Novel perfluorinated dienes

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entitled

NOVEL PERFLUORINATED DIENES

submitted by

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A candidate for the degree of Doctor of Philosophy

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To my late Father

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Memorandum

The work described in this thesis was carried out in the University of Durham between October 1991 and May 1994. 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:

R.D. Chambers, M.W. Briscoe, S.J. Mullins, T. Nakamura, J.F.S. Vaughan and F.G. Drakesmith, *J. Chem. Soc., Perkin Trans. 1*, 1994, 3115.

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July 27th - 30th, 1994.

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Nomenclature

Throughout this work, an `F´ in the centre of a ring denotes that all unmarked bonds are to fluorine.

Abstract

Novel Perfluorinated Dienes

by J F S Vaughan

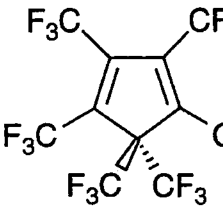
The research described within this thesis may be divided into four areas:

1) Unsaturated perfluorinated systems have been reduced, or defluorinated, using alkali metal amalgams to give products with a higher degree of unsaturation. For example, perfluoro-3,4-dimethylhex-3-ene (**105**) can be reduced to perfluoro-3,4-dimethylhex-2,4-diene (**106**). Remarkably, these reductions have also been performed, with equal success, using an electron rich amine, tetrakis(dimethylamino)ethene (**107**), which avoids the difficult, and potentially hazardous, use of amalgams. A difluoride salt, of amine (**107**), is produced as a by-product, which has potential as a soluble fluoride ion source.

2) Diene (**105**) is highly electron deficient and, therefore, is susceptible to nucleophilic attack, which occurs at the vinylic positions. This compound was reacted with difunctional oxygen nucleophiles, forming potential polymer precursors, which remain reactive towards nucleophiles, suggesting the possibility of their use in block co-polymer syntheses to give highly fluorinated products.

3) Calcium hypochlorite has been utilised to oxidise perfluorinated alkenes and dienes to yield the corresponding epoxide(s). An alternative methodology, using t-butyl hydroperoxide and butyl lithium, has been successfully applied to perfluorinated systems, for the first time, to give previously inaccessible compounds. The diepoxide (**162**) has been shown to undergo an unusual thermal ring opening, and expansion, to form a perfluorinated dioxin (**179**).

4) An efficient route to hexakis(trifluoromethyl)cyclopentadiene (**181**) has been developed *via* an unusual cyclisation process, which is induced by fluoride ion. This diene displays an interesting chemistry, including its reduction by tetraalkylammonium iodides to form the pentakis(trifluoromethyl)cyclopentadienyl anion, as crystalline ammonium salts (tetraethyl show below), in good yields.



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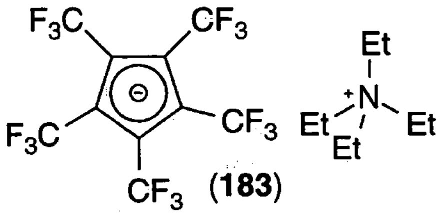

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When these salts are combined with concentrated sulphuric acid, 5H-pentakis(trifluoromethyl)cyclopentadiene (**188**) is produced, which is the strongest non-conjugated carbon acid known.

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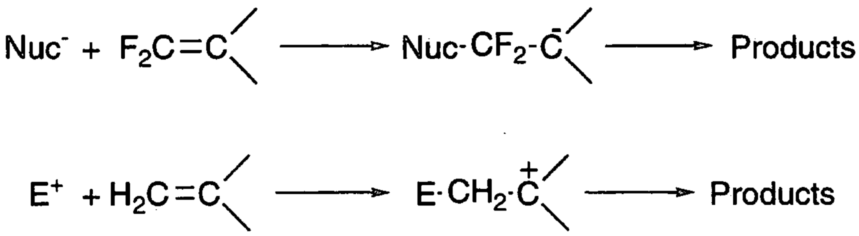
Chapter One
Introduction

I General Introduction

Because of their reactivity, none of the halogens occur in the elemental state. Consequently, fluorine is found in the earth's crust as mineral deposits such as fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$3Ca_3(PO_4)_2Ca(F, Cl)_2$], and has a relatively high abundance (0.065% F: 0.055% Cl).[1] A combination of low F-F bond strength and the high strength of bonds between fluorine and other atoms (*e.g.* carbon) accounts for its reactivity. Many of the remaining differences between fluorine and the other halogens can be explained by its small size and large electronegativity.[1]

However, a high abundance has not resulted in a significant incidence of fluorocarbons occurring in nature and, as a result, new synthetic methods have been developed to incorporate C-F bonds singly and multiply into organic compounds. This has led to a new area of organic chemistry that is often very different to that observed in the corresponding hydrocarbon.[2-4] For example, highly fluorinated alkenes are very electrophilic in nature, readily reacting with nucleophiles, whereas the chemistry of their hydrocarbon equivalents is, of course, the opposite, or `mirrored´.[5]



Worldwide research has led to a huge range of new fluorine containing materials, with greatly varied commercial applications. Some of these are listed below in Table 1.

Table 1 Fluorine Containing Compounds and their Uses

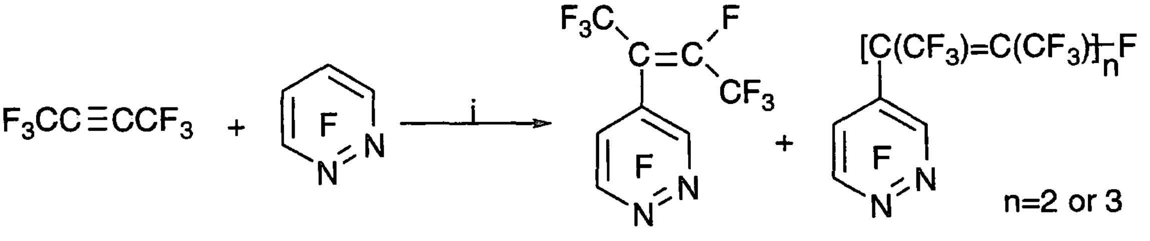
Area of Application	Compound
Refrigerant	CF_2Cl_2
Polymers, elastomers and membranes	$(CF_2CF_2)_n$
Inert fluids	$(CF_2CClF)_n$
Contrast enhancement of X-rays	n-$C_8F_{17}Br$ and $(CF_3)_2CF(CF_2)_4Br$
Artificial blood component	$C_{10}F_{18}$ (perfluorodecalin)
Anaesthetics	$CF_3CHClBr$ (Halothane)
Surfactants	$C_8F_{17}SO_2F$

I.1 Diene Synthesis

The realisation of the vast carbon-fluorine chemistry already available has depended upon development of realistic synthetic methods including, for example, the formation of C-F bonds and of C-C bonds from systems already containing C-F bonds. A vast amount of work has been done concerning the synthesis of highly, or fully, fluorinated dienes as synthetic intermediates, and Sections I.1.A-F of this chapter describe some of the methods employed and give examples of the structural variations encountered. Sections I.2.A-E then review some of the reactions, and often interesting products, of fluorinated dienes.

I.1.A Fluoride Ion Induced Processes

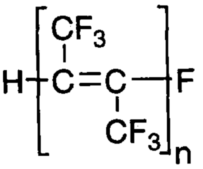
Caesium fluoride was shown to add readily to hexafluorobut-2-yne by Miller[6] in 1969. Further work performed by Chambers[7] and Haszeldine[8] demonstrated that fluoride ion, from caesium fluoride, adds to hexafluorobut-2-yne to give a carbanion which can be trapped by substitution of fluorine in reactive perfluoroaromatic compounds.



(1)

i. CsF, 100°C, Sulpholan Ref 7

Isolation of (1) demonstrated that dimerisation and trimerisation of hexafluorobut-2-yne takes place; if the conditions are not carefully controlled, a homopolymer is formed.[7-9]



$$H\left[\begin{array}{c} CF_3 \\ | \\ C=C \\ | \\ CF_3 \end{array}\right]_n F$$

Work by Miller[10] in 1973 described the fluoride ion induced telomerisation of hexafluorobut-2-yne to give *trans,trans*-2-bromoperfluoro-3,4-dimethyl-2,4-hexadiene (**2**) and perfluoro-3,4-dimethyl-2,4-hexadiene (**3**).

$$F_3CC\equiv CCF_3 + CsF \rightleftharpoons CF_3CF{=}CCsCF_3$$

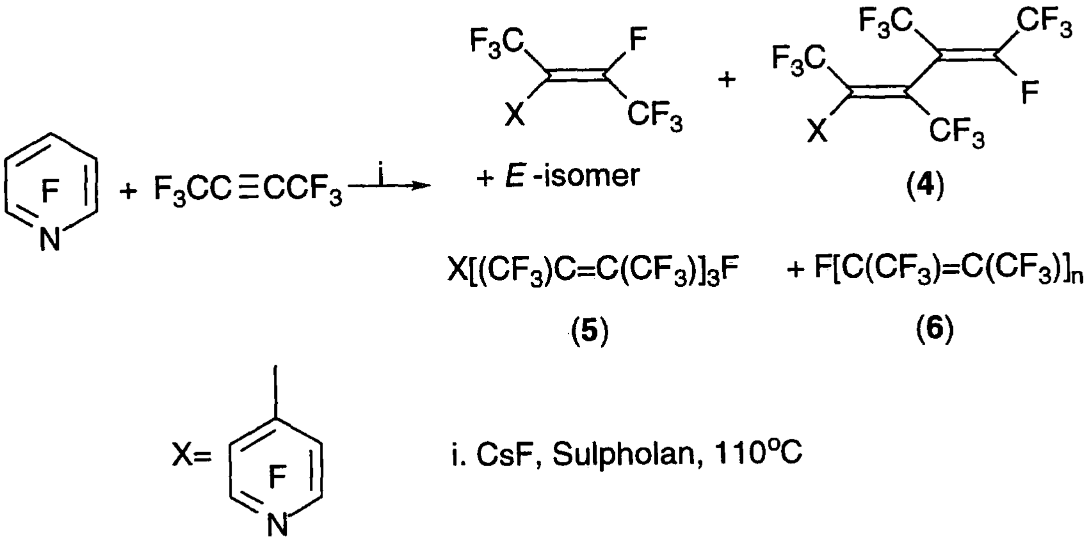
$$CF_3CF{=}CCsCF_3 + F_3CC\equiv CCF_3 \rightleftharpoons CF_3CF{=}CCF_3CCF_3{=}CCsCF_3 \equiv F(CCF_3{=}CCF_3)_2Cs$$

$$F(CCF_3{=}CCF_3)_2Cs + CF_3CF{=}CBrCF_3 \rightleftharpoons \underset{(\mathbf{2})}{F(CCF_3{=}CCF_3)_2Br} + CF_3CF{=}CCsCF_3$$

$$F(CCF_3{=}CCF_3)_2Br + CsF \longrightarrow \underset{(\mathbf{3})}{F(CCF_3{=}CCF_3)_2F} + CsBr$$

Careful modification of the reaction conditions was required to limit the formation of higher telomers.[10]

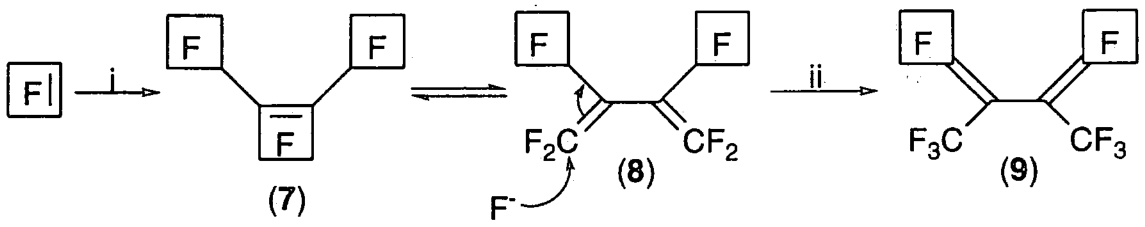
Work in these laboratories has also described diene formation using hexafluorobut-2-yne, fluoride ion and pentafluoropyridine. As mentioned earlier, carbanions generated, after fluoride ion reacts with unsaturated fluorinated systems, will react with activated aromatic systems by displacement of fluoride ion.[2] This has been utilised by Chambers[9] in the formation of a series of highly fluorinated alkenes, dienes and trienes.



As can be seen, two and three molecules of $CF_3C\equiv CCF_3$ have been incorporated into (**4**) and (**5**), giving a diene and triene, respectively. Again, high molecular weight material

(**6**) is observed, which can be limited by minimising the concentration of $CF_3C{\equiv}CCF_3$ and by using a very reactive aromatic system.

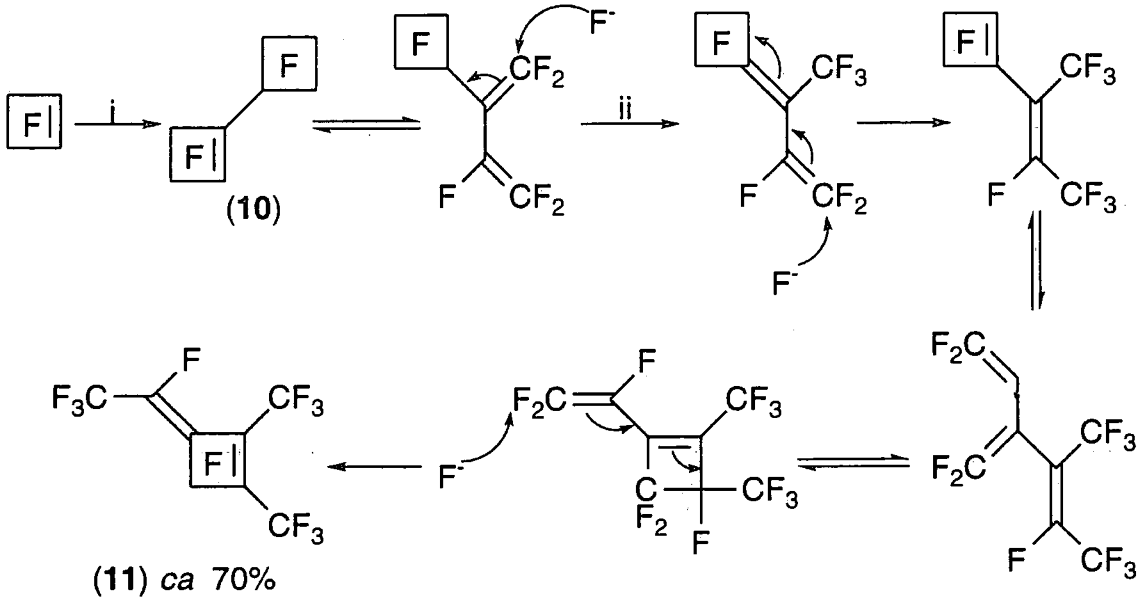
Other interesting diene systems have been synthesised in this group. When the trimer (**7**) of perfluorocyclobutene[11] was heated in a sealed tube with caesium or potassium fluoride, an essentially quantitative yield of diene (**9**) was obtained.[12]



i. Pyridine; ii. CsF or KF, 300°C, sealed tube

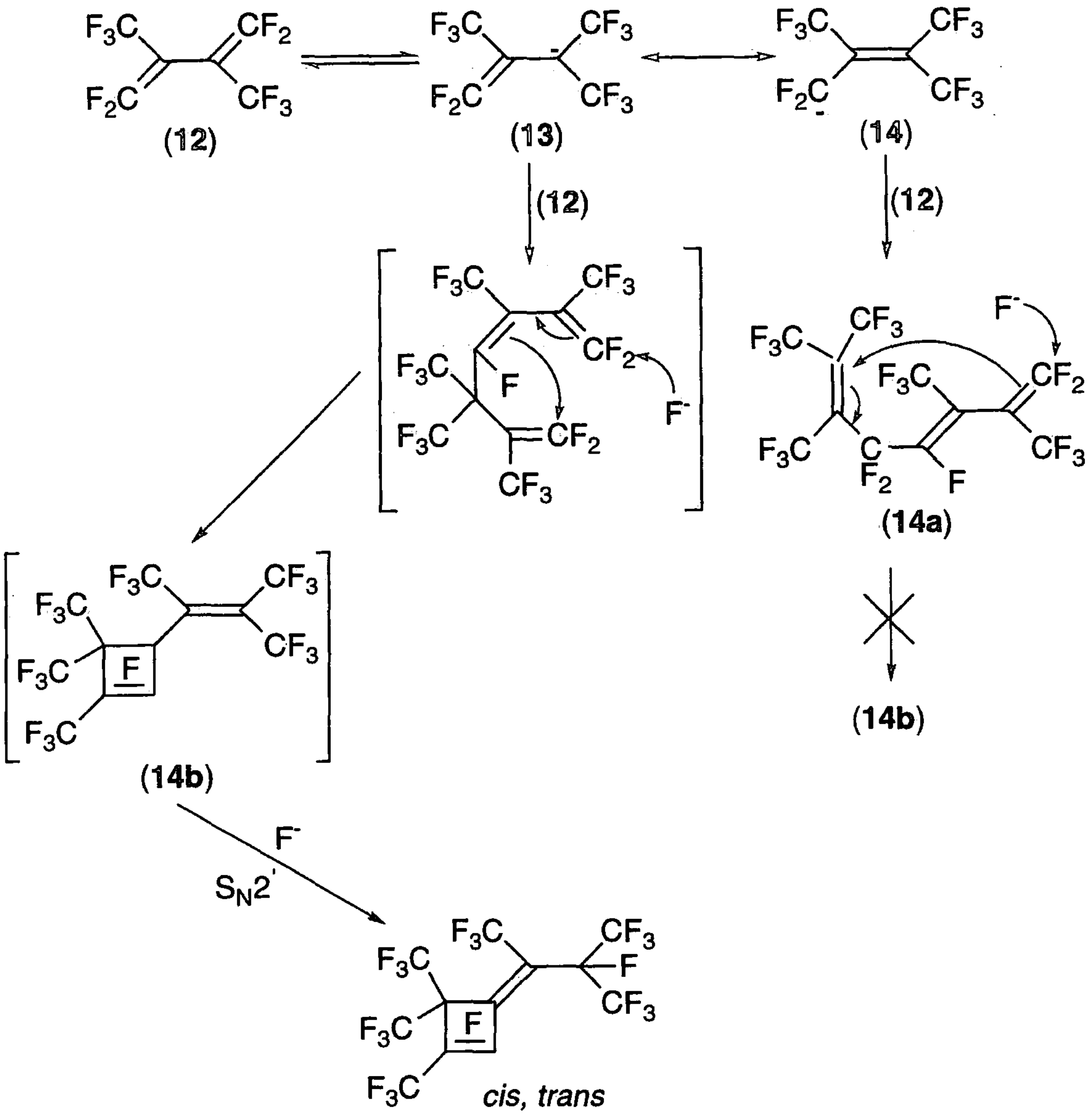
This involves an initial ring opening to give (**8**), followed by attack by fluoride ion.

More remarkably, passage of the dimer (**10**) over potassium fluoride at 510°C gave (**11**) in good yield.[12, 13]



i. Pyridine; ii. KF, 510°C, flow system in N_2

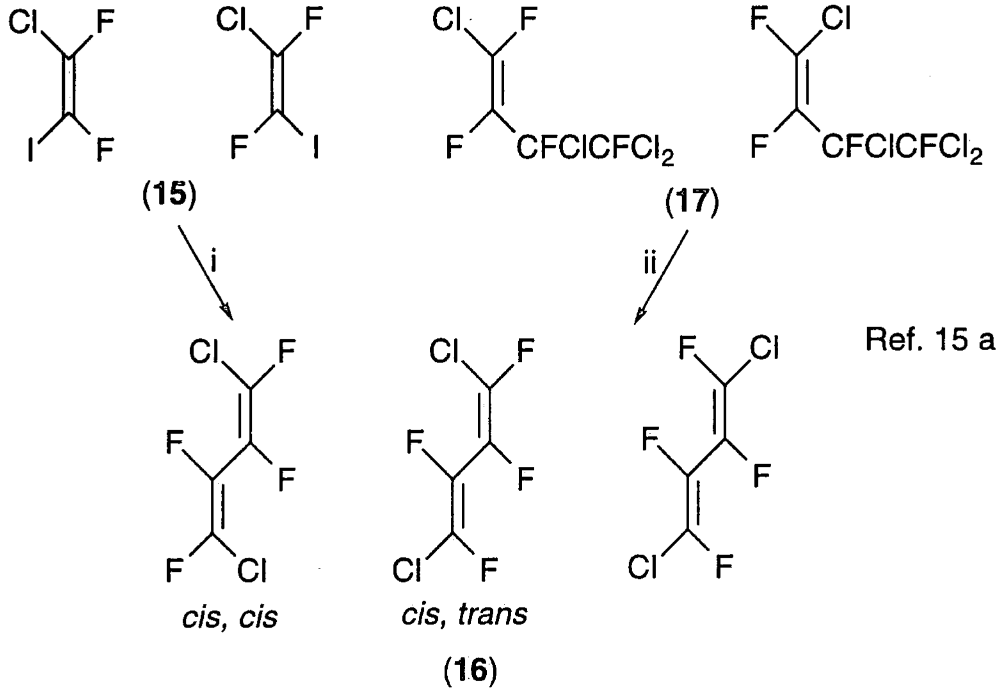
The reaction is thought to proceed *via* a ring opening mechanism similar to that described earlier. Another interesting reaction involves the dimerisation of diene (**12**), followed by a fluoride ion induced cyclisation of one of the products.[14]



More electron density is likely to be localised on the tertiary carbanion centre (**13**) than on centre (**14**). However, attack through (**13**) will be more inhibited, by steric effects, than through (**14**), and this seems to be the dominating influence on the reaction carried out at room temperature, giving largely (**14a**).[14] At elevated temperature it is likely that electron-density distribution is the more important factor, therefore leading to a greater proportion of the reaction through (**13**), giving the cyclic product (**14b**). The cyclisation step involves an internal vinylic substitution of fluoride from a $C{=}CF_2$ group. Cyclisation of the dimer (**14a**) does not occur in an analogous manner, as this would require an internal nucleophilic attack on a much less reactive $C{=}C(CF_3)_2$ group.

I.1.B Reductive Coupling Reactions

Tatlow[15] used hot copper-bronze to couple 1-chloro-1,2-difluoroiodoethene (**15**), which gave three geometrical isomers of 1,4-dichlorotetrafluorobuta-1,3-diene (**16**). Diene (**16**) was previously synthesised using a zinc dust dechlorination of 1,3,4,4-tetrachlorotetrafluorobut-1-ene (**17**)[16] (see section I.1.E), in a different isomeric ratio.

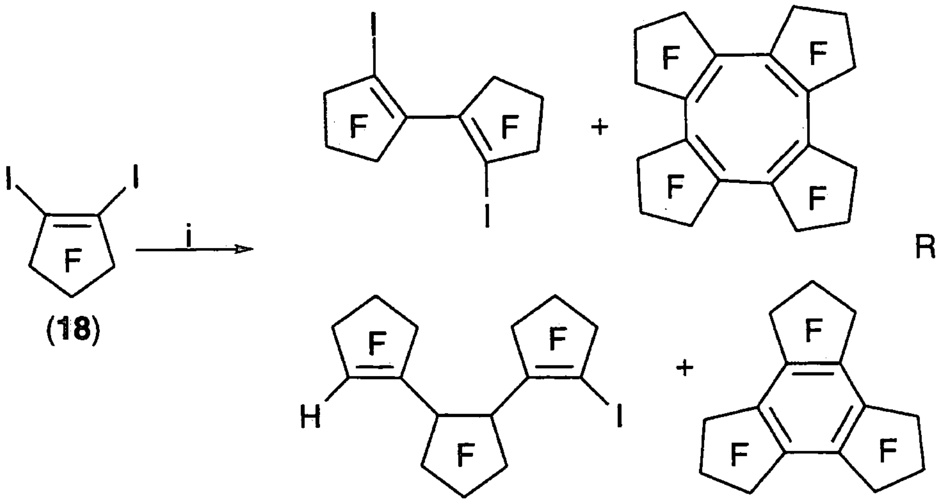


Ref. 15 and 16

i. Cu, 145°C; ii. Zn, MeOH

Work concerning the reductive coupling of 1-iodo-, 1-chloro-2-iodo- and 1,2-di-iodo-fluorinated cyclic alkenes, to give bicyclic dienes and unusual macrocyclic products, has been performed by Park[17], Camaggi[18] and Soulen[19].

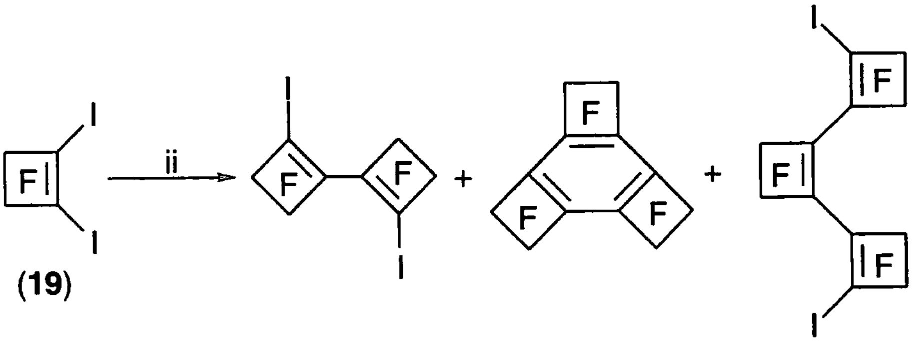
Park and Camaggi prepared 1,2-di-iodohexafluorocyclopentene (18) and 1,2-di-iodotetrafluorocyclobutene (19) from reaction of the corresponding perfluorinated cyclic alkene with sodium iodide.[17, 18] These materials were coupled with copper bronze to give a range of products.



(18)

Ref. 17

i. Copper bronze, 100°C

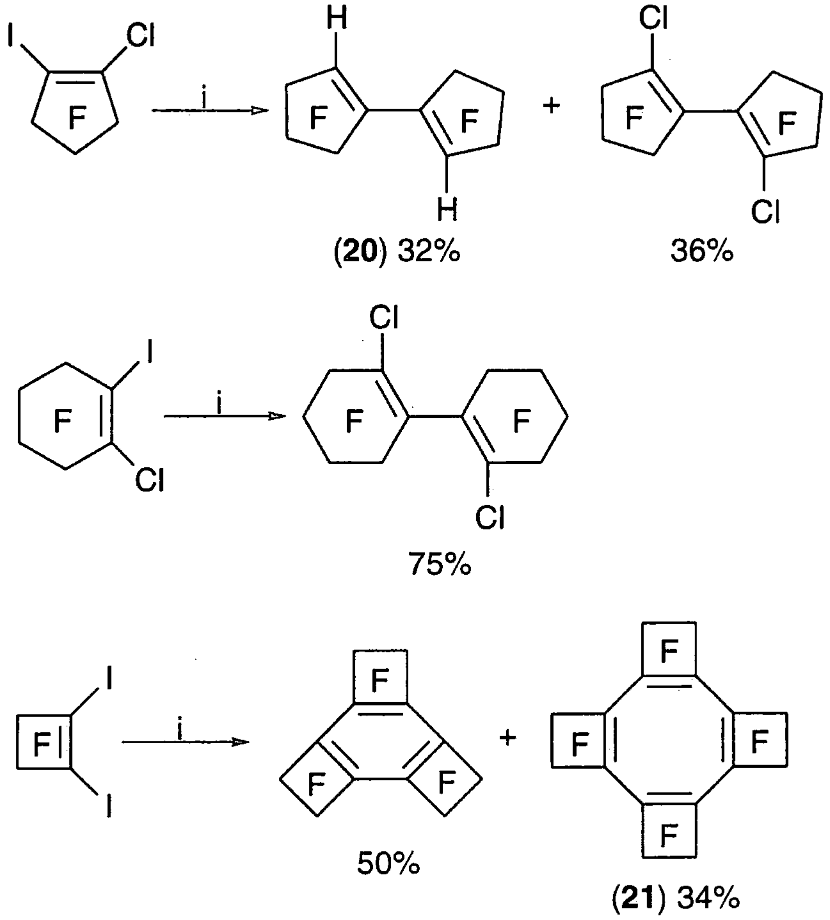


(19)

ii. Copper bronze, 165°C

Ref. 17 and 18

Soulen[19] has performed a series of similar reactions involving 1-iodo-2-chlorohexafluorocyclopentene, 1-iodo-2-chloro-octafluorocyclohexene and 1,2-di-iodotetrafluorocyclobutene with hot copper powder.



(**20**) 32%

36%

75%

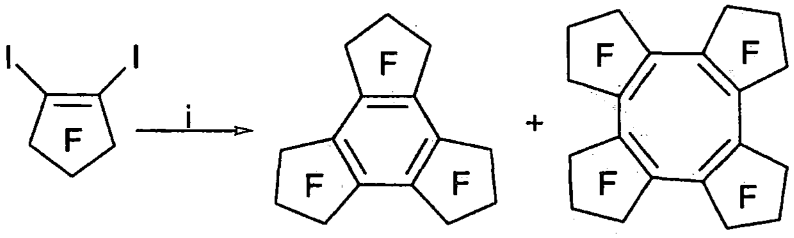
50%

(**21**) 34%

i. Copper powder, 0.5% DMF, 135°C

The appearance of dihydro- product (**20**) was unexpected, and has been attributed to proton abstraction from the solvent. In fact, using dimethylformamide (DMF) as a solvent, in concentrations as low as 0.5 weight percent, had dramatic consequences, allowing coupling of 1,2-di-iodotetrafluorobutene at 130°C or lower, and isolation of the previously unknown tetraene (**21**), which has been found to be one of the most powerful neutral organic oxidants known[20], and has recently been investigated as a sensitiser in photochemical cells.[21]

Also, coupling of 1,2-di-iodohexafluorocyclopentene gave only the cycic trimer (**22**) and tetramer (**23**), and none of the linear coupled products reported by Park and Camaggi.[17, 18]



(**22**) (**23**)

i. Copper powder, DMF (trace), 135°C

Interestingly, the Raman spectrum of (**21**) showed a band (6.25μm) which indicated substantial conjugation of the olefinic carbons; the cyclobutene rings, which link to give the cyclooctatetraene ring, remarkably, force the molecule into a co-planar state. Crystals of (**21**), in fresh alcohol, are reddish purple in colour, which gives further evidence for a highly conjugated anti-aromatic system.[19]

Work by Burton[22], in 1986, involved the direct formation of alkenyl cadmium reagents by reaction of fluorinated alkenyl iodides or bromides with cadmium powder. Their preparation proceeded with total retention of configuration, and subsequent functionalisation was with stereochemical control.[22]

$$R_fCF{=}CFX + Cd \xrightarrow{i} R_fCF{=}CFCdX + (R_fCF{=}CF)_2Cd + CdX_2$$

X=Br, I   i. DMF, r.t. (I), 60°C (Br)

These reagents displayed good thermal stability, with a solution of *Z* -$CF_3CF{=}CFCdBr$ in dry DMF, at room temperature, only losing 15% activity in 35 days. Interestingly, distillation of the reaction mixture, followed by recrystallisation from CH_2Cl_2/pentane, gave white crystals of (*Z* -$CF_3CF{=}CF)_2Cd{\cdot}DMF$ solvate. Structurally similar crystals were also obtained using triglyme as the solvent [(*Z* -$CF_3CF{=}CF)_2Cd{\cdot}TG$].[22] Functionalisation of the alkenyl cadmium reagents occurs readily with, for example, $CH_2{=}CHCH_2Br$, giving a diene.

In the same year, Burton[23] described the preparation of fluorinated vinyl copper reagents, for the first time, which could find useful application in the synthesis of bioactive drugs, polymers and agricultural chemistry.[24] Initially, vinyl zinc or cadmium (previously described) precursors are formed stereospecifically, and their metathesis with copper (I) halides proceeds with retention of configuration.

Attempts to directly generate fluorinated alkenyl copper reagents failed, with only the coupled products (symmetrical dienes) being obtained.

$$2CF_2CFI + 2Cu \longrightarrow CF_2{=}CF{-}CF{=}CF_2 + 2CuI$$

Stereochemical control allows the preparation of either isomeric copper reagent.[23]

$$\begin{tikzcd}[column sep=small] R_fCF{=}CFX + M \arrow[r, "i"] & R_fCF{=}CFMX + & (R_fCF{=}CF)_2M \arrow[d, "ii"] & + MX_2 \\ & & R_fCF{=}CFCu & \end{tikzcd}$$

X=Br, I; M=Cd, Zn

i. DMF, r.t.-60°C; ii. Cu^IX, r.t.

69-99%

Some of the results obtained using this procedure are outlined in Table 2.

Table 2 Preparation of Vinyl Copper Reagents

Alkene	Metal (M)	$R_fCF{=}CFCu$	Yield (%)[a]
$CF_2{=}CFI$	Cd	$CF_2{=}CFCu$	99
$CF_2{=}CFBr$	Zn	$CF_2{=}CFCu$	72
Z-$CF_3CF{=}CFI$	Zn	*Z*-$CF_3CF{=}CFCu$	76
E-$CF_3CF{=}CFI$	Cd	*E*-$CF_3CF{=}CFCu$	83
$CF_3C(Ph){=}CFBr$ *E*/*Z* =59/41	Zn	$CF_3C(Ph){=}CFCu$ *E*/*Z* =59/41	84

[a] Overall ^{19}F NMR yield is based on the starting alkene.

Like the cadmium and zinc reagents, the vinyl copper intermediates show good stability at room temperature, although they are sensitive to oxygen and moisture. They also participate in a range of reactions similar to those of their cadmium analogues.[23]

Coupling:

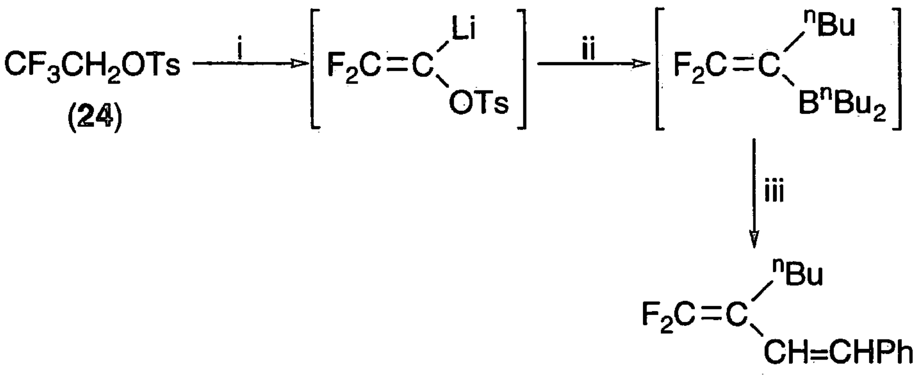
$$Z\text{-}CF_3CF{=}CFCu + E\text{-}CF_3C(Ph){=}CFI \longrightarrow Z,E\text{-}CF_3CF{=}CF{-}CF{=}C(Ph)CF_3 \quad 50\%$$

Alkylation:

$$Z\text{-}CF_3CF{=}CFCu + CH_3I \longrightarrow Z\text{-}CF_3CF{=}CFCH_3 \quad 83\%$$

Burton[25, 26] has recently published two comprehensive reviews (containing 297 references each) on fluorinated organometallic reagents in organic synthesis, and a report on the preparation, stability and reactivity of perfluorobenzyl-cadmium and -copper reagents.[27] Also, a synthesis of partially fluorinated conjugated dienes has been reported by French workers, employing palladium as a catalyst to cross couple iodo- and bromoalkenes.[28, 29]

Finally, another procedure involving a palladium catalyst describes the one pot, stereospecific synthesis of 1,1-difluoro-1,3-dienes *via* the coupling reaction of 2,2-difluorovinylborane.[30] Unlike many of the procedures described in this review, 2,2,2-trifluoroethyl *p* -toluene sulphonate (**24**) is readily available as the starting material. An example of this reaction is shown below.

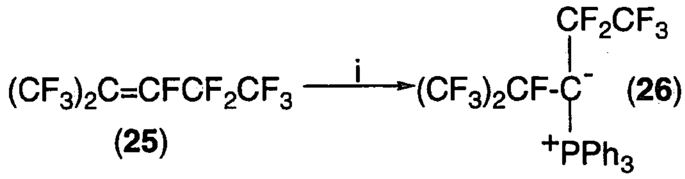


i. 2^{n}BuLi, THF, -78°C, 0.5hr
ii. B^{n}Bu$_3$, -78°C to r.t., 4hr
iii. 2 mol % $Pd_2(dba)_3 \cdot PPh_3$, PhCH=CHBr, THF-HMPA, r.t., 1hr

I.1.C Coupling Reactions involving Phosphorous

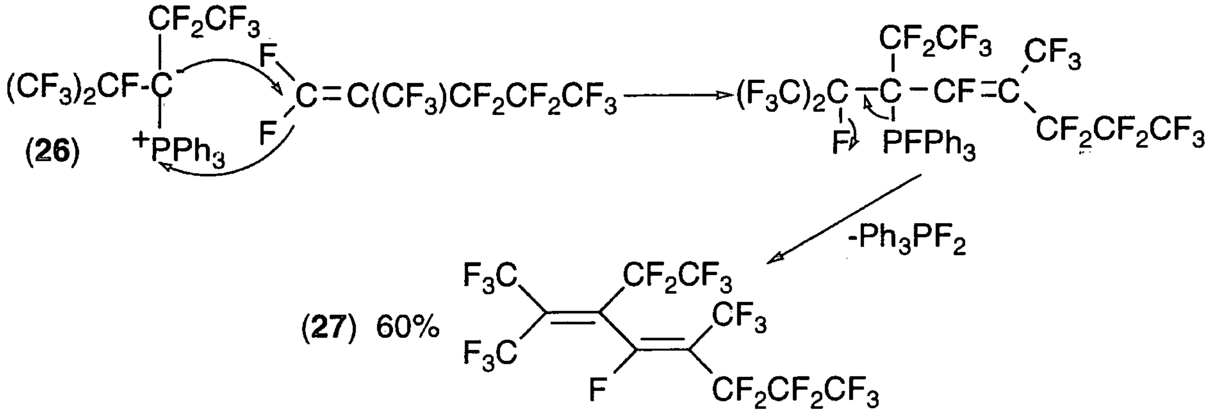
Several research workers have investigated tertiary phosphines as coupling agents for cyclic and acyclic pefluorinated alkenes, forming di- and trienes.[31-33]

In 1981, Stepanov[32] described using triphenylphosphine to dimerise perfluoro-2-methyl-2-pentene (**25**) *via* the corresponding ylide (**26**), which is formed after a 1,2-shift of a fluorine atom.



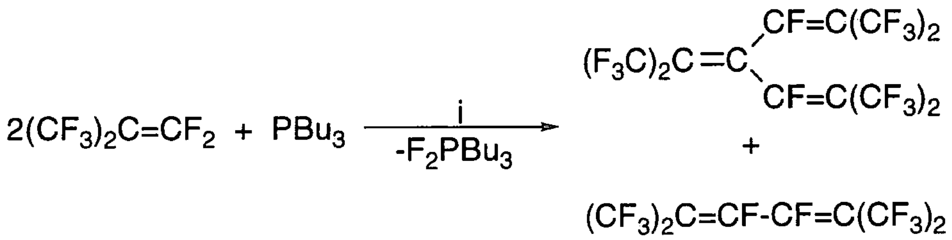
i. PPh_3, Autoclave, CH_3CN, 110°C, 12 hrs

However, attack of ylide (**26**) at the double bond of (**25**) is sterically hindered, and a rearrangement of (**25**) occurs in the presence the phosphine to give an electrophilic, terminal alkene. This is attacked by (**26**) to give diene (**27**), in reasonable yield.[32]



Scheme 1

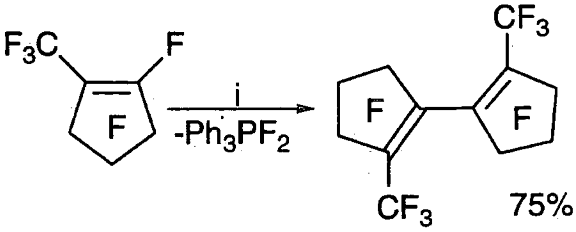
Knunyants[33] described using tributylphosphine with perfluoroisobutene, giving a conjugated di- and triene.



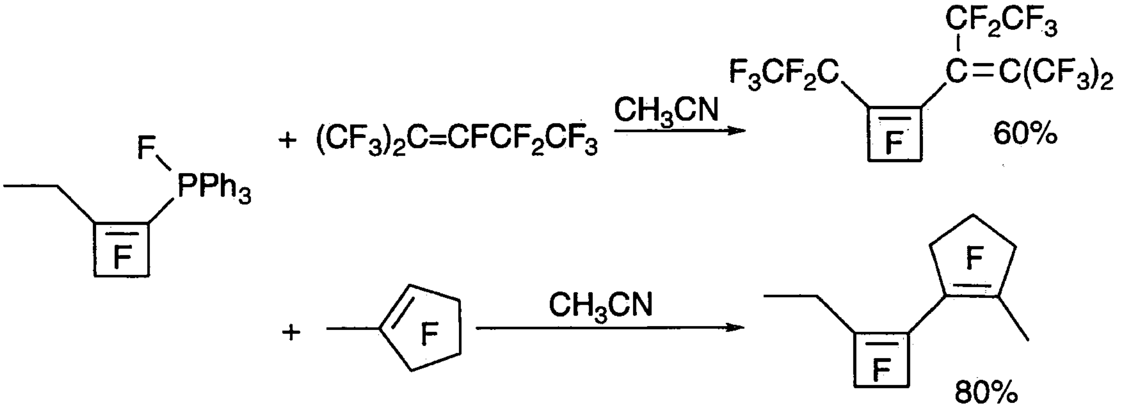
i. CH_3CN, -30°C

Interestingly, the solvent had a great effect on this reaction. When diethyl ether was used only a mixture of phosphoranes was observed, and none of the expected products.[33]

The dimerisation of cyclic perfluoroalkenes has also been described in the literature, following a similar mechanism to that described in Scheme 1.[31, 32]

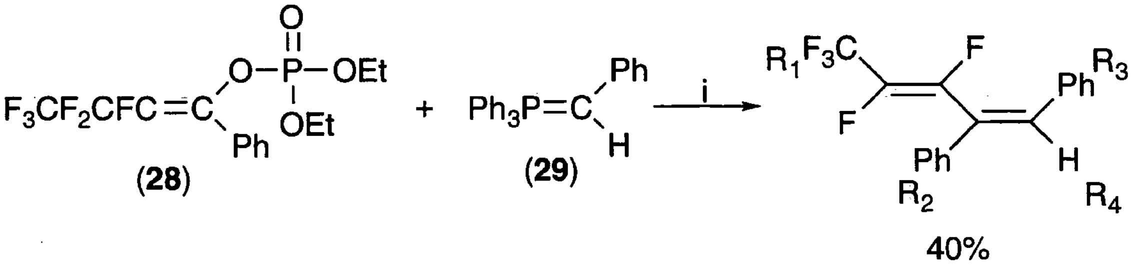


i. PPh_3, CH_3CN, 25°C



As can be seen, the synthetic scope of this type of reaction is very wide.

Finally, in 1988 Ishihara[34] reported a reaction between fluorinated alkenyl phosphates (**28**) and phosphonium ylides (**29**) to give polyfluorinated 1,3-dienes in moderate to good yields.

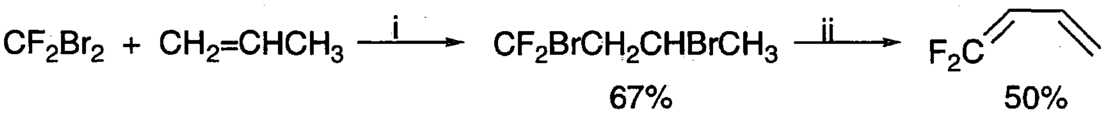


i. THF, r.t., 20 hrs

Eleven different dienes were synthesised, in which substituents R_1, R_2, R_3 and R_4 were varied, with the highest yield being 90%.

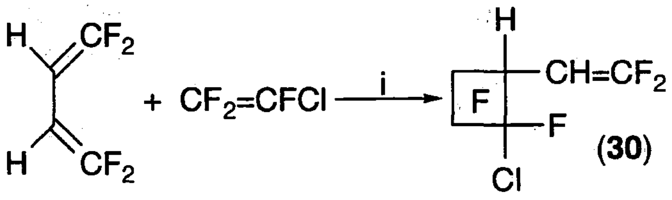
I.1.D Dehydrohalogenation

An early example of diene synthesis *via* dehydrohalogenation was reported by Tarrant[35] in 1954. This involved coupling dibromodifluoromethane with propene to give 1,3-dibromo-1,1-difluorobutane, followed by a base induced dehydrobromination.



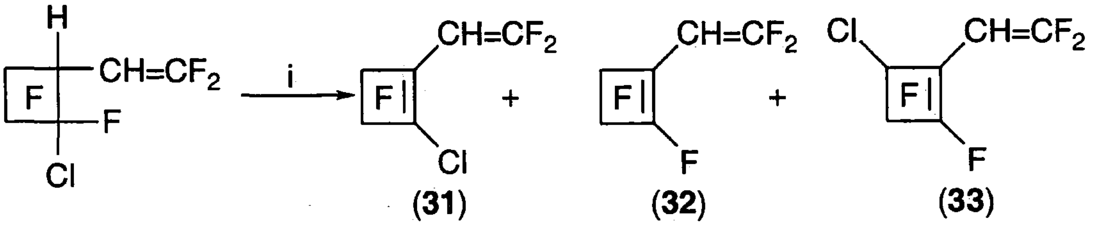
i. $(PhCO_2)_2$, 85°C; ii. NBu_4, 180°C

In 1969, Park investigated the cycloaddition chemistry of 1,1,4,4-tetrafluorobutadiene with, for example, 1-chlorotrifluoroethene leading to the formation of perhalogenated cyclobutane (**30**).[17]



i. Autoclave, 260°C, 18 hrs

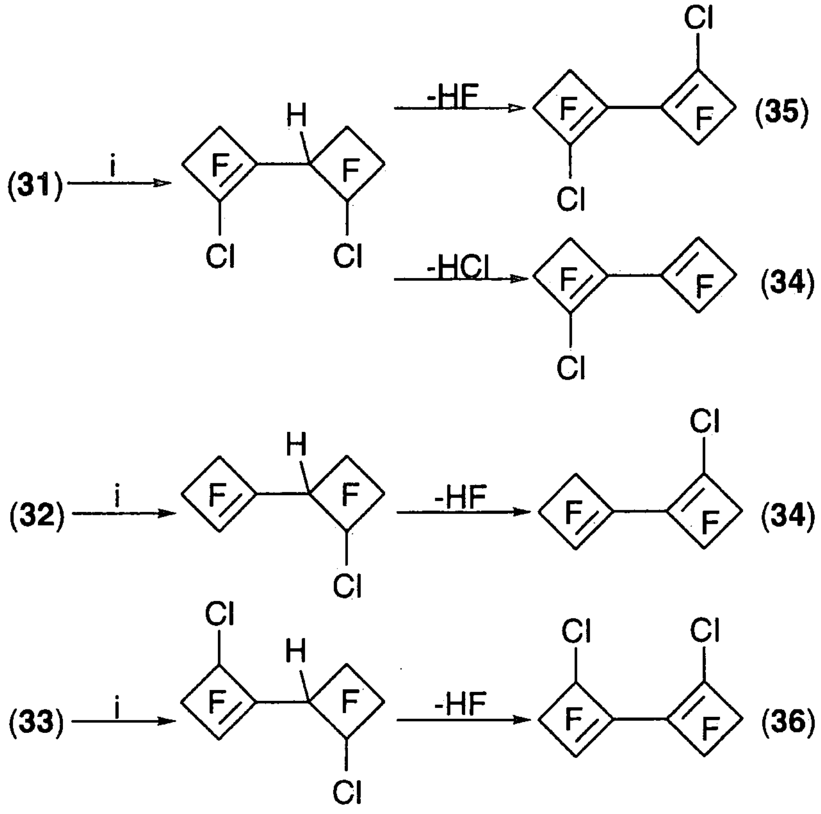
Dehydrohalogenation of (**30**) was initially attempted using potassium ethoxide as the base, to give three isolated products, plus a complex mixture of ethers.[17]



i. KOEt, ethanol, 0-25°C, 6 hrs + ethers

In order to avoid the ethers, silver oxide was employed, which is milder than ethoxide. This method worked well, giving consistently good yields of just the three cyclobutenes.

Dienes (**31**)-(**32**) were then co-reacted with chlorotrifluoroethene to give three bicyclic dienes [(**34**, 8%), (**35**, 10%) and (**36**, 12%).



i. CF_2=CFCl, Autoclave, agitation, 185°C, 42 hrs

The low isolated yields reflect a low conversion of the starting materials to the bicyclic dienes.[17]

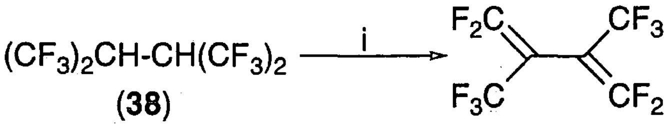
An original route to perfluoro-2,3-dimethyl-1,3-butadiene was reported by Russian workers[36] involving the Kolbe electrochemical dimerisation of fluorinated acids in aqueous solution. The Kolbe electrolysis follows the general pathway described below.[37]

$$2RCO_2 \xrightarrow[\text{anode}]{-e^-} 2RCO_2^{\bullet} \xrightarrow{-CO_2} 2R^{\bullet} \longrightarrow R\text{-}R$$

Fluorocarboxylic acid (**37**) was oxidised at the anode, and the subsequent radical dimerised to give alkane (**38**).

$$\underset{\textbf{(37)}}{2(CF_3)_2CHCOOH} \xrightarrow{\text{Electrolysis}} \underset{\textbf{(38)}}{(CF_3)_2CH\text{-}CH(CF_3)_2} + 2CO_2 + H_2$$

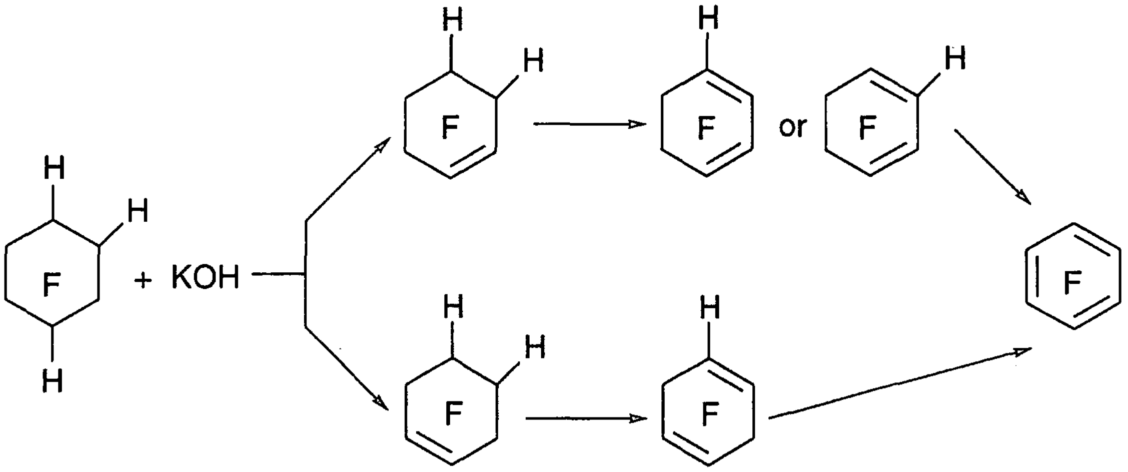
Alkane (**38**) was then treated with base, dehydrofluorinating to give the diene.



(**38**)

i. KOH, dibuty ether, 2 wks

Tatlow[38] reported the base induced dehydrohalogenation of polyfluorocyclohexanes. The products consist of three isomeric dienes, which may be further dehyrohalogenated to give hexafluorobenzene.



Finally, a report from these laboratories has described the synthesis of a diene using a saturated fluorocarbon which was derived from 2-iodo-heptafluoropropane, using standard telomerisation and coupling procedures.[39] The method involved heating the alkane with antimony pentafluoride (SbF_5).

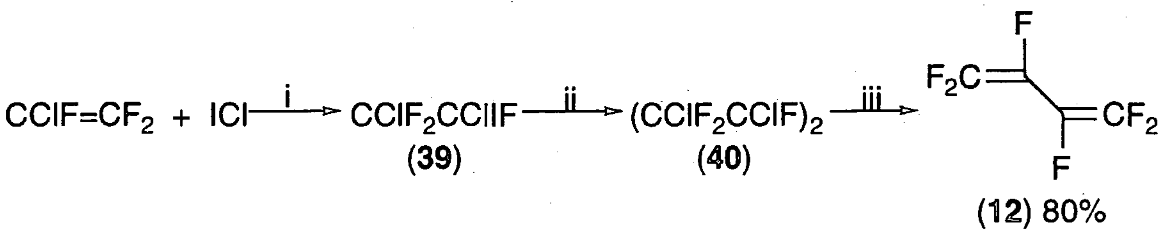
$$[(CF_3)_2CFCH_2CF_2]_2 \xrightarrow{i} [(CF_3)_2C{=}CHCF_2]_2$$

i. SbF_5, 120°C, 2 hrs

I.1.E Dehalogenation

In 1952 Haszeldine[40] reported the synthesis of hexafluorobuta-1,3-diene (**12**) in good yield. This was only the second reported preparation of (**12**); the first being by Miller (1947), involving direct fluorination of 1,2-dichlorodifluoroethene at -78°C, giving the dimer $C_4Cl_4F_6$, which dechlorinated to give the target diene.[41] Disadvantages of this method are that elemental fluorine is required, the optimum yield of $C_4Cl_4F_6$ is low (44%), and several by-products are formed.[40]

The procedure employed by Haszeldine involved the addition of iodine monochloride to chlorotrifluoroethene, giving 1,2-dichloro-1,1,2-trifluoroiodoethane (**39**), in almost quantitative yield, which readily reacted in ultraviolet light, or with zinc in dioxan, to give hexafluoro-1,2,3,4-tetrachlorobutane (**40**). Dehalogenation of (**40**), with zinc and ethanol, gave hexafluorobuta-1,3-diene (**12**).[40]



i. 9 atm., no solvent; ii. Zn, dioxan or Hg, light; iii. Zn, ethanol

However, this reaction was reinvestigated in these laboratories[42], using similar conditions to those of Haszeldine, and $CClF_2CClIF$ as well as ClF_2CCl_2F were isolated, leading to the repeatability of Haszeldines results to be questioned.

In 1986, Dedek[43] reported a different synthesis of hexafluorobuta-1,3-diene (**12**) involving a photochemically initiated reaction between 1,2-dibromo-1-chlorotrifluoroethane and, as earlier, chlorotrifluoroethene, followed by dehalogenation of the products, over zinc, to give dienes and trienes.

$$CClF=CF_2 + Br\text{-}(CClFCF_2)\text{-}Br \xrightarrow{i} Br\text{-}(CF_2CClF)_n(CClFCF_2)_m\text{-}Br$$

i. U.V., 20-30°C, 40 hrs

Where n=m=1 (**41**) 38%
n=1, m=2 (**42**) 19%
n=m=2 (**43**) 43%

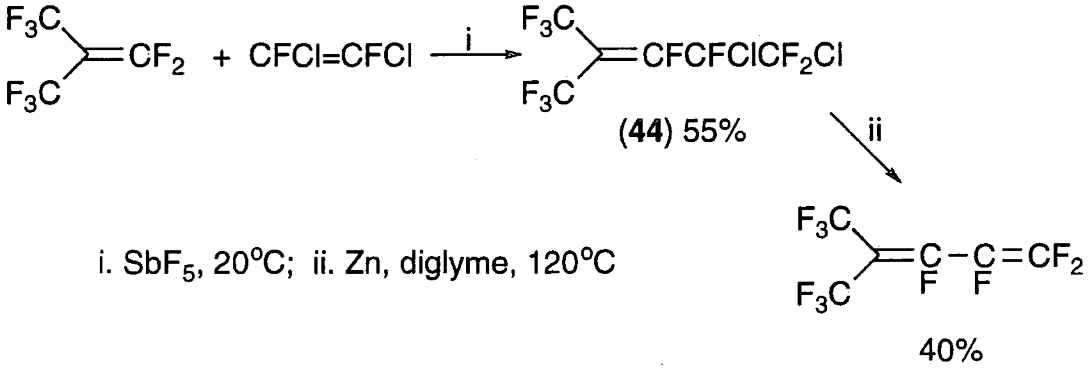
Dehalogenation of (**41**) and (**42**) gave diene (**12**) and perfluoro-1,4,7-octatriene, respectively, whilst dehalogenation of (**43**) gave 3-chlorononafluoro-1,5-hexadiene and perfluoro-1,3,5-hexatriene.

$$\textbf{(41)} \longrightarrow \underset{78\%}{CF_2=CFCF=CF_2}$$

$$\textbf{(42)} \longrightarrow \underset{>50\%}{CF_2=CFCF_2CF=CFCF_2CF=CF_2}$$

$$\textbf{(43)} \longrightarrow \underset{35\%}{CF_2=CFCClFCF_2CF=CF_2} + \underset{65\%}{CF_2=CFCF=CFCF=CF_2}$$

Work by Petrov[44] described the synthesis of perfluoro-2-methyl-2,4-pentadiene. Perfluoroisobutene, which is very toxic, was reacted with 1,2-dichlorodifluoroethene, in the presence of antimony pentafluoride, to give 2-trifluoromethyl-4,5-dichloroperfluoro-2-pentane (**44**) in moderate yield. This was then dechlorinated using zinc to give the diene.[44]



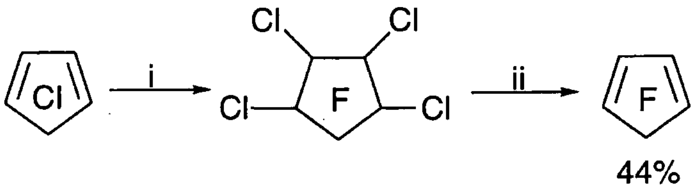
i. SbF_5, 20°C; ii. Zn, diglyme, 120°C

Russian workers[45] have also described the synthesis of dienes by the dehalogenation of a condensation product, which was synthesised for the first time without the use of organometallics.

$$\begin{tikzcd} CClF_2CClIF + CH_2{=}CHCH_2OAc \arrow[r, "i"] & CClF_2CClFCH_2CHICH_2OAc \arrow[d, "ii"] \\ & CF_2{=}CFCH_2CH{=}CH_2 \end{tikzcd}$$

i. $Na_2S_2O_4$, $NaHCO_3$, CH_3CN, H_2O, 40°C, 4hrs; ii. Zinc dust, ethylene glycol

In 1963, Haszeldine[46] reported the synthesis of the potentially very interesting perfluorocyclopentadiene, by the dechlorination of 1,2,3,4-tetrachlorohexafluorocyclopentane.



i. CoF_3 reactor; ii. Zinc dust, dioxan, reflux, 2 hrs

Unfortunately, the chemistry of this system is very limited, as the monomer was found to dimerise at room temperature, with an 80% conversion after 14d.; immediately after isolation, it was necessary to store the diene under vacuum at -196°C.

I.1.F Decarboxylation

Decarboxylation of the salts of polyfluorinated carboxylic acids, containing a terminal double bond, was considered as a route to dienes by Bekker[47] in 1981. The sodium salts were first examined, giving either *Z,Z*-1-chloro-2,3,3,4,5,5-hexafluoro-1,4-pentadiene (**45**) or *Z,Z*-1,2,3,3,4,5,5-heptafluoro-1,4-pentadiene (**46**) on heating the corresponding salt under reduced pressure.

$$CClH{=}CF(CF_2)_3CO_2Na \longrightarrow \underset{\textbf{(45)}\ 78\%}{CClH{=}CFCF_2CF{=}CF_2}$$

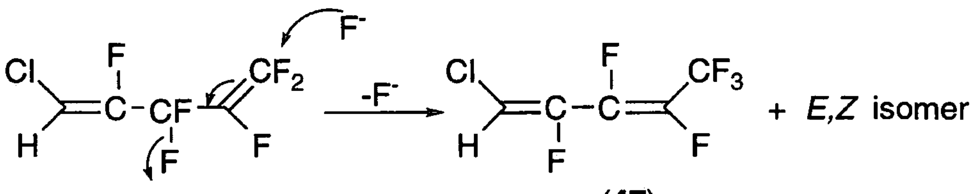
$$CFH{=}CF(CF_2)_3CO_2Na \longrightarrow \underset{\textbf{(46)}\ 95\%}{CFH{=}CFCF_2CF{=}CF_2}$$

i. Heat, 3mmHg; ii. Heat, 1mmHg

However, on heating the potassium salt of the chlorinated carboxylic acid, diene (**45**) was isolated, as expected, plus the *Z,Z*- and *E,Z*- isomers of diene (**47**) [1(**45**):2.8(**47**)].[47]

$$CClH{=}CF(CF_2)_3CO_2K \xrightarrow{\Delta} \textbf{(45)} + \underset{\textbf{(47)}\ Z,Z \text{ and } E,Z}{CClH{=}CFCF{=}CFCF_3}$$

The presence of diene (**47**) can be explained by the isomerisation of (**45**) by potassium fluoride formed in the reaction.

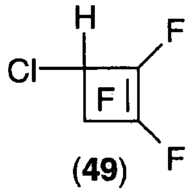


(47)

This did not occur with the sodium salt, since sodium fluoride will not act as a fluoride ion source to induce the isomerisation.

Bekker[47] also performed a similar experiment with the sodium salt of 2,2,3,3,4-pentafluoro-5-chloro-4-penten-1-oic acid to give a mixture of butadiene (**48**) and cyclobutene (**49**), in a 16:1 ratio.

$$CClH{=}CF(CF_2)_2CO_2Na \xrightarrow{i} \underset{\textbf{(48)}}{CClH{=}CF\text{-}CF{=}CF_2} +$$

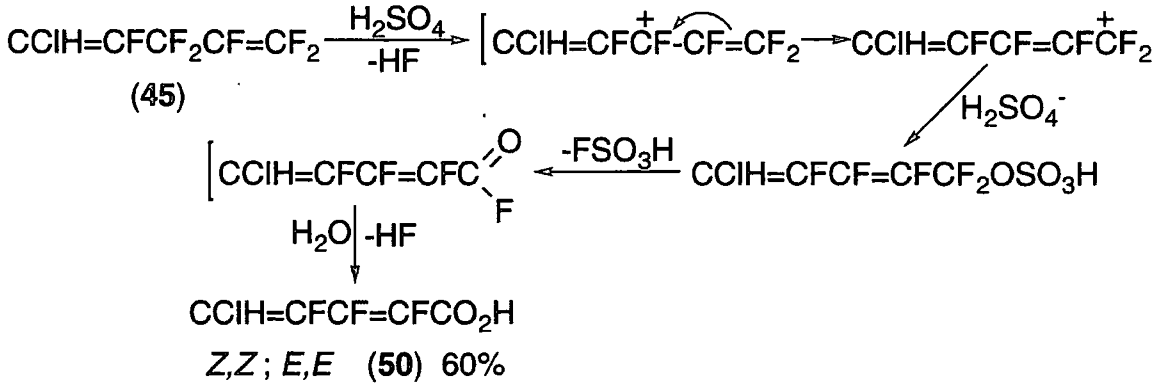


(49)

i. Heat, 1mmHg

Cyclobutene (**49**) arises from the cyclisation of (**48**).

Finally, the conversion of diene (**48**) into the corresponding carboxylic acid (**50**), which is not easily accessible, was demonstrated using concentrated sulphuric acid.[47]

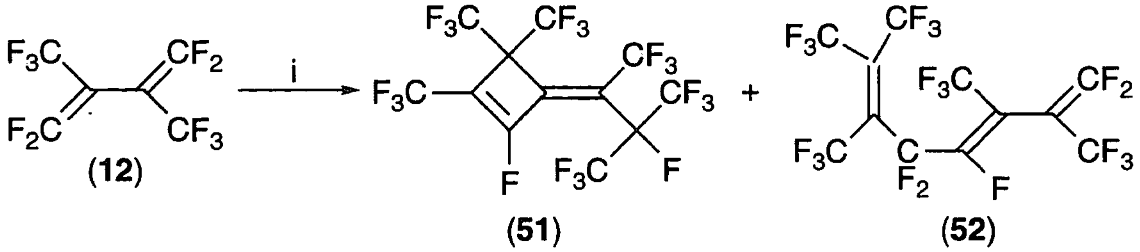


I.2 Reactions of Fluorinated Dienes

I.2.A Reaction with Nucleophiles

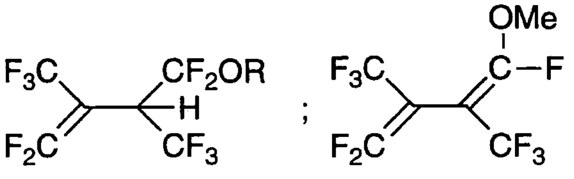
As already mentioned, double bonds with perfluoroalkyl groups attached are extremely electrophilic in nature, and therefore susceptible to nucleophilic attack.

Work done in these laboratories[14] has described the fluoride ion induced dimerisation of perfluoro-2,3-dimethylbuta-1,3-diene (**12**) to give (**51**) and (**52**) as the main products (see section I.1.A).



i. CsF, tetraglyme, r.t., 18hrs

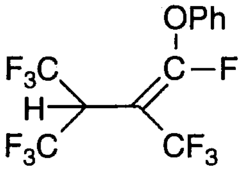
Diene (**12**) has also been shown to undergo reaction with oxygen nucleophiles, such as methanol and phenol, to give a series of 1,2-addition (**53**, **54**) and substitution (**55**) products.[48]



(**53**) R=OMe 17%
(**54**) R=Ph

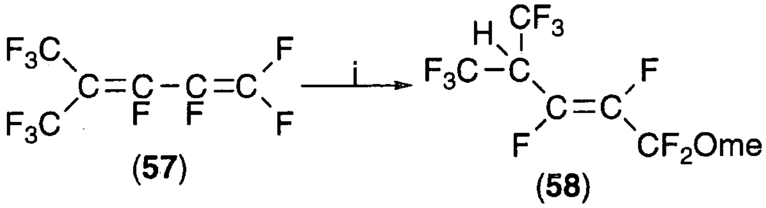
(**55**) 39%

Interestingly, with phenol only product (**56**) was observed, and none of addition product (**54**). This is explained by hydrogen fluoride adding across the double bond of (**54**); unlike with methanol, the reaction occurred in an aprotic solvent (DMF), where fluoride ion is a much better nucleophile.[48]



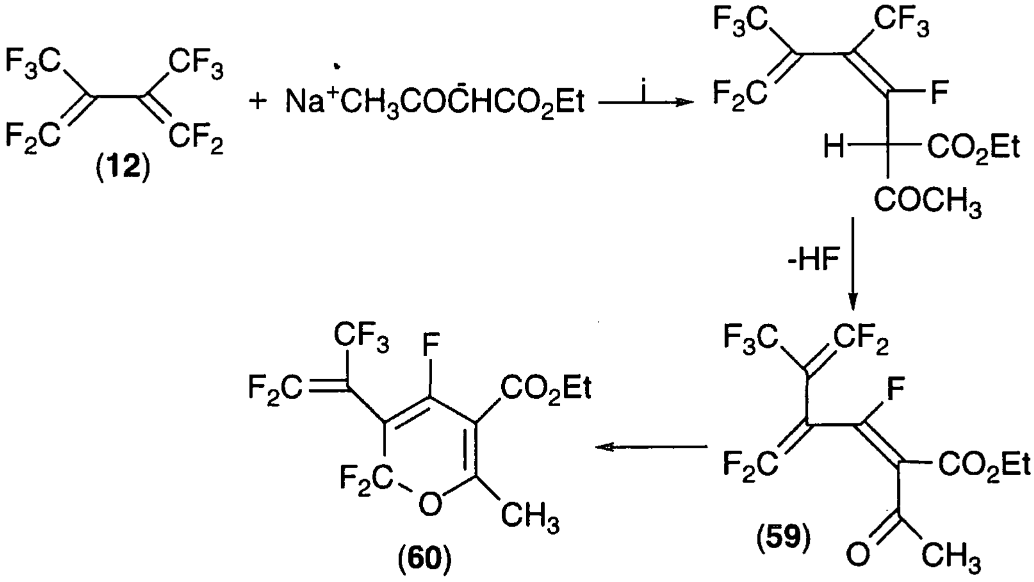
(**56**) 26%

Russian workers observed 1,4- addition of methanol across perfluoro-2-methyl-2,4-pentadiene (**57**) to give (**58**)[44], and similar reactions have been reported by Dedek[49, 50] using fluorinated hexadienes.



i. MeOH, 20°C

Reaction of (**12**) with enolate anions was shown to give a variety of novel heterocyclic compounds. The anion from ethylacetoacetate reacts to give pyran (**60**) as the major product, arising from the electrocyclic ring closure of (**59**).[48]



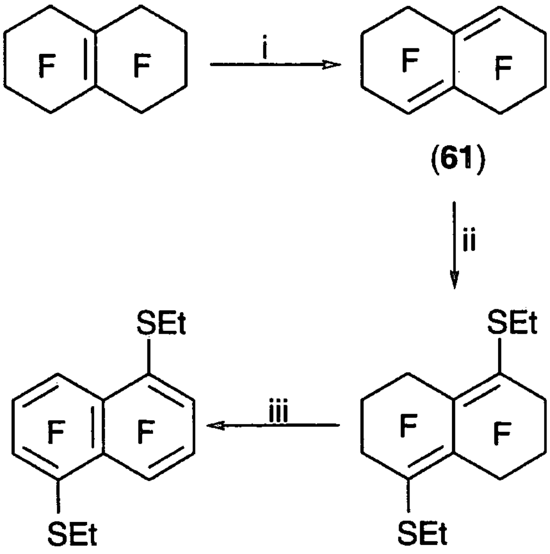
i. Tetraglyme, r.t., 17hrs

Fluorinated dienes are also susceptible to nitrogen and sulphur nucleophiles. Examples using nitrogen have been reported by Dedek[51, 52], and one involves the regioselective reaction between 2-chloroperfluorobuta-1,3-diene and diethylamine, with hydrolysis of the product giving a butenamide.

$$CF_2{=}CFCCl{=}CF_2 \xrightarrow{Et_2NH} CF_2{=}CFCHClCF_2NEt_2 \xrightarrow{H_2O} CF_2{=}CFCHCl\overset{O}{\underset{NEt_2}{C}}$$

Ref 52

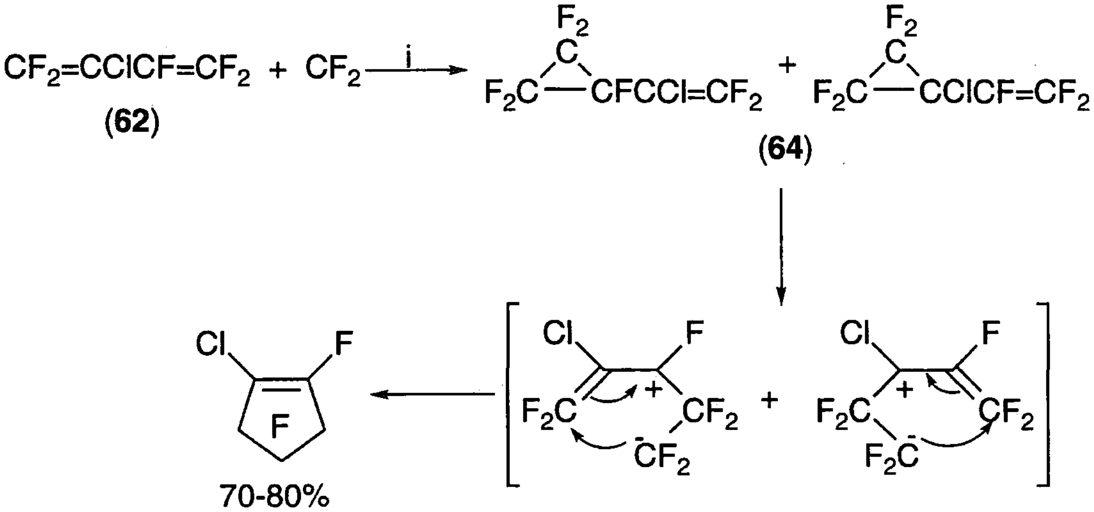
Chinese workers[53] have reacted tetradecafluorobicyclo[4.4.0]dec-1(2),6(7)-diene (**61**) with, amongst others, sulphur nucleophiles to give the disubstituted products, which were then defluorinated, providing a good route to 1,5-disubstituted perfluoronaphthalene derivatives.



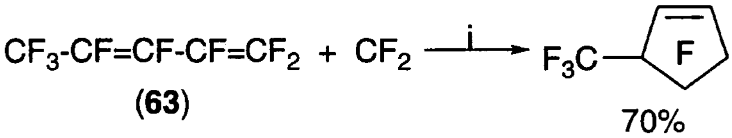
(61)

i. Zn powder, heat; ii. EtSH, Et_3N, -78°C, 3 hrs;
iii. Mg, Et_2O, CH_3CHBr_2, reflux, 2 hrs

Petrov[54], has demonstrated the use of difluorocarbene, generated from the thermolysis of hexafluoropropene oxide, to form cyclopentenes from 2-chloroperfluorobuta-1,3-dienes (**62**) and perfluoropenta-1,3-diene (**63**). Difluorocarbene is extremely electron deficient, and initially attacks electrophilically, forming a negative charge on the carbene carbon, which then effects the cyclopropane ring closure. Isomerisation of (**64**) then gives the cyclopentene in good yield.

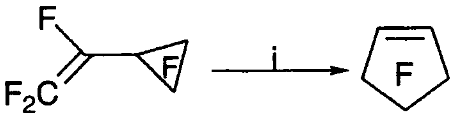


Similarly:



i. Autoclave, 190°C, 5 hrs

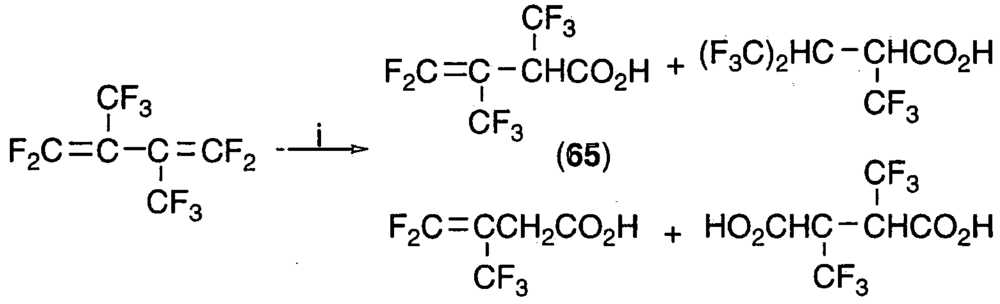
Intermediates (**64**) were proposed in light of work by Neuwar[55] who demonstrated that heating perfluorovinylcyclopropane, from perfluorobuta-1,3-diene and difluorocarbene, gave perfluorocyclopropene.



i. 190°C, 3 hrs

I.2.B Hydration and Dehydration Reactions

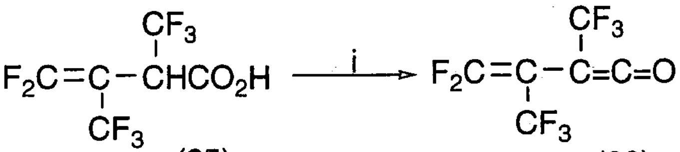
Russian workers have demonstrated the hydration of 2,3-bis(trifluoromethyl)perfluoro-1,3-diene, under mild conditions, to give a mixture of carboxylic acids.[56]



(65)

i. H_2O, $(CH_3)_2CO$, SiO_2, r.t., 1wk

Dehydration of acid (**65**) was performed using phosphorous pentoxide (P_2O_5) to give ketene (**66**), which was later observed in our laboratories.[48]

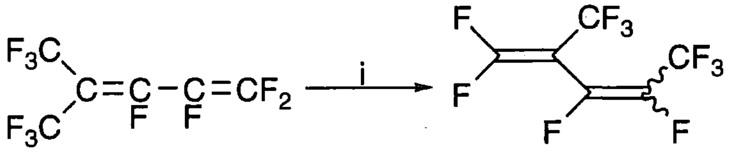


(65) **(66)**

i. xsP_2O_5, heat

I.2.C Electrophilic Attack

Research by Russian workers has demonstrated the use of SbF_5 in isomerisation and condensation reactions involving perfluorinated dienes.[44, 57-59] Perfluoro-2-methyl-2,4-pentadiene (**57**) was treated with SbF_5 to give *cis* and *trans* perfluoro-2-methyl-1,3-pentadiene (**67**) in a 1:1 ratio.[44]

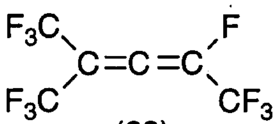


(57)

(67) *cis* , *trans*

i. SbF_5, 0-5°C

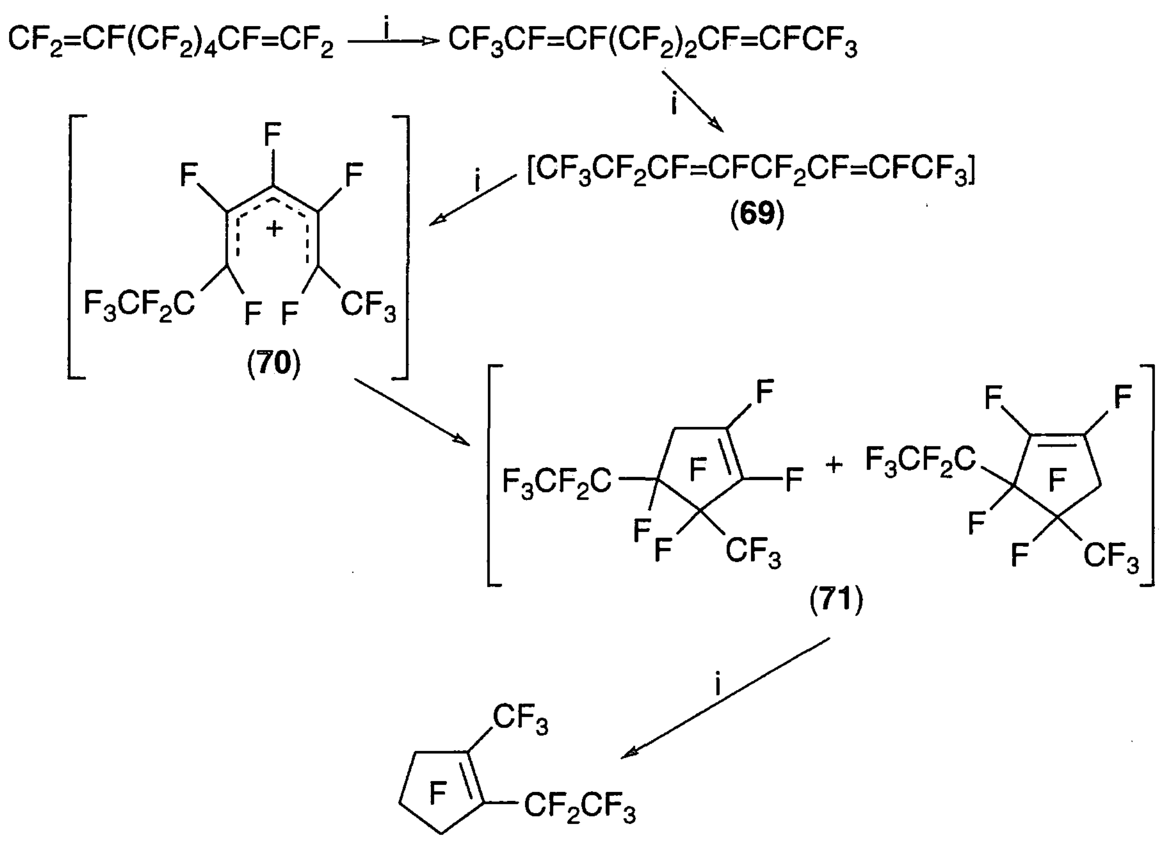
However, at 20°C this reaction gave tris(trifluoromethyl)fluoroallene (**68**) as the sole product.



(68)

Treatment of diene (**67**) under these conditions also gave (**68**), indicating the mechanism involves (**67**) as an intermediate.[44]

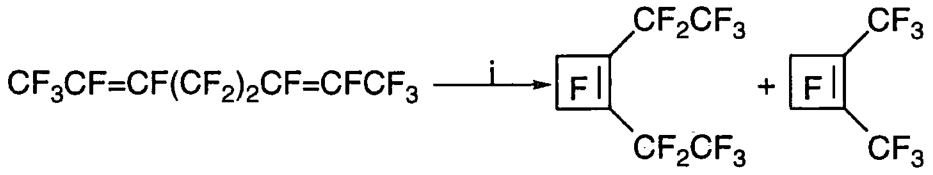
Interestingly, the same workers have observed isomeric transformations, using SbF_5, leading to a series of perfluorocyclopentenes and butenes. An example is shown below.[57, 58]



(**72**) i. xsSbF_5, 100°C, 20-26hrs

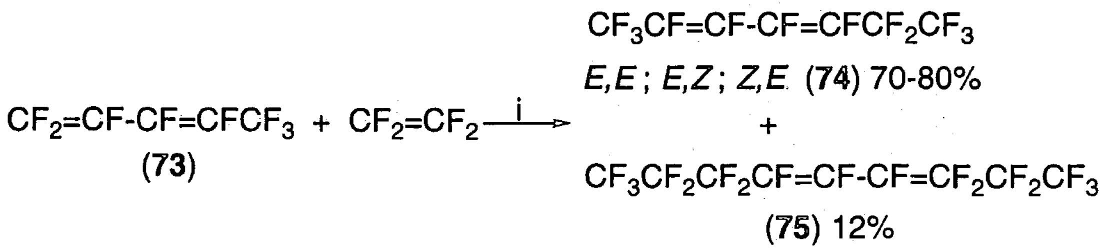
The mechanism involves two SbF_5 initiated isomerisations to give (**69**), followed by a 1,5-cyclisation of the generated pentadienyl cation (**70**) to cyclopentenes (**71**). These isomerise under the reaction conditions to give (**72**). It should be noted that 1,5-cyclisation of pentadienyl cations is well known for hydrocarbons.[60]

Interestingly, when a catalytic amount of SbF_5 was used, perfluorocyclobutenes were observed, due to intramolecular 1,4-cyclisations.[57, 58]



i. SbF_5, 100°C, 20-26hrs

The remarkable electrophilic condensation of perfluoro-1,3-pentadiene (73) with tetrafluoroethene, to give higher dienes, has also been described.[59]



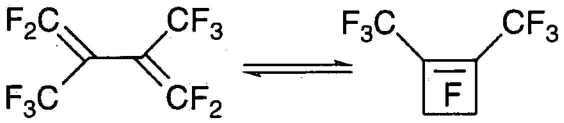
$$\underset{(73)}{CF_2{=}CF{-}CF{=}CFCF_3} + CF_2{=}CF_2 \xrightarrow{i} \begin{array}{c} CF_3CF{=}CF{-}CF{=}CFCF_2CF_3 \\ E,E;\ E,Z;\ Z,E\ (74)\ 70\text{-}80\% \\ + \\ CF_3CF_2CF_2CF{=}CF{-}CF{=}CF_2CF_2CF_3 \\ (75)\ 12\% \end{array}$$

i. Autoclave, SbF_5, r.t., 20hrs

Diene (75) arises from the condensation of a molecule of $CF_2{=}CF_2$ with (74).

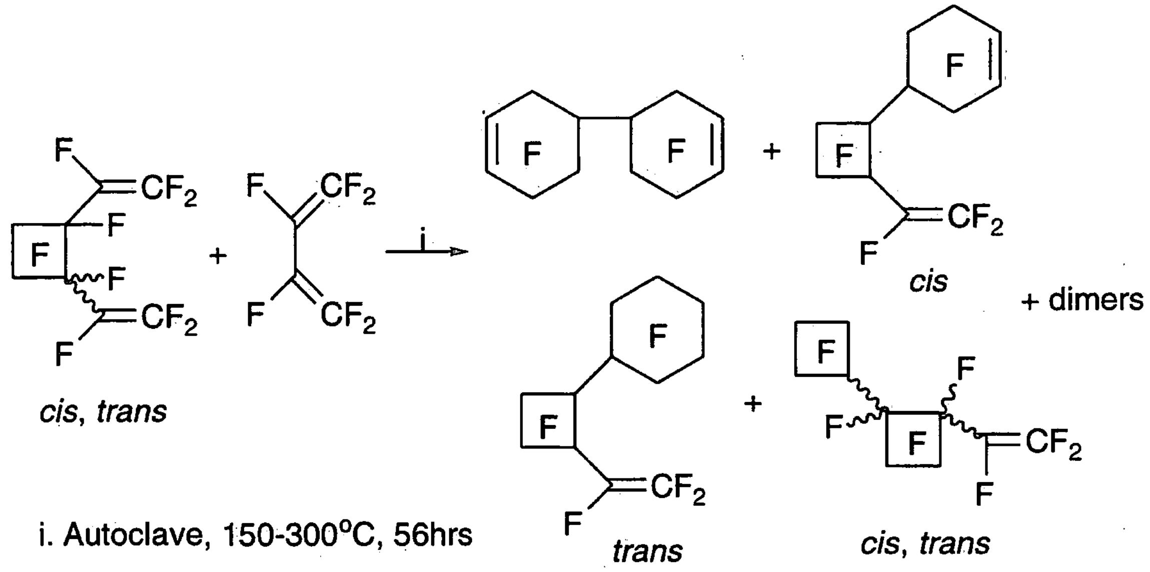
I.2.D Thermal Reactions

Early work by Cheswick[61] compared the kinetics of the thermal interconversion of isomeric perfluoro-1,2-dimethylcyclobutene and perfluoro-2,3-dimethyl-1,3-butadiene, at 290°C and 352°C, with their hydrocarbon equivalents.



