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Some studies of polyfluorinated polycyclic polyenes

Roger R. Hughes

SOME STUDIES OF POLYFLUORINATED POLYCYCLIC POLYENES

by

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ABSTRACT

The attempted addition of difluorocarbene, which was generated from hexafluoropropene epoxide, to polyfluorinated cyclic olefins was largely unsuccessful, although perfluorobicyclo[4,1,0]hept-3-ene was isolated from the addition to perfluorocyclohexa-1,4-diene. It seems that difluorocarbene adds to the polyfluorinated cyclic olefins to form cyclopropanes, which readily eliminate difluorocarbene under the reaction conditions required for their formation.

The attempted photochemical isomerisations of polyfluorobicyclo[2,2,2]octa-2,5-dienes, via the [2π+2π] ring closures to their corresponding tetracycles, were also unsuccessful. However, on irradiation dimethyl 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate formed a tricyclic biradical, which abstracted a hydrogen from the α methylene group of the diethyl ether solvent to give isomers of dimethyl 2-(3'-oxa-2'-pentyl)-1,4,5,6,7,7,8,8-octafluorotricyclo[2,2,2,0^{3,5}]octane-2,3-dicarboxylate. The tricyclic biradical intermediate is similar to that proposed for the photochemical isomerisation of hydrocarbon bicyclo[2,2,2]hepta-2,5-dienes and their analogues. In contrast to their corresponding hydrocarbon analogues the tricyclic biradical intermediates formed on irradiation of polyfluorobicyclo[2,2,2]octa-2,5-dienes do not appear to form tetracycles.

Perfluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene reacted as a diene in the Diels-Alder reactions with ethylene, but-2-yne, acetylene dicarboxylic acid dimethyl ester, perfluoroacetonitrile, tetrafluoroethylene and 1H,2H-hexafluorocyclopentene. As a consequence imposed by the carbocyclic framework of the diene, the addition of 1H,2H-hexafluorocyclopentene gave the exo adduct. The 1,4-alkyne adducts were pyrolysed to give 2,3-disubstituted hexafluoronaphthalenes.

The pyrolysis of perfluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene proceeds via a 1,3-alkyl migration to give perfluorotricyclo[8,2,0,0^{2,7}]dodeca-2,6,8-triene which subsequently eliminates tetrafluoroethylene to give perfluoro-1,2-dihydro-

naphthalene as the major product. The reaction of perfluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,6,9-triene with lithium methyl in ether proceeded preferentially at the diene moiety. The pyrolysis of the monomethyltridecafluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,6,9-trienes gave monomethylnonafluoro-1,2-dihydronaphthalenes which had the methyl label in the non-aromatic ring.

Nucleophilic substitution in perfluoro-1,2-dihydronaphthalene was found to occur only at the vinylic C3 position with sodium borohydride whereas with lithium methyl four monomethyl substitution products were obtained, both the vinylic, the C6 and C7 fluorines being replaced. The gas phase photochemical reaction of perfluoro-1,2-dihydronaphthalene produces the perfluoro-1- and -2-methylenindanes possibly via the perfluorovinyl-o-quinodimethane.

ACKNOWLEDGEMENTS

MEMORANDUM

The work in this thesis was carried out in the Chemistry Laboratories of the University of Durham between October 1972 and July 1975. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

NOTES TO READER

In this thesis compounds previously unreported in the literature are designated by large Roman numbers. [(XIX) and (XXI) have been reported but all of their spectral parameters are not available in the literature]. Other compounds are designated by Arabic numerals.

The diagrams in the Introduction to all Chapters have unmarked bonds to hydrogen and in all Discussion Sections unmarked bonds are to fluorine, unless otherwise stated. A reminder of this is given at the beginning of each Discussion.

Throughout this thesis a number of abbreviations have been used regularly, these are: infrared spectroscopy (i.r.); ultra-violet spectroscopy (u.v.); mass spectroscopy (m.s.); nuclear magnetic resonance spectroscopy (n.m.r.); photoelectron spectroscopy (PES); gas-liquid chromatography (g.l.c.); Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).

Generally the percentage composition of product mixtures has been determined from analytical g.l.c. peak areas which were obtained either by calibration or more usually by direct measurement from the gas density balance.

