Electrochemical reduction of fluorinated systems and derived chemistry

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UNIVERSITY OF DURHAM

A THESIS
entitled

ELECTROCHEMICAL REDUCTION OF FLUORINATED SYSTEMS AND DERIVED CHEMISTRY

submitted by

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(Hatfield College)

A candidate for the degree of Doctor of Philosophy

1989

To Mum,

Dad, Kay,
and Friends.

November 30, 1988

MEMORANDUM:

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

Part of this work has been the subject of the following paper :
M. W. Briscoe, R. D. Chambers, M. J. Silvester, and
F. G. Drakesmith, *Tetrahedron Lett.*,1988, 29(11), 1295.

and has been presented by the author at :
12th. International Symposium on Fluorine Chemistry,
Santa Cruz, California, U.S.A. August 1988.

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Thanks also to the lads in lab 117 and elsewhere - for their help and advice, and for making my stay in Durham so enjoyable. These include Andy Bayliff, Chris Hewitt, Steve Mullins, Pete Hoare, Glenn Apsey, Alan Swales, Robert Fuss, Mike Rock, Paddy Nicholson, and Simon Wait.

Finally, I would like to thank the Science and Engineering Research Council, and the Electricity Research Council for the provision of a C.A.S.E. Award.

ABSTRACT:

The work described in this thesis is divided into four sections:

1. The electrochemical reduction of fluorocarbon derivatives has been investigated. A number of systems have been studied analytically (using cyclic voltammetry); whilst preparatively a range of compounds have been synthesised, including semi-conducting polymers and four-membered perfluorocyclic products.

2. The use of sodium amalgam as an electromimetic medium to facilitate reduction of various fluorocarbon substrates has been studied. A series of volatile cyclic and acyclic F-dienes have been prepared from F-alkenes in good yield and conversion.

The chemistry of these F-dienes is then described:

3. Both mono- and bi- functional nucleophiles have been reacted, giving a range of novel substitution products.

4. A number of free radical and cycloaddition reactions have been attempted without success. However, the complexation of decamethylferrocene as a metallocene one electron donor, with various F-alkenes of low reduction potential, has allowed a radical anion of a perfluorocyclic-diene to be stabilized and fully characterized for the first time.

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CHAPTER 1:

PREPARATIVE ELECTRO-ORGANIC CHEMISTRY OF ORGANO-HALOGEN COMPOUNDS:

1.1: INTRODUCTION TO ELECTRO-ORGANIC CHEMISTRY

"Electro-organic chemistry is one of the most promising tools for organic synthesis"[1] T.Shono 1984

The electrolysis of organic compounds has been studied extensively, however the concept of electrolysis is NOT always the same as that of electro-organic chemistry.
An electro-organic reaction is initiated by transfer of an electron between the electrode and a substrate A; and as shown in equation (1) the substrate A is transferred to an anion radical or cation radical depending on the direction of the electron transfer.

$$A^{2-} \underset{+e}{\rightleftharpoons} A^{-} \underset{+e}{\rightleftharpoons} A \overset{-e}{\rightleftharpoons} A^{+} \overset{-e}{\rightleftharpoons} A^{2+} \qquad (1)$$

Electro-organic chemistry can thus be defined as the investigation of the chemical behaviour of an activated species of A in solution. It therefore not only applies to obvious oxidation and reduction of functional groups - but also includes generation and utilisation of anion radicals.

carbanions, dicarbanions, cation radicals, cations, dications, radicals, acids/electrophiles, bases/nucleophiles. The synthetic chemistry that ensues, however, is dependent upon a number of factors: (i) the intermediates generated are under the influence of a strong magnetic field; (ii) they are in an enviroment where concentration gradients exist, since the precursors are being depleted by the electrode reaction; and (iii) they are formed at, or near, the electrode surface where they may or may not be absorbed.
It is this last "proviso" which is probably the cause of the subtleties observed in electro-organic chemistry. In an electro-organic reaction, the activated species is not formed uniformly in homogeneous solution, but is generated only at the surface of the electrode, whereas in common organic reactions, the active species is often uniformly distributed in solution. This difference in the site of generation, and in the distribution of activated species, can bring about great differences in the reaction of such intermediates.

Viewed from the standpoint of organic synthesis, electro-organic chemistry has a remarkable characteristic. In common organic reactions, the reaction generally takes place between nucleophilic (Nuc) and electrophilic (Elec) reagents, while reaction between reagents of the same polarity is not possible. Inversion of polarity of one of the reagents is therefore essential for carrying out reactions between Nuc and Nuc, or Elec and Elec. This inversion of polarity of reagents is not possible in common organic reactions, however in an electro-organic synthesis the formation of an activated species, by the addition or removal of electrons, does allow such changes to occur. This is just one of a number of attractive and formidable advantages organic electrochemistry has to offer:

1. Precise control of the electrode potential, and therefore of selectivity, is easily obtained. The equivalent of a continuum of oxidizing and reducing agents, all equally accessible, is an attractive proposition.
2. Electrochemical reactions do not require thermal energy to overcome activation barriers, and are therefore generally applicable to thermally sensitive compounds, (the driving force of reaction being the electrode potential).
3. Stoichiometric amounts of oxidants and reductants are not required and therefore their by-products, and any possible pollution effects, are avoided, (although the electricity generating plant may pose different pollution problems!).
4. The relatively stable cost of electricity compared with the steady increase in cost of chemicals/materials has meant electricity becoming an ever more attractive reagent for large scale reactions.
5. Electrochemical synthesis, by its very nature, and by ease of instrumentation, is very suitable for continuous and automatic plant operation. The course of the reaction can be quantitatively monitored quite easily and accurately by coulometry, and of practical convenience is the ease by

which the reaction can be instantly stopped -by turning off the switch!

As with most specialised synthetic techniques however, organic electrochemistry has a number of significant disadvantages. The most practically limiting of these is in the choice of solvent and electrolyte. The solvent must be inert as well as capable of ionizing a suitable electrolyte and dissolving the organic substrate; whilst the electrolyte must be relatively inert, soluble in the solvent used, sufficiently conducting and be easily separable from the product during work-up.
Organic electrochemical reactions are also relatively slow ie.high current densities (current per electrode area) cannot routinely be used. The inherent rate is often related to a rate-limiting electron transfer or adsorption/ desorption step. However, the reputed slowness can usually be attributed to the low surface area to volume ratio of most preparative electrochemical cells.

Organic electrochemical methodology has been used in a way that may surprise the "common or garden" organic chemist. There are now many electrochemical syntheses not duplicated by chemical or catalytic means, and there are numerous possiblities for one-step electrochemical reactions to replace cleverly and laboriously executed multi-stage syntheses.

1.2: GENERAL PRACTICAL ASPECTS

An electrochemical reduction is performed at the cathode (working electrode) with the anode (counter electrode) completing the circuit, and a reference electrode placed as close to the surface of the working electrode as possible. This is commonly achieved by means of a Luggin capillary arrangement, so as to minimise the current-resistance (IR) drop, which causes inaccuracies in the measured electrode potential, and thereby may affect the possible course of the reaction. The reference/working electrode arrangement is used in conjunction with a potentiostat, to control the potential of the working electrode to a pre-selected value (see Fig. 1). Thus, in the case of competing reactions, occuring at different potentials, it is possible to perform a selective reduction. This is known as "controlled potential" electrolysis. Alternative methods of electrolysis are "constant current" and "constant voltage" electrolysis, which, although much simpler experimentally are not as selective[2-4].

The reaction is carried out in a cell containing an inert solvent and supporting electrolyte (the choice of which can often effect the course of a reaction), divided into two compartments by a glass s inter. This separation of the catholyte and anolyte compartments is to prevent species generated by reduction at the working electrode from diffusing across and being oxidized at the counter electrode to give undesired by-products; while at the same time

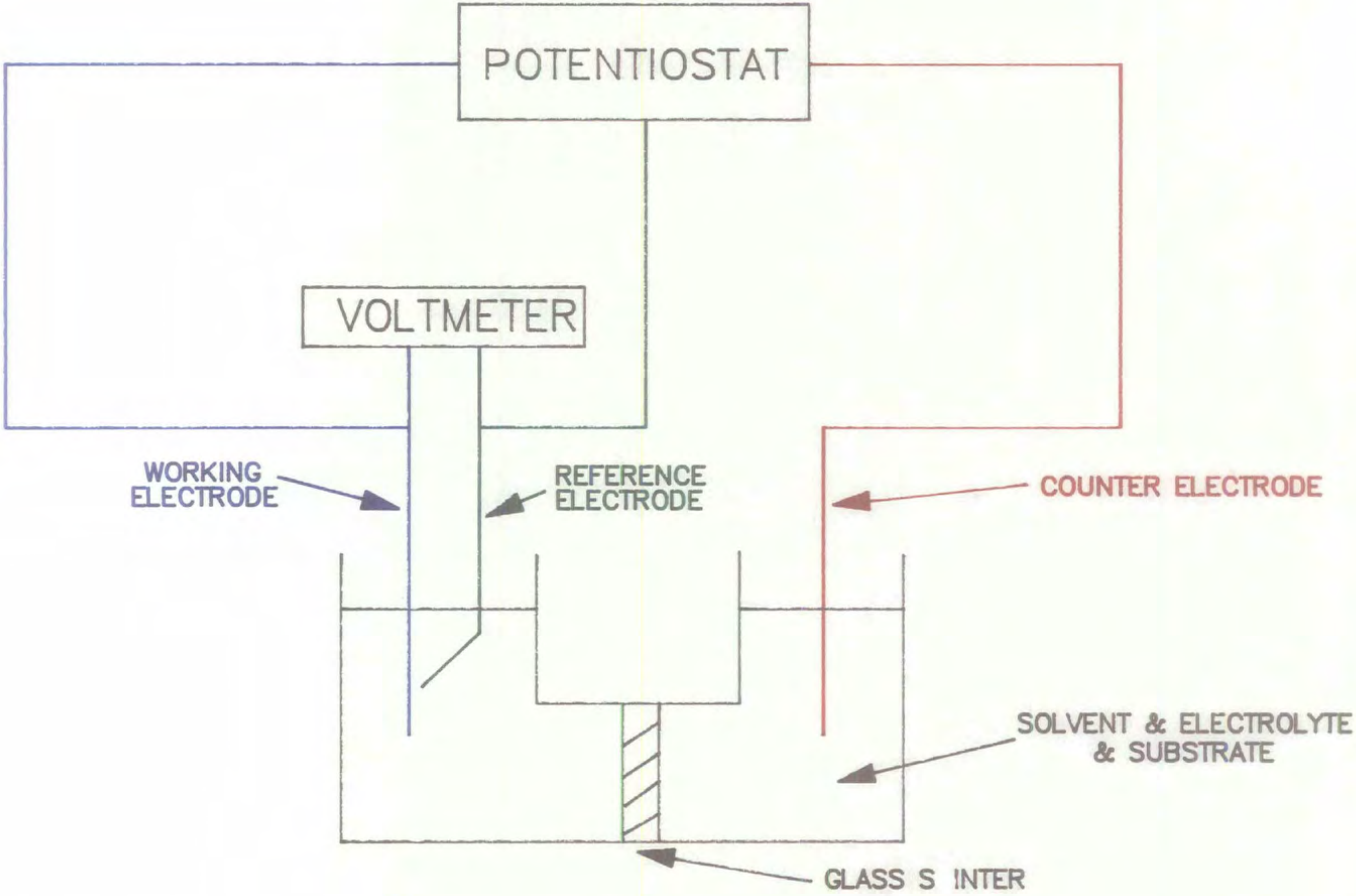


Fig.1: Diagramatic representation of a "Controlled Potential" Electrolysis System.

allowing current to pass, via the ions in solution. The use of a cell divider increases the cell resistance, as does the use of non-aqueous solvents, so to minimise the voltage drop through the electrolyte, the electrodes must be as close together as possible and preferably parallel to facilitate a uniform current density distribution. The cell is also equipped with a dry nitrogen bubbler line to deoxygenate the solvent (as reduction of oxygen may affect the reaction), and a magnetic stirrer bar in the catholyte compartment, to allow the electrochemical processes to be wholly diffusion controlled. A typical arrangement for a three electrode cell is shown in Fig.2.

Please note: All subsequent statements of operating voltage are measured with reference to a saturated calomel electrode

1.3: ELECTROCHEMICAL REDUCTION OF ORGANO-HALOGEN COMPOUNDS:

The electrochemistry of organo-halogen compounds has been extensively reviewed.[2-4] This chapter provides a general discussion of organo-halogen compounds, paying particular attention to the reduction of fluoro-organic compounds.

1.3.1: REDUCTION OF CARBON-HALOGEN BOND:

Ease of reduction of the carbon-halogen bond follows the trend RI > RBr > RCl > RF. Cleavage of the carbon-fluorine bond is therefore relatively hard and often at a reduction potential which is above, or in the same region as the break down potential of the solvent/electrolyte system being used. The difficulty in cleavage of the carbon-fluorine bond may be used as a positive synthetic "handle", when the reactant molecule under investigation contains groups which can be removed at a lower reduction potential, forming either stable products or reactive intermediates.

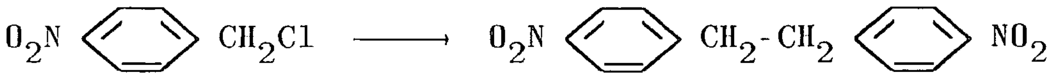
The mechanism of the electrochemical cleavage of the carbon-halogen bond is undecided, and various mechanisms have been proposed which include transition states with radical or anionic character. The mode of "attack" of electrons is also an area of debate. S_N1 or S_N2 displacement reactions with the electron acting as the nucleophile, have been postulated, whilst other workers argue that electrons would prefer to attack on the halogen side of an alkyl halide molecule, especially in crowded molecules. A mechanism in which attack of the electron occurs perpendicular to the carbon-halogen bond, is also possible -this being spatially consistent with the addition of an electron to an anti-bonding orbital.

Cleavage of the carbon-halogen bond can, under the appropriate conditions, lead to a variety of products, and some very reactive intermediates such as carbenes and benzynes. It is the cleavage of carbon-halogen bonds in aprotic solvents, however, that has shown great possibilities for organic synthesis, (the cleavage of such bonds in protic media often leads to the replacement of the halogen with a hydrogen atom).

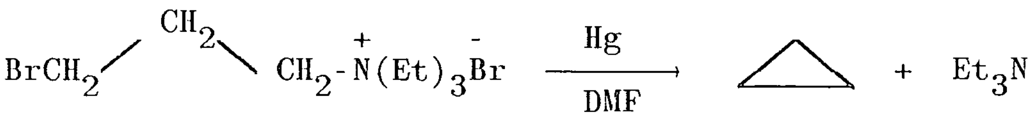
The products derived from the electrochemical reduction of organic halides depends on the nature of the molecule in question, ie.whether it is a monohalide, polyhalide, etc. Consequently each type of halide will be discussed separately.

1.3.2: MONOHALIDES:

The reduction of aliphatic halides in protic and aprotic solvents generally leads to the formation of the corresponding hydrocarbons. There are some exceptions however.



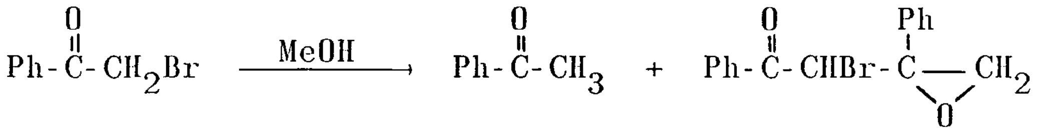
[5]

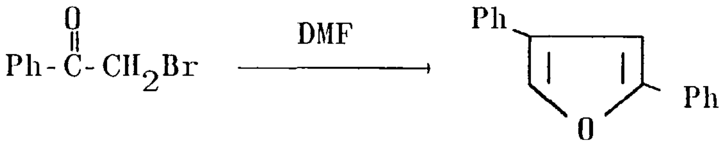


[6]

NB.no dimers or trimers of propane were detectable.

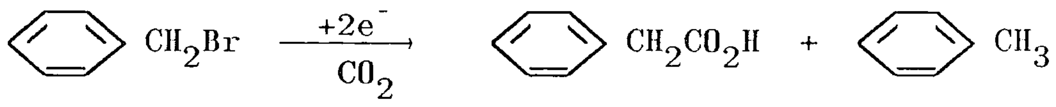
The choice of solvent may dramatically affect the nature of the products formed from an electrochemical reaction. Reduction of phenacyl bromide in methanol has been shown to give very different products from those obtained in DMF^7;





the difference being attributed to the increased acidity of methanol (wrt.DMF), thus allowing methanol to protonate the intermediate enolate anion.

In the presence of CO_2, the cleavage of the carbon halogen bond may yield the corresponding carboxylic acid[8].



The actual mechanism of reduction which is operating, is an area of great debate; be it via radical or anionic intermediates. There appears to be very little compelling evidence for the intervention of radicals as detectable intermediates. The observed coupling products, which some say indicate the presence of discrete radical intermediates, may be formed from the attack of anionic intermediates on the intact alkyl halide. Thus the reduction of alkyl halides may be described by an ECE mechanism (scheme 1)

SCHEME 1

$$R\text{-}X + e^- \xrightarrow{\text{slow}} [\overset{\delta-}{R}\cdots\overset{\delta-}{X}] \longrightarrow R^{\bullet} + X^-$$

$$R^{\bullet} + e^- \xrightarrow{\text{fast}} R^- \longrightarrow \text{PRODUCTS}$$

OR via a $2e^-$ concerted process[4] (scheme 2)

SCHEME 2

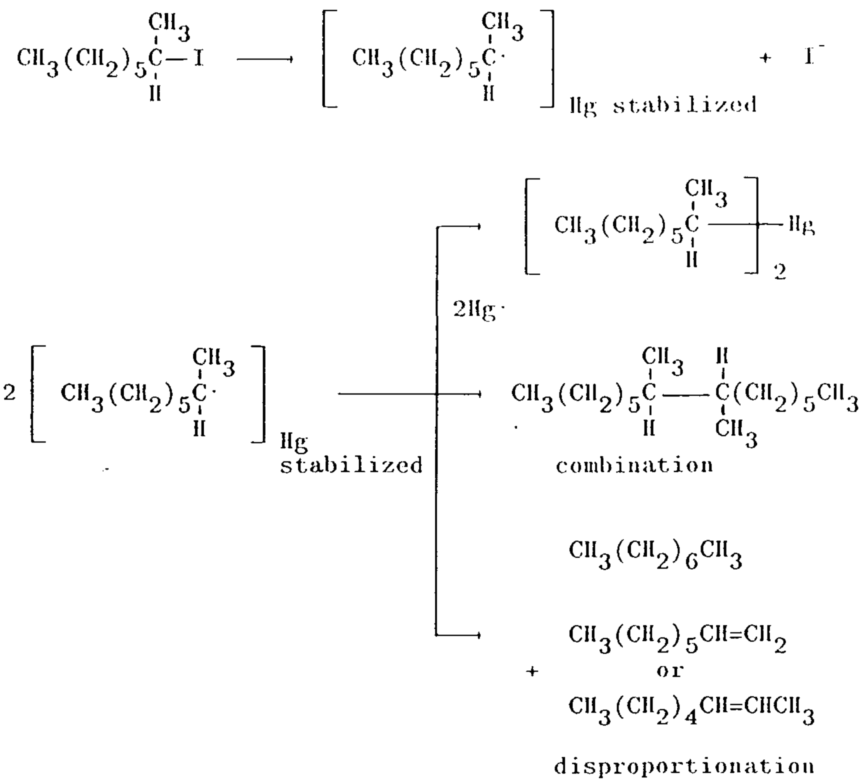
$$R\text{-}X + 2e^- \xrightarrow{\text{slow}} [\overset{\delta-}{R}\cdots\overset{\delta-}{X}] \longrightarrow R^- + X^-$$

Choice of cathode material (allowing stabilisation of intermediate species) may, however, discriminate between a one- or two-electron reduction process. The pulse polarogram of 2-iodo-octane shows two waves of equal height. Reduction at the potential of the first wave gives octane, octene, 7,8-dimethyltetradecane, and di-s-octylmercury (see scheme 3), via an essential initial step generation of a mercury stabilized sec-octyl radical via one electron cleavage of the carbon-iodine bond. Octane was formed at the potential of the second wave together with olefins arising from base elimination from the starting material (see scheme 4). Carbanion intermediates are formed at the potential of the second wave. Thus production of the mercury-stabilized radical is responsible for the stepwise reduction of 2-iodooctane; if the radical was not stabilized, electrolysis of the alkyl iodide would appear as a one-step two-electron process.

In contrast, only one wave is found in the pulse polarogram of 2-bromo-octane, the height of which is equal to the sum of the two waves for the alkyl iodide. Preparative electrochemical reduction gives octane and a mixture of octenes; no di-sec-octylmercury, or 7,8-dimethyltetradecane is formed. Thus reduction of the bromo-derivative appears to be a two-electron breakage of the carbon-bromine bond to yield the sec-octyl carbanion.[9]

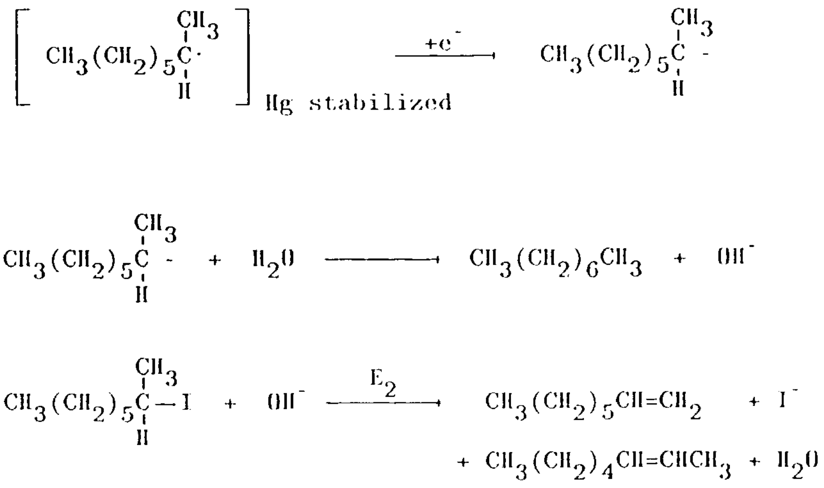
SCHEME 3:

Processes occuring at the potentials of the first wave



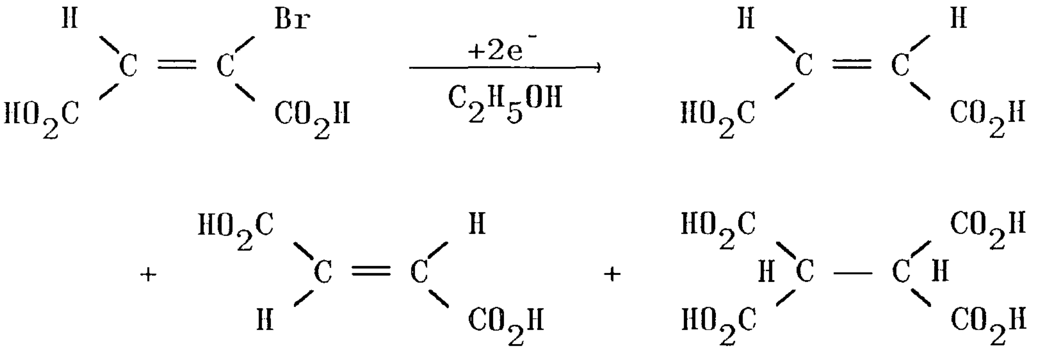
SCHEME 4:

Processes occuring at potentials of the second wave

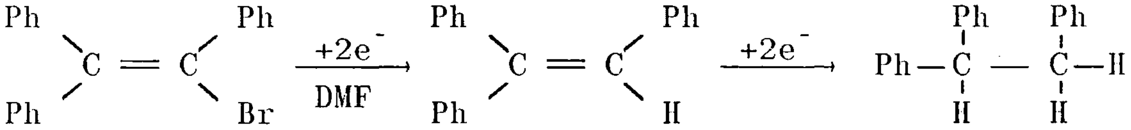


1.3.3: VINYL AND AROMATIC HALIDES:

The reduction of vinyl and aromatic halides is similar to that of aliphatic halides in that similar products are obtained. Cis-trans isomerization may take place[10]:

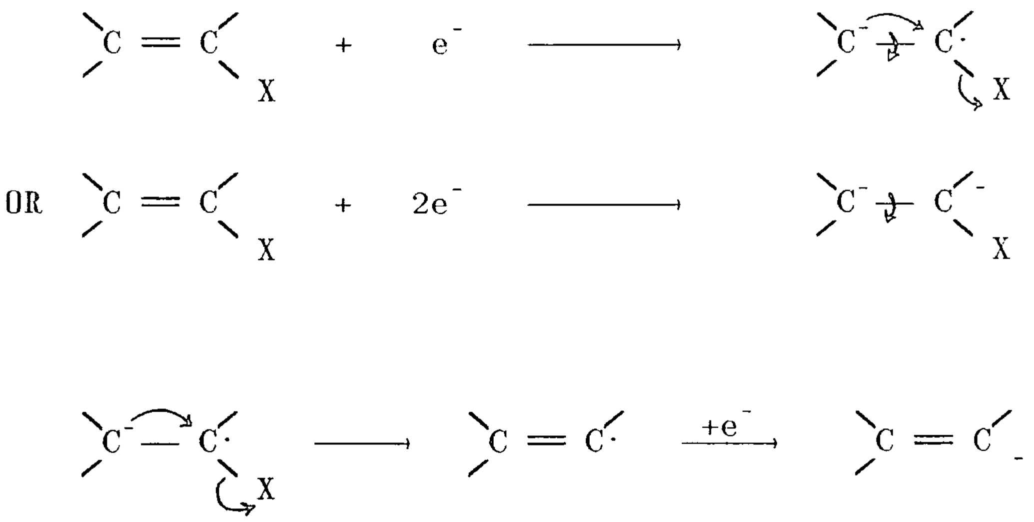


In certain cases, reduction of the double bond may occur, ie. when conjugated with the Π system of phenyl groups[11].



The reduction of vinyl halides may involve an initial addition of electrons to the lowest vacant Π molecular orbital to form the radical anion or dianion (scheme 5), which can rotate about the C-C bond. Elimination of halide anion gives the olefin with the most thermodynamic stability. However, since the cathodic reduction of simple olefins has not been observed, the mechanism detailed in scheme 5, may be applicable only to highly substituted vinyl

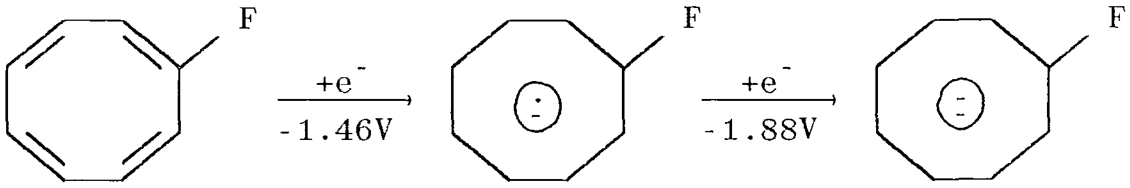
SCHEME 5



halides. The cleavage of simple vinyl halides is therefore considered to be analogous to that of the simple monohalides. Whether the stereochemistry of the olefinic product is determined from a pre-equilibriation of radicals or anions is difficult to ascertain.

The reduction of aromatic halides generally leads to reductive cleavage of the halogen and formation of benzene. Thus bromobenzene affords benzene in quantitative yield[4].

Fluorocyclooctatetraene (FCOT), however, shows two reduction waves in HMPA solvent containing tetrabutylammonium perchlorate as the supporting electrolyte, forming stable products - the radical anion (1) at -1.46V (vs.SCE), and the dianion (2) at -1.88V (vs.SCE)[12].



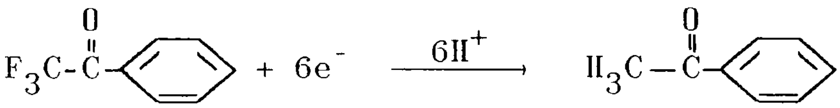
(1) (2)

The anions are unusually stable to fluoride ion elimination, allowing e.s.r. measurements to be made; their stability being attributed to the non-bonding character of the LUMO of FCOT, and the substantial resonance energy of the polar anions.

1.3.4: POLYHALIDES:

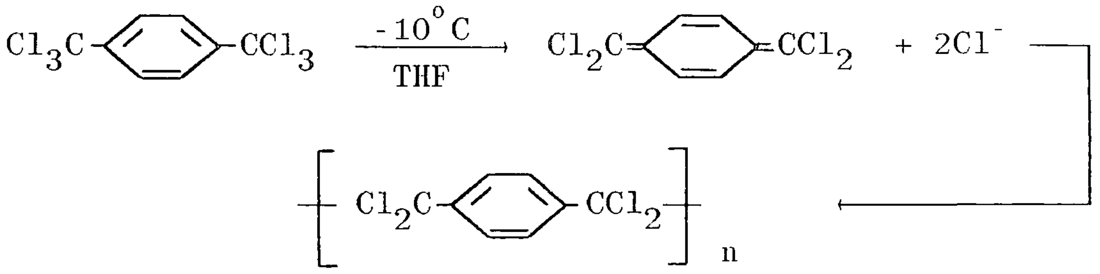
1.3.4.a: GEM HALIDES:

The reduction of gem halides generally yields the corresponding hydrocarbons.

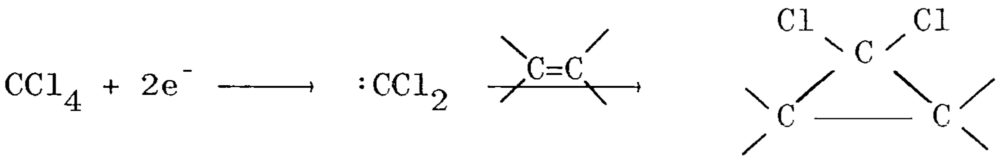


$$F_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5 + 6e^- \xrightarrow{6H^+} H_3C-\overset{O}{\overset{\|}{C}}\text{-}C_6H_5 \qquad [13]$$

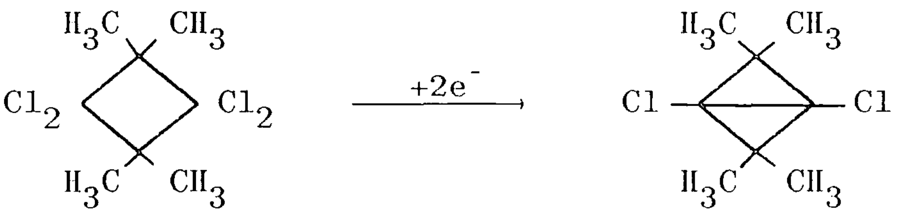
The reduction has also been used for the synthesis of polymers[14].



and reactive intermediates[15].

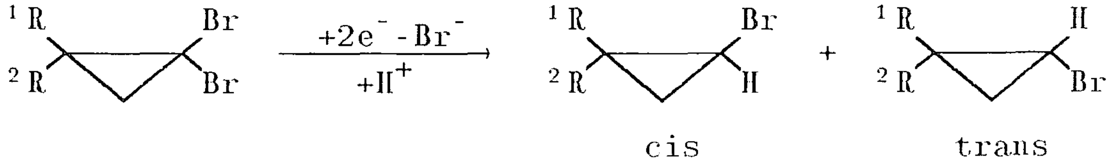


The reduction of gem halides can be allowed to proceed in a stepwise manner, by using controlled potential electrolysis. Thus selective reduction of one of two gem halides allows reduction of (3), to the corresponding bicyclobutane compound (4)[16]



(3) (4)

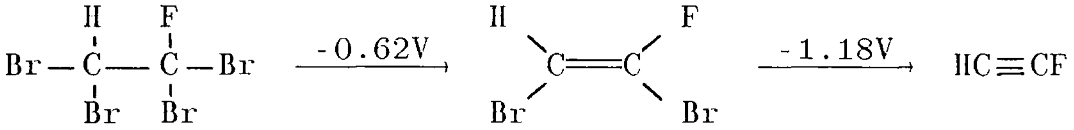
Reduction of gem-dibromocyclopropanes yields the respective monobromocyclopropanes. Stereoselectivity can be achieved particularly when R^2=CO_2Et and R^1=Me, when 99% cis-isomer is obtained[17].



Based on product analysis, the reduction of gem halides is best explained by invoking anionic intermediates.

1.3.4.b: VICINAL HALIDES:

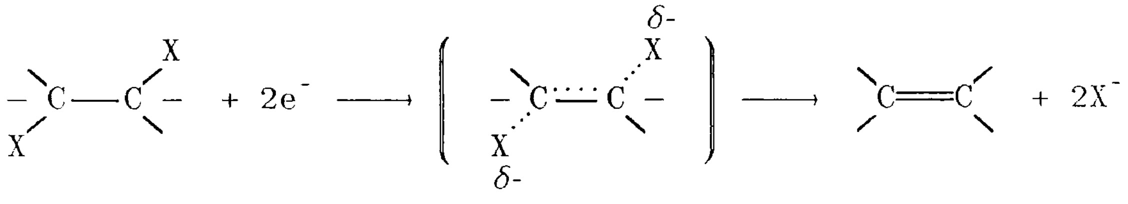
The electrochemical reduction of vicinal dihalides resembles the reduction of the same dihalide with zinc or sodium in that the product is, in general, the corresponding olefin. The reduction of (5), illustrates the principle of an increase in unsaturation on the reduction of vicinal dihalides; the eventual product being fluoroacetylene (6)[18]



(5) (6)

A concerted mechanism in which the transition state bears resemblance to the product olefin, is generally accepted to operate (scheme 6).

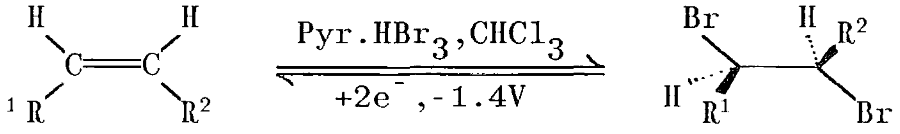
SCHEME 6:



TRANSITION STATE

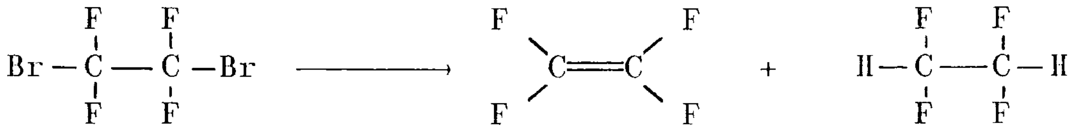
The fact that vicinal polyhalides are reduced at a less negative potential than the corresponding monohalide, is a good indication that a lower energy concerted route is available to them.

Retention of configuration about a carbon-carbon double bond during protection-deprotection by bromination-cathodic debromination has been studied[19].



Specific anti-addition of bromine to the double bond may be achieved with pyridinium hydrobromide perbromide ($Pyr.HBr_3$). Whilst debromination with zinc, magnesium, or KI[20] is not totally stereospecific; retention of configuration is achieved to the extent of 96% or higher with a number of acyclic olefins (of both Z and E configurations), by debromination at a mercury cathode at -1.4V (vs.SCE).

In contrast, the reduction of 1,2-dibromotetrafluoroethane (7) yields a mixture of (8) and (9) -the product distribution being determined by the distribution of rotamers in the reactant[21].



(7) (8) (9)

The difference in behaviour is attributed to trans elimination from the intermediate anion occuring more rapidly than the cis, such that, in the latter case, protonation can occur before elimination.

Chlorofluoroalkanes can be reduced to fluoro-olefins in good yield[22-25]. Reduction of (10) at a lead cathode yields (11),

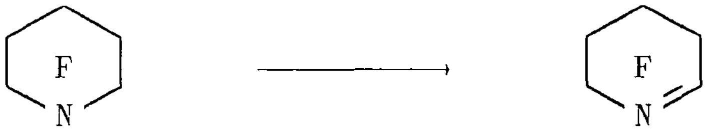
$$\underset{(10)}{CF_2Cl\text{-}CFCl_2} + 2e^- \longrightarrow \underset{(11)}{CF_2{=}CFCl} + 2Cl^-$$

while reduction of (12) at a lead cathode in an alkaline medium gives (13)[22].

$$\underset{(12)}{F_3C\text{-}CHClBr} + 2e^- \longrightarrow \underset{(13)}{F_2C{=}CHCl} \quad (70\%)$$

For molecules containing only one halogen type (as in the case of perfluorinated systems) a site for reductive attack is required.

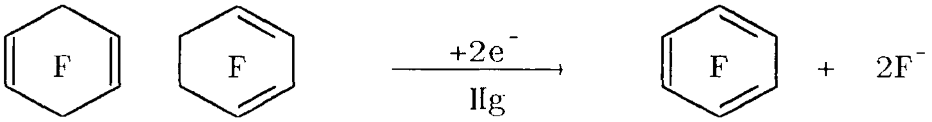
The reduction of perfluoropiperidene occurs via a two step process in acetonitrile at a mercury cathode[26]. Preparative electrolysis of (14) yields (15), which is readily hydrolyzed to give perfluoroglutaric acid as the final product.



(14) (15)

The reaction is very dependent on the electrode material, presumably because of the ability of some metals to form N-metal derivatives.

Aromatic fluorocarbons have been prepared by the reduction of fluorinated cyclohexadienes[27-29]. Reduction of either 1,4- or 1,3 perfluorocyclohexadiene yields hexafluorobenzene.



$$\text{DIENE} + e^- \longrightarrow \text{DIENE}^{-\cdot} \qquad (1)$$

$$\text{DIENE}^{-\cdot} \longrightarrow \text{RADICAL} + F^- \qquad (2)$$

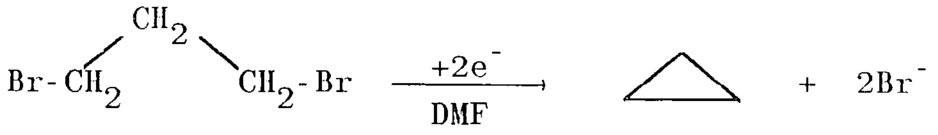
$$\text{RADICAL} + e^- \longrightarrow \text{RADICAL}^- \qquad (3)$$

$$\text{RADICAL}^- \longrightarrow \text{PRODUCT} \qquad (4)$$

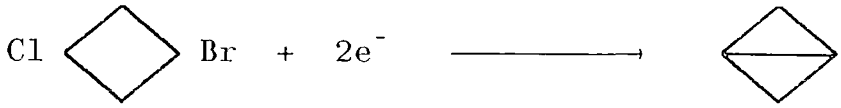
A stepwise mechanism was proposed for this reaction, as detailed above, with either step (1), or steps (1) and (2), as rate determining. As there is no substitution of hydrogen for fluorine, even in the protic medium used, it follows that steps (3) and (4) are rapid in comparison with other possible reactions.

1.3.4.c: α,ω-DIHALIDES:

The electrochemical reduction of α,ω -dihalides, is analogous to that of monohalides. A variety of products may be observed.

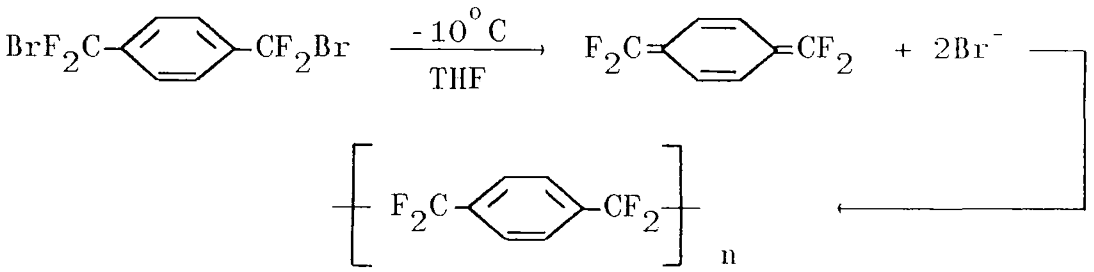


[30]

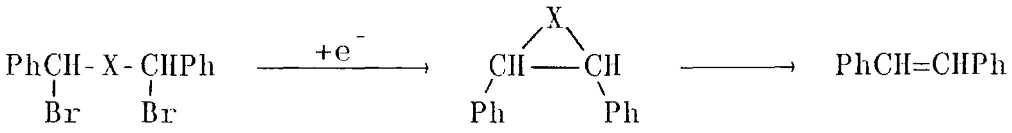


[31]

The reduction has also been used for the synthesis of polymers^{14}.



Reduction of the dibromo-compounds (16), gave stilbene, probably via a three membered-ring heterocyclic

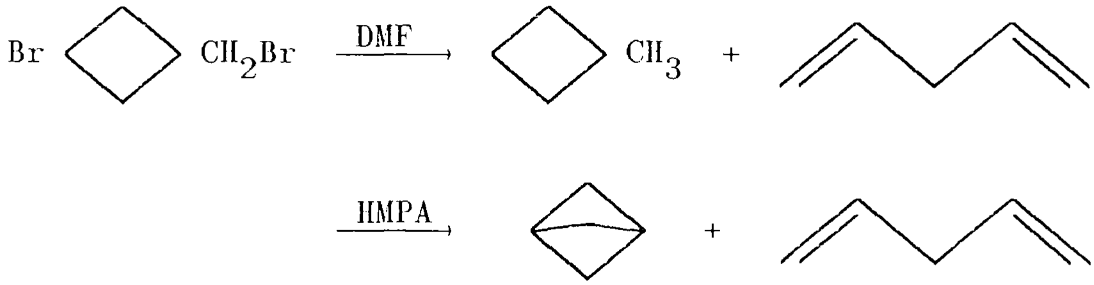


(16)

X = S, SO, or SO_2.

intermediate, with subsequent extrusion of the sulphur containing group. Reduction of either the meso- or the (±)-isomer gave the same mixture of stilbene isomers, so the process is not stereospecific[32].

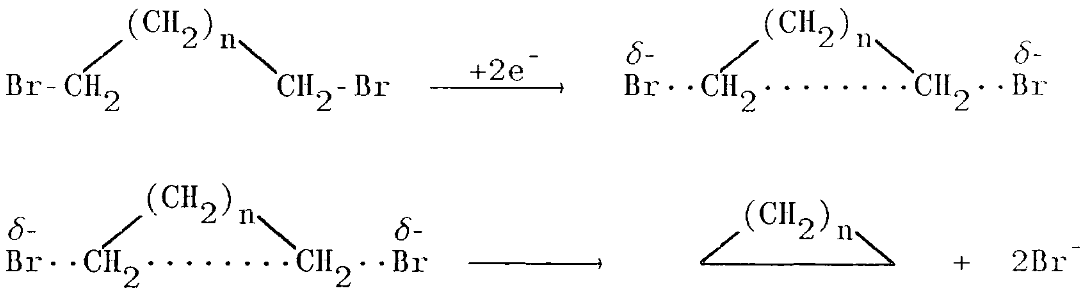
In certain cases different solvents allow the formation of different products[30].



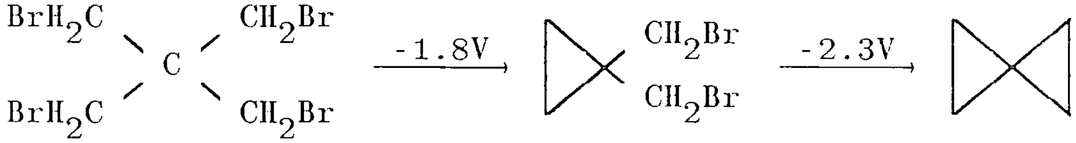
The anionic intermediate from the cleavage of the first carbon-bromine bond abstracts a proton from DMF. This is not possible in hexamethylphosphoramide, and the subsequent bicyclic compound is formed.

While the cyclisation reactions may be explained as proceeding via anionic intermediates, which undergo cyclisation more rapidly than protonation, it is more likely that they proceed in a concerted manner, via transition states similar to those observed for vicinal dihalides (see scheme 7)

SCHEME 7

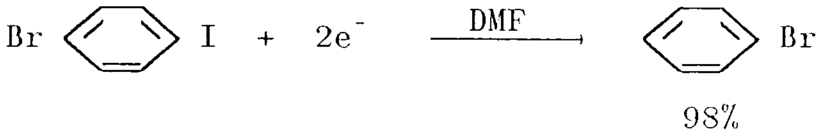


The electrochemical reduction of the tetrabromide (17) under controlled potential, yields either the dibromo intermediate (18) or the spiropentane (19) in high yield, depending on the operating potential[33].



(17) (18) (19)

Controlled potential electrolysis can also be useful in organic synthesis where the reduction of one of two halides in a molecule is desired[34]



CHAPTER 2:

ELECTROCHEMICAL REDUCTION OF VARIOUS FLUORO-ORGANIC COMPOUNDS:

2.A: GENERAL INTRODUCTION:

Electrochemical reduction of fluoro-organic compounds has not received much attention to date (see chapter 1).
The work detailed in this chapter, was therefore undertaken in order to extend the applicability of preparative electro-organic chemistry of fluoro-organic compounds, to allow either:
(i) access to existing compounds by a hopefully cheaper and more direct route than usual synthetic approaches would allow; or
(ii) access to new materials/compounds which have not been previously synthesised.

2.B: ELECTROCHEMICAL REDUCTION OF 4-, 5-, AND 6-MEMBERED PERFLUOROCYCLICOLEFINS:

2.B.1: INTRODUCTION:

Reduction of a compound containing vicinal halogens normally leads to an increase in unsaturation. This is well illustrated by the synthesis of fluoroaromatic compounds from fluorinated cyclohexadienes, which undergo exhaustive defluorination on electrochemical reduction in aqueous ethanol[27-29]. An $EC_EEC_E{}^*$ mechanism was proposed in which steps 2, 3, and 4 are very rapid. In contrast, the

$$\text{DIENE} + e^- \longrightarrow \text{DIENE}^{-\cdot} \tag{1}$$

$$\text{DIENE}^{-\cdot} \longrightarrow \text{RADICAL} + F^- \tag{2}$$

$$\text{RADICAL} + e^- \longrightarrow \text{RADICAL}^{-\cdot} \tag{3}$$

$$\text{RADICAL}^{-\cdot} \longrightarrow \text{F-BENZENE} + F^- \tag{4}$$

reduction of fluorinated substituted cyclopentenes, in acetonitrile, leads to partial defluorination and dimerization via an $EC_EEC_N{}^*$ mechanism[35]. The difference between the two processes has been rationalised on the basis of the enhancement of the double bond towards nucleophilic attack, in the latter case, by the presence of vinylic perfluoroalkyl groups. It is interesting to note that exhaustive defluorination of fluorinated cyclohexenes and cyclohexadienes by hot metals, eg.Fe, is a well known process, whereas the analogous reaction with five and four membered rings is not.

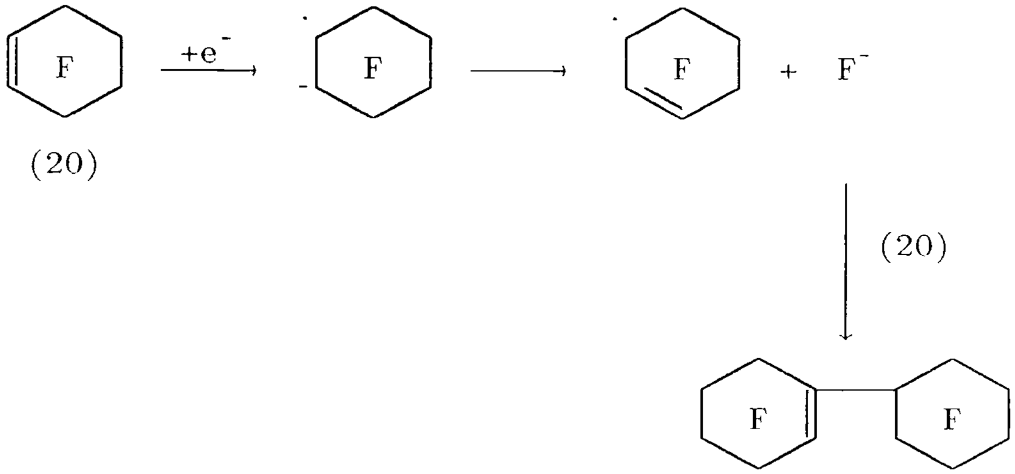
* key E - electrochemical, C_E - chemical (elimination).
C_N - chemical (nucleophilic)

2.B.2: REDUCTION OF PERFLUOROCYCLOHEXENE:

2.B.2.a: INTRODUCTION:

Silvester found that electrochemical reduction of perfluorocyclohexene (20) in DMF at a mercury cathode gave the fluoride induced dimers of (20) as the principle reaction products, and no defluorinated products were observed[34]. The mercury cathode arrangement used is represented diagramatically in Fig.3. The dense perfluorocyclohexene lies at the bottom of the cell in intimate contact with the electrode surface, thus initial reductive elimination of fluoride ion into the highly hydrophobic double layer, via an EC_EEC_E type mechanism, produces an activated fluoride ion which can then readily dimerize (20) to (21) (scheme 8)

SCHEME 8



(21)

It was hoped, that replacement of the horizontal mercury cathode by a platinum foil electrode (see Fig.4), sitting

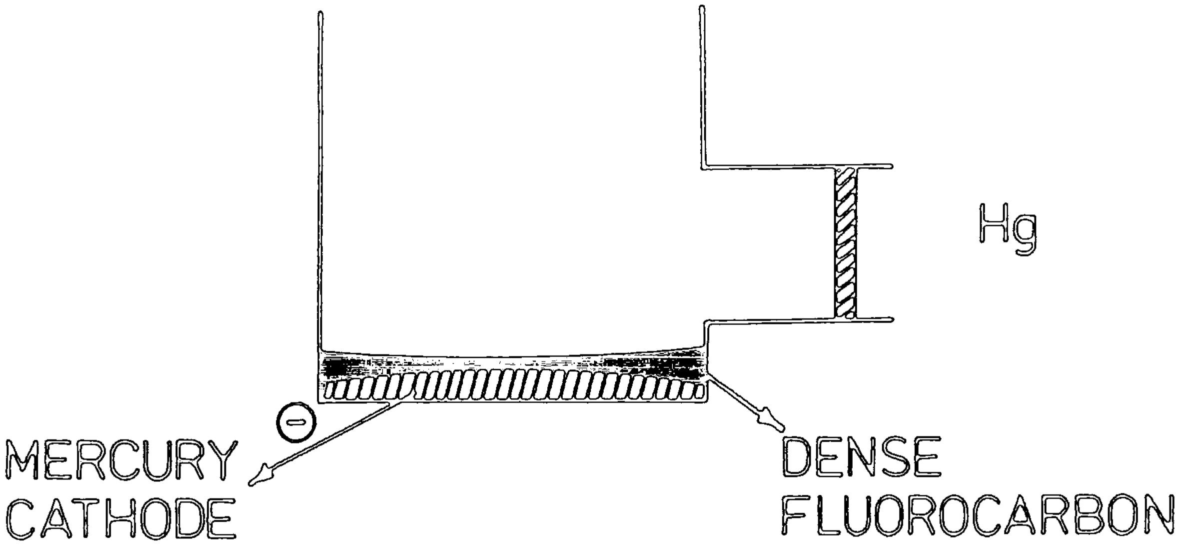


Fig.3: Horizontal mercury cathode arrangement.

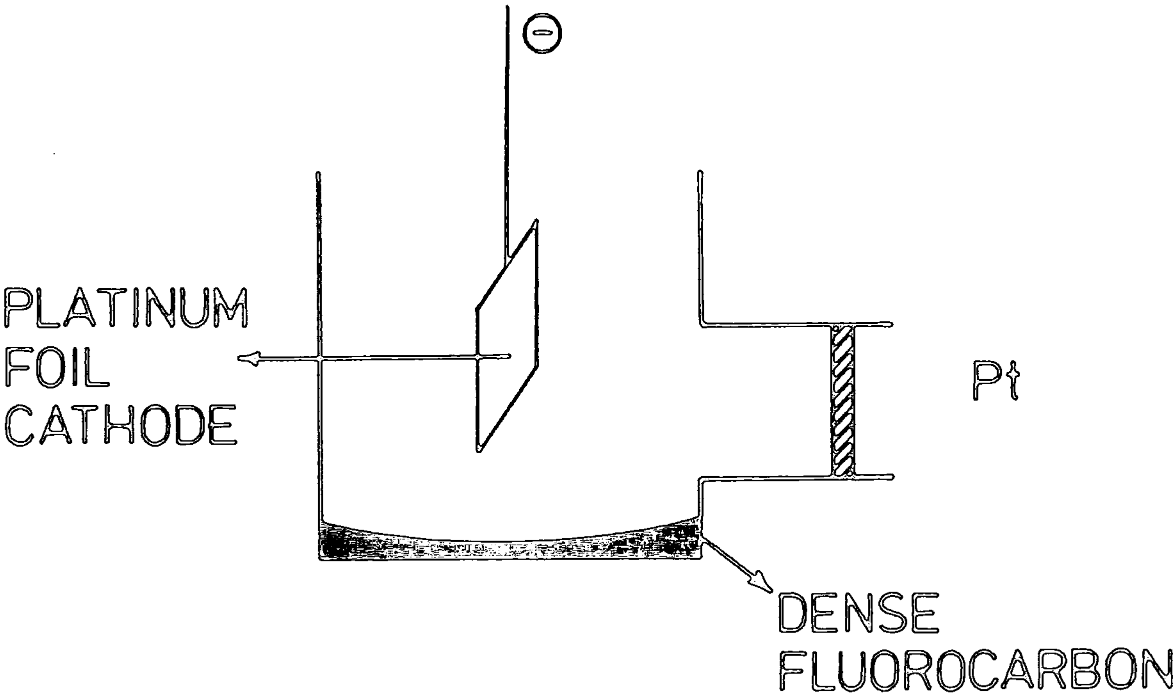


Fig.4: Vertical platinum foil cathode arrangement.

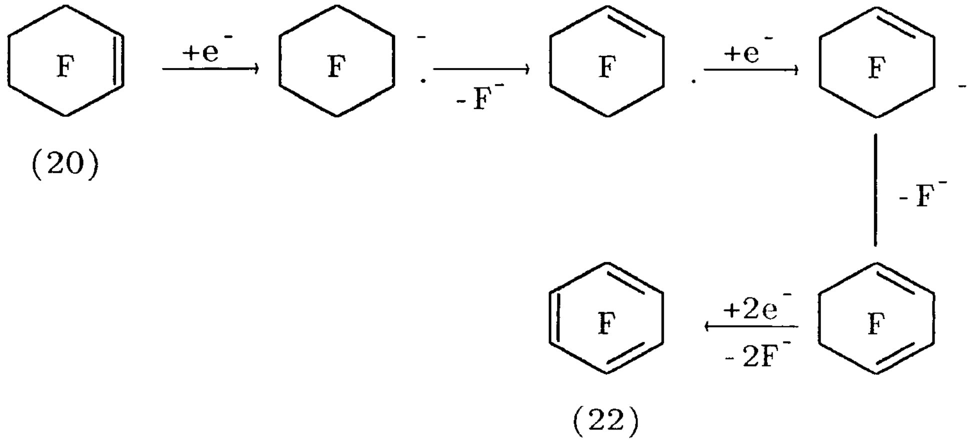
vertically in solution above the dense fluorocarbon (and thereby reducing the area of contact of fluorocarbon with the electrode surface), would allow any electrochemical reaction to run to completion without the unwanted intervention of any activated fluoride ion.

2.B.2.b: ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOHEXENE AT A PLATINUM ELECTRODE:

Reduction of perfluorocyclohexene (20) at -1.6V, at a platinum electrode in anhydrous acetonitrile (or dimethyl formamide) containing tetraethylammonium tetrafluoroborate as a supporting electrolyte, resulted in the formation of hexafluorobenzene (22) as the only isolated product, in high yield.

This is clearly an example of an EC_EEC_E type mechanism, with stepwise reduction and fluoride ion elimination (scheme 9).

SCHEME 9



2.B.3: REDUCTION OF PERFLUOROCYCLOBUTENE:

Electrochemical reduction of perfluorcyclobutene (23) at -1.6V at a platinum cathode in anhydrous DMF containing tetraethylammonium tetrafluoroborate, and at -1.9V at a platinum cathode in anhydrous acetonitrile containing the same electrolyte, resulted in the anode facing side of the cathode becoming rapidly covered with a blue/black coloured material, which very quickly enveloped the entire cathode surface, causing the electrolysis current to fall. The catholyte also became intensely coloured, presumably being caused by fragments from the electrode surface diffusing away from the platinum cathode into solution. At the end of electrolysis the electrode material was scraped off the cathode, washed and dried, to leave a hard fibrous blue/black coloured solid (see Figs.5 and 6). Characterization of this material proved difficult. It was insoluble in common organic solvents, standard infra-red spectroscopy proved difficult due to the polymeric nature of the material, and mass spectrometry showed only that it was a fluorocarbon of some sort. Elemental analysis, however, points to only one feasible gross structure (although irregularities may be contained). Analysis indicates the presence of N and H, in addition to C and F (see table 1).

TABLE 1:
ELEMENTAL ANALYSIS OF POLYMER FROM ELECTROCHEMICAL REDUCTION OF (23)

	C	H	N	F
% mass found	47.8	3.8	2.8	44.9
atomic ratio	20	19	1	12
atomic ratio (- Et_4N^+)*	12	-	-	12

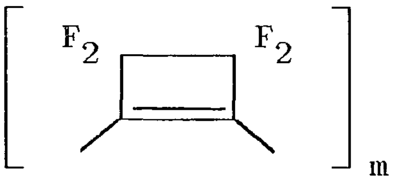
NB. * = corrected atomic ratio allowing for Et_4N^+ incorporation (ie atomic ratio -8C -20H -1N)

Some boron (from the supporting electrolyte) was detected but the percentage mass found was to low to be meaningful.

The H:N ratio of 19:1, corresponds well with that which could be expected if the H and N were present as a Et_4N^+ moiety (H:N = 20:1).
If the H and N found to be present in the polymeric material are assumed to be derived from incorporation of Et_4N^+, then the atomic ratio for carbon must be adjusted accordingly. Thus 8 of the 20 carbon atoms in the atomic ratio are associated with the Et_4N^+ cation, leaving 12 derived from

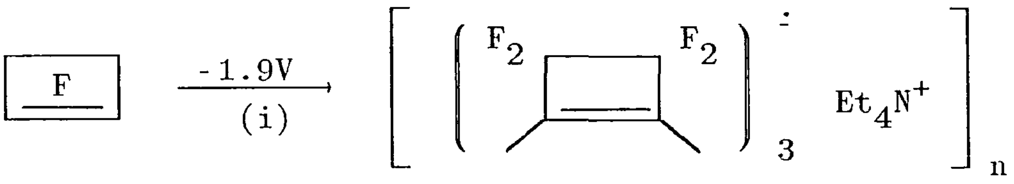
perfluorocyclobutene (23). This allows a maximum F:C ratio of 1:1

ie.



(24)

From table 1, it is clear that 12 carbon atoms from the polymer backbone are associated with each Et_4N^+ cation incorporated; thus m = 3 for each Et_4N^+ unit associated with structure (24). It is therefore reasonable to propose (25) as the best interpretation for structure; and indeed, the



(23) (25)

(i) Pt cathode, divided cell, CH_3CN, Et_4NBF_4

paramagnetic nature of (25) was confirmed by e.s.r. measurements.

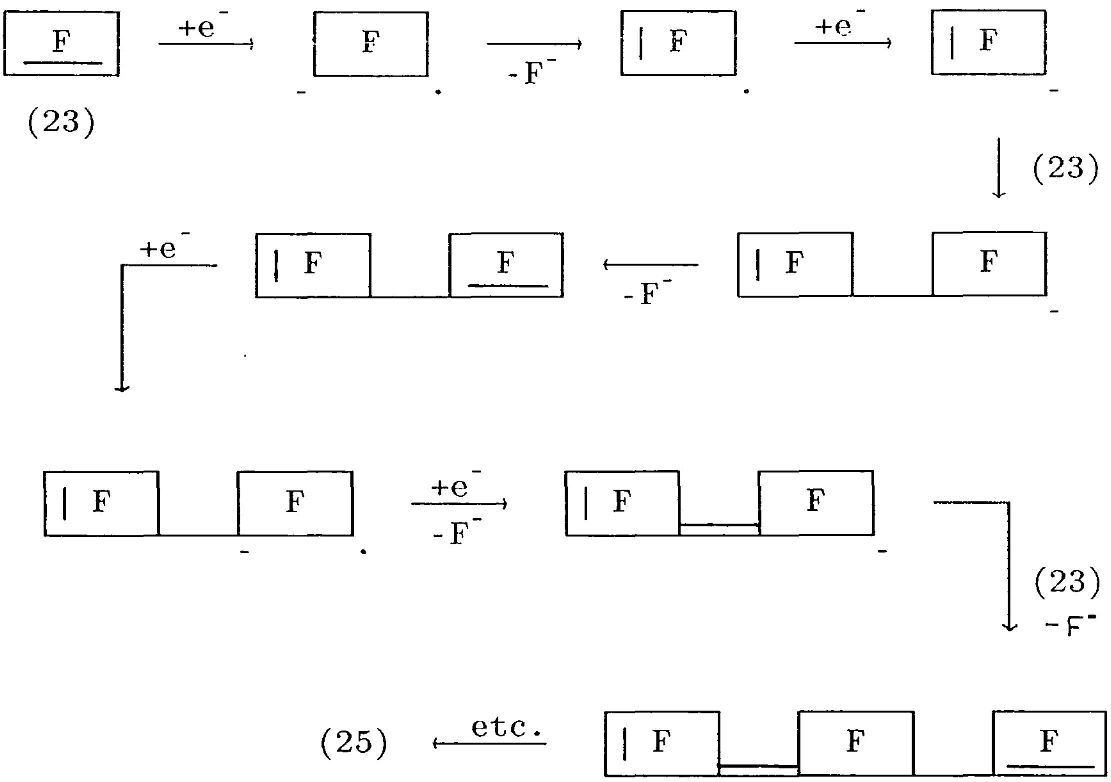
It cannot be ignored that some Et_4N^+ cations may be present in the polymer structure as Et_4NF or Et_4NBF_4; however it is not possible that these salts are present in large quantities as their inclusion would dramatically alter the percentage elemental composition of the polymeric material.

Analysis of the bulk catholyte by high field ^{19}F n.m.r. indicated the presence of unreacted (23) only, although mass spectrometry showed the presence of material which probably formed at the cathode and diffused into the bulk catholyte.

The use of trapping agents proved unhelpful in the elucidation of any possible mechanism. Furan (a Diels-Alder trapping agent for any discrete diene intermediates) did not prevent the formation of the electrode coating. With perfluorocyclohexene (20), as a potential carbanion trap, there was only limited formation of the electrode coating, and (20) was reduced to hexafluorobenzene in good yield. No coupled products were observed.

The results from the electropolymerisation of (23), together with results obtained by Russian workers on dimerisation of perfluoro-1-alkyl-cyclobutene[35], indicate a likely propagation process for the formation of (25) as shown in scheme 10.

SCHEME 10:



2.B.4: REDUCTION OF PERFLUOROCYCLOPENTENE:

In agreement with the results of Silvester[34], electrochemical reduction of perfluorocyclopentene (26) at -1.8V, in anhydrous acetonitrile containing tetraethylammonium tetrafluoroborate as the supporting electrolyte, resulted in dark blue/black needles of polymer being formed at the electrode surface, almost immediately on the passage of current. These "needles" gradually grew and "matted" to envelope the entire cathode surface, causing the electrolysis current to gradually fall.

At the end of electrolysis the electrode material was scraped off the cathode, washed and dried, to leave a hard fibrous blue/black coloured solid. That the material grows on the cathode in itself suggests that it is conducting, and confirmatory measurements of the conductivity of the material gave a value of $10^{-3}\Omega^{-1}cm^{-1}$ - a value indicative of a good semiconductor (conductivity values for comparison: polypyrrole (doped) = $10^{2}\Omega^{-1}cm^{-1}$; polyacetylene (doped) = $10^{5}\Omega^{-1}cm^{-1}$; silicon = $10^{-3}\Omega^{-1}cm^{-1}$)[36,37]. This should be regarded as a minimum value, derived from a multicrystalline sample, and is probably substantially less than the value that would derive from a measurement <u>along</u> a single crystal. This conducting material is of particular interest because, so far as we are aware, it is the first such material to be produced by <u>cathodic</u> electropolymerisation[38], although anodic polymerisation of pyrrole[39] and thiophene[40] are, of course, very well known.

The physical characteristics of this material resembled very closely that of the corresponding material derived from the reduction of (23). It was insoluble in common organic solvents, standard infra-red spectrometry was unhelpful due to the nature of the material, and mass-spectrometry yielded few structural clues. However enough information was obtained from ESCA and elemental analysis for gross structural features to be determined. Elemental analysis shows that in addition to carbon and fluorine, the material contains nitrogen and hydrogen (see table 2), however, as

TABLE 2:

ELEMENTAL ANALYSIS OF POLYMER FROM ELECTROCHEMICAL REDUCTION OF (26)

	C	H	N	F[a]
% mass found	47.3	3.2	2.4	47.1
atomic ratio	23	19	1	15
atomic ratio $(-Et_4N^+)^*$	15	-	-	15

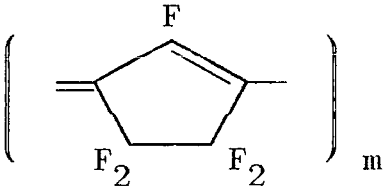
a. %F = 39.6 (measured) + (100 - (%C + %H + %N + %F))

NB. * = corrected atomic ratio allowing for Et_4N^+ incorporation (ie. atomic ratio -8C -20H -1N)

Silvester observed when analysing electrode material from the reduction of (26), the analysis figures do not add up to 100%. As there is no oxygen in the acetonitrile/tetraethylammmonium tetrafluoroborate system, the deficient mass can only be attributed to incomplete decomposition during fusion with potassium in the fluorine analysis, consistent with an extremely stable structure. As for the product from the reduction of perfluorocyclobutene (23), incorporation of Et_4N^+ cations from the supporting electrolyte is clearly indicated by a H:N ratio of 19:1, which corresponds well with the H:N ratio for the Et_4N^+ moiety (20:1); and, furthermore, change to tetrabutylammonium tetrafluoroborate gave a H:N ratio corresponding to Bu_4N^+ cations in the polymeric product. The coating did, however, appear to form more rapidly when using Et_4N^+ than with Bu_4N^+ cation in the supporting electrolyte, this probably being due to the larger cation being more effective in covering the electrode surface (a similar dependence on cation size being observed for the reduction of CF_2Br_2 to PTFE[41]).

A requirement for the presence of tetraalkylammonium cations for polymer growth is borne out by the fact that no polymerisation of (26) was observed using $LiClO_4$ as electrolyte[34], although polymerisation does occur with tetraalkylammonium perchlorate[42]. An E.S.C.A. investigation of the platinum cathode surface, in the former case, indicated that it was covered with a coating approximating to a 1:1 LiF:partially fluorinated carbonaceous material, which was sufficient to obscure the Pt_{4f} signal of the electrode. This coating was not visible, but is presumably passivating, as no gross electrolysis occurred.

