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Electrochemically induced reactions of some fluorocarbon derivatives

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ELECTROCHEMICALLY INDUCED REACTIONS OF

SOME FLUOROCARBON DERIVATIVES

Submitted by

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TO MY PARENTS

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MEMORANDUM

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

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

R.D. Chambers, C.R. Sargent, M.J. Silvester, and F.G. Drakesmith, J. Fluorine Chem., 1980, 15, 257.

ABSTRACT

The oxidation of polyfluoroanisoles gave the corresponding 4,4'-dimethoxybiphenyl derivatives. A vacant _para_ position was shown to be a necessary condition for this coupling reaction. The electron transfer process was found to be thermodynamically irreversible by cyclic voltammetry.

Oxidation of polyfluorinated aromatic amines and phenols generally gave multi-component mixtures, although their voltammetry was simple. The oxidation of pentafluorophenol was greatly improved by the use of trifluoroacetic acid as solvent.

The reaction of octafluorobut-2-ene with some amines was investigated. Products from reaction with primary amines adopted the imine form; the lack of reaction with diethylamine was accounted for by steric hindrance. _Trans_-2H-heptafluorobut-2-ene behaved similarly. The influence of solvent on the reaction between hexafluorobut-2-yne and diethylamine was investigated. Oxidation of fluorinated amino-alkenes gave dimeric products if there was an unsubstituted position at the double bond.

Reduction of perfluorocyclohexene gave oligomers. Reduction of perfluorocyclopentene in N,N-dimethylformamide gave a polymer; no reduction in acetonitrile was noted. Only trapping with perfluorocyclohexene was successful, no polymer was produced and cooligomers were produced.

Reduction of 2,3-dichloro-hexafluorobut-2-ene gave poly(hexafluorobut-2-yne). Hexafluorobut-2-yne could not be reduced electrochemically.

NOMENCLATURE

I. The prefix perfluoro is used before a name to denote that the compound or the part of the compound following the prefix is fully fluorinated.

2. A capital F in a ring (e.g. $\boxed{F}$) denotes that the ring and its unspecified substituents are fully fluorinated.

CONTENTS

INTRODUCTION

CHAPTER I

EXPERIMENTAL METHODS

I.A INTRODUCTION

The technique of electro-organic chemistry has been extensively reviewed.[1-4] This chapter will, therefore, provide only a brief introduction with an emphasis on relevant practical details.

I.B AN ELECTROCHEMICAL REACTION

An electrochemical reaction is a reaction in solution, in which the first step is electron transfer to, (oxidation), or from, (reduction), an electrode. Whether or not this will occur will depend on the potential of the electrode and the energy of the relevant molecular orbital of the substrate. Thus, it would be expected that there should be a correlation between oxidation potential and the gas phase ionisation potential. This will be discussed in more detail later.

When an electron is removed from a neutral substrate, AH, the product is a radical cation, $AH^{\bullet +}$, which can then undergo various reactions (Scheme I.I).

Scheme I.I Reactions of a Radical Cation

(1) Electron Transfer $\qquad\qquad\qquad\qquad AH^{\bullet +} \longrightarrow AH^{2+} + e^-$

(2) Disproportionation $\qquad\qquad\qquad 2AH^{\bullet +} \longrightarrow AH^{2+} + AH$

(3) Coupling $\qquad\qquad\qquad\qquad\qquad 2AH^{\bullet +} \longrightarrow AA + 2H^+$

(4) Reaction with a nucleophile $\quad Nuc^- + AH^{\bullet +} \longrightarrow AHNuc^\bullet$

(5) Reaction with a base $\qquad\qquad B: + AH^{\bullet +} \longrightarrow A^\bullet + BH^+$
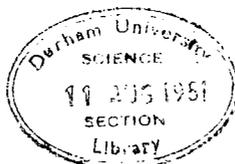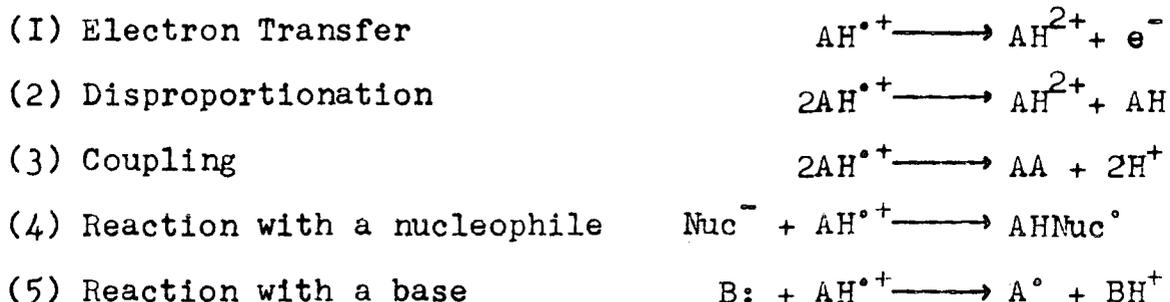
Reactions (4) and (5) are similar and are the source of much discussion.[5] It is usually found that the radical species, AHNuc°, and, A°, are much easier to oxidise than AH, so that their respective cations are readily obtained. Reaction sequences are described in terms of E, (electrochemical), and C, (chemical), stages. For example, initial electron transfer followed by reaction (4), a further electron transfer, and a chemical terminating step would be referred to, in electrochemical nomenclature, as an ECEC reaction.

I.C : PRACTICAL ASPECTS

An electrochemical oxidation is carried out at an anode, (working electrode), with a cathode, (counter electrode), completing the circuit. A reference electrode is placed close to the surface of the working electrode and is used, in conjunction with a potentiostat, to control the potential of the working electrode. An inert solvent and supporting electrolyte are also required. The reaction is normally carried out in a cell divided into two compartments by a diaphragm, such that current will pass but ideally no substrate. Thus, any species produced by oxidation at the anode will not be subsequently reduced at the cathode. A typical arrangement for a three electrode cell is shown in Figure I.I.

Figure I.I A three electrode cell
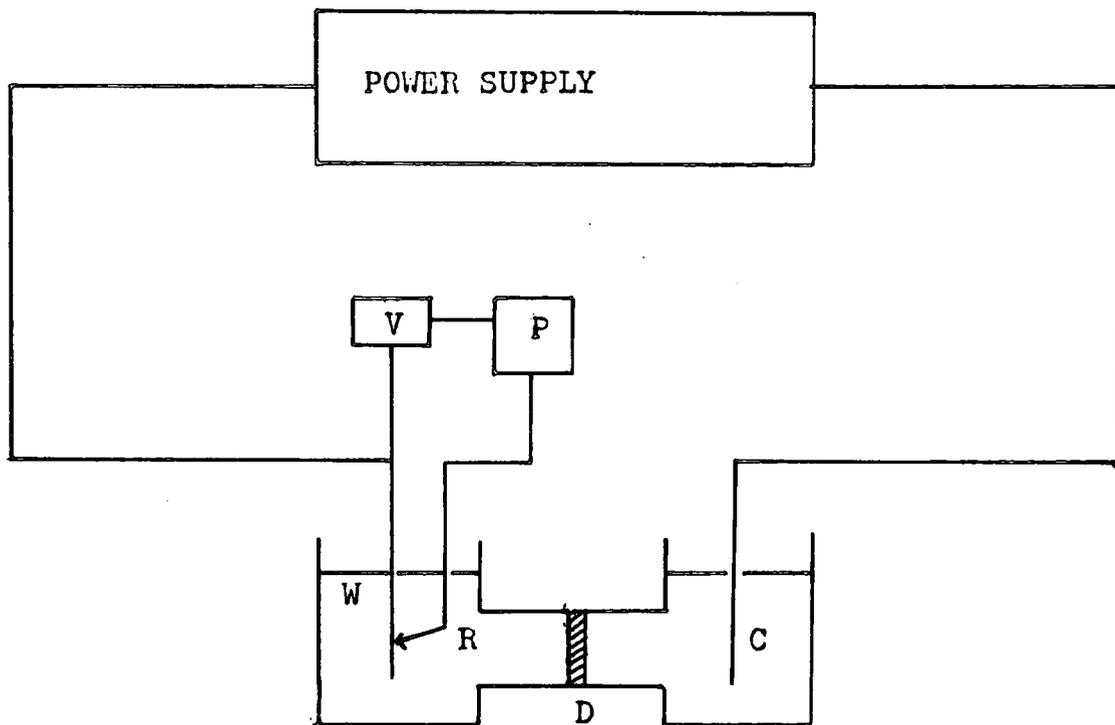
C - counter electrode   D - diaphragm   P - potentiostat
R - reference electrode W - working electrode V - voltmeter

Figure I.I also illustrates the practical arrangement required for a constant potential electrolysis. The potentiostat is a device which maintains the potential between the working electrode and the reference electrode at a pre-selected value. Thus, in the case of competing reactions, occurring at different potentials, it is possible to select only one of these reactions. Alternative methods of electrolysis are constant current and constant voltage. Although these are much simpler in design, they are not as selective.

I. <u>Electrodes</u>

The materials which can be used as an anode are limited because of corrosion during the electrolysis. Platinum has found wide use because of its relative inertness in most environments. However this can be deceptive, as in aqueous solvents at potentials greater than +0·75V (versus the saturated calomel electrode) there is thought to be an oxide coating, such that the electrode material may in fact be platinum oxide.[6] Other materials which can be used are carbon, lead, and lead dioxide.

A much wider choice is available for the cathode material, with the most common being mercury; platinum, lead, copper, zinc, aluminium, and carbon have also been used. The principle advantage of a mercury cathode is that, being a liquid, it can be stirred and hence provide a clean, reproducible surface. In some cathodic reactions it is possible for the electrode to be consumed in the formation of an organometallic compound. This can be used to prepare organomercury and organolead compounds in good yield and therefore may be desirable. (See, for example, the relevant chapters in references I and 2).

The choice of material for the working electrode is important, as the course of the reaction may depend on it. For example, the tendency to further oxidation of an initially formed radical to a carbocation is higher at carbon than at platinum.[7] Adsorption of the substrate onto the metal surface may also affect the reaction. Methanol

has been found to be dissociatively adsorbed at platinum
and the molecular fragments are then oxidised in coupled,
succeeding electrochemical steps.[8]

A reference electrode is a half-cell that defines a
potential to which all other measurements are referred.
The primary standard electrode is the normal hydrogen
electrode. However, it is more convenient to use other
reference electrodes, such as the saturated calomel,
(S.C.E.), whose half-cell reaction is,

$$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$$

The potential of this reference electrode is +0.242V
relative to the normal hydrogen electrode at 25°C. Other
reference electrodes which can be used are Ag/Ag^+,
$Ag/AgCl$, and $Pb/Pb(NO_3)_2$.

2. Supporting Electrolyte and Solvent

Not only can the course of a reaction depend on the
electrode material but it can also depend on the choice of
solvent and supporting electrolyte. For example, in the
electrolysis of acrylonitrile in aqueous solutions,
hydrodimerisation to adiponitrile occurs when the electro-
lyte is a quaternary ammonium salt, whereas simple
saturation leading to propionitrile is favoured when
alkali metal cations are present. It is believed that this
is due to preferential adsorption of onium cations at the
electrode, which then gives rise to a layer at which proton-
ation of the species formed on charge transfer is disfavoured.[9]

The most widely used electrolytes are quaternary ammonium and alkali metal fluoroborates and perchlorates.

Many early electrochemical reactions were carried out in aqueous or aqueous-organic solutions. However this limits the number of reactions which can be studied because of solubility and available potential range. Non-aqueous solvents have become more widely used, especially as they are relatively inert to most reactive species and have a wide potential range. Table I.I shows some common combinations of solvent and supporting electrolyte with their limiting potentials. The limiting potential is that at which either the solvent or the supporting electrolyte becomes electroactive.

Table I.I Limiting potentials on platinum electrodes (v. S.C.E.)[2]

Solvent	Electrolyte	Anodic Limit	Cathodic Limit
Acetonitrile	$LiClO_4$	+2.0V	-3.0V
Acetonitrile	Et_4NBF_4	+3.2V	-I.8V
N,N-Dimethylformamide	$(n-Bu)_4NBF_4$	+I.6V	-2.8V
Methanol	$LiClO_4$	+I.3V	-I.0V
Methylene chloride	$(n-Bu)_4NClO_4$	+I.8V	-I.7V
Sulpholan	Et_4NClO_4	+3.0V	-2.2V
Tetrahydrofuran	$LiClO_4$	+I.6V	-3.2V

3. Cell Design

Numerous cell designs are available, ranging from the simple undivided cell to the more elaborate cells used in physical investigations.[3] Although different in overall design, they should satisfy certain basic requirements. It is desirable to have a uniform current density distribution, therefore the electrodes should be parallel; a high electrode surface area to cell volume ratio is also desirable. To minimise the voltage drop through the electrolyte, the electrodes must be close together and this requirement also affects the choice of diaphragm in a divided cell. Ideally the diaphragm material should be such that there is good electrical conductivity, via the ions in solution, but that no mass transfer of substrate occurs. Sintered glass is generally used but semi-permeable membranes are becoming more widespread.

The position of the reference electrode is important as this will affect the potential of the working electrode and, therefore, possibly the course of the reaction. It is normally positioned close to the surface of the working electrode, by means of a Luggin capillary arrangement, so as to minimise the current-resistance, (I.R.), drop, which would cause inaccuracies in the measured electrode potential.

It is usually necessary to provide some means for the deoxygenation of the solvent. This is especially important in cathodic reactions where the reduction of oxygen may affect the reaction.

4. **Current Efficiency**

In addition to chemical yield, the current efficiency of an electrochemical reaction is important. This is defined as,

Current Efficiency (C.E.) = $\dfrac{n \times \text{no. of moles of product}}{\text{no. of faradays used}} \times 100\%$

where n is the number of electrons required per molecule of product.

I.D **CYCLIC VOLTAMMETRY**

A wide range of electroanalytical techniques is available but only cyclic voltammetry will be discussed here. Linear sweep voltammetry is simply the forward sweep of cyclic voltammetry.

In cyclic voltammetry, the potential of the working electrode is varied linearly with time in an unstirred solution. Initially, the concentration of the electroactive substrate at the electrode surface is greater than that in the bulk solution because of adsorption. On applying a potential sweep, an oxidation (or reduction) occurs such that a concentration gradient is established. The result is that the concentration of the substrate, at the surface of the electrode, is less than that in the bulk solution. The combination of the decrease in the reactant concentration and the increase in the rate of reaction with increasing potential, leads to a maximum in the current-potential curve where the surface concentration of the substrate tends to zero. The current then decreases towards the diffusion-limited value. At some arbitrary point the

direction of the sweep is reversed and returned to its
initial value. Thus, any electrochemical product formed
on the forward sweep, of sufficient stability, will be
reduced (or oxidised) on the reverse sweep.

I. **Reversible electron transfer**

Figure I.2 illustrates the cyclic voltammogram

Figure I.2 Cyclic voltammogram for a reversible reaction
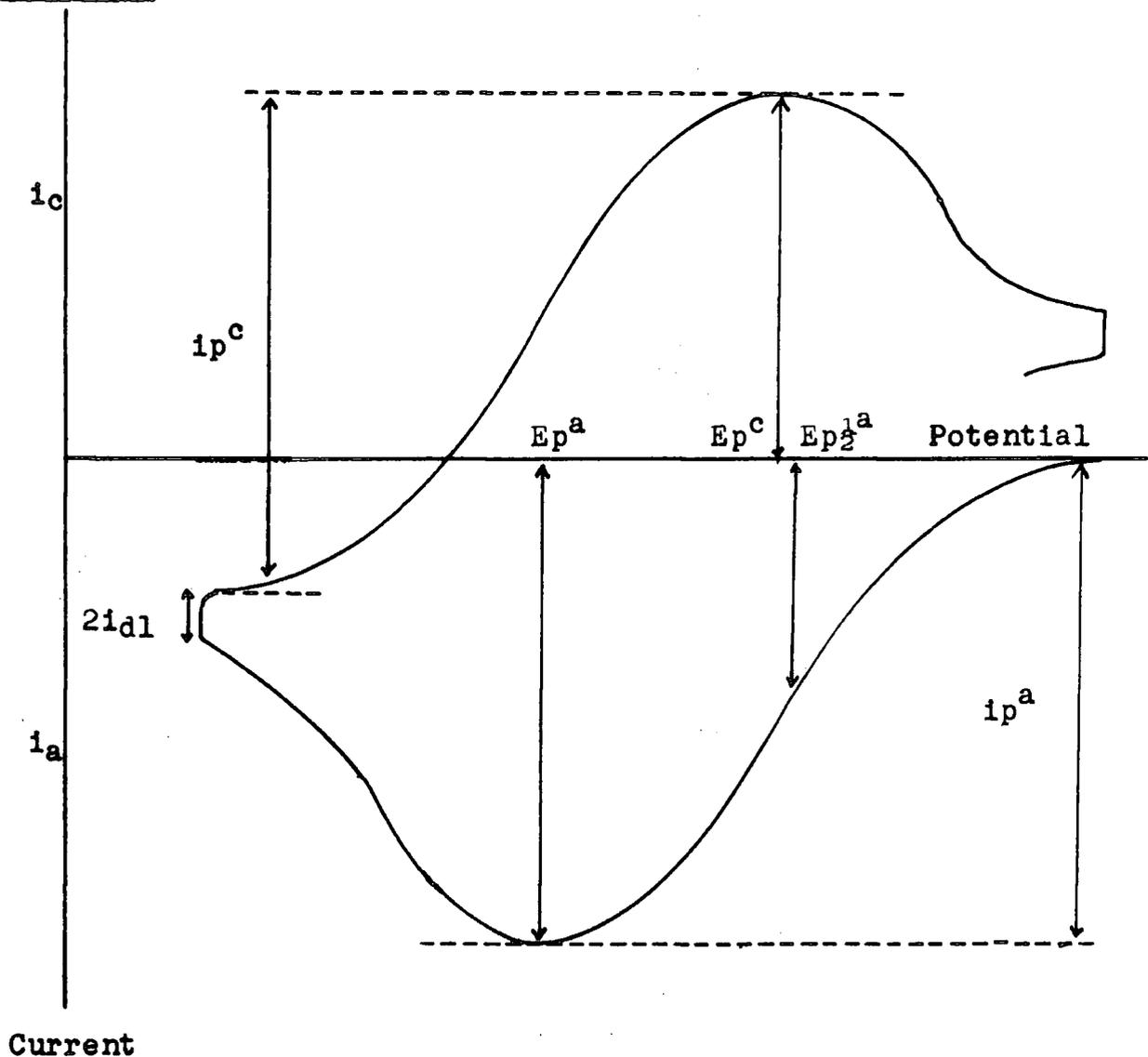
ip - peak current   Ep - peak potential

i_{dl}- double-layer charging current density

$Ep_{\frac{1}{2}}$- half-wave peak potential

a - anodic   c - cathodic

obtained for a reversible electron transfer without
accompanying chemical reactions.

It has been shown that for an electron transfer to be
thermodynamically reversible certain conditions have to be
satisfied.[IO,II] These are:

I. $Ep^a - Ep^c = \dfrac{0.056}{n}$ Volts

2. $ip^a / ip^c = I$

3. Ep is independent of sweep rate

where the symbols correspond to those in Figure I.2. If
these conditions are satisfied it follows that the Nernst
equation is valid at all times. In this equation R' and

Nernst equation: $E = E^o - \dfrac{RT}{nF} \ln \dfrac{R'}{O}$

O are the activities of the reduced and oxidised forms,
respectively, in the reversible reaction,

$O + ne^- \rightleftharpoons R'$

Thus, the half-wave potential of a reversible process
can be related to thermodynamic quantities.

As previously mentioned, the removal of an electron
(oxidation) from a substrate will depend upon the energy of
the highest occupied molecular orbital. Linear correlations
have been found between half-wave potentials and theoretically
calculated energies of the highest occupied molecular
orbitals. Similarly, correlations would be expected with
ionisation potentials. For example, the correlation of
oxidation half-wave potentials for methyl-substituted
aromatic compounds with ionisation potentials was found to
be more satisfactory than a similar correlation with
theoretical molecular orbital energies.[I2,I3] This was

attributed to either a defect in the model used for the effect of the methyl group or in the values of the Huckel coefficients rather than experimental difficulties.

Various correlations have also been found between cathodic half-wave potentials and electron affinities, and energies of the lowest unoccupied molecular orbitals.[14] For example, the latter correlation has been expressed for pyridine-type heteromolecules by the following equation,[15]

$$E_{\frac{1}{2}} = 2.127m_{m+1} - 0.555$$

where m_{m+1} is the energy of the lowest unoccupied molecular orbital.

2. Irreversible electron transfer

The voltammogram of an irreversible electron transfer is dependent on the potential sweep rate. At very high sweep rates the voltammogram will tend towards that of a reversible reaction. On lowering the sweep rate it is found that the peak separation increases and ip^a/ip^c becomes less than unity, until in the limit the reverse peak completely disappears. This type of behaviour is observed for either a slow electron transfer or when the product formed on the forward sweep is unstable, and hence there will be a lower concentration of it on the reverse sweep.

As there is a dependence on both the thermodynamics and kinetics of the reaction, the significance of the half-wave potential of an irreversible reaction is difficult to judge. The theoretical treatment of cyclic voltammetry has been well documented for all the various possibilities.[16-18]

CHAPTER 2

ELECTROCHEMICAL REACTIONS OF ORGANO-FLUORINE COMPOUNDS

2.A INTRODUCTION

This chapter contains a general review of the electro-chemistry of organo-fluorine compounds. Extensive reviews are available on the electrochemistry of organo-halogen compounds. (See, for example, the relevant sections in references I-3).

2.B ELECTROCHEMICAL OXIDATION

Organo-fluorine compounds are difficult to oxidise within the limiting potentials of most solvent systems because of the electron-withdrawing ability of fluorine. Thus, perfluoroaromatic compounds have only been oxidised in solvent systems such as hydrofluoric acid - antimony pentafluoride and fluorosulphonic acid - acetic acid.[19,20]

The voltammetry of some fluoroaromatic compounds has been studied in hydrofluoric acid - antimony pentafluoride and hydrofluoric acid - potassium fluoride.[19] It was concluded that the half-wave potential is independent of pH and that the radical cations produced in the acidic medium are chemically stable if the number of fluorine atoms is greater than four. Pentafluorophenol ($\underline{I}$) was the subject of a more detailed investigation.[21a] In the basic hydrofluoric acid - potassium fluoride medium, three oxidation waves are observed and these have been assigned as follows:

(I) Formation of a radical - pH dependent

$$C_6F_5OH \longrightarrow C_6F_5O^\bullet + H^+$$
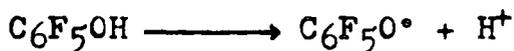
$$(\underline{I})$$

(2) Oxidation of the radical - pH independent:

$$C_6F_5O^\circ \longrightarrow C_6F_5O^+ + e^-$$

(3) Oxidation of the radical after protonation:

$$C_6F_5O^\circ + H^+ \rightleftharpoons C_6F_5OH^{\circ+}$$

$$C_6F_5O^{\circ+} \rightleftharpoons Products + e^-$$

In the acidic medium there are two oxidation waves, with the first being partially reversible. The first step is believed to the formation of a radical, with its stabilisation due to protonation, and the second step is the oxidation of this radical to the products. Controlled potential electrolysis of pentafluorophenol ($\underline{I}$) in the basic medium gives ($\underline{2}$), ($\underline{3}$), and ($\underline{4}$) as products. In the
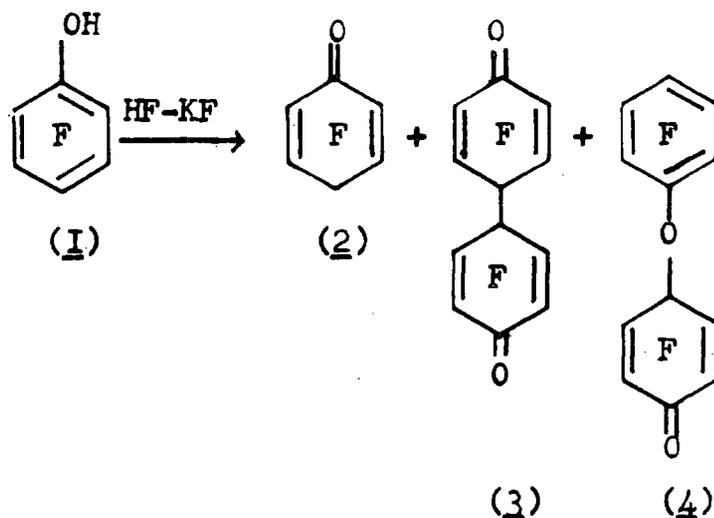
acidic medium, however, only ($\underline{2}$) and ($\underline{4}$) are produced.

Cyclic voltammetry and e.s.r. spectroscopy have been used to observe the radical cations of various fluoroaromatics in fluorosulphonic acid - acetic acid.[20] Their lifetimes are short, with the exception of the radical cation of octafluoronaphthalene whose lifetime is indefinite in this medium. Increasing the acidity of the medium, by the addition of antimony pentafluoride, stabilises all the radical

cations. For example, the hexafluorobenzene radical cation in fluorosulphonic acid - acetic acid has a half-life of seconds, whilst in fluorosulphonic acid - antimony pentafluoride it has a lifetime of hours. Controlled potential electrolyses in the former medium yields fluorosulphonate esters as products.

Hexafluorobenzene (5) and octafluoronaphthalene (6) can be oxidised in trifluoroacetic acid to give, after
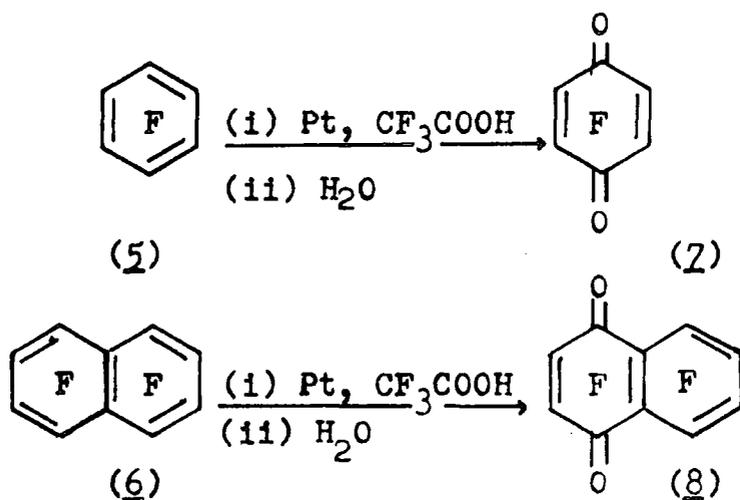
hydrolysis, tetrafluorobenzoquinone (7) and hexafluoronaphthoquinone (8) in 75% and 60% yields, respectively.[2Ib]

The introduction of an electron-donating substituent into an aromatic lowers its oxidation potential. Amino-, NH_2,[22-25] and methoxy-, MeO-,[26] groups have been used successfully in lowering the oxidation potential of polyfluoroaromatic compounds such that less esoteric solvent systems can be used. The electrochemistry of polyfluorinated anisoles will be discussed in Chapter 3.

Electrochemical oxidation of pentafluoroaniline (9) in an aqueous acetone medium gives decafluoroazobenzene (11) and octafluorophenazine (12).[23,24] Two mechanisms have been proposed to account for the dimeric products obtained in the oxidation of aniline and its N-alkyl derivatives. One mechanism involves an initial electron transfer to form a radical cation, $C_6H_5NHR^{\cdot+}$, which can then couple and deprotonate.[27] The alternative mechanism proposes that this radical cation deprotonates to give a radical, $C_6H_4NHR^{\cdot}$, which can then couple.[28] It was concluded that the latter mechanism is more appropriate for the electrochemical oxidation of pentafluoroaniline. The radical cation (10) should be less stable than its hydrocarbon analogue and deprotonation should readily occur in the alkaline medium used.
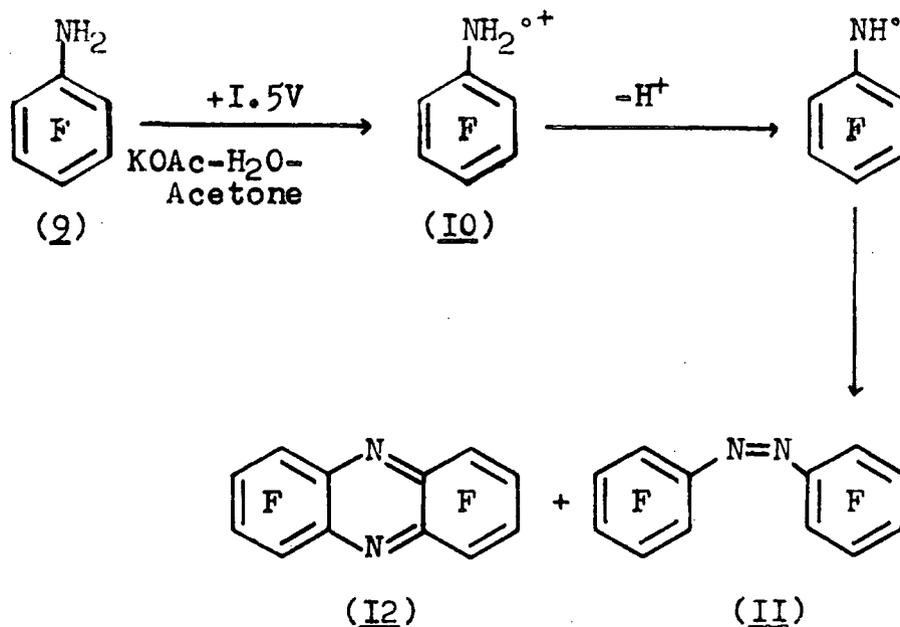
In acetonitrile, however, the oxidation of penta-
fluoroaniline is complex but it is claimed that (II)
is formed in poor yields.[29]

Hexafluoropropene (13) may be oxidised, electro-
chemically, to give hexafluoropropene epoxide (14).[30,31]

$$CF_3CF\!\!=\!\!CF_2 + H_2O \xrightarrow[\text{HNO}_3,\text{PbO}_2]{\text{aq. CH}_3\text{COOH-HF}} CF_3CF\!\!-\!\!CF_2 + 2H^+ + 2e^-$$
$$\quad\quad (13) \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (14)$$
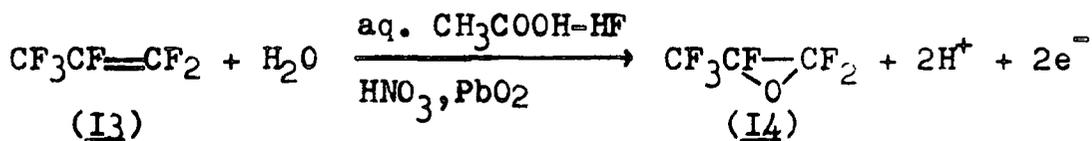
With a potential of about 8V and a current density of
100Adm^{-2} there is 65-75% conversion in this unusual
solvent system.

The oxidation of polyfluorocarboxylic acids can be
used to generate polyfluoroalkyl radicals which can then
be added to various olefins,[32-35] and pyridine.[36] For
example, when trifluoroacetic acid is electrolysed in
aqueous acetonitrile, in the presence of ethylene, I,I,I,6,
6,6-hexafluorohexane (15) is produced in 30% electrochemical
yield.[35] The mechanism is an extension of the Kolbe
reaction and is quite general.

$$CF_3COO^- - e^- \longrightarrow CF_3COO\cdot \xrightarrow{-CO_2} CF_3\cdot$$

$$\downarrow CH_2\!\!=\!\!CH_2$$

$$CF_3CH_2CH_2CH_2CH_2CF_3 \xleftarrow{\text{Dimerisation}} CF_3CH_2CH_2\cdot$$
$$\quad (15)$$
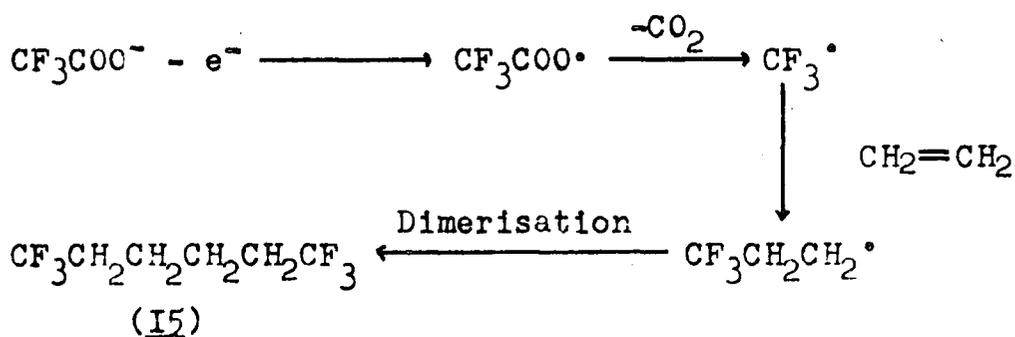
2.C ELECTROCHEMICAL REDUCTION

I. General mechanism

The electrochemical reduction of organic halides is irreversible and usually independent of the pH of the medium.[37] However, the actual mechanism of the electro-chemical cleavage of the carbon - halogen bond is still undecided and various mechanisms have been proposed which include transition states with radical,[38,39] or anionic [40,41] character. Ease of reduction follows the trend $RI > RBr > RCl > RF$ and this has led to comparisons being made with S_N2 (or S_N1) displacement reactions, with the electron acting as the nucleophile.[42] Other workers argue that electrons will prefer to attack on the halogen side and especially in crowded molecules.[43] A later study investig-ated steric effects and their influence on polarographic half-wave potentials.[40] It was concluded that there is an influence, (thus discounting the latter mechanism, where no influence should be observed), but that it is much lower than expected for a straight-forward S_N2 - type attack. A more probable mechanism is believed to be an attack of the electron perpendicular to the carbon - halogen bond and this is also spatially consistent with the addition of an electron to a σ anti-bonding orbital.

2. Alkyl Halides

The reduction of I,I,2,2-tetrabromofluoroethane (16) illustrates the general principle of an increase in unsaturation on the reduction of vicinal dihalides; the eventual product is claimed to be fluoroacetylene (17).[44]

$$Br-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{F}{|}}{C}}-Br \quad \xrightarrow[\text{(v. S.C.E.)}]{-0.62V} \quad \underset{Br}{\overset{H}{>}}C=C\underset{Br}{\overset{F}{<}} \quad \xrightarrow{-1.18V} HC\equiv CF$$

<div align="center">(16)   (17)</div>
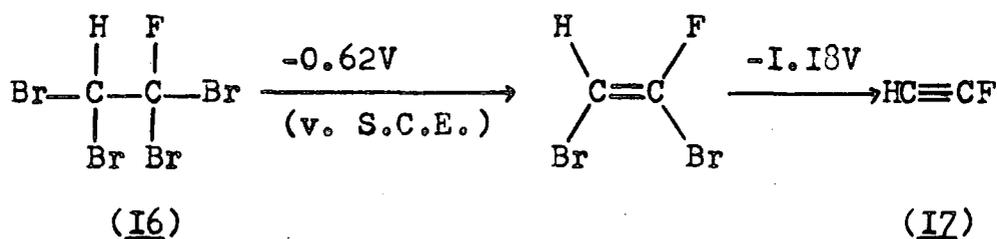
A mixture of tetrafluoroethylene (19) and I,I,2,2-tetrafluoroethane (20) is produced in the reduction of I,2-dibromotetrafluoroethane (18) and it is suggested that the product distribution is determined by the distribution of rotamers in the reactant.[45] Thus, (19) comes from the reduction of the _trans_ rotamer and (20) from the _gauche_ rotamer.

$$Br-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-Br \quad \longrightarrow \quad \underset{F}{\overset{F}{>}}C=C\underset{F}{\overset{F}{<}} \quad + \quad H-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-H$$

<div align="center">(18)   (19)   (20)</div>
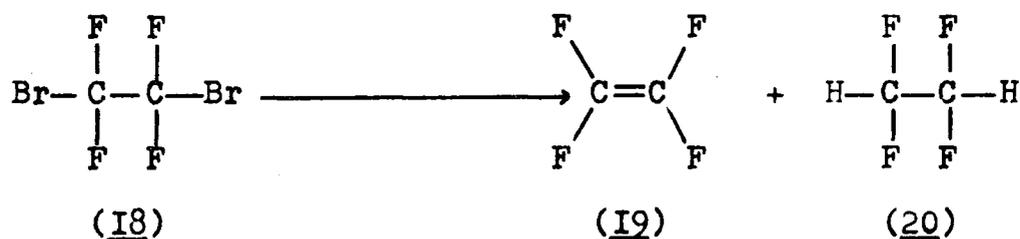
The difference in behaviour is attributed to _trans_ elimination, from the intermediate anion, occurring more rapidly than _cis_ such that, in the latter case, protonation can occur before elimination. The product distribution in the reduction of I,2-dibromo-I,I-difluoroethane and I,I-dibromo-I,2-dichlorodifluoroethane is also claimed to depend on the rotamer distribution.[46,47]

Difluorocarbene has been invoked in a number of electrochemical reductions.[48] The reduction of difluorodichloromethane has been studied at porous electrodes in LiCl-KCl eutectic.[49] Tetrafluoroethylene is produced at high efficiency in low conversions and the reaction is believed to go via difluorocarbene. Yields of up to 60% of I,I-difluoro-

cyclopropanes (<u>22</u>) are obtained when difluorodibromomethane
(<u>2I</u>) is reduced in dichloromethane at platinum electrodes,
in the presence of cyclopropenes.[50] When no suitable
trapping agent is present poly(tetrafluoroethylene) is
produced. Poly(tetrafluoroethylene) layers are formed faster

$$CF_2Br_2 + 2e^- \xrightarrow[\text{CH}_2\text{Cl}_2, \text{ Pt}]{\text{Bu}_4\text{NBr}} \; :CF_2 + 2Br^-$$
(<u>2I</u>)

$$:CF_2 + >C=C< \longleftrightarrow >\overset{\displaystyle |}{C}-\overset{\displaystyle |}{C}< $$
$$\underset{CF_2}{\diagdown\diagup}$$
(<u>22</u>)
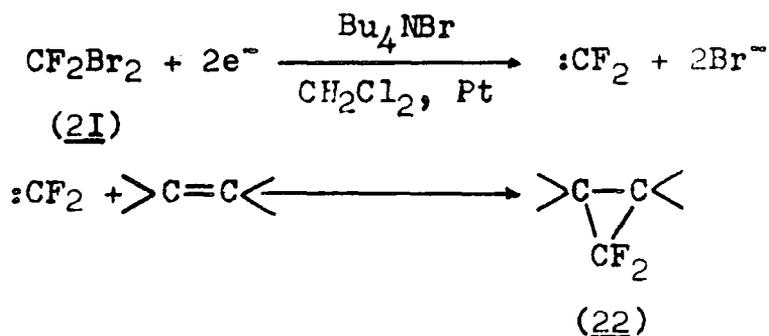
with Et_4NBr as supporting electrolyte than with Bu_4NBr and
it has been suggested that the bulky Bu_4N^+ cations protect
the electrode surface much better than the smaller Et_4N^+
cations.

Chlorofluoroalkanes can be reduced to fluoro-olefins
in good yield.[51-54] For example, reduction of I,I,2-tri-
chlorotrifluoroethane (<u>23</u>) at a lead cathode gives tri-
fluoroethylene (<u>24</u>), with a current efficiency of 53.3%.[52]

$$CF_2ClCFCl_2 + 2e^- \xrightarrow[\substack{KCl, \; 4-7V \\ 2.6A, \; 8-I2^\circ C}]{KOH-isoPrOH} CF_2=CFCl + 2Cl^-$$
(<u>23</u>)   (<u>24</u>)
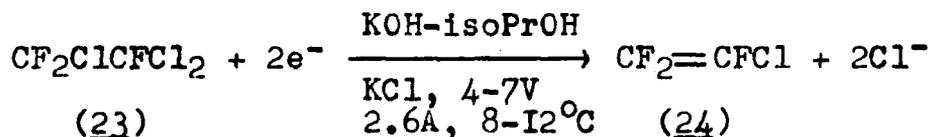
The reduction of perfluoro-n-hexyl iodide (<u>25</u>) is
dependent on the supporting electrolyte.[55,56a]With lithium
chloride as supporting electrolyte two different routes
are apparently in competition. The organometallic route

involves the reaction of (25) with polarised mercury, as indicated in the following scheme, to yield an organo-mercurial (27). This process is in competition with another which involves direct reduction of the carbon-iodine bond. The carbanion (28), thus formed, can either protonate to

Organometallic route:

$$(1) \quad C_6F_{13}I + Hg \xrightarrow{-0.3 - -0.5V} C_6F_{13}HgI$$

(25)   (26)

$$(2) \quad C_6F_{13}HgI + e^- \xrightarrow{-0.85V} C_6F_{13}Hg^\bullet + I^-$$

(26)

$$(3) \quad 2C_6F_{13}Hg^\bullet \longrightarrow (C_6F_{13})_2Hg + Hg$$

(27)

Direct route:

$$(1) \quad C_6F_{13}I + 2e^- \xrightarrow{-0.6V} C_6F_{13}^- + I^-$$

(25)   (28)

$$(2) \quad C_6F_{13}^- \xrightarrow{H^+} C_6F_{13}H$$

(28)   (29)

$$\xrightarrow{-F^-} C_4F_9CF{=}CF_2$$

(30)
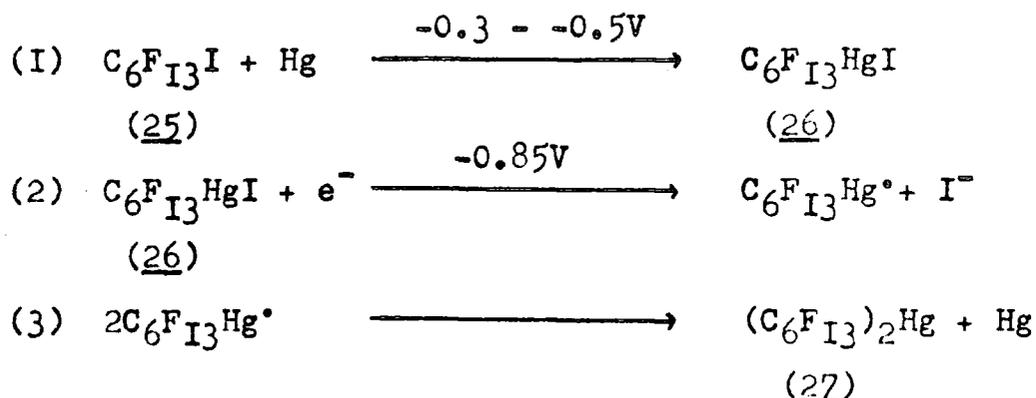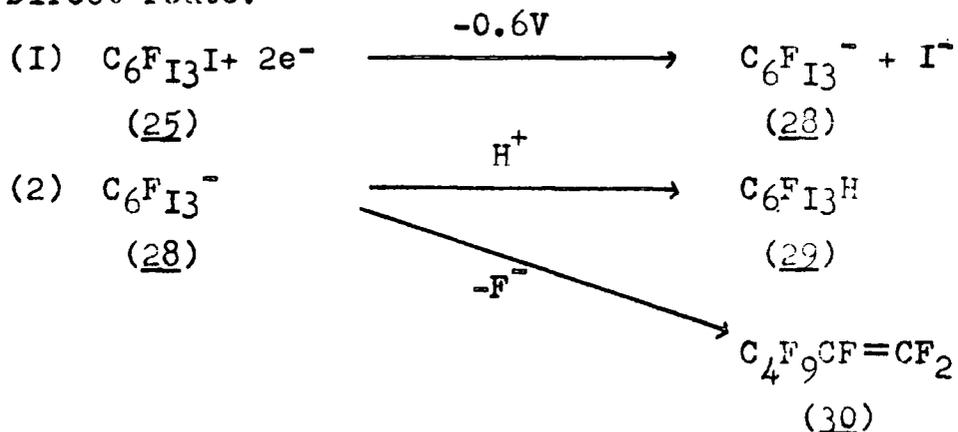
give (29) or lose fluoride ion to yield (30). However, when lithium chloride is used as the supporting electrolyte it is found that the organometallic route is suppressed and the direct route predominates. The difference in behaviour is believed to be due to the effect of the supporting electrolyte on the adsorption of R_FHgI at the cathode surface. In contrast, the reduction of perfluoro-n-butyl-I,4-diiodide (31) follows both routes with either LiCl or

LiClO$_4$ as supporting electrolyte to give the symmetrical organomercurial (32).[56b]

$$I(CF_2)_4I \xrightarrow[\text{D.M.F., Hg}]{-0.75V} H(CF_2)_4\text{-Hg-}(CF_2)_4H$$
$$\text{(31)} \qquad\qquad\qquad\qquad \text{(32)}$$
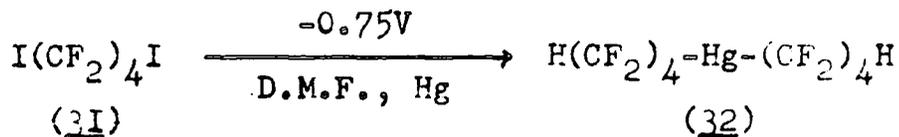
2-Chloromercury-3,3,3-trifluoropropanol has been reduced, in neutral medium, to give difluoroallyl alcohol.[57]

$$CF_3CH(HgCl)CH_2OH \xrightarrow{-1.5V} CF_2{=}CHCH_2OH$$
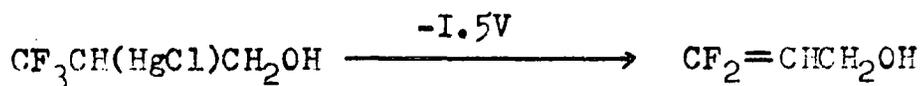
The reduction of perfluoropiperidine (33) is a two-stage process in acetonitrile at a mercury cathode.[58] The reaction is dependent on the electrode material, presumably because of the ability of some metals to form N-metal derivatives. Preparative electrolysis of (33) yields (34), which is readily hydrolysed to give perfluoroglutaric acid as the final product.
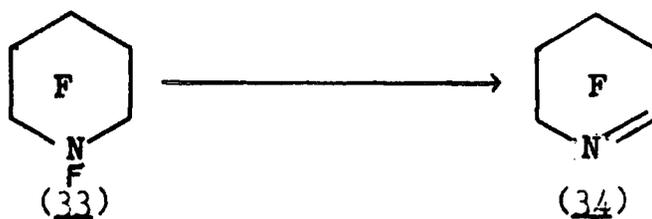
Fluorinated esters (R$_F$COOR) and related compounds have been investigated by preparative and polarographic methods.[59,60] For example, carbon-fluorine bond cleavage occurs on the reduction of ethyl difluoro- and trifluoroacetate at a mercury cathode.[59] The reduction becomes

easier on going from $R_F = CF_3$ to $R_F = CF_3(CF_2)_6$, so that the activation energy relative to electron transfer to $CF_3(CF_2)_n COOEt$ decreases as n increases.[60] The actual electron transfer occurs via the carbonyl group, for example:

$$CHF_2COOEt + e^- \xrightarrow{-2.56V} \left[CHF_2-C\begin{array}{c} O^- \\ OEt \end{array} \right]$$

(35)   (36)

(I)

2H$^+$+e$^-$
(II)

$$F^- + \dot{C}HFCOOEt$$

$$CHF_2-C\begin{array}{c} OH \\ H \\ OEt \end{array}$$
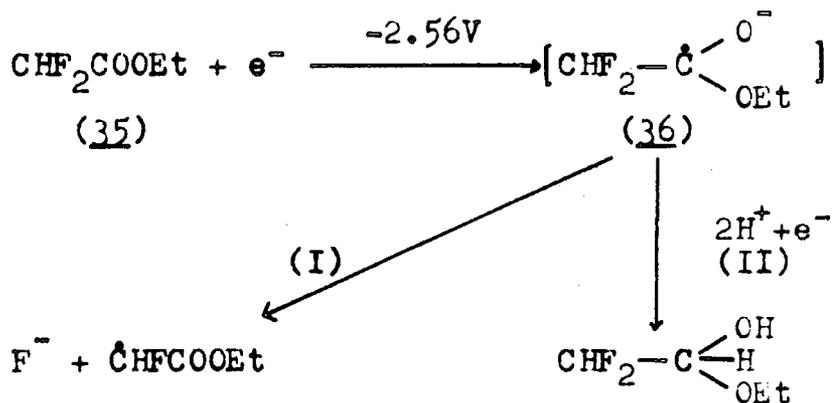
Reduction of (35) at -2.56V produces its radical anion (36) which can decompose by either pathway (I) or (II). Addition of a proton donor leads to protonation of (36) before it can decompose by (I) such that (II) is the preferred pathway. In the case of trifluoroacetic acid only the reduction of the solvated proton was observed.[59] However, this was at a mercury cathode while reduction at a platinum cathode yields I,I,I-trifluoroethane with a current efficiency of 96%.[61] The proposed mechanism involves molecular hydrogen produced at the cathode, which is acting as a catalyst and thus is not a direct reduction.

3.   Alkenes

Reduction of fluorinated cyclohexadienes yields aromatic derivatives.[62-4] For example, the reduction of either I,4- or I,3-perfluorocyclohexadiene yields hexafluoro-

benzene. The mechanism is as follows, with either step
(I) or steps (I) and (2) as rate determining. As there is

(I) Diene + e⁻ ⟶ Diene·⁻

(2) Diene·⁻ ⟶ Radical + F⁻

(3) Radical + e⁻ ⟶ (Radical)⁻

(4) (Radical)⁻ ⟶ Product
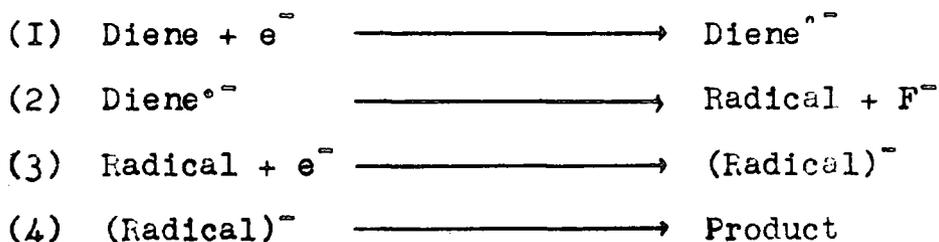
no substitution of hydrogen for fluorine, even in this
protic medium, it follows that steps (3) and (4) are rapid
in comparison with other possible reactions. Not surpris-
ingly, the half-wave potentials for the reduction of I,4-
dienes are more negative than those of the I,3-dienes;
however those of the I,4-dienes do not appear to be repres-
entative of an isolated CF=CF and its first anti-bonding
orbital energy. Although the latter is important in deter-
mining the reduction potential of the dienes its effect on
the half-wave potentials is modified by step (2).