Many of the compounds reported in this thesis have very broad ^{19}F n.m.r. signals that contain many coupling constants, however, in certain cases the actual width of an unresolved resonance has been helpful in ascertaining the presence or absence of large coupling constants and obviously for these systems it is the base line width that is necessarily quoted. The chemical shift positions are quoted with respect to internal $CFCl_3$ and internal T.M.S., unless otherwise stated and refer to the centres of bands. Integrated intensities are given in parentheses and coupling constants in Hz.

The names of the compounds (I) $\longrightarrow$ (XXXXIV) are to be found in Appendix C, which also contains the infrared spectra. Appendix B contains the mass spectra and structures of compounds in numerical order. The ^{19}F n.m.r. data and the

structures of compounds are generally to be found in Tables in the Discussions with the exceptions being (I), (V) and (VI) whose structures are to be found on pages 22, 53 and 95 respectively. The ^{19}F n.m.r. data for the compounds (I) ⟶ (XXXXIV) are to be found on:

		Page
(I)		26
(II) ⟶ (IV)	Table 1	49
(V)		53 ⟶ 54
(VI)		119
(VII) ⟶ (XII)	Table 9	100 ⟶ 101
(XIII) ⟶ (XV)	Table 10	107
(XVI) and (XVII)	Table 14	141
(XVIII)	Table 15	144
(XIX) ⟶ (XXI)	Table 16	148
(XXII)	Table 15	144
(XXIII) ⟶ (XXVIII)	Table 17	153 ⟶ 154
(XXX) ⟶ (XXXVI)	Table 21	191 ⟶ 192
(XXXVII) and (XXXVIII)	Table 11	113
(XXXIX) ⟶ (XXXXI)	Table 23	203
(XXXXII) ⟶ (XXXXIV)	Table 22	201

<div align="center">CONTENTS</div>

Abstract

Acknowledgements

Memorandum

Notes to reader

CHAPTER 4. Vacuum pyrolyses of the Diels-Alder adducts of
tetradecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene
and an investigation into the mechanism of pyrolysis
of tetradecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene

INTRODUCTION

DISCUSSION

EXPERIMENTAL

CHAPTER 5.   Some reactions of perfluoro-1,2-dihydronaphthalene

INTRODUCTION

CHAPTER 1

The Addition Of Difluorocarbene To Polyfluorinated Cyclic Olefins

INTRODUCTION

1.1 Methods of generating difluorocarbene ($:CF_2$)

Difluorocarbene was first postulated as a reaction intermediate by Hine,[1] as a consequence of his classic work on the base catalysed hydrolysis of haloforms. Hine advocated a concerted mechanism for the generation of difluoro-carbene from $CHBrF_2$, which in contrast to $CHCl_3$ did not incorporate solvent deuterium.

$$HO^- \; + \; H\text{-}\underset{F}{\overset{F}{C}}\text{-}Br \; \longrightarrow \; HO\text{-}\text{-}\text{-}H\text{-}\text{-}\text{-}\underset{F}{\overset{F}{C}}\text{-}\text{-}Br \; \longrightarrow \; H_2O \; + \; :CF_2 \; + \; Br^-$$
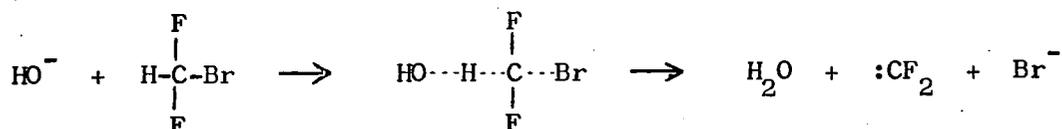
The first addition of difluorocarbene to an olefin was observed in 1960 when thermal breakdown of sodium chlorodifluoroacetate in diglyme at $180^{\circ}C$ in the presence of cyclohexene gave an 11% yield of difluoronorcarane (1).[2] Nucleophilic displacement by iodide ion on trimethyltrifluoromethyl tin under very mild conditions generated difluorocarbene which was trapped as difluoronorcarane.[3] The production of fluoroform when the reaction was performed in aqueous solution was used as evidence for the intermediacy of the trifluoromethyl anion. Nucleophilic displacement by iodide ion on phenyl(trifluoromethyl)mercury also generates difluorocarbene, however in this instance, evidence for the intermediate trifluoromethyl anion was not found.[4]

$$I^- \; + \; Me_3SnCF_3 \; \xrightarrow[\text{Diglyme}]{80^{\circ}C} \; Me_3SnI \; + \; [CF_3^-] \; \xrightarrow{\text{Cyclohexene}} \; \text{(structure)} \; F_2$$