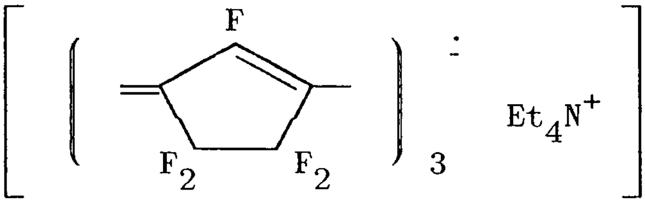
The incorporation of Et_4N^+ in the material requires that the atomic ratio for carbon in table 2 is adjusted accordingly. Thus 8 of the 23 carbon atoms are associated with the Et_4N^+ cation, leaving 15 derived from perfluorocyclopentene (26). A C_1F_1 matrix unit therefore results



(27)

Table 2 clearly shows that 15 carbon atoms from the polymer backbone are associated with each Et_4N^+ cation incorporated; thus m = 3 for each Et_4N^+ unit associated with structure (27).

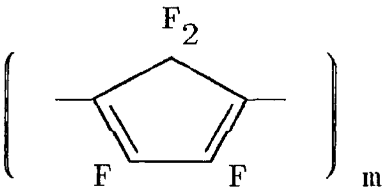
The electrochemical reduction of (26) is therefore analogous to the reduction of (23), and consequently on the basis of elemental analysis alone, it is reasonable to propose (28) as the structure of the polymeric material.



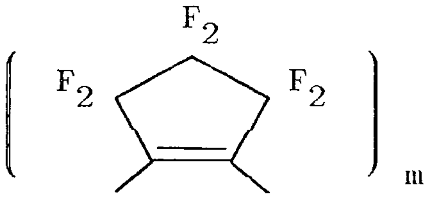
(28)

E.S.C.A. spectra[42] confirm the presence of CF_2 and, hence, the presence of C not attached to F. Although the limitations of E.S.C.A. for the determination of bulk structure should be borne in mind, a combination of elemental analysis with these data suggest (28) as the best interpretation of structure. E.s.r. measurements confimed the paramagnetic nature of (28).

Other structures, giving percentage elemental compositions similar to those detailed in table 2; for example, (29) or



(29)



(30)

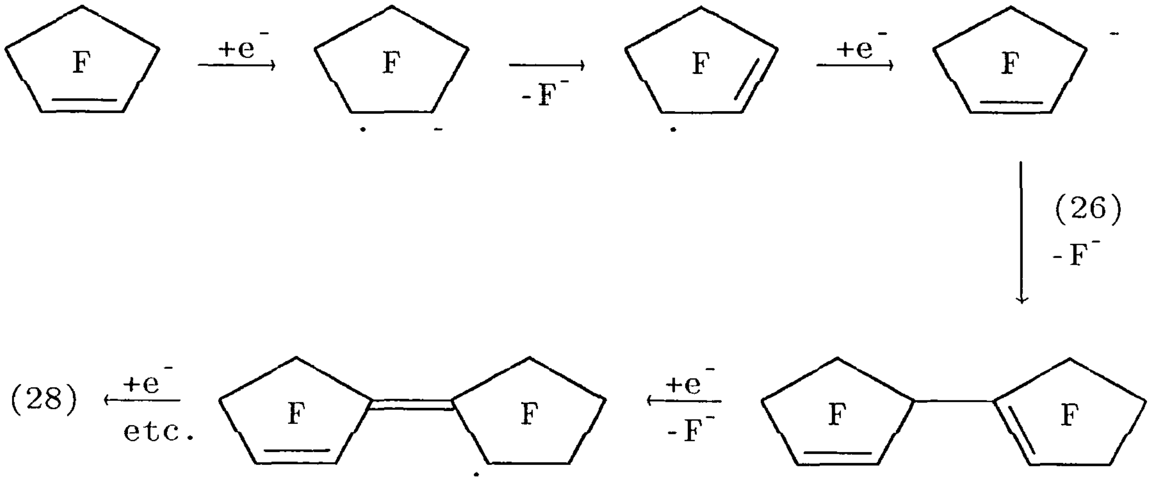
(30) associated with Et_4NF or Et_4NBF_4, are possible. The similarities between the electrochemical reduction of (23) and (26) (- physical and chemical properties, and method of synthesis), suggest that they both possess a similar "basic" structure ie. both materials are polymeric, with a tetraalkylammonium cation associated with three monomer units present as a C_1F_1 matrix, with alternate single and double bonds running through the carbon backbone - see (25) and (28).

Other workers have found that electrochemical reduction of PTFE results in extensive defluorination with the initial formation of $-(C_n)-{}^{-}Bu_4N^{+}$, which is further reduced to $-(C_n)-$ intercalated with Bu_4NF [43,44].

The bulk catholyte was also investigated. Analysis of the catholyte volatiles by high field ^{19}F n.m.r. showed only the presence of perfluorocyclopentene. The involatile fraction was washed with water, which caused a blue/black material to precipitate. This material was then filtered and dried under vacuum, leaving a dark coloured fine particulate powder, which when analysed gave a percentage weight composition similar to that of the electrode material. Clearly the material observed in the bulk catholyte, is caused by fragments of the electrode coating diffusing away from the cathode into solution, as a suspension.

It is clear from the reduction of perfluorocyclohexene (20), which is consistent with the findings of earlier workers for the reduction of perfluorocyclohexadienes[27-29] (see scheme 9), and from the results obtained by Russian workers on dimerisation of perfluoro-1-alkyl-cyclobutene and -cyclopentene[35], that the likely propagation process for the formation of (28) is as shown in scheme 11.

SCHEME 11:



The mechanism of formation of (28) proceeds via an EC_EEC_E mechanism - as observed for the reduction of (20) at a vertical platinum electrode.

A number of experiments were carried out in an attempt to trap any anionic or free radical intermediates. Cyclohexene, as a radical trap, did not stop the formation of the electrode coating, and no products other than those from reduction of (26) were observed. With perfluorocyclohexene (20), as a potential carbanion trap, there was limited formation of the coating and (20) was reduced to hexafluorobenzene. This observation may simply reflect the differing solubilities and absorptivities of (20) and (26), and therefore any wider conclusions cannot be made.

2.B.5: CONCLUSIONS:

These reactions demonstrate the usefulness and subtleties of electro-organic chemistry in the synthesis of novel materials.

The electrochemical reduction of the 4-, 5-, and 6-membered perfluorinated cyclic olefins mirrors the reductive reactions observed over hot metals. Perfluorocyclohexene undergoes exhaustive defluorination to yield hexafluorobenzene in quantitative yield; whilst perfluoro-cyclobutene and -cyclopentene undergo defluorination, coupled with polymerisation, forming novel conducting involatile carbonaceous materials at the cathode surface.

2.C: REDUCTION OF 4- AND 6-MEMBERED 1,2-DICHLOROFLUORO-CYCLICALKANES:

2.C.1: INTRODUCTION:

As was described in chapter 1, the reduction of compounds containing two halogens on adjacent carbon atoms, usually leads to an increase in the unsaturation of the molecule. Thus 1,2-dihaloalkanes give olefins, via a concerted $2e^-$ reduction mechanism. The trans-dihalide, however, is generally reduced at a less negative potential than the cis-isomer; the difference being attributed to steric constraints which affect the approach of the molecule to the electrode surface and subsequent adsorption onto the electrode.

The carbon-chlorine bond is easier to reduce than the carbon-fluorine bond, thus in the 1,2-dichlorofluorocyclic-alkanes, it is reasonable to suppose that the initial step would involve reductive cleavage of the two chlorines to yield the perfluorinated cyclic alkene, which may then itself reduce at the operating potential to yield the respective reduction product, as detailed in section 2B.

This work is precedented by the fact that 1,2-dichlorohexafluorocyclobutane (32) is used in the synthesis of perfluorocyclobutene, by dechlorinating with zinc in ethanol, in a process analogous to the expected initial electrochemical reduction step.

2.C.2: ELECTROCHEMICAL REDUCTION OF 1,2-DICHLORODECAFLUOROCYCLOHEXANE:

2.C.2a: REDUCTION IN DMF AT -1.65V:

1,2-dichlorodecafluorocyclohexane (31) was reduced at -1.65V at a platinum cathode in anhydrous DMF, containing tetraethylammonium tetrafluoroborate as the supporting electrolyte.

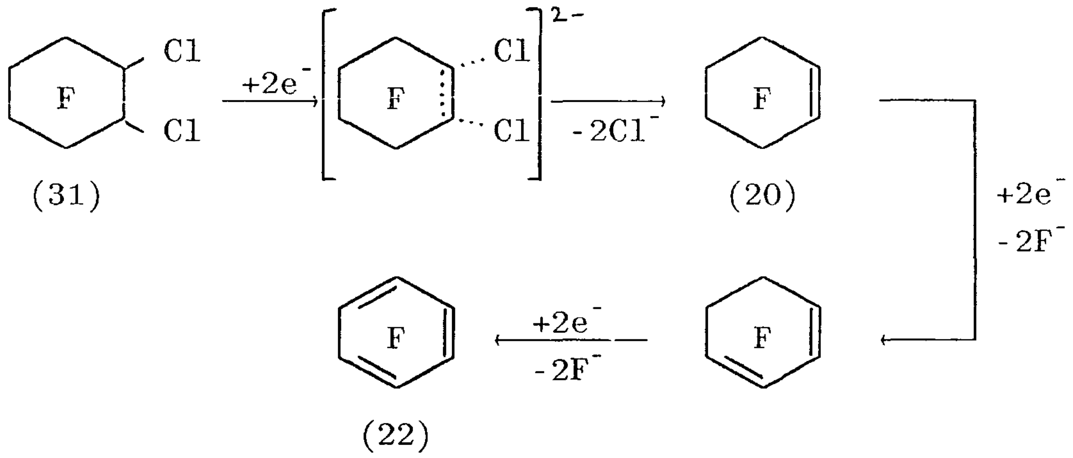
The volatile material collected contained a lower insoluble fluorocarbon layer, which was shown by mass spectrometry-g.l.c., and ^{19}F n.m.r. to contain unreacted (31), and hexafluorobenzene (22) in good yield. Similar analysis of the DMF/volatiles fraction confirmed the presence of (22) as the major product.

2.C.2b: REDUCTION IN ACETONITRILE AT -1.45V:

Reduction of (31) at platinum cathode in anhydrous acetonitrile containing the same supporting electrolyte resulted in the formation of perfluorocyclohexene (20) (40%) in addition to hexafluorobenzene (22) (60%).

Clearly an initial 2e$^-$ reductive cleavage of the two chlorines has occurred to give perfluorocyclohexene (20), which may then itself undergo a 4e$^-$ reduction to yield hexafluorobenzene (22) dependent on the operating reduction potential. (scheme 12).

SCHEME 12:



2.C.3: ELECTROCHEMICAL REDUCTION OF 1,2-DICHLOROHEXAFLUOROCYCLOBUTANE:

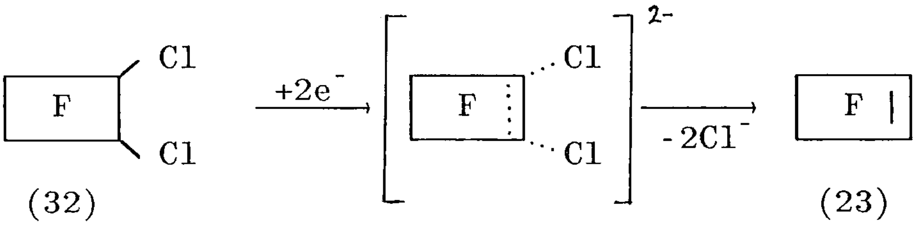
2.C.3a: REDUCTION IN DMF AT -1.5V:

1,2-dichlorohexafluorocyclobutane (32) was reduced at -1.5V at a platinum cathode in anhydrous DMF, with tetraethylammonium tetrafluoroborate as the supporting electrolyte. Throughout the 10hrs of electrolysis the current remained relatively constant at 130mA.

High field ^{19}F n.m.r. of the bulk catholyte showed the presence of (32), and two peaks at 119.6ppm and 138.4ppm, consistent with perfluorocyclobutene (23) in DMF solvent. No film formed on the electrode surface, which would be indicative of (23) being itself reduced at the operating reduction potential (section 2.B.3).

Clearly, reductive cleavage of the two carbon-chlorine bonds has occured via an EC_EEC_E mechanism, forming the volatile perfluorocyclobutene (23), which has not itself been reduced at the operating potential of -1.5V (scheme 13), (indeed, preparative reduction of (23) in DMF, occurs at a potential much greater than -1.5V)

SCHEME 13:



2.C.3b: REDUCTION IN ACETONITRILE AT -1.8V IN THE PRESENCE OF FURAN:

The aim of this experiment was to attempt to modify the reaction pathway of the reduction of (23).

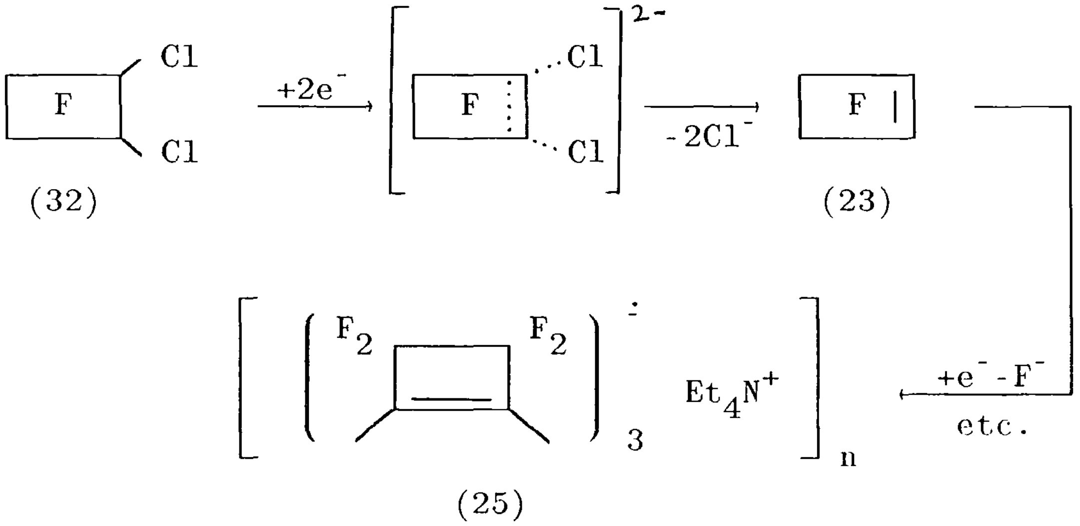
Before the constitution of the material from the electrochemical reduction of perfluorocyclobutene was established, an intriguing possibility was that reduction of (23) may proceed via a perfluorocyclobutadiene intermediate, which could be trapped by Furan (a Diels-Alder trapping agent), particularly when a low concentration of (23) is present at the electrode surface (which would hopefully inhibit propqgative "polymeric" growth)

When 1,2-dichlorohexafluorocyclobutane (32) was reduced at -1.8V at a platinum cathode in acetonitrile containing tetraethylammonium tetrafluoroborate as the supporting electrolyte, and Furan as a "Diels-Alder" trapping agent, a dark blue/black coloured material was deposited on the electrode surface. At the end of electrolysis the catholyte and anolyte were intensely coloured. The polymeric material on the cathode was removed, washed and dried. Subsequent elemental analysis showed its percentage composition to be nearly identical to that of the cathode material obtained on reduction of perfluorocyclobutene (23).

Analysis of the bulk catholyte by ^{19}F n.m.r. showed only the presence of unreacted (32) and perfluorocyclobutene (23).

Reductive cleavage of the two carbon to chlorine bonds has clearly occurred to yield perfluorocyclobutene (23), which has then itself been reduced at the operating potential to yield the polymeric product (25) (scheme 14). The presence of Furan had no modifying effect on the reduction of either (32) or (23).

SCHEME 14:



2.C.4: CONCLUSIONS:

Control of the reduction potential and careful choice of solvent, allows electrochemical reduction of both (31), and (32), to give either their respective perfluorinated cyclic-alkene via a $2e^-$ dechlorination, or the products associated with reduction of the F-alkene.

2.D: ELECTROCHEMICAL REDUCTION OF PERFLUORO-OLEFINS CONTAINING A VINYLIC FLUORINE:

2.D.1: INTRODUCTION:

As was described in chapter 1, the reduction of compounds containing two halogen atoms on adjacent carbon atoms generally leads to an increase in the unsaturation of the molecule. Thus 1,2-dihaloalkanes give olefins, and 1,2-dihaloalkenes give acetylenes. When perfluorinated systems are considered, a carbon to carbon double bond maybe used as a site at which an electrochemical reaction can be initiated, since the reduction of a carbon-fluorine bond in a saturated molecule occurs at a reduction potential which is often above that of the break down voltage of the solvent/electrolyte system being used. Clearly, the ease of electron transfer to a perfluorinated olefin depends on the structure of the molecule, however groups in the immediate vicinity of the double bond which will stabilize the intermediate anion radical, will allow the reduction to take place at a more positive potential.

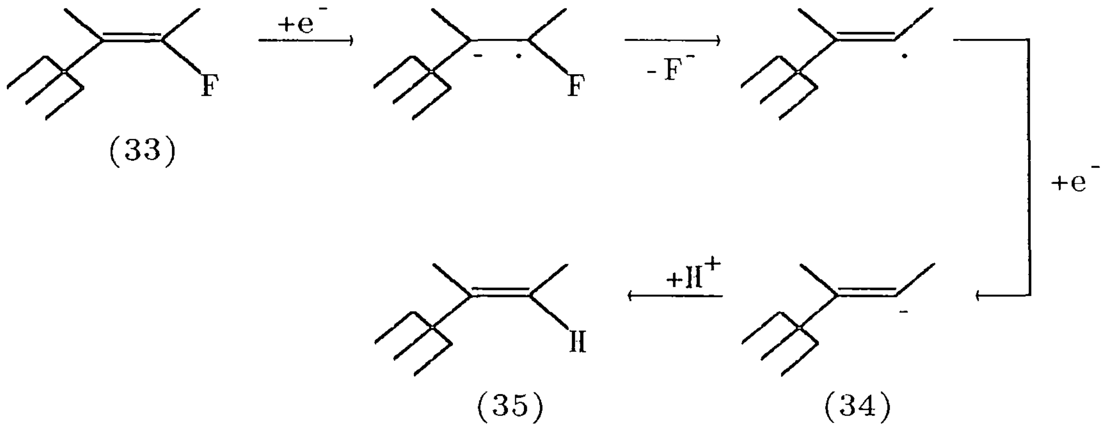
The reduction of perfluoro-3,4-dimethyl-4-ethylhex-2-ene (33), and perfluoro-4-methylpent-3-ene (36), has been investigated -both containing a vinylic fluorine. It was anticipated that the presence of a vinylic fluorine would allow a clear route to fluoride ion elimination, and subsequent carbanionic or radical intermediate formation. Some interesting chemistry may then result from the reaction of these possible reactive intermediates.

2.D.2: ELECTROCHEMICAL REDUCTION OF PERFLUORO-3,4-DIMETHYL-4-ETHYL-HEX-2-ENE (33):

(33) was reduced at -2.0V in acetonitrile at a platinum electrode, with tetraethylammonium tetrafluoroborate as the supporting electrolyte. On the initiation of electrolysis an orange/red colouration began to pervade the cathode compartment. The colour of the catholyte gradually darkened during the reduction.

At the end of electrolysis a lower fluorocarbon layer was still visible at the bottom of the cell. Analysis of this fluorocarbon layer by g.l.c. indicated the presence of only one product in addition to (33). After separation by preparative scale g.l.c, the product was identified as 2H-perfluoro-3,4-dimethyl-4-ethyl-hex-2-ene (35). ^{19}F n.m.r. of (35) gave a spectrum very similar to that of (33); however the vinylic fluorine of (33) was no longer present. Further evidence for structure (35) is a quartet at 4.9ppm in the ^{1}H n.m.r. spectrum (a vinylic proton interacting with an adjacent $-CF_3$ group), and a parent molecular ion M^{-},482,4.7% and M-1,481,32.6% by mass spectroscopy-g.l.c. Scheme 15 shows the most likely route to (35).

SCHEME 15:



Clearly the carbanion (34) must be relatively stable and the pathways for further reaction restricted, to enable (34) to be protonated in a system which has otherwise shown no "protonating" tendency. The origin of the proton source can only be suspected as coming from water impurities in the system.

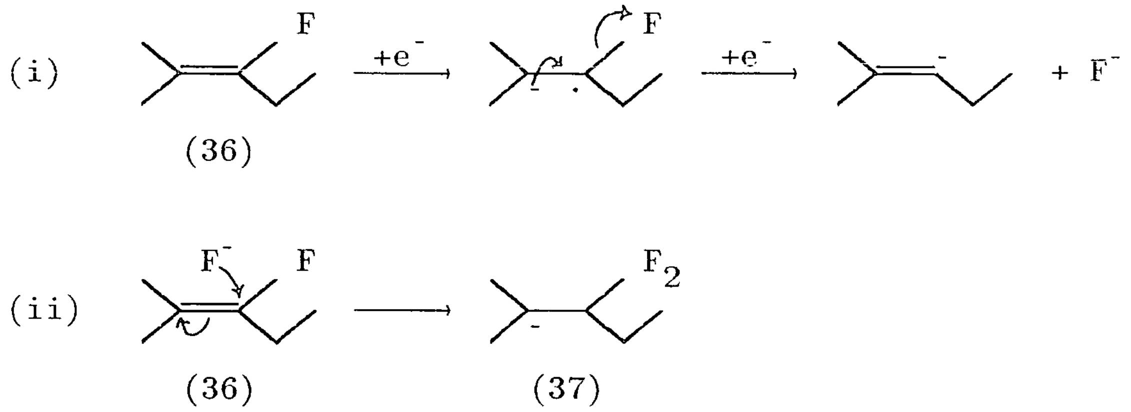
2.D.3: ELECTROCHEMICAL REDUCTION OF PERFLUORO-4-METHYL-PENT-3-ENE (36):

Knunyants[45] reported in 1979 that electrochemical reduction of (36),at a platinum cathode in anhydrous acetonitrile containing tetraethylammonium fluoride as a supporting electrolyte, resulted in the formation of two unusual four membered cyclic dimeric products (38) and (39) (see scheme 17). The electrochemical reduction of (36) was therefore independently studied to confirm these interesting observations.

(36) was reduced at -1.7V at a platinum cathode in acetonitrile containing tetraethylammonium tetrafluoroborate as the supporting electrolyte. On the commencement of reduction an orange/red colouration appeared in the catholyte which gradually turned a dark burgandy red during the course of the electrolysis, as the current fell from 230mA to 16mA.

High field ^{19}F n.m.r. of the bulk catholyte after 1.25hrs and 4.25hrs suggested the presence of a "stable" carbanion (37), which would be formed by fluoride ion attack on (36), the fluoride ion probably coming from initial reductive displacement of the vinylic fluorine in the parent molecule (scheme 16). The presence of carbanion (37) can only be suggested, as reactions of the "carbanion containing catholyte" with various electrophiles failed to form the desired "trapped" adducts.

SCHEME 16:



(36)

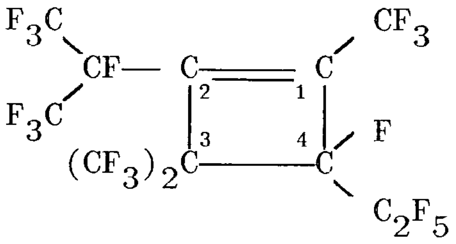
(36) (37)

The counterion of the carbanion is most likely to be Et_4N^+, from the supporting electrolyte -it s interaction with the reaction being not unprecedented (see section 2.B.3, and 2.B.4).

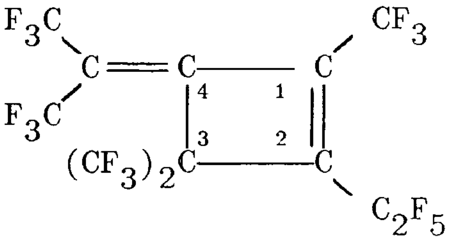
At the end of electrolysis a lower fluorocarbon layer was removed from the catholyte, which was shown by g.l.c. to be a two component mixture. Separation of the two products was achieved by analytical g.l.c. (OPN/Porasil C, 110°C); and by bubbling the exhaust gases from the outlet of the g.l.c. machine through Analar acetone, Fourier transform ^{19}F nmr spectra of the two products could be obtained.

Both the ^{19}F nmr, and mass spectrometry data of the two products agreed with those reported by I.L.Knunyants et al[45]. The two products were therefore identified as: perfluoro-1,3,3-trimethyl-4-ethyl-2-isopropylcyclo-1-butene (38), and;

perfluoro-1,3,3-trimethyl-2-ethyl-4-isopropylidenecyclo-1-butene (39).



(38)



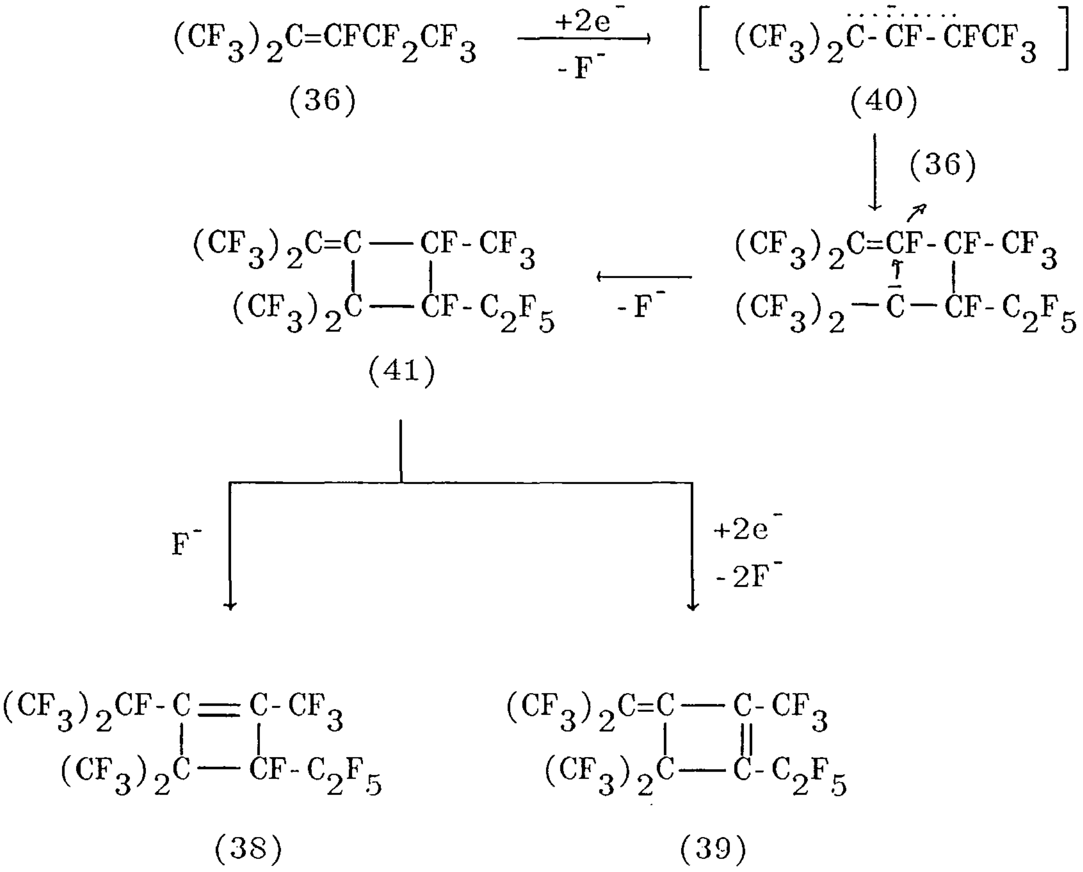
(39)

^{19}F n.m.r. data of (38) shows the presence of two tertiary fluorines, with the $-CF_2$ of the perfluoroethyl group at C-4 split into an AB by the adjacent C-4 tertiary fluorine. Six $-CF_3$ groups are present grouped in three general "environments", with three $-CF_3$'s shifted considerably further downfield than the other three by the presence of the endocyclic double bond. Mass spectrometry-g.l.c. gave a M-19 ion, 543; confirming a $C_{12}F_{22}$ molecular formula.

(39), however, gave a parent molecular ion M^+, 524; indicating that (39) had undergone a greater degree of defluorination than (38). ^{19}F n.m.r. data confirmed this -showing the presence of six $-CF_3$ groups in five environments, and one $-CF_2$ group. No tertiary or vinylic fluorines were present. The downfield shift of the $-CF_2$ in comparison to that observed in (38), suggests that the perfluoroethyl group is now adjacent to the endocyclic double bond; while the absence of a tertiary fluorine indicates that the isopropyl group of (38) is no longer present and has been replaced by an isopropylidene substituent, which is confirmed by the downfield shift of the two respective $-CF_3$ groups. The two perfluoromethyl groups at the C-3 ring position are chemically equivalent in (39), unlike those in (38) which are affected by the tertiary fluorine of the isopropyl group at C-2.

The mechanism proposed for the formation of (38) and (39) involves initial transfer of two electrons to the original pentene (36) accompanied by elimination of fluoride ion to yield the allyl anion (40) (see scheme 17)

SCHEME 17:



Anion (40) then attacks a molecule of the original pentene (36), with subsequent intramolecular substitution of the vinylic fluorine to form the cyclised "dimeric" intermediate (41). It is then suggested that this intermediate is either isomerized by free fluoride ion to form product (38), or is further reduced at the cathode to yield product (39) (see scheme 17). Electrolytic studies confirmed that the diene (39) is NOT a product of cathodic defluorination of cyclobutene (38)[45]; thus their are evidently two independent routes for conversion of intermediate (41) to the two products (38), and (39), dependent on the electrolytic conditions used.

2.D.4: CONCLUSIONS:

These results demonstrate, that reduction of a carbon to carbon double bond in a perfluorinated aliphatic olefin can be efficiently effected, with subsequent reaction yielding interesting, and otherwise difficult to obtain compounds.

CHAPTER 3:

CYCLIC VOLTAMMETRIC STUDIES OF VARIOUS FLUOROCARBON DERIVATIVES:

3.1: INTRODUCTION:

Cyclic voltammetry is an electroanalytical technique which may be used to investigate the electrode processes which occur during an electrochemical reaction.

In cyclic voltammetry the potential of the working electrode, in an unstirred solution, is linearly varied with time.

In the presence of an electro-active material which undergoes reversible electron transfer in a single step, a peak shaped voltammogram results - as shown in Fig 7.

This characteristic shape may be qualitatively understood as follows:

(i) initially, the electrode potential is such that the electroactive material is not able to accept an electron from the cathode (for reduction).

(ii) at a certain potential, current begins to flow as the substrate contained within the electrical double layer surrounding the cathode accepts electrons.

(iii) as the potential becomes more negative so the current rises exponentially. However, as current flows, there results a progressive depletion of electroactive substrate

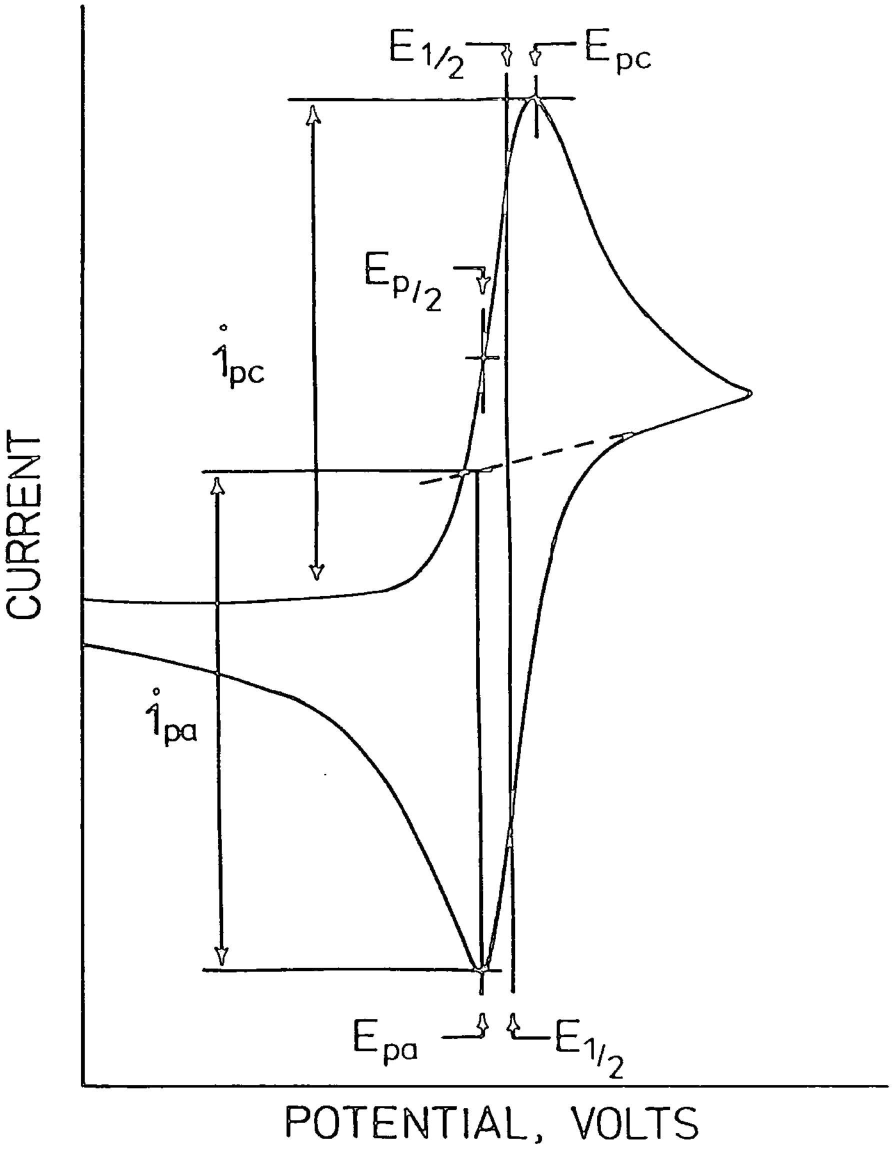


Fig.7: A cyclic voltammogram for a reversible electron transfer.

near the electrode. Although mass transfer delivers more of the active substrate from the bulk to the depleted region, its rate is slow compared with usual rates for electron transfer across the electrical double layer. A peak in the current-potential plot therefore results.

(iv) after the forward scan has been completed, the scan direction is then reversed; thus products which have been formed during the first sweep and which are still in the vicinity of the cathode may themselves undergo electron transfer. For an "ideal" reversible couple the product is reoxidized to the starting material, ie. back electron transfer occurs resulting in current to flow in the opposite direction from that initially observed - thus the reverse current-potential curve is exactly symmetrical to the forward curve. For a <u>reversible</u> process the Nernst equation is valid at all times:

$$E^{o} = E - \frac{RT}{nF} \cdot \ln \frac{[R]}{[0]}$$

where E^{o} is the standard potential of the system, and [R] and [0] are the activities of the reduced and oxidized forms, respectively. From the cyclic voltammogram for such a system it has been shown that[46]

$$E_p^{\,a} - E_p^{\,c} = \frac{0.056 \text{ volts}}{n}$$

(NB. for $E_p^{\,a}$ and $E_p^{\,c}$ - see Fig.7)

The peak potentials are also independent of the scan rate, and the ratio of the peak currents i_p^a/i_p^c is equal to unity[47]. Under these conditions the peak potential may be related to the polarographic $E_{1/2}$ by

$$E_p^c = E_{1/2} - \frac{1.1RT}{nF}$$

which may in turn be related to E^o, and hence to the Gibbs free energy.

If, however, the reduced intermediate is unstable with respect to a competing chemical reaction, its concentration in the double layer will be lower than expected, and a diminished reverse current will be obtained (if at all), dependant on the scan rate - see Fig.8.

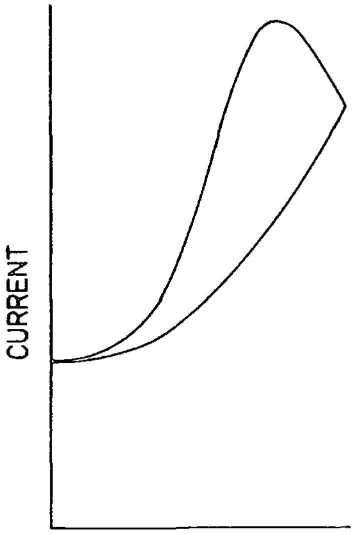


Fig.8: A cyclic voltammogram for a non-reversible electron transfer.

If the scan rate is increased, the chemical reaction following initial electron transfer will proceed to a lesser extent, thus i_p^a/i_p^c increases until, at very fast scan rates, the reaction may appear completely reversible. The expected variations of a wide variety of parameters with scan rate have been calculated for a range of different reaction mechanisms[47,48] - allowing information regarding reaction sequence, and also rate constants[49], to be calculated from the cyclic voltammetric data.

3.2: DISCUSSION:

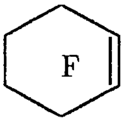
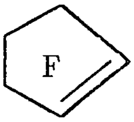
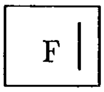
Cyclic voltammetry studies were undertaken to obtain the reduction potentials of the 4-, 5-, and 6- membered F-cycloalkenes and their oligomers, the 4-, and 6- membered 1,2-dichlorofluorocyclicalkanes, and some aliphatic fluoroalkenes, to complement the results reported on the preparative electrochemical reduction of these compounds.

3.2.1: REDUCTION OF THE 4-, 5-, AND 6- MEMBERED F-CYCLOALKENES:

Table 3 shows the results from the cyclic voltammetric investigation of the 4-, 5-, and 6- membered F-cycloalkenes. The results reported in table 3, are the values of E_{pc} (cathodic peak) in volts, measured at 0.1V/s.

These values were found to vary with sweep rate, a phenomenon which is consistent with an irreversible reduction process. Indeed, none of the systems studied showed any reversibility.

TABLE 3: CYCLIC VOLTAMMETRIC RESULTS FROM REDUCTION OF 4-, 5-, AND 6- MEMBERED F-CYCLOALKENES

SUBSTRATE	ACETONITRILE/Bu_4NBF_4	DMF/Bu_4NBF_4
	- 2.15V	- 1.98V & - 2.26V
	- 2.35V	* - 2.28V
	* - 1.65V	- 1.7V
STARTING VOLTAGE OF SOLVENT BREAKDOWN	- 1.9V	- 1.6V

* cyclic voltammogram did NOT produce a clear peak.

NB. all values measured at 0.1 V/s scan rate.

On many occasions a number of sweeps were required before a reduction peak was observed, possibly suggesting that some form of pretreatment of the electrode was necessary before the platinum electrode could "see" any fluorocarbon. This may be attributed to the tetraalkylammonium cation (R_4N^+), from the supporting electrolyte, forming an "impervious sheath" around the electrode. Subsequent multisweeps may allow the R_4N^+ to diffuse away from the electrode as the potential approaches 0V, thus allowing some fluorocarbon to diffuse into the electrode double layer.

Another inherent problem when studying the electrochemistry of fluorocarbons, is their insolubility in the solvents suitable for electrochemistry (ie. DMF, acetonitrile). The actual concentration of fluorocarbon in solution, therefore, is only a fraction of the total quantity added.

The reduction potential of the 4-, 5-, and 6- membered F-cycloalkenes is in the region of the breakdown potential of the solvent. The cyclic voltammogram from the fluorocarbon is therefore superimposed on the increased current response due to the solvent breakdown (Fig.9), thus the observed cyclic voltammogram of the fluorocarbon is a combination of these two responses, (as shown in Fig.10). Detailed conclusions from these results are therefore not possible.

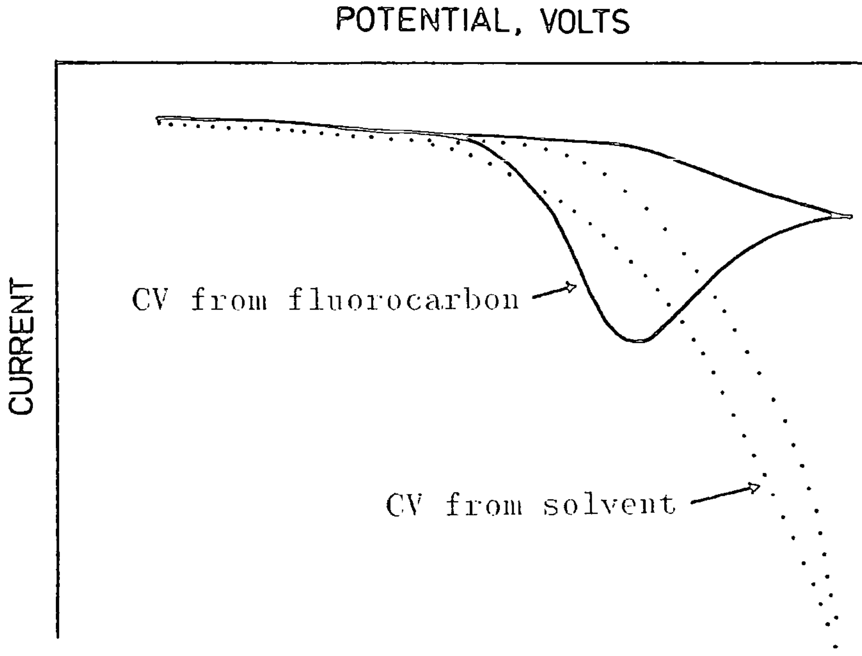


Fig 9: Cyclic voltammograms (CV's) of fluorocarbon and solvent.

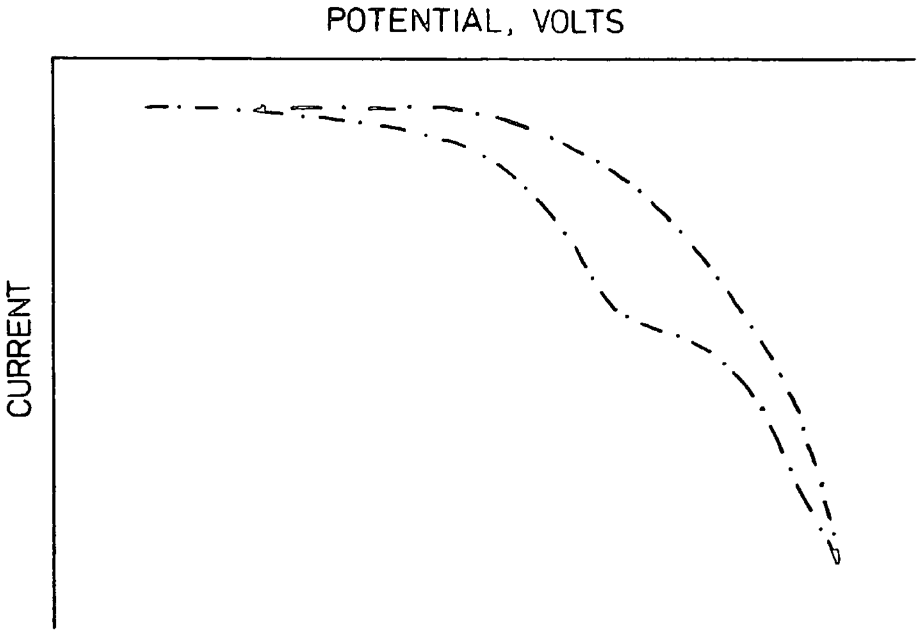


Fig 10: Cyclic voltammogram of the fluorocarbon substrate in the solvent-supporting electrolyte system.

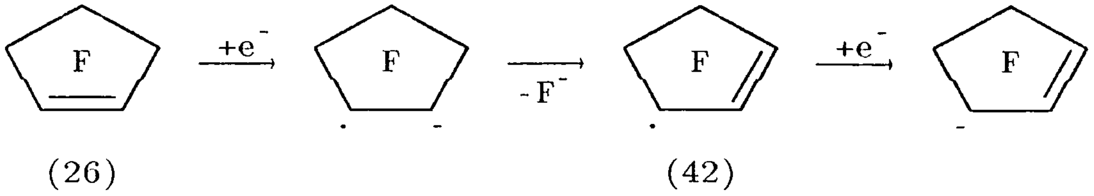
3.2.1a: MULTISWEEP CYCLIC VOLTAMMETRIC STUDIES:

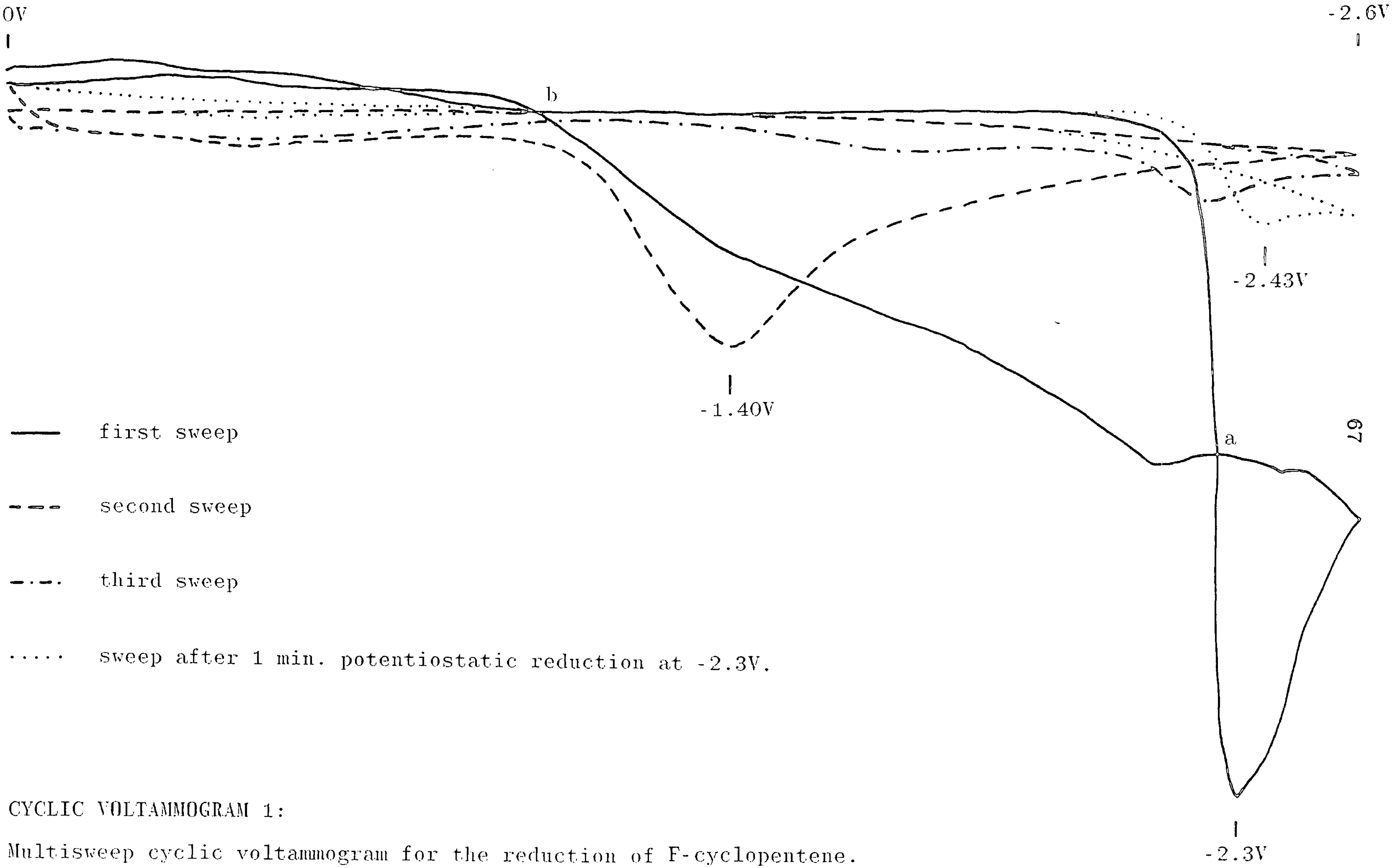
Interesting results were obtained on studying the reduction of perfluorocyclopentene (26) in acetonitrile with tetrabutylammonium tetrafluoroborate as the supporting electrolyte (cyclic voltammogram 1)

On the fist sweep no current response is observed until a potential of ~ - 2.3V is reached -the reduction potential of perfluorocyclopentene. On the return sweep - 2.6V → 0V, a current response is seen upto - 0.92V, forming a "nucleation loop" in the voltammogram. The cross over points observed (marked a and b in cyclic voltammogram 1) are caused by the nucleation overpotential required to deposit the polymer phase on the foreign electrode - a phenomena which is observed during the anodic electropolymerisation of pyrroles and thiophenes[50].

On the second sweep a peak potential of - 1.40V is observed on the forward sweep 0V → - 2.6V. This is presumably the reduction response of the radical intermediate (42) (scheme 18), which has remained in the electrode double layer, and

SCHEME 18:





CYCLIC VOLTAMMOGRAM 1:

Multisweep cyclic voltammogram for the reduction of F-cyclopentene.

which would be expected to reduce at a much lower reduction potential than the parent alkene. No nucleation loop is observed on the reverse sweep.
The third sweep shows a reduction peak at - 2.3V, probably due to reduction of material being deposited on the electrode, or of perfluorocyclopentene itself. The reactive intermediates formed at this stage, are presumably immediately incorporated in the formation of the "polymeric material" at the electrode surface, and are therefore not observed on any subsequent sweeps.
After one minute potentiostatic reduction at -2.3V, a thick coating of material was observable on the electrode; a subsequent sweep showed a peak response at -2.43V. This is either due to reduction of the polymer coating, OR reduction of perfluorocyclopentene at the modified electrode surface (the platinum electrode surface being modified by the polymer coating).

A similar multisweep response should also have been observed when studying perfluorocyclobutene (23), which also forms a polymer at the electrode surface -by an analogous mechanism to that detailed for electrochemical reduction of (26). Despite using a range of sweep rates, no such response was observed. Clearly, a fast enough sweep rate could not be attained to allow an electrochemical response to be recorded for reduction of any radical intermediate. The increased reactivity of the radical intermediates from reduction of

(23) in comparison with those from (26), and the volatile nature of the parent alkene, does not make this a simple problem to overcome.

3.2.2: REDUCTION OF THE OLIGOMERS AND RELATED COMPOUNDS OF THE 4-, 5-, AND 6- MEMBERED PERFLUOROCYCLOALKENES:

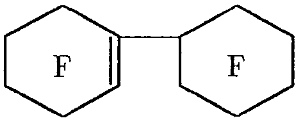
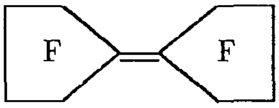
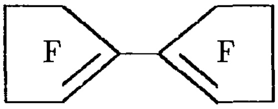
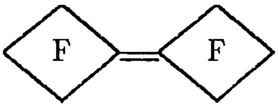
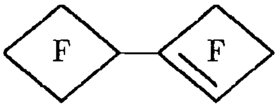
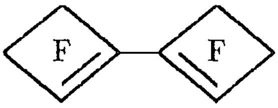
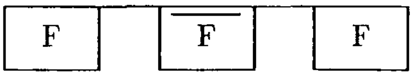
Table 4 shows the results from the cyclic voltammetric investigation of the oligomers and related dienes of the 4-, 5- ,and 6- membered F-cycloalkenes.

In an electrochemical reduction it is assumed that electron transfer is to the lowest unoccupied molecular orbital (LUMO) of the substrate under investigation. The peak potential of an electrochemical reduction is therefore a measure of the relative energetic position of the LUMO of the molecule.

It is well known that replacing fluorine in a F-alkene by perfluoroalkyl groups, reduces the LUMO energy of the molecule[51]. It is therefore not surprising that the dimers and trimer (in the case of F-cyclobutene) of the 4-, 5-, and 6- membered perfluorocyclic olefins, -in which <u>at least</u> one of the vinylic fluorines at the double bond has been replaced by a perfluoroalkyl group,all show reduction potentials, and therefore LUMO energies, which are lower than their monomer precursors.

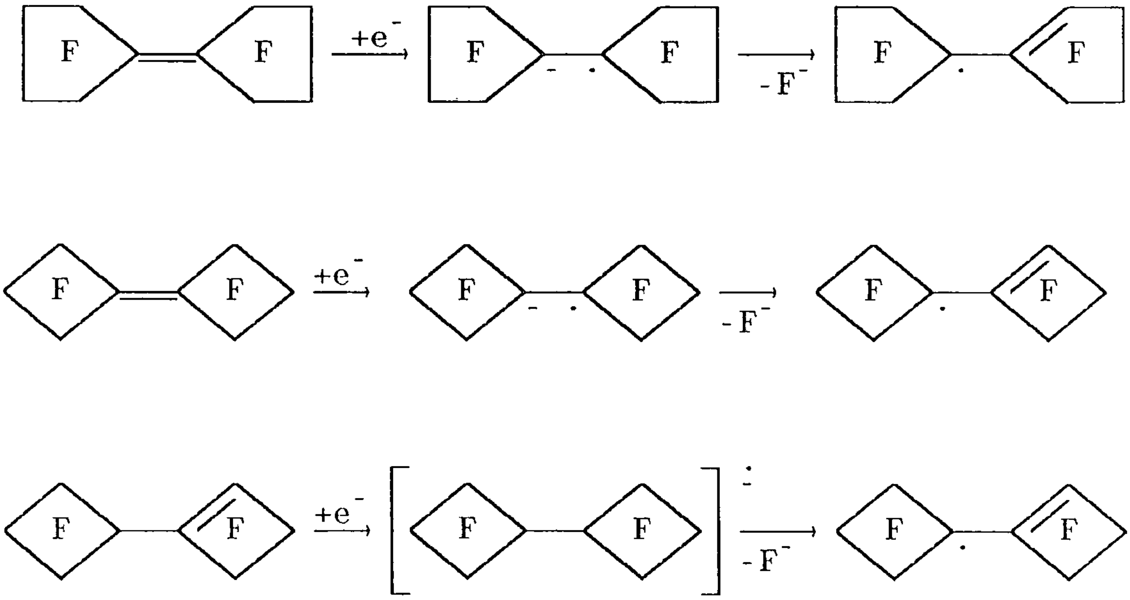
Not ably, both perfluorobicyclopentylidene (43), and the two isomers of the dimer of F-cyclobutene, (44) and (45), exhibit semi-reversible behaviour at a very low reduction

TABLE 4:CYCLIC VOLTAMMETRIC RESULTS FROM REDUCTION OF THE OLIGOMERS AND RELATED DIENES OF THE 4-, 5-, AND 6- MEMBERED PERFLUOROCYCLICOLEFINS:

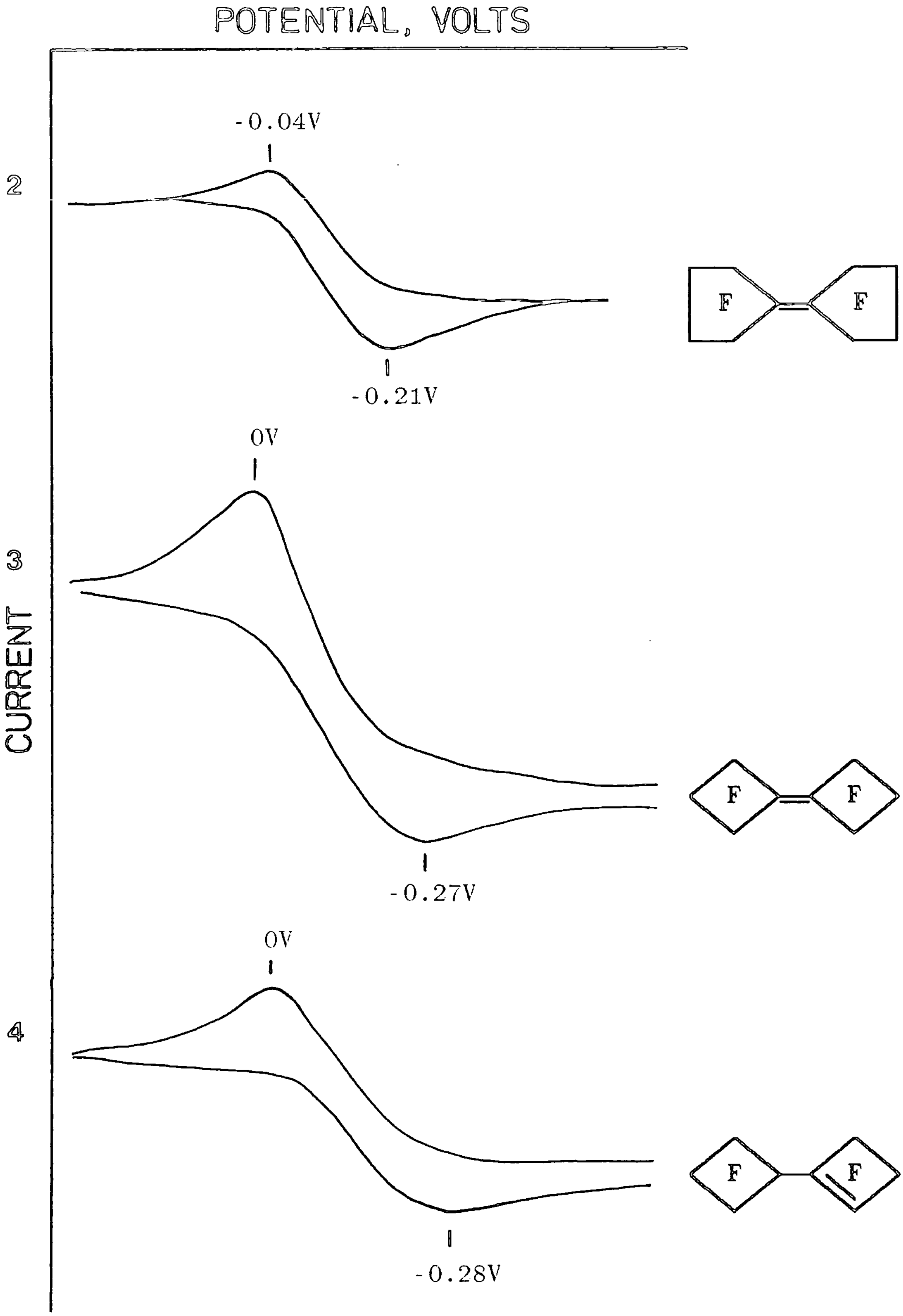
SUBSTRATE	ACETONITRILE/Bu_4NBF_4
	- 1.7V
 (43)	semi-reversible peak - 0.04V - 0.21V & - 1.26V
	- 1.12V
 (44)	semi-reversible peak 0V - 0.27V & - 0.83V
 (45)	semi-reversible peak 0V - 0.28V & - 0.87V
	- 1.19V
	- 1.28V (broad peak)

potential (E_{pc}~ - 0.25V) (cyclic voltammograms 2, 3, & 4). This is indeed surprising, when considering the two isomers of F-cyclobutene in which initial reduction is occurring at double bonds of quite different LUMO energy. The rationale for such an observation may involve the initial steps of electrochemical reduction. As scheme 19 shows, the first one electron reduction and subsequent F^- elimination yields radical anions and radicals of very similar electronic structure.

SCHEME 19:FIRST STEPS OF ELECTROCHEMICAL REDUCTION OF THE DIMERS OF F-CYCLO-PENTENE AND -BUTENE ie.(43), (44), & (45)



The fact that the peaks at E_{pc} ~ - 0.25V are indeed semi-reversible, however, indicates that complete fluoride ion elimination is not occurring. Why the reduction potentials of the dimers, (46) and (47), should be so close,



CYCLIC VOLTAMMOGRAMS 2,3 AND 4:

For reduction of the dimers of F-cyclopentene and F-cyclobutene.

despite their significant differences in LUMO energy is therefore not clear.

Interestingly, the symmetrical double bond of the trimer of F-cyclobutene, reduces at a slightly higher reduction potential than that of the perfluorobicyclobutylidene; due to either (i) the reduced effect of ring strain on the system, and/or (ii) the increased steric bulk of the molecule, preventing satisfactory interaction with the electrode surface.

3.2.3: REDUCTION OF THE 4-, AND 6- MEMBERED 1,2-DICHLOROFLUOROCYCLOALKENES:

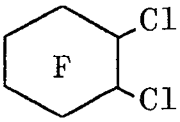
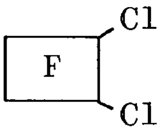
Table 5 shows the results from the cyclic voltammetric investigation of the 4- ,and 6- membered 1,2-dichlorofluorocycloalkenes.

It is interesting to compare the reduction potentials of the compounds under study with the reduction potentials of the analogous F-cycloalkenes. When using acetonitrile (48) gives a reduction potential which is below that of F-cyclohexene; while in DMF the opposite is the case. The differences in the reduction potentials of (49) compared with those of F-cyclohexene in acetonitrile and DMF, are a little less marked.

Preparative reduction of (48) can therefore be controlled to yield either the respective dechlorinated F-cycloalkene, OR the product derived from reductive defluorination of the

F-cycloalkene ie.hexafluorobenzene, by careful choice of solvent and reduction potential (see chap 2).

TABLE 5: CYCLIC VOLTAMMETRIC RESULTS FROM REDUCTION OF THE 4-, AND 6- MEMBERED 1,2-DICHLOROFLUOROCYCLICOLEFINS:

SUBSTRATE	ACETONITRILE/Bu_4NBF_4	DMF/Bu_4NBF_4
 (48)	*- 1.8V	*- 2.0V
 (49)	- 1.7V	- 1.8V
STARTING VOLTAGE OF SOLVENT BREAKDOWN	- 1.9V	- 1.6V

* cyclic voltammogram did NOT produce a clear peak.

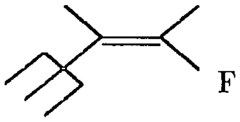
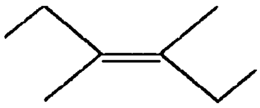
NB. all values measured at 0.1V/s scan rate.

3.2.4: REDUCTION OF ALIPHATIC FLUORO-OLEFINS:

Table 6 shows the results from the cyclic voltammetric investigation of two aliphatic fluoro-olefins readily available in the laboratory - perfluoro-3,4-dimethyl-4-ethyl-hex-2-ene (50), and perfluoro-3,4-dimethyl-hex-3-ene (51)

The results reported in table 6, are the values of E_{pc} (cathodic peak) in volts, measured at a scan rate of 0.1V/s.

TABLE 6: CYCLIC VOLTAMMETRIC RESULTS FROM REDUCTION OF VARIOUS ALIPHATIC FLUORO-OLEFINS:

SUBSTRATE	ACETONITRILE/Bu_4NBF_4
 (50)	- 1.95V (broad peak)
 (51)	- 0.85V, - 1.83V, - 2.23V

As expected the less electrophilic (50), containing a vinylic fluorine, gives a reduction peak at a much higher reduction potential than that of (51), with four perfluoroalkyl groups surrounding the carbon-carbon double bond. Neither olefin showed any sign of reversibility.

CHAPTER 4

A NEW SYNTHETIC APPROACH TO THE PREPARATION OF FLUORO-DIENES AND MONO-ENES

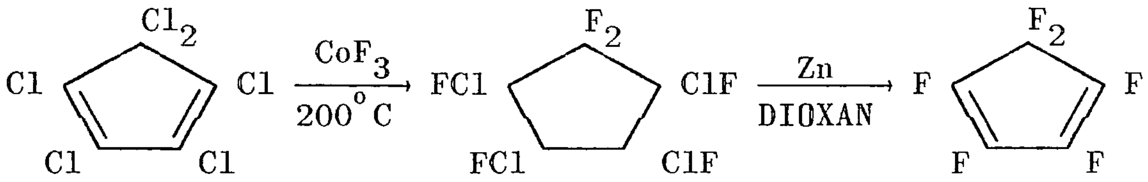
Various methods are available for the preparation of cyclic and acyclic fluoro-dienes. Few, however, have general applicability.

In the introductory section, synthetic approaches for the preparation of fluoro-dienes will be reviewed, followed by a description of a new approach to the synthesis of fluoro-dienes, which may be regarded as an electromimetic process.

4.1: INTRODUCTION:

4.1.1: METAL INDUCED DEHALOGENATION:

Dechlorination with zinc of tetrachlorohexafluorocyclopentane (51), obtained by fluorination of commercial perchlorocyclopentadiene with cobalt trifluoride[52,53], is the most widely used method for preparation of perfluorocyclopentadiene (52).

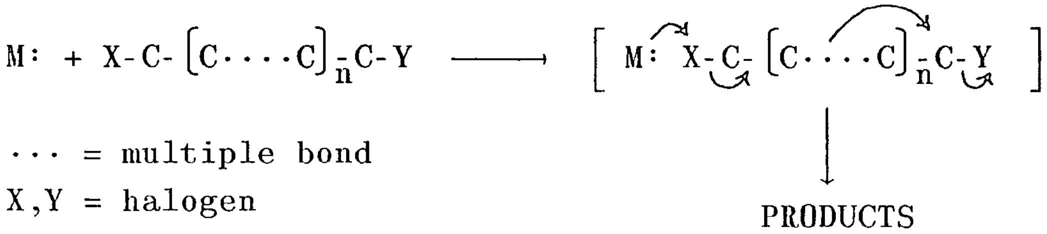


33% (51a) 44% (52)

Use of boiling bis-(2-methoxy-ethyl)ether (bp.161°C), instead of boiling dioxan (bp.102°C), as the reaction medium for the dechlorination, has a significant effect on product yields, increasing the yield of (52) from (51a) from 44 to ca.70%.

The process for zinc initiated reductive dehalogenation is as outlined in scheme 20.

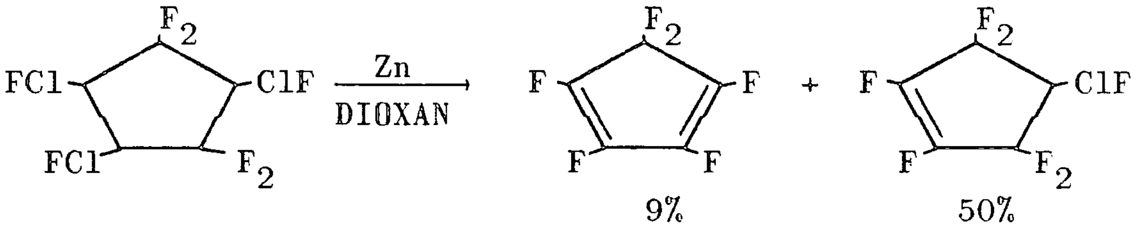
SCHEME 20:



··· = multiple bond
X,Y = halogen
M = metal (Mg, Zn)
n = integer > 0

and as such is limited to substrates containing two halogens in a 1,2 arrangement or linked to a carbon-carbon double bond.

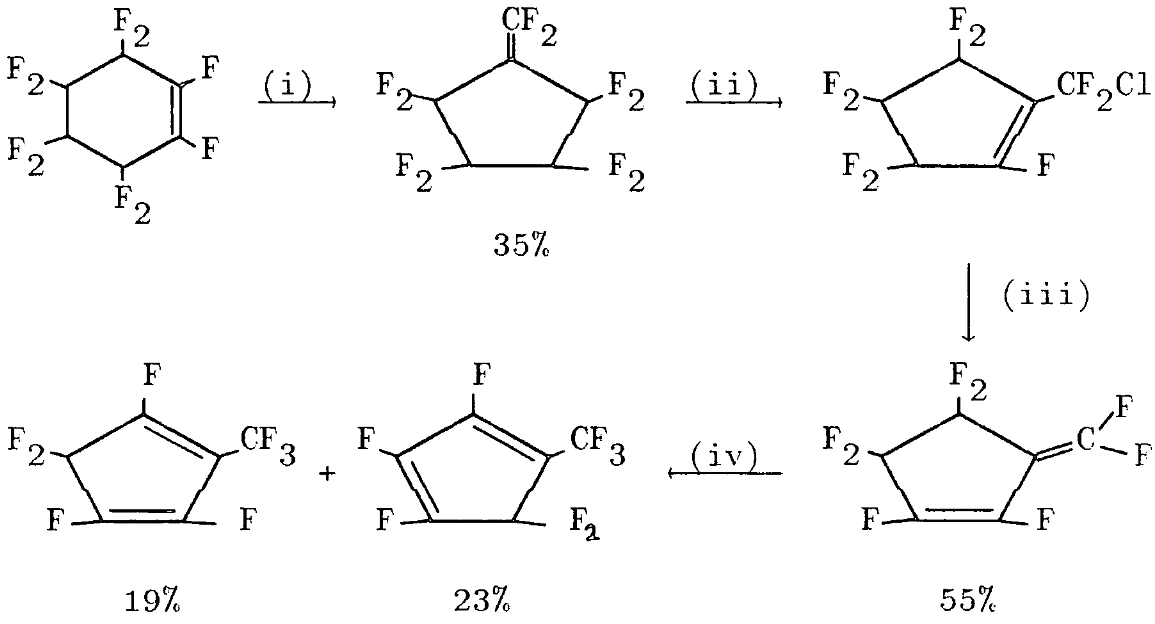
Zinc dechlorination of (53), similarly affords (52) (9%), in addition to 4-chloroheptafluorocyclopent-1-ene (54) (50%)[54].