Perfluoro-2-methyl-2-pentene (37) is reduced at a
platinum cathode in acetonitrile to perfluoro-I,3,3-tri-
fluoromethyl-4-ethyl-2-isopropyl-I-cyclobutene (38) and
perfluoro-I,3,3-trifluoromethyl-2-ethyl-4-isopropylidene-
I-cyclobutene (39). An allylic anion and a dimer are
believed to be the intermediates.[65]

$$\underset{\text{CF}_3}{\overset{\text{CF}_3}{>}}\text{C}=\text{CF}-\text{CF}_2\text{CF}_3 \xrightarrow[\text{(v. Ag/Ag}^+\text{)}]{-1.93\text{V}}$$

(37)

(38)

+

(39)
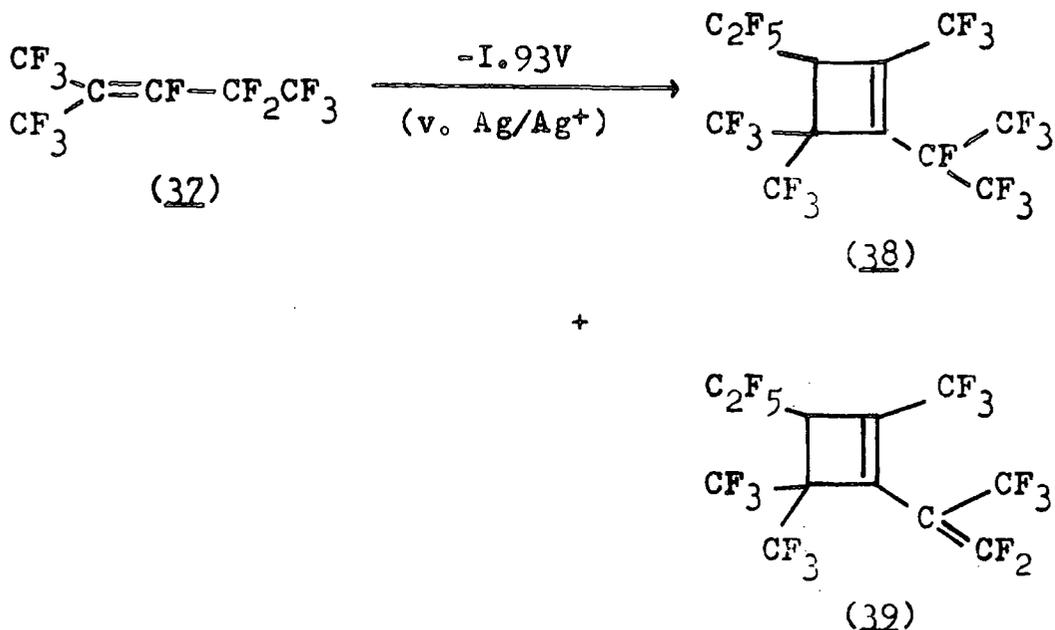
4. Aromatics

The reduction of some polyfluoroaromatic compounds has been studied by polarography.[66-8] In 75% dioxan-water it is found that the overall reaction is, after initial electron transfer, addition of a proton to give a species which is reducible at a more cathodic potential than the initial potential. I.e.,

(I) $\text{ArX} + \text{e}^- \longrightarrow \text{ArX}^{\bullet -}$

(2) $\text{ArX}^{\bullet -} + \text{H}^+ \longrightarrow \text{ArXH}^{\bullet}$

(3) $\text{ArXH}^{\bullet} + \text{e}^- \longrightarrow \text{ArXH}^-$

(4) $\text{ArXH}^- \longrightarrow \text{ArH} + \text{X}^-$
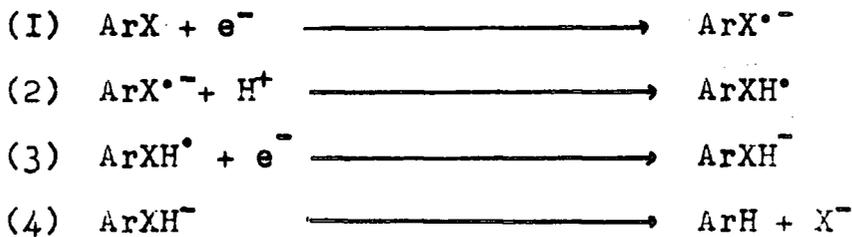
This process is referred to as solvent-assisted reduction.

Further evidence for this mechanism comes from a voltammetric and preparative investigation of the reduction of pentafluorobenzene (40).[68] Preparative electrolysis of (40) yields I,2,4,5-tetrafluorobenzene (41) indicating that the

mechanism shown above is occurring. The proton required in

$$\text{(40)} \quad \xrightarrow[\text{nBu}_4\text{NI}]{\text{Hg, D.M.F.}} \quad \text{(41)}$$
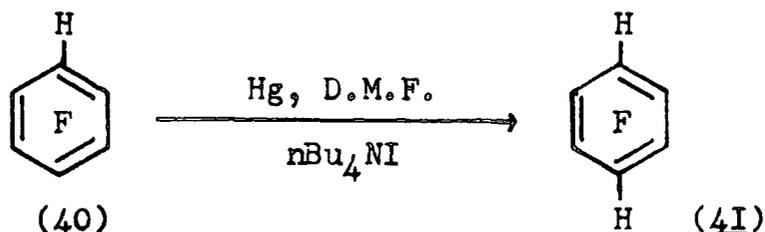
step (2) comes either from an added source, such as hydro-
quinone, or from the supporting electrolyte. If there is
no readily available source of protons it is apparent that
the supporting electrolyte undergoes a Hofmann-type elimin-
ation. With tetrabutylammonium iodide as the supporting
electrolyte, and no added source of protons, tributylamine
was detected.

Two reduction waves are observed in the reduction of
iodopentafluorobenzene (42), with the first being attributed
to a single electron transfer.[67] The radical anion thus
formed readily loses iodide ion to give the radical (43).

$$C_6F_5I + e^- \longrightarrow C_6F_5I^{\cdot -}$$
$$\text{(42)}$$

$$C_6F_5I^{\cdot -} \longrightarrow C_6F_5^{\cdot} + I^-$$
$$\text{(43)}$$
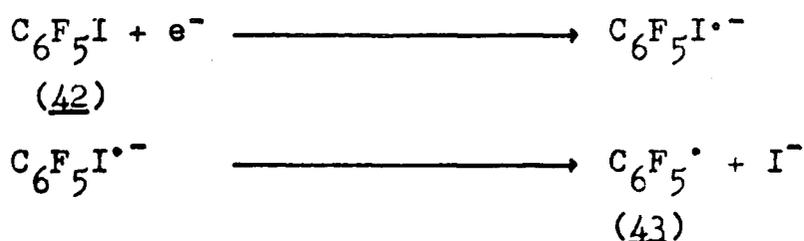
Radical (43) then either dimerises to yield decafluoro-
biphenyl or reacts with the mercury cathode to give (44).

$$2C_6F_5^{\cdot} + Hg \longrightarrow (C_6F_5)_2Hg$$
$$\text{(43)} \qquad\qquad\qquad \text{(44)}$$
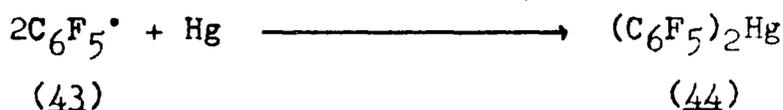
The second wave is believed to be due to another electron

transfer to the radical anion.

$$C_6F_5I^{\cdot-} + e^- \longrightarrow C_6F_5^- + I^-$$

The reduction of I,4-dicyanotetrafluorobenzene (45)
occurs by two different routes, depending on the conditions
used.[69] Either fission of a C-CN bond to give (46) or the
reduction of a nitrile group to give (47) can occur. These
mechanisms are in competition and their rates are a function
of the availability of protons, the concentration of the
non-aqueous co-solvent, and the electrode potential.

NC—⟨F⟩—CN ⟶ H—⟨F⟩—CN + H₂NCH₂—⟨F⟩—CN

(45)   (46)   (47)
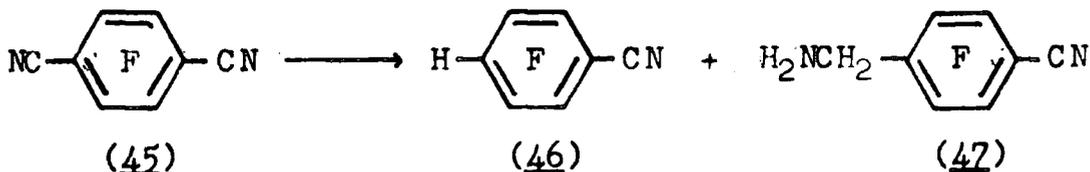
The product distribution in the reduction of penta-
fluorobenzoic acid (48) is, similarly, dependent on the
electrode potential and proton availability.[70,71] At
-I.20V (49) is the major product, while at -I.50V (50) and
(5I) are the products, at a mercury cathode in aqueous
sulphuric acid. The formation of (5I) is also dependent on
the acidity of the medium. Two different mechanisms, I and
II, are operating in low acid media, while in high acid
media protonation of the carbonyl group leads to mechanism
I taking precedence.

(48)   (49)   (50)   (51)

The reduction of pentafluorobenzaldehyde (52) occurs at a lower potential to give (50) and (51) as products, explaining why none is actually isolated.

The reduction of fluoro-substituted aza- aromatic compounds has been investigated by polarography and it was found that it follows the mechanism normally postulated for aryl halides.[72] The stability of the intermediate singly-

charged negative ions is generally higher than for the comparable fluoro-substituted arenes. Poly-halogenated pyridines couple solely through the 4-position.[73] For example, pentafluoropyridine (53) yields the corresponding

(53)   (54)
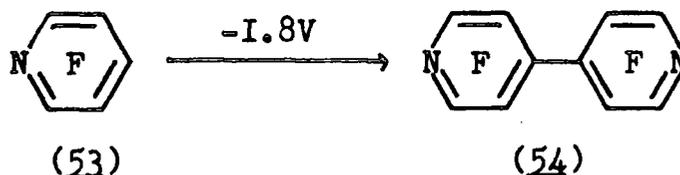
4,4'-bipyridyl (54). The electron distribution in the intermediate radical anions, as indicated by the isolated products, agrees with molecular orbital calculations.

Finally, bis-(pentafluorophenyl) mercury has been

$$(C_6F_5)_2Hg \xrightarrow[\text{MeOH, NaOAc}]{\text{Hg}} C_6F_5H$$
(40)
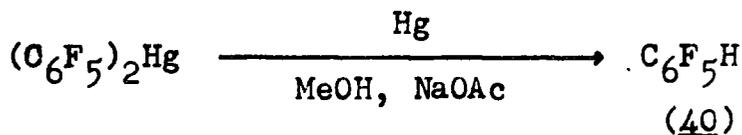
reduced to pentafluorobenzene (40) with the reaction being dependent on factors such as electrolyte concentration.[74]

DISCUSSION

CHAPTER 3

ELECTROCHEMICAL OXIDATION OF FLUORINATED ANISOLES

3.A INTRODUCTION

Electrochemical oxidation of anisole and its derivatives
usually yields coupled products, which are more easily
oxidised than the parent compounds. Thus, the reaction is
complicated by follow-up reactions which result in a low
yield of the dimeric product.[75] For example, the oxidation
of anisole (55) gives 4,4'-dimethoxybiphenyl (56) which is
further oxidised to the radical cation (57) and dication (58).
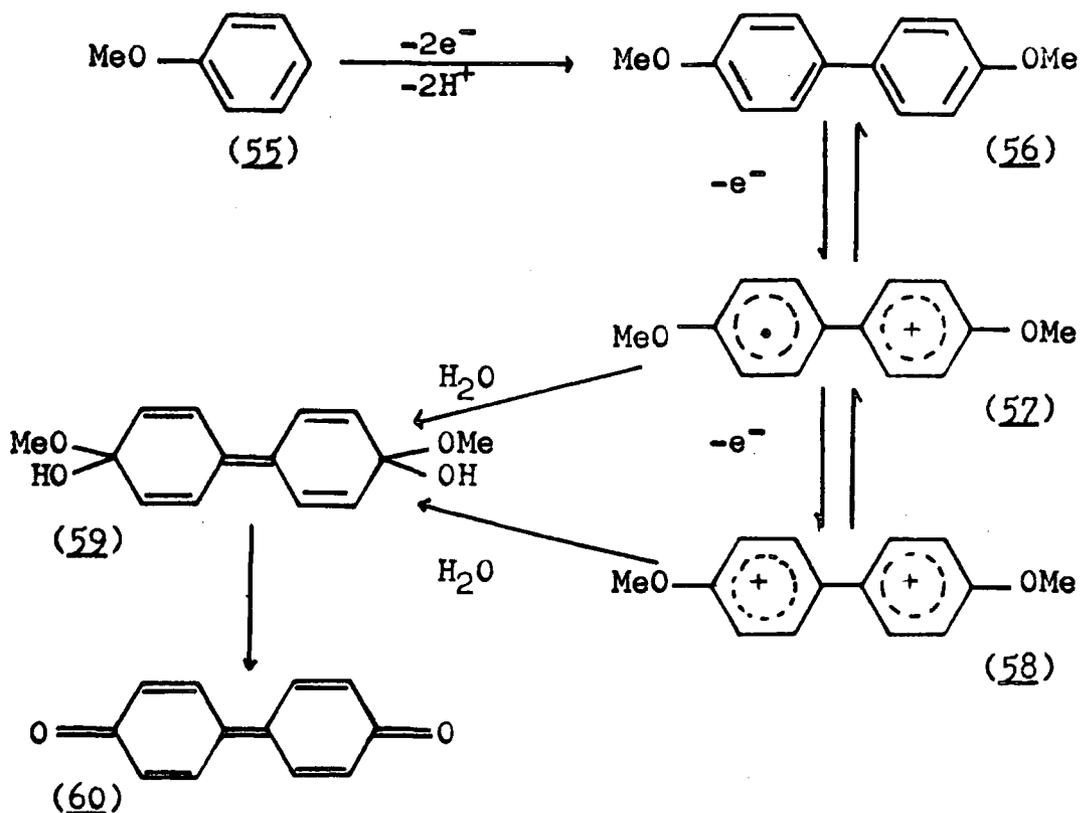
These highly reactive intermediates are readily attacked
by nucleophiles, such as water, which is present even in

'dry' solvents.[76] Water can attack either (57) or (58) to give (59) which can then lose methanol to yield the quinone (60).[77,78] At high radical cation concentrations poly- merisation may occur.

Yields of the coupled product can be increased by the use of solvents, such as dichloromethane, combined with trifluoroacetic acid. Table 3.I shows the variation of yield of (56) with variation in the solvent composition.[79]

Table 3.I Effect of solvent composition on the yield of (56) (3.0F/mol, 20°C, n-Bu$_4$NBF$_4$ (0.1M)).

Trifluoroacetic Acid (ml)	Dichloromethane (ml)	% Yield of (56)
0	100	4
25	75	58
50	50	61
100	0	57

Trifluoroacetic acid stabilises the radical cation (57) which can then be reduced either electrochemically or with zinc to (56). The ability of trifluoroacetic acid to stabilise radical cations is well illustrated by the observation that the thianthrene radical cation is stable in 50/50 water- trifluoroacetic acid, while in acetonitrile it is unstable even with only 10mM of water present.[80,81] How trifluoro- acetic acid deactivates water as a nucleophile is not

understood, it cannot be due to its acidity as it is not sufficiently strong to protonate water.[82]

Coupled products may be formed by two different mechanistic pathways:

(a) Dimerisation of the radical cation, followed by deprotonation.[83]

or (b) Electrophilic attack of the radical cation on the substrate.[84,85]

Support for mechanism (b) has come from the observation that the oxidation of mesitylene, in the presence of benzene, yields mixed coupled products.[85] However, the methoxy group has an ortho/para directing influence in electrophilic aromatic substitution reactions, while electrochemical dimerisation generally occurs through the para position. For example, when the para position is blocked, as in p-methoxytoluene, the radical cation of the biphenyl cannot be detected by cyclic voltammetry and the reaction is complex.[86]

Unsymmetrically substituted diarylalkanes have been used in an attempt to clarify the mechanism but with mixed success. Oxidation of (61) occurs at two potentials to the radical cation (62) at the first and the dication diradical (63) at the second potential.[83] If the reaction is carried out on a preparative scale at +I.2IV a dimer (64) is isolated while at +I.62V the corresponding phenanthrene (65) is obtained. Thus, it would appear that radical cation dimerisation is the dominant dimerisation mechanism for

methoxy-substituted aromatic compounds. This conclusion

(61)   (62)   (64)

+I.2IV

+I.62V

(63)   (65)
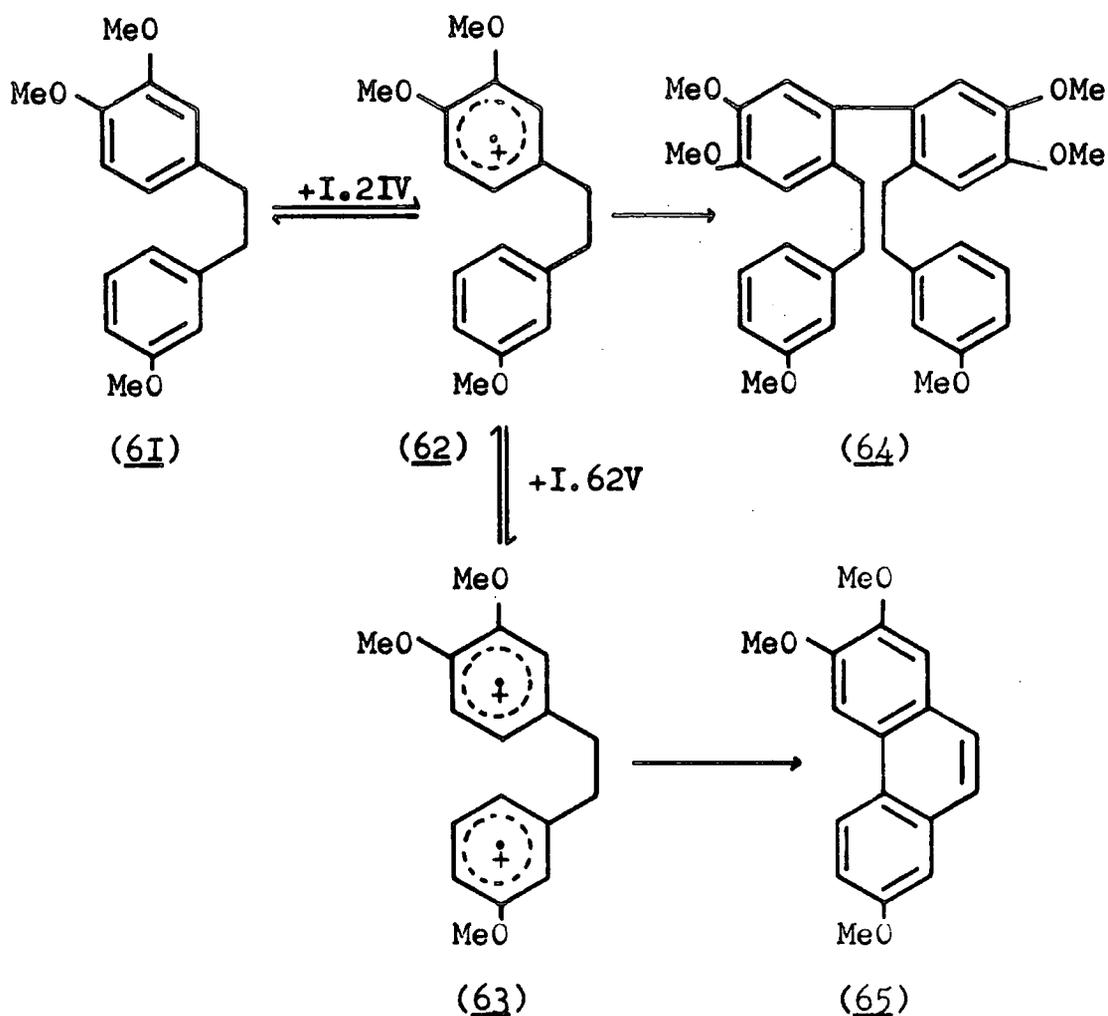
has, however, been critisised.[87]

A later investigation concluded that the dimerisation
of systems such as (61) is dependent on geometrical and
electronic factors, such that both mechanisms (a) and (b)
can occur but with (a) predominant.[88] Although the dimer-
isation of two positive centres may appear unlikely, a
variety of radical cations such as from aromatic hydrocarbons
and amines undergo rapid and reversible dimer formation.[89,90]

3.B ELECTROCHEMICAL OXIDATION OF FLUORINATED ANISOLES

I. Introduction

A series of fluorinated anisoles was investigated by preparative electrochemical oxidation to determine the orientation of dimerisation, utilising fluorine as a blocking substituent.

2. Preparative Oxidations

Oxidation of 2,3,5,6-tetrafluoroanisole (66) and 2,3,6-trifluoroanisole (67) gave the corresponding dimers (68) and (69), in agreement with a previous worker.[91] The
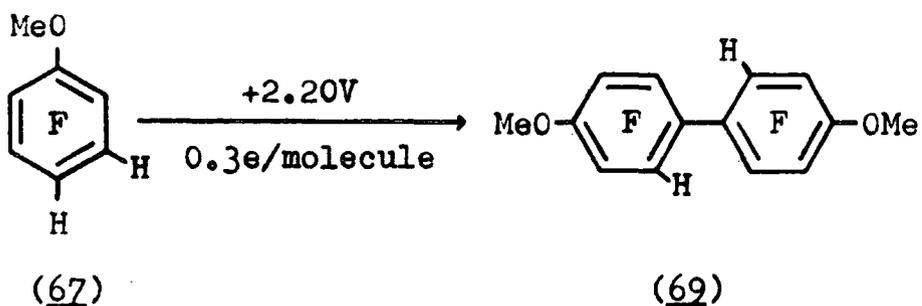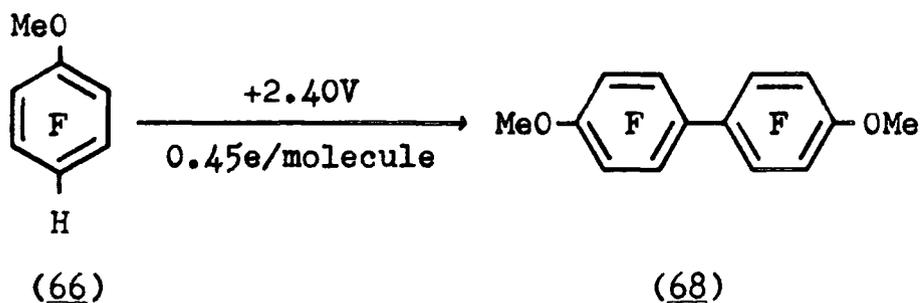
structural assignments of (68) and (69) were based on comparison of n.m.r. and i.r. spectra with those of known samples.[91] 2,3,5,6-Tetrafluoroanisole (66) was also oxidised in a mixed solvent containing acetonitrile/trifluoro-

acetic acid (5:I). The yield of dimer (68) was not greatly altered although the reaction was much cleaner than when no trifluoroacetic acid was present.

MeO—⟨F⟩—H —(+2.40V, CH₃CN: CF₃COOH)→ MeO—⟨F⟩—⟨F⟩—OMe

(66)   (68)
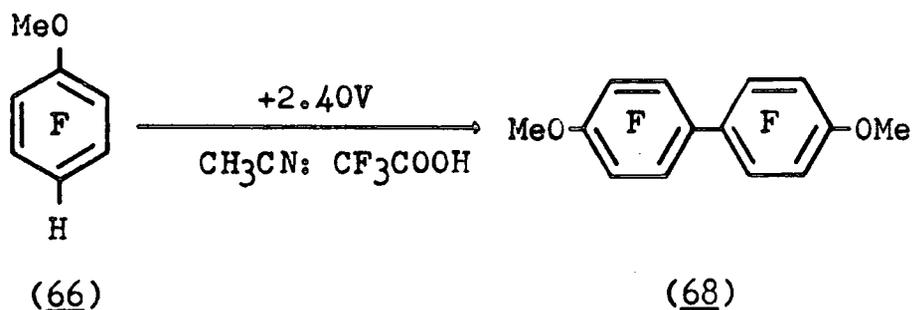
Oxidation of 2,3,5-trifluoroanisole (70) gave a single dimer although dimerisation is possible through either the ortho or para positions. The assignment of this product as the para-para dimer (71) was not conclusively proven by the observation of three signals in the ^{19}F n.m.r. spectrum of equal intensity. It was, therefore, synthesised by an

(70) —(+2.20V, 0.49e/molecule)→ (71)

(70)   (71)
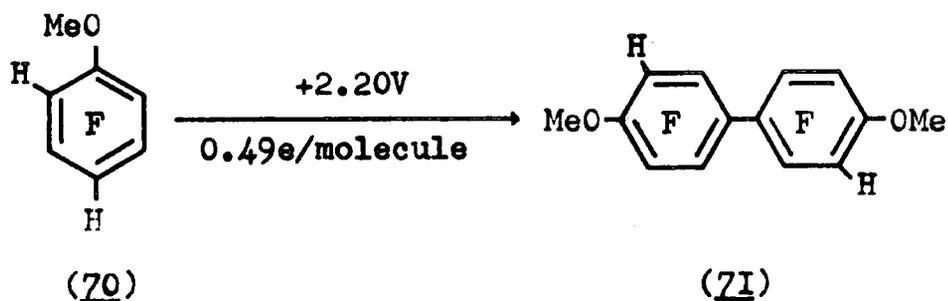
unambiguous route. I-Bromo-2,3,6-trifluoro-4-methoxybenzene (72) was synthesised by a known route[92] and this was coupled, using copper at 200°C, to yield 2,2',3,3',6,6'-hexafluoro-4,4'-dimethoxybiphenyl (71). This coupling

reaction has been used previously to synthesise similar coupled products.

MeO ... Br$_2$/H$_2$SO$_4$ ... MeO ... Cu/200°C ... MeO—⟨F⟩—⟨F⟩—OMe

(70)   (72)   (71)
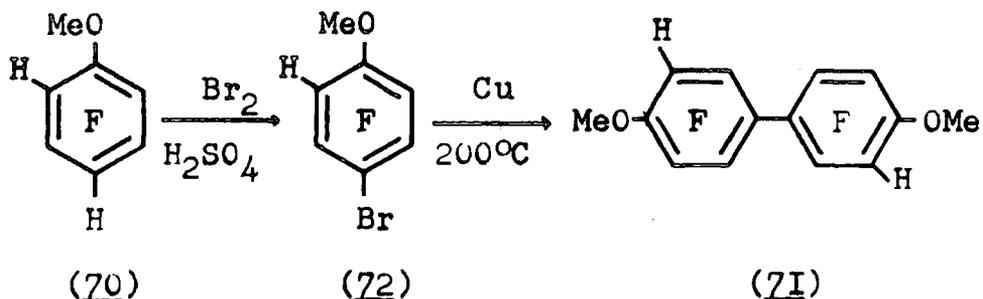
2,4,5-Trifluoroanisole (73) has no para hydrogen and hence it would not be expected to yield any dimeric product on the basis of the above results. In agreement with a previous worker, oxidation of (73) at +2.20V (v. S.C.E.) produced only a multi-component mixture.[9I] Thus, these

MeO ... +2.20V ... Multi-component mixture

(73)
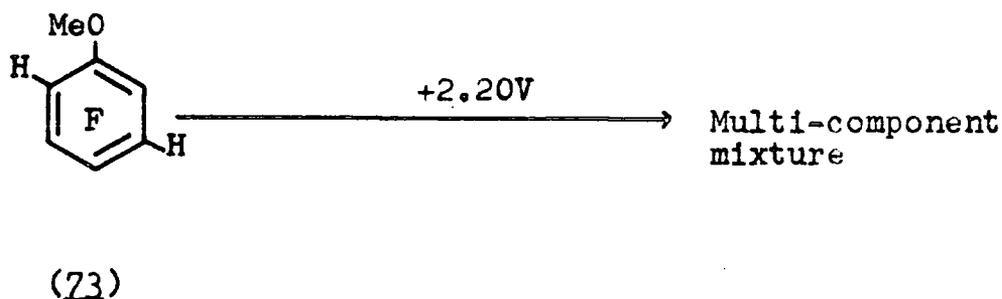
results indicate that dimerisation occurs through the para position in fluorinated aryl methyl ethers.

Oxidation of the parent anisole initially yields a radical cation, which can be considered to be made up of various resonance forms. Using the valence bond description the charge and spin density would be expected to be concentrated at the ortho and para positions, such that the charge is nearest the substituent. However, the results

of the preparative experiments described here, indicate that in the radical cations of fluorinated anisoles, spin and charge density is concentrated at the <u>para</u> position. Theoretical information on these systems is lacking, however, I.N.D.O. calculations at the S.C.F.-M.O. level indicate that the positive charge in the radical cation of anisole is primarily at the <u>α</u> and <u>para</u> positions. [93]

The high yields of dimers (<u>68</u>), (<u>69</u>), and (<u>71</u>) is surprising since they oxidise at potentials lower than that of the parent anisoles. As no reversibility was observed in the voltammetry of (<u>66</u>), (<u>67</u>), and (<u>70</u>) it follows that their radical cations do not have a long lifetime in this medium. Hence the formation of the dimers must occur near the electrode surface and they are protected from oxidation by remaining protonated until transferred to the bulk medium, or because the dimers are not as readily adsorbed onto the electrode.

Fluoro-aromatic compounds are not very reactive towards electrophiles and, therefore, an electrophilic mechanism for dimerisation would appear unlikely. Nitration of 2,3,5,6-tetrafluoroanisole (<u>66</u>) does occur, giving the expected product (<u>74</u>), but under rather forceful conditions. [94]

MeO   MeO

$$\text{(66)} \quad \xrightarrow[\substack{\text{Sulpholan} \\ 60\text{-}70^{\circ}\text{C}, \text{ 2hr}}]{\text{BF}_3\text{-HNO}_3(95\%)} \quad \text{(74)}$$

(<u>66</u>)   (<u>74</u>)
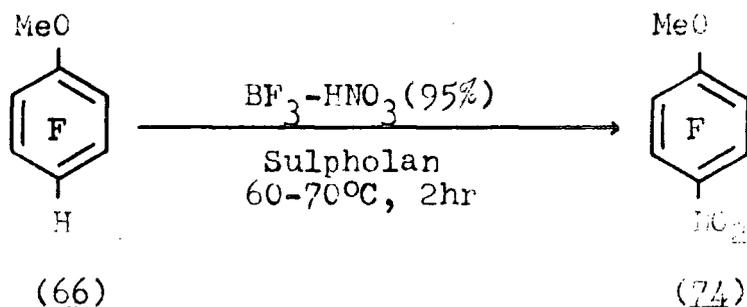
This lack of reactivity towards electrophiles and the isolation of only para-para coupled dimers, indicates that the dimerisation mechanism in the oxidation of fluorinated anisoles is coupling of radical cations, i.e. mechanism (a).

3. Voltammetry

a. Introduction

The cyclic and linear sweep voltammetry of some substituted anisoles was investigated with a view to providing evidence for the structure of their radical cations.

The fact that fluorinated aromatic compounds can be oxidised under the conditions used in this investigation is perhaps surprising. However, the electronic influence of fluorine on a radical cation is one of competition between various effects. From a consideration of its electronegativity, fluorine would be expected to destablise a positive centre $(-I_\sigma)$ but, in opposition, there is a mesomeric interaction $(+M)$ between an unshared pair of electrons on fluorine and the vacant orbital. The net result is that $\overset{+}{C}-F$ is more stable than $\overset{+}{C}-C-F$ and $\overset{+}{C}-H$. Fluorine also stabilises a free radical

<u>Inductive Effect</u>   <u>Mesomeric Effect</u>

$\overset{+}{C} \rightarrow F$ $\overset{+}{C} - \overset{..}{F}$

centre compared to hydrogen by a process which can be explained, as illustrated, by combination of the relevant orbitals leading to stabilisation.[95]

C   F
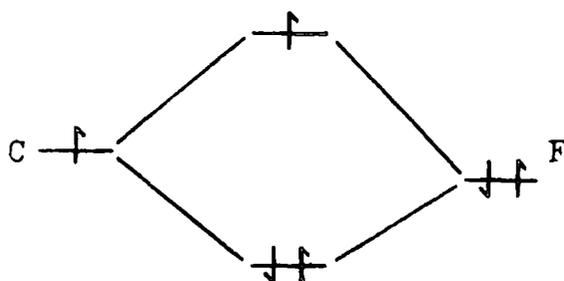
b.   Anisoles

The anisoles investigated by preparative electrochemistry presented a series of similar compounds, where the number and position of fluorine substitution varies. They were investigated using cyclic voltammetry at sweep rates of up to IOV/sec. at the Electricity Council Research Centre, Caperhurst and the results are presented in Table 3.2.

Compounds (66), (67), (70), and (75) were found to be completely irreversible at sweep rates up to ICV/sec.. The variation of potential values with sweep rate is also diagnostic of an irreversible electron transfer. Compound (73), in contrast, had a cathodic peak which was distinguishable at a sweep rate of 500mV/sec.. The peak separation $(Ep_a - Ep_c)$ of 0.09, when inserted into the equation:

$$Ep^a - Ep^c = \frac{0.056}{n} \; V$$

gives $n = 0.62$. This must represent a one-electron oxidation with the deviation from ideality being a consequence of a slow electron transfer.

The replacement of fluorine in the ring by hydrogen leads to a decrease in the oxidation potential, which is in

Table 3.2 <u>Cyclic Voltammetry of some Fluorinated Anisoles</u>
(Ep$\frac{1}{2}$ V v. S.C.E.)

Compound	Sweep Rate (mV/sec.)					
	50	100	200	300	400	500
MeO– (F ortho) (75)	2.36	2.37	2.36	2.38	2.39	-
MeO– (F, H para) (66)	2.28	-	2.28	2.29	2.31	-
MeO– (F, H) (67)	2.09	2.09	2.1	2.1	2.11	2.10
MeO– (H, F, H) (70)	2.02	2.03	2.05	2.05	-	-
MeO– (H, F, H) (73)	1.89	1.88	1.90	1.92	-	1.92 (Anodic)
						1.9 (Cathodic)
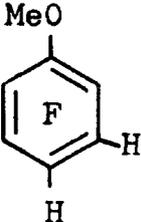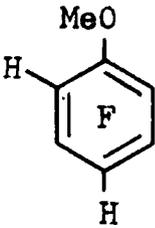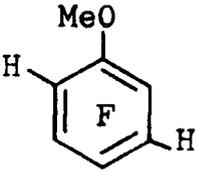
accord with the replacement of an electron-withdrawing substituent. Compound (73) appears to be anomalous, both from the point of view of its low Ep$\frac{1}{2}$ value and the relative stability of its radical cation . The latter observation cannot solely be due to its inability to dimerise, otherwise (75) would show similar behaviour.

A comparison of the resonance canonicals of the radical cation of (73), i.e. (76), with those of (77), the radical cation of (70), which to a first approximation should be more stable, provides a possible reason for this behaviour. In view of the preparative results, only the para resonance canonicals are important:

(76)   (77)
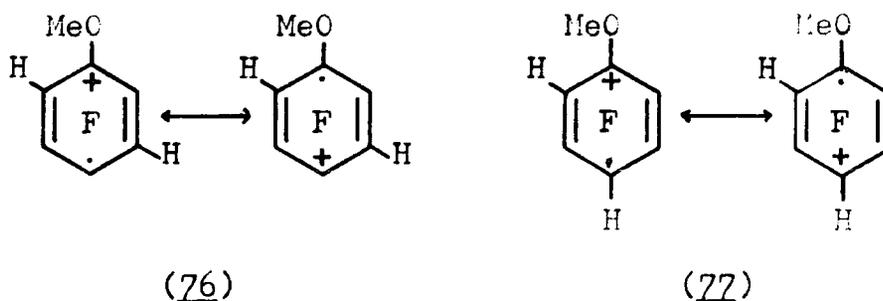
On going from (77) to (76) there is a reduction in the number of destabilising $\overset{+}{C}-C-F$ interactions and, also, replacement of the para hydrogen by a stablising fluorine. The reduction in the Ep$\frac{1}{2}$ value on going from (66) to (67) also illustrates the effect of replacing destabilising fluorine interactions, however in (67) there is an unsubstituted para-position and therefore its radical cation is unstable. Thus, the apparent anomalous behaviour of (73)

is due to the combination of a reduction in the number of destablising fluorines and a substituted _para_-position.

None of the compounds investigated were thermodynamically reversible and, therefore, no quantitative significance can be attached to the potential values. In an attempt to stablise the radical cations methods such as addition of alumina[96] and trifluoroacetic acid[80] , which have been used successfully by other workers, were tried without success. Radical cations are very susceptible to nucleophilic attack and, presumably, the fluorinated ones are even more activated.

Continuous cycling by cyclic voltammetry did not give any new peaks, indicating that the dimers when formed are protected from oxidation. This could either be due to de-activation, through remaining protonated, or because the dimers are not as readily adsorbed onto the electrode surface as the starting materials.

The effect of other halogens was investigated by the method of linear sweep voltammetry, with sweep rates of up to 50 or 100mV/sec. being available. Crude cyclic voltammetry was also possible using this apparatus, however they were all found to be irreversible (Table 3.3). The presence of either a _para_- F, Cl, or Br does not have a great influence on the observed potential. Compound (78) has an anomalously low potential which cannot be explained by the reasoning applied to account for the behaviour of (73).

Table 3.3 Voltammetry of some Halogenated Anisoles[a]

X	MeO / F / X (para)	MeO / F / X,X	MeO / F,X / X	MeO / F / X
I	2.03	–	–	–
Br	2.14	2.16	–	–
Cl	2.24	–	2.03	1.91 (78)
F	2.36[b]	–	–	–

a – $Ep_{\frac{1}{2}}$ V (v. S.C.E.), acetonitrile-T.E.A.F.

   Sweep rate 40mV/sec.

b – Sweep rate 50mV/sec.

c. Dimethoxy compounds

Substitution in an aromatic ring by another methoxy group lowers the oxidation potential and increases the stability of the radical cation, depending on the orientation of the groups. Two dimethoxy compounds were investigated at a variety of sweep rates (at the E.C.R.C., Capenhurst) and the results are presented in Table 3.4.

The voltammogram for (29) is of similar shape to that observed for I,4-dimethoxy-benzene and a similar reaction scheme would be expected:[97,98]
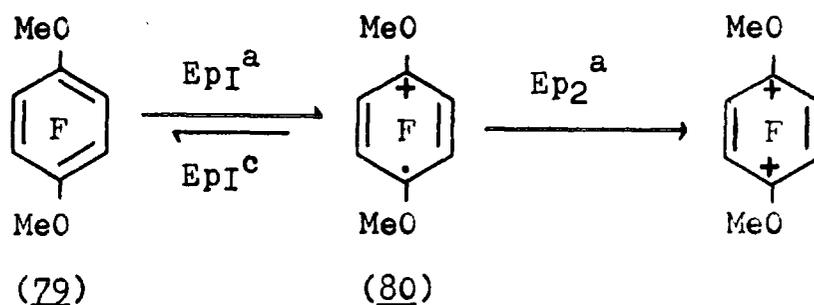
Subsequent demethylation or reaction with water followed by loss of methanol (compare page 29) to give tetrafluoro-p-benzoquinone may then occur, although actual isolation of this product is considered doubtful as it is itself a strong oxidising agent. The first oxidation step was not found to be thermodynamically reversible, having a peak separation of 0.2IV at high sweep rates. At Ep_I^a, a yellow colour formed round the anode and disappeared on reversal of the sweep and was, presumably, the radical cation (80).

Table 3.4 Voltammetry of some dimethoxy compounds

Compound	Assignment	Sweep Rate (mv/sec.)				
a	b	50	100	200	300	400
MeO ⬡ F MeO (79)	$Ep_I{}^a$	1.85	1.87	1.88	1.89	1.90
	$Ep_2{}^a$	2.27	2.30	2.33	2.35	2.35
	$Ep_I{}^c$	1.73	1.72	1.71	1.70	1.69
MeO ⬡ OMe Br F Br (81)	$Ep_I{}^a$	1.79	1.80	1.93	1.94	1.95
	$Ep_2{}^a$	2.06	2.08	2.26	2.27	2.29
	$Ep_I{}^c$	c	c	c	c	1.78
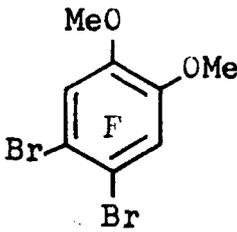
a - acetonitrile, Et_4NBF_4 (0.3M)

b - Volts, v. S.C.E.

c - not properly defined

A similar reaction scheme would be expected for (81), however the stability of its radical cation (82) was less than that of (80). It is likely that this is partially due to elimination of bromine from (82), a process observed to some extent in the oxidation of p-bromo-N,N-dimethylaniline.[102] Changing the solvent from acetonitrile to trifluoroacetic acid led to a marked increase in the stability of (82), with the first oxidation being close to thermodynamic reversibility;

$$Ep^a - Ep^c = 80mV, \quad ip^a = 98 \text{ a}, \quad ip^c = 9I \text{ a}.$$

Oxidation at the first potential caused the formation of a bright pink colour, attributable to (82), which disappeared on reduction.

MeO — OMe $\xrightarrow{Ep_I{}^a}$ $\xleftarrow{Ep_I{}^c}$ MeO(+) — OMe (F, •, Br, Br) $\xrightarrow{Ep_2{}^a}$ MeO(+) — OMe (F, +, Br, Br)

(81) (82)
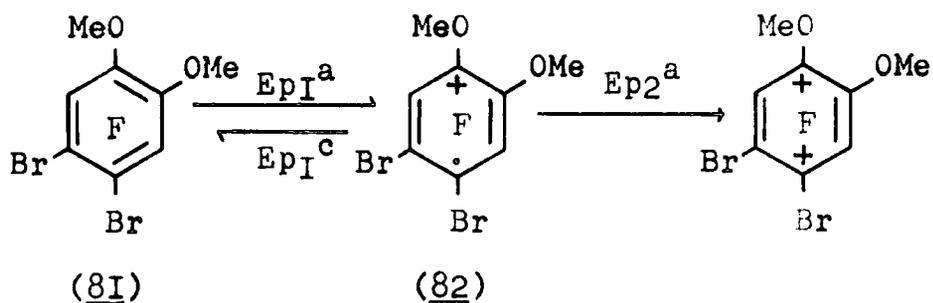
A preparative electrolysis of (81) in acetonitrile was performed at +2.IOV (i.e. at the second oxidation step) but only tar and (81) were recovered.

d. **Methoxy biphenyls**

The dimeric products, obtained by preparative oxidation of anisoles (66), (67), and (70), were investigated by cyclic voltammetry (Table 3.5). As expected, they were oxidised at potentials below those of the starting materials, however, the resultant species did not have any stability in the medium used. Two oxidation waves were observed for (69) and (71) which were assumed to be oxidation to the radical cation and thence to the dication. In the case of (68), the oxidation to the dication would have been beyond the limiting potential of the solvent system.

Groups, other than hydrogen, situated in the o,o' positions can cause restricted rotation and force the molecule

to exist in a conformation in which the rings are non-planar.[98]

Table 3.5 Voltammetry of some methoxy biphenyls

Compound [a]	$Ep\frac{1}{2}(I)$ [b]	$Ep\frac{1}{2}(2)$ [b]
MeO—⟨F⟩—⟨F⟩—OMe (68)	2.26	c
MeO—⟨F⟩—⟨F⟩—OMe (H, H) (69)	I.87	2.3
MeO—⟨F⟩—⟨F⟩—OMe (H, H) (7I)	I.93	2.3
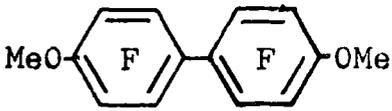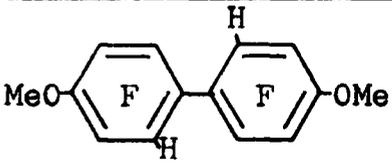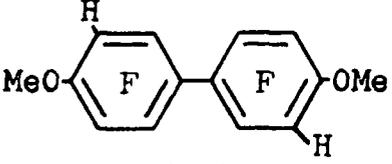
a - acetonitrile, Et_4NBF_4 (0.3M),

b - Volts, v. S.C.E., I00mv/sec.

c - Beyond the limiting potential of the solvent system.

As radical cation stabilisation is dependent on the degree
of conjugation between the rings, contribution of structures
which are twisted should diminish the radical cation stability.
For example, a substantial increase in stability is found
on going from I,4-dimethoxybenzene to 4,4'-dimethoxybenzene,
with a corresponding decrease in oxidation potential, but
the reverse is the case on going to 2,2'-dimethoxybenzene.[98]
As the most stable conformation of the radical cation is
when both rings lie in the same plane, the greater the

interplanar angle between the rings, the greater the energy difference between the radical cation and the starting material. The angle in decafluorobiphenyl is claimed to be 50° from n.m.r. measurements.[99] Thus, oxidation potential of 4,4'-dimethoxyoctafluorobiphenyl (68) should be greater than that of I,4-dimethoxytetrafluorobenzene (79) and this is observed. The observation in the ultra-violet spectrum of (68) of an intense absorption at 244nm (ϵ I8,300) which is not present in the spectrum of (66) indicates that there is substantial conjugation between the rings[9I] but as this is in the excited state it is not directly relevant. Replacement of an _ortho_ fluorine would be expected to lower the oxidation potential by decreasing the interplanar angle. Compound (69) did oxidise at a lower potential but it is difficult to distinguish between removal of an electron-withdrawing substituent and the reduction in the interplanar angle causing this reduction.

CHAPTER 4

ELECTROCHEMICAL OXIDATION OF SOME FLUOROAROMATIC COMPOUNDS

4.A INTRODUCTION

In Chapter 3, the use of the methoxy group to lower the oxidation potential of fluoroaromatic compounds into a more accessible region was described. The results presented in this chapter extend this concept to the N,N-dialkylamino and hydroxyl groups. In the introduction to the discussion of each group of compounds, relevant work from the literature will be briefly discussed so as to provide some background. It was hoped that electrochemical oxidation of the fluorinated compounds would give high yields of dimeric products, by comparison with the results presented in Chapter 3.

4.B OXIDATION OF SOME FLUOROAROMATIC AMINES

I. Introduction

The oxidation of pentafluoroaniline (9) was mentioned in Chapter 2 and will not be discussed further.[22,23]

N,N-dimethylaniline (83) has been extensively investigated by a variety of electrochemical techniques, with the conclusion that the product distribution is dependent on the concentration of (83).[100] Cyclic voltammetry indicates that the major product is para-para tetramethyl benzidine (85), with tritium tracer experiments being required to show the presence of the ortho-para product and that the sterically hindered ortho-ortho product is completely absent.[101] Increasing the concentration of (83) to produce (85) on a synthetic scale leads to

a variety of products being isolated.

At a concentration of 10^{-2}M of ($\underline{83}$) in acetonitrile, some ($\underline{85}$) is isolated but the major product is 4,4'-methylene-bis(N,N-dimethylaniline) ($\underline{87}$). When the concentration of ($\underline{83}$) is increased to about 10^{-1}M leuco crystal violet ($\underline{88}$) is obtained and further oxidation of this gives crystal violet dye ($\underline{89}$). Scheme 4.1 indicates the proposed mechanism. At higher concentrations of ($\underline{83}$) parallel reaction pathways occur because ($\underline{85}$) is always isolated although in varying yield. Other N,N-dialkylanilines give only the benzidines in acetonitrile, even at concentrations of up to 10^{-1}M. In all cases, about half the parent amine is recovered because of deactivation through protonation.[100]

Para-substituted N,N-dimethylanilines, where the substituent is inert, would be expected to yield relatively stable radical cations. For example, para-methoxy N,N-dimethylaniline is oxidised, in acetonitrile, to a highly stable radical cation.[102] The effect of a para-halogen substituent is dependent on the halogen. Thus, para-bromo and para-iodo N,N-dimethylanilines yield fairly unstable radical cations which decompose by the same pathway (Scheme 4.2). As expected, when X=Cl elimination by Scheme 4.2 only occurs to a minor extent in a dilute solution and no elimination occurs when X=F. The radical cation of the latter compound is relatively stable and its decomposition pathway has not been fully elucidated.

Poly-substitution of the aromatic ring leads to

Scheme 4.I

Scheme 4.I cont.

(84) + (87) ⟶ (88)

$$-2e^-$$

(89)

Scheme 4.2 X = Br or I

$$-e^-$$

+ X°

$$2X° \longrightarrow X_2$$
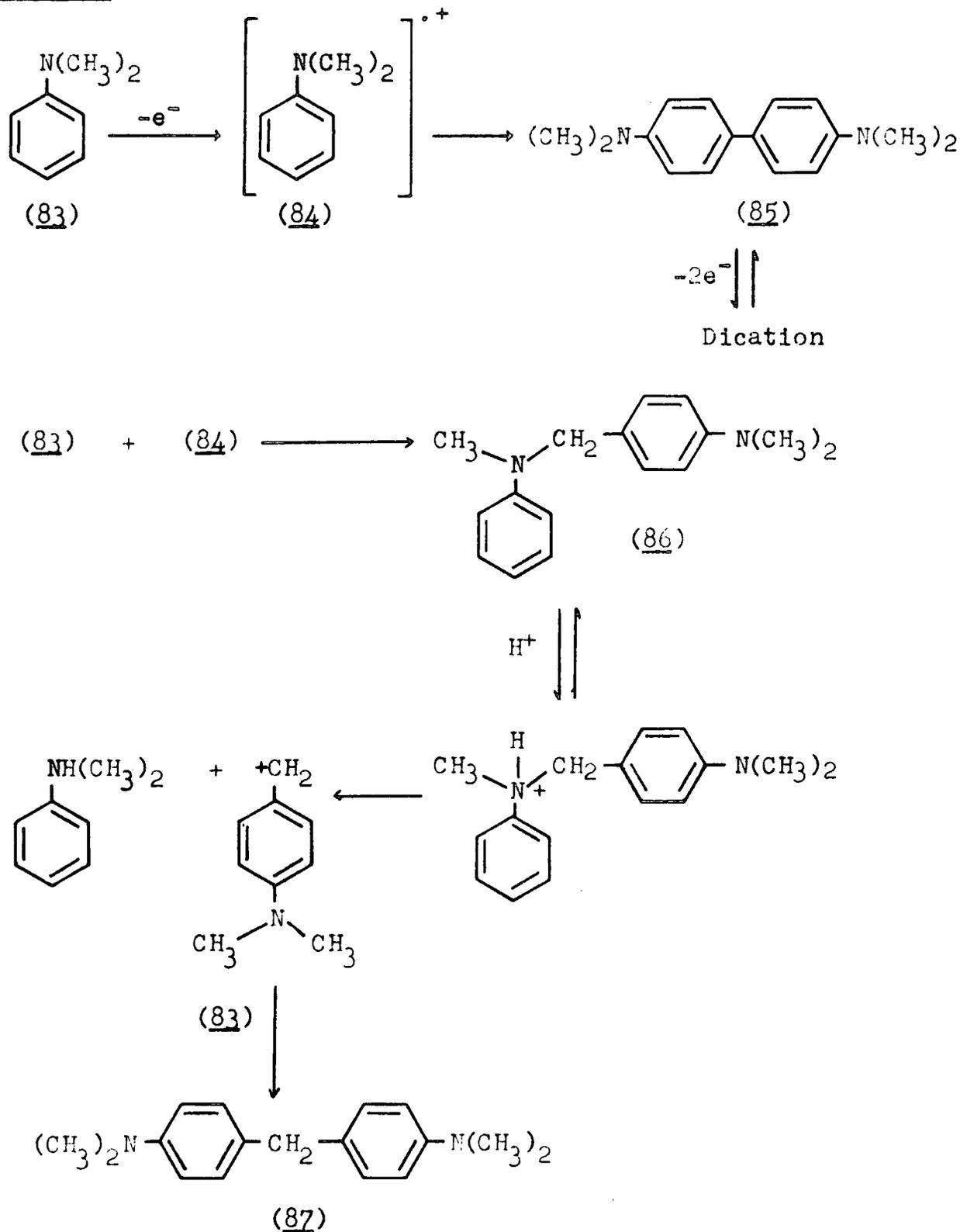
destabilisation of the radical cation by affecting the planarity between the aromatic ring and the N,N-dialkylamino group, such that the electrochemistry is more like that of an aliphatic amine.[103] For example, at 50V/min. para-chloro-N,N-dimethylaniline undergoes a reversible oxidation, while the oxidation of 2,4,6-trichloro-N,N-dimethylaniline is almost completely irreversible at this sweep rate, i.e. its radical cation is considerably less stable.[102]

2.   Oxidation of N,N-dimethylpentafluoroaniline

N,N-dimethylpentafluoroaniline (90) (ca. 1.7×10^{-2}M) was oxidised at +1.20V in acetonitrile-tetraethylammonium fluoroborate (T.E.A.F.). The anolyte turned a bright turquoise blue during the electrolysis but after leaving overnight it had changed to yellow and on work-up only starting material and tar was isolated. The colour was probably due to the radical cation of (90), which would be expected to have a relatively long lifetime as the 4-position is blocked.