(1) 89%

$$I^- + CF_3HgI \xrightarrow[\text{Cyclohexene}]{\text{Refluxing Benzene}}$$

(1) 88%
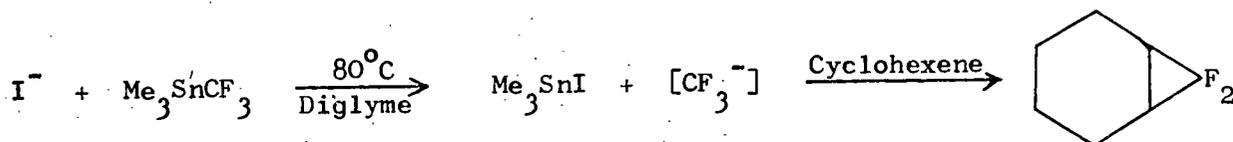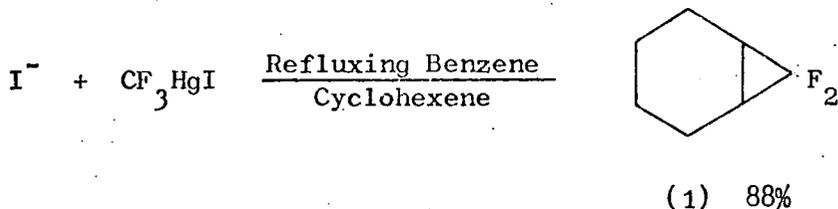
Difluorocarbene can also be generated in a number of pyrolytic reactions; for instance, the manufacture of tetrafluoroethylene is based upon α elimination of HCl from $CHClF_2$ at $650^\circ C$ and 0.5 atm.[5] Pyrolysis of $CHClF_2$ at $600^\circ C$ in the presence of cyclopentadiene produces fluorobenzene and this is also of industrial importance.

$$\xrightarrow{:CF_2} \qquad \xrightarrow[\text{-HF}]{600^\circ C}$$
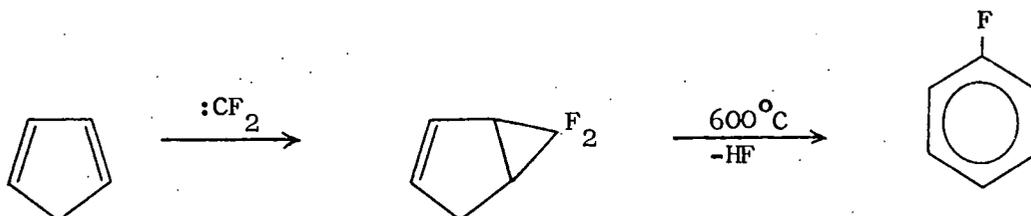
Heating $(CH_3)_3SnCF_3$ at $150^\circ C$ in a sealed tube also generates difluorocarbene which reacts almost quantitively with tetrafluoroethylene to produce perfluoro-cyclopropane.[6] Similarly the trifluoromethylphosphorane (2) will decompose on heating to give difluorocarbene addition products.[7]

	$CF_2{=}CF_2$	(triangle)	$(CF_2)_n$

$(CF_3)_2PF_2$

(2)