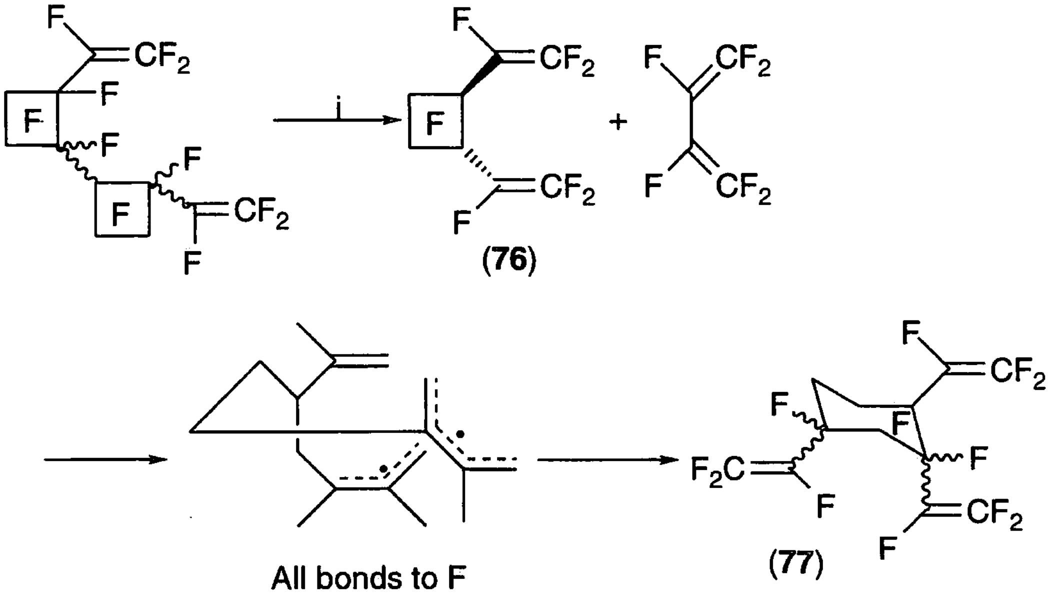
Equilibrium constants were measured, and it was concluded that the reaction follows reversible first order kinetics, and is likely to be a homogeneous unimolecular reaction. More importantly, the effect of fluorine was dramatic, with the equilibrium lying on the cyclobutene side for the fluorocarbon, and on the diene side with the hydrocarbon, as a result of the electron withdrawing CF_3 groups stabilising the π-electron system of the cyclobutene.[61] Dolbier has made similar kinetic studies on the thermal ring opening of various perfluorinated cyclobutenes.[62, 63]

Recent work by Kazmina[64, 65] involved the thermal reactions of hexafluoro-1,3-butadiene with its dimer, forming trimers.



i. Autoclave, 150-300°C, 56hrs

The composition of these complex mixtures varied with temperature and time. Thermal reactions of the trimers were then investigated, giving a variety of products, including (**77**) which arises from the previously unknown insertion of a hexafluorobutadiene molecule into the four membered ring of (**76**), giving a six membered ring.[65]



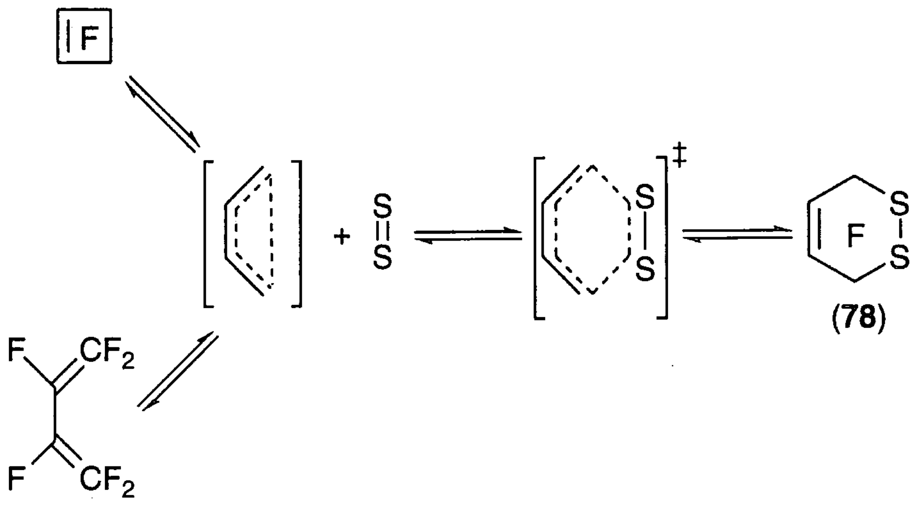
(**76**)

(**77**)

i. Autoclave, 300°C, 64hrs

In the same year, Kazmina[64] focused upon thermally inserting S_2 into hexafluoro-1,3-butadiene. This interest was stimulated by the use of synthetic disulphides as antiviral and anticancer agents, especially with the AIDS virus in mind.[64]

The main product was hexafluoro-3,6-dihydro-1,2-dithi-ine (78). Pyrolysis of sulphur (S_8), at 500°C, gave elemental sulphur (S_2), which inserted *via* the radical mechanism described below.



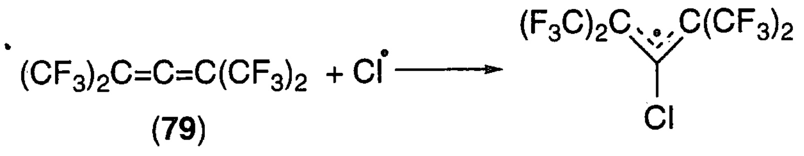
(78)

Again, the composition of the products was time and temperature dependant.[64]

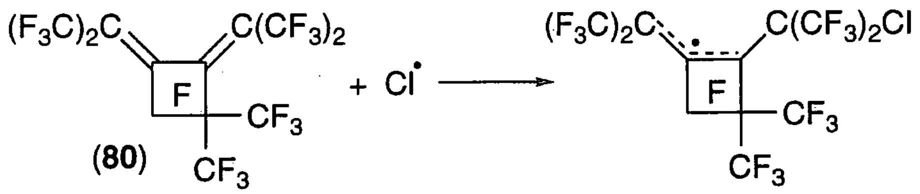
I.2.E Photochemical Reactions

The first stable allyl radicals were detected by Tumanskii[66], in 1989, using electron spin resonance (ESR) spectroscopy, and involved the photochemical chlorination of tetrakis(trifluoromethyl)allene (**79**), cyclic diene (**80**) and conjugated triene (**81**).

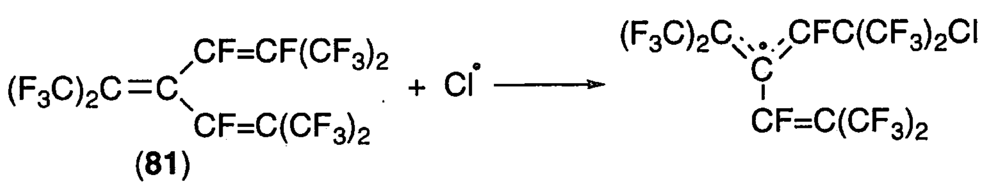
$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$$



(79)



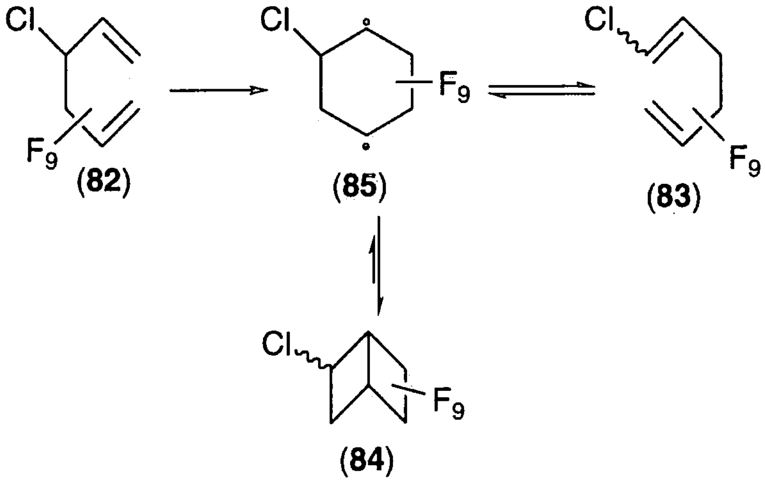
(80)



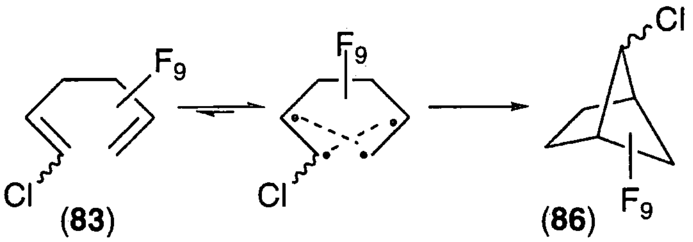
(81)

In all cases, the chlorine atom added regioselectively to give the least sterically strained product.[66]

Recently, Lemal has compared the Cope rearrangement in 1,5-hexadiene with that in its fluorocarbon counterpart, revealing some interesting conclusions.[67] Because the Cope rearrangement product of perfluoro-1,5-hexadiene is degenerate, Lemal used 3-chloroperfluoro-1,5-hexadiene (**82**); the chlorine label did not effect the mechanism. This diene was heated at 210°C for 2.5 days to give (**83**) and (**84**), in a 1:10 ratio.



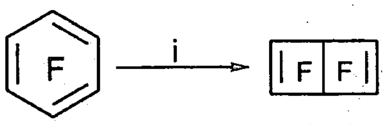
The Cope product (**83**) was then isolated and heated at 250°C for three days, giving (**84**) and (**86**) in an ~1:1 ratio.



No diene (**82**) was detected. These observations show that (**83**) is more stable than (**82**) and, more importantly, that cyclisation to (**84**) occurs more readily than the Cope rearrangement, in either direction. Biradical formation is therefore faster than the Cope rearrangement, and the transition state for a hypothetical concerted Cope rearrangement lies above those leading to the biradical (**85**) from either (**82**) or (**83**).[67] It was concluded that the Cope rearrangement proceeded *via* a biradical in this perfluorinated system, unlike the hydrocarbon system where the Cope transition state requires partial double bond character among all six participating carbons.[67] A detailed review of [1,3]-sigmatropic rearrangements of fluorinated compounds has recently been published by Purrington.[68]

I.2.F Isomerisation

In 1966, Camaggi[69] and Haller[70] described the photoisomerisation of hexafluorobenzene to give hexafluorobicyclo[2.2.0]hexa-2,5-diene (**87**) as the only product.

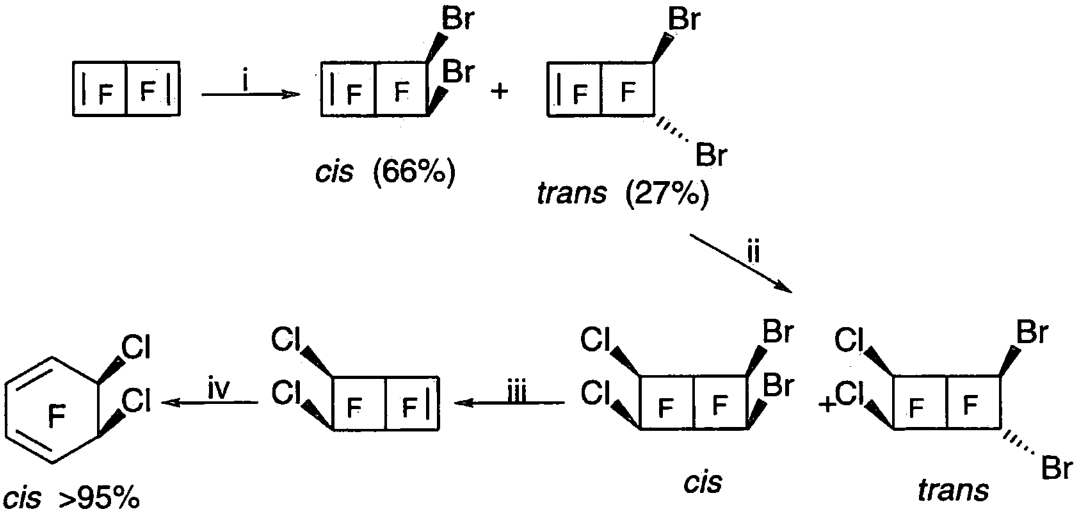


(**87**)

i. U.V., 25°C

It should be noted that (**87**) may detonate as the neat liquid.

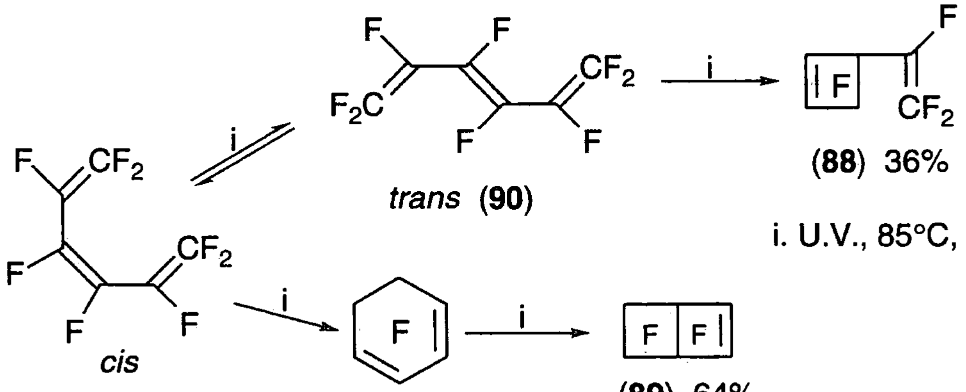
This preparation has been exploited by Lemal[71] to synthesise 5,6-dichloro-hexafluoro-1,3-cyclohexadiene.



i. Br_2, U.V., 0°C; ii. Cl_2, U.V., 0°C; iii. Zinc dust, ether, reflux, *ca.* 4 hrs;
iv. Agitation, 200°C, 4 hrs

Interestingly, the bromine analogue could not be isolated, as aromatisation occurs on the final pyrolytic step, giving hexafluorobenzene and bromine.

More recently, Dedek [72] has demonstrated that irradiation of octafluoro-1,3,5-hexatriene in the vapour phase gave two valence isomers, *i.e.* octafluoro-2-vinylcyclobutene (**88**) and octafluorobicyclo[2.2.0]hex-2-ene (**89**).



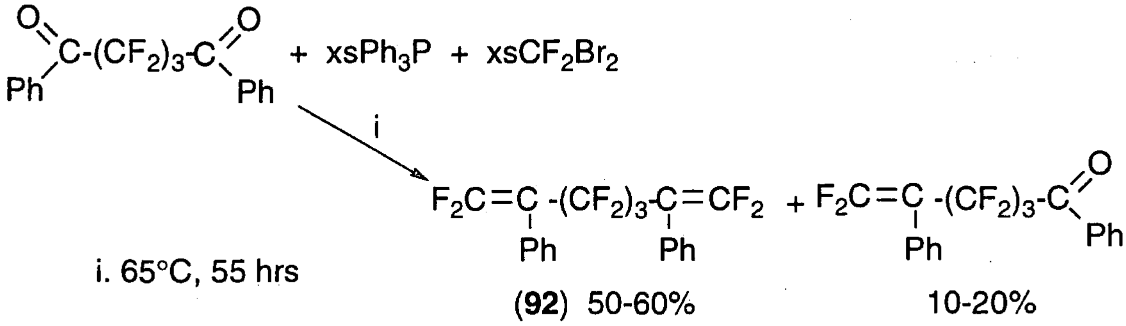
(**88**) 36%

(**89**) 64%

i. U.V., 85°C, 5 hrs

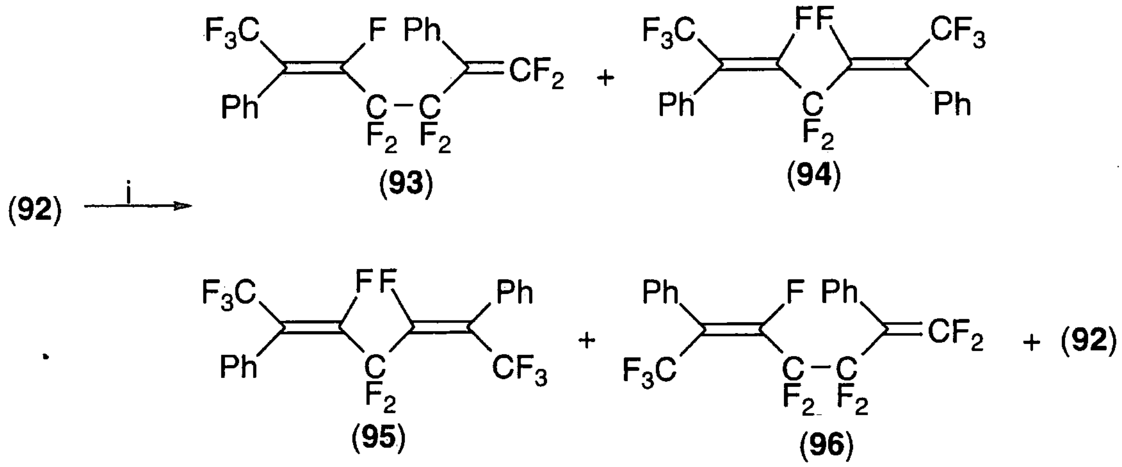
Products (**88**) and (**89**), plus intermediate (**90**), were all isolated, and perfluorocyclohexa-1,3-diene (**91**) was synthesised separately and shown to undergo conversion to (**89**), which supports the pathway.

Burton[73] has described an unusual synthesis of fluorinated heptadienes, and their thermal and fluoride ion induced isomerisations. The procedure employs Wittig chemistry to convert diones into dienes, giving moderate yields (50-60%) of the corresponding diene (**92**).



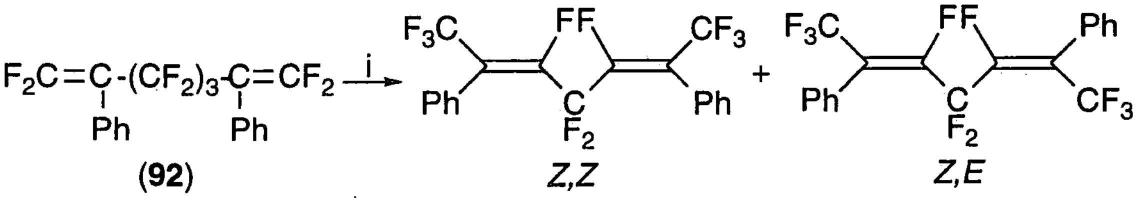
i. 65°C, 55 hrs

Thermal isomerisation of (**92**) yielded four dienes, containing internal double bonds, with the ratio of (**93**):(**94**):(**95**):(**96**):(**92**) being 8.0:6.5:3.1:5.5:1.0.



i. Ampoule, 250°C, 48 hrs

The fluoride ion isomerisation readily gave two internal dienes, with none of the *E,E*-isomer being observed.



i. Et$_4$NF, DMF, r.t., 30 min.

The ease of isomerisation of (**92**) illustrates the value of the Ph_3P/CF_2Br_2 approach, which yielded only the terminal diene.

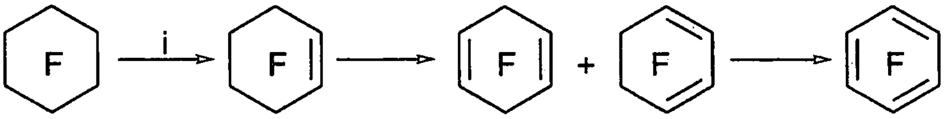
Chapter Two
Defluorination

II Methods of Defluorination

Several methods concerned with defluorinating saturated fluorocarbon systems, to give unsaturated products have been described in the literature. The main system involves using hot metals, although defluorination using electrochemical cells, organometallics and carbon, amongst others, have been detailed. A review of these procedures follows.

II.1 Metal Reactions

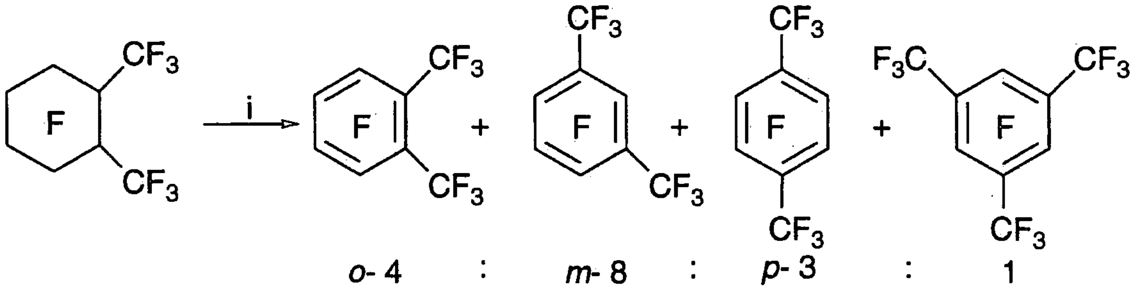
The defluorination of perfluorocyclohexanes, over iron at 300-600°C, to give the corresponding aromatic and diene products has been described by Tatlow.[38, 74-76] For example, perfluorocyclohexane was defluorinated to give hexafluorobenzene and low yields of the intermediate dienes.[38]



i. Fe, 500°C, N_2 flow

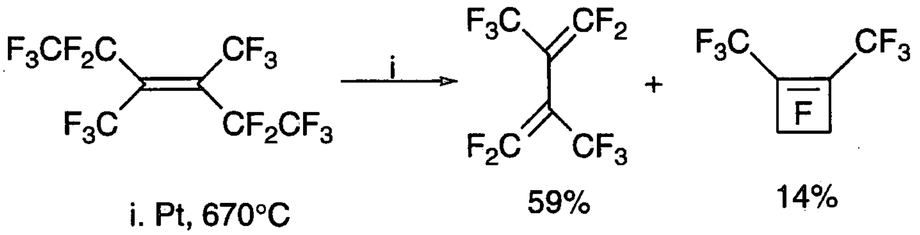
Later publications have described similar reactions, and some of the chemistry of the defluorinated products.[74, 77] Interestingly, the defluorination of cyclohexanes was also observed when perfluorocyclohexane and perfluoro-1,4-dimethylcyclohexane were passed through a reactor containing, as a packing material, caesium trifluorocobaltate, at *ca.* 390°C, to give the corresponding aromatic compounds, and caesium tetrafluorocobaltate III, which is used as a fluorinating agent.[75] Tatlow[76] has also reported the rearrangement of the trifluoromethyl group when perfluoro-1,2-dimethylcyclohexane was defluorinated over nickel at 400-500°C. The observed F-xylene isomer ratios were dependant on temperature and the age of the nickel turnings.

At a temperature of 400°C, and employing nickel that has been used extensively for defluorination, and as a result was finely divided, the products were decafluoro-*p*-, -*m*- and -*o*- xylene, plus dodecafluoromesitylene.



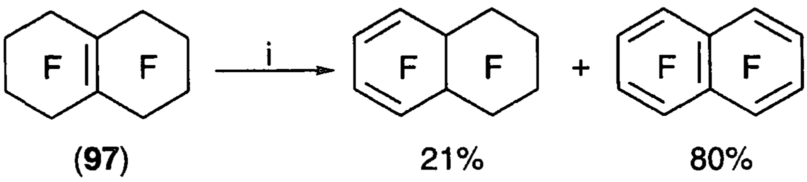
i. Ni, 400°C, N_2 flow

Work in our laboratories has detailed defluorination of perfluoroalkenes, over platinum or iron, at elevated temperatures, to give fluorinated dienes and cyclobutenes.[78]



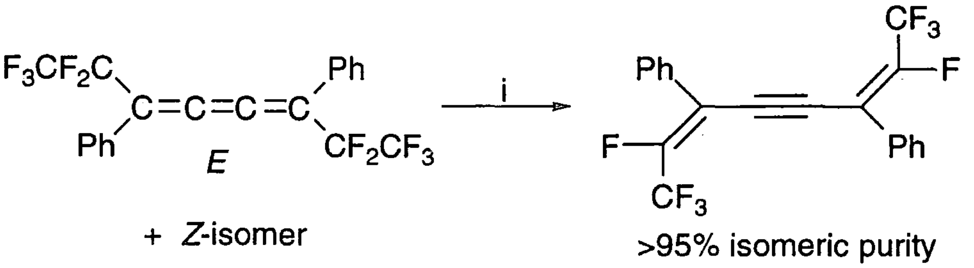
i. Pt, 670°C

Some decomposition also occurred to give C_2F_6 (39%) and C_3F_8 (10%) fragments. It is worth noting that when fresh iron was used, at 540°C, four completely different products were observed, two of which have been explained by intramolecular 1,3-shifts of fluorine.[78] Chinese workers have described the defluorination of hexadecafluorobicyclo[4.4.0]dec-1(6)-ene (**97**) using activated zinc to give the aromatic system. The product ratio depended on solvent polarity and the best results were obtained using dimethylformamide (DMF).[53]



i. Zn, DMF, 80°C, 2 hrs

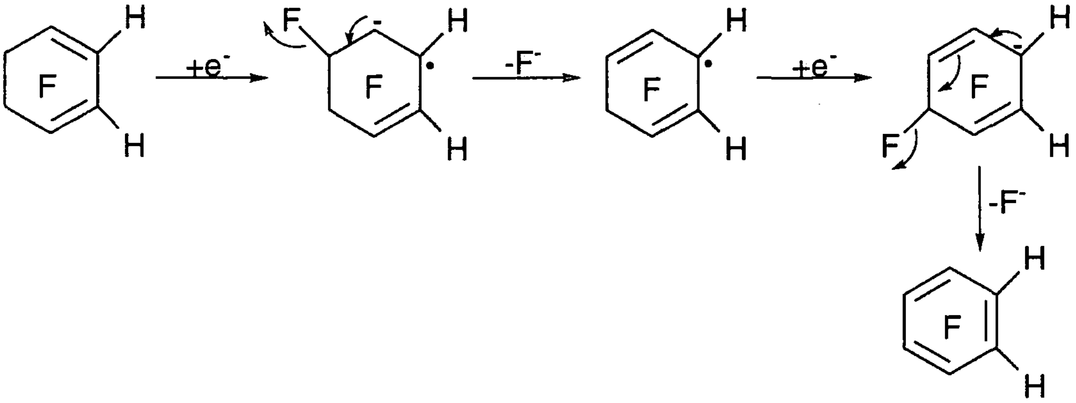
A recent report by Burton[79] described an interesting, mild zinc induced defluorination of butatrienes to give divinylacetylene derivatives. These reactions proceed stereoselectively.



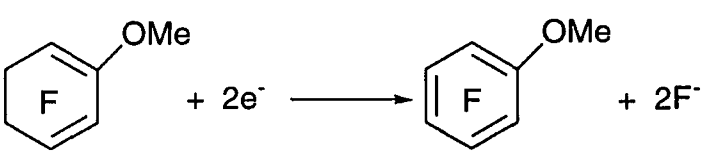
i. Zn, DMF, r.t., 18 hrs

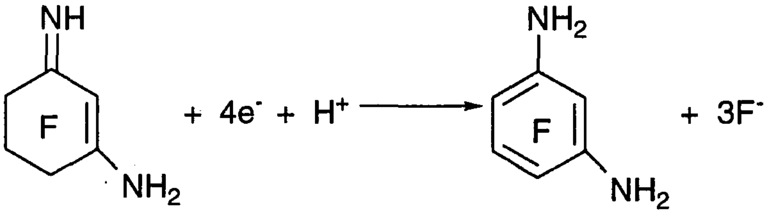
II.2 Single Electron Transfer

Tatlow[80], in 1968, described the reduction of 2H,3H-hexafluorocyclohexa-1,3-diene, at a mercury electrode, to give 1,2,3,4-tetrafluorobenzene as the sole product. A mechanism was suggested which involved the transfer of two electrons to the diene, with the formation of an intermediate radical (see Section II.2.A).

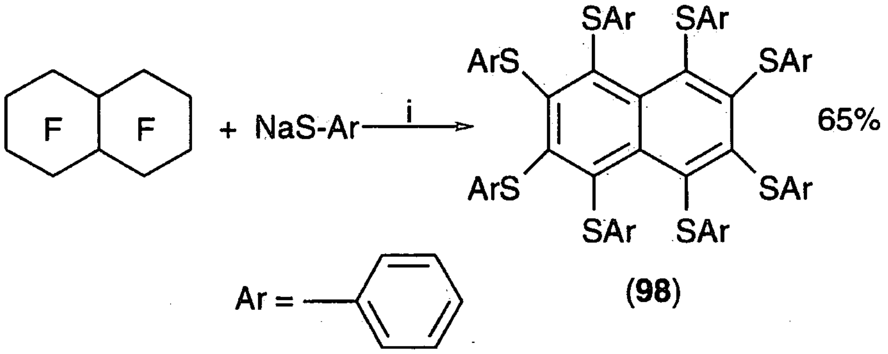


In 1971, Pedler[81] described the reduction of the similar octafluorocyclohexadiene system, and the preparation of substituted fluoroaromatics from various fluorinated dienes.[82]





MacNicol[83], in 1988, described the unusual transformation of perfluorodecalin to octakis(phenylthio)naphthalene (**98**).



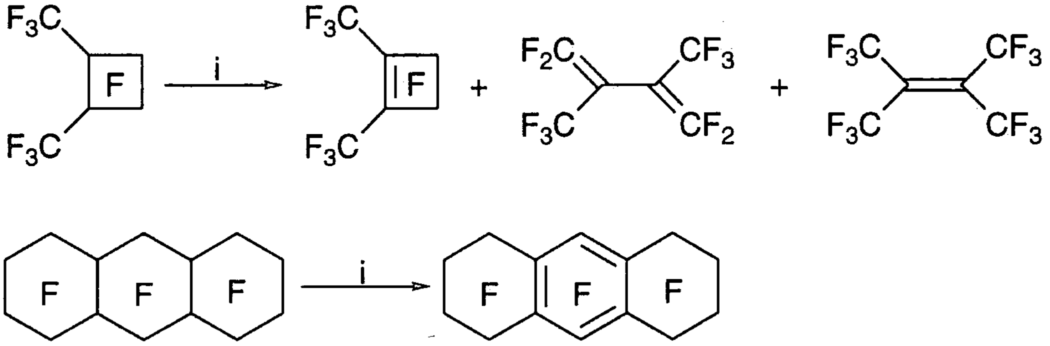
(**98**)

i. 1,3-dimethylimidazolidin-2-one (DMEU), 60-70°C, 10 d

The authors have suggested a mechanism which is likely to involve, as the first step, either nucleophilic attack on a tertiary fluorine leading to a bridgehead carbanion, $C_{10}F_{17}^-$, directly, or single electron transfer, from sulphur, to form a radical anion, $C_{10}F_{18}^{\cdot -}$, capable of eliminating fluoride, to give a tertiary carbon radical which could accept an electron to form $C_{10}F_{17}^-$. The presence of a tertiary centre is very important, and this is demonstrated by the observation that perfluorocyclohexane, without a tertiary centre, does not react under similar conditions.[83] More recently, Pez[84] has described the use of the sodium benzophenone radical anion to reduce perfluoroalkanes, at near room temperature, to give products which still contain fluorine. For example, perfluorodecalin was reduced to perfluoronaphthalene (62%), in tetrahydrofuran, after only 1.5 hrs at room temperature. An interesting application of defluorination techniques has been to enhance the adhesion of fluoropolymers, such as polytetrafluoroethene (PTFE), which are often difficult to adhere to. One procedure discussed at a recent fluoropolymers conference[85] was to use sodium naphthalenide, in tetrahydrofuran, to defluorinate PTFE. Remarkably, a sixty second immersion in a 1M solution resulted in a 15-fold increase in adhesion to an epoxide. Examination of the post-treatment polymer showed almost complete defluorination, with a large increase in the number of oxygen containing functionalities (*e.g.* carbonyl and hydroxyl groups), which arise from the reaction of carbon with atmospheric oxygen.[85] Sodium[86] and lithium[87] in liquid ammonia have also been used to defluorinate PTFE.

II.3 Over Activated Carbon

Weigert[88, 89] has shown that perfluorocarbons defluorinate over activated carbon (*i.e.* high surface area), which will readily accept fluorine, at temperatures below those required for metal defluorinations, giving unsaturated derivatives.

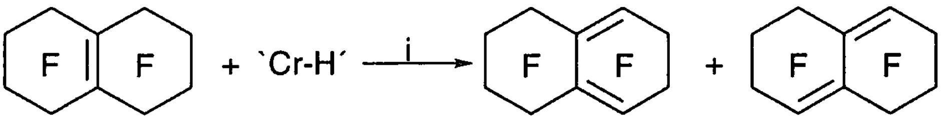


i. Autoclave, carbon, 400°C, 4 hrs

The conversions of perfluoro-1,2-dimethylcyclobutane and perfluoroperhydrophenanthrene were 18% and 100% respectively, although no yields were reported.

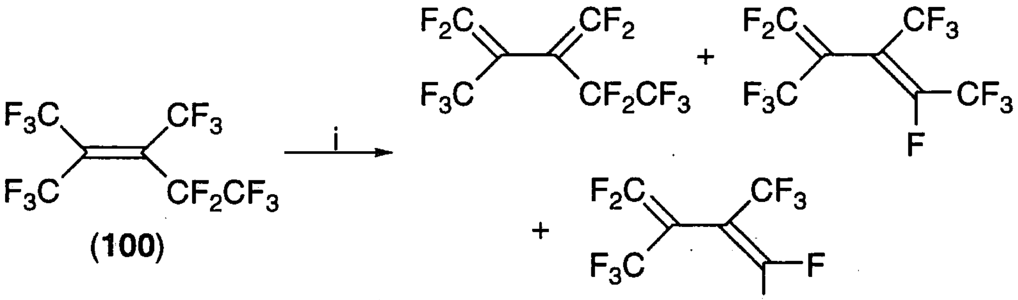
II.4 Organometallics

Various organometallic reagents have been used to activate C-F bonds, often in unsaturated or aromatic substrates. In 1988, M^{c}Donald[90] defluorinated simple F-alkenes and F-alkanes, such as $CF_2{=}CF_2$ and CF_3CF_3, using $Mn(CO_3)^-$ to give product ions of the general structure $F_2Mn(XC_2Y)^-$, where X and Y are F or H. Dienes have been synthesised from alkenes by Huang[91], who has demonstrated the use of a `Cr-H′ species to form bicyclic compounds (**99**), and Watson[92], who used divalent lanthanoid complexes to reduce, for example, perfluoro-2,3-dimethylpent-2-ene (**100**).



(99)

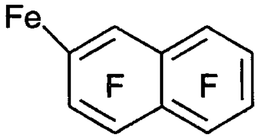
i. THF, -70-20°C, 12 hrs



(100)

i. YbMCp$_2^{**}$THF, r.t.

Recently, Richmond[93] has reported using $CpFe(CO)_2$ to reduce perfluoromethylcyclohexane and perfluorodecalin to the iron bound fluorinated aromatic systems, and Andersen[94] reported employing a uranium complex, $(MeC_2H_4)_3U(t\text{-}Bu)$, to replace a fluorine with hydrogen in perfluorocyclohexane and hexafluorobenzene.



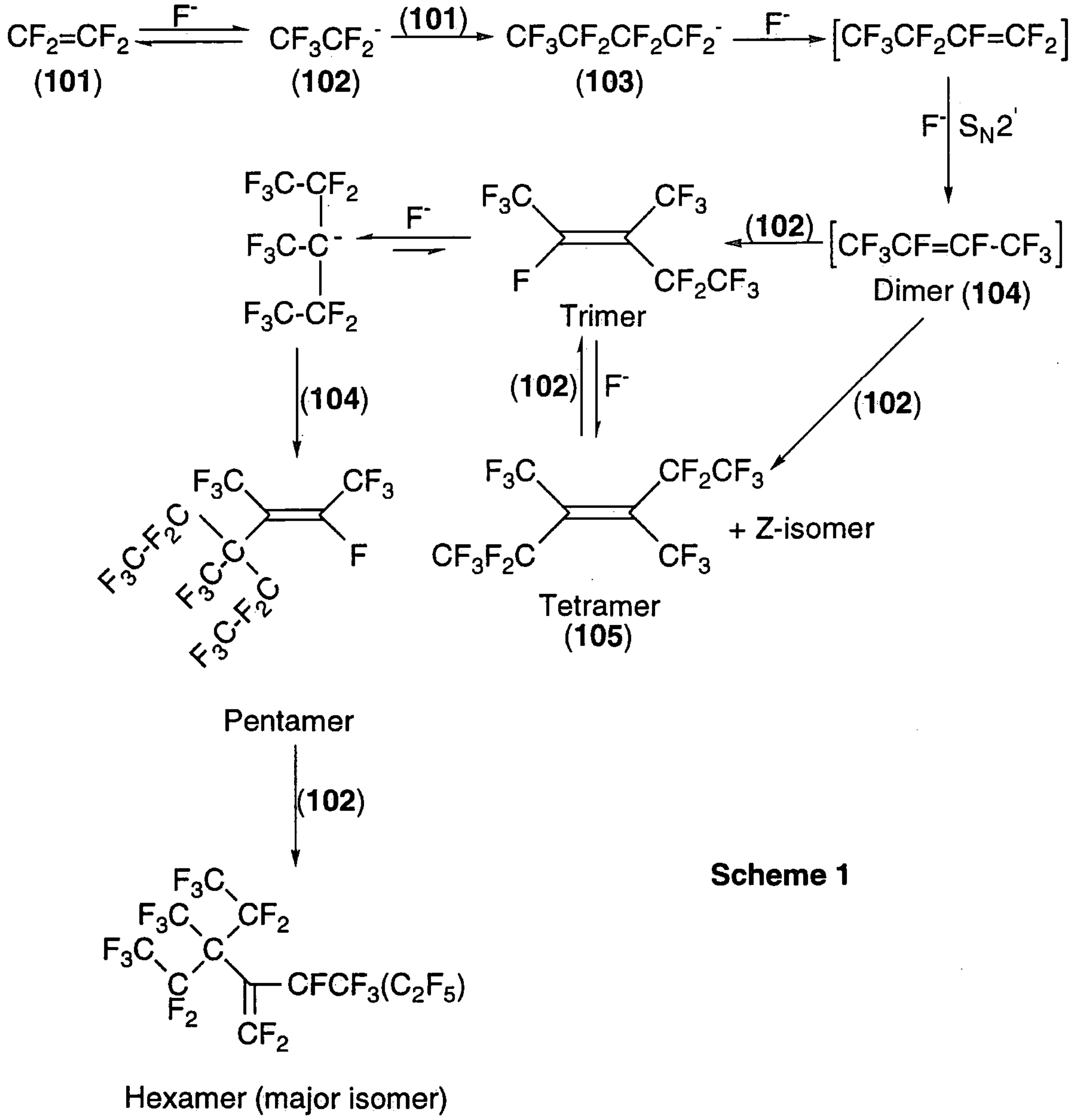
Where Fe=$CpFe(CO)_2$

Ref 93

Although there appears to be some potential in using organometallic for defluorinations, they are unlikely to replace the cheaper, and less hazardous, procedures described earlier.

II.5 The Synthesis of Perfluoro-3,4-dimethylhex-3-ene (105)

Perfluoroalkenes, and -cycloalkenes, may be oligomerised, in fluoride ion induced processes, to give synthetically more sophisticated systems. Tetrafluoroethene has been utilised in this way to synthesise its tetramer (**105**), pentamer and hexamer.[95] Fluoride ion adds to (**101**) to give a carbanion (**102**), which reacts with a second molecule of (**101**), giving carbanion (**103**). Fluoride ion is then eliminated, without any anionic polymerisation of (**103**), giving an external alkene, which rapidly isomerises to the more stable internal alkene (**104**) (see Section II.6.B). Further substitution by (**102**) leads to the tetramer (**105**) of tetrafluoroethene. This process can be extended to form the corresponding pentamer and hexamer (Scheme 1). Formation of the hexamer is intriguing, because it is a rare example of a terminal isomer being thermodynamically favoured over an internal isomer.[5]



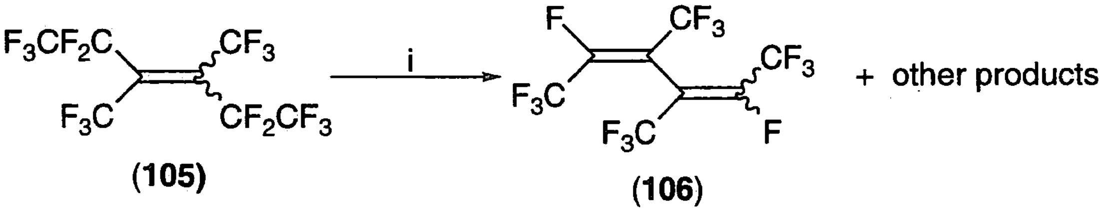
Scheme 1

Tetramer (**105**) is the precursor to the diene used throughout most of this work. Reduction, or defluorination, of (**105**) to give perfluoro-3,4-dimethylhexa-2,4-diene (**106**) has been investigated using electrochemistry, alkali metal amalgams and an interesting electron rich amine, tetrakis(dimethylamino)ethene (**107**), and these systems are described in this Chapter.

II.6 Electrochemical Defluorination of Tetramer (105)

Tatlow[80] and Pedler[81] described the electrochemical defluorination of cyclohexenes and cyclohexadienes to give the aromatic systems (see Section II.2). Whether this kind of process could be applied to highly fluorinated acyclic systems, such as alkene (**105**), to give the corresponding diene, was investigated.

Tetramer (**105**) was added to the working electrode compartment (the cathode) of an electrochemical cell, where a potential of -1.70V was applied for 5.5 hrs. The isolated fluorocarbon was identified as a mixture of (**105**) and perfluoro-3,4-dimethylhexa-2,4-diene (**106**) (15% calculated by ^{19}F NMR spectroscopy).

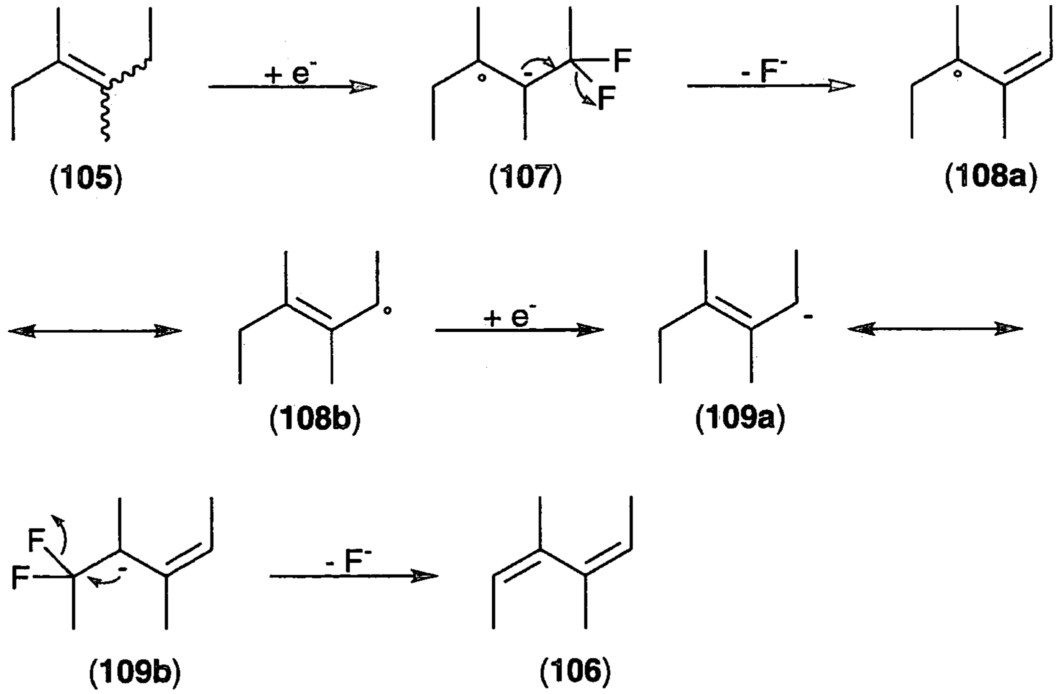


i. Divided cell, CH_3CN, tetrethylammonium tetrafluoroborate

Attempts to characterise the brown solid coating the working electrode failed, and this remains unidentified. However, they may have arisen from side reactions of the substrate (**105**), which have been encountered by previous workers[96], possibly including reaction with the bulk solvent, the electrolyte, or polymerisation. The latter occurs under similar conditions with perfluorocyclobutene and perfluorocyclopentene.[97]

II.6.A The Defluorination Mechanism

The mechanism of the defluorination process is most likely that indicated in Scheme 2, with initial single electron transfer, giving radical anion (**107**), followed by loss of fluoride ion; further reduction of the allyl radical (**108a,b**) would lead to the anion (**109a,b**), from which further loss of fluoride ion could occur, giving (**106**).



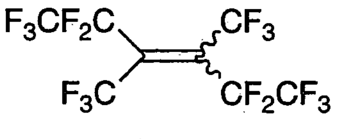
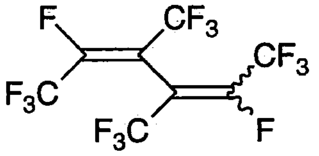
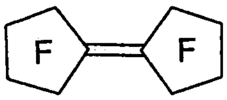
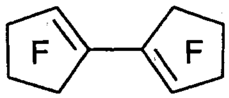
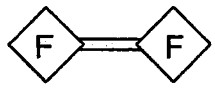
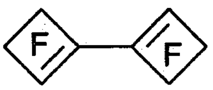
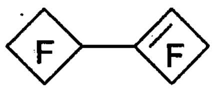
All unmarked bonds to fluorine

Scheme 2 Mechanism of defluorination

II.6.B Reduction Potentials of Fluorinated Systems

The reduction potentials of a number of perfluorinated alkenes have been measured[98], and some of these are shown in Table 1.

Table 1 Reduction potentials of some perfluorinated alkenes and dienes

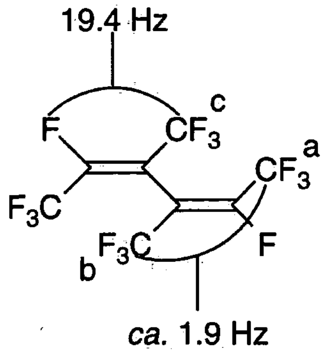
Alkene	Reduction Potential/V*	Diene	Reduction Potential/V*
 **(105)**	-1.62 ± 0.05	 **(106)**	-2.35 ± 0.10
 **(110)**	-1.06 ± 0.03	 **(111)**	-2.03 ± 0.01
 **(112)**	-1.10 ± 0.03	 **(113)**	-2.25 ± 0.01
 **(114)**	-1.23 ± 0.03		

Chambers[2, 13, 99] has suggested that a perfluoroalkyl group attached to a double bond decreases both the HOMO and LUMO orbital energies to a greater extent than when fluorine is attached, due to electron-pair repulsions with the latter. This idea has been supported by Rozhkov[100], who has measured the molecular orbital energies in the perfluoroalkenes obtained by successively substituting all of the fluorine atoms in tetrafluoroethene by trifluoromethyl groups. Therefore, it follows that systems with four perfluoroalkyl groups attached to a double bond have lower frontier orbital energies than those with three and a vinylic fluorine. As the first step in an electrochemical reduction is the addition of one electron to the LUMO, decreasing the energy of this has the consonant effect on the applied potential; all potentials in Table 1 are low. The reduction potentials of alkenes (**105**) and (**110**) appear, at first site, to differ by more than expected, since both can be considered as having four perfluoroalkyl groups attached to a double bond. However, there is considerable angle strain in (**110**), and the addition of an electron to the double bond, giving a radical anion, would relieve such strain, lowering the value for (**110**). In view of this, alkene (**112**), which has angle strain in both rings, should have a significantly lower reduction potential than (**114**), with the angle strain only in one ring. This is not the case, which could be explained by the vinylic fluorine attached to the double bond in (**114**) increasing the orbital energies, and hence decreasing the reduction potential relative to that of (**112**).

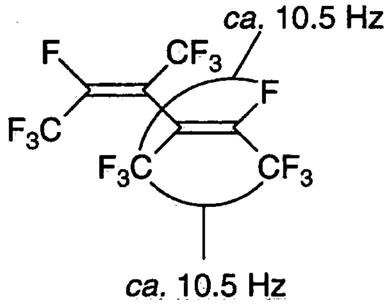
Dienes (**106**), (**111**), and (**113**) can all be considered to have double bonds with three perfluoroalkyl groups and a vinylic fluorine attached and, as expected, the reduction potentials are all about 1V higher than those of the corresponding alkenes. This demonstrates nicely the difference in effect of perfluoroalkyl groups, R_F-C=C, and a vinylic fluorine, F-C=C, at a double bond. As mentioned, the perfluoroalkyl group lowers orbital energies, whereas with a fluorine atom the electron withdrawal is offset by electron-pair repulsions, leading to little difference between hydrogen and fluorine. This fact is essential in the successful isolation of the dienes; lower potentials may have resulted in their reduction.

II.6.C The Structure of Perfluoro-3,4-dimethylhexa-2,4-diene (106)

Reduction of tetramer (**105**) gives both *Z,Z*- and *Z,E*-perfluoro-3,4-dimethylhexa-2,4-diene (**106**), in a ratio of *ca.* 37:10, and identification of each of these isomers followed from analysis of J CF_3,F and J CF_3,CF_3 values.[9, 101]



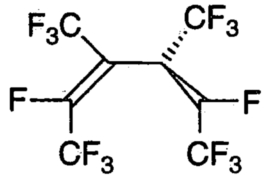
(106a)



(106b)

The large ^{5}J(*cis*-CF_3,CF_3) coupling (*ca.* 10Hz) is very obvious relative to a small ^{5}J(*trans*-CF_3,CF_3) value (*ca.* 2Hz). Also, ^{4}J(*trans*-CF_3,F) values are less than those of ^{4}J(*cis*-CF_3,F). Remarkably, for the *Z,Z*- isomer (**106a**), *pseudo*-septets were observed for CF_3-a and CF_3-b. These arise from the equal coupling of CF_3-b and CF_3-c with CF_3-a, and CF_3-a and CF_3-c with CF_3-b, in an $(A_3)_2(X_3)_2$ system. The J value was 1.9 Hz, which is indicative of a *trans,trans* diene.

A molecular model of diene (**106**) indicates that a planar structure, with a *trans* conformation about the double bonds, is possible. This would be consistent with buta-1,3-diene[102], but gas phase electron diffraction studies by Bauer[103] and *ab initio* molecular orbital studies by Dixon[104] on perfluorobuta-1,3-diene, have shown that a substituent as small as fluorine can lead to non-planarity in the diene, with the minimum energy conformer adopting a skew-*cis* structure. Diene (**106**) has four CF_3 groups, in place of four fluorines in perfluoro-1,3-diene, so there will be considerable steric demands on this system; recent work by Kumadaki[105, 106] has shown the steric effect of a CF_3 group, through the ene reaction of trifluoromethyl ketones, is much larger than a phenyl or isobutyl group, and as large as a *sec*-butyl group. Therefore, it seems reasonable to suggest that diene (**106**) will also adopt a skew-*cis* structure as the minimum energy case. This is shown below for the *Z,Z*- isomer of (**106**).



Support for this argument also arises from the appearance of two C=C stretching bands in the infrared spectrum of diene (**106**), suggesting an asymmetrical structure. This is in contrast, for example, to butadiene, which is symmetrical and only gives one band in the C=C stretch region.[4]

II.7 Defluorination using Alkali Metal Amalgams

II.7.A Introduction

The preparative electrochemical procedure, described in Section II.6, was low yielding and difficult to scale up. As a result, amalgam systems were investigated in an attempt to mimic this process, and to investigate the type of system to which it is applicable.

Previous work in these laboratories has described the successful defluorination of bicyclic alkenes (**110**) and (**112, 114**) to the corresponding dienes (**111**) and (**113**).[96, 98, 107-109] Besides these, few citations involving dehalogenation with amalgams have been reported in the literature. Kavan[110] examined the products from the reduction of hexafluorobenzene and tetradecafluorohexane with lithium amalgam, concluding they consisted of a mixture of lithium fluoride, elemental polymeric carbon, which was electronically conducting and reactive towards oxygen, and a small amount of superstoichiometric lithium. Later, in 1990, Alonso[111] described the selective dehalogenation of halogenoarenes by using sodium amalgam in liquid ammonia.

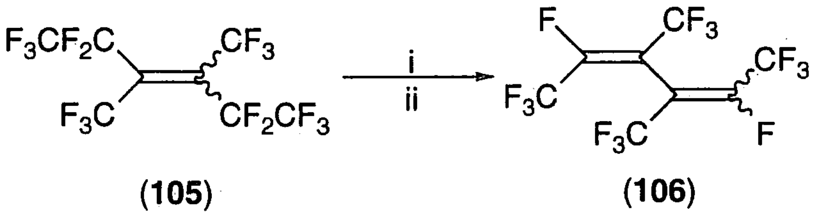
$$P(o)\text{-}X\text{-}C_6H_4Cl + Na(Hg) \xrightarrow{\text{i}} PhCl + X^-$$

i. NH_3, Bu^tOH, r.t.

Interestingly, French workers[112] have recently reported the novel application of sodium amalgam to hydrocarbon systems, producing dienes and trienes in good yield.

II.7.B Perfluoro-3,4-dimethylhex-3-ene (105)

Both sodium and potassium amalgams were used to reduce the tetramer (**105**) of tetrafluoroethene. Tetramer (**105**) was shaken with freshly prepared amalgam, and the volatile material was identified as perfluoro-3,4-dimethylhexa-2,4-diene (**106**) by ^{19}F NMR spectroscopy.

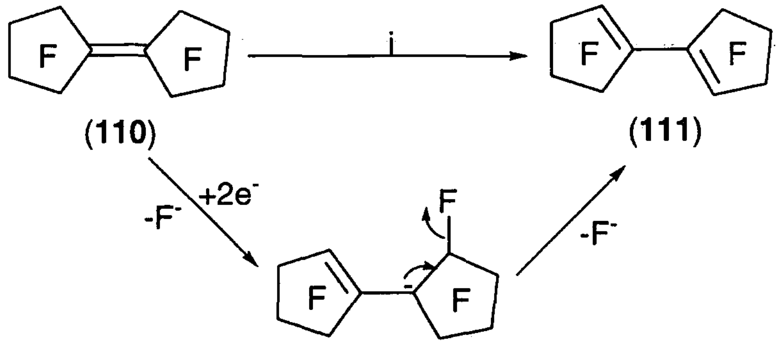


i. Na/Hg, agitate, r.t. (85%); ii. K/Hg, agitate, r.t. (39%)

Ambiguously, the yields of diene (**106**) using lithium and sodium amalgams differed greatly. Lithium has the higher electrode potential[1], *i.e.* is a stronger reducing agent, and should be as efficient as sodium. Another problem with lithium is its low, room temperature, solubility in mercury, causing amalgam preparation to be tedious. Finally, it is worth noting that using fresh amalgam is important; if left over-night, before use, only *ca.* 50% conversion was observed (see Chapter VI, Table 2).

II.7.C Perfluorobicyclopentylidene (110)

The use of sodium amalgam was applied to this bicyclic system. As mentioned earlier, high angle strain in (**110**) facilitates a relatively low reduction potential. Alkene (**110**) was shaken with fresh amalgam [this reaction was much more vigorous than for (**105**)], and volatile material was shown to be perfluoro-1,1′-bicyclopent-1-enyl (**111**)



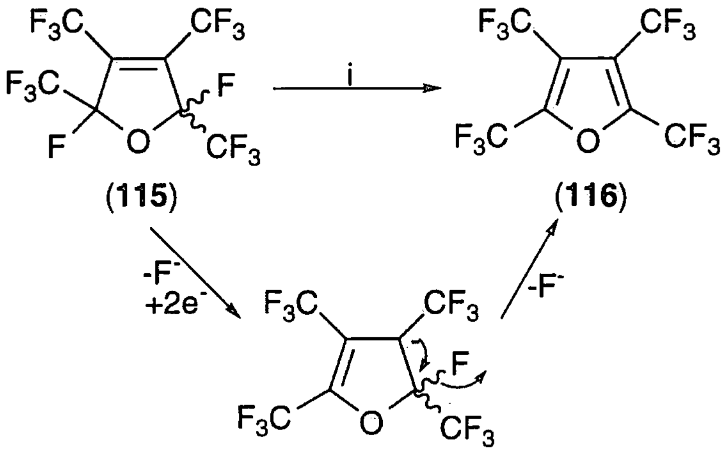
i. Na/Hg, agitation, r.t. (84%)

The mechanism of reduction is analogous to that of tetramer (**105**), involving the transfer of single electrons, and the yield compares well with values previously reported by Nakamura[107] and Mullins.[98] Occasionally, the conversion of alkene (**110**) is low, and it was found that cooling the mixture of (**110**) and (**111**) to *ca.* 60°C led to crystallisation of diene (**111**), which could be obtained pure by low temperature filtration.

II.7.D Perfluoro-2,5-dihydrotetramethylfuran (115)

The alkenes discussed so far, in this Chapter, have contained only carbon and fluorine. It was of interest to investigate whether a sodium amalgam system could be employed to reduce a dihydrofuran to the corresponding furan.

Furan derivative (**115**) was prepared by a method developed in these laboratories.[113] After shaking (**115**) with fresh amalgam, volatile material was identified as tetrakis(trifluoromethyl)furan (**116**), by comparison with an authentic sample.

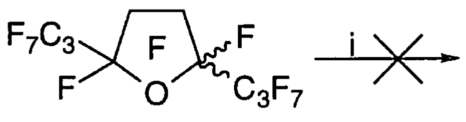


i. Na/Hg, agitation, r.t. (75%)

This reaction proceeded smoothly, in good yield, to give furan (**116**) by the single electron transfer mechanism already described (see Section II.6.A), and the presence of a hetero-atom did not have any detrimental effect, indicating the possibility of increasing the scope of this procedure.

II.7.E Attempted Reduction of Perfluoro-2,5-di-n-propyloxolane (117)

To establish whether unsaturation was necessary for the amalgam system to work, the oxolane (**117**) was used. After agitation with the amalgam, volatile material was found to be only oxolane (**117**) (73% recovery) by ^{19}F NMR spectroscopy.



(117)

i. Na/Hg, agitate, r.t.

This result indicates that unsaturation is required for a compound to accept electrons during the single electron transfer mechanism.

II.7.F Conclusion

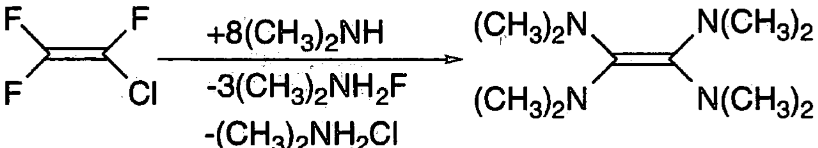
Alkali metal amalgams have provided an efficient route to perfluorinated dienes, by reduction of their alkene precursors. The results described indicate, for the defluorination process to operate successfully, an alkene structure of the type R_FCF_2-$C(R_F)$=$C(R_F)$-

CF_2R_F is required, so that a double bond is available to accept an electron, and a fluorine can be eliminated from difluoromethene in the primary step, to leave an allyl radical. Further reaction then leads to dienes (see Section II.6.A).

II.8 Defluorination using Tetrakis(dimethylamino)ethene (107)

II.8.A Introduction

Tetrakis(dimethylamino)ethene (**107**) is a very interesting electron rich amine, which was first discovered by Pruett[114], in 1950, who synthesised it from chlorotrifluoroethene and dimethylamine.



(**107**) Pale green liquid

A second synthesis has been reported by Weingarten[115], which involves the pyrolysis of tris(dimethylamino)methane, $HC[N(CH_3)_2]_3$.

$$2HC[N(CH_3)_2]_3 \xrightarrow{i} (107) + 2NH(CH_3)_2$$

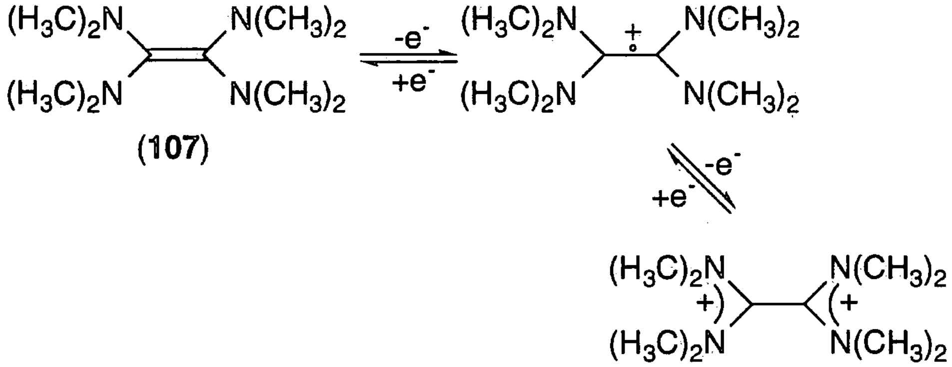
82%

i. 150-190°C, 72 hrs

The structure of (**107**) is unusual, as the molecule is non-planar, with the C=C axis (stretched to 135pm) twisted by 20°, and each two opposite $(CH_3)_2N$ groups are nearly planar.[116] Comparison with literature data confirms that (**107**) is one of the most distorted simple ethenes known, even with respect to sterically overcrowded fulvene derivatives, which have the highest distortion values known (C=C distance up to 141pm and twist angles as high as 40°). In contrast, the tetraisopropyl derivative, $((CH_3)_2CH)_2C=C(CH(CH_3)_2)_2$, which is valence iso-electronic to (**107**), does not display a twist angle. This difference illustrates the spatial requirements of the lone pair, which are facilitated by twisting the N_2C-CN_2 skeleton and flattening the $(CH_3)_2N$ substituents.[116]

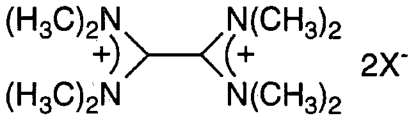
Amine (**107**) is very easily oxidised, with a first ionisation energy of 591kJ mol^{-1}, which is better than that of zinc (906kJ mol^{-1}), and approaches the values for lithium (521kJ mol^{-1}) and sodium (497kJ mol^{-1}).[116] A high reducing power means (**107**) will interact with oxidising agents, and a good example of this is its chemiluminescence with oxygen, which was first reported by Pruett[114], and has been the subject of studies by Fletcher[117] and Toby[118], who concluded that a complex series of reactions takes place to give an electronically excited form of (**107**), which emits light. Also, like the alkali metals, amine (**107**) will react with oxygen free water to liberate hydrogen! The reducing properties of (**107**) have been exploited in many other reactions, including dehalogenation of CCl_3Br[119], reaction with weak acids[120, 121], the formation of charge transfer complexes[122-125] with, for example, tetracyanoethene, and the synthesis of trifluoromethylating agents (Me_3SiCF_3 and Me_2NCF_3).[126, 127] Also, studies of electron mobility[128], and the thermal decomposition[129] of (**107**) have been reported.

When amine (**107**) acts as a reducing agent, a salt is often observed, which arises from the donation of two electrons.



(107)

The intermediate radical cation has been observed by ESR spectroscopy, the results of which suggest the positive charge may be unevenly distributed over the two molecular halves.[130, 131] Amine (**107**) will react, for example, with bromine and chlorine to form a dicationic salt (**118**).[132]

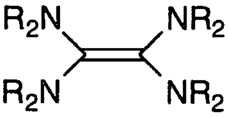


Where X=Br or Cl

(118)

Tremendous structural changes are observed on formation of (**118**). The two $((CH_3)_2N)_2C^+$ molecular halves rotate relative to each other by 76°, and the CC double bond lengthens to a CC single bond. Simultaneously, the CN single bonds shorten by 16pm and the now planar $(CH_3)_2N^{\delta+}$ groups are twisted to different extents out of the two CCN_2 planes. Also, as expected, there is a large change in charge distribution on production of (**118**).[132]

Finally, tetrakis(dimethylamino)ethene (**107**) is not the only tetraaminoethene available. By varying the R groups in (**119**), (**120**) and (**121**), a wide variety of analogues become possible.[124]



(119)

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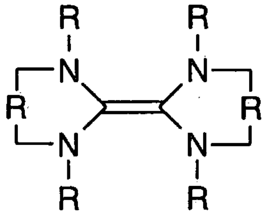

(120)

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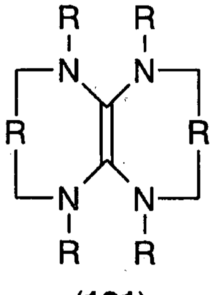


(121)

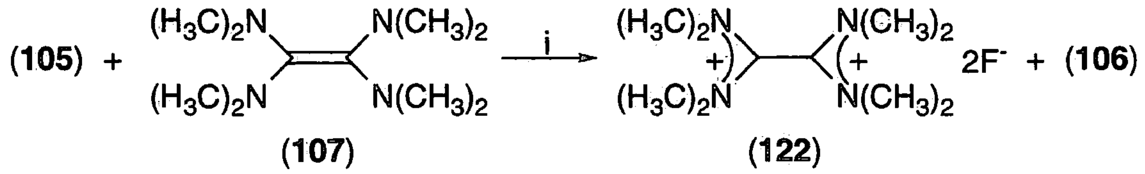
Future work may involve examining the reduction capabilities of some of these.

II.8.B Perfluoro-3,4-dimethylhex-3-ene (105)

II.8.B.(1) Using Dichloromethane as a Solvent

As discussed in the introduction, amine (**107**) is an efficient reducing agent, and whether this could reduce (**105**), which is an oxidising agent, to diene (**106**) was investigated.

A solution of (**107**) was added dropwise to (**105**) in dichloromethane. The lower fluorocarbon layer was isolated, as the only product, and identified as diene (**106**) by ^{19}F NMR spectroscopy.



i. CH_2Cl_2, 0°C to r.t. (90%)

Extraordinarily, this reaction worked with 100% conversion of (**105**), and a 90% yield of (**106**), which is in excess of that obtained using the amalgam systems, and better than reported by Nakamura[107], of these laboratories, when using this procedure (see Chapter VI, Tables 2 and 3). Again, the mechanism can be regarded as single electron transfer mediated.

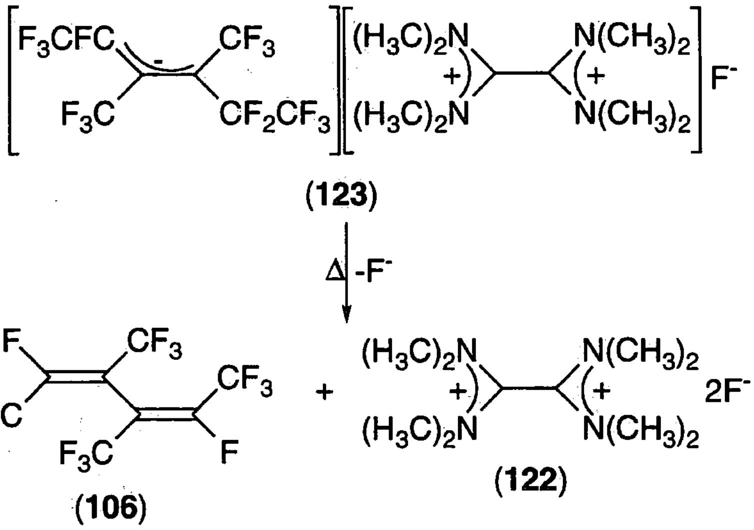
A white precipitate was observed, in the dichloromethane layer, which was filtered and examined primarily by ^{19}F NMR spectroscopy. The ^{1}H NMR spectrum showed two equal intensity peaks (3.5 and 3.3 ppm), which is consistent with results obtained by Bock[132] for the dichloro- and dibromo- dication (**118**), due to the fixation of the R_2N substituents due to drastically shortened R_2N-C bonds (by 16pm), caused by π-charge delocalisation (see Section II.8.A). This contrasts with the neutral molecule (**107**), which shows one signal, even at -53°C, in the ^{1}H NMR spectrum, due to the low inversion barrier of the dimethylamino groups, plus the CN_2 vibrations, which results in the methyl groups being equivalent on the NMR time scale.[116] The ^{19}F NMR spectrum of salt (**122**), in CD_3CN, showed one sharp signal, which supports the structure. However, the chemical shift ranged between -110.0 and -131.0 ppm, depending on how wet this very hygroscopic material had become; values close to -110.0 ppm were obtained when fresh (*i.e.* dry) salt was analysed. Mass spectrometry did not show a molecular ion, and an accurate elemental analysis was not obtained.

Salt (**122**) is soluble in acetonitrile, dimethylsulphoxide, dimethylformamide and sulpholan, which suggests that it could be employed as a soluble fluoride ion source, which is currently being explored in these laboratories.

II.8.B.(2) Without a Solvent

Diene (**106**) was found to be slightly soluble in dichloromethane, so, in an effort to increase the yield, the reaction was attempted without a solvent. Amine (**107**) was added dropwise to tetramer (**105**), and the resultant solid was then heated to 80°C. Volatile material was collected and shown to be diene (**106**), as the only compound, by GLC and ^{19}F NMR spectroscopy. Compared to using a solvent, the yield was only slightly higher (92%).

The red solid produced on mixing amine (**107**) with alkene (**105**) is interesting. The ^{19}F NMR spectrum was extremely complex, and part of this complexity almost certainly resulted from failure to exclude the products formed from the rapid reaction of the solid with air (fumes were observed and the solid blackened); because of this, no further analysis was attempted. However, structure (**123**) can be tentatively suggested, and work in these laboratories[133] supports the decomposition of such carbanions on increasing the temperature.



(123)

(106)

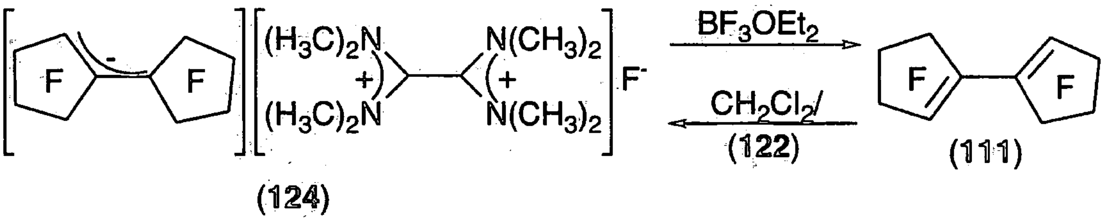
(122)

II.8.C Perfluorobicyclopentylidene (110)

Alkene (**110**) has been successfully reduced, in good yield (*ca.* 83%), by sodium amalgam, and by amine (**107**)[107] in dichloromethane (*ca.* 59%). Whether a similar reduction would occur using (**107**), without a solvent, was explored.

Amine (**107**) was added dropwise to alkene (**110**), and the resultant red solid was then heated, whilst collecting volatile material. A ^{19}F NMR spectrum of this revealed a mixture of alkene (**110**) and diene (**111**), which were separated by crystallisation at 0°C (see Section II.7.C). Disappointingly, the diene (**111**) was isolated in only 14% yield [74% conversion of (**110**)], which could be explained by amine (**107**) reacting with alkene (**110**) to form a carbanion (**124**), which does not significantly decompose at 83°C.

Addition of boron trifluoroetherate (BF_3OEt_2), which abstracts a fluorine from carbanions, to some freshly prepared solid was found to liberate diene (**111**), lending evidence to this argument.



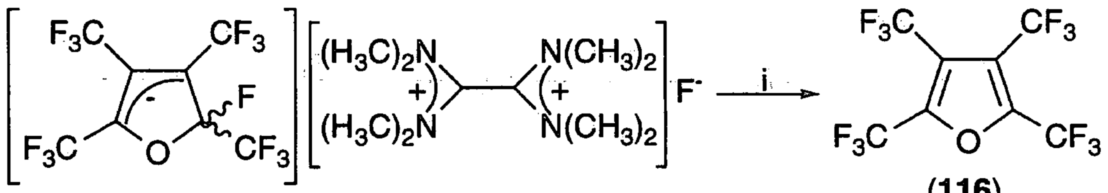
In solution (CH_2Cl_2 and CH_3CN), the difluoride salt (**122**) of amine (**107**) will react with diene (**111**) to give carbanion (**124**)[107]; whether this occurs with the neat liquids is debatable.

Finally, it is worth noting that carbanion (**123**), from tetramer (**105**) [see Section II.8.B.(2)], did not result from salt (**122**) reacting with diene (**106**), as reaction with fluoride ion (caesium fluoride) in tetraglyme, at room temperature, and acetonitrile[98], under reflux, did not result in the formation of a stable carbanion.

II.8.D Perfluoro-2,5-dihydrotetramethylfuran (115)

Whether amine (**107**) would react with (**115**), without a solvent, to give, as with sodium amalgam (see Section II.7.D), tetrakis(trifluoromethyl)furan (**116**) was investigated.

On addition of amine (**107**) to furan derivative (**115**) a red solid formed, after which volatile material was collected whilst heating. Examination by GLC and ^{19}F NMR spectroscopy revealed two components, which were (**115**) (40% calculated by ^{19}NMR spectroscopy) and (**116**) (60% calculated by ^{19}F NMR spectroscopy).



(125)

(116)

i. 100°C, reduced pressure

Again, the amount of material isolated was low, and this could be due to salt (**125**) forming, and remaining stable under the conditions employed. Addition of BF_3OEt_2 may have released furan (**116**).

II.8.E Conclusion

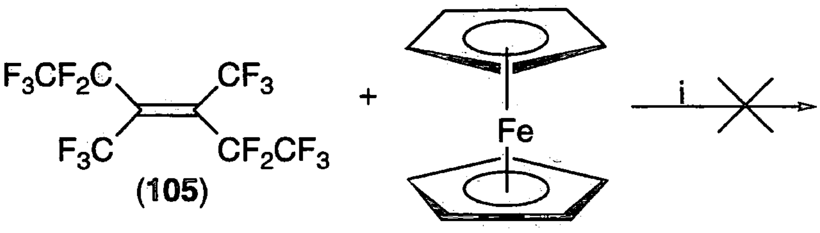
Remarkably, tetrakis(dimethylamino)ethene (**107**) has first and second ionisation energies low enough to reduce, or defluorinate, F-alkenes to give F-dienes. This worked extremely well with tetramer (**105**), giving diene (**106**), although disappointing results were obtained with bicyclic alkene (**110**), compared to using a solvent[107], and furan derivative (**115**), which may have been due to the stability of the intermediate salts.

However, being able to reduce alkene (**105**) to diene (**106**), without using potentially explosive and toxic alkali metal amalgams, and in consistently good yields (see Chapter VI, Tables 2 and 3), is an extremely significant step forward. Also, of course, producing an interesting fluoride ion source (**122**), as a `by-product', is an added bonus!

II.9 Attempted Reduction using Ferrocene

II.9.A Perfluoro-3,4-dimethylhex-3-ene (105)

Ferrocene is an electron rich metallocene, which has a low oxidation potential (*E*°=0.31V[134]), and the possibility of it reducing perfluorinated alkene (**105**), to give diene (**106**), was examined. Alkene (**105**) was stirred with the ferrocene at room temperature. Following the reaction by ^{19}F NMR spectroscopy revealed no reaction had occurred, so the mixture was refluxed, after which volatile material was shown only to contain the starting alkene (**105**).



i. CH_3CN, r.t. and reflux

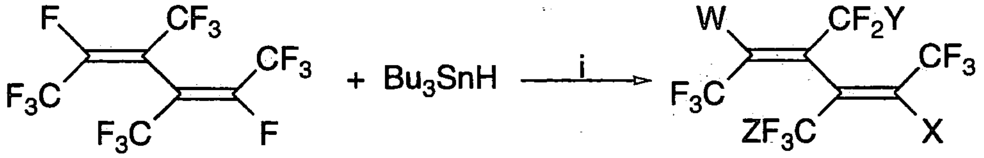
Ferrocene was not sufficiently electron donating, although decamethylferrocene may have been a better choice, since it contains methyl groups which donate electrons into the ring system, decreasing the oxidation potential (*E*°=-0.23V[134]).

II.10 Substitution of Fluorine by Hydrogen in Diene (106)

In order to investigate the effect vinylic fluorines have on the overall reactivity of diene (**106**), an attempt was made to substitute these with similarly sized hydrogen atoms, using tributyl tin hydride as a hydrogen radical source.

After the ultraviolet irradiation of tributyl tin hydride (Bu_3SnH) with diene (**106**), volatile material was shown to be an inseparable mixture by GLC. However, GLC-mass spectrometry revealed the molecular ion for the four main components, which correspond to substitution of one (**130**), two (**131**), three (**132**) and four (**133**) fluorines with hydrogen.

Since more than two hydrogens have been incorporated, some fluorine must have been substituted from the CF_3 groups, and this is confirmed by ^{19}F NMR spectroscopy, which showed a doublet that is characteristic of a CF_2H group (δ_F -199.33, $^2J_{F,H}$ 169.2 Hz).[101] The products may have the structures shown below.

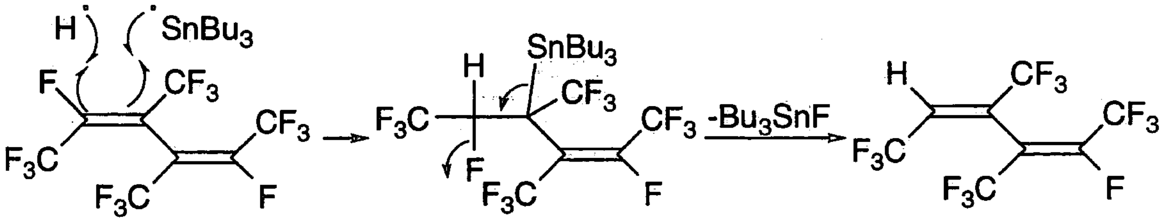


(106)

i. UV irradiation, 2.5 d

Where **(130)** W=H, X=Y=Z=F
(131) W=X=H, Y=Z=F
(132) W=X=Y=H, Z=H
(133) W=X=Y=Z=H

The mechanism involves the radical addition of $H^\bullet$ and $Bu_3Sn^\bullet$ across the double bonds of (**106**). A possible mechanism for vinylic substitution is shown below, involving one double bond.



(133)

Similarly, fluorine can be lost from a CF_3 group, giving a $=CF_2$ moiety, which could then add another molecule of $SnBu_3H$ to form a CF_2H group. However, $SnBu_3H$ can also add to double bonds in the opposite way to that shown, giving different products after fluorine is eliminated. Because of these complexities it is not possible to indicate, from the available data, the definite structures of products (**130**) to (**133**). Finally, since this procedure did not give the 2,5-dihydro- product (**131**) cleanly, it was abandoned.

Chapter Three
Oxygen Nucleophiles

III Introduction

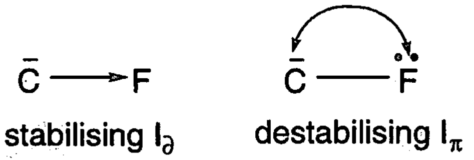
In general, fluorinated alkenes are much more susceptible to attack by nucleophiles than by electrophiles and, in this respect, their chemistry is complementary to that of the corresponding hydrocarbon systems.[2] The result of nucleophilic attack on fluorinated alkenes is the formation of intermediate carbanions, and an understanding of the factors which determine reactivity and orientation of attack is essential in discussing these carbanionic processes.

III.1 Electronic Effects and Fluorine Substitution

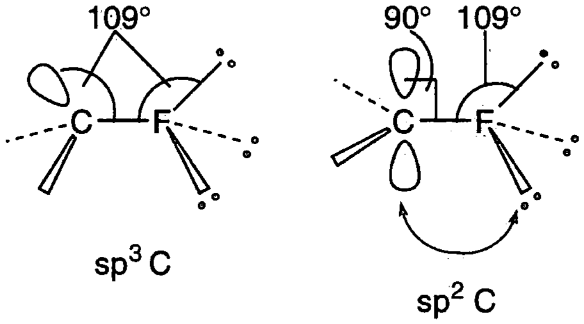
The relationship between structure and kinetic acidity in hydrofluorocarbon systems has been extensively studied, and the results indicate that tertiary carbanions are the most stable, being generated by the strongest acids.[135] The stability of fluorinated carbanions is of the order tertiary > secondary > primary, for example, $(CF_3)_3C^-$ > $(CF_3)_2CF^-$ > $CF_3(CF_2)_5CF_2^-$.[2]

III.1.A What Factors Influence the Stability of these Carbanions ?

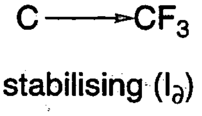
Fluorine substituents have two opposing inductive effects; I_∂ and electron pair repulsion, I_π, whose outcome depends upon the geometry of the system.



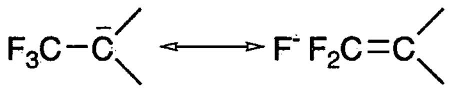
This effect is demonstrated by examination of the relative effects of fluorine attached to sp^3 (tetrahedral) and sp^2 (planar) hybridised carbons.



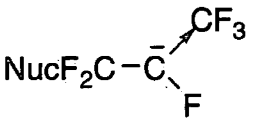
In contrast to fluorine attached to a carbon carrying a negative charge, a perfluoroalkyl group so attached is much more effective at carbanion stabilisation.



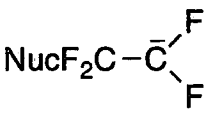
As well as the inductive effect, this stabilisation has partially been attributed to `C-F negative anionic hyperconjugation´. This effect, which involves `no-bond resonance´, was introduced by Roberts[136] in 1950, fell into disrepute around 1970[137] coming back into vogue in 1980[138], and is depicted below.[139]



Although there is now good theoretical evidence for this effect, whether it contributes significantly to the stabilisation of fluorinated carbanions is debatable.[135] The points described above can be used to account for the reactivity of fluorinated alkenes. For example, hexafluoropropene is attacked exclusively at the difluoromethylene group and is more reactive than tetrafluoroethene, and this regiospecificity is attributed to the polar contribution from fluorine, making the difluoromethylene group especially susceptible to nucleophilic attack, and to the fact that a trifluoromethyl group will stabilise adjacent charge (**126**).

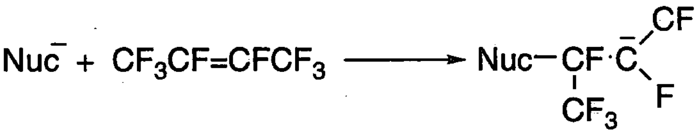


(**126**) stabilised



(**127**) destabilised

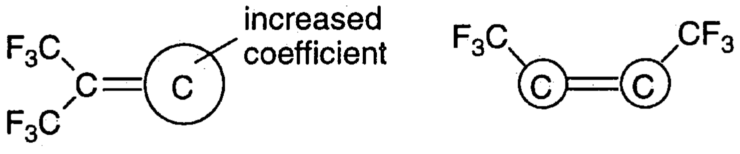
The stability of carbanion (**126**) also accounts for the greater reactivity of tetrafluoroethene, since carbanion (**127**) is the least stable. However, this argument does not sufficiently account for the much greater reactivity of hexafluoropropene over hexafluorobut-2-ene, since the intermediate carbanions, (**126**) and (**128**), will have similar stabilities.



(**128**)

Consequently, a frontier orbital approach has been used to account for reactivity and orientation of attack, which recognises that HOMO-LUMO interaction between nucleophile and fluorinated alkene, respectively, is important, and replacing a fluorine with a trifluoromethyl group in this system reduces the LUMO energy, which increases reactivity.

This is true providing the trifluoromethyl groups are on the same side of the double bond, *i.e.* $CF_2{=}CF_2 < CF_2{=}CFCF_3 < CF_2{=}C(CF_3)_2$, which increases the coefficient in the LUMO of the carbon opposite, and is enhanced for two such groups attached geminally to the double bond (**129**). However, when the trifluoromethyl groups are on opposite sides, *i.e.* (**130**), their coefficients, and hence reactivity, is opposing.

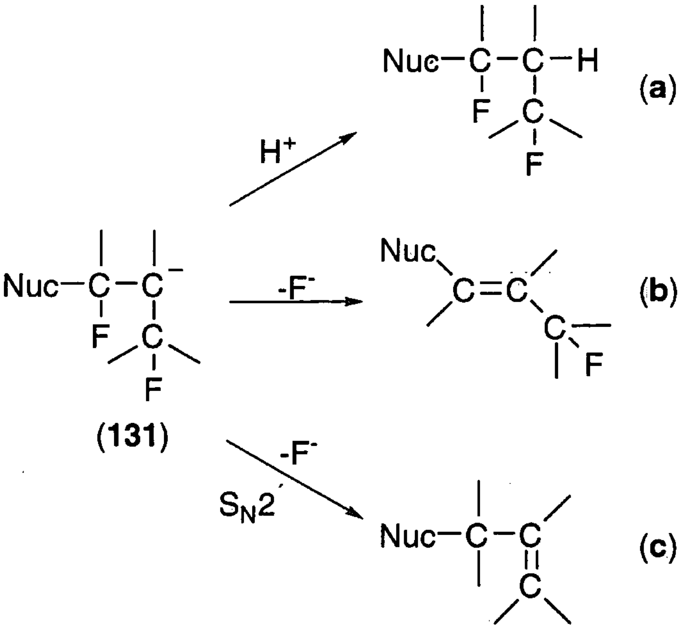


(129) **(130)**

As a result, the reactivity of hexafluorobut-2-ene, with trifluoromethyl groups on opposite sides of the double bond, is decreased relative to hexafluoropropene ($CF_2{=}CF_2 < CF_2CFCF_3 > CF_3CF{=}CFCF_3$).

III.1.B The Products Formed

This is determined by the fate of the intermediate carbanion (**131**), which can follow one of three pathways: a) proton abstraction from the solvent, in effect quenching the carbanion with an electrophile (H^+), b) elimination of fluoride ion, or c) nucleophilic addition, followed by allylic rearrangement and elimination of fluoride ion.

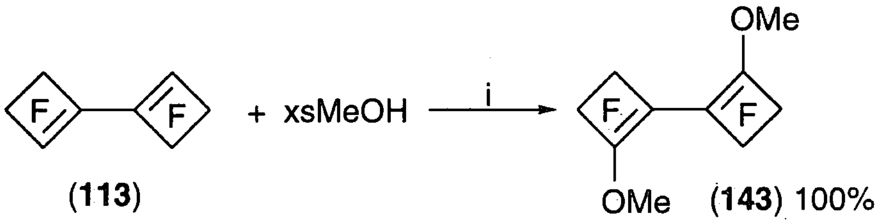


Most of the reactions described in this Chapter involve the nucleophilic elimination of fluoride ion [pathway (b)].

III.2 Prelude

As already mentioned, perfluorinated alkenes and dienes have electron deficient double bonds, making them susceptible to nucleophilic attack, contrasting with the susceptibility to electrophiles of the corresponding hydrocarbon systems.

The reactivity of perfluorinated dienes towards oxygen, sulphur and nitrogen nucleophiles has been extensively explored (Chapter I, Section I.2.A). In these laboratories, a considerable range of reactivity has been observed between bicyclic dienes (**111**) and (**113**) and acyclic diene (**106**).[96, 107] Diene (**113**) reacts exothermically with *neutral* methanol, giving the *bis*-dimethylether (**143**)[96], and this remarkable level of reactivity is usually associated with perfluoroisobutene[140-142], and it is comparatively rare that fluorinated systems will react with neutral methanol.[44, 48]

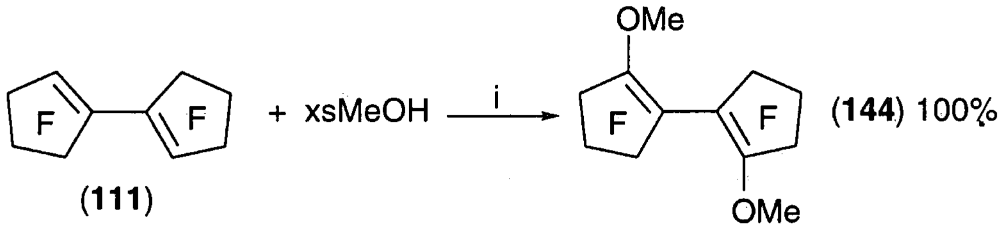


(113)

(143) 100%

i. 1 hr, r.t.

