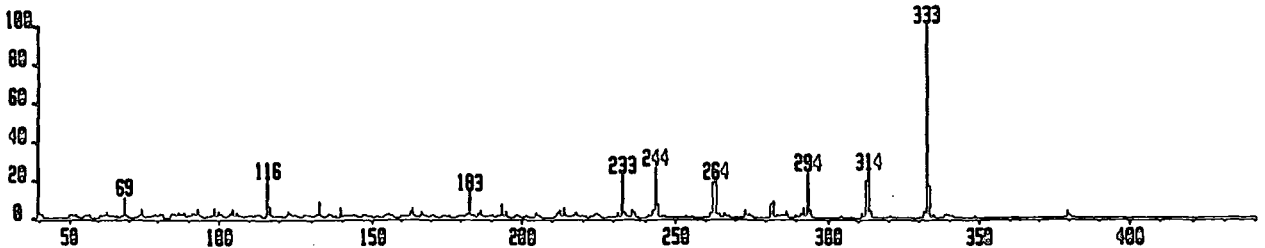
TK2033080 n1 8gd=7 21-ARR-91 14:20:01:06 70E C1-  
 0pH=0 I=10v Hc=379 TIC=136237033 Acnt: Sys:ACE HNR: 65534000  
 TAKA PT= 0° Cel: PFK19ARR MASS: 313



TK20330140 n1 8gd=11 21-ARR-91 14:20:01:30 70E C1-  
 0pH=0 I=6.7v Hc=381 TIC=373520033 Acnt: Sys:ACE HNR: 43753000  
 TAKA PT= 0° Cel: PFK19ARR MASS: 314



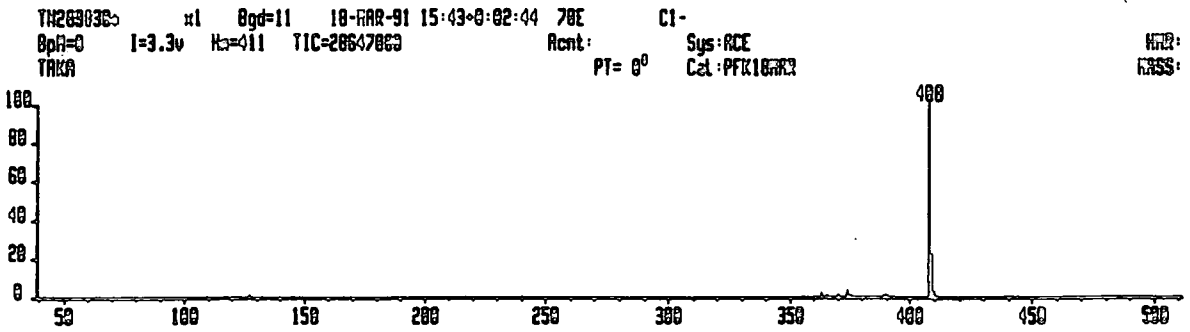
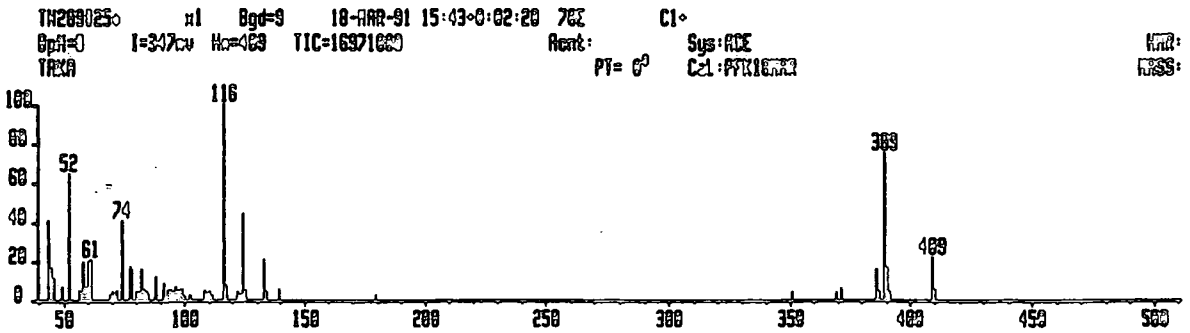
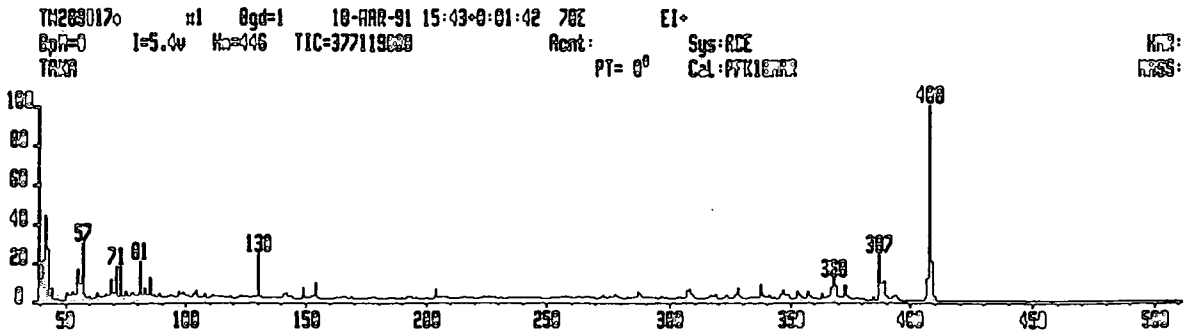
TK20330180 n1 8gd=5 21-ARR-91 14:20:01:49 70E C1-  
 0pH=0 I=7.5v Hc=380 TIC=323379033 Acnt: Sys:ACE HNR: 51445000  
 TAKA PT= 0° Cel: PFK19ARR MASS: 333



MZ	Z	8050	236.69	2.32	313.62	23.40
187.76	0.60	237.69	0.31	314.62	3.16	
189.77	0.46	241.69	1.00	320.62	0.70	
190.72	1.01	242.69	3.99	331.67	3.43	F
191.75	0.39	243.70	29.71	332.60	100.00	F
192.75	0.70	244.70	6.47	333.60	15.88	
193.76	6.88	245.70	0.39	334.60	1.00	
194.77	3.19	246.67	0.36	338.61	1.18	
195.76	0.32	248.67	0.31	339.61	1.12	
197.74	0.70	253.66	0.47	340.61	0.38	
198.73	1.19	255.68	0.86	340.63	0.91	
200.75	0.32	261.67	2.30	379.68	3.22	
201.75	0.74	262.67	18.15	380.67	0.60	
203.73	0.31	263.68	18.90			F
204.73	2.62	263.69	1.84			F
205.73	0.98	264.67	2.13			
211.73	2.92	265.68	0.31			
212.74	3.77	266.69	1.63			
213.74	5.34	267.69	0.93			
214.74	0.64	273.69	3.69			
215.71	0.42	274.69	1.67			
215.71	1.91	275.69	0.74			
217.72	2.46	281.64	7.29			
218.73	0.62	282.69	8.24			
219.72	0.94	283.69	1.00			
220.72	0.94	284.62	0.44			
222.70	0.98	288.62	1.33			
223.71	1.89	286.69	3.43			
224.72	2.46	289.68	0.74			
225.73	1.19	291.61	2.22			
231.71	2.81	292.64	5.21			
232.72	21.60	293.68	22.85			F
233.71	2.44	294.64	3.93			F
234.69	0.42	304.61	0.49			

Spectrum No.18 (EI+ data)

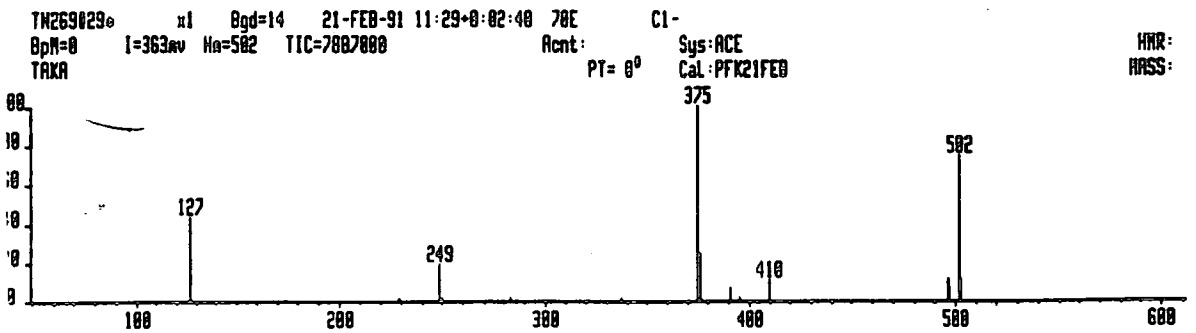
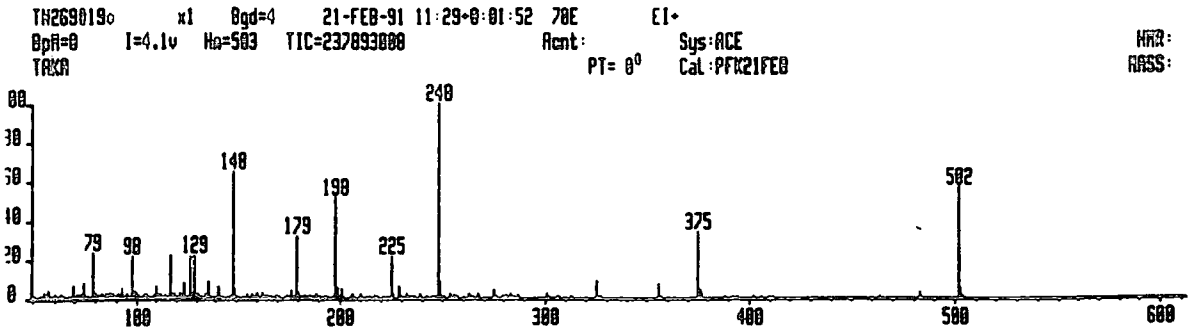
M.W.408



Mass	Z	Base	
44.00	40.41	100.00	4.79
44.99	16.08	109.00	2.99
46.02	10.99	110.00	3.96
48.03	8.29	111.01	2.24
52.05	64.78	116.00	100.00
56.01	4.35	117.01	7.04
58.03	19.39	122.02	3.91
59.03	6.60	123.00	2.73
60.01	20.14	123.99	43.71
61.00	20.76	126.00	4.66
69.00	2.91	133.01	20.84
70.02	3.74	133.99	3.91
72.03	4.22	139.01	5.23
74.01	40.90	179.00	2.86
77.02	16.97	350.91	3.87
78.01	19.30	368.90	3.74
80.00	3.78	370.91	9.72
81.00	3.96	389.92	19.92
82.01	19.70	380.90	3.87
83.00	4.80	388.90	74.89
84.01	3.78	389.90	16.14
85.01	2.60	390.92	3.60
88.01	11.43	408.87	21.90
91.02	8.09	409.89	9.06
92.99	4.44		
94.00	4.88		
95.00	4.13		
96.00	6.33		
97.01	4.18		
98.01	9.08		
99.02	4.80		
100.03	1.90		
102.02	1.72		

Spectrum No.19 (EI+ data)