$\xrightarrow[\text{24 hr.}]{120^\circ C}$: 10 / 80 / 10

$\xrightarrow[\text{10 min.}]{200^\circ C}$: 80 / 10 / 10
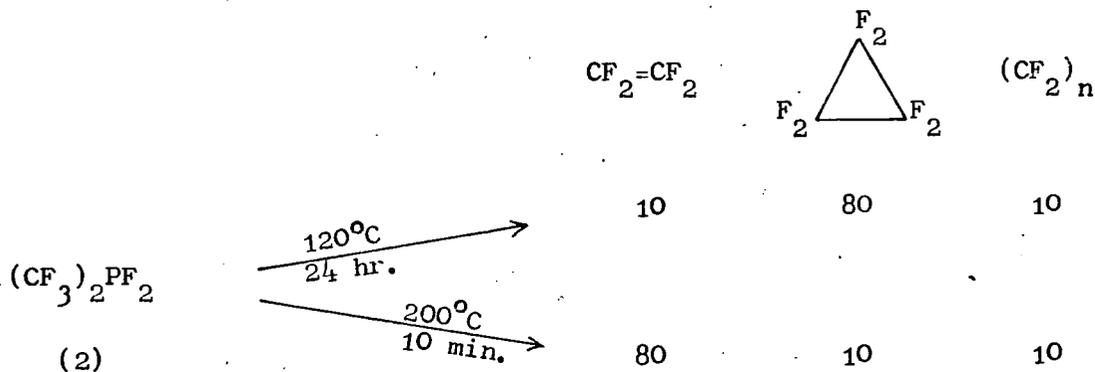
Hexafluoropropene epoxide (HPE) begins to decompose at $180^\circ C$ and forms perfluoroacetyl fluoride and difluorocarbene.[8] Perfluorocyclopropane is the major product when HPE is heated at $200^\circ C$ for 8 hours. Difluorocarbene is produced by the photolysis of the diazirine (3), though better yields are obtained on pyrolysis.[9]

(3)
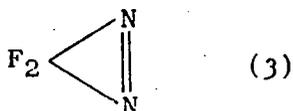
1.2 Generation of perfluoroalkylcarbenes[10]

Perfluoroalkylcarbenes are most conveniently prepared from diazoalkanes

(eg. 4) or the diazirine (5) which on pyrolysis in a helium flow system give:-

$$(CF_3)_2C=N_2 \xrightarrow{250^\circ C} CF_3CF=CF_2 + (CF_3)_2C=C(CF_3)_2$$

(4)

$$(CF_3)_2C\underset{N}{\overset{N}{\big<}} \xrightarrow{250^\circ C} CF_3CF=CF_2 + (CF_3)_2C=NN=C(CF_3)_2$$

(5)
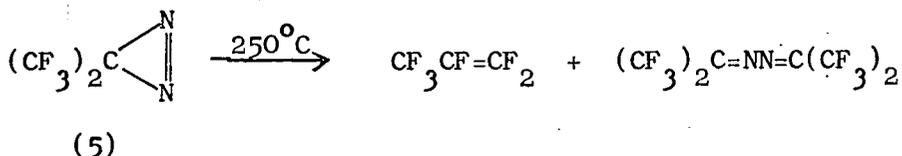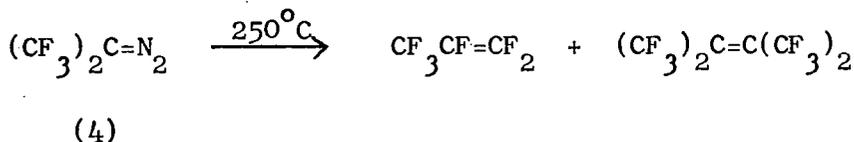
Hexafluoropropene is presumably formed by a 1,2-fluorine shift from the

intermediate carbene $(CF_3)_2C:$. When (4) reacts with cis-but-2-ene at $150^\circ C$

39% of the cis-cyclopropane (4a), 8% of the trans-cyclopropane (4b) and 49% of

(4c) are formed.
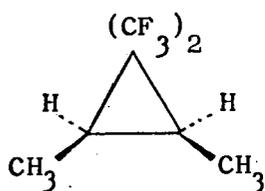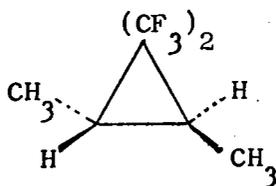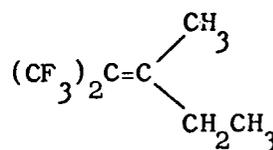
(4a)   (4b)   (4c)

Under the same conditions, the diazirine (5) reacts with cis-but-2-ene to form

55% of the cis-cyclopropane (4a), 8% of the trans-cyclopropane (4b), 2% of (4c),

a vinylic insertion product (8%) and an allylic insertion product (27%).