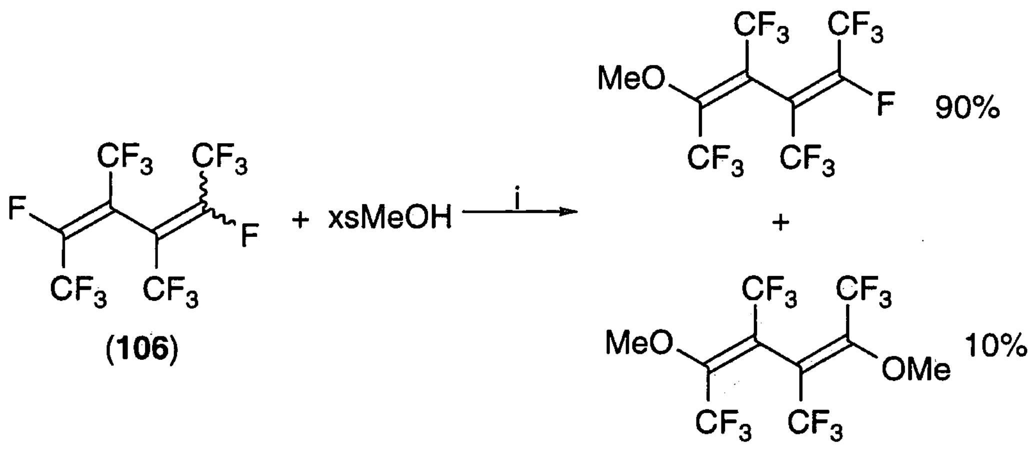
Perfluorobicyclopentenyl (**111**) reacted with neutral methanol, but only over a period of days, giving the dimethylether (**144**)[96], whereas acyclic diene (**106**) required the addition of a base to promote reaction, giving a mixture of mono- and dimethylethers.



(111)

(144) 100%

i. 10 d, r.t.

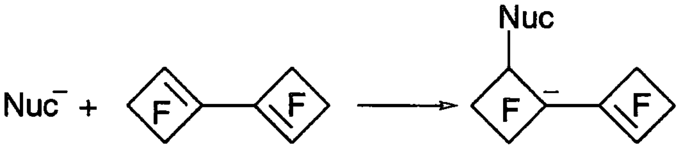


(106)

i. Sodium carbonate, acetonitrile, 7 d, r.t.

(mixture of isomers)

Therefore, the order of reactivity for these systems is (**113**)>(**111**)>>(**106**). Since the electronic effects of these dienes are broadly equivalent, the best explanation for this huge difference in reactivity comes from considering angle strain, which has already been described in the context of the reduction potentials of perfluorinated alkenes (Chapter II, Section II.6.B). Diene (**113**) has two four membered rings, and therefore the most inherent angle strain, which is relieved after nucleophilic attack; a similar argument can be applied to diene (**111**), although obviously the angle strain will be lower than that of (**113**).

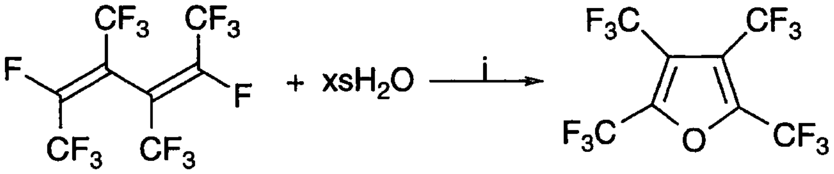


However, diene (**106**) does not have any angle strain to be relieved, and so has the lowest reactivity of the three, giving very little of the dimethyl ether. Another factor which may influence reactivity is the steric effect, which is relatively large in diene (**106**), with its bulky trifluoromethyl groups, and small in the bicyclic dienes (**113**) and (**111**), having double bonds which are unhindered towards nucleophilic attack.

Please note that where necessary, in the following reactions, the stereochemistry of the products was determined by comparing coupling constant data with known values for perfluorinated alkenes (see Chapter I, Section II.6.C).[101]

II.3 Reaction of (106) with Water

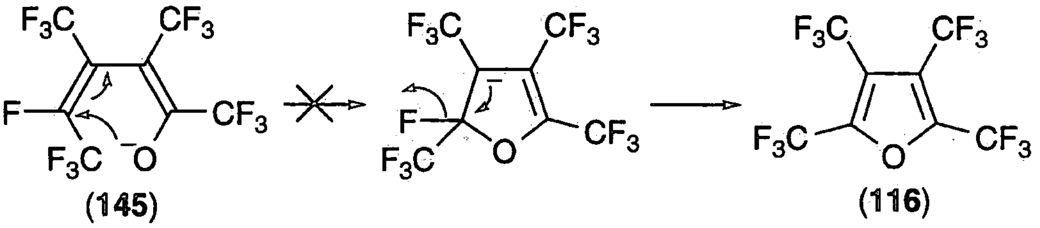
The reaction of diene (**106**) with another simple nucleophile, water, has been investigated by Mullins[98], and others, in these laboratories. This reaction was repeated, and proceeded readily at room temperature, in the presence of a base. By analogy with the reaction of diene (**106**) with methanol, a dihydroxy product would be expected, but instead, perfluorotetramethylfuran (**116**) was observed as the product of cyclisation.



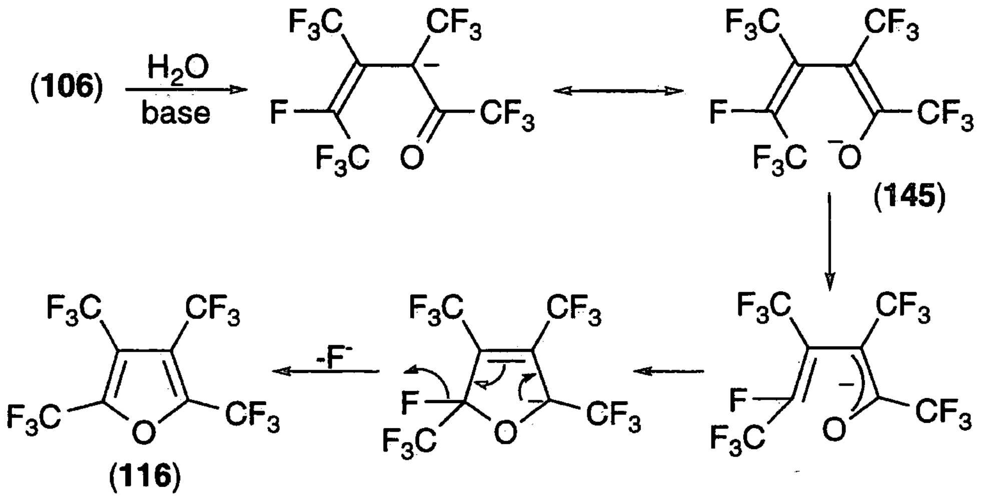
(106) **(116)**

i. caesium carbonate, acetonitrile, 5 d, r.t.

The formation of furan derivative (**116**) *via* a 5-*Endo-Trig* cyclisation is disfavoured, as Baldwins Rules[143] predict that the transition-state geometry necessary to effect ring closure can not be attained.



As a result, an electrocyclisation pathway is suggested, with a 1,5-electrocyclisation allowing ring closure, as shown below.[144]

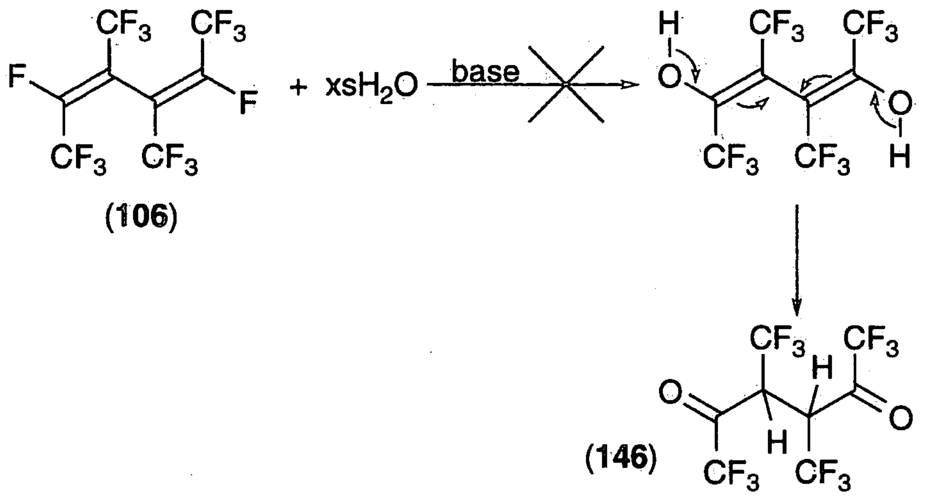


This process proceeds by initial vinylic displacement of fluorine, and then the intermediate ion (**145**) undergoes a rapid electrocyclisation, accompanied by elimination of fluoride ion to give (**116**), and provides a more direct route to the furan derivative (**116**) than previous procedures.[113, 145-147]

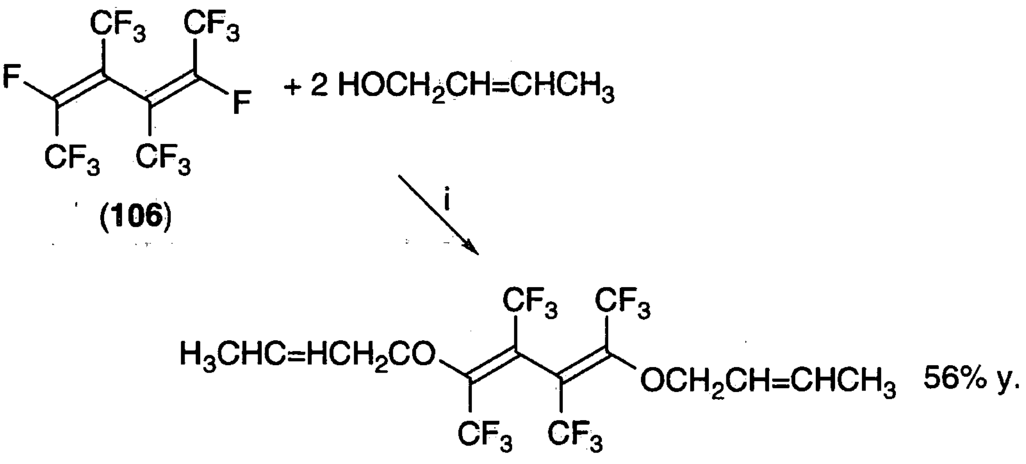
Finally, due to the ease of this cyclisation reaction, furan derivative (**116**) was often observed in the following reactions, even when precautions had been taken to keep reagents and solvents scrupulously dry. This leads to a slight decrease in the yields of the desired products, although no attempts were made to quantify this by isolating the (**116**) formed.

III.4 Reaction of (106) with But-2-en-1-ol

For some time, in these laboratories, there has been interest in the formation, and chemistry, of the diketone (**146**) of (**106**). The reaction of (**106**) with water was considered as a possible route, but cyclisation gave furan derivative (**116**) (Section III.3).



Another possible route was *via* the Claisen Rearrangement, which involves the sigmatropic rearrangement of allyl vinylic ethers or allyl aryl ethers. First of all, the diether was synthesised by reacting diene (**106**) with but-2-en-1-ol, at room temperature, in the presence of a base. This gave the desired product, after distillation, as an inseparable mixture of two isomers (**134a,b**), by ^{19}F NMR spectroscopy.

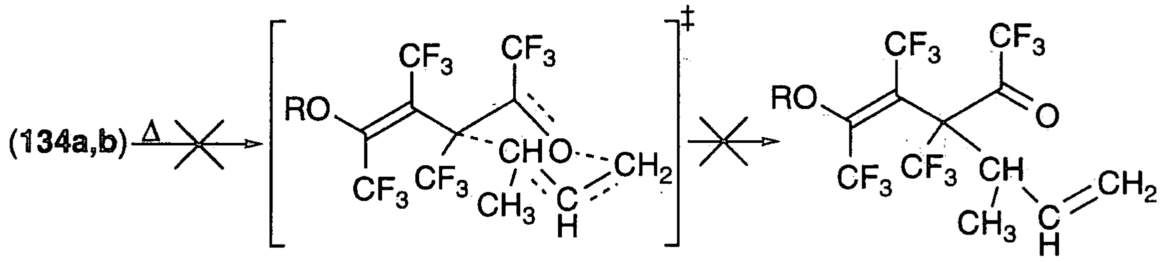


Z,Z- (**134a**) 80% + *Z,E*- (**134b**) 20%

i. Caesium fluoride, acetonitrile, 3.5 hrs, r.t.

The ease at which both vinylic fluorines were substituted is note worthy, and this indicates that the reactive sites are activated towards nucleophilic attack by the electron withdrawing perfluoroalkyl groups.

A small amount of (**134a,b**) was then heated, at 150°C, in an attempt to effect the Claisen rearrangement. However, the colour of the sample changed to dark brown, and the ^{19}F NMR spectrum was extremely complex (more complex than expected, even allowing for the introduction of four chiral centres in the Claisen product), indicating the decomposition of (**134a,b**). Also, the IR spectrum of this material did not show bands indicative of a carbonyl group, indicating that none of the desired product was present.



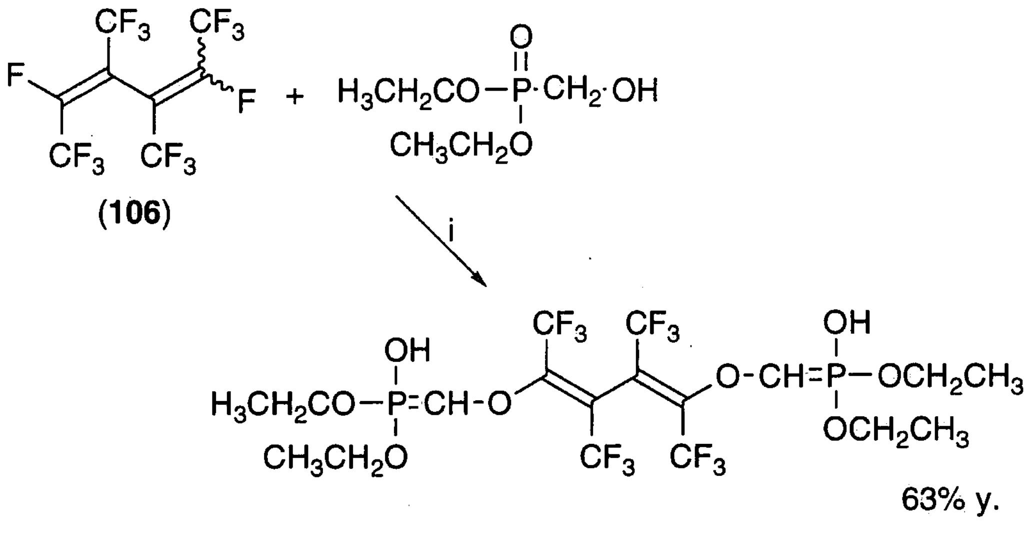
Shown for one half
of the molecule

This reaction was repeated several times, changing the temperature and using a solvent, but to no avail.

III.5 Reaction of (106) with Diethoxyphosphinylmethanol

Whether this type of reaction could be applied to a more complex system, containing a carbonyl group and phosphorous atom, was investigated.

Diene (**106**) was stirred, in the presence of a base, with diethoxyphosphinylmethanol, and the product (**135a,b**) was identified as an inseparable mixture of two isomers by ^{19}F NMR spectroscopy.

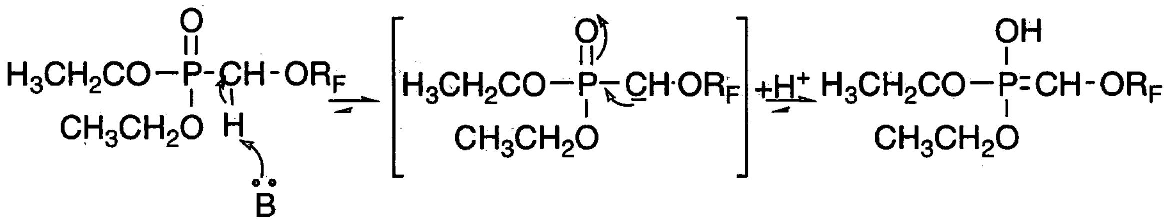


Z,Z- (**135a**) 86% + *Z,E*- (**135b**) 14%

i. Caesium fluoride, acetonitrile, 2.5 d, r.t.

The ^{1}H NMR spectrum of the starting alcohol showed an OCH_2 resonance (δ_H 3.91 ppm) as a doublet, due to coupling with the phosphorous, which was replaced in the product by a signal at δ_H 4.48 ppm, which corresponds to the position expected for a CH= moiety.[148] Also, in the isolated material, there was a broad signal (δ_H 2.98 ppm) which is characteristic of an O*H*, and the correct integration lent further support to the suggested structure.[148] Other evidence for structure (**135a,b**) comes from the IR spectrum, which showed bands corresponding to an OH group (broad, 3480cm^{-1}) and to an HC=C group (*ca.* 2950cm^{-1}). Unfortunately, the absorption bands for a P=O group occur in the same region as the C-F absorptions (*ca.* 1250cm^{-1}), so it was difficult to rule out the presence of the P=O containing tautomer[148], although this could not be distinguished by ^{1}H or ^{19}F NMR spectroscopy. The molecular ion was observed in the mass spectrum, and the elemental analysis was correct, supporting the structure, although not discriminating between the two possible tautomers of (**135a,b**).

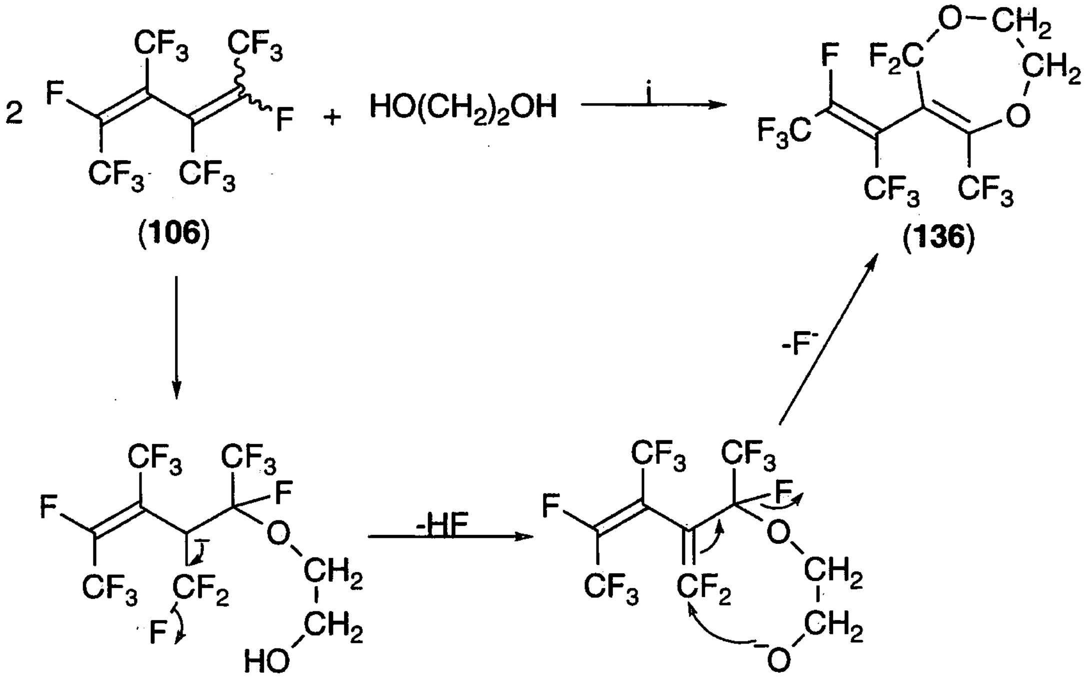
The presence of the base, caesium fluoride, may catalyse the interconversion to give the alcoholic tautomer, as shown below.



III.6 Reaction of (106) with Ethylene Glycol

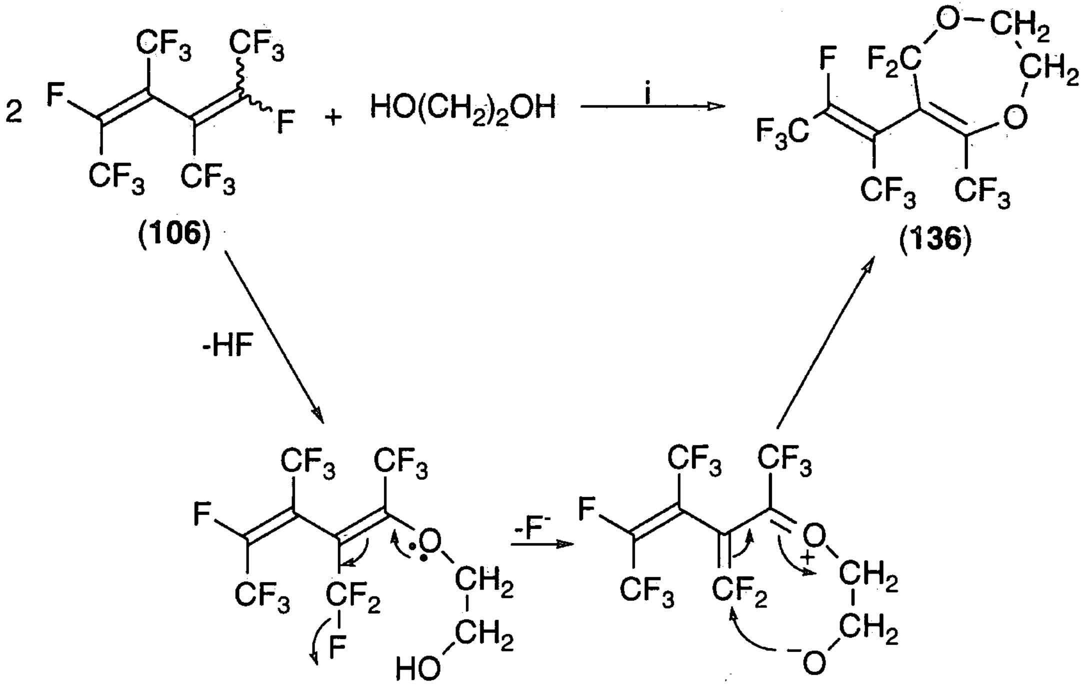
An attempt was made to react two diene (**106**) molecules with a dioxygen nucleophile, in order to synthesise a highly fluorinated diether.

After stirring (**106**) and ethylene glycol at room temperature, in the presence of a base, a single product was isolated, by molecular distillation, which was identified by MS and ^{19}F NMR spectroscopy as diether (**136**).

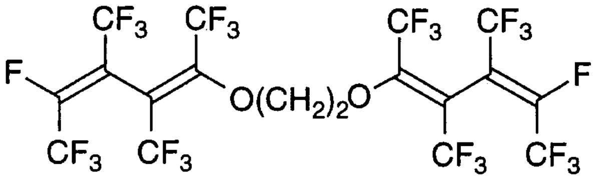


i. Caesium fluoride, acetonitrile, 7 d, r.t.

An alternative mechanism is shown below, involving vinylic substitution and the electrons of one oxygen atom.



Although two equivalents of diene (**106**) were used, the product was not the anticipated acyclic diether (**147**).



(147)

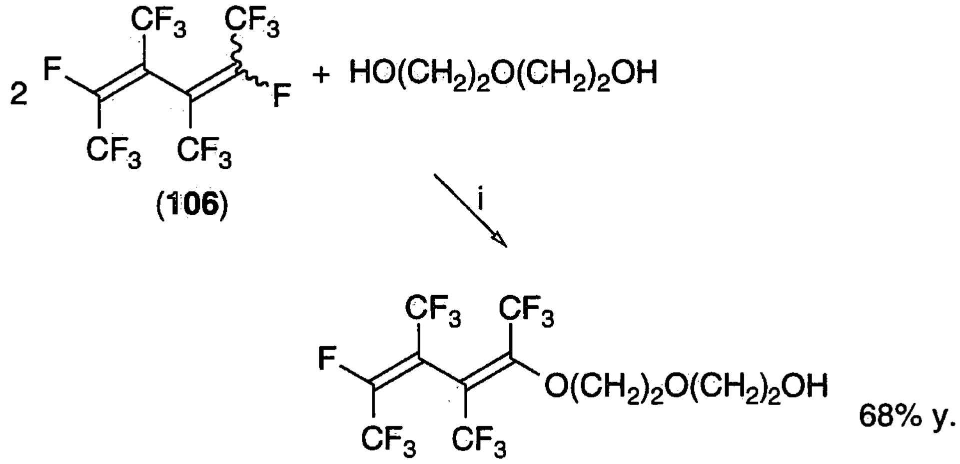
The cyclic product (**136**) arises from nucleophilic addition, followed by elimination of fluorine from a trifluoromethyl group, *via* an S_N2' mechanism, forming a reactive difluoromethylene moiety, which then reacts intramolecularly with the second oxygen atom of the ethylene glycol molecule, effecting ring closure. This result is consistent with that obtained by Briscoe[96], who used different reaction conditions (*i.e.* a different base, solvent and stochiometry).

Interestingly, there was no evidence for the intermolecular reaction between either the difluoromethylene group, or the second unsubstituted double bond, and a glycolic oxygen atom. This observation is most likely due to the intramolecular reaction (*i.e.* cyclisation) being faster than intermolecular attack.

III.7 Reaction of (106) with Diethylene Glycol

Diethylene glycol was used in order to investigate whether a cyclisation similar to that described using ethylene glycol (Section III.6) would occur, giving a larger ring (10 membered).

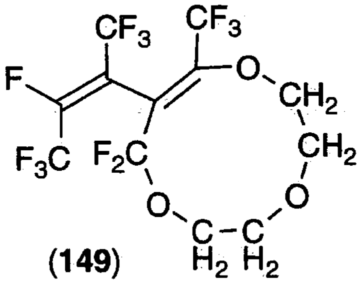
Diene (**106**) was stirred with the diol, in the presence of a base, and the isolated material was identified as an inseparable mixture of two isomers (**137a,b**) by GLC and ^{19}F NMR spectroscopy.



Z,Z-(**137a**) 86% + *Z,E*-(**137b**) 14%

i. Sodium carbonate, acetonitrile, 13 d, r.t.

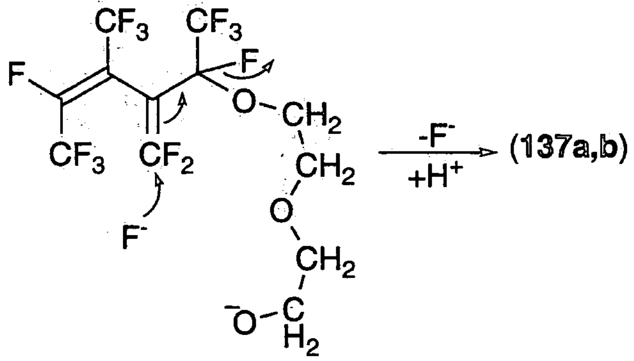
The only product was an acyclic ether (**137a,b**) which appears to have been derived from straight forward elimination of fluoride; no cyclic ether (**149**) was observed.



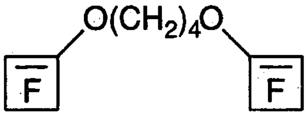
(**149**)

However, in view of the reaction with ethylene glycol, involving elimination of fluorine by an S_N2' mechanism, and subsequent nucleophilic attack, two possible explanations can be offered: a) In this case, simple vinylic substitution of fluorine is successfully competing with the S_N2' mechanism, or, more likely, b) Fluoride *is* lost from a trifluoromethyl group, but the intramolecular reaction with oxygen does not occur due to the long chain of the ether moving the oxygen anion away from the reactive difluoromethylene group.

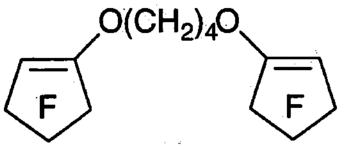
This results in the eliminated fluoride ion quickly reacting with the difluoromethylene group to eliminate the tertiary fluorine, as shown below.



As with ethylene glycol, only one molecular proportion of diene (**106**) reacted with the diol, which is in marked contrast to recent results published by Farnham[149], who has formed diethers from perfluorocyclobutene (**150**) and perfluorocyclopentene (**151**).



(**150**)



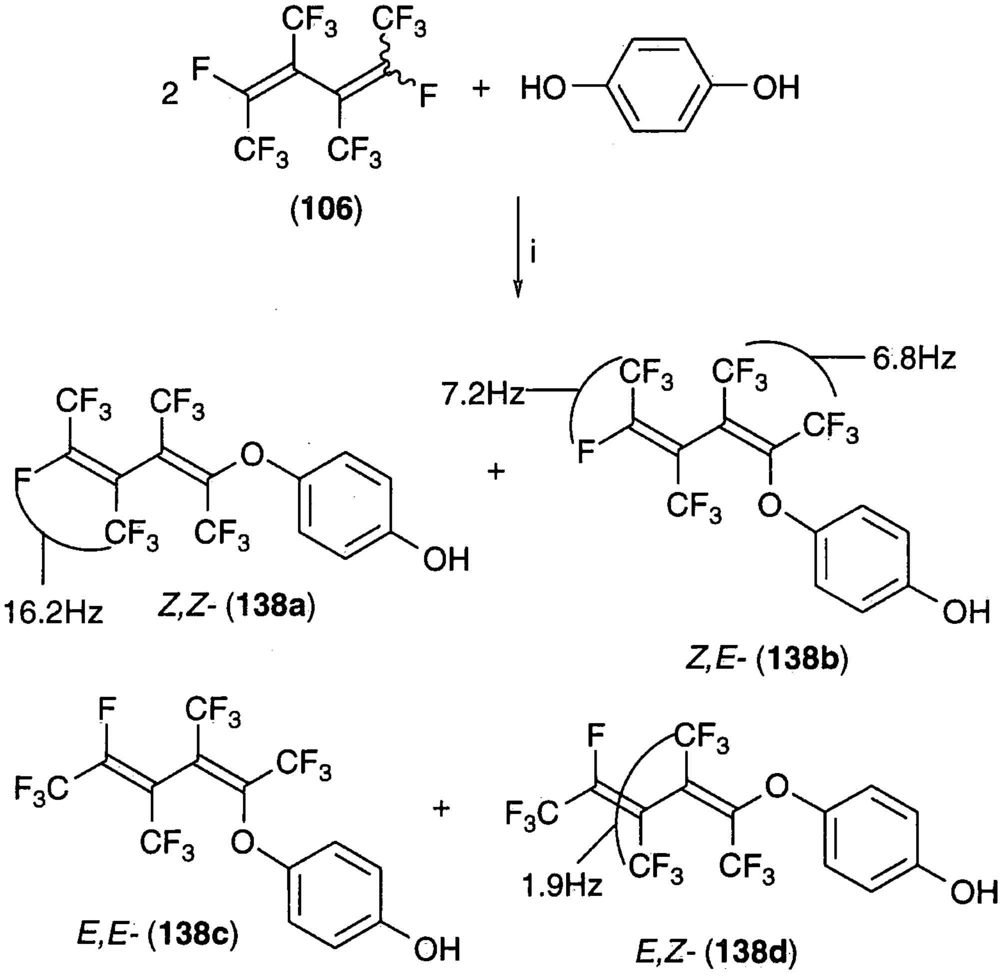
(**151**)

However, two important factors differ with the work reported here: a) Diene (**106**) is far less reactive than perfluorocyclobutene and perfluorocyclopentene, and b) Farnham used a silyl ether, $Me_3SiO(CH_2)_4OSiMe_3$, which may be more reactive than when using the largely heterogeneous base/solvent system with alcohols. These diethers were then converted into polymers of high average molecular weight (*ca.* 64 000).[149]

III.8 Reaction of (106) with Benzene-1,4-diol

So far, the various reactions of acyclic diols towards diene (**106**) have been discussed. The use of systems where reactivity could be more easily controlled were now considered. Diols with the general structure HO-aromatic-OH were employed, since they are rigid and `set-up´ for diether formation, without the possibility for the intramolecular reaction, described for ethylene glycol (Section III.6).

Two equivalents of diene (**106**) were stirred, in the presence of a base, with benzene-1,4-diol, at room temperature. A liquid was isolated by molecular distillation, which crystallised at room temperature, and was identified as an inseparable mixture of four isomers by ^{19}F NMR spectroscopy.

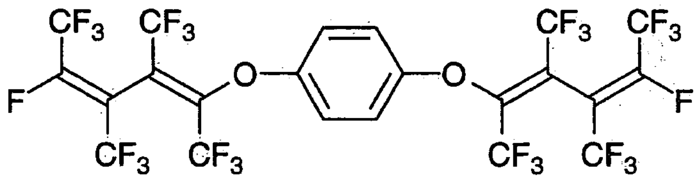


28(**138a**):13(**138b**):5(**138c**):2(**138d**) 32% y.

i. Caesium carbonate, diethyl ether, 4.5 d, r.t.

A solid was then isolated by sublimation, and identified as diether (**139**) by NMR spectroscopy, MS and elemental analysis. This compound was isolated as essentially one isomer, where the trifluoromethyl groups have the all *trans*, or *Z,Z*-, relative arrangement.

Since we begin with a mixture of *E,Z-* and *Z,Z-* diene (**106**), then these reactions must be subject to thermodynamic control of stereochemistry, with the bulky trifluoromethylgroups dominating the outcome.



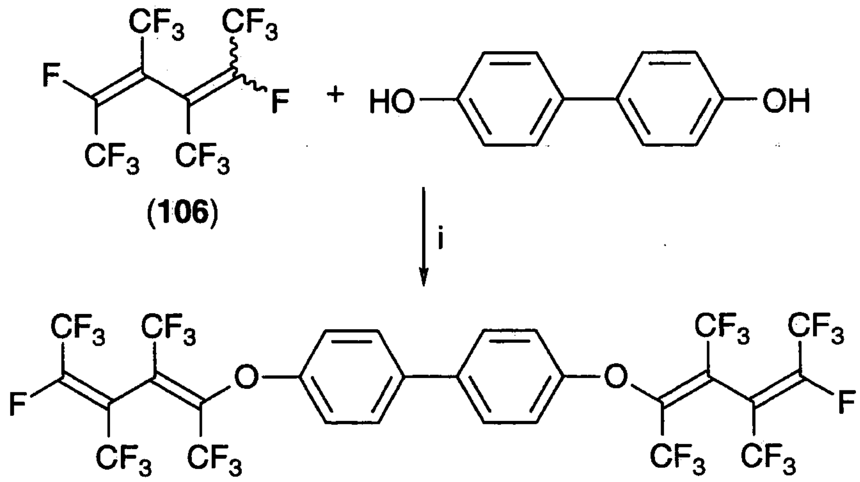
Z,Z- (**139**) 58%

The yield of (**139**) was reasonable, but may have increased over a longer period of time or by using a higher temperature, as more of ether (**138**) reacted. This reaction has demonstrated the possibility of producing diethers, with a similar overall structure to those reported by Farnham[149] (Section III.7), using a diol and a perfluorinated diene (**106**).

III.9 Reaction of (106) with Biphenyl-4,4′-diol

The synthesis of diethers containing two molecules of diene (**106**) was now extended to more complex diols, which still possess the rigidity imparted by aromatic rings.

Diene (**106**) was stirred, in the presence of a base, with biphenyl-4,4′-diol, at room temperature. After purification by sublimation, a white solid was isolated which was identified as the thermodynamically most stable isomer of diether (**140**), by ^{19}F NMR spectroscopy.



Z,Z- (**140**) 78% y.

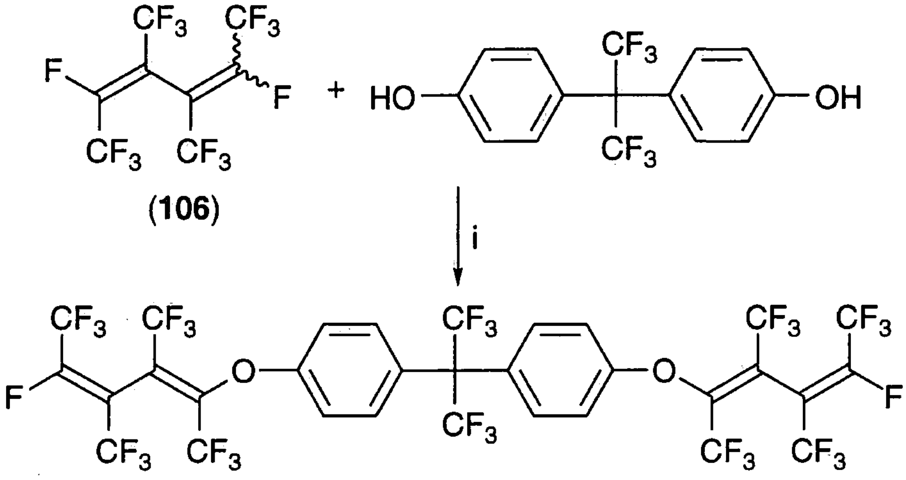
i. Caesium carbonate, diethyl ether/acetone/acetonitrile, 3 d, r.t

A good yield of diether (**140**) was obtained, and interestingly, no monosubstitution product was observed.

III.10 Reaction of (106) with 2,2-Di(4-hydroxyphenyl)hexafluoropropane

A slightly more complex, rigid, diol was employed in order to synthesise a highly fluorinated ether.

A solution of diene (**106**) and 2,2-di(4-hydroxyphenyl)hexafluoropropane were stirred together, at room temperature, in the presence of a base. Recrystallisation of the product gave white needles which were identified, by ^{19}F NMR spectroscopy, as the thermodynamically most stable isomer of diether (**141**).

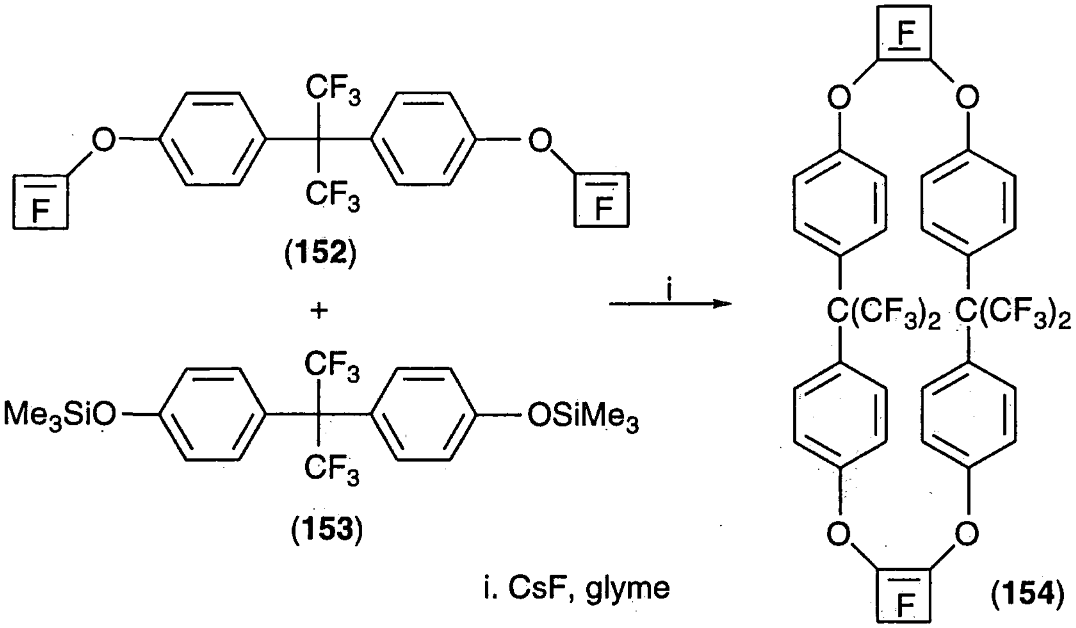


Z,Z-(**141**) 83% y.

i. Caesium carbonate, acetonitrile, 12 d, r.t

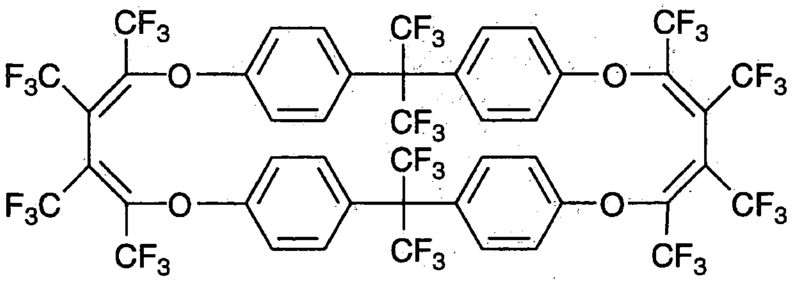
This reaction gave a high yield of ether (**141**), and is a good route to relatively high molecular weight fluorinated diethers. Again, there was no evidence for the monosubstituted product.

Interestingly, Farnham[149] has reported that, during polymerisation studies using fluorinated ether (**152**), and silyl ether (**153**), a cyclic dimer (**154**) was isolated in *ca.* 50% yield.



i. CsF, glyme

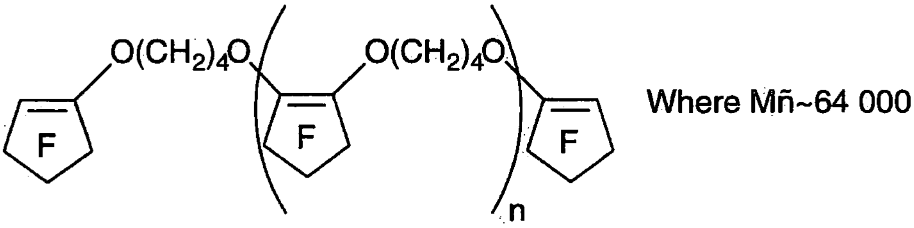
It has been shown that cyclic dimers of this type exhibit remarkable anion binding properties.[149] No such cyclic dimers were observed during the procedures described here, but, if time had allowed, a reaction between diether (**141**) and more diol, or with the silylated equivalent (**153**), may have formed a highly fluorinated macrocycle, such as (**155**).



(155)

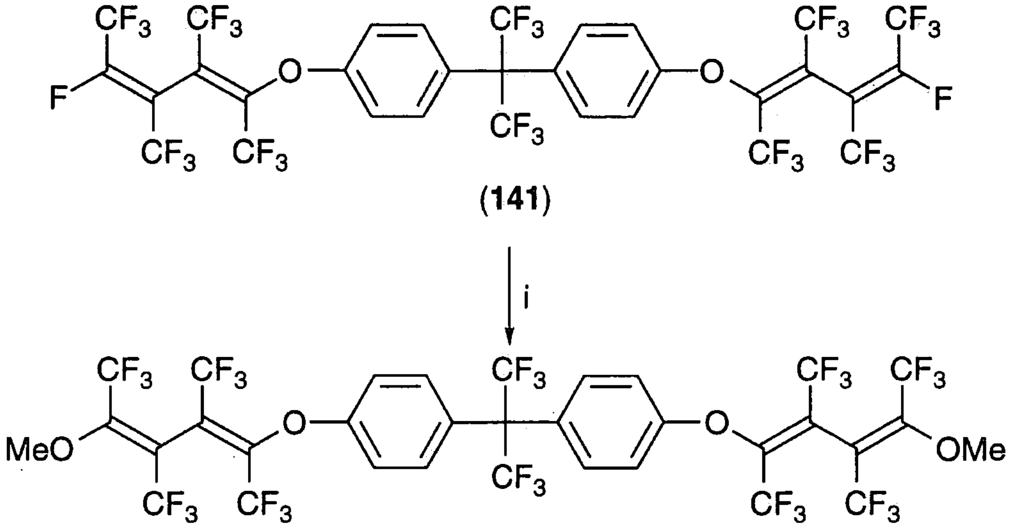
III.11 Reaction of Diether (141) with Sodium Methoxide

In the systems described, the diethers have the general structure diene-O-aromatic-O-diene, where two vinylic fluorines, from the diene, are available for further reaction. As mentioned earlier, Farnham[149] has exploited similar systems to give high molecular weight material, as shown below.



Whether the vinylic fluorines, in the diethers derived from diene (**106**), would be reactive was investigated by reacting (**141**) with methoxide ion.

Diether (**141**) was stirred with sodium methoxide, in methanol, at room temperature, to give a product which, after purification by recrystallisation, was identified as the *Z,Z*-dimethoxy derivative of (**141**) by ^{19}F and ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis.



(**141**)

Z,Z- (**142**) 73% y.

i. NaOMe, methanol, 48 h, r.t.

This reaction proceeded readily, under mild conditions, giving tetraether (**142**) in good yield, which demonstrates that the vinylic fluorines *are* reactive, and reaction of compounds such as (**139**), (**140**) and (**141**) with difunctional nucleophiles could provide a route to high molecular weight fluorinated polymers.

III.12 Conclusion

The susceptibility of diene (**106**) to nucleophilic attack, by oxygen nucleophiles of varying complexity, has been demonstrated, and is due to the inherent electron deficiency within this system. Reaction of diols with diene (**106**) gave highly fluorinated diethers, of high molecular weight, which have been shown to react with oxygen nucleophiles to form tetraethers. This reactivity suggests the possibility of forming novel, fluorinated, polymeric materials whose properties, such as thermal stability and electrical conductivity, would be of interest.

Chapter Four

Perfluorinated Epoxides

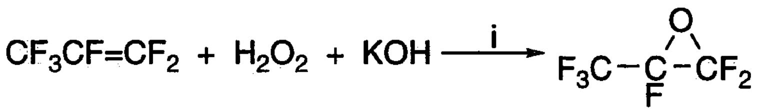
IV Introduction

IV.1 Synthetic Routes

The first reported synthesis of perfluorinated epoxides was in 1962, by the DuPont company, utilising alkaline hydrogen peroxide at reduced temperatures.[150] This method was applied to perfluoroalk-1-enes, perfluorocycloalkenes and some perfluorinated internal alkenes and, since this procedure, several others have been developed: alkali metal hypochlorites, elemental oxygen, elemental fluorine-water-acetonitrile, addition of carbenes to ketones, oxygen difluoride (OF_2) and potassium permanganate-HF. Also, there is a great deal of interest in the chemistry of perfluorinated epoxides, from both synthetic and mechanistic view points, and their potential as monomers for the preparation of fluorinated polyethers of industrial importance is well recognised.[151] The synthetic methods mentioned, and some reactions, of perfluorinated epoxides are described below.

IV.1.A Hydrogen Peroxide

DuPont[152, 153] first applied this methodology to hexafluoropropene, where the corresponding oxide was isolated using distillation or by removal of unreacted alkene after reaction with bromine.



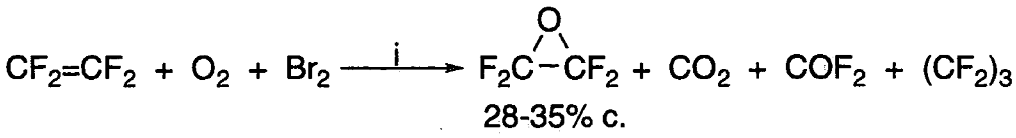
$$CF_3CF{=}CF_2 + H_2O_2 + KOH \xrightarrow{i} F_3C{-}\overset{O}{C(F)}{-}CF_2$$

i. MeOH, *ca.* -40°C

Methanol was added to enable the reaction to be carried out at low temperature without freezing. This method has been applied to many perfluorinated, partially fluorinated and perhalogenated alkenes.[151]

IV.1.B Molecular Oxygen

Interestingly, the peroxide methodology could not be applied to tetrafluoroethene, and most reported procedures for the formation of this oxide involve the use of molecular oxygen, generally in the presence of a free radical source.[151]



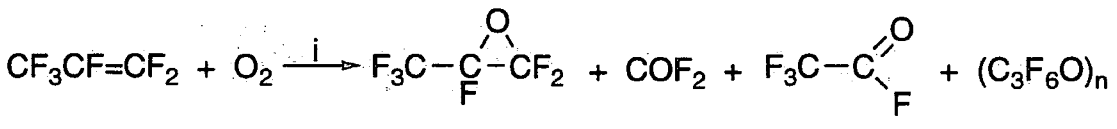
$$CF_2{=}CF_2 + O_2 + Br_2 \xrightarrow{i} F_2C{\overset{O}{-}}CF_2 + CO_2 + COF_2 + (CF_2)_3$$

28-35% c.

45-56% y.

i. UV, 110-120°C

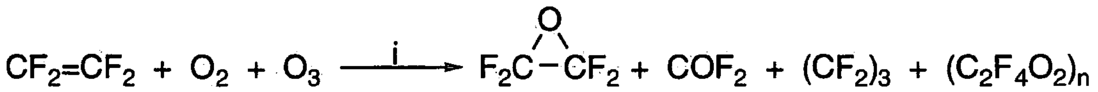
Other alkenes converted to the epoxide by this method include $CF_3CF{=}CF_2$ and $C_5F_{11}CF{=}CF_2$.[151] The formation of tetrafluoroethene oxide has also been extensively investigated by chemists in Italy[154, 155], who used ionising radiation (γ-rays and X-rays). The oxidation led to the formation of tetrafluoroethene oxide, carbonyl fluoride, hexafluorocyclopropene and a polymeric peroxidic liquid $(C_2F_5O_2)_n$. Polymeric material is often observed, as is the case in the ultraviolet initiated epoxidation of hexafluoropropene with molecular oxygen.



i. UV, -75 to -30°C n=1-2

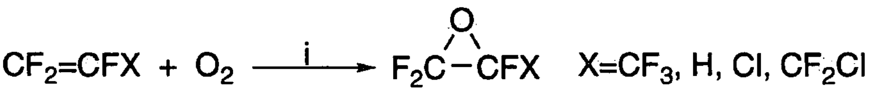
A clear, viscous, polymer was obtained as the major product. However, the epoxide content rises as the molecular weight of the starting alkene increases with, for example, the epoxide being the sole product using perfluorohept-1-ene.[156]

Ozone has been used as an initiator by Gozzo and Camaggi[157], where the reaction with tetrafluoroethene was performed in perfluorinated solvents (*e.g.* hexafluorobenzene and perfluoromethylcyclohexane), in the gas phase.



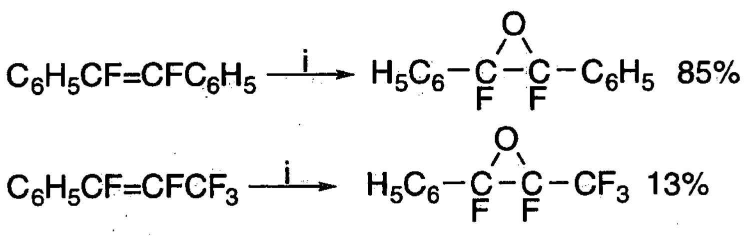
i. -80 to -20°C, solvent

The polymer, $(C_2F_4O_2)_n$, was a rubber-like explosive, which has been eliminated from the products by workers at Montecatini Edison[151] who have modified this procedure. The formation of fluorinated epoxides by heating the alkene with oxygen in an autoclave has also been reported.[151]



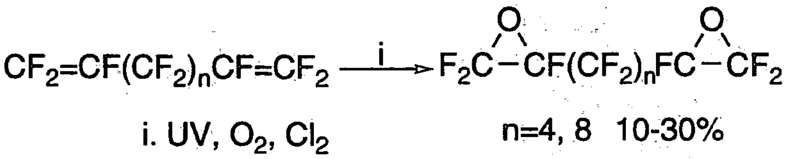
i. 104°C, autoclave

Recent work by Kremlev[158, 159] has described the oxidation of partially fluorinated alkenes using molecular oxygen, chlorine and ultraviolet irradiation.

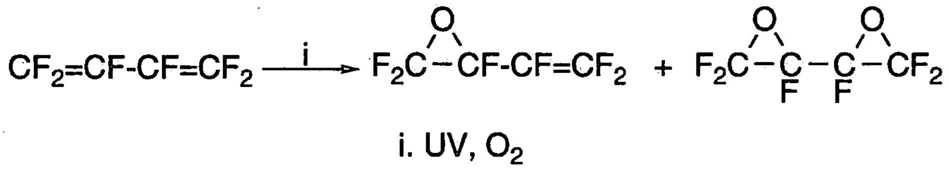


i. O_2, Cl_2, UV

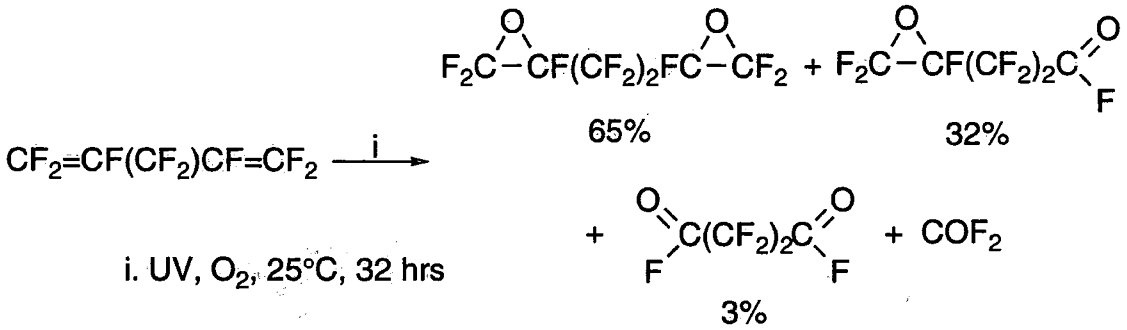
Very few perfluorinated diepoxides have been reported in the literature. The first two such diepoxides were successfully synthesised by Knunyants[160], in 1966, using oxygen in the presence of catalytic amounts of chlorine, and ultraviolet light.



In 1977, the yields of these diepoxides were improved to 65-70% by Sokolov[161], who employed a liquid-phase thermal oxidation. French[161] workers reported the photochemical oxidation of perfluorobutadiene, in 1967, using molecular oxygen. However, the reaction proceeded to give low yields of the mono- and diepoxides, which were difficult to isolate due to their inherent instabilities.

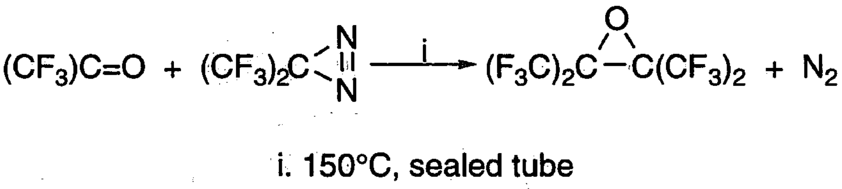


More recently, Filyacova[161] has reported the photochemical oxidation of perfluoro-1,5-hexadiene using atmospheric oxygen.

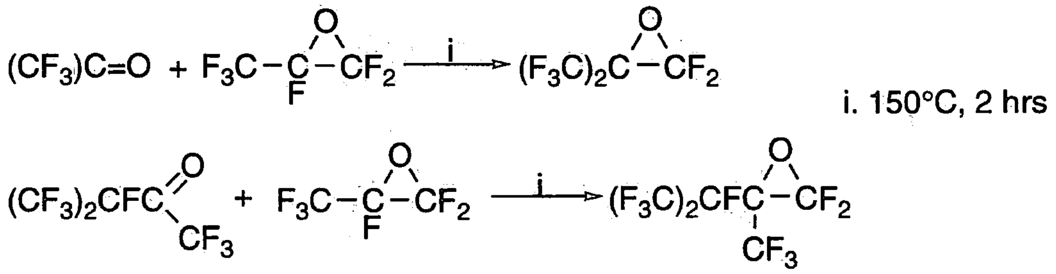


IV.1.C Carbenes and Perfluorinated Ketones

Rokhlin[162] has utilised bis(trifluoromethyl)diazomethane as a source of bis(trifluoromethyl)carbene, which added to hexafluoroacetone to give the corresponding epoxide.



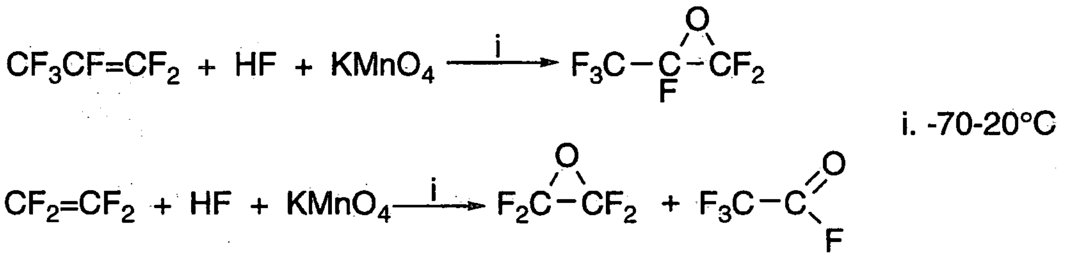
Similar reactions have also been reported by Moore[163], using hexafluoropropene oxide as a source of carbene.



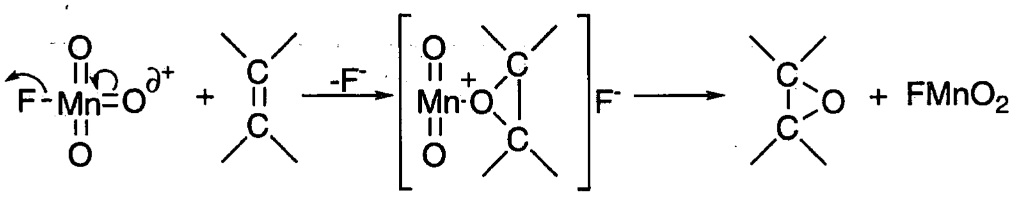
Obviously, this method is limited to the synthesis of epoxides which are stable at the temperatures necessary to generate the carbene.

IV.1.D Potassium Permanganate-Hydrogen Fluoride

Knunyants[164, 165] has reported the preparation of tetrafluoroethene oxide and hexafluoropropene oxide *via* an interesting reaction between the corresponding alkene and potassium permanganate-hydrogen fluoride.

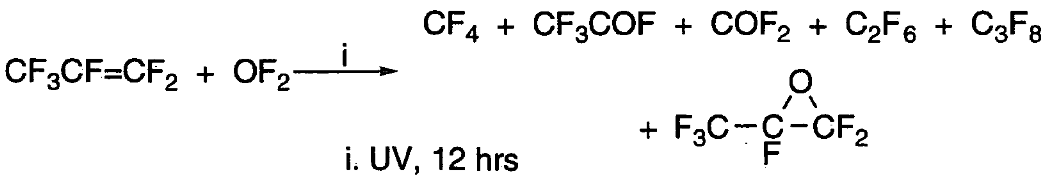


The proposed mechanism involves electrophilic attack on the double bond by the acid fluoride of permanganic acid, which is formed from HF and $KMnO_4$.



IV.1.E Oxygen Difluoride

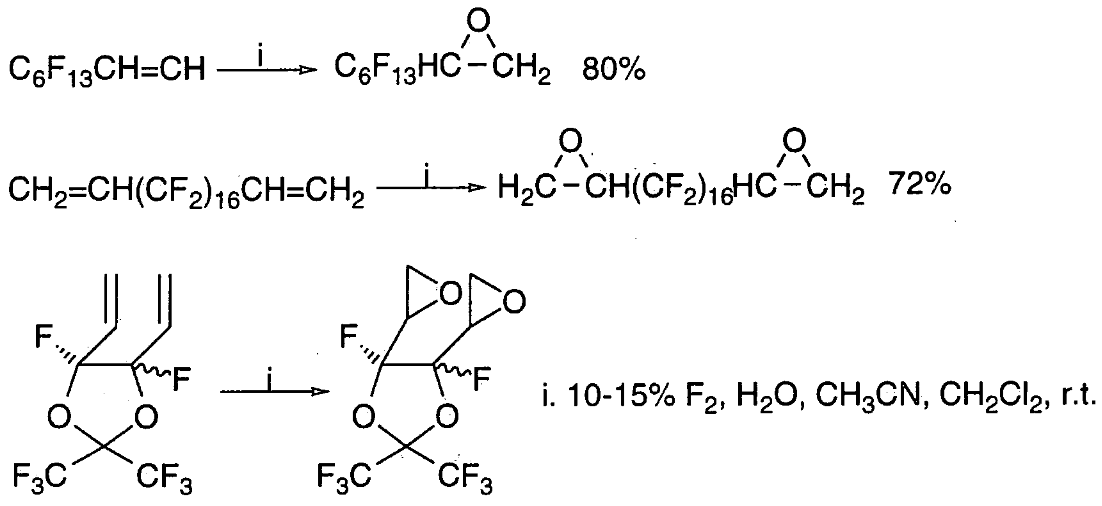
Work by Ruff[166] has described the use of oxygen difluoride to oxidise hexafluoropropene.



The oxide was obtained in low yield, with the formation of many other reaction products. No epoxides were observed when this procedure was repeated using other alkenes (*e.g.* tetrafluoroethene and perfluorocyclobutene).

IV.1.F Elemental Fluorine-Water-Acetonitrile

The DuPont company has recently reported the formation of highly fluorinated mono- and diepoxides.[167, 168] An interesting oxidising complex is used, HOF.CH$_3$CN, which is generated by bubbling 10-15% fluorine (diluted by nitrogen) through a mixture of acetonitrile and water.



$$C_6F_{13}CH{=}CH \xrightarrow{i} C_6F_{13}HC\overset{O}{-}CH_2 \quad 80\%$$

$$CH_2{=}CH(CF_2)_{16}CH{=}CH_2 \xrightarrow{i} H_2C\overset{O}{-}CH(CF_2)_{16}HC\overset{O}{-}CH_2 \quad 72\%$$

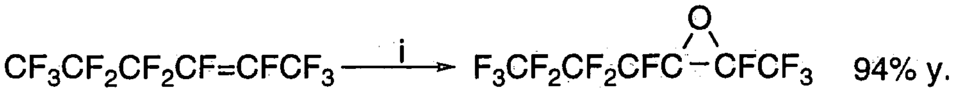
i. 10-15% F$_2$, H$_2$O, CH$_3$CN, CH$_2$Cl$_2$, r.t.

cis + *trans* (**155**) *cis* + *trans* 77%

This method employs very mild reaction conditions and is time efficient; the reaction was complete for dioxole (**155**) in 15 min.

IV.1.G Metal Hypochlorites

Procedures for preparing the oxides of terminal fluoroalkenes are mainly based on the use of hydrogen peroxide or oxygen, as the oxidising agents. Unfortunately, the use of such methods with internal fluoroalkenes does not give satisfactory results, as these systems are electrophilic in nature.[169] Because of this Kolenko[169-171], in 1979, developed an epoxidation method, for electron deficient double bonds, involving aqueous solutions of alkali or alkaline-earth hypohalites, in the presence of aprotic solvents.



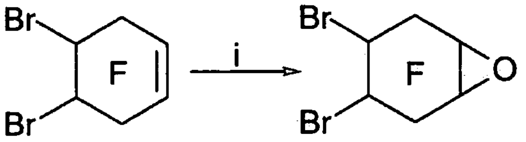
$$CF_3CF_2CF_2CF{=}CFCF_3 \xrightarrow{i} F_3CF_2CF_2CFC\overset{O}{-}CFCF_3 \quad 94\%\ y.$$

i. M(OHal)$_n$, CH$_3$CN

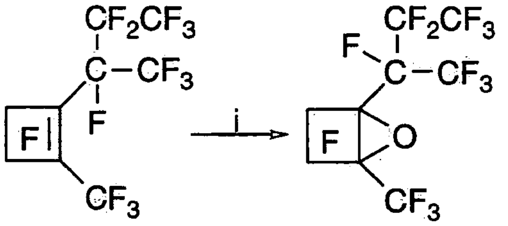
Where M=Na, K, Ba, Ca
Hal=Cl, Br
n=1,2

The aprotic solvents which gave the highest yields were acetonitrile and diglyme. The function of the solvent is to solvate the cation, leaving the anions free, which leads to an increase in the nucleophilicity of the latter, favouring attack of the hypochlorite ions on the double bond of the fluoroalkene. Kolenko and co-workers[172-177] have published many subsequent papers concerning the oxidation of perfluorinated alkenes. This procedure has also been applied to acyclic perfluorobromo-[178] and perfluorochloroalkenes[178, 179] by Chinese and Russian workers.

Tatlow[180, 181] has demonstrated the use of sodium hypochlorite, in the presence of acetonitrile, to epoxidise perhalogenated and perfluorinated cyclohexenes and cyclobutenes, respectively.

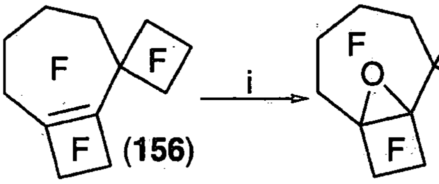


i. NaOCl, CH_3CN, 50°C, 1 hr



i. NaOCl, CH_3CN, 18°C, 1 hr

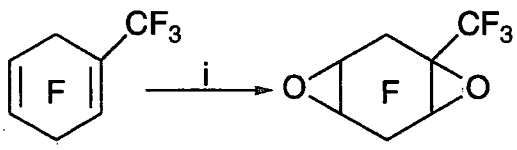
In these laboratories, sodium hypochlorite has been employed to oxidise a series of acyclic and cyclic perfluoroalkenes, including the interesting tricyclic alkene (**156**).[152]



(156) 64% y.

i. NaOCl, CH_3CN

Recently, Tatlow[182] has reported the use of aqueous sodium hypochlorite, in acetonitrile, to synthesise the diepoxide of 1-trifluoromethylheptafluorocyclo-1,4-diene (**157**) in good yield.



i. NaOCl, H_2O, CH_3CN

(157) 60%

Amazingly, this is only the fourth perfluorinated diepoxide to be reported in the literature. The epoxidation of perfluorocyclohexene derivatives was also reported.[182]

Finally, DuPont[183] have recently patented a three-liquid-phase epoxidation procedure for perfluoroalkenes. This is primarily aimed at hexafluoropropene, since it is industrially very important for the synthesis of inert oils and vinyl monomers, and comprises of an aqueous phase containing hypochlorite ions, an epoxide phase containing the bulk of the epoxide and a reaction phase which contains a phase transfer catalyst with a higher affinity for the perfluoroalkene than for its epoxide.

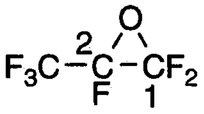
As can be seen, there is a great deal of interest in the synthesis of perfluorinated epoxides, with the safe and cheap Russian originating hypochlorite methodology predominating at the moment.

IV.2 Some Epoxide Chemistry

Perfluorinated epoxides undergo reactions which involve the opening of the oxirane ring with, predominately, nucleophilic reagents, although electrophilic ring opening has been reported. Amongst the possible products are ketones, acid fluorides, alcohols and high molecular weight material. Some of these reactions are detailed below.

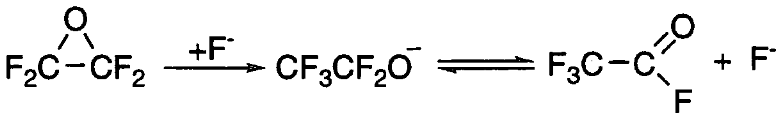
IV.2.A Nucleophilic Ring Opening

In an asymmetrically substituted epoxide, such as hexafluoropropene oxide, there are two possible positions for nucleophilic attack: C_1 or C_2.

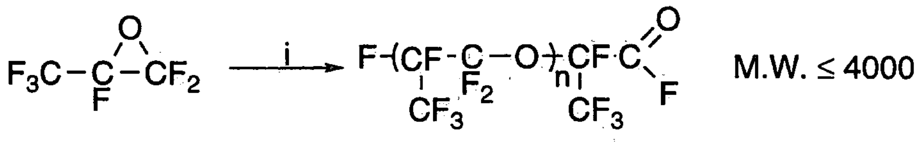


Initial nucleophilic attack will occur preferentially at the more substituted ring carbon (*i.e.* C_2)[184], unless the carbon is very hindered[185], or the nucleophile is very bulky[186], when attack is diverted to the less substituted carbon (*i.e.* C_1). For example, hexafluoropropene oxide will react with ammonia and primary amines at C_2, whereas C_1 is the reactive site in the cases of secondary and tertiary amines, due to their increased steric demands.[185]

The early work involving nucleophilic ring opening reactions concerned simple epoxides such as tetrafluoroethene oxide, where the acid fluoride was observed after reaction with fluoride ion.[187, 188]



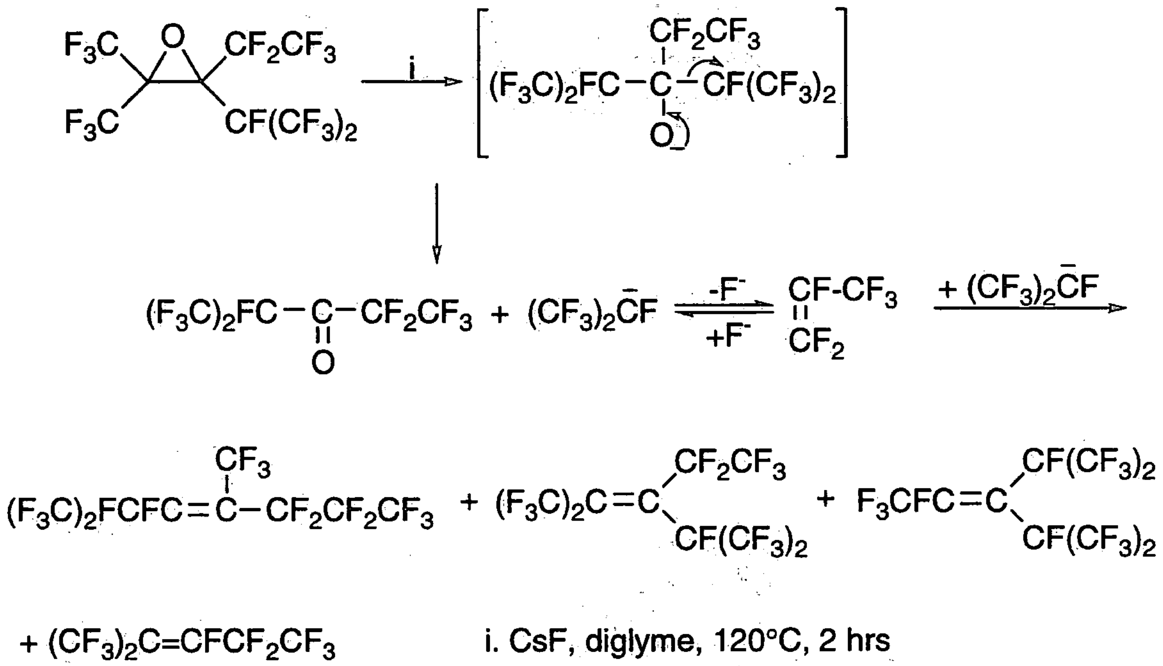
This type of process is known as chain termination, and needs to be avoided for polymerisation to proceed. Interestingly, unlike tetrafluoroethene oxide, hexafluoropropene oxide can be polymerised by fluoride ion (anionic polymerisation), whilst employing a low temperature to suppress the formation of the acid fluoride (CF_3CF_2COF).[187, 188]



i. CsF, tetraglyme, -30 to -50°C, anhydrous media

A great deal of literature exists concerning the fluoride ion induced polymerisation of hexafluoropropene oxide[185], often with co-reactants such as hexafluoropropene[189] or perfluorinated carboxylic acid fluorides.[190]

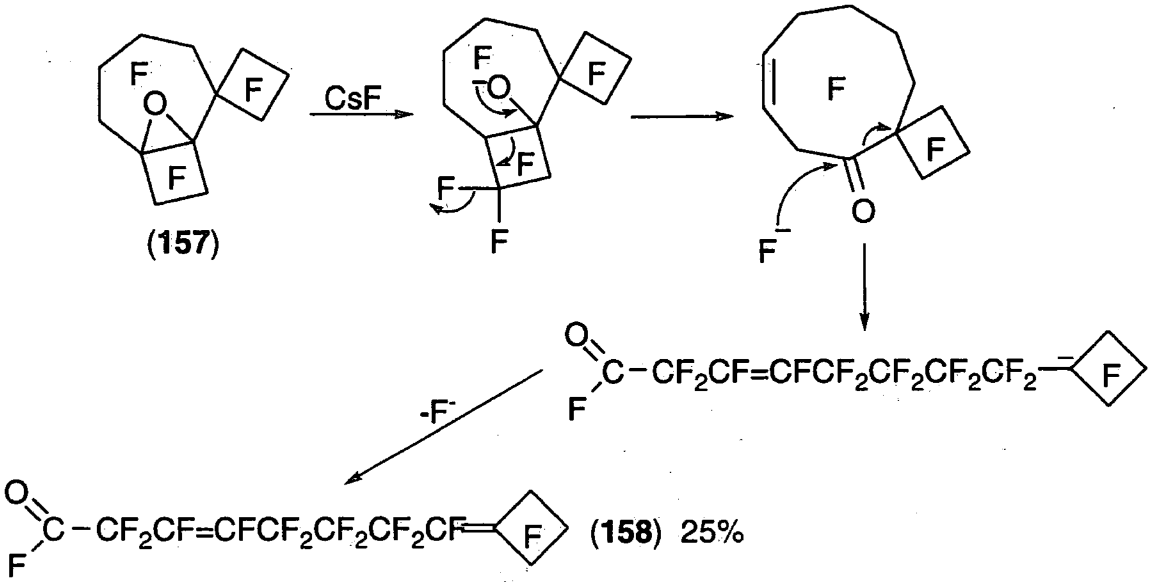
Kolenko[172, 191] has described an interesting fluoride ion induced ring opening, followed by decomposition to give a ketone and a series of perfluorinated alkenes, which are derived from hexafluoropropene and its perfluorinated carbanion.



i. CsF, diglyme, 120°C, 2 hrs

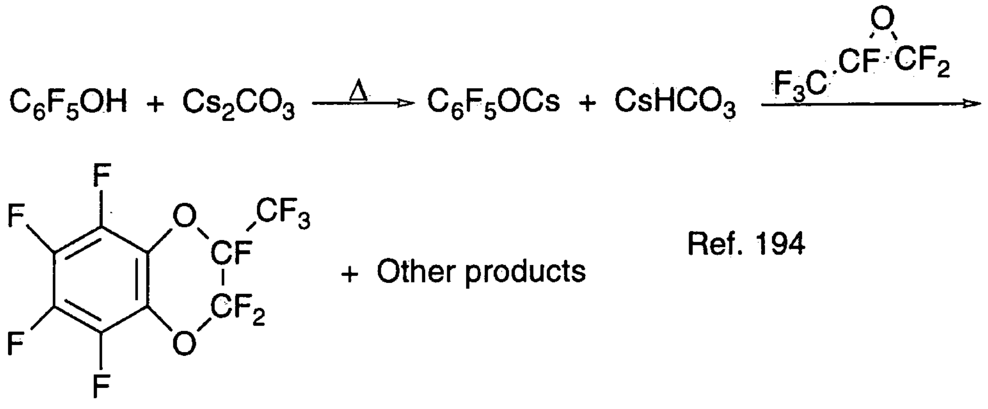
The direction of ring opening is probably determined mainly by steric factors.[172, 191]

In these laboratories, an interesting series of ring openings and expansions was observed on reaction of epoxide (**157**) with fluoride ion.[152]

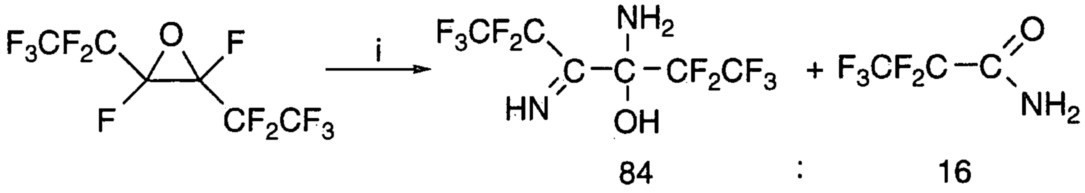


The carbonyl fluoride was the only isolated product from a complex mixture.[152]

Perfluorinated epoxides have also been ring opened by aryloxides[173, 192-195] and amines.[173, 192, 196]

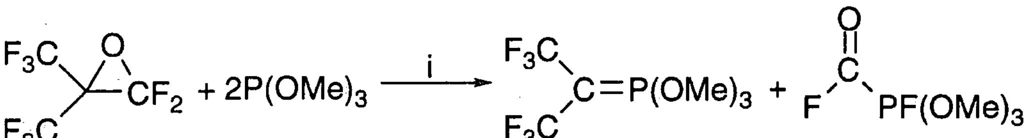


Ref. 194



i. NH_3, diethyl ether Ref. 196

Finally, trialkylphosphites have recently been shown to ring open epoxides.[197] For example, perfluoroisobutene oxide (**159**) reacted with trimethyl phosphite to form isopropylidenetrimethoxyphosphorane (**160**), together with unstable fluorocarbonyltrimethoxyfluorophosphorane (**161**).



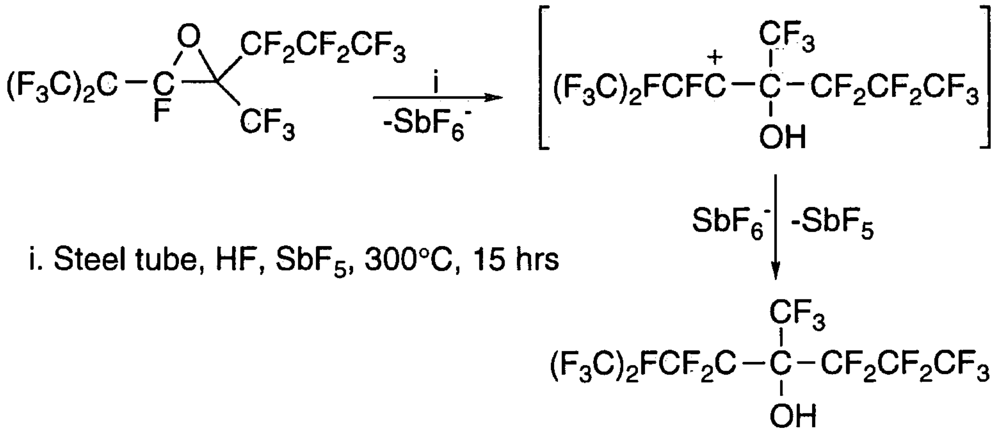
(159) **(160)** **(161)**

i. Diethyl ether, -78°C, 2 hrs

This procedure was applied to a series of perfluorinated epoxides, with similar results.[197]

IV.2.B Electrophilic Ring Opening

As would be expected, perfluorinated epoxides are extremely stable to electrophilic attack, and will only ring open under severe reaction conditions. This has resulted in a limited number of examples, and these originate from Russian laboratories. One such example is the interaction between perfluoro(2,4-dimethyl-3-heptene)oxide and the superacid HF.SbF_5, to give an alcohol.[173, 191]



The reaction requires a powerful electrophile and a high temperature to proceed.

IV.3 Discussion

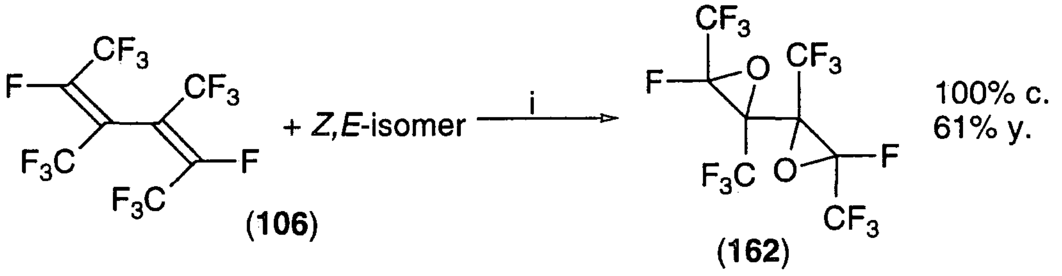
IV.3.A Epoxidations using Calcium Hypochlorite

IV.3.A.(1) Epoxidation of Perfluoro-3,4-dimethyl-2,4-diene (106)

As mentioned in the introduction to this chapter, there are few examples of perfluorinated diepoxides in the literature, and diene (**106**) presented the possibility of adding to this number. The epoxidation of (**106**) was first achieved in these laboratories[98] using calcium hypochlorite and acetonitrile, in a procedure originally described by Kolenko.[169, 170]

This reaction was repeated by stirring diene (**106**) with calcium hypochlorite at room temperature. The diepoxide (**162**) was isolated as a lower layer, and found to be pure by GLC and ^{19}F NMR spectroscopy; the latter showed coupling constants which are characteristic of fluorinated epoxides.[101]

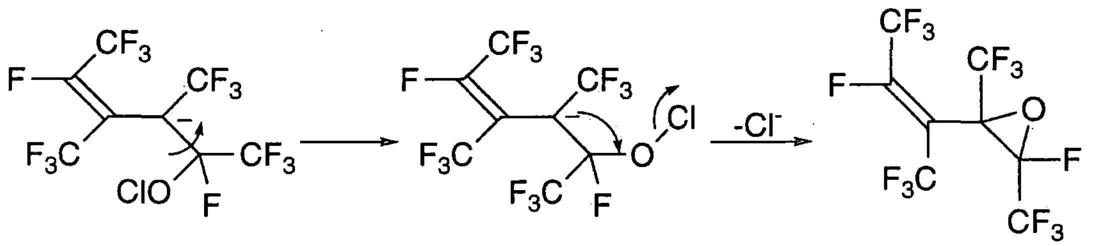
Other evidence for the structure came from mass spectrometry, where addition of oxygen was indicated, elemental analysis and ^{17}O NMR spectroscopy, where one resonance was observed for the single oxygen environment within (**162**).



(106) **(162)**

i. $Ca(OCl)_2$; CH_3CN; r.t.; 1 d

Interestingly, although both isomeric forms of diene (**106**) were present, only <u>one</u> isomer of the diepoxide was observed. This is most likely due to the diepoxide (**162**) being obtained as the thermodynamically most stable product, due to the intermediate carbanion, shown below, being relatively stable, and allowing rotation about the single bond before the ring closes, with chloride ion elimination.



Z,E-isomer

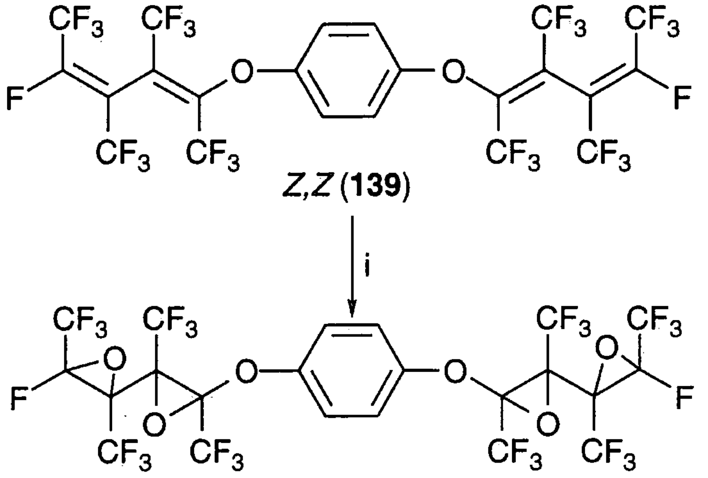
Shown for one double bond

Diepoxide (**162**) has been described, above, as the *trans,trans* isomer, although the thermodynamic product could have a *cis,cis* configuration which remains consistent with two CF_3 environments, one tertiary fluorine environment and a single oxygen environment. However, there is good precedence for the thermodynamic product to be the *trans,trans* isomer, as the steric interactions between the bulky trifluoromethyl groups are minimised[166, 171, 181] and such a configuration is analogous to the nucleophilic epoxidation of a mixture of *cis*- and *trans*- hydrocarbon alkenes, which yields mainly the *trans*- epoxide.[198] This reaction proceeded equally well by refluxing the acetonitrile, using the same reagent stoichiometry, for 5 hrs.

In conclusion, diene (**106**) can be epoxidised, using the hypochlorite methodology, to give the thermodynamic product, which is easily isolated.

IV.3.A.(2) Epoxidation of *Z,Z*-1,4-dioxy-bis(2-perfluoro-3,4-dimethylhexa-2,4-diene)benzene (139)

The synthesis of a tetraepoxide was attempted using calcium hypochlorite, and this is the first reported use of this system with a solid starting material. Tetraene (**139**) was dissolved in acetonitrile, which was refluxed for 43 hrs. After solvent removal and recrystallisation, a white solid was obtained which was identified as the *Z,Z*- isomer of tetraepoxide (**172**) by ^{19}F NMR spectroscopy. Further evidence for (**172**) was supplied by MS, where the molecular ion was observed, and elemental analysis.



Z,Z (**139**)

Z,Z (**172**) 60% y.

i. $Ca(OCl)_2$, CH_3CN, r.t., 43 hrs

By analogy with diepoxide (**162**), it is reasonable to suggest that the tetraepoxide (**172**) is formed as the thermodynamic product, which adopts the *trans,trans*, or *Z,Z*, configuration, again minimising the steric interactions between the trifluoromethyl groups. Interestingly, when this procedure was attempted using diethyl ether as the solvent, no reaction was observed, which emphasises the importance of acetonitrile in solvating the metal cation and leaving the anion uncombined and, therefore, with increased nucleophilicity.[169]

To conclude, the successful application of calcium hypochlorite to a solid tetraene, giving the tetraepoxide, has been demonstrated.