(53) (52) (54)

TABLE 7:

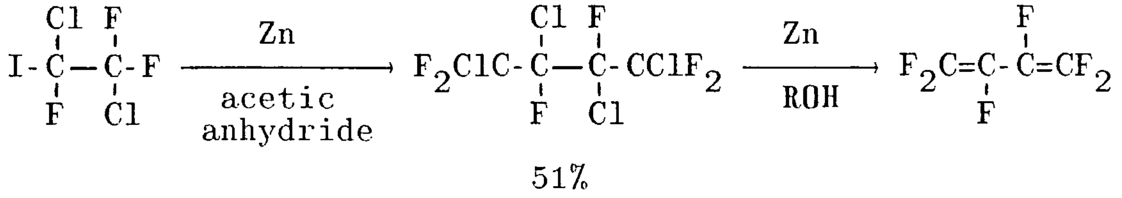
F-DIENE SYNTHESES VIA ZINC DECHLORINATION:



[55]

(i) hν, 185nm (ii) $AlCl_3$-MeI, 0°C
(iii) Zn dust, $(MeO.CH_2.CH_2)_2O$, 160°C (iv) NaF, 320°C

[56] [57]



$$\mathrm{I{-}\overset{Cl}{\underset{F}{C}}{-}\overset{F}{\underset{Cl}{C}}{-}F \xrightarrow[\text{acetic anhydride}]{\text{Zn}} F_2ClC{-}\overset{Cl}{\underset{F}{C}}{-}\overset{F}{\underset{Cl}{C}}{-}CClF_2 \xrightarrow[\text{ROH}]{\text{Zn}} F_2C{=}\underset{F}{C}{-}\overset{F}{C}{=}CF_2}$$

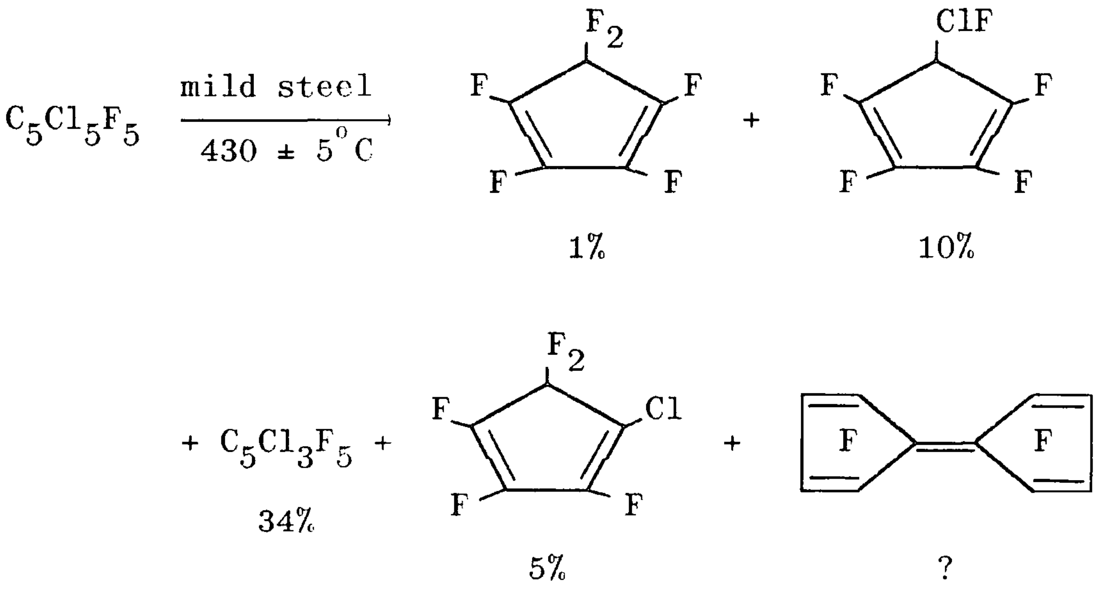
51%

4.1.2. THERMAL ELIMINATION PROCESSES:

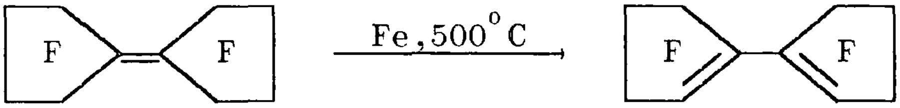
Dehalogenation may also be achieved by thermally induced elimination processes.

Passage of the vapour of pentachloropentafluorocyclopentane (obtained from fluorination of perchlorocyclopentadiene with cobalt trifluoride) over mild steel at 430 ± 5°C under reduced pressure gives various dehalogenated products[54], - see scheme 21

SCHEME 21:



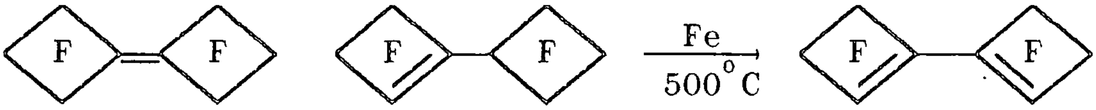
In our laboratories, perfluorobicyclopent-1,1'-enyl (56) has been prepared by the passage of (55) over hot iron[58].



(55)

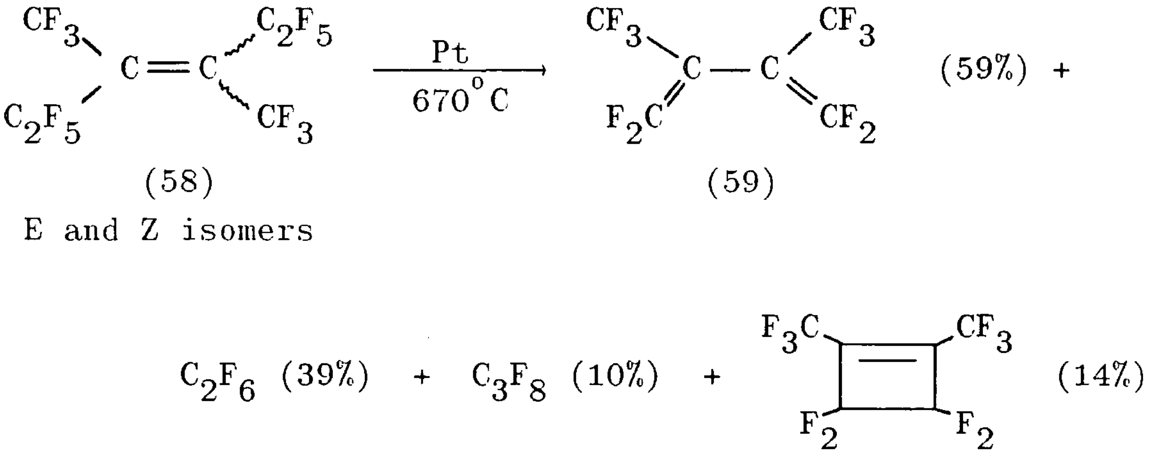
(56)
60% yield
100% conversion

Passage of the dimers of F-cyclobutene, (44) and (45), over hot iron filings gave perfluorobicyclo-1,1'-enyl (57) in approximately 20% yield[59].



(44) (45) (57)

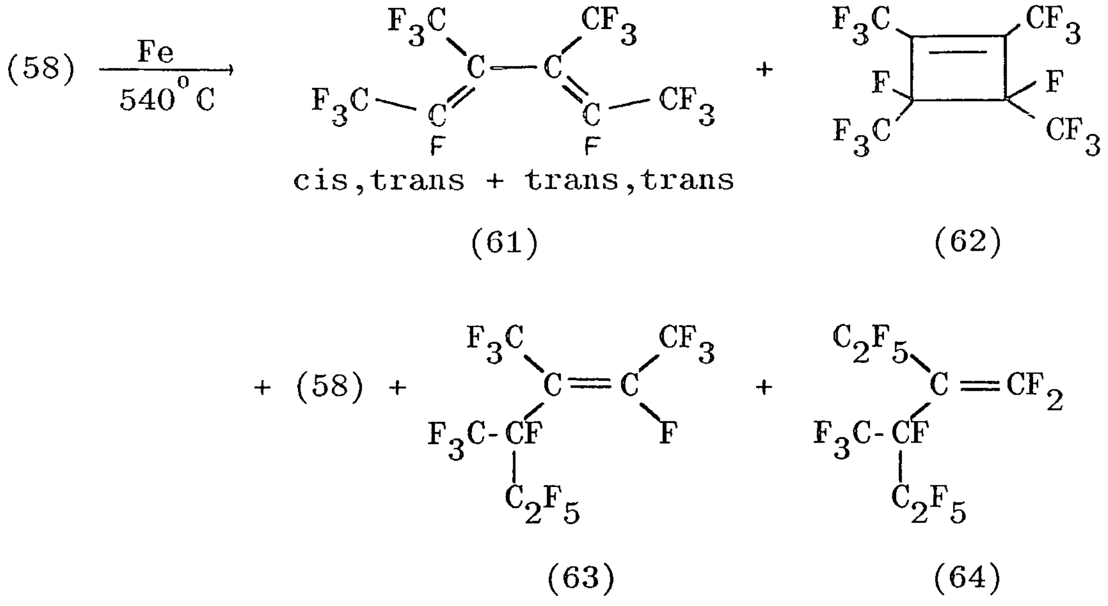
When passed in a stream of nitrogen through a platinum lined tube at 530-700°C, the alkene (58) gave the diene (59) together with lesser amounts of the cyclobutene derivative (60); whilst over hot iron fil ings, diene (61) was formed in addition to the cyclobutene (62) and isomers (63) and (64)[60].



(58)
E and Z isomers

(59)

(60)



cis,trans + trans,trans

(61) (62)

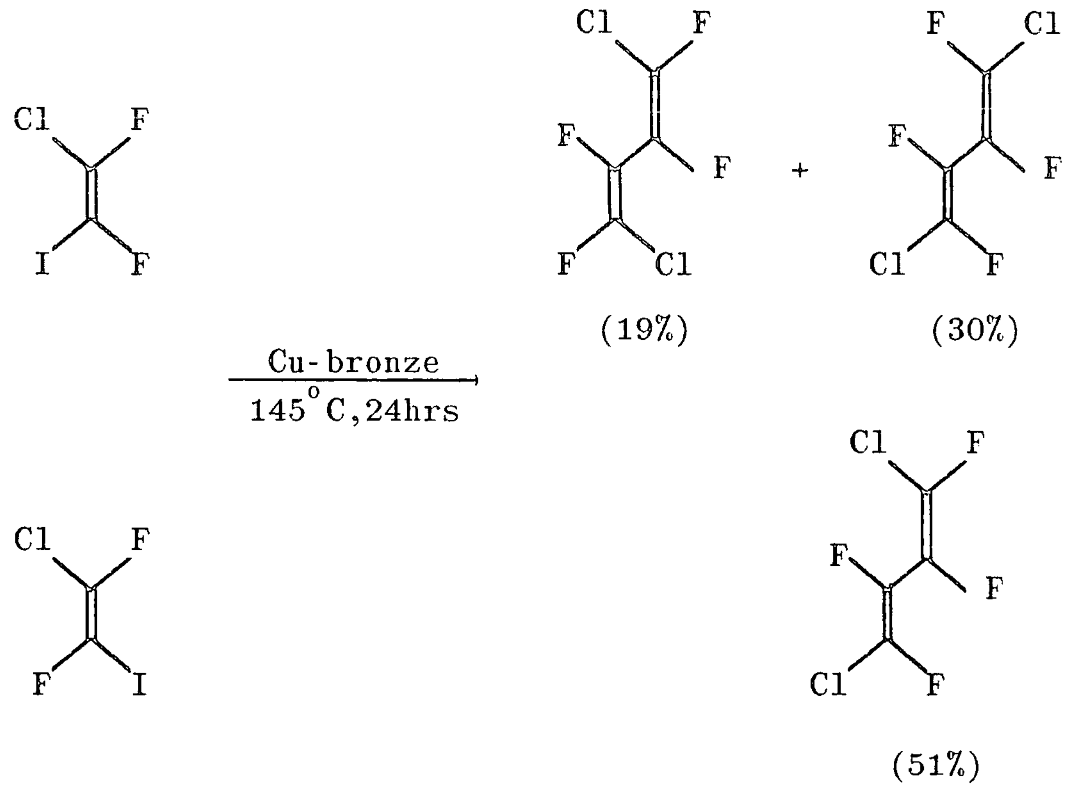
(63) (64)

ratio (58):(63):(64) = 2:2:1

4.1.3: COUPLING REACTIONS:

Intermolecular dehalogenative coupling reactions of polyfluorovinyl-bromides and -iodides in the presence of copper-bronze, allows formation of fluoro-dienes (an analogous reaction to the facile Ullmann reactions of electron deficient aryl bromides and iodides)[61]. When 1-chloro-1,2-difluoroiodoethylene and copper bronze are heated, the three geometrical isomers of 1,4-dichlorotetrafluorobuta-1,3-diene are formed (see scheme 22). Previous syntheses of this diene have involved zinc dust dechlorination of either 1,1,2,3,4,4-hexachlorotetrafluorobutane or 1,3,4,4-tetrachlorotetrafluorobut-1-ene[62].

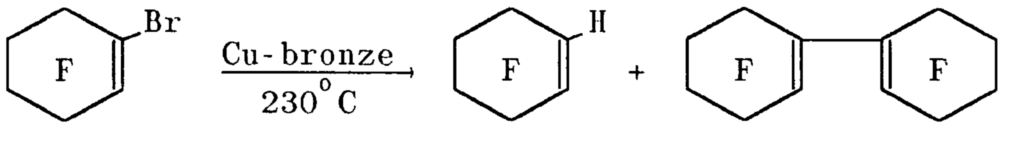
SCHEME 22:



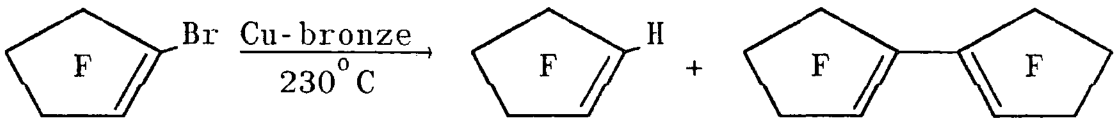
Other synthetically useful copper promoted reductive couplings are detailed in table 8.

TABLE 8:

F-DIENE SYNTHESES VIA METAL PROMOTED REDUCTIVE COUPLINGS:

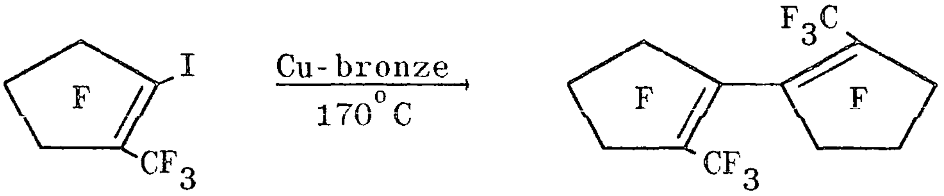


[61]

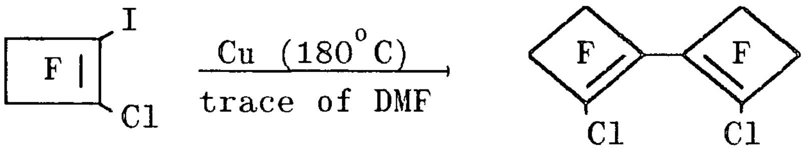


[61]

TABLE 8 CONTINUED:

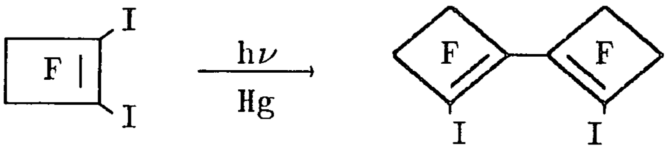


[55]



30-60%

[63]



+ organomercurials

16%

[63]

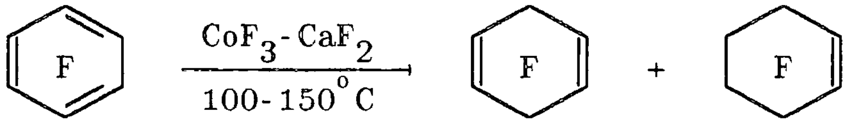
$$(CF_3)_2C{=}CICF_3 \xrightarrow[200^\circ C]{\text{Cu-bronze}} (CF_3)_2C{=}C(CF_3){-}C(CF_3){=}C(CF_3)_2$$

77% [64]

4.1.4: FLUORINATIONS:

Fluorinations of poly unsaturated substrates can be used to prepare certain fluoro-dienes.

Octafluorocyclohexa-1,4-diene, for example, may be synthesized by fluorination of hexafluorobenzene with a mixture of cobalt trifluoride and calcium fluoride[65].

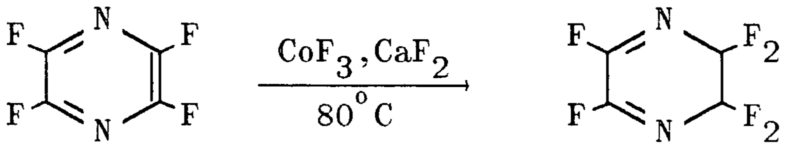


6.7 : 11.4

Other syntheses are detailed in table 9.

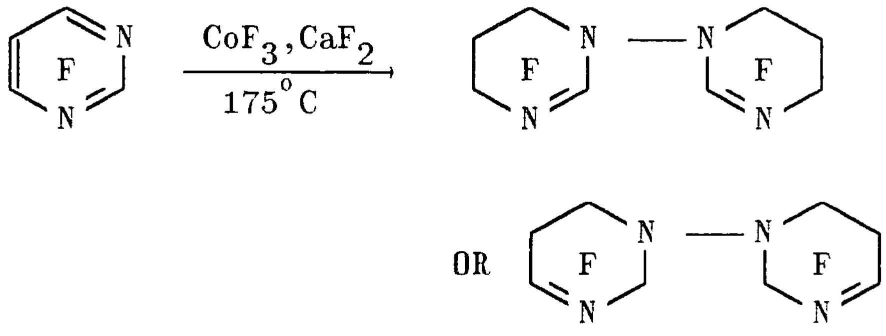
TABLE 9:

F-DIENE SYNTHESES VIA FLUORINATION:



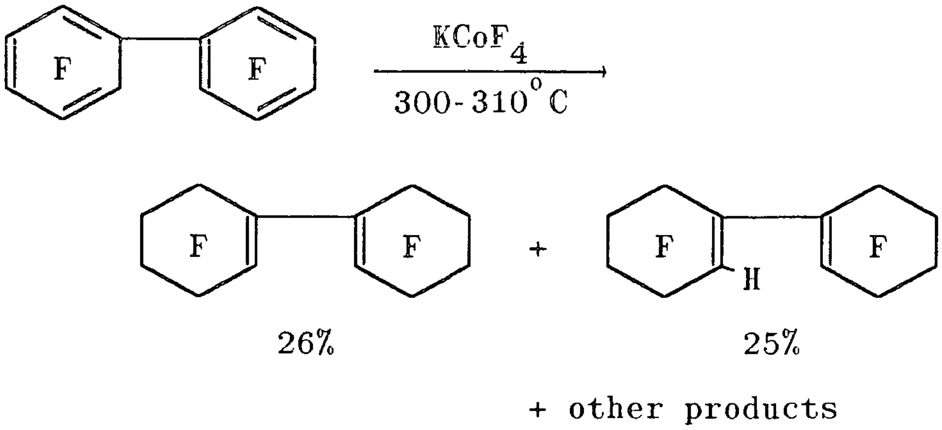
40%

[65]

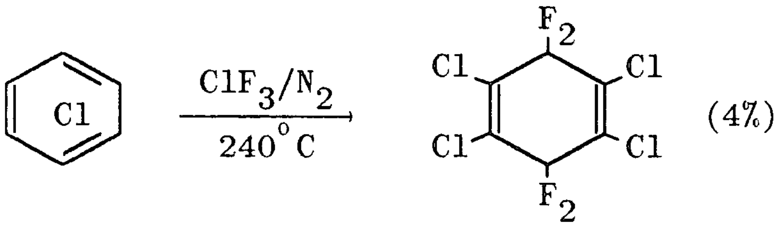


[65]

TABLE 9 CONTINUED:



[66]



[67]

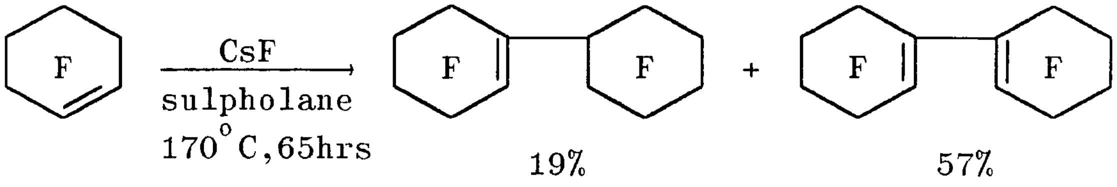
4.1.5: OTHER SYNTHETIC METHODS:

Individual diene syntheses with no general preparative applicability are detailed in table 10.

TABLE 10:

INDIVIDUAL F-DIENE SYNTHESES:-

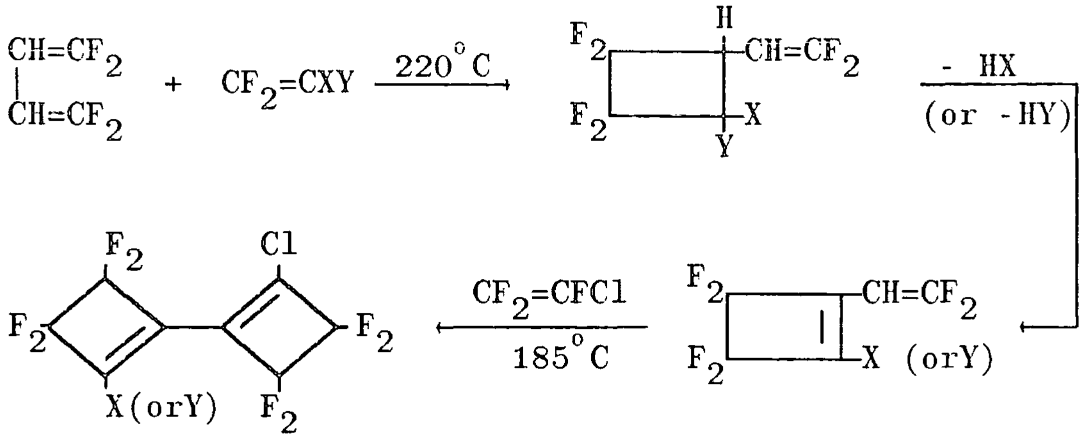
FLUORIDE ION INITIATED DIMERISATION:



[68]

TABLE 10 CONTINUED:

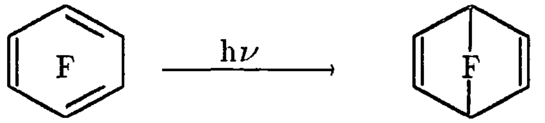
CYCLOADDITION:



[63]

X = Y = Cl
or X = F, Y = Cl

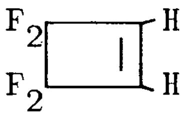
PHOTOISOMERISATION:



ca. 60%

[69]

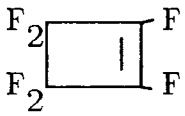
PYROLYSIS OF CYCLOBUTENES:



$\xrightarrow{700^\circ C}$ $CF_2=CH-CH=CF_2$

~ 100%

[70]



$\xrightarrow[Fe]{600-700^\circ C}$ $CF_2=CF-CF=CF_2$

10 - 14%

[71]

$\xrightarrow{550^\circ C}$ $CFCl=C(CO_2CH_3)-CH=CF_2$

80%

[70]

TABLE 10 CONTINUED:

PYROLYSIS OF F-DICARBOXYLIC ACIDS:

$$NaO_2C\text{-}(CF_2)_4\text{-}CO_2Na \xrightarrow{100\text{-}350^\circ C} \underset{30\%}{CF_2{=}CF\text{-}CF{=}CF_2} \qquad [16]$$

4.2: DISCUSSION:

Various attempts have been made in our laboratories to electrochemically reduce polyfluorinated olefins, to allow access to products containing a greater degree of unsaturation than present in the starting material.
Due, however, to the limitations of preparative electrochemistry, (see chapters 1 & 2), this synthetic approach has not yet been generally successful.
Problems involve:
(i) the eliminated fluoride ion interacting with either substrate and/or product;
(ii) movement of the reactive intermediate radical anions and/or anions away from the electrode double layer, thus allowing inter-, rather than intra- molecular reaction; and
(iii) reaction of intermediate species with the solvent/supporting electrolyte.

An alternative chemical method was therefore sought for reduction of polyfluorinated olefins, which would allow fluoride ion elimination from reactive intermediates without the associated problems of electrochemical reduction.

Preliminary studies using apparatus developed at the Electricity Council Research Centre, Capenhurst, showed that reduction of perfluorocyclopentene on potassium amalgam, resulted in formation of a blue-black coloured polymer -similar in appearance to that observed from electrochemical reduction (see chapter 2). Characterization of this polymer proved difficult due to problems of product isolation; the experiment had, however, shown that the potassium amalgam was able to reduce the fluoro-alkene in a manner similar to that observed electrochemically.

This Chapter therefore describes an investigation into the use of sodium amalgam as an electromimetic medium to facilitate reduction of various fluorocarbon substrates.

4.3: SODIUM AMALGAM REDUCTIONS:

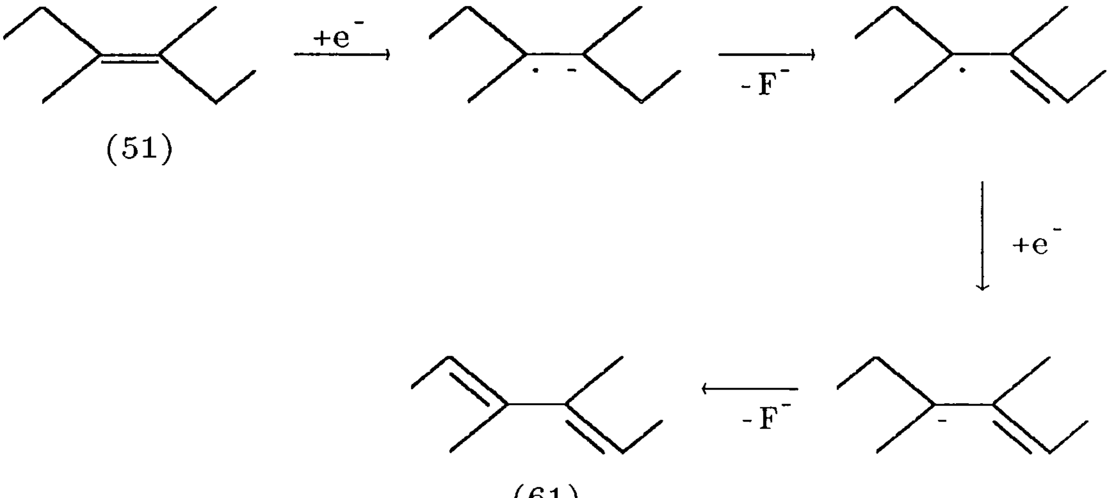
4.3.a: PREPARATION OF FLUORO-DIENES:

4.3.a.1: REDUCTION OF PERFLUORO-3,4-DIMETHYL-HEX-3-ENE (51):

Reduction of (51) with sodium amalgam resulted in a two electron defluorination to give perfluoro-3,4-dimethylhex-2,4-diene (61) in 70% yield, 100% conversion. Only the trans-trans isomer was formed.

The mechanism for this reduction is as outlined in scheme 23, with a one electron addition from the sodium amalgam to the olefinic system, followed by fluoride ion elimination from the -CF_2 group.

SCHEME 23:



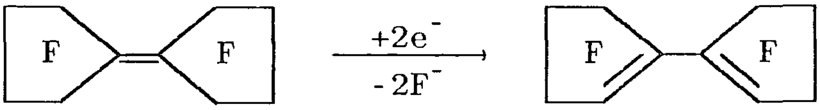
(51)

(61)

The ^{19}F n.m.r. spectrum of (61) is very characteristic -possessing one vinylic fluorine, and two -CF_3 resonances.

4.3.a.2: REDUCTION OF PERFLUOROBICYCLOPENTYLIDENE (43):

Sodium amalgam reduction of (43) gave perfluorobicyclopent-1,1'-enyl (56), as the only product.



(43)

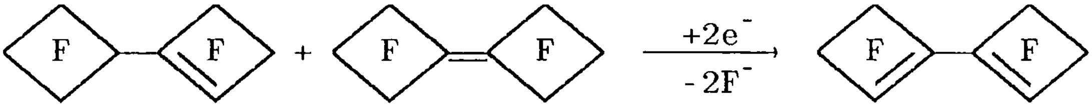
(56)
70% yield
90% conversion

The reaction mechanism is analogous to that detailed for the reduction of (51).

Both the ^{19}F n.m.r. and infra-red spectra of (56) were in agreement with the results reported by E. Marper[58].

4.3.a.3: REDUCTION OF A MIXTURE OF A PERFLUOROBICYCLOBUTYLIDENE (44) AND PERFLUORO-1-CYCLOBUTYLCYCLOBUTENE (45):

Sodium amalgam reduction of the dimers of perfluorocyclobutene (44) and (45) gave, as expected, perfluorobicyclobut-1,1'-enyl (57).

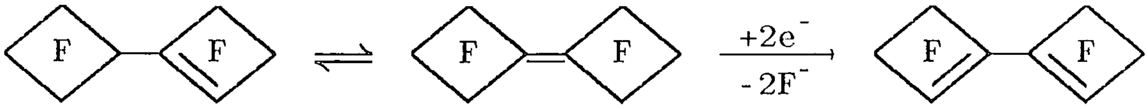


(45) (44) (57)

~ 60% yield
90% conversion

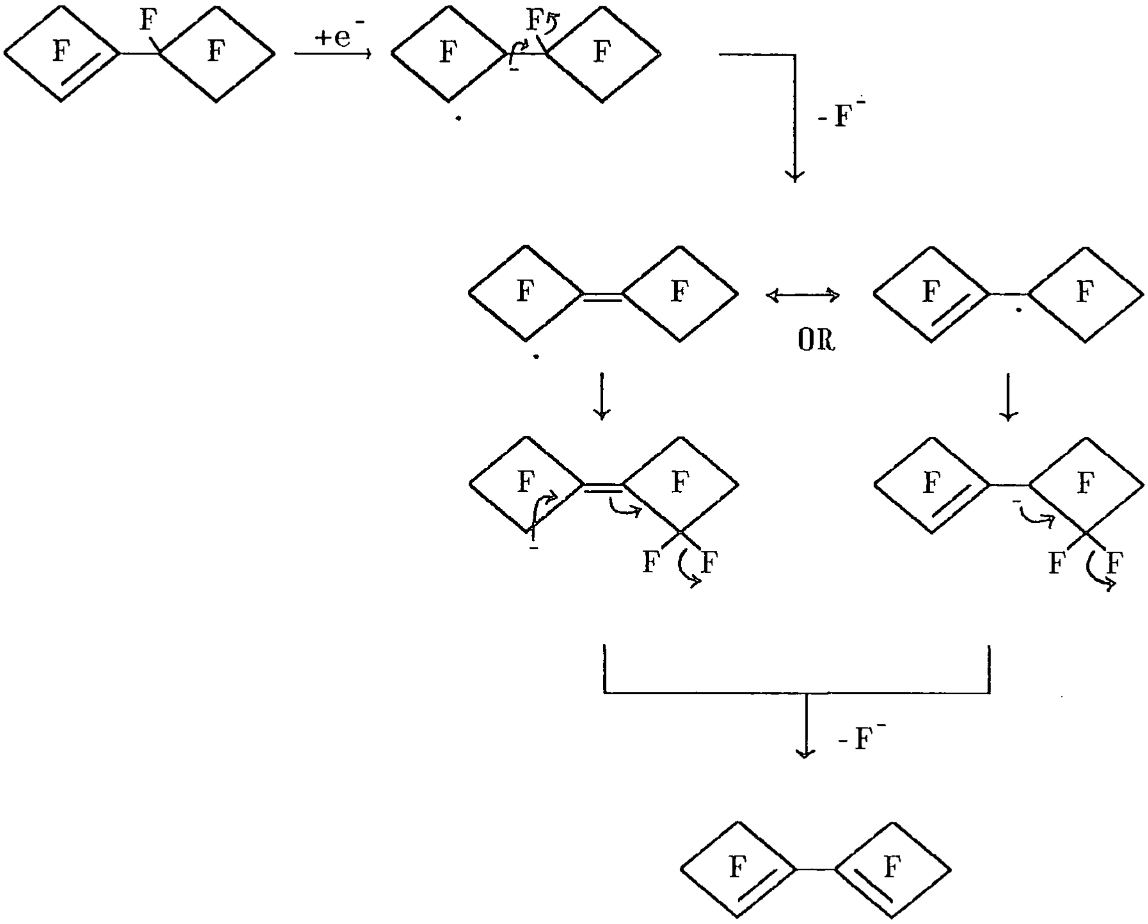
Defluorination of (45) occurs either by released fluoride ion allowing isomerisation of (45) to (44) which then undergoes reduction in a manner analogous to the reduction of perfluorobicyclopentylidene (scheme 24); OR via the mechanism outlined in scheme 25.

SCHEME 24:



(45) (44)

SCHEME 25:



4.3.b: PREPARATION OF TERMINAL FLUORO-MONO-ENES:

4.3.b.1: REDUCTION OF 1,4-DIBROMO-2,3-DICHLOROHEXAFLUOROBUTANE (65):

Reduction of (65) using an exact 2:1 molar ratio of sodium:organic substrate resulted in the formation of two volatile products (66) and (67).

$$\underset{(65)}{BrCF_2\text{-}CFCl\text{-}CFCl\text{-}CF_2Br} \xrightarrow[Na/Hg]{+2e^-} \underset{(66)}{BrCF_2\text{-}CFCl\text{-}CF{=}CF_2} \ (17.6\%)$$

$$+ \underset{(67)}{BrCF_2\text{-}CFCl\text{-}CF{=}CFCl} \ (8.9\%)$$

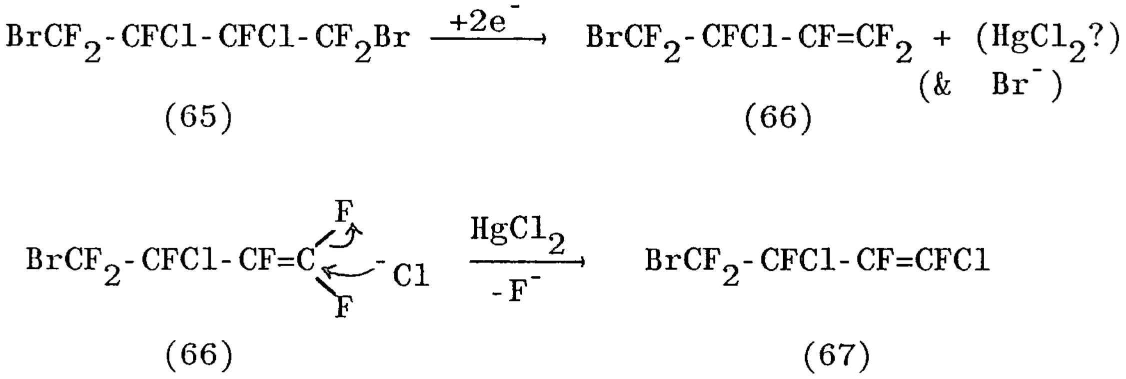
cis & trans isomers

The major product ie.(66) was formed from the expected two electron debromo-chlorination to form the terminal difluoromethylene group, the presence of which was clearly evident by ^{19}F n.m.r.. Mass spectrometry gave a parent molecular ion, isotope ratio, and breakdown pattern consistent with structure (66).

Formation of product (67), however, was a little surprising! Mass spectrometry gave a parent molecular ion, isotope ratio, and breakdown pattern consistent with a $C_4F_5BrCl_2$ molecular formula; whilst ^{19}F n.m.r. showed the presence of two isomers, both of which contained four fluorine resonances in the ratio 2:1:1:1. ^{13}C n.m.r. confirmed the presence of only one $-CF_2$ group, in addition to three -CF- environments. Structure (67) is the only reasonable interpretation of this data.

How (67) is formed, however, is not clear. One explanation may be that (66) is formed first, releasing Cl^- which combines with the mercury to form mercuric chloride. Mercuric chloride is a potential Lewis acid and may therefore attack the terminal difluoromethylene group of (66), exchanging fluoride for chloride ion to form (67) (see scheme 26).

SCHEME 26:



$$BrCF_2\text{-}CFCl\text{-}CFCl\text{-}CF_2Br \xrightarrow{+2e^-} BrCF_2\text{-}CFCl\text{-}CF{=}CF_2 + (HgCl_2?)\ (\&\ Br^-)$$

(65) (66)

$$BrCF_2\text{-}CFCl\text{-}CF{=}CF_2 \xrightarrow[-F^-]{HgCl_2} BrCF_2\text{-}CFCl\text{-}CF{=}CFCl$$

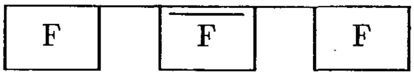
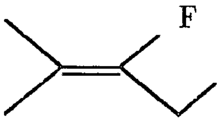
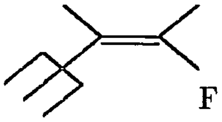
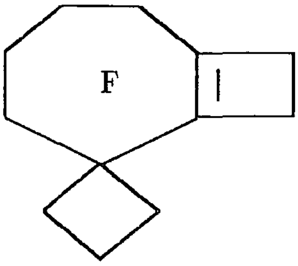
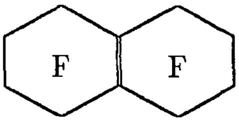
(66) (67)

4.3.c: OTHER ATTEMPTED REDUCTIONS:

Reduction of the substrates detailed in table 11 were attempted using the sodium amalgam reduction system. In each case only the starting fluoro-substrate was identified in the volatile fraction after reaction.

TABLE 11:

ATTEMPTED SODIUM AMALGAM REDUCTIONS:

SUBSTRATE	% AGE RECOVERY OF STARTING MATERIAL
	77%
	60%
	92%
	66%
$C_5F_{11}CF_2I$	88%
	71%

The reduction of perfluoro-2-methylpent-2-ene was attempted in both acetonitrile and THF, but neither solvent had any effect on the course of the reduction.

This is obviously not a definitive study, and further work is clearly necessary to investigate the possible use of solvents, which may (i) affect the course of the reduction; and/or (ii) allow access to less volatile products, which may be formed in the attempted reductions detailed in table 11, but which would not be identified due to the nature of the reaction work-up employed.

4.4: CONCLUSIONS:

Sodium amalgam has been shown to be a useful reagent for the preparation of volatile cyclic and acyclic F-dienes from F-alkenes, in good yield and conversion.

The use of amalgams also allows careful control of the number of available electrons per mole of substrate; allowing reduction of 1,4-dibromo-2,3-dichlorohexafluorobutane (65) to the terminal alkenes (66) and (67), and preventing complete reduction to F-butadiene.

CHAPTER 5:

NUCLEOPHILIC REACTIONS OF FLUORINATED DIENES:

5.1: INTRODUCTION:

Nucleophilic processes in fluoro-olefin chemistry have been extensively studied, and numerous books and review articles are available[73]; however the majority of publications deal with nucleophilic reactions of fluoro "mono-enes". The purpose of this section is to provide some simple illustrative examples of nucleophilic reactions of fluoro-dienes, both cyclic and acyclic, thereby providing an introduction to an area of chemistry which will be further developed later in the chapter.

5.1.A: CYCLIC FLUORO-DIENES:

The most studied cyclic fluoro-diene systems are octafluoro- and hexafluoro- cyclohexadienes (see scheme 27); due mainly to their accessibility.

5.1.A.1: POSITION OF ATTACK:

Consideration of the intermediate carbanion formed from initial nucleophilic attack often explains product distribution. Substitution reactions of octafluorocyclohexa-1,3-diene (68) with methoxide[74], show an orientation effect favouring formation of the 2-substituted product over the 1-substituted (scheme 27).

This stems from the almost cisoid conformation of the 1,3-diene. Attack at C-1 of the 1,3-diene results in the formation of a planar delocalised anionic intermediate, which is <u>destabilised</u> by the fluorine substituents; hence the "1-substituted" product (69) (see scheme 27) is formed in low yield.

α-Fluorine substituents, however, <u>stabilise</u> the non-conjugated (pyramidal) anion (70)[75] resulting from attack at C-2. Further enhancement of stabilisation of this intermediate carbanion is effected by the adjacent electron withdrawing -CF_2 group; consequently (71) is the major product of reaction -resulting from fluoride ion elimination from the weaker tertiary fluorine at C-2 of the intermediate (70).

5.1.A.2: ADDITION vs. SUBSTITUTION:

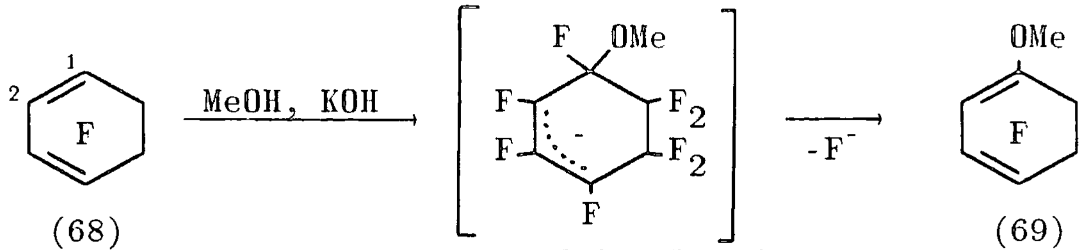
Interestingly perfluorocyclohexa-1,4-diene (72) forms an addition product (74) as well as the expected substitution product (75), while the 1,3-diene (68) forms only substitution products.

This implies that reactions of (72) are more stepwise than those of (68), ie. more charge is developed in the intermediate anion (73) than in anion (70), before C-F bond breaking occurs.

SCHEME 27:

NUCLEOPHILIC ATTACK OF METHANOL ON OCTAFLUOROCYCLOHEXADIENE

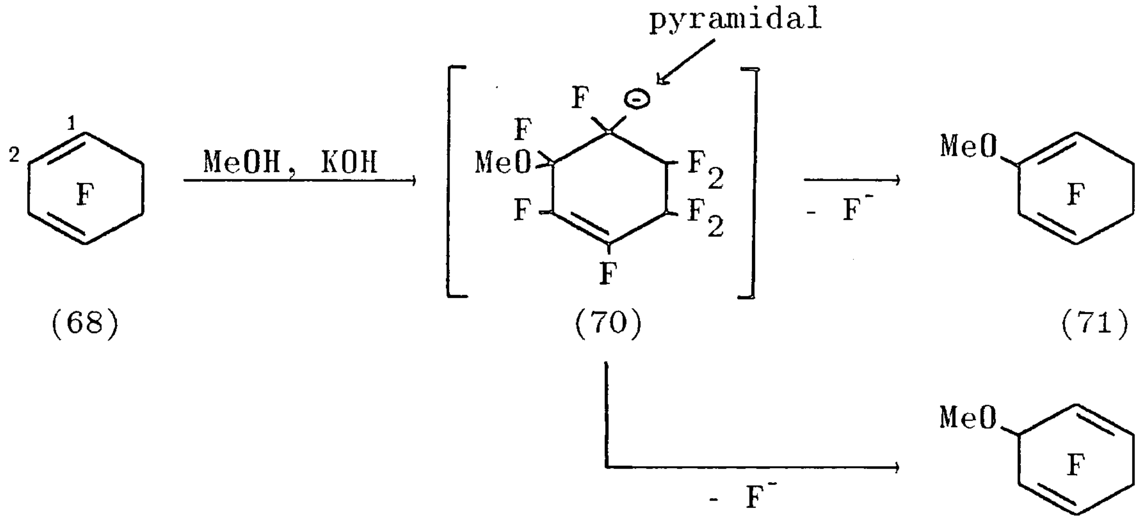
ATTACK AT C-1:



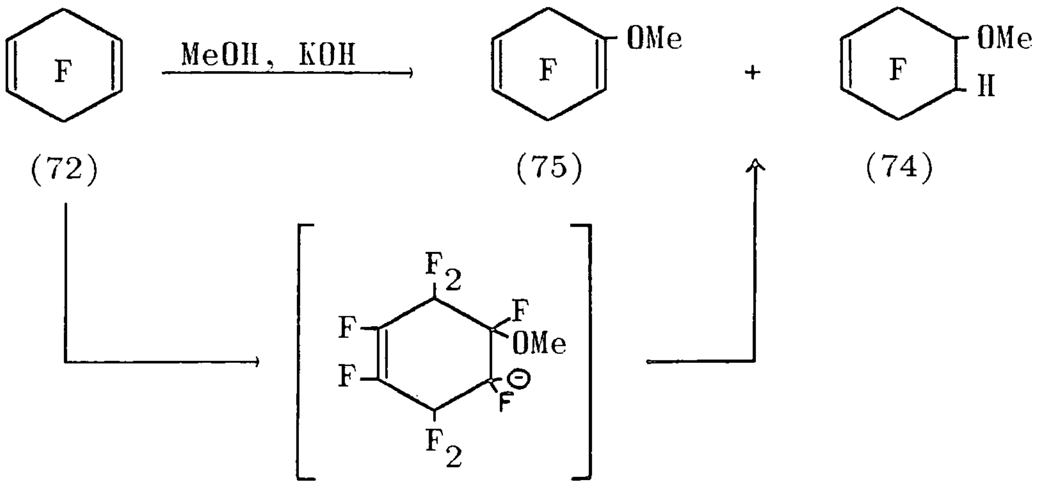
(68) (69)

planar delocalised
anion intermediate

ATTACK AT C-2



(68) (70) (71)



(72) (75) (74)

(73)

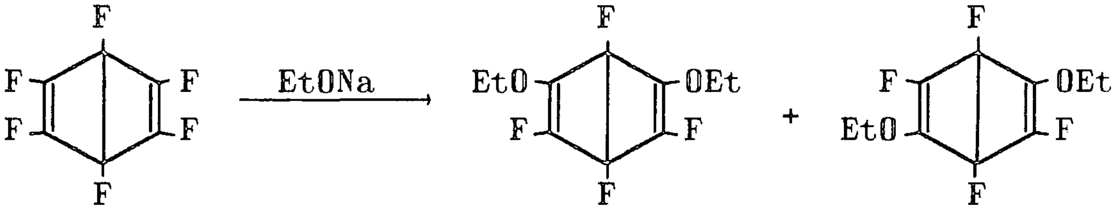
5.1.A.3: MONO vs. DI SUBSTITUTION (ACTIVITY OF NUCLEOPHILE)

Controlled reaction of hexafluorobicyclo-[2,2,0]-hexa-2,5-diene (the para bonded valence bond isomer of hexafluorobenzene, formed by photochemical isomerization of hexafluorobenzene)[76-78] with the moderately active nucleophiles sodium methoxide, sodium ethoxide, methyl lithium and diethylamine produces the corresponding 2-substituted derivative, with further reaction forming the 2,5- and 2,6- disubstituted products. With the very active potassium benzenethiolate, however, only the 2,5-disubstituted derivative is formed[79,80] (see table 12).

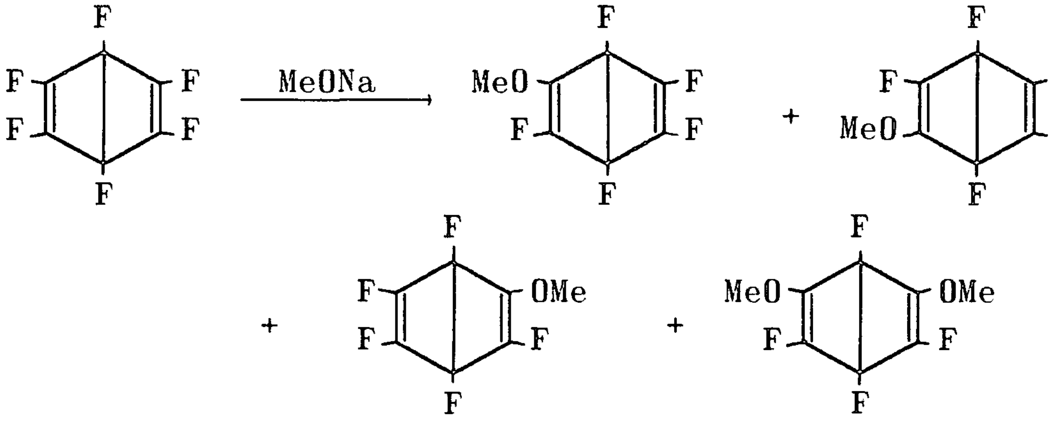
TABLE 12:

REACTIONS OF NUCLEOPHILES WITH CYCLIC FLUORO-DIENES:

OXYGEN NUCLEOPHILES:

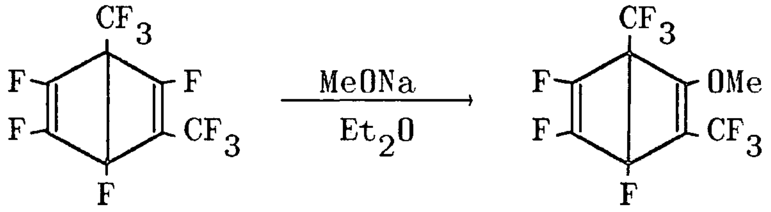


[74] [81]



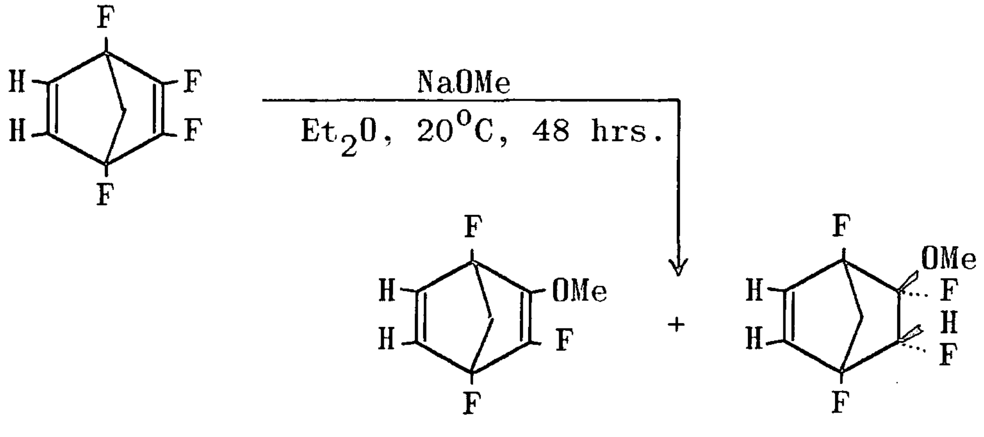
[12]

[15]



40%

[82]

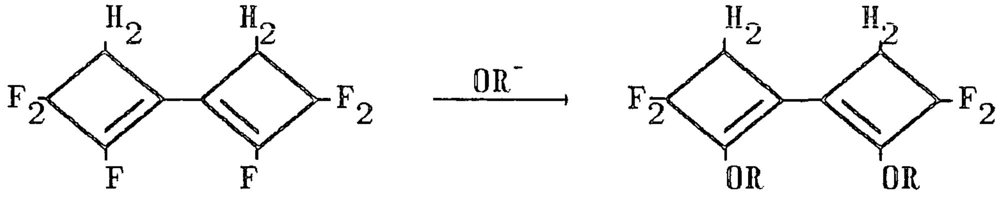


70%

23%

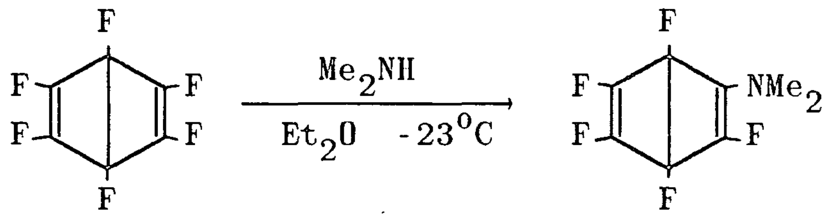
[83]

TABLE 12 CONTINUED:



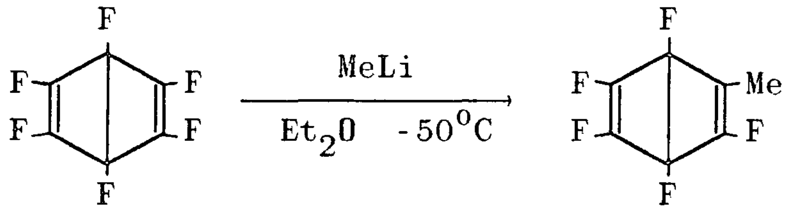
[84]

NITROGEN NUCLEOPHILES

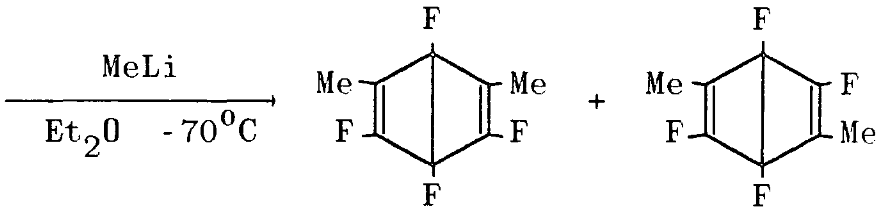


[79]

CARBON NUCLEOPHILES



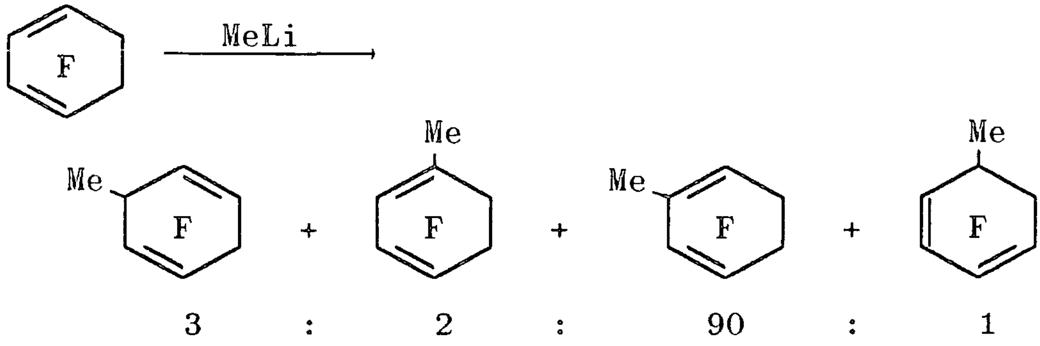
[79]



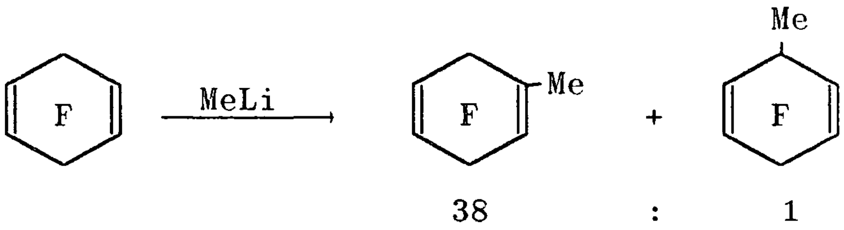
1 : 2

[80]

TABLE 12 CONTINUED:

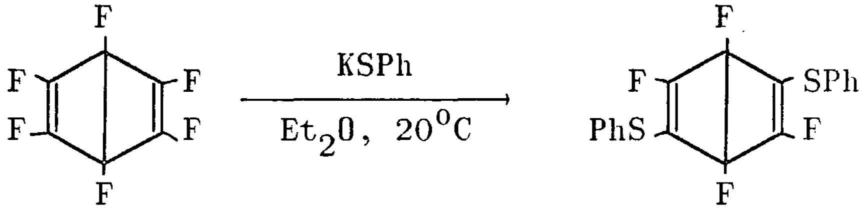


[74]

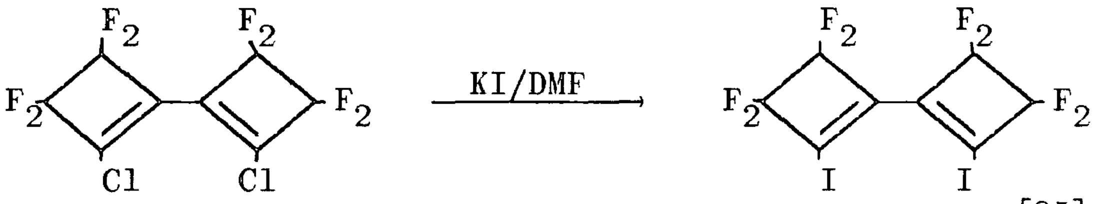


[74]

OTHER NUCLEOPHILES



[79]



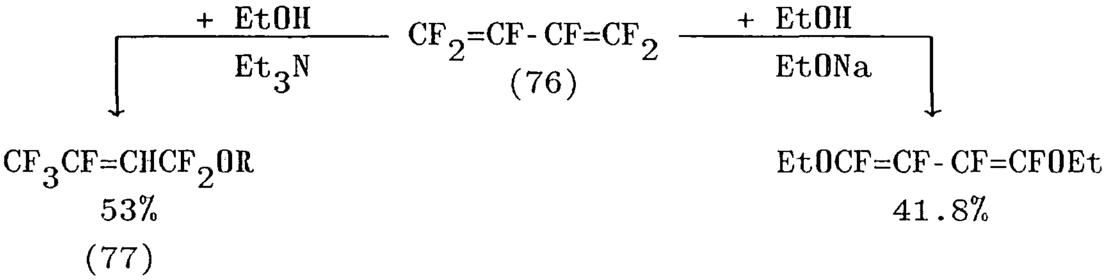
[85]

5.1.B: ACYCLIC FLUORO-DIENES:

The majority of work reported in the literature on the chemistry of aliphatic fluoro-dienes, is confined to the easily accessible perfluorobutadiene (see table 13). In this sub-section some of the factors which affect the nucleophilic reactions of aliphatic fluoro-dienes will be discussed, with examples from the literature on the chemistry of perfluorobutadiene and perfluoro-2,3-dimethylbuta-1,3-diene.

5.1.B.1: EFFECT OF BASE ON REACTION ROUTE:

The effect of base on the direction of a nucleophilic reaction is demonstrated in the different results obtained when perfluorobuta-1,3-diene (76) is treated with ethanol using sodium ethoxide or triethylamine as base.



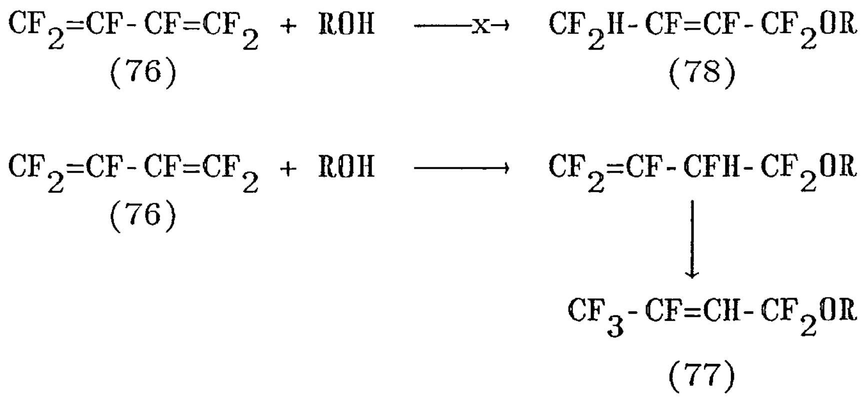
$$CF_3CF{=}CHCF_2OR \xleftarrow[Et_3N]{+\ EtOH} CF_2{=}CF\text{-}CF{=}CF_2 \xrightarrow[EtONa]{+\ EtOH} EtOCF{=}CF\text{-}CF{=}CFOEt$$

(76)

53% (77)

41.8%

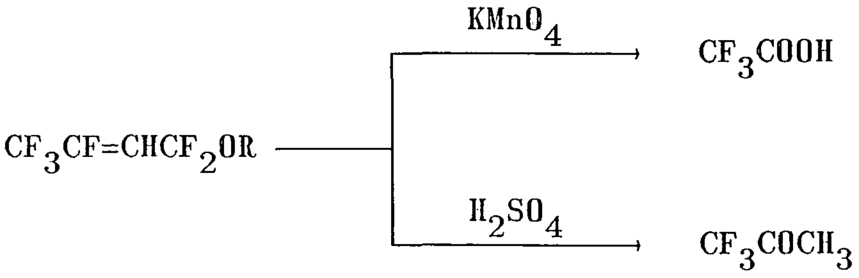
In the former case pure substitution takes place, whereas the triethylamine base catalysed reaction of methanol and ethanol to hexafluorobuta-1,3-diene proceeds via an initial 1,2-addition, followed by an allyl anionotropic regrouping to form alkene (77)[86], and not via a 1,4-addition as previously reported[87].



$$\underset{(76)}{CF_2{=}CF{-}CF{=}CF_2} + ROH \xrightarrow{x} \underset{(78)}{CF_2H{-}CF{=}CF{-}CF_2OR}$$

$$\underset{(76)}{CF_2{=}CF{-}CF{=}CF_2} + ROH \longrightarrow CF_2{=}CF{-}CFH{-}CF_2OR \longrightarrow \underset{(77)}{CF_3{-}CF{=}CH{-}CF_2OR}$$

Oxidation of the reaction product with potassium permanganate did not give difluoroacetic acid, as one would expect from (78), but instead gave trifluoroacetic acid; and hydrolysis with 80% sulphuric acid gave trifluoroacetone - consistent with reaction on alkene (77).



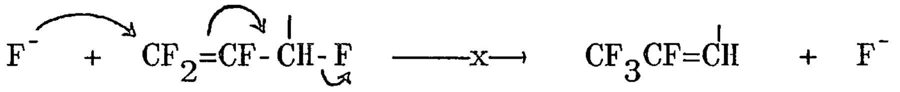
$$CF_3CF{=}CHCF_2OR \xrightarrow{KMnO_4} CF_3COOH$$

$$CF_3CF{=}CHCF_2OR \xrightarrow{H_2SO_4} CF_3COCH_3$$

Thus triethylamine not only catalyzes the addition of alcohol to perfluorobutadiene, but also initiates isomerization of the initial product of reaction. Further experiments showed that in the presence of triethylamine, the dialkylamides of α-hydroperfluoro-vinylacetic acid (79) (formed by the hydrolysis of 1-dialkyl-aminoperfluorobutadienes) isomerized to the dialkylamides of α-hydroperfluorocrotonic acid (80).

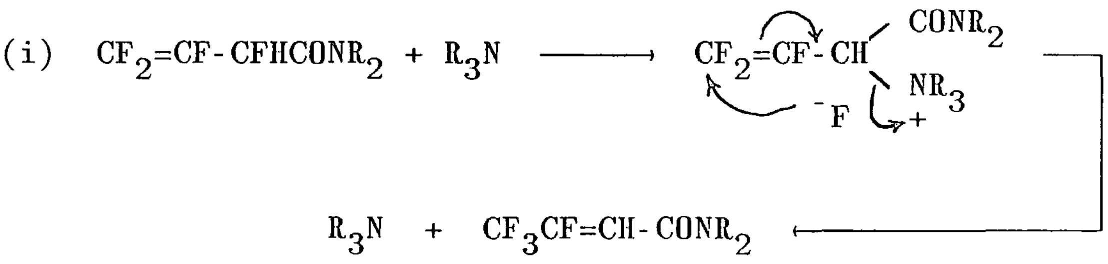
$$\underset{(79)}{CF_2{=}CF\text{-}CFH\text{-}CONR_2} \xrightarrow{Et_3N} \underset{(80)}{CF_3CF{=}CHCONR_2}$$

- an isomerization which could NOT be achieved with anhydrous hydrogen fluoride, or triethylamine hydrofluoride; and which is, consequently, not the usual anionotropic rearrangement under the reaction of fluoride ion.

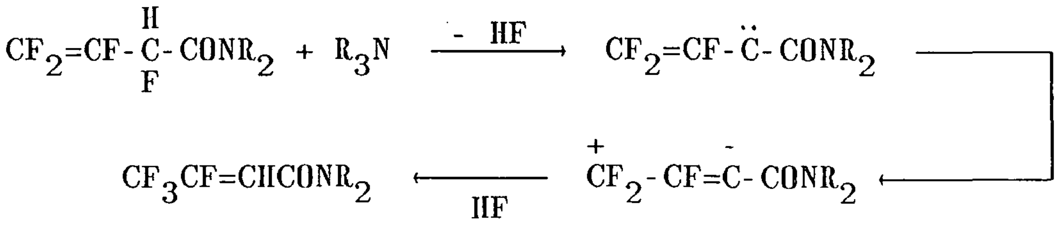


Clearly, the basic character of triethylamine plays an essential role.

Possible mechanisms of rearrangement could therefore be:

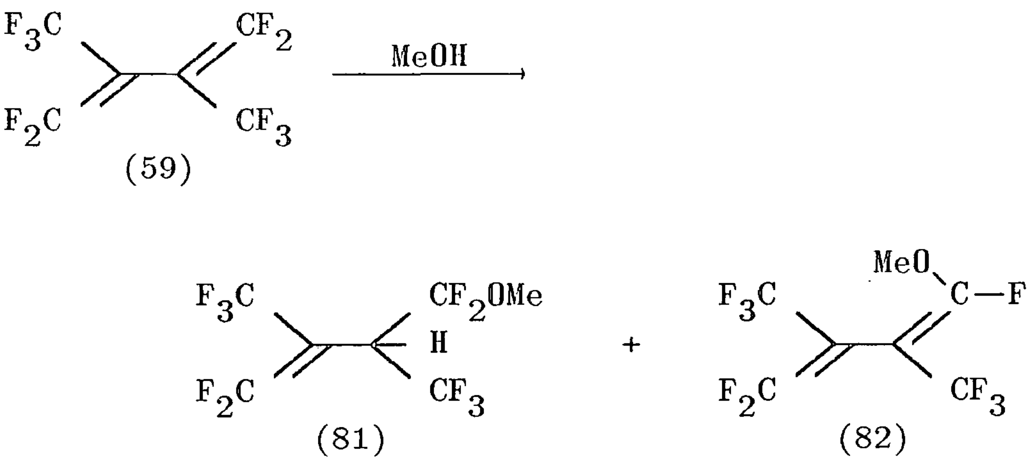


OR (ii)



5.1.B.2: RELATIVE REACTIVITY:

Perfluoro-2,3-dimethylbuta-1,3-diene (59) reacts with an excess of neutral methanol to give a 1,2 addition product (81) and a substitution product (82)[88].