(90)
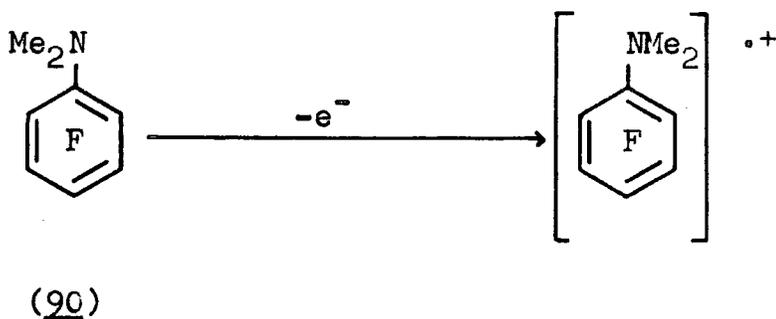
Subsequent decomposition of this radical cation probably occurs through the side chain, yielding products which would be more easily oxidised than (90). Similar behaviour is believed to occur in the oxidation of 4-fluoro-N,N-dimethyl-

aniline; although the exact pathway has not been determined.[102]

Electro-organic reactions can be dependent on the choice of the supporting electrolyte (for example, the synthesis of adiponitrile[9]), however, oxidation at +1.30V in acetonitrile-lithium perchlorate was not successful. The electrolysis initially parallelled that described above but towards the end the anolyte was dark brown, and on work-up only starting material and tar were isolated.

3.   Oxidation of N,N-dimethyl-2,3,5,6-tetrafluoroaniline

In contrast to (90), N,N-dimethyl-2,3,5,6-tetrafluoro-aniline (91) has an unsubstituted 4-position, such that the reactions illustrated in Scheme 4.1 are possible.

Oxidation of (91) (ca. 3×10^{-1}M) at +1.25V in acetonitrile-T.E.A.F. caused none of the colour observed in the oxidation of (90). This is not unexpected as the stability of the radical cation from (91) should be less than that from (90). Mainly starting material and tar were isolated on work-up but sublimation did yield a small quantity of a white solid, which decomposed on standing. The following data, however, were obtained from the solid which suggested structure (92). Mass spectroscopy indicated a molecular weight equivalent to that of (92) and the infra-red spectrum is very similar to that of the starting material (91). The ^{19}F n.m.r. spectrum showed only two resonances but the structure (92) was clearly shown by the ^{1}H n.m.r. spectrum which showed peaks at 3.28, 3.7, and 7ppm, which were assigned to N-methyl, N-methylene,

and an aromatic proton respectively.

The formation of (92) clearly occurs via loss of a proton from the intermediate radical cation, followed by coupling, as shown in the scheme below. It is interesting

(91)

Dimerisation

(92)
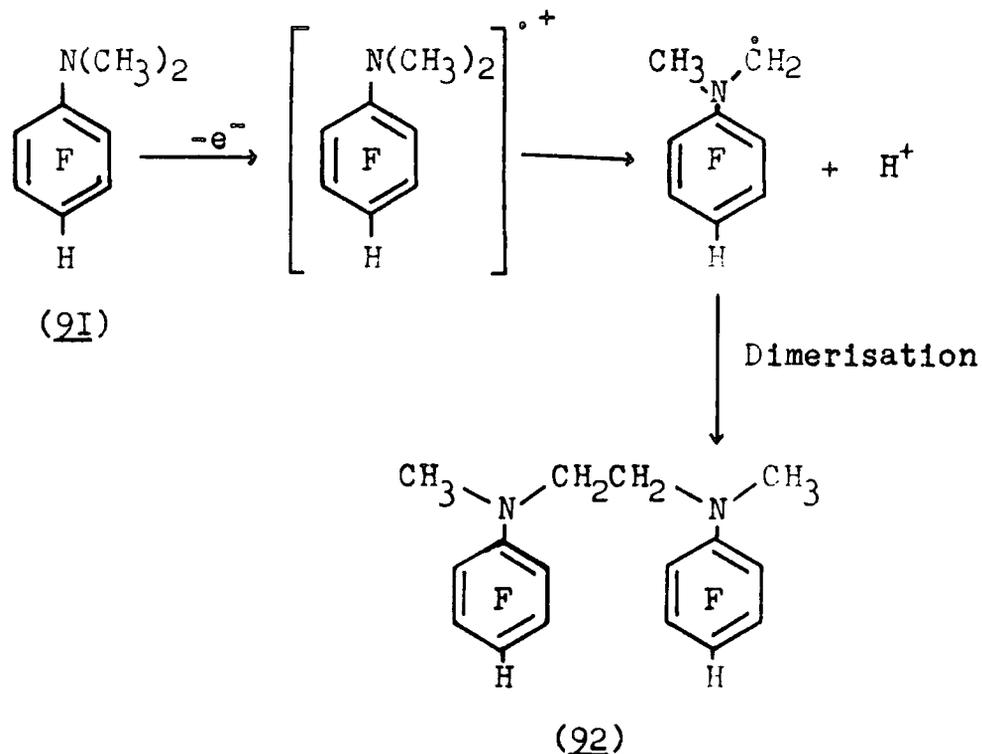
to note that this is similar to an alternative mechanism proposed to account for the formation of some of the products (for example, (86)) in the oxidation of (83).[104] Any products formed by dimerisation through the 4-position are, presumably, further oxidised and it is likely that parallel reaction pathways are occurring.

The supporting electrolyte is important in this reaction because a change from T.E.A.F. to lithium perchlorate led to the formation of an intense red colour during the

electrolysis. Nevertheless, no identifiable product could be isolated.

4. Oxidation of 4-amino-2,3,5,6-tetrafluoropyridine

Oxidation of pentafluoroaniline yields decafluoroazobenzene and octafluorophenazine[22] ; an oxidation of 4-amino-2,3,5,6-tetrafluoropyridine (93) was carried out in an attempt to prepare analogous products, however, only intractable material was obtained.

5. Voltammetry

The difficulty of relating analytical electrochemistry with preparative electrochemistry is well illustrated by the voltammetry of various fluorinated aromatic amines.

None of the compounds investigated were found to undergo thermodynamically reversible electron transfers in acetonitrile. The results were obtained either by linear sweep voltammetry (using the Beckmann instrument) or cyclic voltammetry (at the E.C.R.C., Capenhurst) and are presented in Table 4.I.

Although clearly defined oxidation peaks are observed for each of the systems, i.e. apparently simple electrochemistry, a whole range of products are, in fact, produced on the preparative scale. This illustrates the limitations of analytical electrochemistry in indicating what is to be a preparatively useful reaction. Indeed, as the author sees the present situation, there is little alternative, after

Table 4.I Voltammetry of some fluoroaromatic amines

Compound [a]	Ep$\frac{1}{2}$ [b]	Lit. Value[104]
N(CH$_3$)$_2$ (F ring) (90)	I.I5 [d]	I.I
N(CH$_3$)$_2$ (F ring, H) (91)	I.27 [c]	I.30
N(CH$_2$CH$_3$)$_2$ (F ring, N) (96)	I.6I, I.77, 2.0 [d]	
N(CH$_2$CH$_3$)$_2$ (F ring) (95)	I.27 [c]	
N(CH$_2$CH$_3$)$_2$ (F ring, H) (94)	I.28 [d]	
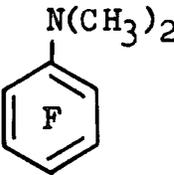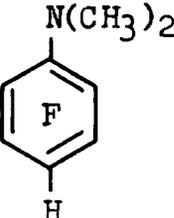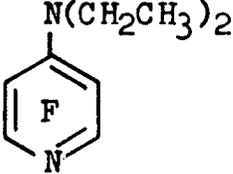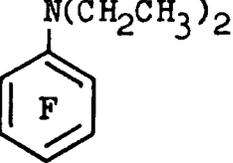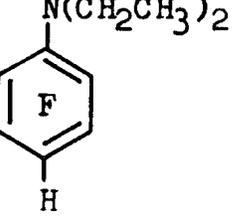
a - acetonitrile-T.E.A.F.,b - V v. S.C.E.,

c - 50mV/sec., d - 40mV/sec.

the analytical stage, to time-consuming screening of various solvent, supporting electrolyte, and electrode combinations.

Comparison of the $Ep_{\frac{1}{2}}$ values of the various amines (Table 4.I) with those of the anisoles (Table 3.2) illustrates how conjugation of the N lone pair with the aromatic system greatly facilitates removal of an electron from an aromatic system. The $Ep_{\frac{1}{2}}$ values of (90) and (91) have been previously reported[104]and these results are also presented in Table 4.I.

In the anisole system, a 4-hydrogen leads to a slightly lower $Ep_{\frac{1}{2}}$ value than the pentafluoro- compound, i.e. compare (66) and (75), whereas in the various amine derivatives shown in Table 4.I the 4-hydrogen derivatives have a slightly higher $Ep_{\frac{1}{2}}$ value. However, these differences are quite small and the point that requires emphasis is that para-fluorine and para-hydrogen have a comparable effect on the $Ep_{\frac{1}{2}}$ value. Clearly, this is yet another illustration of the competing effects of fluorine, as illustrated below. Ring nitrogen,

$$F-\overset{+}{C} \quad \longleftrightarrow \quad \overset{+}{F}=C$$
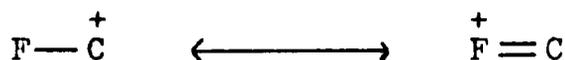
as would be expected, raises the $Ep_{\frac{1}{2}}$ value substantially.

N,N-diethylamino-2,3,5,6-tetrafluorobenzene (94) was found to have a single oxidation peak, with a reduction peak at high sweep rates but true reversibility was not observed. In contrast, the voltammetry of N,N-diethylamino-2,3,5,6-tetrafluoropyridine (96) was complicated, with

three close oxidation peaks being observed.

4.C OXIDATION OF SOME FLUORO-SUBSTITUTED PHENOLS

I. Introduction

Simple phenols yield very reactive initial electrode products which polymerise rapidly; however, when the ortho and para positions are blocked, low molecular weight products can be produced.

While this work was in progress, the oxidation of pentafluorophenol (I) by lead tetra-acetate was reported to give (4) and (97) as products.[105] Lead dioxide similarly
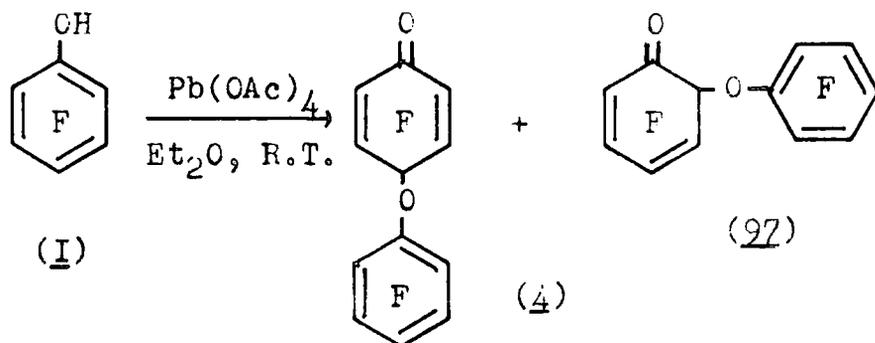
oxidises (I) to (4) (98 is also obtained)[106] and, as both these lead compounds can act as one-electron oxidants, it
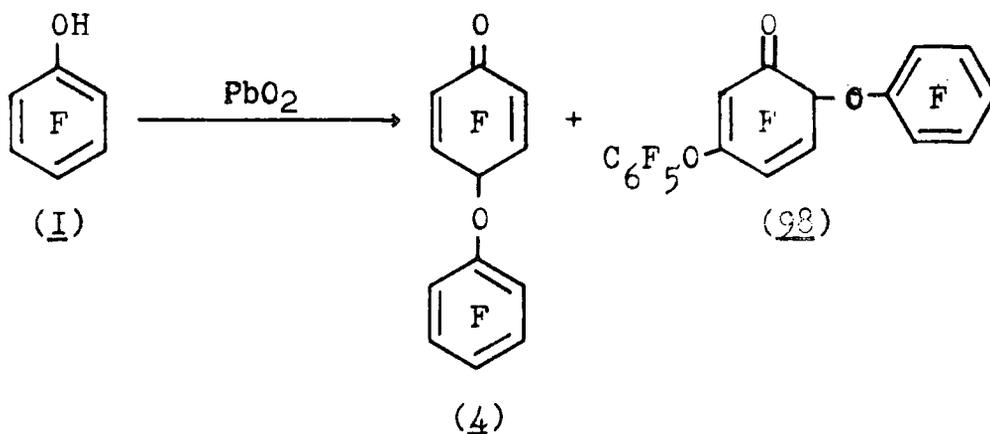
would be expected that electrochemical oxidation would yield the same products. In fact, shortly after the publication of the lead tetra-acetate work, the electrochemical oxidation of (I) in HF-SbF$_5$ and HF-KF was reported to give (4), together with (2) and (3) (the latter compound in HF-KF only).[21a] The formation of (2) was attributed to reaction of the intermediate radical with the solvent media.
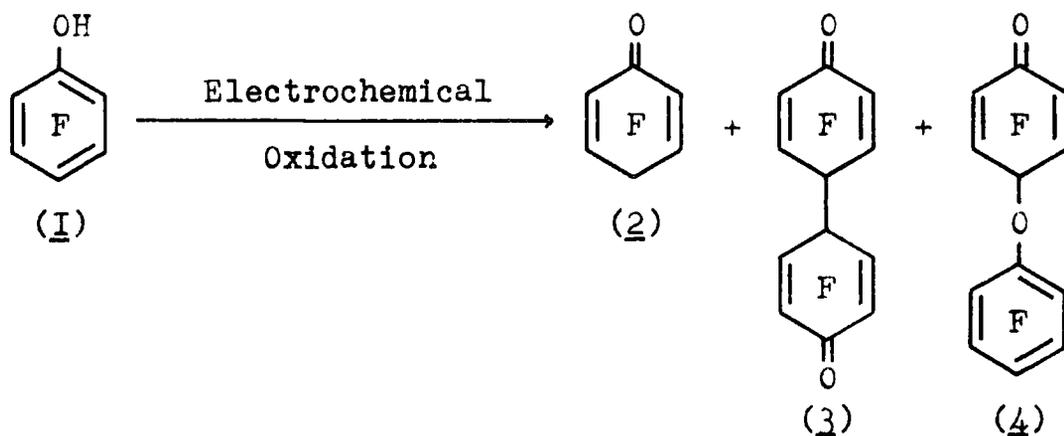
Oxidation of 2,3,5,6-tetrafluorophenol (99) by lead dioxide yields the quinoid compound (100), along with a small quantity of polymer. Addition of a tetraalkylammonium salt was found to enhance polymer formation in this type of oxidation.[107]
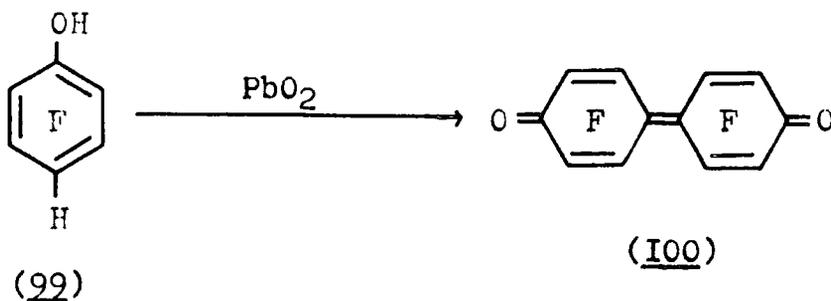
In general, neutralisation of a phenol causes the compound to be more readily oxidised than the parent compound. As with phenols, simple phenoxides yield polymers unless the ortho and para positions are blocked.

2. Oxidation of Pentafluorophenol

a. In Acetonitrile

Pentafluorophenol (I) was oxidised at +2.I5V in acetonitrile-T.E.A.F. to give a dark green anolyte, whose colour was persistent, indicating a long-lived oxidation product. This was confirmed by examination of a sample of the anolyte using the 'Electroscan' instrument; the colour was removed by reduction but did not appear on the oxidation cycle.

Work-up of the anolyte gave (I), together with a compound that was easily identified by its ^{19}F n.m.r. spectrum as (4); i.e. the same product as that obtained previously by chemical oxidation of (I). The formation of (4) occurs via the dimerisation of the radical (IOI), as illustrated in the scheme below.

(I)   (IOI)   (4)
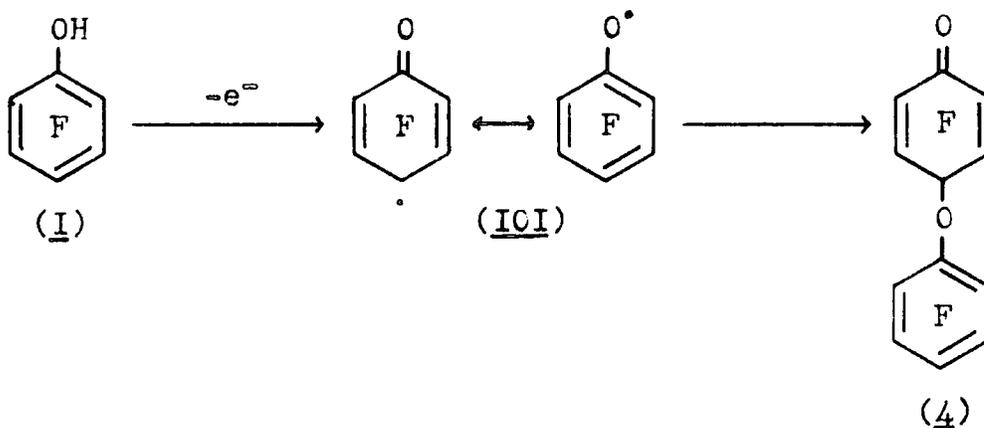
In an attempt to simplify the manipulation of the viscous products from the electrolysis, diazomethane was added. However, only pentafluoroanisole (75) could be detected by mass spectroscopy-g.l.c. and a white solid was also obtained, which could not be identified.

b. **In Trifluoroacetic Acid**

The results presented in Table 3.1 (page 30) illustrate the advantages of using trifluoroacetic acid as a solvent in electrochemical oxidations, because of the stabilisation of the highly reactive radical cations, and the subsequent reduction in side reactions. As the oxidation of (I) in acetonitrile involved numerous side reactions, leading to a reduction in the yield of dimeric products, it was felt that oxidation in trifluoroacetic acid would simplify the reaction.

Oxidation of pentafluorophenol (I) in trifluoroacetic acid at +2.40V produced a golden yellow anolyte. This observation is in stark contrast to the oxidation in aceto-nitrile and clearly indicates an involvement of solvent in the reaction, although the actual influence is not understood. It is interesting to note that the radical (IOI) is yellow,[21a] however, as the products themselves are yellow, it is more likely that the colour observed here is due to the products.

On work-up, a yellow liquid-solid mixture was isolated from which sublimation gave a yellow solid whose ^{19}F n.m.r. spectrum contained two distinctive features, i.e., a triplet of doublets at 115ppm and a multiplet at 124ppm. The former

signal can be assigned to the geminal fluorines in (102)
and the latter signal to the tertiary fluorine in (103), on
the basis of published results.[108] The 2,4-cyclohexadienone
structural unit, which is isomeric with (103), was shown to
be absent by u.v. spectroscopy.[110]
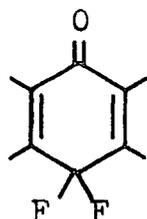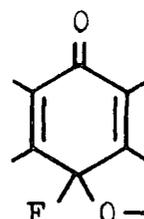
    (102)   (103)

Thin layer chromatography indicated that at least three
components were present in this solid but separation proved
difficult as one, or more, of the components either decomposed
on the silica surface or else readily hydrolysed. This latter
possibility is not unexpected as the tertiary fluorines
would be very susceptible to hydrolysis and especially on a
catalytic surface such as silica. Separation by thick layer
chromatography gave only two identifiable components with
structural assignments being based, principally, on their
^{19}F n.m.r. spectra. One component was identified as (104)
by comparison of its ^{19}F n.m.r. spectrum with published
values.[109]

The identification of the second component was less
certain as, although (105) has been previously prepared,[108]
its ^{19}F n.m.r. spectrum has not been published. However,

the ^{19}F n.m.r. spectrum of the second component contained
certain features which were assigned as follows. A multiplet
at 124.2ppm was readily assigned to the tertiary fluorine
(F-4). The signal at 140.8ppm was a distorted doublet (J =
23.5Hz) and by comparison with the spectrum of (106), and
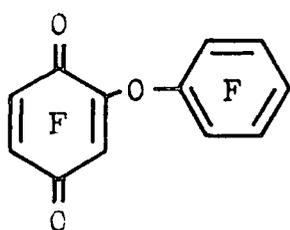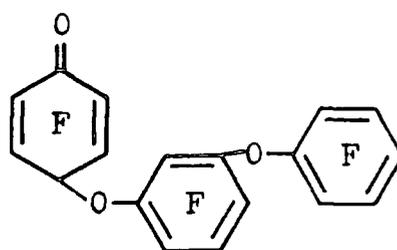
(104)   (105)

similar compounds, this was assigned to F-3 and F-5. At ca.
151ppm, there were two overlapping resonances which were
assigned to F-1 and F-6, once again by comparison with
published spectra of similar compounds.[108] An integration
indicated that this group of signals contained another
fluorine atom which was tentatively attributed to F-2'; a
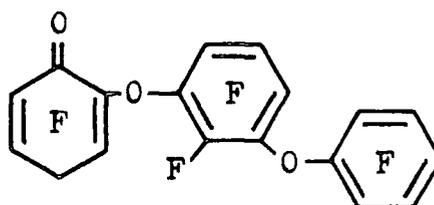
(106)   (107)

multiplet is observed at 151.3ppm for F-2' in (107). Signals
from about 152-161ppm, with an overall integration of 8,
corresponded to the other aromatic fluorine atoms. Thus,

the structure of the second component was believed to be
(105).

All the signals due to (104) and (105) were present in
the ^{19}F n.m.r. spectrum of the original mixture, indicating
that these compounds were not formed by isomerisation on
the silica surface. As previously mentioned, there was also
present a component containing the structural unit (102),
however, none of this component was isolated by column or
thick layer chromatography. Presumably, this was the component
which either hydrolysed or decomposed on the silica.

Scheme 4.3 illustrates the proposed mechanism for the
formation of compound (105). Oxidation of pentafluorophenol
(I) would give the radical (101), which can then dimerise to
give (97) in a process analogous to that proposed in the
lead tetra-acetate oxidation of (I).[105] The trimer (98) is
produced by further reaction of (101) with (97) and this
product is also produced in the lead dioxide oxidation of (I).[106]
The subsequent isomerisation of (98) to (105) has been
previously described, with (105) being formed when (98) is
heated at elevated temperatures (60°C).[108] Nevertheless, the
^{19}F n.m.r. spectrum of the yellow liquid-solid mixture before
sublimation, i.e. before exposure to any prolonged heating,
contained the salient features observed afterwards.

In the presence of an acid, such as HF or BF_3, (98)
isomerises to (108)[108] and it is possible that trifluoro-
acetic acid may perform a similar function. Thus, the compound

Scheme 4.3

(IOI)

(98)

(97)

(IO5)
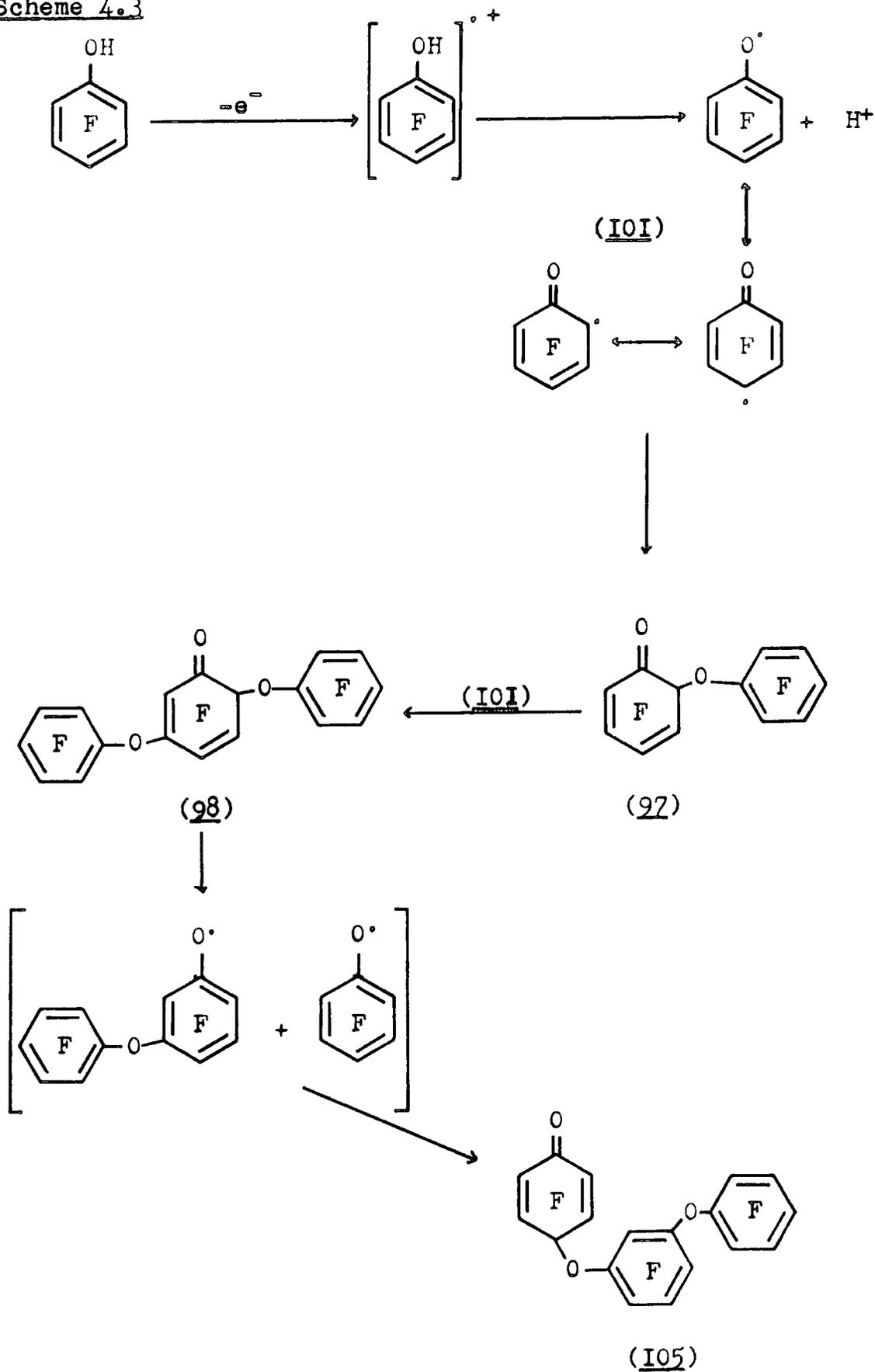
formed in the oxidation, but not actually isolated, may be (I08).

$$C_6F_5O \quad (98) \quad \xrightarrow{BF_3} \quad C_6F_5O \quad (I08)$$
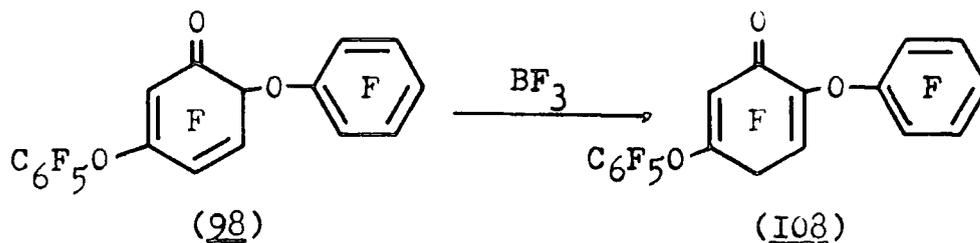
Compound (I04) could be produced by attack of (I0I) on the solvent, as outlined in Scheme 4.4, leading to **tetra-fluoro-p-benzoquinone** (I09) which will readily be attacked by (I0I).

Scheme 4.4   Formation of (I04)

(I0I) + CF$_3$COOH $\longrightarrow$ F   OCOCF$_3$

(I04) $\xleftarrow{\text{(I0I)}}$ (I09)
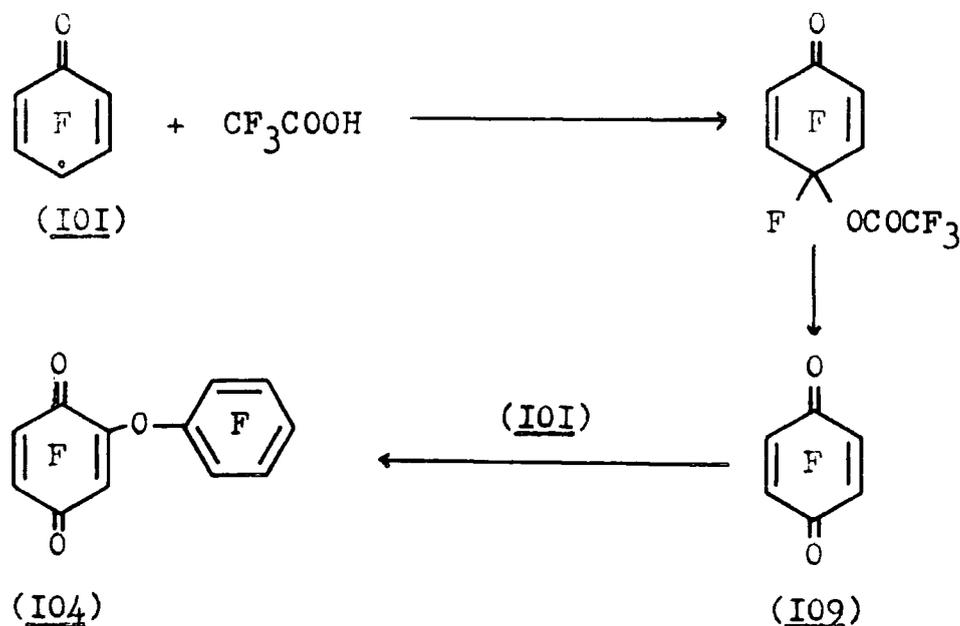
3.   Oxidation of 2,3,5,6-Tetrafluorophenol

2,3,5,6-Tetrafluorophenol (99) was oxidised at +2.20V
in acetonitrile-T.E.A.F. to give a dark green anolyte which,
after standing for a few hours, changed to a dark brown. It
is interesting to compare the oxidation of (99) with that
of (I) in acetonitrile in that both reactions gave a dark
green anolyte, but of different stability. As this colour
developed late in the reaction, it may be due to oxidation
of the products, but it is strange that in none of the other
oxidations carried out by the author (for example, lead
tetra-acetate) was a green colour observed. Lead tetra-
acetate oxidation of (99), in acetonitrile, yielded only
intractable material but even here no distinctive green
colour was observed.

A multi-component mixture was isolated on work-up from
the electrochemical reaction, but separation by column
chromatography gave a yellow liquid whose i.r. spectrum
contained C=O but no hydroxyl group. The ^{19}F n.m.r. spectrum
was complex but contained a multiplet at 123ppm which was
indicative of a tertiary fluorine in a cyclohexadienone
system. As an aid in the identification of this product,
the lead tetra-acetate oxidation of (99) was carried out in
an ether solution. A viscous orange oil was isolated, which
was shown to contain one main component by t.l.c.. The ^{19}F
n.m.r. spectrum indicated the presence of (II2), with
confirmation that it was a 2,4-cyclohexadienone coming from

its u.v. spectrum. Formation of (II2) can be rationalised
by the mechanism proposed in the oxidation of (I) by lead
tetra-acetate[105], (Scheme 4.5).

Scheme 4.5   Lead Tetra-Acetate Oxidation of (99)
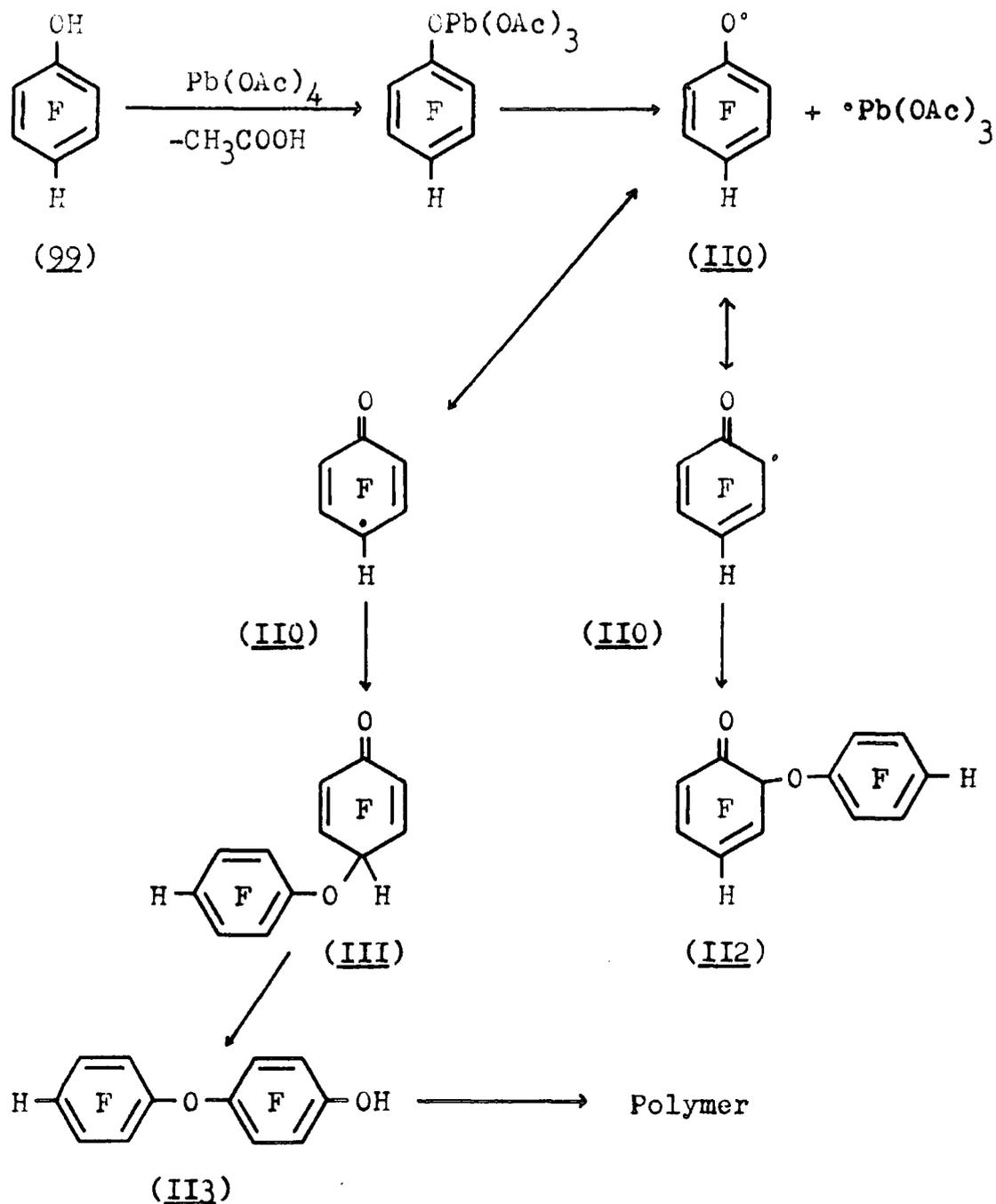
The absence of (III) is not unexpected as this would probably rearrange to (II3), with further oxidation giving a polymer.[III]

Comparison of the [19]F n.m.r. spectrum of the product isolated from the lead tetra-acetate oxidation with that from the electrochemical oxidation indicated that they were the same. Mechanistically, the electrochemical reaction will be similar to Scheme 4.5, with the formation of (IIO) occurring by a rapid deprotonation of the radical cation of (99). The multi-component nature of this reaction will probably be due, in part, to the rearrangement of (III).

As in the oxidation of (I), the products were difficult to manipulate; addition of diazomethane, however, led to the detection of only 2,3,5,6-tetrafluoroanisole (66) by mass spectroscopy-g.l.c. and an involatile white solid was also obtained, which could not be identified.

4. Oxidation of Potassium Pentafluorophenoxide

Potassium pentafluorophenoxide (II4) was readily oxidised in acetonitrile-T.E.A.F. at +0.70V. The current fell off very quickly and this was attributed to polymer formation, which was observed on the anode.

5. Voltammetry

a. Introduction

While the present work was in progress, other workers published the voltammetry of pentafluorophenol (I) in HF-KF and HF-SbF[5] media.[2Ia] In the former medium, the voltammogram

is characterised by two close oxidation waves, with another wave being ill-defined through passivation of the electrode. Only two waves are observed in HF-SbF$_5$, with the first being quasi-reversible. Table 4.2 presents some typical results and the assignments were discussed on pages I2 and I3.

Table 4.2   Voltammetry of Pentafluorophenol (I)[21a]

Medium[a]	pH[b]	Ist Wave[c] E½	2nd Wave[c] E½	3rd Wave[c] E½
KF (IM)	I3.7	0.6I2	0.855	I.35[d]
SbF$_6^-$(0.I5M) + SbF$_5$(0.I2M)	0.92	0.920	I.85[d]	

a - 3mM of (I) in HF.

b - all pH values are with reference to pure HF as solvent.

c - Volts v. Ag/Ag(I), E= +0.230V v. Cu/CuF$_2$.

d - passivation of the platinum electrode.

b.   Results and Discussion

Table 4.3 presents the results obtained by cyclic voltammetry at the E.C.R.C., Capenhurst. None of the electrochemical processes were found to be reversible up to a sweep rate of IOV/sec., in agreement with the general observations of the voltammetry of simple phenols. The voltammograms of penta- and 2,3,5,6-tetra-fluorophenol, (I) and (99), showed two close oxidation waves which merged at sweep rates above

300mV/sec.. By comparison with other work, these two stages presumably represent, firstly, oxidation to the radical cation which rapidly loses a proton, with the second step being oxidation of the radical, thus formed, to the cation.[112]

Table 4.3 Voltammetry of some Fluorinated Phenols and Phenoxide

Compound[a]	1st Wave $Ep_{\frac{1}{2}}$[b]	2nd Wave $Ep_{\frac{1}{2}}$[b]
OH — F (I)	1.94	2.36
O⁻K⁺ — F (114)	0.55	-
OH — F — H (99)	1.97	2.42

a - acetonitrile, Et_4NBF_4

b.- Volts v. S.C.E., sweep rate 200mV/sec.

Step (I)

(II5)

Step (2)

(II5)   (II6)
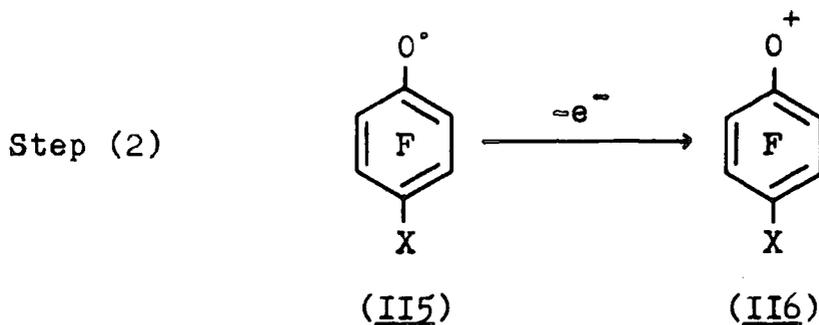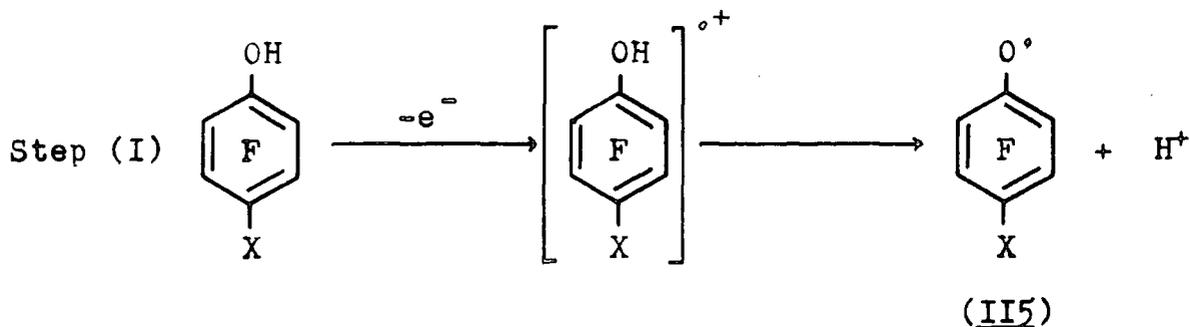
(where X = F or H)

The lack of reversibility is easily understood when one considers the number of possible follow-up reactions. Radical (II5) or cation (II6) can either react with water or another phenol molecule and, in the case of (II5), dimerise. The reactions illustrated below are to be taken together with those previously outlined.

2 ... (II5) ... (X = H)
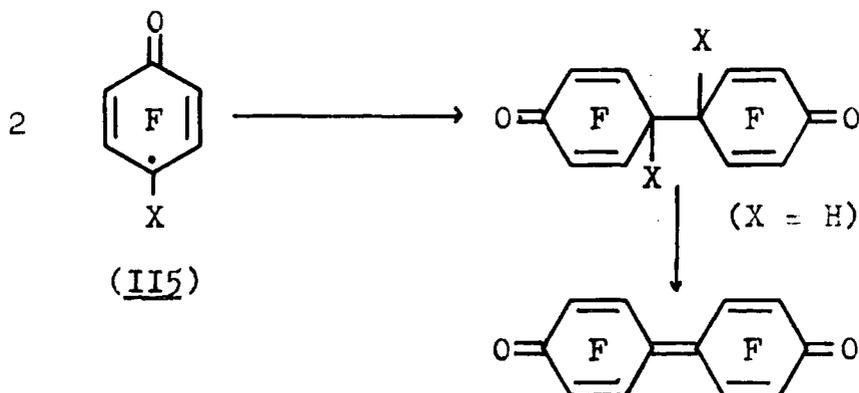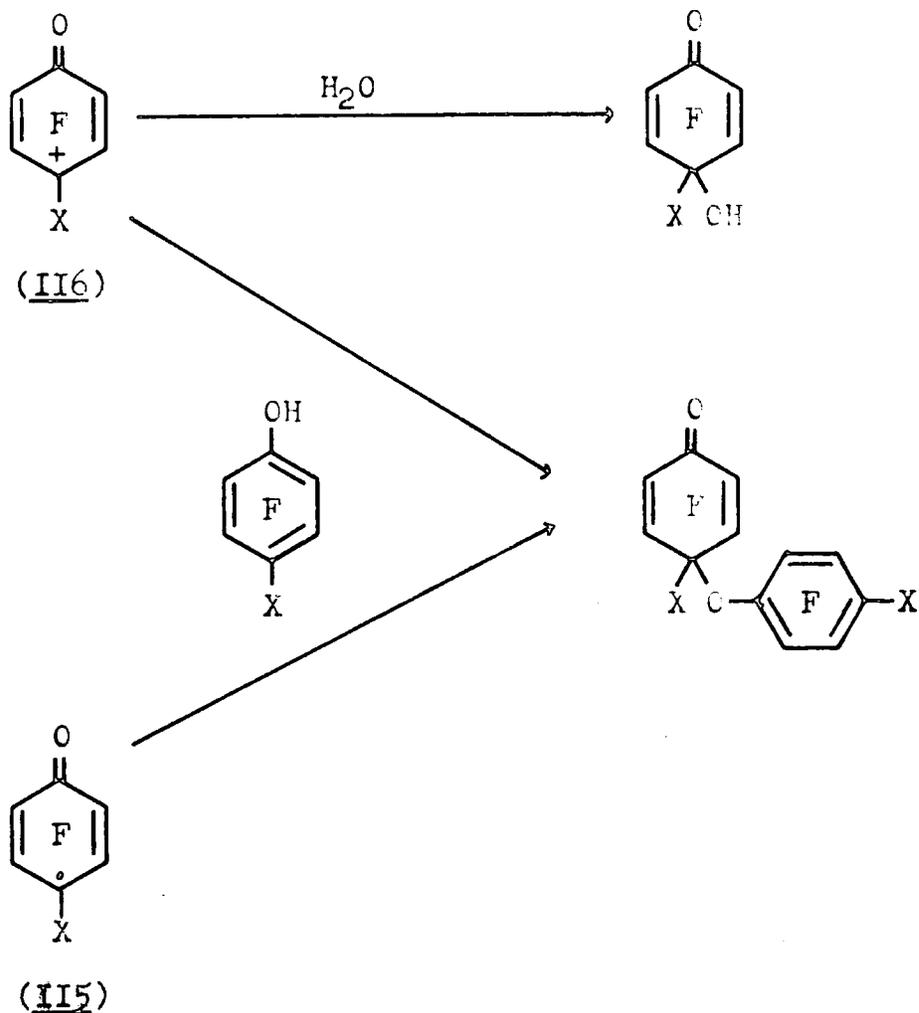
Potassium pentafluorophenoxide (<u>114</u>), as expected, oxidised irreversibly at a much lower potential than the corresponding phenol.

CHAPTER 5

ELECTROCHEMICAL OXIDATION OF SOME SUBSTITUTED FLUOROALKENES

5.A INTRODUCTION

In Chapters 3 and 4 it was shown that the introduction of an electron-donating substituent into a polyfluoroaromatic compound lowered its oxidation potential into a more accessible region. It was decided to extend this concept to poly-fluoro-alkenes, using amino and methoxy groups as substituents. Compounds such as (117) yielded dimeric products on oxidation, but extending the series to (118) was unsuccessful as these compounds were obtained in the imino (118b), rather than amino (118a), form and were not oxidisable under the conditions used.

$$CF_3_{R_2N}C=C_{CF_3}^{H} \qquad CF_3_{RHN}C=C_{CF_3}^{H} \rightleftharpoons CF_3_{RN}C-CH_2CF_3$$

(117)   (118a)   (118b)
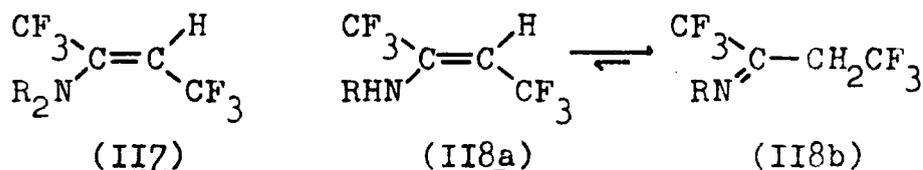
5.B REACTIONS OF SOME FLUOROALKENES WITH AMINES

I. Introduction

Little has been reported of the reactions of octafluoro-but-2-ene (119), trans-2H-heptafluorobut-2-ene (120), and 2-bromoheptafluorobut-2-ene (121) with amines. Octafluoro-but-2-ene (119) reacts with ammonia at low temperature to give I-(trifluoromethyl)-2,3,3,3-tetrafluoroketenimine (122). At higher temperatures (122) is isolated together with 2-aminoheptafluorobut-2-ene (123).[113] It was suggested that

the preference to give the imino form was due to the

$$CF_3CF=CFCF_3 \quad + \quad NH_3 \xrightarrow[\text{-10}^{\circ}\text{C}]{Et_2O} \quad \begin{array}{c} CF_3CHF \\ \diagdown \\ CF_3 \diagup \end{array} C=NH$$

(119)   (122)

$$CF_3CF=CFCF_3 \quad + \quad NH_3 \xrightarrow[\text{50}^{\circ}\text{C}]{Et_2O} \quad \begin{array}{c} CF_3CHF \\ \diagdown \\ CF_3 \diagup \end{array} C=NH \quad +$$

(119)   (122)

$$\begin{array}{c} H_2N \\ \diagdown \\ CF_3 \diagup \end{array} C=C \begin{array}{c} \diagup F \\ \diagdown \\ CN \end{array}$$

(123)
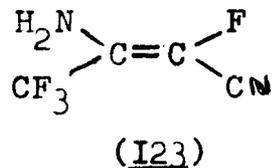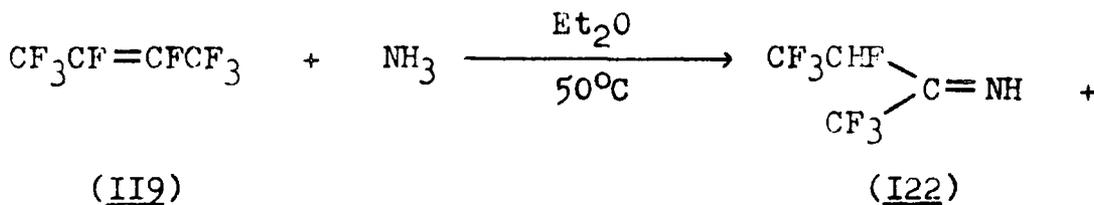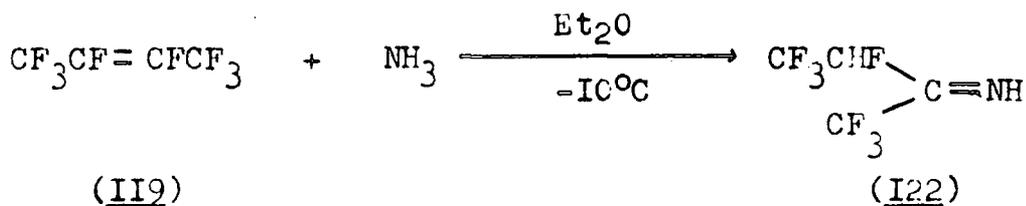
destabilising influence of fluorine attached to an sp^2 hybridised carbon atom.[114,115]

In view of the apparent lack of work in this field and the projected utility of the products in electro-organic synthesis, the reactions of (119), (120), and (121) with various amines were investigated. The results are presented in the following sections.

2.   Octafluorobut-2-ene

a.   Ethylamine

Ethylamine readily reacted with octafluorobut-2-ene (119) to give 2-ethylimino-1,1,1,3,4,4,4-heptafluorobutane (124) in 54% yield. Scheme 5.1 outlines the mechanism by which (124) is believed to be formed.

$$CF_3CF = CFCF_3 \quad + \quad CH_3CH_2NH_2 \longrightarrow CF_3CHF{\diagdown}$$
$${}_{CF_3}{\diagup}C = NCH_2CH_3$$

(119)   (124)
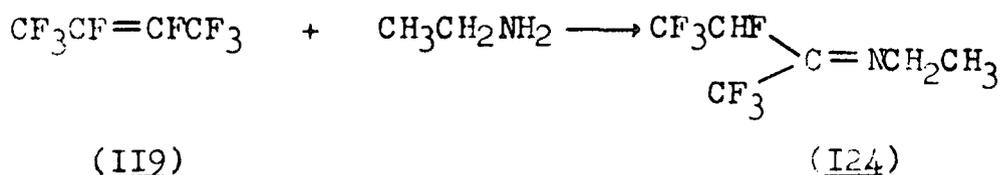
Scheme 5.I   R = CH$_3$ or CH$_3$CH$_2$
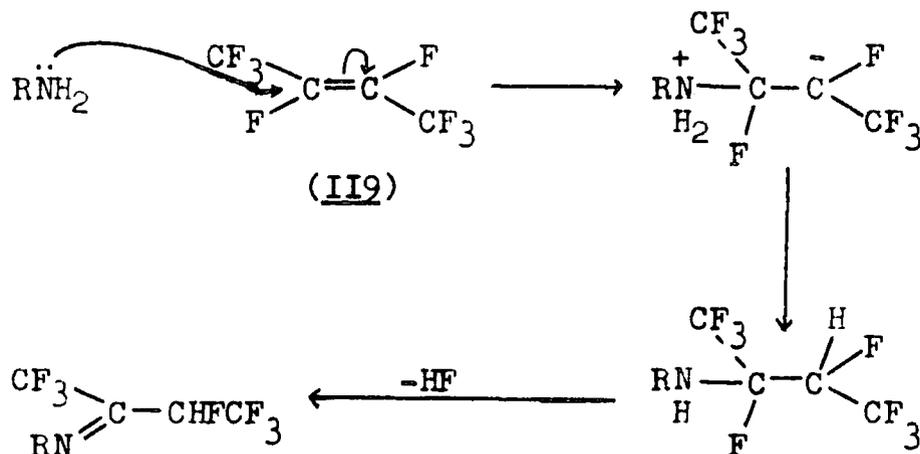
Thus, nucleophilic attack by the amine on (119) results in the formation of a zwitterion, whose carbanionic centre can be protonated either intra- or inter-molecularly. Loss of hydrogen fluoride can then occur to give either the imine or amine. Presumably, as with ammonia, the destabilising influence of a fluorine atom attached to an sp^2 hybridised carbon atom favours the formation of the imine compound.