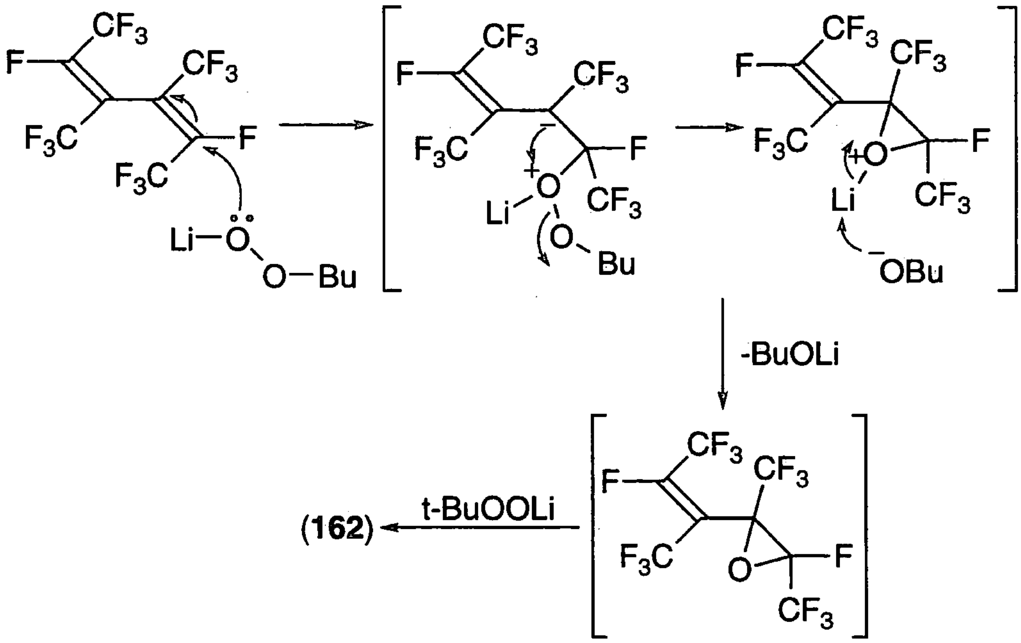
IV.3.B Epoxidations using a t-Butyl Hydroperoxide/Butyl-Lithium System

IV.3.B.(1) Epoxidation of Perfluoro-3,4-dimethyl-2,4-diene (106)

Lithium t-butyl hydroperoxide can be generated from butyl-lithium and t-butyl hydroperoxide, and used as a reagent to epoxidise electron deficient double bonds.[199] This has been applied to hydrocarbon systems, by Meth-Cohn[199, 200], such as α,β-unsaturated esters, sulphones, sulphoximines and amides, with good stereoselectivity. Also, 3-F-alkyl 2-propanoates, which are extremely difficult to epoxidise using established hydrocarbon and fluorocarbon systems, have been oxidised with lithium t-butyl hydroperoxide in good yields, with retention of stereochemistry.[201] Whether this methodology could be applied to perfluorinated alkenes, and a diene, was investigated.

Lithium t-butyl hydroperoxide (Bu^{t}OOLi) was generated *in situ* by mixing butyl lithium with t-butyl hydroperoxide, at -78°C, in tetrahydrofuran. Diene (**106**) was then added and, after 48 hrs, the diepoxide (**162**) was isolated as a lower layer, and identified by ^{19}F NMR spectroscopy [see Section IV.3.A.(1)]. The isolated yield (70%) was slightly better than that obtained using calcium hypochlorite (61%), which suggested that this could be an excellent method for epoxidising perfluorinated systems. The mechanism, shown for one double bond, is given below.

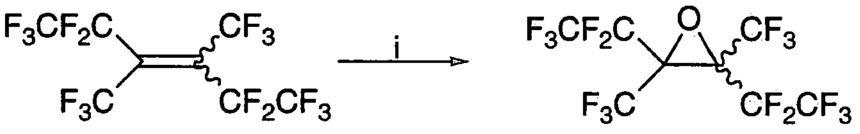
$$\mathrm{BuLi} + \mathrm{Bu^tOOH} \longrightarrow \mathrm{Bu^tOOLi} + \mathrm{BuH}$$



Interestingly, the product, diepoxide (**162**), was obtained as only one isomer, whose data corresponded with that from the epoxidation of diene (**106**) with calcium hypochlorite. This indicates that the epoxidation is not stereospecific with this perfluorinated system, since the *Z,E*-diepoxide, from the *Z,E*- isomer of diene (**106**), was not observed, and that the product stereochemistry is thermodynamically controlled.

IV.3.B.(2) Epoxidation of Perfluoro-3,4-dimethylhex-3-ene (105)

Alkene (**105**) has previously been oxidised, in these laboratories, using sodium hypochlorite in acetonitrile, to give the corresponding oxide (**164**) in 62% yield, with a 1:1 ratio of the *E*- and *Z*- isomers being observed.[202] The lithium t-butyl hydroperoxide methodology was now applied to alkene (**105**). To freshly prepared peroxide, the alkene (**105**) was added, and after 16 hrs fluorinated material was isolated as a lower layer, and identified as a 1:1 mixture of *E* and *Z*-perfluoro-3,4-dimethyl-3,4-epoxyhexane by ^{19}F NMR spectroscopy and GLC.



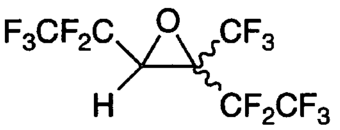
Z + *E* (**105**)

Z (**164a**) + *E* (**164b**) (74% y.)

Z : *E* = 1 : 1

i. Bu^tOOH, BuLi, THF, -78°C to r.t.

The yield (74%) is slightly better than that obtained using the hypochlorite methodology, and none of the previously noted impurity, *E*,*Z*-2H-perfluoro-(3-methyl-3,4-epoxypentane) (**175**, 28%), was observed.[202]



E + *Z* (**175**)

The use of butyl-lithium requires care, due to its moisture sensitivity, and it is relatively expensive. Whether it was possible to replace the lithium counter ion with caesium or potassium was investigated using the fluorides (CsF and KF), which are easy to handle and cheap. When alkene (**105**) was added to a stirred mixture of t-butyl hydroperoxide and caesium fluoride, in tetrahydrofuran, an exotherm was noted. After 72 hrs, product was isolated as a lower layer, and examination by ^{19}F NMR spectroscopy showed, unexpectedly, that only the *Z*-isomer of epoxide (**164**) had formed. It appears that using caesium t-butyl hydroperoxide (Bu^tOOCs) allows the thermodynamically most stable isomer to be formed exclusively. However, GLC-MS and ^{19}F NMR spectroscopy indicated the presence of four other fluorine containing compounds, which remain unidentified. These species may have originated from reactions involving, for example, the hydrogen fluoride produced on forming the salt.

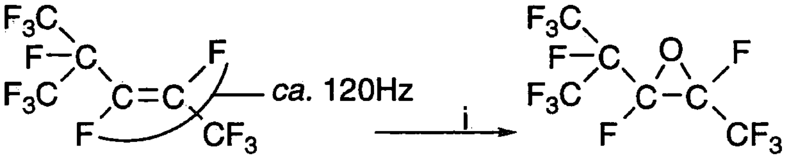
$$Bu^tOOH + CsF \longrightarrow Bu^tOOCs + HF$$

Although using Bu^tOOLi gives a cleaner reaction, it is interesting that Bu^tOOCs reacted as an epoxidising agent, considering its bulk and the crowding around the double bond of alkene (**105**).

The same procedure was applied when using potassium fluoride. Analysis of the isolated lower layer, by ^{19}F NMR spectroscopy, indicated the presence of only (**105**). There was no evidence for epoxide (**164**), even after heating the system to 100°C. This lack of reactivity is most likely due to the K-F bond, unlike the Cs-F bond, being strong enough to prevent the formation of Bu^{t}OOK, and this confirms the observation that, unlike hydrogen peroxide, t-butyl hydroperoxide is unreactive towards most organic substrates in the absence of a catalyst (*e.g.* BuLi or CsF).[203]

IV.3.B.(3) Epoxidation of Perfluoro-2-methylpent-3-ene (165)

The oxidations studied so far have involved F-alkenes which have double bonds with four F-alkyl groups, or three F-alkyl groups and a fluorine attached. Whether double bonds substituted with two vinylic fluorines and two F-alkyl groups (*i.e.* less activated towards nucleophilic attack) would be susceptible to the lithium t-butyl hydroperoxide system was examined. Alkene (**165**) has previously been oxidised, in good yield (72%), using sodium hypochlorite in acetonitrile.[171] Alkene (**165**) was added to freshly prepared lithium t-butyl hydroperoxide and, after 4.5 d, fluorinated material was collected as a lower layer and identified by GLC-MS and ^{19}F NMR spectroscopy as a mixture of alkene (**165**) and *trans*-perfluoro-2-methyl-3-epoxypentane (**166**, 82% by ^{19}F NMR). The epoxide was then isolated by preparative scale gas chromatography.



trans- (**165**) *trans-* (**166**) 82%

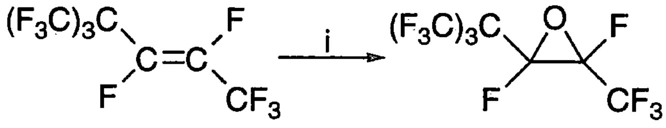
i. Bu^{t}OOH, BuLi, THF, -78°C to r.t.

In perfluorinated alkenes, it is known that $^3J_{trans\text{-FF}}$ coupling is *ca.* 120Hz, whereas $^3J_{cis\text{-FF}}$ coupling is *ca.* 10Hz[101], and examination of the ^{19}F NMR spectrum of (**165**) gave $^3J_{FF}$ values of 135.6Hz, indicating the starting alkene had the vinylic fluorines in the *trans-* conformation.

The ^{19}F NMR spectrum of (**166**) indicated the presence of only one compound which, assuming thermodynamic control of oxidation, is consistent with *trans-* (**166**), since the distance between the bulky perfluoroalkyl groups would be maximised. Further evidence for this configuration comes from a good agreement between this data, and that obtained by Kolenko[171] after the epoxidation of (**165**) using sodium hypochlorite. In conclusion, the presence of two vinylic fluorines did not decrease reactivity towards lithium t-butyl hydroperoxide.

IV.3.B.(4) Epoxidation of Perfluoro-2,2-dimethylpent-2-ene (167)

The t-butyl hydroperoxide and butyl-lithium system was applied to alkene (**167**) (supplied by Yuri Cheburkov, 3M Co.) which, like alkene (**165**), has two vinylic fluorines, plus the more sterically demanding $C(CF_3)_3$ moiety. Alkene (**167**) was added to a solution of lithium t-butyl hydroperoxide, and after 3.5 d a lower layer was isolated and identified as a mixture of (**167**) and perfluoro-2,2-dimethyl-3-epoxypentane (**168**, 80%) by GLC-MS and ^{19}F NMR spectroscopy. The epoxide was then purified by preparative scale gas chromatography in order to obtain carbon and fluorine analysis.



trans- (**167**) *trans*- (**168**)

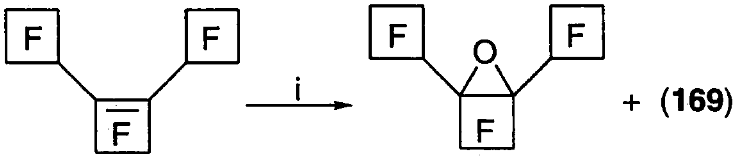
i. Bu^{t}OOH, BuLi, THF, -78°C to r.t.

Both GLC-MS and ^{19}F NMR spectroscopy showed that alkene (**167**) was present as the *trans*- isomer only; a characteristically large $^3J_{trans\text{-}FF}$ coupling of 144.3 Hz was observed[101], and analysis of this data for epoxide (**168**) indicated one isomer was formed, which is most likely *trans*- in configuration since, as with the examples previously described, the steric interactions between the perfluoroalkyl groups are minimised.

Encouragingly, the high steric demands of alkene (**167**) did not inhibit its epoxidation by lithium t-butyl hydroperoxide.

IV.3.B.(5) Epoxidation of Perfluorocyclobutene Trimer (169)

The epoxidation of alkene (**169**) has been successfully accomplished using sodium hypochlorite, in these laboratories[152], to give a reasonable yield of the corresponding epoxide (**170**, 64%). The effectiveness of lithium t-butyl hydroperoxide with this alkene was examined. Alkene (**169**) was added to a solution of lithium t-butyl hydroperoxide, in tetrahydrofuran, and after 3.5 d the fluorinated material was isolated and identified as a mixture of alkene (**169**) and epoxide (**170**) by GLC-MS and ^{19}F NMR spectroscopy.



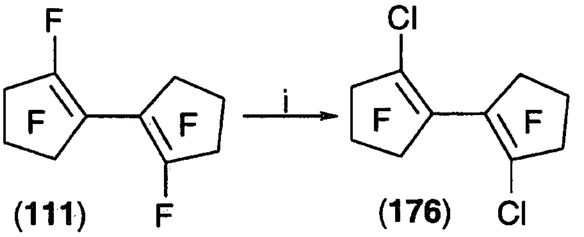
(**169**) (**170**) 16% y.

i. Bu^{t}OOH, BuLi, -78°C to r.t.

The ^{19}F NMR data was consistent with that of Chambers[152] and, unexpectedly, the yield of epoxide (**170**) was very low, and did not compare well to that obtained using hypochlorite. An explanation for this could be that the approach of lithium t-butyl hydroperoxide is inhibited by steric interactions with the bulky perfluorocyclobutane rings, which does not occur with the hypochlorite ion ($^-$OCl).

IV.3.B.(6) Attempted Epoxidation of Perfluoro-1,1′-bicyclopent-1-enyl (111)

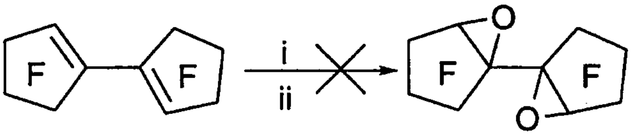
Previous attempts to epoxidise diene (**111**), in order to form an interesting diepoxide, have failed using calcium hypochlorite in acetonitrile.[98] It was found that free chloride ion nucleophilically substituted the vinylic fluorines of this very reactive diene, giving a dichloro compound (**176**).



(111) **(176)**

i. $Ca(OCl)_2$, CH_3CN, r.t., 7 d

The butyl-lithium/t-butyl hydroperoxide system was employed as an alternative method. Diene (**111**) was added to lithium t-butyl hydroperoxide, in tetrahydrofuran, and after 2.5 d a lower layer was isolated.



(100% conv.)

(111) **(176)**

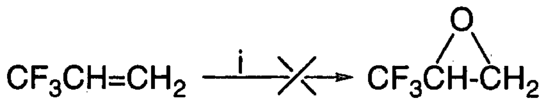
i. Bu^{t}OOH, BuLi, THF, -78°C to r.t.
ii. Bu^{t}OOH, BuLi, THF, -78°C to -20°C

The ^{19}F NMR spectrum was extremely complex, indicating 100% conversion of the diene , but the GLC-MS did not indicate the presence of any diepoxide, and competing side-reactions were obviously taking place. The reaction was repeated, maintaining the temperature at -20°C in an attempt to limit the competing reactions, but this had no effect by GLC-MS and ^{19}F NMR spectroscopy.

IV.3.B.(7) Attempted Epoxidation of 1,1,1-trifluoropropene (171)

Trifluoromethyl containing compounds have received alot of interest because of their physical and biological properties, and many synthetic approaches towards the introduction of trifluoromethyl groups into organic molecules have been reported.[204] Alkene (**171**) gives an epoxide which can be regarded as a potentially versatile building block, but its use has been rarely reported due to limited availability.[205] Recently, optically active epoxide (**177**) was prepared *via* the direct oxidation of alkene (**171**) using a microbial method[205], which is not very practicable, and by Seebach[206] who employed a lengthy five step synthesis. However, it was hoped that direct oxidation could be achieved using the t-butyl hydroperoxide and butyl-lithium system.

The epoxidising mixture was contained in a Carius tube, into which alkene (**171**) was condensed, which was sealed and rotated at room temperature. The ^{19}F NMR spectrum of the volatiles revealed one resonance, which belonged to (**171**) after comparison with the data of an authentic sample.



(171) (177)

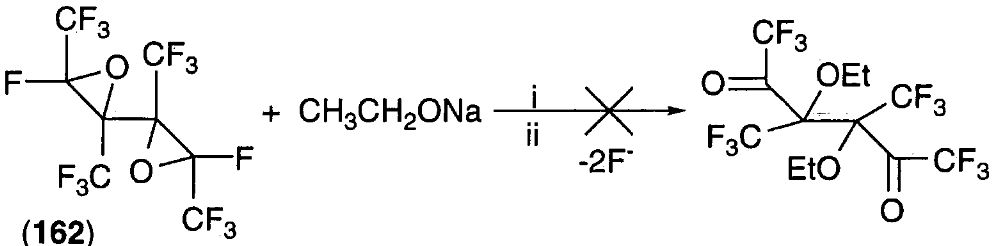
i. t-BuOOH; BuLi; -78°C to r.t.; 4d.

The absence of any reaction could be due to difficulty in mixing (**171**) with the tetrahydrofuran solvent, and/or to the double bond not being sufficiently activated towards nucleophilic attack by only one electron withdrawing CF_3-group.

IV.3.C Ring Opening Reactions with Diepoxide (162)

IV.3.C.(1) Attempted use of Sodium Ethoxide

As mentioned in the introduction to this chapter (Section IV.2), perfluorinated epoxides are susceptible to nucleophilic ring opening reactions, giving products such as ketones and alcohols. The use of diepoxide (**162**) in such reactions seemed a reasonable possibility. Diepoxide (**162**) was stirred with sodium ethoxide, after which fluorinated material was collected as a lower layer and identified as the diepoxide by ^{19}F NMR spectroscopy. As a result, the reaction was repeated in a sealed tube, at 100°C, but without success.



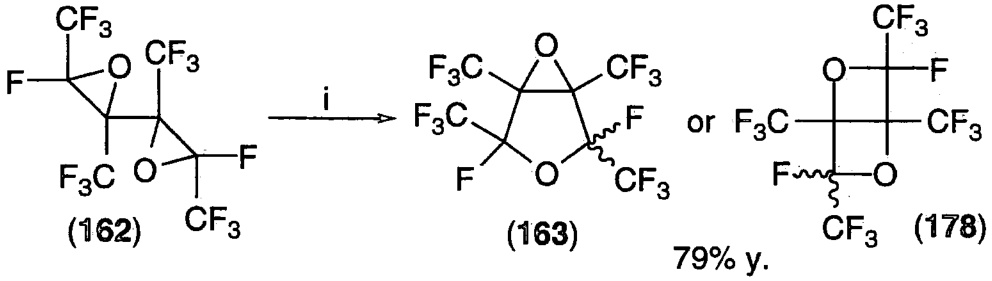
(162)

i. CH_3CN, r.t., 14 d
ii. Sealed tube, CH_3CN, 100°C, 1 d

These results suggest that diepoxide (**162**) is extremely stable to attack by oxygen nucleophiles.

IV.3.C.(2) Attempted use of Caesium Fluoride

In an attempt to ring open diepoxide (**162**), to give a perfluorinated diketone, Mullins[98] used caesium fluoride, which is very effective with epoxides that are substituted with perfluoroalkyl groups (see Section IV.2). This reaction was repeated by adding diepoxide (**162**) to dry caesium fluoride and heating this mixture, using a furnace, in a sealed tube. Volatile material was then isolated and shown to comprise of one component, by GLC, whose structure was suggested as one of the two isomers, shown below, by ^{19}F NMR spectroscopy, MS, IR and elemental analysis. It was found that for the reaction to proceed, temperatures in excess of 120°C were required.



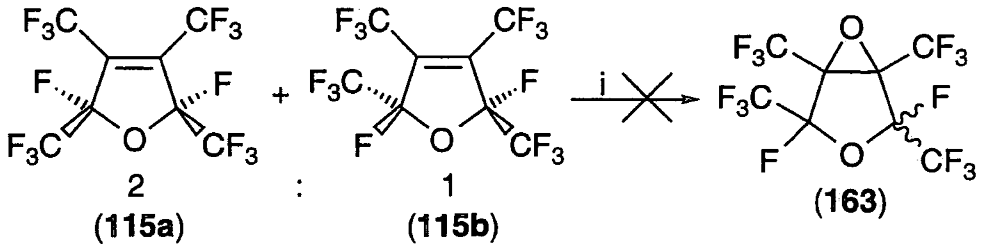
i. Sealed tube, CsF, 200°C, 1 d

The ^{19}F NMR spectrum indicated a symmetrical structure, since only two CF_3 environments and one tertiary fluorine environment were observed, and a carbonyl absorption was absent in the IR spectrum, proving the ketone was not formed. The suggested structures are the only two which fit these criteria, after fluoride ion has opened the epoxide moieties. In an effort to establish the actual isomer formed, attempts were made to synthesise perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane **(163)**.

IV.3.D Attempted Epoxidation of Perfluoro-2,5-dihydrotetramethylfuran (115)

IV.3.D.(1) Using Calcium Hypochlorite

The method developed by Kolenko[169], for electron deficient double bonds was used. Dihydrofuran derivative **(115)**, which was synthesised following a procedure developed in these laboratories[113] (see Chapter 6, Section VI.2.C), provided a potentially convenient route to the desired product, and was added to a mixture of calcium hypochlorite and acetonitrile, which was refluxed.

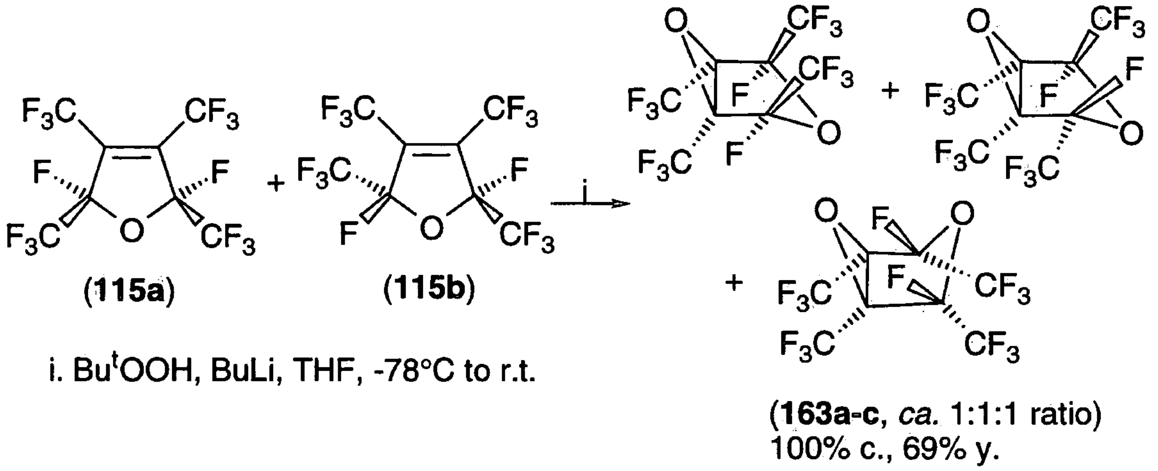


i. $Ca(OCl)_2$, CH_3CN, 90°C, 6 hrs

A lower layer was isolated, which contained several components by GLC-MS and ^{19}F NMR spectroscopy, but there was no evidence for epoxide **(163)**. The isolation of these compounds was not attempted.

IV.3.D.(2) Using Butyl-Lithium/t-Butyl Hydroperoxide

Since the hypochlorite system failed to give the epoxide, the butyl-lithium/t-butyl hydroperoxide system was applied. Dihydrofuran derivative (**115**) was added to a solution of lithium t-butyl hydroperoxide, in tetrahydrofuran, and after 4 d a lower layer was isolated and identified as an inseparable mixture of the three possible isomers of perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane (**163a-c**) by GLC-MS, ^{19}F NMR spectroscopy and elemental analysis.



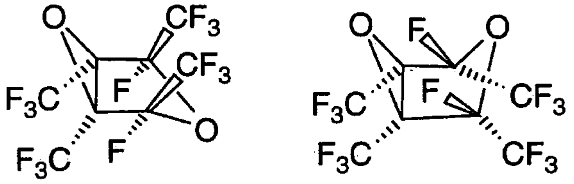
(115a) **(115b)**

i. Bu^{t}OOH, BuLi, THF, -78°C to r.t.

(163a-c, *ca.* 1:1:1 ratio)
100% c., 69% y.

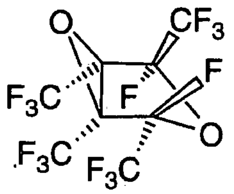
The GLC resolved two closely associated peaks (*i.e.* two isomers), both having identical fragmentation patterns which showed that oxygen had added. Analysis of the ^{19}F NMR spectrum of (**163a-c**) (376MHz) revealed six CF_3 resonances (three grouped at *ca.* 66 ppm and three at *ca.* 80 ppm) and three high frequency resonances belonging to the tertiary fluorines (*cf.* diepoxide (**162**)). These three sets of signals were in the ratio of 3:3:1, indicating the presence of three isomers. It was possible to assign the CF_3 and tertiary fluorine resonances to each isomer, by comparing the relative integration values: isomer 1) 63.9 (CF_3), 79.1 (CF_3) and 122.1 (CF) ppm; isomer 2) 66.3, 80.6 and 127.1 ppm; isomer 3) 66.7, 81.5 and 135.5 ppm. However, it was not possible to identify which structures the peaks represented, due to the observation of complex multiplets, arising from inequivalent long range (*i.e.* ^5J) couplings around the ring systems, which were not interpretable with any accuracy.

On the synthesis of (**115a,b**), one isomer occurred in about twice the concentration as the other, by ^{19}F NMR spectroscopy. After its epoxidation, the product ratio was *ca.* 1:1:1, which implies that (**115a**) is the most abundant isomer, since the oxidation allows both stereoisomers to be formed.



(163)

Whereas, with (**115b**), only one isomer is possible.

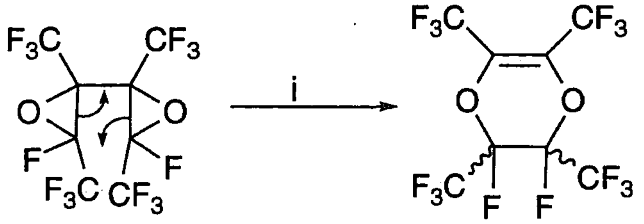


(163)

The product from the isomerisation of diepoxide (**162**) with caesium fluoride did <u>not</u> give a ^{19}F NMR spectrum that corresponded with this data, and was therefore ruled out as a possible structure.

IV.3.E Rearrangement of Diepoxide (162) without Caesium Fluoride

At this point, the control experiment (*i.e.* without CsF) was performed in order to confirm that the fluoride ion source was participating. Diepoxide (**162**) was sealed in a quartz tube, and heated in a furnace at 200°C for 1d. Volatile material contained one component (by GLC), and examination of the ^{19}F NMR spectrum and GLC-MS revealed, surprisingly, data which corresponded exactly with that of the product obtained when using caesium fluoride. Since the action of fluoride ion is not necessary to open the epoxide rings, an intramolecular ring opening is suggested, which relieves the ring strain in forming a perfluorinated dioxin (**179**), whose structure remains consistent with the data.



(162)

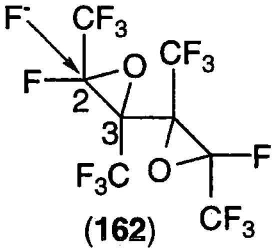
(179)
100% conv.
96% y.

i. Sealed tube, 200°C, 1 d

Also, the ^{17}O NMR spectrum reveals one broad peak, which provides evidence for one oxygen environment, as in (**179**).

This type of rearrangement has not been previously described in the literature and, in an attempt to elucidate the mechanism, diepoxide (**162**) was irradiated with ultraviolet light, but no reaction occured by ^{19}F NMR spectroscopy after 2d and, in view of this, a radical mechanism seems unlikely. However, if the three membered rings in diepoxide (**162**) are considered as double bonds, then the rearrangement described above draws some similarity to the thermal cyclisation of butadiene, which gives cyclobutene.

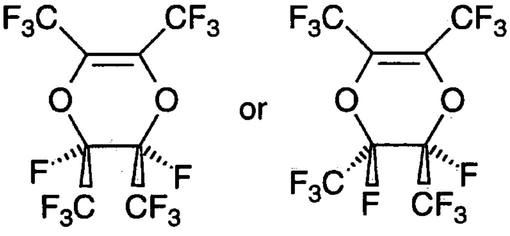
Please note: Diepoxide (**162**) has recently been successfully ring opened with fluoride ion, using tetraglyme as a solvent, at 100°C (100% conversion). Although the products have not yet been characterised, it is clear, by the absence of a tertiary fluorine resonance and the appearance of CF_2 resonances, in the ^{19}F NMR spectrum, that the fluoride ion attacks the tertiary fluorine position (*i.e.* C_2), giving CF_2CF_3 moieties, and not at C_3, which could lead to a perfluorinated ketone.



(162)

IV.3.F The Stereochemistry of Dioxin (179)

Perfluorinated dioxin (**179**) can, potentially, be formed as two isomers, shown below, which both fulfil the symmetrical nature of the ^{19}F NMR spectrum.

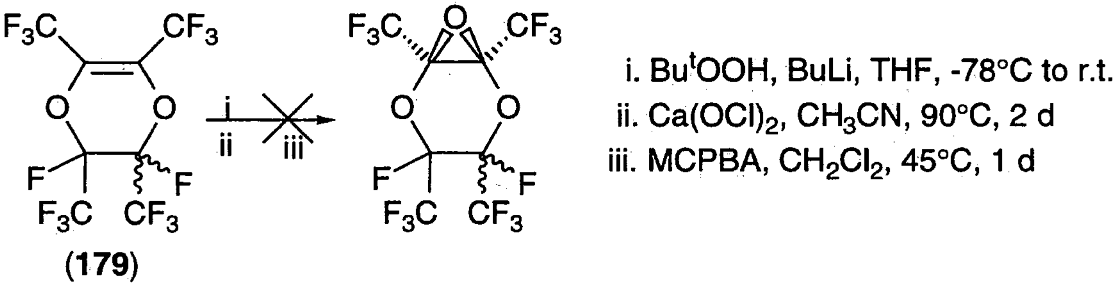


(179a) **(179b)**

On steric grounds dioxin (**179b**) maybe more likely, since the CF_3 interactions are minimised. In order to establish whether this is the case, several experiments were performed, and are described in the following sections.

IV.3.F.(1) Attempted Epoxidation of Dioxin (179)

The most obvious method to decipher the stereochemistry of (**179**) is to functionalise the double bond. An attempt was made to epoxidise the double bond by refluxing (**179**) with calcium hypochlorite, in acetonitrile, but after 2 d only starting material was recovered by ^{19}F NMR spectroscopy. Dioxin (**179**) was then added to a solution of lithium t-butyl hydroperoxide, in tetrahydrofuran, and after 24 hrs only the starting compound was detected.



i. Bu^tOOH, BuLi, THF, -78°C to r.t.
ii. $Ca(OCl)_2$, CH_3CN, 90°C, 2 d
iii. MCPBA, CH_2Cl_2, 45°C, 1 d

Unexpectedly, neither of these procedures worked, suggesting that the double bond is not particularly susceptible to nucleophilic attack, despite being substituted by two trifluoromethyl groups. This may be due to the unshared electron pairs on the oxygen atoms countering the electron withdrawing effect of the F-alkyl groups. As a result, *m*-chloroperoxybenzoic acid, which is used to oxidise electron rich double bonds, was employed as the epoxidising agent. Dioxin (**179**) was refluxed, in dichloromethane, with the acid, but no reaction was evident by ^{19}F NMR spectroscopy.

IV.3.F.(2) Further Attempts to Functionalise Dioxin (179)

Since the oxidation of (**179**) was unsuccessful, a series of other experiments were tried:

i) Chiral shift reagents were used: In separate NMR scale experiments, *ca.* 20mg of tris[3-(heptafluoropropylhydroxymethylene)-(+)-caphorato], europium (III) (Eu-FOD) and 2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane platinum(0)-ethene (prepared following a literature procedure[207]) was added to dioxin (**179**) in deuterated dichloromethane. No change in the ^{19}F NMR shifts of (**179**) were observed.

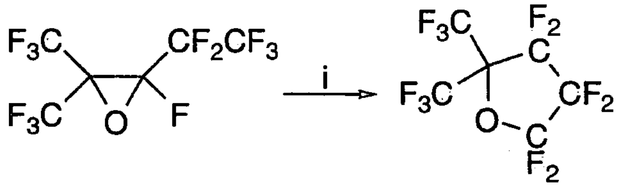
ii) Addition of bromine: Dioxin (**179**) was sealed in a quartz NMR tube, with bromine, and irradiated with ultraviolet light. After 1 d, only the starting material was observed by ^{19}F NMR spectroscopy.

iii) X-ray analysis: Attempts were made, using the departments x-ray crystallographic unit, to obtain a crystal structure from this liquid (**179**). Unfortunately, on freezing (145K), a glass, and not a single crystal, formed which was unsuitable for analysis. This is a problem often encountered with highly fluorinated systems.

So far, attempts to functionalisation the double bond of (**179**), in an effort to establish the stereochemistry, have been unsuccessful.

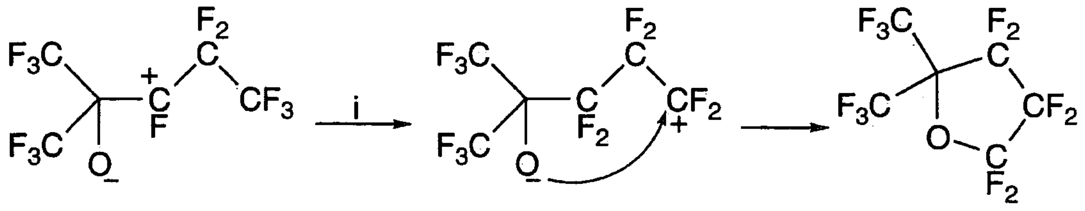
IV.3.G Attempted Ring Opening of Diepoxide (162) using Antimony Pentafluoride

Work by Chepik[208] described the rearrangement of perfluorinated monoepoxides, by initially opening the oxirane functionality using antimony pentafluoride (SbF_5), or a mixture of SbF_5 and octafluorotoluene. This electrophilic ring opening led to unusual cyclised oxolane products, of the type shown below.



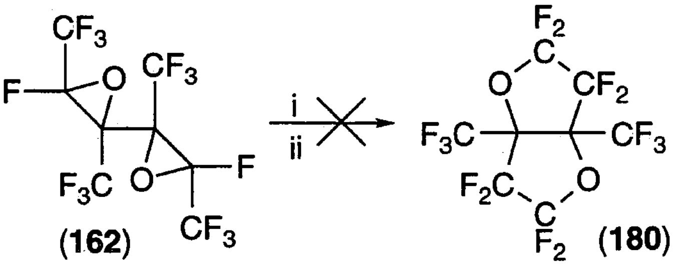
i. $C_6F_5CF_3$, SbF_5, 100°C, 6 hrs

Mechanistically:



i. Rearrangement

Reactions accompanied by the cleavage of a C-F bond in an unactivated CF_3-group, far removed from any functional group, double bond, or aromatic system do not find analogy in the chemistry of organofluorine compounds.[208] Whether this would work with diepoxide (**162**) was of interest, with the possibility of forming two fused five-membered oxolane rings (**180**). The reagents were sealed in a Carius tube and heated, after which volatile material was identified as a mixture of unreacted (**162**) and octafluorotoluene by ^{19}F NMR spectroscopy.



i. $C_6F_5CF_3$, SbF_5, 130°C, 19 hrs

ii. SbF_5, 130°C, 20 hrs

This procedure employed the octafluorotoluene cation as an electrophilic ring opening reagent, and the reaction was repeated, in the absence of octafluorotoluene, using SbF_5 as the attacking electrophile. Again, examination of the volatile material by ^{19}F NMR spectroscopy showed only the starting materials were present.

In conclusion, diepoxide (**162**) is, as would be expected, extremely stable towards electrophilic attack.

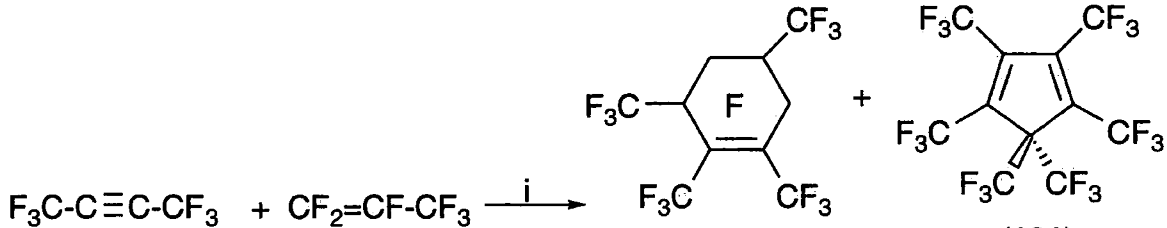
IV.4 Conclusion

Calcium hypochlorite has been successfully applied to perfluorinated alkenes, in accordance with methodology developed by Kolenko[169, 170], to give their corresponding oxides. For the first time, with perfluorinated systems, butyl-lithium and t-butyl hydroperoxide have been used to form epoxides in, generally, good yields. However, the hypochlorite system is cheaper and easy to perform than the peroxide method, although in one instance the latter succeeded where the former failed, giving it merit as an alternative. Both of these methods were used to synthesis diepoxide (**162**), which is surprisingly stable to nucleophilic attack, but will thermally isomerise to give a perfluorinated dioxin (**179**). Similar ring expansions have not been reported in the literature.

Chapter Five
Hexakis(trifluoromethyl)cyclopentadiene (181) and its Chemistry

V.1 Synthesis of Hexakis(trifluoromethyl)cyclopentadiene (181)

Generation of carbanions by the addition of fluoride ion to unsaturated fluoroalkenes[135, 209-211], and to hexafluorobut-2-yne[6-8], is well described in the literature. Such carbanions have been trapped with, for example, bromine and chlorine[210] and have been applied to, amongst other things, the anionic polymerisation of fluoro-alkenes.[211] Work by Jones[212], of these laboratories, exploited the reactivity of hexafluorobut-2-yne with fluoride ion in order to perform a co-oligomerisation reaction with hexafluoropropene. Two interesting cyclic products were observed.

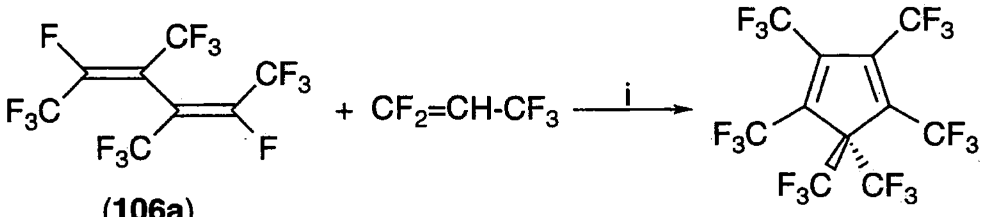


(181)

i. CsF, tetraglyme, r.t. + $C_{10}F_{18}$ + $C_{14}F_{24}$

Diene (**181**) was isolated by preparative scale gas chromatography, in very low yield, and several attempts to increase this failed.[213]

In order to fully characterise and investigate the chemistry of diene (**181**), a realistic stratergy was developed towards its synthesis in a good yield, by limiting the side-reactions and increasing the ease of isolation, and with the use of relatively cheap reagents. Diene (**106**), pentafluoropropene and caesium fluoride, in acetonitrile, were mixed together for 48 hrs, at room temperature. Volatile material was isolated, and a lower layer was shown to contain *one component* (by GLC) which was identified as hexakis(trifluoromethyl)cyclopentadiene (**181**) by ^{19}F NMR spectroscopy, GLC-MS and elemental analysis.

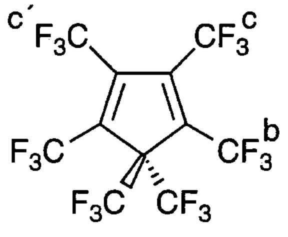


(106a)

(181) 75% y.

i. CsF, CH_3CN, rotating arm, r.t., 48 hrs

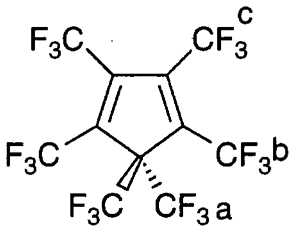
The ^{19}F NMR spectrum revealed three resonances, of equal integration, which is consistent with the three different CF_3 environments present in diene (**181**). Assignment of these peaks to the structure was attempted using a 376 MHz NMR spectrometer. However, two of the peaks [at -55.58 (b) and -59.68 (a) ppm] showed complex second order multiplets, arising from various ^5J and ^6J couplings around the ring, but one peak [at -59.35 (c) ppm] gave a pseudo-septet, which most likely arises from CF_3-b and CF_3-c′ equally coupling with CF_3-c, which occurs since the 'b′ and 'c′ CF_3 groups involved are in the plane of the ring. Also, the coupling constant was 10.9 Hz, which is characteristic for coupling over five bonds ($^5J_{F,F}$).[101, 214]



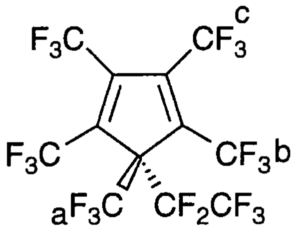
(181)

$J_{c,b}=J_{c,c'}$=pseudo septet

The two remaining resonances were assigned by comparison with the chemical shifts of the corresponding CF_3 groups in diene (**193**).[113]



(181)



(193)

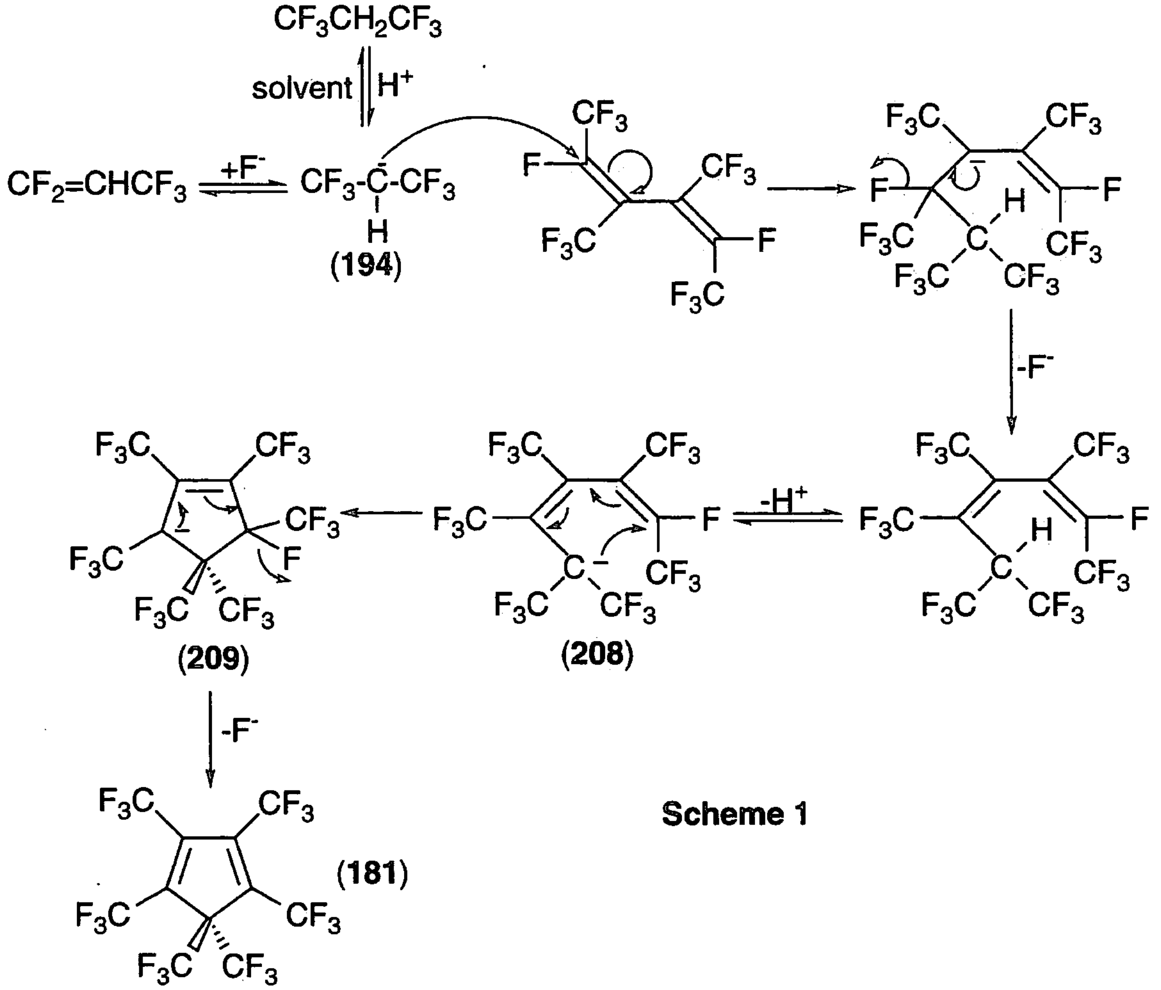
	Shift (ppm)	
CF_3 group	**(181)**	**(193)**
a	-59.68	-60.13
b	-55.58	-57.56
(c	-59.35	-61.80)

Clearly, the resonance for the CF_3-b, attached to the double bond, occurs at a lower frequency than the resonance for the tertiary CF_3-a, and the assignments for CF_3-a and CF_3-b, in diene (**181**), followed accordingly.

The mechanism for the formation of diene (**181**) initially involves nucleophilic attack of fluoride ion on pentafluoropropene, generating a carbanion (**194**) (Scheme 1).

$$\underset{\textbf{(194)}}{CF_3\text{-}\bar{C}H\text{-}CF_3} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} CF_3CH_2CF_3$$

Examination of the solvent layer indicated the presence of $CF_3CH_2CF_3$, by ^{19}F NMR and mass spectrometry, demonstrating that the carbanion (**194**) is in equilibrium with the protonated species. The carbon nucleophile then attacks a vinylic position in diene (**106**), substituting the vinylic fluorine. Caesium fluoride then acts as a base[215], removing the proton from (**208**) to regenerate the carbanion, which then effects ring closure by a second vinylic substitution, giving a highly electron deficient cyclopentadiene derivative.



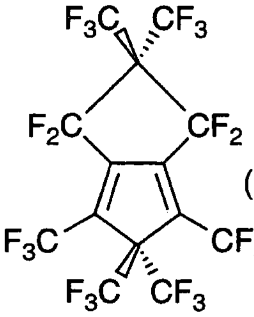
Scheme 1

The cyclisation step is interesting because, as a 5-*endo-trig* process, it is formally disallowed by the Baldwin Rules.[143] It is more likely, therefore, that the process involves the initial electrocyclic ring closure, (**208**) to (**209**), followed by elimination of fluoride ion to give (**181**) (Scheme 1). This is a rare example of an open-chain pentadienyl anion undergoing ring closure to give a carbocyclic system.[144, 216, 217]

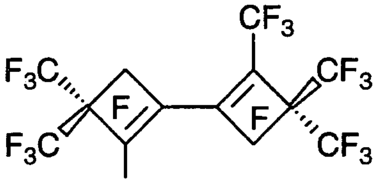
When distilled water was added to the involatile material a lower layer formed, containing *three components* by GLC, although the two minor components were overlapping (ratio of 3 major:1 minor). Several attempts were made to purify the major component by preparative scale gas chromatography, but a little of the minor compounds always remained. Examination of the ^{19}F NMR spectrum of the mixture showed CF_3 and CF_2 resonances, although a 2-D ^{19}F COSY spectrum, from the sample isolated after preparative scale gas chromatography, indicated that the major component (highest retention time) comprised of only five CF_3 groups, with the minor components, therefore, containing the CF_2 groups. The mass spectra for the components had very similar fragmentation patterns, with the highest mass being m/z=586 for each, and the elemental analysis for the mixture supported a formula of $C_{14}F_{22}$, which corresponds to this mass.

In an attempt to prove that two double bonds were present, in each component, the mixture was epoxidised by refluxing with calcium hypochlorite, in acetonitrile. A lower layer was isolated which was analysed by GLC-MS. Two components were observed, and the mass spectra for both indicated that two oxygen atoms had added.

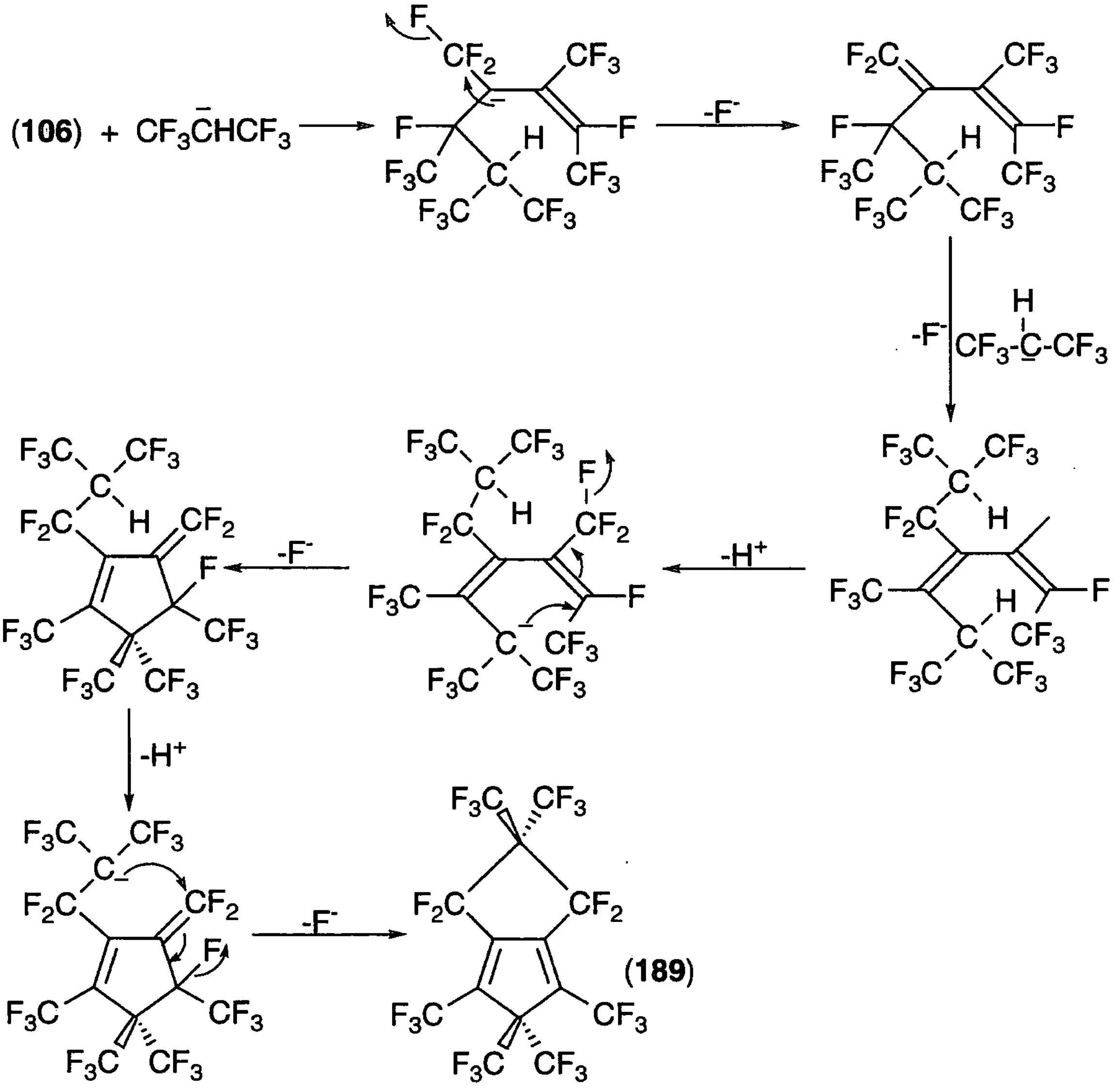
The structure of the involatile components is uncertain, although the evidence indicates that they require the incorporation of diene (**106**) and two equivalents of pentafluoropropene. Two possible structures for the minor components are given below, with a suggested mechanism for the formation of (**189**).



(**189**)



(**190**)

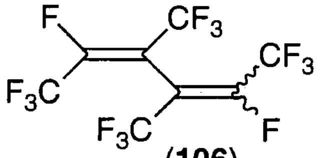
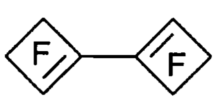
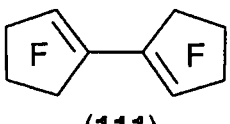
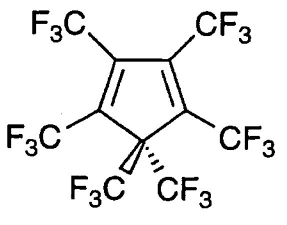


Loss of fluoride ion from two CF_3 groups, *via* an S_N2' mechanism, is required, and the carbanion then reacts with the so generated difluoromethylene groups, to close the ring. The structure of the lower half of diene (**189**) is the same as in diene (**181**), which suggests that these CF_3 groups should have similar chemical shifts in the ^{19}F NMR spectra. Indeed, resonances occuring in similar positions to those of diene (**181**) were observed for both the major and minor components.

V.2 The Extinction Coefficient

Ultraviolet spectroscopy is used to measure the molar absorptivity, or extinction coefficient (ε), in unsaturated compounds. When the double bonds of a diene are conjugated, such as in butadiene, then there is a relatively small energy difference between the HOMO and the LUMO, which is reflected in a high extinction coefficient and a long wavelength.[218] This relationship has been examined for a series of hydrocarbon and fluorocarbon dienes, shown in Table 1.

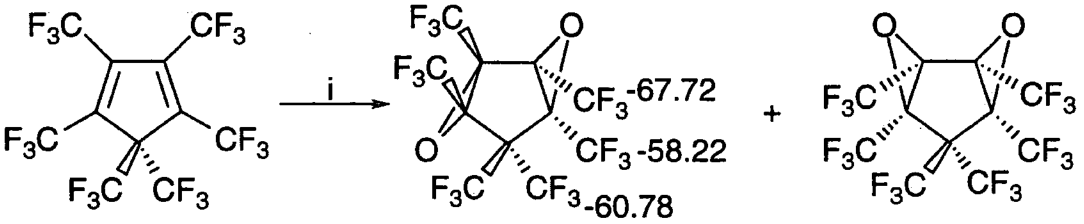
Table 1 Ultraviolet Absorption Data for a Series of Dienes and Fluorinated Dienes.

Diene	λ_{max} (nm)	ε_{max}	Reference
$CH_2=CH-CH=CH_2$	217	21000	219
	256	8000	219
$CF_2=CF-CF=CF_2$	206	2800	40
	215	2350	
 **(106)**	234	272	107
 **(113)**	277	18800	107
 **(111)**	278	10900	107
 **(181)**	253	1674	

The double bonds in butadiene are in the same plane, which allows maximum overlap of the π-orbitals (*i.e.* conjugation). However, with hexafluorobuta-1,3-diene the double bonds are forced out of planarity, into a skew-*cis* structure[219], which decreases the π-orbital overlap and, therefore, the conjugation. Diene (**106**) has four sterically demanding CF$_3$ groups and, as a result, may also adopt an energy minimised skew-*cis* conformation (see Chapter 2, Section II.6.C). This is supported by an extremely low extinction coefficient, which indicates that the double bonds are far less conjugated than in hexafluorobuta-1,3-diene. Interestingly, dienes (**111**) and (**113**) both have high extinction coefficients, which stems from the fact that decreasing bond angles reduces the extent of interaction between the cycloalkyl groups.[107] The extinction coefficient of diene (**181**) was also measured and found to be low, which was unexpected since the cyclopentadiene ring ought to be planar with a high degree of conjugation between the double bonds. This observation is most likely due to interactions between the sterically demanding CF$_3$ groups forcing the ring and, therefore, the double bonds out of planarity, decreasing the conjugation.

V.3 Epoxidation of Diene (181)

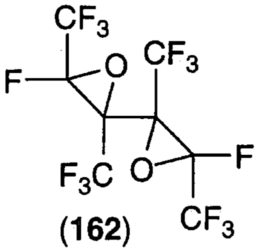
As mentioned in Chapter 4, very few perfluorinated diepoxides have been reported in the literature. Due to this, the oxidation of diene (**181**) was attempted using calcium hypochlorite, in a method similar to that pioneered by Kolenko.[169, 170] A mixture of diene (**181**) and calcium hypochlorite were heated, under reflux, in acetonitrile. A lower layer was isolated and identified as an inseparable mixture of *trans-* (**174a**) and *cis-* (**174b**) perfluorohexakis(trifluoromethyl)-2,4-diepoxycyclopentane by ^{19}F NMR spectroscopy, mass spectrometry, which resolved both isomers and indicated that two oxygen atoms had added to each, and elemental analysis.



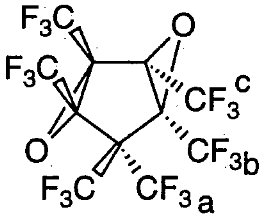
(**181**) *trans-* (**174a**) *cis-* (**174b**)

i. Ca(OCl)$_2$, CH$_3$CN, 90°C, 5 hrs

From examination of molecular models, it is clear that the *trans* diepoxide has three CF$_3$ environments, whilst the *cis* diepoxide has four, and on examination of the ^{19}F NMR spectrum seven resonances were observed, which is in agreement with this (chemical shifts for **174a** are shown above, in ppm). On examination of a high frequency ^{19}F NMR spectrum (376 MHz), most of the resonances, in both isomers, were complex multiplets due to long range F-F couplings around the ring [*cf.* diene (**181**)]. However, in the *trans* isomer, a pseudo septet was observed which can be assigned to CF$_3$-b, arising from this from this coupling equally with CF_3-a and CF_3-c (see NMR spectra 37 and 27 for diene (**181**) and diepoxide (**162**), respectively).

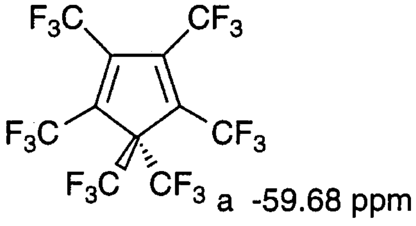


(162)



trans- **(174a)**

Assignment of the other two resonances, in the *trans* isomer, remains unclear, although CF_3-a (at -60.78 ppm), above, possibly occurs at a similar chemical shift to CF_3-a in diene (**181**).

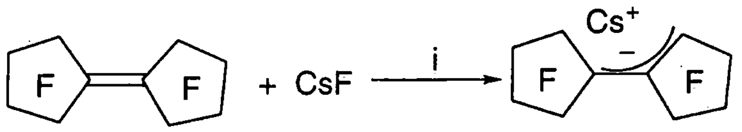


(181)

In conclusion, it was not surprising that the *trans* diepoxide (**174a**) predominated, since steric interactions between the trifluoromethyl groups are minimised, and the hypochlorite methodology has been successfully applied in the synthesis of another perfluorinated diepoxide, whose chemistry is yet to be explored.

V.4 Reaction between Diene (181) and Caesium Fluoride

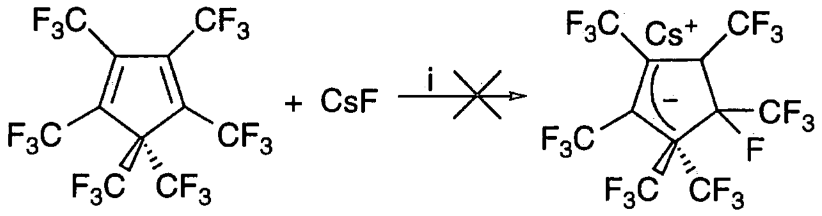
A large amount of effort has been applied to generating observable fluorinated carbanions in these laboratories[107, 209, 210, 220], and world-wide.[221-224] The ceasium salt (**205**), shown below, is one example of where the carbanion was observed by ^{19}F NMR spectroscopy.[222]



(205)

i. Tetraglyme, r.t.

The question of whether diene (**181**) would generate such a carbanion was investigated. On mixing diene (**181**) with tetraglyme and caesium fluoride, an immediate red colour developed. A small amount of volatile material was then isolated, and contained many components by both ^{19}F NMR spectroscopy and GLC-MS (>17 peaks). The ^{19}F NMR spectrum revealed many CF_3 resonances, plus some corresponding to the chemical shift regions of CF_2 and CF groups. The involatile red liquid also gave a complex ^{19}F NMR spectrum, although there were no tertiary fluorine resonances, which suggests that the carbanion of (**181**) was not formed.



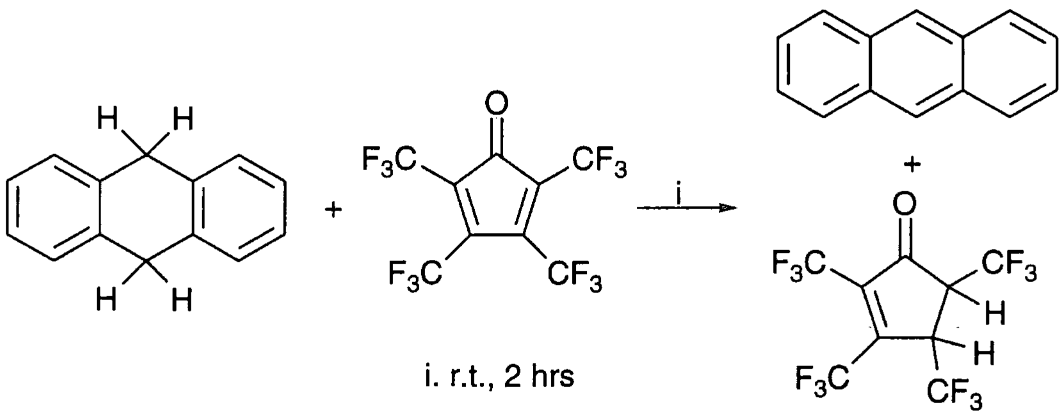
(181)

i. Tetraglyme, r.t.

A small amount of BF_3-etherate, which abstracts fluoride ion from carbanions to release the fluorocarbon, was then mixed with the involatile liquid, but the ^{19}F NMR spectrum was not simplified. Such complexity possibly suggests that diene (**181**) is ring-opening under the reaction conditions.

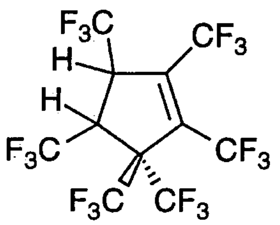
V.5 Attempted Oxidation of 9,10-Dihydroanthracene with Diene (181)

It is known that organic oxidants such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and tetracyanoethene will oxidise the title compound to anthracene.[225] Recently, it has been shown that tetrakis(trifluoromethyl)cyclopentadienone will also effect this oxidation.



i. r.t., 2 hrs

The oxidation was now attempted by heating (no reaction at room temperature) diene (**181**) with 9,10-dihydroanthracene, in diethyl ether. Volatile material was isolated and the only fluorocarbon component, by ^{19}F NMR spectroscopy, was diene (**181**), and the solid residue was identified as 9,10-dihydroanthracene by ^{1}H NMR spectroscopy. No analogous reaction had occured to form the dihydro product, shown below.

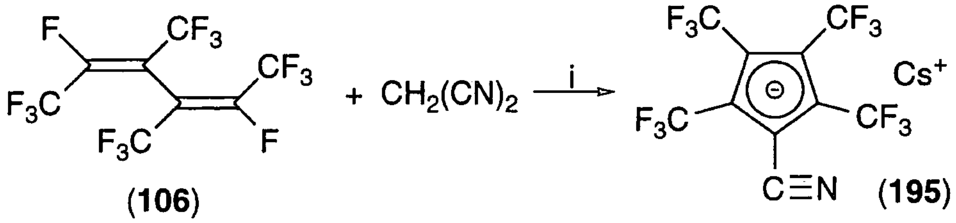


This result indicates that diene (**181**), unlike tetrakis(trifluoromethyl)cyclopentadienone, is not sufficiently oxidising to form anthracene from its dihydro- precursor.

V.6 Synthesis of Pentakis(trifluoromethyl)cyclopentadienyl Salts

V.6.A Introduction

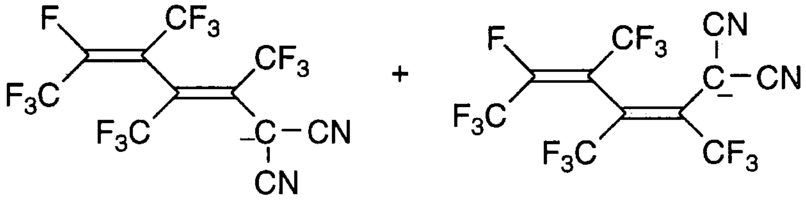
In these laboratories there has been great interest in synthesising highly fluorinated cyclopentadienyl anions. Work by Greenhall[5, 216, 226] has demonstrated that, for example, the reaction between diene (**106**) and $CH_2(CN)_2$, under reflux, gives the tetrakis(trifluoromethyl)cyclopentadienyl derivative (**195**).


(**106**)

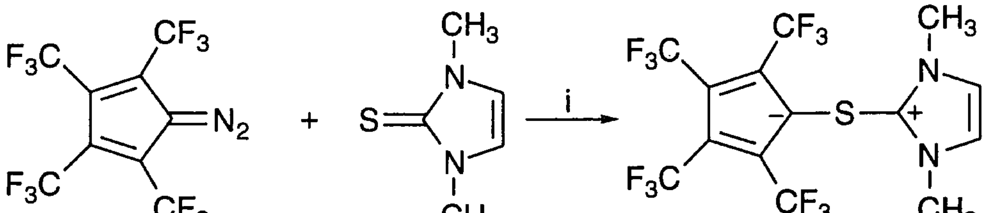
(**195**) 100% c.

i. CsF, CH_3CN, reflux, 1 hr

Interestingly, if the reaction mixture was at room temperature, the two intermediate open chain cyclopentadienyl anions were observed by ^{19}F NMR spectroscopy.

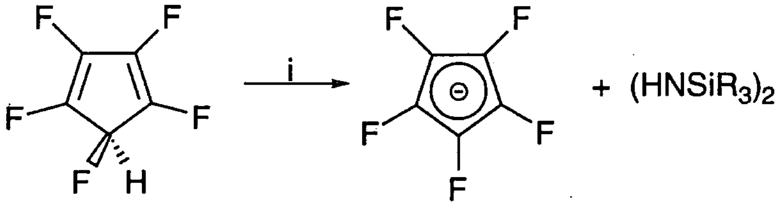

3 : 1

Other workers[227] have synthesised highly fluorinated cyclopentadiene derivatives, such as diazotetrakis(trifluoromethyl)cyclopentadiene, which has been used to form an interesting ylide (**196**).


(**196**)

i. Ultraviolet light, THF, 0°C, 5 min

Finally, Seppelt[228] has formed the pentafluorocyclopentadienyl anion from 1,2,3,4,5-pentafluorocyclopentadiene.

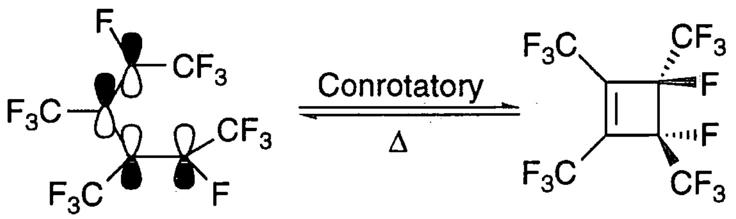

i. $M^+N(SiR_3)_2^-$, THF

The $Na^+[18\text{-crown-}6]C_5F_5^-$ salt, in tetrahydrofuran, was the most stable, being observed for several hour at room temperature. The compound gradually decomposed, forming the metal fluoride and polymeric material.

Research published, by other workers, concerning the formation of cyclopentadienyl salts will be discussed later in this chapter, where relevant.

V.6.B Synthesis of Caesium Pentakis(trifluoromethyl)cyclopentadienyl (182)

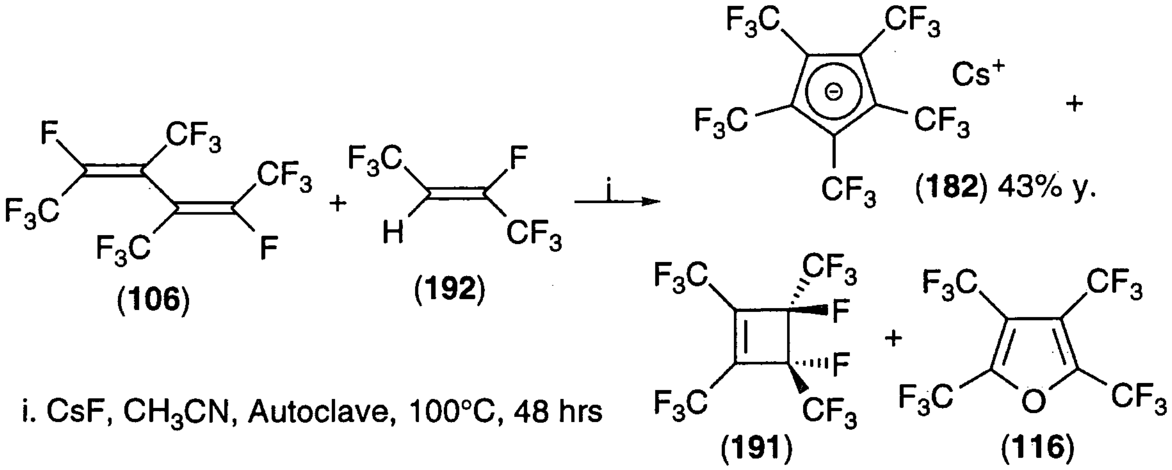
Mullins[5, 98] has demonstrated that diene (**106**) will react with heptafluorobut-2-ene to give a moderate yield of caesium pentakis(trifluoromethyl)cyclopentadienyl (**182**). This reaction was repeated by heating diene (**106**) with heptafluorobut-2-ene (**192**), caesium fluoride and acetonitrile, in an autoclave. Examination of the volatile material by ^{19}F NMR spectroscopy showed the presence of diene (**106**) and heptafluorobut-2-ene, plus perfluorotetramethylfuran (**116**) and perfluorocyclobutene derivative (**191**). The latter is formed from the thermal cyclisation of diene (**106**).[98, 229]



(106)

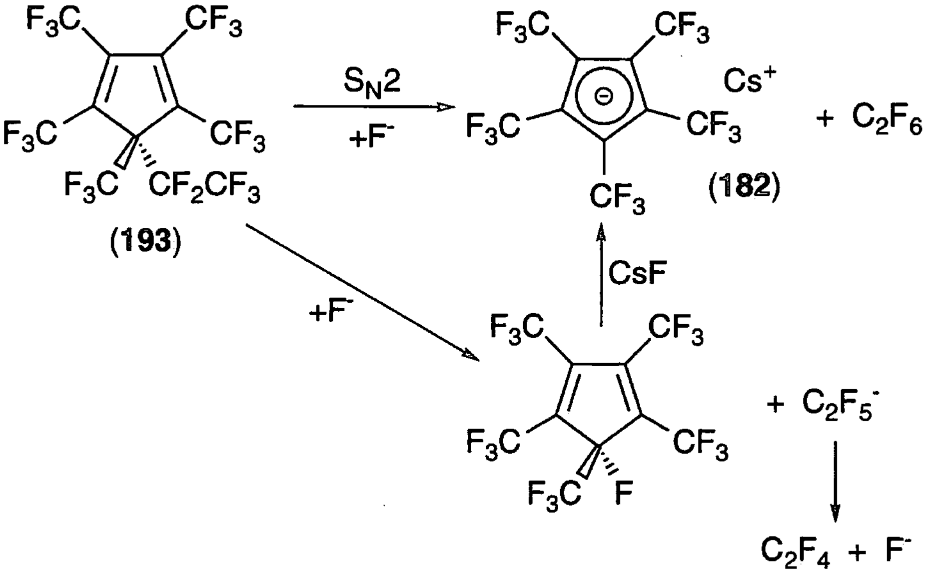
(191) *ca.* 50%

An off-white solid was then isolated from the residue, and shown to be caesium pentakis(trifluoromethyl)cyclopentadienyl (**182**) by ^{19}F NMR spectroscopy , where one sharp signal was observed due to the equivalence of the CF_3 environments, and FAB mass spectrometry, where both the cation and anion were observed. Purification of this material proved difficult, preventing an accurate elemental analysis from being obtained.



i. CsF, CH_3CN, Autoclave, 100°C, 48 hrs

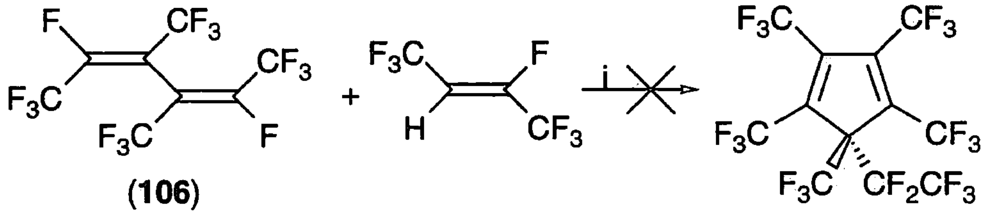
The mechanism is of interest, and Mullins[98] proposed that diene (**193**) is an intermediate, which then loses the 5-pentafluoromethyl group in preference to the 5-trifluoromethyl group.



Which pathway is invoked is unclear, although the pentakis(trifluoromethyl)-cyclopentadienylide anion is a very stable leaving group, due to the stabilising electron withdrawing capacity of the CF_3 moieties, which supports an S_N2 type mechanism, even though nucleophilic attack at a saturated F-alkyl group is unusual. The second pathway involves the nucleophilic substitution of a pentafluoroethyl group by fluoride ion, followed by a fluoride ion induced defluorination, which is known.[78] The gaseous products, C_2F_6 and C_2F_4, were not observed by GLC-MS, although unassigned resonances in the ^{19}F NMR spectrum of the volatiles could be consistent with either compound.

V.6.B.(1) Attempted Synthesis of Perfluoro-1,2,3,4,5-pentamethyl-5-ethylcyclopentadiene (193)

Diene (**181**) was successfully synthesised using pentafluoropropene as a source of $^{-}C(CF_3)_2H$, and it was of interest to similarly use heptafluorobut-2-ene to generate $CF_3CF_2(H)(CF_3)C^-$, in order to form cyclopentadiene derivative (**193**). Diene (**106**) and heptafluorobut-2-ene were mixed with caesium fluoride, in acetonitrile, at room temperature. A lower layer was isolated which was shown to be a mixture of diene (**106**) and heptafluorobut-2-ene by ^{19}F NMR spectroscopy. There was no evidence for the formation of diene (**193**).



(**106**)

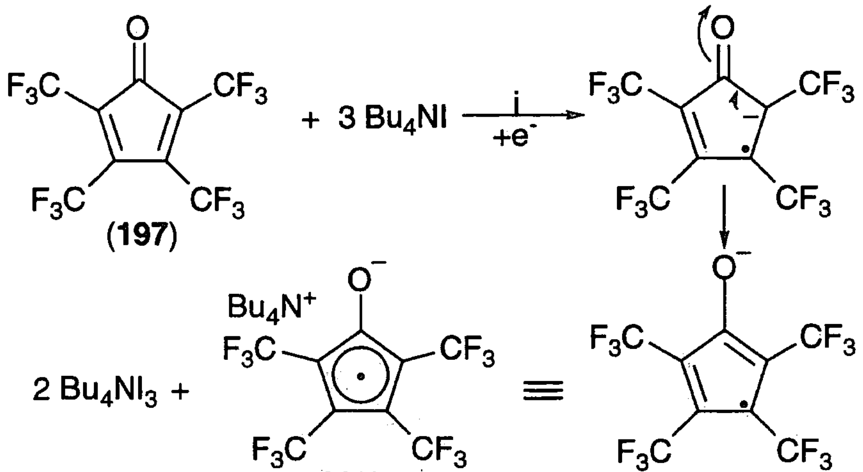
(**193**)

i. CsF, CH_3CN, r.t., 5 d

This lack of reactivity is most likely due to heptafluorobut-2-ene not being susceptible to nucleophilic attack by fluoride ion at room temperature.

V.6.C The Synthesis of Tetraalkylammonium Cyclopentadienyl Salts

In 1963, Wilkinson and Dickson[225, 230] reported the discovery of tetrakis(trifluoromethyl)cyclopentadienone (**197**), which was prepared by the coupling of hexafluorobut-2-yne and carbon monoxide, under high pressure, in the presence of the catalyst $[Rh(CO)_2Cl]_2$. Burk[225], in 1991, described the synthesis of cyclopentadienyl systems bearing multiple trifluoromethyl substituents, with a view to using these as ligands for transition metals (see Section V.11). Reaction between tetrakis(trifluoromethyl)cyclopentadienone and tetraethylammonium iodide gave the tetrabutyl ammonium salt (**198**), as a blue radical anion, in good isolated yield.

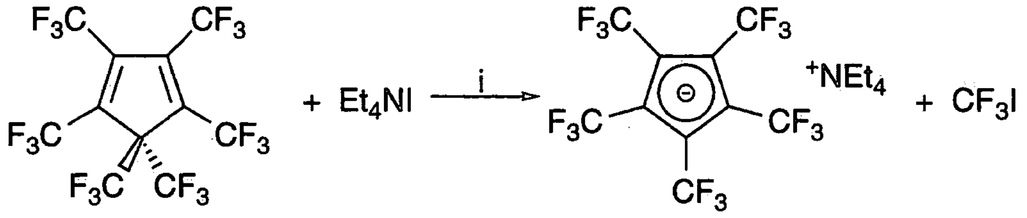


(**197**)

62% y.

i. CH_2Cl_2, 25°C, 20 min

Because the iodide has a high reducing power, it will transfer an electron to the ketone, reducing it to the radical anion. This reaction led to the idea that hexakis(trifluoromethyl)cyclopentadiene (**181**) could be reduced, using tetraalkylammonium iodides, to the pentakis(trifluoromethyl)cyclopentadienyl salt. Diene (**181**) was slowly added to a refluxing solution of tetraethylammonium iodide in acetonitrile. After removal of the solvent the resultant residue was recrystallised, giving colourless crystals, which were identified as tetraethylammonium pentakis(trifluoromethyl)cyclopentadienyl (**183**) by NMR spectroscopy, FAB mass spectrometry, where both the cation and anion were observed, and elemental analysis.



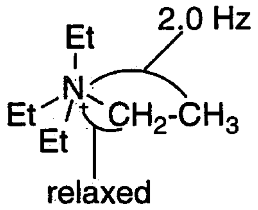
(181) **(183)** 100% c.; 75% y.

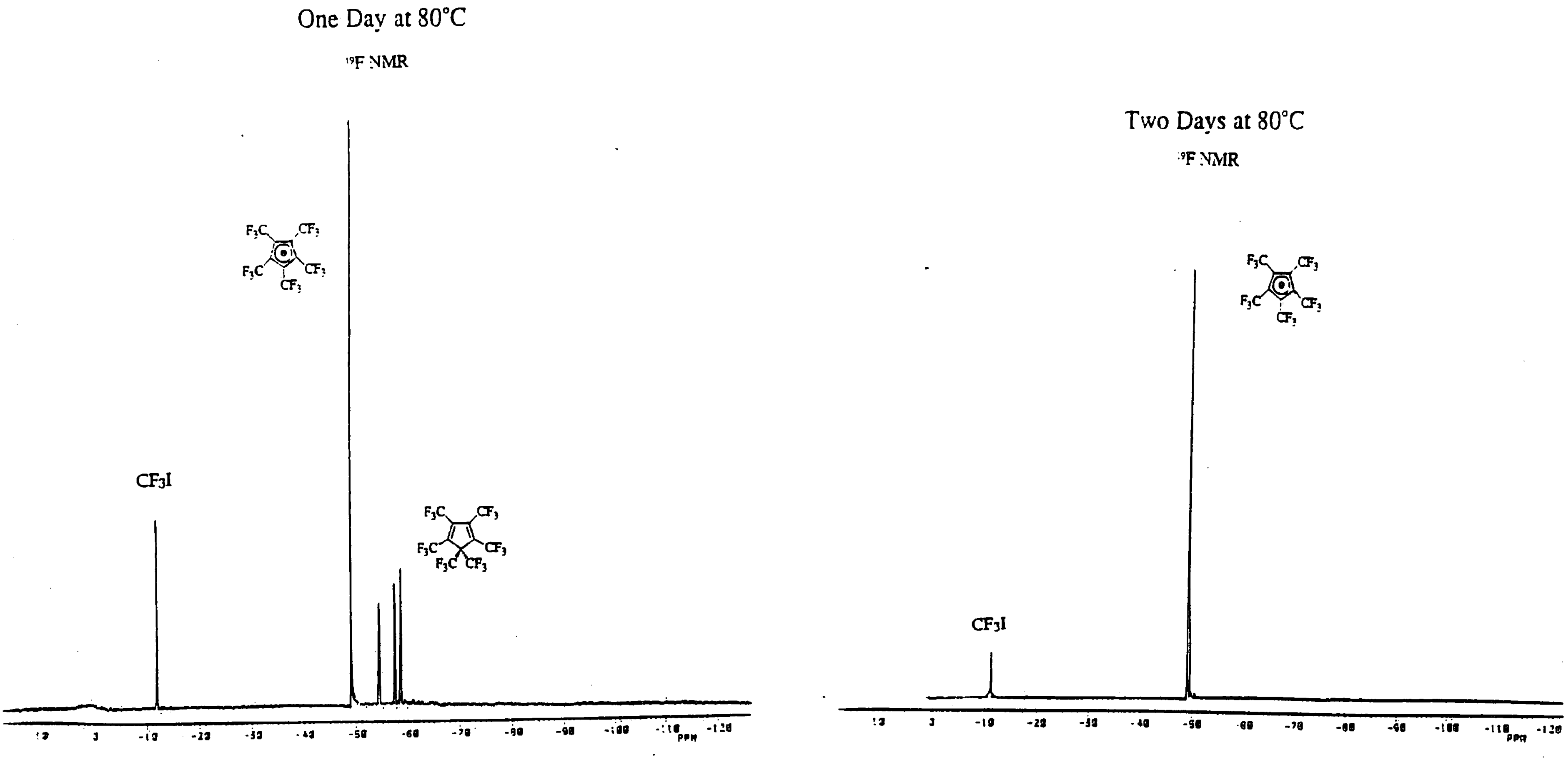
i. CH_3CN, 80°C, 48 hrs

This is the first time that a pentakis(trifluoromethyl)cyclopentadienyl salt has been obtained pure and in good yield. Iodotrifluoromethane (CF_3I) was observed when the reaction was performed in a sealed quartz NMR tube. Figure 1 shows two ^{19}F NMR spectra, from this experiment, which indicate the appearance of CF_3I and the full conversion of diene (**181**) to the salt (**183**).

The ^1H NMR spectrum of the product was interesting, since nitrogen coupling with the methyl protons ($^3J_{H,N}$) of the ethyl group was observed, which is unusual, giving triplets of equal line intensity, since ^{14}N has a spin number of one (Figure 2).

However, it would be expected that the $^2J_{H,N}$ coupling would be larger than the $^3J_{H,N}$ coupling, and reflected as four equal intensity triplets in the quartet (Figure 2). This is not the case since protons next to nitrogen are efficiently relaxed; because of its electric quadrupole, nitrogen can flip rapidly among its spin states, broadening the ^1H signal.[214] No such N/H coupling was observed in the starting iodide, which is most likely due to the fact that this effect is dependant upon the nitrogen environment, the sample concentration and the solvent used.




One Day at 80°C

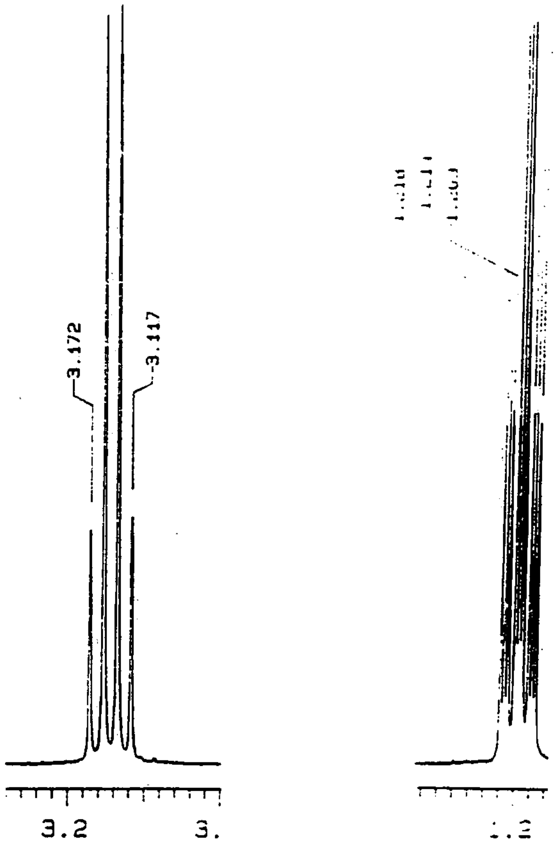
^{19}F NMR

Two Days at 80°C

^{19}F NMR

Figure 1

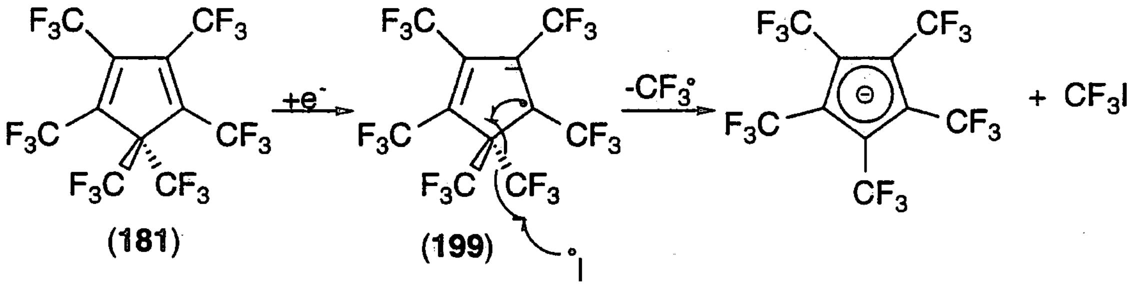
Figure 2 Nitrogen/Hydrogen Coupling in Salt (183)



V.6.C.(1) Mechanism

Mechanistically, this reaction is very interesting. Two mechanisms are possible which involve the transfer of single electrons (SET), as described in Chapter 2, and earlier in this chapter for the reduction of tetrakis(trifluoromethyl)cyclopentadienone. The third mechanism is of the S_N2 type.

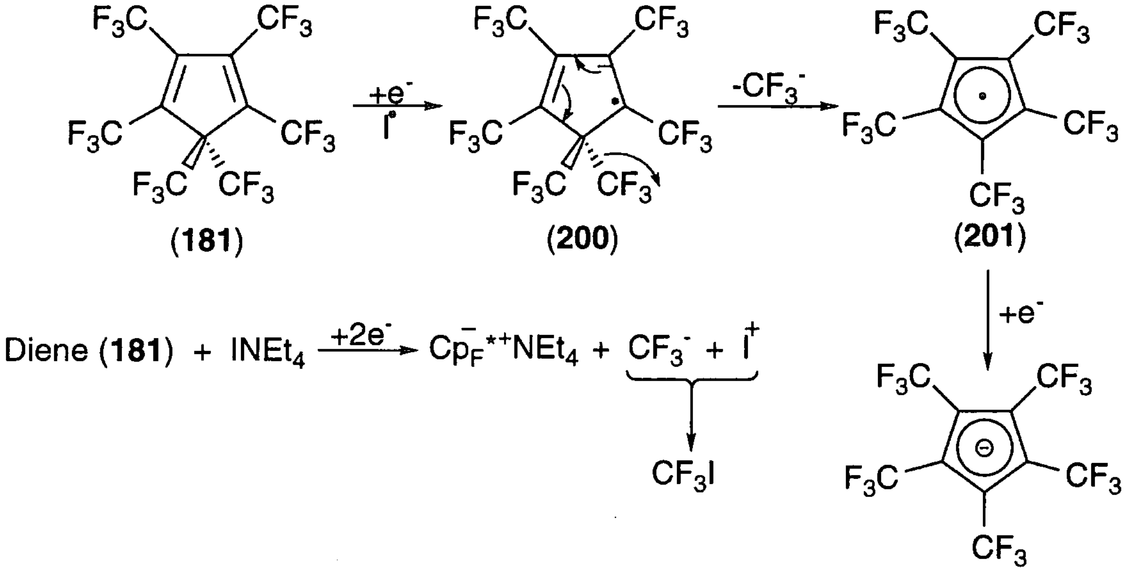
(a) Single electron transfer (SET): The most likely mechanism of the two involves the transfer of one electron to the diene (**181**), generating a radical anion and an iodine atom (**199**). The iodine atom then cleaves a geminal C-CF_3 bond, forming CF_3I and the aromatic pentakis(trifluoromethyl)cyclopentadienyl anion.