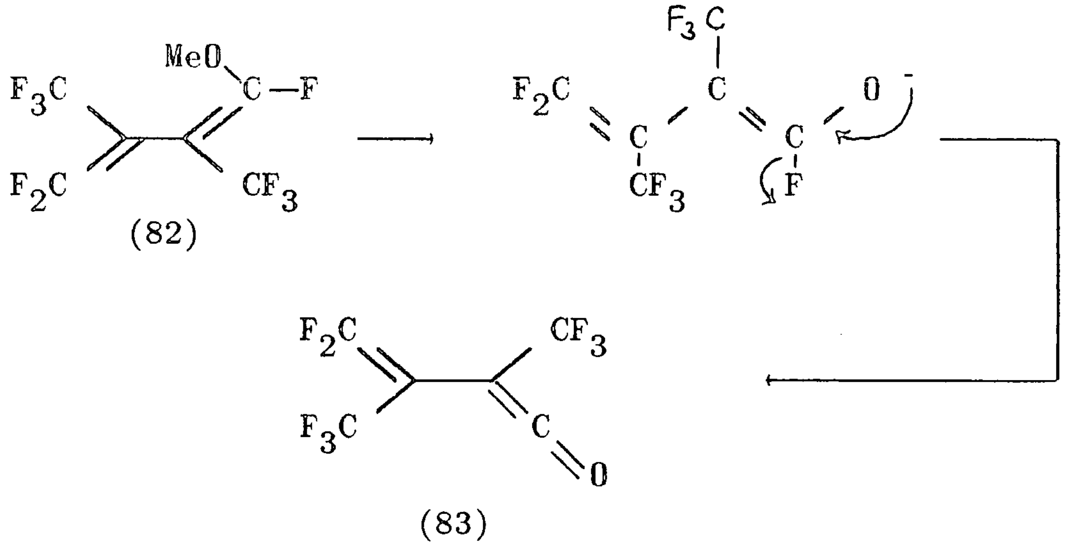


Reaction of the diene (59) with sodium methoxide, however, afforded a complex mixture of products from which only the di-substituted product (30%) could be isolated as a mixture of isomers.

The reaction of diene (59) with neutral methanol places it as a fairly reactive olefinic system in common more with $(CF_3)_2C = CF_2$ than $CF_3CF = CF_2$; however, once one of the double bonds in diene (59) has reacted, far stronger nucleophilic conditions are required to bring about reaction with the second double bond ie. the reactivity of the system is lowered.

Treatment of the substitution product (82) with iodotrimethylsilane under conditions known to cleave ethers[89], led to formation of the ketene (83) via a novel

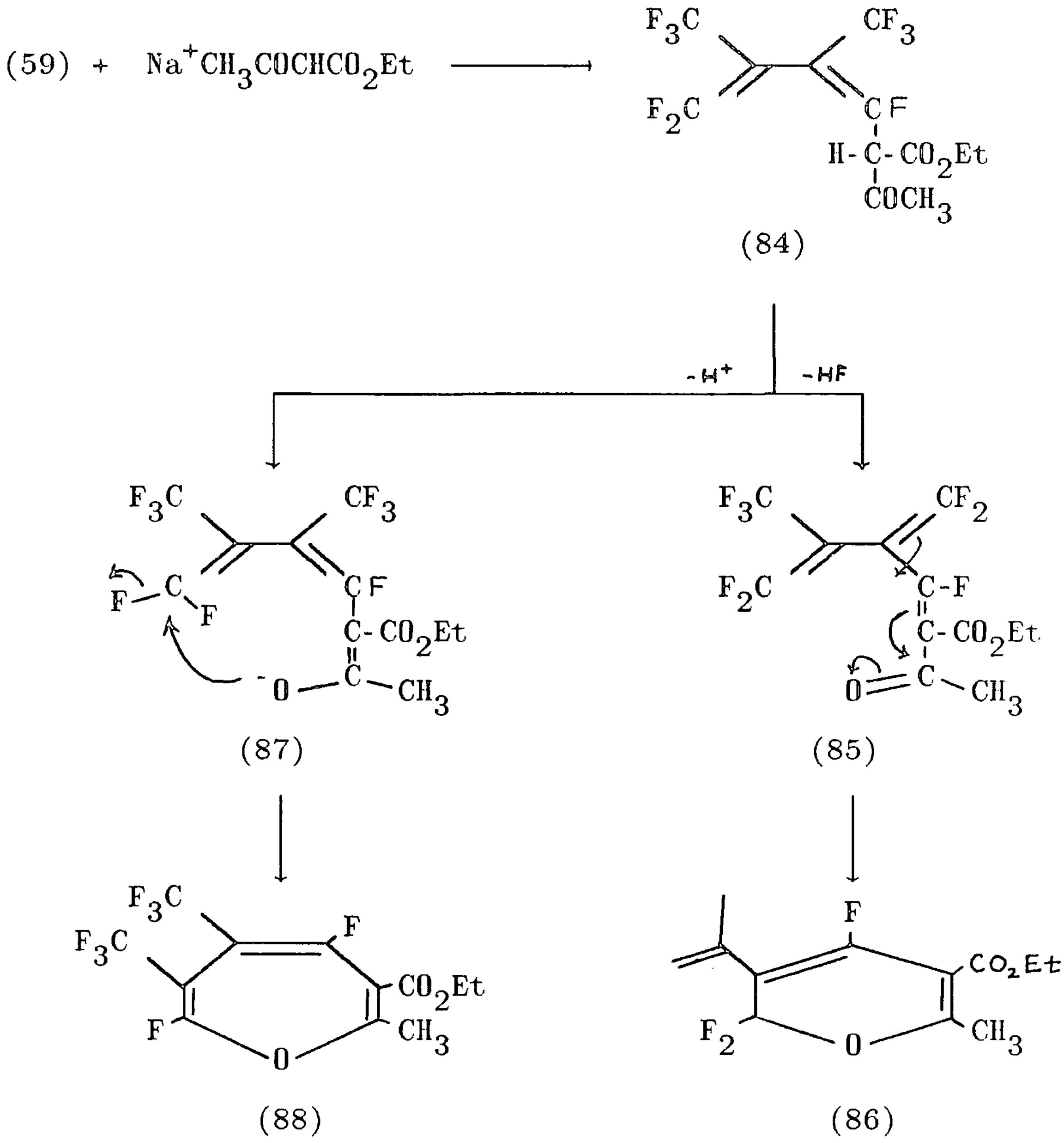
SCHEME 28:



elimination of fluoride ion from a position *α* to the incipient oxyanion (see scheme 28).

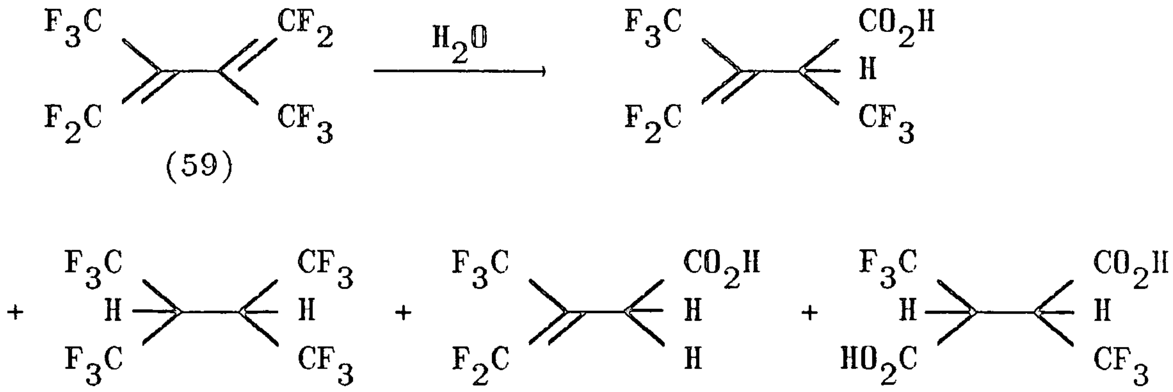
Reaction of diene (59) with the anion derived from ethyl acetoacetate yielded two isomeric products. The major product (30%) (86) was a pyran derivative arising from an electrocyclic ring closure of the intermediate ester ketone (85). Formation of the minor oxepine product (2%) (88) can be explained by loss of a proton from the initial substitution intermediate (84) followed by cyclisation through the resultant oxyanion (87) - see scheme 29.

SCHEME 29:



5.1.B.3: CONJUGATION OF DOUBLE BONDS:

Examination of the Dewar model of diene (59)[90,91] reveals that the angle between the planes of the double bonds is close to 90°, while rotation around the C - C central bond is hindered by the two CF_3 groups. Although this does not exclude the possibility of a partial conjugation of the double bonds, Russian workers have considered diene (59) to be non-conjugated in the light of the reaction of (59) with water to give a mixture of acids, in which the expected 1,4-addition products could NOT be detected[92].



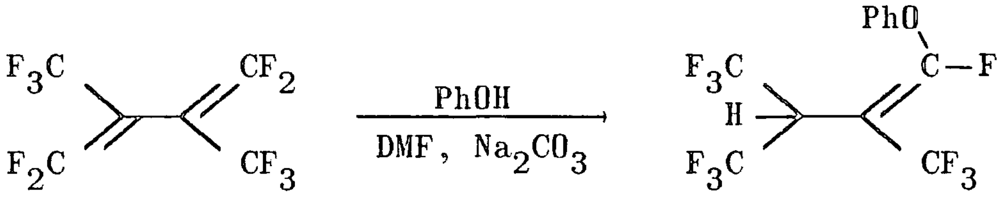
(59)

However, preferred reaction at only one of the double bonds of perfluoro-2,3-dimethylbuta-1,3-diene due to a decreased reactivity of the monosubstituted product over the parent diene; and u.v. data (λ_{max} = 242 nm)[88], contradicts their assumptions and suggests that the double bonds of the diene are indeed conjugated.

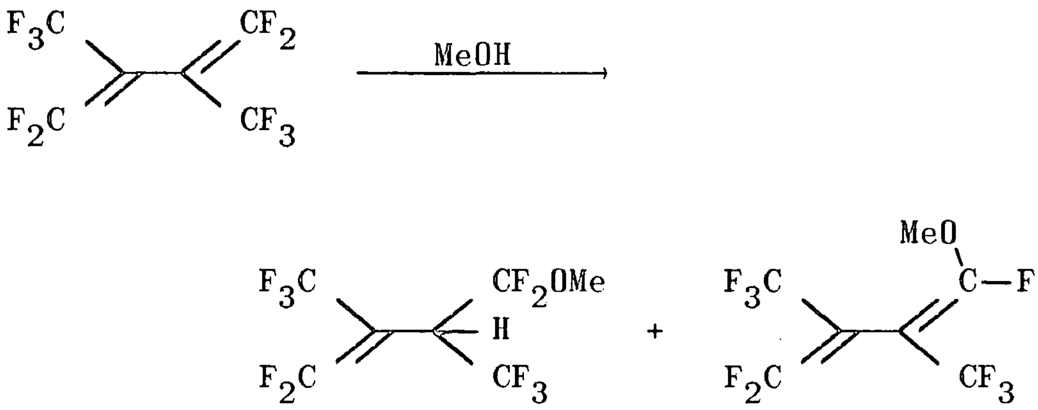
TABLE 13:

REACTIONS OF NUCLEOPHILES WITH ALIPHATIC FLUORO-DIENES

OXYGEN NUCLEOPHILES



[88]

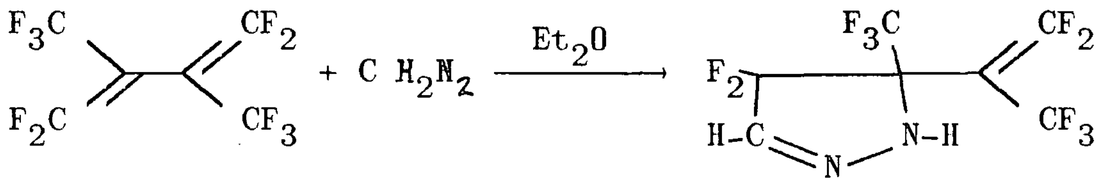


[88]

NITROGEN NUCLEOPHILES

$$CF_2{=}CF\text{-}CF{=}CF_2 + NH(Et)_2 \xrightarrow{Et_2O} CF_2{=}CF\text{-}CF\text{-}CFN(C_2H_5)_2$$

[87]



[88]

5.2: DISCUSSION:

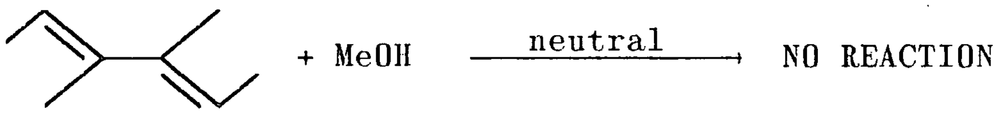
Most of the work described in this chapter centres around investigating the chemistry of perfluoro-3,4-dimethylhex-2,4-diene (61) with various mono- and bi- functional nucleophiles, although some preliminary studies on the nucleophilic reactions of perfluorobicyclo -pent-1,1'-enyl (56), and -but-1,1'-enyl (57) will be discussed.

5.2.A: OXYGEN NUCLEOPHILES:

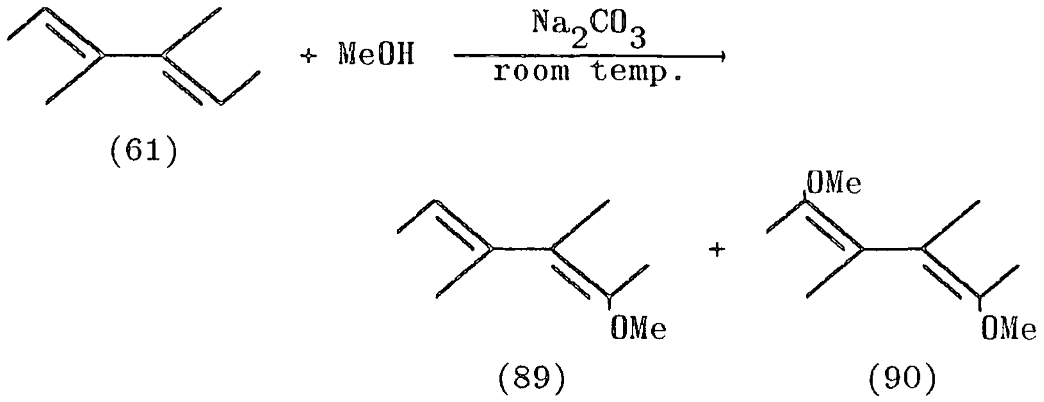
5.2.A.1: REACTIONS WITH ALCOHOLS:

5.2.A.1a: DIENE (61) WITH METHANOL:

No reaction occured when perfluoro-3,4-dimethylhex-2,4-diene (61) was added to an excess of neutral methanol. After making the reaction mixture basic with sodium carbonate, however, a mixture of the mono- (89) and di- derivatives (90), were isolated.



(61)

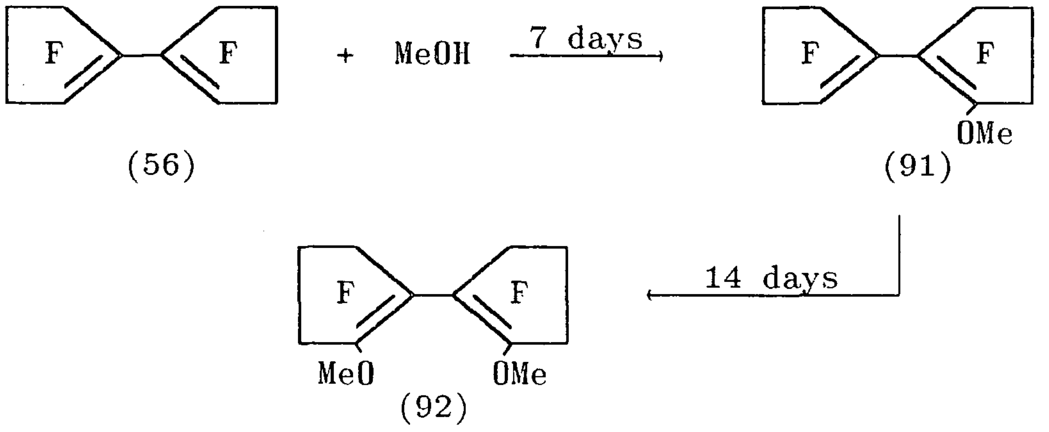


(61)

(89) (90)

5.2.A.1b: DIENE (56) WITH METHANOL:

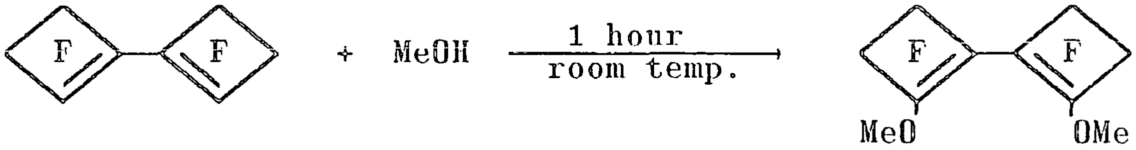
Reaction of perfluorobicyclopent-1,1'-enyl (56) with an excess of neutral methanol proceeded slowly to give, after seven days, almost exclusively the monomethoxy derivative (91). Further reaction allowed compound (91) to be converted to the dimethoxy derivative (92).



(56) (91) (92)

5.2.A.1c: DIENE (57) WITH NEUTRAL METHANOL:

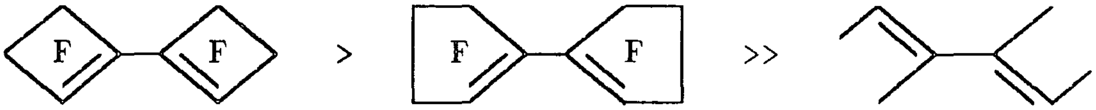
The addition of perfluorobicyclobut-1,1'-enyl (57) to an excess of neutral methanol resulted in a very rapid exothermic reaction to give, after approximately one hour, the crystalline dimethoxy derivative (93).



(57) (93)

4.2.A.1d: CONCLUSIONS:

By considering the reaction times and conditions of reaction of the three dienes with neutral methanol, it is clear that the relative reactivities are as outlined below; with both perfluorobicyclo-pent-1,1'-enyl, and -but-1,1'-enyl reacting with neutral methanol, and perluoro-3,4-dimethyl -hex-2,4-diene reacting with methanol, only in basic media.



(57) (56) (61)

It is interesting to note, that only perfluoroisobutene of the aliphatic fluoro mono-enes will react with neutral methanol.

These differences in reactivity may be explained in a number of ways:

(i) RING STRAIN:

Increased reactivity of perfluorobicyclobutylidene over its five membered analogue perfluorobicyclopentylidene, has been rationalised on the basis of increased ring strain aiding nucleophilic attack[93]. A similar approach may therefore be used to explain the reactivities of the dienes (57), (56), and (61)

Nucleophilic reaction of (57) clearly releases greater ring strain than in diene (56); whilst no such effect is relevant when considering the reactivity of the acyclic diene (61).

(ii) STERIC HIND RANCE TO ATTACK:

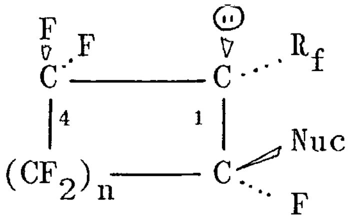
The double bonds of the diene (61) are surrounded by sterically bulky $-CF_3$ groups, which present a greater "barrier" to nucleophilic attack than the $-CF_2$ groups of the essentially planar ring systems of dienes (57) and (56).

(iii) STABILITY OF THE INTERMEDIATE CARBANION:

Although all three dienes are "electronically" very similar, the geometries of the intermediate carbanions (formed after initial nucleophilic attack), are very different.

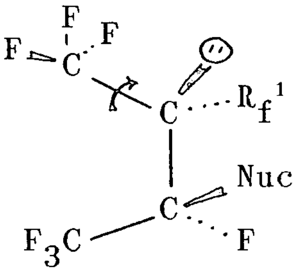
The intermediate carbanions of the cyclic dienes (56) and (57) may be represented as in Fig 11, in which the

FIG.11: DIAGRAMATIC REPRESENTATION OF THE INTERMEDIATE CARBANION FORMED FROM (56) OR (57)



negative charge on C-1 is in an sp^2 orbital which is in line with an F of the $-CF_2$ on C-4, in a fixed orientation.
It has been suggested that this <u>fixed</u> arrangement (due to the cyclic nature of the molecule), offers a greater degree of stabilisation to the intermediate carbanion, than when the adjacent R_f group on C-4 is a freely rotating $-CF_3$ group, as in diene (61) - Fig 12..

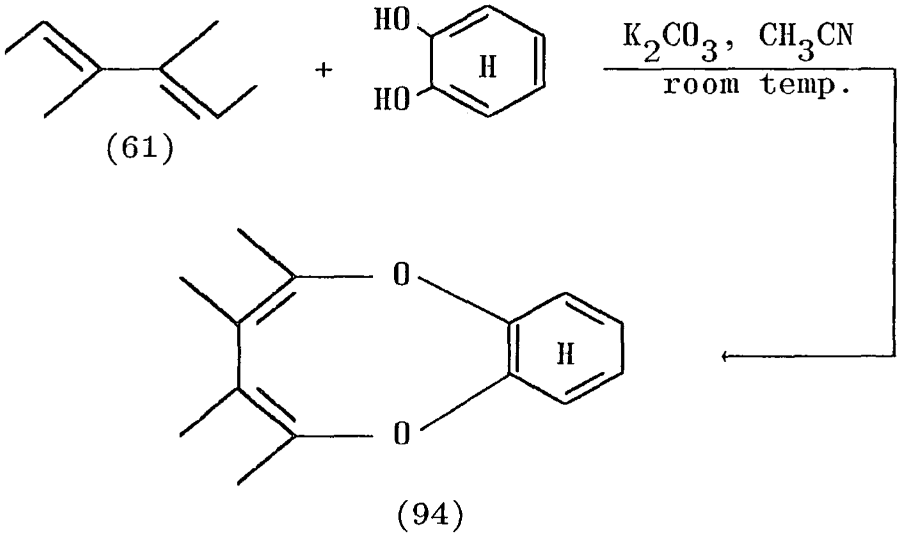
FIG.12: DIAGRAMATIC REPRESENTATION OF THE INTERMEDIATE CARBANION FORMED FROM (61)



5.2.A.2: REACTIONS WITH BIFUNCTIONAL OXYGEN NUCLEOPHILES:

5.2.A.2a: DIENE (61) WITH CATECHOL:

Reaction of diene (61) with catechol gave the expected 8-membered ring product (94), by successive substitution of the two vinylic fluorines of the parent diene, the absence of which were clearly indicated by ^{19}F n.m.r. spectroscopy.



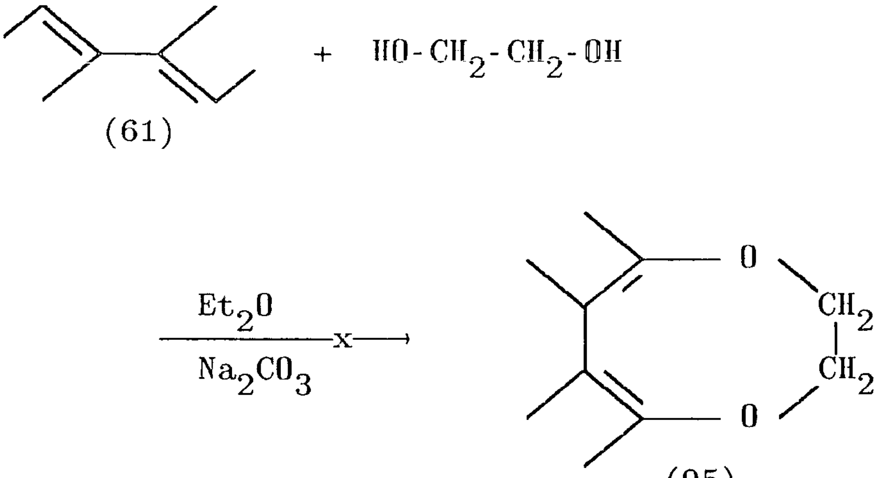
(61)

(94)

U.v. spectroscopy showed no bathochromic shift in the spectrum of (94) compared with that of catechol. It must therefore be concluded that (94) is not a 10π aromatic system.

5.2.A.2b: DIENE (61) WITH ETHYLENE GLYCOL:

When diene (61) and ethylene glycol were mixed together in the presence of a large amount of ether as solvent, the expected 8-membered product (95) was NOT formed.



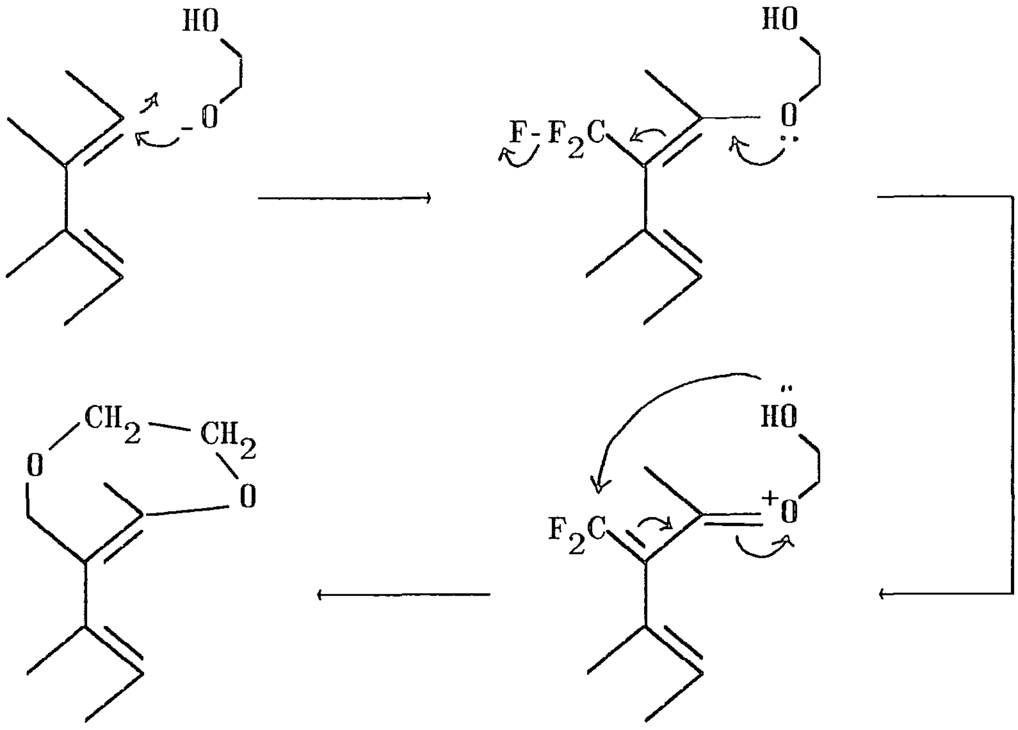
(61)

(95)
NOT FORMED

Instead a seven membered cyclic product (97) was obtained. ^{19}F n.m.r. of (97) clearly shows the presence of three -CF$_3$ groups, one vinylic fluorine, and two fluorines in a -CF$_2$-O- environment. Two peaks at 4.2 and 4.3 ppm in the ^{1}H n.m.r. suggest that the -O-CH$_2$-CH$_2$-O- group is in a non-symmetrical environment. Further evidence for (97) is given by i.r. data which indicates the presence of two C-C double bonds, and mass-spectrometry which gives a parent molecular ion M$^+$, 384, and a breakdown consistent with structure (97).

A possible mechanism of formation of (97) is detailed in scheme 30; the final step of which involves an "allowed" 7-endo trig cyclisation, with the "free" end of the ethylene glycol unit attacking the terminal difluoromethylene group of the intermediate cation (96) - see scheme 30.

SCHEME 30:



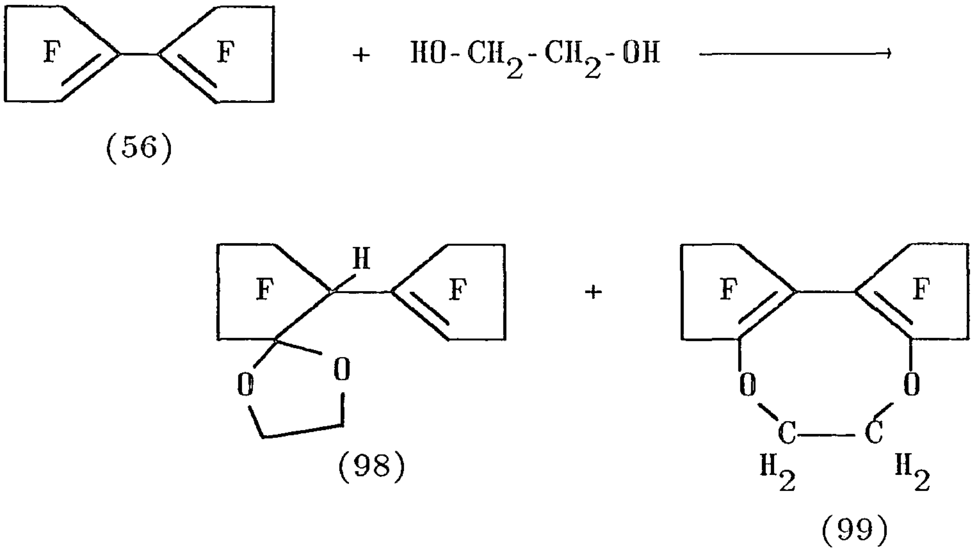
(97) (96)

5.2.A.2c: DIENE (56) WITH ETHYLENE GLYCOL:

This is another example of the enhanced reactivity of diene (56) over (61).

Reaction of diene (56) with ethylene glycol in ether proceeds in <u>neutral</u> conditions to give two products (98) and (99).

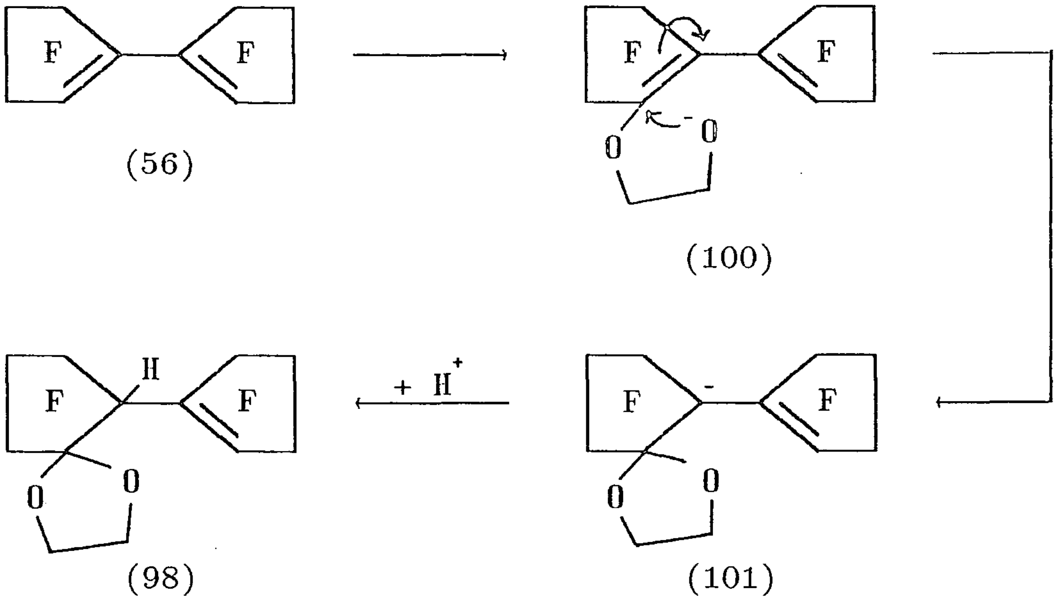
^{19}F n.m.r. of product (99) shows the presence of only three $-CF_2$ enviroments; vinylic fluorine resonances being notably absent. ^{1}H n.m.r. confirms the presence of protons in a symmetrical ether environment, while mass spectrometry and elemental analysis confirmed the molecular formula of $C_{12}H_4F_{12}O_2$.



Mass spectrometry data of (98) gave a parent molecular ion M^+,428, for $C_{12}H_5F_{13}O_2$, however only one C-C double bond was evident by i.r. ^{19}F n.m.r. showed the presence of six A,B $-CF_2$ resonances and one vinylic fluorine; while ^1H n.m.r. gave a resonance at 3.7ppm (tertiary proton), and 4.1ppm (spiro-ketal)

Formation of the five-membered spiro-ketal probably occurs via an initial substitution of one of the vinylic fluorines of diene (56) to give intermediate (100), which then undergoes an "allowed" 5-exo trig cyclisation to form the five membered spiro-ketal anion intermediate (101), which is then protonated to give product (98) - see scheme 31.

SCHEME 31:

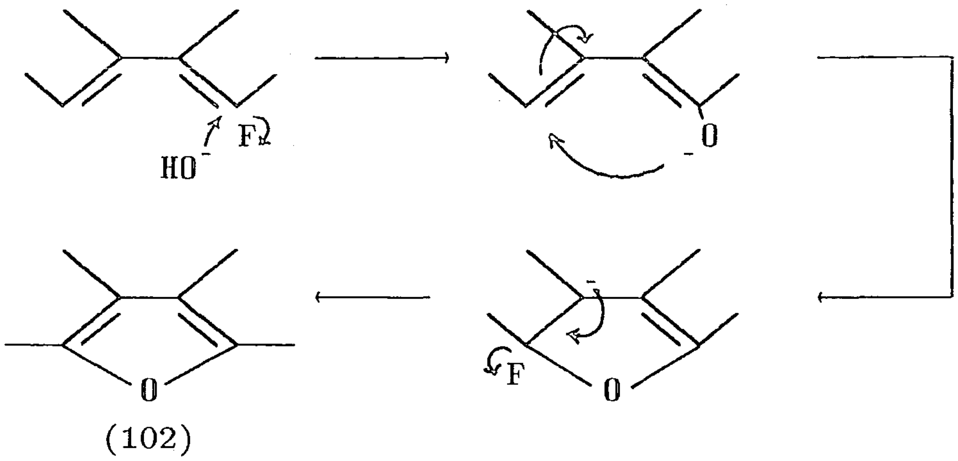


5.2.A.3: REACTION WITH POTASSIUM HYDROXIDE:

5.2.A.3a: DIENE (61) WITH POTASSIUM HYDROXIDE:

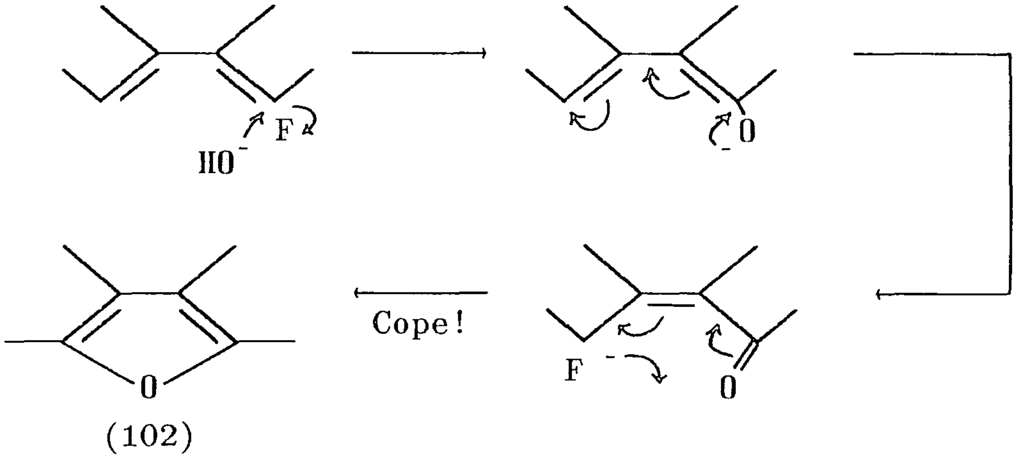
Reaction of diene (61) with potassium hydroxide in dimethyl formamide as solvent, gave perfluorotetramethylfuran (102) as the only product, identified by a comparison of spectroscopic data with that of an authentic sample[94]. Formation of this product by scheme 32, would violate Baldwins ring closure rules, since a "forbidden" 5-endo trig cyclisation step would be involved.

SCHEME 32:



However, scheme 33 - a "Cope-type" cyclisation, involving nucleophilic attack by carbon, overcomes the problems of necessary geometrical orbital overlap, encompassed within the set of ring-closure rules outlined by Baldwin[95].

SCHEME 33

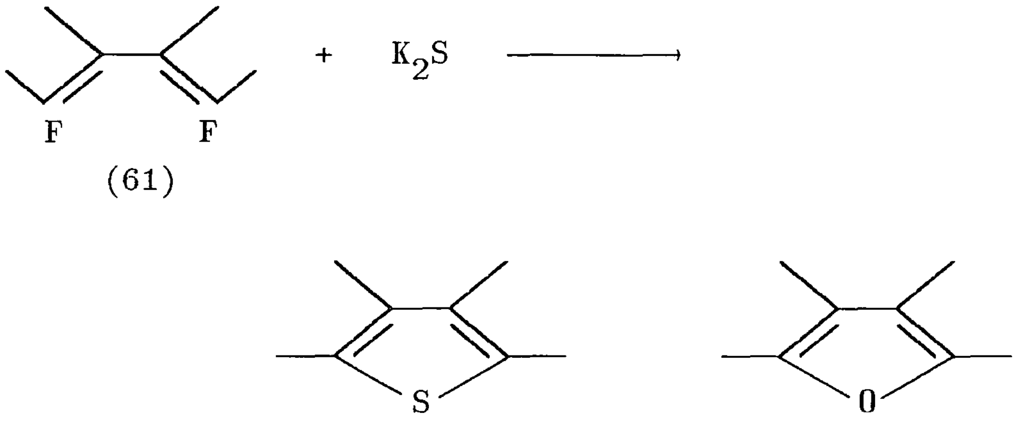


5.2.B: SULPHUR NUCLEOPHILES:

5.2.B.1: REACTIONS WITH POTASSIUM SULPHIDE:

5.2.B.1a: DIENE (61) WITH POTASSIUM SULPHIDE:

Diene (61) when reacted with potassium sulphide in dimethyl formamide gave two products - perfluorotetramethylthiophene (103), and perfluorotetramethylfuran (102).



(61)

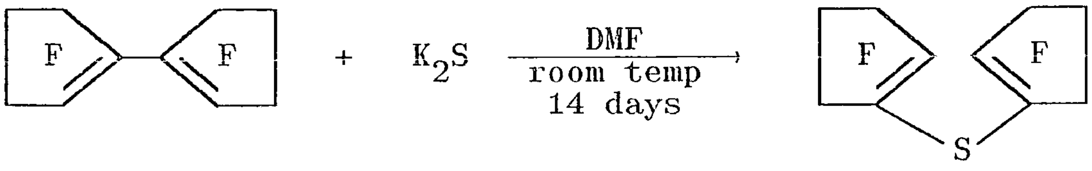
(103)

(102)

- the furan (102) is formed from the reaction of the diene with potassium hydroxide, available either as impurities in the potassium sulphide sample used, or from reaction of the released potassium cation with water in the system.

5.2.B.1b: DIENE (56) WITH POTASSIUM SULPHIDE:

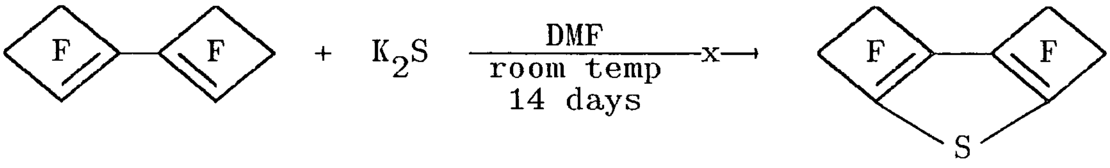
As expected, thiophene (104) was the only isolated product from reaction of (56) with potassium sulphide. ^{19}F n.m.r. of the product thiophene showed the presence of only three $-CF_2$ enviroments, while mass spectrometry and elemental analysis confimed the molecular formulae to be $C_{10}F_{12}S$.



(56) (104)

5.2.B.1c: DIENE (57) WITH POTASSIUM SULPHIDE:

The reaction of perfluorobicyclobut-1,1'-enyl with potassium sulphide did <u>not</u> yield thiophene (105), but instead gave a mixture of products which were involatile to transference *in vacuo*. This suggests that inter- rather than intra- molecular coupling with the sulphide ion had occurred, but attempts to isolate components of this mixture were unsuccessful. Reactions in high dilution may overcome this problem, and allow intra- molecular substitution of the second vinylic fluorine by the sulphide to form the desired thiophene (105).

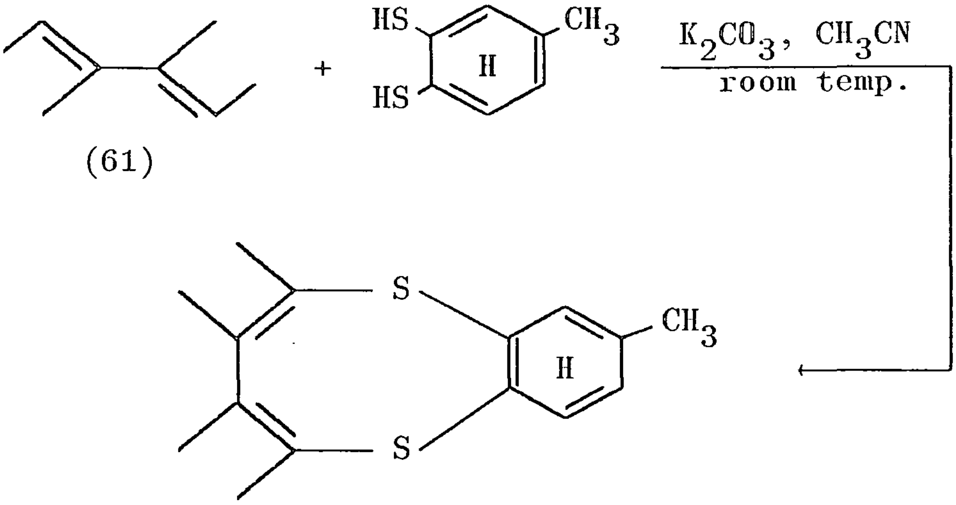


(57) (105)

5.2.B.2: REACTION WITH BIFUNCTIONAL SULPHUR NUCLEOPHILES:

5.2.B.2a: DIENE (61) WITH 3,4-DIMERCAPTOTOLUENE:

Diene (61) reacted readily with 3,4-dimercaptotoluene in the presence of potassium carbonate to afford (106) in good yield.



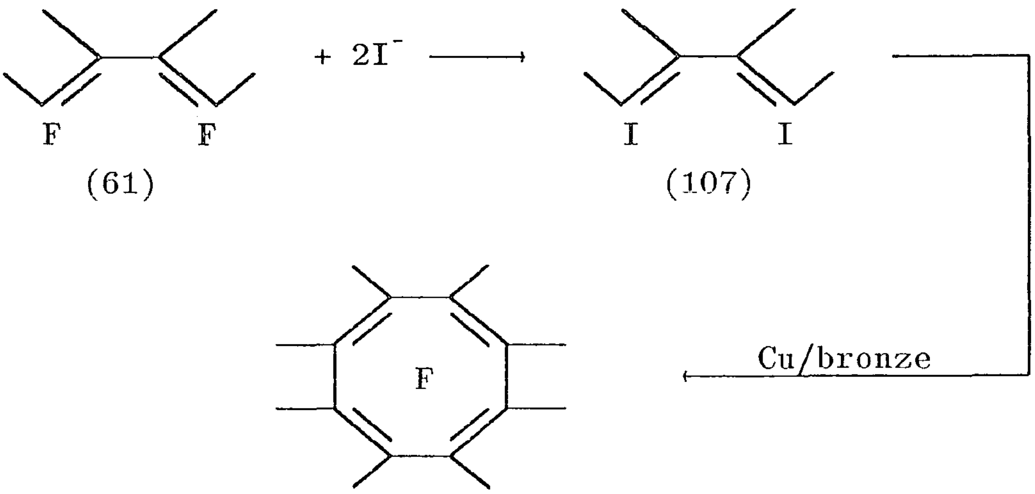
(106)

U.v. spectroscopy indicated that (106) was not a 10π aromatic system.

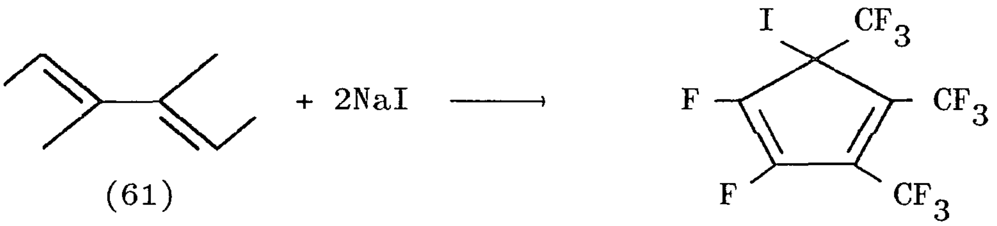
5.2.C: IODIDE NUCLEOPHILE:

5.2.C.1: DIENE (61) WITH IODIDE:

The aim of this reaction was to attempt to synthesise the di-iodide (107), which could then be coupled using Cu-bronze, and thereby act as a convenient route to perfluorooctamethylcyclooctatetraene.



The reaction of diene (61) with sodium iodide in acetonitrile at 140°C, however, did not yield the expected product. Instead, the major product from reaction was the cyclic mono-iodide (109).



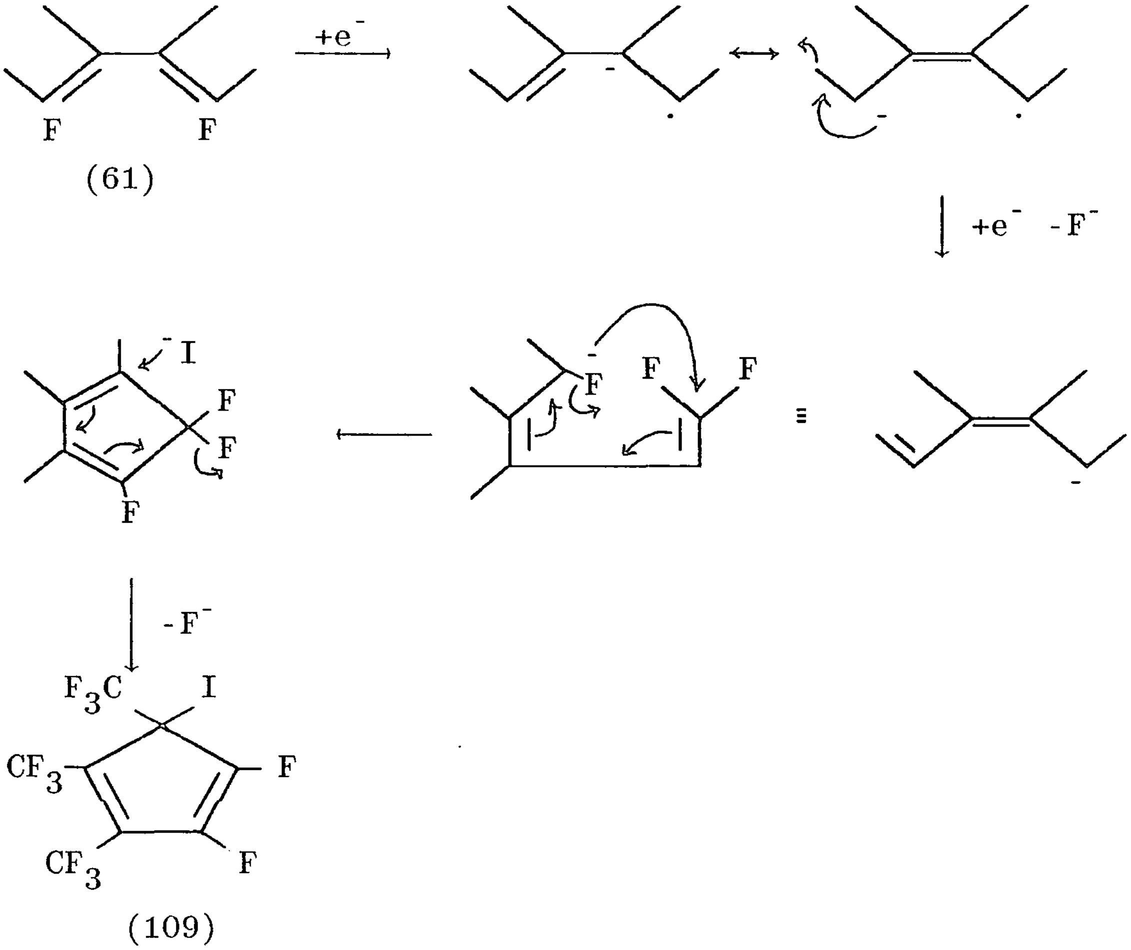
(61)

(109)

The formation of product (109) was surprising. ^{19}F n.m.r. of (109) clearly showed the presence of three $-CF_3$ groups, and two vinylic fluorines. I.r. data indicated the presence of two olefinic enviroments, with both elemental analysis and mass spectrometry confirming a molecular composition of $C_8F_{11}I$.

A proposed mechanism of formation of (109) is outlined in scheme 34, involving the iodide ion acting as a one electron reducing agent in a single electron transfer process similar to that reported for the reaction of sulphur containing nucleophiles with perfluorodecalin to yield various substituted napthalene derivatives[96].

SCHEME 34:



4.2.D: FLUORIDE ION REACTIONS:

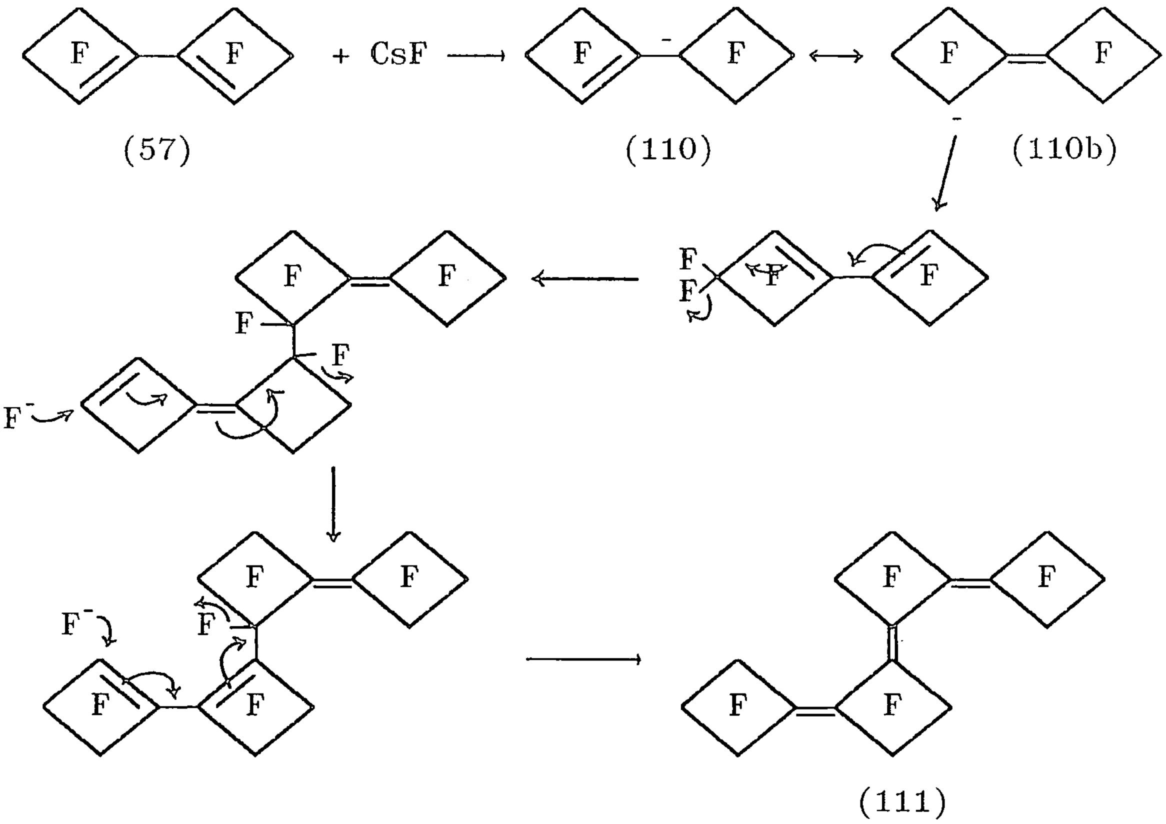
4.2.D.1: DIENE (57) WITH CAESIUM FLUORIDE:

In an attempt to observe the hopefully stable carbanion (110), perfluorobicyclobut-1,1'-enyl was reacted with caesium fluoride in tetraglyme solvent under an atmosphere of nitrogen - conditions which have previously been successfully used in our laboratories for the preparation of perfluoroalkyl anions[97].

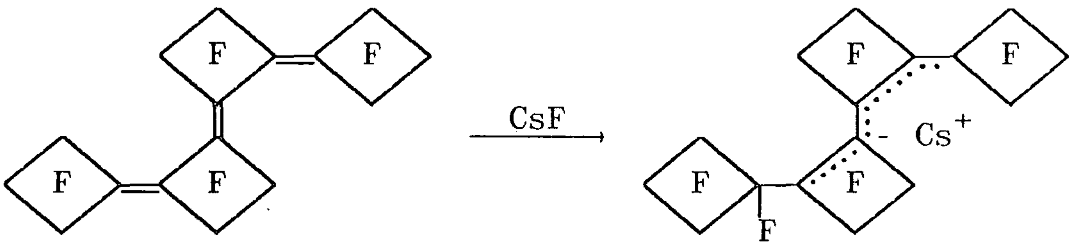
Analysis of the tetraglyme layer by ^{19}F n.m.r. highlighted the possible formation of a carbanionic species by the appearance of $-CF_2-$ resonances downfield from those of the parent diene - as would be expected for $-CF_2-$ groups adjacent to the charge centre; however a complete assignement of the ^{19}F n.m.r. spectrum could not be made. Removal of the product volatiles from the tetraglyme layer, however, showed formation of the crystalline solid (111). ^{19}F n.m.r. of (111) showed the presence of three $-CF_2$ enviroments integrating 2:2:1, with those integrating to 2 being at a low field position, characteristic of $-CF_2$'s adjacent to a C-C double bond. I.r. confirmed these observations -showing the presence of two C-C double bonds; while mass spectrometry and elemental analysis confirmed the molecular formula to be $C_{16}F_{16}$.
Clearly, in the presence of caesium fluoride perfluorobicyclobut-1,1'-enyl had oligomerised to form the diene dimer, via attack of the carbanionic intermediate (110b) on the parent diene (57), and subsequent fluoride ion initiated rearrangements (see scheme 35).

SCHEME 35:

Fluoride ion initiated oligomerisation of diene (57)



The diene dimer (111) when reacted with caesium fluoride in tetraglyme gave the stable carbanion (112).



(111) (112)

The ^{19}F n.m.r. of the carbanion (112) showed six $-CF_2-$ resonances shifted downfield, which suggests that the negative charge is delocalised through the double bonds, as shown in the above structure.

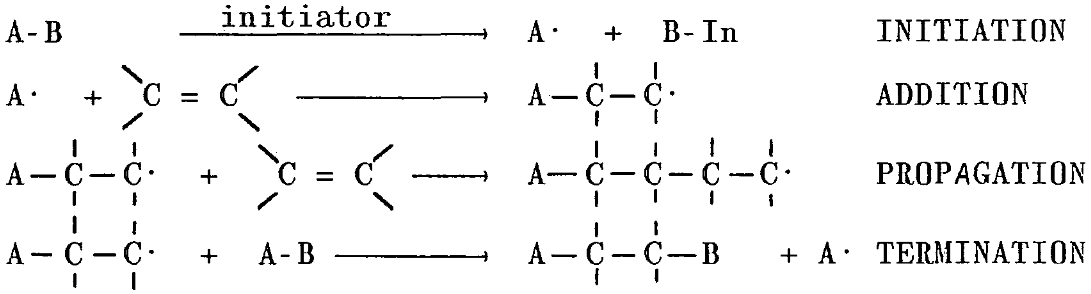
CHAPTER 6:

ADDITION REACTIONS OF PERFLUORO-DIENES:

6.1: INTRODUCTION:

6.1.A: FREE RADICAL ADDITIONS:

The general process for free radical additions can be described as shown below:



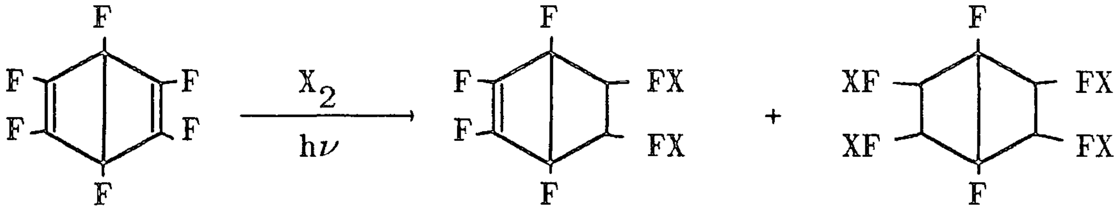
If the bond A-B is weak, and the concentration of AB is sufficiently high, the main product from reaction will arise from addition to the double bond, ie. termination competes successfully over propogation.

Little work has been done on a systematic study of the relationship between structure and reactivity; however free radical additions of functional groups to fluorinated alkenes is a potential synthetic route to a whole range of functionalised fluorocarbon compounds[98-100].

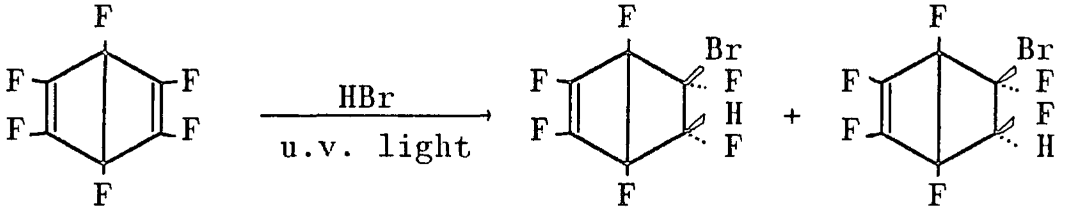
Table 14 is a summary of some free radical addition reactions of various cyclic and acyclic fluoro-dienes.

TABLE 14:

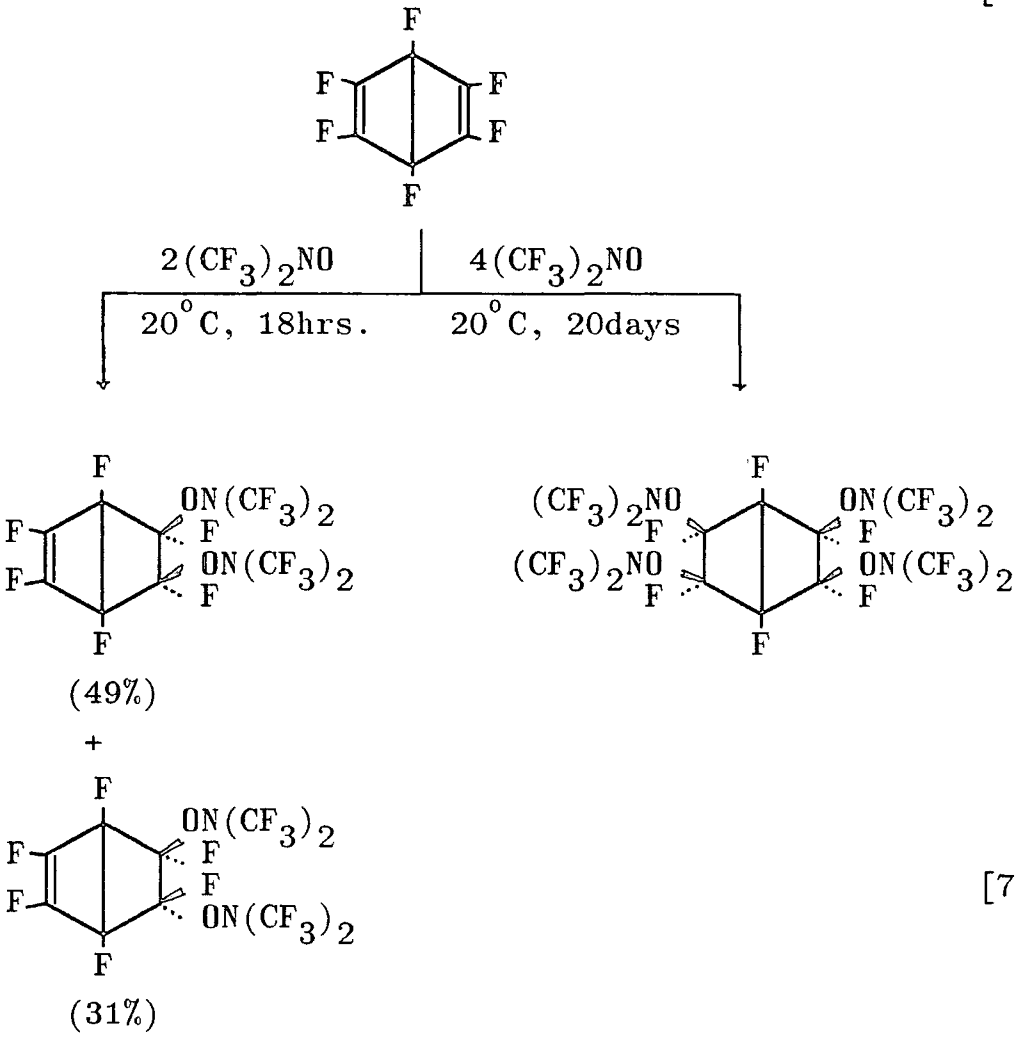
CYCLIC FLUORO-DIENES:



X = Br,Cl [79,80]

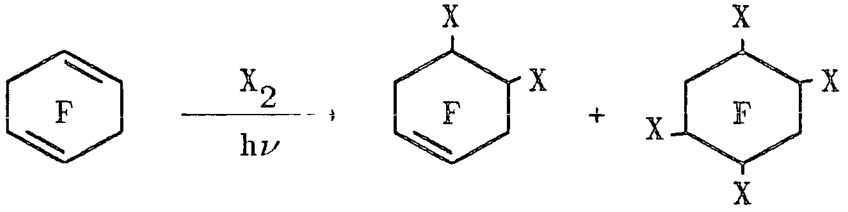


[79]



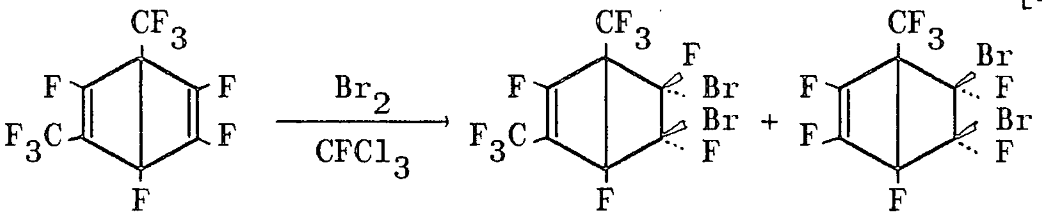
[79]

TABLE 14 CONTINUED:



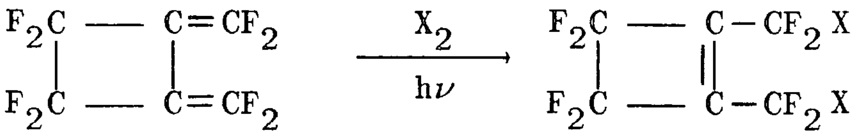
X = Br,Cl

[101]



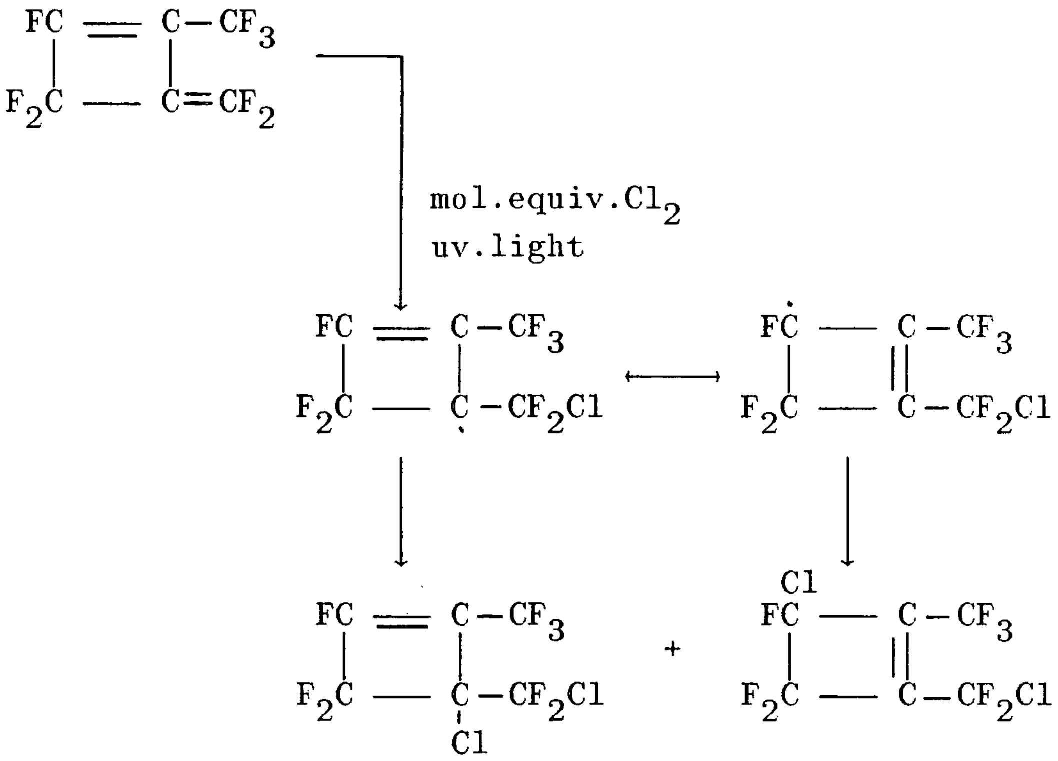
7 : 1 (73%)

[104]



X = Br,Cl

[103]



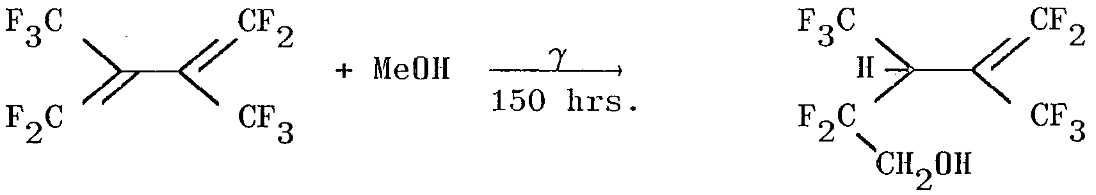
43% 46% [103]

TABLE 14 CONTINUED:

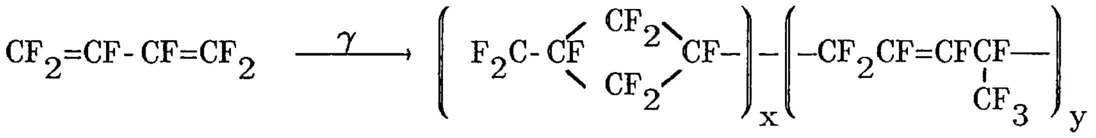
ACYCLIC FLUORO-DIENES:

$$F_2C{=}CF\text{-}CF{=}CF_2 + CH_3S\text{-}SCH_3 \xrightarrow{h\nu} CH_3SCF_2CF{=}CFCF_2SCH_3$$

[105]



76% [88]



[106]

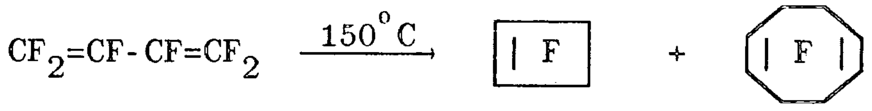
6.1.B: CYCLOADDITION REACTIONS OF FLUORO-DIENES:

Cycloaddition reactions can be divided into three areas: reactions involving (2+2) cycloadditions; reactions involving (4+2) cycloadditions ie. Diels-Alder reactions; and reactions involving dipolar species. Dienes allow the possibility of competition between 1,2 cycloaddition and Diels Alder 1,4 cycloaddition.