Compound (124) was identified on the basis of its n.m.r. spectra, with correct elemental analyses and mass spectrum being obtained. Table 5.I contains some typical ^{19}F n.m.r. chemical shifts and Table 5.2 contains the relevant n.m.r. data of compounds containing the required structural units, which were used as aids in the assignment of (124) and

Table 5.I ^{19}F n.m.r. Chemical Shifts for Aliphatic
         Perfluorocarbons[116]

Structural Type[b]	Approximate Chemical Shift Range[a] (ppm)
CF$_3$—C$\lesseqgtr$	60-70
CF$_3$—C=C$<$	60-70
C̲F̲$_3$—CF$<$	70-80
C̲F̲$_3$—CF$_2$—	80-90
$>$C=CF—	100-120
—CF$_2$—	100-140
—CF$<$	160

a - with respect to CFCl$_3$.

b - all unmarked substituents are carbon.

Table 5.2   <u>Model Compounds</u> [113,117]

Compound	Assignment	Chemical Shift		Relevant
		^{19}F	^{1}H	Multiplicity (Hz)
a bc d CF_3＼$\underset{\underset{N}{\parallel}}{C}$／$CHFCF_3$ N＼H (<u>122</u>)	a	75.2		D, J_{ac} = 10.2
				Q, J_{ad} = 3.4
	b		4.53	D, J_{bc} = 43.8
				Q, J_{bd} = 5.9
	c	208.8		D, J_{cb} = 43.8
				Q, J_{cd} = 11.9
				Q, J_{ca} = 10.2
	d	78.3		D, J_{dc} = 11.9
				Q, J_{db} = 5.9
				Q, J_{da} = 3.4
a c b CF_3＼C／CH_2CF_3 N＼H (<u>126</u>)	a	77.2		
	b	63.8		T, J_{bc} = 10
				Q, J_{ba} = 2.6
	c		3.31	Q, J_{cb} = 10

CF_3CF_2＼C／CF_3
CF_3＼C／CF_2CF_3
   N
   CH_2 b
   CH_3 c
	a	70.5		

	b		3.6	
	c		1.3	

similar structures. The ^{19}F n.m.r. spectrum of (124) consisted

of two sets of resonances which were attributed to syn and

anti isomers. Assignment of the imine structure followed

from the observation of a broad doublet (J = 46Hz) at 203.4

or 208.8ppm. This is readily attributed to the -CHF- group

by comparison with the ^{19}F n.m.r. spectrum of (122), with

confirmation being obtained from the ^1H n.m.r. spectrum.

Also present in each set were two groups of resonances, at

72.4 and 77.2ppm, and 66.7 and 78.1ppm, which were assigned

to the two CF_3 groups in each isomer. It was not possible

to assign resonances to either a syn or anti structure.

b. Methylamine

Methylamine readily reacted with octafluorobut-2-ene

(119) to give syn and anti 2-methylimino-1,1,1,3,4,4,4-

heptafluorobutane (127), by the mechanism outlined in

Scheme 5.I. The structural assignment was made on the basis

$$CF_3CF=CFCF_3 \quad + \quad CH_3NH_2 \quad \longrightarrow \quad \begin{array}{c} CF_3CHF \\ CF_3 \end{array} C=NCH_3$$

$$(119) \qquad\qquad\qquad\qquad\qquad\qquad (127)$$
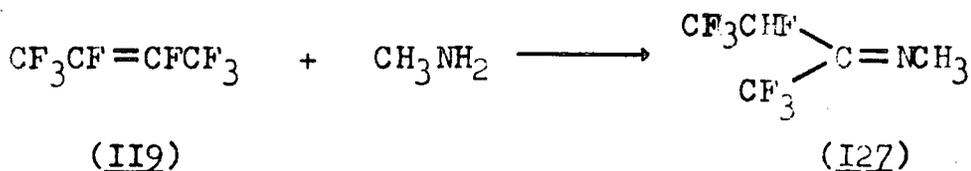
of information given in the previous section and, as with

(124), syn and anti isomers were shown to be present by ^{19}F

n.m.r. spectroscopy.

c. Diethylamine

In contrast to the reactions with primary amines, octa-

fluorobut-2-ene (119) was found to be relatively unreactive

towards diethylamine. Table 5.3 illustrates some typical experiments.

Table 5.3   Reaction of Octafluorobut-2-ene (II9) with diethylamine

Solvent	Temperature (°C)	Reaction Time (hours)	Ratio of Amine:(II9)	Recovery of (II9) (%)
Diethyl	0	48	0.8:I	63.5
Ether	22	75.5	I:I	35
	22	94	3:I	5I
Sulpholan	50	I43	I:0.9	47
	50	I66	2.I:I	35

This lack of reactivity is perhaps surprising, especially as (II9) readily reacted with dimethylamine (section 5.B.2.d.). Evidence that the expected product, N,N-diethylamino-I,I,I-2,4,4,4-heptafluorobut-2-ene (I28) was produced, albeit in small yields, came from n.m.r. spectroscopy (IO.B.3.b.i). By comparison with the shifts recorded in Table 5.I, the two resonances at 62.5 and 66.Ippm were assigned to two CF_3 groups, and that at I33.Ippm to the vinylic fluorine. The ^{19}F n.m.r. spectrum was that expected for the overall structure (I28), but the stereochemistry must be inferred from the

Table 5.4 Characteristic Coupling Constants [118]
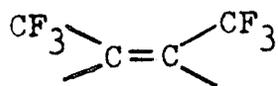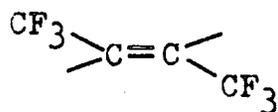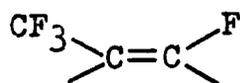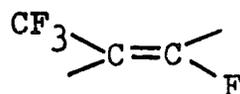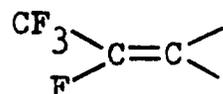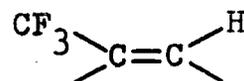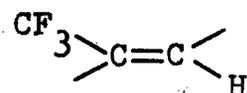
Structure	J
CF_3 and CF_3 cis on $C=C$	J = 11 - 13 Hz
CF_3 and CF_3 trans on $C=C$	J = 1 - 2 Hz
CF_3 and F cis on $C=C$	J = 18 - 25 Hz
CF_3 and F trans on $C=C$	J = 8.5 - 11 Hz
CF_3 and F geminal on $C=C$	J = 4 - 8 Hz
CF_3 and H cis on $C=C$	J = 0 - 2 Hz
CF_3 and H trans on $C=C$	J = 0 - 1 Hz

complexity of the spectrum. Table 5.4 indicates some characteristic coupling constants and, as can be seen from this table, the coupling constant for a _trans_ arrangement is very much smaller than for a _cis_ arrangement. Thus, if

$$CF_3\!\!>\!\!C\!=\!C\!\!<\!\!CF_3 \qquad\qquad CF_3\!\!>\!\!C\!=\!C\!\!<\!\!CF_3$$

$$J_{CF_3/CF_3} \qquad > \qquad J_{CF_3/CF_3}$$
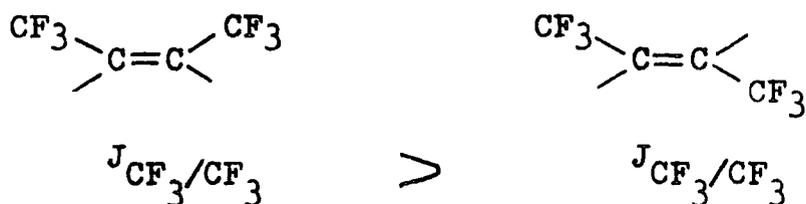
it was the _trans_ isomer, the resonances assigned to the CF_3 groups should be simple in form and as they are not, this implies that it is the _cis_ isomer which was isolated.

$$CF_3CF\!=\!CFCF_3 \;+\; (CH_3CH_2)_2NH \;\xrightarrow{1}\; CF_3\!\!>\!\!C\!=\!C\!\!<\!\!CF_3 \atop F \qquad\quad N(CH_2CH_3)_2$$

(**119**)   (**128**)
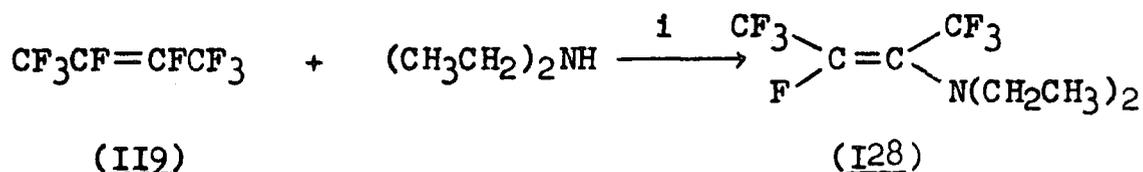
1 - sulpholan, $50^{\circ}C$, I:I ratio.

When the reaction was carried out in the presence of excess diethylamine at $50^{\circ}C$ in sulpholan, the only product which was isolated was a white solid which could not be identified.

The contrast in behaviour between dimethylamine and diethylamine suggests that the low reactivity is due to steric hindrance, with the relatively bulky diethylamine restricted in its approach to the double bond. An explanation to account for this steric effect can be modelled on the steric mechanism proposed in elimination reactions.[119]

(A)   (B)

Thus, the approach of the nucleophile towards the alkene (A) leads to a transition state which could be represented by (B). In moving towards (B) there will be steric interaction between a trifluoromethyl group and the nucleophile, and, therefore, the more bulky the nucleophile the greater the interaction.

It might be anticipated that we should observe similar behaviour in other crowded fluoroalkenes, for example, perfluoro-4-methyl-pent-2-ene (129). However, (129) reacts quite readily with diethylamine to give I-N,N-diethylamino-2-trifluoromethyloctafluoropent-I-ene (130).[120] This higher reactivity may be attributed to a different process in that the isolation of (130) is due to the production of fluoride ion in the initial step, which then causes a rapid fluoride ion induced isomerisation to give (131). As the terminal $CF_2 = C<$ group is very activated towards nucleophilic attack, diethylamine preferentially attacks (131) rather than (130) (Scheme 5.2).

Scheme 5.2

$$(CF_3)_2CF-\underset{F}{\overset{}{C}}=\underset{F}{\overset{}{C}}-CF_3 \xrightarrow[-F^-]{+Et_2NH} \underset{CF_3}{\overset{CF_3}{>}}C=CF-\underset{\overset{|}{{}^+HNEt_2}}{CF}-CF_3$$

(129)

$$\downarrow \begin{array}{c} -Et_2NH \\ +F^- \end{array}$$

$$\underset{CF_3}{\overset{CF_2}{>}}C-CF_2CF_2CF_3 \xleftarrow[-F^-]{+F^-} \underset{CF_3}{\overset{CF_3}{>}}C=CFCF_2CF_3$$

(131)

$$\downarrow \begin{array}{c} +Et_2NH \\ -HF \end{array}$$

$$Et_2NCF=C\overset{CF_2CF_2CF_3}{\underset{CF_3}{<}}$$

(130)

Similar behaviour has been reported with related fluoro-alkenes[121] and herein lies the possible reason as to why octa-fluorobut-2-ene is unreactive towards diethylamine. The reactivity of fluoroalkenes such as (129) towards diethylamine is not dependent on the direct reaction, but on the fluoride ion induced isomerisation to a more reactive compound. As the principle aim of this work was to synthesise (128) in useful quantities this reaction was not investigated further.

In an attempt to overcome this lack of reactivity,

lithium diethylamide was synthesised but its reaction with

(II9) was not found to be synthetically useful. A small

quantity of a mixture was isolated and separated by preparative

g.l.c.. Mass spectroscopy-g.l.c. indicated that the mixture

contained 2-N,N-diethylamino-1,1,1,3,4,4,4-heptafluorobut-2-ene

(128) and 2,3-bis(N,N-diethylamino)-1,1,1,4,4,4-hexafluoro-

but-2-ene (133), and a probable mechanism for their formation

is outlined in Scheme 5.3.

Scheme 5.3
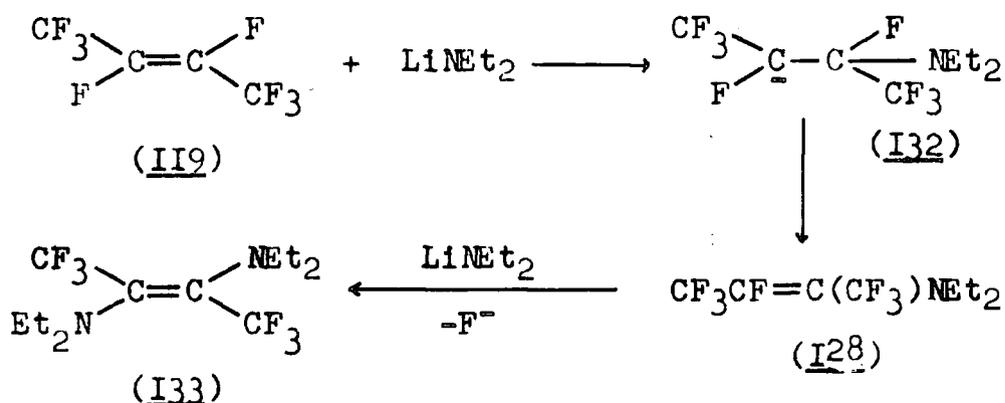
^{19}F n.m.r. spectroscopy was used to confirm the presence

of (133), with its structure following directly from the

observation of a singlet attributable to the two CF_3 groups.

A tentative assignment of the stereochemistry as trans was

based on the assumption that the bulky N,N-diethylamino

groups are unlikely to be cis.

From the ^{19}F n.m.r. spectrum, (128) was shown to be a

mixture of cis and trans isomers with the assignment following

directly from the information presented in Tables 5.I and
5.4.

d. **Dimethylamine**

Dimethylamine readily reacted with octafluorobut-2-ene
(**II9**), presumably reflecting the smaller steric requirement
of this amine compared to diethylamine, to give cis and trans
-2-N,N-dimethylamino-I,I,I,3,4,4,4-heptafluorobut-2-ene, (**I34**)
and (**I35**) respectively. The isomers were separated by prep-
arative g.l.c., with the cis isomer being isolated in a larger
amount.

$$CF_3CF{=}CFCF_3 \quad + \quad (CH_3)_2NH \quad \longrightarrow \quad \underset{F}{\overset{CF_3}{>}}C{=}C\overset{N(CH_3)_2}{\underset{CF_3}{<}} \quad +$$

(**II9**)   (**I35**)

$$\underset{F}{\overset{CF_3}{>}}C{=}C\overset{CF_3}{\underset{N(CH_3)_2}{<}} \quad + \quad \underset{}{\overset{CF_3CH{=}C(CF_3)}{N(CH_3)_2}}$$

(**I34**)   (**I36**)
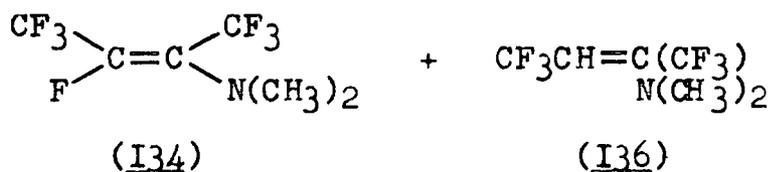
Correct elemental analyses were obtained on a mixture
of (**I34**) and (**I35**), and parent peaks were observed in their
mass spectra. The assignment of structures was based on
information presented in Tables 5.I and 5.4.

A third fraction was also obtained by preparative g.l.c.
which contained (**I34**) as an impurity. A mass spectrum of this
fraction contained an intense m/e 207 which was not present
in the mass spectrum of either (**I34**) or (**I35**). In the [1]H n.m.r.

spectrum of this fraction there was present a resonance with a chemical shift similar to that of the olefinic proton in (136).[122] Thus, it appears reasonable to suggest that a small quantity of (136) (M 207) was produced in this reaction, possibly by an electron transfer or radical mechanism. The latter mechanism has been postulated to account for some anomalous products in similar reactions.[123]

3. Trans-2H-heptafluorobut-2-ene

a. Ethylamine

Ethylamine readily reacted with trans-2H-heptafluorobut-2-ene (120) to yield 2-ethylimino-1,1,1,4,4,4-hexafluorobutane (137). The high electronegativity of fluorine causes C-3 to be highly electrophilic, such that nucleophilic attack occurs at this position. This also results in the formation of the

$$CF_3 \diagdown C=C \diagup F \atop H \diagup \diagdown CF_3 \quad + \quad CH_3CH_2NH_2 \longrightarrow \quad CF_3CH_2 \diagdown C=NCH_2CH_3 \atop CF_3 \diagup$$

$$(120) \qquad\qquad\qquad\qquad (137)$$
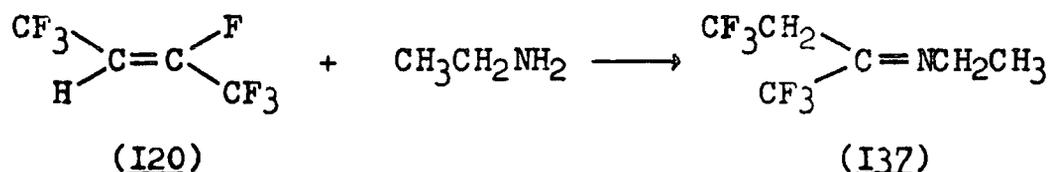
most stable carbanion, with hydrogen preferentially stabilising the negative centre compared to fluorine.[124] Protonation of this carbanion, followed by loss of hydrogen fluoride gives the imine (Scheme 5.4).

Compound (137) had correct elemental analyses and mass spectrum, and the assignment of its structure was based on n.m.r. spectroscopy and comparison with model compounds (Table 5.2). The ^{1}H n.m.r. spectrum of (137) contained a triplet (0.87ppm, J = 7Hz) and a quartet (3.18ppm, J = 7Hz)

Scheme 5.4 R = CH₃ or C₂H₅

$$\text{RNH}_2 \quad \overset{CF_3}{\underset{F}{\diagdown}} C=C \overset{H}{\underset{CF_3}{\diagup}} \quad \longrightarrow \quad RN\overset{CF_3}{\underset{H_2}{\overset{+}{\diagdown}}}-\overset{|}{\underset{F}{C}}-\bar{C}\overset{H}{\underset{CF_3}{\diagup}}$$

(120)

$$\overset{CF_3}{\underset{RN}{\diagdown}}CCH_2CF_3 \quad \overset{-HF}{\longleftarrow} \quad \overset{CF_3}{\underset{RNH}{\overset{|}{\underset{F}{\diagdown}}}}\overset{|}{\underset{H}{C}}-\overset{|}{C}\overset{H}{\underset{CF_3}{\diagup}}$$
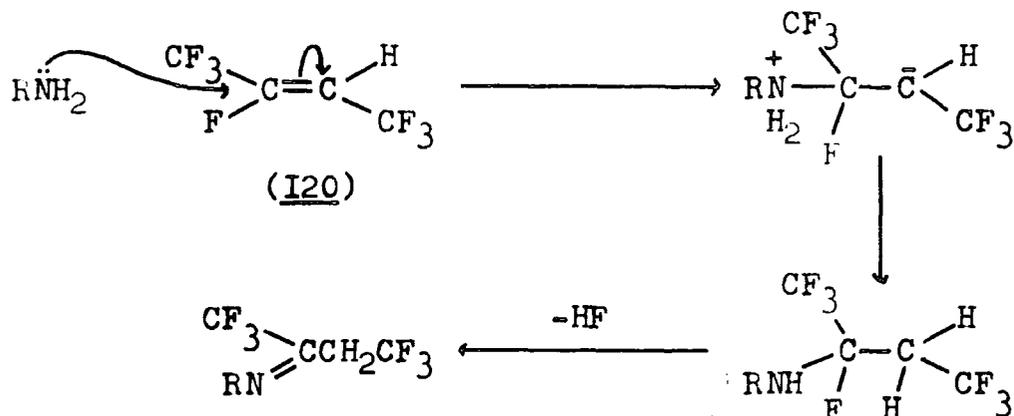
which were assigned to the ethyl group. Overlapping with the
latter group was a quartet (2.88ppm, J = IOHz) which was
assigned, by comparison with (126) (Table 5.2), to the other
methylene group. ^{19}F n.m.r. spectroscopy showed the presence
of two CF_3 groups but, in contrast to (124) and (127), no
syn or anti isomers were discernible.

b. Methylamine

Methylamine readily reacted with trans-2H-heptafluoro-
but-2-ene (120) to give 2-methylimino-I,I,I,4,4,4-hexafluoro-
butane (138), by the mechanism outlined in Scheme 5.4.

$$\overset{CF_3}{\underset{F}{\diagdown}}C=C\overset{H}{\underset{CF_3}{\diagup}} \quad + \quad CH_3NH_2 \quad \longrightarrow \quad \overset{CF_3CH_2}{\underset{CF_3}{\diagdown}}C=NCH_3$$

(120)   (138)
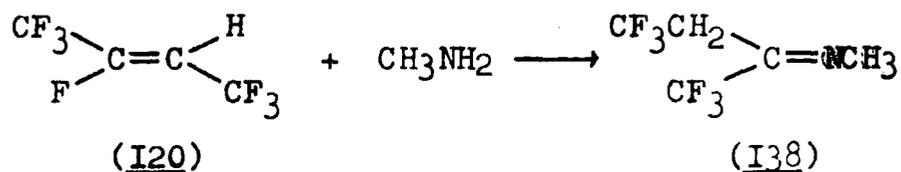
Compound (138) was identified on the basis of its ^{1}H
n.m.r. spectrum, which contained a singlet overlapping a
quartet. The singlet (3ppm) was assigned to the methyl group
and the quartet (2.92ppm, J = IOHz) was assigned to the

methylene group, by comparison with (I26) (Table 5.2).
Correct elemental analyses and mass spectrum were also
obtained.

c. Diethylamine

As with (II9), trans-2H-heptafluorobut-2-ene (I20) was
found to be fairly unreactive towards diethylamine. A mixture
was obtained, one component of which was assumed to be 2H-
3-N,N-diethylamino-I,I,I,4,4,4-hexafluorobut-2-ene (I39) on
the basis of a parent peak in the mass spectrum. However, as
the product was required in synthetically useful quantities
this reaction was not investigated further, and (I39) was
prepared by a known route.[II8] Presumably, steric factors are
affecting this reaction, as discussed earlier.

d. Dimethylamine

A reaction readily occurred to yield the desired product,
2H-3-N,N-dimethylamino-I,I,I,4,4,4-hexafluorobut-2-ene (I36),
which was identified by comparison of its n.m.r. data with
those of a known sample.[I22]

$$CF_3 \diagdown C=C \diagup H \atop F \diagup \diagdown CF_3 \quad + \quad (CH_3)_2NH \longrightarrow \quad CF_3 \diagdown C=C \diagup N(CH_3)_2 \atop H \diagup \diagdown CF_3$$

(I20)   (I36)
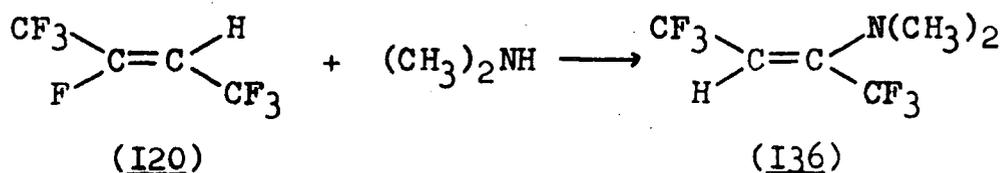
4. 3-Bromo-heptafluorobut-2-ene

a. Dimethylamine

In view of the comments made previously, only a reaction
with dimethylamine was attempted. The reaction readily occurred

to give a mixture, which mass spectroscopy-g.l.c. indicated was two components with a parent peak of 287 and a minor component with a parent peak of 250. N.m.r. spectroscopy indicated that the main components were _cis_ and _trans_ 2-bromo-3-N,N-dimethylamino-I,I,I,4,4,4-hexafluorobut-2-ene, (140) and (141), in a ratio of 4:I. The assignment of structures followed directly from information presented previously. The minor component was probably 2,3-bis(N,N-dimethylamino)-I,I,-I,4,4,4-hexafluorobut-2-ene (142) on the basis of its mass spectrum. This reaction illustrates the preferential ability

Scheme 5.5
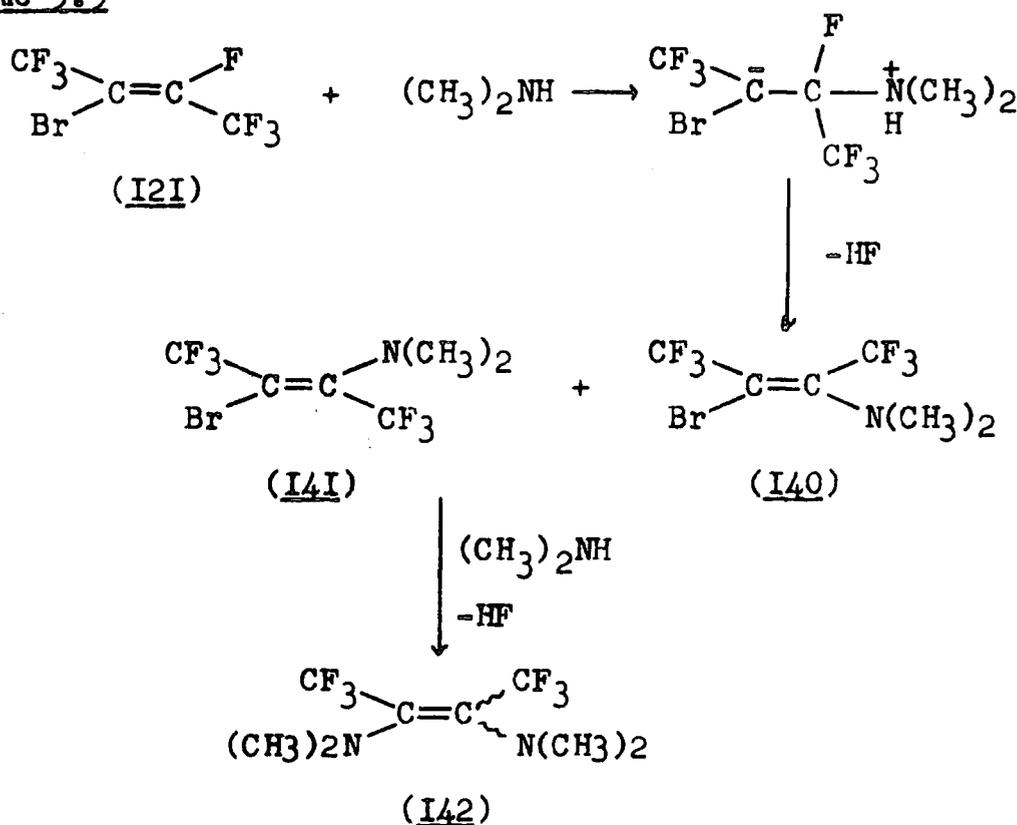
of a bromine atom to stabilise a carbanionic centre, compared

to a fluorine atom (Scheme 5.5).[118]

5.C REACTION OF HEXAFLUOROBUT-2-YNE WITH DIETHYLAMINE

In order to synthesise (139) in a useful quantity, the reaction between hexafluorobut-2-yne (143) and diethylamine was used,[118] and the effect of solvent on the product isomer ratio was investigated. The area of nucleophilic addition to acetylenes has been well investigated, but it has been found that an overall explanation for the observed isomer ratios is lacking.[125] The steric course of the reaction depends on several factors such as the solvent, the nature of the acetylene and amine, and the mixing process.[126]

$$CF_3C \equiv CCF_3 \quad + \quad (CH_3CH_2)_2NH \longrightarrow CF_3(H)C = C(CF_3)N(CH_2CH_3)_2$$
$$(143) \hspace{8cm} (139)$$
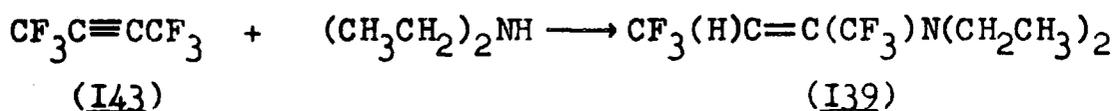
In this investigation, the reactions were carried out at atmospheric pressure and on termination of the experiment, the isomer distribution present in the crude reaction mixture was determined by ^{19}F n.m.r. spectroscopy. The results obtained are presented in Table 5.5. Isomer ratios in the isolated product were also determined; these indicated that the _trans_ isomer was the more volatile component, as vacuum transference was found to offer a crude separation on work-up from involatile solvents.

There are believed to be two possible mechanisms for this reaction.[118] Mechanism I requires the formation of a four-centre intermediate; charge formation would be small and the _cis_ isomer should predominate

Mechanism I

$$CF_3C \equiv CCF_3 \xrightarrow{\hspace{2cm}} \overset{\delta-}{CF_3}C \equiv CCF_3 \xrightarrow{\hspace{2cm}} \underset{(CH_3CH_2)_2N}{CF_3} C = C \underset{H}{CF_3}$$
$$+$$
$$H-N(CH_2CH_3)_2 \qquad H\cdots \underset{\delta+}{N}(CH_2CH_3)_2$$
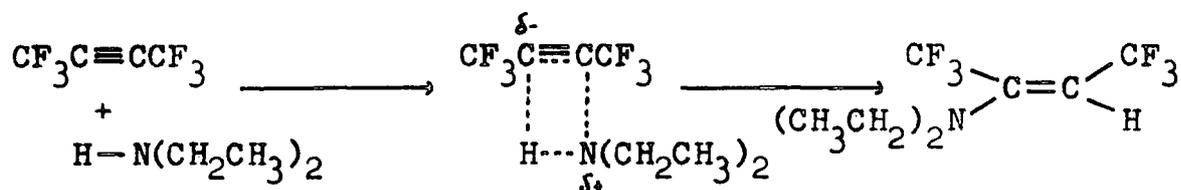
In mechanism II there is the formation of _cis_ and _trans_ zwitterions, i.e. full charge transfer, and protonation can then occur either inter- or intra-molecularly. Isomerisation

Mechanism II

$$CF_3C \equiv CCF_3 \xrightarrow{\hspace{1cm}} \underset{(CH_3CH_2)_2N\atop H}{\overset{CF_3}{\underset{+}{}}}C = C \underset{CF_3}{\overset{-}{}} \xrightarrow{\hspace{1cm}} \underset{(CH_3CH_2)_2N}{CF_3}C = C \underset{CF_3}{\overset{H}{}}$$
$$+$$
$$(CH_3CH_2)_2NH \xrightarrow{\hspace{1cm}} \underset{(CH_3CH_2)_2N\atop H}{\overset{CF_3}{\underset{+}{}}}C = C \underset{\underset{\ominus}{}}{CF_3} \xrightarrow{\hspace{1cm}} \underset{(CH_3CH_2)_2N}{CF_3}C = C \underset{H}{\overset{CF_3}{}}$$
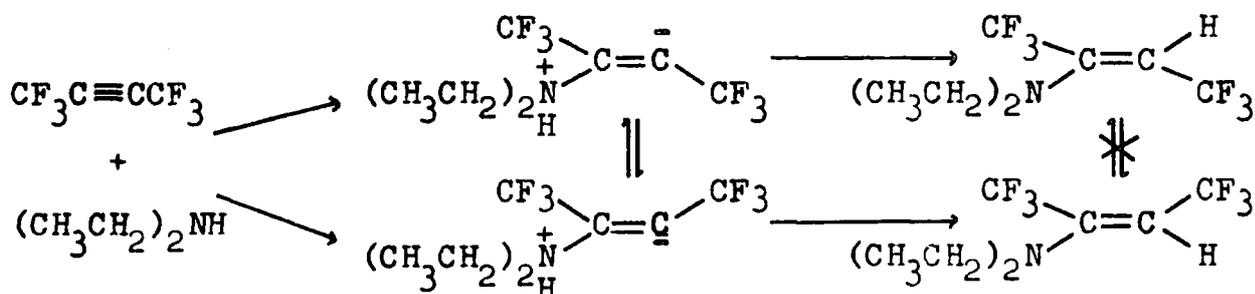
of either the products and/or the intermediate zwitterions may occur. However, results obtained in this investigation, and by another worker,[118] indicate that isomerisation of the products does not occur. The possibility of isomerisation of the intermediate zwitterions is difficult to assess and their relative stabilities may be solvent dependent. Theoretical calculations indicate that the barrier to inversion is high for fluorinated vinyl anions and an experimental result is in agreement with this.[127,128] Thus, reaction of butyl lithium with _trans_-IH-pentafluoropropene (_144_) yields an organolithium compound which can be trapped with, for

Table 5.5 Effect of solvent on the isomer ratio

Solvent	Volume (ml)	ε [a]	Ratio of reactants Amine: (143)	Product (139) Cis: Trans [b]
-	-		I:I	30: 70
Diethyl	IO	4.3	I:I	47:53
Ether	25		I:I	65:35
Dichloro- methane	IO	8.9	I:I	I4:86
H.M.P.A. [c]	IO	30	I:I	67:33
Sulpholan	IO	44	I:I	6I:39

a - dielectric constant of the solvent[1],

b - determined by ^{19}F n.m.r. spectroscopy on the crude reaction mixture,

c - Hexamethyl phosphoramide.
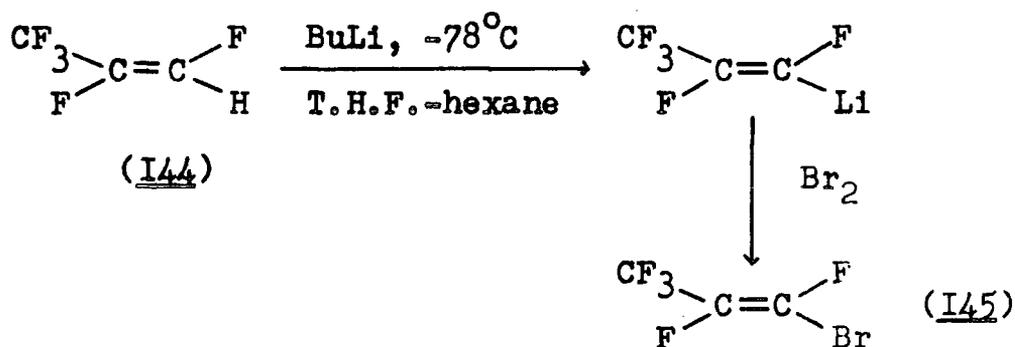
example, bromine to give <u>trans</u>-I-bromo-pentafluoropropene

(<u>145</u>). However, a direct comparison of this result with the

zwitterion (<u>147</u>) is not valid, as in the vinyl anion (<u>146</u>)

a destabilising $\bar{C}$—F interaction is present, while in (<u>147</u>)

a stabilising CF_3 group is attached to the carbanionic centre.

$$CF_3 \diagdown C=C \diagup F$$
$$F \diagup \qquad \diagdown \underset{=}{C}$$

$$CF_3 \diagdown C=C \diagup CF_3$$
$$R_2\overset{+}{\underset{H}{N}} \diagup \qquad \diagdown \underset{=}{C}$$
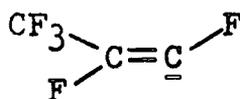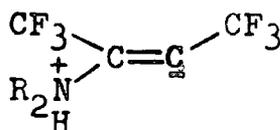
(<u>146</u>)   (<u>147</u>)

In an attempt to obtain more applicable experimental evidence,

(<u>143</u>) was reacted with lithium diethylamide, at low temperature,

and then bromine was added to trap any vinyl anions. Unfort-

unately, hexafluorobut-2-yne is susceptible to polymerisation

by organolithium compounds,[129] and only polymeric material

was isolated.

Assuming that the barrier to inversion is high, then

it follows that the isomer ratio depends on the orientation

of initial attack. Therefore, it must be the stability of

the intermediate which is dependent on the solvent. High

dielectric constant solvents will stabilise charge separation

whereas low dielectric constant solvents will prefer little

or no charge separation. Thus, a change in mechanism may

occur on changing the solvent and, hence, probably a change

in the isomer distribution. As can be seen from Table 5.5

this is the case, however, the change does not appear to

solely dependent on the solvent dielectric constant, although
this would appear to be the principal factor. The _cis_ isomer
was formed predominantly in the solvents of high dielectric
constant, and this can be accounted for by mechanism I.
Preferential formation of the _trans_ isomer in solvents of
low dielectric constant cannot be readily explained by either
mechanism I or II, and it is suggested that mechanism III is
operating. This latter mechanism involves a concerted ter-

Mechanism III

$$CF_3C\equiv CCF_3 \longrightarrow \underset{Et_2N}{\overset{CF_3}{>}}C\!\!=\!\!C\underset{CF_3}{\overset{H\text{-}NEt_2}{<}} \longrightarrow \underset{Et_2N}{\overset{CF_3}{>}}C\!\!=\!\!C\underset{CF_3}{\overset{H}{<}}$$

$$+ \qquad\qquad\qquad H \qquad\qquad\qquad +$$

$$2Et_2NH \qquad\qquad\qquad\qquad\qquad\qquad Et_2NH$$

molecular process such that there is no charge separation.
This mechanism should be dependent on the concentration of
amine and, indeed, dilution of the reactants in diethyl ether
led to a reduction in the amount of the _trans_ isomer formed.

5.D ELECTROCHEMICAL OXIDATION OF SOME SUSTITUTED FLUOROALKENES

I. Introduction

Electrochemical oxidation of ethylene occurs at a high
potential ($+2.90$V v. Ag/Ag$^+$) to give its radical cation.[130]
Substitution at the double bond by electron-donating groups
lowers the oxidation potential into a more accessible region
and also affects the stability of the radical cation.

Thus, the oxidation of alkenes completely substituted with amino groups results in the formation of stable radical cations and dications. However, when one of the ethylenic carbon atoms is unsubstituted, rapid dimerisation reactions occur. For example, tetrakis(N,N-dimethylamino)-ethylene (148) undergoes a two-stage oxidation at a dropping mercury electrode to produce, initially, the radical cation and then the dication.[131] In contrast, vinylidene-bis(N,N-dimethylamino)-(149) is oxidised to I,I,4,4-tetrakis(N,N-dimethylamino)-butadiene (150). It is interesting to note that a radical cation dimerisation mechanism is favoured for these dimerisation reactions.[132,133]

$$
\underset{(148)}{\overset{Me_2N}{\underset{Me_2N}{>}}C=C\overset{NMe_2}{\underset{NMe_2}{<}}} \xrightleftharpoons{-0.75} \overset{Me_2N}{\underset{Me_2N}{>}}\overset{+}{C}-\overset{\cdot}{C}\overset{NMe_2}{\underset{NMe_2}{<}} \xrightleftharpoons{-0.6IV} \text{Dication}
$$

$$
2\ \underset{(149)}{\overset{Me_2N}{\underset{Me_2N}{>}}C=C\overset{H}{\underset{H}{<}}} \xrightarrow{-2e^-} \underset{(150)}{\overset{Me_2N}{\underset{Me_2N}{>}}C=C\overset{H}{\underset{\underset{H}{>}C=C\overset{NMe_2}{\underset{NMe_2}{<}}}{}}} + 2H^+
$$
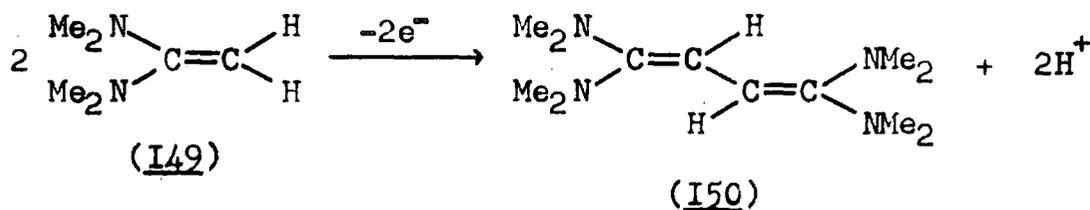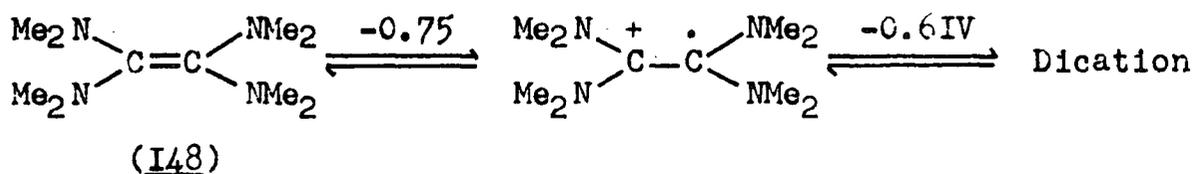
The ease of oxidation is primarily dependent on the number of amino groups substituted on the double bond. Beyond this, the extent of the π-system, the degree of alkyl or aryl substitution and steric interactions affect the oxidation potential. Table 5.6 presents some relevant information

obtained in an extensive study of amino-alkenes.[132] As expected, the oxidation potential increases with substitution of an ethylenic hydrogen by an electron-withdrawing substituent. However, the difference in lifetimes of the radical cations is quite dramatic. It is suggested by the authors that this is due to delocalisation of the positive charge over six atoms (i.e. including the chlorine atoms) and that the reactive site is hindered.

Table 5.6 [132]

Compound	E^{o}(a)	$t_{\frac{1}{2}}$(b)
Me_2N, Me_2N $C=C$ H, H	0.48	0.005
Me_2N, Me_2N $C=C$ Cl, Cl	0.52	250
Me_2N, Me_2N $C=C$ F, F	0.7	0.005

a - Formal potential, V v. S.C.E., see ref. II

b - Half-life of the radical cation in seconds.

The oxidation of vinyl ethers, similarly, yields coupled products, for example: [134]

$$EtOCH=CH_2 \xrightarrow[\text{C Anode}]{\text{MeOH-KOH}} \begin{array}{c} EtO \quad\quad\quad OEt \\ \diagdown \quad\quad\quad \diagup \\ CHCH_2CH_2CH \\ \diagup \quad\quad\quad \diagdown \\ MeO \quad\quad\quad OMe \end{array}$$
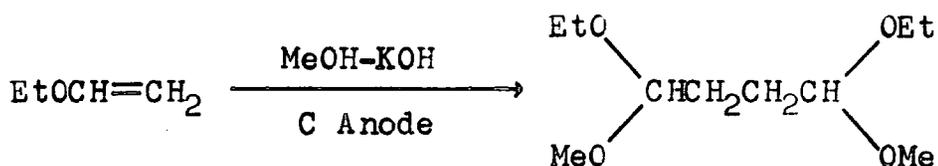
Oxidation of fluorinated alkenes, appropriately substituted, would be expected to yield similar products and, hence, provide a route to difunctionalised fluoroalkenes. Unfortunately, the choice of systems was limited, with the synthesis of suitable starting materials, as described earlier, proving difficult. Nevertheless, it is felt that this preliminary study introduces an interesting development.

2. Trans-2H-3-methoxy-I,I,I,4,4,4-hexafluorobut-2-ene

Linear sweep voltammetry, using the 'Electroscan' instrument, indicated that the title compound was not oxidised below the limiting potential of the solvent system. The trifluoromethyl group is a strongly electron-withdrawing substituent[95] and, presumably, the electron-donating ablility of the methoxy group is insufficient to compensate for this.

3. 2H-3-N,N-diethylamino-I,I,I,4,4,4-hexafluorobut-2-ene

The voltammogram of 2H-3-N,N-diethylamino-I,I,I,4,4,4-hexafluorobut-2-ene (139) consisted of a single wave which was irreversible at I00mV/sec. and had an $Ep\frac{1}{2}$ of +I.69V (v. S.C.E.), in acetonitrile, at 50mV/sec.. Comparison of this result with that for trans-2H-3-methoxy-I,I,I,4,4,4-hexafluorobut-2-ene, once again, illustrates the advantage of having an amino group as substituent.

Oxidation of (139) at +1.90V gave the dimer (151) with a current efficiency of 29%. Compound (151) was identified on the basis of a correct elemental analysis and a parent peak in the mass spectrum. ^{1}H n.m.r. spectroscopy clearly showed the absence of an olefinic proton, with only resonances attributable to the diethylamino groups being present. As previously mentioned, assignment of stereochemistry can be based on ^{19}F n.m.r. coupling constants, however, only broad resonances were observed in the CF_3 region (see Table 5.4) and no assignment was possible.

Oxidation of (139) will give its radical cation which can then dimerise, subsequent loss of two protons will give (151) as an isomeric mixture. 1,3-Butadienes generally oxidise

$$CF_3 \diagdown_{H} C = C \diagup^{CF_3}_{NEt_2} \xrightarrow{-e^-} CF_3 \diagdown_{H} \overset{\cdot}{C} - \overset{+}{C} \diagup^{CF_3}_{NEt_2}$$

(139)

Dimerisation
-2H+

$$Et_2N \diagdown_{CF_3} C = C \diagup^{CF_3} \diagdown_{CF_3} C = C \diagup^{CF_3}_{NEt_2}$$

(151)
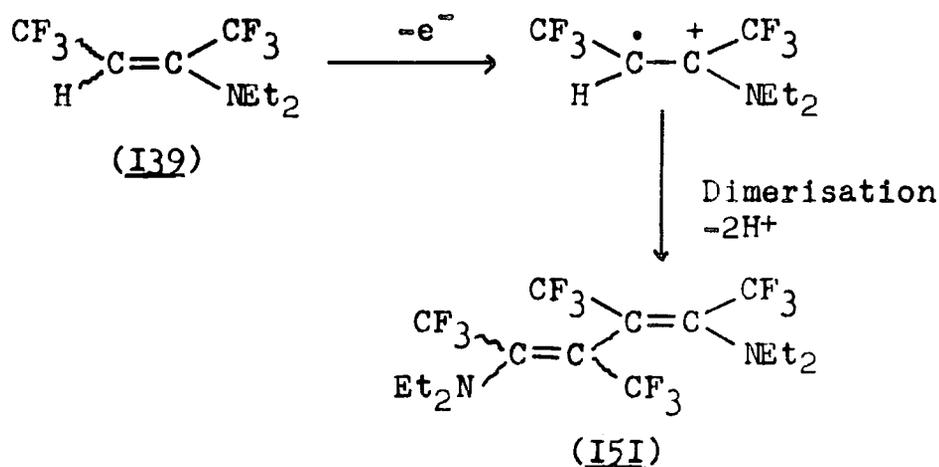
at a lower potential than an isolated double bond because of the extended conjugation and, thus, (151) may have been expected to oxidise at a lower potential than (139). However, (152) is believed to be non-planar and have essentially[117] unconjugated double bonds, and it is reasonable to suggest

that (<u>151</u>) is similarly non-planar; coupled with protonation

$$F_2C=C\begin{smallmatrix}CF_3\\\\C=CF_2\\CF_3\end{smallmatrix}$$

(<u>152</u>)

this would protect (<u>151</u>) from further oxidation.

4. <u>2H-3-N,N-dimethylamino-I,I,I,4,4,4-hexafluorobut-2-ene</u>

As expected, the voltammogram of 2H-3-N,N-dimethylamino-I,I,I,4,4,4-hexafluorobut-2-ene (<u>136</u>) was not very different to that of (<u>139</u>)with an Ep½ of +I.62V at 40mV/sec.. Preparative oxidation of (<u>136</u>) at +I.8V gave the expected dimer (<u>153</u>),

$$\begin{smallmatrix}CF_3\\H\end{smallmatrix}C=C\begin{smallmatrix}CF_3\\NMe_2\end{smallmatrix} \xrightarrow{-e^-} \begin{smallmatrix}CF_3\\H\end{smallmatrix}\overset{\cdot}{C}-\overset{+}{C}\begin{smallmatrix}CF_3\\NMe_2\end{smallmatrix}$$

(<u>136</u>)

Dimerisation
-2H⁺

$$\begin{smallmatrix}CF_3\\Me_2N\end{smallmatrix}C=C\begin{smallmatrix}CF_3\\\\C=C\\CF_3\end{smallmatrix}\begin{smallmatrix}CF_3\\NMe_2\end{smallmatrix}$$

(<u>153</u>)

and the comments applied to (<u>151</u>) will also be valid for (<u>153</u>). Identification of (<u>153</u>) followed from the absence of an olefinic proton in its [I]H n.m.r. spectrum and a parent peak in the mass spectrum; as with (<u>151</u>), no assignment of stereochemistry was possible.

5. <u>2-N,N-dimethylamino-I,I,I,3,4,4,4-heptafluorobut-2-ene</u>

Dimerisation of the radical cation of an amino-alkene can generally only occur if there is an un-substituted position on the double bond. It was of interest to determine the reaction pathway when these positions were blocked, and 2-N,N-dimethylamino-I,I,I,3,4,4,4-heptafluorobutene (<u>134-5</u>) presented an ideal example for comparison with (<u>136</u>). As the
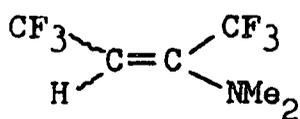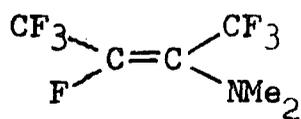
(<u>136</u>)   (<u>134-5</u>)

2-position is blocked, it was hoped that dimerisation would occur through the amino group, in a process analogous to that described on page 53.

Using the 'Electroscan' instrument, it was found that oxidation of (<u>134-5</u>) occurred at $Ep^{\frac{1}{2}}$ = +I.I5V at 40mV/sec.. This is surprisingly low (compare (<u>136</u>), +I.69V) and cannot be readily explained on the basis of the relative stabilities of $\overset{+}{C}$—F and $\overset{+}{C}$—H or $\overset{\cdot}{C}$—F and $\overset{\cdot}{C}$—H, as this would be observed for those compounds shown in Table 5.6 (page 96).

A preparative oxidation of (<u>134-5</u>), however, was unsuccessful and only a multi-component mixture was isolated. In view of this result an oxidation of (<u>140-I</u>) was not attempted.

CHAPTER 6

ELECTROCHEMICAL REDUCTION OF SOME PERFLUOROCYCLOALKENES

6.A INTRODUCTION

The reduction of a compound containing vicinal halogens normally leads to an increase in unsaturation. This is well illustrated, as mentioned in Chapter 2, by the synthesis of fluoroaromatic compounds from fluorinated cyclohexadienes.[62]

The reduction of three perfluorocycloalkenes (i.e. cyclohexene, cyclopentene, and cyclobutene) was investigated in an attempt to observe similar behaviour. Defluorination, a process analogous to the expected electrochemical reaction, of either perfluorocyclopentene or perfluorocyclobutene has not been performed and even if this did not occur, potentially interesting polymers may result.