Diene (**181**) + $INEt_4 \xrightarrow{+e^-} Cp_F^{-}{}^{*+}NEt_4 + CF_3I$

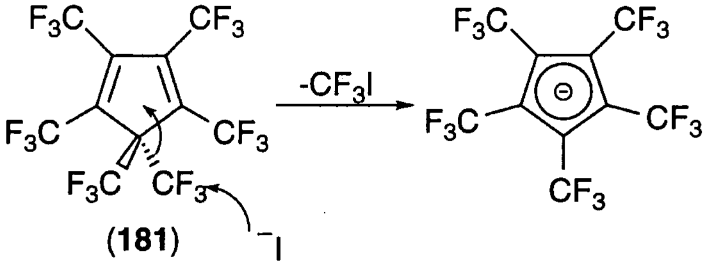
This type of reaction could possibly be used to generate, for example, R-S-CF_3 bonds, where the sulphur anion is oxidised to give S˙, which then cleaves a geminal C-CF_3 bond.

The second mechanism, like the first, initially involves the transfer of a single electron to (**181**), which is followed by the elimination of CF_3^- (**200**), and transfer of a second electron to the radical (**201**), giving the desired product.



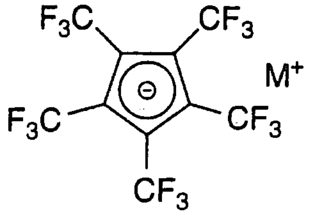
Since the yield is high, the reaction stoichiometry must be *ca.* 1 diene (**181**):1 iodide, *i.e.* both electrons must originate from the same iodide ion, generating I^+, if the reaction proceeds *via* this route. However, the first ionisation energy of I^- is 1010 kJ mol^{-1}, but the second is substantially higher at 1840 kJ mol^{-1}, which possibly disfavours the loss of a second electron under the conditions employed, suggesting that the first route is more likely as this involves the loss of only one electron from the iodide ion.[231]

(b) The S_N2 Mechanism: Since the pentakis(trifluoromethyl)cyclopentadienyl anion is a very good leaving group, an S_N2 type reaction mechanism does not seem unreasonable, as described for the formation of caesium pentakis(trifluoromethyl)cyclopentadienyl (**182**, Section V.6.B).



Unlike the reaction with tetrakis(trifluoromethyl)cyclopentadienone, heat was required to promote a reaction with (**181**), which is in agreement with the decreased reactivity observed in some reactions previously described in this chapter.

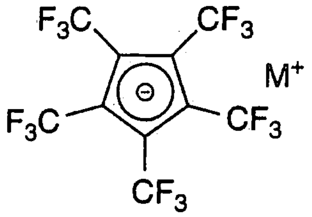
Diene (**181**) was also reacted with tetrapropylammonium iodide and tetrabutylammonium iodide, under the same conditions, to give the corresponding salts (**184**) and (**185**) in good yield.



(184)

$M^+ = NPr_4$ 73% y.

;



(185)

$M^+ = NBu_4$ 70% y.

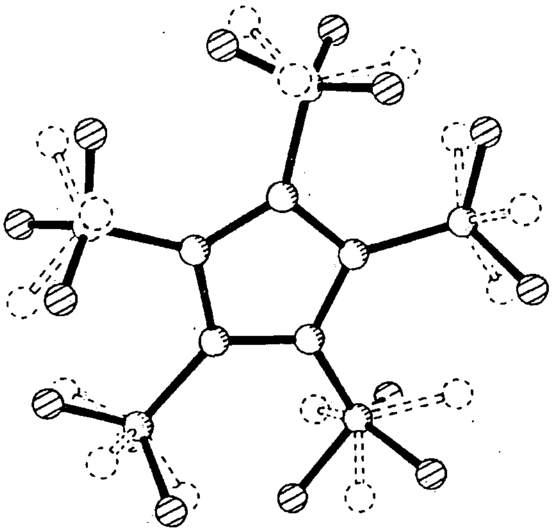
Interestingly, there was a large difference in the melting points of the three cyclopentadienyl salts, (**183**)-(**185**), with the tetraethylammonium salt melting at a temperature 100°C higher than that for the tetrapropylammonium salt.

(185) < **(184)** < **(183)**

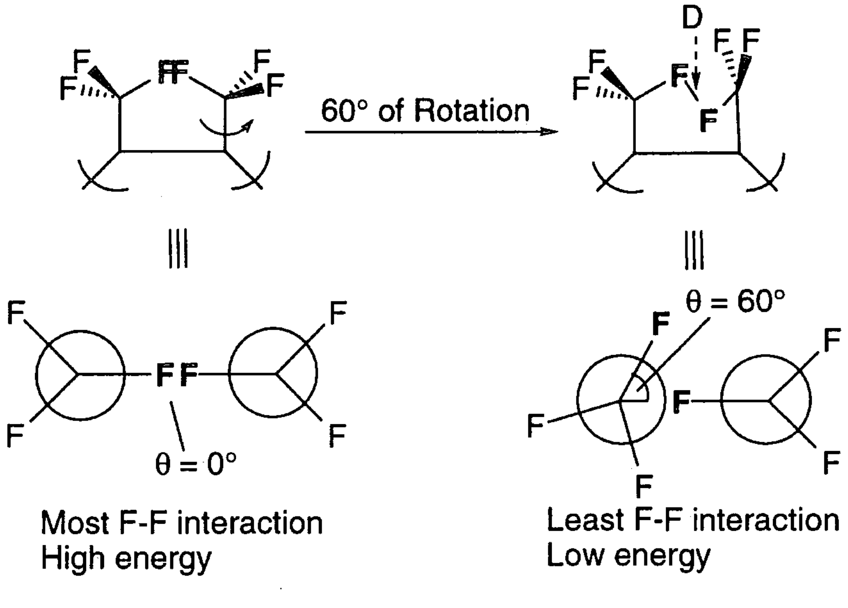
112°C < 136°C < 236°C

Crystals of salt (**185**) were the easiest to isolate and were cuboidal in nature. These were found to be suitable for X-ray analysis, performed within the department (Rasaku AFC 6S diffractometer), which resolved the anion and the tetrabutylammonium group (Figure 3). However, the high fluorine content caused vibrations within the crystal, even at low temperature (performed at 150K), preventing an accurate determination of bond lengths and angles. The crystallographic analysis indicated that the CF_3 groups were rotating, and whether they were interlocked, *via* the fluorine atoms and, therefore, rotating consecutively around the ring was of interest. Using a molecular modelling programme (Insight 2-version 2.30), a space filling model of the pentakis(trifluoromethyl)-cyclopentadienyl anion strongly suggested that the fluorine atoms of adjacent CF_3 groups could impinge upon each other.

Figure 3



The same program was used to measure the energy, and the distance (D), between the nuclei of two designated fluorine atoms, on adjacent CF_3 groups, as one such group was rotated through 60°, in 10° intervals, as shown below.



F=Designated fluorine

The results from this analysis are given in Table 1.

Table 1 The Distance and Energy between Two Fluorines, on Adjacent CF_3 Groups, as their Relative Orientation is Changed in the Perfluoropentakis(trifluoromethyl)-cyclopentadienyl Anion

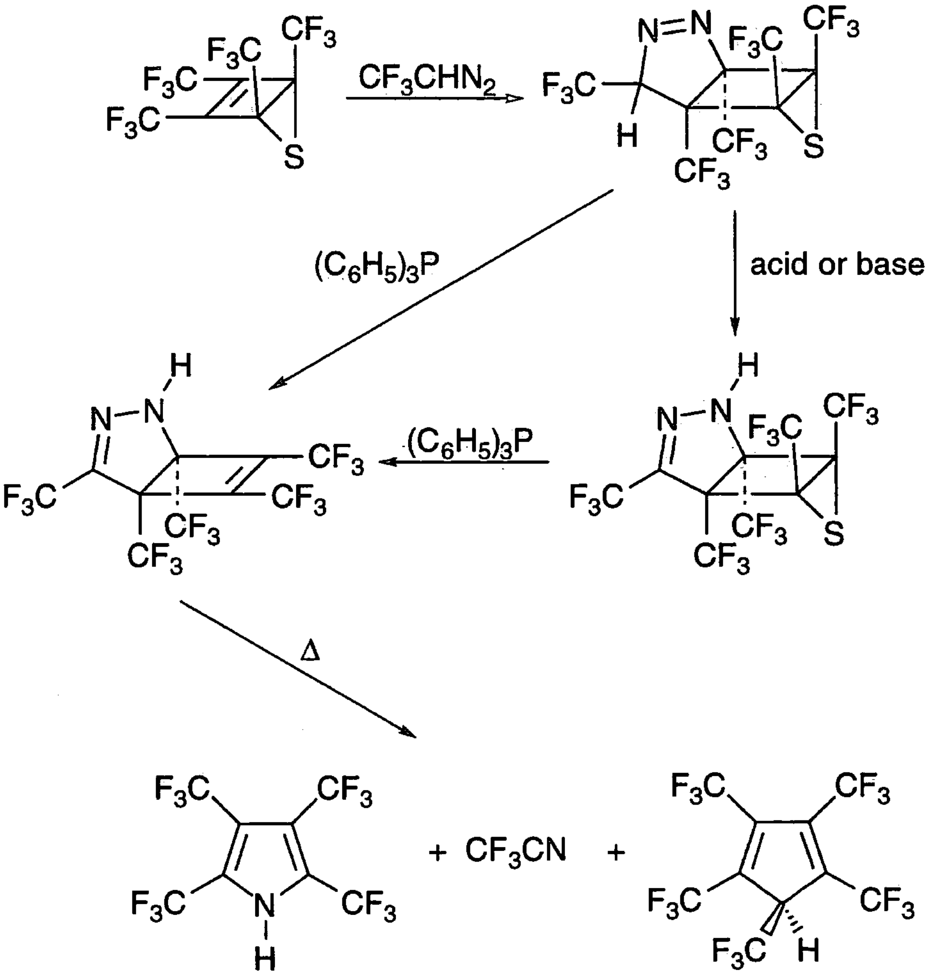
Angle of Rotation (Deg.)	Energy (kJ)	Distance 'D' (pm)
0	16.30	165
10	12.00	167
20	5.40	176
30	2.50	189
40	0.50	206
50	0.10	223
60	0.05	244

The van der Waals' radius for fluorine is 135 pm[231], and clearly when the fluorine atoms are eclipsed (*i.e.* at 0° of rotation), with a distance of only 165 pm between the two nuclei, there is substantial overlap. Not surprisingly, this is the highest energy state. However, once the fluorines are staggered (*i.e.* after 60° of rotation) the distance is still only 244 pm, which is within two van der Waals' radii for fluorine (270 pm), indicating that the fluorine atoms may indeed inter-lock with the possibility that the CF_3 groups will rotate in order, as with a series of cogs, around the ring. After a rotation of 60°, the energy is at a minimum.

In conclusion, an efficient methodology has been developed to generate a series of organic salts containing the very interesting pentakis(trifluoromethyl)cyclopentadienyl anion, which is an addition to the family of hydrocarbon and fluorocarbon cyclopentadienyl anions already available.

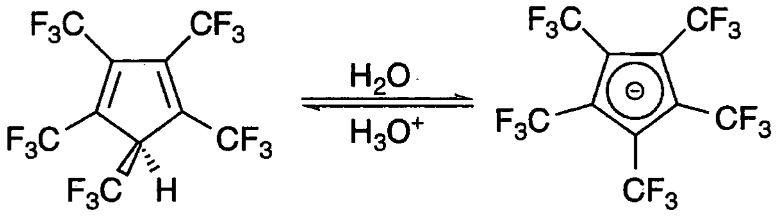
V.7 The Formation of 5H-Perfluoropentamethylcyclopentadiene (188)

In 1980, Lemal[232] described the first synthesis of the extraordinary carbon acid (**188**), which exceeds nitric acid in strength, despite its lack of conjugating substituents. The interesting, but rather esoteric, route developed was low yielding (*e.g.* only 11% for the last step), and involved preparative scale gas chromatography to isolate the product.



(188) ≤11%

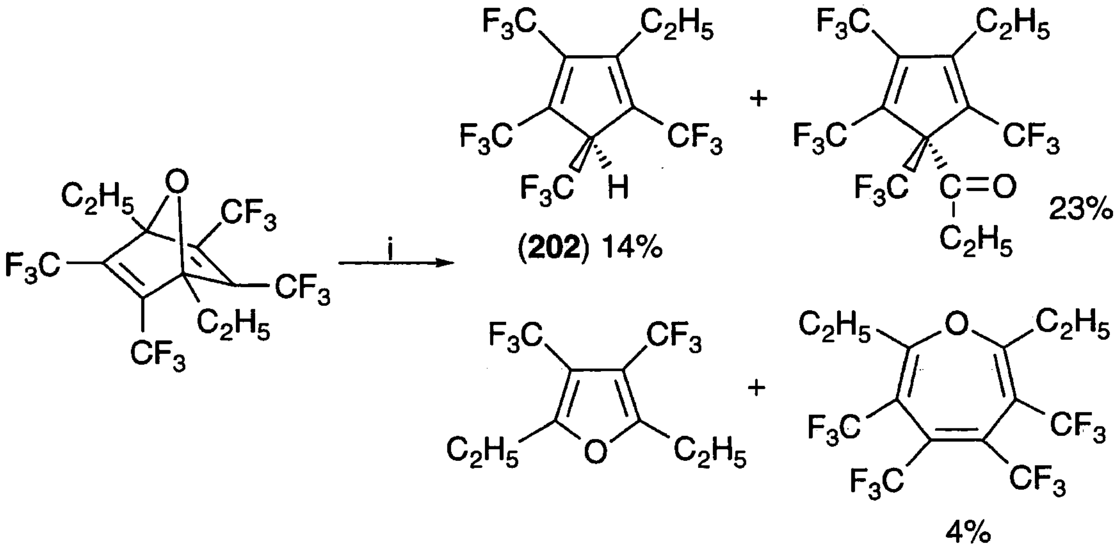
Diene (**188**) was soluble in water, where it ionised to give the pentakis(trifluoromethyl)cyclopentadienyl anion which, on acidification with concentrated sulphuric acid, gave the original diene.[232]



(188)

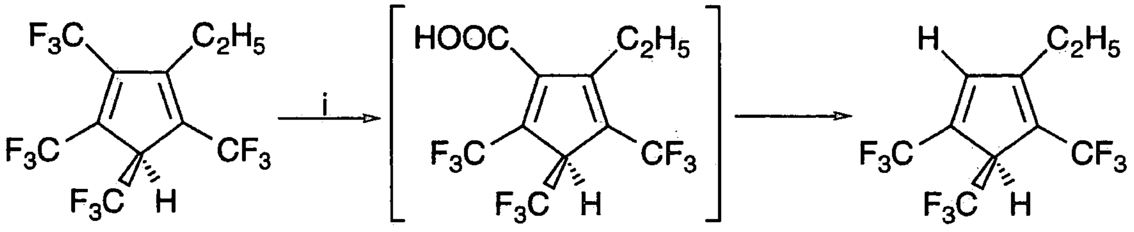
The pK_a of (**188**) was measured at ≤ -2, which is eighteen orders of magnitude more acidic than cyclopentadiene itself (pK_a= 16), due to the presence of five trifluoromethyl groups. The strongest acid known is 1,2,3,4,5-pentacyanocyclopentadiene (pK_a≤ -11), but an acid without conjugated substituents to approach the acidity of (**188**) is unknown.[232]

Work recently published by Muramatsu[233], detailed the synthesis of 1-ethyl-2,3,4,5-tetrakis(trifluoromethyl)-1,4-cyclopentadiene (**202**), which is very similar in structure to diene (**188**).



i. Ultraviolet light, ether, r.t., 184 hrs

Interestingly, when diene (**202**) was mixed with water one of the trifluoromethyl groups hydrolysed, after only 5 hrs, to give 1-ethyl-2,3,4-tris(trifluoromethyl)-1,4-cyclopentadiene (**203**).

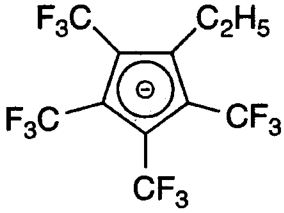


(**202**)

(**203**) 38% y.

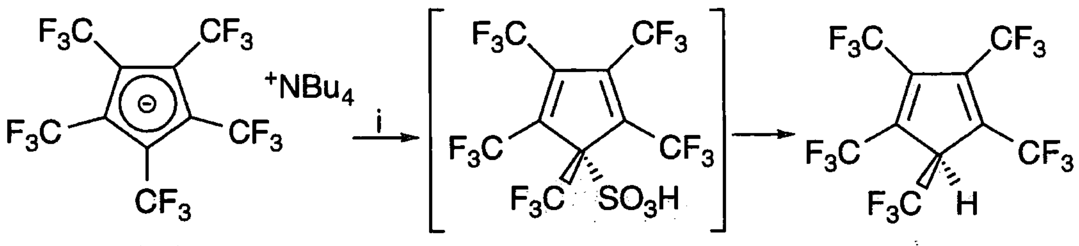
i. H_2O, r.t., 5 hrs

The formation of the anion (**204**) was not observed, which emphasises the importance of five trifluoromethyl groups in such a process.



(**204**)

A synthesis of diene (**188**) was pursued by adding concentrated sulphuric acid to crystals of tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienyl (**185**). When this mixture was immediately examined by ^{19}F NMR spectroscopy, three resonances were observed, with a peak integration of 2:1:2, which was in agreement with the results of Lemal[232], for diene (**188**), but the chemical shifts differed from those reported. None of the pentakis(trifluoromethyl)anion was observed. When the sample of acid (**185**), in sulphuric acid, was re-examined after 1 hr, by ^{19}F NMR spectroscopy, a second component had appeared, with all the peaks at a slightly lower frequency, but with the same 2:1:2 integration, and the chemical shifts of resonances were now in agreement with those attributed to diene (**188**) (ratio of 1.8 diene (**188**): 1.0 unknown).[232]



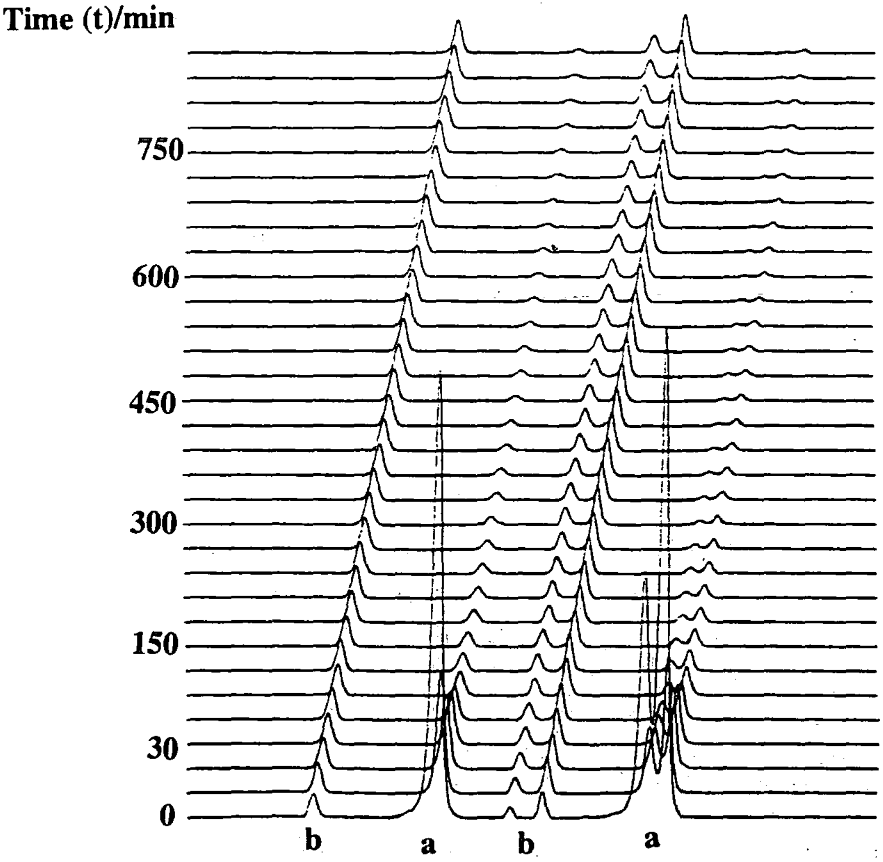
(**185**)

(**188**) 100% c.

i. Conc. H_2SO_4, 48 hrs

After 48 hrs, the unknown compound had disappeared, and this observation suggested that this was being converted into diene (**188**). Since the unknown compound had the same 2:1:2 integration as diene (**188**), it is reasonable to suggest that the species initially formed has a group at the tertiary position, such as SO_3H from the sulphuric acid, which is gradually replaced by a proton to give diene (**188**) (Figure 4). An NMR experiment was performed to investigate this idea further. A sample of tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienyl (**185**) was added to concentrated sulphuric acid, in an NMR tube which was sealed. The NMR spectrometer recorded the ^{19}F NMR spectrum every 10 min, for 30 min, and then every 30 min thereafter. The signal to noise ratio of each spectrum was compared to that of the sample at t=0, and is represented diagrammatically in Figure 5. Peaks `a´ represent the unknown, which has a high concentration at t=0 and rapidly decreases, but the concentration of compound `b´, diene (**188**), does not increase beyond the amount formed after the initial mixing (*i.e.* at t=0). This suggests that diene (**188**) is possibly rapidly reacting with, for example, the NMR tube, removing it from solution and giving a low equilibrium concentration. However, the uniformity of the diene (**188**) peaks, `a´, remains difficult to explain, since an initial increase in concentration would have been expected. Figure 4 shows the actual ^{19}F NMR spectrum after 5 hrs which, in the light of this data, indicates that the signals attributable to diene (**188**) are increasing along with the background noise, and are <u>not</u> as a result of an increase in concentration.

Figure 5



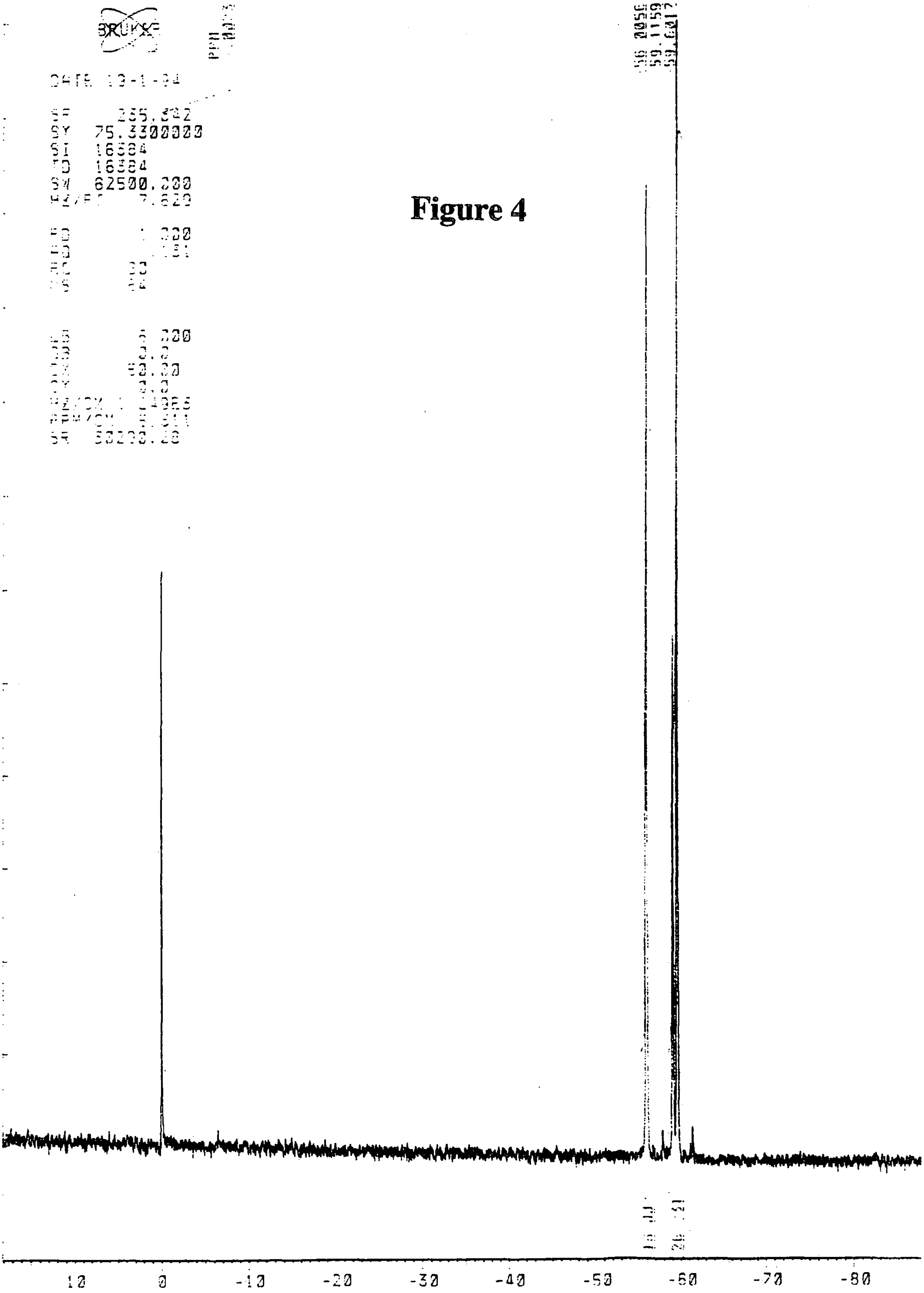

BRUKER
PPM
DATE 13-1-94
SY 75.3300000
SI 16384
TD 16384
SW 62500.000
56.2056
59.1159
59.6417
10
0
-10
-20
-30
-40
-50
-60
-70
-80

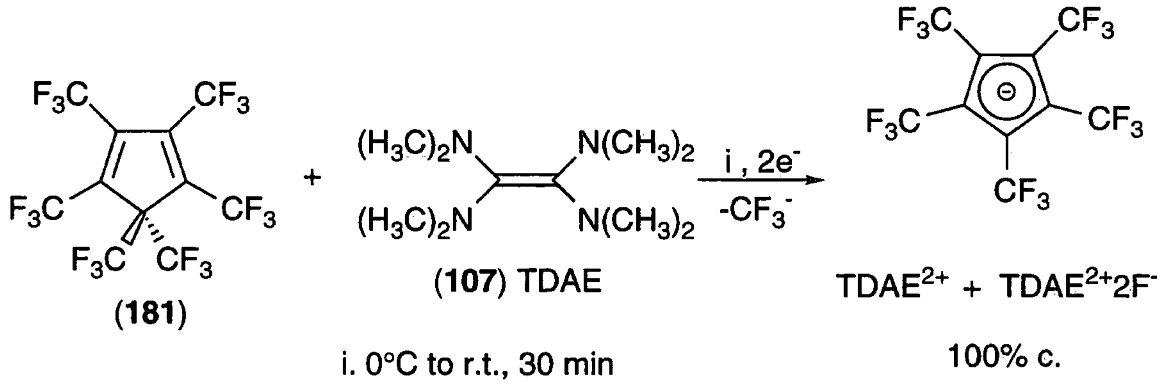
Figure 4

Pure diene (**188**) was obtained by repeating the reaction under reduced pressure, whilst collecting volatile material in a cold trap. The molecular ion was observed in the mass spectrum, and both the ^{1}H and ^{13}C NMR spectra (in $CDCl_3$) lent further support to the structure of (**188**), with a very convincing quartet [C*H*(CF_3)] being observed in the ^{1}H NMR spectrum. This material gradually, over a period of several days, reacted with the sample bottle.

Thus, a new route to diene (**188**), in good yield, has been developed, which is an alternative to the largely academic route described by Lemal.[232]

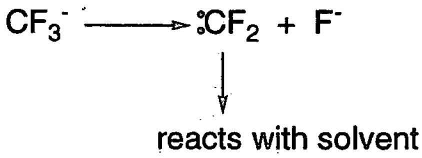
V.8 Reaction of Diene (181) with Tetrakis(dimethylamino)ethene (107)

Tetrakis(dimethylamino)ethene (**107**) is easily oxidised, see Chapter 2, with each molecule donating two electrons. An attempt was made to reduce diene (**181**) to the pentakis(trifluoromethyl)cyclopentadienyl anion, using this amine. Diene (**181**) was mixed with amine (**107**) at 0°C, with the formation of a red solid. Addition of acetone to this mixture then precipitated a white solid, leaving the colour in the acetone, which was identified as the salt $(TDAE)^{2+}2F^{-}$ (**122**), by ^{19}F NMR spectroscopy. Several attempts were made to recrystallise the residue obtained after solvent removal, but without success, although the ^{1}H NMR spectrum showed two resonances, corresponding to the $TDAE^{2+}$ dication and the ^{19}F NMR spectrum gave one sharp singlet, indicative of the symmetrical pentakis(trifluoromethyl)cyclopentadienyl anion. Also, FAB mass spectrometry revealed both the cation and the anion, but an accurate elemental analysis could not be obtained.



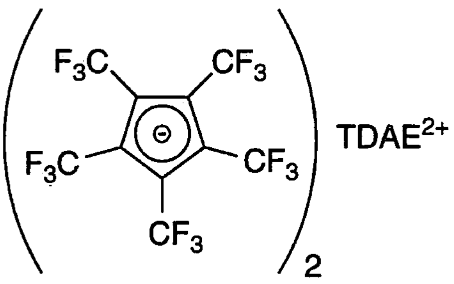
Clearly, diene (**181**) was reduced by the amine (**107**), most likely by the second single electron transfer mechanism described in Section V.6.C.(1), involving the transfer of two electrons and the loss of CF_3^-. A similar experiment was performed in a sealed vessel, and the volatile material showed the presence of trifluoromethane, CF_3H, supporting the production of CF_3^-. Since the difluoride salt, $(TDAE^{2+})2F^-$ (**122**), was isolated, the formation of fluoride ion needs to be accounted for.

This may arise from the decomposition of CF_3^- to give difluorocarbene as a by-product.



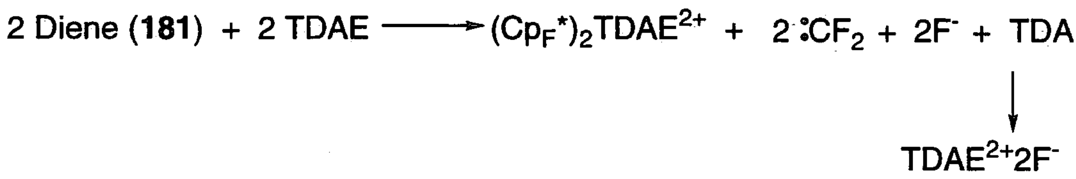
$$CF_3^- \longrightarrow :CF_2 + F^- \quad \downarrow \text{ reacts with solvent}$$

From these observations, the most likely structure is (**186**), as shown below.



(**186**)

The overall reaction is represented as follows:



$$2\text{ Diene } (\mathbf{181}) + 2\text{ TDAE} \longrightarrow (Cp_F^*)_2TDAE^{2+} + 2\,:CF_2 + 2F^- + TDAE^{2+} \downarrow TDAE^{2+}2F^-$$

(**122**)

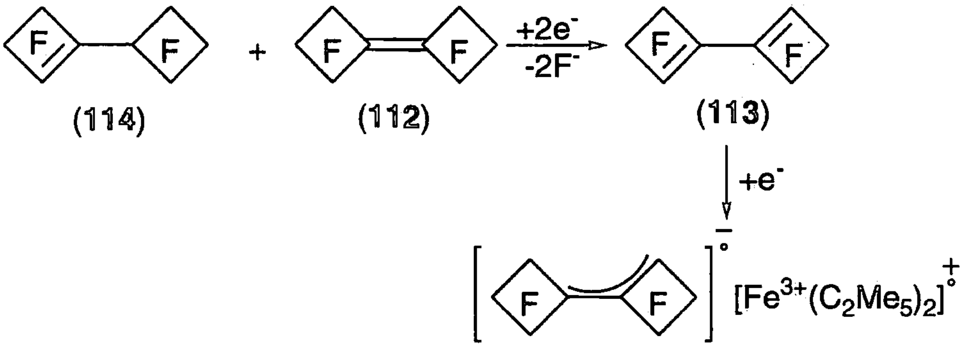
The CF_3^- anion which is generated supplies the fluoride ion for salt (**122**).

As well as defluorination (Chapter 2), this remarkable amine has now been applied to generating of the pentakis(trifluoromethyl)cyclopentadienyl anion.

V.9 Reaction of Diene (181) with Decamethylferrocene

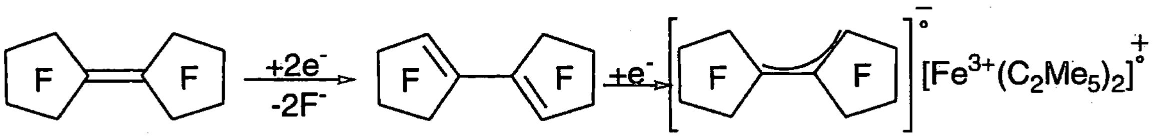
Magnets have fascinated man since the observation that iron is attracted to lodestone, which was exploited by the Chinese who invented the compass.[234] In recent years, there has been a great deal of interest in charge transfer salts with respect to their ferromagnetism and electrical conductivity.[235, 236] Miller[235], in 1987, discovered that decamethylferrocene will interact with tetracyanoethene to give a crystalline charge transfer salt, $[Fe(C_2Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$, which, remarkably, displayed ferromagnetism at temperatures below 4.8 K, and has been dubbed the first organic magnet. Decamethylferrocene has an electrode potential of -0.1V[134], which indicates the ease at which it is oxidised, or donates electrons. Work by Briscoe[96] and Mullins[98] has demonstrated the formation of metallocene charge transfer complexes with fluorocarbon acceptor molecules, for the first time.

Fluorinated alkenes (**112**), (**114**)[98] and (**110**)[96] were reacted with decamethylferrocene, under mild conditions, to give green charge transfer complexes, derived from the three electron reduction of the alkenes.



(**114**) (**112**) (**113**)

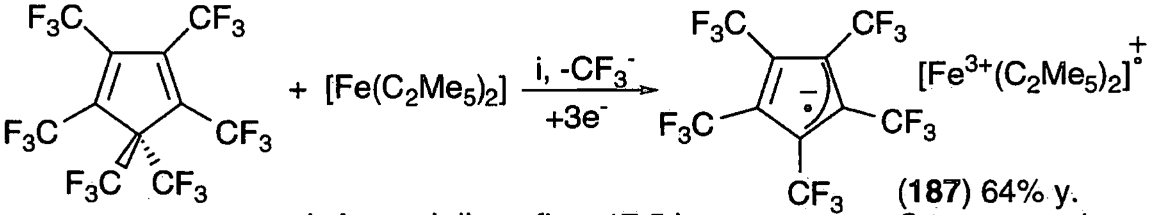
Similarly:



(**110**) (**111**)

Interestingly, the alkenes are first reduced to the corresponding dienes (*i.e.* defluorination), emphasising how easily these materials are reduced (see Chapter 2). Unfortunately, crystals of these charge transfer salts did not show any ferromagnetic coupling.[98] Diene (**181**) was examined with a view to synthesising a similar charge transfer complex.

To a refluxing solution of decamethylferrocene, in acetonitrile, diene (**181**) was added. An immediate green colouration developed, and after solvent removal the residue was recrystallised to give dark green crystals which were identified as decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienyl (**187**), by NMR spectroscopy, FAB mass spectrometry, where the cation and anion were observed, and elemental analysis.



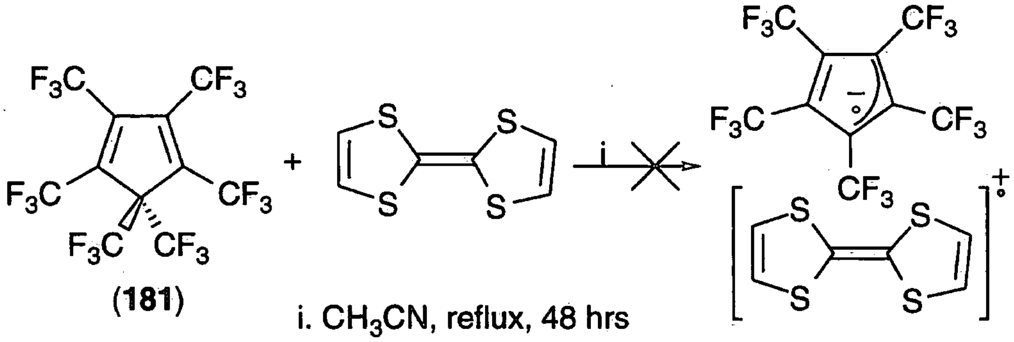
(**181**) i. Acetonitrile, reflux, 17.5 hrs (**187**) 64% y.
Green crystals

The second single electron transfer mechanism described in Section V.6.C.(1) can be applied here, with the pentakis(trifluoromethyl)anion accepting the third electron to give the radical anion (**187**). Crystals which were suitable for X-ray analysis could not be grown, preventing the ferromagnetic properties from being measured.

Finally, diene (**181**) can be reduced to the radical anion, by accepting three electrons, to give only the third known metallocene-fluorocarbon charge transfer salt.

V.10 Attempted Reaction between Diene (181) and Tetrathiofulvalene

In the early 1970's it was discovered that single crystals of a tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) charge transfer complex showed metal-like electrical conductivity.[237, 238] The tetrathiofulvalene acts as the reducing agent, as it is easily oxidised. Whether diene (**181**) could be reduced by tetrathiofulvalene was investigated by heating this, and the diene, in acetonitrile. The reaction was followed by ^{19}F NMR spectroscopy, and only the starting diene was observed.



(181)

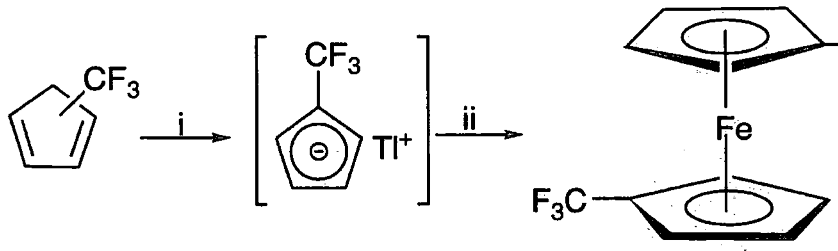
i. CH_3CN, reflux, 48 hrs

Unfortunately, under these conditions tetrathiofulvalene could not be oxidised, in order to reduce diene (**181**), to give a charge transfer complex with the pentakis(trifluoromethyl)cyclopentadienyl anion.

V.11 Cyclopentadienyl Anions as Transition Metal Ligands

Ferrocene is probably the best known compound bearing the cyclopentadienyl ligand attached to a transition metal. The introduction of electron rich substituents into the cyclopentadienyl backbone is well known to dramatically effect the reactivity of transition metals containing these ligands (*e.g.* decamethylferrocene).[239] However, metal centres which contain cyclopentadienyl groups bearing electron withdrawing substituents remain relatively unexplored.

Work by Gassman[134], in 1986, demonstrated the formation of bis(trifluoromethyl)ferrocene (**206**) from the thallous salt of the (trifluoromethyl)cyclopentadienyl group.

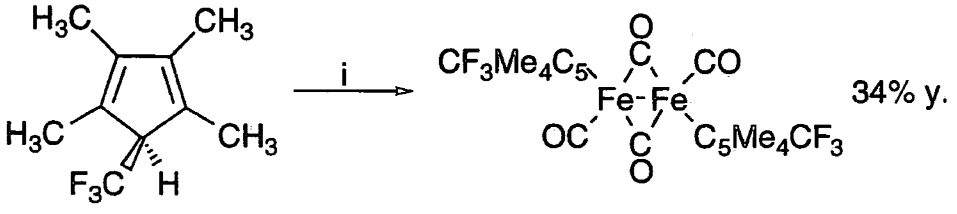


(206) *ca.* 60%

i. $TlOC_2H_5$, -10°C to -15°C; ii. $FeCl_2$

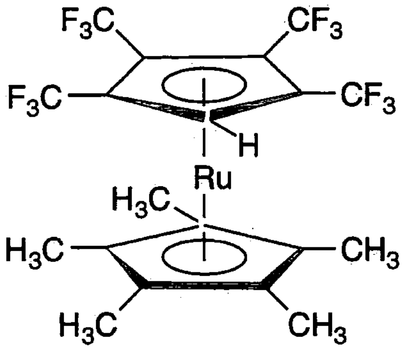
The incorporation of one CF_3 group had a dramatic effect on the electronic properties of (**206**), when compared to ferrocene. This group has also been attached to transition metals such as rhodium, iridium[134] and cobalt.[240]

In a recent Ph.D. thesis, by a student of Gassman[241], other interesting complexes were reported, including the one shown below.



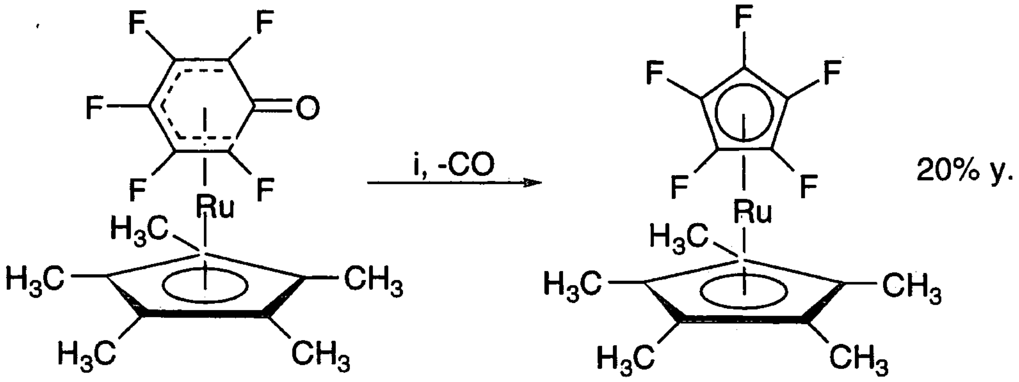
i. $Fe(CO)_5$, octane, reflux, 48 hrs

In 1989, Burk[239] reported the preparation of several transition metal complexes containing the tetrakis(trifluoromethyl)cyclopentadienyl ligand. One such complex with ruthenium gave compound (**207**), below.



(207)

In 1992, the first transition metal complex containing a perfluorocylopentadienyl ligand was reported by Hughes.[242] Ironically, the synthesis did not involve the perfluorocyclopentadienyl ligand itself.



i. Flash photolysis

The carbonyl compound was recovered in 60% yield. Finally, this year an extensive review, containing 400 references, has been published by Richmond[243], concerning the formation of fluorocarbon-transition metal complexes.

As can be seen, a great deal of interest would be generated if transition metal complexes containing the pentakis(trifluoromethyl)cyclopentadienyl anion could be synthesised, and collaborative work, within this department, using the tetraalkylammonium salts is currently pursuing this goal.

V.12 Conclusion

An efficient synthesis of hexakis(trifluoromethyl)cyclopentadiene (**181**) has been reported. From this a new perfluorinated diepoxide has been synthesised, and (**181**) has been used to form pure organic salts of the very interesting pentakis(trifluoromethyl)cyclopentadienyl anion, using a readily accessible, high yielding method. Reaction of tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienyl (**185**) with concentrated sulphuric acid gives a good route to 5-H-perfluoropentamethylcyclopentadiene (**188**), which is the strongest non-conjugated carbon acid known.[232]

Instrumentation

Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B (60MHz), a Bruker AC250 (250.13MHz) and a Varian VXR400S (399.95MHz) NMR spectrometer. The internal reference was tetramethylsilane (TMS).

^{19}F NMR spectra were recorded on a Varian EM3601 (56.45MHz), the Bruker AC250 (235.34MHz) and the Varian VXR400S (376.29MHz) NMR spectrometer. The internal reference was fluorotrichloromethane ($CFCl_3$).

^{13}C NMR spectra were recorded on the Bruker AC250 (62.9MHz) and the Varian VXR400S (100.58MHz) NMR spectrometer. The internal reference was tetramethylsilane (TMS).

^{31}P NMR spectra were recorded on a Bruker AC250 (101.26MHz) NMR spectrometer. The external reference was orthophosphoric acid (H_3PO_4; 85%).

Unless stated otherwise, all spectra were recorded using $CDCl_3$ or $(CD_3)_2CO$ as a solvent.

Infra Red Spectrometry (IR)

Infra red spectra were recorded on a Perkin-Elmer 577 Grating Spectrophotometer. Solid samples were run as KBr discs, liquid samples were run as a thin film between two polished KBr plates and gases and very volatile liquids were run in a sealed gas cell fitted with KBr plates.

Mass Spectrometry

Mass spectra of solid samples were recorded on a VG 7070E spectrometer. GLC mass spectra were recorded on a VG Trio 1000 spectrometer linked to a Hewlett Packard 5890 series II gas chromatograph, fitted with a 25m cross-linked methyl silicone capillary column.

Elemental Analysis

Carbon, hydrogen and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba Strumentazione 1106 Elemental Analyser. Analysis for halogens was performed as described in the literature.[244]

Gas Chromatography (GLC)

Gas chromatography analysis was carried out on a Hewlett Packard 5890A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column.

Preparative scale GLC was performed on a Varian Aerograph Model 920 (catharometer detector) gas chromatograph, fitted with a 3m 10% SE30 packed column.

Distillation

Fractional distillation of product mixtures was carried out using a Fischer Spahltrohr MMS 255 small concentric tube apparatus. Boiling points were recorded during the distillation.

Melting Points

Melting points were measured at atmospheric, using a Gallenkamp apparatus, and remain uncorrected.

Reagents and Solvents

Unless otherwise stated, reagents were used as supplied by the manufacturers. Solvents were predried by standard methods and stored over molecular sieve (type 4A), under dry nitrogen. A current of dry nitrogen was maintained for removal of the solvent with a syringe.

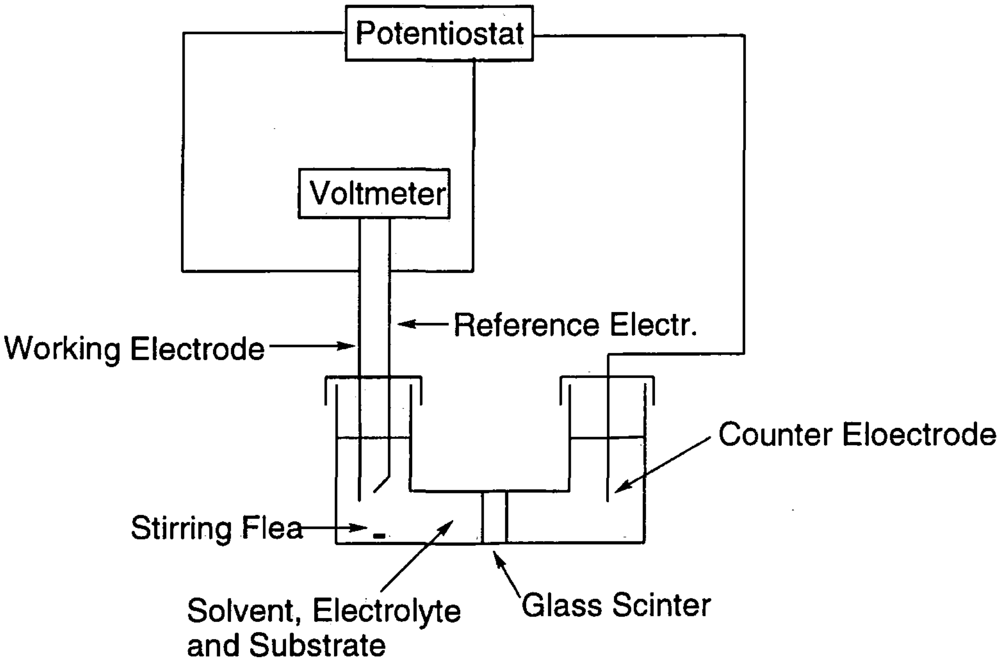
Chapter Six
Experimental to Chapter Two

VI.1 Electrochemical Defluorination

VI.1.A Defluorination of Perfluoro-3,4-dimethylhex-3-ene (105)

Alkene (**105**) was reduced using a Wenking ST 72 potentiostat, which allowed exact control of the applied reduction potential. The supporting electrolyte (tetraethylammonium tetrafluoroborate) facilitated the passage of current, *via* the ions in solution, and a cell divider, plus the use of a non-aqueous solvent, increases the cell resistance, which minimises the voltage drop (measured by the voltmeter). Three electrodes were used: the working and counter were made from platinum, whilst the reference was a saturated calomel electrode (see Figure 1).

Figure 1 The Electrolysis System



An electrolyte solution was prepared by dissolving tetraethylammonium tetrafluoroborate (5.45g, 25.1mmol) in acetonitrile (150 cm^3). This was then degassed, by bubbling nitrogen through it, and poured into the working electrode side of the cell, where it diffused across the sinter and into the Luggin capillary, which housed the calomel electrode. At all times there was a flow of nitrogen through the cell compartments. Alkene (**105**) (5.00g, 12.5mmol) was then pipetted into the working electrode compartment, and the mixture stirred. A potential of 1.70V was applied, with a current of 4.40mA, and after 5.5 hrs the current had plateaued at 8.45mA, when the reaction was stopped. A clear, colourless, lower layer (2.9g) remained at the working electrode, which was isolated and identified as a mixture of (**105**) plus *Z,Z* and *E,Z* diene (**106**) (6%, calculated by ^{19}F NMR spectroscopy); NMR spectra 1-4; Mass spectra 1-3.

An attempt was made to characterise a brown coating which formed on the working electrode. The material was isolated, dissolved in a minimum of acetonitrile (14 cm^3) and refrigerated (-15°C). However, the material which precipitated from solution, and the supernatant liquid, gave extremely complex ^{19}F NMR spectra, and as a result no further attempts at purification were made.

VI.2 Defluorination using Alkali Metal Amalgams

VI.2.A General Procedure

To a Schlenk tube, containing a pre-weighed amount of mercury, small pieces of diethyl ether washed sodium were added, under a positive flow of dry nitrogen. The Schlenk tube was then gently shaken, and the sodium dissolved with the generation of heat and grey fumes. The exotherm was carefully monitored, because of the possibility of vaporising the mercury, and controlled by periodic water cooling. Once the concentration of sodium had reached *ca.* 0.5% w/w, the fluoroalkene was added, under dry nitrogen, and the Schlenk tube was sealed using a Suba-Seal bung. The contents were then vigorously shaken, again with the production of heat which was controlled by water cooling. The consistancy of the amalgam changed during the reduction; lumpy and wet, to a solid lump, to dark grey dust. The end of reaction was indicated by the reappearance of liquid mercury, after which volatile material was isolated by transferring to a cold finger, under reduced pressure. A lithium amalgam was formed using the same procedure.

VI.2.B Defluorination of Perfluoro-3,4-dimethylhex-3-ene (105)

VI.2.B.(1) Using Sodium Amalgam

Fluoroalkene (**105**) (10.10g, 25.3mmol) was reduced by vigorously shaking with sodium amalgam (Na 3.00g, 130.4mmol; Hg 519.10g; 0.58%w/w). The isolated volatile components (7.3g, 80%) were identified as an inseparable mixture, by GLC, of the isomeric dienes *Z,Z*- and *E,Z*- perfluoro-3,4-dimethylhexa-2,4-diene (**106a,b**) (37:10 by ^{19}F NMR spectroscopy). For the mixture: b.p. 73-74°C; (Found: C, 26.3; F, 72.8. Calc. for C_8F_{14} C, 26.5; F, 73.5%); NMR spectra 3 and 4; IR spectrum 2; Mass spectra 2 and 3.

Table 2 Reduction of Alkene (**105**) using Sodium Amalgam

Alkene (**105**)/g	Sodium/g	Mercury/g	% w/w	Diene (**106**) Yield/%
20.00	3.00	519.10	0.58	80
20.00	2.90	525.00	0.55	80
20.00	2.85	520.00	0.55	50*
10.10	1.40	260.10	0.54	81
10.00	1.70	259.20	0.66	79
10.05	1.65	295.00	0.60	78
10.00	1.60	290.10	0.55	86

* 50% conversion, based on ^{19}F NMR Spectroscopy measurements.

VI.2.B.(2) Using Potassium Amalgam

Fluoroalkene (**105**) (5.00g, 12.5mmol) was reduced by vigorously shaking with potassium amalgam (K 1.30g, 33.3mmol; Hg 260.00g; 0.50%w/w). The isolated volatile material (1.78g, 39%) consisted of one component by GLC, and was identified as *Z,Z*- and *E,Z*- perfluoro-3,4-dimethylhexa-2,4-diene (**106a,b**) by comparison with the data of an authentic sample.

VI.2.C Preparation of Perfluoro-2,5-dihydrotetramethylfuran (115a,b)

Fluoroalkene (**105**) (20.00g, 50.0mmol) and anhydrous pyridine (9.30g, 117.7mmol) were added to tetraglyme (35cm^3). This mixture was heated to 80°C, with stirring, and ethanol (2.0g, 43.5mmol) was then added. The temperature was increased to 105°C, and the mixture refluxed for 5.5 hrs, after which the reaction vessel was allowed to cool, and water (150 cm^3) was added. A lower layer was collected, washed with water (4x50 cm^3), and volatile material was then isolated under reduced pressure, leaving a small amount of brown tar (*ca.* 0.05g).

Fractional distillation of the volatile material yielded, as a pair of isomers, dihydrofuran derivative (**115a,b**, 2:1 ratio, respectively) (third fraction, 1.9g, 5.1mmol, 10%), whose structure was consistent with literature values reported in these laboratories[113]; (Found: C, 25.2; F, 70.15. Calc. for C_8F_{14} C, 25.4; F, 70.4%); NMR spectrum 7.

VI.2.D Defluorination of Perfluoro-2,5-dihydrotetramethylfuran (115a,b)

Furan derivative (**115a,b**) (1.55g, 4.6mmol) was reduced by vigorously shaking with sodium amalgam (Na 0.30g, 13.1mmol; Hg 59.76g; 0.50%w/w). A clear, colourless liquid was isolated under reduced pressure, and shown to contain one component by GLC. This was subsequently identified as perfluorotetramethylfuran (**116**) (1.1g, 3.1mmol, 75%). b.p. 100-102°C (lit.: 104-105°C[21]); NMR spectrum 8; IR spectrum 6; Mass spectrum 7.

VI.2.E Defluorination of Perfluorobicylopentylidene (110)

Fluoroalkene (**110**) (6.00g, 14.1mmol) was reduced by vigorously shaking with sodium amalgam (Na 0.80g, 34.8mmol; Hg 150.00g; 0.53%w/w). The isolated volatile components were purified by crystallisation at 0°C to give perfluoro-1,1′-bicyclopent-1-enyl (**111**) (4.6g, 84%). b.p. 130°C, (Found: C, 31.0; F, 68.5. Calc. for $C_{10}F_{14}$ C, 31.1; F, 68.9%); NMR spectrum 6; IR spectrum 5; Mass spectrum 9.

VI.2.F Attempted Defluorination of Perfluoro-2,5-di-n-propyloxolane (117)

Fluoroalkane (**117**) (0.55g, 1.1mmol) was vigorously shaken with sodium amalgam (Na 0.10g, 4.4mmol; Hg 20.00g; 0.50%w/w). The isolated volatile material had one component by GLC, which was identified as unchanged alkane (**117**), by comparison of the ^{19}F NMR spectrum with that of an authentic sample; NMR spectrum 9.

VI.3 Defluorination using Tetrakis(dimethylamino)ethene (107)

VI.3.A Defluorination of Perfluoro-3,4-dimethylhex-3-ene (105)

VI.3.A.(1) Using a Solvent

A solution of amine (**107**) (5.00g, 2.5mmol, 5.80cm^3) in CH_2Cl_2 (5cm^3), was added dropwise, under nitrogen, to a mixture of (**105**) (11.00g, 27.5mmol) and CH_2Cl_2 (10cm^3) at 0°C, with the development of a deep red colour and a fine precipitate. Cooling was discontinued after 30 min, and the mixture was stirred at room temperature for a further 30 min. A lower layer was then isolated by syringe, and found to contain one component by GLC, which was identified as *Z,Z-* and *E,Z-* perfluoro-3,4-dimethylhexa-2,4-diene (**106a,b**) (9.0g, 24.7mmol, 90%) by comparison of the ^{19}F NMR spectrum with that of an authentic sample; NMR spectra 3 and 4.

The precipitate was then filtered, under dry nitrogen, and washed with CH_2Cl_2 ($3x5cm^3$) to afford a white solid which was identified as octamethyloxamidium difluoride (**122**) [4.5g, 18.9mmol, 68.6% based on (**122**)]; NMR spectrum 11; Mass spectrum 5. This solid was extremely hygroscopic, causing accurate analysis to be difficult.

Table 3 Reduction of Alkene (**105**) using Tetrakis(dimethylamino)ethene (**107**)

Alkene (**105**)/g	Amine (**107**)/cm^3	Dichloromethane/ cm^3	Diene (**106**) Yield* /%
11.00	5.80	50	50
11.00	5.75	15	87
11.20	5.80	15	84
11.00	5.80	15	90
11.10	5.80	15	87

* All isolated yields.

VI.3.A.(2) Without a Solvent

Amine (**107**) (5.00g, 25.0mmol, $5.80cm^3$) was added dropwise, under nitrogen, at 0°C to alkene (**105**) (11.00g, 27.5mmol). A dark red colour immediately developed, with the appearance of solid material. After *ca.* 15 min stirring stopped, due to the formation of a red solid, which was allowed to stand at room temperature for 30 min. This salt was then heated , under vacuum, at 80°C for 30 min (in order to decompose it), whilst collecting volatile material in a cold finger. Volatiles were purified by distillation, and found to contain one component by GLC, which was identified as *Z,Z-* and *Z,E-* perfluoro-3,4-dimethylhexa-2,4-diene (**106a,b**) (9.2g, 25.4mmol, 92%) by comparison of the ^{19}F NMR spectrum with that of an authentic sample; NMR spectra 3 and 4.

VI.3.B Defluorination of Perfluorobicyclopentylidene (110)

To stirred (**110**) (3.57g, 8.4mmol), amine (**107**) (1.54g, 7.7mmol, $1.78cm^3$) was added, dropwise, at 0°C, under an atmosphere of dry nitrogen. The reactants became orange, with the appearance of solid, and the reaction mixture was allowed to increase to room temperature, over 0.5 hrs, during which time white fumes were liberated. After this period, a moist, dark red, solid lump had appeared, and stirring was no longer possible. The solid was then heated to 85°C for 1.5 hrs, under reduced pressure. A pale yellow liquid was collected in a cold finger which, after distillation (1.3g), was shown to consist of two components by GLC, which were identified as (**110**) (first peak, 74%, calculated by ^{19}F NMR spectroscopy); NMR spectrum 5; Mass spectrum 8, and pefluoro-1,1′-bicyclopent-1-enyl (**111**) (26%, calculated by ^{19}F NMR); NMR spectrum 6; Mass spectrum 9, by comparison with the data of an authentic sample.

Fresh carbanion (**124**) was prepared to investigate the effect of BF_3OEt_2: Amine (**107**) (0.26g, 1.3mmol, $0.30cm^3$) was added to alkene (**110**) (0.50g, 1.2mmol), and volatile material was removed, under reduced pressure, from the resultant solid and identified as alkene (**110**) (0.10g, 0.3mmol). The solid was then dissolved in CH_3CN (10cm^3), and the solution was filtered. Addition of BF_3OEt_2 (0.20g, 1.3mmol) to the filtrate produced a lower layer, which was shown to be diene (**111**) (0.25g, 69% based on 0.40g of alkene reacting), by examination of ^{19}F NMR values.

VI.3.C Defluorination of Perfluoro-2,5-dihydrotetramethylfuran (115)

Amine (**107**) (0.58g, 2.9mmol; 0.67cm^3) was added dropwise, under a nitrogen atmosphere, to stirred (**115**) (1.00g, 2.7mmol) at 0°C. On addition, a red/orange solid developed, which made stirring difficult, and white fumes were liberated. The reaction was then allowed to warm to room temperature for 1 hr, after which the solid was heated to 100°C, whilst collecting volatile material, in a cold trap, under reduced pressure. Volatiles (0.4g) consisted of two components by GLC, which were identified as (**115**) (40%, calculated by ^{19}F NMR); NMR spectrum 7; IR spectrum 3, and perfluorotetramethylfuran (**116**) (60%, calculated by ^{19}F NMR); NMR spectrum 8; IR spectrum 6 and Mass spectrum 7, by comparing the data with literature values.[113]

VI.3.D Attempted Defluorination using Ferrocene

VI.3.D.(1) Attempted Defluorination of Perfluoro-3,4-dimethylhex-3-ene (105)

To a stirring mixture of acetonitrile (10 cm^3) and ferrocene (2.83g, 15.2mmol), alkene (**105**) (2.00g, 5mmol) was added. After 24 hrs at room temperature, no reaction had occurred, by ^{19}F NMR spectroscopy, so the temperature was increased to 100°C for 4 hrs, after which volatile material was shown to contain only alkene (**105**), by ^{19}F NMR spectroscopy; NMR spectra 1 and 2.

VI.3.D.(2) Substitution of Fluorine by Hydrogen in Diene (106)

Tributyl tin hydride (7.05g, 24.2mmol) was pipetted into a Carius tube (60cm^3), under an atmosphere of dry nitrogen, and diene (**106**) (4.00g, 11.1mmol) was then transferred, under reduced pressure, onto the hydride. The contents were degassed three times, and the tube was sealed under vacuum, after which irradiation with ultraviolet light commenced, using a fan to maintain a constant temperature. After 2.5 d the reaction was discontinued, and a large amount of white solid (Bu_3SnF) was present. Volatile material was collected under reduced pressure to give a colourless liquid (2.7g), which was shown to be a complex mixture of products by GLC and ^{19}F NMR spectroscopy. These could not be separated, but GLC-mass spectrometry indicated the four main components were derived from introduction of one to four hydrogens; Mass spectra 10, 11, 12 and 13, respectively.

Chapter Seven
Experimental to Chapter Three

VII.1 Reactions with Oxygen Nucleophiles

VII.1.A Diene (106) with Water

A mixture containing diene (**106**) (2.00g, 5.5mmol), distilled water (0.40g, 22.2mmol), caesium carbonate (7.20g, 22.1mmol), and acetonitrile (15cm^3) was stirred at room temperature for 5 d. Volatile material was transferred under vacuum to a cold trap and more water (15cm^3) was added. The lower layer was removed, purified by distillation, and identified as perfluorotetramethylfuran (**116**) (1.2g, 64%) by comparison with literature data. b.p. 101-103°C (lit.: 104-105°C[145-147]); NMR spectrum 8; IR spectrum 6; Mass spectrum 7.

Note: During the following reactions, precautions were taken to rigorously exclude water in an attempt to avoid the cyclisation of diene (106), as described in Section VII.1.A, above. However, some tetrakis(trifluoromethyl)furan (116) was observed in the volatile material from most of the reactions, decreasing the yield of the desired products slightly.

VII.1.B Diene (106) with But-2-en-1-ol ($HOCH_2CH{=}CHCH_3$)

To a stirring mixture of diene (**106**) (5.00g, 13.8mmol), caesium fluoride (5.00g, 32.9mmol) and acetonitrile (10cm^3), but-2-en-1-ol (2.20g, 30.5mmol) was added dropwise, under an atmosphere of nitrogen. The reaction was very exothermic, and was allowed to stir for 3.5 hrs at room temperature, after which water (30cm^3) was added to the homogenous liquid to give a lower layer (5.0g). This was isolated and distilled to yield a colourless liquid (3.6g, 56%), consisting of two components, which were identified as an inseparable mixture of *Z,Z-* (**134a**) and *E,Z-* (**134b**) *Z,Z-* and *E,Z-2,5-di-(butoxy-2-ene)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene* (8:2 respectively, by ^{19}F NMR spectroscopy). For the mixture (Found: C, 41.3; H, 3.1; F, 49.3. $C_{16}H_{14}F_{12}O_2$ requires C, 41.2, H, 3.0; F, 48.9%); IR spectrum 9; Mass spectrum 17; for (**134a**) NMR spectrum 12; for (**134b**) NMR spectrum 13.

VII.1.B.(1) The Attempted Claisen Rearrangement of (134a,b)

Diether (**134a,b**) (0.50g, 1.1mmol) was transferred, under vacuum, into a quartz NMR tube (4mm internal diameter), which was then sealed under reduced pressure and furnace heated at 150°C for 48 hrs, after which the material had become brown in colour. The ^{19}F NMR spectrum was very complex, and no carbonyl resonances were observed in the IR spectrum.

This reaction was repeated at various temperatures, with either no reaction (upto 120°C), or a reaction giving a ^{19}F NMR spectrum of similar complexity. Also, the use dimethylformamide, as a polar solvent, did not facilitate a reaction.

VII.1.C Diene (106) with Diethoxyphosphinylmethanol [$HOCH_2P(O)(OCH_2CH_3)_2$]

Diethoxyphosphinylmethanol (0.93g, 5.5mmol) was slowly added to a stirring mixture of diene (**106**) (1.00g, 2.8mmol), caesium fluoride (0.90g, 5.9mmol) and acetonitrile (7cm^3), under an atmosphere of nitrogen. After 2.5 d at room temperature, the solid was filtered off and volatile material was removed under reduced pressure. The involatile liquid (1.28g) was then purified by molecular distillation (100°C, 0.5mmHg) to give a pale yellow liquid (1.1g, 63%), which was identified as an inseparable mixture (by GLC) of *Z,Z-* (**135a**) and *E,Z-* (**135b**) *2,5-bis[oxymethene(diethoxylphosphinol)]-3,4-bis(trifluoromethyl)perf;uorohexa-2,4-diene* (86:14 respectively, by ^{19}F NMR spectroscopy). For the mixture (Found C, 32.6; H, 3.9; F, 34.25. $C_{18}H_{24}F_{12}O_8P_2$ requires C, 32.8; H, 3.65; F, 34.65%); IR spectrum 7; Mass spectrum 14; for (**135a**) NMR spectrum 14; for (**135b**) NMR spectrum 15. For the starting alcohol, δ_H(250MHz, $CDCl_3$, $CFCl_3$) 1.35 (3H, t, $J_{H,H}$ 6.8 Hz, OCH_2CH_3), 3.91 (2H, d, $J_{H,P}$ 6.0 Hz, $HOCH_2P$), 4.17 (2H, q, $J_{H,H}$ 7.0 Hz, OCH_2CH_3), 4.44 (1H, br s, OH) ppm; δ_P (100MHz, $CDCl_3$, H_3PO_4) 25.38 (s) ppm.

VII.1.D Diene (106) with Diethylene Glycol ($HOCH_2CH_2OH$)

To a stirring mixture of diene (**106**) (3.00g, 8.3mmol), sodium carbonate (1.72g, 16.2mmol) and acetonitrile (20cm^3), a solution of dry diethylene glycol (0.43g, 4.1mmol), in acetonitrile (10cm^3), was slowly added under an atmosphere of nitrogen. After 13 d at room temperature, volatile material was removed under reduced pressure, and a lower layer (0.87g) was identified as unreacted diene (**106**) by ^{19}F NMR spectroscopy. The remaining liquid was purified by molecular distillation (35°C, 0.5mmHg) to give a colourless product (1.6g, 68% based on 2.13g of (**106**) reacting) which was identified as an inseparable mixture (by GLC) of *Z,Z-* (**137a**) and *E,Z-* (**137b**) *2-ethoxy-[2-ethoxy(2-hydroxy)]-3,4-bis(trifluoromethyl)perfluoro-2,4-diene* (84:16 respectively, by ^{19}NMR spectroscopy). For the mixture (Found C, 32.0; H, 2.05; F, 54.8. $C_{12}H_9F_{13}O_3$ requires C, 32.1; H, 2.0; F, 55.1%); IR spectrum 8; Mass spectrum 16; for (**137a**) NMR spectrum 16; for (**137b**) NMR spectrum 17.

VII.1.E Diene (106) with Ethylene Glycol ($HOCH_2CH_2OCH_2CH_2OH$)

Dry ethylene glycol (0.25g, 4.0mmol) was slowly added to a mixture of diene (**106**) (3.00g, 8.3mmol), caesium carbonate (5.26g, 16.1mmol) and acetonitrile (40cm^3), under an atmosphere of dry nitrogen. After 7d at room temperature, the solid was filtered off, and volatile material was transferred, under reduced pressure, to a cold finger. Water (20cm^3) was then added to the volatiles, giving a lower layer (2.5g) which was found to contain two components by GLC, which were identified as perfluorotetramethylfuran (**116**); NMR spectrum 8; Mass spectrum 7, and 5-fluoro-6-(perfluoro-3-methylprop-2-ene)-7-difluoro-1,4-dioxep-5-ene (**136**) (*ca.* 55% by ^{19}F NMR spectroscopy); NMR spectrum 18; Mass spectrum 15, by comparison with literature values.[96]

VII.1.F Diene (106) with Benzene-1,4-diol

Benzene-1,4-diol (0.30g, 2.7mmol) in diethyl ether (10cm^3) was added dropwise to a stirred mixture containing (**106**) (2.00g, 5.5mmol), dry caesium carbonate (4.00g, 12.3mmol) and diethyl ether (30cm^3). After 4.5 d at room temperature, the solvent was removed, and molecular distillation of the residue (30°C, 0.8mmHg) gave a colourless liquid, which crystallised at room temperature, and was identified as a 28:13:5:2 mixture of *Z,Z-* (**138a**), *Z,E-* (**138b**), *E,E-* (**138c**), and *E,Z-* (**138d**) *2-phenoxy-(4-hydroxy)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene* (0.4g, 32.5%). For the mixture (Found: C, 37.0; H, 1.2. $C_{14}H_5F_{13}O_2$ requires C, 37.2; H, 1.1%); ^{1}H NMR spectrum 18; IR spectrum 10; Mass spectrum 18; for (**138a**) ^{19}F NMR spectrum 19; for (**138b**) ^{19}F NMR spectrum 20; for (**138c**) ^{19}F NMR spectrum 21; for (**138d**) ^{19}F NMR spectrum 22.

The remaining solid was purified by sublimation (50°C, 0.8mmHg) to give a white material, which was shown to be one product by NMR, and identified as *Z,Z-p-phenylenedioxy-2,2′-bis[3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene]* (**139**) (1.25g, 58%), (Found: C, 33.0; H, 0.5. $C_{22}H_4F_{26}O_2$ requires C, 33.25; H, 0.5%); NMR spectrum 23; IR spectrum 11; Mass spectrum 19.

VII.1.G Diene (106) with Biphenyl-4,4′-diol

A solution of biphenyl-4,4′-diol (0.77g, 4.1mmol), in diethyl ether (5cm^3) and acetone (5cm^3), was added dropwise to a mixture of diene (**106**) (3.00g, 8.3mmol), caesium carbonate (5.400g, 16.6mmol) and acetonitrile (30cm^3). After stirring for 72 hrs, at room temperature, the solid was filtered off, and the organic material was dissolved in CH_2Cl_2 (30cm^3) and dried ($MgSO_4$). Solvent was removed under reduced pressure, and the residue sublimed under vacuum (80°C, 0.05mmHg) to give a white solid which was identified as *biphenyl-4,4′-diyldioxy)-2,2′-bis[3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene]* (**140**) (2.8g, 78%), (Found: C, 38.8; H, 0.85. $C_{28}H_8F_{26}O_2$ requires C, 38.6; H, 0.9%); NMR spectrum 24; IR spectrum 12; Mass spectrum 20.

VII.1.H Diene (106) with 2,2-Di(4-hydroxyphenyl)hexafluoropropane

A solution of 2,2-di(4-hydroxyphenyl)hexafluoropropane (1.39g, 4.1mmol) in acetonitrile (10cm^3) was added dropwise to a stirred mixture of diene (**106**) (3.00g, 8.3mmol), caesium carbonate (5.40g, 16.6mmol) and acetonitrile (30cm^3), and after 12 d at room temperature, the solid was filtered off, and the organic material was dissolved in acetone (25cm^3) and dried ($MgSO_4$). The solvent was then removed, under reduced pressure, and the residue sublimed under vacuum (80°C, 0.10mmHg) to give a white solid, which was recrystallised from acetone as white needles, and subsequently identified as *bis(trifluoromethyl)methylenedi-p-phenylenedioxy-2,2′-bis[3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene]* (**141**) (3.5g, 83%), (Found: C, 36.8; H, 0.7. $C_{31}H_8F_{32}O_2$ requires C, 36.5; H, 0.8%); NMR spectrum 25; IR spectrum 13; Mass spectrum 21.

VII.1.I Bis(trifluoromethyl)methylenedi-p-phenylenedioxy-2,2′-bis[3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] (141) with Sodium Methoxide

A solution of sodium methoxide (0.20g, 3.7mmol) in methanol (5cm^3) was added to a mixture of (**141**) (0.20g, 0.2mmol) in methanol (10cm^3), and stirred at room temperature for 48 hrs. Removal of the solvent gave a residual solid which was extracted with diethyl ether and dried ($MgSO_4$). Subsequent solvent removal, and recrystallisation from acetone, gave an off white solid which was identified as *bis(trifluoromethyl)methylenedi-p-phenylenedioxy-2,2′-bis[5-methoxy-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene]* (**142**) (0.15g, 73%), (Found: C, 38.1; H, 1.4. $C_{33}H_{14}F_{30}O_4$ requires C, 37.9; H, 1.3%); NMR spectrum 26; IR spectrum 14; Mass spectrum 22.

Chapter Eight
Experimental to Chapter Four

VIII.1 Epoxidation of Perfluoro-3,4-dimethyl-2,4-diene (106) with Calcium Hypochlorite

Diene (**106**) (5.00g, 13.8mmol) was added dropwise to a stirred mixture of acetonitrile (20cm^3) and calcium hypochlorite (7.04g, 49.2mmol), which had been dried by gently heating under vacuum. After stirring for one week, at room temperature, a colourless liquid was isolated by distillation, under reduced pressure, and identified as perfluoro-3,4-dimethyl-2,4-diepoxyhexane (**162**) (3.29g, 8.35mmol, 61%), (Found: C, 24.4; F, 68.0. Calc. for $C_8F_{14}O_2$ C, 24.4; F, 67.5%); ^{19}F NMR spectrum 27; IR spectrum 23; Mass spectrum 24.

This reaction was also performed, with equivalent success, by refluxing the reaction mixture at 90°C for 5 hrs.

VIII.2 Reaction of Perfluoro-3,4-dimethyl-2,4-diene (106) with Butyl-lithium and tert-Butyl Hydroperoxide

An anhydrous (as supplied by the Aldrich Co.) solution of t-butyl hydroperoxide in toluene (3.0M solution: 8.4cm^3, 12.6mmol, 1.5 equiv. w.r.t. (**106**)) was added to freshly distilled tetrahydrofuran (15cm^3) at -78°C, under an atmosphere of dry nitrogen. This was followed by the addition of a solution of butyl-lithium in hexane (1.6M solution: 11.4cm^3, 9.1mmol, 1.1 equiv. w.r.t. (**106**)); the resulting solution was stirred at -78°C for 5 min, after which diene (**106**) (3.00g, 8.29mmol) was added. The reaction mixture was stirred at ambient temperature for 48 hrs. After its completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatile material was then isolated under reduced pressure and cooled to -15°C, which ensured that the majority of the fluorinated material separated from the solvent, forming a lower layer (2.3g) which was identified as perfluoro-3,4-dimethyl-2,4-diepoxyhexane (**162**) (70%, 100% conversion by ^{19}F NMR) by comparison of ^{19}F NMR data with that of an authentic sample; ^{19}F NMR spectrum 27 (see above for other data).

VIII.3 Attempted Epoxidation of Perfluoro-2,5-dihydrotetramethylfuran (115) with Calcium Hypochlorite

Alkene (**115**) (0.60g, 1.6mmol) was added to a mixture of calcium hypochlorite (0.75g, 5.2mmol) and acetonitrile (10cm^3), which was refluxed at 85°C for 6 hrs. Volatile material was then isolated as a lower layer (0.2g), under reduced pressure, and shown to contain several components, by GLC-MS and ^{19}F NMR spectroscopy, of which none could be attributed to the epoxide. No attempt was made to isolate any of the components.

VIII.4 Epoxidation of Perfluoro-2,5-dihydrotetramethylfuran (115) with Butyl-lithium and tert-Butyl Hydroperoxide

An anhydrous (as supplied by the Aldrich Co.) solution of t-butyl hydroperoxide in toluene (3.0M solution: 3.3cm^3, 9.9mmol, 1.5 equiv. w.r.t. (**115**)) was added to freshly distilled tetrahydrofuran (15cm^3) at -78°C under an atmosphere of dry nitrogen. This was followed by the addition of a solution of butyl-lithium in hexane (1.6M solution: 4.6cm^3, 7.3mmol, 1.1 equiv. w.r.t. (**115**)); the resulting solution was stirred at -78°C for 5 min, after which furan derivative (**115**) (2.50g, 6.6mmol) was added. The reaction mixture was stirred at ambient temperature for 96 hrs. After its completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatile material was then isolated under reduced pressure and cooled to -15°C, which ensured that the majority of the fluorinated material separated from the solvent, forming a lower layer (1.8g) which was identified as a mixture containing three isomers of *perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane* (**163a-c**) (69%, *ca.* 1:1:1 ratio, 100% conversion by ^{19}F NMR) (Found C, 24.4; F, 67.3. $C_8F_{14}O_2$ requires C, 24.4; F, 67.5%); ^{19}F NMR spectrum 28; IR spectrum 18; Mass spectrum 26.

VIII.5 Epoxidation of Perfluoro-3,4-dimethylhex-3-ene (105) with Butyl-lithium and tert-Butyl Hydroperoxide

An anhydrous (as supplied by the Aldrich Co.) solution of t-butyl hydroperoxide in toluene (3.0M solution: 6.2cm^3, 18.6mmol, 1.5 equiv. w.r.t. (**105**)) was added to freshly distilled tetrahydrofuran (30cm^3) at -78°C under an atmosphere of dry nitrogen. This was followed by the addition of a solution of butyl-lithium in hexane (1.6M solution: 8.5cm^3, 13.6mmol, 1.1 equiv. w.r.t. (**105**)); the resulting solution was stirred at -78°C for 5 min, after which alkene (**105**) (5.00g, 12.5mmol) was added. The reaction mixture was stirred at ambient temperature for 16 hrs. After its completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatile material was then isolated under reduced pressure and cooled to -15°C, which ensured that the majority of the fluorinated material separated from the solvent, forming a lower layer (4.1g) which was identified as a mixture of alkene (**105**); ^{19}F NMR spectra 1 and 2, *E*-perfluoro-3,4-dimethyl-3,4-epoxyhexane (**164a**) (37%, calculated by ^{19}F NMR); ^{19}F NMR spectrum 29 and *Z*-perfluoro-3,4-dimethyl-3,4-epoxyhexane (**164b**) (37%, calculated by ^{19}F NMR); ^{19}F NMR spectrum 29, by comparison of the ^{19}F NMR values with those in the literature.[152]

VIII.6 Reaction of (105) with Caesium Fluoride and tert-Butyl Hydroperoxide

An anhydrous solution of t-butyl hydroperoxide in toluene (3.0M solution: 3.8cm^3, 11.3mmol, 1.5 equiv. w.r.t. (**105**)) was added to dried caesium fluoride (1.7g, 11.3mmol) in freshly distilled tetrahydrofuran (15cm^3), at -78°C, under an atmosphere of dry nitrogen. This then stirred for 10 min, after which alkene (**105**) (2.5g, 6.3mmol) was added. The reaction was stirred at ambient temperature for 72 hrs. After its completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatiles were then isolated, under reduced pressure, and examination by ^{19}F NMR spectroscopy and GLC showed a mixture containing *Z*-perfluoro-3,4-dimethyl-3,4-epoxyhexane (**164**) (44%, calculated by ^{19}F NMR); ^{19}F NMR spectrum 29; Mass spectrum 23, by comparison with data in the literature[152], and four other fluorine containing components, which remain unidentified.

VIII.7 Attempted Epoxidation of (105) with Potassium Fluoride and tert-Butyl Hydroperoxide

An anhydrous solution of t-butyl hydroperoxide in toluene (3.0M solution: 2.5cm^3, 7.5mmol, 1.5 equiv. w.r.t. (**105**)) was added to dried potassium fluoride (0.4g, 7.6mmol) in freshly distilled tetrahydrofuran (10cm^3), at -78°C, under an atmosphere of dry nitrogen. This then stirred for 10 min, after which alkene (**105**) (3.0g, 7.5mmol) was added and the reaction stirred at ambient temperature for a further 51 hrs. After completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatiles were then isolated, under reduced pressure, and identified as alkene (**105**), ^{19}F NMR spectra 1 and 2, by comparison with the literature values.[152]

The reaction was repeated at 100°C for 93 hrs, with only (**105**) shown to be present by ^{19}F NMR spectroscopy.

VIII.8 Epoxidation of Perfluoro-2-methylpent-3-ene (165) with Butyl-lithium and tert-Butyl Hydroperoxide

An anhydrous (as supplied by the Aldrich Co.) solution of t-butyl hydroperoxide in toluene (3.0M solution: 4.8cm^3, 14.2mmol, 1.5 equiv. w.r.t. (**165**)) was added to freshly distilled tetrahydrofuran (15cm^3) at -78°C under an atmosphere of dry nitrogen. This was followed by the addition of a solution of butyl-lithium in hexane (1.6M solution: 6.5cm^3, 10.5mmol, 1.1 equiv. w.r.t. (**165**)); the resulting solution was stirred at -78°C for 5 min, after which alkene (**165**) (3.00g, 9.5mmol) was added. The reaction mixture was stirred at ambient temperature for 108 hrs. After its completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatile material was then isolated under reduced pressure and cooled to -15°C, which ensured that the majority of the fluorinated material separated from the solvent, forming a lower layer (2.6g) which was identified as a mixture of (**165**); ^{19}F NMR spectrum 31 and perfluoro-2-methyl-3-epoxypentane (**166**) (82%, calculated by ^{19}F NMR), which was separated from the starting alkene by preparative scale gas chromatography; ^{19}F NMR spectrum 32; IR spectrum 19 and Mass spectrum 29.

VIII.9 Epoxidation of Perfluoro-2,2-dimethylpent-3-ene (167) with Butyl-lithium and tert-Butyl Hydroperoxide

An anhydrous (as supplied by the Aldrich Co.) solution of t-butyl hydroperoxide in toluene (3.0M solution: 3.2cm^3, 9.6mmol, 1.5 equiv. w.r.t. (**167**)) was added to freshly distilled tetrahydrofuran (6cm^3) at -78°C under an atmosphere of dry nitrogen. This was followed by the addition of a solution of butyl-lithium in hexane (1.6M solution: 4.0cm^3, 6.4mmol, 1.1 equiv. w.r.t. (**167**)); the resulting solution was stirred at -78°C for 5 min, after which alkene (**167**) (2.00g, 5.7mmol) was added. The reaction mixture was stirred at ambient temperature for 84 hrs. After its completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatile material was then isolated under reduced pressure and cooled to -15°C, which ensured that the majority of the fluorinated material separated from the solvent, forming a lower layer (1.6g) which was identified as a mixture of (**167**); ^{19}F NMR spectrum 33; IR spectrum 20 and Mass spectrum 30 and *E- and Z-perfluoro-2,2-dimethyl-3-epoxypentane* (**168**) (80% calculated by ^{19}F NMR), which was separated from the starting alkene by preparative scale gas chromatography. (Found: C, 22.7; F, 72.5. $C_7F_{14}O$ requires C, 22.95; F, 72.7%); ^{19}F NMR spectrum 34; IR spectrum 21; Mass spectrum 31.

VIII.10 Epoxidation of Perfluoro-1,2-biscyclobutyl-cyclobutene (169) with Butyl-lithium and tert-Butyl Hydroperoxide

An anhydrous (as supplied by the Aldrich Co.) solution of t-butyl hydroperoxide in toluene (3.0M solution: 3.1cm^3, 9.3mmol, 1.5 equiv. w.r.t. (**169**)) was added to freshly distilled tetrahydrofuran (4cm^3) at -78°C under an atmosphere of dry nitrogen. This was followed by the addition of a solution of butyl-lithium in hexane (1.6M solution: 4.3cm^3, 6.9mmol, 1.1 equiv. w.r.t. (**169**)); the resulting solution was stirred at -78°C for 5 min, after which alkene (**169**) (3.00g, 6.2mmol) was added. The reaction mixture was stirred at ambient temperature for 84 hrs. After its completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatile material was then isolated under reduced pressure and cooled to -15°C, which ensured that the majority of the fluorinated material separated from the solvent, forming a lower layer (2.5g) which was identified as a mixture of (**169**) (80%, calculated by ^{19}F NMR); ^{19}F NMR spectrum 35, IR spectrum 16 and Mass spectrum 27 and perfluoro-1′,2′-epoxytercyclobutane (**170**) (20%, calculated by ^{19}F NMR); ^{19}F NMR spectrum 36; IR spectrum 17; Mass spectrum 28, by comparison with data in the literature.[107, 152]

VIII.11 Epoxidation of *p*-Phenylenedioxy-2,2′-bis[Z,Z-3,4-bis(trifluoromethyl)-perfluorohexa-2,4-diene] (139) with Calcium Hypochlorite

Tetraene (**139**) (0.20g, 0.25mmol) was added, under nitrogen, to a mixture of dried calcium hypochlorite (0.60g, 4.2mmol) and acetonitrile (30cm^3), which was refluxed at 90°C for 43 hrs. Solid material was then filtered off, and removal of the solvent from the filtrate gave an off white residue which recrystallised from dichloromethane/hexane (1:1) to yield a white solid, subsequently identified as *p-Phenylenedioxy-2,2′-bis[Z,Z-3,4-bis(trifluoromethyl)perfluoro-2,4-diepoxy-hexane]* (**172**) (0.13g, 60%), m.p. 72°C. (Found: C, 30.5; H, 0.4; F, 57.2. $C_{22}F_{26}H_4O_6$ requires C, 30.8; H, 0.5; F, 57.6%); ^{19}F NMR spectrum 38; IR spectrum 25; Mass spectrum 32.