Table 15 is a summary of some cycloaddition reactions of various cyclic and acyclic fluoro-dienes.

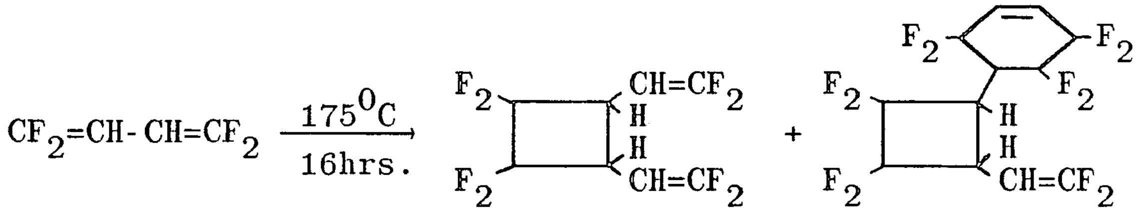
TABLE 15:

CYCLOADDITION REACTIONS OF CYCLIC-FLUORO-DIENES



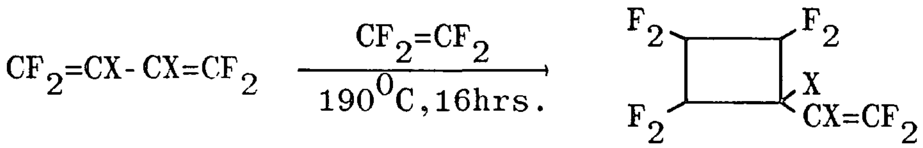
67%

[104,107]



36% 22%

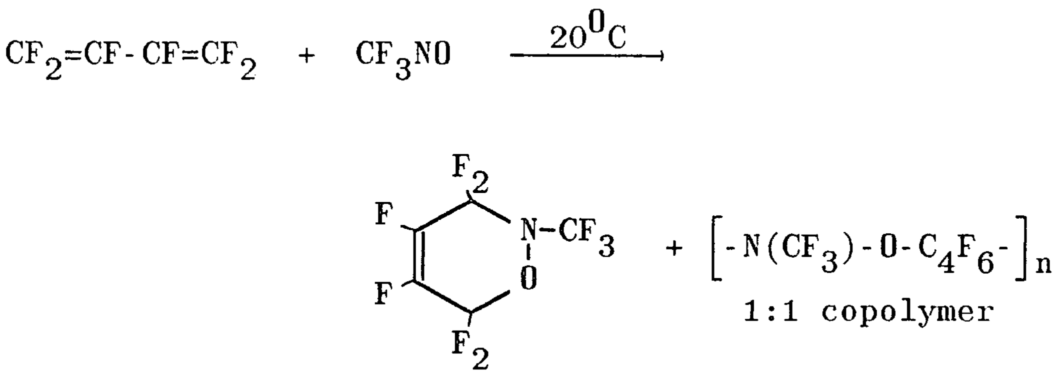
+ high polymers [108]



X = H,F

X = H, 56%

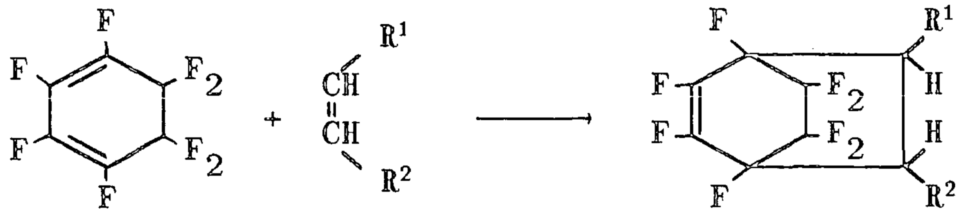
X = F, 21% [108]



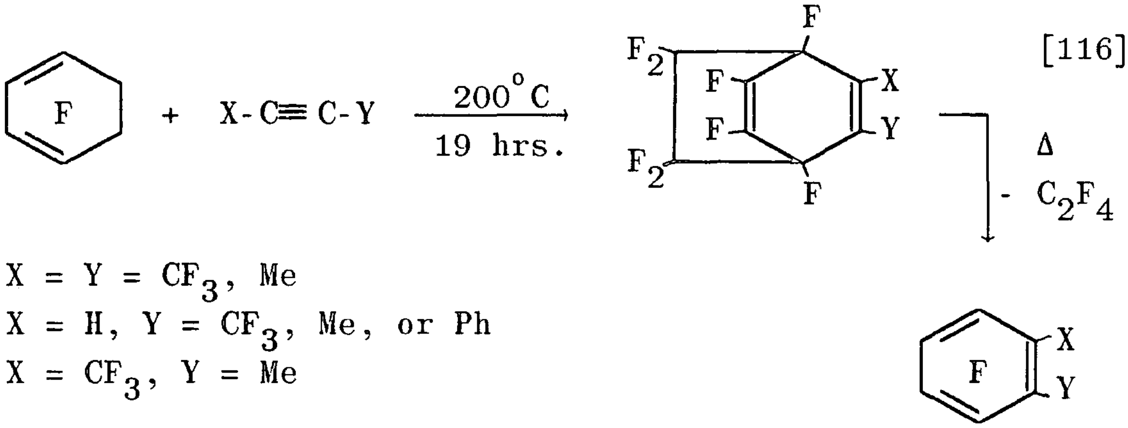
1:1 copolymer

6 : 1 [109,110]

TABLE 15 CONTINUED:

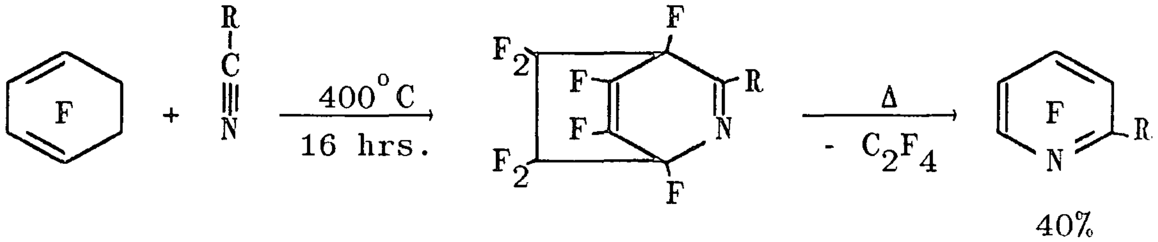


R^1 = H, R^2 = COMe, OC_2H_5, CN, C_6H_5, COOMe [111]



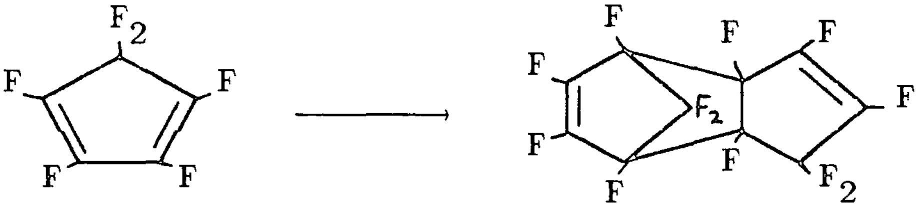
[116]

X = Y = CF_3, Me
X = H, Y = CF_3, Me, or Ph
X = CF_3, Y = Me



R = Br, CF_3, C_6F_5

[117]



[112]

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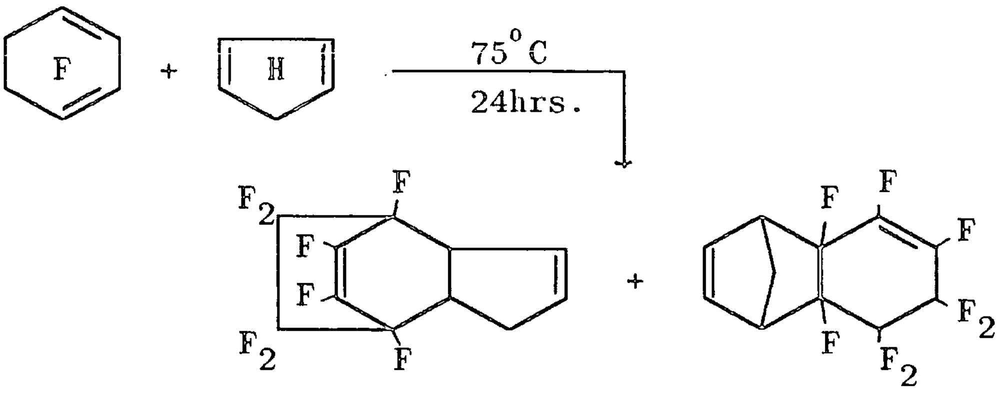
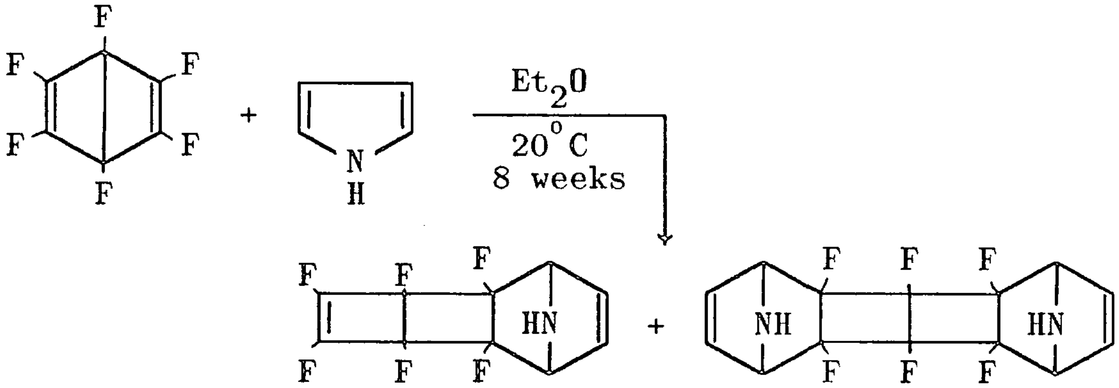
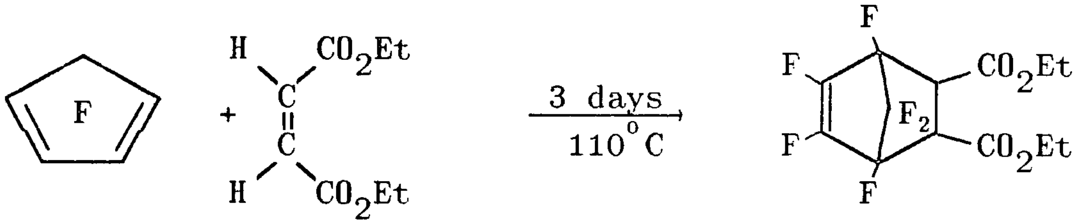


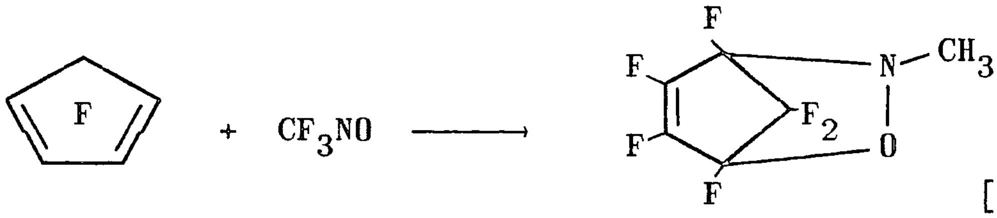
16% 70% [114]



58% 7% [115]

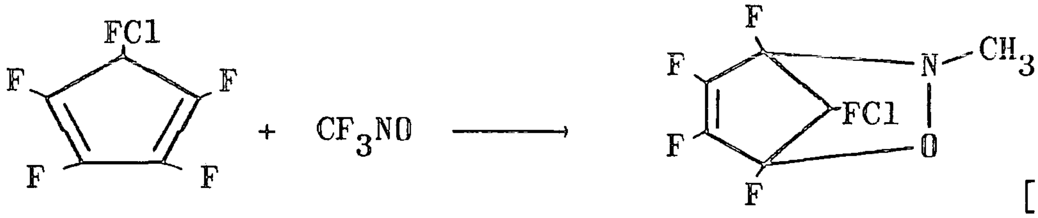


66% [113]

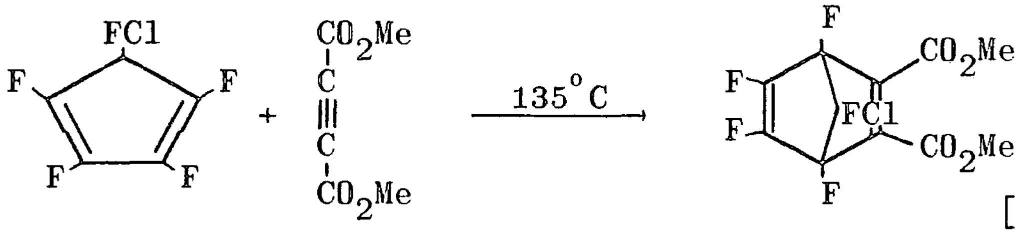


[118]

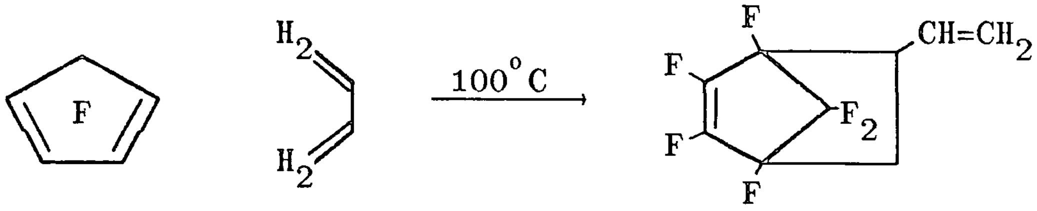
TABLE 15 CONTINUED:



[118]



[118]



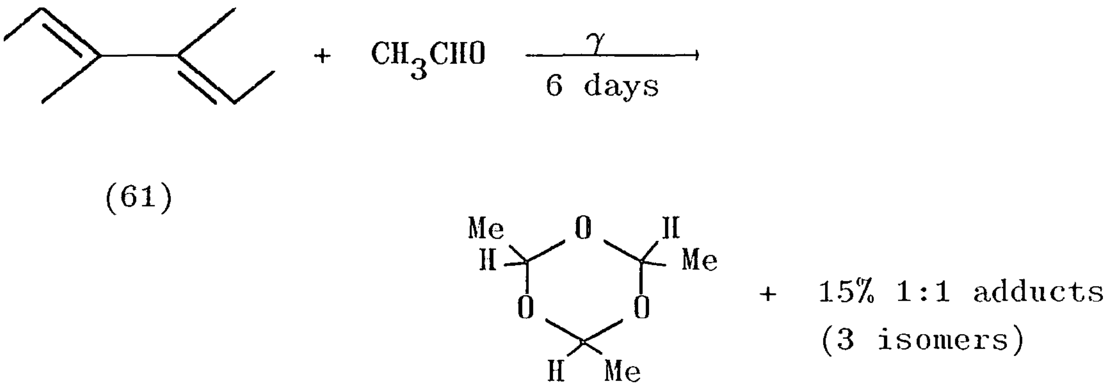
64% [119]

6.2: DISCUSSION:

6.2.A: FREE RADICAL ADDITION REACTIONS OF DIENES (56) AND (61):

6.2.A.1: REACTION OF DIENE (61) WITH ACETALDEHYDE:

Gamma ray initiated free radical addition of acetaldehyde to perfluoro-3,4-dimethylhex-2,4-diene (61) resulted in the formation of a 15% yield of three isomers of a 1:1 adduct; the major product from the reaction, however, was the cyclo-triether (113) formed by acid catalyzed trimerisation of acetaldehyde[98].



(61)

(113)

Separation and purification of the 1:1 adducts was not attempted due to their low yield.

6.2.A.2: REACTION OF DIENE (61) WITH DIMETHYL ETHER:

In an attempt to minimise steric restrictions to attack, and eliminate the problems of hydrocarbon oligomerisation, a gamma-ray initiated free radical addition reaction of dimethyl ether to diene (61) was attempted. After six days a 10% yield of three isomers of a 1:1 adduct was isolated. Further purification was again not attempted due to the low yield of the reaction.

6.2.A.3: REACTION OF DIENE (56) WITH DIETHYL ETHER:

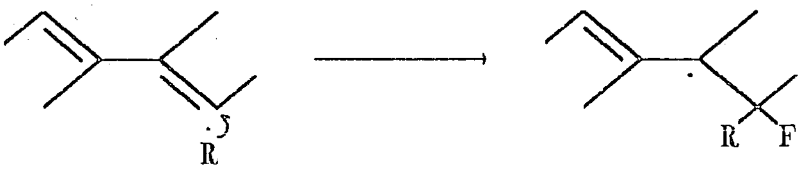
A less than 3% yield of a 1:1 adduct was obtained from a gamma-ray initiated addition reaction of diethyl ether to diene (56).

6.2.A.4: CONCLUSIONS:

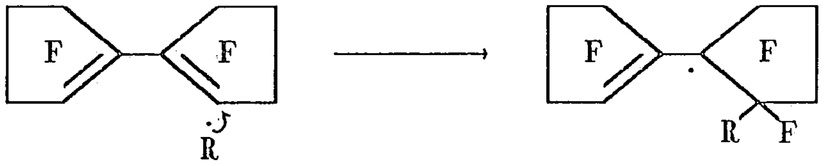
There are two factors which are probably contributing to the low yield of products obtained from the attempted free radical addition reactions to dienes (56) and (61).

1. INTERMEDIATE RADICAL STABILITY:

Radical attack on dienes (56) and (61) would result in the formation of allylic radical intermediates (114) and (115)

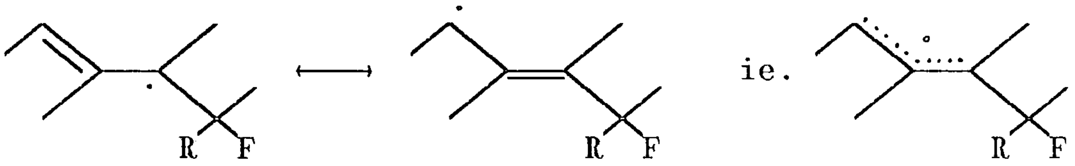


(61) (114)



(56) (115)

-which are known to be exceedingly stable due to resonance delocalization with the remaining double bond.

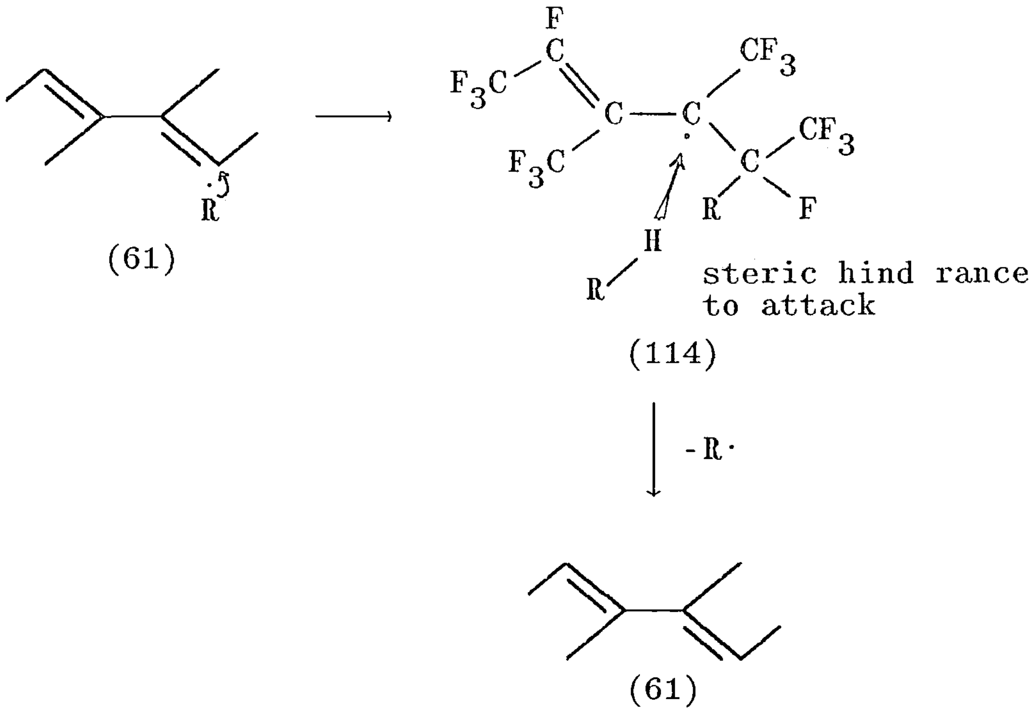


These radical intermediates are consequently unreactive to further radical attack, and therefore decay to reform the parent diene.

2. STERIC FACTORS:

The bulky -CF_3 groups of perfluoro-3,4-dimethylhex-2,4-diene, in particular, may (i) restrict interaction of the attacking free radical on the double bond of the parent diene, thereby preventing bond formation; OR (ii) prevent secondary radical attack on the intermediate allylic radical

(114) (if formed), thus favouring decay of the intermediate radical back to the parent diene.



Clearly, further work is required to ascertain to what extent each of these factors affects the reactivity of perfluoro-dienes in free radical initiated reactions..

6.2.B: CYCLOADDITION REACTIONS:

6.2.B.1: DISCUSSION:

Numerous 4+2 cycloaddition reactions have been attempted, using perfluoro-3,4-dimethylhex-2,4-diene (61) and perfluorobicyclopent-1,1'enyl (56), with various dienophiles of differing electron densities -see table 16.

In each case the reactants were mixed together under the conditions shown, but only starting material was recovered, with no formation of any Diels-Alder adduct by the mechanism shown below.

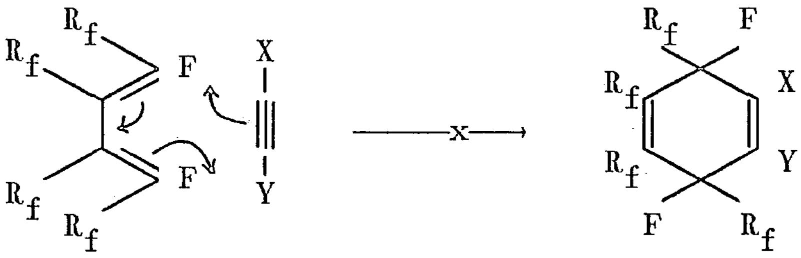
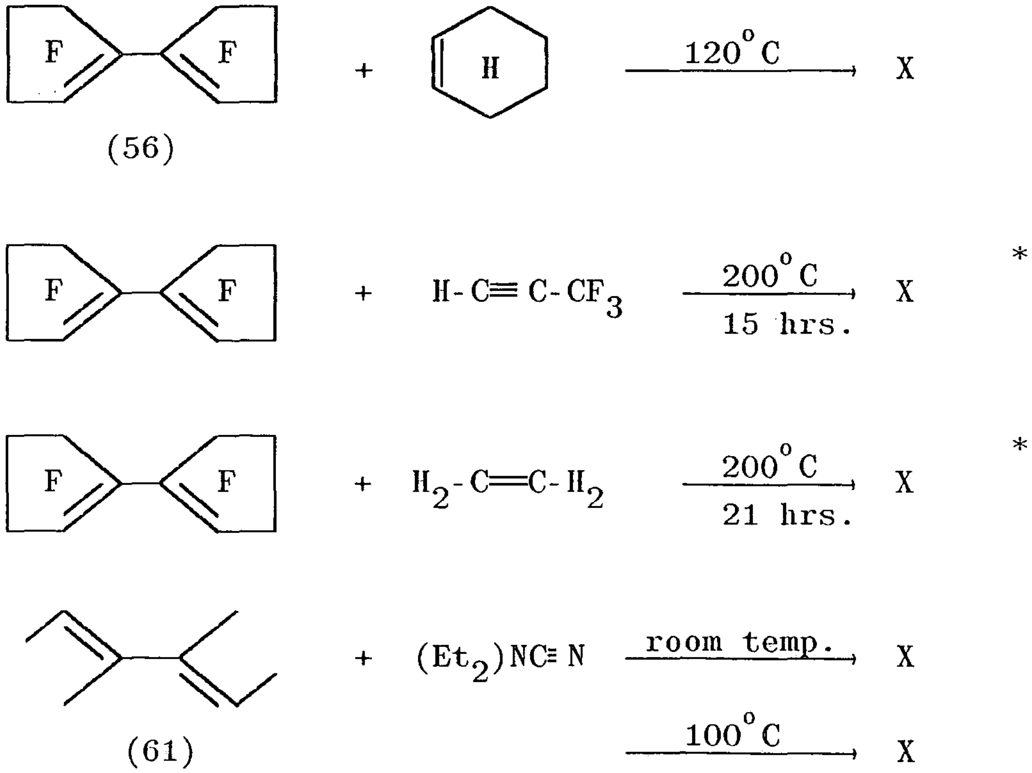


TABLE 16:

ATTEMPTED DIELS-ALDER REACTIONS OF DIENES (56) AND (61)



NB. * reactions - performed by E. Marper (ref 58)

6.2.B.2: CONCLUSIONS:

The non-reactivity of dienes (56) and (61) in the Diels-Alder cycloaddition reaction may be explained by:

(i) the difficulty with which dienes (56) and (61) can adopt the required cisoid conformation; and/or

(ii) the inability to obtain satisfactory overlap of the participating π orbitals, due to steric restrictions imposed by the bulky perfluoroalkyl groups of the perfluoro-dienes.

6.3:CHARGE-TRANSFER SALTS:

6.3.1:INTRODUCTION

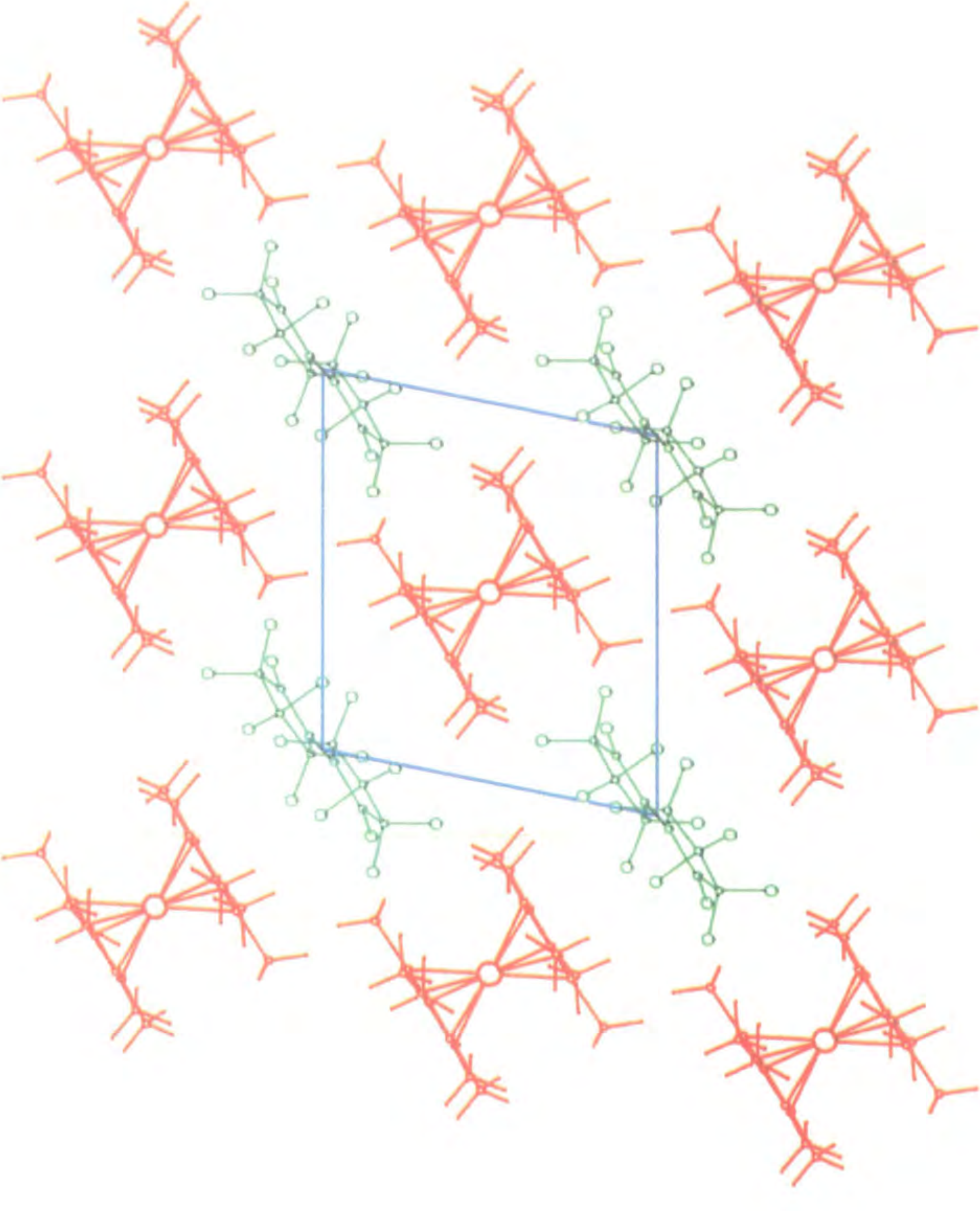
Charge transfer salts are currently a major research interest, since some have been shown to exhibit properties of one dimensional electrical conductivity; while others of the type $[D]^{+\cdot}[A]^{-\cdot}$, where D = a metallocene donor, and A = an organic acceptor, have been shown to demonstrate novel magnetic properties. Miller et al[120], in 1987, reported that a one electron transfer salt of decamethylferrocene and tetracyanoethylene exhibited the first organo-ferromagnetic behaviour. Magnetic measurements on $[Fe(cp^*)_2]^{+\cdot}[TCNE]^{-\cdot}$ showed that below 15K the magnetisation was no longer proportional to the applied magnetic field, and at temperatures below 4.5K the compound displayed conventional ferromagnetic properties, ie. spontaneous magnetisation was observed.

Cyclic voltammetry has shown that a series of perfluorocyclic-olefins have relatively low reduction potentials (see Chapter 3), and would therefore readily accept an electron from a suitable metallocene "donor". The radical anions so formed from perfluorobicyclopentylidene (43) would ex ist in a planar conformation in the solid state and therefore effectively replace TCNE in an analogous series of compounds with donors such as Decamethylferrocene. Decamethylferrocene, as a metallocene "donor", has an oxidation potential of +0.81V, which allows it to effectively donate electron(s) to the perfluorocyclicolefins under study. It therefore offered a unique opportunity to stabilise a series of perfluoro-radical anions which had NOT been previously trapped, whilst also offering the possibility of forming the first fluoro-organo ferromagnet.

6.3.2:DISCUSSION

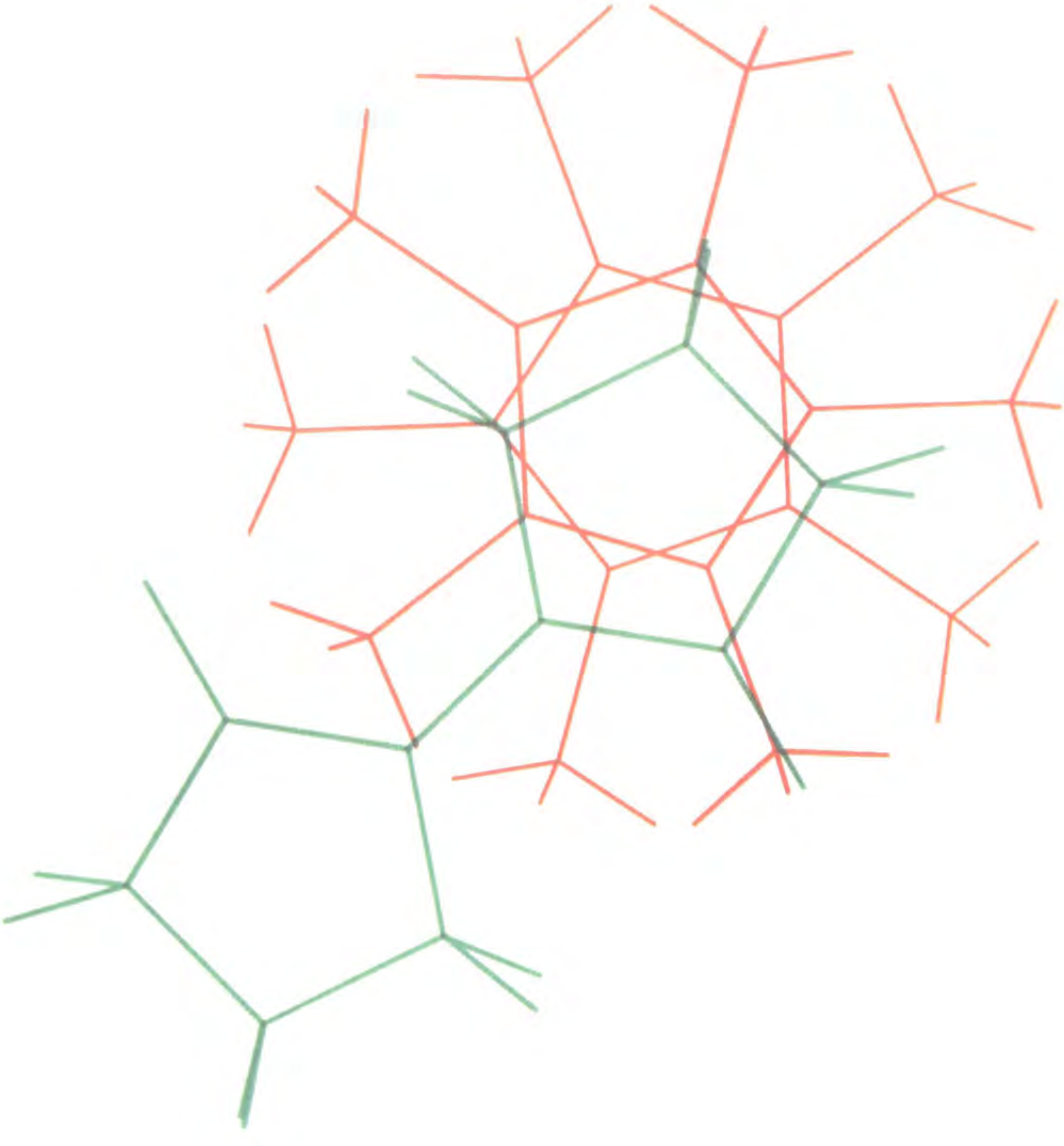
REACTION OF DECAMETHYLFERROCENE AND PERFLUORO-BICYCLOPENTYLIDENE:

The addition of perfluorocyclopentylidene(43) to a solution of decamethylferrocene in acetonitrile, resulted in an immediate colour change from yellow (due to $(\eta - C_5Me_5)_2Fe$) to a deep green colour - indicative of formation of a charge transfer complex. After ten days, a deep green crystalline solid was isolated in approx.25% yield, which was subsequently shown by X-ray crystallographic analysis to be a charge transfer salt of decamethyl ferrocene with perfluorobicyclopentenyl ie. $[Fe(C_5Me_5)_2]^{+\cdot}$ $[C_{10}F_{14}]^{-\cdot}$



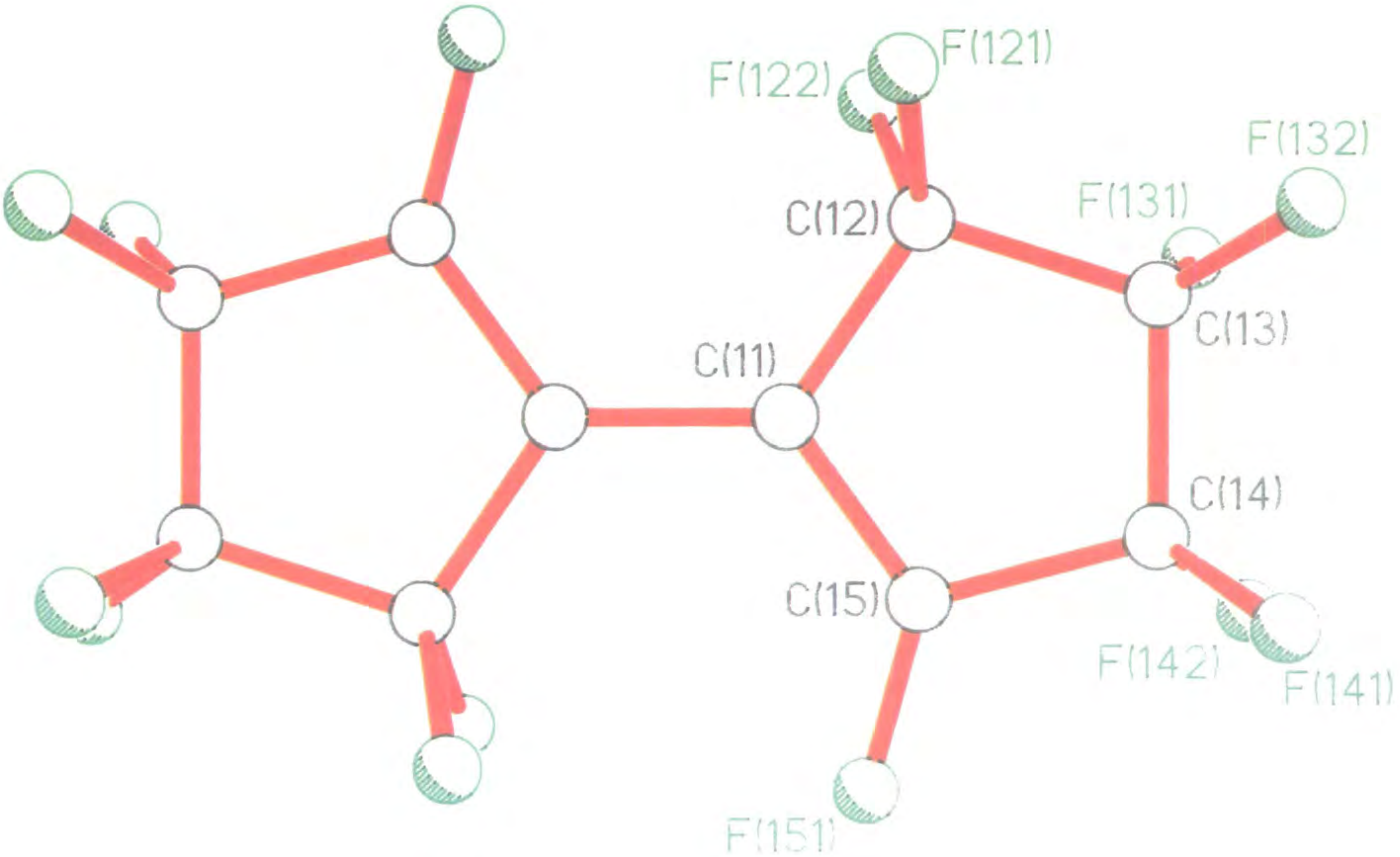
X-ray analysis 1:

Plot showing 3D stacking of $[Fe(C_5Me_5)_2]^{+\cdot}$ $[C_{10}F_{14}]^{-\cdot}$



X-ray analysis 2:

Plot showing the relative positioning of the $[Fe(C_5Me_5)_2]^{+\cdot}$ radical cation w.r.t. the $[C_{10}F_{14}]^{-\cdot}$ radical anion.



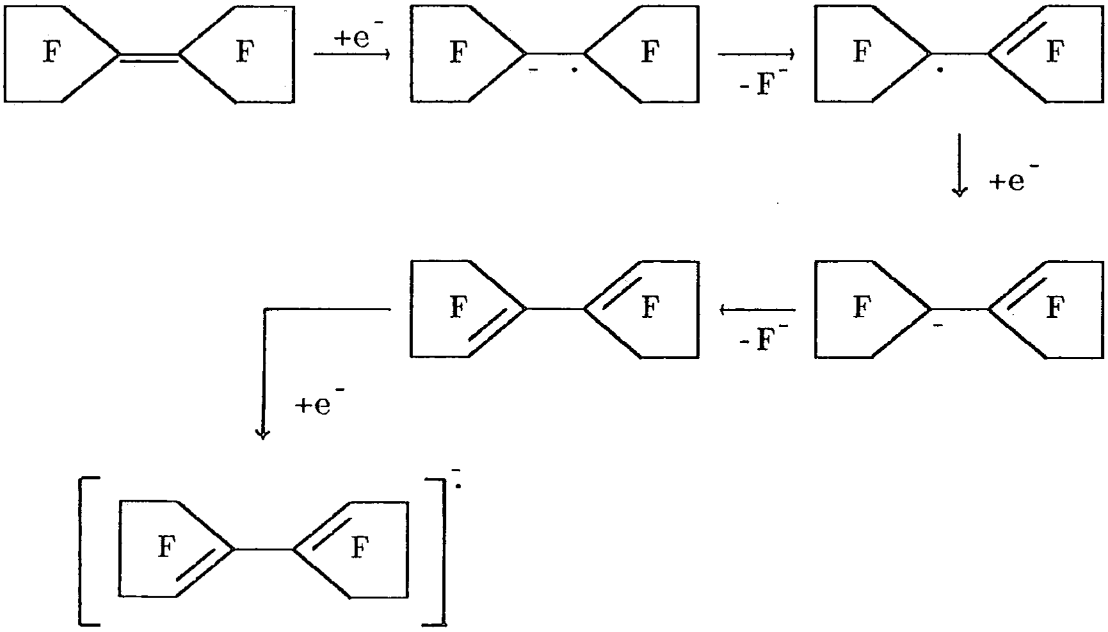
X-ray analysis 3:

Plot showing the $[C_{10}F_{14}]^{-\cdot}$ radical anion in isolation.

6.3.2.a: THE $[C_{10}F_{14}]^-$ ANION

X-ray crystallographic data shows that the perfluorocyclopentylidene has undergone a $3e^-$ reduction to give the perfluorobicyclopentenyl radical anion (see scheme 36) -the first reported structural characterization of a fluoro-radical anion.

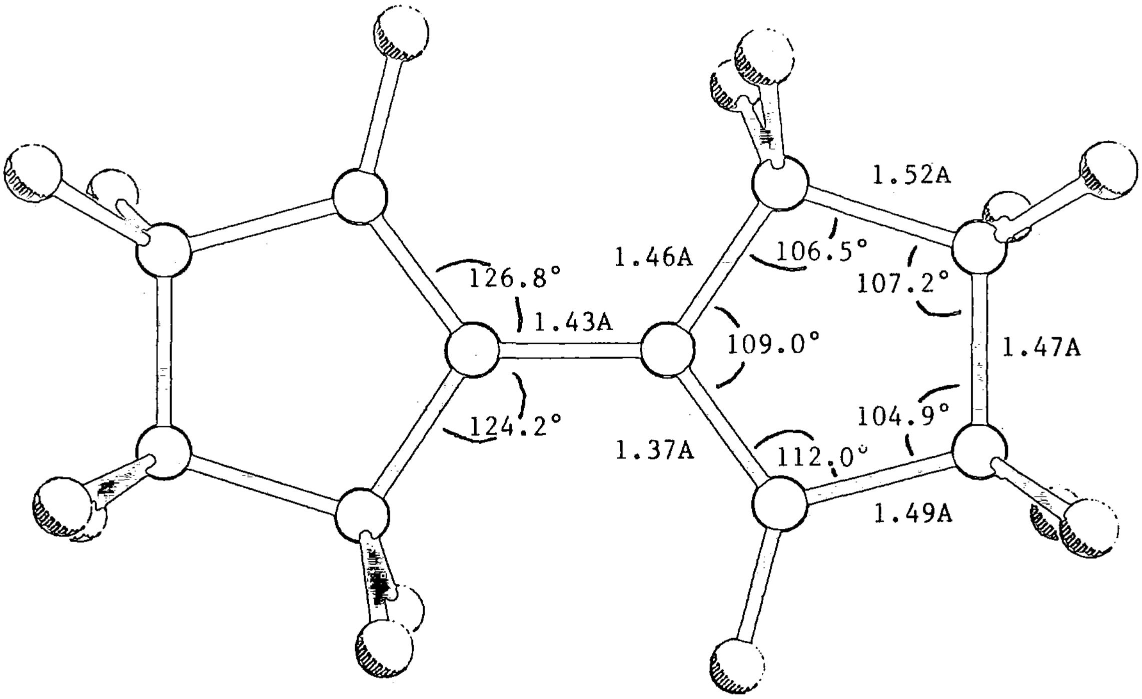
SCHEME 36:



Indeed, reaction of perfluorobicyclopentenyl (56) with decamethylferrocene, in acetonitrile, gave the charge transfer salt in quantitative yield, by a direct $1e^-$ transfer complexation.

The perfluorobicyclopentenyl radical anion possesses a trans arrangement of double bonds, with bond lengths and angles as shown in Fig.13.

FIG.13



The bond lengths suggest that a degree of conjugation exists between the two double bonds, with the carbon to carbon double bond length longer than in a non-conjugated system (~ 1.34 Å), and the adjoining carbon to carbon single bond shorter than normal (~ 1.48 Å)

6.3.2.b:THE $[Fe(C_5Me_5)_2]^+$ CATION

The decamethylferrocenium radical cation possess two pentamethylcyclopentadienyl rings in a staggered arrangement with local D_{5d} symmetry. The same arrangement is observed in decamethylferrocene[122], and for the decamethyl-ferrocenium radical cation in the $[TCNQ]^-$ [123]and $[TCNE]^-$ [121] charge transfer salts.

6.3.2.c:SOLID STATE STRUCTURE

The bulk structure of the decamethylferrocene -perfluorobicyclopentenyl salt is very similar to that of the decamethylferrocene-TCNE complex[121]. Each layer in the crystal is made up of discrete pairs of donor and acceptor radical ions. Moreover, each layer of donor-acceptor pairs is out of register with neighbouring layers by half a unit, so that the distance between donors in one layer and acceptors in an adjacent layer is approximately the same as the distance between donors and acceptors in the same layer. The complex has, therefore, a true three dimensional structure.

Elemental and infra-red analysis of the crystalline solid provided confirmatory evidence for these findings. Fourier transform ^{19}F n.m.r. of the analytically pure charge transfer salt failed to show resonances from the radical anion of perfluorobicyclopentenyl due to its paramagnetic nature; howvever, the presence of trace diamagnetic impurities was evident. ^{1}H nmr also showed, as expected, the absence of any resonance.

6.3.3:MAGNETIC SUSCEPTIBILITY MEASUREMENTS:

6.3.3.1:INTRODUCTION

In the mid 1960's McConnell published proposals for the preparation of molecular based ferromagnetic materials[124-125], which were later expanded upon by

Breslow[126-128]. This model requires a charge transfer complex to contain 1-D chains of alternating S=1/2 donors, D, and acceptors, A, ie. ....$D^{\cdot +}$ $A^{\cdot -}$ $D^{\cdot +}$ $A^{\cdot -}$...., such that upon charge transfer a triplet is formed and thus ferromagnetic coupling may result. Such ferromagnetic behaviour was observed for the decamethylferrocene-TCNE charge transfer salt[121].

A similar physical and electronic structure has been identified in the decamethylferrocene -perfluorobicyclopentenyl charge transfer salt, and consequently the ferromagnetic behaviour of this complex was investigated at Cambridge.

6.3.3.2:DISCUSSION

Magnetic susceptibility was measured using a Faraday balance in the range 5-300K using two magnetic field strengths (0.76 & 0.87τ). The susceptibility χ was fitted to the Curie-Weiss equation:

$$\chi = \chi_0 + C(T - \theta)$$

and plotted as agraph of $1/(\chi - \chi_0)$ vs.τ (see graph 1)

Recorded parameters were estimated as:

$\chi_0 = -(5\pm4) \times 10^{-4}$ emu/mole

$C_{(molar)} = 0.95 \pm 0.1$

$\theta = -2 \pm 2K$

(NB. θ for $[Fe(C_5Me_5)_2]^+$ $[TCNE]^-$ = 30 @ T>60K)

A value for θ close to zero, indicates that the material either possess very weak intermolecular exchange, or that ferromagnetic and anti-ferromagnetic contributions balance each other.

6.3.4:OTHER CHARGE-TRANSFER REACTIONS (PRELIMINARY OBSERVATIONS)

The addition of perfluorobicyclopentylidene to a solution of bis-benzene chromium in acetonitrile caused an immediate colour change from green to yellow, suggesting that formation of a charge transfer complex had occured. Purification and subsequent isolation of the crystalline product was however unsuccessful.

Decamethylferrocene has been reacted with a number of fluoro-olefins (namely: perfluorobicyclobutylidene (44), perfluorobicyclobut-1,1'-enyl (57), perfluorotrisisopropyltriazine, and perfluoro-3,4-dimethyl -hex-2,4-diene (61)), in an attempt to isolate other charge transfer salts. Despite colour changes indicative of decamethylferrocene being converted to its d^5 radical cation, no complex has yet been isolated and fully characterized.

Further work is clearly required to extend these preliminary observations, in the light of the exciting results obtained with decamethylferrocene and perfluorobicyclopent-1,1'-enyl.

6.3.5:CONCLUSIONS

Suitable one electron organometallic donors (eg.decamethylferrocene) have been shown to interact with a range of fluoro-olefins of low reduction potential, to form charge-transfer complexes. This approach, has for the first time, allowed a radical anion of a fluorinated olefin to be trapped (the radical anion of perfluorobicyclopent-1,1'enyl), and consequently enabled bond lengths and angles to be determined from X-ray crystallographic data. Further work in this area should allow other fluorinated radical anionic species to be trapped, with the crystalline solids so formed possessing potentially interesting physical properties of ferromagnetism or electrical conductivity.

INSTRUMENTATION:

N.M.R. SPECTRA: Standard fluorine and proton spectra were recorded on a Varian EM360L spectrometer operating at 56.4 and 60 MHz respectively. High resolution spectra were recorded on a Bruker AC250 operating at 62.9 MHz for ^{13}C, 250.1 MHz for ^{1}H, and 235.3 MHz for ^{19}F. Chemical shifts for ^{13}C and ^{1}H signals are quoted in ppm relative to external Me_4Si reference with downfield taken as positive. Chemical shifts of ^{19}F signals are quoted in ppm relative to external $CFCl_3$ reference with upfield taken as positive.

INFRARED SPECTRA: Infrared spectra were recorded on a Perkin Elmer 457 grating i.r. spectrophotometer using KBr discs for solid samples, or as thin films between KBr plates for liquid samples.

MASS SPECTRA: Mass spectra of pure materials were recorded on a VG 7070E spectrometer with electron impact, chemical ionisation and negative ionisation modes as appropriate. G.l.c. mass spectra were recorded on a VG Micromass 12B spectrometer fitted with a Pye 104 gas chromatograph (packed columns) or a VG 7070E spectrometer equipped with a capillary column gas chromatograph (25m fused silica column with O_{v1} coating).

ELEMENTAL ANALYSES: Carbon, hydrogen and nitrogen analyses were obtained using a Perkin Elmer 240 elemental analyser. Analysis for halogens was performed as described in the literature.

GAS LIQUID CHROMATOGRAPHIC ANALYSIS: Gas liquid chromatographic analyses were carried out using: Pye 104 (packed column), Pye GCD (packed column), and Hewlett Packard 5890A (0_{v1} coated fused silica capillary column) gas chromatographs equipped with flame ionisation detectors. Preparative g.l.c. was performed on a Varian aereograph model 920 (packed column) with a Cathodometer detector. Column packing most commonly used: Col. 0 (5% or 10% silicone gum rubber).

REAGENTS AND SOLVENTS: Unless otherwise stated reagents were used as supplied. 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 solvent.

CHAPTER 7:

EXPERIMENTAL TO CHAPTER 2

7.1:REDUCTION OF PERFLUOROCYCLOHEXENE

7.1.1:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOHEXENE AT A PLATINUM ELECTRODE IN ACETONITRILE

Perfluorocyclohexene (20) (5.50g, 21.0m.moles), was reduced at -1.6V at a platinum cathode in anhydrous acetonitrile containing tetraethylammonium tetrafluoroborate. The perfluorocyclohexene formed an insoluble layer which, by the end of the electrolysis had disappeared.

The bulk catholyte was analysed by high field ^{19}F n.m.r. which indicated the presence of unreacted (20), and a sharp resonance at 163.3ppm, characteristic of hexafluorobenzene (22), as the only product.

Product volatiles were removed by transference *in vacuo* to a cold trap. Analysis by mass spectrometry-g.l.c. (capillary, temperature programmed) confirmed the presence of (22) M^+, 186, 41.6%, in good yield.

7.1.2:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOHEXENE AT A PLATINUM ELECTRODE IN DMF

Perfluorocyclohexene (20) (6.08g, 23.2m.moles), was reduced at -1.6V in anhydrous DMF containing tetraethylammonium tetrafluoroborate as a supporting electrolyte, at a platinum cathode.

The product volatiles were removed from the bulk catholyte by transference *in vacuo* to a cold trap. Analysis of this volatile "fraction" by ^{19}F n.m.r and mass spectrometry-g.l.c. (capillary, temperature programmed), confirmed the presence of hexafluorobenzene (22) in excellent yield, in addition to a number of minor products -whose breakdown pattern indicated that they were not fluorocarbons.

The involatile residue from the catholyte was not investigated.

7.2:REDUCTION OF PERFLUOROCYCLOBUTENE

7.2.1:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOBUTENE AT A PLATINUM CATHODE IN DMF

Perfluorocyclobutene (23) (10g, 61.7m.moles), was reduced at -1.6V at a platinum cathode in anhydrous DMF containing tetraethylammonium tetrafluoroborate as a supporting electrolyte, with the cell externally cooled to under $2^{o}C$ with an ice-salt bath. After approx. 5 minutes from the start of electrolysis, a black coloured material began to form on the electrode, which continued to "envelope" the entire cathode surface. The bulk catholyte became intensely coloured, and the current fell from 32mA to 9mA, as the coating on the electrode thickened.

Analysis of the bulk catholyte by high field ^{19}F n.m.r.

indicated the presence of (23) only.

At the end of reduction, the solid material was scraped off the electrode, washed and dried under vacuum to leave a black fibrous solid (0.21g). The infra red spectrum of this material proved difficult to obtain due to the nature of the solid. The solid was insoluble in common organic solvents, and mass spectral data proved to be unhelpful in product identification.

The bulk catholyte was concentrated by removal of excess solvent by transference *in vacuo* to a cold trap, leaving an intensely coloured residue. Mass spectrometry showed it to be a multicomponent mixture. Analysis of the catholyte volatiles by ^{19}F n.m.r and mass spectrometry-g.l.c., indicated the presence of unreacted (23) only.

7.2.2:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOBUTENE AT A PLATINUM CATHODE IN ACETONITRILE

Perfluorocyclobutene (23) (9.62g, 59.4m.moles), was reduced at -1.9V at a platinum cathode in acetonitrile containing tetraethylammonium tetrafluoroborate as the supporting electrolyte.

Observations and work up as for 7.2.1, except: Analysis of the polymer coating showed C, 47.8; H, 3.8; N, 2.8; F, 44.9%

7.2.3:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOBUTENE IN THE PRESENCE OF PERFLUOROCYCLOHEXENE

Perfluorocyclobutene (23) (6.29g, 38.8m.moles), was reduced at -1.8V in the presence of perfluorocyclohexene (20) (4.34g, 16.6m.moles) at a platinum electrode in anhydrous acetonitrile containing tetraethylammonium tetrafluoroborate. During the 4hrs. of electrolysis the current fell from 150mA to 25mA. At the end of electrolysis, polymer formation was restricted to the lower edge of the electrode.

The catholyte volatiles were analysed by mass spectrometry-g.l.c (capillary, temperature programmed), and ^{19}F n.m.r, which showed the presence of unreacted (23) and (20), and hexafluorobenzene (22) in good yield. The catholyte "involatile" fraction was not investigated.

7.3:REDUCTION OF PERFLUOROCYCLOPENTENE

7.3.1:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOPENTENE AT A PLATINUM ELECTRODE IN DMF

Perfluorocyclopentene (26) (7.0g, 33.0m.moles), was reduced at -1.5V at a platinum cathode in anhydrous DMF containing tetraethylammonium tetrafluoroborate. The electrolysis was allowed to continue for approx. 3.5hrs, during which time the current fell from 40mA to 9mA, and a dark blue/black coloured deposit formed on the electrode, as well as pervading the bulk catholyte.

At the end of the reduction, the solid material was scraped off the cathode (0.86g), and dried under vacuum to leave a black fibrous solid. Analysis found C, 43.1; H, 2.51; N, 2.67; F, 40.13%. The infra-red spectrum of this material proved difficult to obtain due to the nature of the solid, and therefore contained broad absorptions which could not be interpretated with any degree of certainty. The solid was not soluble in common organic solvents, and mass spectral data proved to be unhelpful in product identification.

The bulk catholyte was concentrated by removal of excess solvent by transference *in vacuo* to a cold trap, leaving a dark blue/black coloured suspension which yielded two ^{19}F n.m.r. resonances at

126.2ppm (m) and 173.0ppm (m). Mass spectrometry again failed to confirm the presence of possible products.

7.3.2:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOPENTENE AT A PLATINUM CATHODE IN ACETONITRILE

Perfluorocyclopentene (26) (6.0g, 28.3m.moles), was reduced at -1.8V at a platinum cathode in anhydrous acetonitrile containing tetraethylammonium tetrafluoroborate as the supporting electrolyte. During the 5hrs of elecrolysis the current rose initially to 36mA and a dark blue film immediately formed on the electrode surface. The current then gradually fell to 10mA as the electrode was enveloped in the dark blue material, and the catholyte became intensely coloured.

At the end of electrolysis the blue/black coloured material was scraped off the electrode, washed and dried under vacuum to leave a black fibrous solid (0.17g). Analysis found: C, 47.3; H, 3.2; N, 2.4; F, 39.6%. Subsequent analysis by mass spectrometry, and infra-red spectroscopy yielded no structural clues on the identity of this material (as for 7.3.1).

The bulk catholyte was concentrated by removal of excess solvent by transference *in vacuo* to a cold trap, leaving a dark blue/black coloured involatile viscous residue, which gave two ^{19}F n.m.r. signals at 126.2ppm (m) and 173.0ppm (m). This involatile residue was then washed with water. The resulting suspension was filtered and dried under vacuum, leaving a dark coloured fine particulate powder (0.04g). Analysis found: C, 44.9; H, 2.5; N, 4.3; F, 31.5%. Mass spectrometry and infra-red spectroscopy gave no structural clues on the identity of this material.

7.3.3:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOPENTENE IN ACETONITRILE CONTAINING TETRABUTYLAMMONIUM TETRAFLUOROBORATE

Perfluorocyclopentene (26) (7.0g, 33.0m.moles), was reduced at -1.8V at platinum cathode in anhydrous acetonitrile containing tetrabutylammonium tetrafluoroborate as the supporting electrolyte. During the 8hrs of electrolysis the current remained between 10-16mA. A blue/black coloured film formed on the electrode, but only after the electrolysis had been running for some 20 minutes.

At the end of electrolysis the electrode material was scraped off the cathode, washed with water, and dried under vacuum to leave a black fibrous solid (0.13g). Analysis found C, 52.6; H, 5.4; N, 2.5; F, 34.2%.
Investigation of the catholyte was not attempted in the light of earlier results (see 7.3.1. and 7.3.2.)

7.3.4:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOPENTENE AT A NICKEL ELECTRODE

Perfluorocyclopentene (26) (6.16g, 29.1m.moles), was reduced at -2.3V at a nickel electrode in anhydrous acetonitrile containing tetraethylammonium tetrafluoroborate. The current rose to 120mA, and then gradually fell as the electrode became "enveloped" in a blue/black coloured material.
Analysis and product work-up was as described in 7.3.2 with the exception: Analysis of the fine particulate powder (0.04g) from the bulk catholyte found C, 52.2; H, 2.8; N, 2.4; F, 27.1%.

7.3.5:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOPENTENE IN THE PRESENCE OF CYCLOHEXENE

Perfluorocyclopentene (26) (5.13g, 24.2m.moles) was reduced at -1.6V in the presence of cyclohexene (6.32g, 77.1m.moles) at a platinum cathode in anhydrous DMF containing tetraethylammonium tetrafluoroborate. The electrolysis current rose from 8.0mA to 16.0mA, and then gradually fell to 10.0mA as the electrode became coated in a blue/black coloured material. Analysis of the bulk catholyte by ^{19}F nmr showed only the presence of unreacted (26).

7.3.6:ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOPENTENE IN THE PRESENCE OF PERFLUOROCYCLOHEXENE

Perfluorocyclopentene (26) (3.14g, 14.8m.moles), was reduced at -1.9V in the presence of perfluorocyclohexene (20) (4.10g, 15.6m.moles), at a platinum cathode in anhydrous acetonitrile containing tetraethylammonium tetrafluoroborate as the supporting electrolyte. During the 6.5hrs of electrolysis the current rose from 25.0mA to 70.0mA. At the end of electrolysis, polymer formation was restricted to the lower edge of the electrode (covering approx.5% of the total electrode area).

The bulk catholyte was analysed by high field ^{19}F n.m.r. which indicated the presence of unreacted (26) and (20), a sharp singlet at 163.3ppm -characteristic of hexafluorobenzene (22), and two minor peaks at 126.3ppm (m) and 172.2ppm (m), characteristic of the reduction product from the reduction of (26).

Product volatiles were removed by transference *in vacuo* to a cold trap. Analysis by mass spectrometry-g.l.c. (capillary, temperature programmed), confirmed the presence of (22) M^+, 186, 41.6%, as the only product.

7.4:ELECTROCHEMICAL REDUCTION OF 1,2-DICHLORODECAFLUORO-CYCLOHEXANE

7.4.1: AT -1.65V

1,2-Dichlorodecafluorocyclohexane (31) (7.13g, 21.4m.moles), was reduced at -1.65V in a solution of tetraethylammonium tetrafluoroborate in anhydrous DMF at a platinum cathode. During the electrolysis the lower fluorocarbon layer formed by (31) disappeared, and the catholyte darkened from a pale yellow to an orange/brown colour.

Solvent and catholyte volatiles were removed from any catholyte involatiles (eg.tetraethylammonium salts, etc.) by transference *in vacuo* to a cold trap. A lower insoluble fluorocarbon layer (0.48g) was removed and shown by g.l.c. (capillary, temperature programmed), and by^{19}F n.m.r. to contain unreacted (31), and hexafluorobenzene (22) in good yield.

Subsequent analysis of the solvent/volatile fraction by mass spectrometry-g.l.c. (capillary, temperature programmed) indicated the presence of (22), M^+; 186, 15.5%, as the only volatile fluorocarbon product. ^{19}F n.m.r. confirmed the presence of (22) by a single resonance at 165.1ppm (s).

7.4.2: AT -1.45V

1,2-Dichlorodecafluorocyclohexane (31) (4.1g, 12.3m.moles) was reduced at -1.45V in a solution of tetraethylammonium tetrafluoroborate in anhydrous acetonitrile at aplatinum cathode.

During the electrolysis the lower fluorocarbon layer formed by (31) disappeared, and the catholyte darkened from a pale yellow to a dark brown colour.

Product volatiles were removed by transference *in vacuo* to a cold trap. Analysis by ^{19}F n.m.r. and mass spectrometry-g.l.c. (capillary, temperature programmed) showed the presence of perfluorocyclohexene (20) (41%), and hexafluorobenzene (22) (59%) in addition to (31).

7.5:ELECTROCHEMICAL REDUCTION OF 1,2-DICHLOROHEXAFLUORO-CYCLOBUTANE

7.5.1:AT -1.5V

1,2-dichlorohexafluorocyclobutane (32) (7.14g, 30.6m.moles), was reduced at -1.5V at a platinum cathode in anhydrous DMF containing tetraethylammonium tetrafluoroborate as the supporting electrolyte.

A sample of the bulk catholyte at the end of the electrolysis was removed. Analysis by high field ^{19}F n.m.r. showed it to contain unreacted (32), and two peaks at 119.6ppm (d) and 138.4ppm (t), which correspond to the chemical shifts observed for perfluorocyclobutene (23) dissolved in DMF.

7.5.2:AT -1.8V IN THE PRESENCE OF FURAN

1,2 dichlorohexafluorocyclobutane (32) (7.02g, 30.3m.moles), was reduced at -1.8V at a platinum cathode in anhydrous acetonitrile containing tetraethylammonium tetrafluoroborate as a supporting electrolyte, and Furan (2.06g, 30.3m.moles) as a Diels-Alder trapping agent. Within 20 mins. the catholyte was intensely coloured and a dark blue/black coloured film began to cover the anode facing side of the cathode. After 3.5hrs. both the cathode and the anode were cleaned, in order to maintain a reasonable current flow. The material which had been removed from the cathode was washed with water, and dried "in vacuo" to leave a black coloured solid (0.12g) - similar in appearance to that formed from reduction of perfluorocyclobutene (23) (see 7.2.2). Elemental analysis found: C, 49.3; H, 2.8; N, 2.9; F, 35.5; Cl, 1.46%.

Analysis of the bulk catholyte by ^{19}F n.m.r. indicated the presence of a low concentration of perfluorocyclobutene (23), in addition to unreacted (32).

^{19}F n.m.r. of the catholyte involatile fraction showed a complex mixture of products. Characterization was therefore not pursued further.

7.6:ELECTROCHEMICAL REDUCTION OF PERFLUORO-3,4-DIMETHYL-4-ETHYL-HEX -2-ENE

Perfluoro-3,4-dimethyl-4-ethyl-hex -2-ene (33) (7.4g, 14.8m.moles), was reduced at -2.0V at a platinum cathode in anhydrous acetonitrile containing tetraethylammonium tetrafluoroborate. (33) formed an insoluble layer at the bottom of the electrolysis cell. During electrolysis the catholyte darkened from an orange/red to a very dark brown colour.

A lower fluorocarbon layer (5.15g) was removed from the bottom of the catholyte compartment at the end of the electrolysis. Analysis by g.l.c. (capillary, temperature programmed) showed the presence of (33) (ca.83%), and one other component (ca.17%), which was subsequently isolated by preparative scale g.l.c. (column O), and shown to be: 2H-perfluoro-3,4-dimethyl-4-ethyl-hept-2-ene (35); (found: C, 24.6; H, 0.2; F, 74.5; $C_{10}H_1F_{19}$ requires: C, 24.9; H, 0.2; F, 74.9%); mass spectrum number 1; n.m.r. spectrum number 1; i.r. spectrum number 1.

^{19}F n.m.r. of the bulk catholyte, showed that very little fluorocarbon material had entered solution, consequently the "acetonitrile fraction" was not investigated further.