M.W.502



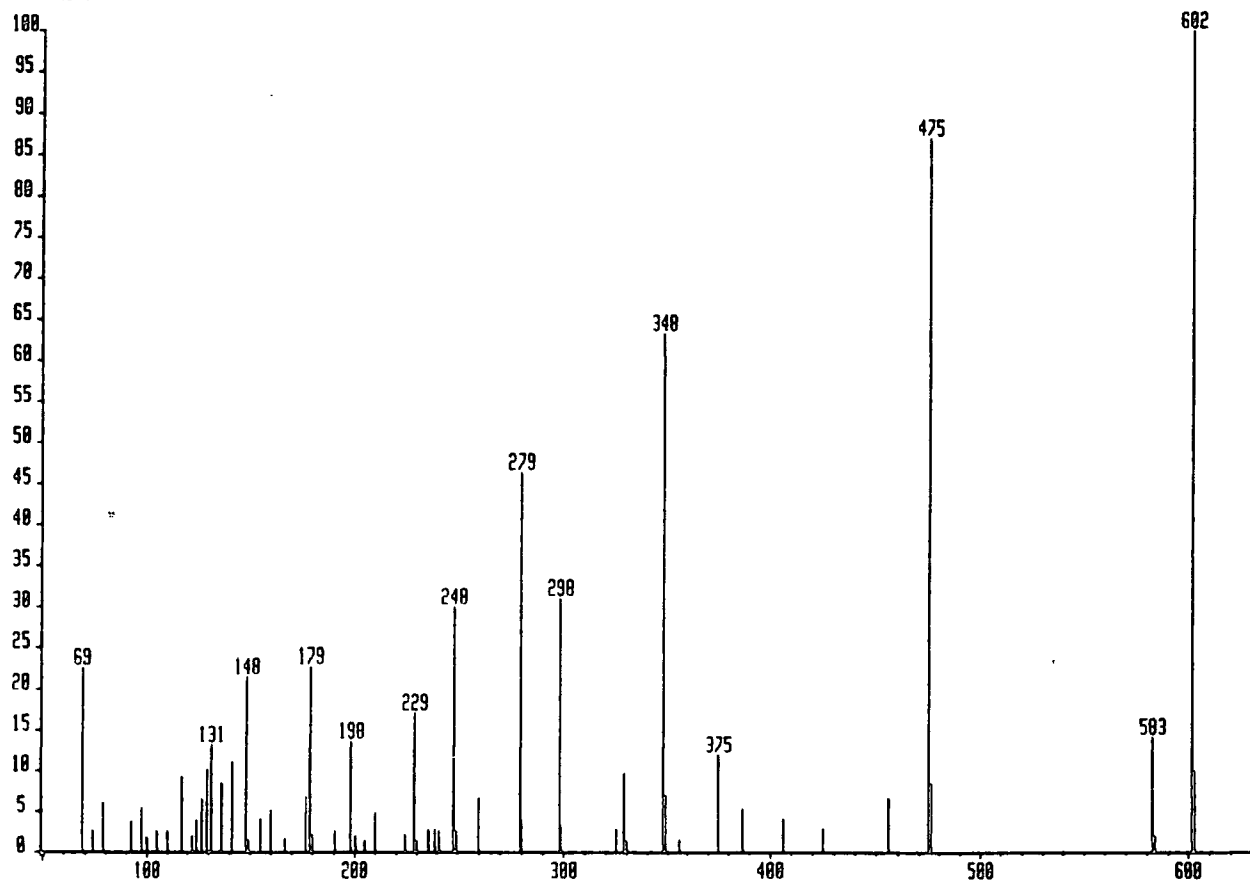
Mass	% Base	Mass	% Base
140.88	5.96	209.88	1.67
140.96	0.92	212.79	0.96
141.89	0.96	214.09	0.88
142.88	0.96	216.89	1.57
143.00	0.96	217.81	0.88
145.79	0.55	221.01	0.88
146.85	0.96	222.99	0.96
147.68	1.06 F	224.79	21.02
147.88	64.75 F	225.79	1.72
148.89	4.78	228.88	5.73
149.90	0.96	229.89	0.96
152.83	0.34	231.79	0.96
154.88	1.67	232.89	1.82
157.79	1.67	234.84	0.96
157.84	0.92	235.88	0.55
158.23	0.88	236.79	0.96
158.98	0.92	238.79	1.81
159.88	2.87	242.11	0.86
159.99	0.91	244.87	0.96
160.89	0.96	246.84	0.91
162.34	2.51	246.92	0.86
162.82	1.67	247.86	100.00
163.58	0.89	248.30	0.88
163.83	0.96	248.49	0.88
164.12	0.87	248.87	7.88
164.82	0.96	249.88	0.96
165.85	0.91	250.78	0.96
166.88	0.96	253.69	1.91
168.88	0.37	255.79	1.10
169.11	0.85	256.81	0.87
169.79	1.29	262.78	1.67
171.02	0.96	263.85	0.94
173.88	0.96	266.87	1.72
174.79	1.58	274.77	3.55 F
176.79	3.82	274.84	1.67 F
177.85	0.96	324.78	8.60
178.57	0.87	325.79	0.96
178.88	31.70	326.81	0.88
179.89	2.87	355.77	6.90
180.89	0.96	356.78	0.96
181.80	0.96	374.77	33.51
182.86	0.97	375.77	3.82
183.07	1.59	376.81	1.86
193.79	0.96	483.73	0.96
196.85	0.96	501.71	56.38
197.87	51.49	502.22	0.36
198.87	5.17 F	502.73	4.78
198.93	1.67 F	503.75	0.96

## Spectrum No.20 (EI+ data)

M.W.602

TH2440992o x1 Bgd=978 11-DEC-98 10:59:08 13:57 70E EI+  
 BpA=0 I=3.3v Ha=603 TIC=152230000 Acnt: Sys:NAKAFURA  
 FA3 0.1 ASEC GC= 168<sup>o</sup> Cal:PFK7DEC  
 \*x1=0

HAR:  
 MASS:



Mass	% Base	Mass	% Base	Mass	% Base
55.00	0.68	177.96	0.79	260.03	6.56
69.00	22.41	179.01	22.59	261.04	0.39
74.00	2.38	180.01	1.98	279.02	46.21
79.00	5.95	186.01	0.77	280.02	3.85
80.01	0.31	191.02	2.39	298.01	30.92
86.00	0.60	198.01	13.50	299.03	2.99
93.00	3.57	199.02	0.59	324.93	2.75
98.01	5.25	200.93	1.82	325.96	0.35
99.01	0.41	205.01	1.26	329.01	9.51
100.02	1.69	210.02	4.76	330.02	1.19
103.01	0.58	211.05	0.33	336.93	0.32
105.01	2.38	217.02	0.80	348.02	63.14
110.01	2.39	224.02	0.64	349.02	6.76
112.01	0.74	224.93	1.99	355.95	1.31
117.01	9.08	227.96	0.53	374.94	11.89
118.02	0.38	229.01	17.02	386.96	5.15
122.02	1.80	230.02	1.29	387.95	0.30
124.01	3.76	236.01	2.62	405.95	4.01
126.93	6.41	238.92	2.62	424.96	2.74
129.01	10.01	241.01	2.38	455.97	6.50
130.02	0.49	247.99	29.88	456.99	0.63
131.01	13.08	249.01	2.42	474.91	86.98 F
136.01	8.33	253.85	0.78	475.94	8.38 F
139.91	0.64	255.29	0.63	476.92	0.50
141.02	10.86			582.88	14.11
142.01	0.79			583.89	1.77
143.02	0.31			601.89	100.00 F
148.01	21.40			602.93	9.79 F
149.01	1.41			603.95	0.39
155.01	3.92				
160.01	4.93				
162.46	0.32				
167.01	1.44				
172.01	0.57				
174.01	0.41				
176.92	6.67				

## Spectrum No.21 (EI+ data)

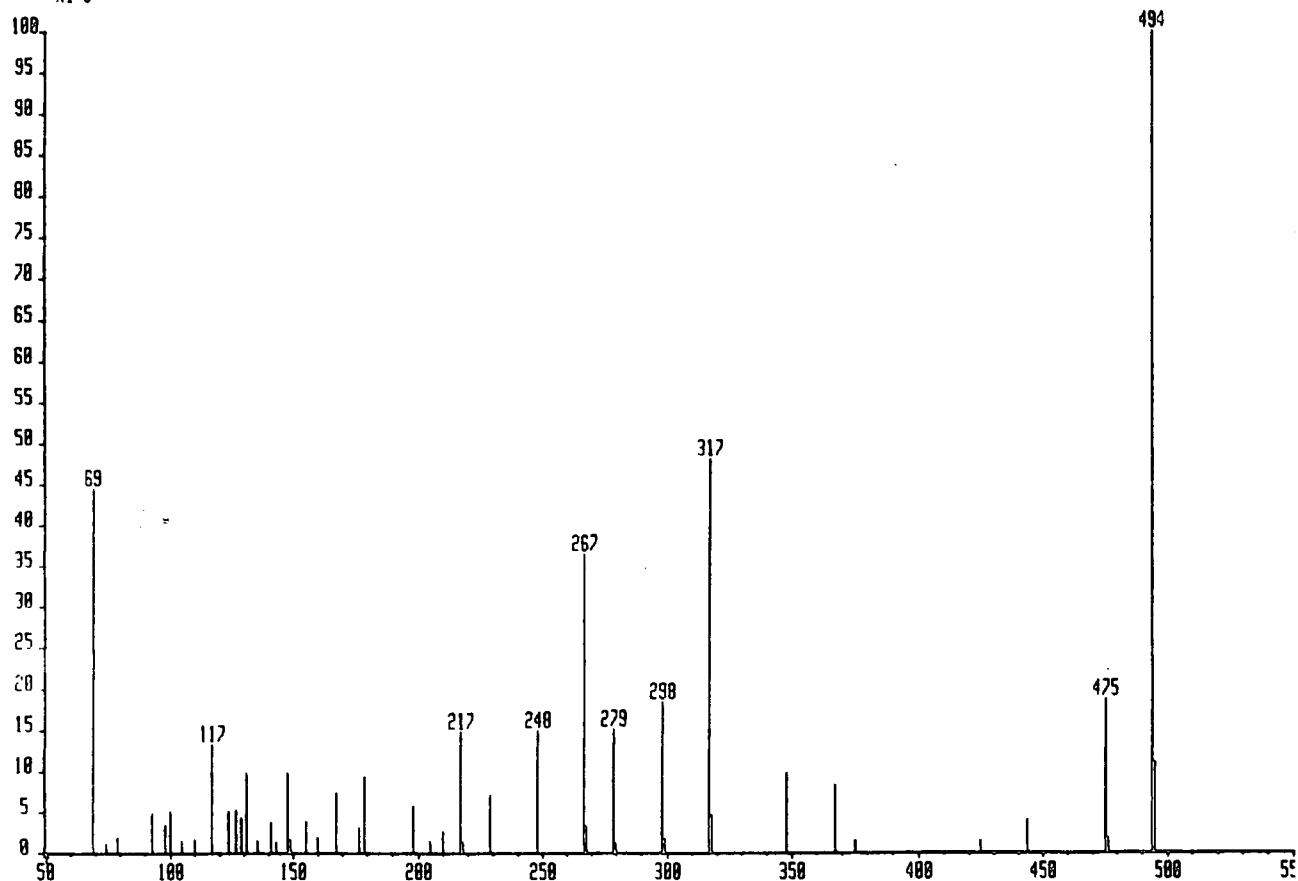
M.W.493

TH2440500o x1 Bgd=571 11-DEC-90 10:59:00:00:00 70C EI+

BpA=0 I=4.7u Ha=496 TIC=151753000 Acnt:

FA3 0.1 ASEC GC= 110° Sys:NAKAURA

\*x1.0 Cal:PFK7DEC

NRR: 385  
RASS:

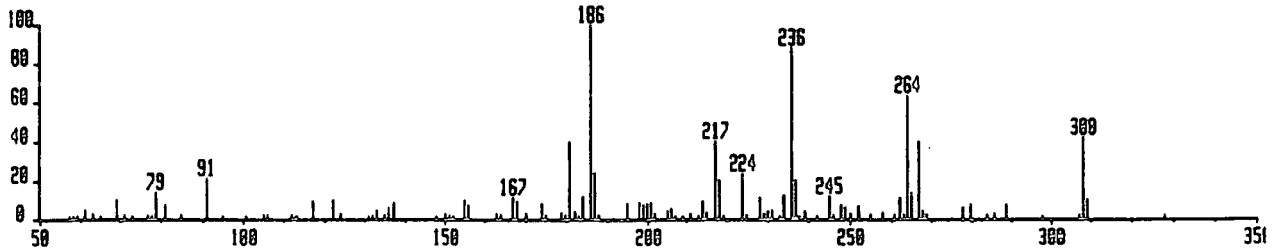
Mass	Base		
55.01	0.33	217.03	14.63
69.01	44.40	218.03	1.25
70.01	0.50	221.99	0.38
74.01	1.09	224.83	0.60
79.01	1.86	229.03	6.93
86.01	0.92	230.03	0.51
93.01	4.72	238.95	0.39
98.02	3.37	241.04	0.56
100.01	4.97	243.03	0.52
105.03	1.31	248.03	14.85
108.52	0.49	249.03	0.91
110.02	1.49	255.02	0.89
112.02	0.37	260.02	0.89
117.02	13.23	267.01	36.31
118.04	0.45	268.02	3.23
122.01	0.34	273.71	0.32
124.02	4.93	279.04	14.93
126.94	5.18	280.04	1.10
129.02	4.20	298.03	18.28
131.02	9.77	299.03	1.68
136.02	1.32	317.02	48.08
141.03	3.71	318.03	4.54
143.02	1.17	329.05	0.54
148.02	9.70	348.05	9.66
149.01	1.47	349.04	0.92
153.02	3.72	367.04	8.18
160.02	1.81	368.06	0.84
167.02	7.27	374.96	1.42
174.03	0.54	406.01	0.31
176.93	2.99	424.99	1.39
179.03	9.21	443.97	3.97
180.02	0.84	445.01	0.35
181.03	0.33	474.96	18.58
186.03	0.84	475.98	1.68
191.03	0.93	493.94	100.00 F
196.99	0.37	494.97	10.95 F
198.03	5.58	496.01	0.84
205.03	1.41		

Spectrum No.22 (EI+ data)

M.W.328

TH4560812o x1 Bgd=775 25-FEB-92 16:32:0:10:06 78E EI+  
 BpH=0 I=195uv Hn=327 TIC=12040003 Acnt: Sys:MAXAMURA  
 FA3 0.1ASEC GC= 129<sup>o</sup> Cal:PFK25FEB

HR: 121  
 MASS:



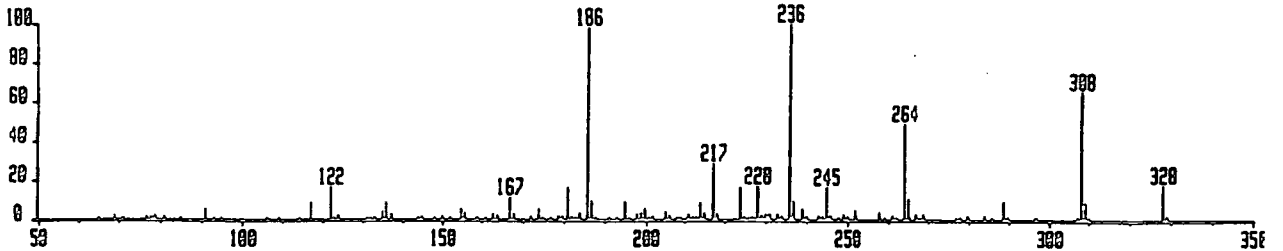
Mass	% Base	Mass	% Base
57.02	1.33	198.89	7.11
58.02	1.09	199.88	7.81
58.03	1.41	200.89	8.20
59.04	1.25	201.87	2.66
60.99	4.61	204.87	3.99
62.98	2.34	205.88	5.08
64.97	1.48	206.87	1.33
68.95	9.30	208.89	1.48
71.02	1.72	210.86	2.27
72.98	1.33	212.89	1.17
73.02	1.33	213.85	8.75
76.96	2.03	214.88	3.28
77.92	1.48	216.87	40.00
77.94	1.17	217.89	20.00
77.98	1.17	218.88	1.09
78.95	13.36	223.87	22.97
80.94	7.11	224.85	2.03
84.90	1.64	227.90	10.86
90.95	20.47	228.89	2.73
94.94	1.09	229.86	4.06
100.95	1.41	230.88	4.53
104.98	2.19	232.91	1.56
105.94	2.11	233.87	12.42
111.94	1.64	235.85	88.13
112.90	1.09	236.86	20.00
112.98	1.56	238.86	3.67
116.92	8.75	241.84	1.17
121.95	9.30	244.85	11.33
123.93	2.42	245.85	1.88
130.93	1.41	247.86	6.95
131.92	1.88	248.83	6.02
132.91	4.30	249.87	2.34
134.91	2.19	251.85	6.41
135.91	9.99	254.86	2.03
136.91	8.28	257.84	3.28
147.89	1.41	260.81	1.95
149.94	2.50	261.85	10.86
150.90	2.03	262.78	1.95
151.88	1.17	263.84	63.67
154.88	9.30	264.84	13.59
155.89	7.34	266.84	40.00
162.93	2.58	267.83	3.83
163.92	1.88	268.86	1.88
166.90	11.17	277.82	5.78
167.90	8.98	279.82	6.95
169.91	2.27	283.83	1.64
173.90	7.73	285.85	2.73
174.90	1.88	288.85	7.03
178.91	3.13	297.90	1.33
179.88	2.03	306.80	1.80
180.90	40.00	307.84	41.95
181.89	3.67	308.85	9.61
182.03	0.94	327.82	1.64
182.88	1.25		
183.88	11.48		
189.87	100.00		
186.87	23.52		
187.89	1.64		
194.86	7.97		
197.88	8.20		

Spectrum No.23 (EI+ data)

M.W.328

TH45609380 x1 Bgd=914 25-FEB-92 16:32:0:11:34 78E EI+  
 BpA=0 I=478uv Ha=320 TIC=21660000 Acnt: GC= 144° Sys:MAXAMURA  
 RA3 0.1A5EC Cal:PFK25FEB

MR: 31:  
 MASS:



Mass	% Base				
49.98	0.91	199.90	0.73	296.84	0.57
49.98	0.38	197.88	2.33	306.85	1.34
64.98	0.89	198.89	3.09	307.89	65.33
68.96	1.89	199.89	4.88	308.86	8.33
70.99	0.73	200.89	0.97	309.85	0.45
76.97	1.08	201.84	1.96	327.87	17.10
77.95	0.99	204.87	3.94	328.89	2.11
78.95	1.98	205.89	1.85		
80.95	1.05	207.93	0.70		
84.91	0.45	208.90	0.96		
90.96	5.14	210.62	0.48		
92.95	0.93	210.90	2.39		
94.94	0.97	211.91	1.21		
94.98	0.54	212.91	1.08		
105.94	0.80	213.88	8.17		
106.02	0.35	214.88	3.41		
108.96	0.51	216.89	27.91		
113.93	0.96	217.89	2.42		
116.94	8.17	223.88	16.33		
121.95	16.33	224.91	1.21		
122.96	0.64	225.88	0.77		
123.94	1.98	226.24	0.64		
130.89	0.51	226.33	0.41		
130.98	0.73	226.60	0.51		
131.93	0.41	226.87	0.70		
132.92	1.47	227.91	16.87		
134.95	3.67	228.91	1.82		
135.92	8.17	229.88	2.87		
136.93	2.52	230.89	2.62		
143.89	0.64	232.89	2.26		
143.93	0.48	233.87	1.34		
144.95	1.15	235.87	100.00		
147.91	0.64	236.88	9.19		
149.92	1.37	238.90	4.85		
152.00	0.38	239.91	1.05		
154.90	5.20	242.87	1.88		
155.91	2.90	243.89	1.15		
158.88	0.51	244.87	16.33		
158.96	0.64	245.88	1.66		
160.96	0.57	247.83	0.73		
162.92	2.26	248.87	2.87		
163.91	2.01	249.85	1.08		
166.92	10.62	251.85	4.66		
167.92	2.30	257.88	3.92		
171.91	1.37	258.91	0.73		
173.92	4.98	260.86	1.69		
174.91	0.80	261.83	0.77		
176.86	0.41	263.85	49.03		
178.93	1.63	264.86	10.21		
179.91	1.18	266.86	2.42		
180.92	16.33	267.87	0.54		
181.93	1.44	268.88	2.58		
182.91	0.96	276.89	0.51		
183.90	3.16	277.86	1.59		
185.90	97.99	279.85	2.14		
186.90	9.09	283.85	1.63		
187.88	0.61	285.89	0.48		
190.94	0.70	288.87	8.71		
192.92	0.54	289.88	0.99		
194.87	8.90	296.79	0.57		



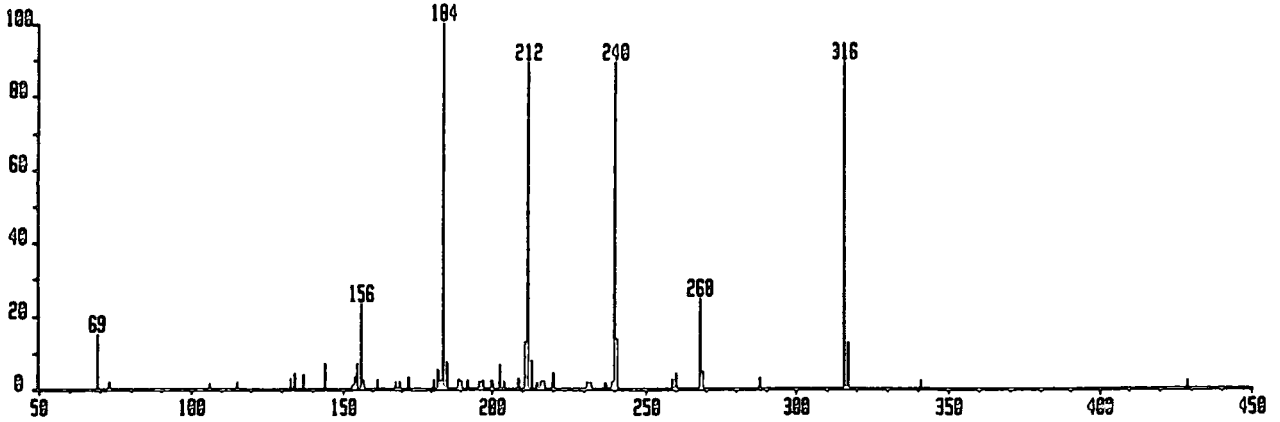
## Spectrum No.24 (EI+ data)

M.W.428

TN46001235o x1 Bgd=1056 26-FEB-92 10:24:0:15:20 70E  
 BpA=0 I=175cv Ma=428 TIC=6874803 Acnt: GC= 102°  
 FA3 0.1FSEC