VIII.12 Attempted Epoxidation of Perfluoro-1,1′-bicyclopent-1-enyl (111) with Butyl-lithium and tert-Butyl Hydroperoxide

An anhydrous (as supplied by the Aldrich Co.) solution of t-butyl hydroperoxide in toluene (3.0M solution: 2.6cm^3, 7.8mmol, 1.5 equiv. w.r.t. (**111**)) was added to freshly distilled tetrahydrofuran (5cm^3) at -78°C under an atmosphere of dry nitrogen. This was followed by the addition of a solution of butyl-lithium in hexane (1.6M solution: 3.6cm^3, 20.7mmol, 1.1 equiv. w.r.t. (**111**)); the resulting solution was stirred at -78°C for 5 min, after which diene (**111**) (1.00g, 2.6mmol) was added. The reaction mixture was stirred at ambient temperature for 60 hrs. After its completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatile material was then isolated under reduced pressure and cooled to -15°C, which ensured that the majority of the fluorinated material separated from the solvent, forming a lower layer (0.6g) which was found to contain several components by GLC, and the ^{19}F NMR spectrum was extremely complex (100% conversion by ^{19}F NMR). Masses corresponding to the mono- or diepoxide were not observed by GLC-MS, and no further work-up was attempted. The reaction was repeated, whilst maintaining the temperature at -20°C, using a cryostat, but without success.

VIII.13 Attempted Epoxidation of 1,1,1-Trifluoropropene (171) with Butyl-lithium and tert-Butyl Hydroperoxide

A Carius tube (60cm^3) was charged with freshly distilled tetrahydrofuran (3cm^3) and t-butyl hydroperoxide in toluene (3.0M solution: 10.4cm^3, 31.2mmol, 1.5 equiv. w.r.t. (**171**)), at -78°C, under an atmosphere of dry nitrogen, with periodic agitation. Butyl-lithium in hexane (1.6M solution: 14.3cm^3, 22.9mmol, 1.1 equiv. w.r.t. (**171**)) was then slowly added, with mixing. Alkene (**171**) was then condensed into the tube, which was sealed under vacuum and rotated at ambient temperature for 4 d. Volatile material was isolated under reduced pressure, as a homogeneous layer. The only fluorine containing component was (**171**) by comparison of the ^{19}F NMR spectroscopy values with those of an authentic sample; δ_F(250MHz, $CFCl_3$).-67.0 (s, CF_3) ppm.

VIII.14 Thermal Reaction of Diepoxide (162) with Caesium Fluoride

Diepoxide (**162**) (1.01g, 2.6mmol) was condensed into a Carius tube (60cm^3) containing dry caesium fluoride (0.50g, 3.3mmol), which was sealed under vacuum and heated in a furnace at 200°C for 24 hrs. Volatile material was isolated under reduced pressure to give a colourless liquid, which contained one component by GLC, and was identified as *perfluoro-2,3,5,6-dimethyl-5,6-dihydro-1,4-dioxin* (**179**) (0.8g, 79%). (Found: C, 24.2; F, 67.4. $C_8F_{14}O_2$ requires C, 24.4; F, 67.5%); NMR spectrum 30; IR spectrum 24; Mass spectrum 25.

VIII.15 Thermal Reaction of Diepoxide (162) without Caesium Fluoride

Diepoxide (**162**) (1.00g, 2.5mmol) was condensed into a Carius tube (60cm^3), which was then sealed under vacuum and heated in a furnace at 200°C for 24 hrs. Volatile material was isolated under reduced pressure to give a colourless liquid, which contained one component by GLC, and was identified as *perfluro-2,3,5,6-tetramethyl-5,6-dihydo-1,4-dioxin* (**179**) (0.95g, 95%). (Found: C, 24.3; F, 67.2. $C_8F_{14}O_2$ requires C, 24.4; F, 67.5%); NMR spectrum 30; IR spectrum 24; Mass spectrum 25.

VIII.16 Attempted Epoxidation of Dioxin (179) with Calcium Hypochlorite

Dioxin (**179**) (0.64g, 1.6mmol) was added to a mixture of calcium hypochlorite (0.93g, 6.5mmol) and acetonitrile (10cm^3), which was refluxed at 85°C for 2 d. Volatile material was then isolated under reduced pressure, and a lower layer (0.4g) was shown to contain only dioxin (**179**) by GLC and ^{19}F NMR spectroscopy; NMR spectrum 30.

VIII.17 Attempted Epoxidation of Dioxin (179) with Butyl-lithium and tert-Butyl Hydroperoxide

An anhydrous (as supplied by the Aldrich Co.) solution of t-butyl hydroperoxide in toluene (3.0M solution: 1.0cm^3, 3.0mmol, 1.5 equiv. w.r.t. (**179**)) was added to freshly distilled tetrahydrofuran (3cm^3) at -78°C under an atmosphere of dry nitrogen. This was followed by the addition of a solution of butyl-lithium in hexane (1.6M solution: 1.4cm^3, 1.6mmol, 1.1 equiv. w.r.t. (**179**)); the resulting solution was stirred at -78°C for 5 min, after which alkene (**179**) (0.80g, 2.0mmol) was added. The reaction mixture was stirred at ambient temperature for 42 hrs. After its completion (monitored by ^{19}F NMR), solid sodium sulphite (*ca.* 1g) was added, to destroy any remaining peroxide, and the mixture stirred for a further 15 min. Volatile material was then isolated under reduced pressure and cooled to -15°C, which ensured that the majority of the fluorinated material separated from the solvent, forming a lower layer (0.6g) which contained a single component by GLC, and was identified as dioxin (**179**) by ^{19}F NMR spectroscopy; ^{19}F NMR spectrum 30.

VIII.18 Attempted Epoxidation of Dioxin (179) using *m*-Chloroperoxybenzoic Acid

Dioxin (179) (1.00g, 2.5mmol) was added to a solution of *m*-chloroperoxybenzoic acid (0.88g, 5.1mmol) in dichloromethane (10cm^3), which was refluxed at 45°C for 1d. Volatile material was then collected under reduced pressure, and the lower layer (0.6g) was shown to contain only dioxin (179) by GLC and ^{19}F NMR spectroscopy; ^{19}F NMR spectrum 30.

VIII.19 Preparation of 2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane Platinum(0)-ethene

DIOP-platinum-(II)-dichloride (191mg, 0.25mmol) was dissolved in dried dichloromethane (4cm^3) and dried ethanol (4cm^3), and the solution cooled to -78°C. A fierce stream of ethene was bubbled through the solution. Sodium borohydride (21.9mg, 0.6mmol) was dissolved in dried ethanol (4cm^3) and also cooled to -78°C, before being slowly injected into the solution of the platinum complex. The mixture was stirred at -78°C under a stream of ethene for 1h, then slowly allowed to warm to room temperature. At the first sign of darkening (*ca.* -20°C) the solution was transferred into degassed, dried ethanol (30cm^3) and, after 15 min, the product precipitated as off white micro-crystals (90mg, 50%); δ_H (250MHz, $CDCl_3$, $SiMe_3$) 7.65 (4H, m, ArH), 7.50 (4H, m, ArH), 7.37 (12H, m, ArH), 3.87(2H, m, CH_2), 3.43 (2H, m, CH_2), 2.45 (2H, m), 2.10 (2H, m, CH_2), 1.80 (2H, m, CH_2), 1.31 (6H, s, $C(CH_3)_2$), which was consistent with literature values.[207]

VIII.20 Attempted Derivatisation of Dioxin (179) using Chiral Shift Reagents

In two separate NMR scale experiments, tris[3-(heptafluoropropylhydroxymethylene)-(+)-caphorato], europium (III) (Eu-FOD, from Aldrich) and freshly prepared 2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane platinum(0)-ethene (*ca.* 20mg) were added, under an atmosphere of nitrogen, to dioxin (**179**) (*ca.* 40mg) which was previously dissolved in deuterated dichloromethane. The shift reagents were mixed until dissolved, and the solutions transferred to NMR tubes, again under nitrogen. Examination of the ^{19}F NMR spectra from both experiments revealed only the starting dioxin (**179**), and there was no evidence for interaction with the double bond; ^{19}F NMR spectrum 30.

VIII.21 Attempted Addition of Bromine to Dioxin (179)

Bromine (0.03g, 0.2mmol) was added under nitrogen, by pipette, to a quartz NMR tube (I.D. 4mm), and dioxin (**179**) (0.08g, 0.2mmol) was then condensed into the tube, which was sealed under vacuum. After irradiation with ultraviolet light (Hanovia UVS 1000W medium pressure lamp), for 1d, only (**179**) was identified after examination of the ^{19}F NMR spectrum; spectrum 30.

VII.22 Attempted Electrophilic Ring Opening of Diepoxide (162)

A Carius tube (60cm^3) was charged, under nitrogen, with freshly distilled antimony pentafluoride (SbF_5) (6.50g, 29.8mmol) and octafluorotoluene (4.80g, 20.3mmol). Diepoxide (**162**) (2.00g, 5.1mmol) was then condensed into the tube, which was sealed under vacuum and heated at 130°C for 19 hrs. Volatile material (6.0g) was then isolated under reduced pressure, and identified as a mixture of octafluorotoluene and diepoxide (**162**) by comparison of the ^{19}F NMR data with that of authentic samples; NMR spectrum 27. The same procedure was repeated without the octafluorotoluene, attempting to use antimony pentafluoride as the attacking electrophile, without success.

Chapter Nine
Experimental to Chapter Five

IX.1 The Synthesis of Hexakis(trifluoromethyl)cyclopentadiene (181)

Samples of 1,1,3,3,3-pentafluoropropene (2.20g, 16.7mmol), perfluoro-3,4-dimethyl-2,4-diene (**106**) (3.00g, 8.3mmol) and dry acetonitrile (5 cm^3) were condensed into a Carius tube (60 cm^3), containing dried caesium fluoride (5.00g, 32.9mmol), which was then sealed under reduced pressure and rotated, using a mechanical arm, at ambient temperature for 48 hrs. Volatile material was then isolated under vacuum, and the lower layer contained one component (by GLC) which was identified as hexakis(trifluoromethyl)cyclopentadiene (**181**) (2.9g, 6.1mmol, 74%) (Found: C, 27.6; F, 72.3. $C_{11}F_{18}$ requires C, 27.8; F, 72.2%); $\lambda_{max}(CH_2Cl_2)$/nm 253 (ε/dm^3 mol^{-1} cm^{-1} 1674); NMR spectra 37; IR spectrum 27; Mass Spectrum 33. The upper solvent layer was found to contain 1,1,1,3,3,3-hexafluoropropane; δ_F(250 MHz; CH_3CN; $CFCl_3$) 62.9 (s); m/z 133 (M^+-19).

Distilled water (10 cm^3) was then added to the involatile material, and a lower layer formed (1.76g), which contained two resolved components by GLC (28% and 72%), both with m/z=586 as the highest value. The ^{19}F NMR spectrum showed *ca.* eleven CF_3 resonances (54-80 p.p.m.), and several which could be attributed to a CF_2 group (98-108 p.p.m.). Preparative scale gas chromatography was attempted to separate the components, with only limited success; IR spectrum 28.

IX.2 Epoxidation of Hexakis(trifluoromethyl)cylopentadiene (181) using Calcium Hypochlorite

Diene (**181**) (0.62g, 1.31mmol) was added dropwise to a stirred mixture of calcium hypochlorite (0.60g, 4.20mmol) and acetonitrile (3cm^3), and the reaction mixture was heated under reflux, at 90°C, for 5 hrs. Volatile material was then isolated under reduced pressure and the lower layer (0.45g, 70%) was identified as an inseparable mixture of *trans-perfluorohexakis(trifluoromethyl)-2,4-diepoxycyclopentane* (**174a**) (86% calculated by ^{19}F NMR) (Found: C, 25.9; F, 67.2; $C_{11}F_{18}O_2$ requires C, 26.1, F 67.6; M, 506); NMR spectrum 39; IR spectrum 22; Mass spectrum 34 and *cis-perfluorohexakis(trifluoromethyl)-2,4-diepoxycyclopentane* (**174b**) (14% calculated by ^{19}F NMR); NMR spectrum 39; IR spectrum 22; Mass spectrum 34.

IX.3 Epoxidation of Isomers (189) and (190) using Calcium Hypochlorite

A mixture of calcium hypochlorite (1.40, 9.8mmol) and acetonitrile (5cm^3) was heated under reflux, and the isomers (**189**) and (**190**) (1.00g, 1.7mmol) were then added. After 48 hrs volatile material was collected under reduced pressure and a lower layer (0.7g, 66%) was isolated. This was shown to comprise of two components by GLC, which both gave mass spectra fragmentation patterns which indicated that two oxygen atoms had added; m/z=599 (M$^+$-19). The ^{19}F NMR spectrum of the mixture was complex, but showed chemical shifts that are characteristic of CF_3 and CF_2 groups. No separation of these components was attempted.

IX.4 Reaction between Diene (181) and Caesium Fluoride

Dry caesium fluoride (0.58g, 3.8mmol) and freshly distilled tetraglyme (5cm^3) were added, under nitrogen, to a sealable round bottomed flask. Diene (**181**) (0.50g, 1.1mmol) was then condensed into the flask, which was sealed under vacuum and allowed to warm to ambient temperature. A deep red colouration immediately developed, intensifying as the flask warmed, and the reaction stirred for 24 hrs, after which a small amount of volatile material was isolated under reduced pressure. The ^{19}F NMR spectrum of this was extremely complex, showing resonances in the chemical shift regions of CF_3, CF_2 and C-F moieties. The GLC-MS showed >17 peaks, and the mass spectra remain unassigned. Similarly, the involatile material also gave a complex, unassignable, ^{19}F NMR spectrum, and the addition of BF_3-etherate to the NMR sample did not simplify the spectrum. No further work-up was attempted.

IX.5 Attempted Dehydrogenation of 9,10-dihydroanthracene with Diene (181)

Diene (**181**) (0.50g, 1.1mmol) was condensed, under reduced pressure, into a quartz tube (*ca.* 60cm^3) containing 9,10-dihydroanthracene (0.19g, 1.1mmol) and diethyl ether (8cm^3), which was heated in a furnace for 24 hrs. Volatile material was isolated under reduced pressure, and contained only diene (**181**) and solvent by NMR spectroscopy; NMR spectrum 37. The solid residue was found to be 9,10-dihydoanthracene by comparison of the ^{1}H NMR spectrum with that of an authentic sample.

IX.6 Attempted Reaction between Diene (106) and Heptafluorobut-2-ene (192), at Room Temperature

Diene (**181**) (3.00g, 8.3mmol) and alkene (**192**) (1.66g, 9.1mmol) were condensed, under reduced pressure, into a quartz Carius tube (60cm^3), which contained dry caesium fluoride (5.10g, 33.6mmol) and acetonitrile (10cm^3), which was then sealed under vacuum. This was rotated, using a mechanical arm, for 5 d at room temperature, and volatile material was then isolated under reduced pressure. The fluorinated components were subsequently identified as diene (**181**) and alkene (**192**) by ^{19}F NMR spectroscopy; NMR spectra 37 and 42, respectively.

IX.7 Reaction between Diene (106) and Heptafluorobut-2-ene, using Heat

Heptafluorobut-2-ene (1.94g, 10.7mmol) was condensed into an autoclave tube (150cm^3) which was previously charged with dry acetonitrile (25cm^3), diene (**106**) (3.02g, 8.3mmol), and a large excess of dry caesium fluoride (7.77g, 51.2mmol). The tube was then heated in a furnace at 100°C, for 48 hours. After this time, the tube was allowed to cool and volatile material was isolated under reduced pressure and analysed by ^{19}F NMR spectroscopy, which revealed a mixture of heptafluorobut-2-ene (**192**, ^{19}F NMR spectrum 42), perfluorotetramethylfuran (**116**, ^{19}F NMR spectrum 8) and perfluoro-1,2,3,4-tetramethylcyclobutene (**191**, ^{19}F NMR spectrum 41) by comparison with the data from authentic samples. A dark brown liquid was isolated by pipette, filtered, and the filtrate was combined with washings from the tube (3x10cm^3 of acetone). Solvent was then removed, under reduced pressure, to give a brown oil which crystallised over 14 d. This partially crystalline oil was then washed with dichloromethane (15cm^3) to give an off white powder, and analysis by ^{19}F NMR spectroscopy and FAB mass spectrometry identified the powder as caesium pentakis(trifluoromethyl)cyclopentadienyl (**182**) (1.9g, 43%); NMR spectrum 40; IR spectrum 26; Mass spectrum 35.

IX.8 Reaction of Diene (181) with Tetraethylammonium Iodide

Tetraethylammonium iodide (0.49g, 1.91mmol) was added to dry acetonitrile (10cm^3), and heated under reflux at 80°C. Diene (**181**) (1.00g, 2.11mmol) was then slowly added, with the formation of a red colour, and the mixture refluxed for 48 hrs, after which the solution was cooled and filtered. Solvent was then removed under reduced pressure and the residue redissolved in dichloromethane (10cm^3), which was then washed with a saturated solution of sodium metabisulphite (10cm^3 of water) in order to remove any iodine which was present. The lower layer was then isolated, combined with hexane (10cm^3) and refrigerated (-15°C) for two days. Colourless crystals formed, which were identified as *tetraethylammonium pentakis(trifluoromethyl)cyclopentadienyl* (**183**) (0.85g, 1.59mmol, 75%), m.p. 236°C (Found: C, 40.2; H, 3.8; N, 2.5. $C_{18}H_{20}F_{15}N$ requires C, 40.4; H, 3.7; N, 2.6%); NMR spectrum 43; IR spectrum 29; Mass spectrum 37.

IX.9 Reaction of Diene (181) with Tetrapropylammonium Iodide

Tetrapropylammonium iodide (0.59g, 1.89mmol) was added to dry acetonitrile (10cm^3), which was refluxed at 80°C. Diene (**181**) (1.00g, 2.11mmol) was then slowly added, with the formation of a red colour, and the mixture refluxed for 48 hrs, after which the solution was cooled and filtered. Solvent was then removed under reduced pressure and the residue redissolved in dichloromethane (10cm^3), which was then washed with a saturated solution of sodium metabisulphite (10cm^3 of water) in order to remove any iodine which was present. The lower layer was then isolated, combined with hexane (10cm^3) and refrigerated (-15°C) for two days. Colourless crystals were isolated and identified as *tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienyl* (**184**) (0.90g, 1.47mmol, 73%), m.p. 136°C (Found: C, 44.7; H, 4.8; N, 2.5. $C_{22}H_{28}F_{15}N$ requires C, 44.9; H, 4.8; N, 2.4%); NMR spectrum 44; IR spectrum 30; Mass spectrum 38.

IX.10 Reaction of Diene (181) with Tetrabutylammonium Iodide

Tetrabutylammonium iodide (0.70g, 1.90mmol) was added to dry acetonitrile (10cm^3), which was refluxed at 80°C. Diene (**181**) (1.00g, 2.11mmol) was then slowly added, with the formation of a red colour, and the mixture refluxed for 48 hrs, after which the solution was cooled and filtered. Solvent was then removed under reduced pressure and the residue redissolved in dichloromethane (10cm^3), which was then washed with a saturated solution of sodium metabisulphite (10cm^3 of water) in order to remove any iodine which was present. The lower layer was then isolated, combined with hexane (10cm^3) and refrigerated (-15°C) for two days. Colourless cuboidal crystals formed which were identified as *tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienyl* (**185**) (0.95g, 1.47mmol, 70%), m.p. 112°C (Found: C, 48.2; H, 5.4; N, 2.2. $C_{26}H_{36}F_{15}N$ requires C, 48.2; H, 5.6; N, 2.2%); NMR spectrum 45; IR spectrum 31; Mass spectrum 39.

IX.11 Reaction between Tetrabutylammonium Pentakis(trifluoromethyl)-cyclopentadienyl (185) and Concentrated Sulphuric Acid

Concentrated sulphuric acid (20cm^3) was slowly added to salt (**185**) (0.20g, 0.3mmol), which had been powdered. The system was under reduced pressure and the volatile material, which was continually condensed into a cold finger, was identified as 5H-perfluoropentamethylcycopentadiene (**188**) (0.08g, 64%); NMR spectra 46; Mass spectrum 40. The ^{19}F NMR data was consistent with that reported by Lemal.[232]

IX.12 Reaction of Diene (181) with Tetrakis(dimethylamino)ethene (107)

Diene (**181**) (0.50g, 1.05mmol) was cooled to 0°C and, under an atmosphere of nitrogen, tetrakis(dimethylamino)ethene (**107**) (0.21g, 1.05mmol) was added dropwise, with stirring. Immediately, a red solid was observed and stirring quickly became impossible. The solid was then warmed to ambient temperature and left for 60 min, after which it was dissolved in dry acetone (30 cm^3) and an insoluble white solid remained, which was filtered and identified as octaoxamidinium difluoride (**122**) [0.1g, 80% based on 50% of amine (**107**) forming the difluoride salt (**122**)] by comparison of the ^{19}F NMR data with that of an authentic sample. Solvent was then removed to give a red solid, which was identified as *octaoxamidinium di[pentakis(trifluoromethyl)cyclopentadienyl]* (**186**) (0.8g, 75%) by NMR spectroscopy and FAB-mass spectrometry; NMR spectrum 47; Mass spectrum 40. Attempted recrystallisations from CH_3CN/petroleum spirit (30-40°C) and CH_2Cl_2/hexane were unsuccessful, and an accurate elemental analysis could not be obtained. When this experiment was repeated in a sealed vessel, volatile material was found to contain trifluoromethane by comparison of the ^{19}F NMR spectroscopy data with that in the literature[101, 245]; δ_F(250MHz, $CFCl_3$) -81.73 (d, $J_{F,H}$ 77.2 Hz, CF_3H).

IX.13 Attempted Reaction between (181) and Tetrathiofulvalene

Tetrathiofulvalene (0.47g, 2.3mmol) was added to a mixture of diene (**181**) (1.00g, 2.1mmol) and acetonitrile (10cm^3), which was heated under reflux for 24 hrs. The reaction was monitored by ^{19}F NMR spectroscopy, and only unreacted diene (**181**) was observed throughout; NMR spectrum 37.

IX.14 Reaction of Diene (181) with Decamethylferrocene

A mixture of decamethylferrocene (0.60g, 1.84mmol) and dry acetonitrile (70 cm^3), were heated under reflux at 85°C. Diene (**181**) (1.00g, 2.1mmol) was then slowly added, and a green colour formed immediately, and turned almost black after 30 seconds. The mixture refluxed for 17.5 hrs, after which the solvent was evaporated to half its volume, and the solution cooled to -30°C for 6 hrs, using a cryostat. No crystalline material was observed, so the solvent was removed, and the resultant residue recrystallised from a minimum of dry acetonitrile to give small, dark green crystals (0.86g, 64%) which were identified as *decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienyl radical anion* (**187**), m.p. >330°C (Found C, 49.2; H, 4.2; Fe, 8.2. $C_{30}H_{30}F_{15}Fe$ requires C, 49.3; H, 4.10; Fe, 7.7); NMR spectrum 48; IR spectrum 32; Mass spectrum 187.

Appendix One

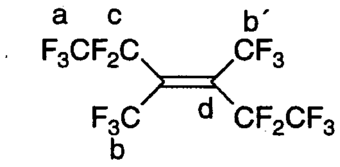
NMR Data

1. *E*-Perfluoro-3,4-dimethylhex-3-ene (**105a**)
2. *Z*-Perfluoro-3,4-dimethylhex-3-ene (**105b**)
3. *Z,Z*-Perfluoro-3,4-dimethyl-2,4-diene (**106a**)
4. *E,Z*-Perfluoro-3,4-dimethyl-2,4-diene (**106b**)
5. Perfluorobicyclopentylidine (**110**)
6. Perfluoro-1,1′-bicyclopent-1-enyl (111)
7. *cis*- and *trans*-Perfluoro-2,5-dihydrotetramethylfuran (**115a,b**)
8. Perfluorotetramethylfuran (**116**)
9. Perfluoro-2,5-di-n-propyloxolane (**117**)
10. Tetrakis(trimethylamino)ethene (**107**)
11. Octamethyloxamidium difluoride (**122**)
12. *Z,Z*-2,5-Di-(butoxy-2-ene)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene (**134a**)
13. *E,Z*-2,5-Di-(butoxy-2-ene)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene (**134b**)
14. *Z,Z*-2,5-bis[oxymethene(diethoxyphosphinol)]-3,4-bis(trifluoromethyl)perfluoro-hexa-2,4-diene (**135a**)
15. *E,Z*-2,5-bis[oxymethene(diethoxyphosphinol)]-3,4-bis(trifluoromethyl)perfluoro-hexa-2,4-diene (**135b**)
16. *Z,Z*-2-ethoxy-[2-ethoxy(2-hydroxy)]-3,4-bis(trifluoromethyl)perfluoro-2,4-diene (**137a**)
17. *E,Z*-2-ethoxy-[2-ethoxy(2-hydroxy)]-3,4-bis(trifluoromethyl)perfluoro-2,4-diene (**137b**)
18. 5-fluoro-6-(perfluoro-3-methylprop-2-ene)-7-difluoro-1,4-dioxep-5-ene (**136**)
19. *Z,Z*-2-Phenoxy-(4-hydroxy)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene (**138a**)
20. *Z,E*-2-Phenoxy-(4-hydroxy)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene (**138b**)
21. *E,E*-2-Phenoxy-(4-hydroxy)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene (**138c**)
22. *E,Z*-2-Phenoxy-(4-hydroxy)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene (**138d**)
23. *p*-Phenylenedioxy-2,2′-bis[*Z,Z*-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] (**139**)
24. (Biphenyl-4,4′-diyldioxy)-2,2′-bis[*Z,Z*-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] (**140**)
25. Bis(trifluoromethyl)methylenedi-*p*-phenylenedioxy-2,2′-bis[*Z,Z*-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] (**141**)
26. Bis(trifluoromethyl)methylenedi-*p*-phenylenedioxy-2,2′-bis[*Z,Z*-5-methoxy-3,4-bis-(trifluoromethyl)perfluorohexa-2,4-diene] (**142**)
27. *Z,Z*-Perfluoro-3,4-dimethyl-2,4-diepoxyhexane (**162**)
28. Perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane (**163a-c**)
29. *E* and *Z*-Perfluoro-3,4-dimethyl-3,4-epoxyhexane (**164a,b**)
30. *trans*- or *cis*-Perfluoro-2,3,5,6-tetramethyl-5,6-dihydo-1,4-dioxin (**179**)
31. *trans*-Perfluoro-2-methylpent-3-ene (**165**)
32. *trans*-Perfluoro-2-methyl-3-epoxypentane (**166**)
33. *trans*-Perfluoro-2,2-dimethylpent-3-ene (**167**)
34. *trans*-Perfluoro-2,2-dimethyl-3-epoxypentane (**168**)
35. Perfluoro-1,2-biscyclobutyl-cyclobutene (**169**)
36. Perfluoro-1′,2′-epoxytercyclobutane (**170**)
37. Hexakis(trifluoromethyl)cyclopentadiene (**181**)

38 *p*-Phenylenedioxy-2,2′-bis[*Z*,*Z*-3,4-bis(trifluoromethyl)perfluoro-2,4-diepoxyhexane] (**172**)

39. *trans*- and *cis*-Perfluorohexakis(trifluoromethyl)-2,4-diepoxycyclopentane (**174a,b**)
40. Caesium pentakis(trifluoromethyl)cyclopentadienyl (**182**)
41. Perfluoro-1,2,3,4-tetramethylcyclobutene (**191**)
42. *Z*-Heptafluorobut-2-ene (**192**)
43. Tetraethylammonium pentakis(trifluoromethyl)cyclopentadienyl (**183**)
44. Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienyl (**184**)
45. Tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienyl (**185**)
46. 5H-perfluoropentamethylcyclopentadiene (**188**)
47. Octaoxamidinium di[pentakis(trifluoromethyl)cyclopentadienyl] (**186**)
48. Decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienyl radical anion (**187**)

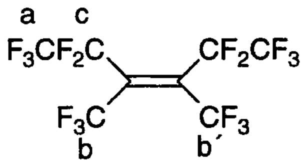
Spectrum No. 1



(105a)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-57.66	tq	$J_{b,c}$ 21.8, $J_{b,a}$ 3.4	3	b
-74.08	*pseudo*-sept	$J_{a,b+b'}$ 3.4	3	a
-99.34	br s	-	2	c
^{13}C data				
118.89	q	J 278.5	-	a or b
112.90	q	J 265.4	-	a or b
110.48	t	J 43.9	-	c
117.94	qt	$J_{d,b}$ 289.2, $J_{d,c}$ 34.3	-	d

Spectrum No. 2



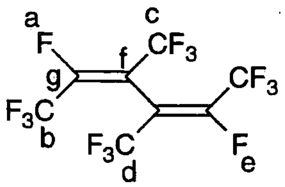
(105b)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-57.15	qt	$J_{b,b'}$ 20.3, $J_{b,c}$ 6.8	3	b
-73.95	*pseudo*-sept	$J_{a,b+b'}$ 6.4	3	a
-99.34	br s	-	2	c

^{13}C data

Spectrum was coincidental with isomer (**105a**)

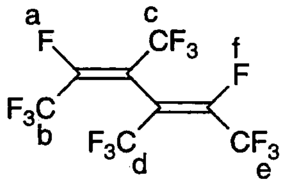
Spectrum No. 3



(106a)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-60.50	d *pseudo*-septets	$J_{c,a}$ 19.2, $J_{c,b+d}$ 1.9	3	c
-68.25	d *pseudo*-septets	$J_{b,a}$ 8.3, $J_{b,c+d}$ 1.7	3	b
-100.94	qq	$J_{a,c}$ 19.3, $J_{a,b}$ 7.5	1	a
^{13}C data				
107.33	qdd	$J_{C,F(c)}$ 38.8, $J_{f,a}$ 17.5, $J_{f,e}$ 5.8	-	f
116.87	qd	$J_{C,F(c)}$ 276.6, $J_{c,a}$ 38.1	-	c
119.89	qd	$J_{C,F(b)}$ 277.3, $J_{b,a}$ 12.6	-	b
152.68	dq	$J_{g,a}$ 291.2, $J_{C,F(b)}$ 40.4	-	g

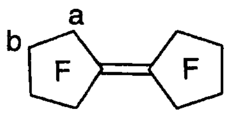
Spectrum No. 4



(106b)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-56.60	overlapping dqq	$J_{d,a+b+d}$ 1.9	3	d
-60.30	dqq	$J_{c,a}$ 18.8, $J_{c,d}$ 2.3, $J_{c,b}$ 1.1	3	c
-67.90	qd	$J_{b,c}$ 10.5, $J_{b,a}$ 7.5	3	e
-68.80	dq	$J_{b,a}$ 7.1, $J_{b,c}$ 2.3	3	b
-97.43	qq	$J_{f,d}$ 14.1, $J_{f,e}$ 3.8	1	f
-102.20	qq	$J_{a,c}$ 19.2, $J_{a,b}$ 6.8	1	a

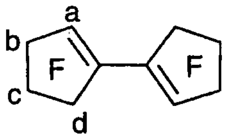
Spectrum No. 5



(110)

Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-110.03	s	-	1	a
-135.59	s	-	1	b

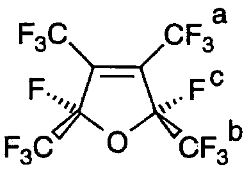
Spectrum No. 6



(111)

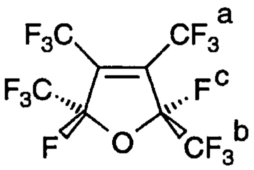
Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-107.20	t	$J_{d,c}$ 15.2	2	d
-109.10	tt	$J_{a,b}$ 44.0, $J_{a,c \text{ or } d}$ 14.7	1	a
-119.07	d	$J_{b,a}$ 14.7	2	b
-129.80	s	-	2	c

Spectrum No. 7



2
(**115a**)

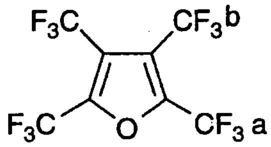
:



1
(**115b**)

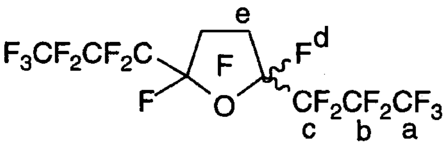
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data: Isomer (**115a**)				
-60.4	s	-	3	a
-82.0	s	-	3	b
-120.0	s	-	1	c
^{19}F data: Isomer (**115b**)				
-59.9	s	-	3	a
-80.5	s	-	3	b
-109.7	s	-	1	c

Spectrum No. 8



Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-57.62	m	-	1	b
-62.40	q	$J_{a,b}$ 9.4	1	a

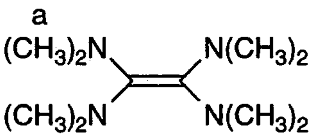
Spectrum No. 9



(117) Two isomers

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-81.42	s	-	3	a
-127.22	d	J_{AB} 259.0	2	b
-131.00	d	J_{AB} 259.0	2	b
-125.52	d	J_{AB} 268.4	2	c
-132.68	d	J_{AB} 268.3	2	c
-121.21	s	-	1	d
-122.55	s	-	1	d
-119.98	d	J_{AB} 307.0	2	e
-123.80	d	J_{AB} 307.0	2	e
-120.51	d	J_{AB} 306.2	2	e
-123.92	d	J_{AB} 306.2	2	e

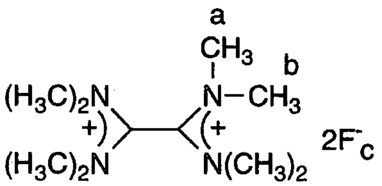
Spectrum No. 10



(107)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
2.45	br s	-	-	a

Spectrum No. 11

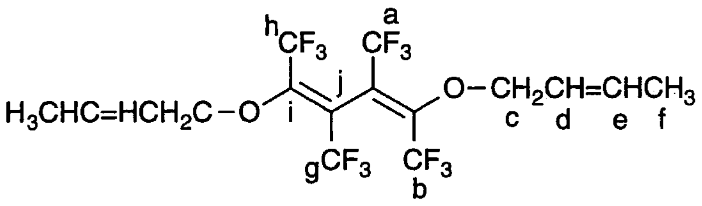


(122)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.2	s	-	1	a or b
3.6	s	-	1	a or b
^{19}F data				
-110.2*	s	-	-	c

* This value moves to higher frequencies when (**122**) is exposed to moisture.

Spectrum No. 12



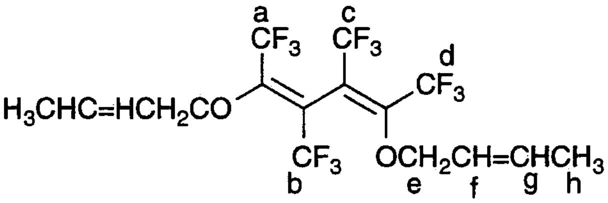
(134a)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
1.75	d	$J_{f,e}$ 6.0	3	f
4.48	dd	$J_{c,d}$ 12.8, $J_{c,e}$ 6.8	2	c
5.70	ABtq	J_{AB} 15.4, $J_{d,c}$ 6.8, $J_{d,f}$ 1.6	1	d
5.88	ABqt	J_{AB} 14.8, $J_{e,f}$ 7.0, $J_{e,c}$ 1.2	1	e
^{19}F data				
-63.86	s	-	1	a
-60.92	q	$J_{b,a}$ 2.1	1	b

^{13}C data

18.00	s	-	-	f
75.95	s	-	-	c
124.20	s	-	-	e
134.05	s	-	-	d
121.25	q	$^{1}J_{CF}$ 212.77	-	g or h
121.05	q	$^{1}J_{CF}$ 276.60	-	g or h
131.70	s	-	-	i or j
132..08	s	-	-	i or j

Spectrum No. 13

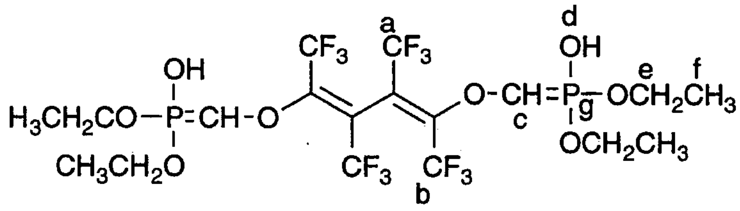


(134b)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
1.75	d	$J_{h,e}$ 5.2	3	f
4.48	*	-	2	e
5.70	m	-	1	f
5.88	m	-	1	g
^{19}F data				
-65.01	s	-	1	a
-60.35	s	-	1	b
-57.29	q	$J_{c,d}$ 11.7	1	c
-64.56	q	$J_{d,c}$ 12.5	1	d

* coincidental with isomer (**134a**)

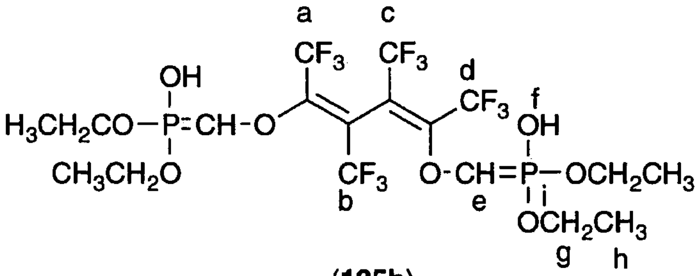
Spectrum No. 14



(135a)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
1.33	t	$J_{f,e}$ 6.8	6	f
2.98	br s	-	1	d
4.19	q of m	$J_{e,f}$ 7.2	4	e
4.48	m	-	1	c
^{19}F data				
-62.37	s	-	1	a
-59.85	q	$J_{b,a}$ 2.3	1	b
^{31}P data (overlapping the resonance for isomer **135b**)				
14.95	s	-	-	g

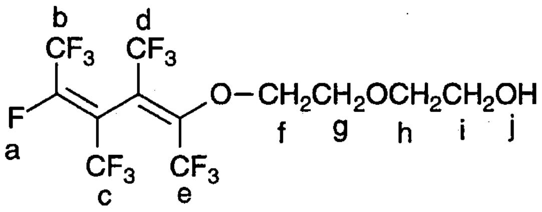
Spectrum No. 15



(135b)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
Spectrum coincidental with isomer (**135a**)				
^{19}F data				
-63.38	s	-	1	a
-59.25	s	-	1	b
-56.32	q	$J_{c,d}$ 12.4	1	c
-63.50	q	$J_{d,c}$ 12.6	1	d

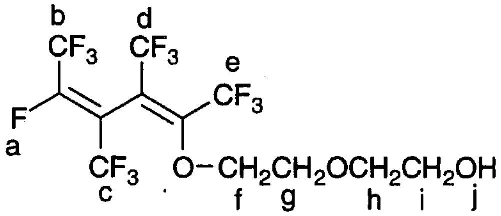
Spectrum No. 16



(137a)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
4.27	dt	$J_{i,j}$ 21.2, $J_{i,h}$ 4.7	2	i
3.82	t	$J_{g,f}$ 4.6	2	g
3.76	t	$J_{h,i}$ 4.6	2	h
3.63	t	$J_{f,g}$ 4.4	2	f
1.77	br s	-	-	j
^{19}F data				
-60.16	s	-	3	e
-61.13	d	$J_{c,a}$ 17.2	3	c
-63.24	s	-	3	d
-68.56	s	-	3	a
-105.79	qq	$J_{a,c}$ 16.4, $J_{a,b}$ 7.9	1	a

Spectrum No. 17

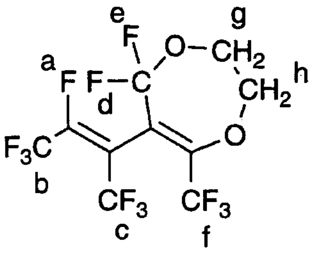


(137b)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
4.29	dt	$J_{i,j}$ 20.7, $J_{i,h}$ 4.1	2	i
3.82	*	-	2	g
3.73	t	$J_{h,i}$ 4.1	2	h
3.58	t	$J_{f,g}$ 4.1	2	f
1.77	br s*	-	-	j
^{19}F data				
-56.38	q	$J_{e,d}$ 12.4	3	e
-60.65	d	$J_{c,a}$ 16.2	3	c
-63.69	q	$J_{d,e}$ 12.4	3	d
-69.47	d	$J_{b,a}$ 7.9	3	b
-108.8	qq	$J_{a,c}$ 16.4, $J_{a,b}$ 7.5	1	a

* coincidental with isomer (**137a**)

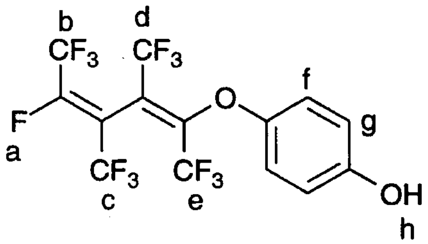
Spectrum NO. 18



(**136**)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
4.25	overlapping m	-	-	g and h
^{19}F data				
-61.14	d	$J_{b,a}$ 16.2	3	c
-68.89	s	-	1	d or e
-69.76	q	$J_{d\text{ or }e,c\text{ or }f}$ 10.9	1	d or e
-70.53	d	$J_{b,a}$ 4.1	3	b
-83.07	m	-	3	f
-107.64	qq	$J_{a,c}$ 16.2, $J_{a,b}$ 8.3	1	a

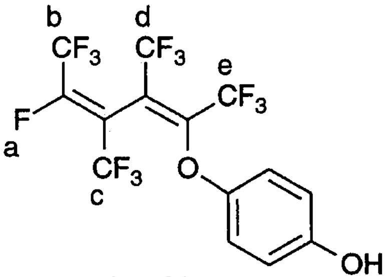
Spectrum No. 19



(138a)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.36	AB	J_{AB} 8.8	2	f
7.32	AB	J_{AB} 8.8	2	g
2.84	br s	-	-	h
^{19}F data				
-61.12	s	-	3	d
-62.34	s	-	3	e
-61.26	d	$J_{c,a}$ 16.2	3	c
-69.61	s	-	3	b
-104.76	qq	$J_{a,c}$ 15.8, $J_{a,b}$ 7.9	1	a

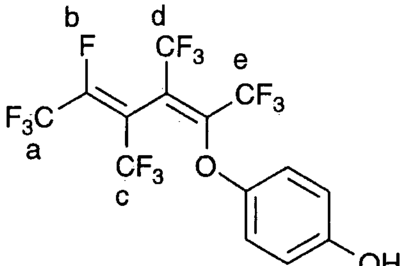
Spectrum No. 20



(138b)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
Spectrum was coincidental with isomer (**138a**)				
^{19}F data				
-58.14	m	containing J 8.0	3	d
-63.50	q	$J_{e,d}$ 6.8	3	e
-60.56	d	$J_{c,a}$ 15.4	3	c
-70.54	d	$J_{b,a}$ 7.2	3	b
-106.41	qq	$J_{a,c}$ 15.4, $J_{a,b}$ 7.9	1	a

Spectrum No. 21



(138c)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment

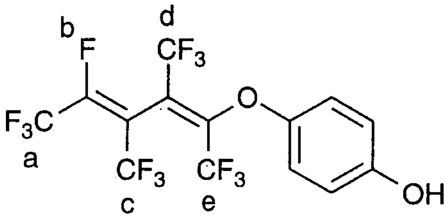
^{1}H data

Spectrum coincidental with isomer (**138a**)

^{19}F data

-57.33	q	$J_{d,e}$ 9.0	3	d
-61.00	s	-	3	e
-63.50	s	-	3	c
-69.25	dq	$J_{b,a}$ 10.5, $J_{b,c}$ 2.1	3	b
-103.03	m	-	1	a

Spectrum No. 22



(138d)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment

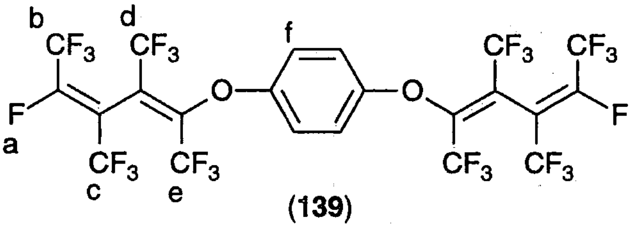
^{1}H data

Spectrum coincidental with isomer (**138a**)

^{19}F data

-56.99	m	containing J 2.2	3	d
-63.30	m	containing J 1.8	3	e
-63.30	dq	$J_{c,a}$ 3.8, $J_{c,d}$ 1.9	3	c
-69.17	s	-	3	b
-101.12	m	-	1	a

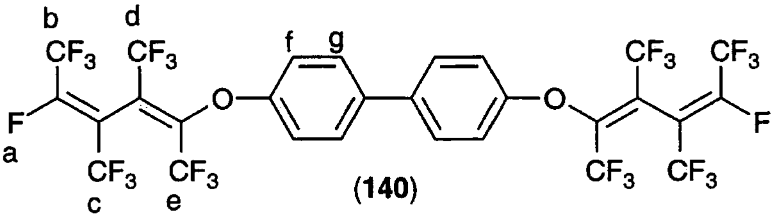
Spectrum No. 23



(139)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.02	s (*pseudo*-AB system)	-	-	f
^{19}F data				
-60.52	d *pseudo*-septets	$J_{c,a}$ 16.2, $J_{c,b+d}$ 1.5	3	c
-60.58	q	$J_{d,e}$ 1.5	3	d
-61.85	q	$J_{e,d}$ 1.1	3	e
-68.93	d *pseudo*-septets	$J_{b,a}$ 4.1, $J_{b,c+d}$ 1.1	3	b
-104.16	qq	$J_{a,c}$ 15.8, $J_{a,b}$ 7.5	1	a

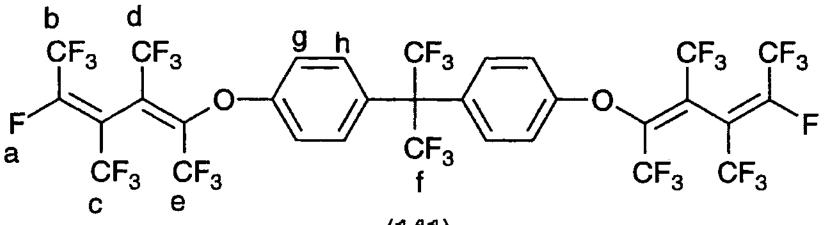
Spectrum No. 24



(140)

Chemical shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.06	AB	J_{AB} 8.6	1	f
7.55	AB	J_{AB} 8.6	1	g
^{19}F data				
-60.14	d	$J_{c,a}$ 23.7	3	c
-60.51	s	-	3	d
-61.75	s	-	3	e
-68.91	dm	$J_{b,a}$ 5.9	3	b
-104.26	qqq	$J_{b,a}$ 23.7, $J_{a,b}$ 7.9, $J_{a,d}$ 1.4	1	a

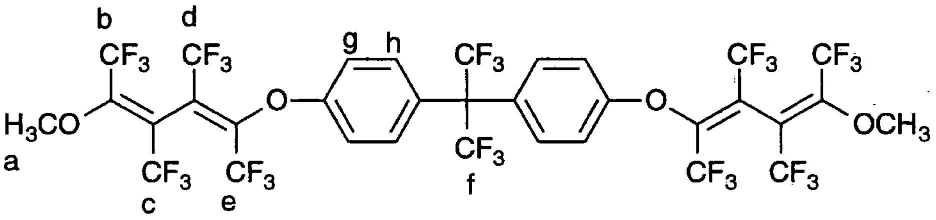
Spectrum No. 25



(141)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.31	AB	J_{AB} 8.8	1	h
7.62	AB	J_{AB} 8.8	1	g
^{19}F data				
-61.14	s	-	6	d and e
-62.62	s	-	3	c
-64.63	s	-	3	f
-69.52	s	-	3	b
-104.52	qq	$J_{a,c}$ 20.5, $J_{a,b}$ 8.3	1	a

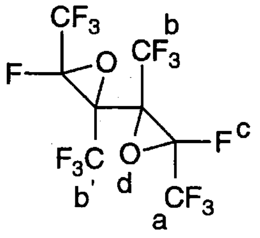
Spectrum No. 26



(141)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.99	s	-	3	a
7.01	AB	J_{AB} 8.4	2	h
7.39	AB	J_{AB} 8.4	2	g
^{19}F data				
-60.20	s	-	1	e
-60.96	s	-	1	c or d
-60.95	s	-	1	c or d
-63.58	s	-	1	b
-64.02	s	-	1	f

Spectrum No. 27

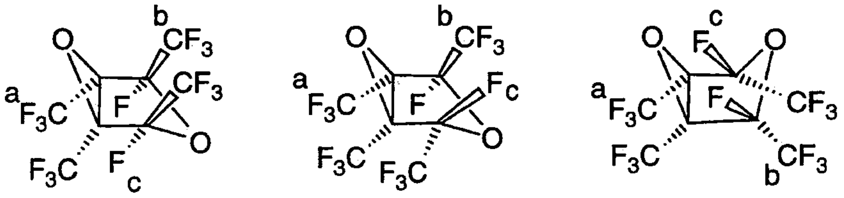


(162)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data*				
-66.08	d *pseudo*-sept	$J_{a,c}$ 16.2, $J_{a,b+b'}$ 2.9	3	a
-76.33	*pseudo*-sept	$J_{b,a+b'}$ 2.4	3	b
-154.70	q	$J_{c,a}$ 15.7	1	c
^{17}O data*				
64.00	br s	-	-	d

* 470MHz spectrum

Spectrum No. 28



(163a-c)

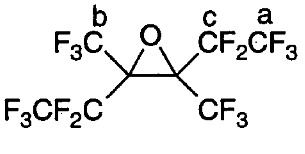
Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data-Isomer `a´				
-63.87	q	$J_{b,a}$ 7.9	3	b
-79.10	m	-	3	a
-122.08	m	-	1	c
^{19}F data-Isomer `b´				
-66.25	s	-	3	b
-80.58	s	-	3	a
-127.10	s	-	1	c

^{19}F data-Isomer `c´

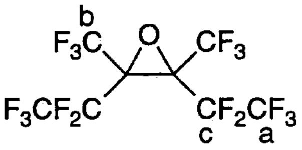
-66.65	m	containing *J* 9.0	3	b
-81.55	s	-	3	a
-135.57	m	-	1	c

NB Resonances were allocated to the isomers by the relative integration of the ^{19}F NMR peaks

Spectrum No. 29



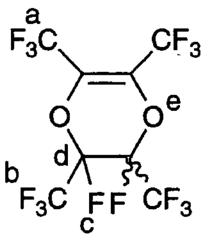
E-isomer (**164a**)



Z-isomer (**164b**)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data:*Z*-isomer				
-63.50	br s	-	3	a
-76.56	br s	-	3	b
-104.91	br s	-	2	c
^{19}F data:*E*-isomer				
-64.22	br s	-	3	a
-77.93	br s	-	3	b
-108.44	m	-	2	c

Spectrum No. 30

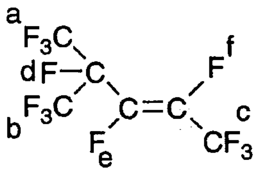


(173)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data*				
-66.76	qd	$J_{a,b}$ 5.0, $J_{a,c}$ 2.4	3	a
-77.30	dq	$J_{b,c}$ 11.0, $J_{b,a}$ 4.3	3	b
-151.24	qq	$J_{c,b}$ 10.5	1	c
^{13}C data†				
89.60	dq	$J_{d,c}$ 298.8, $J_{d,b}$ 47.8	-	d
^{17}O data*				
66.65	br s	-	-	e

* 470MHz spectrum; † 125MHz spectrum

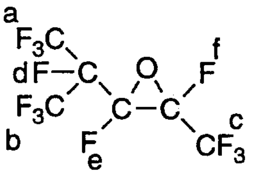
Spectrum No. 31



E-(**165**)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-68.92	dd	$J_{c,f}$ 21.8, $J_{c,e}$ 9.0	3	c
-75.65	m	containing J 4.9	6	a+b
-156.74	AB spectrum	J_{AB} 137.6	1	e or f
-158.93	AB spectrum	J_{AB} 137.6	1	e or f
-188.22	m	containing J 7.9	1	d

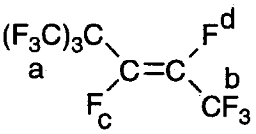
Spectrum No. 32



E-(**166**)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-73.70	qd	$J_{a,b}$ 8.3, $J_{a,d}$ 2.3	3	a or b
-75.43	qd	$J_{b,a}$ 8.7, $J_{b,d}$ 2.3	3	b or a
-75.93	dd	$J_{c,f}$ 11.8, $J_{c,e}$ 2.1	3	c
-147.71	dq	$J_{f,e}$ 19.9, $J_{f,c}$ 10.5	1	f
-156.87	dm	$J_{e,d}$ 31.6	1	e
-184.65	dq	$J_{d,e}$ 32.9, $J_{d,a\ \mathrm{or}\ b}$ 7.9	1	d

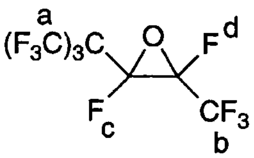
Spectrum No. 33



E-(**167**)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-62.53	dd	$J_{a,c}$ 17.3, $J_{a,d}$ 12.0	9	a
-67.52	dd	$J_{b,d}$ 21.8, $J_{b,c}$ 7.5	3	b
-148.74	ABm	J_{AB} 144.3	1	c
-150.23	ABm	J_{AB} 144.3	1	d

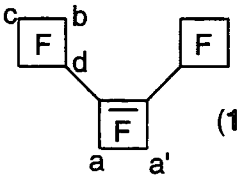
Spectrum No. 34



E- **(168)**

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-63.17	t	$J_{a,c+d}$ 12.0	9	a
-74.85	d	$J_{b,d}$ 14.7	3	b
-130.50	mdq	$J_{c,d}$ 12.8, $J_{c,b}$ 4.9	1	c
-157.15	qdm	$J_{d,b}$ 25.6, $J_{d,c}$ 12.8	1	d

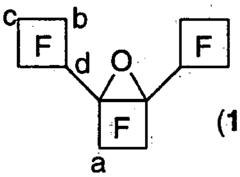
Spectrum No. 35



(169)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-110.33	t	$J_{a,a'}$ 4.0	2	a
-125.49	AB spectrum	J_{AB} 246.4	2	b
-129. 83		J_{AB} 246.4	2	b
-127.32	AB spectrum	J_{AB} 242.4	1	c
-131.11		J_{AB} 242.4	1	c
-178.63	s	-	1	d

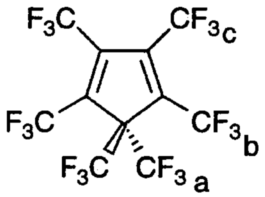
Spectrum No. 36



(170)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-116.33	AB spectrum	J_{AB} 207.6	1	a
-125.05		J_{AB} 207.9	1	a
-127.11	AB spectrum	J_{AB} 239.7	2	b
-129.86		J_{AB} 236.1	2	b
-129.23	AB spectrum	J_{AB} 234.6	1	c
-131.47		J_{AB} 227.5	1	c
-183.21	s	-	1	d

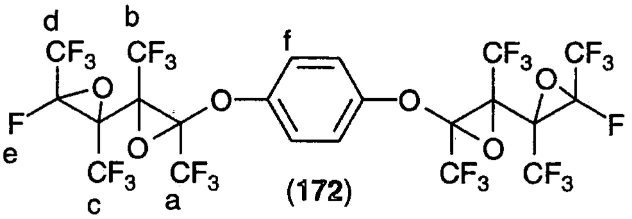
Spectrum No. 37



(181)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-55.58	m	containing $J_{F,F}$ 10.5	1	b
-59.35	pseudo septet	$J_{c,b+c'}$ 10.9	1	c
-59.68	m	containing $J_{F,F}$ 12.4	1	a
^{13}C data				
66.51	s	-	-	a
117.83	q	$J_{C,F}$ 276.5	-	b or c or d
118.83	q	$J_{C,F}$ 274.7	-	b or c or d
120.23	q	$J_{C,F}$ 288.5	-	b or c or d
137.69	q	$J_{C,F}$ 40.7	-	e or f

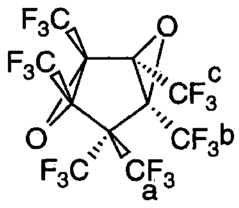
Spectrum No. 38



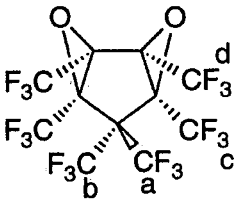
(172)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
7.41	s	-	-	f
^{19}F data				
-58.99	s	-	3	a
-64.19	*pseudo*-septet	$J_{c,d+e}$ 6.0	3	c
-69.38	dqq	$J_{d,e}$ 10.2, $J_{d,c+b}$ 3.4	3	d
-76.52	q	$J_{b,a}$ 5.3	3	b
-155.40	q	$J_{e,c}$ 16.4	1	e

Spectrum No. 39



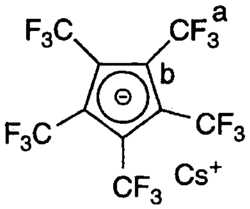
trans- **(174a)**



cis- **(174b)**

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data:*trans* isomer				
-58.22	*pseudo*-septet	$J_{b,c+a}$ 11.3	1	b
-60.78	m	containing J 7.1	1	a
-67.72	m	containing J 6.0	1	c
^{19}F data:*cis* isomer				
-57.10	m	-	1	a or b
-60.42	m	-	1	a or b
-61.49	m	-	2	c
-64.61	m	-	2	d

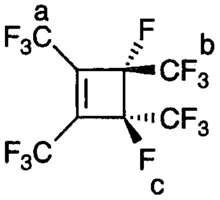
Spectrum No. 40



(182)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-49.74	s	-	-	a
^{13}C data				
124.67	q	$J_{C,F}$ 270.6	-	a
110.63	q	$J_{C,F(a)}$ 19.2	-	b

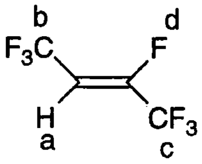
Spectrum No. 41



(191)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{19}F data				
-63.05	m	-	3	a
-71.80	d	$J_{b,c}$ 6.3	3	b
-165.84	m	-	1	c

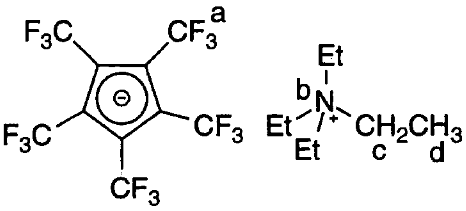
Spectrum No. 42



Z- (**192**)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
5.41	dq	$J_{a,d}$ 28.4, $J_{a,b}$ 5.3	-	a
^{19}F data				
-59.07	dd	$J_{b,d}$ 17.9, $J_{b,a}$ 7.4	3	b
-73.28	d	$J_{c,d}$ 9.5	3	c
-117.10	m	-	1	d

Spectrum No. 43

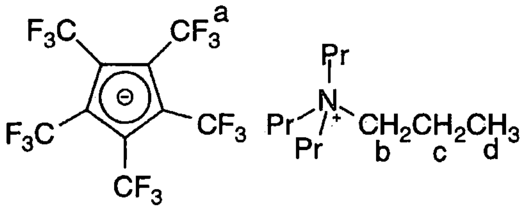


(**183**)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data†				
3.15	q	$J_{c,d}$ 7.2	2	c
1.20	tt	$J_{d,c}$ 7.20, $J_{d,b}$ 1.60	3	d
^{19}F data†				
-50.99	s	-	-	a
^{13}C data* †				
15.67	s	-	-	d
53.04	t	$J_{c,b}$ 2.6	-	c
124.63	q	$J_{C,F}$ 270.9	-	a

* Proton decoupled; † In CD_3CN solvent.

Spectrum No. 44

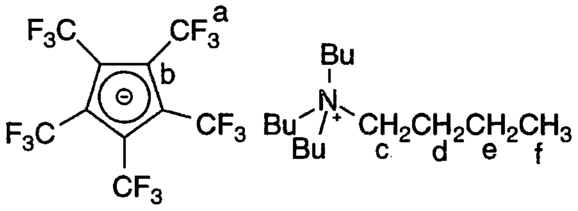


(184)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data†				
0.94	t	$J_{d,c}$ 7.2	3	d
1.65	sextet	$J_{c,b+d}$ 7.6	2	c
3.04	m	-	2	b
^{19}F data†				
-50.99	s	-	-	a
^{13}C data*				
15.28	s	-	-	d
30.95	s	-	-	c
55.20	s	-	-	b
123.31	q	$J_{C,F}$ 269.7	-	a

* Proton decoupled; † In CD_3CN solvent.

Spectrum No. 45

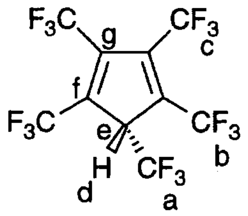


(185)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data†				
0.96	t	$J_{d,e}$ 7.2	3	f
1.35	sextet	$J_{e,f+d}$ 7.6	2	e
1.60	quintet	$J_{d,e+c}$ 8.4	2	d
3.08	m	-	2	c
^{19}F data†				
-50.51	s	-	-	a
^{13}C data* †				
13.13	s	-	-	f
19.22	s	-	-	e
23.43	s	-	-	d
58.46	s	-	-	c
123.57	q	^{J}C,F 269.0	-	a
109.62	q	$J_{C,F(a)}$ 13.4	-	b

* Proton decoupled; † In CD_3CN solvent.

Spectrum No. 46

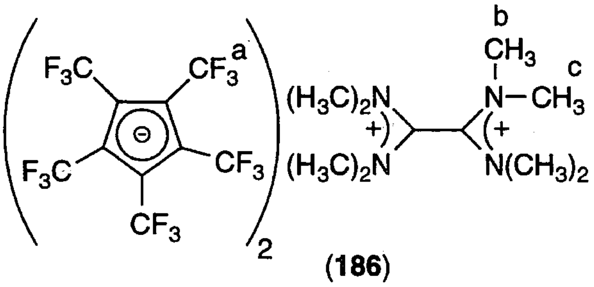


(188)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
4.82	q	$J_{d,a}$ 5.7	-	d
^{19}F data				
-55.99	md	$J_{b,d}$ 3.4	2	b
-59.10	m	-	1	a
-60.20	m	-	2	c
^{13}C data*				
58.37	q	$J_{C,F(a)}$ 32.2	-	e
119.19	q	$J_{C,F}$ 272.7	-	b or c
120.17	q	$J_{C,F}$ 272.4	-	b or c
122.54	q	$J_{C,F}$ 284.2	-	a
139.64	q	$J_{C,F(c\ or\ b)}$ 40.0	-	f or g
139.78	q	$J_{C,Fc\ or\ b)}$ 40.3	-	f or g

* Proton decoupled.

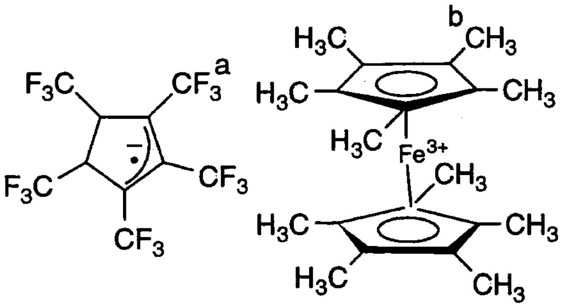
Spectrum No. 47



(186)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data				
3.85	s	-	1	b or c
3.61	s	-	1	b or c
^{19}F data				
-49.74 s	-	-	a	

Spectrum No. 48



(187)

Chemical Shift (ppm)	Multiplicity	Coupling constants (Hz)	Integral	Assignment
^{1}H data†				
5.45	s	-	-	b
^{19}F data†				
-49.73	s	-	-	a
^{13}C data* †				
55.38	s	-	-	b
124.70	q	$J_{C,F}$ 270.8	-	a

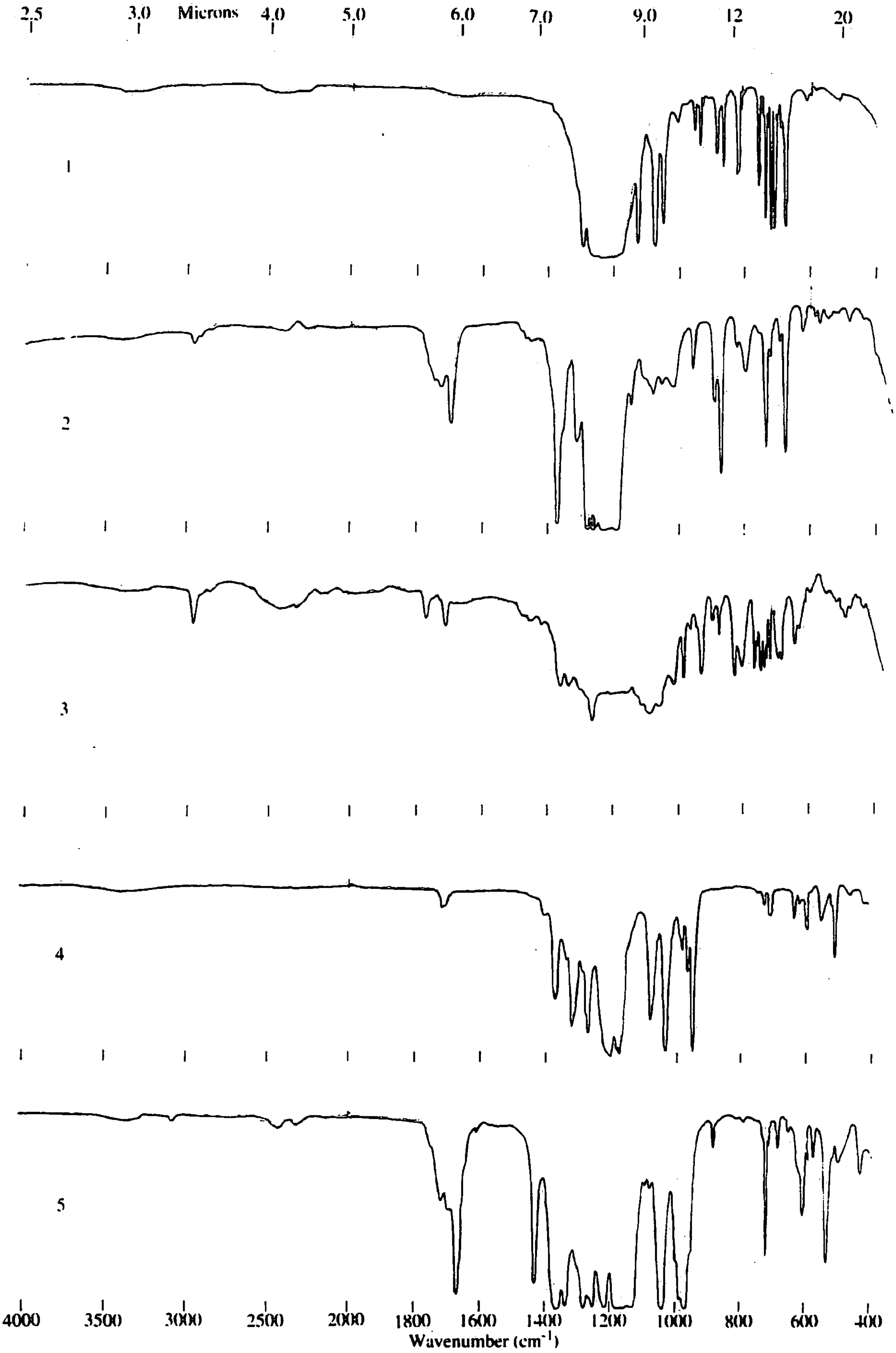
* Proton decoupled; † In CD_3CN solvent.

Appendix Two

Infra Red Spectra

1. *E*- and *Z*-Perfluoro-3,4-dimethylhex-3-ene (**105**)
2. *Z,Z*- and *E,Z*-Perfluoro-3,4-dimethyl-2,4-diene (**106**)
3. *cis*- and *trans*-Perfluoro-2,5-dihydrotetramethylfuran (**115**)
4. Perfluorobicyclopentylidine (**110**)
5. Perfluoro-1,1′-bicyclopent-1-enyl (**111**)
6. Perfluorotetramethylfuran (**116**)
7. *Z,Z*- and *E,Z*-2,5-bis[oxymethene(diethoxyphosphinol)]-3,4-bis(trifluoromethyl)-perfluoro-hexa-2,4-diene (**135a,b**)
8. *Z,Z*- and *E,Z*-2-ethoxy-[2-ethoxy(2-hydroxy)]-3,4-bis(trifluoromethyl)perfluoro-2,4-diene (**137a,b**)
9. *Z,Z*- and *E,Z*-2,5-Di-(butoxy-2-ene)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene (**134a,b**)
10. *Z,Z*-, *Z,E*-, *E,E* -and *E,Z*-2-Phenoxy-(4-hydroxy)-3,4-bis(trifluoromethyl)perfluoro-hexa-2,4-diene (**138a-d**)
11. *p*-Phenylenedioxy-2,2′-bis[*Z,Z*-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] (**139**)
12. (Biphenyl-4,4′-diyldioxy)-2,2′-bis[*Z,Z*-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] (**140**)
13. Bis(trifluoromethyl)methylenedi-*p*-phenylenedioxy-2,2′-bis[*Z,Z*-3,4-bis(trifluoro-methyl)perfluorohexa-2,4-diene] (**141**)
14. Bis(trifluoromethyl)methylenedi-*p*-phenylenedioxy-2,2′-bis[*Z,Z*-5-methoxy-3,4-bis-(trifluoromethyl)perfluorohexa-2,4-diene] (**142**)
15. *E* and *Z*-Perfluoro-3,4-dimethyl-3,4-epoxyhexane (**164a,b**)
16. Perfluoro-1,2-biscyclobutyl-cyclobutene (**169**)
17. Perfluoro-1′,2′-epoxytercyclobutane (**170**)
18. Perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane (**163a-c**)
19. *trans*-Perfluoro-2-methyl-3-epoxypentane (**166**)
20. *trans*-Perfluoro-2,2-dimethylpent-3-ene (**167**)
21. *trans*-Perfluoro-2,2-dimethyl-3-epoxypentane (**168**)
22. *trans*- and *cis*-Perfluorohexakis(trifluoromethyl)-2,4-diepoxycyclopentane (**174a,b**)
23. *Z,Z*-Perfluoro-3,4-dimethyl-2,4-diepoxyhexane (**162**)
24. *trans*- or *cis*-Perfluoro-2,3,5,6-tetramethyl-5,6-dihydo-1,4-dioxin (**179**)
25. *p*-Phenylenedioxy-2,2′-bis[*Z,Z*-3,4-bis(trifluoromethyl)perfluoro-2,4-diepoxy-hexane] (**172**)
26. Caesium pentakis(trifluoromethyl)cyclopentadienyl (**182**)
27. Hexakis(trifluoromethyl)cyclopentadiene (**181**)

28. Perfluoro-3,3,7,7-tetramethyl-[3.3.0]-oct-1,4-diene (**189**) and perfluoro-1,1′-bicyclo-2,2′,3,3,3′,3′-hexamethyl-1-enyl (**190**) (plus another isomer)
29. Tetraethylammonium pentakis(trifluoromethyl)cyclopentadienyl (**183**)
30. Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienyl (**184**)
31. Tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienyl (**185**)
32. Decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienyl radical anion (**187**)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5.0
6.0
7.0
9.0
12
20
1
2
3
4
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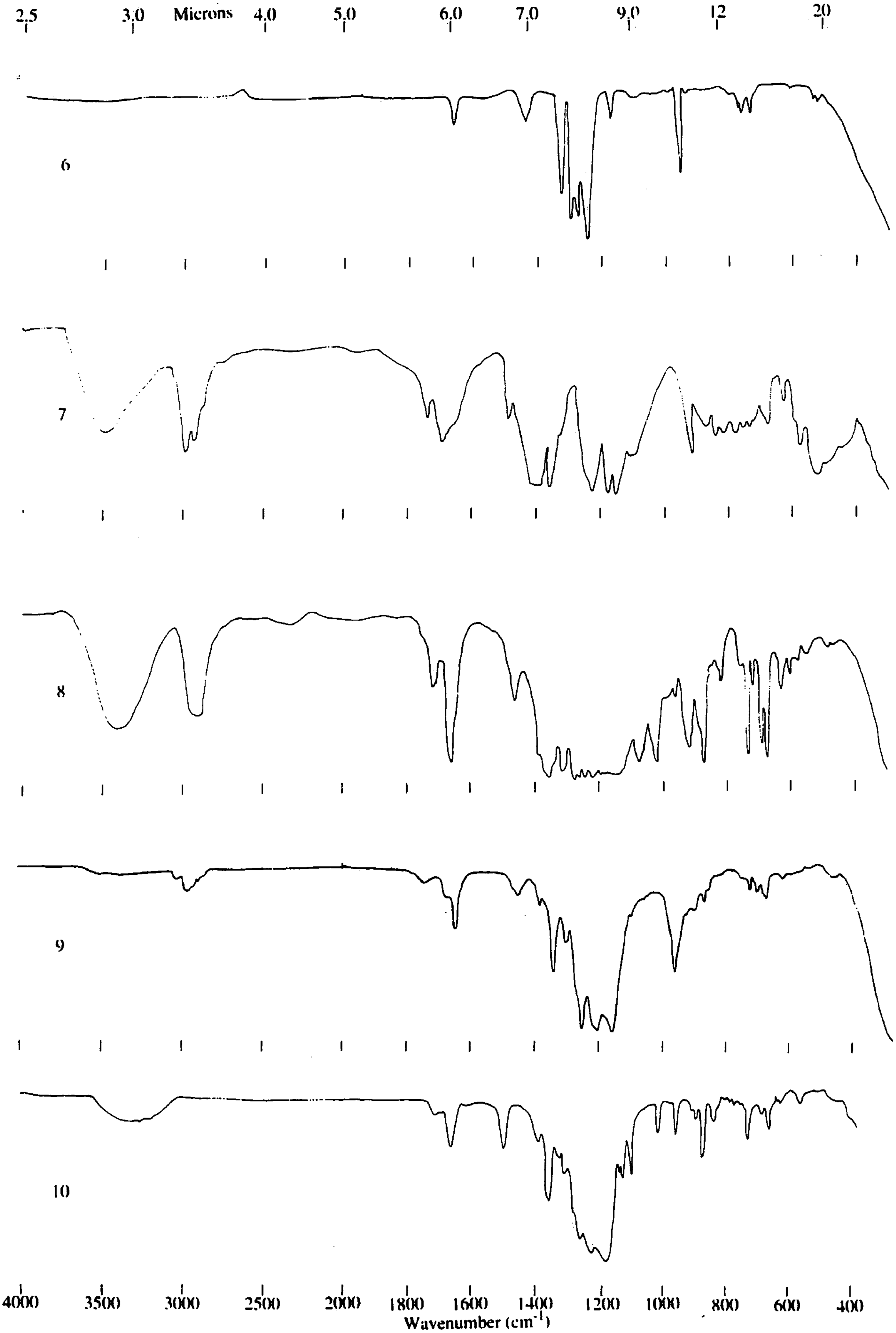
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber (cm^{-1})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Microns
4.0
5.0
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7.0
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6
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3000
2500
2000
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1200
1000
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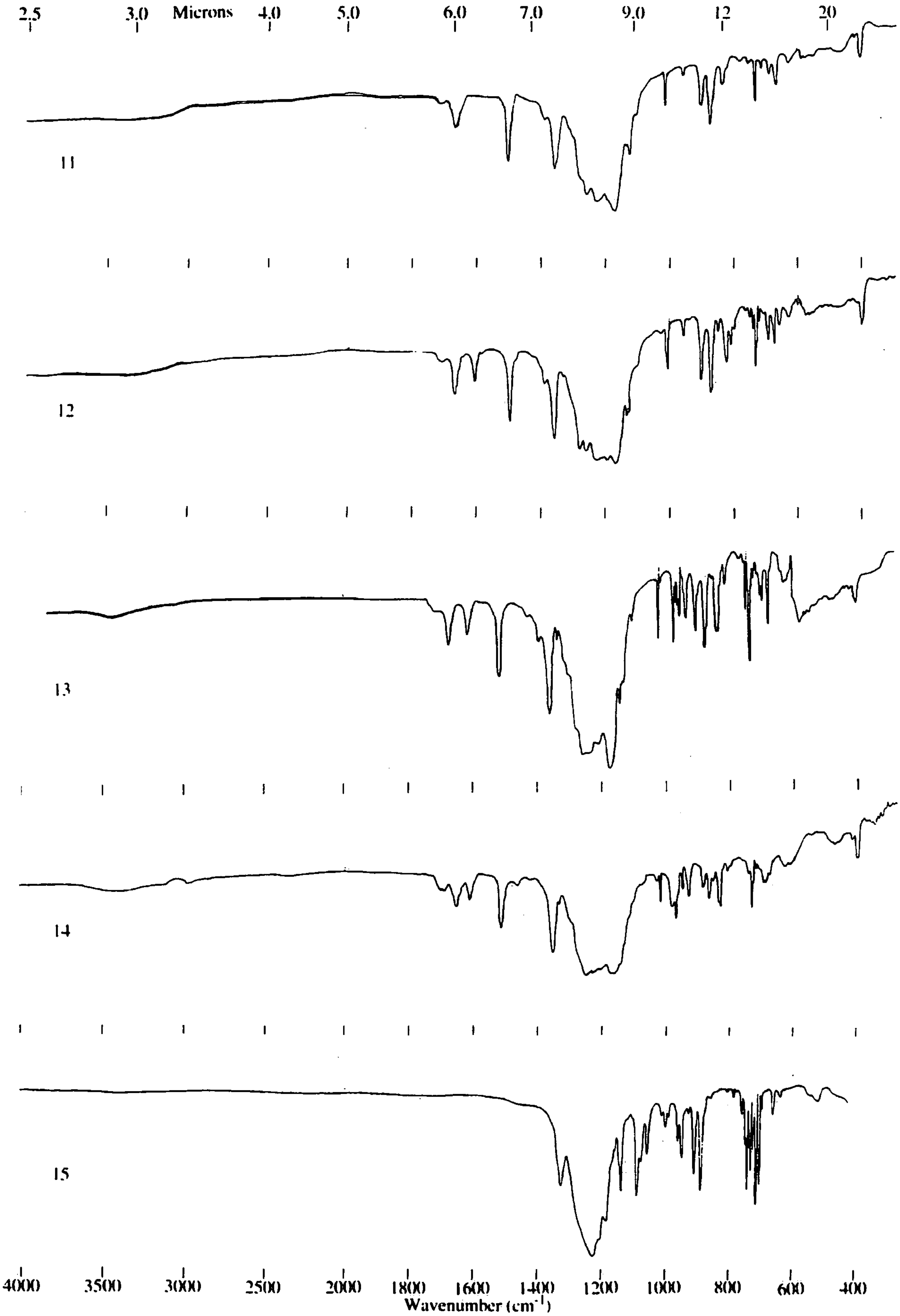
Wavenumber (cm^{-1})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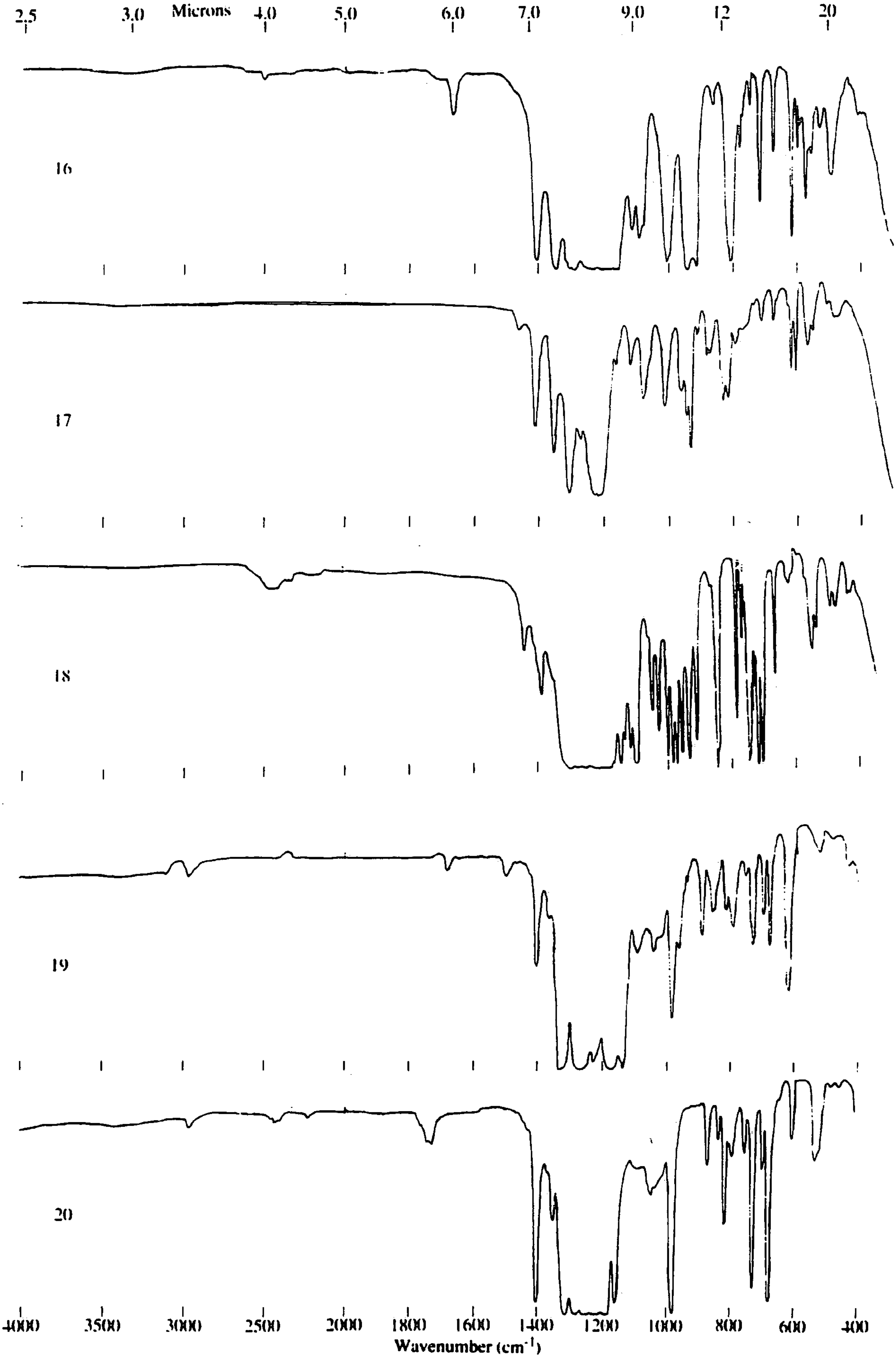
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber (cm^{-1})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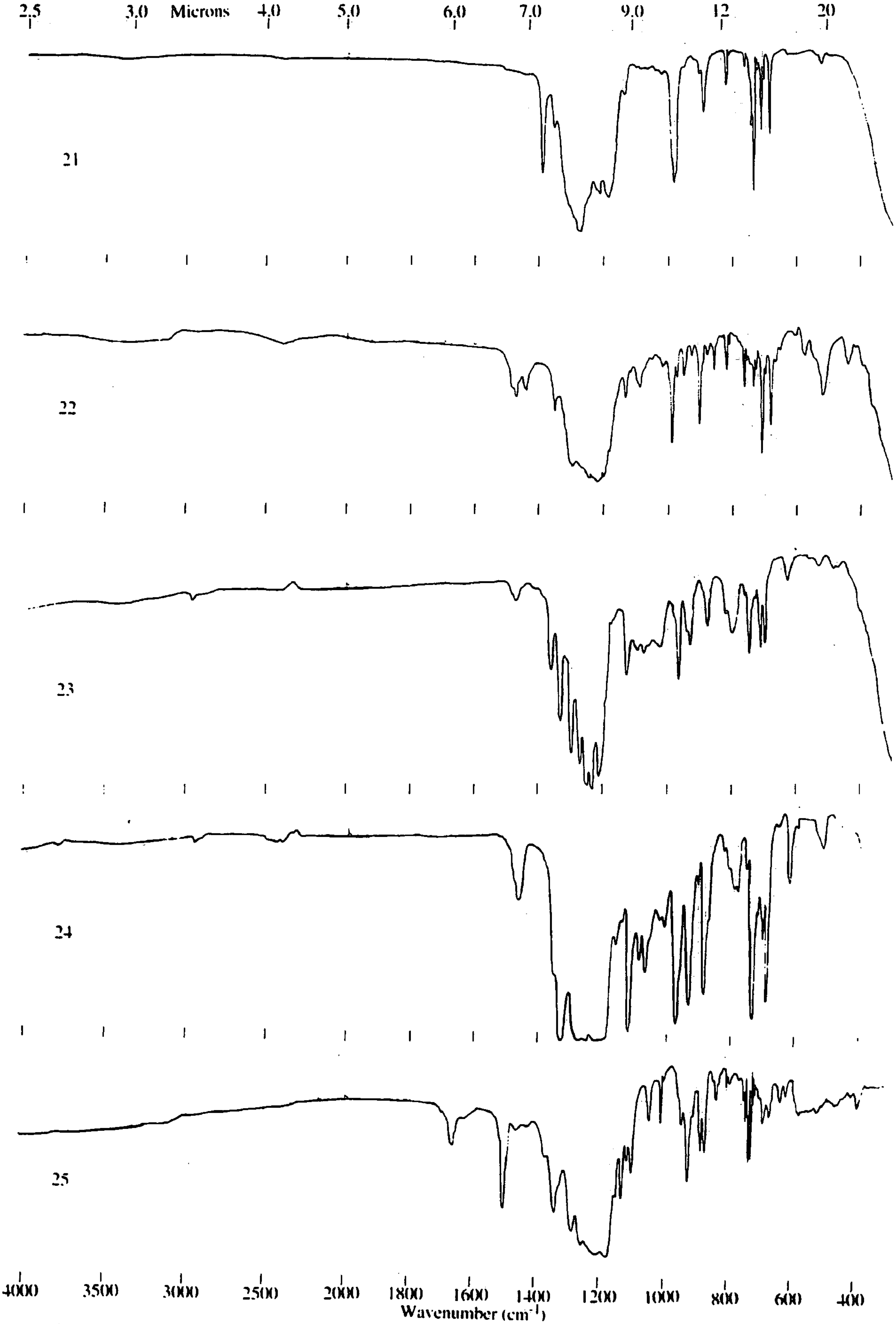
600
400
Wavenumber (cm^{-1})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1200
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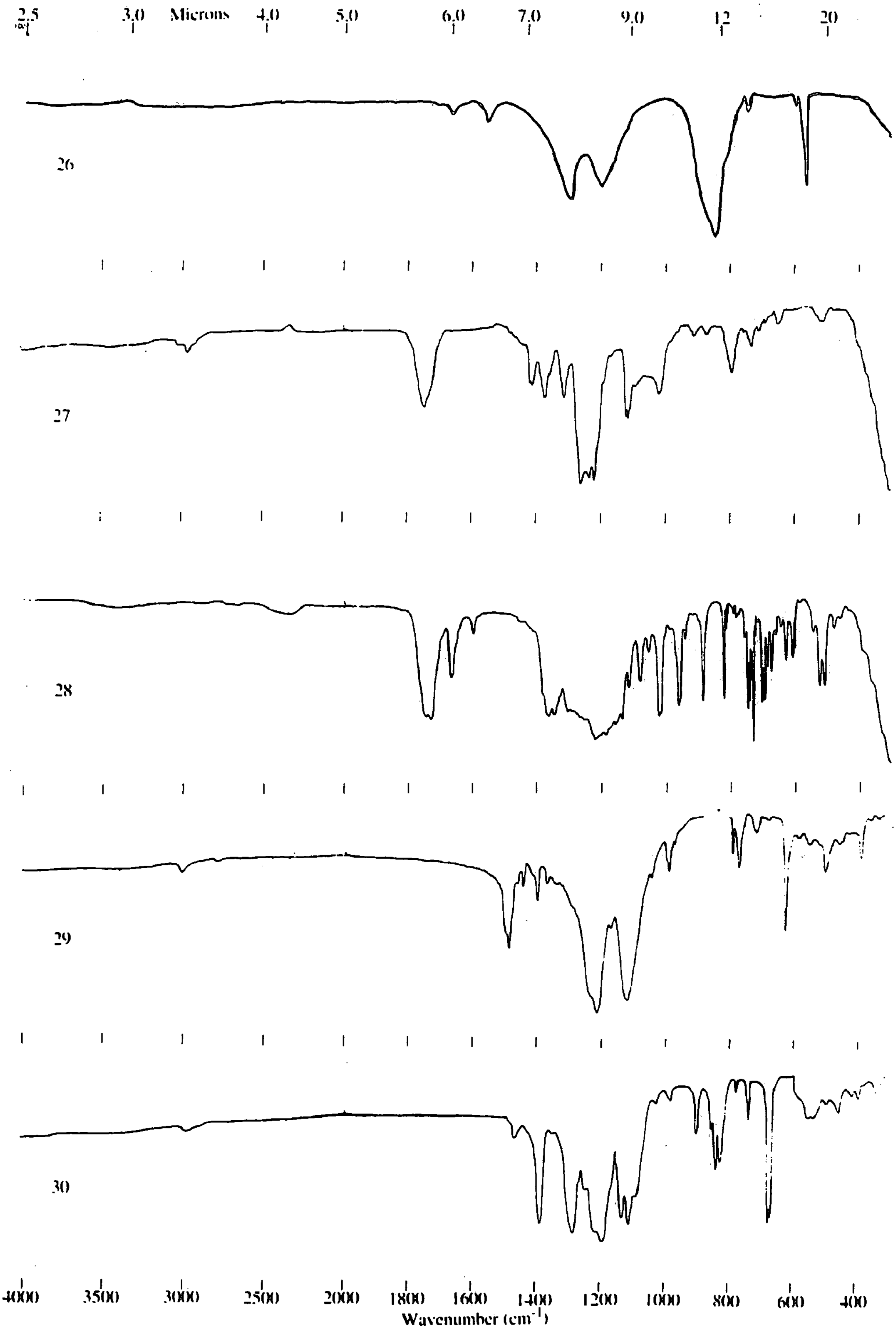
600
400
Wavenumber (cm^{-1})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3000
2500
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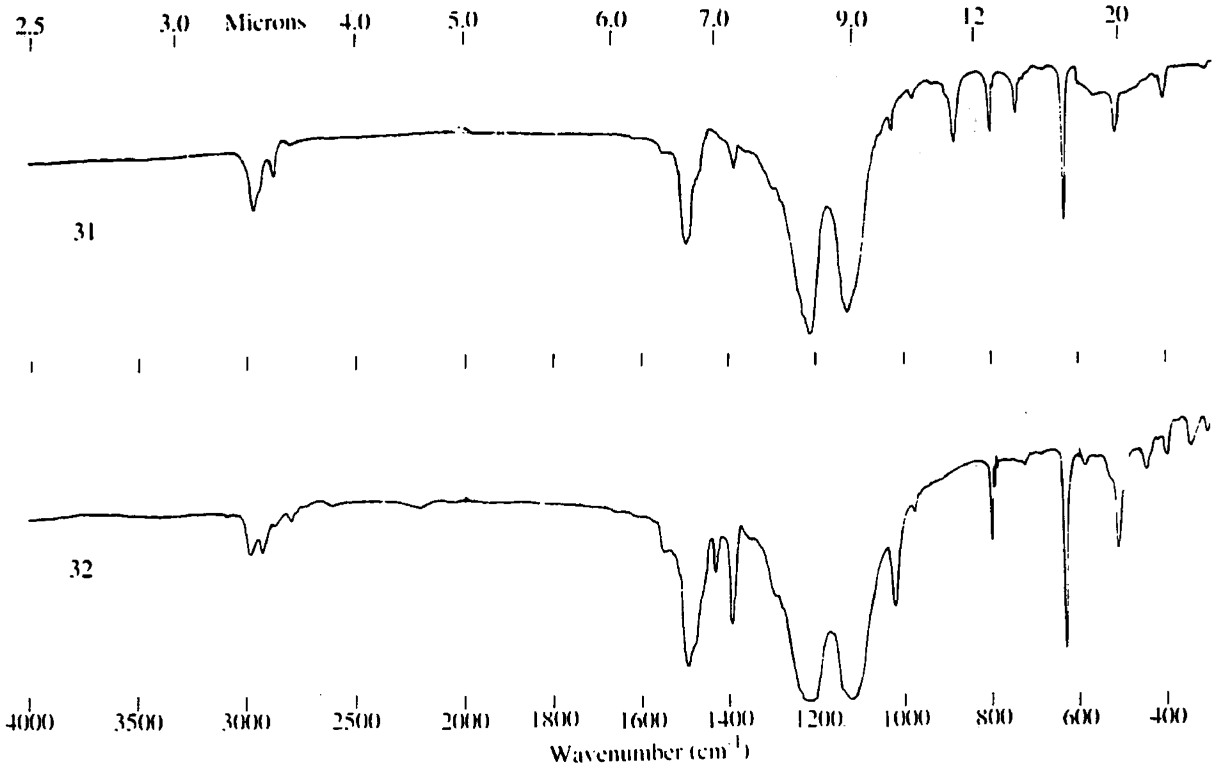
1600
1400
1200
1000
800
600
400
Wavenumber (cm^{-1})