Naturally, there would be the production of fluoride ion associated with the reduction and, hence, it would be expected that products from fluoride ion induced oligomerisations would be obtained. As oligomers were isolated, it would be appropriate to discuss briefly this type of reaction, using the relevant alkenes as examples.

6.B FLUORIDE ION INDUCED OLIGOMERISATIONS

I. Perfluorocyclohexene

Perfluorocyclohexene (154) is dimerised by fluoride ion in a polar aprotic solvent such as sulpholan at 150°C.[135] A trace of the defluorinated dimer (156) is also produced under these conditions, but the major product is the dimer (155).
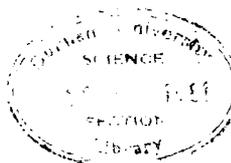
Only the <u>endo</u> isomer is obtained under equilibrium control, i.e. in the presence of fluoride ion, and the <u>exo</u> isomer has to be synthesised by an alternative route.[136]
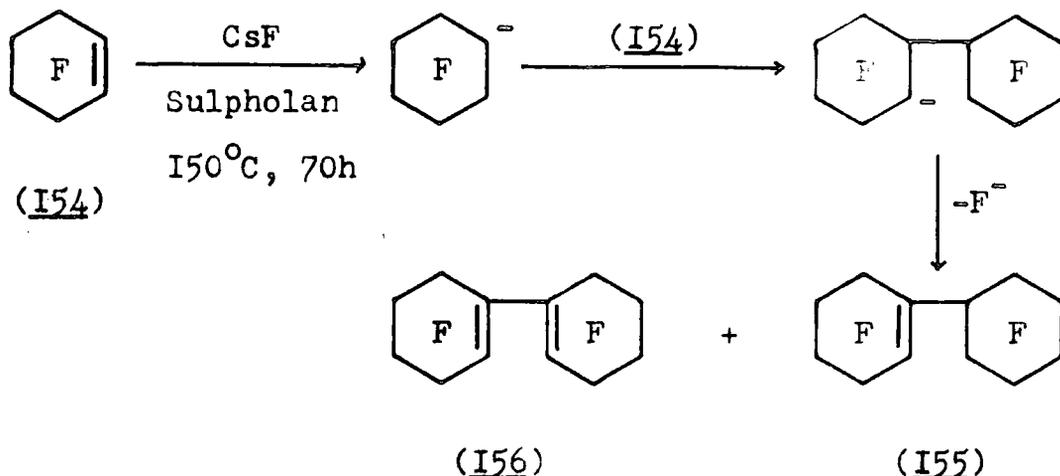
Three factors have to be considered when rationalising why only one isomer is produced under equilibrium control:

    a.   the presence of vinylic fluorine atoms

    b.   conformational interactions

    c.   angle strain

As mentioned before, it has been found that vinylic fluorine atoms raise the energy of the system through repulsions between the fluorine lone pairs and the π-system.[95] Conformational interactions between fluorine atoms are important,[137] with an unsaturated site in a five-membered ring decreasing eclipsing interactions while in a six-membered ring increasing them. Therefore, it is preferable to have two unsaturated sites in a six-membered ring. The importance of the relative angle strain between <u>exo</u> and <u>endo</u> isomers is difficult to

judge.[138] Thus, isomer (155) is preferred because it reduces eclipsing interactions.

Co-oligomerisations are also possible, as illustrated by the reaction of perfluorocyclohexene (154) and perfluoro-cyclopentene (157) with fluoride ion in N,N-dimethylformamide (D.M.F.).[139] Perfluoro-I-cyclohexylcyclopentene (158) is isolated together with the dimers of (154) and (157). Compound (158) clearly indicates the preference towards having no unsaturated sites in a six-membered ring.

(154)   (157)   (158)   +

(155)   (159)

2. Perfluorocyclopentene

The fluoride ion induced oligomerisation of perfluoro-cyclopentene (157) produces a single dimer but this time it is the exo isomer which is preferred.[135] Taking into account the factors mentioned above, it follows that the isolation of dimer (159) can be rationalised on the basis that there are no vinylic fluorine atoms and that, more importantly, eclipsing interactions are minimised.

(159)

6.C REDUCTION OF PERFLUOROCYCLOHEXENE

Perfluorocyclohexene (154) was reduced at -I.6V in D.M.F. on a mercury cathode. Passage of enough charge to perform a two-electron reduction on I.Ig of (154) gave 0.55g of a volatile mixture containing:

(155)   (156)
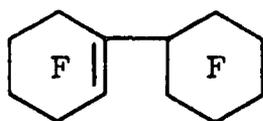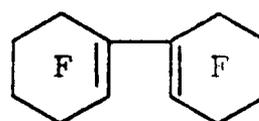
98%   I.8%

Both these products can be accounted for by the fluoride ion reaction described in section 6.B.I.; nevertheless, they are produced under remarkably mild conditions when compared to the conditions required for the CsF induced reaction. Compound (156) could also be formed electrochemically by dimerisation of the radical (160) and a fluoride ion induced rearrangement of (161), as shown in the following scheme.

(154)　　　　　　　　(160)　　　　　　　(161)

(156)
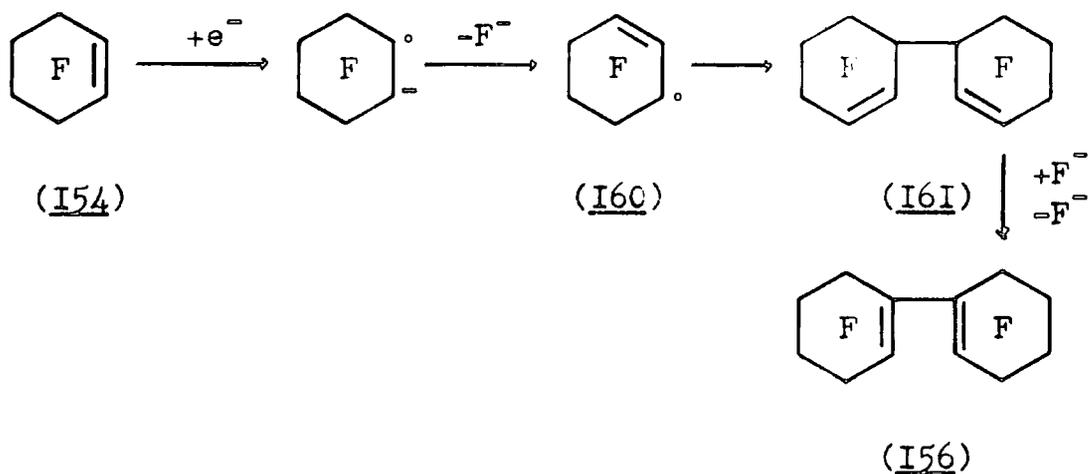
The involatile residue was shown by g.l.c. to be a
several component mixture. Its i.r. spectrum contained C—H
stretching vibrations and an absorption similar to the C=O
frequency in D.M.F., although none was present by g.l.c..
Fluorine was shown to be present by n.m.r. spectroscopy, with
shifts similar to those expected for $-CF_2-$ groups being
observed. Thus, it would appear that the solvent has become
incorporated into the electrochemical product, in agreement
with similar observations made in the reduction of some acyclic
perfluoroalkenes.[91]

By comparison with previous work, the following reaction
scheme appeared possible.[62]

(154)　　　　　　(162)　　　　　　(160)　　　　　(163)

(164)
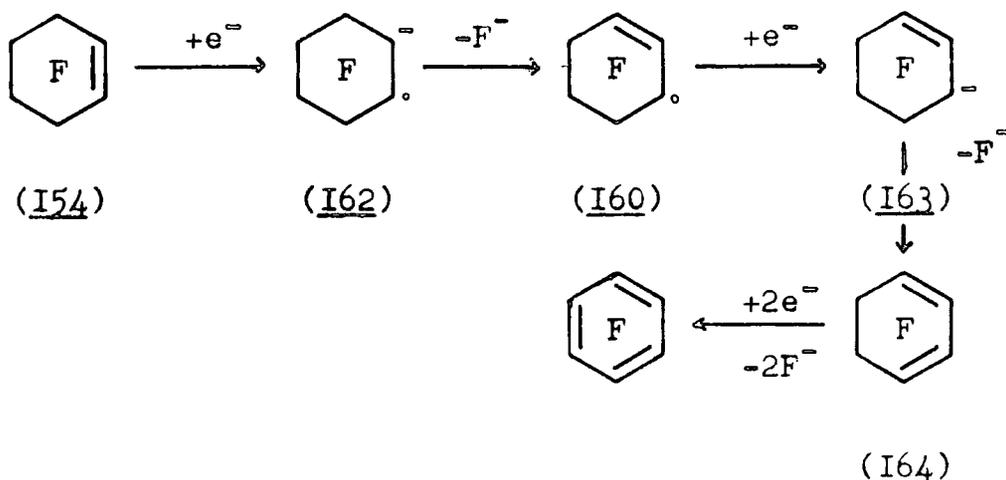
As no hexafluorobenzene was isolated, it seems reasonable to suggest that reduction to perfluorocyclohexa-I,3-diene (**I64**) did not occur. Fluoride ion reactions usually occur in D.M.F. without any incorporation of the solvent, thus discounting any reaction between the anion (**I63**) and the solvent. As no hydrogen substitution occurs in the reduction of (**I64**) in a protic medium, it appears unlikely that radical (**I60**) is involved. Thus, it must be the radical anion (**I62**) which is attacking the solvent, which implies that the loss of fluoride ion to give (**I60**) is a slow step. This is in agreement with similar work which indicates that reduction, followed by loss of fluoride ion, is rate-determining (see page 23).[62]

A mechanism has been proposed to account for the reduction of organic halides in D.M.F. which involves initial attack on the solvent to give a complex, which is then reduced.[I40] Although this hypothesis was found interesting, it has received no support, however, it does present a mechanism for solvent incorporation.

$$RX \ + \ H-\underset{\underset{O}{\|}}{C}-N(CH_3)_2 \longrightarrow \left[H\overset{\overset{OR}{|}}{C} = \underset{+}{N}(CH_3)_2 \right] X^-$$
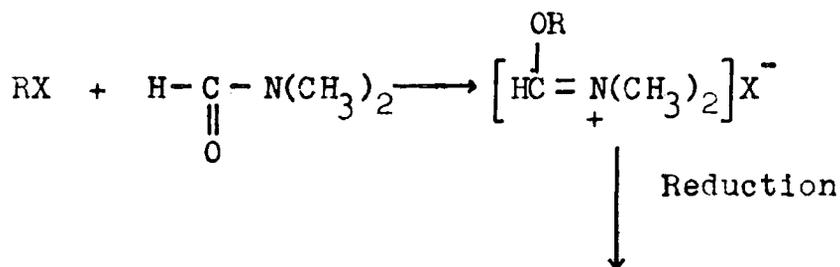
↓ Reduction

6.D REDUCTION OF PERFLUOROCYCLOPENTENE

I. Electrochemical Reduction in D.M.F.

a. Mercury Cathode

When perfluorocyclopentene (157) was reduced at -I.3V
on a mercury cathode in D.M.F., with tetraethylammonium
bromide as supporting electrolyte, a dark blue film formed
on the electrode surface. This film gradually thickened,
causing the current to become erratic and foulling both the
stirrer and the electrode surface. Towards the end of the
electrolysis the bulk catholyte was also blue and this,
presumably,was caused by fragments from the electrode covering.

A cap of material was removed from the electrode surface
and dried to leave a black fibrous solid which was insoluble
in common organic solvents. Unfortunately, the physical nature
of the material made it very difficult to obtain an i.r.
spectrum and the spectra obtained were broad and indefinable,
e.g. we were not able, with certainty, to determine the absence
of $C=0$. This product will be discussed in more detail in
section 6.D.I.c..

Extraction of the catholyte yielded a viscous residue
which had ^{19}F n.m.r. signals in the $-CF_2-$ region, and it is
possible that this represents a low molecular weight version
of the black solid. No oligomers were isolated in this reaction
but a preliminary experiment, under similar conditions, a
small quantity of (159) was detected by mass spectroscopy-g.l.c..
This suggests that oligomer formation may be dependent on the

electrode coating. Reduction of (I57) will occur at the
electrode surface such that any fluoride ion would, be trapped
by the surface coating and, thus, would be unable to promote
oligomerisation.

b. **Platinum Cathode**

Reduction of perfluorocyclopentene (I57) at -I.5V at a
platinum cathode in D.M.F. containing tetraethylammonium
fluoroborate (T.E.A.F.) gave a similar solid to that described
in section 6.D.I.a.. Thus, the formation of this solid is
independent of bromide ion or interaction with mercury. Its
formation is, however, dependent on electron transfer, as no
increase in the surface coating was noted when the current
was initially switched on for only a few seconds. The electrolysis
was continued until the platinum cathode was completely
covered with material and, typically, the current had dropped
from I20 to I8mA. In order to continue with the electrolysis
it was necessary for an incision to made into the coating
which could then be peeled off the electrode. At the end of
the electrolysis the solid samples were dried under vacuum
to leave a hard black fibrous solid. As in the other experi-
ments described,unidentifiable oils were also produced.

c. **Structure and Composition of the Solid**

It seems reasonable to suggest that this solid, which is
formed in the reduction of perfluorocyclopentene, is polymeric
for a number of reasons:

i. insoluble in common solvents,

ii. involatile, hence no mass spectrum was possible,

iii. its growth, especially on the platinum cathode.

As it is black, it must be highly conjugated and hence a large amount of defluorination (i.e. a low fluorine analysis compared to (157)) would be expected. The analysis figures obtained on various samples are given in Table 6.I; however, they do not add up to 100%. Only some of the deficiency could be made up by oxygen 'coming from the solvent'; since the N:O ratio in D.M.F. is only 0.9, only 2-3% can be attributed to oxygen. Therefore, there must be incomplete decomposition during the fusion with potassium (i.e. in the fluorine analysis) which is consistent with a very stable structure. Even assuming that the deficiency is made up of fluorine, the subsequent percentage leads to a much lower value than in perfluorocyclopentene (F-71.7%).

Table 6.I Elemental Analyses on the Solid

C	H	N	F
42.82	2.00	2.14	44.11
42.86	5.04	3.03	40.55
44.31	2.46	2.05	-
31.68	2.93	2.82	-

There are numerous mechanistic possibilities to account

for the formation of a polymer in the reduction of (157), but

the requirement that it has to be highly conjugated is a

limiting factor. The following scheme outlines the reaction

pathway which was expected:

(157)

(165)
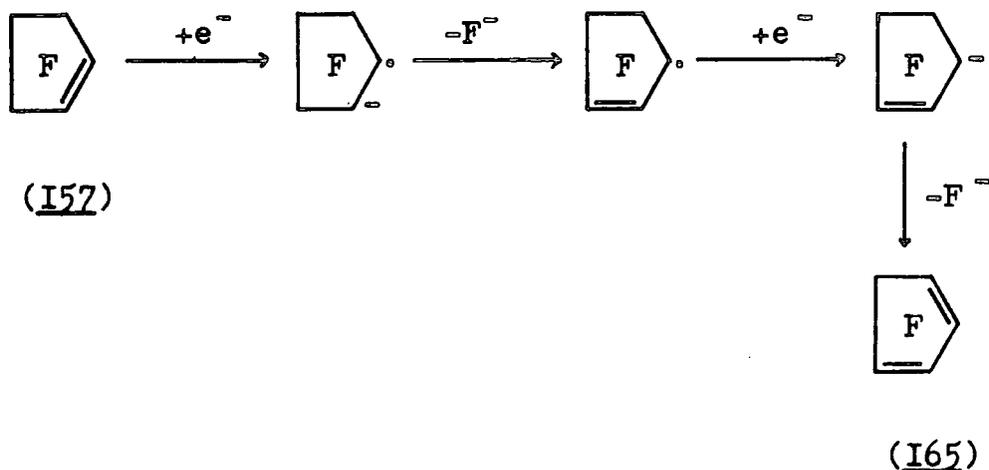
Subsequent reduction of (165) would lead to a radical anion

or anion which may then polymerise by attack either on (157)

or (165). Dimerisation of (165) would be a competing pathway [142]

but it is not obvious how further reduction of the Diels-Alder

adduct (166) would yield a conjugated polymer. A possible

(165) (166)
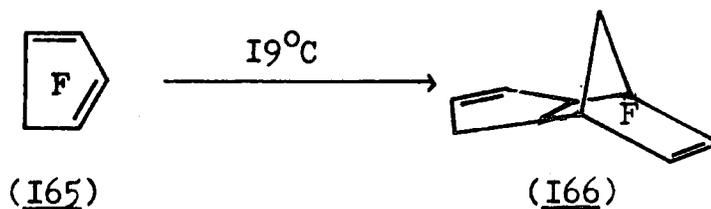
mechanism is outlined in the following scheme for polymer

formation occurring via reduction of (165):
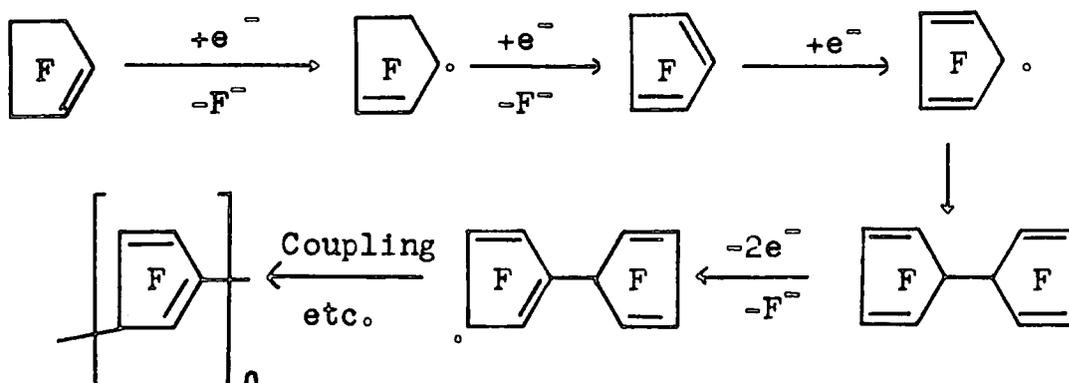
The analysis of the resultant polymer is C, 44% and F, 56%; certainly the carbon figure is in the right region.

Well investigated model systems are lacking, although the reduction of perchlorocyclopentene (167) has been briefly investigated.[141] The authors conclude that the mechanism is as follows:

(168)
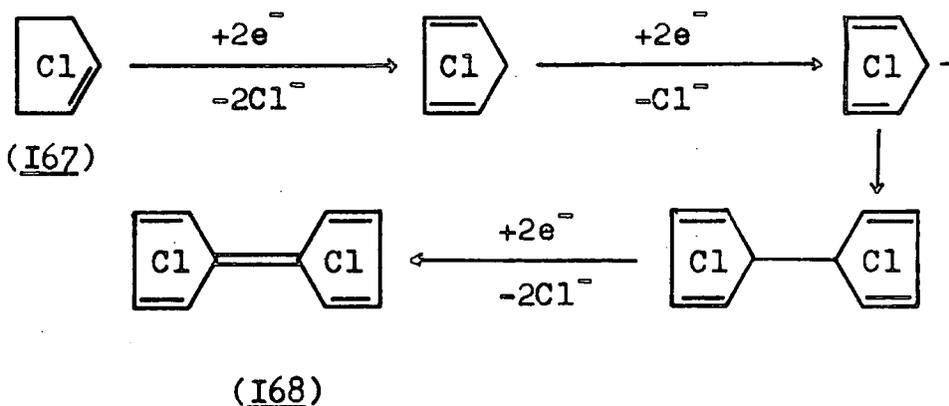
It is natural to draw comparisons between the reduction of (167) and (157), however, the evidence for the formation of (168) is not particularly definite and it should be more readily reduced than the starting material. The analogous fluorinated compound to (168) is claimed to be formed in the pyrolysis of pentachloropentafluorocyclopentane over mild steel at about 430°C.[143]

In the discussion above, it was concluded that the solid formed in the reduction of (157) is a highly conjugated system. On standing, some of the samples became coated with a white powder, suggesting aerial oxidation or hydrolysis and, hence, a few reactions were attempted. No change occurred when a sample was placed in an atmosphere of wet or dry oxygen, and addition to bromine and chlorine in carbon tetrachloride were similarly unsuccessful. A sample was added to liquid chlorine and allowed to stand by a window for a few weeks but there was no visible change. On allowing the chlorine to evaporate, a red-brown solid was isolated which we were unable to identify. Its mass spectrum was clearly not of a perfluorocarbon but its i.r. spectrum showed no characteristic C—Cl absorptions.

d.   **Trapping Experiments**

The aim of these experiments was to, hopefully, modify, the reaction pathway of the reduction of (157).

i.   **Perfluorocyclohexene**

If the polymer was formed from an anionic intermediate it would be expected that the reaction would be modified by the presence of perfluorocyclohexene.

Reduction of perfluorocyclopentene (157) in the presence of perfluorocyclohexene (154) at -1.5V produced no solid. Thus, the reaction has been substantially modified by the addition of an anionic trap; however, apart from the fluoride ion reaction products, no other product was identified.

It is unfortunate that no direct electrochemical product could be identified as this means that the function of (154) can only be supposed. The reaction could be dependent on the relative rate of defluorination (a process analogous to the electrochemistry) such that a reduced form of (157) reduces (154). Another possibility is that fluoride ion is intimately involved in the polymerisation process and the addition of (154) aids its removal.

One of the remarkable facts about this reaction is the ease with which the oligomers of (154) and (157) are produced, thus illustrating the potential utility of electrochemical generation of fluoride ion as a synthetic tool. All three possible dimers were isolated.

(154)   (157)   (158)

(155)   (159)
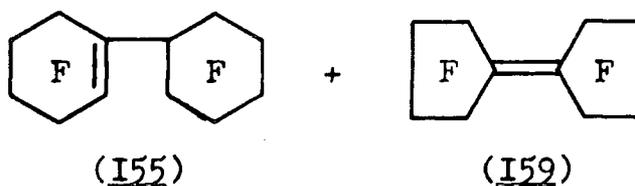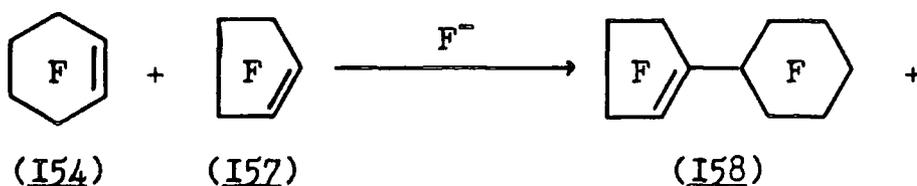
ii. <u>Cyclohexene</u>

The other possible reactive intermediate in the reduction of perfluorocyclopentene (157) is a radical and we reasoned that cyclohexene may act as a trap for these radicals, thus modifying the reaction.
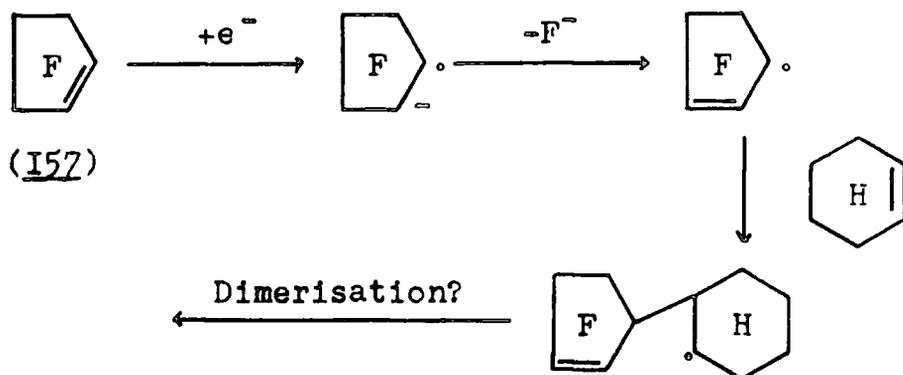
On reduction of perfluorocyclopentene (157) in the presence of cyclohexene a black solid was produced and, therefore, the process has not been substantially modified. In agreement with this the recovery of cyclohexene was high (i.e. 85%). Enough charge was passed to perform a two-electron reduction on 0.7Ig of (157), however, 0.94g of this black solid was isolated, clearly indicating that it is not a simple electrochemical process.

As before, an oil was also isolated which we were unable to identify.

iii. Chloropentafluorobenzene

As the reduction of perfluorocyclopentene (157) was modified by the addition of anion trap (i.e. perfluorocyclohexene) it was hoped that addition of a system readily attacked by nucleophiles, but not available for fluoride ion induced oligomerisations would be more useful. For example, a process such as that illustrated could be envisaged:

(157)
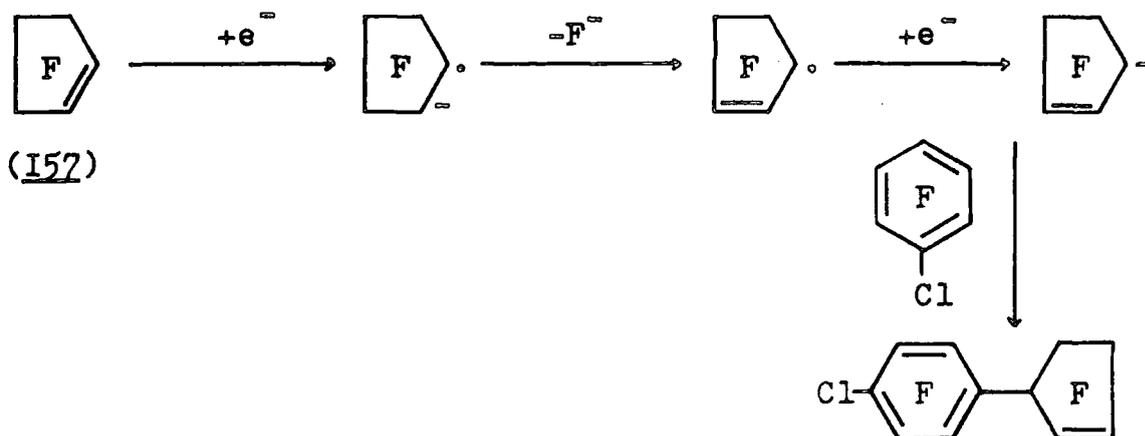
However, reduction of perfluorocyclopentene (157) in the presence of chloropentafluorobenzene gave this black solid again and it is considered that there was no incorporation of chloropentafluorobenzene as its recovery was high (93%). It is interesting to note that on this occasion the solid was green, whereas in the other experiments it was blue, however, on removing it from the catholyte and drying it went black.

In conclusion, therefore, the reaction pathway was not apparently altered by the addition of an anion trap such as chloropentafluorobenzene.

2. Electrochemical Reduction in Acetonitrile

In the previous discussions it was suggested that attack on the solvent occurs in the reduction of (157) and, therefore, it was decided to carry out the reaction in a different solvent.

The limiting potential of acetonitrile, with a tetraalkyl ammonium salt as supporting electrolyte, is low and, therefore, lithium perchlorate was used (limiting potential -3.0V).[2]

Although the electrode potential was increased to the break-down point of the solvent system, no reduction of (157) was detected. Voltammetric investigations using acetonitrile-Et_4N^+, acetonitrile-Li^+, D.M.F.-Et_4N^+, and D.M.F.-Li^+ as solvent systems concluded that the reduction of (157) to this black solid only occurred in D.M.F.-Et_4N^+. This behaviour is not understood and further work would be of value.

3. **Chemical Reduction**

Electrochemical reduction involves electron transfer and it is possible to achieve this chemically; hence, it should be possible to reduce perfluorocyclopentene chemically and it was of interest to determine whether chemical electron transfer gave the same product as electrochemical electron transfer.

Sodium in hexamethyl phosphoramide (H.M.P.A.) produces a blue solution of 'solvated electrons' and would be expected to reduce (157). This reaction is apparently the first reported investigation of the reaction of a fluorocarbon with the 'solvated electron' and as such was only preliminary in nature.

On allowing perfluorocyclopentene into the reaction vessel, the blue colour was immediately replaced by pale yellow. Over a period of a few hours, the solution darkened and on work-up a quantity of hard black chips was isolated. As with the electrochemical product, this solid was involatile (thus no mass spectrum was obtainable) and it was insoluble in the common organic solvents. Elemental analysis was un-

helpful as incomplete combustion was obviously occurring.

4. **Conclusions**

The electrochemical reduction of perfluorocyclopentene
is very dependent on the solvent and supporting electrolyte.
On reduction, a black solid is produced which is believed
to be a highly-conjugated non-conducting stable polymer. It
is interesting to note that perfluorocyclopentene has not
been homopolymerised, although copolymerisation readily
occurs.[144] The mechanism of its formation is not understood
and, of the trapping experiments, only the addition of
perfluorocyclohexene had any major effect; an investigation
of the reduction of perfluorocyclopentadiene would be useful
in elucidating the mechanism.

6.E **REDUCTION OF PERFLUOROCYCLOBUTENE**

The experimental technique used here was crude and, hence,
no major conclusions can be made. Nevertheless, a small
quantity of a black solid was produced and it is interesting
to note that perfluorocyclobutene, as with (157),[144b] is very
stable towards defluorination over, for example, platinum.[144a]

CHAPTER 7

REDUCTION OF 2,3-DICHLORO-I,I,I,4,4,4-HEXAFLUOROBUT-2-ENE

AND RELATED STUDIES

7.A INTRODUCTION

Electrochemical reduction of vicinal dihalides can lead
to an increase in unsaturation such that an acetylenic
compound is obtained (for example, see ref. 44). However, as
described in Chapter 6, the reduction of perfluoroalkenes
is complicated by the production of fluoride ion and the
reactions induced by this ion. It was decided to investigate
the reduction of a chlorofluoroalkene such that the fission
of a carbon-chlorine bond occurred with the concurrent
formation of the relatively unreactive chloride ion. 2,3-Di-
chloro-I,I,I,4,4,4-hexafluorobut-2-ene (169) is used as a
precursor in the synthesis of hexafluorobut-2-yne (143). [145]
Dechlorination of (169) by zinc, in a suitable solvent, yields
(143) in a process analogous to the expected reduction
pathway and, thus, (169) would appear to be an ideal compound

$$CF_3ClC=CClCF_3 \xrightarrow{Zn} CF_3C\equiv CCF_3$$
$$(169) \qquad\qquad (143)$$
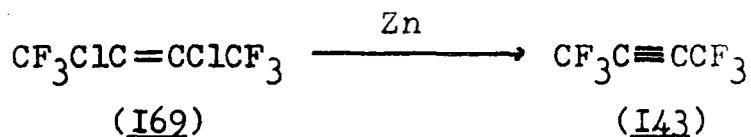
for reduction to a synthetically useful compound. In connection
with this work, the reduction of (143) was also investigated.

7.B ELECTROCHEMICAL REDUCTION OF 2,3-DICHLORO-I,I,I,4,4,4-HEXAFLUOROBUT-2-ENE

I. Introduction

I,2-Dichloroalkenes lose both halogens in a single two-

electron step to give acetylenes which are reduced at a more
negative potential. The _trans_-dihalide is generally reduced
at a less negative potential than the _cis_-isomer, with the
difference being attributed to steric hindrance affecting
the approach of the molecule to the electrode surface and
adsorption onto the electrode.[146,147]

2.   Reduction at -I.20V

2,3-Dichloro-I,I,I,4,4,4-hexafluorobut-2-ene (_169_) was
reduced at -I.20V on a mercury cathode in N,N-dimethylformamide
(D.M.F.) and tetraethylammonium bromide (T.E.A.B.). No gas
evolution was observed during the electrolysis, but it was
noticed that a solid was deposited on the floor of the cell.
The volatile material which was isolated contained, principally,
(_169_) but mass spectroscopy-g.l.c. also detected a minor
component which was deduced to be (_170_), on the basis of its
high mass and breakdown pattern.

$$CF_3 \diagdown C=C \diagup CF_3$$
$$Cl \diagup \qquad \diagdown C=C \diagup CF_3$$
$$CF_3 \diagup \qquad \diagdown Cl$$

(_170_)
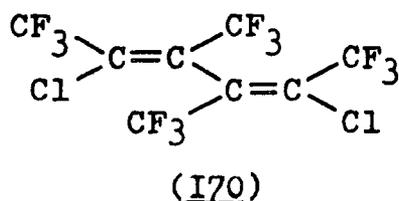
The involatile material consisted of a small quantity
of tar together with a pale yellow solid. The i.r. spectrum
of this solid was identical to that of poly(hexafluorobut-2-yne)
and elemental analysis confirmed the absence of chlorine,
with the low fluorine analysis being due to incomplete fusion.

There are two possible mechanisms for the formation of
the polymer in what is the first reported electro-initiated
polymerisation to give a fluorinated polymer. In mechanism

I, (169) is reduced to a carbanion (171) which can then lose chloride ion to give hexafluorobut-2-yne (143). Compound (143)

Mechanism I

$$CF_3ClC=CClCF_3 \xrightarrow[-Cl^-]{+2e^-} CF_3\overset{-}{C}=CClCF_3 \xrightarrow{-Cl^-} CF_3C\equiv CCF_3$$

(169)   (171)   (143)

$$CF_3C\equiv CCF_3 \xrightarrow{Cl^- \text{ or } Br^-} \left(\begin{matrix} CF_3 \\ | \\ C=C \\ | \\ CF_3 \end{matrix}\right)_n$$

(143) $+e^-$

$$CF_3\overset{-}{C}=\overset{\circ}{C}CF_3$$

(172)
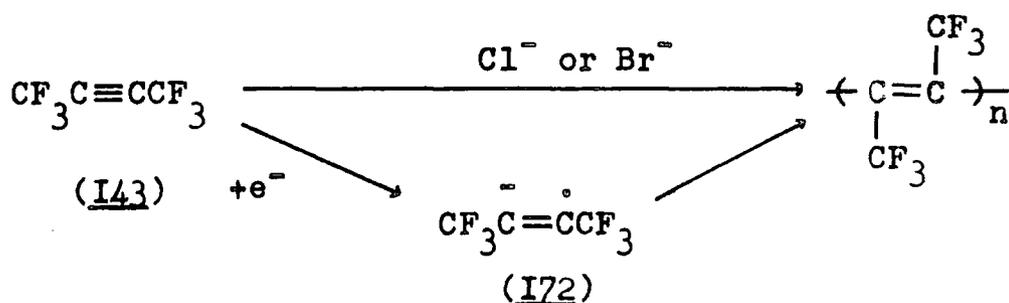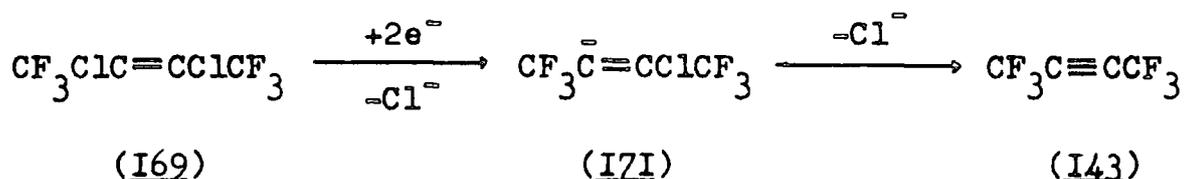
can polymerise by nucleophilic attack of either chloride ion, which is formed in the reduction, or bromide ion, which is present as the electrolyte, in a process analogous to the fluoride ion induced polymerisation.[148] An alternative pathway is reduction of (143) to its radical anion (172), which can either polymerise anionically or by a free radical mechanism.

Mechanism II requires the formation of the radical anion of (169) which can then dimerise to form a dianion (173). Loss of chloride ions gives (170) and further reduction of this leads to a step growth formation of a polymer. Detection of (170) would appear to favour this latter mechanism; however, even with a large n, the chlorine percentage is significant.

Mechanism II

$$CF_3ClC = CClCF_3 \xrightarrow{+e^-} CF_3Cl\overset{-}{C}-\overset{\circ}{C}ClCF_3$$

(**169**)

Dimerisation

$$CF_3, \overset{-}{C}-\overset{Cl}{\underset{CF_3}{C}}-\overset{CF_3}{\underset{Cl}{C}}-\overset{-}{\underset{Cl}{C}}$$

(**173**)

$-2Cl^-$

$$CF_3, C=C-\overset{CF_3}{\underset{CF_3}{C}}=C-\overset{CF_3}{\underset{Cl}{}}$$

(**170**)

etc.

$$CF_3, C=C-\overset{CF_3}{}C=C-\overset{CF_3}{}C=C-\overset{CF_3}{\underset{Cl}{}}$$
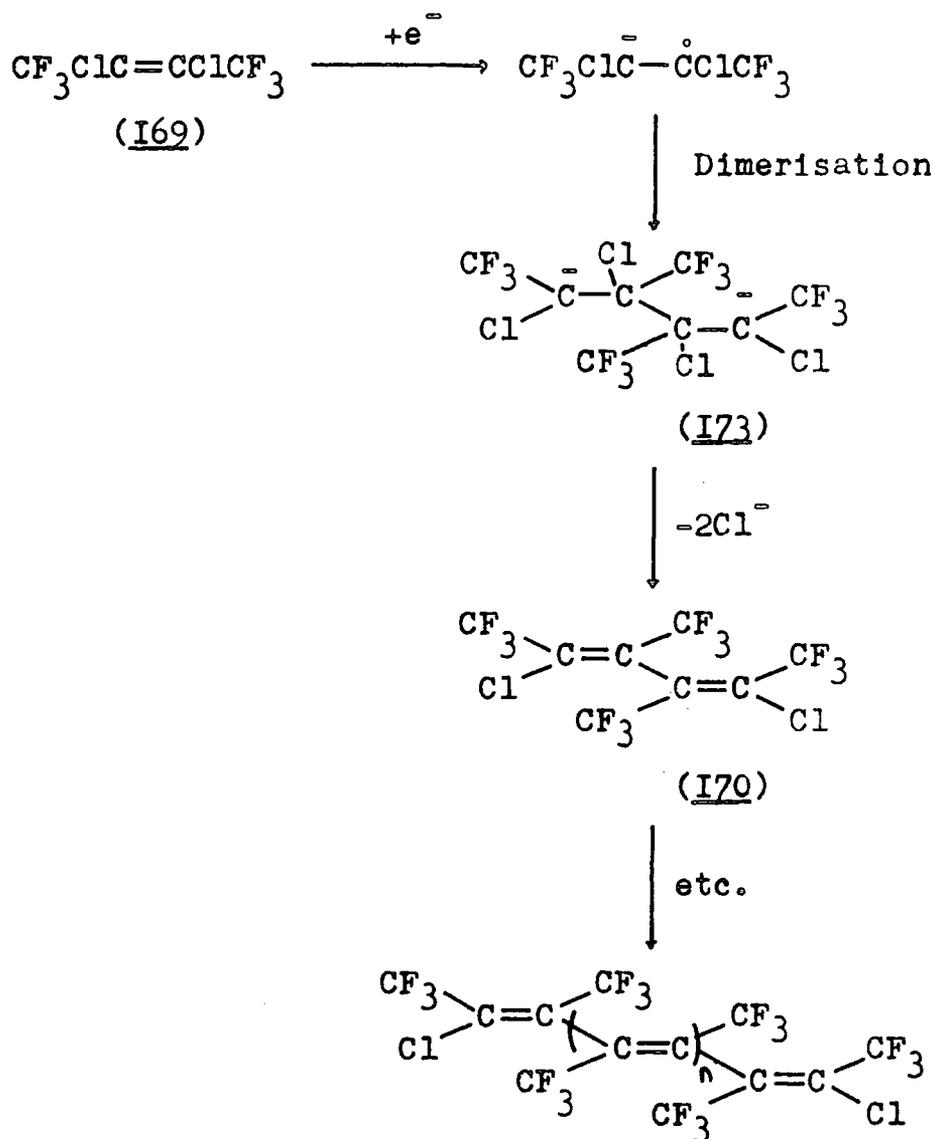
It seems likely, therefore, that (**170**) is produced via mechanism II and that polymerisation occurs by mechanism I.

It was possible that bromide ion itself may initiate the polymerisation of (**169**), but a control experiment gave no polymeric products and the results presented in section 7.B.3. indicate that bromide ion is not involved, at least initially.

3. **Reduction at -1.0V**

2,3-Dichloro-1,1,1,4,4,4-hexafluorobut-2-ene (169) was reduced at -1.0V and with tetraethylammonium fluoroborate as supporting electrolyte. As described in 7.B.2., a yellow-white solid was isolated whose i.r. spectrum was identical with that of poly(hexafluorobut-2-yne). Elemental analysis again indicated the absence of chlorine in this solid.

Thus, the formation of the polymer is independent of the supporting electrolyte and the only difference between this reaction and that described in 7.B.2 is the absence of (170). It is impossible, solely on the basis of these experiments, to determine whether this is significant or not.

7.C **REDUCTION OF HEXAFLUOROBUT-2-YNE**

I. **Introduction**

Electrochemical reduction of acetylenes is confined to activated compounds, that is, those containing double bonds or electron-withdrawing substituents conjugated with the triple bond.[149] Thus, in principle, hexafluorobut-2-yne (143) should be readily reduced as it is an electron-deficient acetylene, with the CF_3 groups being able to stabilise any carbanionic centre. Initial one-electron transfer would

$$CF_3C\equiv CCF_3 \xrightarrow{+e^-} CF_3\overset{\bullet}{C}\!\!=\!\!\overset{-}{C}CF_3 \longrightarrow \text{Polymerisation}$$
$$(143)$$
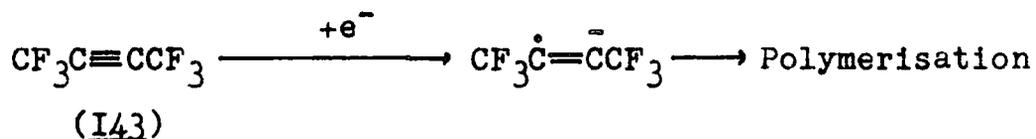
yield a radical anion which could then polymerise either by an anionic or radical mechanism.

2. Attempted Electrochemical Reduction

Hexafluorobut-2-yne (I43) is readily attacked by nucleophiles and, therefore, the choice of supporting electrolyte is critical. A control experiment was performed by stirring T.E.A.B. in D.M.F. under an atmosphere of (I43). A rapid reaction occurred to give poly(hexafluorobut-2-yne), which was identified by i.r. spectroscopy, and the reaction is, presumably, aided by the presence of a large cation causing a reduction in ion-pairing in solution.

Reduction of (I43) in acetonitrile-lithium perchlorate was attempted but no reduction occurred, even at the breakdown potential of the system. The practical method adopted in this reaction, although crude, gave a surprisingly good recovery of (I43). In view of the comments made in Chapter 6, it is possible that it is the solvent system which is inapplicable and that hexafluorobut-2-yne could be reduced in a different system.

3. Solvated Electron Reduction

a. Introduction

The reduction of acetylenes by chemical methods (e.g. sodium-hexamethyl phosphoramide (H.M.P.A.)) has been considered to go via a radical anion, followed by a dianion.[150] However, later work concluded that this hypothesis was incorrect.[151] Conjugated acetylenes (with a carbonyl or aryl group) can be reduced electrochemically to the radical anion in aprotic media at -2 to -2.9V. Non-conjugated acetylenes

(i.e. when R = H or alkyl) are normally considered to be
electrochemically inert by a process which involves electron
transfer to form a radical anion.[152] The reduction potential
of sodium-H.M.P.A. is -2.96V[153] and is, therefore, barely
adequate to produce a radical anion let alone a dianion.
Therefore, to explain the process of reduction by chemical
means, an organometallic route has been invoked where there
is the simultaneous addition of an electron and Na^+ (Scheme
7.I). A similar intermediate to (<u>I74</u>) has been proposed in

<u>Scheme 7.I</u>
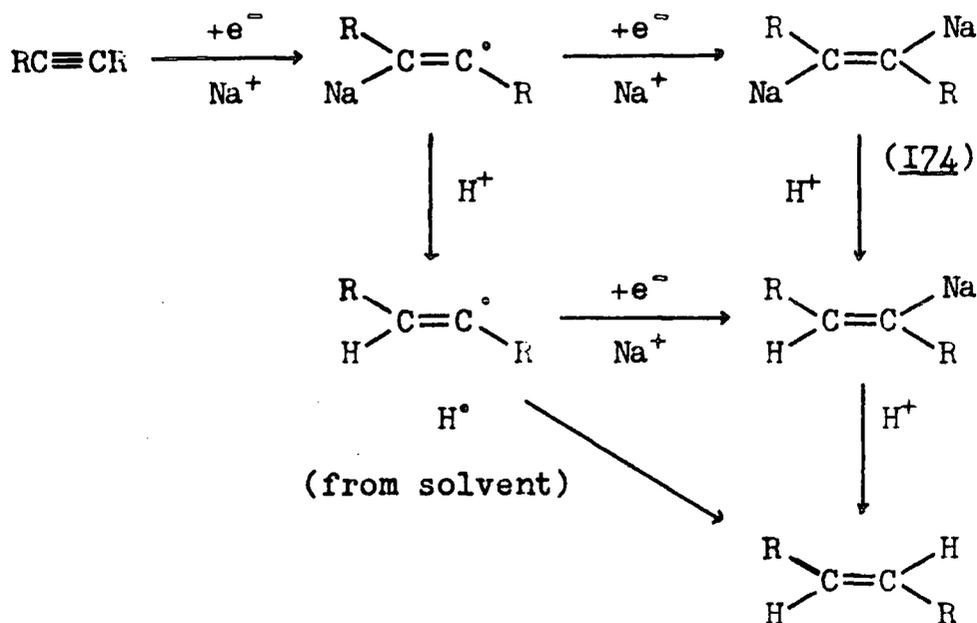
the reaction of diphenylacetylene with alkali metals at low
temperature, with the <u>trans</u> configuration minimising the
electrostatic repulsion between C—Na dipoles.[154,155]

In view of the failure to reduce hexafluorobut-2-yne
electrochemically, it was of interest to determine whether

it could be carried out using the solvated electron.

b. **Reduction of Hexafluorobut-2-yne**

Sodium was partially dissolved in degassed H.M.P.A. to give a blue solution, and then small quantities of hexafluoro-but-2-yne (143) were allowed in. The blue colour was immediately replaced by an orange colour, with undissolved black sodium still present. On the surface of the liquid a transparent film had formed and on further addition of (143), and swirling the flask, this material collected into a bright red ball. Presumably, the colour was due to charge transfer between the solvent and the polymer. ^{31}P n.m.r. spectroscopy only detected H.M.P.A. in this solid and this indicated that there was no chemical incorporation of the solvent in the polymer (i.e. it was only physically bound). Addition of water to the solid, followed by filtration, gave a white fibrous solid which was identified as poly(hexafluorobut-2-yne) on the basis of correct elemental analyses and its i.r. spectrum.

Assuming that the mechanism outlined in Scheme 7.I is occurring, then the initially-formed radical (175) will readily polymerise by a radical pathway. Radical polymerisation of (143) initiated by γ-rays is a very efficient route to poly-(hexafluorobut-2-yne).[156]

$$CF_3C\equiv CCF_3 \xrightarrow[\text{Na}^+]{+e^-} \underset{\text{Na}}{\overset{CF_3}{\diagup}}C=C\overset{\circ}{\underset{CF_3}{\diagdown}} \quad (\underline{175})$$

(143)

↓ (143)

$$\underset{\text{Na}}{\overset{CF_3}{\diagup}}C=C\underset{CF_3}{\overset{CF_3}{\diagdown}}C=C\overset{\circ}{\underset{CF_3}{\diagdown}}$$

↓ etc.

$$-\!\!\!\left(C_4F_6\right)\!\!\overline{_n}$$
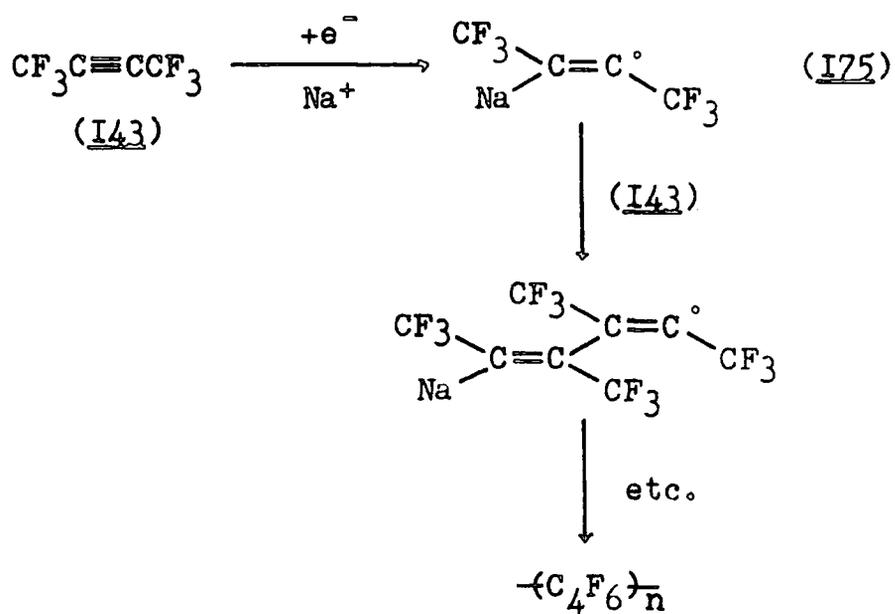
To confirm that the formation of the polymer was not due to a reaction with the solvent, a control experiment was performed, however, no reaction occurred.

EXPERIMENTAL

Instrumentation

Infra-red spectra were recorded on Perkin-Elmer Model 457 or 577 'Grating Infra-red Spectrophotometers'. Solid samples were pressed into homogeneous thin discs with potassium bromide. Liquids were recorded as contact films between potassium bromide plates. Gaseous samples were recorded in gas cells with potassium bromide windows.

Raman spectra were recorded using a Cary 82 Laser Raman Spectrophotometer with either a Spectra-Physics Model I64 argon-ion laser at 5I4.5nm (green) or a Spectra-Physics Model I25 helium-neon laser at 632.8nm (red).

Ultra-violet spectra were recorded using a Unicam SP 8000 Spectrophotometer.

Mass spectra were recorded on an A.E.I. M.S. 9 Spectrometer or on a V.G. Micromass I2B Spectrometer fitted with a Pye I04 gas chromatograph. Both spectrometers were linked with a V.G. Datasystem 2000.

Proton and fluorine n.m.r. spectra were recorded on either a Varian A56/60D spectrometer or, latterly, on a Varian EM360L, operating at 60.0 and 56.4 MHz respectively. Chemical shifts are quoted relative to external TMS or $CFCl_3$ unless otherwise stated. The standard probe temperature of the A56/60D was $40^{\circ}C$ and of the EM360L was $20^{\circ}C$. The phosphorous n.m.r. spectra were recorded on a Fourier transform spectrometer operating at 24.29 MHz. Chemical shifts are quoted relative to external H_3PO_4.[157]

Gas liquid chromatographic analyses were carried out on a Varian Aerograph Model 920 or Pye IO4 Gas Chromatograph using columns packed with 30% silicone gum rubber SE-30 on chromosorb P (column O) or 20% diisodecylphthalate on chromosorb P (column A). Preparative scale gas liquid chromatography was performed on a Varian Aerograph Model 920 using either column O or A.

Carbon, hydrogen, and nitrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analyses for halogens were performed by the literature method.[158]

Melting points and boiling points were determined at atmospheric pressure and are uncorrected. Boiling points were determined by the Siwoloboff method.

CHAPTER 8

EXPERIMENTAL FOR CHAPTER 3

8.A GENERAL

I. Reagents

Methoxy-derivatives were prepared by nucleophilic substitution reactions on the corresponding polyfluoro-benzenes using published routes unless otherwise stated.[159-165]

Acetonitrile was purified using a published route [166] and stored under an atmosphere of dry nitrogen. 'Spectrosol' acetonitrile was occasionally used in some of the voltammetric experiments without further purification. Trifluoroacetic acid was purified by fractional distillation in an atmosphere of dry nitrogen.