[1°  
 Sys: HAKKURU  
 Cal: PFK25FEB

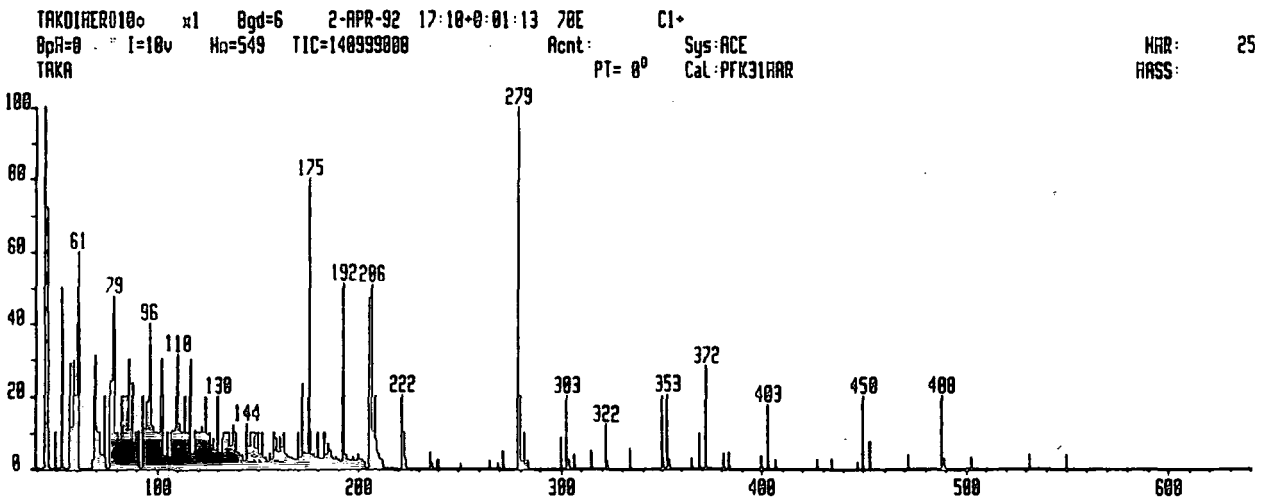
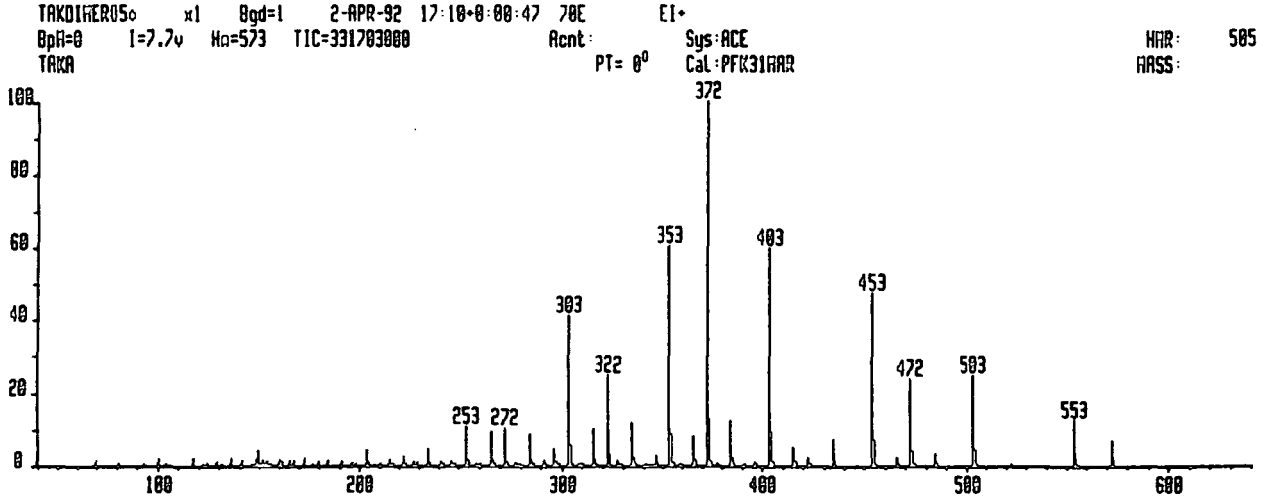
HFR: 1152  
 MASS:



m/z	% Base
68.98	14.76
73.02	1.56
109.97	1.39
106.00	1.30
115.00	1.74
132.96	2.69
133.96	4.08
136.97	3.91
143.99	6.86
152.96	1.13
153.95	3.04
154.94	6.86
155.94	23.00
156.98	2.00
161.93	2.26
167.94	1.56
169.03	1.82
171.96	2.99
180.94	2.34
181.93	5.30
182.89	2.08
183.01	2.08
183.93	100.00
184.95	7.20
188.90	2.26
189.89	1.56
191.92	2.17
195.93	1.74
196.99	2.08
200.00	2.17
202.93	6.34
203.91	1.82
208.93	2.69
210.92	12.99
211.92	88.89
212.93	7.95
214.90	1.48
215.00	1.13
215.93	1.56
216.92	1.82
219.91	4.08
230.91	1.65
231.85	1.39
232.02	1.39
237.00	1.30
238.93	1.65
239.91	88.89
240.92	13.28
258.89	2.43
259.94	4.17
267.92	24.48
268.93	4.43
287.90	2.86
315.93	88.89
316.89	12.24
340.87	1.91
428.81	1.91

Spectrum No.25 (EI+ data)

M.W.572

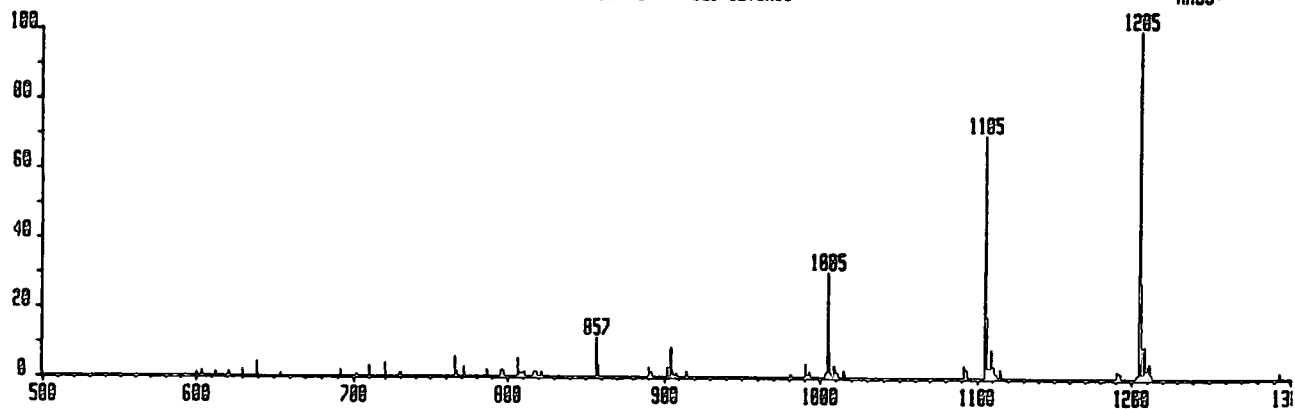


Mass	% Base								
68.98	1.48	207.94	0.09	283.94	8.59	346.94	0.52	464.97	2.03
80.98	0.63	209.95	0.51	284.95	1.53	352.93	60.37	465.98	0.51
92.98	0.51	214.95	1.50	285.95	0.20	353.94	8.39	471.97	23.68
99.97	1.79	216.96	0.51	290.92	1.52	354.95	0.54	472.98	3.66
104.00	0.18	221.95	2.53	291.92	0.24	357.98	0.09	473.99	0.51
116.97	2.03	223.01	0.51	295.94	4.57	358.74	0.20	483.98	3.07
121.97	0.51	226.95	0.88	296.95	1.01	359.99	0.15	484.98	0.60
123.97	0.55	228.95	0.70	297.94	0.23	364.94	7.95	502.98	24.55
129.00	0.87	233.95	4.32	302.93	40.97	365.95	1.39	503.99	4.23
130.96	0.51	234.95	0.62	303.94	5.42	371.91	100.00	504.99	0.51
135.96	2.22	240.95	1.15	304.95	0.51	372.94	12.52	521.99	0.51
140.96	1.54	241.95	0.21	307.93	0.18	373.95	1.01	553.00	12.23
145.97	0.19	245.94	1.01	308.40	0.09	376.95	0.51	554.01	2.10
147.96	1.55	246.96	0.51	308.62	0.08	383.95	12.44	555.02	0.17
148.99	4.20	247.95	0.51	309.02	0.17	384.95	2.06	572.01	7.00
149.99	0.51	252.94	10.63	309.86	0.27			573.01	1.25
151.46	1.30	253.95	1.52	314.94	9.94	389.95	0.22		
151.96	0.15	257.95	0.51	315.95	1.52	390.95	0.19		
152.96	1.13	258.94	0.14	316.94	0.15	395.95	1.01		
154.96	0.51	259.95	0.51	319.95	0.15	396.96	0.51		
159.00	0.09	264.94	9.34	321.93	24.78	402.94	59.73		
159.96	1.40	265.95	1.52	322.95	3.04	403.32	0.07		
160.96	1.01	266.95	0.23	326.94	0.16	403.95	9.12		
164.96	1.54	271.95	10.17	327.94	1.52	404.96	0.88		
166.96	1.50	272.94	1.13	328.94	0.51	414.95	4.77		
171.96	2.01	273.96		333.94	11.66	415.96	1.01		
176.46	0.51	276.93	0.11	334.62	0.07	421.95	2.18		
178.96	1.18	277.11	0.60	334.94	0.07	422.96	0.51		
183.96	1.52	277.40	0.07	335.96	2.11	433.96	7.17		
189.96	1.01	277.40	0.07	335.96	0.19	434.97	1.21		
195.96	0.61	277.98	0.08	340.94	0.51	446.01	0.16		
197.96	0.49	278.00	0.51	341.97	0.14	452.96	47.28		
202.95	4.20	278.83	0.51	342.99	0.11	453.97	8.55		
203.96	0.58	279.24	0.08	344.32	0.16	454.98	0.51		

## Spectrum No.26 (Cl- data)

TH145R0230 ml Bgd=17 8-AUG-98 11:45:00:58 78E Cl-  
 SpA=0 I=1.0v Ma=1314 TIC=35387888 Acnt: Sys:ACE2000  
 TRKA PT= 0° Cat:ULTRUG