Microns
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6.0
7.0
9.0
12
20
31
32
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber (cm^{-1})

Appendix Three

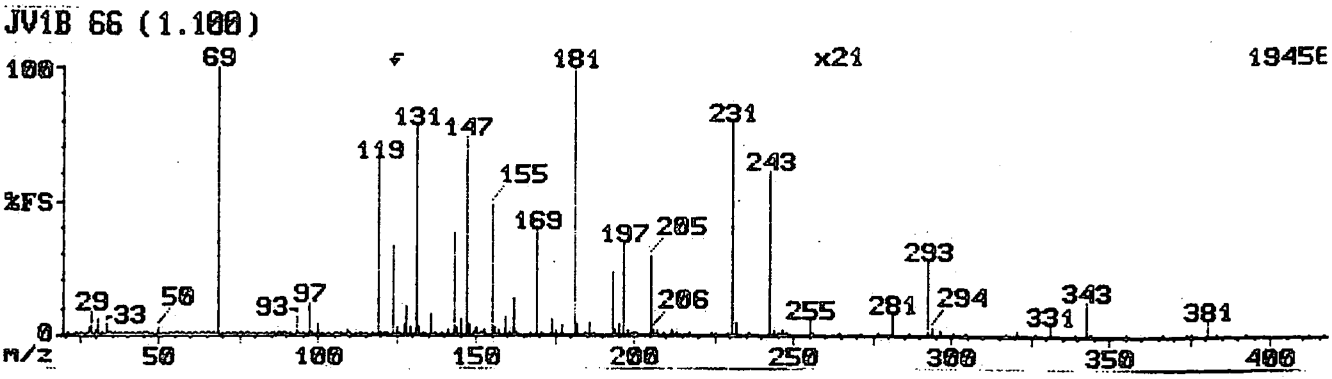
Mass Spectra
(EI unless stated otherwise)

1. *E*-Perfluoro-3,4-dimethylhex-3-ene (**105a,b**)
2. *Z,Z*-Perfluoro-3,4-dimethyl-2,4-diene (**106a**)
3. *E,Z*-Perfluoro-3,4-dimethyl-2,4-diene (**106b**)
4. Octamethyloxamidium difluoride (**122**)
5. *cis*- and *trans*-Perfluoro-2,5-dihydrotetramethylfuran (**115a,b**)
6. Perfluorotetramethylfuran (**116**)
7. Perfluorobicyclopentylidine (**110**)
8. Perfluoro-1,1′-bicyclopent-1-enyl (**111**)
9. Monohydrogenated diene (**130**)
10. Dihydrogenated diene (**131**)
11. Trihydrogenated diene (**132**)
12. Tetrahydrogenated diene (**133**)
13. *Z,Z*- and *E,Z*-2,5-bis[oxymethene(diethoxyphosphinol)]-3,4-bis(trifluoromethyl)-perfluoro-hexa-2,4-diene (**135a,b**)
14. 5-fluoro-6-(perfluoro-3-methylprop-2-ene)-7-difluoro-1,4-dioxep-5-ene (**136**)
15. *Z,Z*- and *E,Z*-2-ethoxy-[2-ethoxy(2-hydroxy)]-3,4-bis(trifluoromethyl)perfluoro-2,4-diene (**137a,b**)
16. *Z,Z*- and *E,Z*-2,5-Di-(butoxy-2-ene)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene (**134a,b**)
17. *Z,Z*-, *Z,E*-, *E,E* -and *E,Z*-2-Phenoxy-(4-hydroxy)-3,4-bis(trifluoromethyl)perfluoro-hexa-2,4-diene (**138a-d**)
18. *p*-Phenylenedioxy-2,2′-bis[*Z,Z*-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] (**139**)
19. (Biphenyl-4,4′-diyldioxy)-2,2′-bis[*Z,Z*-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] (**140**)
20. Bis(trifluoromethyl)methylenedi-*p*-phenylenedioxy-2,2′-bis[*Z,Z*-3,4-bis(trifluoro-methyl)perfluorohexa-2,4-diene] (**141**)
21. Bis(trifluoromethyl)methylenedi-*p*-phenylenedioxy-2,2′-bis[*Z,Z*-5-methoxy-3,4-bis-(trifluoromethyl)perfluorohexa-2,4-diene] (**142**)
22. *E* and *Z*-Perfluoro-3,4-dimethyl-3,4-epoxyhexane (**164a,b**)
23. *Z,Z*-Perfluoro-3,4-dimethyl-2,4-diepoxyhexane (**162**)
24. *trans*- or *cis*-Perfluoro-2,3,5,6-tetramethyl-5,6-dihydo-1,4-dioxin (**179**)
25. Perfluoro-1,2,4,5-tetramethyl-3,6-dioxabicyclo[3.1.0]hexane (**163a-c**)
26. Perfluoro-1,2-biscyclobutyl-cyclobutene (**169**)
27. Perfluoro-1′,2′-epoxytercyclobutane (**170**)
28. *trans*-Perfluoro-2-methyl-3-epoxypentane (**166**)

29. *trans*-Perfluoro-2,2-dimethylpent-3-ene (**167**)
30. *trans*-Perfluoro-2,2-dimethyl-3-epoxypentane (**168**)
31. *p*-Phenylenedioxy-2,2′-bis[*Z,Z*-3,4-bis(trifluoromethyl)perfluoro-2,4-diepoxyhexane] (**172**)
32. Hexakis(trifluoromethyl)cyclopentadiene (**181**)
33. *trans*- and *cis*-Perfluorohexakis(trifluoromethyl)-2,4-diepoxycyclopentane (**174a,b**)
34. Caesium pentakis(trifluoromethyl)cyclopentadienyl (**182**)
35. Octaoxamidinium di[pentakis(trifluoromethyl)cyclopentadienyl] (**186**)
36. Tetraethylammonium pentakis(trifluoromethyl)cyclopentadienyl (**183**)
37. Tetrapropylammonium pentakis(trifluoromethyl)cyclopentadienyl (**184**)
38. Tetrabutylammonium pentakis(trifluoromethyl)cyclopentadienyl (**185**)
39. 5H-perfluoropentamethylcyclopentadiene (**188**)
40. Decamethylferrocenium pentakis(trifluoromethyl)cyclopentadienyl radical anion (**187**)

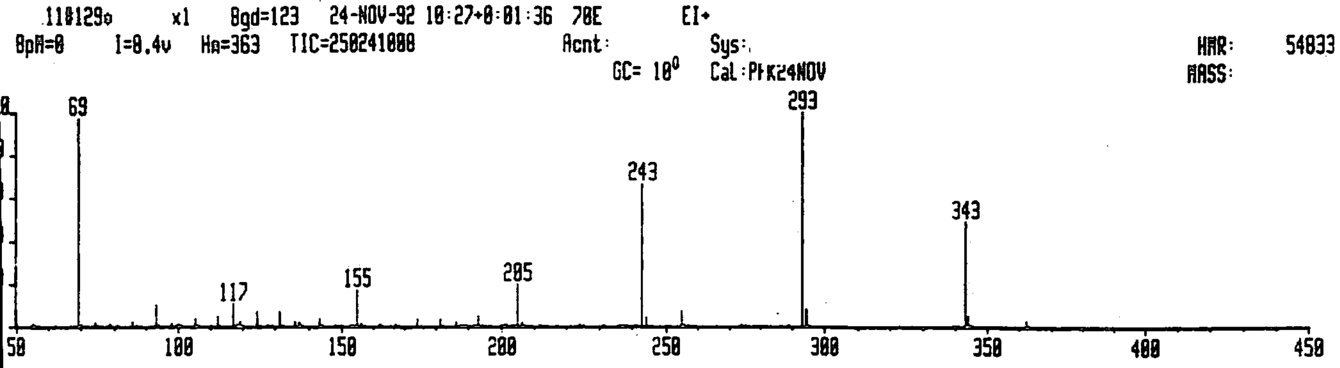
Fast atom bombardment (FAB) mass spectra were recorded using glycerol as the liquid matrix. Peaks corresponding to masses of 92_n+1 (FAB+) and 92_n-1(FAB-) originate from the matrix solvent.

Mass Spectrum 1



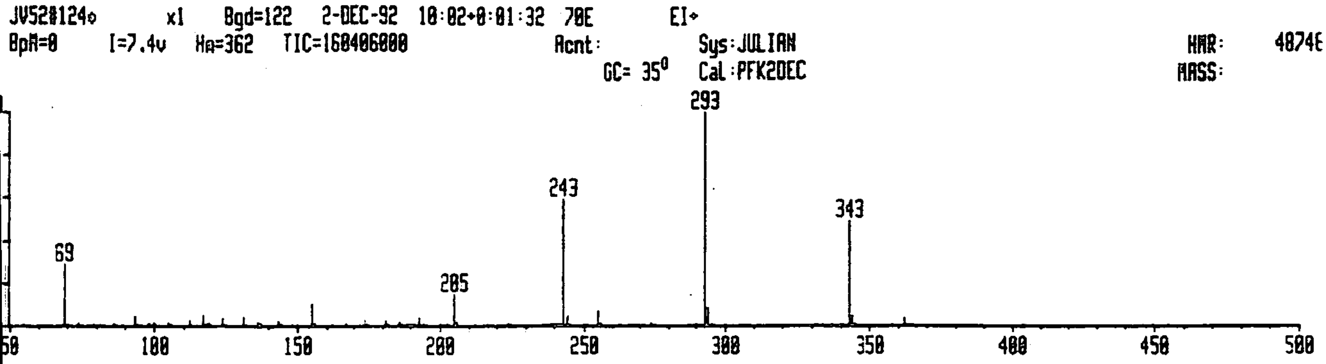
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.18	72	0.03	129	0.12	207	0.09
24	0.04	73	0.22	131	3.75	209	0.05
25	0.07	74	1.06	132	0.16	212	0.12
26	0.30	75	0.32	133	0.06	213	0.04
27	0.77	76	0.11	134	0.05	217	0.07
28	2.43	77	0.15	136	0.36	224	0.04
29	8.68	78	0.50	137	0.06	225	0.06
30	2.11	79	0.17	139	0.05	229	0.06
31	6.05	80	0.07	141	0.09	231	3.85
32	0.85	81	1.41	143	1.86	232	0.22
33	3.85	82	0.16	144	0.13	236	0.03
34	0.09	83	0.20	145	0.27	243	2.96
35	0.04	84	0.14	147	3.59	244	0.11
36	0.10	85	0.12	148	0.20	245	0.06
37	0.08	86	0.24	149	0.04	247	0.10
38	0.14	87	0.06	150	0.12	248	0.05
39	0.30	88	0.04	151	0.06	255	0.28
40	0.27	89	0.03	152	0.05	256	0.06
41	0.76	90	0.04	153	0.07	265	0.04
42	0.33	91	0.17	155	2.37	271	0.06
43	1.09	93	6.71	156	0.16	277	0.03
44	1.23	94	0.29	157	0.07	281	0.39
45	0.71	95	0.20	159	0.35	287	0.04
46	0.10	97	11.71	161	0.05	293	1.34
47	0.31	98	0.44	162	0.67	294	0.12
48	0.04	100	4.34	163	0.07	297	0.10
50	2.66	101	0.22	167	0.05	301	0.05
51	0.83	103	0.35	169	1.88	305	0.05
52	0.05	105	0.66	171	0.07	317	0.05
53	0.11	106	0.10	174	0.30	321	0.08
54	0.11	107	0.05	175	0.09	327	0.04
55	0.53	109	1.71	177	0.18	331	0.20
56	0.19	110	0.11	181	5.03	340	0.04
57	0.37	112	0.93	182	0.20	343	0.60
58	0.09	113	0.23	185	0.04	344	0.07
59	0.50	114	0.04	186	0.24	356	0.04
60	0.20	115	0.04	187	0.06	367	0.04
61	0.16	117	0.96	193	1.14	374	0.04
62	0.20	119	65.26	194	0.09	375	0.04
63	0.09	120	1.39	195	0.17	381	0.28
64	0.15	121	0.08	197	1.66		
65	0.42	122	0.05	198	0.10		
66	0.05	124	1.60	199	0.05		
67	0.17	125	0.14	200	0.03		
69	100.00	126	0.05	201	0.03		
70	1.20	127	0.21	205	1.41		

Mass Spectrum 2



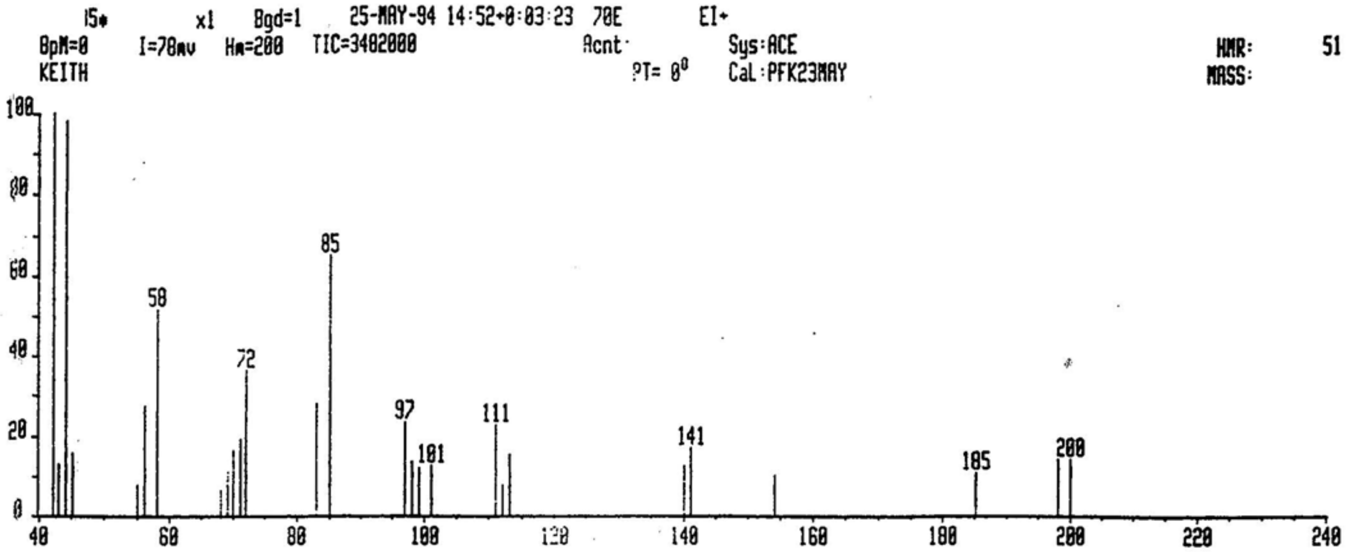
Mass	% Base	
50.00	0.93	
55.01	0.60	
69.00	97.30	
70.00	0.93	
74.00	1.50	
79.01	0.55	
86.01	1.87	
93.01	9.87	
98.02	1.27	
100.02	0.95	
105.02	3.11	
112.01	4.74	
117.02	10.51	
118.02	0.59	
119.01	1.72	
124.02	6.31	
131.01	6.18	
136.02	2.13	
137.01	1.17	
143.01	3.28	
155.00	16.95	
156.00	0.81	
162.01	0.44	
167.02	0.70	
174.02	2.94	
181.02	3.15	
186.02	1.90	
193.02	4.21	
201.62	0.35	
205.01	19.06	
206.02	1.23	
224.03	1.13	
243.01	66.62	
244.02	4.12	
255.02	6.82	
256.03	0.47	
274.03	0.57	
293.04	100.00	F
294.03	7.45	F
343.04	48.47	F
344.03	4.19	F
362.03	2.82	

Mass Spectrum 3



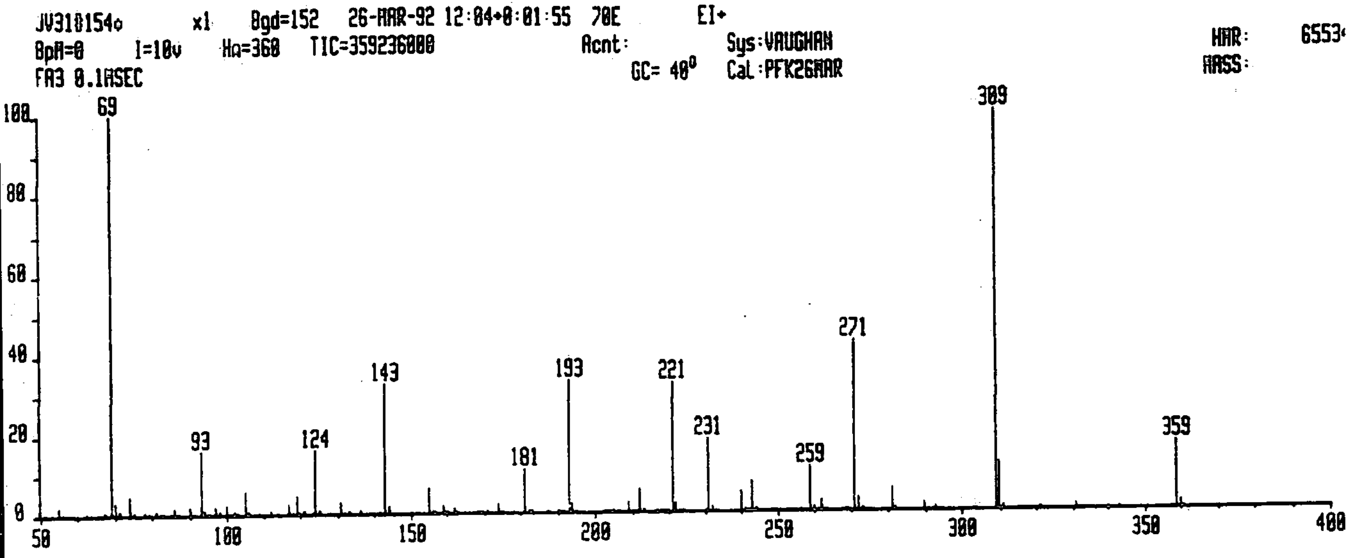
Mass	% Base	
68.98	28.50	
69.98	0.30	
73.98	0.43	
85.97	0.58	
92.97	3.88	
97.97	0.42	
99.97	0.38	
104.97	1.27	
111.97	2.01	
116.97	4.54	
118.97	0.84	
123.96	3.17	
130.97	3.53	
135.96	1.15	
136.97	0.70	
142.96	1.84	
154.95	9.79	
155.96	0.54	
161.95	0.32	
166.94	0.36	
173.95	1.78	
180.95	2.40	
185.95	1.37	
192.95	2.97	
204.95	14.40	
205.96	0.97	
223.94	0.94	
242.93	58.74	
243.94	3.76	
254.94	6.69	
255.95	0.48	
273.93	0.45	
292.92	100.00	F
293.93	7.48	F
342.88	48.46	F
343.90	4.14	F
361.90	3.29	

Mass Spectrum 4



Mass	% Base
42.10	100.00
43.11	12.62
44.11	97.86
45.12	15.53
55.07	7.57
56.08	27.18
58.09	51.46
68.04	6.21
69.03	10.87
70.05	16.12
71.05	18.83
72.03	35.92
83.04	27.77
85.05	64.66
97.06	23.30
98.06	13.40
99.07	11.65
101.09	12.43
111.06	22.52
112.07	7.38
113.09	14.95
140.08	12.23
141.09	16.89
154.10	9.90
185.15	10.68
198.16	13.98
200.16	14.17

Mass Spectrum 5

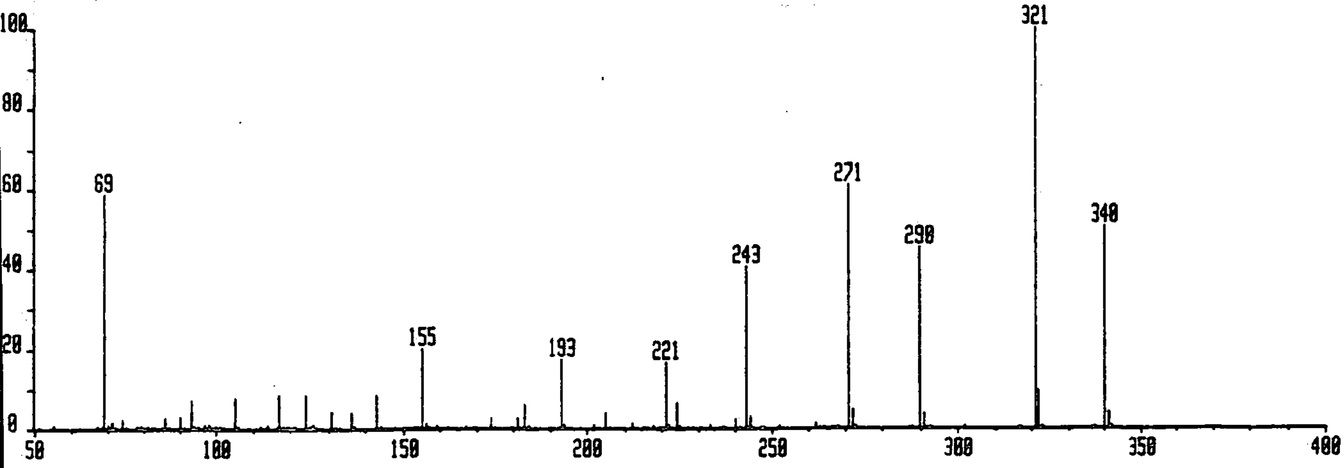


Mass	% Base
49.98	3.13
54.98	1.61
68.98	100.00 0
69.97	2.84
70.97	0.81
73.97	4.34
77.97	0.39
80.98	0.78
85.98	1.24
89.97	1.56
92.97	15.72
93.98	0.78
96.97	1.56
97.98	0.39
99.97	2.05
101.97	0.39
104.97	5.35
105.97	0.39
111.97	0.78
116.97	2.34
118.97	4.32
120.97	0.78
123.97	16.07
124.98	0.78
130.97	2.73
132.97	0.39
135.97	0.78
142.95	32.42
143.97	1.56
154.96	6.25
155.97	0.39
158.96	1.60
161.96	1.17
170.96	0.39
173.96	2.09
180.95	10.94
181.96	0.42
182.95	0.39
189.89	0.39
192.93	33.29

Mass	% Base
208.95	2.34
211.95	5.86
212.96	0.39
220.94	32.54
221.95	1.96
230.95	18.06
231.95	0.99
239.95	4.69
240.96	0.39
242.94	7.13
243.95	0.41
258.93	10.94
259.94	0.78
261.94	2.34
270.93	42.97
271.94	3.17
280.94	5.62
281.94	0.43
289.93	1.56
292.94	0.85
308.97	100.00
309.93	11.72
310.94	0.78
330.94	1.17
358.91	16.80
359.92	1.56

Mass Spectrum 6

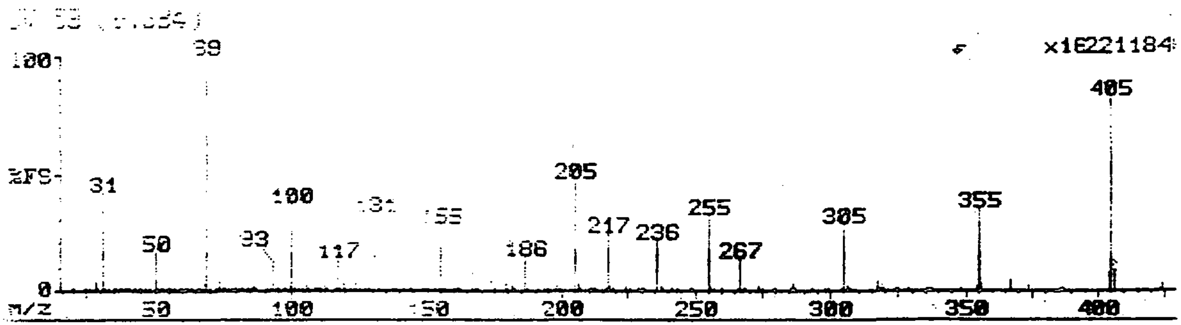
```
JV310187o        x1    Bgd=180   26-MAR-92 12:04+0:02:19  70E        EI+
BpM=0    I=10v   Ha=341   TIC=352535000             Acnt:        Sys:VAUGHAN                        HMR:     6553
FA3 0.1MSEC                                   GC= 40°   Cal:PFK26MAR                       MASS:
```



Mass	% Base
49.98	1.17
54.98	0.79
66.98	0.39
68.96	58.60
69.97	0.78
70.97	1.32
73.97	1.96
77.97	0.39
78.98	0.39
80.97	0.39
85.98	2.37
89.97	2.73
92.97	6.73
93.98	0.39
94.97	0.48
96.97	0.78
97.98	0.83
99.98	0.39
100.97	0.39
104.97	7.42
105.98	0.39
113.97	0.78
116.97	8.20
117.97	0.43
118.97	0.39
123.97	8.33
124.97	0.39
125.97	0.78
130.97	4.22
135.97	3.65
136.97	0.39
142.96	8.20
143.97	0.39
154.96	20.02
155.97	0.95
173.96	2.52
180.88	2.36

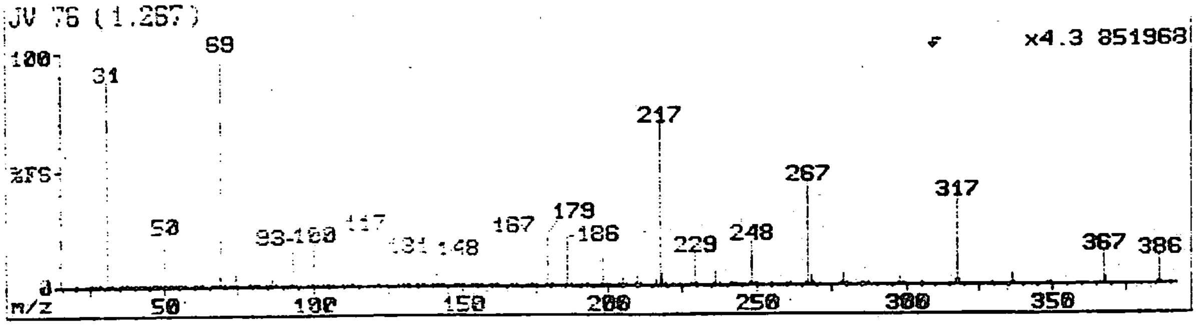
Mass	% Base	
182.94	5.86	
183.95	0.39	
192.94	16.99	
193.96	0.80	
201.95	0.84	
204.95	3.91	
211.95	0.94	
220.94	16.41	
221.95	0.79	
223.95	6.32	
224.96	0.40	
232.96	0.78	
239.94	1.95	
242.94	40.42	
243.95	2.73	
251.95	0.39	
261.95	1.18	
270.93	61.05	F
271.94	4.31	F
272.95	0.39	
289.92	45.10	
290.93	3.27	
301.95	0.39	
320.95	100.00	FO
321.93	9.27	F
322.95	0.49	
339.90	50.26	F
340.93	3.91	F
341.95	0.39	

Mass Spectrum 7



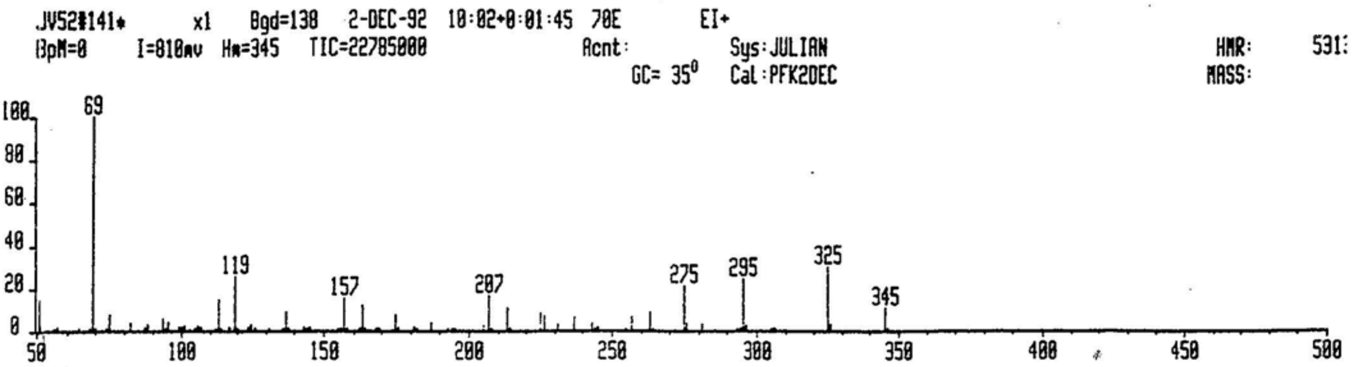
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
12	0.20	148	1.73	248	1.40
14	0.22	149	0.37	249	0.17
15	0.07	150	0.44	255	31.87
16	0.14	153	0.01	256	2.05
18	1.83	154	1.59	257	0.09
19	0.29	155	22.15	260	0.04
31	41.85	156	1.35	266	0.33
32	0.58	160	0.35	267	13.70
50	16.30	161	0.04	268	1.09
67	0.28	162	0.60	269	0.04
68	3.38	167	5.47	274	1.30
69	100.00	168	0.70	275	0.16
70	1.12	169	0.14	279	0.24
72	0.03	172	0.05	280	0.23
73	0.11	174	3.47	285	0.07
74	3.89	175	0.17	286	3.01
75	0.43	179	3.06	287	0.33
76	0.02	180	0.22	293	0.03
77	0.02	181	2.19	298	0.22
92	0.33	182	0.08	299	0.24
93	10.69	186	14.63	304	0.35
94	0.36	187	0.95	305	28.15
95	0.01	191	0.03	306	2.21
97	0.05	193	1.37	307	0.09
98	1.91	194	0.07	317	2.47
99	1.52	198	2.07	318	0.30
100	37.22	199	0.30	319	0.02
101	0.84	205	47.22	324	0.82
116	0.36	206	2.47	325	0.07
117	13.33	207	0.09	329	0.03
118	0.79	210	0.35	336	0.45
119	3.33	211	0.03	337	0.03
120	0.06	212	0.07	348	0.02
122	0.10	216	0.38	354	0.12
123	0.26	217	24.63	355	2.20
124	9.40	218	1.59	356	0.20
125	0.42	219	0.05	367	0.28
128	0.15	224	1.81	374	0.12
129	0.56	225	0.10	385	0.02
131	32.59	229	0.93	386	0.15
		230	0.08	387	0.03
		231	0.04	404	0.46
		236	21.67	405	5.14
		237	1.47		
		238	0.06		
		241	0.07		
		243	0.72		

Mass Spectrum 8



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.29	75	0.41	143	3.85	224	0.07
21	0.02	76	0.08	144	0.10	228	0.25
24	0.23	79	3.79	147	0.30	229	13.70
25	0.11	80	0.42	148	12.26	230	1.24
26	0.14	81	1.54	149	0.82	235	0.12
27	0.43	82	0.06	150	0.09	236	6.22
28	4.24	84	0.04	153	0.08	237	0.29
29	0.42	85	0.14	154	0.29	241	0.99
31	87.02	86	2.94	155	10.10	242	0.10
32	1.23	87	0.15	156	0.48	243	0.10
33	0.08	91	0.22	159	0.06	247	0.45
35	0.11	92	0.45	160	2.73	248	18.39
36	0.59	93	17.07	161	0.38	249	0.82
37	0.21	94	0.59	162	0.39	250	0.05
38	0.11	98	5.44	166	0.35	255	0.53
39	0.22	99	1.17	167	22.60	260	0.37
40	0.24	100	18.15	168	1.50	261	0.07
41	0.15	101	0.33	172	0.36	266	0.86
42	0.07	103	0.29	173	0.03	267	43.27
43	1.01	104	0.10	174	0.92	268	3.61
44	0.33	105	2.88	175	0.06	269	0.17
45	0.06	106	0.16	178	0.52	278	0.11
46	0.04	109	0.08	179	20.43	279	4.90
47	1.13	110	1.75	180	1.50	280	0.45
48	0.19	111	0.17	181	0.45	285	0.04
49	1.04	112	1.14	185	0.34	286	1.43
50	21.88	113	0.05	186	18.39	287	0.08
51	0.99	117	23.32	187	1.14	297	0.08
52	0.06	118	1.36	191	0.74	298	2.79
53	0.05	119	0.71	192	0.11	299	0.31
54	0.09	121	0.03	193	0.88	305	0.06
55	2.76	122	0.75	197	0.16	316	0.38
56	0.26	124	0.77	198	[illegible]	317	[illegible]
57	0.05	125	0.16	199	1.10	318	0.49
60	0.23	128	0.13	200	0.05	[illegible]	0.06
61	0.11	129	5.05	203	0.05	336	1.03
62	1.49	130	0.59	205	3.25	337	0.08
63	0.08	131	13.34	206	0.21	367	3.25
66	0.11	132	0.44	209	0.09	[illegible]	0.66
67	0.51	134	0.09	210	4.00	[illegible]	0.23
68	4.09	135	0.11	211	0.38	386	2.73
69	100.00	136	4.84	216	1.58	387	0.29
70	1.14	137	0.34	217	63.22		
72	0.06	140	0.13	218	4.87		
73	0.16	141	4.87	219	0.18		
74	5.29	142	0.42	222	0.05		

Mass Spectrum 9



Mass	% Base
49.99	0.92
50.99	14.29
56.00	0.96
57.01	1.43
64.00	0.49
68.00	0.58
68.98	100.00
69.99	0.83
73.99	0.47
74.99	6.81
81.99	3.11
86.99	1.28
87.99	2.43
92.98	5.40
93.99	0.94
94.99	3.95
98.99	1.51
99.98	1.24
100.99	1.86
102.98	0.30
104.98	0.38
105.98	2.22
106.99	1.28
111.98	0.43
112.98	13.83
113.99	0.83
116.98	1.52
118.97	25.16
119.98	0.60
123.98	1.04
124.98	2.33
126.00	0.70
130.98	0.75
135.97	0.45
136.98	8.04
137.98	0.75
142.97	1.45
143.99	0.45
144.99	1.51
154.96	0.75
155.96	0.79
156.97	14.59
157.99	0.94
161.96	0.36
162.97	11.56
174.96	7.28
175.97	1.30
180.94	1.39
206.97	16.17
207.98	0.90
212.97	10.07
213.99	0.38
224.96	7.64
225.97	6.64
230.96	2.80
236.97	5.68
242.96	3.09
243.97	0.36
244.98	1.17
254.96	0.56
256.97	5.63
262.97	8.24
264.00	0.30
274.95	20.70
275.97	3.31
280.95	2.56
292.98	0.36
293.99	0.38
294.66	0.60
294.96	23.60
295.96	1.75
304.94	0.81
305.98	0.55
306.20	0.45
324.94	29.53
325.95	2.47
344.95	10.24
345.95	0.88

Mass Spectrum 10

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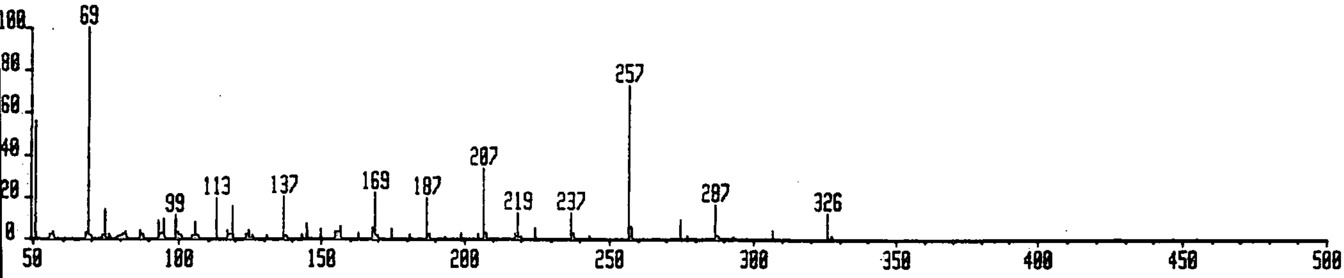
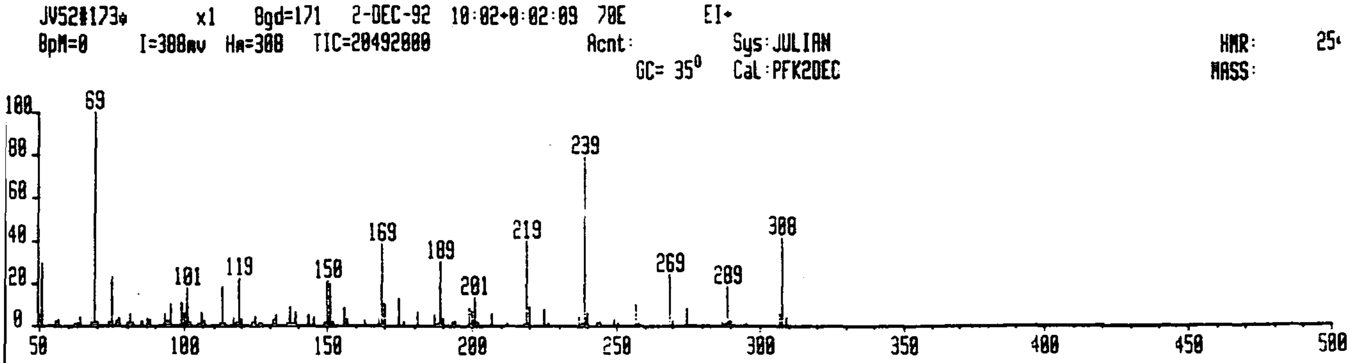
JV520191o       x1    Bgd=100   2-DEC-92  10:02+0:02:22  70E        EI+
BpA=0      I=407av  Ha=327   TIC=16016000              Acnt:          Sys:JULIAN                                   HAR:       26730
                                                          GC= 35⁰   Cal:PFK2DEC                                  MASS:
```



Mass	% Base
50.00	1.31
50.99	55.85
56.00	1.76
57.01	3.11
68.00	2.77
68.98	100.00
69.99	1.42
73.99	1.38
74.99	13.43
76.00	2.13
78.99	0.75
80.00	1.50
31.00	2.91
81.99	3.44
86.99	3.78
88.00	1 76
92.98	9.49
93.99	2.62
95.00	8.83
98.99	11.15
99.99	2.43
100.98	1.31
104.98	1.20
105.99	8.01
107.01	1.01
112.99	19.15
116.98	4.08
117.99	1.91
118.99	15.49
123.99	2.06
124.99	3.93
125.99	1.20
130.98	1.46
136.98	19.94
137.98	1.53
142.97	1.95
144.99	6.92
149.99	4.19
154.97	3.11
155.97	3.07
156.99	5.84
162.98	2.43
167.98	5.16
168.98	21.74
169.98	0.97
174.97	4.38
180.98	1.65
186.97	19.15
187.99	2.84
192.99	0.86
198.99	2.24
204.97	1.72
206.98	33.30
208.00	2.39
217.99	2.84
218.98	12.46
220.00	0.94
224.97	5.09
236.97	12.23
237.99	2.39

Mass	% Base
242.98	1.16
256.98	72.95
257.99	5.46
274.98	9.24
276.99	1.46
286.97	16.24
287.97	1.42
292.98	0.75
306.98	4.15
325.97	11.97
327.00	1.53

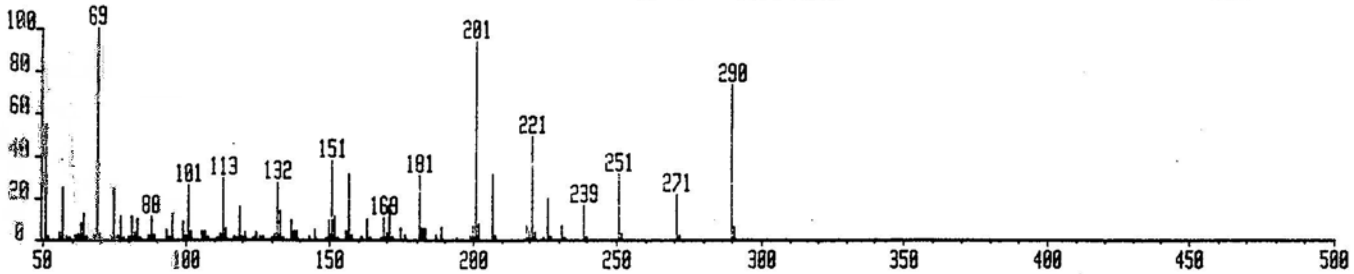
Mass Spectrum 11



Mass	% Base
50.00	4.21
51.00	29.10
56.00	1.89
57.00	2.79
62.00	0.79
63.01	1.06
64.00	3.70
68.00	1.26
68.98	100.00
70.00	1.49
73.98	1.45
74.99	22.22
76.00	2.01
77.01	3.26
79.99	1.26
81.00	5.07
82.00	1.53
95.00	2.12
86.99	3.15
88.00	2.63
92.98	5.43
93.99	1.73
95.00	9.79
98.99	10.46
39.99	5.03
101.00	17.18
102.01	0.98
104.99	0.90
105.99	5.66
107.00	1.93
111.99	1.18
112.99	18.01
113.99	0.51
116.98	2.99
117.98	1.34
118.99	21.82
120.00	2.44
123.99	1.42
124.99	3.85
125.98	0.47
127.02	0.79
130.99	2.44
132.00	4.72
136.00	0.75
136.98	8.45
137.99	0.79
139.00	5.66
142.98	4.52
145.00	3.03
148.98	1.42
149.99	20.68
150.99	19.19
152.01	0.98
155.97	7.63
156.99	2.67
162.98	1.93
167.97	2.28
168.98	38.03
169.98	9.75
174.97	12.39
175.97	1.14
180.98	5.51
186.98	4.64
187.99	0.71
188.99	29.73
190.00	2.36
192.99	1.22
193.98	1.77
198.97	7.90
199.98	6.25
200.39	0.98
200.47	0.94
200.54	0.94
200.68	0.87
200.75	1.06
200.98	12.70
202.01	1.10
206.99	5.07
212.02	0.79
217.99	1.45
218.98	39.17
219.99	8.30
224.97	7.04
225.98	0.90
236.97	3.70
237.99	1.18
238.99	79.08
240.00	5.66
243.00	1.10
243.99	1.49
248.98	2.36
250.46	0.79
256.99	9.67
258.00	0.67
268.98	23.67
269.99	2.04
274.97	7.79
286.99	1.49
287.96	0.63
288.98	17.85
290.00	1.69
295.00	0.87
306.98	4.92
307.98	40.98
309.00	3.42

Mass Spectrum 12

```
JV52#256*       x1    Bgd=241   2-DEC-92  10:02+0:03:11  70E        EI+
BpM=0     I=533mv  Hm=290   TIC=37700000            Rcnt:          Sys:JULIAN                         HMR:       349
                                                       GC= 35⁰    Cal:PFK2DEC                         MASS:
```

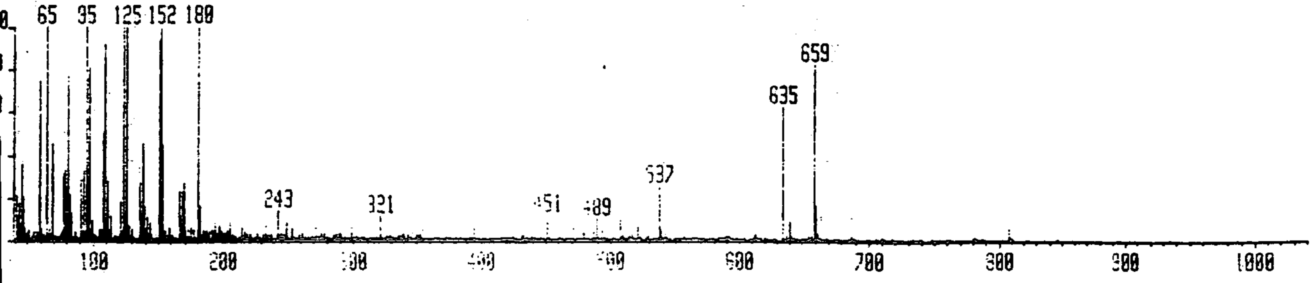


Mass	% Base
50.00	4.40
50.99	54.56
52.00	0.97
55.99	3.00
57.00	24.52
58.01	1.46
59.02	0.69
61.00	1.63
62.01	2.46
63.01	7.86
64.00	12.00
65.01	1.20
67.99	2.20
68.98	100.00
70.00	2.26
73.99	1.14
74.99	24.52
76.00	2.20
77.00	10.89
78.03	0.57
79.99	1.06
80.99	10.69
81.99	3.43
83.01	9.46
84.03	0.43
87.00	1.71
88.00	11.03
89.00	1.91
92.98	4.32
93.99	1.26
95.00	12.49
98.99	8.03
99.99	2.03
101.00	25.55
102.01	4.00
105.98	4.09
106.99	3.74
108.00	0.97
110.99	0.71
111.99	2.29
112.99	28.95
114.00	5.26
116.98	1.31
117.99	0.54
118.99	15.55
120.00	1.49
121.01	3.06
123.99	0.83
124.99	3.17
126.00	1.11
127.00	1.54
130.00	0.66
130.99	2.26
132.00	26.64
133.00	13.38
134.01	0.89
136.99	9.26
137.99	4.00
139.00	3.60
142.99	1.03

Mass	% Base
144.99	4.29
148.98	0.89
149.99	8.89
150.99	37.30
152.00	10.69
153.01	0.80
155.97	3.77
156.98	30.84
157.99	2.09
160.97	1.23
162.98	9.72
164.01	0.57
167.99	0.91
168.98	10.20
169.99	3.29
171.00	15.83
172.00	0.97
174.96	5.37
175.97	1.80
180.97	29.84
181.99	4.94
182.21	0.63
182.42	0.80
182.66	1.17
182.98	4.94
186.99	1.74
189.00	5.83
193.98	0.71
198.98	1.94
199.99	6.14
200.99	93.83
202.00	7.63
206.98	31.07
207.99	1.89
218.97	6.20
219.99	3.72
220.99	48.41
222.00	3.26
224.98	0.60
225.98	19.06
226.99	1.26
230.98	6.37
232.01	0.71
238.99	16.15
239.99	1.51
250.98	31.04
252.00	2.37
270.99	21.15
272.00	1.91
289.98	73.25
290.98	5.89

Mass Spectrum 13

```
JV42#17+        x1    Bgd=3     25-JUN-92 18 43+0 01 49  70E          EI+
BpM=0      I=10v    Ha=935   TIC=2066262992              Acnt         Sys:ACE                                          HMR:      6553
J.VAUGHAN                                                   PT= 8⁰    Cal:PFK7SJUN                                     MASS:
```

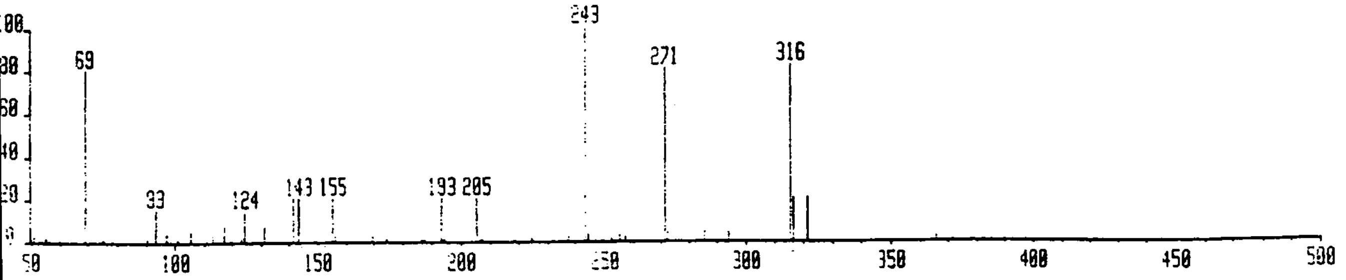


Mass	% Base	
41.06	10.38	F
42.06	3.94	F
43.04	17.29	F
43.07	10.94	F
44.04	6.81	F
45.05	35.50	F
46.99	19.81	F
48.00	5.56	
59.08	74.49	
65.01	100.00	FO
67.01	3.56	F
69.03	44.94	F
78.02	10.54	F
79.02	11.43	F
80.04	14.32	
81.00	17.12	F
82.01	11.31	F
83.02	13.12	F
91.03	26.10	
93.05	32.58	
95.02	100.00	FO
96.03	28.37	F
97.03	30.66	F
99.04	9.24	
108.07	49.85	
109.04	91.55	
110.06	12.40	
111.04	27.79	F
113.04	10.59	
121.08	17.79	
123.07	100.00	O
124.07	13.10	
125.08	100.00	O
126.08	6.76	
127.05	6.25	
136.11	26.74	
137.09	12.58	
138.09	45.33	
139.08	16.06	
140.08	5.52	
141.06	11.00	
143.04	8.60	
151.09	93.65	F
152.10	100.00	FO
153.12	45.12	F
159.03	5.54	
166.13	23.25	
167.11	11.68	
168.12	23.24	
169.12	27.01	
175.05	5.64	
177.04	5.35	
180.15	100.00	FO
181.14	16.07	F
191.05	5.32	
193.06	6.96	
196.15	7.01	
205.07	8.56	
215.10	6.60	
233.10	7.03	

Mass	% Base	
243.11	14.06	
249.07	8.13	
253.08	5.59	
271.07	6.22	
273.14	5.14	
299.08	6.67	
321.09	11.29	
353.10	6.64	
393.01	7.03	F
395.08	5.47	F
451.04	12.48	F
489.14	10.16	F
507.16	9.79	F
521.18	7.63	F
537.22	25.47	F
634.54	63.12	
639.34	8.20	F
659.35	82.69	F
660.37	16.34	F
801.53	0.12	
803.60	0.17	
805.56	0.10	
807.55	5.12	F
808.57	1.56	F
809.60	1.57	F
810.60	0.44	
811.58	0.12	
823.59	0.07	
835.65	0.19	
845.65	0.39	
846.65	0.08	
857.64	0.12	
907.70	0.16	
929.75	0.09	

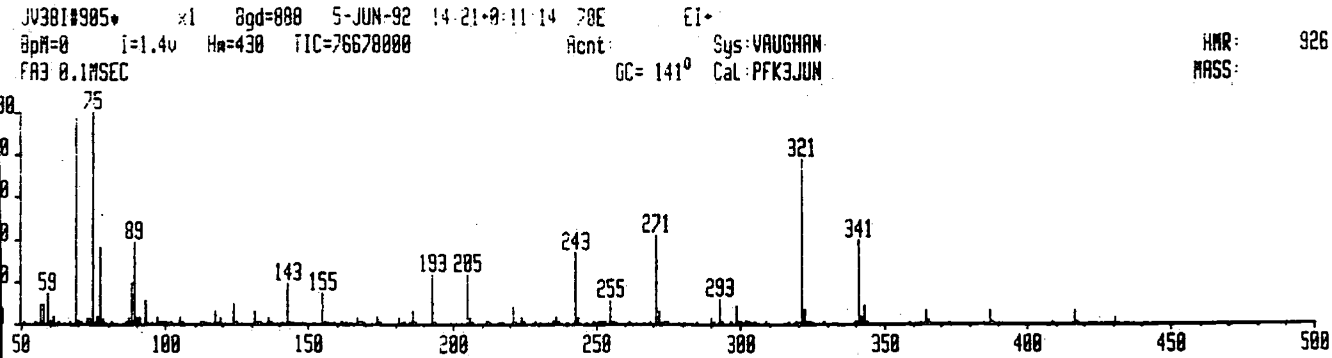
Mass Spectrum 14

```
JV37E8722o      xl    Bgd=182   10-JUN-92 16:48+0:08:57  70E          EI+
BpM=0     I=195mv  Hm=365   TIC=7729000                  Acnt:          Sys:VAUGHAN                                   HMR:      1280
FA3 0.1MSEC                                                      GC= 79⁰   Cal:PFK8JUN                                   MASS:
```



Mass	% Base
50.09	1.48
51.10	1.38
55.11	1.25
69.11	80.00
74.14	1.95
75.15	1.25
90.17	1.56
93.17	14.61
97.16	2.89
101.18	1.56
105.19	4.38
113.23	2.58
117.21	7.73
123.24	1.56
124.22	14.30
131.23	6.95
141.27	20.00
143.25	20.00
155.26	20.00
156.28	2.81
169.29	2.03
174.30	2.73
186.31	1.80
187.31	1.33
193.32	20.08
194.34	1.72
205.33	20.00
206.34	1.48
207.39	1.41
218.24	1.48
224.36	3.59
235.40	2.81
237.38	1.80
243.39	100.00
244.40	6.64
249.39	1.33
252.43	2.03
255.42	4.53
257.47	2.03
271.42	80.00
272.44	3.75
285.43	4.53
293.47	3.67
315.51	62.34
316.51	20.00
321.50	20.00

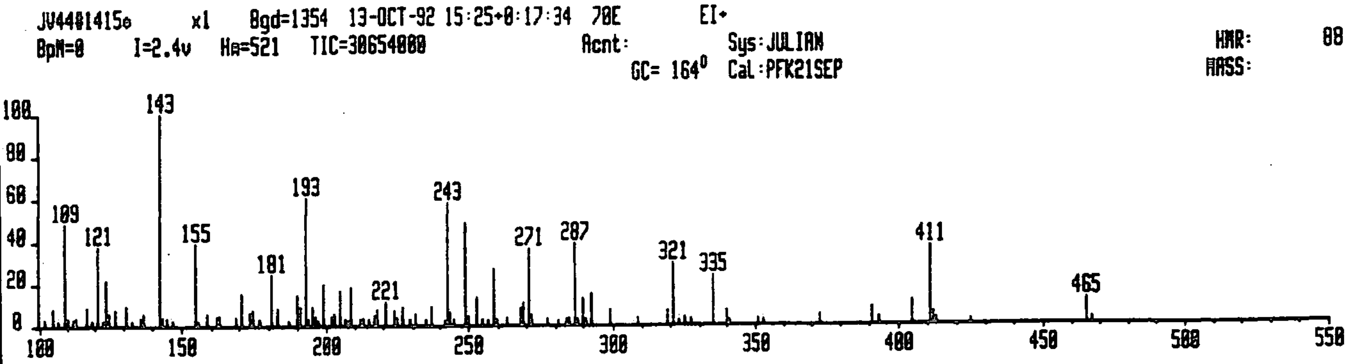
Mass Spectrum 15



Mass	% Base
47.99	3.30
49.94	1.19
50.95	0.91
54.95	0.77
56.99	3.76
57.99	3.97
58.99	13.99
59.97	1.17
60.97	3.02
62.96	0.35
66.93	0.44
68.93	36.69
69.93	0.99
70.96	0.51
72.97	2.76
73.93	2.75
74.97	100.00
75.98	3.44
76.97	36.12
77.96	1.77
80.93	0.35
85.92	0.63
86.96	2.76
87.97	19.34
88.98	38.67
89.97	2.76
90.98	2.76
92.92	11.05
96.91	2.76
142.87	18.48
143.88	0.37
154.86	13.81

Mass	% Base
185.84	5.52
186.85	0.81
192.83	22.76
193.84	0.88
204.80	23.00
205.81	2.76
206.82	0.55
211.83	0.99
212.85	0.38
216.83	0.42
220.81	7.46
221.83	0.53
223.81	2.76
224.83	0.80
228.86	0.45
234.82	1.10
235.81	2.76
236.81	0.45
242.79	33.55
243.80	2.76
254.78	11.06
255.79	0.77
270.76	41.44
271.76	5.52
292.75	11.45
293.75	0.93
320.72	77.45
321.73	6.12
340.71	39.07
341.71	3.23
342.71	8.31
416.68	5.75
417.69	0.65
430.71	2.76

Mass Spectrum 16

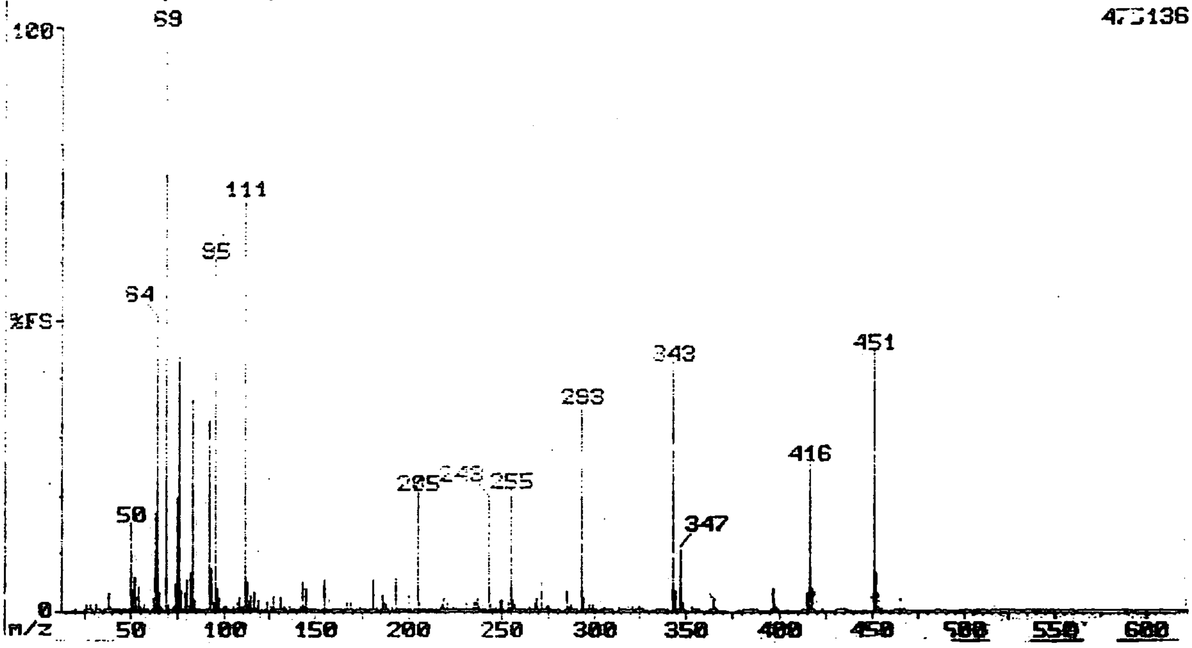


Mass	% Base
49.95	0.82
50.96	1.62
51.97	1.06
52.98	8.06
53.99	3.52
55.00	100.00
56.00	4.54
68.94	6.15
69.98	0.33
70.98	1.10
72.98	1.54
92.93	2.10
95.01	0.47
96.94	0.42
104.93	0.43
109.03	2.76
116.93	0.49
120.91	2.13
123.92	1.22
126.96	0.39
130.92	0.51
142.91	5.76
154.92	2.20
158.93	0.31
170.93	0.84
173.94	0.35
174.95	0.42
180.91	1.37
182.91	0.43
189.90	0.80
190.90	0.47
192.90	3.48
194.94	0.49
198.88	1.10
202.92	0.31
204.91	0.91
208.92	1.04
217.90	0.40
220.91	0.62
223.92	0.36
226.90	0.47
236.92	0.47
242.91	3.32
243.92	0.32
248.90	2.77
252.93	0.72
258.91	1.53
267.90	0.44
268.93	0.58
270.92	2.06
286.91	2.21
289.92	0.69
292.92	0.85
298.94	0.40
318.90	0.38
320.91	1.67
334.92	1.34
339.93	0.38
391.01	0.43
404.99	0.61
410.98	2.09
411.96	0.31
465.03	0.66

Mass Spectrum 17

Name:Julian Ion Mode:EI+ 11-Mar-94 15:39

JV40M 790 (13.168)

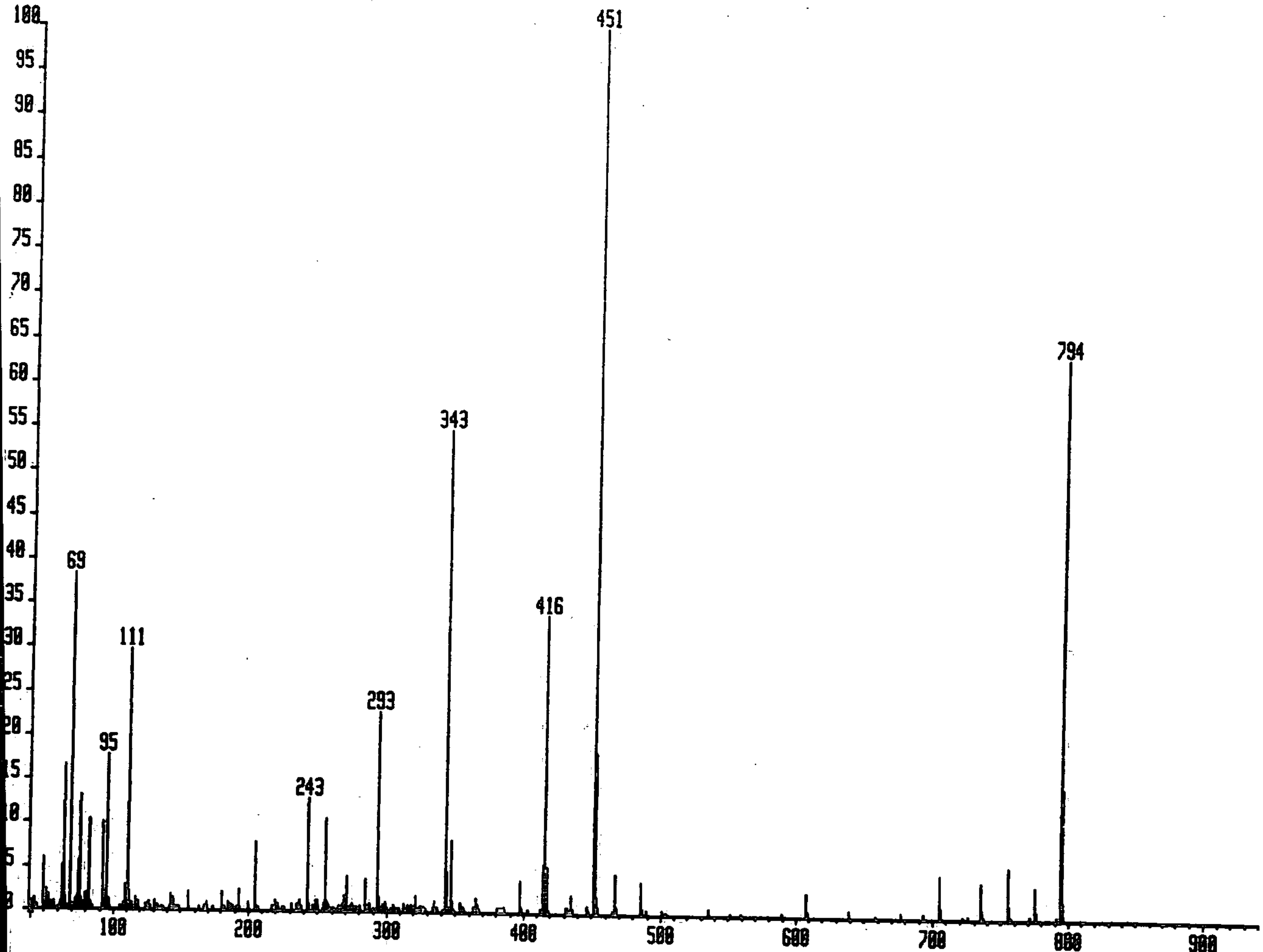


Mass	Rel Int
50	15.30
51	3.50
52	5.82
53	2.20
54	4.15
57	1.27
58	0.07
59	0.06
61	0.49
62	2.49
63	16.59
64	49.78
65	3.08
66	0.61
67	0.12
69	100.00
70	1.27
71	0.29
72	0.06
73	0.62
74	4.80
75	19.40
76	43.75
77	3.50
78	0.15
79	3.13
80	5.55
81	0.84
82	6.57
83	36.21

Mass	Rel Int
92	22.76
93	7.44
94	1.64
95	60.34
96	4.04
97	2.48
111	70.69
112	5.06
113	1.37
114	2.72
115	0.21
117	3.61
204	0.43
206	1.48
255	21.12
~~293~~	~~35.34~~
294	2.45
343	42.67
344	3.43
345	0.33
346	0.29
347	10.45
415	2.95
416	25.65
417	3.77
451	44.61

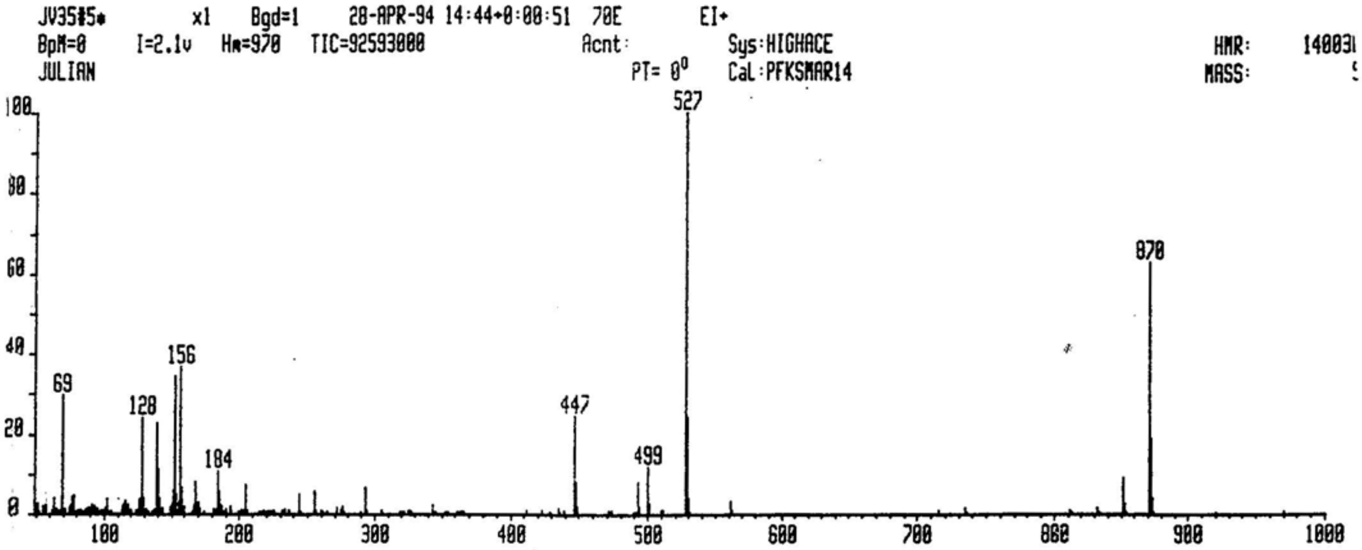
Mass Spectrum 18

```
JV40S05o        x1    Bgd=1     8-MAR-94  12:48+0:00:46  70E         EI+
BpM=0     I=2.1v   Ha=894   TIC=97348000            Acnt:          Sys:ACE                        MAR:    14011
JULIAN VAUGHAN                                          PT= 0°    Cal:PFKS7MAR                    MASS:
+X1.0
```



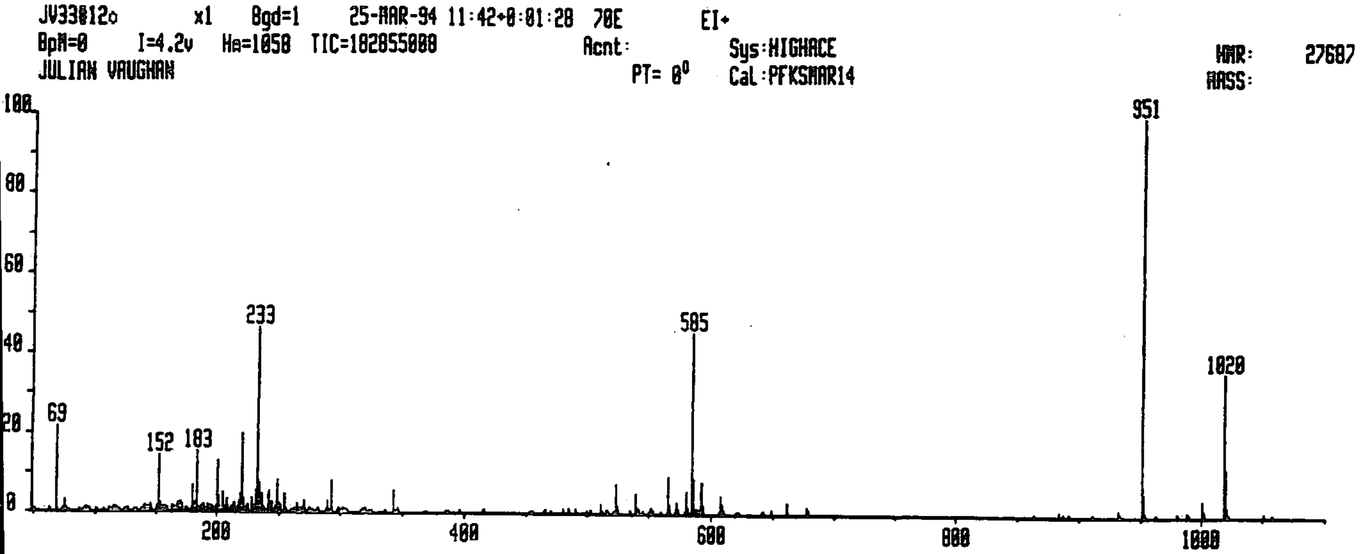
Mass	% Base
63.10	4.98
64.10	16.47
65.10	1.48
69.04	38.27
70.04	0.37
71.13	0.46
73.08	1.10
74.05	1.41
75.06	5.57
76.06	12.93
77.06	1.23
79.05	0.77
80.05	1.68
81.08	0.84
82.04	1.86
83.07	10.23
84.08	0.67
92.08	9.99
93.07	1.84
94.08	0.42
95.09	17.72
96.09	1.11
97.05	1.03
107.09	0.36
108.09	0.68
109.10	2.78
110.10	0.59
111.09	29.61
243.13	12.80
244.14	0.75
247.17	0.57
249.15	1.21
250.17	1.16
254.16	0.86
255.14	10.54
343.18	54.71
415.25	5.48
416.25	33.94
417.26	5.25
418.26	0.34
431.26	0.60
432.26	0.74
435.27	2.02
436.27	0.38
446.42	0.81
451.24	100.00 F
452.27	18.27 F
794.48	63.69 F
795.54	14.90 F
796.55	1.91

Mass Spectrum 19



Mass	% Base	
67.17	0.79	
69.12	29.50	
126.23	3.56	
127.24	3.66	
128.25	24.12	
129.25	3.66	
139.25	22.70	
151.26	5.88	
152.27	34.24	
153.28	4.79	
154.28	0.38	
155.23	2.97	
156.27	36.71	
157.27	6.51	
184.29	10.78	
185.29	5.58	
186.27	2.14	
187.29	1.87	
446.53	24.17	
447.53	7.86	
448.55	1.58	
492.43	7.89	
493.45	1.59	
499.44	11.60	
500.45	2.29	
510.43	0.70	
511.44	0.67	
527.42	100.00	F
528.46	24.12	F
529.46	3.66	
851.43	8.99	F
852.46	2.54	F
853.50	0.50	
870.42	63.10	F
871.42	18.89	F
872.45	3.66	F

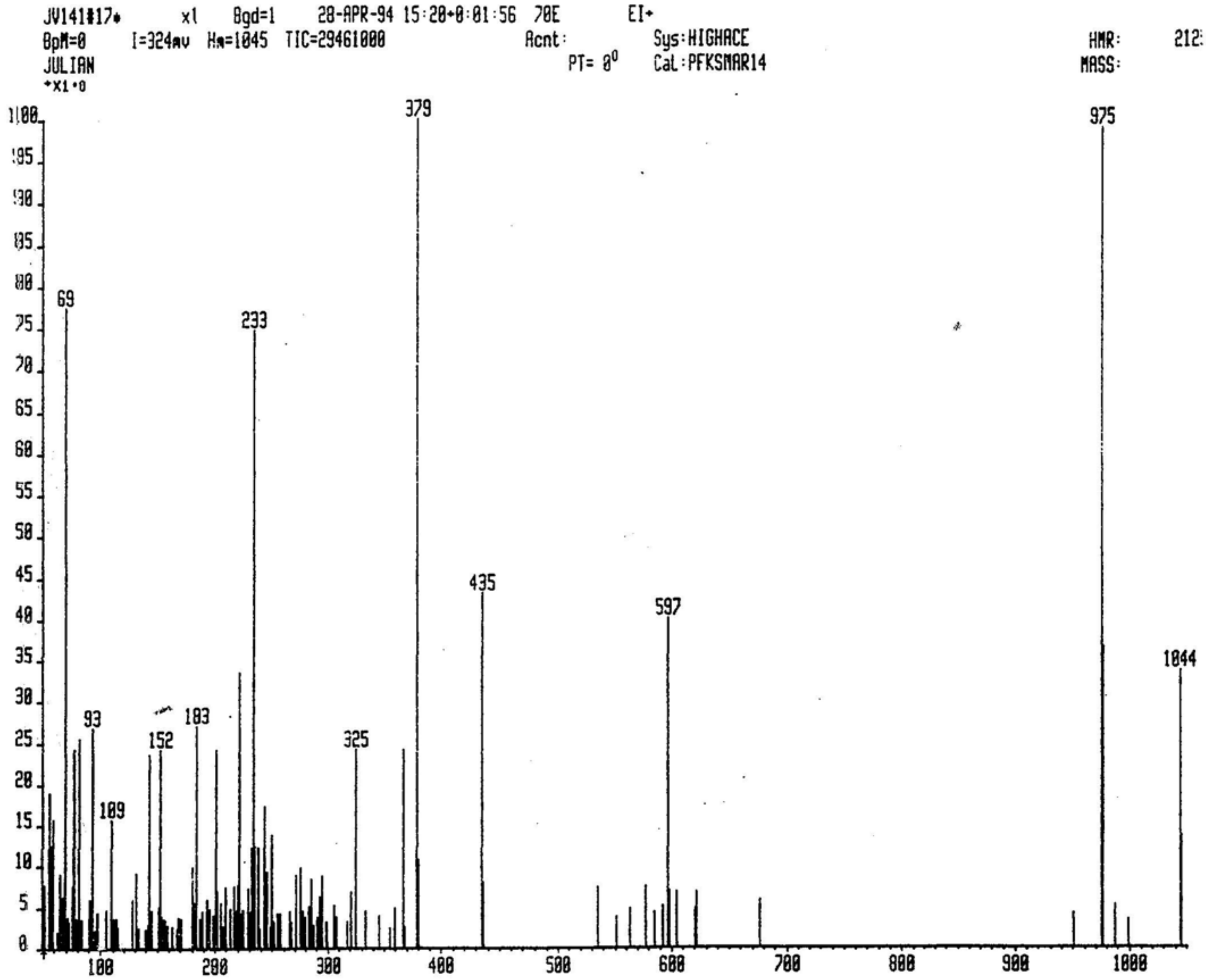
Mass Spectrum 20



Mass	% Base
52.11	1.48
56.07	0.88
58.09	5.51
59.09	0.77
60.09	2.72
61.07	2.16
70.09	0.91
72.11	1.28
74.10	2.18
77.10	1.50
78.09	1.60
81.10	0.72
82.10	0.77
83.10	0.43
84.10	0.88
86.12	0.73
88.11	2.22
90.09	0.60
91.12	1.09
93.09	0.71
94.10	2.21
95.11	1.12
96.11	1.10
97.11	0.49
98.12	1.00
99.12	0.81
100.13	0.87
102.13	1.53
105.14	0.64
107.11	0.56
108.12	1.52
109.10	5.39
110.11	1.33
111.12	0.79
112.13	0.66
113.13	0.66
114.14	0.61

Mass	% Base
144.15	0.49
145.13	0.39
146.14	0.59
147.15	0.51
148.15	0.53
149.17	0.40
150.17	0.48
152.12	6.17
153.13	1.37
154.15	0.47
155.15	0.37
156.18	0.43
157.14	0.68
158.15	0.49
159.15	0.54
160.15	0.47
161.16	0.39
162.16	0.40
163.18	0.67
164.15	0.47
165.14	1.06
166.14	0.49
167.15	0.46
168.13	1.52
169.14	0.79
170.14	0.77
171.14	0.82
172.17	0.51
173.17	0.49
174.18	1.07
175.17	0.66
176.17	0.43
178.20	0.62
180.14	5.83
181.14	2.15
182.15	0.85
183.13	7.66
585.00	42.36
951.00	100.00
1020.00	40.34

Mass Spectrum 21

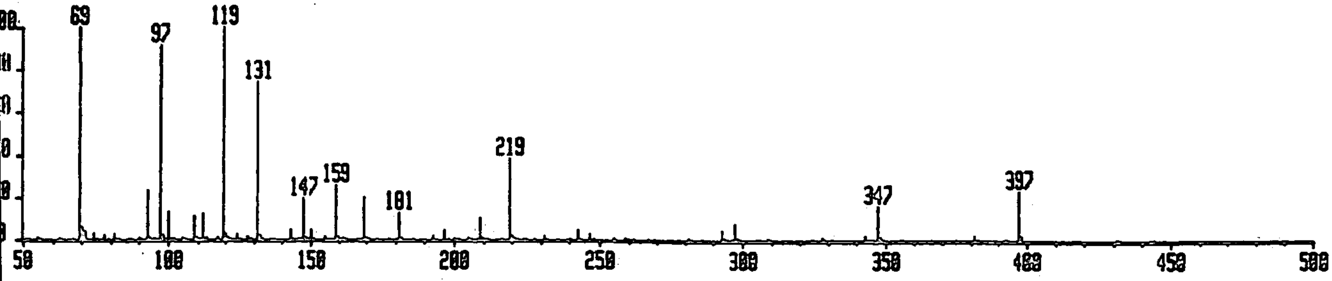