Tetraethylammonium fluoroborate (T.E.A.F.) was prepared by mixing hot, saturated aqueous solutions of tetraethylammonium bromide and sodium fluoroborate and allowing to cool. The solid was filtered off and recrystallised from aqueous methanol, until no bromide could be detected using silver nitrate solution. It was dried by alternatively heating to 150°C under vacuum and crushing to a fine powder.

Thin layer and column chromatography were carried out using either silica or alumina as the support material.

2. Apparatus and Experimental Procedure

All preparative-scale electrochemical oxidations were carried out in an 'H-cell', as illustrated in Figure 8.I.

Figure 8.I   The H-cell
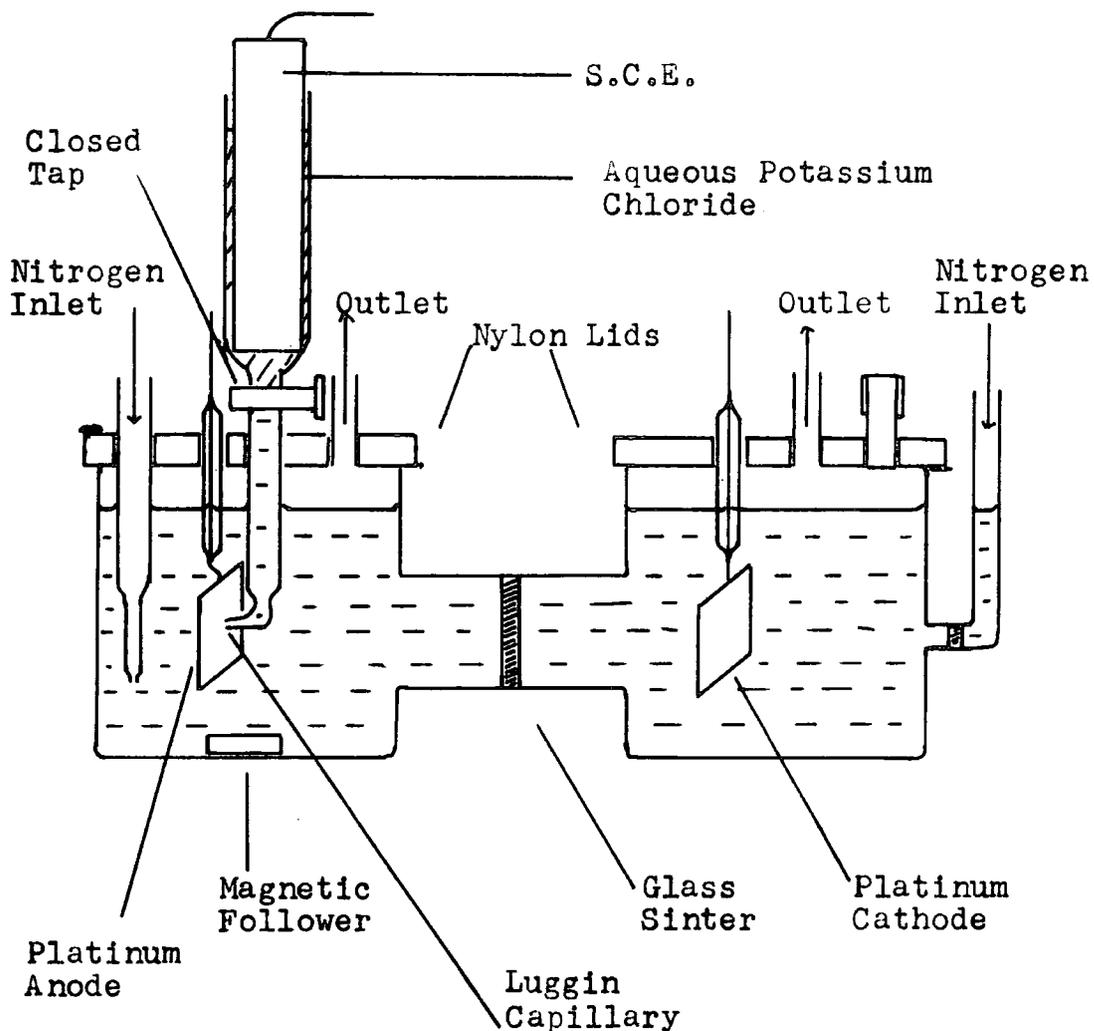
The electrodes were platinum foil, approximately $6cm^2$ in area, which were cleaned prior to use with concentrated nitric acid, distilled water, and acetone. The reference electrode was a Pye-Unicam 303NS saturated calomel electrode which was protected from the bulk solution by a built-in sinter and used in conjunction with a salt bridge. The salt bridge consisted of a modified dropping funnel which had solvent-supporting electrolyte in the lower part, separated by an ungreased, closed tap from aqueous potassium chloride in the upper part. Thus, all values of potential

referred to in the experimental sections are with respect to the saturated calomel electrode.

The potentiostat was a custom built model, loaned by the Electricity Council, incorporating a DC 300 watt amplifier which had two channels that could be used independently. Figure 8.2 shows a diagrammatic representation of the controls and wiring involved in using Channel I (and similarly for Channel 2). To operate the potentiostat it is switched on at the main switch and at the switch marked 'AMP'. The fan is also switched on and the dials marked 'CHANNEL I' and 'CHANNEL 2' turned fully clockwise. The potentiostat is then allowed to warm up for I5 minutes.

The working electrode (in this case the anode) is connected to the terminal 'WE' and the reference electrode to 'REF'. A voltmeter is connected between the two terminals so as to measure the potential between them and in this project a Fluke 8000A digital multimeter was used. The counter electrode is connected, via an ammeter, to 'SE' such that it measures the current through the cell. To perform oxidations the switch designated '+/-' is set to '-'.

With a solution in the cell, the 'ON ELECTRODE' switch can be turned on and the required potential of the working electrode, relative to the reference, can now be set using the dial marked 'POT'. The voltmeter on the potentiostat measures the total voltage across the cell and its full scale deflection is either IO or IOOV, depending on the setting.

Figure 8.2 Potentiostat wiring for an oxidation using

Channel I
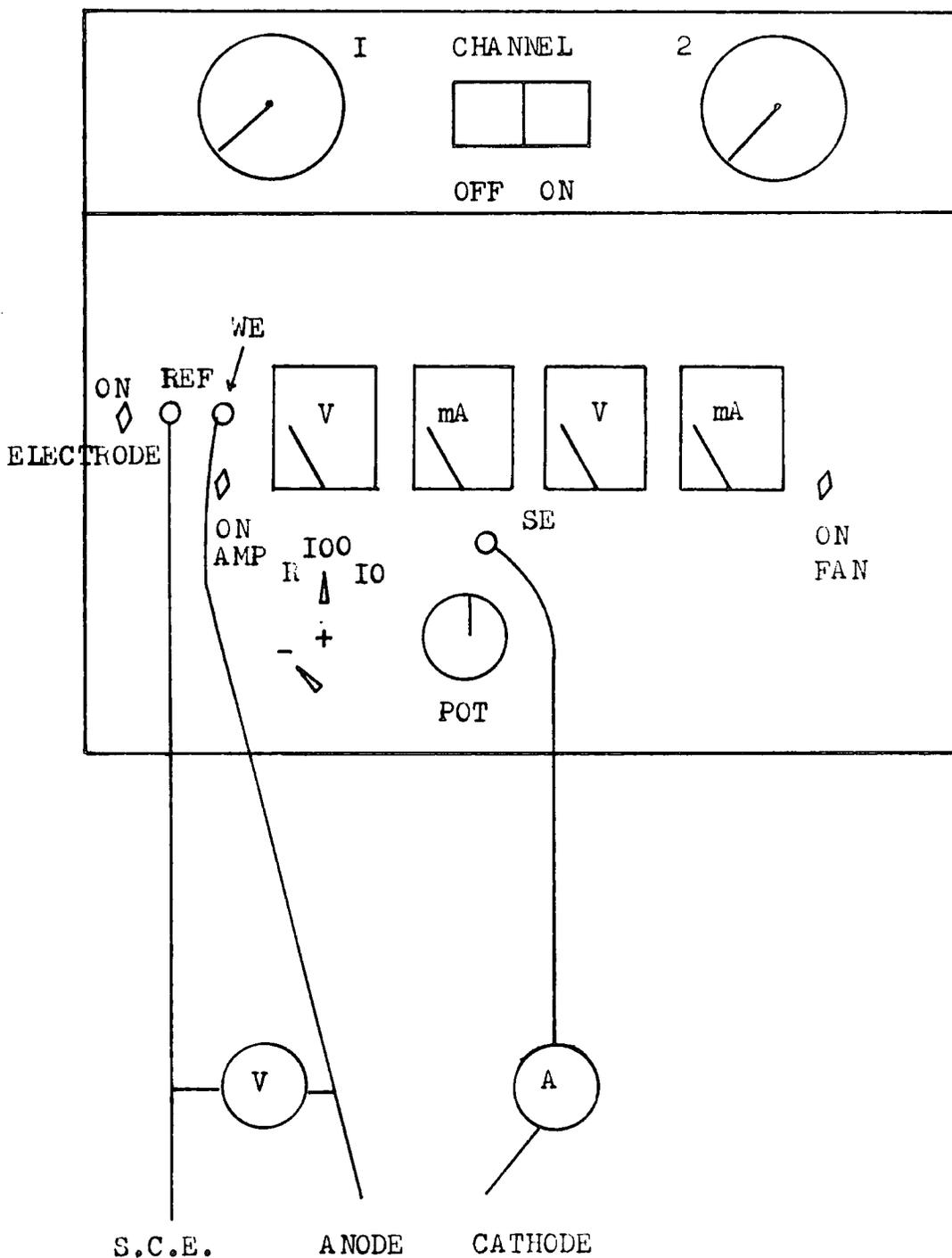
The experimental procedure was to fill the 'H-cell' with the solvent (I70 ml unless otherwise stated) and supporting electrolyte (6g). The solution was then de-oxygenated by bubbling dry nitrogen through it. The cell was normally cooled with a water bath during the electrolysis. The experiment was carried out at a potential in the region of the peak potential which had been obtained by linear sweep voltammetry. The amount of charge passed was followed either graphically or by using an Amel 558 integrator (which had been standardised), loaned by the Electricity Council.

3. **Linear Sweep Voltammetry**

Linear sweep voltammetry was carried out using a Beckmann Electroscan 30 combined with a Fluke 8000A digital multimeter. Sweep rates of up to I00mV/sec were available using this instrument. The electrodes were parallel, cylindrical platinum wires of 0.5mm diameter, sealed in glass to maintain a constant cell geometry of a separation of 2.5mm and exposed length of 20mm. The cell had a capacity of approximately 2.5ml and the reference electrode was an S.C.E. with a side arm containing agar gel-KCl as the salt bridge. Figure 8.3 illustrates the cell. The solutions were 0.35M tetraethylammonium fluoroborate in acetonitrile containing the substrate in either 4 or 40mM concentration. The solutions were deoxygenated prior to running each voltammogram by bubbling dry nitrogen through the cell and this was also to stir the solutions between runs.

Figure 8.3   Micro-cell for Linear Sweep Voltammetry

Cathode   Anode

Nitrogen
Inlet

Saturated Calomel

Electrode (S.C.E.)

Saturated KCl solution

Mercurous and Potassium
Chloride Paste

Mercury

Copper Connection

Agar gel-KCl

Bridge
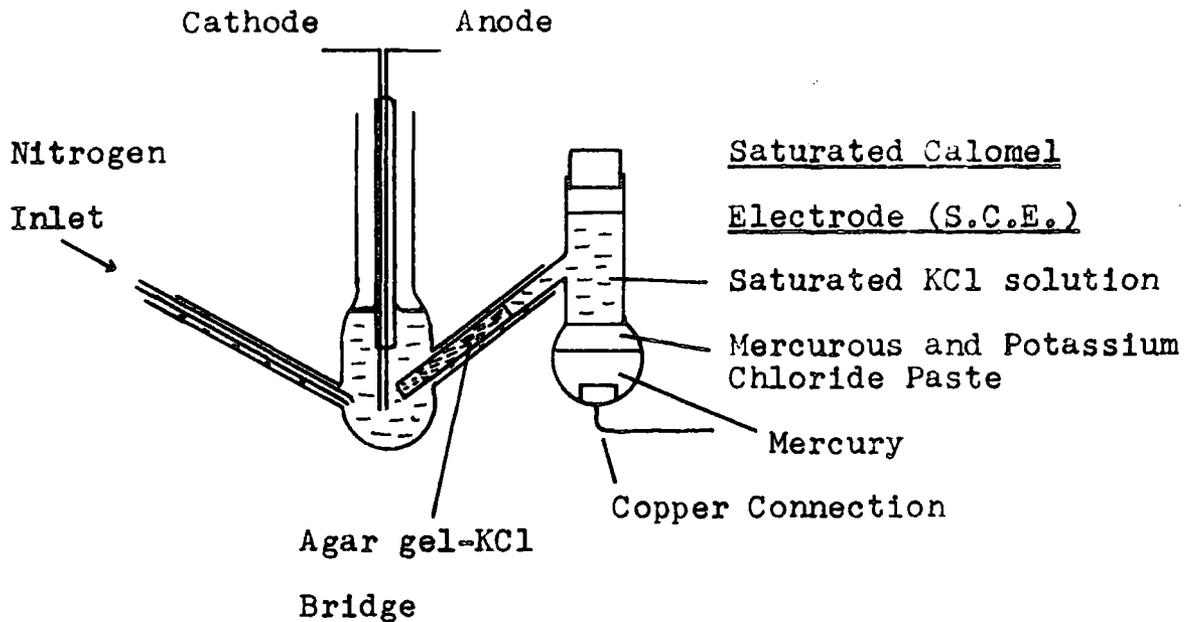
4.   Cyclic Voltammetry

Cyclic voltammetry was performed at the Electricity
Council Research Centre, Capenhurst. The cell which was
used is shown in Figure 8.4.

Figure 8.4   Cell for Cyclic Voltammetry

Platinum
Anode

Reference
Electrode

N₂
Inlet

Platinum
Cathode

Luggin
Capillary

Three-way Tap
(open)
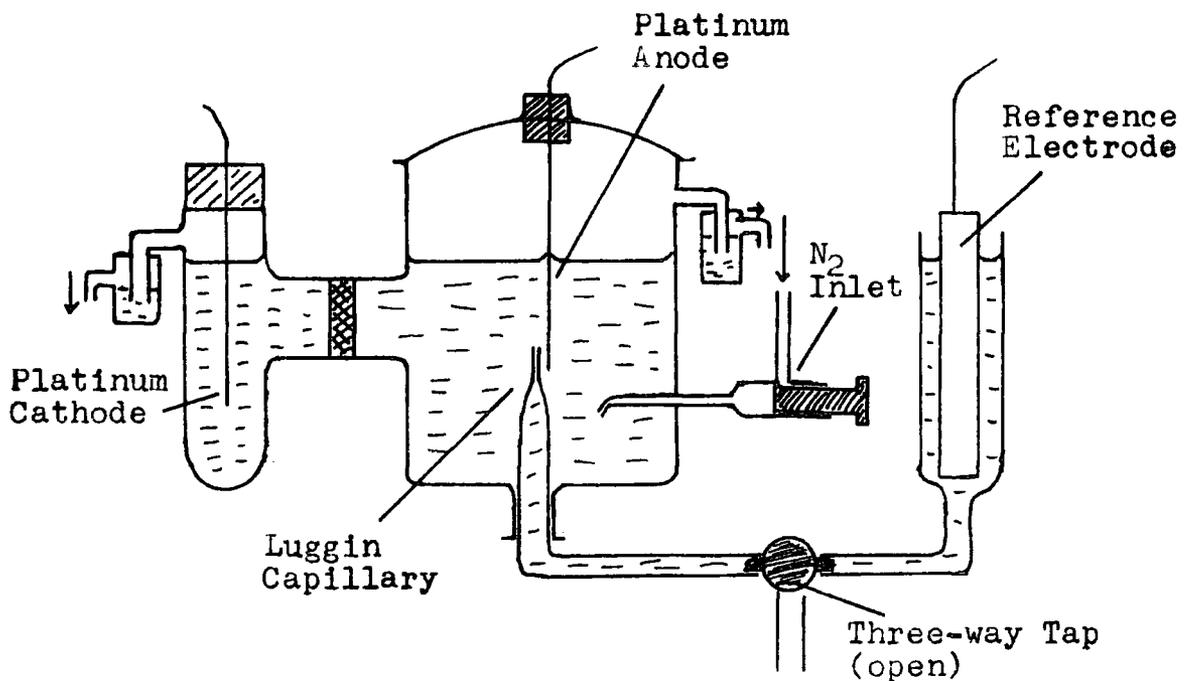
The electrodes were platinum wire, with a saturated calomel electrode as reference. Solutions were 0.3M tetra-ethylammonium fluoroborate in acetonitrile containing the substrate at I0mM concentration. The anolyte was deoxygenated with nitrogen and this was also used to stir the solutions in between each run. Voltammograms were run from 0.05 to I0V/sec. by means of a function generator coupled to a potentiostat. At over 0.5V/sec. the traces were recorded on a cathode ray oscilloscope and photographed.

8.B OXIDATION of 2,3,5,6-TETRAFLUOROANISOLE

I. In Acetonitrile

2,3,5,6-Tetrafluoroanisole (66) (6.04g, 33.6mmol) was oxidised at +2.40V in acetonitrile and tetraethylammonium fluoroborate (T.E.A.F.). The electrolysis was stopped after 0.015 faradays of charge had been passed, which was equivalent to 0.45e/molecule of (66), and turned the anolyte dark brown.

The anolyte was removed, diluted with water and extracted with ether. The ethereal extracts were dried $(MgSO_4)$ and concentrated by distillation. The remainder of the volatiles were removed by vacuum transference into a cold trap and subsequent distillation left a residue containing (66) (1.2g) by g.l.c.. The involatile residue, after vacuum transference, was sublimed (0.005mmHg, 95-100°C) to yield a white sublimate which was identified as I,I'-dimethoxy-2,2',3,3',5,5',6,6'-octafluorobiphenyl (68) (1.59g, current efficiency (C.E.) 59%), m.p. 85-85.5°C (lit.[167] 83-84.5°C). (Found: M+, 358. Calc. for $C_{14}H_6F_8O_2$: M, 358). The intractable residue (0.56g) was shown to be a multi-component mixture by thin layer chromatography (t.l.c.).

2. In Acetonitrile-Trifluoroacetic Acid

2,3,5,6-Tetrafluoroanisole (66) (4.0g, 22.2mmol) was oxidised at +2.40V in acetonitrile (150ml), trifluoroacetic acid (30ml), and T.E.A.F. (6g). The electrolysis was terminated after 0.013 faradays of charge had passed (equivalent to 0.51e/molecule of (66)),turning the anolyte

yellow. The anolyte was treated as in 8.B.I. to yield (66) (1.85g), by vacuum transference, and a sublimate which was identified as 1,1'-dimethoxy-2,2',3,3',5,5',6,6'-octafluoro-biphenyl (68) (1.03g, C.E. 51%), m.p. 84-85°C (lit.[167] 83-84.5°C). (Found: M$^+$, 358; Calc. for $C_{14}H_6F_8O_2$: M, 358).

An intractable residue (0.16g) was also obtained.

8.C OXIDATION OF 2,3,6-TRIFLUOROANISOLE

2,3,6-Trifluoroanisole (67) (4.8g, 29.6mmol) was oxidised at +2.20V in acetonitrile-T.E.A.F.. The electrolysis was stopped after 0.0065 faradays of charge had passed (equivalent to 0.22e/molecule of (67)). Following a similar procedure to that described in 8.B.I., volatiles containing (67) (0.7g) were obtained by vacuum transference. Sublimation (0.1mmHg) of the residue gave two fractions:

(i) 20-40°C, (67) (1.1g), identified by n.m.r. spectroscopy.

(ii) 100-120°C, Hexafluoro-2,2'-dihydro-4,4'-dimethoxybiph-enyl(69) (0.25g, C.E. 24%), m.p. 122-125 C (lit.[168] 125-126°C). (Found: M$^+$, 322; Calc. for $C_{14}H_8F_6O_2$: M, 322).

The intractable residue (0.61g) was shown to be a multi-component mixture by t.l.c..

8.D OXIDATION OF 2,3,5-TRIFLUOROANISOLE

I. Electrochemical Oxidation

2,3,5-Trifluoroanisole (70) (5.0g, 30.9mmol) was oxidised at +2.20V in acetonitrile-T.E.A.F.. The electrolysis was terminated after 0.015 faradays of charge had passed,

which was equivalent to 0.49e/molecule of (70). The solvent
was removed from the anolyte under vacuum to leave a red-
brown residue which was washed with dry ether and filtered.
Removal of the solvent by distillation and vacuum transfer-
ence left a residue from wich sublimation (0.05mmHg) gave
two fractions:

    (i)   30-40°C, (70) (I.32g), by n.m.r. spectroscopy.

    (ii) I00-200°C, white solid (0.85g)

Column chromatography, with dichloromethane as eluant,
gave a further quantity (0.5Ig) of this white solid from
the residue (I.86g) after sublimation. Both samples were
shown to be the same by t.l.c., thus giving an overall
yield of I.36g (C.E. 56%) of a white solid which was ident-
ified as 2,2',3,3',6,6'-hexafluoro-4,4'-dimethoxybiphenyl
(7I) m.p. I57-I58°C. (Found: C,52.49; H,2.52; F, 35.72%;
M$^+$, 322. $C_{I4}H_8F_6O_2$ requires: C, 52.18; H, 2.50; F, 35.38%;
M, 322). ^{I9}F and $^I H$ n.m.r. spectra no. I, i.r. spectrum no.I.

2.   Synthesis of (7I) by an alternative route

    I,2,4-Trifluoro-3-bromo-6-methoxybenzene[92] (72) (I.0g,
4.Immol) was heated with activated copper bronze (3g) in
a sealed glass tube at 220°C for 2 days. The mixture was
then extracted with ether and removal of the solvent left
a residue from which repeated sublimation yielded a white
sublimate, 2,2',3,3',6,6'-hexafluoro-4,4'-dimethoxybenzene
(7I) (0.35g, 35%), whose spectra were comparable with those
of the sample obtained in 8.D.I..

8.E OXIDATION OF 2,4,5-TRIFLUOROANISOLE

2,4,5-Trifluoroanisole (73) (1.0g, 6.2mmol) was oxidised at +2.20V in acetonitrile-T.E.A.F.. The electrolysis was terminated after 0.0038 faradays of charge had passed, which was equivalent to 0.62e/molecule of (73). Following the procedure outlined in 8.B.I., a residue was obtained from which sublimation gave (73)(0.09g), identified by n.m.r. spectroscopy, and a residue (0.62g), which was shown to be a multi-component mixture by t.l.c..

8.F OXIDATION OF 1,2-DIBROMO-3,6-DIFLUORO-4,5-DIMETHOXY-
BENZENE

I. Synthesis of 1,2-dibromo-3,6-difluoro-4,5-dimethoxy-
benzene

Sodium (2.6g, 113mmol) was dissolved in dry methanol (100ml) and 1,2-dibromotetrafluorobenzene (12.48g, 40.5mmol) was added. The mixture was refluxed for 43hrs. and, after cooling, was added to a large volume of water and extracted with ether. The ethereal extracts were dried (MgSO$_4$), concentrated by distillation, and the remainder of the solvent removed under vacuum. The residue was recrystallised from methanol to give a white solid which was identified as 1,2-dibromo-3,6-difluoro-4,5-dimethoxybenzene (81) (10.7g, 79%), m.p. 64.5-65.5°C. (Found: C, 28.77; H, 1.83; Br, 47.8; F, 11.5%. C$_8$H$_6$Br$_2$F$_2$O$_2$ requires: C, 28.95; H, 1.83; Br, 48.2; F, 11.5%). ^{19}F and ^{1}H proton n.m.r. spectra no. 2, i.r. spectrum no. 2, mass spectrum no. I.

2. Electrochemical oxidation

I,2-Dibromo-3,6-difluoro-4,5-dimethoxybenzene (<u>81</u>) (3.25g, 9.8mmol) was oxidised at +2.10V in acetonitrile-T.E.A.F.. During the electrolysis, the anode was covered with a red haze which 'fell off' whilst the rest of the anolyte was yellow. The electrolysis was terminated after 0.0060 faradays of charge had passed, which was equivalent to 0.62e/molecule of (<u>81</u>). The anolye was worked-up as in 8.D.I., to leave a residue from which sublimation gave (<u>81</u>) (2.30g), identified by ^{19}F n.m.r. and i.r. spectroscopy, and tar (0.24g), which was shown to be a multi-component mixture by t.l.c..

CHAPTER 9

EXPERIMENTAL TO CHAPTER 4

9.A GENERAL

I. Reagents

N,N-dimethylpentafluoroaniline (90) and N,N-dimethyl-2,3,5,6-tetrafluoroaniline (91) were prepared by the technical staff, using literature methods.[169,170] Pentafluorophenol (1) was supplied by Imperial Smelting Corporation Ltd., and other compounds were prepared by published routes.[160,170-2]

Lithium perchlorate was supplied by BDH Chemicals Ltd., and was purified by recrystallisation from aqueous solution and dried at 50°C under vacuum. Solvents and other supporting electrolytes were described on page I29.

Lead tetra-acetate was recrystallised from glacial acetic acid and dried under vacuum. Diazomethane was prepared in an ethereal solution using a standard method.[173]

2. Experimental Procedure

The procedure for the electrochemical oxidations was as described on page I29.

9.B ELECTROCHEMICAL OXIDATION OF N,N-DIMETHYLPENTAFLUOROANILINE

I. With Tetraethylammonium Fluoroborate as Electrolyte

N,N-dimethylpentafluoroaniline (90) (3.Ig, I4.7mmol) was oxidised at +I.20V in acetonitrile and tetraethylammonium fluoroborate (T.E.A.F.). A greenish-blue haze formed around the anode almost immediately and 'fell off' during the electrolysis, turning the anolyte turquoise-blue. After 0.0024 faradays of charge had been passed (equivalent to 0.I6e/molecule), the electrolysis was stopped and the anolyte removed.

After leaving overnight, the anolyte had turned yellow in colour. It was diluted with water and extracted with ether; the ethereal extracts were dried (MgSO$_4$) and the solvent removed by distillation to leave a yellow liquid. Vacuum transference, followed by distillation, gave a liquid (1.20g) which was found by mass spectroscopy-g.l.c. (Col. 0, 150°C) to contain components with (i) m/e 211, (ii) m/e 316, and (iii) m/e 249. Component (i) was identified as (90) (99%) on the basis of its mass spectrum and g.l.c. retention time. An involatile residue (0.41g) remained after the final vacuum transference and this was shown to be a multi-component mixture by thin layer chromatography (t.l.c.).

It was found that the aqueous phase from the initial extraction was acidic, and neutralisation yielded a further quantity of (90) (0.08g).

2. With Lithium Perchlorate as Electrolyte

N,N-dimethylpentafluoroaniline (90) (3.3g, 15.6mmol) was oxidised at +1.30V in acetonitrile (170ml) and lithium perchlorate (8.36g). As before, a turquoise blue colour 'fell off' the anode thus colouring the anolyte, however, towards the end of the oxidation the anolyte had turned dark brown. 0.0069 Faradays of charge were passed, which was equivalent to 0.44e/molecule of (90).

The solvent was removed from the anolyte by vacuum transference to leave a red-brown semi-solid residue. Addition of ether to this residue resulted in the formation of a two layer system. The upper layer was removed and concentrated by distillation to leave a red-brown residue (1.78g).

Molecular distillation gave (90)(0.25g), by n.m.r. spectroscopy

and g.l.c. retention time, and an intractable residue (0.69g).

The lower layer was diluted with water and extracted with

ether, the ethereal extracts were dried (MgSO$_4$) and concentrated

by distillation to leave a liquid (2.45g). Molecular distill-

ation gave (90) (0.52g), by g.l.c. retention time, and an

intractable residue (0.32g).

The solvent which had been originally removed from the

anolyte by vacuum transference was found to contain (90)

(0.44g) by g.l.c..

9.C   ELECTROCHEMICAL OXIDATION OF N,N-DIMETHYL-2,3,5,6-
      TETRAFLUOROANILINE

I.   With Tetraethylammonium Fluoroborate as Electrolyte

N,N-dimethyl-2,3,5,6-tetrafluoroaniline (91) (4.86g,

25.2mmol) was oxidised at +I.25V in acetonitrile-T.E.A.F..

During the electrolysis, the anolyte went slightly yellow

but there was no definite colour change as observed in 9.B.I..

0.006I Faradays of charge were passed, which was equivalent

to 0.24e/molecule of (91).

Following the procedure as described in 9.B.I., a residue

was isolated from which sublimation (0.005mmHg, 60°C) gave

a white solid (0.I8g) on the cold finger. This solid was

identified as I,2-bis(N-methyl-2,3,5,6-tetrafluoroanilino)-

ethane (92) (C.E.I5%), m.p. 8I-2°C. (Found: C, 49.I8; H, 2.86;

N, 7.30%; M$^+$ 384. C$_{16}$H$_{12}$F$_8$N$_2$ requires C, 50.00; H, 3.I3;

N, 7.29%; M 384.); n.m.r. spectrum no. 3, i.r. spectrum no. 3.

This solid decomposed on standing.

Distillation of the liquid obtained by vacuum transference

gave a liquid (I.25g) whose mass spectroscopy-g.l.c. (Col.
0, 170°C) was inconclusive but ^{19}F n.m.r. spectroscopy
suggested that it was mainly starting material.

2. **With Lithium Perchlorate as Electrolyte**

N,N-dimethyl-2,3,5,6-tetrafluoroaniline (91) (3.0g, 15.5
mmol) was oxidised at +1.30V in acetonitrile (170ml) and
lithium perchlorate (8g). The anode surface was initially
pale blue, but after about 5mins. this was replaced by red
and the anolyte, itself, turned dark red during the electrolysis.
The initial current was 180mA, but at the end of the electro-
lysis it had increased to 300mA. 0.0082 Faradays of charge
were passed, which was equivalent to 0.53e/molecule of (91).

Vacuum transference of the solvent from the anolyte
left a purple residue. Distillation of the volatiles left
a liquid containing (91) (0.58g) by g.l.c. retention time
(Col. 0, 140°C).

Part of the purple residue was added to water giving a
purple solution, however, on extraction with dichloromethane
the colour disappeared. The extracts were dried (MgSO$_4$) and
the solvent removed under vacuum to leave an intractable
residue (0.09g). The remainder of the purple residue was
diluted with ether and washed with water. The ethereal extracts
were dried (MgSO$_4$) and distilled to leave a liquid (I.33g),
from which molecular distillation (0.05mmHg, 100-120°C)
yielded (91) (0.70g) by g.l.c. retention time and n.m.r.
spectroscopy. An intractable residue (0.48g) remained behind.

9.D ELECTROCHEMICAL OXIDATION OF 4-AMINO-2,3,5,6-TETRA-FLUOROPYRIDINE

4-Amino-2,3,5,6-tetrafluoropyridine (93) (I.2g, 7.2mmol) was oxidised at +2.20V in acetonitrile-T.E.A.F.. 0.0036 Faradays of charge were passed (equivalent to 0.5e/molecule of (93)) which turned the anolyte red-brown.

Most of the solvent was removed from the anolyte by vacuum transference to leave a residue which was diluted with water. This was then ether extracted, the ethereal extracts dried ($MgSO_4$), and the solvent removed by distillation. The remaining solvent was removed by vacuum transference to leave a solid; sublimation gave a white-yellow solid (0.3g) whose i.r. spectrum was the same as that of (93). An intractable residue (0.8Ig) remained behind. Column chromatography separated this residue into various coloured solids in minor quantities (<0.05g) which were unidentified.

9.E ELECTROCHEMICAL OXIDATION OF PENTAFLUOROPHENOL

I. In Acetonitrile

Pentafluorophenol (I) (6.5g, 35.3mmol) was oxidised at +2.I5V in acetonitrile-T.E.A.F.. 0.007I Faradays of charge were passed (equivalent to 0.2e/molecule of (I)) which turned the anolyte dark green. An investigation of a sample of the anolyte with the 'Electroscan' instrument only led to the removal of the colour on the reduction cycle, and there was no regeneration on the oxidation cycle.

Removal of the solvent from the anolyte by vacuum

transference left a dark green liquid-solid mixture. Addition
of ether to this mixture gave a red-brown ether solution
and a small quantity of a purple solid. The i.r. spectrum
of this solid contained absorptions at 1050 and 1100cm^{-1}, and
very little else. After filtration of the ethereal solution,
the solvent was removed by distillation; molecular distillation
(0.1mmHg, 70°C) gave a yellow liquid (3.39g) whose ^{19}F n.m.r.
spectrum identified it as (I). The involatile material (2.1g)
was run on a silica column to yield only two identifiable
fractions, one of which was (I)(0.2g). The other fraction
had a distinctive ^{19}F n.m.r. spectrum which, by comparison
with the product from the lead tetra-acetate oxidation of
(I), was identified as (4) (0.3g). In an attempt to simplify
the other fractions, diazomethane was added; however, only
pentafluoroanisole (75) could be detected by mass spectroscopy-
g.l.c. and a white solid was also formed. The i.r. spectrum
of this solid contained absorptions attributable to C—F,
amongst others; however, it could not be identified.

2. **In Trifluoroacetic Acid**

Pentafluorophenol (I) (5.0g, 27mmol) was oxidised at
+2.40V in trifluoroacetic acid (170ml) and T.E.A.F. (6g).
0.0104 Faradays of charge were passed (equivalent to 0.38e/
molecule of (I)), which turned the anolyte yellow.

Removal of the solvent by vacuum transference left a
viscous yellow residue which was washed with ether. The
solvent was removed by vacuum transference to leave a yellow-

liquid-solid (4.94g). Molecular distillation (0.05mmHg) gave three fractions:

(i)   yellow-brown liquid (0.54g), identified as (I) by g.l.c. and ^{19}F n.m.r.

(ii)   yellow liquid (0.3g), containing (I) (0.25g) by g.l.c. and ^{19}F n.m.r.

(iii) yellow liquid (0.7g), containing (I) (0.56g) by g.l.c. and ^{19}F n.m.r.

The latter two fractions contained minor quantities of two compounds which were later identified as indicated below. The residue was a bright yellow liquid-solid mixture (I.48g) and removal of most of the liquid, by decanting, left a yellow solid (0.92g). The liquid was shown to be mainly (I) by ^{19}F n.m.r. spectroscopy.

Sublimation of this yellow solid did not succeed in affording a separation. Analysis found: C, 39.2; F, 45.54%. Its u.v. spectrum in acetonitrile contained λ_{max} 260nm and no apparent absorption around 344nm . The ^{19}F n.m.r. spectrum of this solid contained numerous resonances, including a triplet of doublets at II5ppm and a multiplet at I24ppm. Thin layer chromatography indicated that it was a mixture and a separation, using a silica column, was attempted. However, as the column developed the yellow components went purple in colour and only tar was isolated. Thick layer chromatography, with a dichloromethane-carbon tetrachloride (50:50) mixture as eluant, similarly led to

decomposition of some of the material; however, enough material was isolated to allow the identification of two components:

(i) yellow solid, identified as trifluoro-(pentafluoro-phenoxy)-1,4-benzoquinone (<u>104</u>) m.p. 108-110°C (lit. value[109] 116-7°C), by comparison of its ^{19}F n.m.r. spectrum with published values.[109] I.r. spectrum no. 4.

(ii) yellow solid, identified as perfluoro-4-(3'-phenoxyphenoxy)-2,5-cyclohexadienone (<u>105</u>) on the basis of its ^{19}F n.m.r. spectrum. N.m.r. spectrum no. 4.

Both fractions (i) and (ii) from the molecular distill-ation contained (<u>104</u>) and (<u>105</u>) as minor impurities.

The trifluoroacetic acid which had been originally removed by vacuum transference contained (<u>I</u>) (0.38g), by g.l.c. Similarly, the ether which had been used to extract the involatile fraction, and subsequently vacuum transferred, was found to contain (<u>I</u>) (0.36g) by g.l.c.

9.F <u>ELECTROCHEMICAL OXIDATION OF 2,3,5,6-TETRAFLUOROPHENOL</u>

I. <u>Electrochemical Oxidation</u>

2,3,5,6-Tetrafluorophenol (<u>99</u>) (5.0g, 30.1mmol) was oxidised at +2.20V in acetonitrile-T.E.A.F.. 0.0055 Faradays of charge were passed (equivalent to 0.18e/molecule of (<u>99</u>)) which turned the anolyte dark green. However, after standing for a few hours it had altered to a dark brown.

The solvent was removed by vacuum transference from the anolyte to leave a semi-solid residue which was then washed

with ether. Concentration of these washings by distillation left a red-brown residue which was shown to contain (99) and a product by ^{19}F n.m.r. spectroscopy. Molecular distillation (0.05mmHg, 70-80°C) of the residue gave (99) (2.80g), which was identified by g.l.c. retention time and ^{19}F n.m.r. spectroscopy. A residue (1.70g) remained behind.

T.l.c. indicated that this residue contained one main component and column chromatography, using a silica column and dichloromethane-methanol (80:20) as eluant, gave seven fractions. Fractions 2-5 were found to be the same by t.l.c. and were, therefore, combined (0.13g). An i.r. spectrum of this yellow liquid contained a C O absorption and no O H. Its u.v. spectrum had a λ_{max} (acetonitrile) 325nm, amongst others, and its ^{19}F n.m.r. spectrum was distinctive.

Addition of diazomethane to the column fractions gave only 2,3,5,6-tetrafluoroanisole (66), which was identified by mass spectroscopy-g.l.c., and a white solid which could not be identified.

2. Lead Tetra-acetate Oxidation

2,3,5,6-Tetrafluorophenol (99) (1.02g, 6.1mmol) was added to lead tetra-acetate (2.67g, 6.02mmol) in ether (10ml). After stirring at room temperature for 65 minutes, the solution was filtered and the solvent removed under vacuum to leave a yellow liquid (1.3g). Molecular distillation gave two fractions which were shown to be the same by t.l.c.:

(i) 0.02mmHg, 85°C, (0.34g), yellow liquid.

(ii) 0.01mmHg, 85-90°C, (0.08g), orange liquid.

The product was identified as 2,3,5,6-tetrafluoro-6-(2',3',
5',6'-tetrafluorophenoxy)-2,4-cyclohexadien-1-one (112)
(Found: M$^+$ 330; $C_{12}H_2F_8O_2$ requires M 330). N.m.r. spectra
no. 5, i.r. spectrum no. 5.

Comparison of the ^{19}F n.m.r. spectrum of (112) with the
product isolated in the electrochemical oxidation (9.F.I.)
showed that they were the same.

9.G OXIDATION OF POTASSIUM PENTAFLUOROPHENOXIDE

Potassium pentafluorophenoxide (114) (dehydrated by
the literature method[160]) (5.0g, 22.5mmol) was oxidised at
+0.70V in acetonitrile-T.E.A.F.. The current was initially
140mA but after 5mins. it had dropped to 42mA, and after
52mins. it was only 2mA. The electrolysis was terminated
after 0.0006 faradays of charge were passed and the anolyte
was then filtered to give a caramel-brown solid (1.15g),
identified as (114) by i.r. spectroscopy. Removal of the
solvent from the anolyte by vacuum transference left a
yellow-brown solid (5.74g). I.r. spectroscopy indicated
that this solid contained supporting electrolyte and (114).
No other fluorocarbon was isolated.

The anode was found to be covered with a very thin
film of white solid, i.e. the electrode had been passivated.

CHAPTER IO

EXPERIMENTAL TO CHAPTER 5

IO.A GENERAL

I. Reagents and Solvents

Octafluorobut-2-ene (II9) was obtained from Bristol

Organics Ltd.. Trans-2H-heptafluorobut-2-ene (I20) was

prepared by the technical staff[174] and 2-bromo-heptafluoro-

but-2-ene (I2I), trans-2H-3-methoxy-I,I,I,4,4,4-hexafluoro-

but-2-ene (I25), and 2H-3-N,N-diethylamino-I,I,I,4,4,4-hexa-

fluorobut-2-ene (I39) were synthesised by known routes.[118,174]

Hexafluorobut-2-yne (I43) was available in this laboratory.

Amines were used as supplied . Methyl lithium was supplied

as a solution in ether, approximately I.7M, and was not

standardised prior to use.

Diethyl ether was dried over sodium wire, and sulpholan

was purified by fractional distillation under reduced pressure

and stored over molecular sieve (Type 4.A) under an atmosphere

of nitrogen. Hexamethyl phosphoramide was dried over molecular

sieve (Type 4.A), and dichloromethane was dried over

anhydrous magnesium sulphate. Other solvents and supporting

electrolyte were described on page I29.

2. Apparatus and Experimental Procedure

The reactions between amines and alkenes were either

carried out in glass Carius tubes of approximately IOOcm^3

volume or at atmospheric pressure, with the alkene being

introduced from a variable reservoir (football bladder)
attached to the reaction vessel. Standard vacuum line
techniques were employed to manipulate gaseous reagents and
products.

The electrochemical apparatus and procedure was described
on page I29.

I0.B <u>REACTIONS OF OCTAFLUOROBUT-2-ENE WITH AMINES</u>

I. <u>Ethylamine</u>

Octafluorobut-2-ene (<u>II9</u>) (8.Ig, 40.5mmol) and ethyl-
amine (3.8g, 84.4mmol) were sealed in a Carius tube and
allowed to warm up to room temperature, during which time a
white solid and liquid were produced. After 24hrs., volatiles
were removed by vacuum transference to yield a pale yellow
liquid (4.3g) in the cold trap. A viscous orange residue
remained behind and no gas was recovered. G.l.c. (Col. 0,
II0°C) indicated that the volatiles contained one major
component. This was separated by preparative g.l.c. (Col. 0,
I05°C) to give a mixture of <u>syn</u> and <u>anti 2-ethylimino-I,I,I,3-
4,4,4-heptafluorobutane</u> (<u>I24</u>) (3.05g, 34%) (Found: C, 32.I3;
H, 2.76; N, 6.I6; F, 59.6I%. $C_6H_6F_7N$ requires C, 32.00; H,
2.67; N, 6.22; F, 59.II%.). $\lambda_{max.}$ (acetonitrile) 274nm ($\leq$ 72),
n.m.r. spectra no. 6 , i.r. spectrum no. 6 , mass spectrum
no. 2.

2. <u>Methylamine</u>

Methylamine (2.Ig, 67.7mmol) and octafluorobut-2-ene
(<u>II9</u>) (5.7g, 28.5mmol) were sealed together in a Carius tube

and vigorously shaken for 24hrs.. A colourless liquid (5.09g) was obtained by vacuum transference and a white-yellow solid (presumably, the amine hydrofluoride) remained behind. The liquid was found to contain one major component by g.l.c. (Col. 0, 120°C). This was separated by preparative g.l.c. (Col. 0, 120°C) and identified as <u>syn</u> and <u>anti</u> 2-methylimino-1,1,1,3,4,4,4-heptafluorobutane (<u>127</u>) (4.8g, 80%), (Found: C, 28.26; H, 2.05; N, 6.44%. $C_5H_4F_7N$ requires C, 28.44; H, 1.9; N, 6.6%.), n.m.r. spectra no. 7, i.r. spectrum no. 7, mass spectrum no. 3.

3. <u>Diethylamine</u>

A number of experiments were carried out under a variety of conditions and only typical experiments are described here.

a. <u>At Room Temperature</u>

i. <u>In Ether</u>

Diethylamine (8.65g, 118.5mmol) in ether (25ml) was stirred at room temperature, while octafluorobut-2-ene (<u>119</u>) (7.9g, 39.5mmol) was allowed to enter the reaction vessel over a period of 15 minutes, at atmospheric pressure. After 94hrs., vacuum transference yielded volatiles (4.56g) which contained (<u>119</u>)(89%), by i.r. spectroscopy, and ether (11%), by g.l.c. retention time. The involatile residue was found to contain dissolved (<u>119</u>), ether, diethylamine, and a minor component by g.l.c..

ii. <u>No Solvent</u>

Diethylamine (2.3g, 31.5mmol) and octafluorobut-2-ene

(II9) (2.0g, I0mmol) were sealed in a Carius tube and vigorously shaken for 73½hrs. at room temperature. On opening the tube, distilled water was added and a red lower layer (0.08g) was obtained. This reaction was not investigated further.

b. At 50°C

i. Approximately Equimolar Quantities

Diethylamine (4.0g, 54.5mmol) in sulpholan (50ml) was stirred at 50°C and a trap containing octafluorobut-2-ene (II9) (I0.0g, 50mmol) was attached. After I43hrs. unreacted (II9) (4.7g), identified by i.r. spectroscopy, was condensed into a cold trap. The reaction mixture was heated up to I00°C, under vacuum, to give a colourless liquid (2.97g) in the cold trap. Dilution of the involatile residue with a large quantity of water did not give a lower fluorocarbon layer.

The colourless liquid which had transferred was added to water, extracted with dichloromethane and the extracts dried (MgSO$_4$). Concentration by distillation left a yellow-green liquid (0.5g) which was found by g.l.c. (Col. O, I40°C) to contain a minor product. This product was shown to be (I28) by comparison of its g.l.c. retention time with that of (I28) prepared in I0.B.3.c.. N.m.r. spectra no. 8.

ii. Excess Amine

Diethylamine (I4.6g, 200mmol) in sulpholan (25ml) was stirred at 40-50°C and a trap containing octafluorobut-2-ene (II9) (I9g, 95mmol) was attached. After I66hrs., unreacted (II9) (6.62g) was recovered by vacuum transference and the residue was diluted with water. The red lower layer was removed, washed with water, diluted with ether, and dried

(MgSO$_4$). Reduced pressure distillation (ImmHg, up to 90°C)
yielded no material and on opening the apparatus to the
atmosphere the sample solidified. Molecular distillation
(0.05mmHg, 175°C) gave a liquid which solidified to a
colourless solid (0.25g). (Found: C, 50.04; H, 7.81; N, 9.36%).
^{19}F n.m.r. 73.6 (D, J = 20Hz) and 182.1 (Q, J = 20Hz) (ppm
w.r.t. external CFCl$_3$), relative intensity 3:1. ^{1}H n.m.r.
1.17 (T, J = 7Hz) and 3.35 (Q, J = 7Hz) (ppm w.r.t. external
T.M.S.), relative intensity 3:2. Mass spectrum, m/e 284.

c. **Methyl Lithium and Diethylamine**

Methyl lithium (0.43g, 1.7M, 11.5ml) was added to diethyl-
amine (1.45g, 19.9mmol) in ether (25ml), under an atmosphere
of dry nitrogen. The reaction mixture was allowed to evolve
methane over a short period, after which the pale green
solution was frozen down, let down to vacuum, and allowed to
warm up to room temperature. Octafluorobut-2-ene (<u>119</u>) (5g,
25mmol) was allowed in in small quantities while the reaction
vessel was cooled with a water bath. There was an immediate
red colouration, which darkened on the addition of more (<u>119</u>)
until the reaction mixture was red-brown. After stirring for
2hrs. at 10°C, octafluorobut-2-ene (<u>119</u>) (1.9g) was recovered
by vacuum transference. Distilled water (50ml) was added to
the reaction mixture and this was then ether extracted. The
ethereal extracts were dried (MgSO$_4$) and the solvent removed
by distillation to leave a red-brown residue. Molecular
distillation yielded a liquid (1.60g) which was shown, by

g.l.c. (Col. O, I75°C) to contain three components, one of which was ether. An intractable residue (0.95g) remained behind. Preparative g.l.c. (Col. O, I62°C) gave two fluoro-carbon fractions:

(i) 2-N,N-diethylamino-I,I,I,3,4,4,4-heptafluorobut-2-ene (I28) (0.2Ig), n.m.r. spectra no. 8, i.r. spectrum no. 8, and mass spectrum no. 4.

(ii) 2,3-bis(N,N-diethylamino)-I,I,I,4,4,4-hexafluoro-but-2-ene (I33) (0.26g), n.m.r. spectra no. 9, i.r. spectrum no. 9 , and mass spectrum no. 5.

4. **Dimethylamine**

Dimethylamine (4.3g, 96.7mmol) and octafluorobut-2-ene (II9) (8.3g, 4I.5mmol) were sealed in a Carius tube and vigorously shaken for an hour at room temperature. Vacuum transference at room temperature gave a colourless liquid (4.9g) in the cold trap. A further quantity of liquid (4.8g) was obtained by vacuum transference, with warming, and both fractions were found to contain the same three components. These were separated by preparative g.l.c. (Col. O, IIO°C);

(i) cis-2-N,N-dimethylamino-I,I,I,3,4,4,4-heptafluoro-but-2-ene (I34) (2.62g, 28.I%), b.p. 84°C, n.m.r. spectrum no. I0, i.r. spectrum no. I0, mass spectrum no. 6.

(ii) trans-2-N,N-dimethylamino-I,I,I,3,4,4,4-heptafluoro-but-2-ene (I35) (2.24g, 24%), n.m.r. spectra no. II, i.r. spectrum no. II, mass spectrum no. 7.

Analysis of a mixture of (i) and (ii).(Found: C, 31.85;

H, 2.76; N, 6.15; F, 59.02%. $C_6H_6F_7N$ requires C, 32.0; H, 2.67; N, 6.22; F, 59.11%).

(iii) A mixture of (136) (90%) and (134) (10%) (0.08g). ^{19}F n.m.r. 53.8 (D, J = 9.5Hz), 67.0ppm (broad singlet), (w.r.t. external $CFCl_3$), relative intensity I:I. ^{1}H n.m.r. 2.99 (S, assigned to the impurity), 3.15 (S), and 5.33ppm (Q, J = 9.5Hz) (w.r.t. external T.M.S.), relative intensity 2:5:I. A mass spectrum of this sample contained an intense m/e 207, (136) requires M 207.

IO.C REACTIONS OF TRANS-2H-HEPTAFLUOROBUT-2-ENE WITH AMINES

I. Ethylamine

Ethylamine (4.6g, I02.2mmol) and trans-2H-heptafluoro-but-2-ene (120) (8.3g, 45.6mmol) were sealed in a Carius tube and on allowing to warm up to room temperature, a white solid and liquid were produced. After 3hrs., vacuum trans-ference gave a colourless liquid (6.66g) which consisted of one major component. This was separated by preparative g.l.c. (Col. O, I35°C) and identified as 2-ethylimino-I,I,I,4,4,4-hexafluorobutane (137) (5.Ig, 54%), (Found: C, 34.95; H, 3.56; N, 6.70; F, 54.96%. $C_6H_7F_6N$ requires C, 34.78; H, 3.38; N, 6.76; F, 55.07%). λ_{max} (acetonitrile) 244nm (ε 223), n.m.r. spectra no. I2, i.r. spectrum no. I2, and mass spectrum no. 8.

2. Methylamine

Methylamine (2.5g, 80.7mmol) and trans-2H-heptafluoro-but-2-ene (120) (5.5g, 30.2mmol) were sealed in a Carius tube and allowed to warm up to room temperature. After 36hrs. ,

vacuum transference gave a liquid (3.4g) which was shown by
g.l.c. (Col. 0, I50°C) to consist of one major component.
This was separated by preparative g.l.c. and identified as
2-methylimino-I,I,I,4,4,4-hexafluorobutane (I38)(2.63g, 45%) b.p.36°C,
(Found: C, 30.97; H, 2.73; N, 7.09; F, 59.42%. $C_5H_5F_6N$
requires C, 3I.09; H, 2.59; N, 7.25; F, 59.07%). N.m.r.
spectra no. I3, i.r. spectrum no. I3, mass spectrum no. 9.