7.7:ELECTROCHEMICAL REDUCTION OF PERFLUORO-4-METHYL-PENT-3-ENE

Perfluoro-4-methyl-pent-3-ene (36) (6.54g, 21.8m.moles), was reduced at a platinum cathode in anhydrous acetonitrile containing tetraethylammonium tetrafluoroborate as the supporting electrolyte. The current passing fell from 230mA to 16mA during the 7hrs. of electrolysis, while the catholyte darkened in colour from a pale orange to a burgundy red.

Two 3ml. samples were removed from the bulk catholyte after

1.25 hrs. and 4.25 hrs. Analysis by high field ^{19}F n.m.r. suggested the presence of carbanion (37), by comparison of chemical shifts with those of an authentic sample provided by A.E.Bayliff.

After a period of 24hrs., a lower fluorocarbon layer was removed. Analysis by mass spectrometry-g.l.c. (capillary, 35^0C) showed it to contain two products (i) (ca.55%), and (ii) (ca.45%). Separation was achieved by analytical scale g.l.c. (OPN/Porasil C,110^0C), and by bubbling the exhaust gases from the outlet of the g.l.c. machine through Analar acetone, Fourier transform ^{19}F n.m.r. spectra of the two products was obtained. The two products were identified as:

(i) **perfluoro-1,3,3-trimethyl-4-ethyl-2-isopropylcyclo-1-butene (38)**; mass spectrum number 2; n.m.r. spectrum number 2.

(ii) **perfluoro-1,3,3-trimethyl-2-ethyl-4-isopropylidenecyclo-1-butene (39)**; mass spectrum number 3; n.m.r. spectrum number 3.

Approx. 3ml. of methyl iodide was added to 10ml. of the bulk catholyte, in an attempt to methylate any carbanion (37) which may have been formed. No fluorocarbon was eliminated from the solution; however subsequent analysis of the bulk catholyte by ^{19}F n.m.r. showed the absence of some peaks attributable to the carbanion.

Volatile material was removed from the bulk catholyte by transference *in vacuo* to a cold trap. Subsequent analysis by g.l.c. (capillary column, temperature programmed) showed the presence of acetonitrile as the major component. This fraction was not investigated further.

CHAPTER 8:

EXPERIMENTAL TO CHAPTER 4:

8.1:GENERAL PROCEDURE:

Typically one mole of substrate was added, under an atmosphere of dry nitrogen, to two moles of sodium predissolved as a 0.5% (by weight) sodium amalgam. A Schlenk containing the mixture was stoppered, and then carefully shaken manually, allowing adequate mixing of the fluorocarbon substrate with the sodium amalgam. After approximately one minute from the commencement of mixing, a vigorous exothermic reaction occurs; the Schlenk was therefore regularly cooled under a running cold water tap. During the exothermic reaction the visual appearance of the mixture dramatically changes from a metallic/mercury coloured globular mass to a fine black coloured powder, from which mercury droplets seperate during agitation.

After the exothermic rection had subsided, volatiles were transferred *in vacuo* to a cold trap, and analysed by g.l.c.-mass spectrometry.

[CAUTION: the reaction is carried out in a sealed system, and consequently safety procedures should be carefully adhered to; ie.the reaction should be carried out behind a blast screen, especially in the knowledge that a vigorous exotherm accompanies the reaction.]

8.2:REDUCTION OF PERFLUORO-3,4-DIMETHYLHEX-3-ENE (51):

Perfluoro-3,4-dimethylhex-3-ene (51) (10.3g, 25.6mmol) was added to a 0.5% sodium amalgam (containing Na:1.2g, 52.2mmol; Hg:234.6g) as detailed in the general procedure. After reaction, a volatile fraction (7.7g) was removed by transference *in vacuo* to a a cold trap. Subsequent analysis by g.l.c.(capillary, temperature programmed) showed only one product, which was identified as:

perfluoro-3,4-dimethylhex-2,4-diene (61) (75.1%)
(Found: C, 27.0; F, 72.8. C_8F_{14} calc. for: C, 26.5; F, 73.5%); n.m.r. spectrum number 4; i.r. spectrum number 2; mass spectrum number 4.

A number of such reductions were performed, the details of which are tabulated below:

(51) (g,mmol)	Na (g,mmol)	Hg (g)	YIELD (61) %	CONVERSION %
10.2, 28.2	1.4, 3.5	228	85	100
10.8, 29.8	1.5, 3.8	239	85	100
10.4, 28.7	1.4, 3.5	239	80	100
10.0, 27.6	1.3, 3.3	230	74	100

8.3:REDUCTION OF PERFLUOROBICYCLOPENTYLIDENE (43):

Perfluorobicyclopentylidene (43) (2.5g, 5.8mmol) was added to a 0.5% sodium amalgam (containing Na:0.4g, 16.1mmol; Hg:74.0g) as detailed in the general procedure. After

reaction a volatile fraction (1.9g) was removed by transference *in vacuo* to a a cold trap. Subsequent analysis by g.l.c.(capillary, temperature programmed) showed the presence of only one product, which was identified as:
perfluorobicyclopent-1,1'-enyl (56) (66.1%)
(Found: C, 31.0; F, 68.5. $C_{10}F_{14}$ calc. for: C, 31.1; F, 68.9%); n.m.r. spectrum number 5; i.r. spectrum number 3; mass spectrum number 5.

8.4:REDUCTION OF PERFLUOROCYCLOBUTENE DIMERS (44) & (45):

The dimers of perfluorocyclobutene (44) & (45) (1.9g, 6.0mmol) were added to a 0.5% sodium amalgam (containing Na:0.30g, 13.05mmol; Hg:54.2g) as detailed in the general procedure. After reaction a volatile fraction (1.0g) was removed by transference *in vacuo* to a a cold trap. Subsequent analysis by g.l.c.(capillary, temperature programmed) showed the presence of only one product, which was identified as:
perfluorobicyclobut-1,1'-enyl (57) (78.0%) (Found: C,33.9; F,66.2; C_8F_{10} calc. for: C,33.6; F,66.4%); n.m.r. spectrum number 6; i.r. spectrum number 4; mass spectrum number 6.

8.5:REDUCTION OF 1,4-DIBROMO-2,3-DICHLOROHEXAFLUOROBUTANE (65):

1,4-dibromo-2,3-dichlorohexafluorobutane (65) (4.4g, 11.1mmol) was added to a 0.5% sodium amalgam (containing Na:0.52g, 22.62mmol; Hg:107.13g) as detailed in the general procedure. After reaction a volatile fraction (2.1g) was removed by transference *in vacuo* to a cold trap. Subsequent analysis by g.l.c. (capillary column, temperature programmed) showed the presence of two products: (i) (17.6%), and (ii) (8.9%). The two products were isolated by preparative scale g.l.c. (Column O, 110^{o}C) and identified as:

(i) **1-bromo-2-chlorohexafluorobut-3-ene (66)**

(Found: C, 17.9; C_4BrClF_6 requires: C, 17.3%); n.m.r. spectrum number 7; i.r. spectrum number 5; mass spectrum number 7

(ii) **1-bromo-2,4-dichloropentafluorobut-3-ene (67)**

(Found: C, 16.6; $C_4BrCl_2F_5$ requires: C, 16.3%); n.m.r. spectrum number 8; i.r. spectrum number 6; mass spectrum number 8

8.6:OTHER ATTEMPTED REDUCTIONS:

The table below summarises attempted reductions of various fluorocarbon substrates, all of which failed to yield any volatile products -analysed by g.l.c.(capillary column)

SUBSTRATE (g, mmol)	Na (g,mmol)	Hg g	%AGE RECOVERY OF SUBSTRATE
F-1,2-dicyclobutyl-cyclobutene (3.0g,6.2mmol)	0.3, 13.9	59.4	77
F-2-methylpent-2-ene (5.06g, 16.9mmol)	0.8, 34.8	158.2	60
F-spiro(cyclobutane-1',2-bicyclo(5.2.0)-non-(1,7)-ene (2.5g, 5.2mmol)	0.3, 14.4	53.3	66
1-iodofluorohexane (5.9g, 13.3mmol)	0.6, 27.0	104.7	88
F-3,4-dimethyl-4-ethylhex-2-ene (6.1g, 12.2mmol)	0.6, 26.1	114.4	92

CHAPTER 9:

EXPERIMENTAL TO CHAPTER 5:

OXYGEN NUCLEOPHILES:

9.1:REACTIONS WITH ALCOHOLS:

9.1.1:DIENE (61) WITH NEUTRAL METHANOL

A mixture containing diene (61) (2.0g, 5.5mmol), methanol (0.7g, 22.2mmol), and acetonitrile (2ml) was stirred at room temperature for 7 days. Volatile material was transferred *in vacuo* to a cold trap, and shown by g.l.c (capillary column) to contain only diene (61), methanol, and acetonitrile.

9.1.2:DIENE (61) WITH METHANOL UNDER BASIC CONDITIONS

To experiment 9.1.1 was added sodium carbonate (0.9g, mmol). Stirring was continued for a further 7 days, after which time volatile material was transferred *in vacuo* to a cold trap. The lower layer (1.4g) was removed and shown by g.l.c. (capillary column) to contain two products (i) (90.2%) and (ii) (9.8%) which, when purified by preparative scale g.l.c. (Col DNP, 110°C), were identified as:

(i) <u>2-methoxy-perfluoro-3,4-dimethylhex-2,4-diene (89)</u> (Found: C, 28.8; H, 0.7; F, 65.9; $C_9F_{13}H_3O$ requires: C, 28.9; H, 0.8; F, 66.0%); n.m.r. spectrum number 9; i.r. spectrum number 7; mass spectrum number 9

(ii) 2,5-dimethoxy-perfluoro-3,4-dimethylhex-2,4-diene (90)
n.m.r spectrum number 10; i.r. spectrum number 8; mass spectrum number 10

9.1.3:DIENE (56) WITH NEUTRAL METHANOL:

Perfluorobicyclopent-1,1'-enyl (56) (2.0g, 5.2 mmol) and methanol (0.8g, 25.0 mmol) were mixed at room temperature, whereupon an immediate exothermic reaction occured. The mixture was stirred and, after 48hrs, a sample from the homogeneous mixture was taken and shown by g.l.c.(capillary column) to contain one product (90%), which was identified as: 2-methoxy-perfluorobicyclopent-1,1'-enyl (91)
(Found: C, 33.4; H, 0.8; F, 57.9; $C_{11}F_{13}H_3O$ requires: C, 33.2; H, 0.8; F, 62.1%); n.m.r. spectrum number 11; i.r. spectrum number 9; mass spectrum number 11.

The reaction was allowed to continue for a further 10 days. Volatile material was transferred *in vacuo* to a cold trap and shown by g.l.c. to contain only methanol. The crystalline solid which remained was identified as:
2,2'-dimethoxy-perfluorobicyclopent-1,1'-enyl (92)
(Found: C, 35.0; H, 0.9; F, 55.7; $C_{12}F_{12}H_6O_2$ calc. for: C, 35.1; H, 1.5; F, 55.6%); n.m.r. spectrum number 12; i.r. spectrum number 10; mass spectrum number 12.

9.1.4:DIENE (57) WITH NEUTRAL METHANOL

Upon the addition of perfluorobicyclobut-1,1'-enyl (57) (2.0g, 6.99mmol) to methanol (1.0g, 31.3 mmol) an immediate exothermic reaction occured forming a white crystalline solid within 1hr. Volatile material was transferred *in vacuo* to a cold trap which was subsequently shown to be methanol by comparison of g.l.c. (capillary column) retention time with that of an authentic sample. The crystalline solid which remained was identified as:

2,2'-dimethoxy-perfluorobicyclobut-1,1'-enyl (93)

(Found: C, 39.5; H, 1.8; $C_{10}F_8H_6O_2$ requires: C, 38.7; H, 1.9%) n.m.r. spectrum number 13; i.r. spectrum number 11; mass spectrum number 13

9.2:REACTION WITH CATECHOL

9.2.1:DIENE (61) WITH CATECHOL

A mixture of diene (61) (2.0g, 5.5mmol), catechol (0.6g, 5.7mmol), potassium carbonate (1.73g, 12.5mmol) and acetonitrile (30ml) was stirred at room temperature for 7 days. After filtration of solids, water was added to the reaction mixture, and the lower layer thus formed (1.1g) was removed. Volatile material (1.0g) was transferred *in vacuo* to a cold trap and shown by g.l.c.(capillary column) to be a single compound, identified as:

2,3,4,5-tetrakis-(trifluoromethyl)-1,6-benzodioxocin (94)

(Found: C, 38.6; H, 0.8; $C_{14}F_{12}H_4O_2$ requires: C, 38.9; H, 0.9%) n.m.r. spectrum number 14; i.r. spectrum number 12; mass spectrum number 14.

9.3:REACTIONS WITH ETHYLENE GLYCOL

9.3.1:DIENE (61) WITH ETHYLENE GLYCOL

A mixture of diene (61) (2.05g, 5.7mmol), ethylene glycol (0.4g, 6.1mmol), potassium carbonate (1.8g, 12.9 mmol) and sodium dried diethyl ether (30ml) was stirred at room temperature. After 5 days volatile material was transferred *in vacuo* to a cold trap and shown by g.l.c.(capillary column) to contain one product in addition to the diethyl ether solvent. Water was added to the volatile fraction and the lower layer thus formed was removed, purified by preparative scale g.l.c.(column O, 100°C), and shown to be: **5-fluoro-6-(perfluoro-3-methylprop-2-ene)-7-difluoro-1,4-dioxep-5-ene (97)**

n.m.r. spectrum number 15; i.r. spectrum number 13; mass spectrum number 15.

9.3.2:DIENE (56) WITH ETHYLENE GLYCOL

Bicyclopent-1,1'-enyl (56) (2.0g, 5.2mmol) and ethylene glycol (0.4g, 6.6mmol) in sodium dried diethyl ether (30ml) were stirred at room temperature. After 14 days volatile material was transferred *in vacuo* to a cold trap. The lower layer (1.4g) was removed and shown by g.l.c. (capillary) to consist of two components, (i) (71.1%) and (ii) (21.8%), which were isolated by preparative scale g.l.c. (column O, 165°C) and shown to be:

(i) [Ethane-1,2-dialkoxy]-2',2'-tridecafluoro-1H-di[cyclopentan-6-ene] (98) (Found: C, 33.9; H, 1.1; F; 57.1; $C_{12}F_{13}H_5O_2$ requires: C, 33.6; H, 1.2; F, 57.7%) n.m.r. spectrum number 16; i.r. spectrum number 14; mass spectrum number 16.

(ii) [Ethane-1,2-dialkoxy]-2',7'-dodecafluorodi-[1-cyclopentenyl] (99) (Found: C, 35.5; H, 0.7; F; 55.3; $C_{12}F_{12}H_4O_2$ requires: C, 35.3; H, 1.0; F, 55.9%) n.m.r. spectrum number 17; i.r. spectrum number 15; mass spectrum number 17.

9.4:REACTION WITH POTASSIUM HYDROXIDE

9.4.1:DIENE (61) WITH POTASSIUM HYDROXIDE

A mixture of diene (61) (1.5g, 4.2 mmol), powdered potassium hydroxide (0.28g, 5.0 mmol) and dimethyl formamide (15ml) was stirred at room temperature for 14 days. Product volatiles were removed by transferrence *in vacuo* to a cold trap. Subsequent analysis by g.l.c. (capillary) showed the presence of one product only, which was identified as:

perfluorotetramethylfuran (102)

n.m.r. spectrum number 18; i.r. spectrum number 16; mass spectrum number 18.

SULPHUR NUCLEOPHILES:

9.5:REACTIONS WITH POTASSIUM SULPHIDE

9.5.1:DIENE (61) WITH POTASSIUM SULPHIDE:

A mixture of diene (61) (1.5g, 4.2 mmol), potassium sulphide (0.6g, 5.5 mmol) and dimethyl formamide (20ml) was stirred at room temperature for 14 days. Volatile material was transferred *in vacuo* to a cold trap. The upper layer was shown by g.l.c.(capillary column) to contain two products and dimethyl formamide, and the lower layer to contain the same two products and unreacted diene (61). Separation of the two products was afforded by preparative scale g.l.c. (column O, 100°C), and were subsequently identified as:

(i) perfluorotetramethylfuran (102); and

(ii) **perfluorotetramethylthiophene (103)**

n.m.r. spectrum number 19; i.r. spectrum number 17; mass spectrum number 19.

9.5.2:DIENE (56) WITH POTASSIUM SULPHIDE

A mixture of perfluorobicyclopent-1,1'-enyl (56) (1.7g, 4.4mmol), potassium sulphide (0.59g, 5.4mmol) and dimethyl formamide (20ml) was stirred at room temperature. After 14 days volatile material was transferred *in vacuo* to a cold trap and shown by g.l.c.(capillary column) to contain one product. Water was added to the volatile fraction, and the solid product thus formed, was extracted with diethyl ether (3 x 100ml), dried ($MgSO_4$), and evaporated to yield a white coloured solid. Sublimation *in vacuo* of this material gave a crystalline solid (0.4g), pure by ^{19}F n.m.r. and t.l.c., which was subsequently identified as:

perfluoro-1,2,3,5,6,7-hexafluoro-dicyclopenta [b,d]-thiophene (104)

n.m.r. spectrum number 20; i.r. spectrum number 18; mass spectrum number 20.

9.5.3:DIENE (57) WITH POTASSIUM SULPHIDE

A mixture of perfluorobicyclobut-1,1'-enyl (57) (1.5g, 5.2mmol), potassium sulphide (0.65g, 5.9mmol) and dimethyl formamide (20ml) was stirred at room temperature for 14 days. Product volatiles were removed by transferrence *in vacuo* to a cold trap and subsequent analysis (g.l.c.-mass spectrometry) showed the presence of a small quantity of unreacted diene and dimethyl formamide only. ^{19}F n.m.r. of the involatile fraction showed a complex mixture of products. The reaction was not pursued further.

9.6:REACTION WITH 3,4-DIMERCAPTOTOLUENE:

9.6.1:DIENE (61) WITH 3,4-DIMERCAPTOTOLUENE:

A mixture of diene (61) (2.0g, 5.6mmol), 3,4-dimercaptotoluene (0.9g, 5.6mmol), potassium carbonate (1.8g, 13.0mmol), and acetonitrile (30ml) was stirred at room temperature for 5 days. After filtration of solids, water (150ml) was added. The product was then extracted with diethyl ether (2 x 100ml), dried ($MgSO_4$), and the ether removed on a rotary evaporator to leave a yellow coloured oil. Volatile material was transferred *in vacuo* to a cold trap and shown by g.l.c.-mass spectrometry to contain two isomers of one product, subsequently identified as:

2,3,4,5-tetrakis-(trifluoromethyl)-1,6-benzodithiocin (106)

(Found: C, 38.3; H, 0.9; $C_{15}F_{12}H_6S_2$ requires: C, 36.7; H, 1.2%) n.m.r. spectrum number 21; i.r. spectrum number 19; mass spectrum number 21.

OTHER NUCLEOPHILES:

9.7:REACTIONS WITH SODIUM IODIDE

9.7.1:DIENE (61) WITH SODIUM IODIDE

Diene (61) (3.3g, 9.0mmol), sodium iodide (2.9g, 19.1 mmol) and acetonitrile (7ml) were sealed in a carius tube and heated at 140°C for 4 days in a rocking autoclave. The tube was opened and the volatiles transferred *in vacuo* to a cold trap. Analysis by g.l.c. (capillary column) of the lower layer showed the presence of one major product (22%), and a number of minor products in addition to unreacted diene (61). The upper solvent layer was shown to contain the same major product (21%) without the presence of the minor products. The upper solvent layer was therefore isolated and mixed with water (50 ml). The lower layer thus formed was removed, and purified by preparative scale g.l.c. (column O, 110°C) to give the major product which was subsequently identified as:

5-iodo-perfluoro-1,2,5-trimethylcyclopentadiene (109)
(Found: C, 22.3; F, 48.5; I, 28.6; $C_8F_{11}I$ requires: C, 22.2; F, 48.4; I, 29.4%) n.m.r. spectrum number 22; i.r. spectrum number 20; mass spectrum number 22.

Purification of the minor products by preparative scale g.l.c. proved difficult, and was therefore not pursued.

9.8:REACTIONS WITH FLUORIDE ION

9.8.1:DIENE (57) WITH CAESIUM FLUORIDE

Perfluorbicyclobut-1,1'-enyl (57) (2.0g, 7.0mmol) was added to a sample of well dried and ground caesium fluoride (1.13g, 7.4 mmol) in tetraglyme (6ml), whereupon an exothermic reaction occured immediately, and the solution turned a deep orange/red in colour. Stirring was continued for 4 days, after which time the mixture was allowed to settle for ca. 0.5hr. to allow unreacted caesium fluoride and diene (57) to settle as a lower layer. A sample from the transparent coloured homogeneous upper layer was removed. Analysis by ^{19}F n.m.r. showed the sample to contain a mixture of products, none of which could be identified from the n.m.r. data alone.

Mixing was continued for a further 6 days. The mixture was again allowed to settle, and the homogeneous upper layer removed. Sublimation *in vacuo* gave a transparent crystalline solid, as the only isolated product, which was subsequently identified as:

2,6-Di-[1'-cyclobutylidene]-dicyclobutylidene (111)

(Found: C, 33.3; F, 67.0; $C_{16}F_{20}$ requires: C, 33.6; F, 66.4%); n.m.r. spectrum number 23; i.r. spectrum number 21; mass spectrum number 23.

9.8.2:REACTION OF TRIENE (111) WITH CAESIUM FLUORIDE

A small quantity of dry caesium fluoride was carefully introduced into a dry n.m.r. tube, to which was added tetraglyme (4ml) and a sample of triene (111) (in molar deficiency to fluoride). The mixture was vigorously shaken for ca. 0.5hr. Analysis by ^{19}F n.m.r. identified the presence of carbanion (112) ^{19}F n.m.r. spectra number 24.

CHAPTER 10:

EXPERIMENTAL TO CHAPTER 6:

10.1:FREE RADICAL ADDITION REACTIONS:

10.1.1:DIENE (61) WITH ACETALDEHYDE:

A mixture of diene (61) (1.2g, 3.3mmol) and acetaldehyde (0.9g, 20.4mmol) contained in a carius tube was degassed and sealed *in vacuo*. After six days irradiation with gamma-rays, volatile material was transferred *in vacuo* to a cold trap. The upper layer was removed and shown by g.l.c.(capillary column) to contain one major product (83%), which was identified as 2,4,6-trimethyl-1,3,5-trioxane (113) by a comparison of its mass spectrum and ^{1}H n.m.r. spectra with an authentic sample. The lower layer was shown by mass spectrometry-g.l.c.(capillary column) to contain four products: (113) (73%), and three isomers of a 1:1 adduct of acetaldehyde and diene (61) (27%). The reaction was not pursued further due to the low yield and difficulty of purification of products.

10.1.2:DIENE (61) WITH DIMETHYL-ETHER

Diene (61) (1.5g, 4.14mmol) was contained in a Carius tube and degassed. Dimethyl ether (1.5g, 32.6mmol) was then transferred *in vacuo* into the tube, which was then sealed and irradiated with gamma rays for 21 days. Volatile material was transferred *in vacuo* to a cold trap and shown by mass spectrometry-g.l.c.(capillary column) to contain three isomers of a 1:1 adduct of dimethyl ether and diene (61) (10%). The reaction was not pursued further due to the low yield, and difficulty of purification of products.

10.1.3:DIENE (56) WITH DIETHYL ETHER

A mixture of diene (56) (2.1g, 5.4mmol) and diethyl ether (1.1g, 14.6mmol) contained in a Carius tube was degassed, sealed *in vacuo*, and irradiated with gamma rays for 4 days. Volatile material was transferred *in vacuo* to a cold trap and shown by mass spectrometry-g.l.c.(capillary column) to contain only diene (56) and diethyl ether. The involatile material (0.06g) was subjected to a second vacuum transference, and subsequently shown by mass spectrometry-g.l.c.(capillary column) to contain a mixture of isomers of a 1:1 adduct of diethyl ether and diene (56). In view of the low yield and difficulty of purification of products, the reaction was not pursued further.

10.2:ATTEMPTED CYCLO-ADDITION REACTIONS:

10.2.1:REACTION OF DIENE (56) WITH CYCLOHEXENE

Diene (56) (2.05g, 5.2mmol) and cyclohexene (0.4g, 5.2mmol) were contained in a rotaflo tube, and heated at 120°C for 11 days. Volatile material was transferred *in vacuo* to a cold trap, and shown by g.l.c.(capillary column) to contain only diene (56) and cyclohexene.

10.2.2:REACTION OF DIENE (61) WITH DIETHYLCYANAMIDE

10.2.2a:AT 18°C

A mixture containing diene (61) (2.1g, 5.8mmol), diethylcyanamide (0.6g, 6.0mmol), and dichloromethane (25ml) was stirred at room temperature for 3 weeks. Volatile material was transferred *in vacuo* to a cold trap, and shown by g.l.c.(capillary column) to contain only diene (61), diethyl cyanamide and dichloromethane.

10.2.2b:AT 100°C

Diene (61) (2.0g, 5.4mmol), diethylcyanamide (0.6g, 6.0mmol) and dichloromethane (25ml) were sealed in a Carius tube and heated at 100°C for 4 days in a rocking autoclave. The tube was opened and volatile material transferred *in vacuo* to a cold trap. Subsequent analysis by g.l.c.(capillary column) showed only the presence of diene (61), diethylcyanamide and dichloromethane.

10.3:CHARGE-TRANSFER REACTIONS:

10.3.1:GENERAL PROCEDURES:

All syntheses were carried out at room temperature and atmospheric pressure.

Acetonitile (doubly distilled from P_2O_5, and stored over dry nitrogen) was used as solvent for all reactions.

Decamethylferrocene (provided by Dr. V.C.Gibson) was purified before use by sublimation *in vacuo*.

10.3.2:REACTION OF DIENE (43) WITH DECAMETHYLFERROCENE

Perfluorobicyclopentylidene (129.9mg, 0.306mmol) was added to a solution of decamethylferrocene (100mg, 0.307mmol) in acetonitrile (20ml), whereupon an immediate colour change occurred (light orange to dark green). The mixture was stirred at room temperature for a further 3 days. After evaporation of all but approx. 3ml of the solvent, the solution was refrigerated overnight at -20°C. The dark green crystals which formed were isolated and dried *in vacuo* and identified as:

$\underline{[Fe(\eta\text{-}C_5Me_5)_2]}^{\cdot +}\underline{[C_{10}F_{14}]}^{\cdot -}$ (Found: C, 50.78; H, 4.21; $C_{30}H_{30}F_{14}Fe$ requires: C, 50.58; H, 4.24%)

i.r. spectrum number 22

10.3.3:OTHER CHARGE TRANSFER REACTIONS

Other attempted charge transfer complexation reactions, conducted in a similar manner to 9.3.1, are detailed below. No complex has yet been fully characterized from any of these reactions.

1: REACTION:

Decamethylferrocene (100mg, 0.307mmol) + mixture of the dimers of perfluorocyclobutene (99.3mg, 0.307mmol)

colour change: yellow to dark green (immediate)

elemental analysis: C, 55.3; H, 4.7%
C, 51.7; H, 5.4%
C, 49.5; H, 4.7%

2: REACTION:

Decamethylferrocene (101mg, 0.310mmol) + perfluorobicyclobut-1,1'-enyl (92mg, 0.322mmol)

colour change: yellow to dark green (immediate)

elemental analysis: C, 57.2; H, 5.4; F,23.2%
C, 57.7; H, 5.2; F, 23.8%
C, 57.3; H, 5.1%

3: REACTION:

Decamethylferrocene (100mg, 0.307mmol) + perfluoro-3,4-dimethylhex-2,4-diene (117mg, 0.322mmol)

colour change: yellow to green (v.slow reaction)

elemental analysis: C, 50.7; H, 5.7; F,29.8%
C, 50.3; H, 5.4%

4: TEST REACTION:

Decamethylferrocene + perfluoro-trisisopropyltriazine

colour change: yellow to dark green (immediate)

elemental analysis: C, 41.6; H, 5.5; N, 1.8%

C, 41.9; H, 5.1; N, 2.0%

5: TEST REACTION:

Bisbenzene chromium + perfluorobicyclopentylidene

colour change: green to yellow (immediate)

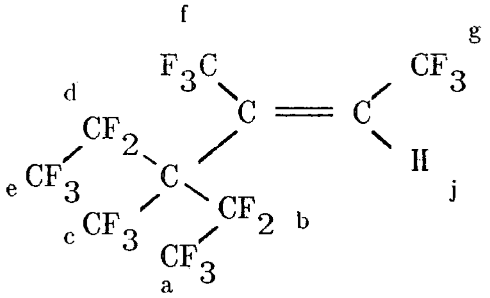
elemental analysis: none available.

APPENDIX 1: N.M.R. SPECTRA

1. 2H-perfluoro-3,4-dimethyl-4-ethylhex -2-ene (35)
2. Perfluoro-1,3,3-trimethyl-4-ethyl-2-isopropyl-cyclo-1-butene (38)
3. Perfluoro-1,3,3-trimethyl-2-ethyl-4-isopropylidene-cyclo-1-butene (39)
4. Perfluoro-3,4-dimethylhex-2,4-diene (61)
5. Perfluorobicyclopent-1,1'-enyl (56)
6. Perfluorobicyclobut-1,1'-enyl (57)
7. 1-Bromo-2-chlorohexafluorobut-3-ene (66)
8. 1-Bromo-2,4-dichloropentafluorobut-3-ene (67)
9. 2-Methoxyperfluoro-3,4-dimethylhex-2,4-diene (89)
10. 2,5-Dimethoxyperfluoro-3,4-dimethylhex-2,4-diene (90)
11. 2-Methoxyperfluorobicyclopent-1,1'-enyl (91)
12. 2,2'-Dimethoxyperfluorobicyclopent-1,1'-enyl (92)
13. 2,2'-Dimethoxyperfluorobicyclobut-1,1'-enyl (93)
14. 2,3,4,5-Tetrakis-(trifluoromethyl)-1,6-benzo-dioxocin (94)
15. 5-Fluoro-6-(perfluoro-3-methylprop-2-ene)-7-difluoro-1,4-dioxep-5-ene (97)
16. (Ethane-1,2-dialkoxy)-2,2'-tridecafluoro-1H-di(cyclopentan-6-ene) (98)
17. (Ethane-1,2-dialkoxy)-2,7'-dodecafluoro-di(1-cyclopentenyl) (99)

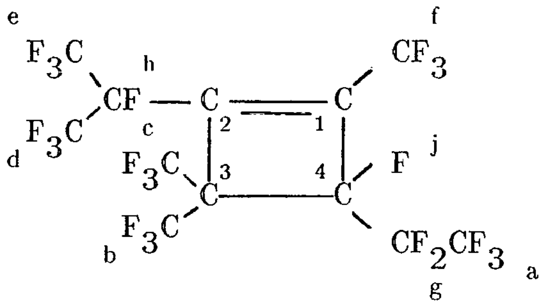
18. Perfluorotetramethylfuran (102)
19. Perfluorotetramethylthiophene (103)
20. Perfluoro-1,2,3,5,6,7-hexafluorodicyclopenta-[b,d]thiophene (104)
21. 2,3,4,5-Tetrakis-(trifluoromethyl)-1,6-benzo-dithiocin (106)
22. 5-Iodoperfluoro-1,2,5-trimethylcyclopentadiene (109)
23. 2,6-di(1'-cyclobutylidene)dicyclobutylidene (111)
24. 2,6-di(1'-cyclobutylidene)dicyclobutyl anion (112)

N.M.R. NUMBER: 1



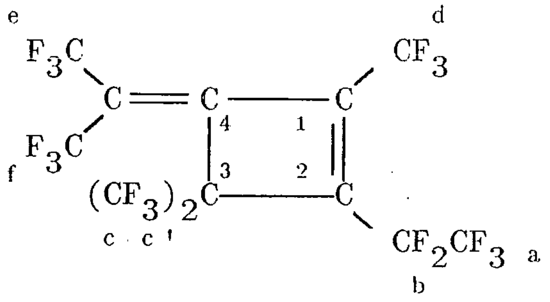
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
^{19}F n.m.r. data			
58.8	broad d (J 38)	3	f
63.0	m of d (J 6.5)	3	g
78.3	d (J 11.8)	3	c
80.1	d (J 10.6)	3	e
80.8	d(J 39) of q(J 13.4)	3	a
101.8 & 108.5	AB (J 273) lower limb q (J 38)	2	d
104.5 & 108.6	AB (J 305) lower limb d (J 30)	2	b
^{1}H n.m.r. data			
5.0	q (J 6.6)		j

N.M.R. NUMBER: 2



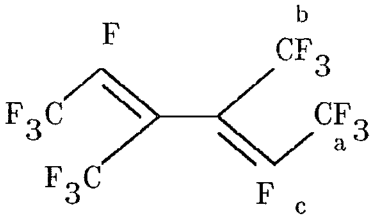
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
62.0	m	3	f
62.8	m	3	e
63.6m	m (J 10)	3	d
72.3	m	3	c
74.2	m	3	b
79.3	m	3	a
111.6 & 118.2	AB (J 290) upper limb q (J 33)	2	g
159.9	m (J 10)	1	h
175.5	m	1	j

N.M.R. NUMBER: 3



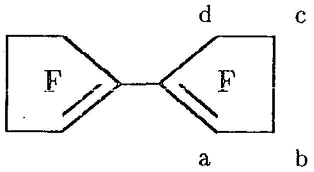
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
59.7	m	3	e
60.8	m	3	f
63.0	m	3	d
64.3	m	6	c and c'
81.4	broad s	3	a
109.2	m	2	b

N.M.R. NUMBER: 4



CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
63.0	d (J 18.4)	3	a
71.1	s	3	b
105.0	broad d (J 9.2)	1	c

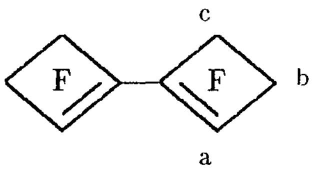
N.M.R. NUMBER: 5



CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
107.1	t? (J 15)	2	d
108.9	m	1	a
119.0	d? (J 15)	2	b
129.7	m	2	c

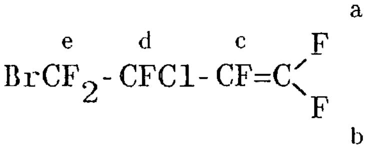
NB. the molecule is behaving as a $[AA'NN'QQ'X]_2$ system.

N.M.R. NUMBER: 6



CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
99.3	broad s	1	a
117.6	m	2	c
119.4	m	2	b

N.M.R. NUMBER: 7

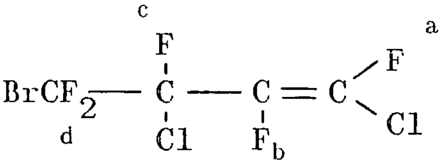


$$\overset{e}{\mathrm{BrCF_2}}\text{-}\overset{d}{\mathrm{CFCl}}\text{-}\overset{c}{\mathrm{CF}}{=}\mathrm{C}\begin{matrix}\diagup \mathrm{F}^{a}\\ \diagdown \mathrm{F}_{b}\end{matrix}$$

CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
61.7 & 63.4	AB (J 177)	2	e
91.9	d(J 56) of d(J 38)	1	b
105.4	d(J 169) of d(J 94) of d(J 47)	1	a
129.0	m	1	d
178.7	d(J 115) of m	1	c

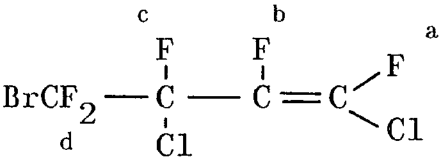
N.M.R. NUMBER: 8

isomer 1:



CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
61.1	AB (see *)	2	d
106.2	d(J 132) of d(J 48)	1	a
127.5	m	1	c
149.3	d(J 129) of m	1	b

isomer 2:



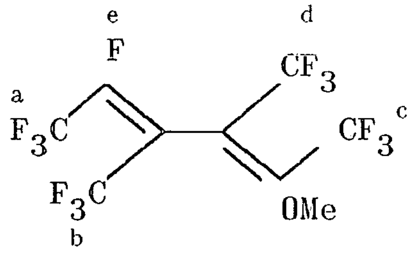
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
61.1	AB (see *)	2	d
88.2	d (J 20)	1	a
123.8	d(J 16) of t(J 15)	1	c
137.9	m	1	b

* resonance at 61.1 = overlapping AB for both isomers 1 & 2

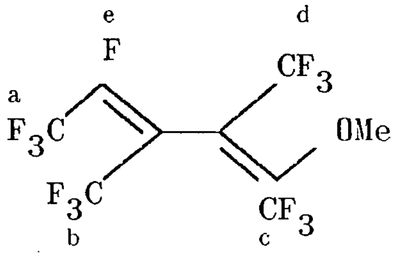
NB. ratio 1:2 = 5:4 (from integration)

^{13}C n.m.r. shows only one triplet at 117.6 (J 315), other peaks between 145.6 and 103.3 unassigned.

N.M.R. NUMBER: 9

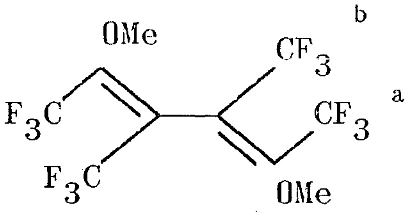


CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
61.1	s	3	c
61.7	d (J 17)	3	a
64.1	s	3	d
69.1	s	3	b
106.5	m	1	e



CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
56.8	q (J 11.8)	3	c
61.5	d (J 16.9)	3	a
64.1	s	3	d
69.9	d (J 6.6)	3	b
109.2	m	1	e

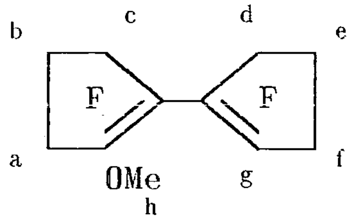
N.M.R. NUMBER: 10



(three isomers)

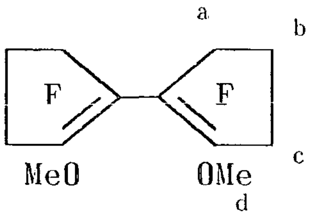
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
isomer 1:			
57.2	m	1	a
64.3	q (J 11.6)	1	b
isomer 2:			
61.3	s	0.56	a
64.0	s	0.56	b
isomer 3:			
61.1	s	0.68	a
64.9	s	0.68	b

N.M.R. NUMBER: 11



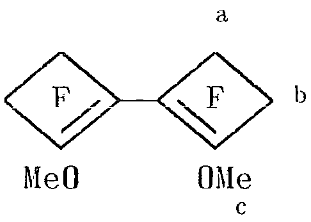
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
^{19}F n.m.r data			
105.6	s	2	c
107.8	s	2	d
113.0	s	2	a
114.4	m	1	g
119.5	d (J 14)	2	f
129.7	s	2	b
130.5	s	2	e
^{1}H n.m.r data			
4.2	s		h

N.M.R. NUMBER: 12



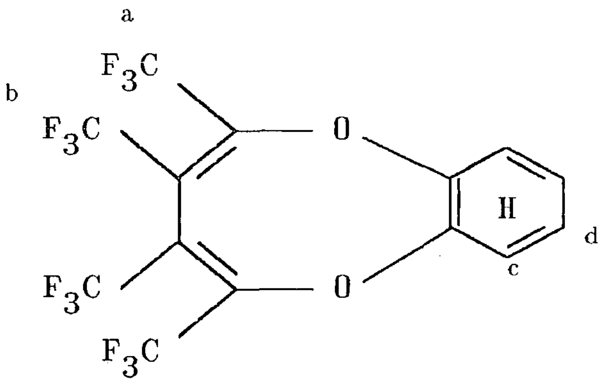
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
^{19}F n.m.r. data			
106.5	s	1	a
115.6	s	1	c
131.0	s	1	b
^{1}H n.m.r data			
4.1	s		d

N.M.R. NUMBER: 13



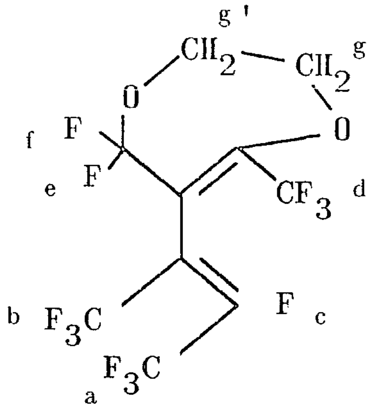
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
^{19}F n.m.r. data			
111.1	m	1	a
113.9	m	1	b
^{1}H n.m.r. data			
4.2	s		c

N.M.R. NUMBER: 14



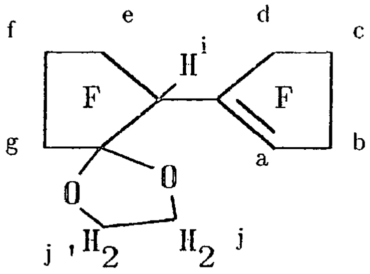
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
^{19}F n.m.r. data			
57.5	m	3	a
66.2	m	3	b
^{1}H n.m.r. data			
6.97	m	1	c
7.03	m	1	d

N.M.R. NUMBER: 15



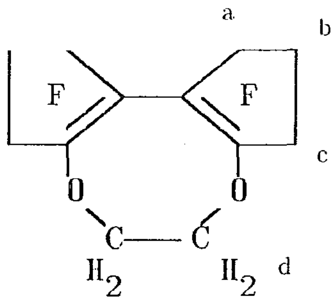
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
^{19}F n.m.r. data			
61.4	d (J 16)	3	a
70.0	s	1	f
70.5	q (J 11)	1	e
70.7	s	3	b
83.3	m	3	d
106.8	m	1	c
^{1}H n.m.r. data			
4.2	m		g and g'
4.3	m		

N.M.R. NUMBER: 16



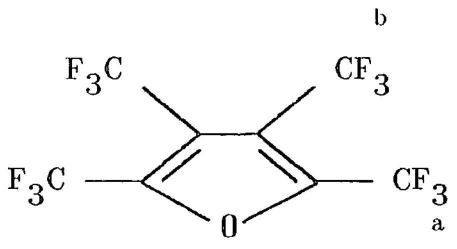
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
^{19}F n.m.r. data			
108.2 & 109.6 each limb d (J 10.4)	AB (J 258)	2	d
109.8 & 117.1	AB (J 244)	2	b
114.4	m	1	a
119.0 & 120.7 each limb d (J 16.2)	AB (J 263)	2	c
128.2 & 135.3	AB (J 249)	2	e
130.3 & 131.5	AB (J 242)	2	f
132.1 & 133.5	AB (J 255)	2	g
^{1}H n.m.r. data			
4.1	m	4	j & j'
3.7	m	1	i

N.M.R. NUMBER: 17



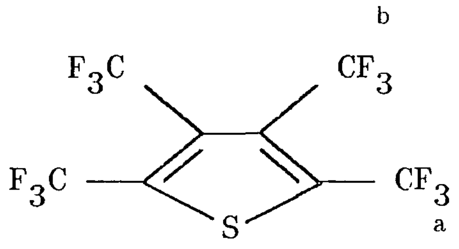
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
^{19}F n.m.r. data			
106.8	s	1	a
119.5	m	1	c
131.2	s	1	b
^{1}H n.m.r. data			
2.2	s		d

N.M.R. NUMBER: 18



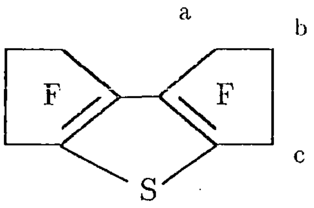
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
57.0	m	1	a
61.7	m	1	b

N.M.R. NUMBER: 19



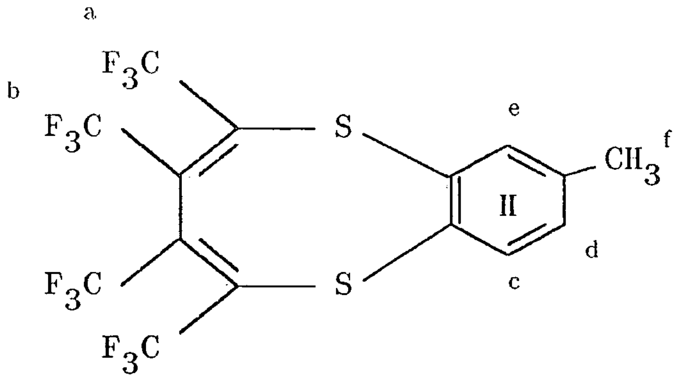
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
54.4	m	1	a
56.5	m	1	b

N.M.R. NUMBER: 20



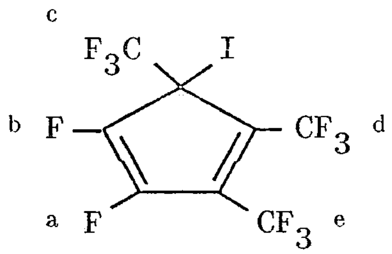
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
102.6	s	1	a
106.0	s	1	c
124.2	s	1	b

N.M.R. NUMBER: 21



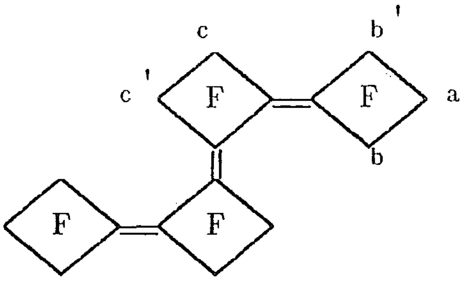
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
^{19}F n.m.r. data			
58.8	m	3	a
59.4	m	3	b
^{1}H n.m.r. data			
2.40	s	3	f
7.28 & 7.52	AX (J 8)	2	c and d
7.47	s	1	e

N.M.R. NUMBER: 22



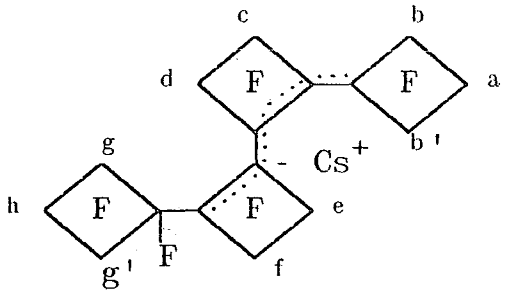
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
61.1	broad s	3	c
64.5	m	3	d
71.2	d(J 3.9) of q(J 3.3)	3	e
77.6	d(J 13.6) of q(J 7.4)	1	b
80.1	d(J 12.7) of q(J 9.4)	1	a

N.M.R. NUMBER: 23



CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
109.7	s	2	c & c'
117.7	s	2	b & b'
129.5	s	1	a

N.M.R. NUMBER: 24



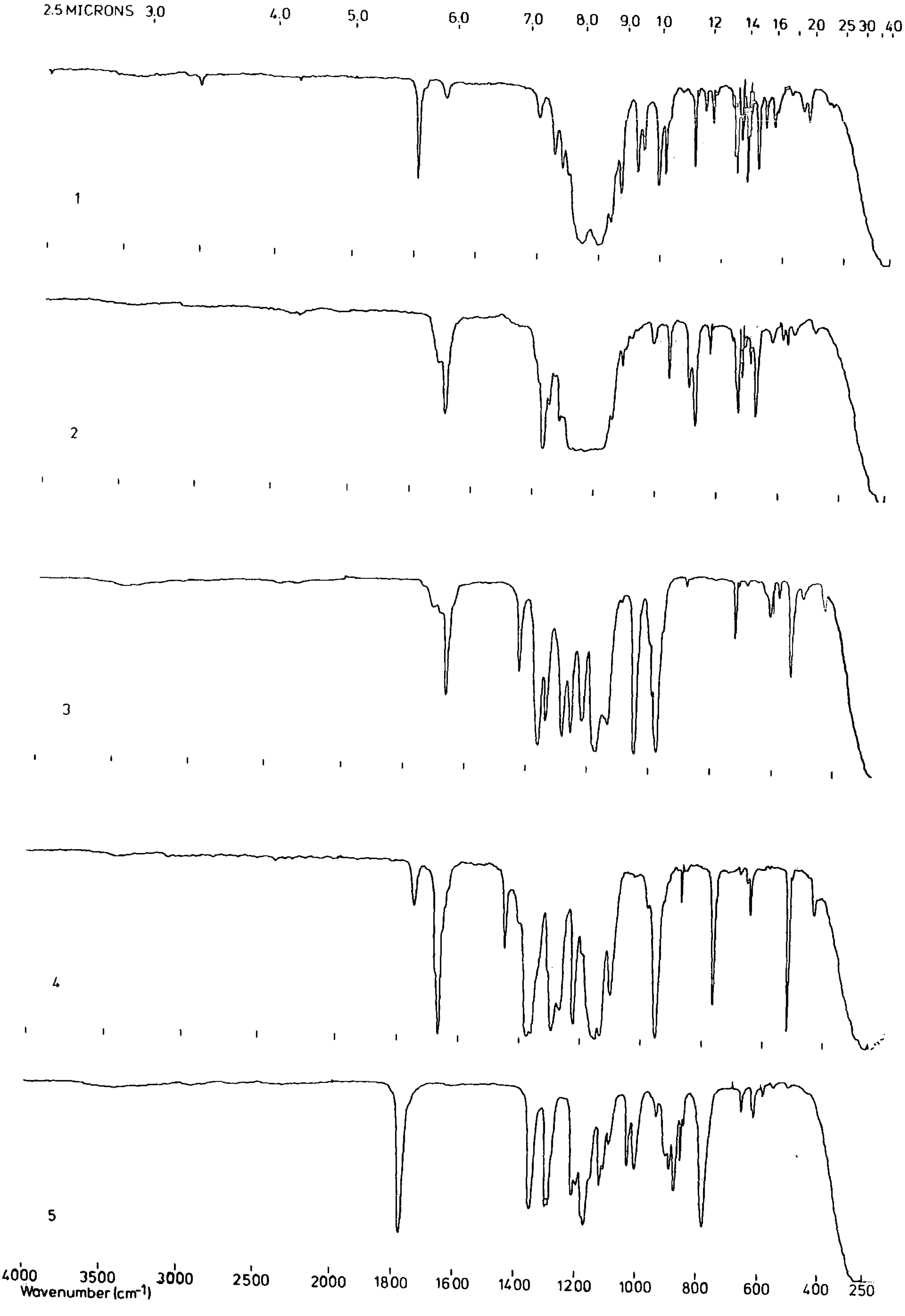
CHEMICAL SHIFT (ppm)	MULTIPLICITY (J in Hz)	INTEGRAL	ASSIGNMENT
93.4	s	4	b & b'
100.8	s	2	c
109.0	s	2	d
112.6	s	2	e
114.2	s	2	f
117.6 & 120.1	AB (J 214)	4	g & g'
125.6	s	2	a
129.7	s	2	h

NB. the tertiary fluorine resonance was lost in the background arising from the PTFE base in the ^{19}F probe.

APPENDIX 2: INFRARED SPECTRA

1. 2H-perfluoro-3,4-dimethyl-4-ethylhe -2-ene (35)
2. Perfluoro-3,4-dimethylhex-2,4-diene (61)
3. Perfluorobicyclopent-1,1'-enyl (56)
4. Perfluorobicyclobut-1,1'-enyl (57)
5. 1-Bromo-2-chlorohexafluorobut-3-ene (66)
6. 1-Bromo-2,4-dichloropentafluorobut-3-ene (67)
7. 2-Methoxyperfluoro-3,4-dimethylhex-2,4-diene (89)
8. 2,5-Dimethoxyperfluoro-3,4-dimethylhex-2,4-diene (90)
9. 2-Methoxyperfluorobicyclopent-1,1'-enyl (91)
10. 2,2'-Dimethoxyperfluorobicyclopent-1,1'-enyl (92)
11. 2,2'-Dimethoxyperfluorobicyclobut-1,1'-enyl (93)
12. 2,3,4,5-Tetrakis-(trifluoromethyl)-1,6-benzodioxocin (94)
13. 5-Fluoro-6-(perfluoro-3-methylprop-2-ene)-7-difluoro-1,4-dioxep-5-ene (97)
14. (Ethane-1,2-dialkoxy)-2,2'-tridecafluoro-1H-di(cyclopentan-6-ene) (98)
15. (Ethane-1,2-dialkoxy)-2,7'-dodecafluoro-di(1-cyclopentenyl) (99)
16. Perfluorotetramethylfuran (102)
17. Perfluorotetramethylthiophene (103)
18. Perfluoro-1,2,3,5,6,7-hexafluorodicyclopenta-[b,d]thiophene (104)

19. 2,3,4,5-Tetrakis-(trifluoromethyl)-1,6-benzodithiocin (106)
20. 5-Iodoperfluoro-1,2,5-trimethylcyclopentadiene (109)
21. 2,6-di(1'-cyclobutylidene)dicyclobutylidene (111)
22. $[Fe(\eta\text{-}C_5Me_5)_2]^{\cdot+}$ $[C_{10}F_{14}]^{\cdot-}$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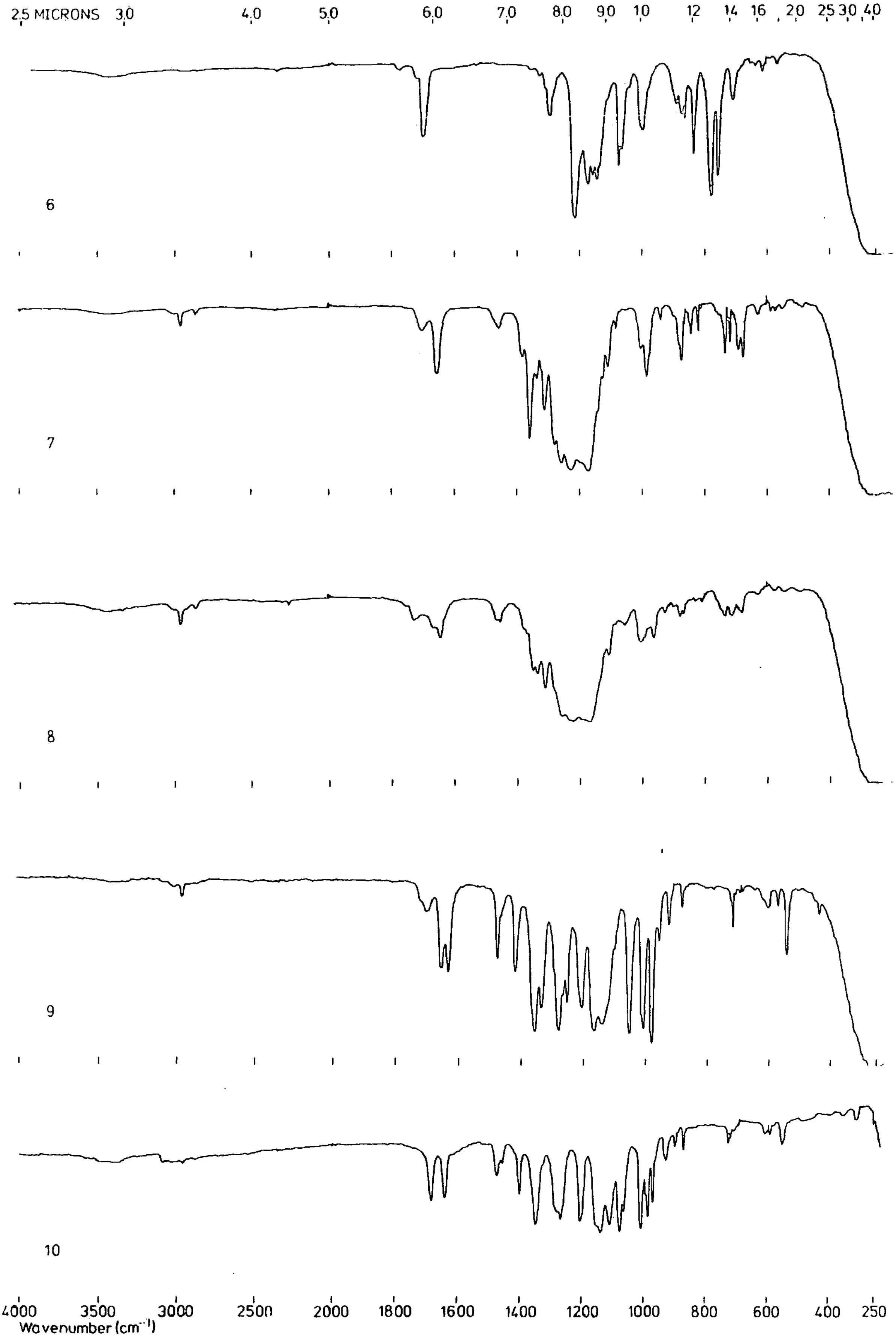
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
1
2
3
4
5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm-1)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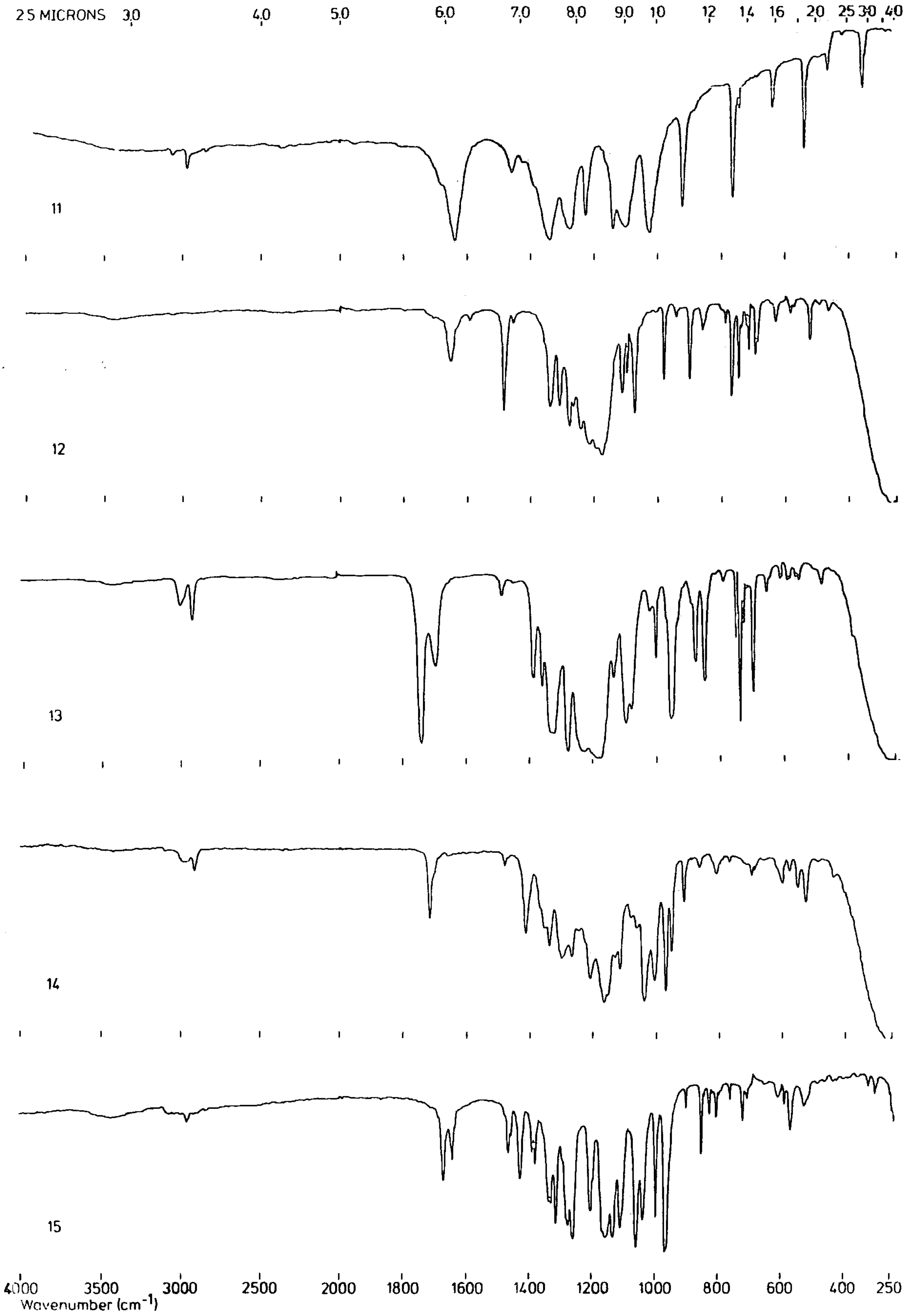
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
6
7
8
9
10
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)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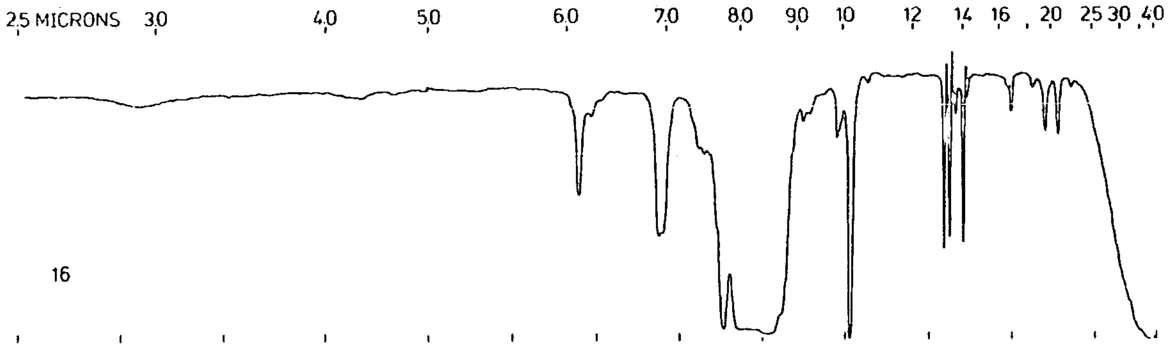
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
11
12
13
14
15
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)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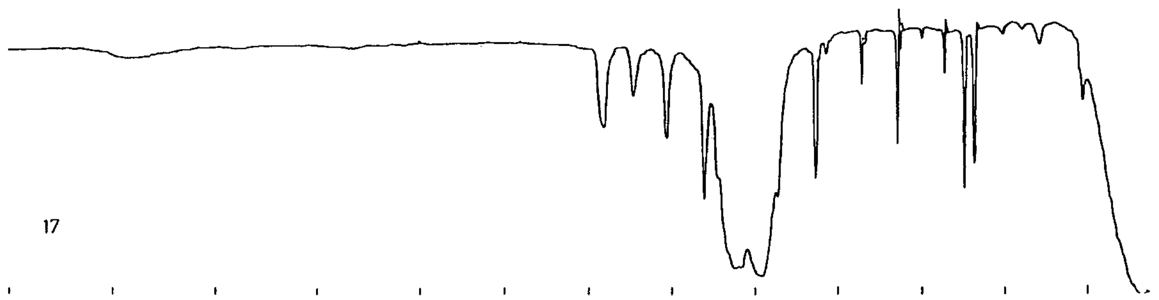
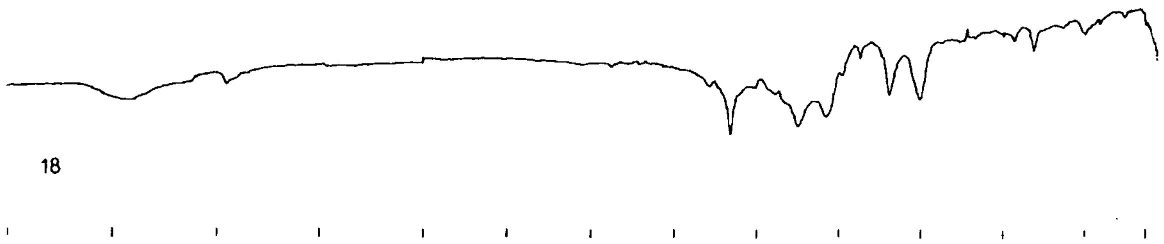
6,0
7,0
8,0
9,0
10
12
14
16
20
25
30
40

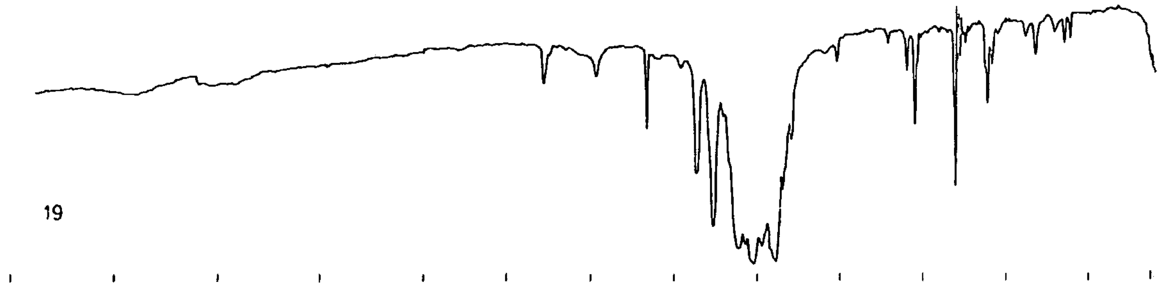
16



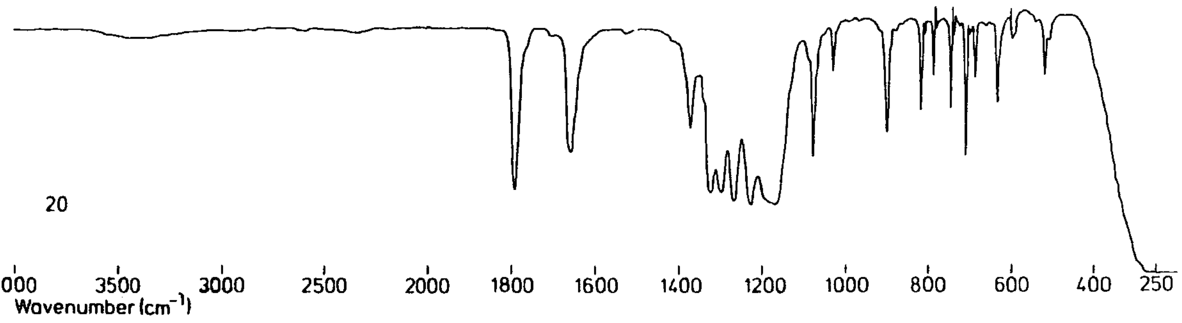
17



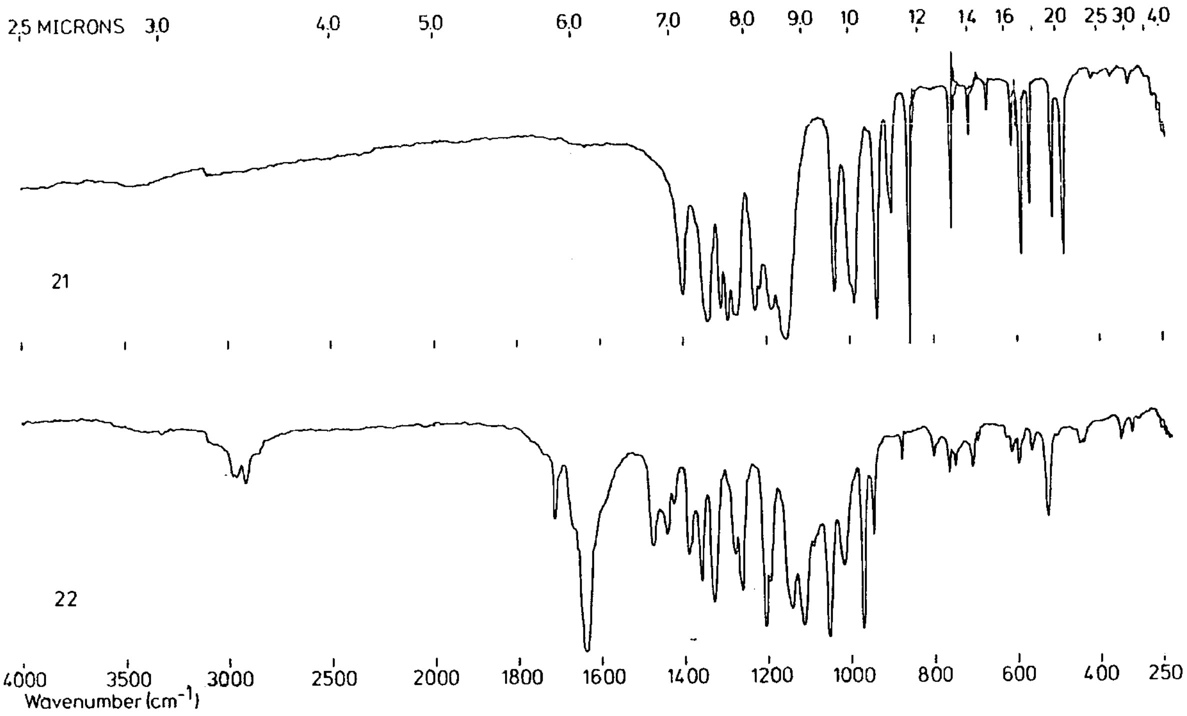
18



19


4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm^{-1})