```
JV141#17*        xl    Bgd=1     28-APR-94 15:20+0:01:56  70E         EI+
BpM=0     I=324mv  Hm=1045  TIC=29461000               Acnt:           Sys:HIGHACE                    HMR:      212:
JULIAN                                                        PT= 0°   Cal:PFKSMAR14                  MASS:
*X1*0
```

Mass	% Base	
69.11	77.32	
71.20	3.72	
73.15	3.06	
76.14	7.39	
77.15	24.09	
79.17	3.48	
81.14	25.36	
83.20	3.29	
91.17	5.84	
93.16	26.73	
143.20	23.48	
145.20	4.56	
151.20	4.89	
152.25	24.09	
221.29	33.36	
222.29	4.14	
223.28	2.59	
225.24	4.56	
229.28	7.11	
231.28	4.42	
232.28	12.09	
233.31	74.68	
234.30	12.28	
237.26	12.19	
238.27	2.16	
243.24	17.18	
325.27	24.09	
333.28	4.42	
345.30	3.86	
355.30	2.35	
359.29	4.80	
367.30	24.09	
368.29	2.54	
379.32	100.00	
380.33	10.73	
435.39	43.06	
597.33	40.05	
598.33	6.92	
604.37	6.73	
620.37	4.71	
621.37	6.78	
676.29	5.74	
951.23	4.05	
975.21	99.15	F
976.41	36.47	F
987.27	5.08	
999.26	3.29	
1044.16	33.51	F
1045.19	13.60	F

Mass Spectrum 22

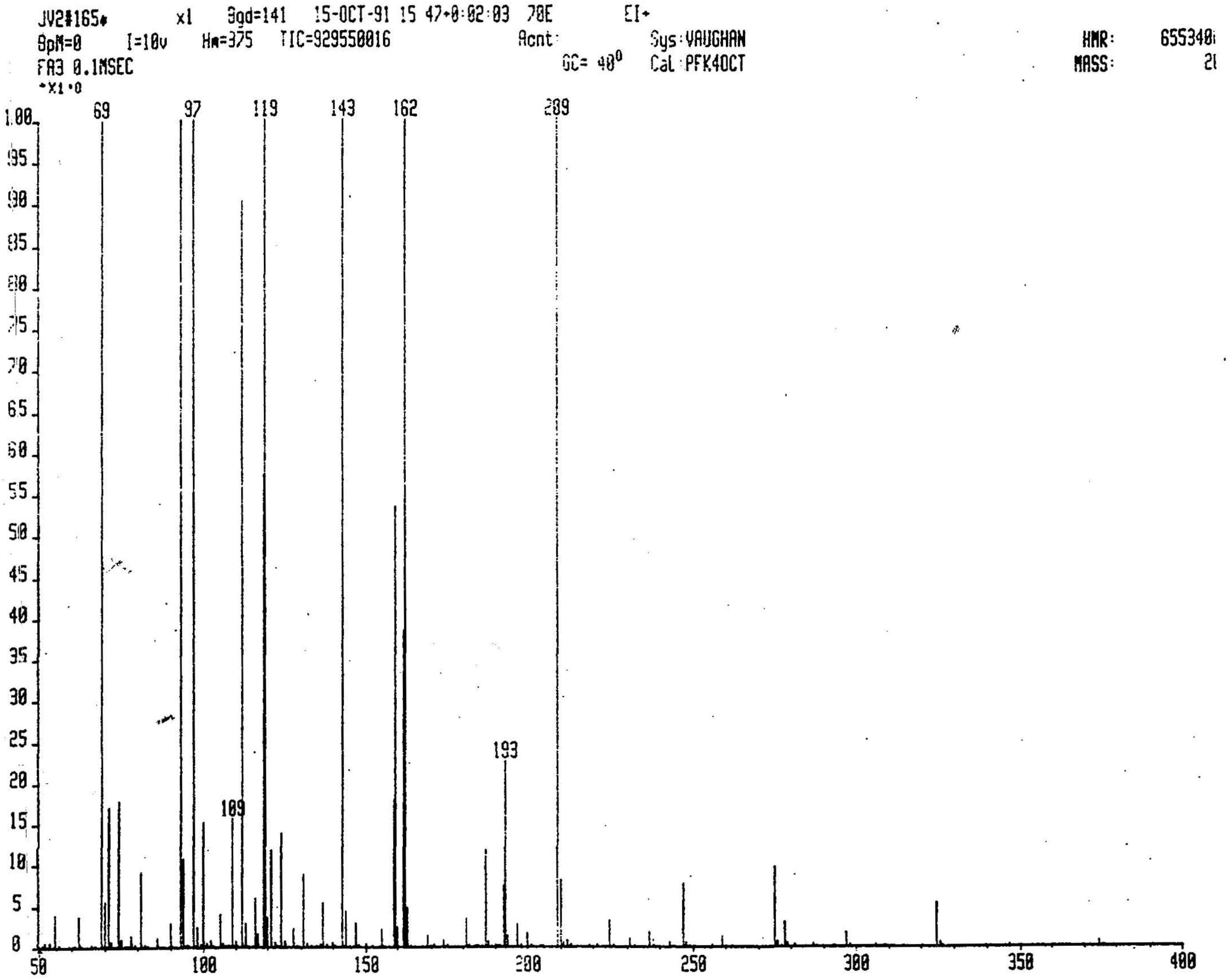
```
JV460136o      x1   Bgd=123   15-SEP-92 11:17+0:01:41  70E        EI+
BpA=0    I=10v   Ha=443   TIC=456956992             Acnt:        Sys:JULIAH                             HRR:      655340
FA3 0.1ASEC                                            GC= 40°   Cal:PFK27AUG                           MASS:          1
```



Mass	% Base	
49.93	6.94	
54.92	0.60	
61.92	0.81	
68.93	100.00	O
69.91	6.03	
70.91	3.87	
73.91	2.33	
77.90	1.71	
80.90	2.39	
89.90	0.71	
92.91	23.01	
93.91	0.75	
96.89	91.44	
97.89	2.11	
99.89	12.62	
104.89	0.90	
108.87	11.01	
109.88	0.36	
111.88	12.04	
112.88	0.43	
116.88	0.80	
118.88	100.00	O
119.87	2.25	F
120.87	0.46	F
123.88	2.87	
127.87	1.45	
130.87	74.08	
131.88	2.23	
142.87	4.48	
146.86	19.11	
147.87	0.62	
149.86	4.24	
154.86	1.48	
158.85	25.75	
159.86	1.11	
161.86	0.92	
168.84	19.97	
169.85	0.62	
180.85	12.85	
181.85	0.54	
192.85	1.94	
196.83	4.19	
199.84	0.37	
204.83	0.67	
208.82	10.25	
209.83	0.59	
218.83	38.38	F
219.83	1.61	F
220.84	0.42	
230.84	2.00	
242.85	4.30	
243.85	0.31	
246.84	2.82	
254.86	0.34	
258.85	0.92	
280.86	0.51	
292.86	4.27	
293.87	0.33	
296.85	7.57	
297.86	0.50	

Mass	% Base	
308.86	0.91	
327.87	1.13	
342.88	2.03	
346.86	16.33	F
347.88	1.29	F
380.89	2.23	
392.87	0.37	
396.89	23.26	F
397.96	1.99	F
430.94	0.73	

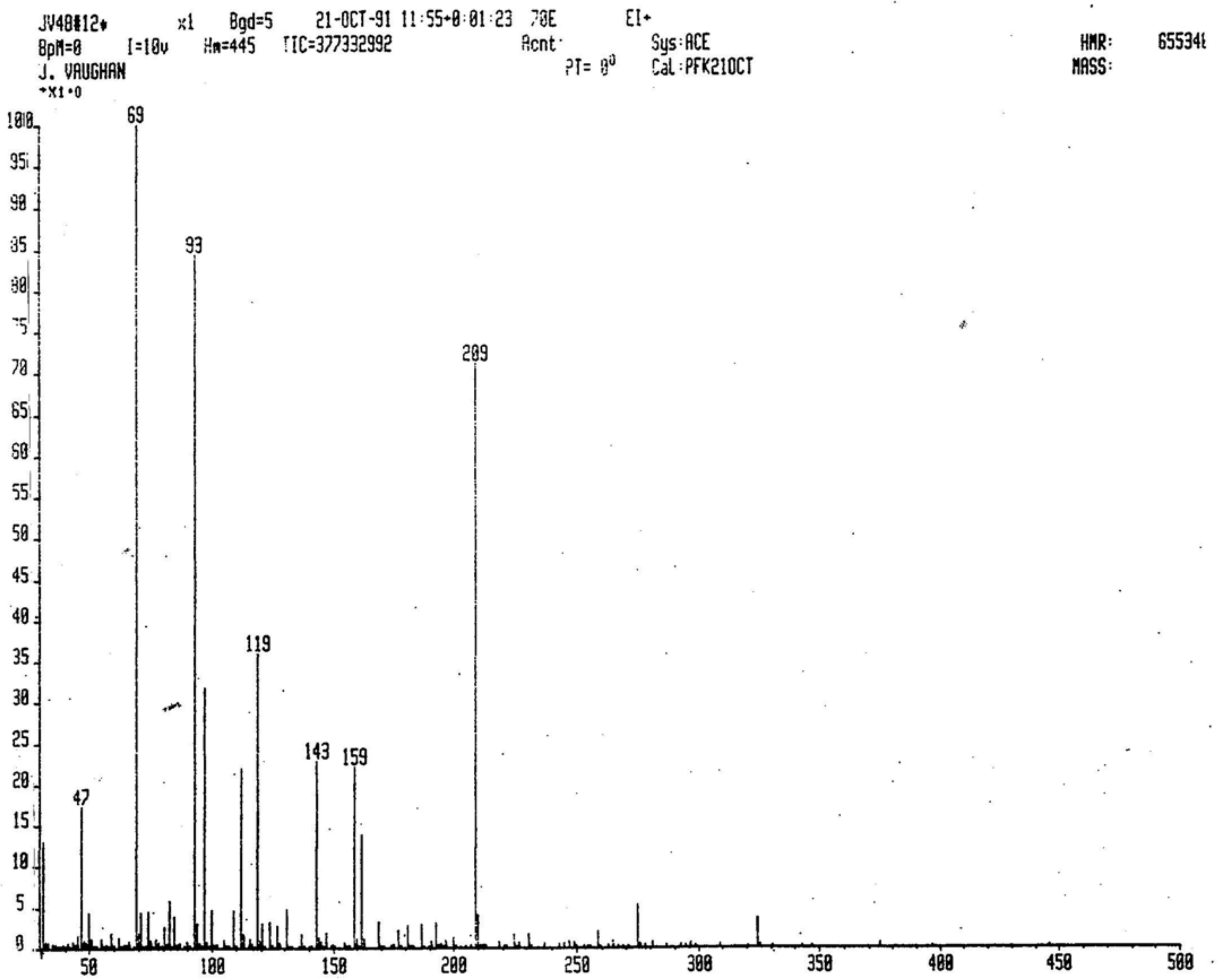
Mass Spectrum 23



Mass	% Base	
69.01	100.00	O
69.98	5.47	
70.97	16.95	
71.98	0.55	
73.98	17.86	
74.98	0.91	
77.97	1.34	
80.97	8.99	
85.97	1.01	
89.97	2.73	
93.01	100.00	FO
93.97	10.67	F
96.91	38.33	F
96.98	100.00	FO
97.97	2.35	
99.96	15.23	
108.96	15.69	
109.97	0.53	
111.89	30.79	F
111.98	90.20	F
112.96	2.79	
115.95	5.83	
116.94	1.46	F
118.89	57.44	F
118.98	100.00	FO
119.95	3.52	F
120.97	11.63	F
121.96	0.47	F
123.96	13.84	

Mass	% Base	
142.87	31.42	F
142.98	100.00	FO
143.96	4.30	
146.95	2.73	
154.94	2.06	
158.85	18.02	F
158.96	53.60	F
159.93	2.34	F
161.84	38.49	F
161.97	100.00	FO
192.96	22.60	F
193.92	1.33	
196.91	2.61	
199.91	1.56	
208.78	49.04	F
208.93	100.00	FO
209.91	8.05	F
286.91	0.33	
296.88	1.61	
324.87	5.24	
325.88	0.41	
374.87	0.57	

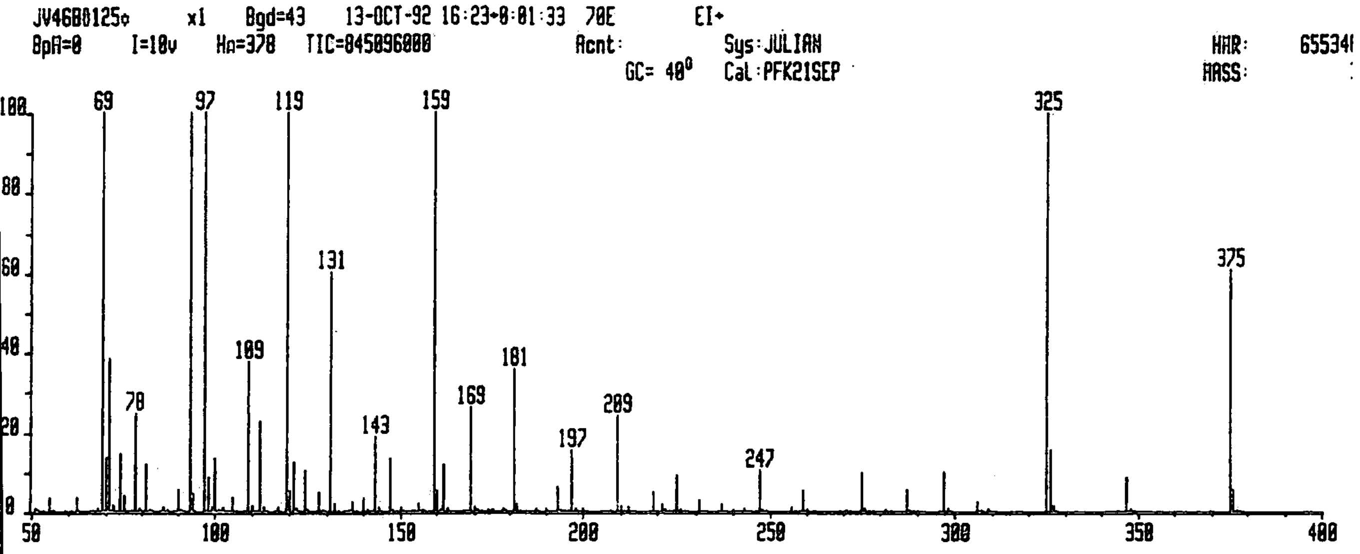
Mass Spectrum 24



```
JV40#12+        x1   Bgd=5    21-OCT-91 11:55+0:01:23  70E        EI+
BpM=0    I=10v   Hm=445   TIC=377332992              Acnt           Sys:ACE                      HMR:    65534
J. VAUGHAN                                              PT= 0°    Cal:PFK210CT                   MASS:
+X1.0
```

Mass	% Base	
68.94	100.00	O
69.95	1.80	
70.94	4.23	
73.94	4.32	F
92.93	84.21	
93.93	2.94	
94.94	0.39	
96.92	31.69	
111.91	21.86	
112.92	1.56	
115.91	0.98	
116.90	0.44	
118.91	35.87	
142.90	22.73	
143.90	1.13	
144.91	0.80	
146.89	1.69	
154.89	0.52	
158.88	22.03	
159.88	1.02	
161.88	13.72	
208.84	70.90	
209.85	3.91	
325.76	0.33	
374.73	0.51	

Mass Spectrum 25



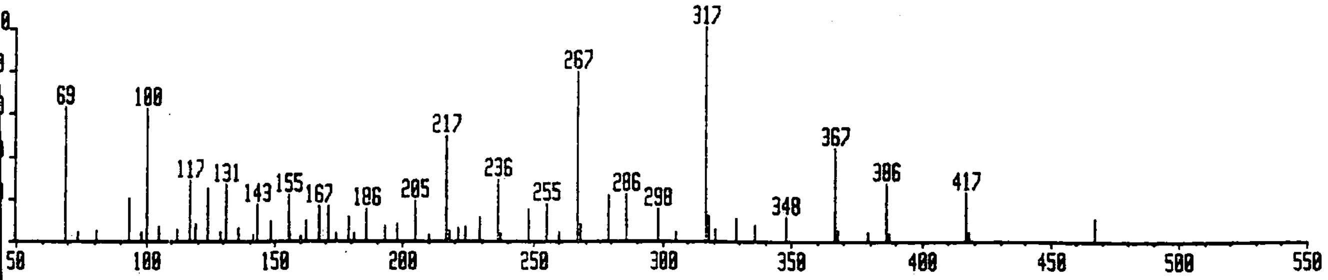
```
JV46B0125o      x1    Bgd=43    13-OCT-92 16:23+0:01:33  70E        EI+
BpA=0     I=10v    Ha=370   TIC=845096000              Acnt:        Sys:JULIAN                    HMR:     65534
                                                   GC= 40°   Cal:PFK21SEP                      MASS:
```

Mass	% Base	
49.94	17.26	
50.95	0.37	
54.95	2.60	
61.94	3.24	
68.96	100.00	O
69.94	12.65	
70.93	38.74	
71.94	1.37	
73.94	14.49	
74.93	3.99	
77.93	26.89	
78.94	0.61	
80.93	13.05	
81.94	0.40	
85.94	1.12	
89.93	6.66	
92.95	100.00	O
93.93	5.63	
96.96	100.00	O
97.93	9.89	
98.93	1.14	
99.93	16.80	
100.91	0.55	
101.93	1.27	
104.93	4.69	
108.92	53.03	
109.93	1.70	
111.92	32.16	
112.93	1.25	
116.93	1.62	F
118.96	100.00	FO
119.93	7.39	
120.92	17.37	F
121.92	0.85	F
123.93	14.74	
124.93	0.78	
127.92	7.03	
130.93	88.86	
131.93	2.87	
135.92	0.48	
136.92	3.73	
139.92	5.43	
140.93	0.41	
142.92	31.03	
143.93	1.15	
146.92	20.40	
147.93	0.63	
149.93	1.40	
154.92	3.19	
158.96	100.00	O
159.93	8.23	
160.93	0.61	
161.93	18.87	
162.94	0.98	
168.93	42.41	

Mass	% Base	
180.92	59.30	F
181.92	2.73	
186.90	1.01	
189.89	1.63	
192.90	10.89	
193.97	0.60	
196.92	26.27	
197.92	0.98	
199.92	1.25	
208.91	44.58	F
209.92	2.38	F
211.93	1.55	
218.93	9.31	
219.94	0.40	
220.93	3.23	
224.92	15.99	
225.92	0.90	
230.93	5.35	
231.94	0.33	
236.92	2.76	
239.93	0.79	
242.93	1.65	
246.91	18.77	
247.93	1.03	
255.92	1.93	
258.92	9.89	
259.93	0.69	
271.18	0.68	
274.93	18.48	
275.94	1.17	
280.95	0.50	
286.93	11.20	
287.95	0.86	
296.93	19.83	
297.93	1.29	
305.93	4.38	
306.94	0.46	
308.93	1.86	
325.02	100.00	FO
325.93	31.29	F
326.94	2.73	F
346.92	18.69	F
347.95	1.45	F
375.03	100.00	FO
375.94	19.20	F
376.94	1.69	F

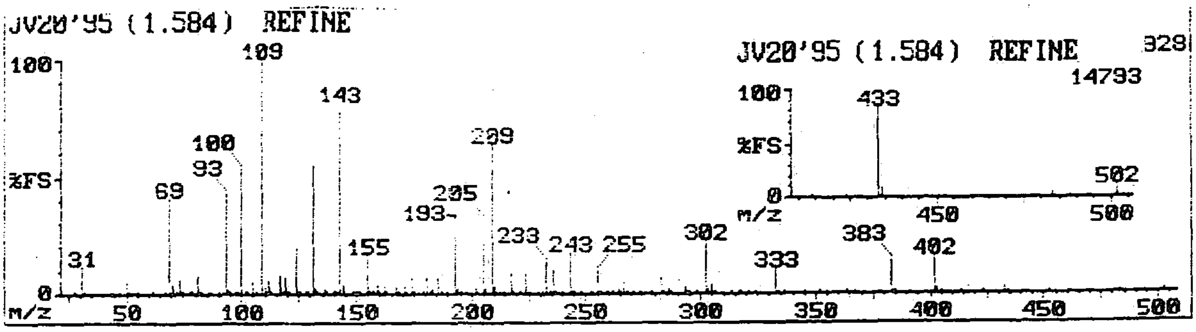
Mass Spectrum 26

```
JV300#325+      x1    Bgd=202   30-OCT-92 14:34+0:04:02  70E        EI+
BpM=0     I=111mv  Hm=466   TIC=7202000                Acnt:       Sys:JULIAN                              HMR:      7320
                                                           GC= 35°  Cal:PFK200CT                            MASS:        3
```



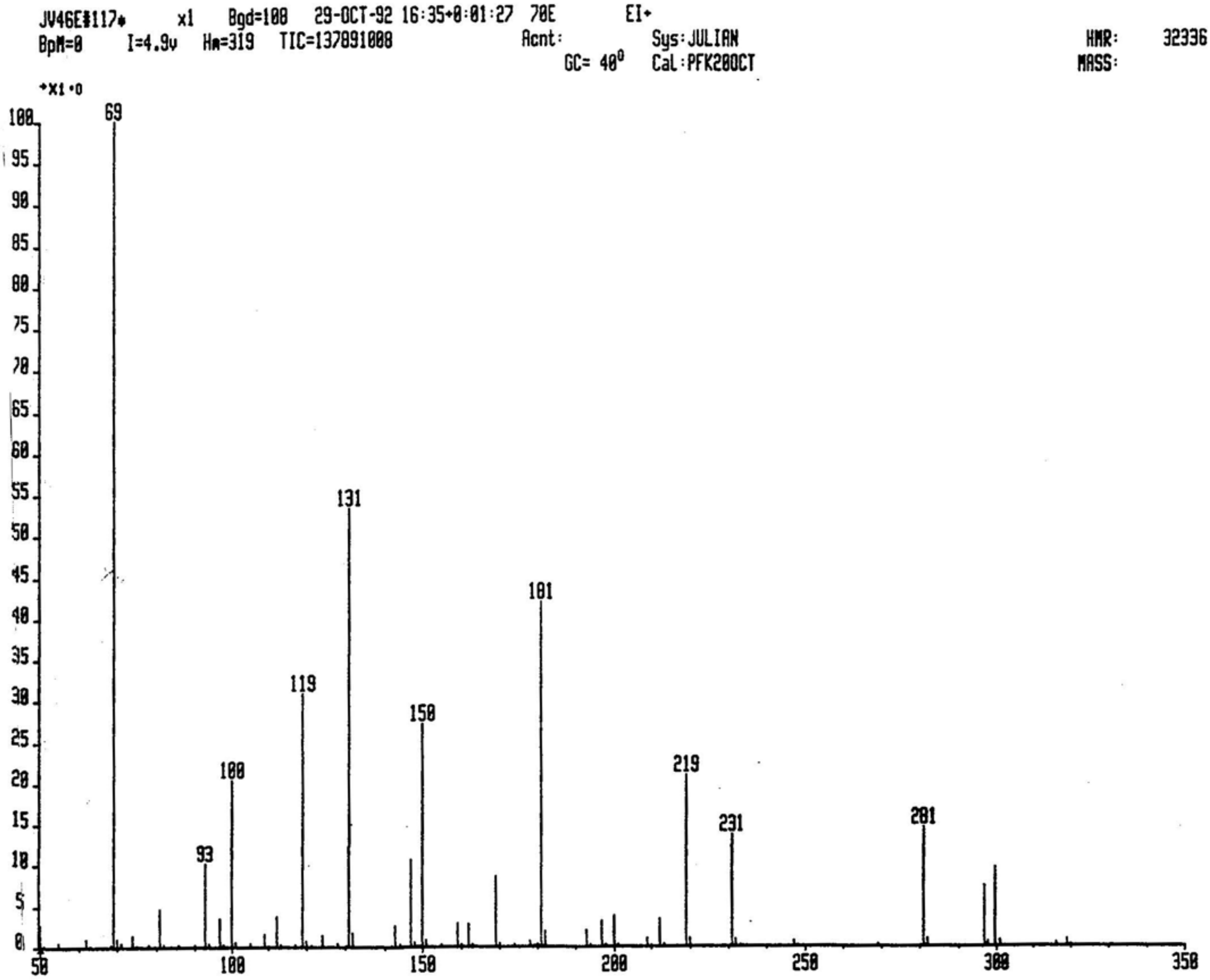
Mass	% Base
50.00	2.32
68.99	62.57
73.99	3.96
81.00	4.64
92.98	19.81
97.98	3.55
99.98	62.02
104.98	6.69
111.98	4.92
116.97	28.14
118.97	7.38
123.97	24.32
128.96	3.96
130.97	26.09
135.97	5.60
140.97	2.73
142.96	16.53
147.96	8.74
154.96	21.04
155.96	3.42
159.85	2.19
161.96	8.74
166.96	16.12
170.95	15.98
173.96	3.01
178.95	11.07
180.94	3.42
185.93	14.62
192.92	6.28
197.93	7.38
204.94	18.44
209.94	2.73
216.93	49.18
217.93	4.37
220.93	5.60
223.93	6.28
228.93	10.66
235.93	28.55
236.94	3.42
247.91	14.89
254.90	17.08
259.91	3.55
266.89	79.51
267.90	7.92
278.89	20.90
285.90	21.86
297.88	14.48
304.85	3.55
316.85	100.00
317.87	11.75
320.85	4.92
328.86	10.25
335.85	7.24
347.83	11.20
366.82	43.31
367.84	4.51
378.84	3.55
385.81	26.91
386.85	3.42
416.78	22.54
417.83	4.10
466.76	9.97

Mass Spectrum 27



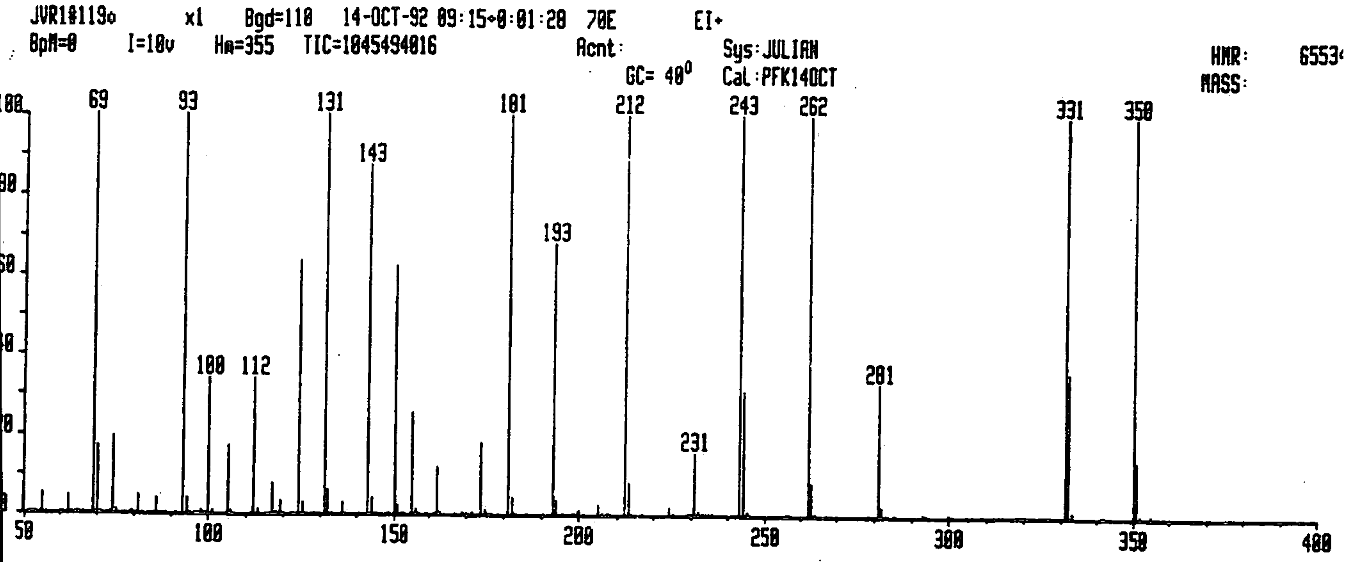
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
28	0.30	119	6.38	190	0.67	279	0.20
31	11.49	120	0.14	193	31.18	283	5.59
32	0.05	121	0.31	194	1.50	284	0.46
43	0.17	124	19.62	195	0.12	286	1.76
44	0.11	125	0.83	198	0.74	287	0.11
47	0.67	126	0.27	202	1.88	293	3.21
50	4.50	128	0.14	203	0.09	294	0.24
51	0.12	129	0.50	205	31.39	295	0.44
55	1.34	131	55.38	206	2.32	298	0.34
62	0.70	132	1.97	209	64.25	302	22.58
67	0.08	133	0.39	210	3.24	303	1.76
69	40.86	136	1.85	211	0.22	305	3.98
70	0.52	137	0.14	212	0.73	306	0.32
71	3.86	140	1.21	214	0.58	314	0.73
72	0.12	141	0.39	217	8.53	317	1.31
74	6.18	143	31.72	218	0.58	318	0.13
75	0.30	144	3.44	221	1.01	321	0.39
78	1.29	148	1.09	224	9.21	324	0.16
79	0.37	149	0.06	225	0.52	333	10.42
81	8.20	150	0.78	229	0.47	334	0.75
82	0.24	151	0.09	231	0.31	336	0.44
83	0.04	152	0.10	233	13.44	345	0.25
86	1.09	155	16.47	234	0.95	352	0.33
87	0.09	156	0.86	236	9.81	355	1.02
90	1.06	157	0.09	237	0.66	364	0.75
93	42.47	159	4.30	240	0.32	367	0.22
94	1.48	160	0.27	243	17.20	383	13.78
95	0.07	162	3.58	244	1.02	384	1.36
97	0.49	163	0.15	245	0.74	385	0.09
98	0.83	167	2.69	248	0.75	402	15.19
100	52.96	168	0.16	252	2.20	403	1.50
101	1.44	169	0.84	253	0.17	405	0.61
102	0.93	171	3.09	255	10.15	414	0.11
105	4.57	172	0.18	256	0.69	424	0.06
106	0.25	174	6.99	259	1.00	433	3.24
109	100.00	175	0.42	262	0.47	434	0.35
110	3.38	179	1.00	264	1.83	452	0.08
111	0.20	181	7.19	265	0.14	483	0.18
112	6.18	182	0.37	267	4.84	502	0.45
113	0.26	183	1.56	268	0.39		
117	7.33	186	7.06	271	1.19		
118	0.38	187	0.45	274	0.82		

Mass Spectrum 28



Mass	% Base
50.01	2.66
55.01	0.48
62.02	0.90
69.01	100.00
81.01	4.52
93.02	10.08
94.02	0.36
97.01	3.43
100.02	20.28
119.02	30.83
120.02	0.60
124.02	1.33
131.02	53.23
132.02	1.64
143.02	2.55
147.01	10.46
148.01	0.38
150.01	27.12
181.01	41.83
219.00	20.86
220.01	0.81
231.00	13.51
232.01	0.73
246.99	0.54
280.99	14.41
281.99	0.85
296.97	7.28
297.97	0.43
299.97	9.48
300.99	0.56
315.97	0.32

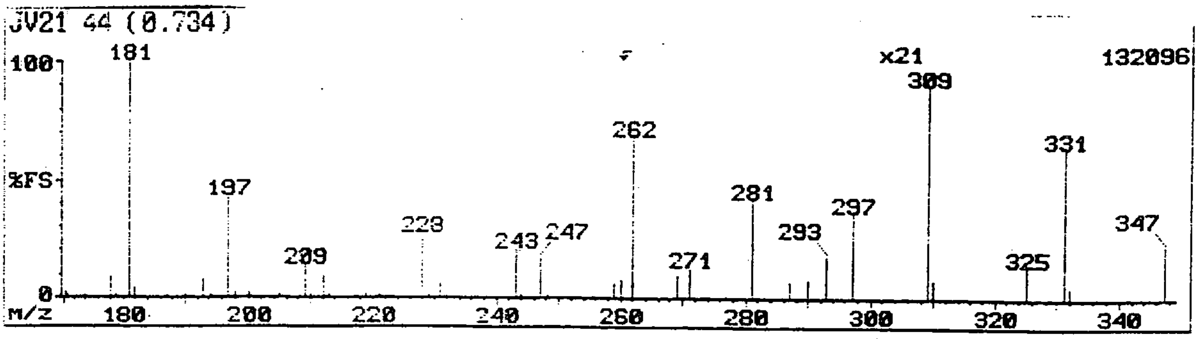
Mass Spectrum 29



Mass	% Base
49.99	11.10
55.00	4.79
62.00	4.18
69.02	100.00 O
70.00	16.85
73.99	19.08
75.00	0.63
80.99	4.30
86.00	3.87
93.01	100.00 O
94.00	3.60
98.00	0.73
100.01	33.95
123.99	63.19
125.00	2.76
131.02	100.00 O
132.00	5.82
135.99	2.73
142.99	87.50
143.99	3.76
150.00	62.14
151.00	2.02
154.97	25.40
155.98	1.19
161.98	11.49
162.99	0.46
171.49	0.41 F
173.98	17.88 F
174.99	0.99
181.00	100.00 O
181.99	4.27
192.97	67.93
193.98	3.55
199.99	1.06
204.98	2.44
212.02	100.00 FO
212.99	7.82 F
223.99	1.58
230.98	15.52
232.00	0.78
243.09	100.00 FO
244.00	30.89 F
245.01	0.67
262.03	100.00 FO
263.00	7.92 F
280.98	32.71
281.98	1.95
293.01	0.68
331.12	100.00 FO
331.99	35.63 F
333.09	1.10 F
350.06	100.00 FO

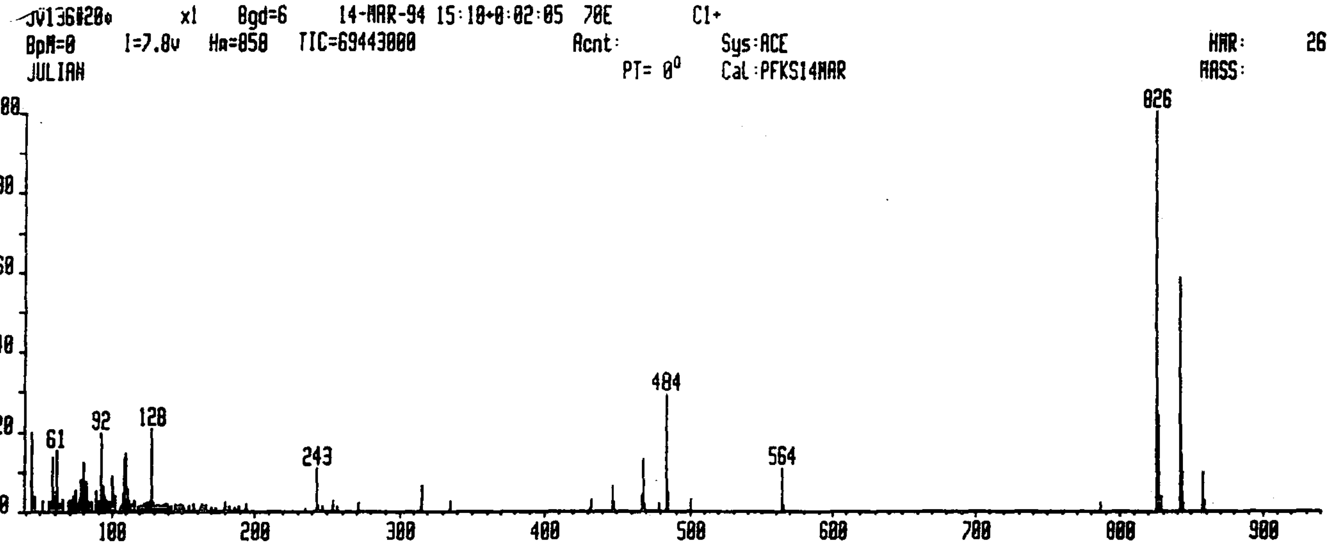
Mass	% Base
350.98	13.68 F
351.95	0.51 F

Mass Spectrum 30



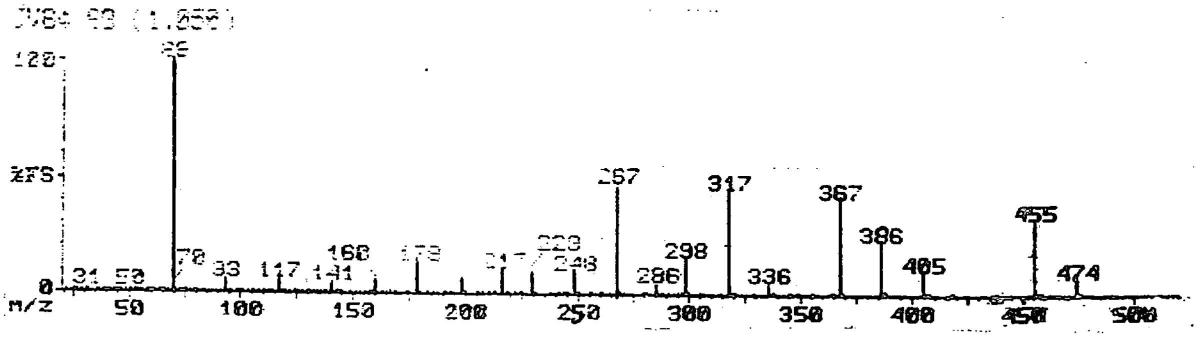
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
170	0.22	197	5.40	229	0.21	281	0.31
171	0.07	198	0.29	231	0.81	287	0.05
174	0.17	200	0.28	243	3.08	290	0.06
178	1.30	205	0.07	244	0.19	293	0.13
179	0.10	209	2.01	247	2.44	297	0.26
181	15.00	210	0.11	248	0.13	309	0.65
182	0.63	212	1.24	259	0.81	310	0.05
187	0.06	213	0.08	260	0.06	325	0.10
190	0.03	219	0.33	262	0.49	331	0.47
193	1.18	221	0.16	269	0.07	332	0.03
194	0.09	228	4.01	271	0.09	347	0.16

Mass Spectrum 31



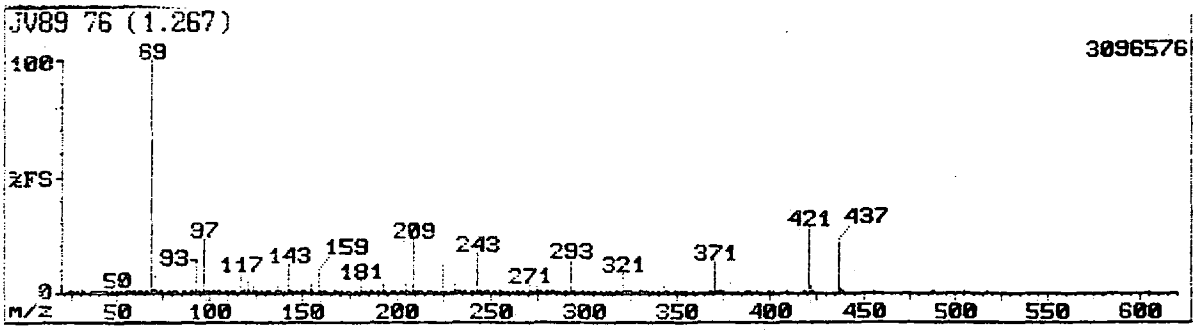
Mass	% Base	
44.04	1.00	
58.06	0.69	
61.03	0.77	
78.05	0.38	
80.04	0.62	
82.04	0.37	
92.01	1.00	
93.04	0.32	
100.05	0.44	
109.05	0.67	
110.03	0.74	
128.04	1.06	
242.96	0.56	
316.00	0.32	
447.11	0.32	
467.96	0.65	
483.97	1.51	
563.94	0.56	
825.83	5.18	F
826.88	1.23	F
841.85	3.02	F
842.89	0.72	F
857.87	0.50	

Mass Spectrum 32



Mass	Rel Int
69	100.00
117	6.07
124	4.12
179	13.54
217	10.85
229	10.61
267	47.32
317	44.39
367	40.98
386	22.32
455	40.20
474	10.31

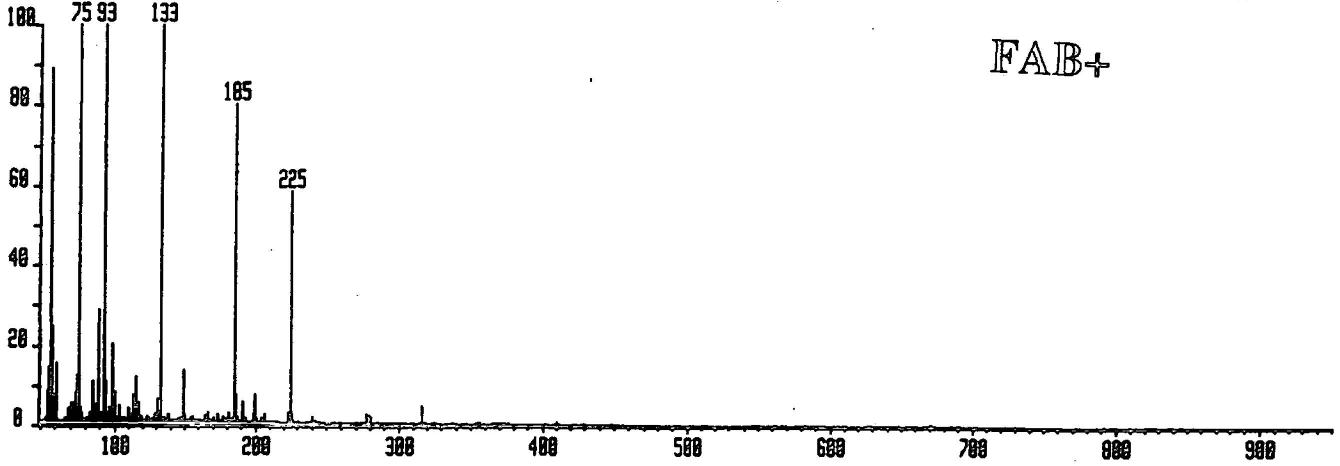
Mass Spectrum 33



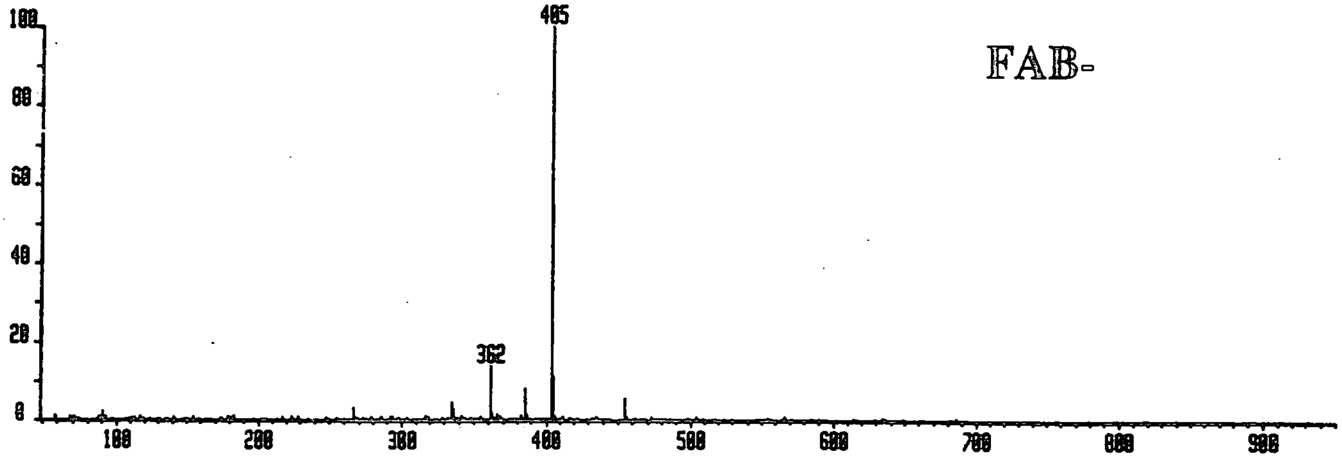
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
69	100.00	184	0.04	265	0.01	419	0.01
70	1.74	186	0.62	267	0.68	421	28.57
71	2.15	187	0.45	268	0.07	422	2.61
72	0.09	190	0.39	271	4.07	423	0.18
74	1.38	191	0.04	272	0.26	437	21.30
75	0.09	193	3.54	273	0.01	438	1.93
78	1.07	194	0.18	275	2.48	439	0.16
79	0.16	197	0.06	276	0.13		
81	0.53	198	0.14	277	0.01		
82	0.03	199	0.03	280	0.02		
83	0.02	202	0.05	281	0.10		
86	0.29	203	0.02	283	0.49		
87	0.03	205	3.74	284	0.04		
90	1.46	206	0.20	286	0.13		
91	0.07	207	0.01	287	0.09		
93	11.38	209	22.88	290	0.55		
94	0.36	210	1.04	291	0.04		
95	0.16	211	0.06	293	2.68		
97	23.28	212	0.75	294	0.18		
98	0.82	213	0.05	295	0.03		
99	0.11	214	0.06	299	0.89		
143	12.70	217	0.80	300	0.07		
144	0.51	218	0.07	302	0.36		
145	0.08	219	0.01	303	0.04		
147	0.23	221	0.88	305	1.12		
148	0.53	222	0.05	306	0.08		
150	0.39	224	0.51	309	0.05		
151	0.02	225	14.81	312	0.14		
152	0.01	226	0.69	314	0.02		
155	4.20	227	0.07	317	0.08		
156	0.22	229	0.09	318	0.01		
159	8.47	231	3.74	321	8.73		
160	0.43	232	0.18	322	0.64		
161	0.06	233	0.43	323	0.04		
162	0.55	234	0.03	324	0.05		
163	0.06	236	0.93	325	0.08		
167	1.81	237	0.13	330	0.02		
168	0.12	240	0.16	331	0.01		
169	0.19	241	0.01	333	0.42		
171	0.06	243	17.86	334	0.04		
174	0.37	244	1.03	337	0.15		
175	0.05	245	0.07	340	0.11		
178	0.31	247	0.02	343	3.08		
179	0.28	248	0.08	344	0.22		
181	5.82	249	0.08	345	0.01		
182	0.20	252	0.07	349	0.72		
183	0.62	253	0.02	350	0.05		
		255	2.18	352	0.13		
		256	0.16	353	0.03		
		257	0.02	355	0.08		
		259	1.34	359	0.05		
		260	0.08	368	0.20		
		262	0.07	369	0.03		
		264	0.04	371	13.89		

Mass Spectrum 34

```
JV1402o          x1    Bgd=1      15-JAN-91 12:14+0:00:38  70E        FB+
BpM=0      I=10v    Hm=751   TIC=711624000              Acnt:          Sys:FAB                          HMR:     65
J. VAUGHAN                                                    PT= 0°    Cal:PFK14JAN                     MASS:
```



```
JV1400*          x1    Bgd=6      15-JAN-91 12:14+0:01:21  70E        FB-
BpM=0      I=6.8v   Hm=931   TIC=90241000               Acnt:          Sys:FAB                          HMR:     4477
J. VAUGHAN                                                    PT= 0°    Cal:PFK14JAN                     MASS:
```



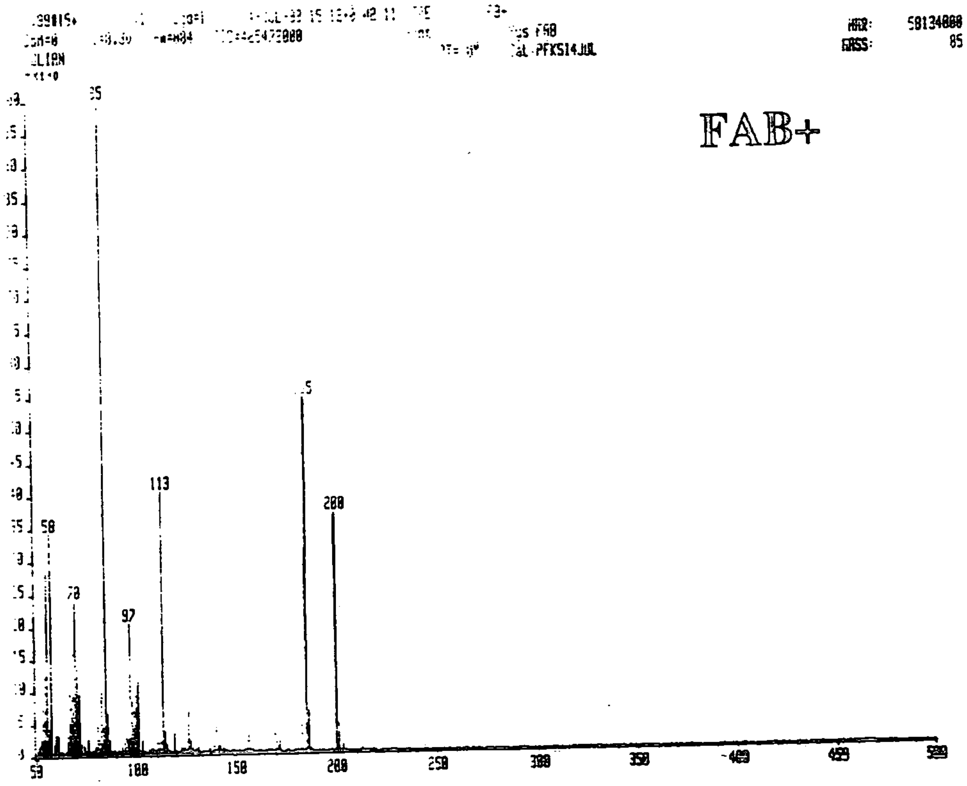
FAB+

Mass	% Base
130.81	6.64
131.85	1.17
132.68	100.00 0
133.84	0.94
134.83	1.57

FAB-

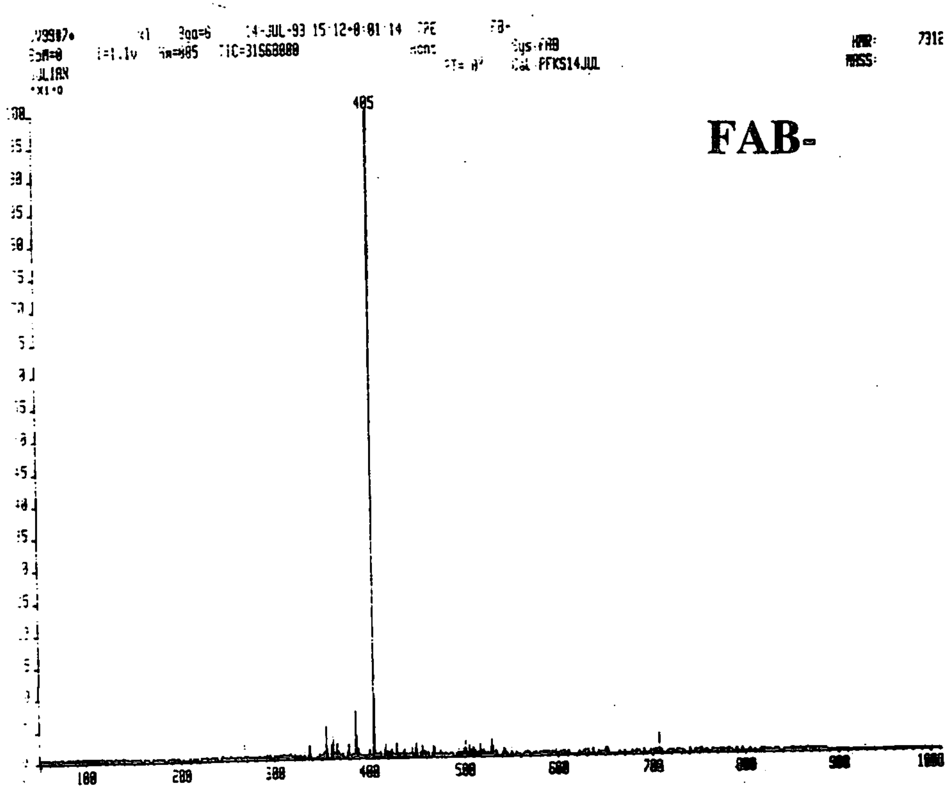
Mass	% Base
386.68	1.36 F
404.65	100.00 F
405.66	10.86 F
406.69	0.62 F

Mass Spectrum 35



FAB+

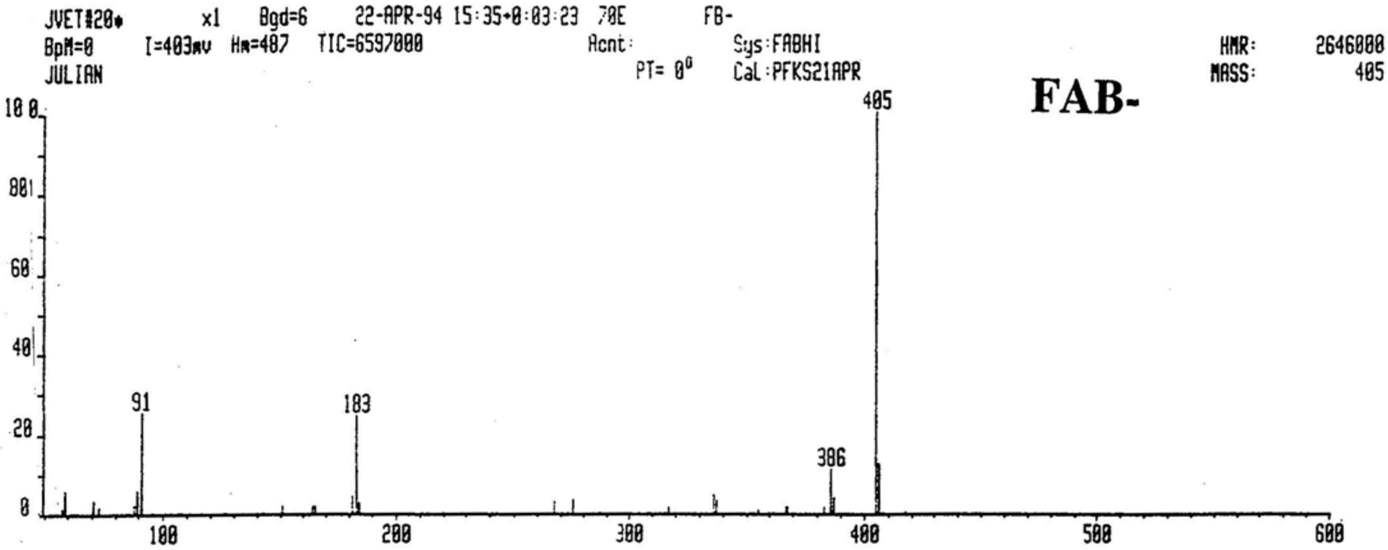
Mass	% Base
199.28	6.03
200.29	37.11
201.27	4.42

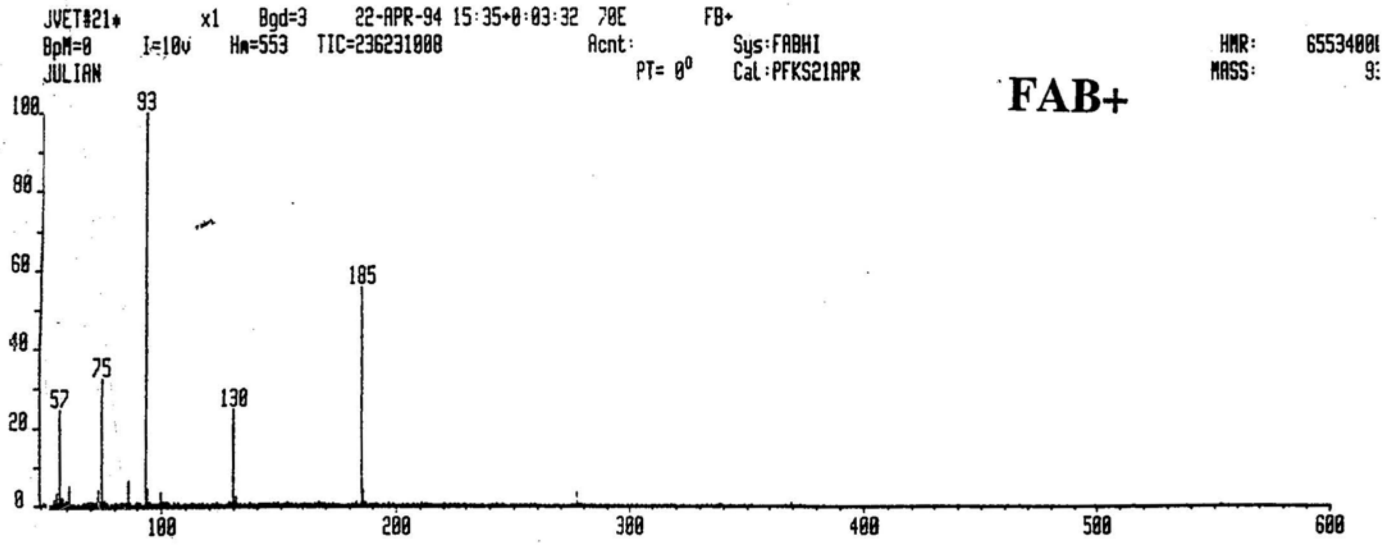


FAB-

Mass	% Base
403.15	0.36
405.49	100.00
406.51	9.89

Mass Spectrum 36





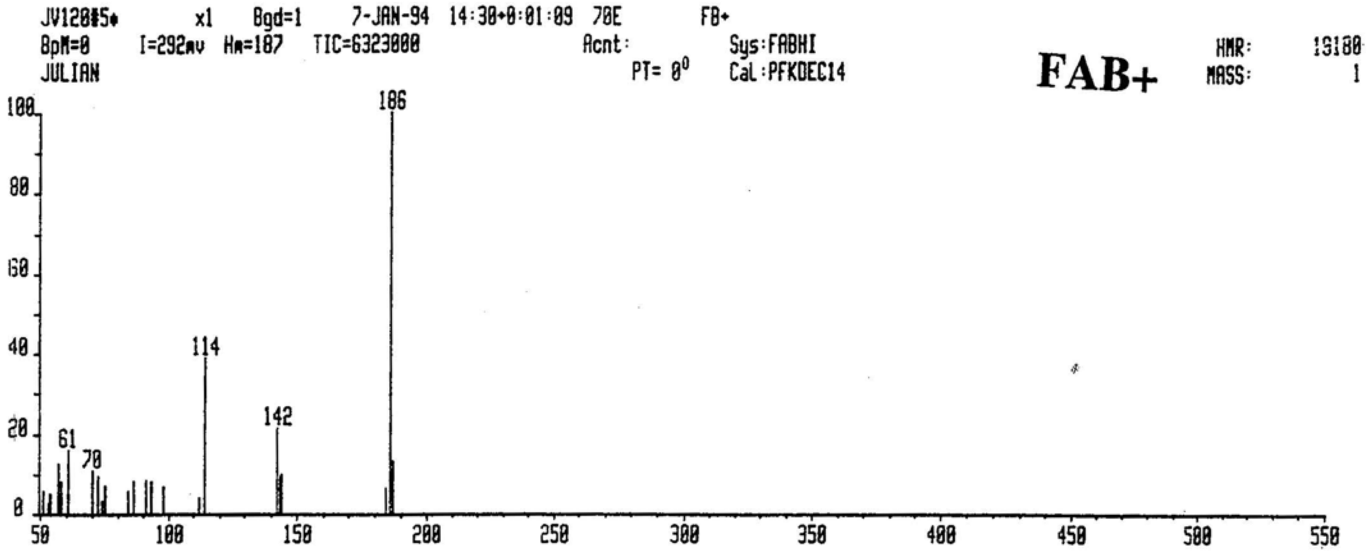
FAB-

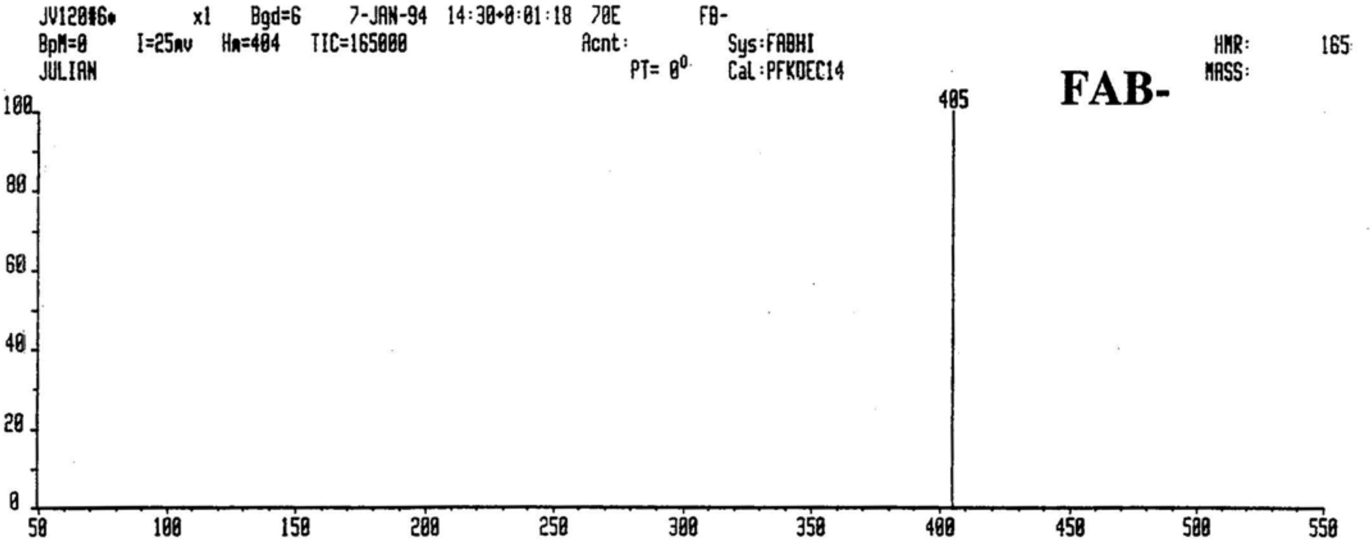
Mass	% Base
58.00	1.06
59.00	5.52
71.00	3.10
73.02	1.28
88.01	2.04
88.04	1.59
89.02	5.44
91.03	25.17
151.05	1.70
151.09	1.10
164.09	1.63
165.05	1.70
165.11	1.55
181.08	4.27
183.11	24.23
184.10	2.49
267.04	2.76
275.18	3.33
317.08	1.55
336.04	4.57
337.06	3.21
354.99	0.72
367.02	0.98
367.12	1.44
367.24	1.44
382.92	1.44
383.03	1.28
386.04	11.11
387.03	3.85
405.04	100.00
406.05	12.24

FAB+

Mass	% Base
129.04	0.79
130.00	5.30 F
130.11	24.82 F
131.09	2.36

Mass Spectrum 37





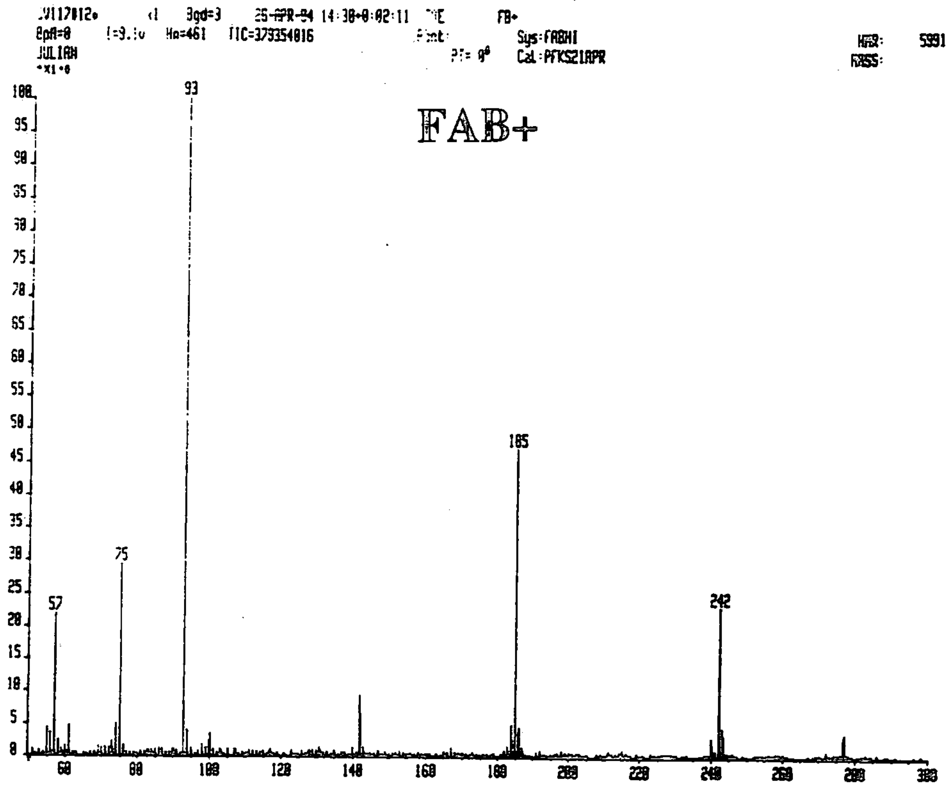
FAB+

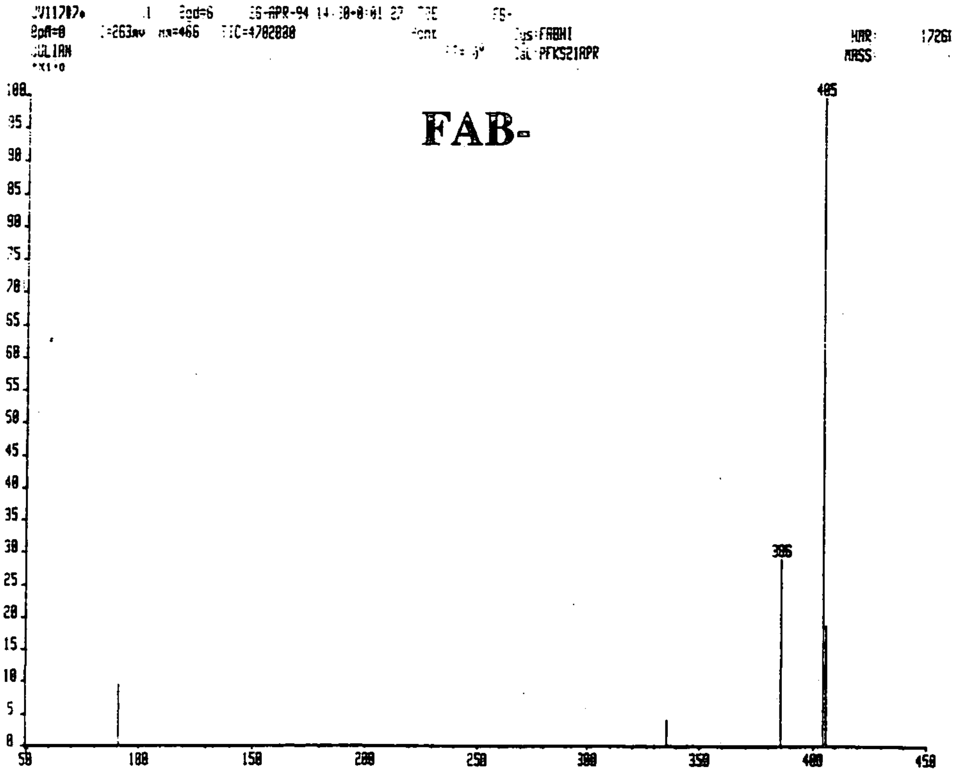
Mass	% Base
51.01	5.58
53.02	2.50
54.02	4.64
57.01	12.25
58.04	7.98
61.00	15.80
70.02	7.51
70.04	10.74
72.04	9.33
73.98	3.02
75.00	6.78
84.04	5.53
86.05	7.87
91.01	8.34
93.01	7.98
98.04	6.57
112.05	3.02
112.08	3.75
114.07	38.53
142.08	21.06
143.09	9.02
144.10	9.59
184.11	6.31
184.14	3.08
186.13	100.00
187.13	12.88

FAB-

Mass	% Base
404.73	100.00

Mass Spectrum 38





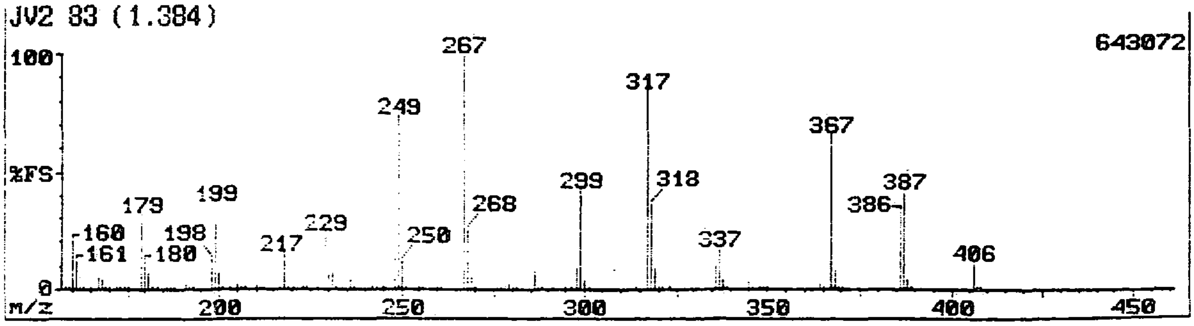
FAB+

Mass	% Base
241.17	0.85
242.22	23.12
243.06	2.30 F

FAB-

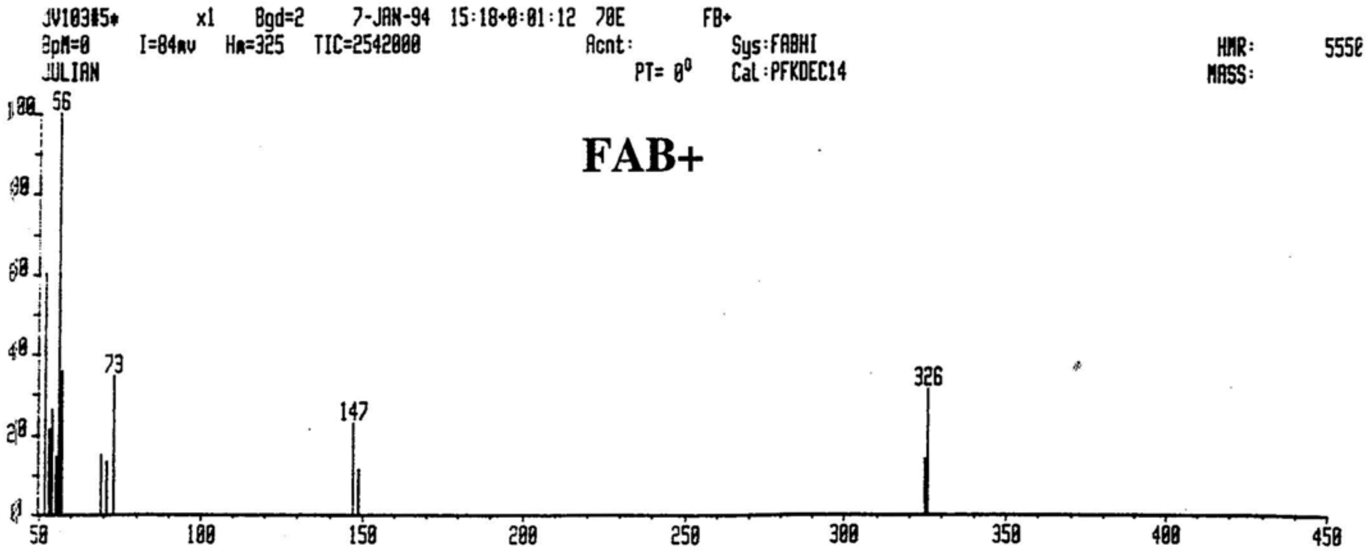
Mass	% Base
404.53	11.30
404.76	100.00 F
404.90	88.99 F
405.83	18.71

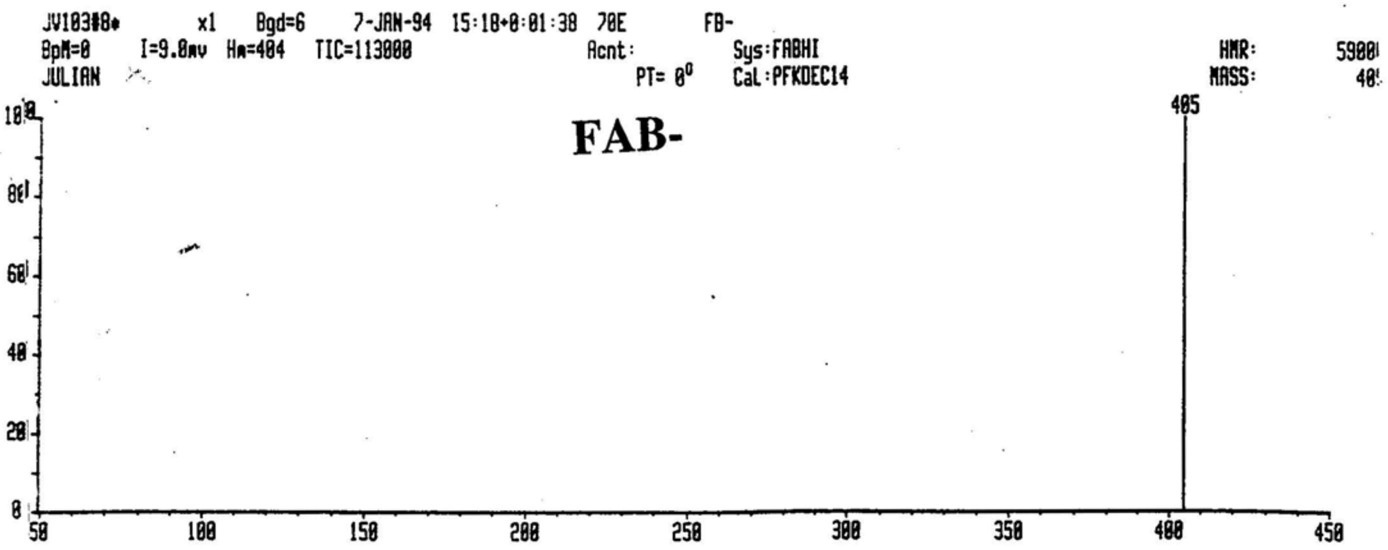
Mass Spectrum 39



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
157	0.03	200	1.72	250	2.89	319	2.14
159	0.02	201	0.10	251	0.18	320	0.16
160	4.88	203	0.01	255	0.02	321	0.01
161	2.93	205	0.36	256	0.00	323	0.01
162	0.28	206	0.03	260	0.05	329	0.01
163	0.04	207	0.03	261	0.03	336	2.49
165	0.01	210	0.56	267	24.53	337	4.38
167	1.27	211	0.27	268	6.29	338	0.88
168	1.03	212	0.03	269	1.16	339	0.07
169	0.11	217	3.87	270	0.08	345	0.81
170	0.01	218	3.75	276	0.01	346	0.09
172	0.18	219	0.31	277	0.02	348	0.19
173	0.02	220	0.02	279	0.68	349	0.19
174	0.16	223	0.02	280	0.21	350	0.02
175	0.04	224	0.02	281	0.03	364	0.43
179	7.93	227	0.01	286	1.97	365	0.05
180	2.77	229	6.05	287	0.30	367	16.09
181	1.66	230	1.51	288	0.03	368	1.82
182	0.11	231	1.63	291	0.01	369	0.12
184	0.22	232	0.13	295	0.21	370	0.01
186	0.15	236	1.04	296	0.03	386	7.77
187	0.18	237	0.20	298	2.21	387	10.31
188	0.01	241	0.14	299	10.47	388	1.05
191	0.36	242	0.01	300	0.92	389	0.05
192	0.10	243	0.01	301	0.04	406	2.85
193	0.10	245	0.06	314	0.04	407	0.30
198	3.09	248	4.57	317	20.78	408	0.01
199	8.95	249	18.13	318	8.79	456	0.01

Mass Spectrum 40





FAB+

Mass	% Base
51.91	60.00
52.90	10.09
52.91	21.08
52.92	9.55
53.91	11.53
53.92	25.95
54.98	14.41
55.90	100.00
56.91	35.68
56.99	29.01
68.89	14.77
70.90	13.15
72.89	34.41
146.88	22.52
148.89	10.99
324.92	13.69
325.94	31.17

FAB-

Mass	% Base
404.56	91.53
404.66	100.00

Appendix Four

Colloquia, Conferences and Induction Courses

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

3) details of the postgraduate induction course.

Research Colloquia, Seminars and Lectures

1991 - 1994

(an asterisk indicates those attended)

1991

October 17*	Dr. J. A. Salthouse, University of Manchester *Son et Lumiere - a demonstration lecture.*
October 31	Dr. R. Keely, Metropolitan Police Forensic Science *Modern Forensic Science.*
November 6	Prof. B. F. G. Johnson†, University of Edinburgh *Cluster-Surface Analogies.*
November 7	Dr. A. R. Butler, St. Andrews University *Traditional Chinese Herbal Drugs.*
November 13*	Prof. D. Gani†, St. Andrews University *The Chemistry of PLP Dependant Enzymes.*
November 20*	Dr. R. More O'Ferrall†, Dublin *Some Acid-Catalysed Rearrangements in Organic Chemistry.*

November 28	Prof. I. M. Ward, Leeds University *The Science & Technology of Orientated Polymers.*
December 4*	Prof. R. Grigg†, Leeds University *Palladium Catalysed Cyclisation and Ion Capture Processes.*
December 5*	Prof. A. L. Smith, ex Unilever *Soap Detergents and Black Puddings.*
December 11	Dr. W. A. Cooper†, Shell Research *Colloid Science, Theory, and Practice.*

1992

January 9*	Dr. E. Snyder, U.S. Air Force *Perfluoropolyethers*
January 16	Dr. N. J. Long, University of Exeter *Metallocenophanes-Chemical sugar-tongs.*
January 22	Dr. K. D. M. Harris†, University of St. Andrews *Understanding the Prperties of Solid Inclusion Compounds.*
January 29*	Dr. A. Holmes†, University of Cambridge *Cycloaddition Reactions in the Service of the Synthesis of Piperidine and ndolizidine Natural Products.*
January 30	Dr. M. Anderson, Sittingbourne Research Centre, Shell Research *Recent Advances in the Safe and Selective Chemical Control of Insect Pests.*
February 12*	Dr. D. E. Fenton†, University of Sheffield *Polynuclear Complexes of Molucular Clefts as Models for Copper Biosites.*
February 13	Dr. J. Saunders, Glaxo Group Research Limited *Molecular Modelling in Drug Discovery.*
February 19*	Prof. E. J. Thomas†, University of Manchester *Application of Organo-Stannanes to Organic Synthesis.*

February 20	Prof. E. Vogel, University of Cologne *The Musgrave Lecture: Porrphyrins, Molecules of Interdisciplinary Interest.*
February 25	Prof. J. F. Nixon, University of Sussex *Phosphoalkylenes, New Building Blocks in Inorganic and Organometallic Chemistry.*
February 26	Prof. M. L. Hitchman†, University of Stratheclyde *Chemical Vapour Deposition.*
March 5	Dr. N. C. Billingham, University of Sussex *Degradable Plastics - Myth or Magic ?*
March 10*	Dr. H. Fielding, ICI Polymers (retired) *Fluoropolymers*
March 11*	Dr. S. E. Thomas†, Imperial College London *Recent Advances in Organoiron Chemistry.*
March 12	Dr. R. A. Hann, ICI Image Data *Electronic Photography - An Image of the Future*
March 18*	Dr H. Maskill†, University of Newcastle *Concerted or stepwise fragmentation in a deamination-type reaction.*
April 7	Prof. D. M. Knight, Philosophy Department, University of Durham *Interpreting experiments: the begining of electrochemistry.*
April 30*	Dr. A. Marhold, Bayer Co., Leverkusen *Fluorine Chemistry in the Bayer Company.*
May 13	Dr. J-C. Gehret, Ciba Geigy, Basel *Some aspects of Industrial Agrochemical Research.*
July 3*	Dr. V. Palmer, University of Delhi *Biological systems in Organic Synthesis*

October 15	Dr M. Glazer & Dr. S. Tarling, Oxford University & Birbeck College, London *It Pays to be British! - The Chemist's Role as an Expert Witness in Patent Litigation.*
October 20	Dr. H. E. Bryndza, Du Pont Central Research *Synthesis, Reactions and Thermochemistry of Metal (Alkyl) Cyanide Complexes and Their Impact on Olefin Hydrocyanation Catalysis.*
October 22	Prof. A. Davies, University College London *The Ingold-Albert Lecture The Behaviour of Hydrogen as a Pseudometal.*
October 28	Dr. J. K . Cockcroft, University of Durham *Recent Developments in Powder Diffraction.*
October 29	Dr. J. Emsley, Imperial College, London *The Shocking History of Phosphorus.*
November 4	Dr. T. P. Kee, University of Leeds *Synthesis and Co-ordination Chemistry of Silylated Phosphites.*
November 5	Dr. C. J. Ludman, University of Durham *Explosions, A Demonstration Lecture.*
November 11*	Prof. D. Robins†, Glasgow University *Pyrrolizidine Alkaloids : Biological Activity, Biosynthesis and Benefits.*
November 12	Prof. M. R. Truter, University College, London *Luck and Logic in Host - Guest Chemistry.*
November 18	Dr. R. Nix†, Queen Mary College, London *Characterisation of Heterogeneous Catalysts.*
November 25*	Prof. Y. Vallee. University of Caen *Reactive Thiocarbonyl Compounds.*
November 25	Prof. L. D. Quin†, University of Massachusetts, Amherst *Fragmentation of Phosphorous Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding.*

November 26	Dr. D. Humber, Glaxo, Greenford *AIDS - The Development of a Novel Series of Inhibitors of HIV.*
December 2*	Prof. A. F. Hegarty, University College, Dublin *Highly Reactive Enols Stabilised by Steric Protection.*
December 2*	Dr. R. A. Aitken†, University of St. Andrews *The Versatile Cycloaddition Chemistry of* $Bu_3P.CS_2$.
December 3	Prof. P. Edwards, Birmingham University *The SCI Lecture - What is Metal?*
December 9*	Dr. A. N. Burgess†, ICI Runcorn *The Structure of Perfluorinated Ionomer Membranes.*

1993

January 5*	Prof. J. O'Donnell, University of Queensland *NMR studies of the Radiation Chemistry of Polymers*
January 20	Dr. D. C. Clary†, University of Cambridge *Energy Flow in Chemical Reactions.*
January 21	Prof. L. Hall, Cambridge *NMR - Window to the Human Body.*
January 27*	Dr. W. Kerr, University of Strathclyde *Development of the Pauson-Khand Annulation Reaction : Organocobalt Mediated Synthesis of Natural and Unnatural Products.*
January 28	Prof. J. Mann, University of Reading *Murder, Magic and Medicine.*
February 3*	Prof. S. M. Roberts, University of Exeter *Enzymes in Organic Synthesis.*
February 10	Dr. D. Gillies†, University of Surrey *NMR and Molecular Motion in Solution.*
February 11*	Prof. S. Knox, Bristol University *The Tilden Lecture: Organic Chemistry at Polynuclear Metal Centres.*

February 17	Dr. R. W. Kemmitt†, University of Leicester *Oxatrimethylenemethane Metal Complexes.*
February 18	Dr. I. Fraser, ICI Wilton *Reactive Processing of Composite Materials.*
February 22	Prof. D. M. Grant, University of Utah *Single Crystals, Molecular Structure, and Chemical-Shift Anisotropy.*
February 24*	Prof. C. J. M. Stirling†, University of Sheffield *Chemistry on the Flat-Reactivity of Ordered Systems.*
March 10	Dr. P. K. Baker, University College of North Wales, Bangor *'Chemistry of Highly Versatile 7-Coordinate Complexes'.*
March 11	Dr. R. A. Y. Jones, University of East Anglia *The Chemistry of Wine Making.*
March 17*	Dr. R. J. K. Taylor†, University of East Anglia *Adventures in Natural Product Synthesis.*
March 24*	Prof. I. O. Sutherland†, University of Liverpool *Chromogenic Reagents for Cations.*
May 13	Prof. J. A. Pople, Carnegie-Mellon University, Pittsburgh, USA *The Boys-Rahman Lecture: Applications of Molecular Orbital Theory*
May 21	Prof. L. Weber, University of Bielefeld *Metallo-phospha Alkenes as Synthons in Organometallic Chemistry*
May 24*	Dr. A. Bader, Aldrich *Two lectures: 'The Adventures of a Chemist collector' and 'Josef Loschmidt'.*
June 1	Prof. J. P. Konopelski, University of California, Santa Cruz *Synthetic Adventures with Enantiomerically Pure Acetals*
June 2	Prof. F. Ciardelli, University of Pisa *Chiral Discrimination in the Stereospecific Polymerisation of Alpha Olefins*

June 7	Prof. R. S. Stein, University of Massachusetts *Scattering Studies of Crystalline and Liquid Crystalline Polymers*
June 16	Prof. A. K. Covington, University of Newcastle *Use of Ion Selective Electrodes as Detectors in Ion Chromatography.*
June 17	Prof. O. F. Nielsen, H. C. Arsted Institute, University of Copenhagen *Low-Frequency IR - and Raman Studies of Hydrogen Bonded Liquids.*
July 23*	Prof. F. Wadi, University of California, Santa Barbara *Recent Adventures in the Chemistry of Buckminsterfullerene* C_{60}.
September 13	Prof. Dr. A. D. Schlüter, Freie Universität Berlin, Germany *Synthesis and Characterisation of Molecular Rods and Ribbons.*
September 13	Prof. K. J. Wynne, Office of Naval Research, Washington, U.S.A. *Polymer Surface Design for Minimal Adhesion*
September 14	Prof. J. M. DeSimone, University of North Carolina, Chapel Hill, U.S.A. *Homogeneous and Heterogeneous Polymerisations in Enviromentally Responsible Carbon Dioxide.*
September 28*	Prof. H. Ila., North Eastern University, India *Synthetic Strategies for Cyclopentanoids via OxoKetene Dithiacetals.*
October 4	Prof. F. J. Feher†, University of California at Irvine *Bridging the Gap between Surfaces and Solution with Sessilquioxanes.*
October 14	Dr. P. Hubberstey, University of Nottingham *Alkali Metals: Alchemist's Nightmare, Biochemist's Puzzle and Technologist's Dream.*
October 20*	Dr. P. Qualye†, Unversity of Manchester *Aspects of Aqueous Romp Chemistry.*
October 23	Prof. R. Adams†, University of S. Carolina *The Chemistry of Metal Carbonyl Cluster Complexes Containing Platinum and Iron, Ruthenium or Osmium and the Development of a Cluster Based Alkyne Hydrogenating Catalyst.*

October 27*	Dr. R. A. L. Jones†, Cavendish Laboratory *'Perambulating Polymers'.*
November 10	Prof. M. N. R. Ashfold†, University of Bristol *High-Resolution Photofragment Translational Spectroscopy: A New Way to Watch Photodissociation.*
November 17*	Dr. A. Parker†, Laser Support Facility *Applications of Time Resolved Resonance Raman Spectroscopy to Chemical and Biochemical Problems.*
November 24	Dr. P. G. Bruce†, University of St. Andrews *Synthesis and Applications of Inorganic Materials.*
November 25	Dr. R.P. Wayne, University of Oxford *The Origin and Evolution of the Atmosphere.*
December 1*	Prof. M. A. McKervey†, Queens University, Belfast *Functionlised Calixerenes.*
December 8*	Prof. O. Meth-Cohen, Sunderland University *Friedel's Folly Revisited.*
December 16	Prof. R. F. Hudson, University of Kent *Close Encounters of the Second Kind.*

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January 26	Prof. J. Evans†, University of Southhampton *Shining Light on Catalysts.*
February 2	Dr. A. Masters†, University of Manchester *Modelling Water Without Using Pair Potentials.*
February 9*	Prof. D. Young†, University of Sussex *Chemical and Biological Studies on the Coenzyme Tetrahydrofolic Acid.*
February 16	Prof. K. H. Theopold, University of Delaware, U.S.A *Paramagnetic Chromium Alkyls: Synthesis and Reactivity.*

February 23	Prof. P. M. Maitlis†, University of Sheffield *Why Rodium in Homogenous Catalysis.*
March 2*	Dr. C. Hunter†, University of Sheffield *Non Covalent Interactions between Aromatic Molecules.*
March 9	Prof. F. Wilkinson, Loughborough University of Technology *Nanosecond and Picosecond Laser Flash Photolysis.*
March 10	Prof. S.V. Ley, University of Cambridge *New Methods for Organic Synthesis.*
March 25	Dr. J. Dilworth, University of Essex *Technetium and Rhenium Compounds with Applications as Imaging Agents.*
April 20*	Prof. P. Parsons, University of Reading *New Methods and Strategies in Natural Product Synthesis*
April 28	Prof. R. J. Gillespie, McMaster University, Canada *The Molecular Structure of some Metal Fluorides and OxoFluorides: Apparent Exceptions to the VSEPR Model.*
May 12	Prof. D. A. Humphreys, McMaster University, Canada *Bringing Knowledge to Life*

† Invited specially for the graduate training programme.

Research Conferences Attended

1991	
December	Modern Aspects of Sterochemistry, Sheffield University.
1992	
April	North East Graduate Symposium, Durham.
December	Modern Aspects of Sterochemistry, Sheffield University.
1993	
July	2nd Anglo-Russian-Ukranian Symposium on Fluorine Chemistry, Durham.
December	Modern Aspects of Sterochemistry, Sheffield University.
1994	
April	North East Graduate Symposium, University of Northunbria at Newcastle.
July	15th International Symposium on Fluorine Chemistry, Yokohama, Japan.

First Year Induction Course

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

Departmental Organisation	Dr. E.J.F. Ross
Safety Matters	Dr. G.M. Brooke
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 / Mr. G. Haswell

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