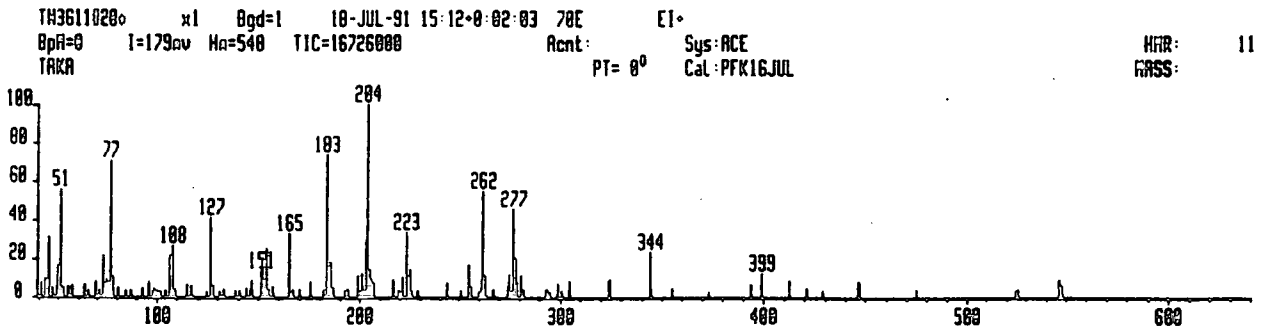
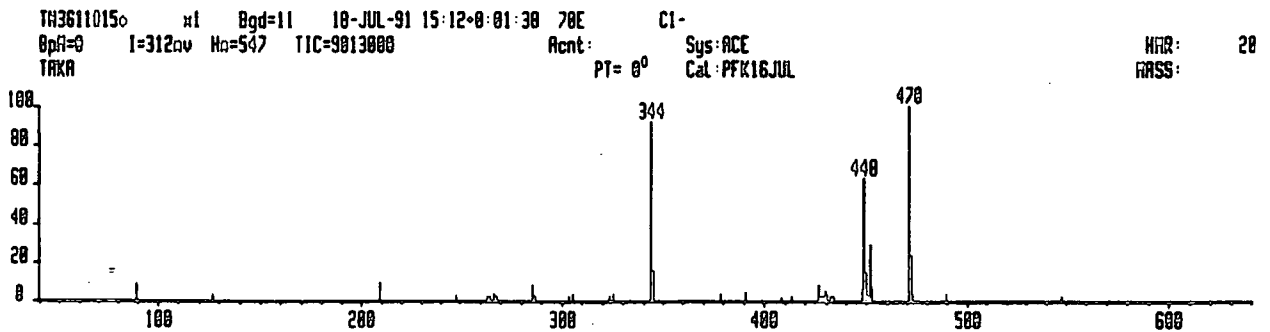
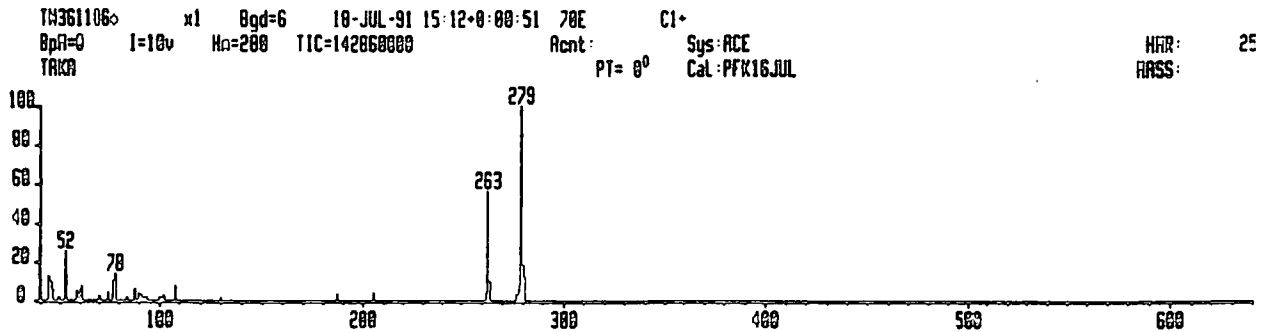
MAR: 66  
 MASS:



Mass	% Base	Retention Time (min)	Relative Intensity (%)
599.30	0.70	1115.04	2.00
603.19	1.57	1191.02	1.85
612.53	0.94	1193.01	1.91
620.24	1.24	1203.87	0.70
629.48	1.66	1205.02	100.00 F
638.67	3.87	1206.21	27.14 F
639.44	0.61	1208.07	0.88
694.19	0.69	1209.02	8.85
691.97	1.91	1210.04	2.30
701.76	0.36	1211.03	3.35
710.18	2.90	1212.07	3.86
720.30	3.72	1212.99	0.54
729.51	0.81	1213.17	0.72
730.40	0.70	1293.06	1.33
765.41	5.47		
766.24	1.03		
771.22	2.48		
786.43	1.66		
795.73	1.36		
796.67	1.88		
797.60	0.94		
808.89	9.17		
807.81	0.87		
808.78	0.75		
810.57	1.23		
817.09	0.91		
818.04	1.21		
821.63	0.34		
821.79	0.91		
888.90	10.95		
887.82	3.24		
890.08	2.47		
892.12	0.96		
902.22	2.53		
904.26	8.08		
905.24	1.34		
908.27	0.88		
914.37	1.37		
981.13	0.79		
981.07	3.74		
982.15	0.46		
993.07	1.97		
1003.09	1.17		
1005.04	29.90		
1006.03	7.19		
1007.06	0.97		
1008.98	3.23		
1010.00	1.17		
1011.03	1.15		
1015.04	1.87		
1091.01	3.14		
1092.04	0.78		
1093.00	2.00		
1104.99	69.96 F		
1105.97	17.01 F		
1106.98	2.60		
1108.93	7.92		
1109.94	1.95		
1110.91	2.76		
1112.02	0.60		

Spectrum No.27 (EI+ data)

M.W.548



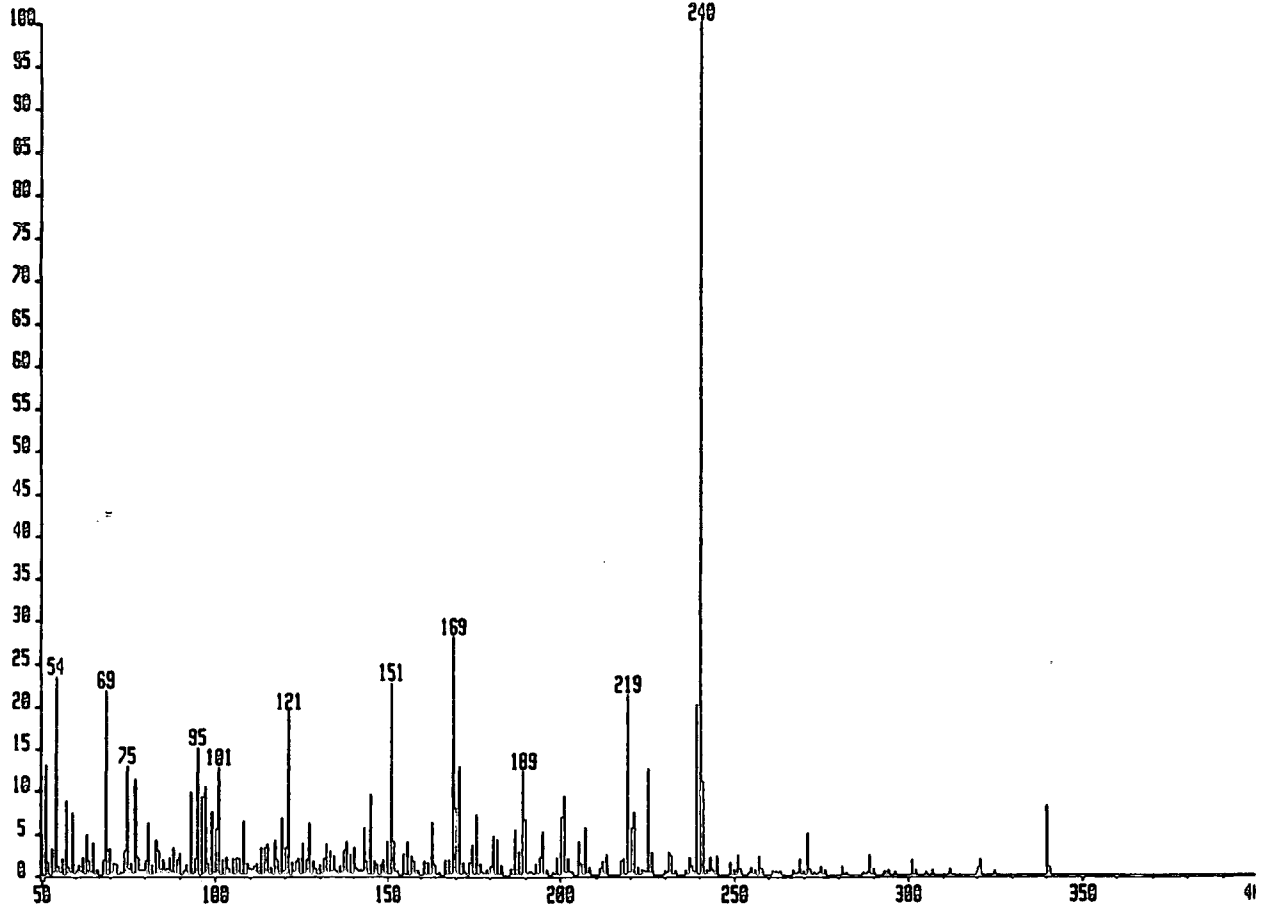
Mass	% Base	Mass	% Base	Mass	% Base	Mass	% Base
41.02	6.88	115.03	6.20	206.00	9.18	345.02	3.91
43.01	8.92	116.97	5.78	207.00	6.97	355.05	4.33
43.98	9.26	124.99	2.38	216.96	8.67	373.09	2.63
45.01	30.84	126.99	41.12	219.00	2.89	393.99	6.20
46.96	4.50	128.02	5.99	220.02	2.72	399.02	12.06
48.99	5.44	130.97	2.80	221.04	10.03	412.99	8.50
49.99	16.14	132.99	4.16	223.01	33.22	421.04	4.33
51.00	55.90	139.02	3.40	224.00	10.98	429.07	2.97
52.01	4.42	141.03	3.06	225.01	13.93	446.15	7.82
55.03	9.10	144.00	4.76	226.03	2.97	447.10	7.90
56.98	3.65	145.98	4.23	229.00	3.31	475.08	3.97
57.05	9.52	147.03	8.07	244.00	7.22	525.09	3.23
63.01	6.63	151.01	13.51	251.02	3.14	526.10	4.08
65.02	3.14	152.02	18.78	254.99	16.65	547.10	9.26
68.97	7.73	153.03	9.18	256.00	4.84	548.10	5.69
69.05	3.82	154.04	24.89	260.04	2.80		
71.07	3.23	155.02	4.08	261.05	8.92		
73.02	20.90	156.99	4.84	262.06	55.14		
74.00	6.80	164.98	32.46	263.06	10.96		
74.99	9.01	166.01	2.72	266.98	3.91		
76.01	7.05	166.97	3.65	274.00	5.35		
77.01	70.39	170.00	3.65	275.00	11.81		
78.02	10.45	175.01	7.56	276.03	2.97		
80.97	4.42	182.00	3.74	277.05	45.71		
84.99	3.40	183.00	73.49	278.05	19.63		
87.00	3.48	184.01	15.55	279.06	7.73		
92.97	4.76	185.02	17.67	281.04	10.62		
96.01	7.56	186.00	4.42	282.04	3.65		
97.99	2.38	192.99	3.48	293.00	3.91		
98.98	3.57	194.00	4.16	294.01	3.82		
99.97	2.97	199.00	10.71	295.06	2.38		
100.99	2.80	200.00	3.06	299.03	6.88		
102.02	2.95	201.01	12.49	301.04	3.14		
104.99	3.14	202.02	5.27	304.99	8.16		
106.97	20.99	203.01	28.63	323.98	8.07		
107.98	26.00	204.02	100.00	325.00	8.67		
108.99	3.65	205.02	14.10	344.00	23.02		

Spectrum No.28 (EI+ data)

M.W.342

TN34120700 x1 8gd=700 23-MAY-91 12:31:09:46 70C EI+  
 BpA=0 I=913uv No=341 TIC=50136000 Acnt: Sys: NAKAFUDA  
 FA3 0.1ASEC GC= 125° Cal: PFKRAY21  
 \*x1.0