3. Diethylamine

Diethylamine (2.4g, 32.9mmol) in sulpholan (25ml) was
stirred at room temperature and a trap containing trans-2H-
heptafluorobut-2-ene (I20) (6.4g, 35.2mmol) was attached.
After 3½hrs., little reaction had occurred (by g.l.c.) and
more diethylamine (0.5g, 6.8mmol) was added. After 63½hrs.,
vacuum transference gave a yellow-green liquid (I.36g) which
was shown by mass spectroscopy-g.l.c. (Col. 0, I45°C) to
contain: (i) diethylamine, (ii) (I20),(iii) (I39), (iv)
m/e 279, (v) m/e 284. ^{19}F n.m.r. spectroscopy confirmed the
presence of (I39) by comparison with a known spectrum. The
reaction was not synthetically useful and, therefore, was
not investigated further.

4. Dimethylamine

Dimethylamine (4.0g, 88.9mmol) and trans-2H-heptafluoro-
but-2-ene (I20) (6,5g, 35.7mmol) were sealed in a Carius
tube. On allowing to warm up to room temperature, a white
solid (presumably, the amine hydrofluoride) and a pale yellow
liquid were produced..After 2½hrs., vacuum transference gave

a liquid (8.2g) which contained one major component by g.l.c..

This was separated by preparative g.l.c. (Col. O, 115°C)

and identified as <u>trans</u>-2H-3-N,N-dimethylamino-I,I,I,4,4,4-

hexafluorobut-2-ene (<u>136</u>) (4.8g, 65%), by comparison of its

n.m.r. spectra with those of a known sample.[122]

10.D <u>REACTION OF 2-BROMO-HEPTAFLUOROBUT-2-ENE WITH DIMETHYL-</u>

   <u>AMINE</u>

2-Bromo-heptafluorobut-2-ene (<u>121</u>) (2.98g, 11.42mmol)

and dimethylamine (1.93g, 42.89mmol) were sealed together

in a Carius tube and allowed to warm up to room temperature.

After Ihr., vacuum transference gave a pale yellow liquid

and solid (3.95g) in the cold trap. An orange liquid (2.78g)

was removed and found to contain one minor component and

two major components by g.l.c. (Col. A, 95°C). Mass spectro-

scopy-g.l.c. (Col. A, 105°C) indicated the following:

   (1) $C_8H_{12}F_6N_2$, M^+ 250. Identified as <u>2,3-bis(N,N-dimethyl-</u>

<u>amino)-I,I,I,4,4,4-hexafluorobut-2-ene</u> (<u>142</u>), mass spectrum

no. II.

   (11) $C_6H_6BrF_6N$, M^+ 285, M+2 287. Identified as <u>cis</u>- and

<u>trans-2-bromo-3-N,N-dimethylamino-I,I,I,4,4,4-hexafluoro-</u>

<u>but-2-ene</u>, (<u>140</u>) and (<u>141</u>); N.m.r. spectra nos. I4 and I5,

i.r. spectrum no. I6, and mass spectrum no. IO.

10.E <u>REACTION OF HEXAFLUOROBUT-2-YNE WITH DIETHYLAMINE</u>

I. <u>General</u>

Numerous reactions were carried out and Table IO.I

presents the information obtained. The method of reaction

was the same in each experiment, i.e. diethylamine was present in a vigorously stirred solvent at room temperature and all the hexafluorobut-2-yne (I43) was allowed in under the action of atmospheric pressure. Thus, the rate of mixing was rapid and reasonably constant from experiment to experiment. Isomer ratios in the crude reaction mixture were determined using ^{I9}F n.m.r. spectroscopy and, in particular, the signals attributable to the trifluoromethyl groups.

Table IO.I

Solvent	Volume (ml)	Ratio of Reactants Amine:(I43)(mmol)	Reaction Time(min)	ε b	Product (I39) Cis:Trans
-		22.9:22.8	35		30:70
Diethyl	IO	34.2:34.6	45	4.3	47:53
Ether	25	II:I0.9	65		64.7:35.3
Dichloro-methane	IO	26:26	40	8.9	I4:86
H.M.P.A.[a]	IO	25.34:25.3	34	30	67:33
Sulpholan	IO	30.I:29.6	30	44	49:5I

a - Hexamethyl Phosphoramide

b - Solvent dielectric constant[I]

2. Reaction of hexafluorobut-2-yne with lithium diethylamide

Diethylamine (1.8g, 24.7mmol) was dissolved in n-pentane (25ml). Methyl lithium (1.7M, 14ml, 0.48g) was added by means of a syringe, under a dry nitrogen atmosphere. The reaction vessel was then frozen down, evacuated, and allowed to warm up to about -70°C (acetone-CO$_2$). Hexafluorobut-2-yne (143) (4.0g, 24.7mmol) was allowed into the reaction vessel from a trap in small quantities over 15 minutes. The colour of the solution was initially purple-red, but this darkened on addition of more (143) and the viscosity of the solution increased. After all of the (143) had been added, bromine (3.95g, 24.7mmol) was added in small quantities from a dropping funnel over 5-10 minutes. The colour immediately disappearred and quantities of white fumes were formed. On allowing the reaction to warm up to room temperature, it was noted that the surface of the liquid was covered with a white-yellow solid. Vacuum transference left an involatile residue which was washed with dichloromethane and ether. Drying under vacuum left a white-yellow solid (1.7g), whose i.r. spectrum was comparable to that of poly(hexafluorobut-2-yne).

The washings were combined, washed with water and dried (MgSO$_4$). The solvent was removed by distillation to leave a viscous red-brown oil (4.9g); it was deduced that the fluorocarbon content was low from the n.m.r. spectrum and, therefore, the experiment was terminated.

10.F ELECTROCHEMICAL OXIDATION OF 2H-3-N,N-DIETHYLAMINO-
   1,1,1,4,4,4-HEXAFLUOROBUT-2-ENE

2H-3-N,N-diethylamino-1,1,1,4,4,4-hexafluorobut-2-ene
(139) (4.0g, 17mmol) was oxidised at +1.90V in acetonitrile-
T.E.A.F.. The electrolysis was terminated after 0.0082
faradays of charge had passed, which was enough to perform
a 2e/molecule oxidation on 0.96g of (139).

Vacuum transference from the anolyte gave a liquid
containing (139) (1.71g, by g.l.c.) in the cold trap. The
involatile residue was washed with ether; the washings were
then combined and concentrated by distillation to leave a
red-brown oil. Molecular distillation (0.05mmHg) gave two
fractions and an intractable residue (0.38g).

(i) R.T.-40°C, (139) (0.24g), identified by g.l.c.
retention time.

(ii) 40-60°C, yellow liquid, identified as 2,5-bis(N,N-
diethylamino)-3,4-bis(trifluoromethyl)-1,1,1,6,6,6-hexa-
fluorohexa-2,4-diene (151) (0.56g, C.E. 29%), (Found: C,
41.14; H, 4.41; N, 6.16%. $C_{16}H_{20}F_{12}N_2$ requires C, 41.03; H,
4.27; N, 5.98%). N.m.r. spectra no. 16, i.r. spectrum no. 17
and mass spectrum no. 12.

10.G ELECTROCHEMICAL OXIDATION OF 2H-3-N,N-DIMETHYLAMINO-
   1,1,1,4,4,4-HEXAFLUOROBUT-2-ENE

2H-3-N,N-dimethylamino-1,1,1,4,4,4-hexafluorobut-2-ene
(136) (4.8g, 23.2mmol) was oxidised at +1.80V in acetonitrile-
T.E.A.F.. 0.0104 Faradays of charge were passed (equivalent
to 0.48e/molecule of (136)) which turned the anolyte orange.

The solvent was removed from the anolyte by vacuum transference and the residue was washed with ether and filtered. After removal of the ether by vacuum transference, molecular distillation (0.01mmHg) of the residue gave three fractions and an intractable residue (0.24g).

(i)   20-60°C, (136) (0.92g), by g.l.c. retention time.

(ii)   60-80°C, (0.07g), containing one major component (96%) by g.l.c.

(iii) 80-110°C, yellow liquid, identified as 2,5-bis(N,N-dimethylamino)-3,4-bis(trifluoromethyl)-1,1,1,6,6,6-hexafluorohexa-2,4-diene (153) (0.52g, C.E. 24%) (Found: C, 35.07; H, 2.87; N, 6.58%. $C_{12}H_{12}F_{12}N_2$ requires C, 34.95; H, 2.87; N, 6.80%). N.m.r. spectra no. 17, i.r. spectrum no. 18, and mass spectrum no. 13. The major component in fraction (ii) was shown to be (153) by comparison of g.l.c. retention time.

The volatile part of the anolyte was found to contain (136) (1.21g) by g.l.c.

IO.H ELECTROCHEMICAL OXIDATION OF 2-N,N-DIMETHYLAMINO-1,1,1,-3,4,4,4-HEPTAFLUOROBUT-2-ENE

2-N,N-dimethylamino-1,1,1,3,4,4,4-hexafluorobut-2-ene (134-5) (4.2g, 18.7mmol, 1:1 isomer mixture) was oxidised at +2.0V in acetonitrile-T.E.A.F.. 0.0083 Faradays of charge were passed (equivalent to 0.44e/molecule of (134-5)) which turned the anolyte dark brown.

The solvent was removed from the anolyte by vacuum transference to leave a red-brown solid which was washed with

ether. Filtration, followed by removal of the solvent left
an intractable residue (0.87g). The filtrand was added to
water and extraction with dichloromethane, followed by drying
and distillation gave a red-brown oil (0.75g) which could
not be identified.

The solvent originally removed from the anolyte was
found to contain (<u>134-5</u>) (1.3g, cis:trans 60:40) by g.l.c.

CHAPTER II

EXPERIMENTAL FOR CHAPTER 6

II.A GENERAL

I. Reagents

Perfluorocyclohexene (154) was obtained from Bristol
Organics Ltd. and chloropentafluorobenzene from Imperial
Smelting Corporation Ltd.. Perfluorocyclopentene (157) and
perfluorocyclobutene were prepared by the technical staff
using literature methods.

N,N-dimethylformamide (D.M.F.) was purified by fractional
distillation under reduced pressure from anhydrous sodium
carbonate onto molecular sieve (Type 4.A), and stored under
dry nitrogen. Other solvents and electrolytes were as
described previously.

Mercury was doubly distilled. Sodium was obtained from
BDH Chemicals Ltd. and cleaned in petroleum ether (60-80°C)
prior to use.

2. Apparatus and Experimental Procedure

The electrochemical cell and instrumentation were as
described on page 129, except that the potentiostat was used
in its reduction mode. When a mercury cathode was used, the
reference electrode was directly immersed into the solvent
such that the tip was close to the cathode surface.

The solvent and supporting electrolyte solution was
degassed for at least 15mins. with dry nitrogen, and then
the substrate was added to the catholyte. For the reduction

of perfluorocyclobutene the catholyte and anolyte were
separately degassed under vacuum, with the anolyte being let
down to an atmosphere of dry nitrogen. Perfluorocyclobutene
was vacuum transferred into the catholyte and, whilst cool,
this solution was poured into the cathode compartment of the
cooled cell. Although crude, this method was considered
adequate for this preliminary investigation.

II.B ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOHEXENE

Perfluorocyclohexene (154) (4.51g, 17.21mmol) was
reduced at -1.60V in a solution of tetraethylammonium bromide
(T.E.A.B.) in D.M.F. on a mercury cathode. Perfluorocyclo-
hexene formed an insoluble layer which, by the end of the
electrolysis, had disappeared. 0.0084 Faradays of charge
were passed, which was enough to perform a 2e/molecule reduction
on 1.1g of (154).

The volatiles were removed from the catholyte by vacuum
transference to yield a D.M.F.-lower layer system. The lower
layer (0.55g) was analysed by mass spectroscopy-g.l.c. (Col.
0, 100°C) and shown to contain (i) $C_{12}F_{20}$(155) (M+, 524; 98%)
(ii) $C_{12}F_{18}$ (156) (M+ not observed, M+-19, 467; 1.8%) and
(iii) m/e 464 (0.2%)- the breakdown pattern indicated that
(iii) was not a perfluorocarbon. Comparison of the ^{19}F n.m.r.
spectrum with that of a known sample confirmed the presence
of perfluoro-(1-cyclohexyl)cyclohexene (155).

The involatile residue from the catholyte was washed

with ether, and the residue from this was then added to water which was ether extracted. The ether extracts were combined, dried (MgSO$_4$), and the solvent removed by distillation to leave a red-brown semi-solid residue (I.83g). ^{19}F n.m.r. spectroscopy of this residue indicated the presence of -CF$_2$- groups and ^{1}H n.m.r. spectroscopy indicated the presence of CH$_3$ and CH$_2$ groups. The i.r. spectrum contained numerous absorptions with, in particular, bands at I730, I670, and I6I0cm^{-1}. The absorption at I670cm^{-1} is reminiscient of the C=O in D.M.F. but none was present by g.l.c. which showed several components (Col. O, 230°C). Sublimation (0.05mmHg, 200°C) of some of this residue yielded a yellow-white solid (0.03g) on the cold finger. The i.r. spectrum of this solid was found to contain absorptions at 3400 (broad), I650, and 735 (intense)cm^{-1} with little else.

II.C ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOPENTENE

I. Reduction in D.M.F.

a. On a Mercury Cathode

Perfluorocyclopentene (<u>I57</u>) was reduced at -I.30V in a solution of T.E.A.B. in D.M.F. on a mercury cathode. Initially, I.68g of (<u>I57</u>) was present as an insoluble layer on the cathode surface and when the current was switched on a dark blue film immediately formed on the electrode surface. Over a period of about 30mins. 6.34g of (<u>I57</u>) was added and the electrolysis continued until 0.008 faradays of charge had passed, which was enough to perform a 2e/molecule reduction on 0.84g of (<u>I57</u>). This coating formed a non-conducting layer

on the electrode thus causing the electrolysis to be terminated much earlier than expected.

A 'cap' of blue material was removed from the cathode surface and dried under vacuum to leave a black fibrous solid (0.22g). Analysis found, C, 31.68; H, 2.93; N, 2.82%. Its i.r. spectrum contained numerous broad absorptions which could not be interpreted with any degree of certainty.

The residue which remained after removal of all liquid from the catholyte by vacuum transference was washed with ether, water, and acetone to leave a bronze coloured film (0.03g). No mass spectrum was obtainable and a laser raman spectrum using the green laser was unobtainable as the sample fluoresced. The ether washings were distilled at atmospheric pressure to leave a viscous tar (0.26g), which had i.r. absorptions for C—F, C—H, and C=O, and a ^{19}F n.m.r. spectrum containing resonances in the -CF$_2$- region.

The transferred liquid from the catholyte was found to have a lower layer which was found to be (157) (4.4g) by g.l.c. retention time.

b. At a Platinum Cathode

Perfluorocyclopentene (157) (6.89g, 32.5mmol) was reduced at -1.50V at a platinum cathode in D.M.F.-T.E.A.F.. The current was switched on for only a second and immediately a small quantity of blue material formed on the cathode. Over a period of a few minutes there appeared to be no growth and hence the electrolysis was continued with in the normal

manner. As the coating was non-conducting, it was necessary to periodically remove it so that a reasonable current could flow. 0.0069 Faradays of charge were passed and this was enough to perform a 2e/molecule reduction on 0.74g of (157).

The solid which had been removed from the cathode was washed with D.M.F. and ether, and dried 'in vacuo' to leave a black solid (0.34g). Analysis found, C, 42.82; H, 2.00; N, 2.14; F,44.11%. This solid was not soluble in common organic solvents and no mass spectrum was obtainable. Its i.r. spectrum was ill-defined,and the sample was found to strongly fluoresce at 514.5nm and have virtually no spectrum at 632.8nm such that no laser raman spectrum could be obtained.

Vacuum transference of all the liquid from the catholyte left a blue-black solid which was washed with dry acetonitrile and filtered to leave <0.01g of a blue-black solid. The washings were added to water and extracted with ether. The extracts were dried (MgSO$_4$) and distilled at atmospheric pressure to leave a yellow liquid (0.7g) which was found to be a multi-component mixture by g.l.c.. The liquid which had been vacuum transferred was found to have a lower layer (2.54g) which contained mainly (157) but also a minor quantity of (159) by g.l.c..

c.   Attempted Reactions of the Solid from the reduction of (157)

A small quantity of this solid was added to bromine and allowed to stand overnight; there was no apparent reaction. A sample of this solid was kept in an atmosphere of dry oxygen without any apparent reaction; addition of some water

similarly, had no apparent effect. Pyrolysis under vacuum
produced no visible change. Chlorine in carbon tetrachloride
had no visible effect and, hence, a sample was allowed to
stand in liquid chlorine, by the window, for a few weeks.
On allowing the chlorine to evaporate, a solid was isolated
whose i.r. spectrum did not contain any characteristic
C—Cl adsorptions and was similarly insoluble in common
solvents.

d.   In the presence of Perfluorocyclohexene

Perfluorocyclopentene (157) (3.66g, 17.26mmol) and
perfluorocyclohexene (154) (4.94g, 18.85mmol) were reduced
at -1.50V in D.M.F.-T.E.A.B. on a mercury cathode. The
reduction was terminated after 0.010 faradays of charge were
passed, which was enough for a 2e/molecule reduction to be
performed on 1.06g of (157). At the end of the reduction the
catholyte was red-brown in colour, but no black solid was
present.

A colourless liquid (2.95g) was transferred from the
catholyte under vacuum and without warming. Mass spectroscopy-
g.l.c. (Col. A, 40°C) indicated that this liquid contained,
(i) m/e 214 (1%), (ii) (154) (M$^+$, 262; 73%), (iii) (159)
(M-19, 405; 1%), (iv) m/e 305 (1%), (v) (158) (M$^+$, 474; 7%),
(vi) m/e 486, (vii) (155) (M$^+$, 524; 10%); fraction (i) was
tentatively assigned as 1,2-dihydrooctafluorocyclopentane
on the basis of the mass spectrum and no assignment was
possible for fractions (iv) and (vi), although the break-

down pattern of the latter indicated that it was not a perfluorocarbon. Comparison of mass spectra was made with those of known samples of (ii), (iii), (v), and (vii).

The remaining liquid was transferred from the catholyte under vacuum and with warming to give a D.M.F.-lower layer system. Mass spectroscopy-g.l.c. (Col. A, 78°C) of the lower layer (0.76g) indicated the presence of the following; (i) (154) (M+, 262; I.7%), (ii) (159) (M+, 424 (weak); I7%), (iii) (158) (M+, 474; 79%), and (iv) (155) (M+, 524; I.7%) I.r. spectroscopy and ^{19}F n.m.r. confirmed the presence of perfluoro-(I-cyclohexyl)cyclopentene (158).

The involatile residue was washed with a large quantity of ether. The washings were dried (MgSO$_4$), and the solvent removed by distillation and vacuum transference to leave a red-brown semi-solid residue (I.75g). Molecular distillation (0.05mmHg, 80°C) gave a yellow liquid (0.3Ig) which solidified on standing; however, sublimation up to 200°C was unsuccessful. The ^{19}F n.m.r. spectrum of this solid was complex, but it contained one tertiary and one olefinic fluorine such that the overall integration was equivalent to 32 fluorines. Any further identification proved impossible.

e.   In the presence of Cyclohexene

Perfluorocyclopentene (157) (3.65g, I7.22mmol) was reduced at -I.50V in the presence of cyclohexene (7.34g, 89.5 mmol) on a mercury cathode in D.M.F.-T.E.A.F.. The electro-

lysis had to be stopped sooner than intended because of fouling of the cathode by the black solid, and, therefore, only 0.003 faradays of charge were passed. This was enough charge to perform a 2e/molecule reduction on 0.7Ig of (157).

Transference of the volatiles from the catholyte, without warming, yielded a liquid (2.2Ig) which was shown by mass spectroscopy-g.l.c. (Col. 0, 122°C) to contain; (i) (157) (M^+, 212; I4.5%) and (ii) cyclohexene (M^+, 82; 85.5%). I.r. spectroscopy confirmed these assignments.

The remaining liquid from the catholyte was removed by vacuum transference to leave a blue-black residue which was washed with water and ether. The ether washings were dried ($MgSO_4$) and the solvent removed by distillation to leave a red-brown oil (0.78g). Mass spectroscopy-g.l.c. (Col. 0, II8°C) found one broad component with m/e 283 whose breakdown pattern indicated that it was not a perfluorocarbon. The ^{19}F n.m.r. spectrum was complex and could not be identified. The aqueous washings were extracted with dichloromethane, dried ($MgSO_4$), and distilled to leave a residue which contained cyclohexene (I.98g), by mass spectroscopy-g.l.c. (Col. 0, II8°C) and ^1H n.m.r..

The solid which was insoluble in either water or ether was dried to leave a black solid (0.94g), whose i.r. spectrum was poorly defined and which strongly fluoresced under the green laser.

The D.M.F. which was originally transferred did not have a lower layer and, therefore, was diluted with water

and extracted with ether. The ether extracts were dried
(MgSO$_4$) and the solvent was removed by distillation to leave
an oil containing cyclohexene (1.83g) by g.l.c.. Extraction
of the anolyte yielded a further quantity of cyclohexene
(0.5g), by mass spectroscopy-g.l.c. (Col. 0, 118°C) and ^{19}F
n.m.r. spectroscopy indicated that there was a trace of a
fluorocarbon in this sample.

f.   In the presence of Chloropentafluorobenzene

Perfluorocyclopentene (157) (6.2g, 29.3mmol) was reduced
at -1.30V in the presence of chloropentafluorobenzene (7.06g,
34.9mmol) in D.M.F.-T.E.A.F. on a mercury cathode. The
reduction produced the solid, as before, but this time it
was green in solution. The reaction was terminated after
0.0095 faradays of charge were passed, which was enough to
perform a 2e/molecule reduction on 1.01g of (157).

All the liquid was vacuum transferred from the catholyte
to leave a solid which was washed with a large quantity of
chloroform to remove the supporting electrolyte. The solid
which remained was dried under vacuum to leave a black solid
(0.27g). Analysis found, C, 42.86; H, 5.04; N, 3.03; F, 40.55
%. This solid was insoluble in common organic solvents and
no mass spectrum was obtainable. Distillation of the chloro-
form washings left a residue containing chloropentafluoro-
benzene (0.14g) by g.l.c..

The liquid which had originally transferred was trans-
ferred again but this time without the application of heat,
to give in the cold trap a liquid which was shown by g.l.c.

to contain chloropentafluorobenzene (I.4Ig), perfluoro-
cyclopentene (0.49g), and perfluorocyclopentene dimer (<u>159</u>)
(0.08g). The involatile liquid was extracted with ether,
and the ether extracts dried (MgSO$_4$) and the solvent removed
by distillation to leave a liquid containing chloropenta-
fluorobenzene (4.95g) by g.l.c. and ^{19}F n.m.r. spectroscopy.
A sample of the catholyte which was removed during the electro-
lysis was found to contain chloropentafluorobenzene (0.09g),
perfluorocyclopentene (<u>157</u>) (0.02g), and perfluorocyclo-
pentene dimer (<u>159</u>) (<0.0Ig) by g.l.c.

2. Reduction in Acetonitrile

Lithium perchlorate (9.75g) was dissolved in acetonitrile
(I70ml) and introduced into the cell. Perfluorocyclopentene
(<u>157</u>) (3.5g, I6.5mmol) was added to the catholyte. The
electrodes were platinum foil and the reference electrode
was placed in a salt bridge, i.e. as in the oxidation reactions.
The potential of the cathode was increased up to the limiting
potential of the solvent system with only background current
being observed. Therefore, the experiment was terminated
and it was found that the cathode was covered with a grey
substance which reacted with water and, presumably, was lithium.

3. Solvated Electron Reduction

Hexamethyl phosphoramide (H.M.P.A.) (I0ml) was degassed
'in vacuo' and sodium (0.20g, 8.7mmol) was added in small
pieces, under an atmosphere of nitrogen. A blue colouration
was obtained in the solution around the sodium, which itself

went black. On evacuation, effervescence was noted (although there was no apparent increase in pressure) with a concomitant increase in the blue colour. Perfluorocyclopentene (**157**) (4.3g, 20.3mmol) was allowed in over a period of 10mins., under vacuum. The blue colour immediately disappeared and was replaced by a pale brown colour which progressively darkened until after 2hrs. it was black. After 24hrs., the reaction vessel was let down to dry nitrogen and aqueous methanol was added to destroy any remaining sodium. The solution was filtered to leave a black solid (0.35g). Analysis found C, 16.03; H, 4.40; N, 5.89; F, 28.76%. Only a mass spectrum of H.M.P.A. could be obtained from this solid and the presence of this was confirmed by ^{31}P n.m.r. spectroscopy, which gave a single resonance at -24.2ppm.

II.D ELECTROCHEMICAL REDUCTION OF PERFLUOROCYCLOBUTENE

Perfluorocyclobutene (7.3g, 45.1mmol) was reduced at -1.50V at a mercury cathode in D.M.F.-T.E.A.B.. The procedure was as described on page165 and the cell was cooled to under 5°C with an ice-water bath. 0.004 Faradays of charge were passed which was enough to perform a 2e/molecule reduction on 0.32g of the fluorocarbon.

Perfluorocyclobutene (0.34g) was recovered from the catholyte by vacuum transference without warming. Transference of the remaining liquid gave only D.M.F. with no lower layer. The involatile residue was washed with chloroform to remove the supporting electrolyte to leave a black solid (0.05g) which was not investigated.

CHAPTER 12

EXPERIMENTAL FOR CHAPTER 7

12.A GENERAL

1. Reagents

2,3-Dichlorohexafluorobut-2-ene (169) was available in this laboratory and hexafluorobut-2-yne (143) was obtained from Bristol Organics Ltd.. Other reagents, solvents, and supporting electrolytes have been previously described.

2. Apparatus and Experimental Procedure

The electrochemical cell and instrumentation was described on page129, with the potentiostat being used in its reduction mode.

The attempted electrochemical reduction of hexafluoro-but-2-yne was carried out using a modified procedure. The cell and its contents were cooled to around -30°C, using an acetone-carbon dioxide bath, and hexafluorobut-2-yne was condensed into the cathode compartment from a variable reservoir arrangement. The majority of the gas condensed and formed a mobile lower layer.

12.B ELECTROCHEMICAL REDUCTION OF 2,3-DICHLORO-1,1,1,4,4,4-HEXAFLUOROBUT-2-ENE

1. At -1.20V and with tetraethylammonium bromide as electrolyte

2,3-Dichloro-1,1,1,4,4,4,-hexafluorobut-2-ene (169) (7.5g, 32.3mmol) was reduced at -1.20V in D.M.F. and tetra-ethylammonium bromide (T.E.A.B.), on a mercury cathode. The catholyte was pale yellow after a few minutes but towards the end of the electrolysis was red-brown. The electrolysis

was stopped after 0.0I90 faradays of charge had passed, which was enough to perform a 2e/molecule reduction on 2.2g of (169).

Transference of volatiles under vacuum, without warming, from the catholyte gave a colourless liquid (2.39g) in the cold trap. Mass spectroscopy-g.l.c. (Col. A, 84°C) showed this liquid to be a mixture of (169) (M^+, 232; 99%) and a component with m/e 394. On the basis of the high mass and breakdown pattern, this latter component was deduced to be $C_8Cl_2F_{12}$ (170) (I%).

All the remaining liquid was removed from the catholyte to leave a solid which was washed with ether and water. A yellow solid did not dissolve in either solvent and this was dried to leave a yellow powder (I.09g) identified as poly-(hexafluorobut-2-yne), (Found: C, 29.42; H, I.67; N, I.37: F, 40.6I%. Calc. for $(C_4F_6)_n$: C, 29.63; F, 70.37%), i.r. spectrum no. I9.

The ether washings were combined, dried ($MgSO_4$), and the solvent removed by distillation to leave an intractable residue (0.I5g). Reduced pressure distillation of the transferred D.M.F. gave (169) (I.3Ig), which was identified by g.l.c. retention time and ^{I9}F n.m.r. spectroscopy.

2. Control Experiment

2,3-Dichloro-I,I,I,4,4,4-hexafluorobut-2-ene (169) (I.5g, 6.47mmol) was stirred for 48hrs. in D.M.F. (I0ml) and T.E.A.B. (0.3g, I.43mmol). No reaction occurred.

3. <u>At -I.00V and with tetraethylammonium fluoroborate as</u>
   <u>electrolyte</u>

2,3-Dichloro-I,I,I,4,4,4-hexafluorobut-2-ene (<u>I69</u>)
(8.42g, 36.29mmol) was reduced at -I.00V in D.M.F. and tetra-
ethylammonium fluoroborate on a mercury cathode. The reduction
was terminated after 0.0I50 faradays of charge were passed,
which was enough to perform a 2e/molecule reduction on I.74g
of (<u>I69</u>).

Vacuum transference of the volatiles from the catholyte
gave (<u>I69</u>) (7.39g) which was identified by g.l.c retention
time and ^{19}F n.m.r. spectroscopy. Filtration of the involatile
material, with washing (water and ether), gave a yellow-
white solid (0.I9g) identified as poly(hexafluorobut-2-yne),
(Found: C, 30.33; H, 0.80; N, I.34; F, 62.I6%. Calc. for
$(C_4F_6)_n$: C, 29.63; F, 70.37%). Intractable material (0.I5g)
was isolated from ether washings.

I2.C <u>REDUCTION OF HEXAFLUOROBUT-2-YNE</u>

I. <u>Attempted Electrochemical Reduction of Hexafluorobut-2-yne</u>

Lithium perchlorate (8.5g) was dissolved in D.M.F. (I70
ml) and the solution was poured into the cooled cell. As
described in section I2.A.2., hexafluorobut-2-yne (<u>I43</u>) (9g,
56mmol) was transferred into the catholyte. The potential of
the platinum cathode was increased up to the breakdown
potential (ca. -3.2V) of the solvent system, with only the
background current being noted. The cell was allowed to warm
up to ca. -I.0°C where-upon gas started leaking from the cell,

but once again no reduction was observed when the potential was increased. The potential of the cathode was kept around the breakdown potential for about 5mins., but no reaction appeared to be occurring and, therefore, the electrolysis was stopped.

Volatiles were transferred out of the cathode compartment, and then vacuum transferred to give hexafluorobut-2-yne (143) (6g, 67% recovery) identified by i.r. spectroscopy.

2. **Reaction with T.E.A.B.**

T.E.A.B. (1.05g, 5mmol) was dissolved in D.M.F. (15ml) and hexafluorobut-2-yne (143) (2.9g, 17.9mmol) was allowed in under vacuum. The colourless solution was stirred at room temperature; after a few minutes, the solution became yellow and, after a few hours, very viscous. After 16hrs. volatiles (0.49g) were recovered by vacuum transference and water was added to the involatile residue. Filtration, followed by washing with ether and drying 'in vacuo' left a white solid (1.91g) whose i.r. spectrum was the same as that of poly(hexafluorobut-2-yne).

3. **Solvated Electron Reduction**

a. **Solvated Electron Reduction of Hexafluorobut-2-yne**

Sodium (0.27g, 11.74mmol) was added to hexamethyl phosphoramide (H.M.P.A.) (10ml) under an atmosphere of dry nitrogen. The sodium immediately went black and some of the solvent surrounding it went blue. After allowing the mixture to stand for 45mins. hexafluorobut-2-yne (143) (0.72g, 4.44 mmol) was allowed in in small amounts under vacuum. The blue

colour immediately disappeared to be replaced by an orange colour, with pieces of black sodium still present in the liquid. On the surface of the liquid there was a clear film which increased in quantity on further addition of (143), and it was found that when the flask was swirled, the film collected into a bright red ball. A sample of this gelatinous material was removed and shown by ^{31}P n.m.r. spectroscopy that it contained only physically bound H.M.P.A. (-24.2ppm). Addition of water to this sample did not immediately remove the red colour, although eventually it went colourless.

Water was added to the bulk sample and filtered to leave a solid which was washed with ether and dried 'in vacuo' to give a yellow solid (0.50g) identified as poly(hexafluoro-but-2-yne), (Found: C, 29.35; F, 70.92%. Calc. for $(C_4F_6)_n$: C, 29.63; F, 70.37%).

b. **Control Experiment**

H.M.P.A. (10ml) was repeatedly degassed 'in vacuo' and then hexafluorobut-2-yne (143) (0.21g, 1.3mmol) was transferred in under vacuum. The reaction mixture was stirred at room temperature, however, the solution only turned pale yellow. After 96hrs., the solution was diluted with water, ether extracted and the ethereal extracts dried (MgSO$_4$). The solvent was removed, leaving <0.01g of a yellow oil which was not investigated further.

APPENDICES

APPENDIX I

N.M.R. SPECTRA

1) 2,2',3,3',6,6'-hexafluoro-4,4'-dimethoxybiphenyl (71)

2) 1,2-dibromo-3,6-difluoro-4,5-dimethoxybenzene (81)

3) 1,2-bis(N-methyl-2,3,5,6-tetrafluoroanilino)-ethane (92)

4) Perfluoro-4-(3'-phenoxyphenoxy)-2,5-cyclohexadienone (105)

5) 2,3,5,6-tetrafluore-6-(2',3',5',6'-tetrafluorophenoxy)-2,4-cyclohexadien-1-one (112)

6) Syn and anti 2-ethylimino-1,1,1,3,4,4,4-heptafluoro-butane (124)

7) Syn and anti 2-methylimino-1,1,1,3,4,4,4-heptafluoro-butane (127)

8) 2-N,N-diethylamino-1,1,1,3,4,4,4-heptafluorobut-2-ene (128)

9) 2,3-bis(N,N-diethylamino)-1,1,1,4,4,4-hexafluorobut-2-ene (133)

10) Cis-2-N,N-dimethylamino-1,1,1,3,4,4,4-heptafluoro-but-2-ene (134)

11) Trans-2-N,N-dimethylamino-1,1,1,3,4,4,4-heptafluoro-but-2-ene (135)

12) 2-ethylimino-1,1,1,4,4,4-hexafluorobutane (137)

13) 2-methylimino-1,1,1,4,4,4-hexafluorobutane (138)

14) Cis-2-bromo-3-N,N-dimethylamino-1,1,1,4,4,4-hexafluoro-but-2-ene (140)

15) <u>Trans</u>-2-bromo-3-N,N-dimethylamino-1,1,1,4,4,4-hexa-
fluorobut-2-ene (<u>141</u>)

16) 2,5-bis(N,N-diethylamino)-3,4-bis(trifluoromethyl)-
1,1,1,6,6,6-hexafluorohexa-2,4-diene (<u>151</u>)

17) 2,5-bis(N,N-dimethylamino)-3,4-bis(trifluoromethyl)-
1,1,1,6,6,6-hexafluorohexa-2,4-diene (<u>153</u>)

The following abbreviations are used in this appendix:
S, singlet; D, doublet; T, triplet; Q, quartet; P, pentet;
M, multiplet.

Unless otherwise stated spectra were recorded using
neat liquids.

For ^{1}H spectra downfield shifts are quoted as positive
(delta scale), whilst for ^{19}F spectra, upfield shifts are
quoted as positive.

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment

I. <u>2,2',3,3',6,6'-hexafluoro-4,4'-dimethoxybiphenyl</u> (<u>7I</u>)

$\underline{19}_F$

II2.9	M	I	a
I34	M	I	b
I62.9	M	I	c

$\underline{I}_H$

4.2	Broad S	3	d
7.I3	M	I	e

Recorded as a solution in acetonitrile.

(<u>7I</u>)   (<u>8I</u>)

2. <u>I,2-dibromo-3,6-difluoro-4,5-dimethoxybenzene</u> (<u>8I</u>)

$\underline{19}_F$

I2I.4	S	-	a

$\underline{I}_H$
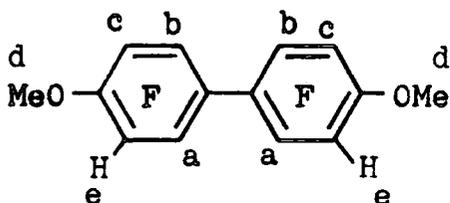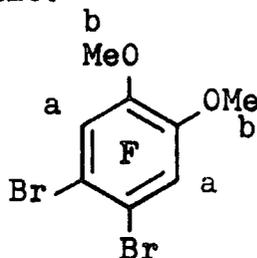
4.I6	S	-	b

Recorded as a solution in ether.

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment
3. I,2-bis(N-methyl-2,3,5,6-tetrafluoroanilino)-ethane (92)			
19F			
I40.I	P, J = I0	I	a
I50.7	M	I	b
1H			
3.28	Broad	3	c
3.7	Broad	2	d
7.0	M	I	e

Recorded in $CDCl_3$.

(92)   (I05)

4. Perfluoro-4-(3'-phenoxyphenoxy)-2,5-cyclohexadienone (I05)

19F
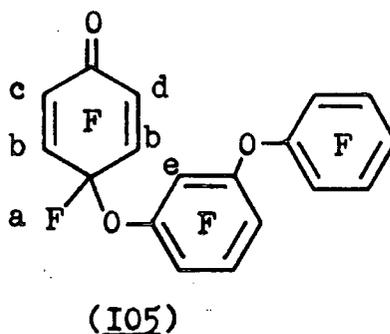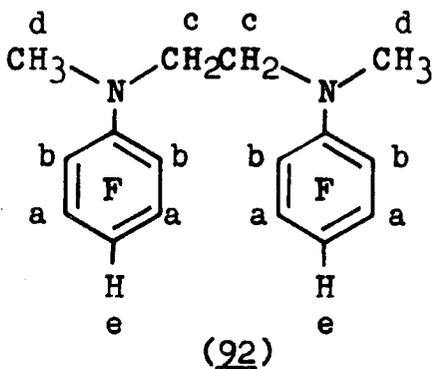
Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment
I24.2	M	I	a
I40.8	Distorted D,		
	J = 23.5	2	b
ca. I5I		3	c,d,e

Signals from I52-I6Ip.p.m. (relative intensity 8) were unassigned.

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment
5. 2,3,5,6-tetrafluoro-6-(2',3',5',6'-tetrafluorophenoxy)- 2,4-cyclohexadien-I-one (II2)			
^{19}F			
II2.9	M	I	a
II4.9	T, $J_{be}= J_{bc}=$ 22.5; D, $J_{bg}=$ 8.5; D, $J_{ba}= 5$	I	b
I27.7	M	I	c
I40.2	P, J = 9.9 of M	2	d
I53.8	M	I	e
I64	M	2	f
^{I}H			
6.3	Broad M	-	g, h

Recorded in a CDCl$_3$ solution.

(II2)
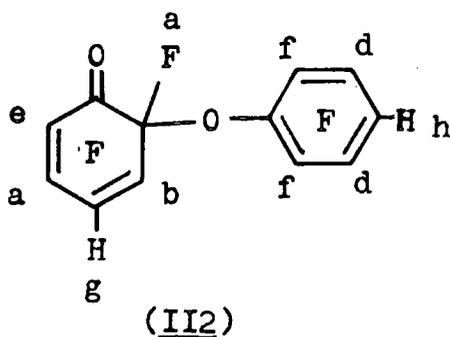
Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment

6. syn and anti 2-ethylimino-I,I,I,3,4,4,4-heptafluoro-butane (I24)

$\underline{^{19}F}$

(a)

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment
72.4	Broad	3	a
77.2	Broad	3	b
208.8	D, J_{cf}= 46	I	c

(b)

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment
66.7	Broad	3	a
78.I	Broad	3	b
203.4	D, J_{cf}= 46	I	c

$\underline{^{1}H}$

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment
I.33	T, J_{de}= 7	3	d
3.84	Q, J_{ed}= 7	2	e
5.49	D, J_{fc}= 46 of Q, J_{fb}= 7	I	f

$$\underset{a}{CF_3}\overset{b\quad fc}{CF_3CHF}\diagdown C\!=\!N\!-\!\overset{e\quad d}{CH_2CH_3}$$

(I24)
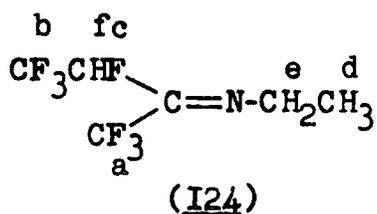
Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment

7. **syn and anti 2-methylimino-I,I,I,3,4,4,4-heptafluoro-butane (127)**

^{19}F

(a)

67.2	M	3	a
78.4	M	3	b
203.4	D, J_{ce}= 44	I	c

(b)

72.5	Broad	3	a
77.3	M	3	b
2I0.3	D, J_{ce} = 44	I	c

^{I}H

3.62	S	3	d
5.52	D, J_{ec} = 44 of		
	Q, J_{eb}= 7	I	e

$$\underset{b}{CF_3}\underset{ec}{CHF} \diagdown \underset{a}{CF_3} \diagup C{=}N{-}\underset{d}{CH_3}$$
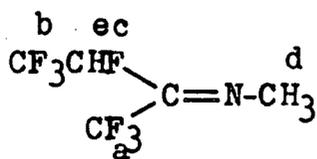
(127)

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment

8. 2-N,N-diethylamino-I,I,I,3,4,4,4,-heptafluorobut-2-ene (I28)

^{19}F

62.5	M	3	a
66.I	M	3	b
I33.I	M	I	c

^{I}H

| I.52 | T, J_{de}= 7 | 3 | d |
| 3.53 | Q, J_{ed}= 7 | 2 | e |

$$\underset{c}{\overset{b}{CF_3}}\overset{F}{\underset{}{}}C=C\overset{CF_3\,a}{\underset{e\quad d}{N(CH_2CH_3)_2}}$$

(I28)

$$\underset{b\quad c}{(CH_3CH_2)_2N}\overset{a}{\underset{}{CF_3}}C=C\overset{N(CH_2CH_3)_2}{\underset{a}{CF_3}}$$

(I33)

9. 2,3-bis(N,N-diethylamino)-I,I,I,4,4,4-hexafluorobut-2-ene (I33)

^{19}F

| 76.97 | S | - | a |

^{I}H
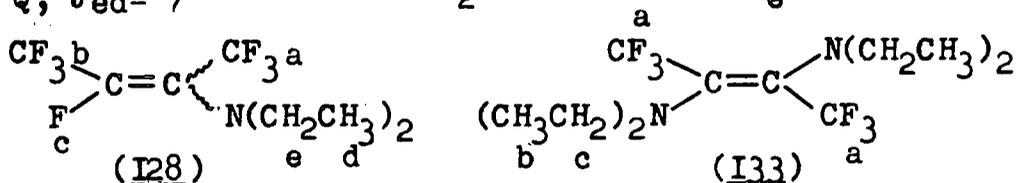
| I.I9 | T, J_{bc}= 7 | 3 | b |
| 2.94 | Q, J_{cb}= 7 | 2 | c |

IO. Cis-2-N,N-dimethylamino-I,I,I,3,4,4,4-heptafluorobut-2-ene (I34)

^{19}F

| 63.6 | M | 3 | a |

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment
10. cont.			
67.3	M	3	b
138.7	Broad	1	c
^1H			
2.68	S		d
2.74	S	-	

(134)   (135)

11. Trans-2-N,N-dimethylamino-1,1,1,3,4,4,4-heptafluoro-but-2-ene (135)

^{19}F			
66.2	D, J_{ac} = 23	3	a
69.8	D, J_{bc} = 6	3	b
131.7	D, J_{cb} = 6 of		
	Q, J_{ca} = 23	1	c
^1H			
2.66	S	-	d

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment

I2. <u>2-ethylimino-I,I,I,4,4,4-hexafluorobutane</u> (<u>I37</u>)

$\underline{I9_F}$

63.7	Broad	I	a
74.2	Broad	I	b

$\underline{I_H}$

0.87	T, $J_{ce}= 7$	3	c
2.88	Q, $J_{db}= I0$	2	d
3.I8	Q, $J_{ec}= 7$	2	e

(<u>I37</u>)   (<u>I38</u>)

I3. <u>2-methylimino-I,I,I,4,4,4-hexafluorobutane</u> (<u>I38</u>)

$\underline{I9_F}$

63.2	Broad M	3	a
74.I	M	3	b

$\underline{I_H}$

2.92	Q, $J_{db}= I0$	2	d
3.0	S	3	c

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment

I4. <u>Cis-2-bromo-3-N,N-dimethylamino-I,I,I,4,4,4-hexafluoro-</u> <u>but-2-ene</u> (I40)

$\underline{^{19}F}$

57.5	Q, J_{ab}= I3.8	I	a
60.8	Q, J_{ba}= I3.8	I	b

$\underline{^{1}H}$

2.53	S	‒	c

$$\underset{b}{CF_3}\diagdown \underset{Br}{}C{=}C\diagup \underset{a}{CF_3} \quad N(CH_3)_2 \underset{c}{}$$

(I40)

$$\underset{b}{CF_3}\diagdown \underset{Br}{}C{=}C\diagup \underset{c}{N(CH_3)_2} \quad \underset{a}{CF_3}$$

(I4I)
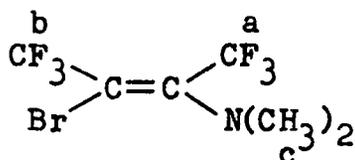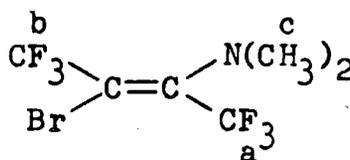
I5. <u>Trans-2-bromo-3-N,N-dimethylamino-I,I,I,4,4,4-hexa-</u> <u>fluorobut-2-ene</u> (I4I)

$\underline{^{19}F}$

62.I	S	I	a
62.9	S	I	b

$\underline{^{1}H}$

2.07	S	-	c

Spectrum recorded as a mixture of (<u>I40</u>) and (<u>I4I</u>).