20


2,5 MICRONS
3,0
4,0
5,0
6,0
7,0
8,0
9,0
10
12
14
16
20
25
30
40
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm^{-1})

21

22

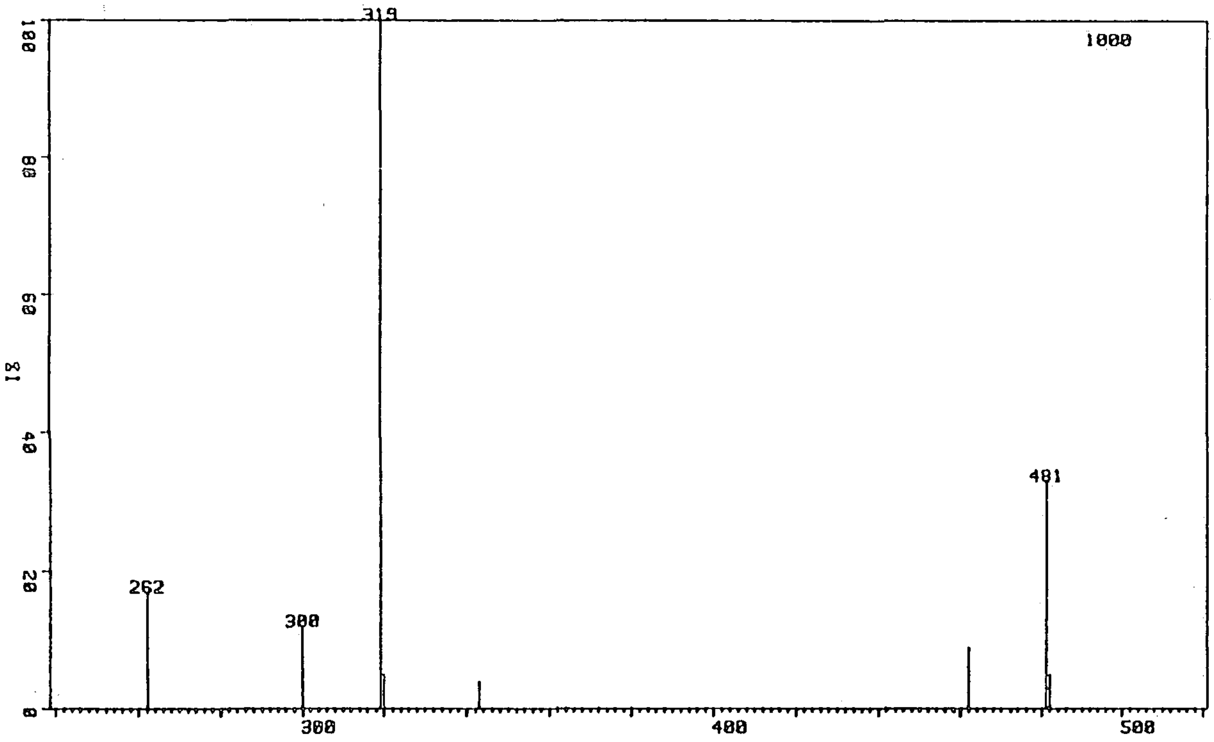
APPENDIX 3: MASS SPECTRA

1. 2H-perfluoro-3,4-dimethyl-4-ethylhex -2-ene (35)
2. Perfluoro-1,3,3-trimethyl-4-ethyl-2-isopropyl-cyclo-1-butene (38)
3. Perfluoro-1,3,3-trimethyl-2-ethyl-4-isopropylidene-cyclo-1-butene (39)
4. Perfluoro-3,4-dimethylhex-2,4-diene (61)
5. Perfluorobicyclopent-1,1'-enyl (56)
6. Perfluorobicyclobut-1,1'-enyl (57)
7. 1-Bromo-2-chlorohexafluorobut-3-ene (66)
8. 1-Bromo-2,4-dichloropentafluorobut-3-ene (67)
9. 2-Methoxyperfluoro-3,4-dimethylhex-2,4-diene (89)
10. 2,5-Dimethoxyperfluoro-3,4-dimethylhex-2,4-diene (90)
11. 2-Methoxyperfluorobicyclopent-1,1'-enyl (91)
12. 2,2'-Dimethoxyperfluorobicyclopent-1,1'-enyl (92)
13. 2,2'-Dimethoxyperfluorobicyclobut-1,1'-enyl (93)
14. 2,3,4,5-Tetrakis-(trifluoromethyl)-1,6-benzo-dioxocin (94)
15. 5-Fluoro-6-(perfluoro-3-methylprop-2-ene)-7-difluoro-1,4-dioxep-5-ene (97)
16. (Ethane-1,2-dialkoxy)-2,2'-tridecafluoro-1H-di(cyclopentan-6-ene) (98)
17. (Ethane-1,2-dialkoxy)-2,7'-dodecafluoro-di(1-cyclopentenyl) (99)

18. Perfluorotetramethylfuran (102)
19. Perfluorotetramethylthiophene (103)
20. Perfluoro-1,2,3,5,6,7-hexafluorodicyclopenta-[b,d]thiophene (104)
21. 2,3,4,5-Tetrakis-(trifluoromethyl)-1,6-benzodithiocin (106)
22. 5-Iodoperfluoro-1,2,5-trimethylcyclopentadiene (109)
23. 2,6-di(1'-cyclobutylidene)dicyclobutylidene (111)

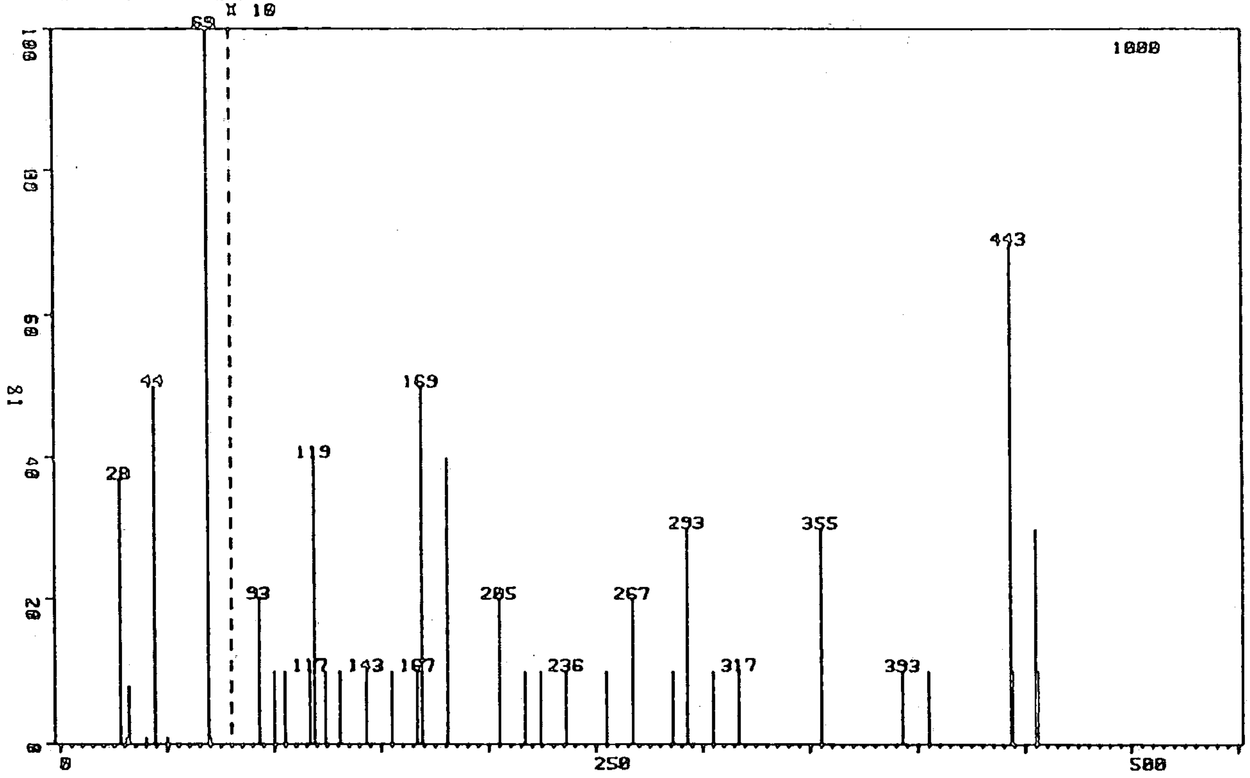
MB3245 0
CAL:LIB STA:

28-OCT-9.
0:0

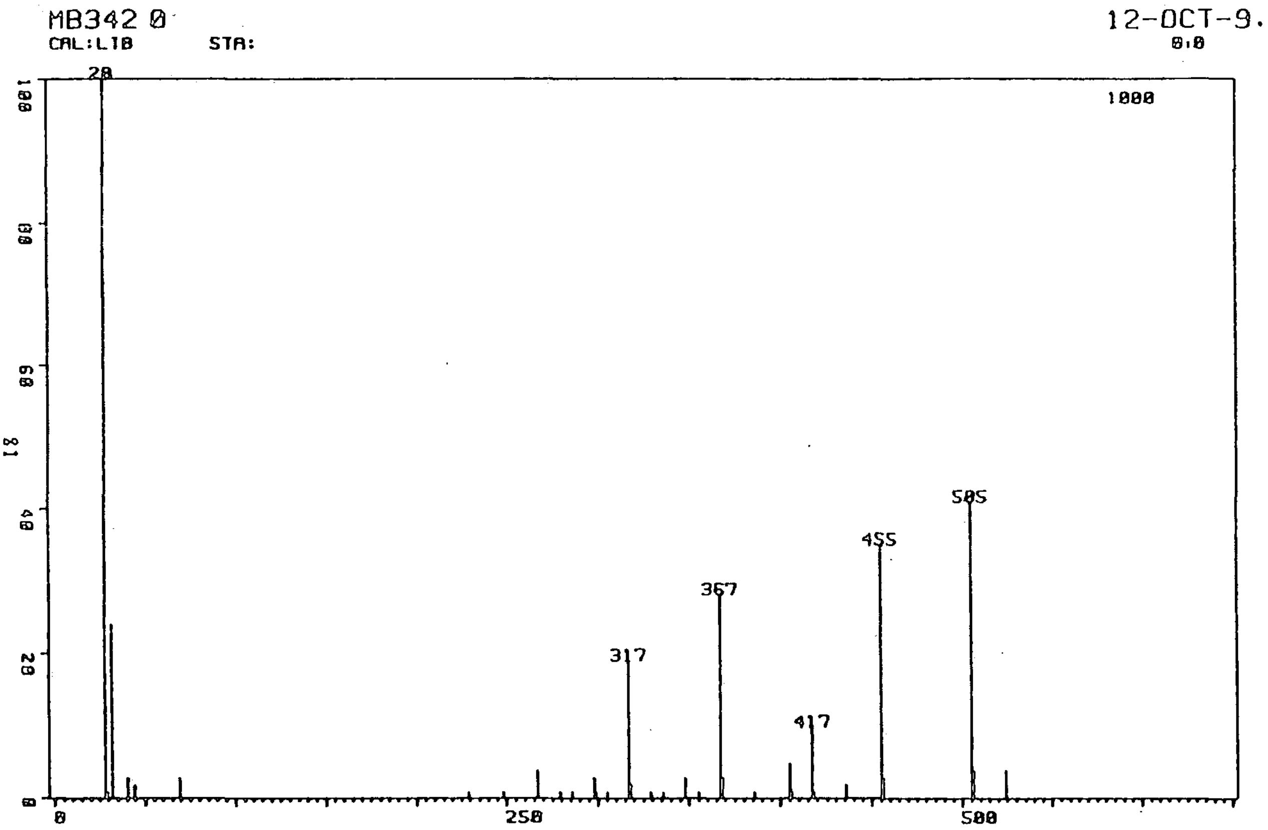


MASS	%HT. BASE
262.21	17.31
300.23	12.02
319.27	100.00
320.28	5.09
343.33	4.07
462.47	8.76
481.45	32.59
482.49	4.68

MB341 0 M.BRISCOE 12-OCT-9.
CAL:LIB STA: 0.0



MASS	%HT. BASE
28.10	37.48
30.86	1.20
31.97	8.34
39.80	0.62
44.09	0.46
49.87	0.42
68.97	100.00
69.91	0.85
93.02	1.66
99.92	1.37
105.04	0.49
117.03	1.11
118.97	4.46
124.03	0.59
130.97	1.30
143.01	0.62
155.01	1.24
166.99	0.94
168.96	5.24
180.95	3.55
205.00	2.41
216.99	0.72
223.98	0.49
235.96	1.01
254.99	0.62
266.96	2.05
285.96	0.49
292.96	2.61
304.95	0.91
316.96	0.91
354.95	3.19
392.96	0.59
404.94	0.75
442.87	6.77
443.94	0.62
454.92	2.70
455.93	0.46
473.94	0.36
542.91	1.99

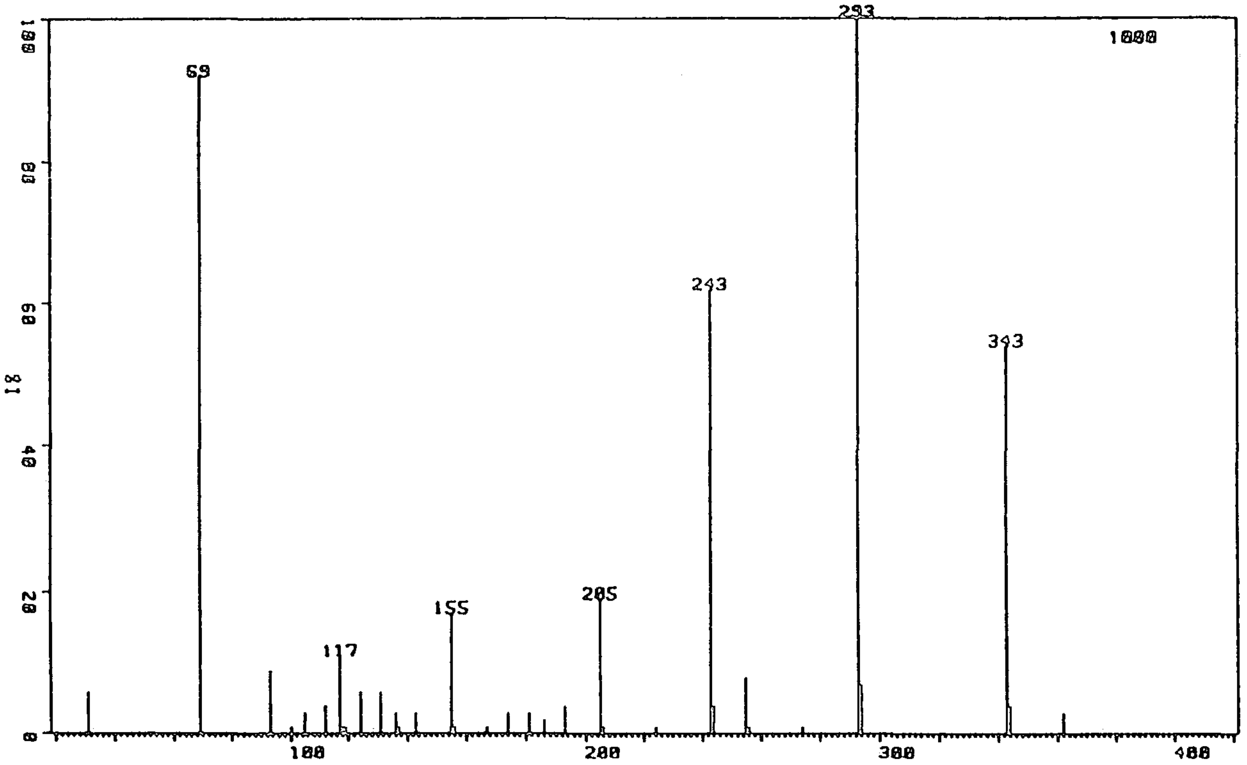


MASS	%HT. BASE
28.10	100.00
28.96	0.89
31.97	23.89
39.81	2.68
44.09	1.52
68.98	2.50
228.98	0.76
247.98	0.85
266.98	3.89
278.96	1.30
285.99	1.38
297.98	3.39
299.00	0.58
304.98	0.94
316.96	18.94
317.99	1.56
329.00	1.30
336.00	1.30
342.97	3.44
354.98	0.89
366.95	27.87
367.96	2.64
385.98	1.30
404.98	4.60
405.99	0.58
416.96	10.36
418.00	1.03
435.98	2.57
454.98	34.75
455.98	3.17
504.95	41.40
505.97	4.29
523.94	3.97

4

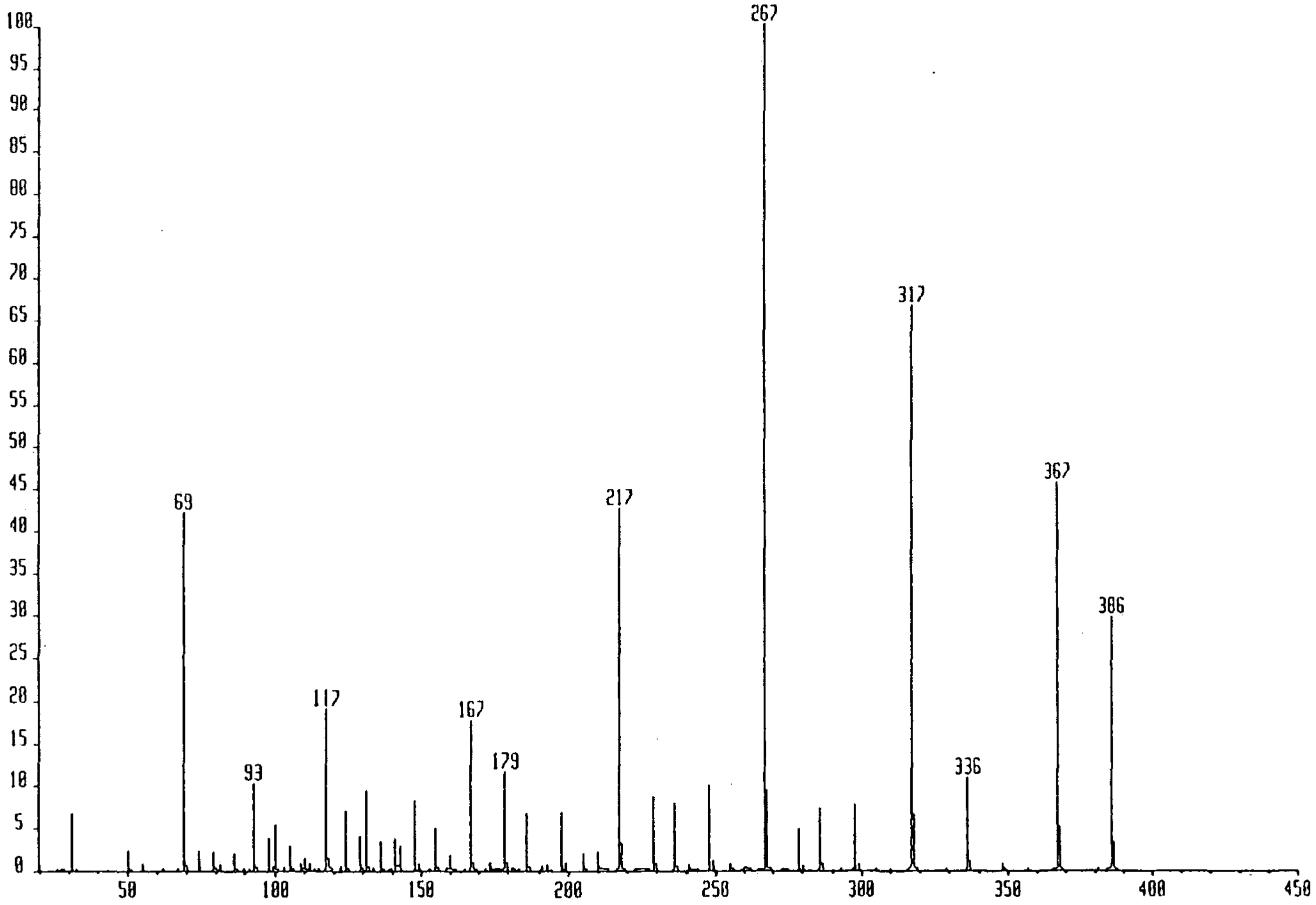
MB71 0
CAL:LIB STR:

12-OCT-9.
0:0



Mass	% Base
31.04	5.53
69.09	91.65
93.13	8.97
100.14	1.03
105.15	3.49
106.16	0.18
112.16	3.50
112.66	0.19
117.16	11.00
118.17	0.54
119.17	1.48
124.17	5.77
125.18	0.27
129.18	0.08
131.18	5.65
132.11	0.06
132.19	0.14
136.19	2.57
137.19	0.95
143.20	3.04
144.20	0.12
148.21	0.31
150.21	0.15
155.21	17.04
156.22	0.91
162.22	0.30
167.23	0.70
174.23	2.89
175.24	0.12
181.23	2.68
182.24	0.14
186.23	1.89
187.24	0.08
193.26	3.77
194.27	0.26
201.19	0.08
201.28	0.08
201.37	0.07
201.43	0.08
201.48	0.12
201.60	0.15
201.85	0.19
202.11	0.12
202.22	0.08
202.42	0.08
205.27	18.77
206.28	1.31
212.29	0.11
217.30	0.21
224.30	1.12
225.31	0.07
231.31	0.07
236.32	0.09
243.31	62.19
244.32	3.91
255.34	7.66
256.35	0.48
274.36	0.57
275.37	0.05
292.78	0.06
293.38	100.00
294.38	7.16
295.40	0.32
342.74	0.06
343.44	53.88
343.72	0.06
344.45	4.47
345.45	0.19
362.48	3.13
363.49	0.26

A8690144o x1 Bgd=129 28-OCT-88 10:1+0:02:34 70E EI+
BpA=0 I=5.1v Ha=300 TIC=202452000 Acnt: Sys:ORIS HAR: 3340200P
GC= 54° Cal:PFK MASS: 267



Mass	% Base
31.01	6.65
50.02	2.24
69.03	42.05
74.03	2.27
79.03	2.08
86.03	1.92
93.04	10.28
98.03	3.73
100.03	5.38
105.03	2.79
110.04	1.28
117.03	19.02
118.04	1.34
124.03	7.03
129.04	3.95
131.03	9.27
136.04	3.46
141.04	3.66
143.04	2.87
148.03	8.22
155.03	4.85
160.03	1.79
167.03	17.59
179.03	11.62
186.04	6.63
198.04	6.88
205.04	1.87
210.04	2.03
217.04	42.47
218.04	3.10
229.04	8.65
236.03	7.84
248.04	9.97
267.04	100.00
268.05	9.28
279.04	4.92
286.03	7.30
298.03	7.75
317.03	66.52
318.03	6.53
336.03	10.78
337.04	1.00
367.02	45.44
368.03	5.06
381.26	0.07
384.24	0.10
384.53	0.10
385.40	0.10
385.46	0.13
385.65	0.39
386.02	29.56
386.51	0.10
387.02	3.28
388.04	0.20

6

```
AB01030o       x1    Bgd=20    12-AUG-87 12:1+0:02:00   70E        EI+
BpA=0     I=1Gv    Ma=287   TIC=250427060             Rcnt:          Sys:BRIS                                    HRR:     65534000
                                                          GC= 40°   Cal:PFK                                     MASS:         217
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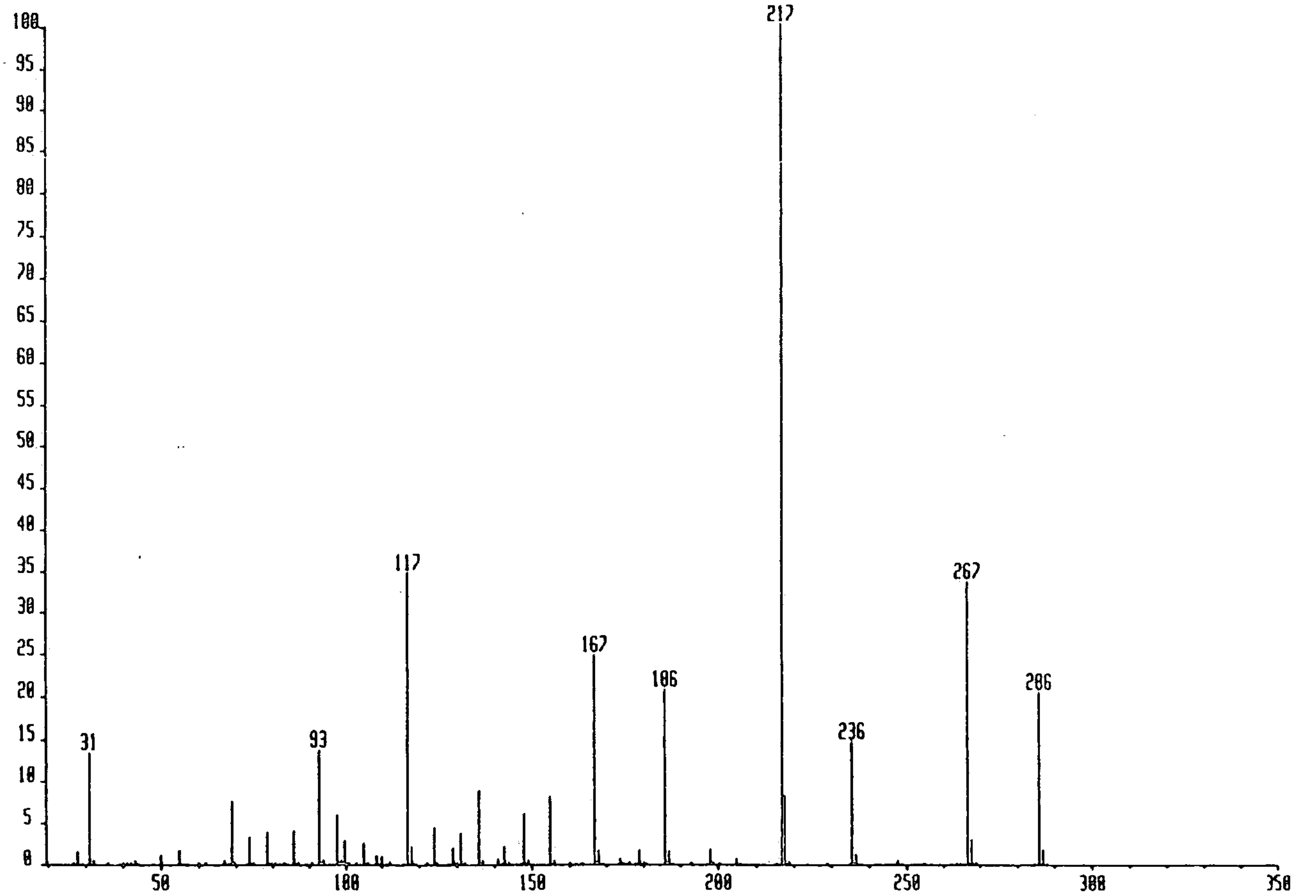

Mass	% Base	
27.97	1.52	
30.96	13.33	
31.96	0.43	
39.92	0.13	
40.99	0.17	
42.00	0.11	
43.00	0.42	
49.94	1.05	
54.94	1.60	
61.93	0.16	
66.93	0.42	
68.92	7.56	
73.91	3.26	
74.92	0.11	
78.91	3.83	
79.91	0.20	
80.90	0.14	
83.40	0.14	
85.90	3.99	
86.90	0.16	
92.89	13.62	
93.90	0.41	
97.89	5.98	
98.89	0.41	
99.89	2.75	
104.88	2.59	
105.89	0.11	
108.38	1.07	
109.88	0.82	
111.87	0.37	
116.87	34.59	
117.87	2.13	
121.87	0.16	
123.86	4.50	
124.86	0.21	
128.86	1.93	
129.86	0.12	
130.86	3.74	
131.86	0.14	
135.85	8.86	
136.86	0.48	
140.85	0.56	
142.84	2.07	
147.84	6.04	
148.84	0.41	
154.84	8.14	

Mass	% Base	
155.84	0.45	
159.83	0.13	
166.82	24.77	
167.83	1.64	
173.82	0.66	
178.81	1.64	
179.82	0.13	
185.81	20.63	
186.81	1.42	
192.80	0.22	
197.80	1.72	
198.80	0.17	
204.79	0.53	
216.80	100.00	FO
217.78	8.14	F
218.78	0.26	
235.77	14.45	
236.77	1.12	
247.77	0.38	
266.73	33.53	F
267.74	2.99	F
268.74	0.11	
285.73	20.22	F
286.73	1.75	F

7

```
AB720143o      x1   Bgd=139   25-OCT-88 12:4+0:02:32   70E        EI+
BpA=0     I=3.0v   Ha=279   TIC=93490000            Acnt:         Sys:BRIS                        MAR:      24655000
                                                          GC= 54°   Cal:PFK                        MASS:          147
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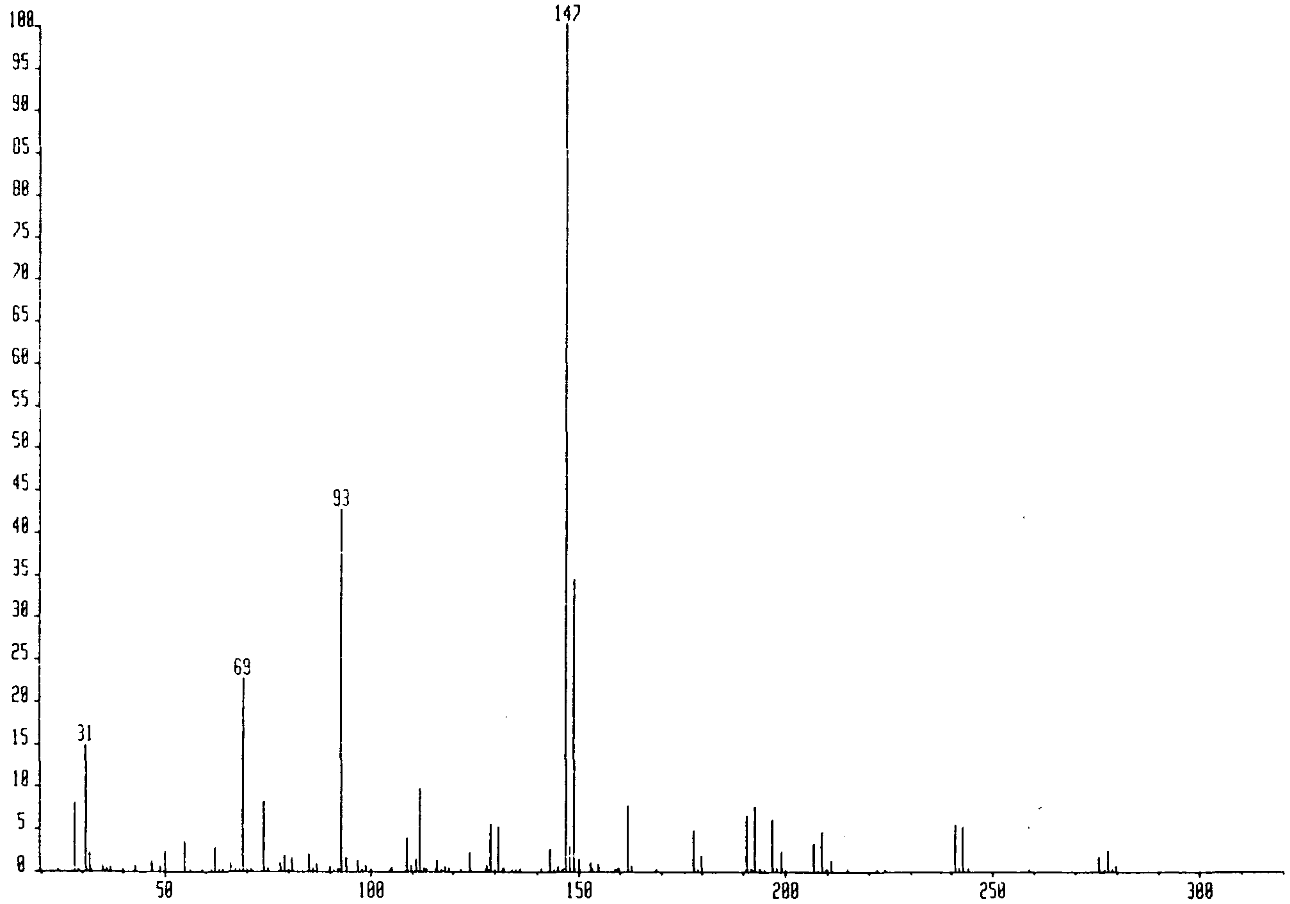
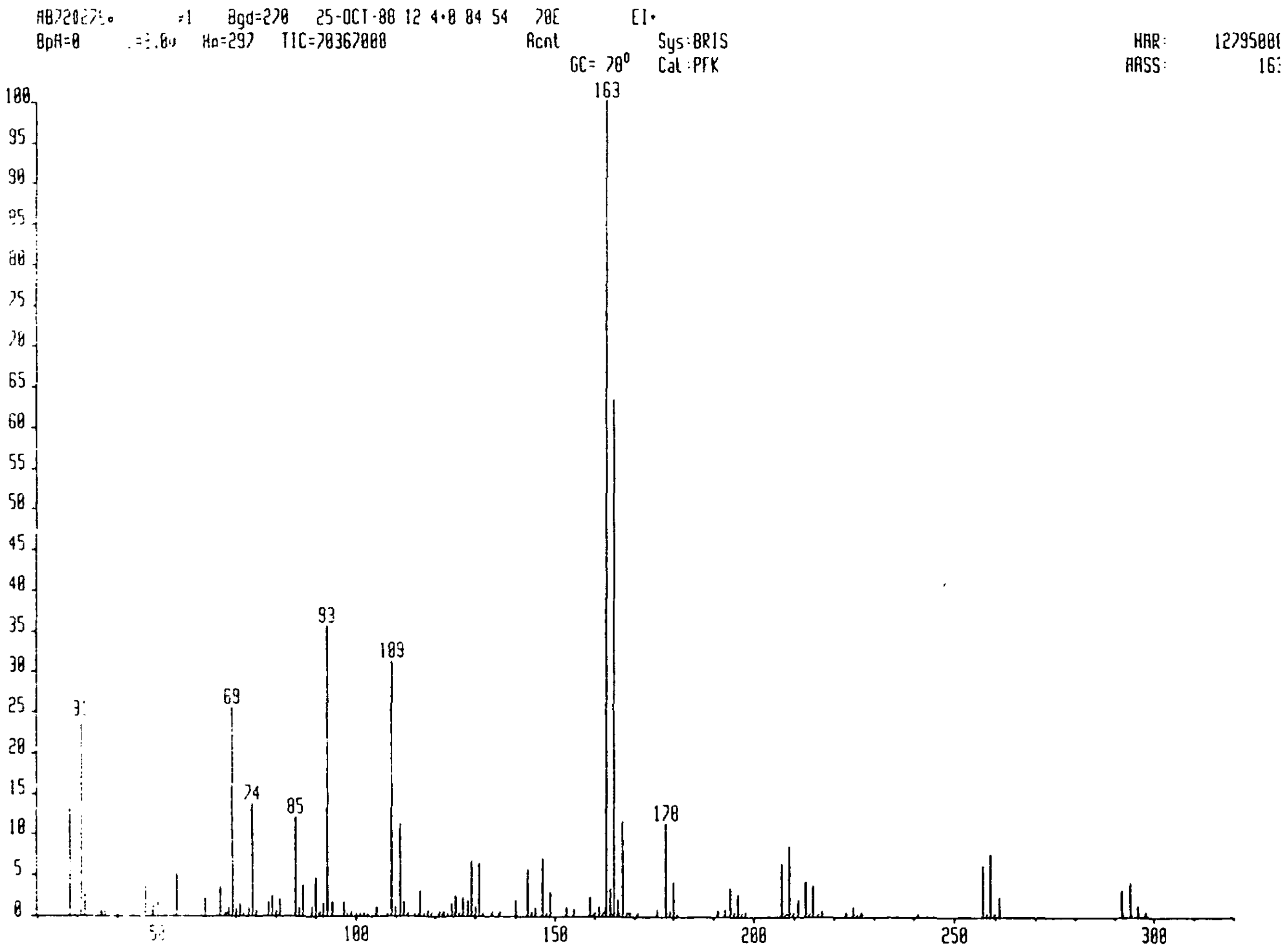


Mass	% Base
28.02	8.03
31.00	14.78
31.99	2.14
46.98	1.08
50.01	2.27
55.01	3.42
62.01	2.61
69.00	22.72
74.01	8.18
78.93	1.73
80.92	1.33 F
81.00	1.46 F
84.97	1.95
93.01	42.62
94.01	1.55
96.97	1.15
108.97	3.82
110.97	1.32
111.99	9.67
115.97	1.18
123.99	2.12
128.92	5.50
130.91	5.17 F
130.99	4.98 F
142.99	2.53
146.95	100.00
147.95	2.88
148.95	34.37
149.95	1.33
161.98	7.69
177.93	4.68
179.93	1.76
190.89	6.55
192.89	7.49
196.93	6.11
198.94	2.21
206.86	3.31
208.86	4.58
210.86	1.14
240.88	5.49
242.87	5.25
258.87	0.10
275.85	1.66
276.82	0.13
277.84	2.35
278.84	0.28
279.85	0.65

8

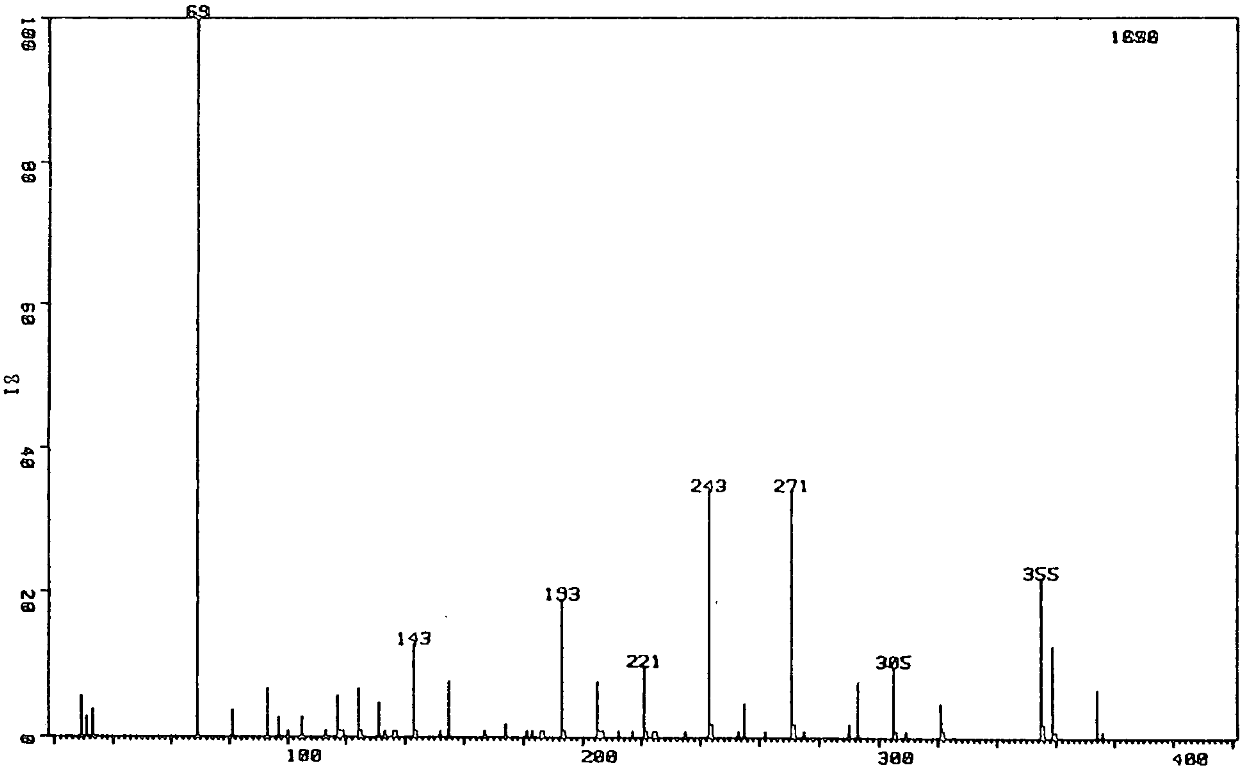


Mass	% Base
28 02	13 08
31 00	24 01
31 99	3 12
34 97	1 43
46 98	4 06
48.97	1 15
50 01	2 05
55 01	5 25
62 01	2.06
65 98	3 70
69 00	25.46
70 98	1 37
74 01	13 64
77.98	1 57
78 93	2 34
80 93	1 90
84 97	11 95
86.97	3 70
88.99	1 09
89.98	4.59
91.98	1 45
93.01	35 60
94.01	1 62
96.98	1.70
105.00	1 06
108.97	31 33
109 96	1.09
110.97	11.14
111.97	1.59
115.97	2.99
123.99	1.52
124.94	2.31
126 94	2.09
127 96	1.81
128.92	6.65
130.91	6.34
139.96	1.82
142.99	5.62
146.95	6.97
148.95	2.82
158.95	2.21
160.95	1.09
162.92	100.00
163.92	3.31
164.92	63.35
165.92	1.87
166.91	11.53
177.93	11.26
179.92	4.19
193.92	3.37
195.92	2.62
206.86	6.34
208.85	8.45
210.86	1.87
212.90	4.21
214.90	3.71
224.82	1.07
256.85	6.03
257.85	0.37
258.85	7.52
259 82	0 37
260 85	2 20
291 80	3 09
293 80	4 03
295 78	1 21
297 81	0 50

9

MB7521 0
CRL:LIB STR:

12-OCT-9.
0:0



Mass	% Base
29. 04	6. 20
31. 04	3. 02
33. 06	3. 86
69. 08	100. 00
81. 13	3. 81
93. 13	7. 09
97. 13	2. 81
100. 14	0. 64
101. 16	0. 09
102. 14	0. 29
105. 15	2. 80
106. 16	0. 19
109. 15	0. 30
110. 16	0. 07
112. 16	0. 29
113. 16	0. 75
114. 16	0. 15
117. 16	5. 72
118. 16	0. 45
119. 16	0. 66
121. 17	0. 20
124. 17	7. 48
125. 18	0. 46
131. 19	4. 62
132. 19	0. 14
133. 18	0. 81
136. 18	1. 07
137. 19	0. 73
139. 21	0. 28
143. 19	12. 74
144. 20	0. 74
145. 21	0. 23
148. 21	0. 20
152. 20	0. 48
155. 21	7 90
156. 21	0. 28
157. 22	0 21
159 21	0 08
162. 21	0 18
163. 22	0 33
167. 22	0. 79
168. 22	0 21
169 22	0 30
171 19	0. 06
174. 21	1. 50
175 22	0. 26
181. 24	0. 97
183. 24	0. 81
185 25	0 13
186 25	0. 91
187 25	0 63
189 28	0 13
193. 25	18 99
194. 25	1. 01
195. 27	0. 06
202. 26	0. 24
203. 26	0 31
205. 26	7 83
206. 27	0. 45
207. 28	0 64
212. 27	1. 05
213. 28	0. 13
216. 30	0. 10
217. 29	0. 62
217. 56	0. 10
217. 76	0. 06
217. 82	0. 06
218. 05	0. 10
218. 18	0. 12
218. 35	0. 18
218. 53	0. 08
218. 65	0. 06
218. 71	0. 10
221. 28	10. 45
222. 28	0. 64
224. 29	0. 79
225. 30	1. 07
231. 30	0. 29
233. 31	0. 12
235. 31	0. 79
236. 31	0. 35
237. 30	0. 29
240. 30	0. 32
241. 17	0. 05
241. 30	0. 08
241. 48	0. 08
242. 95	0. 08
243. 30	34. 24
244. 31	2. 34
252. 31	0. 16
253. 33	0. 60
255. 34	4. 93
256. 34	0. 34
257. 34	0. 36
259. 33	0. 11
262. 32	0. 99
267. 34	0. 13
271. 33	34. 01
272. 34	2. 48
273. 36	0. 13
274 35	0. 12
275. 35	1. 14
285 36	0. 12
286. 37	0. 40
290. 34	2. 15
290. 77	0. 14
290. 94	0. 10
291. 03	0. 13
291. 10	0. 14
291. 35	0. 22
291. 47	0. 08
291. 51	0. 09
293. 35	8. 49
294. 36	0. 43
303. 39	0. 18
305. 40	10. 19
306. 41	0. 79
309. 38	1. 14
310. 37	0. 12
321. 38	4 66
322. 39	0. 52
325. 41	0. 30
340. 44	0. 28
344. 41	0. 11
344. 51	0. 10
344. 80	0. 12
345. 11	0. 18
345. 28	0. 13
345. 68	0. 06
355. 47	22. 07
356. 42	1. 98
357. 47	0. 17
359. 43	12. 94
360. 45	1. 11
374. 49	6. 86
375. 50	0. 75

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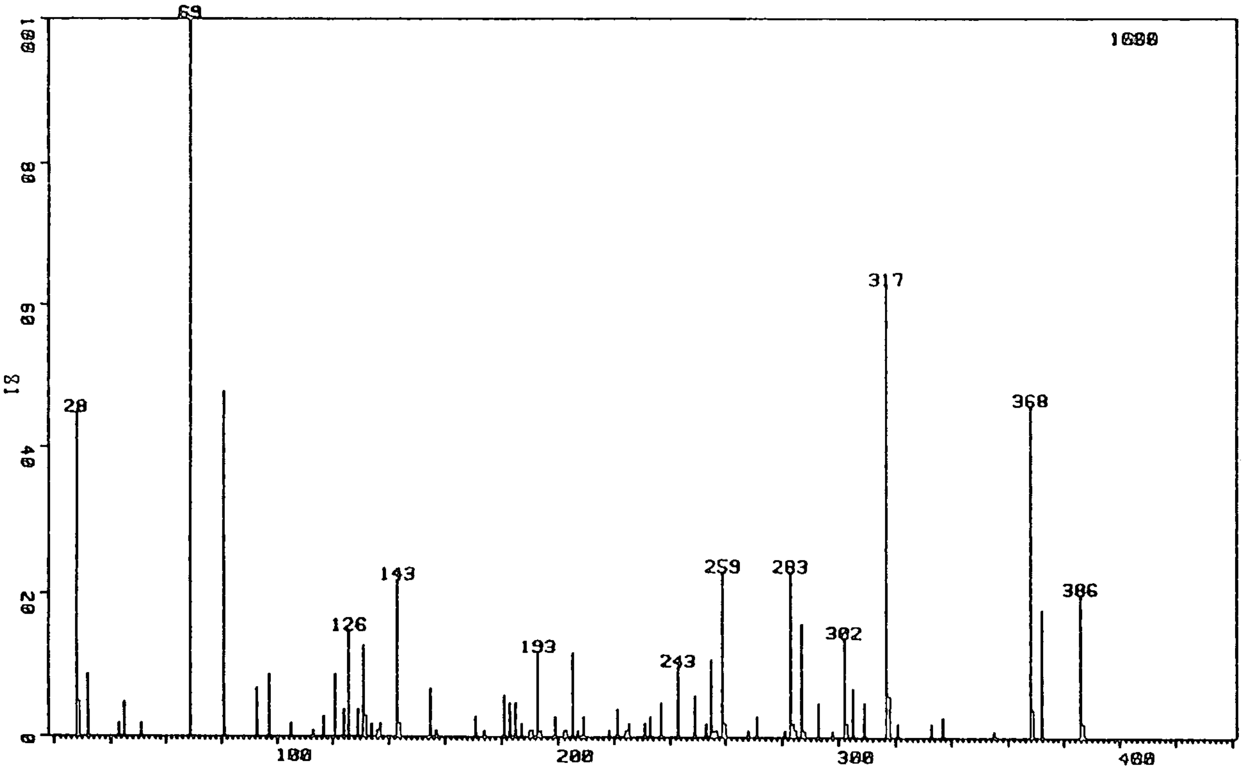

Mass	% Base
28. 03	45. 19
29. 03	5. 44
32. 03	9. 15
43. 08	2. 38
45. 10	4. 83
51. 08	2. 38
69. 08	100. 00
81. 13	47. 78
93. 13	7. 14
97. 13	9. 30
105. 14	1. 95
113. 17	1. 41
117. 17	3. 24
121. 15	8. 72
124. 17	4. 18
126. 21	15. 10
129. 08	3. 53
131. 09	2. 70
131. 20	12. 90
132. 09	3. 10
134. 10	1. 51
136. 10	1. 37
137. 20	1. 66
143. 19	22. 41
144. 20	1. 80
155. 21	6. 77
157. 21	1. 37
157. 24	0. 79
171. 21	3. 46
174. 21	0. 79
181. 23	5. 55
183. 24	5. 41
185. 26	4. 86
187. 24	1. 80
190. 26	1. 23
191. 25	1. 37
193. 25	12. 32
194. 28	1. 37
199. 25	3. 14
202. 25	0. 83
203. 26	1. 23
205 28	11. 89
207. 31	1. 37
209. 26	3. 24
218. 27	1. 08
221. 29	3. 82
224. 29	1. 41
225. 30	1. 84
231. 30	1. 66
233. 30	2. 52
237. 29	4 83
243 30	10. 16
249. 32	5. 55
253. 33	1. 66
255. 35	11. 21
256. 36	1. 37
257. 36	0. 94
259. 32	22. 85
260. 33	1 95
268. 33	1. 37
271. 34	3. 46
281. 35	1. 37
283. 36	22. 70
284. 34	0. 94
284. 39	1. 55
285. 39	1. 37
287. 35	16. 36
288. 38	1. 41
293. 38	4. 54
298. 44	1. 08
302. 40	13. 51
303. 40	1. 51
305. 41	7. 42
309. 37	4. 86
317. 42	62. 52
318. 43	5. 98
321. 39	1. 80
333. 45	2. 38
337. 43	3. 10
355. 46	1. 23
367. 52	46. 38
368. 52	4. 25
371. 50	17. 51
372. 49	1. 37
386. 52	19. 68
387. 51	1. 66

A01130371◇ x1 Bgd=361 25-OCT-00 12:0+0:06:35 70E EI+
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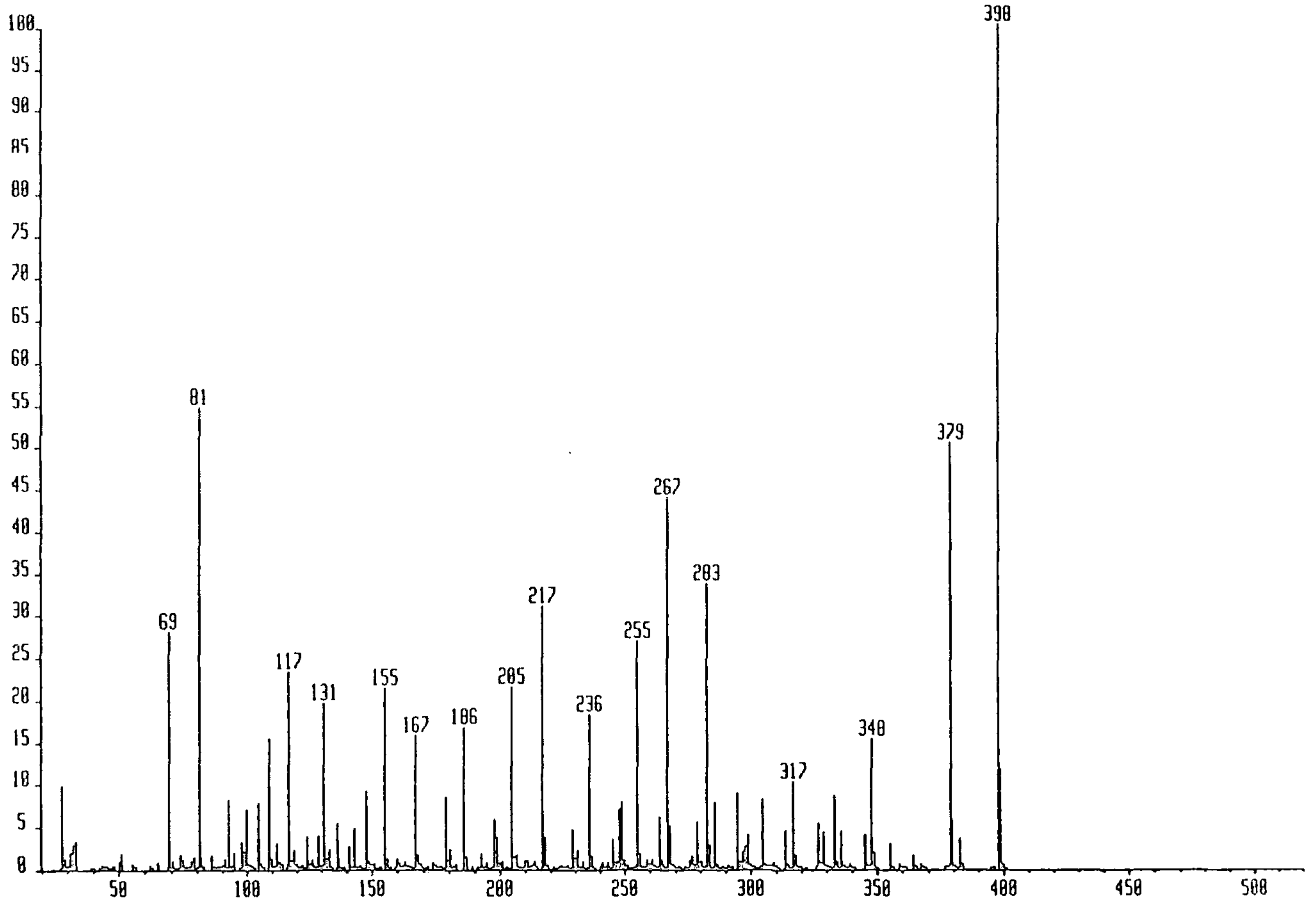
MAR 1924100
MASS 39

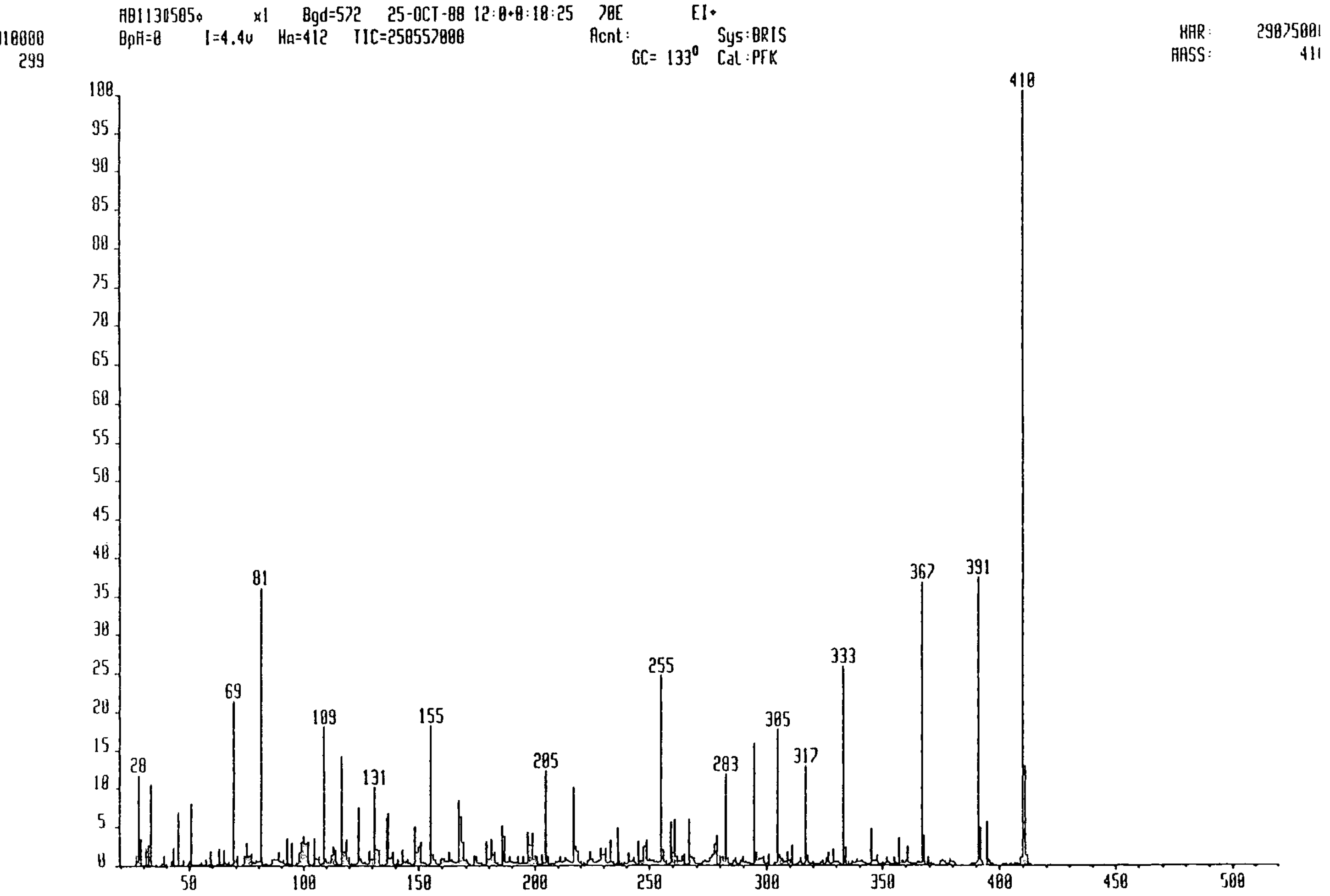


Mass	% Base
28.02	9.72
29.01	1.23
31.00	1.91
31.99	2.63
33.01	2.32
51.01	1.79
69.01	27.94
74.01	1.57
75.02	1.04
79.01	1.30
81.02	54.72
82.02	1.33
86.01	1.56
91.01	1.22
93.01	8.11
95.02	1.87
98.01	3.13
99.01	2.05
100.00	6.94
105.01	7.67
109.00	15.36
110.01	1.16
112.01	2.97
117.01	23.25
118.01	1.08
119.00	2.28
124.01	3.71
126.02	1.04
129.00	3.83
131.00	19.51
132.01	1.18
133.00	2.29
136.00	5.40
137.01	1.24
141.00	2.66
143.00	4.73
148.00	9.19
155.00	21.39
155.99	1.18
159.99	1.24
166.99	15.71
168.00	1.57
178.99	8.39
180.00	1.03
180.99	2.32
185.97	16.71

Mass	% Base
186.98	1.53
192.96	1.71
197.97	5.83
198.97	3.76
204.98	21.50
205.98	1.50
206.98	1.60
209.98	1.07
211.00	1.08
216.98	30.90
217.98	3.74
228.99	4.63
229.96	1.37
230.98	2.25
235.97	16.15
236.98	1.41
244.97	2.38
247.97	6.99
248.97	7.64
249.99	1.07
254.96	26.79
255.97	1.81
258.99	1.06
263.96	6.11
264.97	1.03
266.97	43.80
267.97	5.05
276.96	1.44
278.98	5.46
282.95	33.58
283.94	2.88
285.95	7.85
294.94	8.90
296.96	2.07
297.95	2.68
298.95	4.07
304.94	8.14
313.93	4.50
316.93	10.24
317.94	1.57
326.94	5.37
328.96	4.34
332.93	8.60
335.94	4.45
344.94	4.07
347.94	15.21

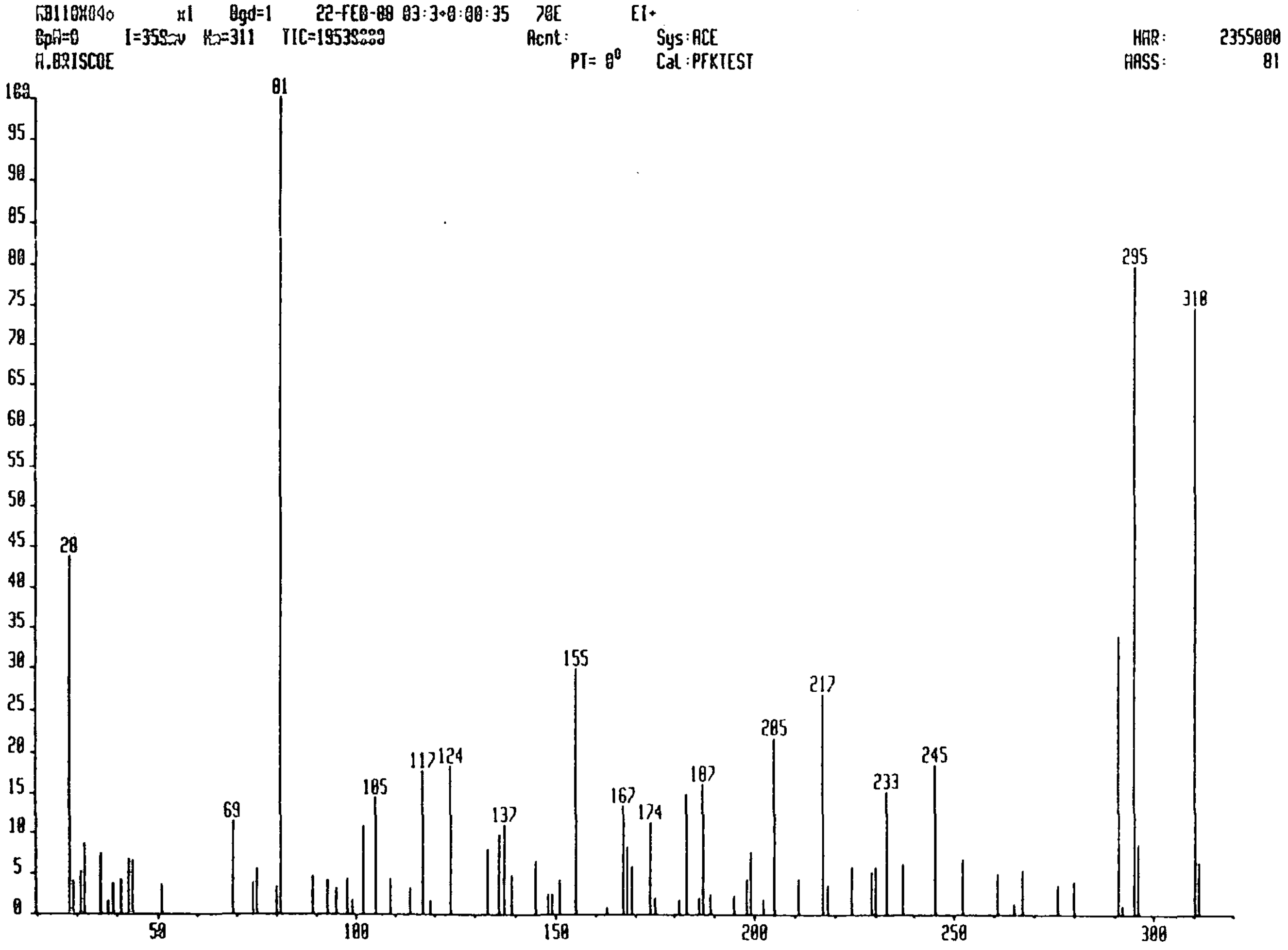
Mass	% Base
348.95	1.88
354.93	2.91
363.92	1.67
378.94	50.27
379.93	5.59
380.95	0.41
381.82	0.17
382.63	0.08
382.89	3.50
383.92	0.54
394.84	0.17
395.53	0.16
395.71	0.16
395.83	0.13
396.02	0.24
396.21	0.18
396.27	0.15
396.43	0.20
396.66	0.24
397.91	100.00
398.30	0.15
398.39	0.12
398.46	0.13
398.53	0.14
398.60	0.18
398.92	11.69
399.95	0.64
401.30	0.14