HR: 5  
 MASS:



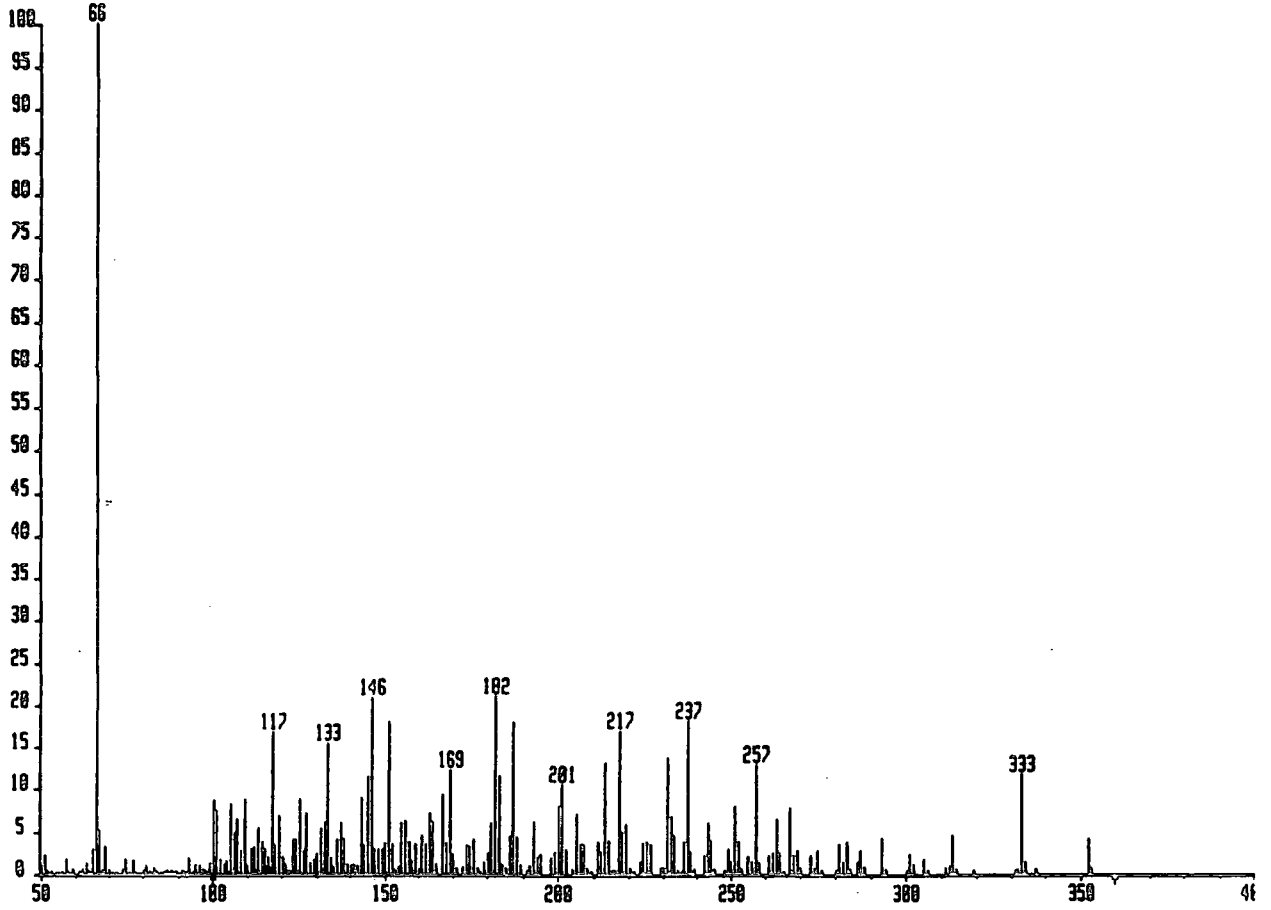
m/z	Relative Intensity (%)	Other Data
49.04	0.32	144.10
50.04	4.46	145.11
51.04	12.99	146.12
92.07	1.49	147.13
93.07	3.11	148.09
93.92	0.32	149.10
94.08	23.37	190.09
115.11	3.66	191.12
116.09	0.84	192.13
117.07	4.13	169.13
118.09	1.82	167.09
119.09	6.73	168.12
120.11	3.17	169.12
121.11	19.33	170.13
122.11	1.45	171.14
123.08	1.59	172.14
124.08	1.89	173.12
125.10	3.69	174.11
126.10	1.82	175.12
127.12	6.18	176.13
128.12	1.65	177.13
129.09	0.80	179.12
130.09	1.24	180.12
131.09	1.92	181.10
132.10	3.67	182.13
133.12	2.79	183.14
134.12	2.19	186.10
135.10	0.48	187.12
136.08	1.07	188.14
137.09	2.99	189.14
138.11	3.96	217.12
139.12	2.32	218.13
140.13	3.27	219.13
141.11	0.68	219.65
142.09	0.58	220.15
143.09	5.61	221.16
	1.62	237.56
	9.54	238.19
	1.97	238.50
	1.22	239.15
	1.12	240.16
	1.70	241.17
	3.91	242.19
	22.97	243.14
	3.89	244.17
	0.32	245.15
	1.77	249.16
	1.72	222.16
	28.01	223.12
	7.90	224.14
	12.88	225.13
	1.49	226.14
	0.35	230.15
	1.40	231.15
	3.94	232.15
	7.12	233.19
	1.27	236.13
	0.92	237.14
	1.09	290.16
	4.74	291.17
	4.24	292.18
	1.24	294.14
	0.79	299.19
	5.41	296.17
	2.77	297.16
	12.21	298.19
	1.99	291.17
	1.84	262.19
	21.30	263.19
	0.30	267.13
	9.60	268.17
	7.43	269.17
	0.32	270.17
	0.99	271.18
	0.30	272.19
	20.13	274.15
	100.00	279.15
	10.89	276.17
	0.62	281.17
	2.04	282.19
	0.98	289.18
	2.19	290.19
	1.44	293.18
	0.92	294.14
	0.63	296.23
	0.47	301.18
	12.91	302.20
	2.86	307.19
	0.47	312.19
	2.64	320.19
	2.19	321.20
	0.43	329.19
	0.92	340.20
	2.02	341.21
	0.92	0.92

Spectrum No.29 (EI+ data)

M.W.352

TN34110856 x1 Bgd=839 23-MAY-91 11:51:0:10:36 70E EI+  
 BpA=0 I=7.1u Mo=353 TIC=98876000 Acnt: Sys:MARKAREA  
 PA3 0.1A5EC GC= 134° Cal:PFKRAY21

HAR: 46  
 MASS: H10.0°



MASS	Z	BASE	MASS	Z	BASE	MASS	Z	BASE
50.05	0.96	101.11	0.74	164.16	0.61	244.20	0.39	
51.06	2.14	105.09	0.81	167.12	0.93	251.20	0.79	
53.08	0.39	106.10	0.49	168.13	0.37	252.21	0.38	
56.05	0.32	107.11	0.64	169.15	1.22	257.20	1.28	
57.06	1.79	109.12	0.88	174.13	0.33	263.21	0.64	
59.08	0.63	112.09	0.32	175.15	0.32	267.17	0.78	
62.07	0.59	113.10	0.53	176.15	0.41	281.20	0.34	
63.07	1.36	114.12	0.38	181.14	0.60	283.22	0.38	
64.09	0.39	117.09	1.67	182.16	2.10	293.21	0.42	
65.09	2.95	118.10	0.34	183.17	1.15	313.23	0.45	
66.10	100.00	119.11	0.68	188.13	0.48	333.25	1.17	
67.10	5.06	123.11	0.41	187.15	1.79	352.25	0.41	
68.07	0.39	124.10	0.40	188.16	0.44			
69.05	3.28	125.13	0.87	193.15	0.61			
70.07	0.50	127.14	0.72	200.14	0.80			
74.06	0.64	131.11	0.54	201.15	1.06			
75.07	1.81	132.13	0.62	205.14	0.70			
77.08	1.60	133.14	1.54	206.16	0.35			
80.07	0.49	136.10	0.41	207.17	0.36			
81.07	1.06	137.12	0.59	211.16	0.39			
83.09	0.71	138.14	0.41	213.18	1.32			
84.10	0.33	143.11	0.89	214.18	0.40			
86.07	0.33	144.14	0.34	217.14	1.70			
87.09	0.49	149.14	1.14	218.15	0.50			
88.09	0.47	146.14	2.08	219.17	0.59			
91.09	0.46	150.13	0.36	224.18	0.36			
92.09	0.34	151.15	1.79	225.19	0.38			
93.08	1.94	152.15	0.35	226.18	0.35			
94.09	0.33	155.11	0.60	231.19	1.37			
95.10	1.11	156.13	0.62	232.19	0.67			
96.12	0.98	157.14	0.38	233.21	0.46			
97.13	0.62	159.16	0.34	236.16	0.37			
98.09	0.36	161.13	0.45	237.18	1.81			
99.09	1.35	162.14	0.36	243.18	0.59			
100.09	0.86	163.14	0.71					

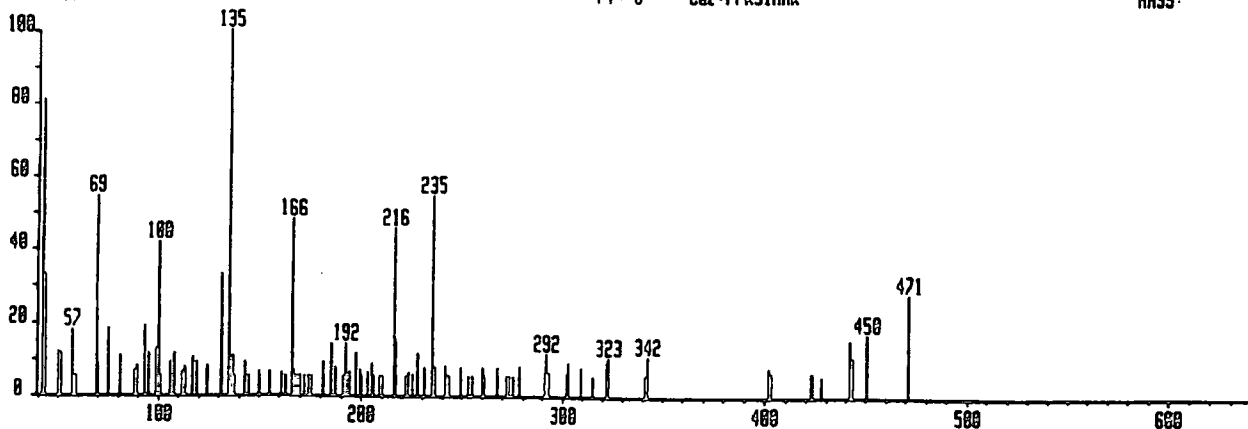


Spectrum No.31 (EI+ data)

M.W.470

TN449P035o x1 Bgd=34 0-APR-92 16:16:0 03:23 78E [I+  
 BpA=0 I=3.1v Mn=601 TIC=391132000 Acnt: Sys:ACE  
 TAKA PT= 0° Cal:PFK31ARR