Obviously different intermediates must be involved in each case and it is

probable that the diazirine (5) reacts via the free bis-trifluoromethyl carbene

whereas the diazoalkane (4) reacts via a cyclic nitrogen adduct since the cyclic

adduct (6) was isolated from the reaction of (4) with but-2-yne. (6) loses

nitrogen on heating to give the cyclopropene (7).
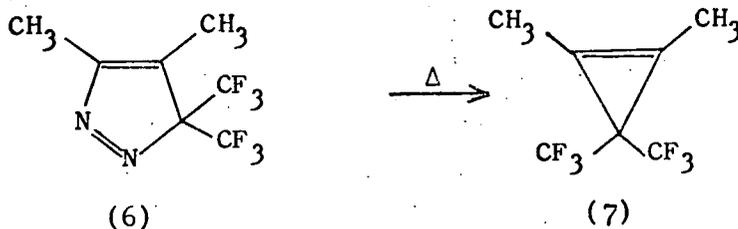
(6)   (7)

1.3 The preparation of polyfluorinated cyclopropanes from difluorocarbene

With difluorocarbene being the least reactive halocarbene and fluorinated olefins not being particularly susceptible to electrophilic attack, then the generation of difluorocarbene with fairly high energy is required to ensure the production of fluorinated cyclopropanes. The heating of fairly simple polyfluorinated olefins with either HPE[8] or with trifluoromethylphosphoranes[7,11] at high temperatures and pressures in the absence of solvent have been the methods most widely employed for the production of polyfluorinated cyclopropanes. Moore, in a U.S. patent,[12] claimed to have achieved addition of difluorocarbene to cyclic fluorinated olefins such as perfluorocyclohexene and perfluorocyclo-pentene though neither experimental conditions nor details of reaction products (compositions and yields) were given.

The generating of $:CF_2$ from $(CF_3)_3PF_2$ was used in the following examples:

(ref. 7)

(ref. 11)

X = Y = H	12% yield
X = F, Y = Cl	91% yield
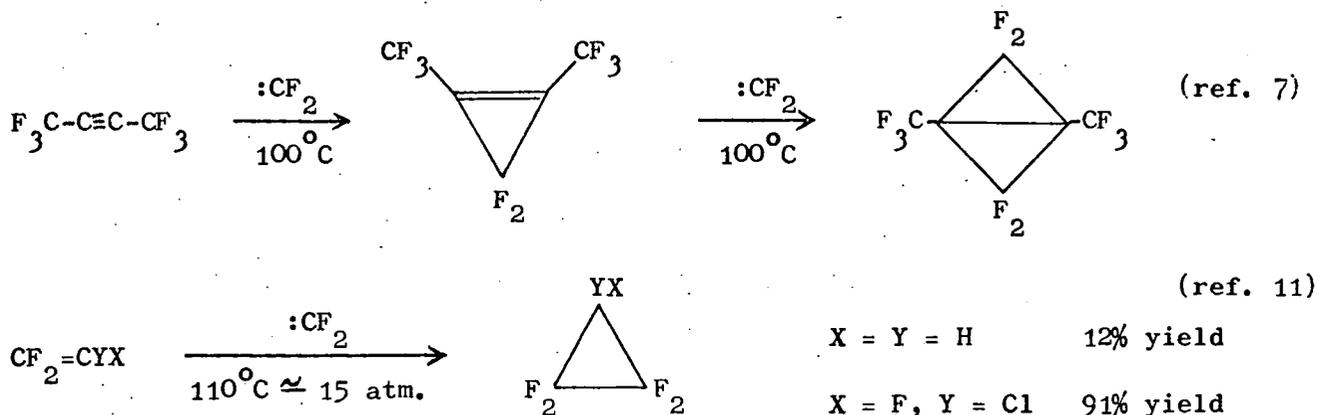
Moore did document the following reaction and state that reaction temperatures of $300°C$ promoted undesirable side reactions of HPE.[12]