Shift p.p.m.	Fine structure J values in Hz	Relative Intensity	Assignment

16. **2,5-bis(N,N-diethylamino)-3,4-bis(trifluoromethyl)-1,1,1,6,6,6-hexafluorohexa-2,4-diene (151)**

^{19}F

56.6		⎤	
58.4		Overlapping	a, b
60.0	Broad S	Resonances	c, d
60.6	Broad S	⎦	

^{1}H

0.55	Broad T, $J_{ef}= 7$	3	e
2.47	Broad Q, $J_{fe}= 7$	2	f
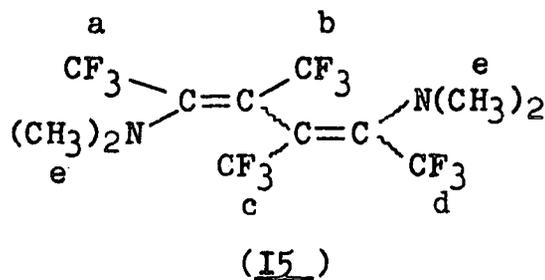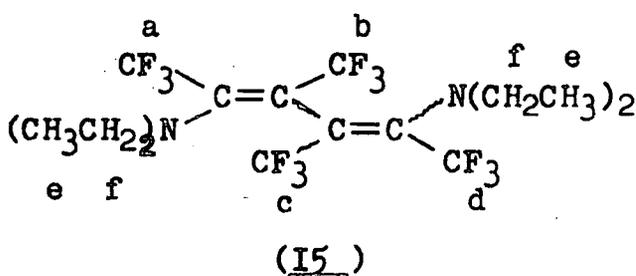
(15)   (15)

17. **2,5-bis(N,N-dimethylamino)-3,4-bis(trifluoromethyl)-1,1,1,6,6,6-hexafluorohexa-2,4-diene (153)**

^{19}F

55-65	Broad M	-	a, b
			c, d

^{1}H

2.3	Broad	-	e

APPENDIX II

INFRARED SPECTRA

1) 2,2',3,3',6,6'-hexafluoro-4,4'-dimethoxybiphenyl (<u>71</u>)

2) 1,2-dibromo-3,6-difluoro-4,5-dimethoxybenzene (<u>81</u>)

3) 1,2-bis(N-methyl-2,3,5,6-tetrafluoroanilino)-ethane (<u>92</u>)

4) Trifluoro(pentafluorophenoxy)-1,4-benzoquinone(<u>104</u>)

5) 2,3,5,6 -tetrafluoro-6-(2',3',5',6'-tetrafluoro-phenoxy)-2,4-cyclohexadien-1-one (<u>112</u>)

6) 2-ethylimino-1,1,1,3,4,4,4-heptafluorobutane (<u>124</u>)

7) 2-methylimino-1,1,1,3,4,4,4-heptafluorobutane (<u>127</u>)

8) 2-N,N-diethylamino-1,1,1,3,4,4,4-heptafluorobut-2-ene (<u>128</u>)

9) 2,3-bis(N,N-diethylamino)-1,1,1,4,4,4-hexafluorobut-2-ene (<u>133</u>)

10) <u>Cis</u>-2-N,N-dimethylamino-1,1,1,3,4,4,4-heptafluorobut-2-ene (<u>134</u>)

11) <u>Trans</u>-2-N,N-dimethylamino-1,1,1,3,4,4,4-hexafluoro-but-2-ene (<u>135</u>)

12) 2-ethylimino-1,1,1,4,4,4-hexafluorobutane (<u>137</u>)

13) 2-methylimino-1,1,1,4,4,4-hexafluorobutane (<u>138</u>)

14) 2H-3-N,N-diethylamino-1,1,1,4,4,4-hexafluorobut-2-ene (<u>139</u>)

15) 2H-3-N,N-dimethylamino-1,1,1,4,4,4-hexafluorobut-2-ene (<u>136</u>)

16) 2-bromo-3-N,N-dimethylamino-1,1,1,4,4,4-hexafluorobut-2-ene (<u>140</u>) and (<u>141</u>)

I7) 2,5-bis(N,N-diethylamino)-3,4-bis(trifluoromethyl)-I,I,-I,6,6,6-hexafluorohexa-2,4-diene (<u>I5I</u>)

I8) 2,5-bis(N,N-dimethylamino)-3,4-bis(trifluoromethyl)-I,-I,I,6,6,6-hexafluorohexa-2,4-diene (<u>I53</u>)

I9) Poly(hexafluorobut-2-yne) (prepared by the electrochemical reduction of (<u>I69</u>))
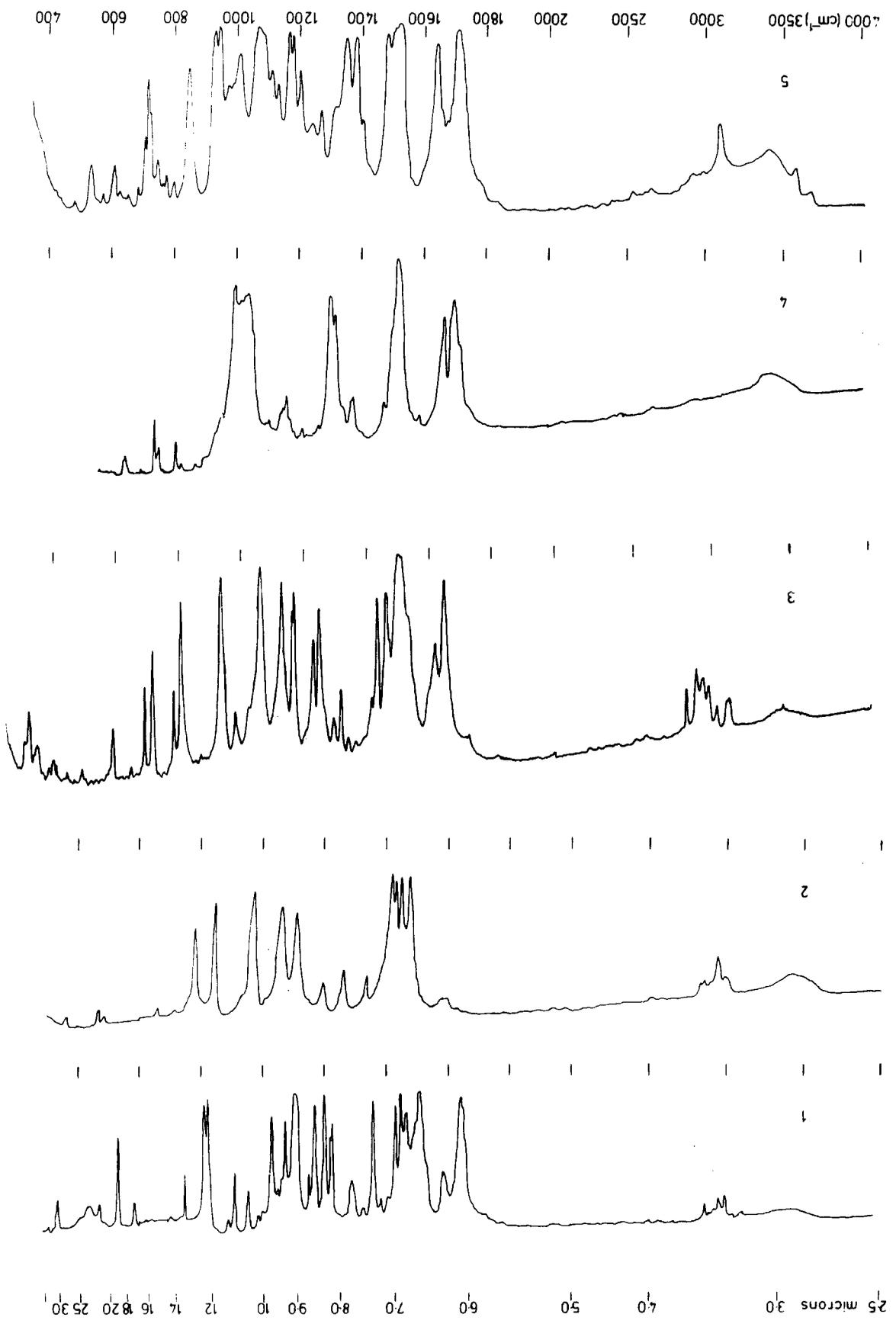
25 microns 3·0   4·0   5·0   6·0   7·0   8·0   9·0   10   12   14   16 18 20 25 30

6

7

8

9

10
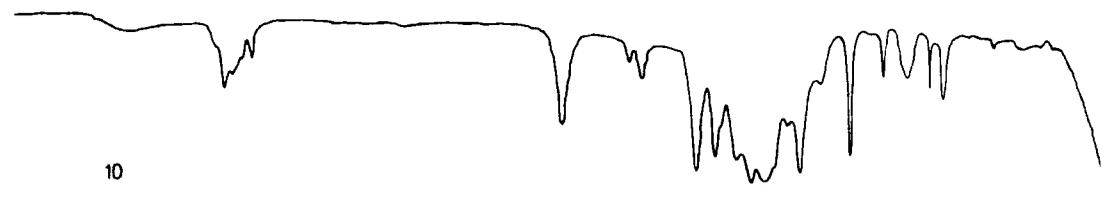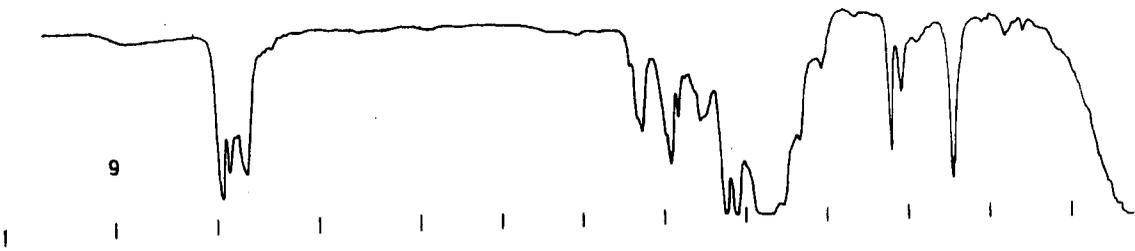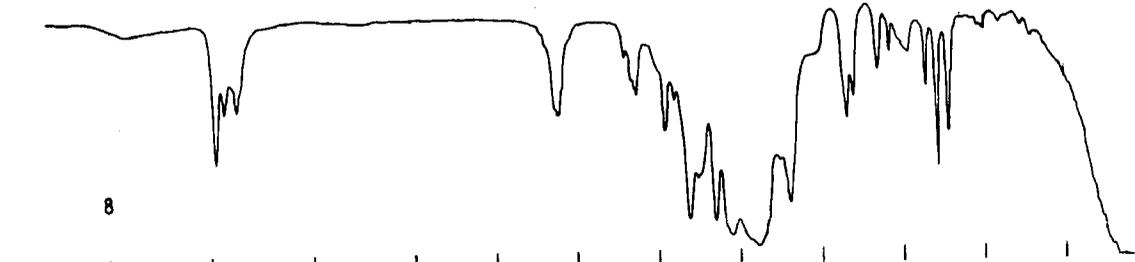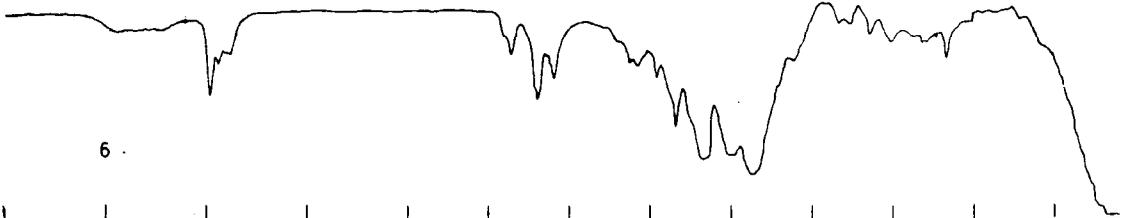
4000 (cm⁻¹) 3500   3000   2500   2000   1800   1600   1400   1200   1000   800   600   400
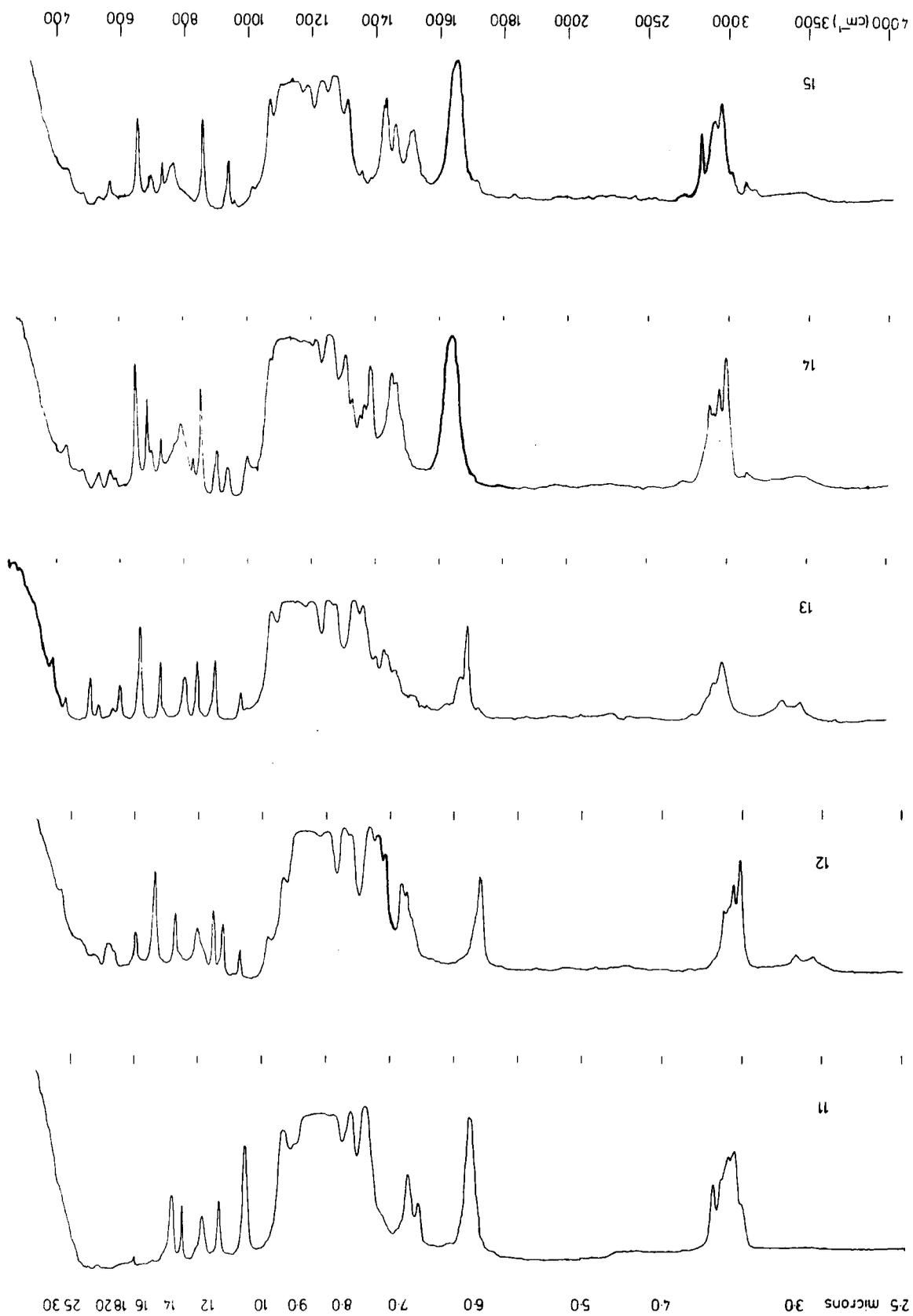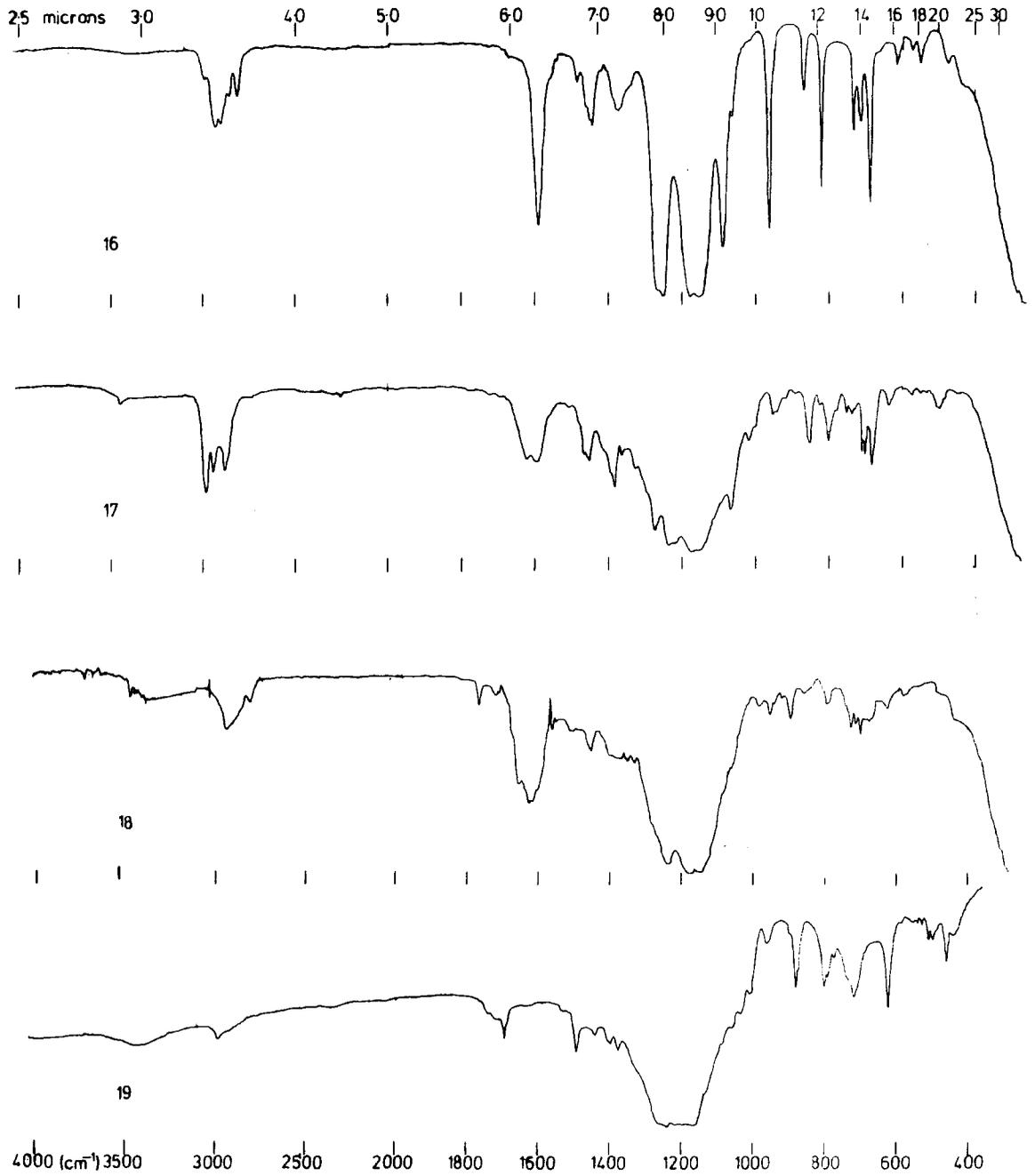
APPENDIX III

MASS SPECTRA

I) I,2=dibromo=3,6=difluoro=4,5=dimethoxybenzene (8I)

2) 2-ethylimino-I,I,I,3,4,4,4=heptafluorobutane (I24)

3) 2-methylimino=I,I,I,3,4,4,4=heptafluorobutane (I27)

4) 2-N,N-diethylamino-I,I,I,3,4,4,4=heptafluorobut=2=ene (I28)

5) 2,3-bis(N,N-diethylamino)-I,I,I,4,4,4=hexafluorobut=2=ene (I33)

6) Cis-2-N,N-dimethylamino=I,I,I,3,4,4,4-heptafluorobut=2=ene (I34)

7) Trans-2-N,N-dimethylamino-I,I,I,3,4,4,4-heptafluorobut=2=ene (I35)

8) 2-ethylimino-I,I,I,4,4,4-hexafluorobutane (I37)

9) 2=methylimino-I,I,I,4,4,4-hexafluorobutane (I38)

I0) 2-bromo-3-N,N=dimethylamino-I,I,I,4,4,4-hexafluorobut=2-ene (I40)

II) 2,3-bis(N,N-dimethylamino)-I,I,I,4,4,4-hexafluorobut=2-ene (I42)

I2) 2,5-bis(N,N-diethylamino)-3,4-bis(trifluoromethyl)-I,I,I,6,6,6-hexafluorohexa-2,4=diene (I5I)

I3) 2,5-bis(N,N-dimethylamino)=3,4-bis(trifluoromethyl)=I,I,I,6,6,6-hexafluorohexa=2,4=diene (I53)

MJS21B 18   No.2 x 3

PEAK NO.	MASS	% INT BASE			
1	26.31	2.00			
2	27.25	19.59			
3	28.14	21.38			
4	29.02	100.00			
5	29.86	2.16			
7	32.01	3.19			
8	33.12	4.69	64	140.92	2.39
12	42.05	2.66	65	141.95	1.33
15	46.12	3.09	67	153.96	3.59
16	47.10	4.19	68	154.99	2.00
17	50.91	2.13	69	155.97	46.39
23	58.98	1.96	70	156.98	2.83
26	68.95	8.98	71	157.92	2.00
29	72.01	2.23	72	159.89	5.49
37	86.04	1.36	74	177.93	1.83
39	89.98	2.16	77	205.94	2.10
44	95.99	7.45	78	206.94	0.30
49	107.93	1.83	79	208.87	0.43
50	108.91	1.76	80	209.85	17.29
57	123.98	16.26	81	210.90	1.03
60	127.92	66.48	82	223.97	3.53
61	128.90	2.53	83	224.99	2.16
63	139.84	10.08	84	225.99	0.67

MJS20A 13 　　　No.3　　　X 10
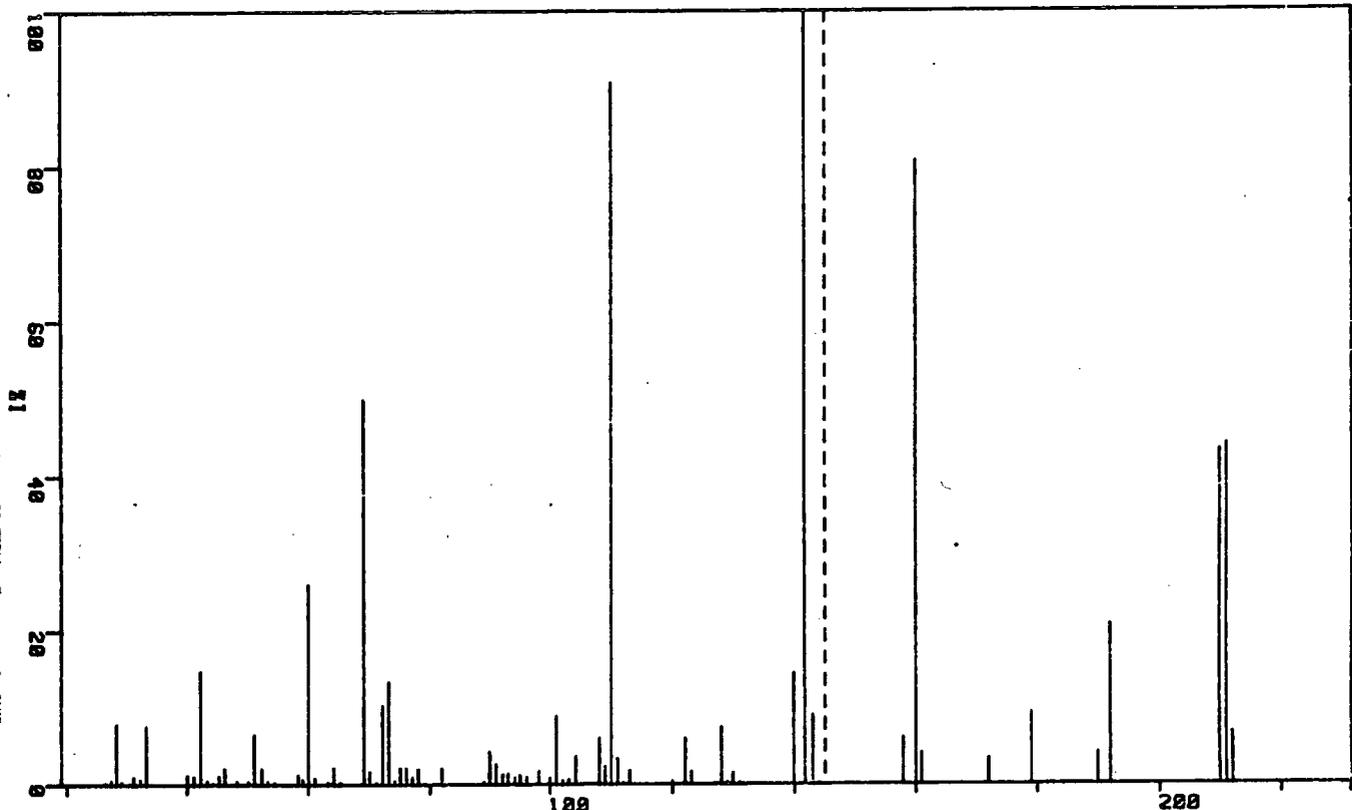
PEAK NO.	MASS	% INT BASE			
3	28.14	7.91			
7	33.12	7.64			
10	42.05	14.80			
14	46.13	2.10			
17	50.92	6.54			
18	52.01	2.03			
23	59.90	25.93			
26	64.08	2.22			
28	68.94	49.96			
31	72.01	10.38			
32	73.05	13.36			
34	75.04	2.17			
35	76.03	2.15			
39	81.96	2.17			
41	89.88	4.32	65	127.95	7.45
42	90.95	2.61	69	139.87	14.51#
50	100.93	8.89	70	141.55	100.00#
53	104.04	3.61	71	142.90	9.04#
55	107.97	6.06	74	159.91	8.13
56	108.94	2.37	79	191.92	2.10
57	109.91	90.77	80	209.83	4.37
58	110.94	3.39	81	210.90	4.44
62	121.97	5.98	82	211.93	0.71

MJS291 29

No. 4

PEAK NO.	MASS	% INT BASE
1	27.16	14.12
2	28.05	14.12
3	28.95	100.00
4	29.79	2.42
5	31.93	2.14
7	40.93	1.01
8	42.03	5.12
10	47.10	2.48
11	50.93	1.18
13	56.12	2.76
16	68.96	3.10
17	69.95	2.70
18	71.01	3.38
22	95.03	1.97
23	96.03	1.13
24	107.97	2.53
26	112.96	1.29
29	124.02	3.15
30	126.98	1.97
31	127.96	4.00
33	135.98	1.13
34	139.88	6.70
36	154.02	1.52
38	156.03	6.08
39	157.96	1.74
41	171.95	0.96
42	177.95	1.97
43	184.02	5.35
45	185.90	2.53
46	189.89	18.85
47	190.95	1.29
48	203.96	4.78
49	205.98	5.85
50	207.01	0.51
51	207.95	3.10
52	208.90	1.41
53	209.92	37.70
54	210.96	2.14
55	221.96	1.63
56	223.99	6.08
57	225.03	0.73
58	234.03	4.22
59	235.96	0.51
60	237.96	48.62
61	238.97	4.00
62	251.94	1.58
63	252.97	15.03
64	254.01	1.18

MJS179 42
CAL:CA

No.5

MJS282 28   No.6 x 2

PEAK NO.	MASS	% INT BASE
1	27.16	1.85
2	28.05	20.62
3	28.95	28.55
4	31.94	3.61
5	33.05	7.58
6	40.94	2.38
7	42.03	47.93
8	43.10	10.31
9	44.15	1.23
10	46.13	0.79
11	47.10	0.70
12	50.93	5.02
13	58.98	0.79
14	59.90	7.49
15	65.10	0.79
16	68.96	16.83
17	72.03	1.65
18	77.06	1.67
19	78.02	1.94
20	86.08	3.26
24	95.04	3.79
25	96.04	1.76
26	99.91	3.44
27	104.06	1.85
28	106.05	1.85
29	108.96	1.32
30	109.92	21.76
31	113.00	1.67
32	122.01	5.64
33	127.02	1.50
34	127.99	3.61
35	130.93	0.88
36	136.04	2.73
37	139.92	7.58
38	140.95	24.23
39	141.98	1.32
40	145.01	1.67
41	154.03	1.94
42	156.02	100.00
43	157.03	5.81
44	157.97	3.17
45	159.92	2.64
46	171.98	0.97
47	174.02	2.38
48	205.97	19.47
49	206.97	1.32
50	207.91	2.20
51	209.91	1.50
52	221.96	0.97
53	223.96	16.8:
54	224.98	35.1:
55	225.98	2.3:

MJS281 20　　　　　　No.7　x 2
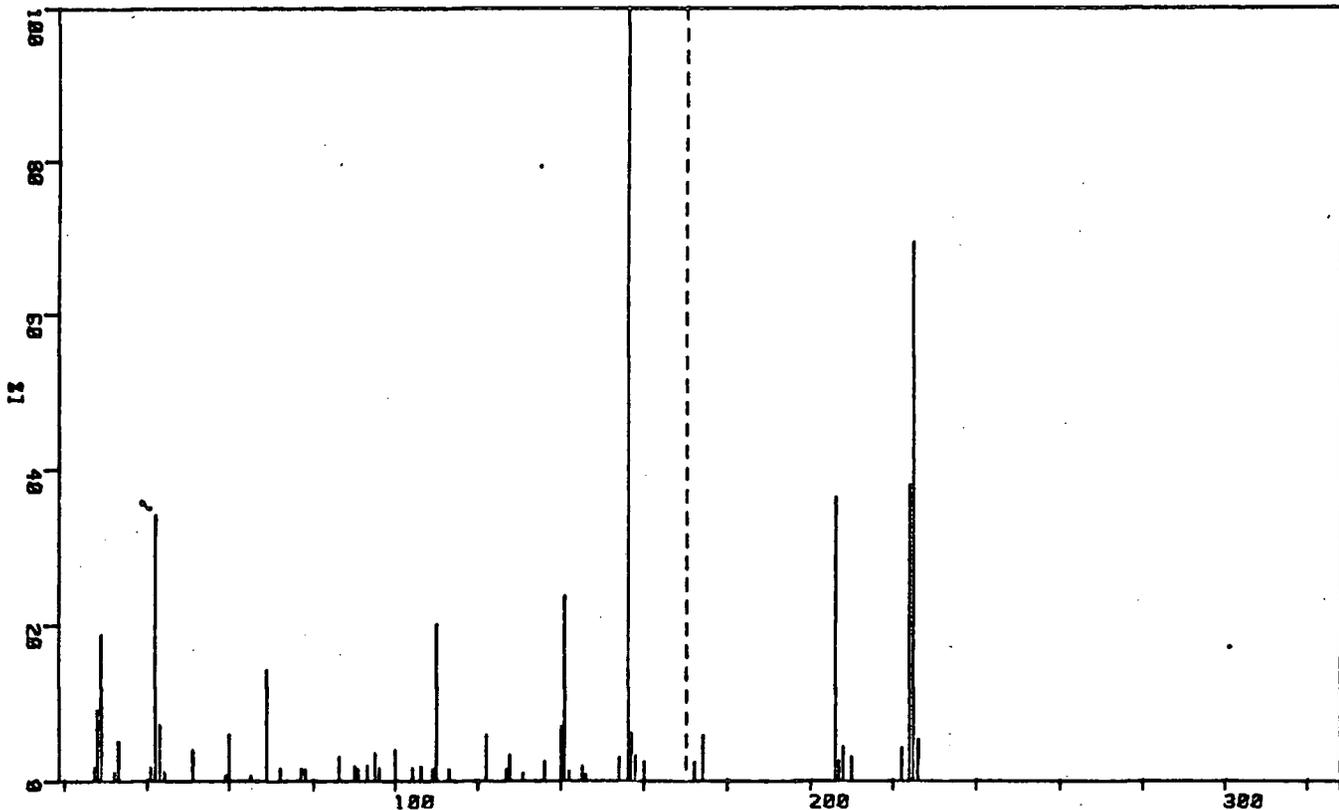
PEAK NO.	MASS	% INT BASE
1	27.17	1.65
2	28.05	8.96
3	28.95	18.71
4	31.93	1.13
5	33.05	4.96
6	40.94	1.74
7	42.03	34.03
8	43.10	7.14
9	44.15	1.13
10	50.93	3.83
11	58.98	0.70
12	59.90	5.92
13	65.09	0.70
14	68.96	14.19
15	72.04	1.57
16	77.06	1.57
17	78.02	1.48
18	86.08	3.05
19	89.92	1.83
20	90.97	1.48
21	93.01	1.91
22	95.04	3.48
23	96.04	1.65

PEAK NO.	MASS	% INT BASE
24	99.91	3.83
25	104.07	1.57
26	106.05	1.74
27	108.96	1.48
28	109.92	20.10
29	113.00	1.48
30	122.00	5.74
31	127.03	1.48
32	127.99	3.22
33	130.95	0.96
34	136.04	2.44
35	139.91	6.88
36	140.94	23.59
37	141.98	1.31
38	144.99	1.83
39	145.98	0.78

PEAK NO.	MASS	% INT BASE
40	154.01	2.87
41	156.02	100.00
42	157.01	6.09
43	157.95	3.22
44	159.93	2.52
45	171.98	1.22
46	174.02	2.87
47	205.97	18.19
48	206.98	1.31
49	207.93	2.18
50	209.90	1.48
51	221.96	2.09
52	223.87	18.97
53	224.85	34.73
54	226.03	2.61

MJS115 6　　　　　No. 8　　　　x 4
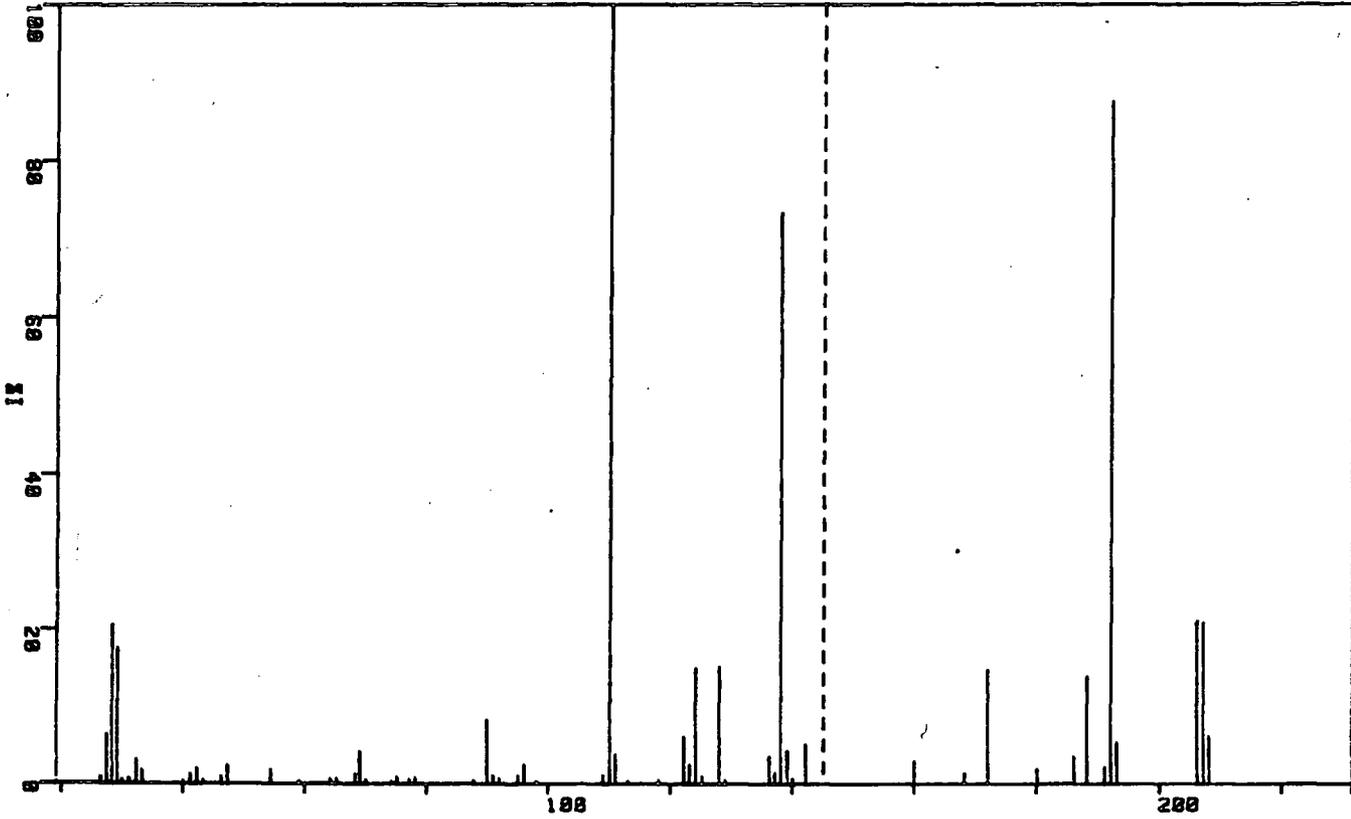
PEAK NO.	MASS	% INT BASE
2	27.23	6.46
3	28.12	20.52
4	29.01	17.56
7	32.01	3.18
11	42.07	1.99
14	47.12	2.34
20	68.99	4.20
27	89.95	8.31
31	96.07	2.57
34	109.96	100.00
35	111.01	3.80
38	122.03	6.24
39	123.06	2.57
40	124.08	14.95
42	128.03	15.17
44	136.09	3.54
46	138.06	73.37
47	139.05	4.33
49	142.04	5.17
52	172.04	3.72
55	188.07	3.49

PEAK NO.	MASS	% INT BASE
57	192.03	21.89
59	206.07	5.31
60	207.08	5.26
61	208.07	1.55

MJ1191 B M.J.SILVESTER   No.9   28-APR-
CAL: CALM23
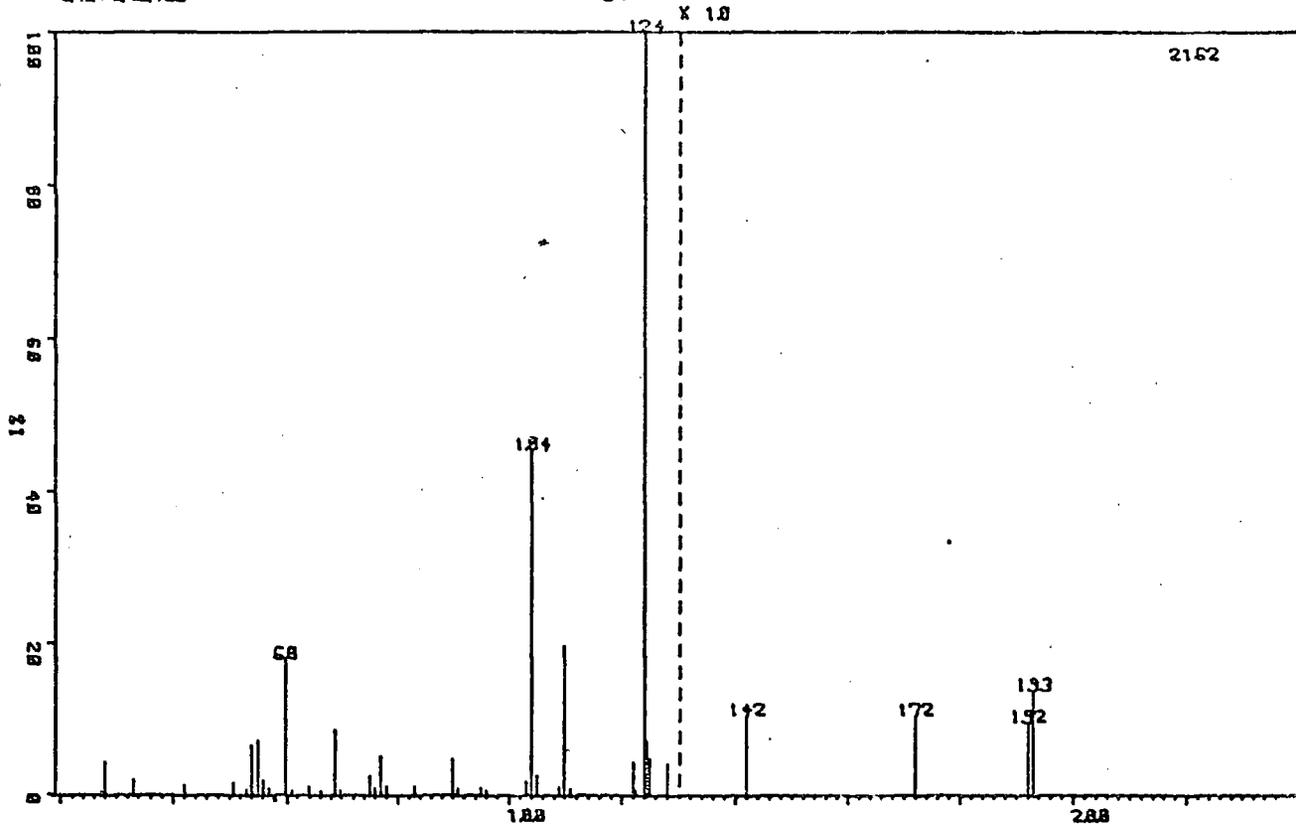
PEAK NO.	MASS	%HT. BASE			
1	27.25	0.51			
2	28.13	4.39			
3	33.12	2.04			
4	42.07	1.34			
5	50.94	1.62			
6	53.08	0.69	24	95.06	0.88
7	54.13	6.66	25	96.08	0.60
8	55.16	7.35	26	103.08	1.90
9	56.15	1.99	27	104.10	45.56
10	57.10	0.83	28	105.07	2.73
11	59.93	17.90	29	109.00	1.20
12	61.01	0.60	30	109.95	19.84
13	64.11	1.16	31	110.99	0.83
14	66.16	0.56	32	122.04	4.39
15	68.92	8.65	33	122.68	0.69
16	69.88	0.60	34	124.05	100.00
17	75.08	2.59	35	124.34	7.26
18	76.07	0.97	36	125.07	4.90
19	77.05	5.27	37	128.02	4.26
20	78.02	1.25	38	142.09	1.06
21	83.03	1.25	39	172.13	1.06
22	89.92	4.81	40	192.09	0.97
23	90.98	0.79	41	193.13	1.39

MJS201 61 M.J.SILVESTER   No.10   27-NOV-

CAL:CAL27

205

1687

118

28

42

69

136

205

100   200   300

			36	111.00	12.72
			37	113.05	2.43
				115.03	1.10
	74.03	1.02	39	116.05	0.80
	78.14	42.74	40	117.05	0.70
	81.02		45	118.02	
	84.05		46	119.03	1.07
			47	121.06	0.69
	87.13		48	123.11	1.05
	91.05		49	124.07	1.30
	92.07	1.18	50	127.02	
	93.92		51	131.06	1.60
	94.04		52	134.00	0.53
	96.95	19.87	54	136.09	13.29
		0.97		143.04	
19		0.83		145.92	1.19
20	95.09		70	167.98	1.01
21	97.05		71	171.97	2.67
	95.01		80	200.92	8.12
	96.07		83	201.92	1.54
	101.08		84	202.95	8.48
45	103.03	1.48		204.02	1.13
46	104.03		86	204.03	100.00
	106.03		87	205.00	13.15
	107.00		88	207.01	0.77
49	108.00	0.96	89	211.06	

90	216.00	6.46
91	217.01	0.45
92	217.93	0.81
93	219.04	0.71
94	245.95	2.13
95	267.99	1.22
96	284.66	17.72
97	286.91	17.49
98	287.61	11.30

MJS20I 44 M.J.SILVESTER No.11 27-NOV-
CAL:CAL27

MJS223 74　　　　　No.12

PEAK NO.	MASS	% INT BASE
1	27.16	3.32
2	28.05	8.80
3	28.95	92.93
6	42.03	5.92
8	44.13	7.22
9	47.09	3.61
10	56.13	21.21
13	68.96	3.03
14	69.96	3.17
15	71.02	6.64
16	72.08	6.06
18	98.01	7.36
21	124.04	7.94
22	125.04	2.45
23	126.05	21.07
28	154.05	52.09
29	155.06	3.61
30	164.03	13.71
32	166.05	6.93
34	181.00	6.49
37	204.97	6.20
39	217.95	14.29
40	218.94	3.03
43	232.95	2.60
45	245.96	14.14
47	251.86	2.60
49	271.87	5.34
55	285.94	6.64
58	295.96	9.81
60	299.86	9.24
65	313.95	9.24
66	314.98	2.60
67	315.98	2.45
70	327.94	7.94
74	334.86	2.60
75	339.77	2.45
78	354.89	5.19
84	383.14	5.48
87	408.85	2.45
88	410.96	15.73
89	419.46	4.18
90	420.84	1.59
91	438.95	100.00
92	467.91	51.08

MS1265 7   No.13   23-MAY-
CAL:CA

PEAK NO.	MASS	%HT. BASE
2	28.14	29.50
7	32.02	6.05
8	33.13	2.14
11	42.07	22.12
12	43.14	11.91
13	44.17	12.69
14	45.19	8.19
18	55.14	3.38
21	58.10	6.20
23	59.92	2.45
27	66.13	4.68
30	68.93	16.44
33	73.04	3.44
36	76.07	4.62
48	94.00	6.11
62	109.84	50.06
64	110.92	2.70
65	111.96	6.67
72	124.00	5.65
73	124.97	6.67
74	126.06	100.00
84	136.00	3.29
85	136.99	3.91

PEAK NO.	MASS	%HT. BASE
87	138.01	2.20
89	138.96	47.39
90	139.91	3.19
94	143.99	8.06
99	148.91	6.45
109	161.93	2.95
111	163.93	4.65
119	170.92	2.14
142	195.94	2.33
144	198.06	12.31
151	205.93	7.38
162	218.14	38.71
170	229.83	6.82
185	247.89	6.54
196	259.02	2.64
202	265.69	19.51
203	267.89	16.97
205	273.91	3.13
207	279.95	4.87
210	286.44	9.77
213	292.96	2.11
218	297.89	19.51
219	299.57	7.51
224	308.23	2.33
226	313.03	6.42
231	323.91	3.78

PEAK NO.	MASS	%HT. BASE
232	327.79	9.27
234	334.00	7.66
243	356.39	4.00
247	366.50	3.91
249	377.83	5.12
253	397.05	41.78
254	400.45	0.37
255	408.73	0.31
256	409.09	0.34
257	412.03	59.58

APPENDIX IV

DEPARTMENTAL COLLOQUIA AND FIRST YEAR INDUCTION COURSE

FOR POSTGRADUATES

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

(a) all research colloquia, research seminars and lectures arranged by the Department of Chemistry during the period of the writer's residence as a postgraduate student;

(b) all research conferences attended and papers read out by the writer of the thesis, during the period when the research for the thesis was carried out; and

(c) details of the first-year induction course.

Events in (a) which were attended are marked +.

Research Colloquia, Seminars and Lectures

I. University of Durham Chemistry Colloquia

Academic Year 1977-78

I9 Oct. Dr. B. Heyn (U. of Jena, D.D.R.), "Sigma-organo molybdenum complexes as alkene polymerisation catalysts".

+ 27 Oct. Professor R.A. Filler (Illinois Institute of Technology, U.S.A.), "Reactions of organic compounds with xenon fluorides".

2 Nov. Dr. N. Boden (U. of Leeds), "N.m.r. spin-echo experiments for studying structure and dynamical properties of materials containing interacting spin Y_2-pairs".

9 Nov. Dr. A.R. Butler (U. of St. Andrews), "Why I lost faith in linear free energy relationships".

7 Dec. Dr. P.A. Madden (U. of Cambridge), "Raman studies of molecular motions in liquids".

14 Dec. Dr. R.O. Gould (U. of Edinburgh) , "Crystallography to the rescue in ruthenium chemistry".

+ 25 Jan. Dr. G. Richards (U. of Oxford), "Quantum Pharmacology".

+ I Feb. Professor K.J. Ivin (Queens U. Belfast), "The olefin metathesis reaction, mechanism of ring opening polymerisation of cycloalkenes".

3 Feb. Dr. A. Hartog (Free U., Amsterdam), "Surprising recent studies in organomagnesium chemistry".

+ 22 Feb. Professor J.D. Birchall (Mond Division, I.C.I.), "Silicon in the biosphere".

+ I Mar. Dr. A. Williams (U. of Kent), "Acyl group transfer reactions".

3 Mar. Dr. G. van Koten (U. of Amsterdam), "Structure and reactivity of aryl-copper cluster compounds".

15 Mar. Professor G. Scott (U. of Aston), "Fashioning plastics to match the environment".

22 Mar. Professor H. Vahrenkamp (U. of Freiburg, Germany), "Metal-metal bonds in organometallic complexes".

19 Apr. Dr. M. Barber (UMIST), "Secondary ion mass spectra of surfaces and adsorbed species".

+ 16 May Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface plasma waves and adsorbed species on metals".

<u>18 May</u> Professor M. Gordon (U. of Essex), "Three critical points in polymer chemistry".

+ <u>22 May</u> Professor D. Tuck (U. of Windsor, Ontario), "Electrochemical synthesis of inorganic and organo-metallic compounds".

+ <u>24 & 25 May</u> Professor P. von Schleyer (U. of Erlangen, Nurnberg),

I "Planar tetra-coordinate methanes, perpendicular ethenes, and planar allenes".

II "Aromaticity in three dimensions".

III "Non-classical carbo-cations".

<u>21 June</u> Dr. S.K. Tyrlik (Acad. of Sci., Warsaw), "Dimethylglyoxime cobalt complexes - catalytic black boxes".

<u>23 June</u> Professor G. Mateescu (Case Western Reserve U., Ohio), "A concerted spectroscopy approach to the characterisation of ion and ion-pairs: facts, plans, and dreams".

+ <u>8 Sept.</u> Dr. A. Diaz (I.B.M., San Jose, California), "Chemical behaviour of electrode surface bonded molecules".

<u>15 Sept.</u> Professor W. Siebert (Marburg, W. Germany), "Boron heterocycles".

<u>22 Sept.</u> Professor T. Fehlner (Notre Dame, U.S.A.), "Ferraboranes: synthesis and photochemistry".

Academic Year 1978-79

+ 12 Dec. Professor C.J.M. Stirling (U. of Bangor), "Parting is such sweet sorrow - the leaving group in organic chemistry".

+ 31 Jan. Professor P.D.B. de la Mare (U. of Auckland, New Zealand), "Some pathways leading to electrophilic substitution".

14 Feb. Professor B. Dunnel (U. of British Columbia), "The application of n.m.r. to the study of motions of molecules in solids".

+ 14 Mar. Dr. J.C. Walton (U. of St. Andrews), "Pentadienyl radicals".

+ 28 Mar. Dr. A. Reiser (Kodak Ltd.), "Polymer photography and the mechanism of cross-link formation in solid polymer matrices".

+ 25 Apr. Dr. C.R. Patrick (U. of Birmingham), "Chlorofluorocarbons and statospheric ozone: an appraisal of the environmental problem".

I May Dr. G. Wyman (European Research Office, U.S. Army), "Excited state chemistry of indigoid dyes".

2 May Dr. J.D. Hobson (U. of Birmingham), "Nitrogen-centred reactive intermediates".

8 May Professor A. Schmidpeter (Inst. of Inorg. Chem., Munich U.), "Five-membered Phosphorous heterocycles containing dicoordinate phosphorous".

+ 9 May Professor G. Maier (Lahn Giessen U.), "Tetra-tert-butyltetrahedrane".

+ <u>9 May</u> Dr. A.J. Kirkby (U. of Cambridge), "Structure and reactivity in intramolecular and enzymic catalysis".

<u>16 May</u> Dr. J.F. Nixon (U. of Sussex), "Some recent developments in platinum-phosphine complexes".

+ <u>23 May</u> Dr. B. Wakefield (U. of Salford), "Electron transfer in reaction of metals and organometallic compounds with polychloropyridine derivatives".

+ <u>13 June</u> Professor I. Ugi (U. of Munich), "Synthetic uses of super nucleophiles".

+ <u>25 Sept.</u> Professor R. Soulen (Southwestern U., Texas), "Applications of HSAB theory to vinylic halogen substitution reactions and a few copper coupling reactions".

Academic Year 1979-80

+ <u>21 Nov.</u> Dr. J. Muller (U. of Bergen), "Photo-chemical reactions of ammonia".

+ <u>28 Nov.</u> Dr. B. Cox (U. of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity".

<u>5 Dec.</u> Dr. G.C. Eastmand (U. of Liverpool), "Synthesis and properties of some multicomponent polymers".

<u>12 Dec.</u> Dr. C.I. Ratcliffe, "Rotor motions in solids".

<u>18 Dec.</u> Dr. K.E. Newman (U. of Lausanne), "High pressure multinuclear n.m.r. in the elucidation of mechanism of simple fast inorganic reactions".

<u>30 Jan</u>. Dr. M.J. Barrow (U. of Edinburgh), "The structures of some simple inorganic compounds of silicon and germanium - pointers to structural trends in group 4".

+ <u>6 Feb</u>. Dr. J.M.E. Quirke (U. of Durham), "Degradation of chlorophyll - a in sediments".

+ <u>23 Apr</u>. B. Grievson B.Sc. (U. of Durham), "Halogen radio-pharmaceuticals".

+ <u>14 May</u> Dr. R. Hutton (Waters Associates), "Recent developments in multi-milligram and multi-gram scale preparative high performance liquid chromatography".

<u>21 May</u> Dr. T.W. Bentley (U. of Swansea), "Medium and structural effects on solvolytic reactions".

+ <u>10 July</u> Professor D. Des Marteau (U. of Heidelberg), "New developments in organonitrogen fluorine chemistry".

2. <u>Durham University Chemical Society</u>

<u>Academic Year 1977-78</u>

<u>13 Oct</u>. Dr. J.C. Young and Mr. A.J.S. Williams (U. of Aberystwyth), "Experiments and considerations touching colour".

+ <u>20 Oct</u>. Dr. R.L. Williams (Metropolitan Police Forensic Science Dept.), "Science and crime".

+ <u>3 Nov</u>. Dr. G.W. Gray (U. of Hull), "Liquid crystals - their origins and applications".

<u>24 Nov</u>. Mr. G. Russel (Alcan), "Designing for social acceptability".

I Dec. Dr. B.F.G. Johnson (U. of Cambridge), "Chemistry of binary metal carbonyls".

+ 2 Feb. Professor R.A. Raphael (U. of Cambridge), "Bizarre reactions of acetylenic compounds".

16 Feb. Professor G.W.A. Fowles (U. of Reading), "Home winemaking".

+ 9 Mar. Professor H. Suschitzky (U. of Salford), "Fruitful fissions of benzofuroxans".

+ 4 May Professor J. Chatt (U. of Sussex), "Reactions of coordinated dinitrogen".

+ 9 May Professor G.A. Olah (Case Western Reserve U., Ohio), "Electrophilic reactions of hydrocarbons".

Academic Year 1978-79

+ IO Oct. Professor H.C. Brown (U. of Purdue), "The tool of increasing electron demand in the study of cationic processes".

+ I9 Oct. Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is death in the pot".

26 Oct. Professor W.J. Albery (Imperial College, London), "Photogalvanic cells for solar energy conversion".

+ 9 Nov. Professor A.R. Katritsky (U. of East Anglia), "Some adventures in heterocyclics".

+ I6 Nov. Dr. H.C. Fielding (Mond Division, I.C.I.), "Fluorochemical surfactants and textile finishes".

23 Nov. Dr. C. White (Sheffield U.), "The magic of Chemistry".

I8 Jan. Professor J.C. Robb (Birmingham U.), "The plastics revolution".

8 Feb. Mr. C.G. Dennis (Vaux Ltd.),"The art and science of brewing".

I Mar. Professor R. Mason (Govt. Scientific Advisor), "The scientist in defence policy".

10 May Professor G. Allen (Chairman S.R.C.), "Neutron scattering for polymer structures".

Academic Year 1979-80

18 Oct. Dr. G. Cameron (U. of Aberdeen), "Synthetic polymers - twentieth century polymers".

25 Oct. Professor P. Gray (U. of Leeds), "Oscillatory combustion reactions".

+ I Nov. Dr. J. Ashby (I.C.I. Toxicological Laboratory), "Does chemically-induced cancer make chemical sense".

+ 8 Nov. Professor J.H. Turnbull (R.M.C. Shrivenham), "Luminescence of drugs".

15 Nov. Professor E.A.V. Ebsworth (U. of Edinburgh), "Stay still, you brute: the shape of simple silyl complexes".

+ 24 Jan. Professor R.J.P. Williams (U. of Oxford), "On first looking into biology's chemistry".

+ 14 Feb. Professor G. Gamlen (U. of Salford), "A yarn with a new twist - fibres and their uses".

21 Feb. Dr. M.L.H. Green (U. of Oxford), "Synthesis of highly reactive organic compounds using metal vapours".

+ 28 Feb. Professor S.F.A. Kettle (U. of East Anglia), "Molecular shape, structure and chemical blindness".

6 Mar. Professor W.D. Ollis (U. of Sheffield), "Novel molecular rearrangements".

Research Conferences Attended

9th International Symposium On Fluorine Chemistry,

Avignon, 3-7 September 1979.

3rd Annual Congress of the Chemical Society, Durham,

9-II April I980.

First Year Induction Course

In each part of the course, the use and limitations of

the various services available are explained by the

people responsible for them.

Departmental organisation	Dr. E.J.F. Ross
Safety matters	Dr. M.R. Crampton
Electrical appliances and infra-red spectroscopy	Mr. R.N. Brown
Chromatography and microanalysis	Mr. T.F. Holmes
Library facilities	Mr. W.B. Woodward (Keeper of science books)
Atomic absorptiometry and inorganic analysis	Mr. R. Coult
Mass spectrometry	Dr. M. Jones
N.m.r. spectroscopy	Dr. R.S. Matthews
Glassblowing techniques	Mr. W.H. Fettis and Mr. R. Hart

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REFERENCES

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