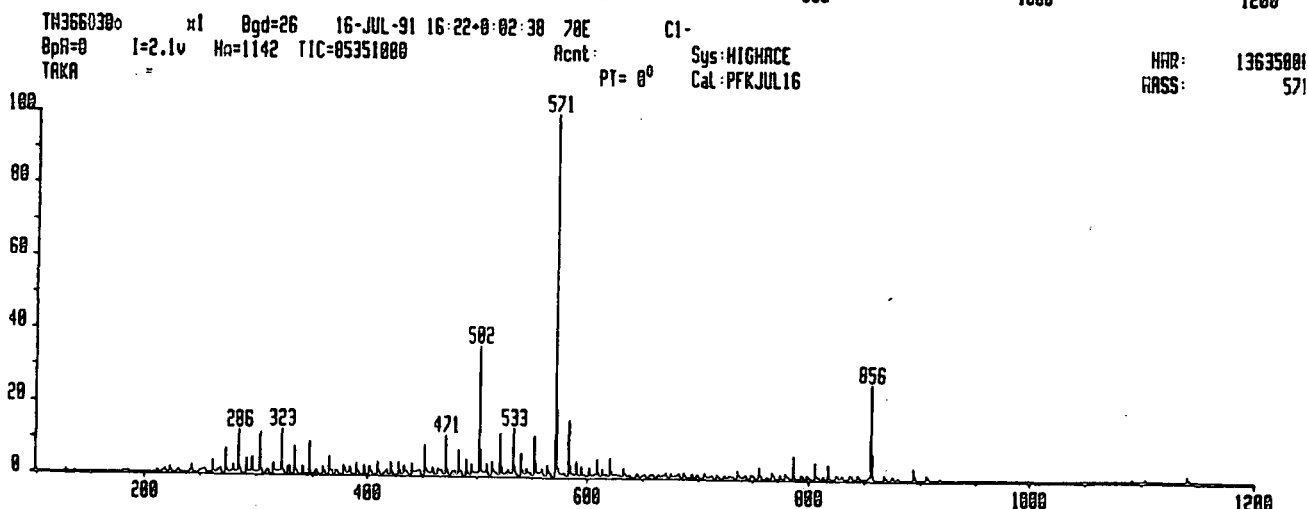
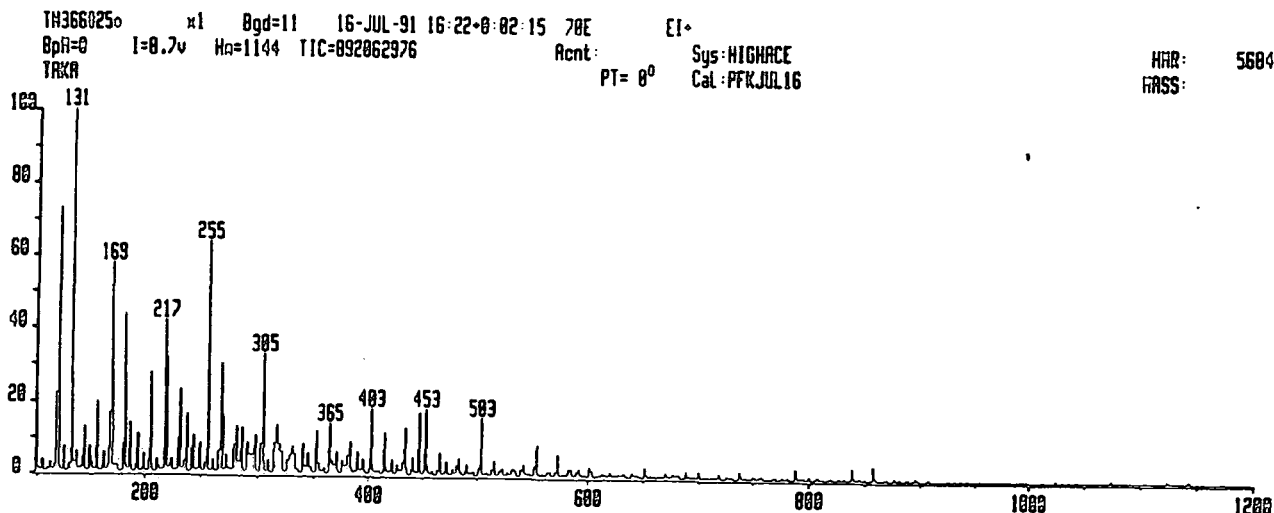
HAR: 202200  
 HASS: 13



Mass	% Base		
42.01	80.79	216.00	45.67
43.02	32.91	217.00	15.19
49.99	11.53	222.01	5.06
51.00	11.33	223.01	6.33
57.01	17.72	225.01	5.47
58.01	5.07	228.01	11.46
59.03	5.06	231.01	7.59
69.99	54.43	235.00	54.43 F
70.00	8.56	236.01	7.64 F
75.00	18.14	241.02	7.95
80.99	10.71	242.02	5.46
88.00	6.41	243.01	5.06
89.01	7.84	249.02	7.60
92.98	18.99	253.02	5.06 F
95.00	11.39	255.01	5.06
98.99	12.66	260.03	7.60
99.98	41.77	261.02	5.06
101.00	5.06	267.00	7.59
105.99	8.86	272.04	5.06
106.99	5.06	273.04	5.06
107.99	11.41	278.02	5.06
111.99	6.33	278.03	7.93
112.99	7.59	291.03	6.33 F
116.99	10.13	292.05	11.39 F
118.99	8.87	293.04	6.33
123.98	8.01	302.02	5.87 F
130.98	32.91	303.04	8.86 F
135.00	100.00	309.04	7.59
136.00	8.86	315.04	5.06
136.99	10.78	322.04	9.32 F
137.99	5.27	323.06	10.28 F
142.98	8.86	341.05	5.37 F
145.01	5.21	342.05	10.66 F
149.99	6.33	401.54	7.59 F
154.98	6.33	403.06	6.33 F
160.99	5.60	422.28	6.33 F
163.00	5.12	423.30	6.33 F
166.00	48.10	427.88	5.22 F
166.99	6.76	442.14	15.21 F
167.98	5.07	443.26	10.13 F
168.99	5.06	480.10	16.78 F
170.00	5.62	471.19	27.86 F
172.01	5.06		
173.99	5.06		
175.00	5.06		
180.99	9.04		
185.00	13.92		
186.99	7.59		
191.01	5.06		
192.01	13.92		
193.00	5.60		
194.00	6.33		
197.00	11.36		
198.99	6.69		
199.99	5.06		
203.01	6.33		
204.99	8.72		
208.00	5.06		
209.00	5.06		



# Spectrum No.32 (CI- data)



Mass	% Base											
96.64	2.11	F	210.03	3.29	303.00	7.25	430.96	3.61	1081.45	0.10		
97.68	2.42		212.02	2.01	304.98	31.15	F 433.91	11.22	1086.49	0.07		
99.68	22.41		217.02	39.26	305.99	2.81	F 434.95	2.12	1093.93	0.16		
104.76	3.32		218.04	3.33	309.97	3.22	F 440.95	4.28	1112.73	0.09		
111.85	2.65		219.02	33.44	314.99	7.97	446.05	17.29	F 1124.56	0.40		
114.95	2.15		222.03	2.29	316.99	12.07	447.11	5.67	F 1125.93	0.13		
116.92	20.22		224.03	3.84	318.98	8.54	452.90	15.86	F 1143.98	0.49		
118.94	79.08		229.03	8.98	321.99	5.48	453.96	2.73	F 1144.94	0.16		
123.99	6.88		231.02	23.53	326.99	3.30	464.97	5.45	1162.89	0.11		
129.04	2.40		234.03	2.39	328.99	4.85	471.98	3.65	1183.04	0.13		
131.04	100.00	0	236.02	15.58	330.98	7.68	480.93	2.93				
132.04	3.67		237.03	2.63	333.99	4.80	483.93	4.27				
136.04	5.12		241.02	6.39	340.99	7.24	490.93	2.82				
141.07	3.38		243.01	10.31	342.98	2.47	502.87	13.90	F			
143.03	11.80		248.01	6.94	345.99	5.19	503.95	2.36	F			
148.03	5.86		253.01	2.68	352.99	10.72	514.99	3.97				
149.06	4.06		255.00	60.30	F 354.99	2.78	540.93	3.14				
150.03	2.72		256.01	4.65	364.96	12.45	550.93	2.20				
155.03	17.70		260.03	3.92	365.99	2.06	552.92	7.38	F			
162.03	5.59		265.02	5.75	366.98	3.15	571.92	5.79	F			
167.03	12.45		267.00	27.20	368.98	2.75	600.89	2.52				
168.07	2.68	F	268.02	2.96	371.97	5.60	650.88	2.50				
169.03	70.03	F	269.01	15.88	376.98	3.34	780.88	2.60				
170.04	2.42		272.01	4.35	378.96	2.57	838.93	2.94	F			
179.04	7.12		279.01	7.18	380.97	5.04	857.90	3.65	F			
181.03	45.82		281.00	13.60	383.97	7.96	1005.66	0.10				
182.04	2.13		284.01	3.24	390.96	5.50	1012.71	0.10				
186.03	13.32				393.97	3.97	1024.68	0.21				
193.03	10.91		286.00	11.76	F 402.93	15.92	1025.66	0.09				
198.03	4.95		291.00	7.82	403.97	2.39	1030.69	0.13				
203.04	2.64		293.00	5.83	414.96	10.57	1036.61	0.15				
205.03	29.40		298.01	4.53	F 421.96	3.73	1043.98	0.11				
206.03	2.11		297.99	9.89	F 426.95	2.48	1074.46	0.30				
							1075.47	0.12				

## Appendix Four

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

- (1) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;
- (2) lectures organised by Durham University Chemical Society;
- (3) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out;
- (4) details of the postgraduate induction course.

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS.

April 1989 - March 1992

(Those attended are marked \*)

- |         |  |
|---------|--|
| 20.4.89 | Dr. M. Casey (Salford University)<br><i>Sulphoxides in Stereoselective Synthesis</i>                                 |
| 27.4.89 | Dr. D. Crich (University College, London)<br><i>Some Novel Uses of Free Radicals in Organic Synthesis</i>            |
| 3.5.89  | Dr. P. C. B. Page.(University of Liverpool)<br><i>Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides</i> |
| 10.5.89 | Prof. P. B. Well (Hull University)<br><i>Catalyst Characterisation and Activity</i>                                  |

- 11.5.89 Dr. J. Frey (Southampton University)  
*Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl*
- 16.5.89 Dr. r. Stibr (Czechoslovak Academy of Science)  
*Recent Developments in the Chemistry of Intermediate-Sited Carboranes*
- 17.5.89 Dr. C. J. Moody (Imperial College)  
*Reactive Intermediates in Heterocyclic Synthesis*
- 23.5.89 Prof. P. Paetzold (Aachen)  
*Iminoboranes  $XB\equiv NR$  : Inorganic Acetylenes ?*
- 15.6.89 Prof. J. Pola (Czechoslovak Academy of Science)  
*Carbon Dioxide Laser Induced Chemical Reactions-New Pathways in Gas-Phase Chemistry*
- 10.11.89 Prof. J.I.G. Cadogan (B.P.)  
\* *From Pure Science to Profit*
- 17.10.89 Dr. F. Palmer (Nottingham University)  
\* *Thunder and Lightning*
- 25.10.89 Prof. C. Floriani (Lausanne University, Switzerland)  
*Molecular Aggregates - A Bridge Between Homogeneous and Heterogeneous Systems*
- 1.11.89 Dr. J.P.S. Badyal (Durham University)  
\* *Breakthroughs in Heterogeneous Catalysis*
- 9.11.89 Prof. N.N. Greenwood (Leeds University)  
*Novel Cluster Geometries in Metalloborane Chemistry*
- 10.11.89 Prof. J.E. Bercaw (California Institute of Technology)  
\* *Synthetic and Mechanistic Approaches to Ziegler-Natta Polymerisation of Olefins.*
- 13.11.89 Dr. J. Becher (Odense University)  
\* *Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks*