53% yield
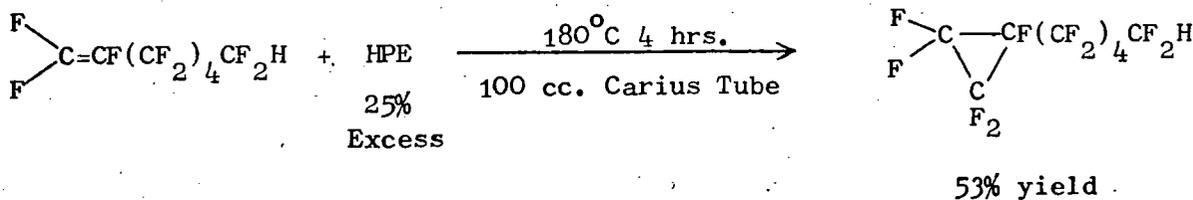
Sargent has prepared a large number of polyfluorinated cyclopropanes by the expedient use of HPE.[8] For instance he obtained a 50% yield of perfluoromethylcyclopropane by reaction of perfluoropropene and a 50% excess of HPE at 200°C. Difluorocarbene derived from HPE adds to the <u>cis</u> (8) and <u>trans</u> (9) olefins in a stereospecific manner to produce the <u>cis</u> (10) and <u>trans</u> (11) cyclopropanes, respectively. The situation is complicated by the <u>cis/trans</u> isomerisation of (10) and (11), nevertheless after 4 hours at 200°C the stereospecificity of each reaction was greater than 95%.

$$F \diagdown C=C \diagup F \qquad \xrightarrow{:CF_2} \qquad (75\% \text{ yield})$$

(8)   (10)

$$(9) \qquad \xrightarrow{:CF_2} \qquad (11) \qquad (80\% \text{ yield})$$
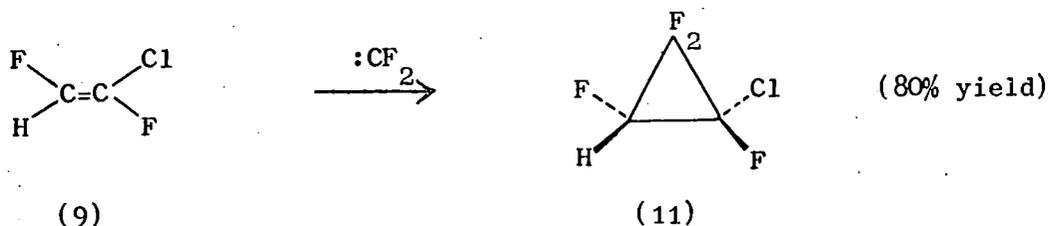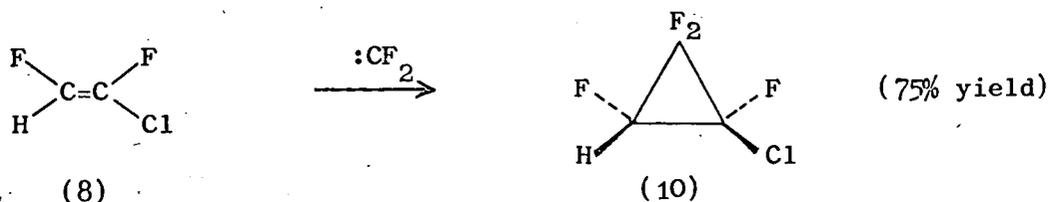
1.4 Structure and reactivity of difluorocarbene

Hine[1] established that the order of stability of the dihalocarbenes ($:CX_2$) is $F >> Cl > Br > I$. The inductive effect of fluorine is more than offset by the π-bonding between fluorine and the electron deficient carbon atom. An excellent discussion by Simons[13] leads to the conclusion that extensive π-bonding exists in $:CF_2$ and the difluoroamino radical, $:NF_2$. The dissociation energy of the π-bond in tetrafluoroethylene is about 70 Kcals.[14] whilst that in ethylene is about 160 Kcals.[15] in spite of the latter having a slightly longer bond length. The salient factor here is that $:CF_2$ is much more stable than $:CH_2$. Simons has also shown that the extent of π-bonding for each C-F is about 31 Kcals/mole from a consideration of the dissociation energy of C-F in CF_3 and in CF_2. The only electronic transition in $:CF_2$ occurs at 2650Å and corresponds to an energy of

4.66 eV.[16] This was assigned by Simons to the $^1B_1 \leftarrow {}^1A_1$ transition. The assignment was confirmed by a detailed analysis of the rotational fine structure[17] and requires difluorocarbene to be a ground state singlet. The infrared spectrum of difluorocarbene trapped in a rigid matrix of argon or nitrogen at $4^\circ K$ suggests that the bond angle is 108°.[18]