12

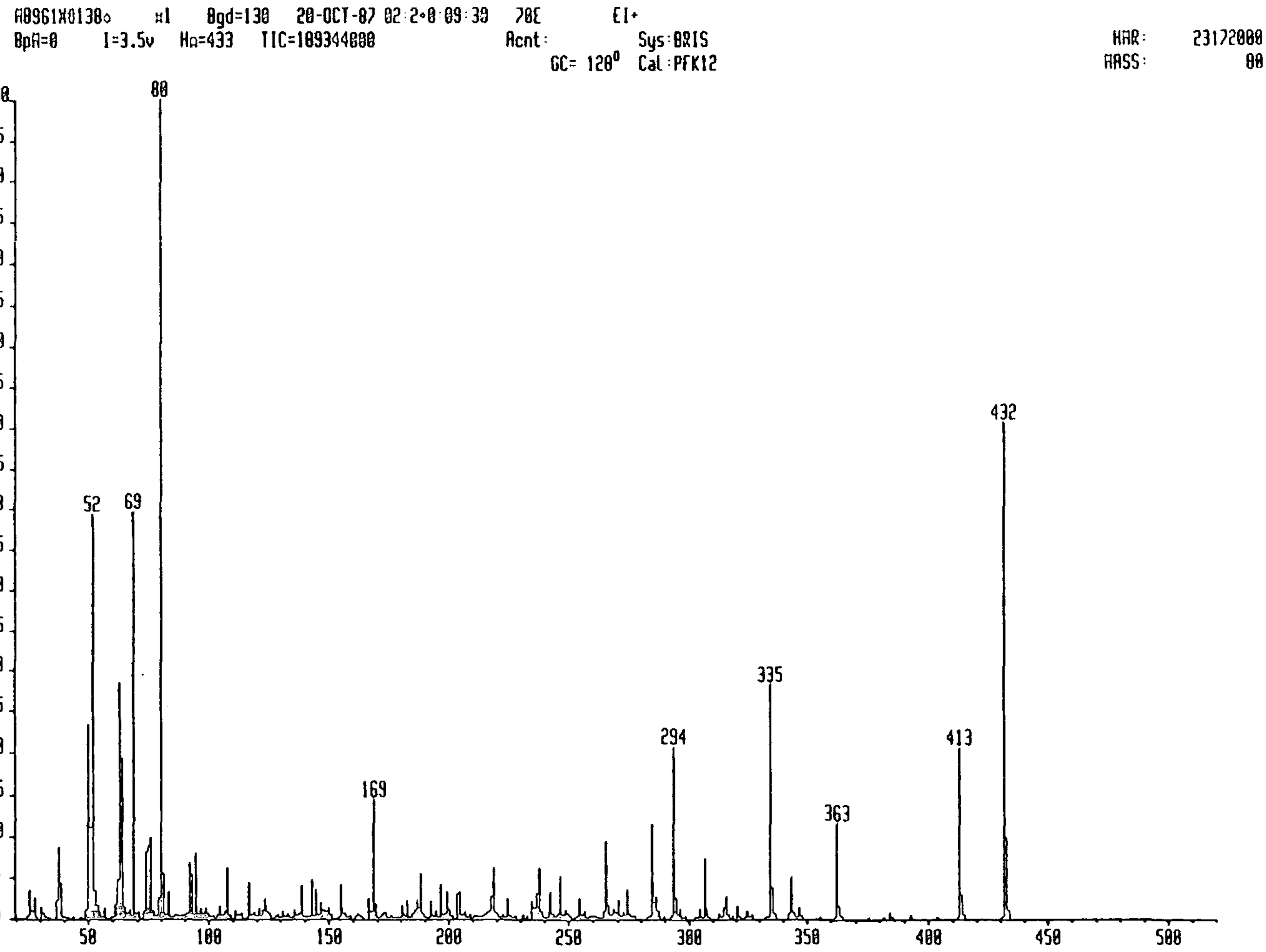


Mass	% Base
27.04	1.33
28.02	11.72
29.02	3.41
31.01	2.25
31.99	2.79
33.01	10.46
39.03	1.11
43.03	2.24
45.04	6.86
51.02	8.01
59.03	1.74
63.04	2.10
65.04	2.00
69.01	21.35
71.01	1.14
74.01	1.37
75.02	2.87
76.04	1.15
77.04	1.51
81.02	35.94
89.04	1.65
93.02	3.46
95.02	2.78
98.02	1.63
99.02	3.02
100.01	3.63
101.04	2.75
102.01	3.04
105.02	3.39
107.04	1.01
109.01	17.92
112.02	1.35
113.02	2.36
114.01	1.91
117.02	14.02
118.02	1.79
119.02	3.33
120.04	1.03
124.01	7.34
129.02	1.73
131.01	10.12
132.03	2.03
133.01	1.87
136.01	6.10
137.02	6.66
138.02	1.02
139.03	1.63
143.01	1.98
148.01	4.89
149.01	1.58
150.02	2.42
151.03	3.02
155.00	18.05
156.01	1.33
163.02	1.59
167.00	8.36
168.01	6.17
169.01	2.95
174.00	1.19
175.01	1.01
179.00	2.90
181.00	3.33
182.03	1.40
182.99	1.57
185.99	5.09
186.99	3.75
189.00	1.06
192.98	1.10
194.98	1.04
197.00	4.08
198.01	2.54
199.00	3.94
200.01	1.26
201.02	1.01
202.99	1.37
204.99	12.19
206.01	1.04
211.01	1.03
217.00	9.99
218.00	2.35
219.01	1.84
223.99	1.56
229.00	2.02
230.00	1.37
231.01	2.12
232.99	3.06
235.99	4.78
236.99	1.52
240.99	1.43
244.98	3.01
246.99	2.25
248.00	2.43
248.98	3.08
254.98	24.50
255.99	1.91
259.01	5.48
260.01	1.69
260.99	5.76
262.00	1.26
263.99	1.15
265.00	1.30
267.00	5.71
268.01	1.04
277.00	1.37
277.99	2.60
278.99	3.72
279.99	1.12
281.00	1.06
282.01	1.03
282.97	11.66
290.01	1.07
294.99	15.66
295.99	1.62
300.99	1.41
304.97	17.54
305.97	1.34
308.98	1.63
310.97	2.56
316.99	12.67
317.99	1.28
326.96	1.54
329.01	1.98
332.96	25.67
333.96	2.27
344.98	4.66
347.98	1.12
356.98	3.39
360.97	2.34
366.96	36.45
367.98	3.75
380.24	0.14
380.51	0.33
380.70	0.09
380.88	0.14
381.11	0.20
381.29	0.12
387.99	0.11
388.39	0.12
389.04	0.07
389.10	0.09
389.44	0.12
390.01	0.26
390.56	0.45
391.00	37.09
392.01	4.67
393.02	0.51
394.97	5.48
395.96	0.59
396.85	0.09
401.91	0.11
402.72	0.09
404.75	0.11
406.16	0.11
406.21	0.11
406.59	0.11
406.87	0.19
407.13	0.16
407.37	0.14
407.69	0.22
407.85	0.08
407.94	0.08
408.03	0.11
409.11	1.01
409.96	100.00
410.97	12.69
411.40	0.09
411.44	0.11
411.65	0.12
411.97	1.28
412.97	0.11

13



Mass	% Base
28.02	43.69
29.02	3.99
31.01	5.14
32.01	8.66
35.99	7.39
37.99	1.44
39.04	3.65
41.06	4.12
43.04	1.87
43.07	6.62
43.08	2.55
44.01	6.54
51.03	3.48
69.03	11.46
74.03	3.91
75.04	5.44
80.02	1.15
80.03	3.23
81.05	100.00
89.06	4.63
93.03	4.16
95.02	3.14
95.05	1.06
98.04	4.33
99.04	1.66
102.03	10.83
105.05	14.31
109.03	4.33
114.03	3.10
117.04	17.66
119.05	1.44
124.04	18.22
133.04	8.03
136.05	9.77
137.05	11.00
139.07	4.67
145.06	6.54
148.05	2.42
149.04	2.34
149.07	1.32
151.08	4.12
155.05	29.85
163.07	0.76
167.06	13.38
168.06	8.24
169.07	5.73
174.05	11.21
175.06	1.95
181.09	1.66
183.06	14.82
186.05	2.00
187.06	15.97
189.07	2.42
195.06	2.25
198.07	4.33
199.07	7.77
202.05	1.83
205.05	21.70
211.07	4.29
217.08	26.75
218.08	3.61
224.05	5.86
229.08	5.14
230.07	5.82
233.06	15.16
237.09	6.07
245.08	18.39
252.06	6.67
261.06	4.84
265.09	1.19
267.09	5.35
276.08	3.61
280.06	3.95
291.11	33.84
292.10	1.06
295.09	79.58
296.09	8.58
310.12	74.35
311.12	6.33

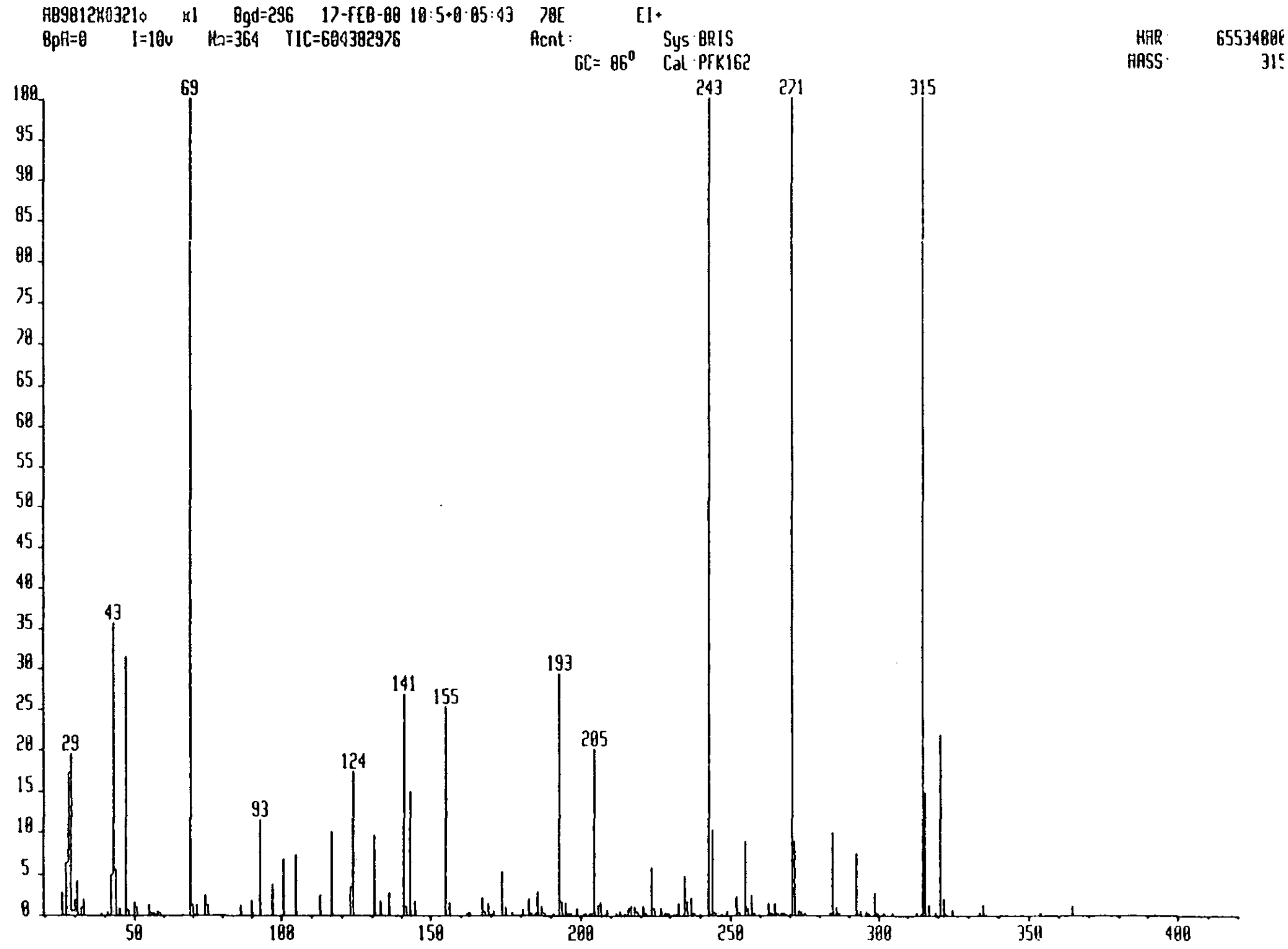


Mass	% Base
36.65	2.16
37.66	8.72
38.67	4.24
49.74	23.32
50.76	11.10
51.77	49.31
52.77	3.46
53.77	1.58
60.84	1.67
61.78	0.27
61.85	4.76
62.87	28.39
63.89	19.30
64.90	1.28
68.91	49.62
74.04	8.20
75.07	8.82
76.10	9.91
79.16	2.46
80.19	100.00
81.21	5.48
82.20	0.47
83.19	3.25
92.08	6.77
93.04	5.38
94.04	0.50
95.05	8.02
96.05	0.57
96.99	1.22
98.00	0.66
98.99	1.36
104.94	1.48
107.93	6.16
116.87	4.49
120.84	1.22
122.87	1.06
123.35	0.14
123.85	2.41
135.84	1.00
138.86	3.94
142.84	4.73
144.87	3.59
145.88	0.38
146.84	1.99
147.84	1.03
148.86	0.91

Mass	% Base
154.83	4.11
166.80	2.52
168.82	14.35
169.82	1.77
180.79	1.64
182.77	2.21
185.77	1.09
186.79	2.29
187.80	1.26
188.79	5.54
192.76	2.08
196.79	4.19
199.78	3.32
200.78	0.99
203.77	2.95
204.75	3.30
216.75	0.92
217.77	2.72
218.78	6.25
224.76	2.44
234.75	2.13
235.73	1.36
236.74	3.06
237.49	0.25
237.74	6.27
242.71	3.25
246.74	5.26
247.74	0.48
248.73	1.04
254.71	2.49
255.71	0.49
256.74	0.94
264.70	0.86
265.71	9.50
266.70	1.64
267.69	0.51
268.27	0.13
268.70	1.19
269.69	0.80
270.67	2.28
274.69	3.53
284.69	11.57
285.23	0.15
285.69	1.86
286.68	2.64
287.68	0.82

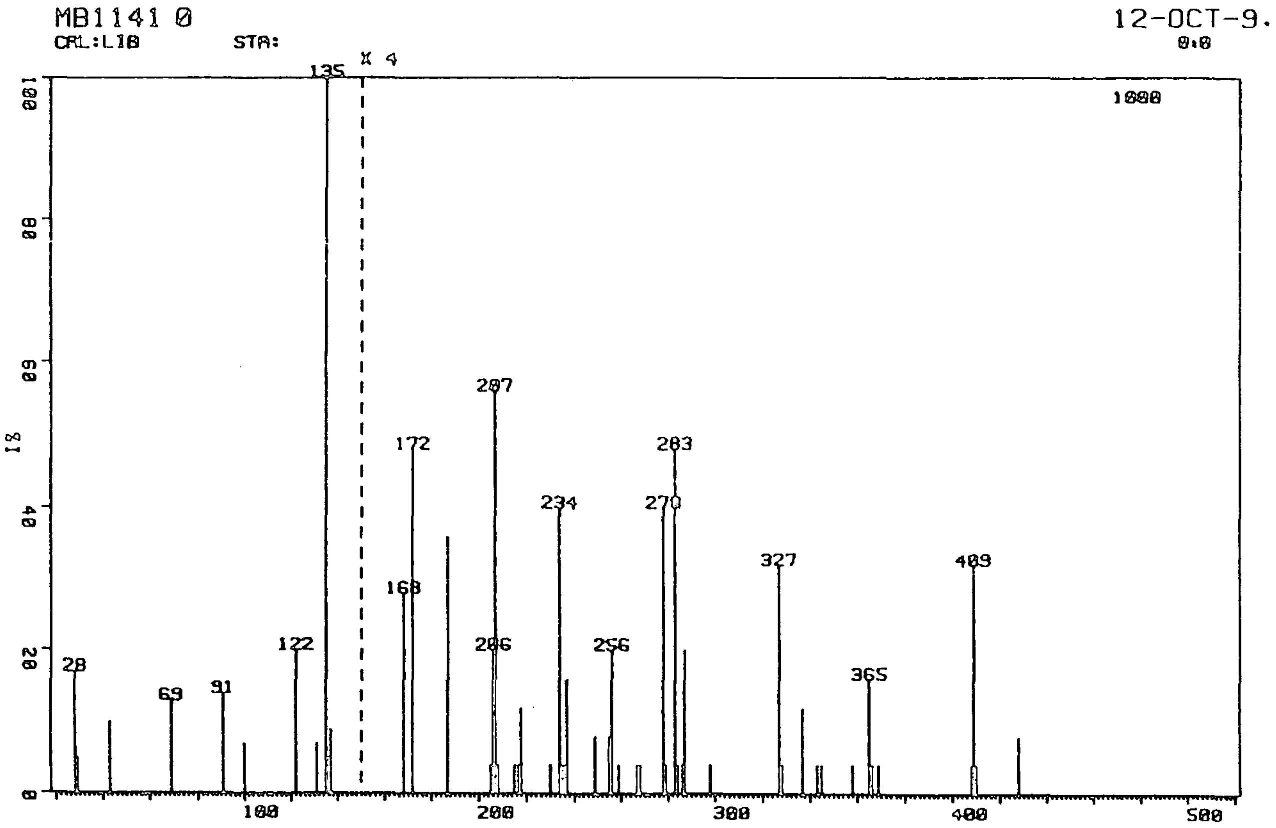
Mass	% Base
293.68	20.59
294.68	2.46
295.67	0.48
296.68	1.11
304.63	1.24
306.66	7.42
307.67	1.18
314.64	1.33
315.66	2.66
320.62	1.46
321.64	0.14
324.64	0.95
325.62	0.14
326.62	0.46
332.66	0.13
333.64	0.16
334.00	0.14
334.64	28.19
335.65	3.71
336.65	0.55
342.62	0.55
343.63	4.98
344.63	0.73
345.61	0.16
345.70	0.13
346.62	1.38
347.61	0.26
361.61	0.22
362.61	11.55
363.61	1.46
363.82	0.28
364.59	0.35
375.59	0.13
384.58	0.69
392.58	0.40
411.98	0.12
412.56	20.52
413.56	2.90
414.54	0.39
430.25	0.17
431.57	60.56
432.58	9.96
433.56	1.02

15



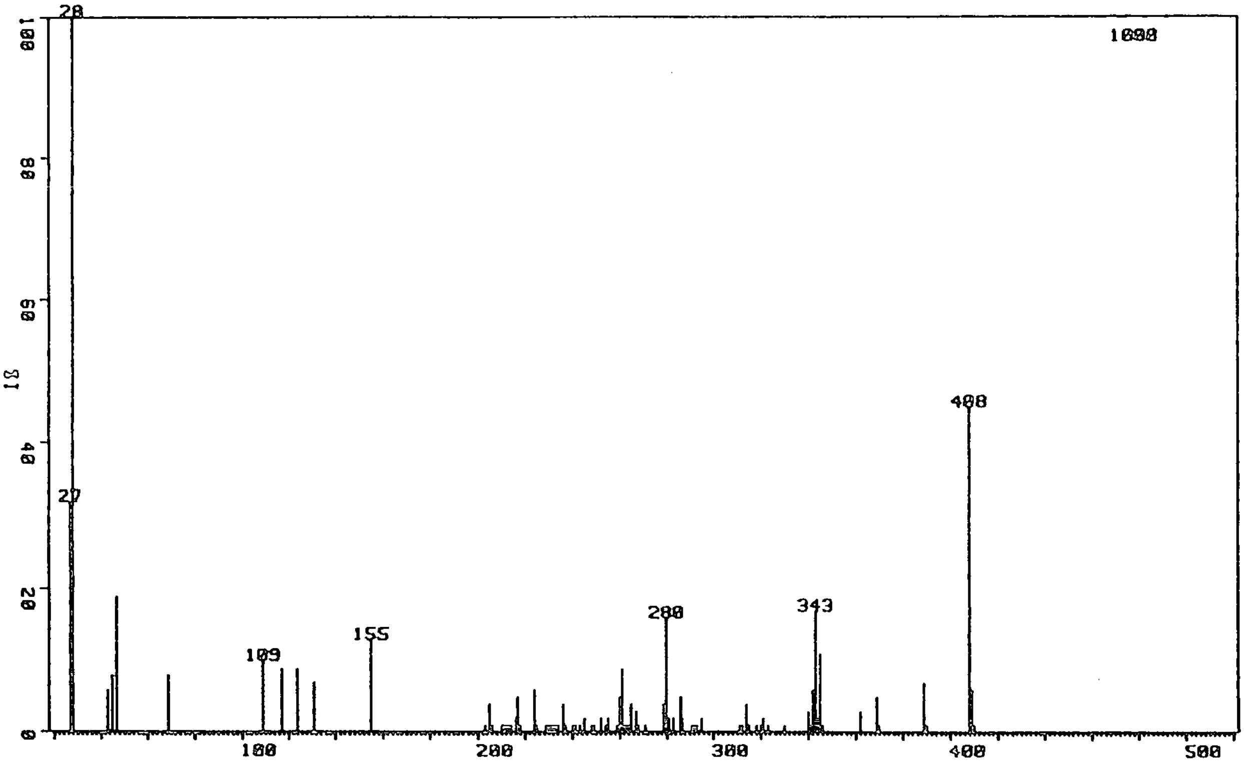
Mass	% Base
26 02	2 60
27.02	6 40
28 00	3 50 F
28.03	17 25 F
29.00	19 40
30 00	1 83
30 99	4 16 F
33 00	1 90
42 00	4 86
43 01	35 57
43 98	1 00 F
44 01	5 50 F
47 02	31 35
49 99	1.45
51 00	0.95
54 99	1.20
56.00	0.20
57.00	0.15
58.03	0 47
64.00	0.25
64.99	0.16
66.98	0.25
67.98	0.09
68.98	100 00 0
69.98	1.19
70.98	1.16
73.98	2.37
74.98	1.20
77.97	0.67
78 98	0.30
85.97	1.20
86.97	0.62
87.99	0.13
89.97	1.84
90.98	0.50
92.97	11.35
93.98	0.38
94.98	0.61
96.96	3.65
97.97	0.94
98 98	0.45
99.97	0.46
100.96	6.81
101 96	0 60
104.96	7.25
105.97	0.61
106.97	0.08
107.98	0.10
108.97	0.10
111.96	0.53
112.98	2.40
113.97	0.15
114.97	0.22
116.96	10.07
117.96	0.62
118.97	0.88
120.95	0.73
121.98	0.30
122.97	3.39
123.47	0.28
123.95	17.15
124.96	0.99
125.95	0.68
130.95	9.61
131.87	0.05
131.96	0.34
132.95	1.57
133.97	0.16
135.95	2.71
136.96	0.94
140.97	26.78
141.97	1.03
142.94	14.77
143.95	0.79
144.96	1.64
147.95	0.86
151.94	0.78
154.94	25.24
155.95	1.44
156.95	0.25
158.93	0.53
161.93	0.12
162.94	0.27
166.92	2.02
167.94	0.44
168.94	1.30
170.92	0.39
173.92	5.28
174.92	0.89
176.94	0.35
180.93	0.66
182.92	1.89
185.93	2.83
186.94	0.98
187.94	0.27
190.93	0.10
192.93	29.32
193.93	1.66
194.94	1.54
195.95	0.16
196.94	0.13
198.92	0.74
201.92	0.18
202.94	0.10
203.94	0.10
204.92	19.98
205.93	1.22
206.93	1.69
208.91	0 55
211.92	0.16
212.92	0.43
214.92	0.16
215.92	0.77
216.73	0.05
216.91	1.08 F
217.91	1.08 F
218.98	0.45 F
223.91	5.85
224.92	0.71
226.94	0.72
228.32	0.10
228.77	0.18
232.71	1.27 F
232.96	0.58 F
234.92	4.75
235.91	1.69
236.91	2.03
237.92	0.16
239.91	0.05
242.89	100.00 0
243.90	10.20
244.91	0.27
246.92	0.06
248.90	0.46
251.90	2.23
252.91	0.37
254.90	8.95
255.90	0.74
256.91	2.33
257.92	0.14
262.90	1.28
263.89	0.08
263.93	0.06
264.90	1.33
265.92	0.14
266.92	0.13
270.91	100.00 0
271.49	0.08
271.89	8.91
272.89	0.47
273.90	0.24
274.91	0.13
283.89	0.08
284.89	9.87
285.90	0.82
286.90	0.08
292.87	7.42
293.88	0.46
295.90	0.45
296.91	0.11
298.87	2.60
299.88	0.19
301.87	0.10
304.88	0.14
312.88	0.27
313.90	0.04
313.99	0.06
314.88	100.00 0
315.89	14.72
316.90	1.23
318.87	0.23
320.53	0.03
320.86	21.84
321.87	1.91
322.87	0.07
324.87	0.55
333.88	0.32
334.90	1.15
335.93	0.07
340.88	0.06
353.87	0.13
364.89	1.00

16

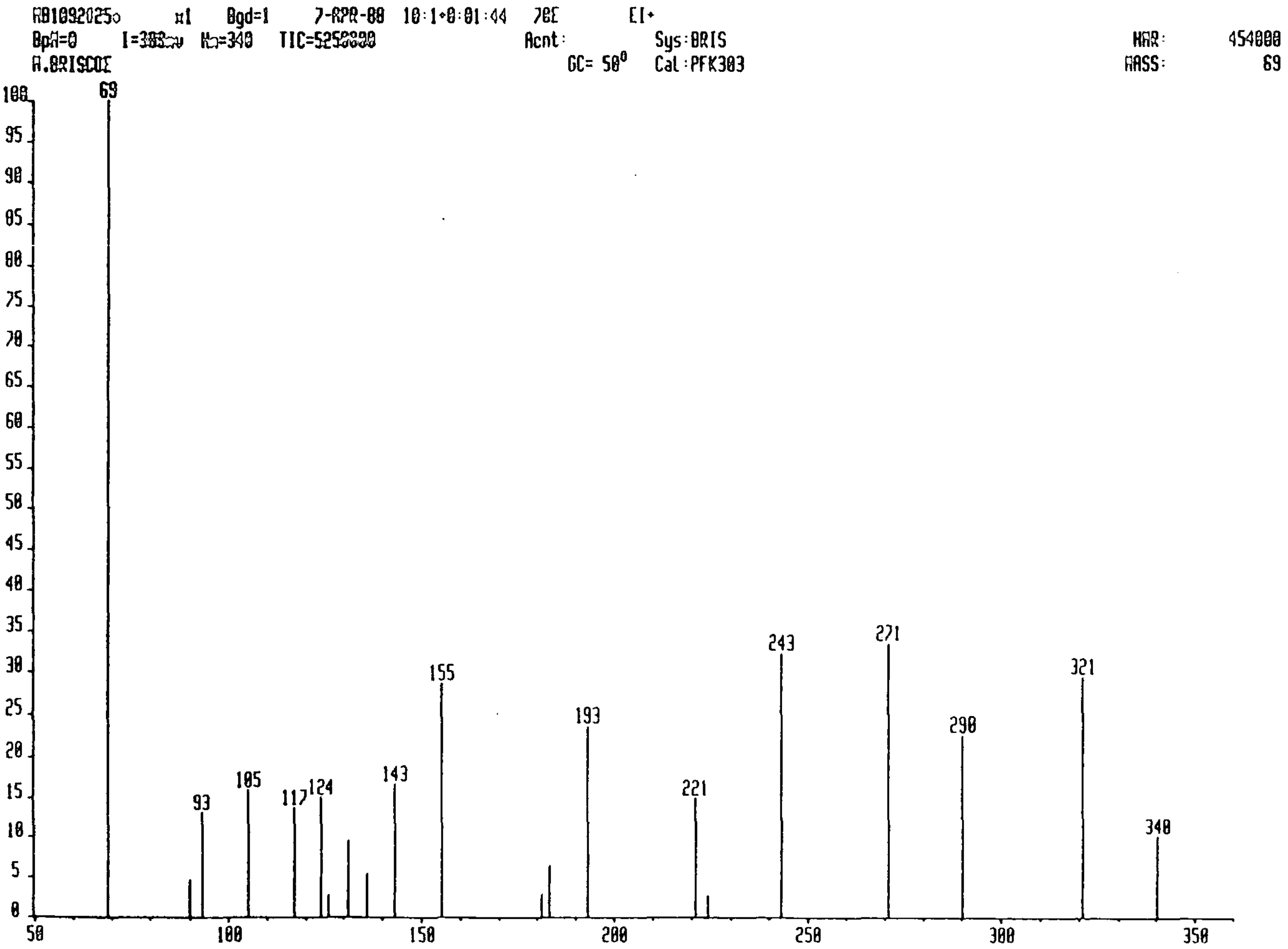


Mass	% Base	Mass	% Base	Mass	% Base
27.79	16.63	249.00	1.63	337.03	2.86
28.77	5.27	250.01	0.23	338.04	0.26
42.85	10.44	251.04	0.09	343.03	0.55
68.95	12.78	254.99	2.49	345.03	0.48
90.99	14.08	256.00	4.91	346.04	0.19
99.98	7.35	257.01	0.34	358.06	0.88
122.00	19.50	258.02	0.05	359.07	0.19
130.98	6.82	259.03	0.62	363.05	0.10
135.01	100.00	260.02	0.08	364.04	0.25
136.01	5.44	261.00	0.19	365.05	4.48
136.99	9.45	264.00	0.12	366.06	0.51
167.97	6.70	265.01	0.44	369.07	0.91
172.00	11.93	266.99	1.32	370.08	0.11
186.99	8.55	268.00	0.85	378.07	0.16
201.02	0.25	269.01	0.11	384.04	0.17
204.99	0.97	270.03	0.19	389.08	0.25
206.00	5.00	275.98	0.04	408.11	1.23
207.01	14.36	276.04	0.07	409.11	8.04
208.01	0.90	277.03	0.07	410.11	0.96
209.99	0.07	278.04	9.93	411.12	0.07
211 00	0.15	279.04	1.12	428.12	1.91
212.01	0.04	280.03	0.17	429.12	0.26
214.99	0.76	281.04	0.12		
216.01	0.06	283.02	11.95		
216.98	1.45	284.02	1.18		
217.98	3.23	285.03	0.08		
218.99	0.32	286.01	0.61		
220.01	0.13	287.02	4.94		
223 97	0.04	288.04	0.43		
225.00	0.11	289.06	0.05		
228.02	0.12	295.02	0.16		
228.99	0.27	295.99	0.04		
229 43	0.04	297.05	0.11		
229 52	0.05	298.04	1.21		
229.76	0.05	299.03	0.29		
229.99	0.46	301.04	0.06		
230.18	0.04	305.00	0.11		
231 01	0.18	306.01	0.05		
232 99	0.08	308.03	0.20		
233 99	9 52	309.04	0.22		
235 00	0.77	311.12	0.09		
235 99	1 00	311.45	0.07		
237 00	4.50	311.64	0.04		
238.00	0.38	314.00	0.30		
243.00	0.09	315.01	0.26		
244 47	0.07	317.01	0.28		
244.54	0.06	318.03	0.08		
244 69	0.08	321.04	0.05		
245 07	0.23	327.04	7.65		
245 62	0.04	328.04	1.13		
246 00	0 10	329.06	0.16		
247 04	0.07	334.01	0.08		
248 00	0.38	336.02	0.11		

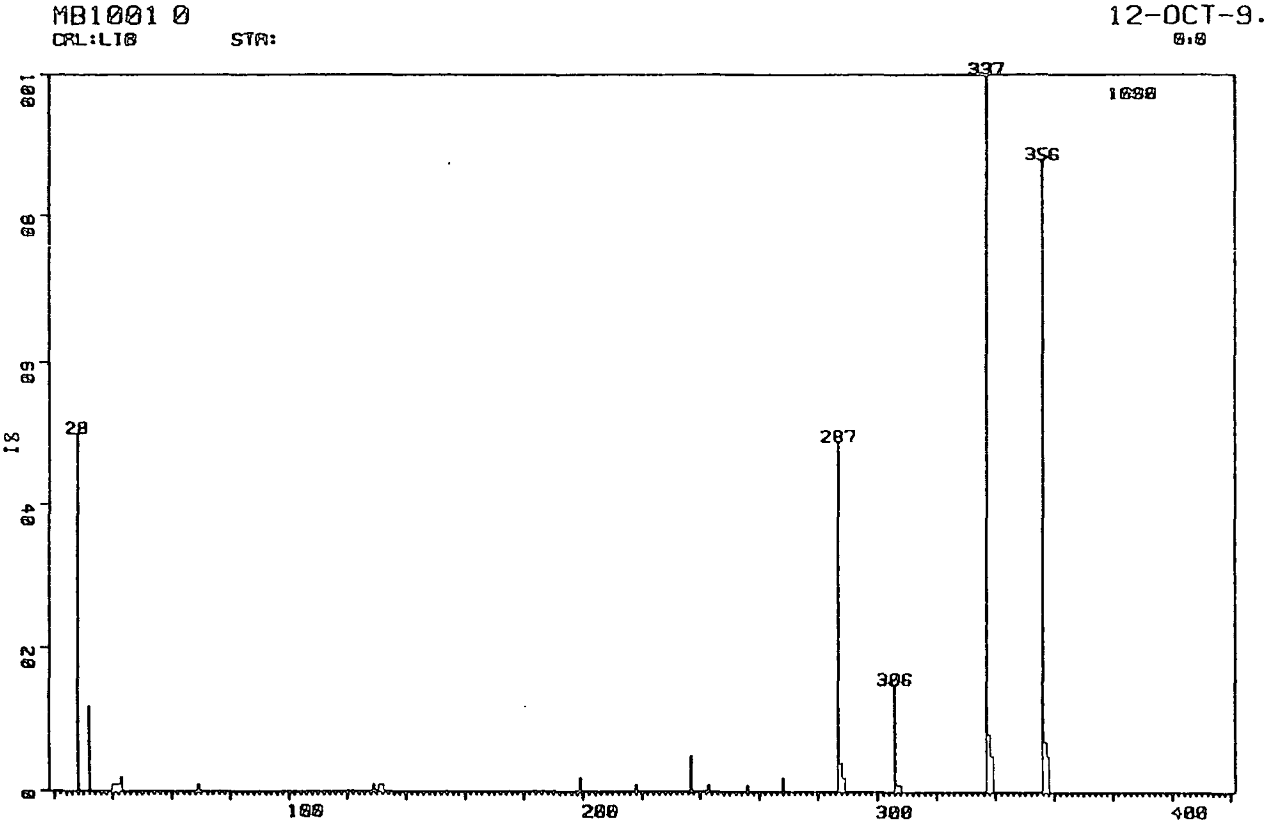
MB1142 0 12-OCT-9.
CAL:LIB STA: 0:0



Mass	% Base	Mass	% Base	Mass	% Base
26.78	32.42	242.99	1.16	310.01	0.25
27.79	100.00	244.01	0.20	311.00	0.55
42.85	6.42	244.98	1.58	312.00	1.06
44.88	7.66	245.99	0.22	313.02	0.24
46.89	19.11	246.99	0.38	313.99	3.50
68.95	7.57	247.98	0.84	314.99	0.48
108.97	9.64	248.99	0.49	316.98	0.16
116.97	9.05	251.98	1.62	318.00	0.59
123.97	8.92	252.98	0.19	318.53	0.09
130.97	6.74	254.00	1.34	318.69	0.08
154.97	12.92	254.98	1.86	318.97	0.22
201.00	0.40	256.00	0.32	320.00	0.66
202.00	0.28	257.00	0.09	321.01	2.33
202.99	0.50	258.99	1.23	322.02	0.32
204.00	0.19	260.00	4.59	323.00	0.80
204.98	4.14	260.98	9.44	323.97	0.13
205.98	1.40	261.99	1.17	327.00	0.18
206.99	0.14	263.00	1.15	330.01	1.15
208.99	0.21	263.98	0.68	331.02	0.14
209.99	1.20	264.98	3.79	332.03	0.44
210.99	0.62	266.00	0.31	333.01	0.33
211.99	0.73	266.98	3.00	334.01	0.20
213.00	1.00	267.99	0.53	335.98	0.11
213.98	0.60	270.99	0.71	339.00	0.12
214.98	0.27	272.01	0.14	340.02	2.65
215.98	1.99	272.98	0.29	341 03	0.72
216.97	4.52	273.99	0.21	342.00	6.41
217.98	0.60	275.99	0.16	343.01	17.29
220.98	0.22	276.99	0.36	344.02	1.88
222.98	0.13	278.02	0.32	345.01	11.32
223.97	6.16	279.02	4.09	346.01	1.23
224.98	0.62	280.03	15.83	347.07	0.12
225.96	0.12	281.02	2.01	349.02	0.37
226.98	0.11	282.02	0.28	354.00	0.11
228.99	1.45	282.99	1.95	358.04	0.15
230.00	1.06	284.01	0.25	359.03	0.42
230.99	0.60	285.02	0.23	360.03	0 21
232.00	1.00	286.01	4.85	361.01	0 12
232.99	0.64	287.02	1.51	362.02	3 23
233.99	0.53	288.03	0.33	363.03	0 35
235.97	4.42	289.00	0.17	364 02	0.29
236.98	1.18	290.02	0.29	368.04	0.41
238.97	0 20	291.03	0.96	369.04	5.12
239 99	0.49	292.02	0.71	370.05	0.79
241 00	1.01	293.03	0.64	380.00	0.15
241.20	0.12	293.98	0.09	389 05	6.91
241.28	0.11	295.00	2.36	390.06	0.93
241 41	0.15	296.00	0.43	405.06	0.19
241.54	0.14	299.01	0.26	408.08	45 03
241.70	0 13	301.00	0.18	408 48	0 09
241.81	0.11	301.99	0.12	409 09	5.81
241.98	0 40	305.00	0.29	410 09	0 52



Mass	% Base
28.03	100.00
32.02	24.71
36.01	4.15
38.01	1.33
40.00	1.33
44.03	2.55
69.06	17.78
90.07	0.82
93.08	2.31
105.08	2.82
117.09	2.43
124.10	2.66
126.10	0.47
131.10	1.68
136.10	0.94
143.11	2.94
155.12	5.09
181.13	0.51
183.13	1.14
193.14	4.19
221.15	2.62
224.15	0.47
243.16	5.72
271.17	5.91
290.18	3.99
321 19	5.21
340.20	1.80



Mass	% Base
26.94	0.34
27.92	49.66
28.92	0.41
28.96	0.18
31.91	11.79
35.91	0.20
38.96	0.26
39.90	0.75
40.98	0.67
41.99	0.51
43.00	1.77
43.94	0.42
57.02	0.20
68.99	0.97
74.03	0.16
93.01	0.16
106.00	0.16
113.00	0.16
128.94	0.96
129.99	0.38
130.94	0.73
131.93	1.00
133.93	0.42
135.94	0.30
143.03	0.17
149.00	0.31
181.03	0.20
193.04	0.22
199.02	2.00
200.04	0.13
205.03	0.18
218.02	0.47
237.02	5.21
238.02	0.40
239.02	0.23
243.05	0.78
249.02	0.23
256.03	1.05
268.03	1.73
269.03	0.18
287.04	49 11
288.04	3.64
289.03	2.21
306.05	15.37
307.05	1.23
308.05	0.78
318.06	0.41
337.05	100.00
338.05	7.81
339.04	5.11
340.05	0.28
355.25	0.10
355.53	0.12
355.63	0.16
356.06	88.28
356.49	0.14
357.06	7.29
358.05	4.59
359.05	0.29

20

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AB1003X0367o    x1    Bgd=357    10-FEB-00 12:1+0:06:32    70E        EI+
BpA=0    I=10v    Ma=382    TIC=453400992                Acnt:        Sys:ORIS                    MAR:    65534000
                                                          GC= 94°     Cal:PFK162                  MASS:        330
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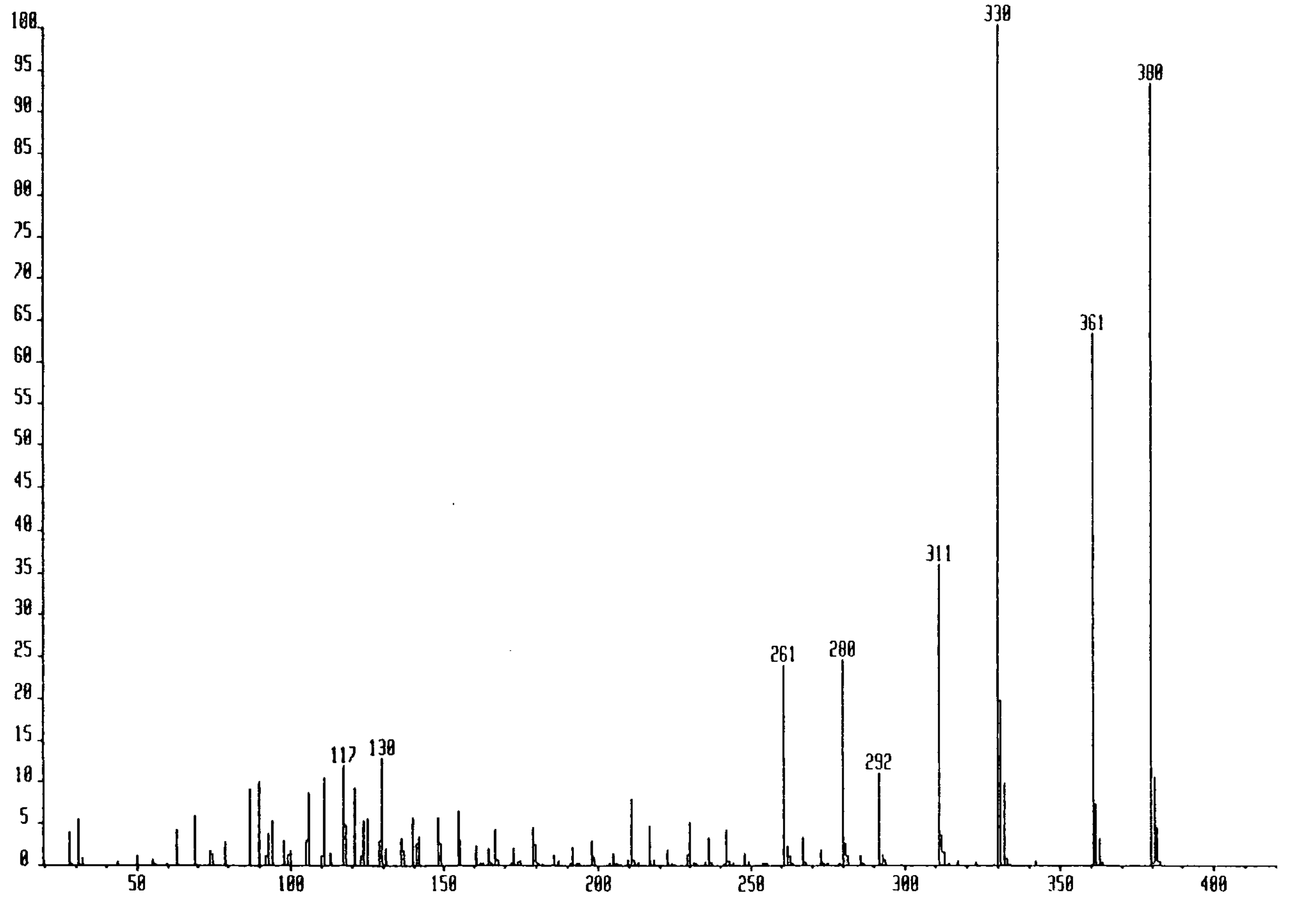

Mass	% Base
28.01	3.91
31.00	5.54
50.00	1.07
55.00	0.65
55.97	0.03
60.00	0.07
62.97	4.10
67.97	0.47
68.99	5.83
70.97	0.84
73.04	0.20
73.99	1.59
74.96	1.16
76.96	0.07
78.99	2.66
79.97	0.47
80.47	0.60
86.96	9.07
87.96	0.32
88.96	0.37
89.49	0.15
89.97	9.92
90.47	0.66
90.97	0.52
91.96	1.02
92.98	3.65
93.96	5.19
94.96	0.10
95.96	0.28
97.98	2.88
98.96	1.13
99.98	1.61
104.98	2.69
105.47	2.91
105.95	8.64
109.98	1.09
110.95	10.35
111.46	0.08
111.96	0.62
112.95	1.37
114.47	0.05
114.96	0.81
115.47	0.06
115.96	0.08
116.98	11.89
117.95	4.79

Mass	% Base
119.95	0.14
120.96	9.26
121.46	0.78
121.97	0.89
122.95	1.02
123.97	5.24
124.95	5.45
125.95	0.13
126.95	0.22
128.97	2.85
129.95	12.79
130.46	0.70
130.96	1.96
131.94	0.60
134.95	0.64
135.97	3.09
136.45	0.14
136.94	1.58
139.96	5.58
140.46	0.60
140.97	2.46
141.94	3.24
147.96	5.70
148.94	2.56
154.96	6.36
155.44	2.83
155.94	0.96
156.45	0.08
159.95	0.91
160.92	2.25
166.94	4.19
167.93	0.65
171.94	0.08
172.92	1.86
178.96	4.43
179.93	2.42
197.95	2.83
198.93	0.94
203.92	0.14
204.95	1.29
210.92	7.86
211.92	0.66
212.92	0.36
216.94	4.64
217.93	0.54
222.92	1.76

Mass	% Base	
228.94	1.21	
229.92	5.03	
230.92	0.34	
231.92	0.20	
234.93	0.23	
235.94	3.26	
236.10	0.04	
236.94	0.35	
240.95	0.17	
241.91	4.21	
242.92	0.42	
243.91	0.16	
247.93	1.35	
260.91	23.86	
261.91	2.20	
262.91	1.10	
263.91	0.10	
266.93	3.31	
267.94	0.27	
272.91	1.71	
279.90	24.47	
280.91	2.45	
281.90	1.11	
285.91	1.05	F
286.00	0.58	F
291.89	10.92	
292.31	0.05	
292.34	0.05	
292.41	0.05	
292.57	0.06	
292.95	1.22	
293.58	0.05	
293.88	0.55	
298.88	0.03	
310.89	35.80	
311.90	3.59	
312.89	1.55	
313.90	0.12	
316.92	0.38	
322.89	0.27	
328.75	0.05	
329.94	100.00	
330.89	19.78	
331.89	9.79	
332.89	0.77	
333.92	0.03	

Mass	% Base
341.89	0.49
360.29	0.04
360.88	63.08
361.89	7.19
362.89	3.10
363.90	0.27
379.88	93.03
380.35	0.09
380.88	10.56
381.88	4.48
382.88	0.49

```
RB105X0476◇     x1     Bgd=466   4-DEC-87  15:0+0:00:29   70E          EI+
BpM=121   I=6.9v   Hm=482   TIC=272230016              Acnt:            Sys:BRIS                                KnR:     45190
                                                             GC= 183°  Cal:PFK412                              MASS:
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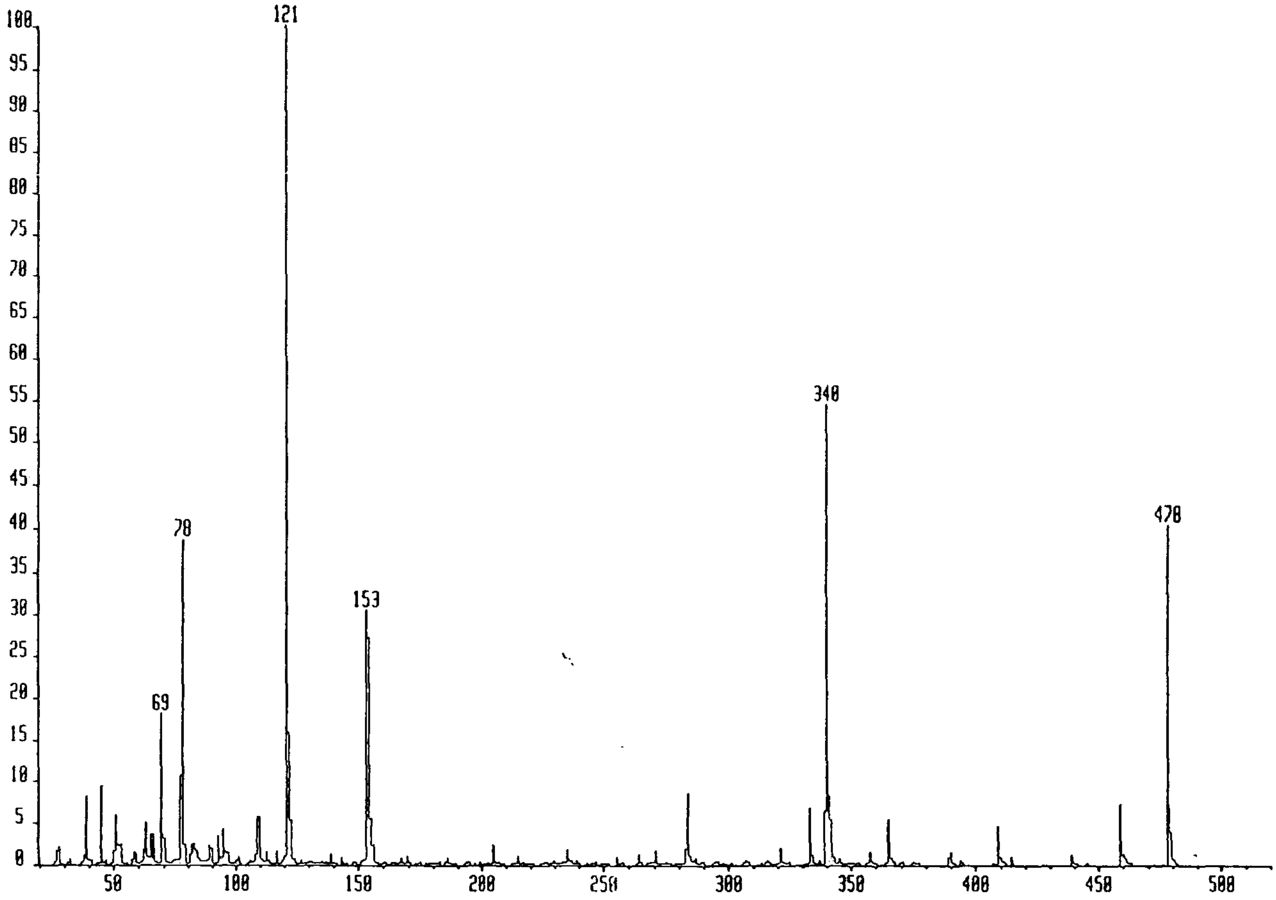
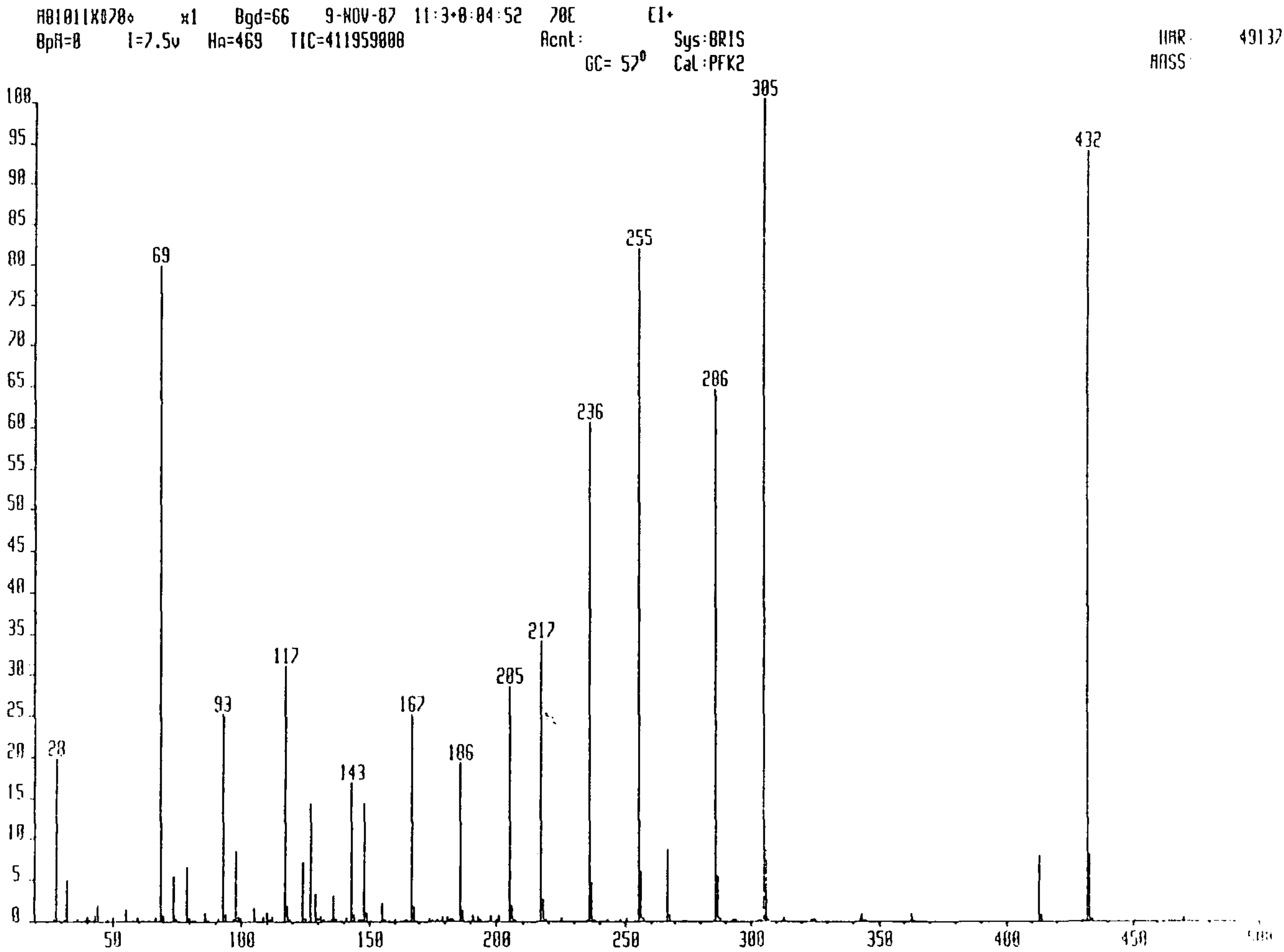
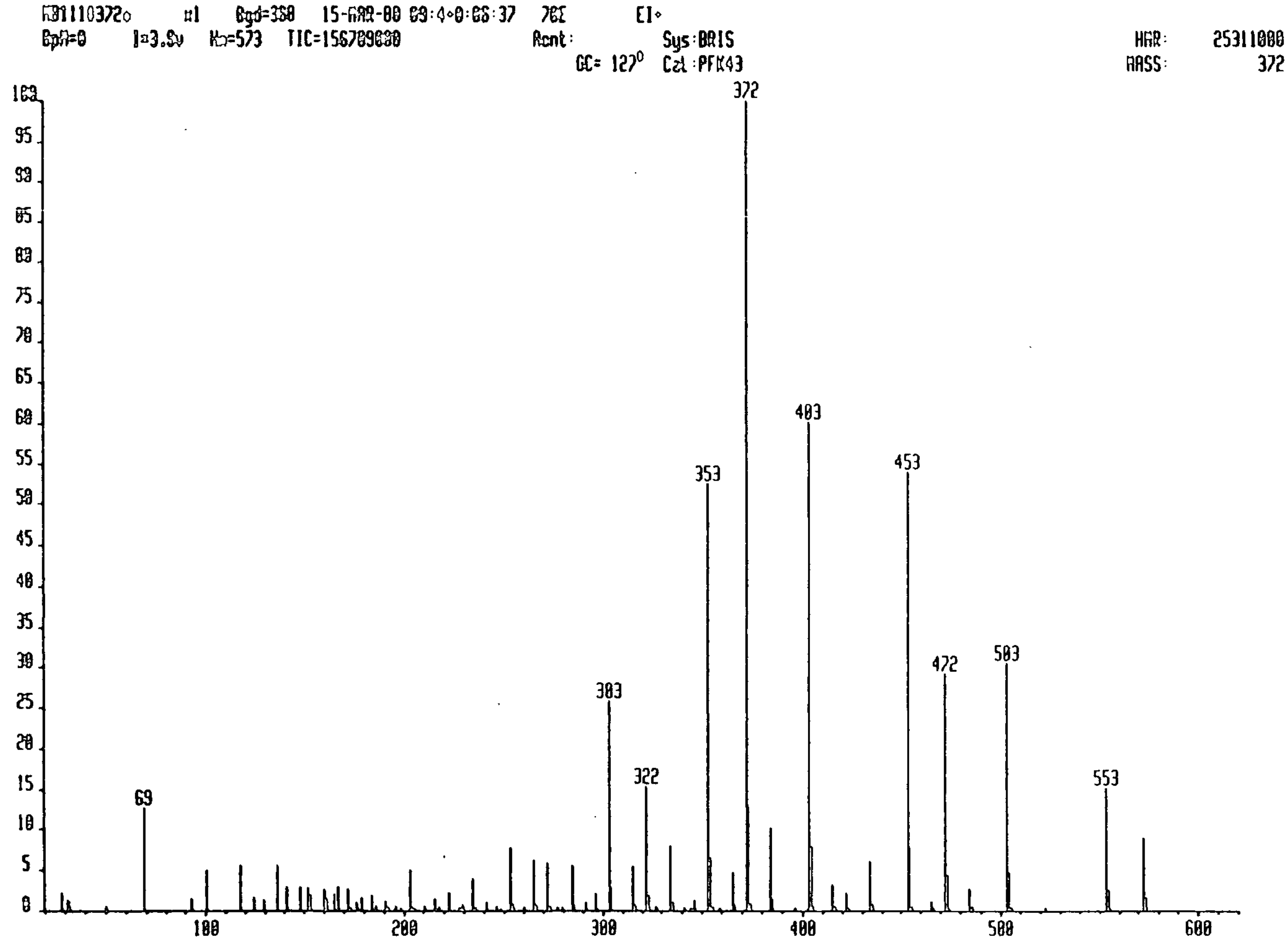


Mass	% Base
25.99	0.23
27.00	1.65
27.98	2.02
37.98	1.00
39.00	8.12
40.00	0.56
44.94	9.30
49.98	1.68
50.99	5.94
52.00	2.38
53.01	2.30
57.96	1.53
58.96	1.15
61.98	1.77
62.99	4.99
63.91	0.37
63.99	0.90
65.00	3.51
66.01	3.61
68.96	18.08
69.04	0.10
69.95	3.56
70.96	3.18
77.00	10 73
78.01	38 68
79.02	2.41
80.94	1.15
81.95	2 31
83.96	1.58
84.97	0.75
89.00	2.22
92.95	3.36
93.95	0.85
94.96	4.13
95.97	1.42
96.97	1.35
107.96	1.15
108.97	5.85
112.92	1.43
120.97	100.00
121.09	0.07
121.97	15.87
122.97	5.34
138.93	1.21
152 93	30 47
153.94	27 22
154.94	5.45
155.94	2.40
166.95	0.68
169.94	1.08
185.95	0.78
204.94	2.39
214.98	1 00
234.95	1.81
235.95	0.66
236.93	0.50
237.96	0.21
238.95	0.44
254.94	1.11
255.94	0.28
256.95	0.23
257.95	0.08
262.96	0.12
263.98	1.25
268.93	0.25
269.94	0.32
270.94	1.67
271.95	0.19
272.95	0.18
273.94	0.12
274.94	0.23
275.95	0.12
276.94	0.12
278.84	0.08
279.93	0.09
280.96	0.14
281.31	0.04
281.98	0.17
282.22	0.10
282.91	1.91
283.95	8.65
284.26	0.07
284.95	1.06
285.95	0.40
286.91	0.68
287.92	0.20
288.93	0.37
289.93	0.29
293.97	0.08
294.95	0.23
295.95	0.35
306.96	0.51
307.97	0.28
312.94	0.17
314.96	0.26
315.93	0.46
318.92	0.11
319.94	0.19
320.94	1.94
321.94	0.35
322.93	0.19
323.95	0.08
324.92	0.25
330.97	0.06
331.97	0.12
332.97	6.66
333.98	1.08
334.98	0.08
336.91	0.44
338.92	6.30
339.92	54.31
340.93	8.35
341.92	5.31
342.92	0.90
343.92	0.20
344.96	0.79
345.99	0.12
349.99	0.16
352.30	0.11
352.47	0.10
352.87	0.08
355.92	0.15
356.92	0.32
357.94	1.48
358.94	0.35
359.94	0.14
360.01	0.08
363.95	0.08
364.95	5.41
365.96	0.67
366.95	0.32
369.94	0.12
370.93	0.36
374.92	0.35
375.96	0.19
376.93	0.15
388.92	0.92
389.93	1 49
390.94	0.35
391.93	0.18
393.90	0.46
394.90	0.11
406.92	0.12
407.91	0.06
408.94	4.62
409.94	0.90
410.95	0.42
411.94	0.12
413.99	0.82
415.00	0.14
438.93	1.20
439.93	0.21
440.94	0.12
444.93	0.21
458.93	7.20
459.94	1.21
460.93	0.76
461.95	0.11
462 91	0 09
475.92	0 07
477.89	40.19
478.90	7 09
479.90	3.89
480.90	0 54
481.91	0 12



Mass	% Base	Mass	% Base	Mass	% Base
26.93	0.14	135.99	3.01	237.01	4.54
27.92	19.71	136.14	0.04	238.01	0.16
28.92	0.18	136.40	0.03	242.99	0.08
28.95	0.08	136.99	0.19	248.00	0.12
30.92	0.20	138.91	0.06	250.91	0.24
31.91	4.88	141.00	0.28	255.00	81.82
35.90	0.11	142.99	16.75	255.56	0.04
39.90	0.39	144.00	0.67	255.64	0.05
40.97	0.22	145.91	0.19	256.00	5.99
41.98	0.16	146.95	0.17	257.00	0.26
42.95	0.04	147.46	0.04	267.00	8.58
42.99	0.54	148.00	14.16	268.00	0.81
43.93	1.74	149.00	0.91	274.01	0.05
47.93	0.10	150.88	0.04	285.30	0.05
49.93	0.43	155.00	2.11	286.01	64.43
54.94	1.35	155.99	0.12	286.39	0.02
59.95	0.23	157.92	0.05	287.01	5.41
61.95	0.03	159.99	0.10	288.01	0.24
66.97	0.31	167.00	24.96	293.00	0.14
68.97	79.64	168.00	1.59	293.92	0.12
69.98	0.60	169.02	0.07	305.01	100.00 F
73.98	5.28	174.00	0.33	306.02	8.55
74.98	0.17	176.91	0.21	307.02	0.36
78.99	6.54	179.00	0.41	312.93	0.31
80.00	0.36	181.00	0.47	324.01	0.13
91.00	0.13	181.93	0.12	324.94	0.10
92.99	25.09	186.00	19.11	343.01	0.23
94.00	0.73	187.00	1.23	343.92	0.74
96.99	0.09	190.95	0.61	344.85	0.04
98.00	8.47	192.99	0.41	345.00	0.03
99.00	0.43	197.99	0.66	362.93	0.67
99.99	0.26	199.72	0.14	363.94	0.05
105.00	1.45	200.02	0.06	412.93	7.92
105.99	0.07	200.07	0.09	413.93	0.72
106.02	0.06	200.22	0.04	430.01	0.03
108.49	0.46	200.91	0.56	430.24	0.03
110.00	0.85	204.99	28.38	430.44	0.06
117.00	30.99	205.99	1.85	431.91	93.58
118.00	1.75	207.03	0.18	432.93	7.98
124.00	7.17	216.99	33.98	433.93	0.28
125.00	0.29	218.00	2.50	450.98	0.06
126.91	14.20	219.00	0.10	469.95	0.47
129.00	3.19	224.92	0.36		
130.00	0.26	236.00	60.45		
130.97	0.53	236.32	0.06		
131.91	0.15	236.47	0.03		



Mass	% Base
28.05	2.05
31.05	1.16
50.07	0.47
69.09	12.60
74.09	0.21
79.10	0.17
81.09	0.21
86.10	0.70
93.10	1.35
98.11	0.47
100.12	4.95
101.62	0.34
103.12	0.39
105.12	0.34
110.14	0.13
117.13	5.51
118.13	0.21
119.12	0.18
122.13	0.48
124.13	1.41
126.63	0.34
129.13	1.17
131.14	0.72
132.05	0.17
132.65	0.13
134.14	0.28
136.14	5.49
136.65	0.09
141.15	2.77
142.15	0.49
143.14	0.20
146.15	0.15
148.14	2.84
151.64	2.61
152.13	0.17
153.15	1.81
155.15	0.85
160.15	2.58
161.15	1.29
165.15	1.97
167.14	2.81
172.15	2.52
173.13	0.10
176.64	0.86
177.13	0.15
179.16	1.49
184.17	1.83
186.16	0.38
191.17	1.00
192.17	0.32
196.17	0.50
198.18	0.18
203.18	4.94
204.18	0.34
205.19	0.09
210.19	0.38
215.19	1.29
217.17	0.34
222.19	2.02
229.20	0.53
234.20	3.80
235.19	0.29
241.20	0.92
246.20	0.43
248.22	0.20
253.21	7.75
254.21	0.72
260.20	0.23
265.22	6.00
266.22	0.53
272.22	5.84
273.22	0.50
277.20	0.28
279.22	0.32
284.22	5.44
285.23	0.58
291.23	0.88
296.24	1.98
297.21	0.10
297.26	0.20
303.22	25.83
303.43	1.54
304.23	2.65
315.27	5.33
316.27	0.62
322.24	15.24
323.24	1.79
327.25	0.48
334.25	7.85
335.25	0.91
341.25	0.28
343.97	0.10
344.39	0.19
344.52	0.10
346.26	1.15
353.26	52.41
354.27	6.44
355.28	0.32
358.60	0.13
358.83	0.15
359.20	0.10
359.24	0.11
365.27	4.57
366.26	0.58
371.21	0.07
372.26	100.00
373.27	12.80
374.27	0.76
384.28	10.03
385.28	1.40
396.28	0.26
402.77	0.12
403.28	60.14
404.28	7.91
405.27	0.40
415.30	3.15
416.28	0.37
422.30	2.05
423.31	0.20
434.29	6.04
435.29	0.77
453.31	53.89
454.31	7.67
455.31	0.40
465.34	1.04
466.34	0.12
472.31	29.17
473.31	4.36
474.34	0.18
484.31	2.73
485.31	0.37
503.33	30.52
504.34	4.58
505.34	0.28
522.34	0.26
553.36	15.10
554.37	2.55
555.33	0.13
572.37	8.92
573.38	1.48

APPENDIX 4:

(A) UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKER:

1st AUGUST 1985 TO 31st JULY 1986

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

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

(B)

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

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

13.11.86* Prof. Sir G. Allen (Unilever Research)
Biothechnology and the Future of the Chemical Industry

6.5.87 Dr. R. Bartsch (University of Sussex)
Low Co-ordinated Phosphorus Compounds

27.5.87 Dr. M. Blackburn (University of Sheffield)
Phosphonates as Analogues of Biological Phosphate

9.5.87* Prof. F.G. Bordwell (Northeastern University, U.S.A.)
Carbon Anions, Radicals, Radical Anions and Radical Cations

26.11.86 Dr. N.D.S. Canning (University of Durham)
Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis

11.5.87 Dr. R.D. Cannon (University of East Anglia)
Electron Transfer in Polynuclear Complexes

28.1.87 Dr. W. Clegg (University of Newcastle-upon-Tyne)
Carboxylate Complexes of Zinc; Charting a Structural Jungle

5.11.86 Prof. D. Döpp (University of Duisberg)
Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes

8.12.86 Prof. T. Dorfmuller (University of Bielefeld)
Rotational Dynamics in Liquids and Polymers

12.5.87* Dr. E.M.Goodger (Cranfield Institute of Technology)
Alternative Fuels for Transport

16.10.86* Prof. N.N. Greenwood (University of Leeds)
Glorous Gaffes in Chemistry

7.5.87 Dr. M. Harmer (I.C.I. Chemicals and Polymer Group)
The Role of Organometallics in Advanced Materials

5.2.87* Dr. P. Hubbersley (University of Nottingham)
Demonstration Lecture on Various Aspects of Alkali Metal Chemistry

17.3.87 Prof. R.F. Hudson (University of Kent)
Aspects of Organophosphorus Chemistry

15.3.87 Prof. R.F. Hudson (University of Kent)
Homolytic Rearrangements of Free Radical Stability

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

(C)

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

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

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

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

25.2.88	Prof. A. Underhill (University of Bangor) Molecular Electronics
26.11.87	Dr. D.H. Williams (University of Cambridge) Molecular Recognition
15.10.87	Dr. M.J. Winter (University of Sheffield) Pyrotechnics (Demonstration Lecture)

NB. The lectures marked * were attended.

(D) RESEARCH CONFERENCES ATTENDED

R.S.C. (N.E. section) General Poster Meeting
University of Newcastle-upon-Tyne, December 1985

Graduate Symposium, University of Durham, April 1986

R.S.C. Postgraduate Heterocyclic Symposium,
University of Aston, July 1986

International Symposium to celebrate the
"Centenary of the discovery of Fluorine"
University of Paris, Paris, France, August 1986

R.S.C. Postgraduate Heterocyclic Symposium,
University of Keele, July 1987

21st Sheffield Symposium on "Modern Aspects
of Stereochemistry"
University of Sheffield, December 1987

Graduate Symposium, University of Durham, April 1988

12th. International Symposium on Fluorine Chemistry,
University of California, Santa Cruz, U.S.A., August 1988

(E) FIRST YEAR INDUCTION COURSE OCTOBER 1985

The course consists of a series of one hour lectures, explaining the uses and limitations of the various services available in the Department.

(1) Departmental Organisation - Dr. E. J. F. Ross

(2) Safety Matters - Dr. M. R. Crampton

(3) Electrical appliances and infrared spectroscopy

(4) Chromotography and microanalysis - Mr. T. F. Holmes

(5) Atomic absorptiometry and inorganic analysis
- Mr. R. Coult

(6) Library Facilities - Mr. R. B. Woodward

(7) Mass Spectroscopy - Dr. M. Jones

(8) Nuclear Magnetic Resonance Spectroscopy
- Dr. R. S. Matthews

(9) Glass blowing techniques - Mr. R. Hart and Mr. G. Haswell

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