- 16.11.89 Dr. D. Parker (Durham University)  
*Macrocycles, Drugs and Rock 'n' Roll*
- 29.11.89 Prof. D.J. Cole-Hamilton (St. Andrews University)  
\* *New Polymers from Homogeneous Catalysis*
- 30.11.89 Dr. M.N. Hughes (King's College, London)  
*A Bug's Eye View of the Periodic Table*
- 4.12.89 Dr. D. Graham (B.P. Research Centre)  
*How Proteins Absorb on Interfaces*
- 6.12.89 Dr. R.L. Powell (ICI)  
\* *The Development of CFC Replacements*
- 7.12.89 Dr. A. Butler (St. Andrews University)  
\* *The Discovery of Penicillin: Facts and Fancies*
- 13.12.89 Dr. J. Klinowski (Cambridge University)  
*Solid State NMR Studies of Zeolite Cages*
- 15.12.89 Prof. R. Huisgen (Universitat Munchen)  
*Recent Mechanistic Studies of [2+2] Additions*
- 24.1.90 Dr. R.N. Perutz (York University)  
*Plotting the Course of C-H Activations with Organometallics*
- 31.1.90 Dr. U. Dyer (Glaxo)  
\* *Synthesis and Conformation of C-Glycosides*
- 1.2.90 Prof. J.H. Holloway (Leicester University)  
*Noble Gas Chemistry*
- 7.2.90 Dr. D.P. Thompson (Newcastle University)  
*The role of Nitrogen in Extending Silicate Crystal Chemistry*
- 8.2.90 Rev. R. Lancaster (Kimbolton Fireworks)  
*Fireworks - Principles and Practice*
- 12.2.90 Prof. L. Lunazzi (University of Bologna)  
\* *Application of Dynamic NMR to the Study of Conformational Isomerism*

- 14.2.90 Prof. D. Sutton (Simon Fraser University, Vancouver B.C.)  
*Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium*
- 15.2.90 Prof. L. Crombie (Nottingham University)  
*The Chemistry of Cannabis and Khat*
- 21.2.90 Dr. C. Bleasdale (Newcastle University)  
*The Mode of Action of some Anti-tumour Agents*
- 22.2.90 Prof. D.T. Clark (ICI Wilton)  
*Spatially Resolved Chemistry using Nature's Paradigm in the Advanced Materials Area*
- 28.2.90 Dr. R.K. Thomas (Oxford University)  
*Neutron Reflectometry from Surfaces*
- 1.3.90 Dr. J.F. Stoddart (Sheffield University)  
\* *Molecular Lego*
- 8.3.90 Dr. A.K. Cheetham (Oxford University)  
*Chemistry of Zeolite Cages*
- 21.3.90 Dr. I. Powis (Nottingham University)  
\* *Spinning off in a huff: Photodissociation of Methyl Iodide*
- 23.3.90 Prof. J.M. Bowman (Emory University)  
*Fitting Experiment with Theory in Ar-OH*
- 9.7.90 Prof. L.S. German (USSR Academy of Sciences - Moscow)  
\* *New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes*
- 9.7.90 Prof. V.E. Platonov (USSR Academy of Sciences - Novosibirsk)  
\* *Polyfluoroindanes: Synthesis and Transformation*
- 9.7.90 Prof. I.N. Rozhkov (USSR Academy of Sciences - Moscow)  
\* *Reactivity of Perfluoroalkyl Bromides*
- 11.10.90 Dr. W.A. MacDonald (ICI Wilton)  
*Materials for the Space Age*

- 24.10.90 Dr. M. Bochmann (U.E.A.)  
*Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls*
- 26.10.90 Prof. R. Soulen (South Western University, Texas)  
*Chemistry of some Fluorinated Cyclobutenes*
- 31.10.90 Dr. R. Jackson (Newcastle University)  
\* *New Synthetic Methods:  $\alpha$ -aminoacids and Small Rings*
- 1.11.90 Dr. N. Logan (Nottingham University)  
\* *Rocket Propellants*
- 6.11.90 Dr. P. Kocovsky (Uppsala University)  
\* *Stereo-controlled Reactions Mediated by Transition and Non-Transition Metals*
- 7.11.90 Dr. D. Gerrard (B.P.)  
*Raman Spectroscopy for Industrial Analysis*
- 7.11.90 Dr. W. Dolbier (Gainesville, Florida)  
\* *Rearrangements of bis CF<sub>3</sub> Vinyl Aromatics: a Route to 1,3,5-Hexatrienes*
- 8.11.91 Dr. S.K. Scott (Leeds University)  
*Clocks, Oscillations and Chaos*
- 14.11.90 Prof. T. Bell (SUNY, Stony Brook , U.S.A)  
\* *Functional Molecular Architecture and Molecular Recognition*
- 21.11.90 Prof. J. Pritchard (Queen Mary and Westfield College, London)  
*Copper Surfaces and Catalysts*
- 28.11.90 Dr. B.J. Whitaker (Leeds University)  
*Two-dimensional Velocity Imaging of State-selected Reaction Products*
- 29.11.90 Prof. D. Crout (Warwick University)  
\* *Enzymes in Organic Synthesis*
- 5.12.90 Dr. P.G. Pringle (Bristol University)  
*Metal Complexes with Functionalised Phosphines*
- 13.12.90 Prof. A.H. Cowley (University of Texas)  
\* *New Organometallic Routes to Electronic Materials*

- 15.1.91 Dr. B.J. Alder (Lawrence Livermore Labs., California)  
*Hydrogen in all its Glory*
- 17.1.91 Dr. P. Sarre (Nottingham University)  
*Comet Chemistry*
- 23.1.91 Prof. J.S. Higgins (Imperial College, London)  
\* *Rheology and Molecular Structure of Ionomer Solutions*
- 24.1.91 Dr. P.J. Sadler (Birkbeck College, London)  
*Design of Inorganic Drugs: Precious Metals, Hypertension and HIV*
- 30.1.91 Prof. E. Sinn (Hull University)  
*Coupling of Little Electrons in Big Molecules. Implications for the active Site of Macromolecules*
- 31.1.91 Dr. D. Lacey (Hull University)  
\* *Liquid Crystals*
- 6.2.91 Dr. R. Bushby (Leeds University)  
*Biradicals and Organic Magnets*
- 14.2.91 Dr. M.C. Petty (Durham University)  
*Molecular Electronics*
- 20.2.91 Prof. B.L. Shaw (Leeds University)  
\* *Synthesis with Coordinated, Unsaturated Phosphine Ligands*
- 28.2.91 Dr. J. Brown (Oxford University)  
\* *Can Chemistry Provide Catalysts Superior to Enzymes?*

- 6.3.91 Dr. C.M. Dobson (Oxford University)  
*NMR Studies of Dynamics in Molecular Crystals*
- 7.3.91 Dr. J. Markam (ICI Pharmaceuticals)  
\* *DNA Fingerprinting*
- 24.4.91 Prof. R.R. Schrock (MIT)  
*Metal-ligand Multiple Bonds and Metathesis Initiators*
- 25.4.91 Prof. T. Hudlicky (Virginia Polytechnic Institute)  
\* *Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products*
- 20.6.91 Prof. M.S. Brookhart (University of North Carolina)  
\* *Olefin Polymerisations, Oligomerisations and Dimerisations Using Electrophilic Late Transition Metal Catalysts*
- 29.7.91 Dr. M.A. Brimble (Massey University, New Zealand)  
\* *Synthetic Studies Towards the Antibiotic Griseusin-A*
- 3.10.91 Dr. R. Keeley (Metropolitan Police)  
*Modern Forensic Science*
- 17.10.91 Dr. J. A. Salthouse (Manchester University)  
*Son et Lumiere*
- 6.11.91 Prof. B. F. G. Johnson (Edinburgh University)  
\* *Cluster-Surface Analogies*
- 7.11.91 Dr. A. R. Butler (St. Andrews University)  
\* *Traditional Chinese Herbal Drugs*
- 13.11.91 Prof. D. Gani (St. Andrews University)  
\* *The Chemistry of PLP Dependant Enzymes*
- 20.11.91 Dr. R. More O'Ferrall (Dublin)  
*Some Acid-Catalysed Rearrangements in Organic Chemistry*
- 28.11.91 Prof. I. M. Word (Leeds University)  
\* *The Science & Technology of Orientated Polymers*
- 4.12.91 Prof. R. Grigg (Leeds University)  
*Palladium Catalysed Cyclisation and Ion Capture Processes*



- 5.12.91 Prof. A. L. Smith (ex Unilever)  
\* *Soap Detergents and Black Puddings*
- 11.12.91 Dr. W. A. Cooper (Shell Research)  
*Colloid Science, Theory, and Practice*
- 16.1.92 Dr. N. J. Long (Exeter University)  
\* *Metallocenophanes-Chemical sugar-tongs*
- 22.1.92 Dr. K. D. M. Harris (St. Andrews University)  
*Understanding the Properties of Solid Inclusion Compounds*
- 29.1.92 Dr. A. Holmes (Cambridge University)  
\* *Cycloaddition Reactions in the Service of the Synthesis of Piperidine and  
indolizidine Natural Products*
- 12.2.92 Dr. D. E. Fenton (Sheffield University)  
\* *Polynuclear Complexes of Molecular Clefts as Models for Copper  
Biosites*
- 19.2.92 Prof. E. J. Thomas (Manchester University)  
*Application of Organo-Stannanes to Organic Synthesis*
- 25.2.92 Prof. J. F. Nixon (University of Sussex)  
\* *Phosphoalkylenes, New Building Blocks in Inorganic and Organometallic  
Chemistry*
- 26.2.92 Prof. M. L. Hitchman (Strathclyde University)  
*Chemical Vapour Deposition*
- 11.3.92 Dr. S. E. Thomas (Imperial College)  
*Recent Advances in Organoirron Chemistry*
- 18.3.92 Dr. H. Maskill (Newcastle University)  
\* *Mechanistic Studies of Organic Group Transfer Reactions*

Research Conferences Attended

- 5.7.89 Royal Society of Chemistry Heterocyclic Group, Postgraduate Heterocyclic Symposium, Sheffield University.
- Aug. 89 European Symposium on Fluorine Chemistry, Leicester University.
- 13.12.89 Modern Aspects of Stereochemistry, One Day Meeting, Sheffield University
- 15.12.89 Royal Society of Chemistry Perkin Division, One Day Meeting, Durham University.
- 7.3.90 SCI Graduate Symposium, York University.
- 2.4.90 North East Graduate Symposium, Newcastle University.
- 22.10.90 Fluorine Chemistry Symposium, Japan
- Sept 91 13th International Symposium on Fluorine Chemistry, Ruhr Universität, Bochum, Germany.

FIRST YEAR INDUCTION COURSE

This course consists of a series of one hour lectures on the services available in the department.

Departmental Organisation - Dr. E.J.F. Ross

Safety Matters - Dr. M.R. Crampton

Electrical Appliances - Mr. B.T. Barker

Chromatography and Microanalysis - Mr. T.F. Holmes

Atomic Absorptiometry and Inorganic Analysis - Mr. R. Coult

Library Facilities - Mr. R.B. Woodward

Mass Spectroscopy - Dr. M. Jones

Nuclear Magnetic Resonance Spectroscopy - Dr. R.S. Matthews

Glass-blowing Techniques - Mr. R. Hart and Mr. G. Haswell

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