, A more theoretical study employing extended Hückel calculations[19] suggests that difluorocarbene should be a ground state singlet in contrast to the triplet ground state of methylene. The calculated bond angle for $:CF_2$ is $98 \pm 1^\circ$ and the σ^2 configuration means that there is a vacant p orbital. A symmetrical approach of difluorocarbene to an olefin may be considered in terms of a correlation diagram for levels and states:
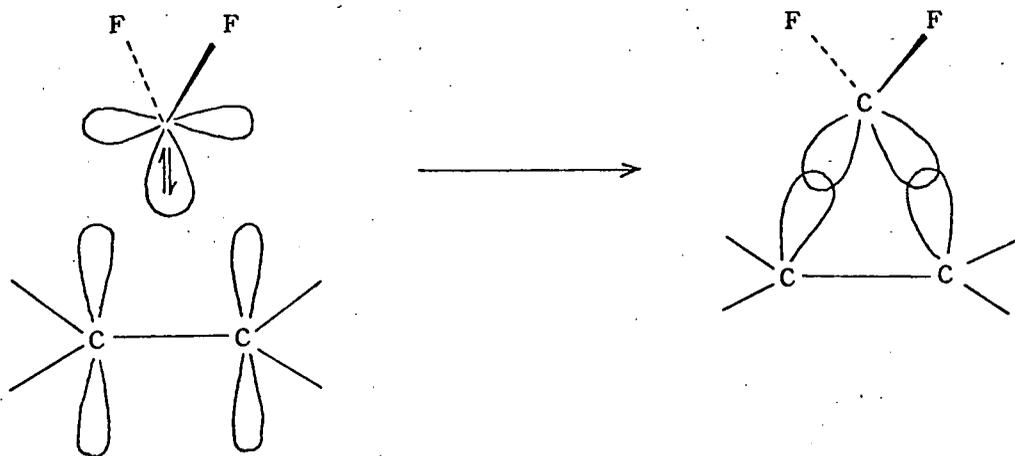
Consider the plane of symmetry passing through $\diagup C = C \diagdown$ and $\overset{F}{\underset{\cdot\cdot}{\diagup}} C \overset{F}{\diagdown}$ and the cyclopropane (i.e. $C_{2\upsilon}$). The p orbital is placed at the non-bonding level, and an orbital correlation diagram can be constructed:

Carbene   π bond   Cyclopropane
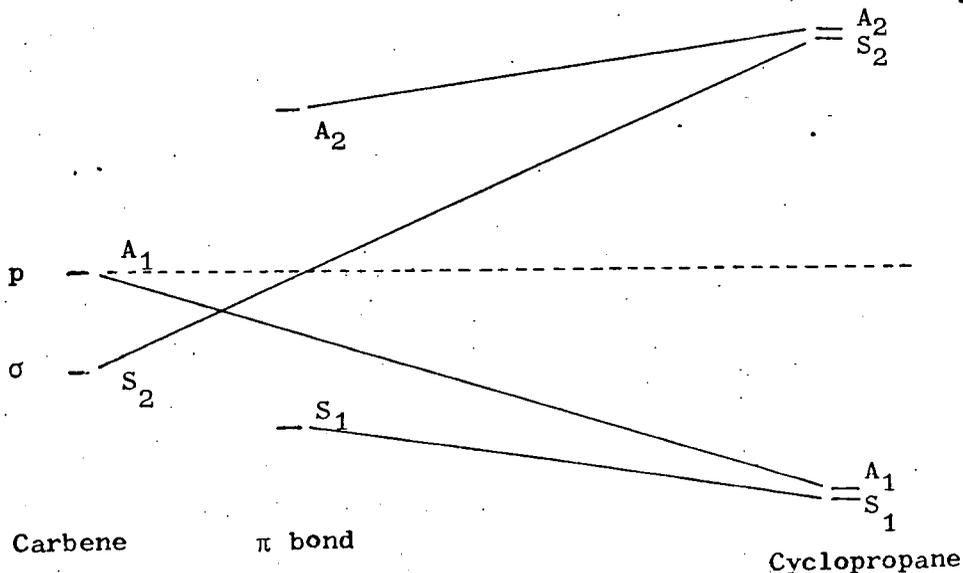
From which we can construct the state correlation diagram:

$$^1S \quad —— \quad S_1{}^2 S_2{}^2$$

$$^1A \quad —— \quad S_1{}^2 A_1{}^1 S_2{}^1$$

$$S_1{}^2 A_1{}^2 \quad —— \quad ^1S$$

$$S_1{}^2 S_2{}^1 A_1{}^1 \quad —— \quad ^3A$$

$$^3A \quad —— \quad S_1{}^2 A_1{}^1 A_2{}^1$$

$$A_1{}^2 S_2{}^2 \quad —— \quad ^1S$$

$$^1S \quad —— \quad S_1{}^2 A_1{}^2$$

Reactants   Product
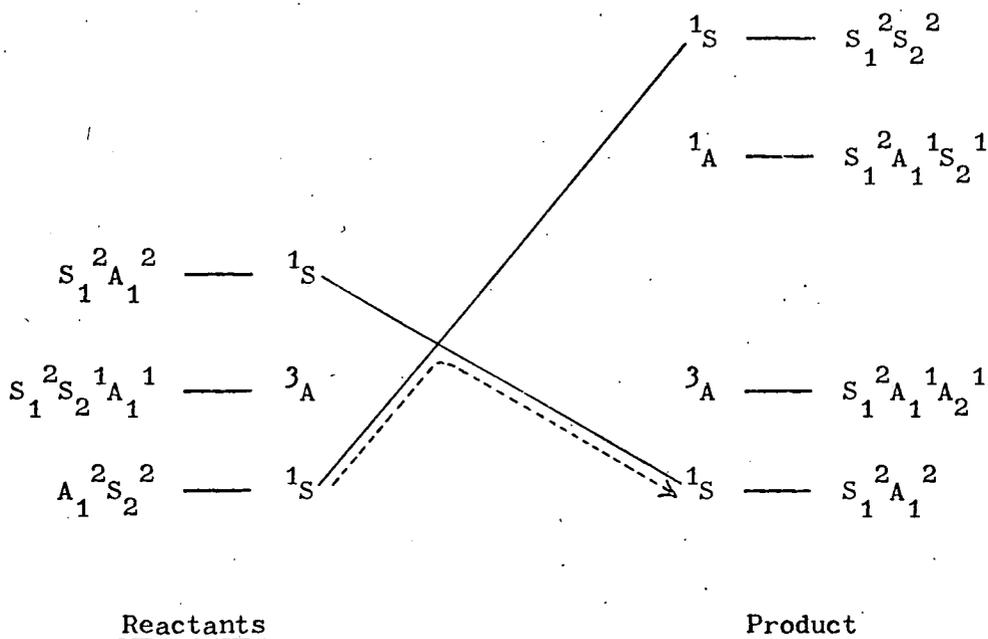
Hence for the symmetrical approach of a singlet (^1S state with σ^2 configuration) the state correlation diagram requires that species of the same symmetry cross over. This is not allowed and the reaction is symmetry forbidden. (A triplet with σp configuration would involve an allowed process). The transition state for the computed non-symmetrical approach of difluoro-carbene involves the p-orbital pointing towards carbon atom B whilst the 'carbene carbon' is nearer to carbon atom A.[20]
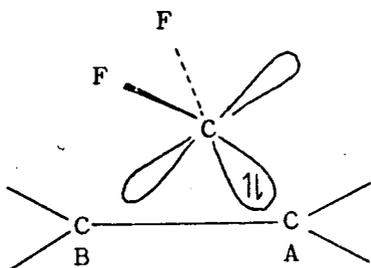
The primary interaction is then between the unoccupied methylene p-orbital and the π-bond rather than between the carbene lone pair and the π-bond. Hence there is a development of charge in the transition state which results in the olefinic moiety developing some carbonium ion character. The computed

activation energy of difluorocarbene addition to ethylene was 20 Kcals., and

this compares with the known value of 11-12 Kcals.[21] The energy of activation

for difluorocarbene addition to tetramethylethylene was zero and to propene was

5.20 Kcals.

Ab initio calculations by Harrison[22] suggest that difluorocarbene is a ground

state singlet with a bond angle of 105° and that methylene is a triplet with a

bond angle of 132.5^o. Both the extended Hückel and ab initio calculations

predict that the order of stability is $:CF_2 > :CHF > :CH_2$ whilst the former also

predict that $:CF_2$ is more stable than $:CCl_2$. $:CHF$ and $:CHCl$ have been confirmed

as ground state singlets by analysis of their long wavelength transitions.[23]

Harrison also assigns $:CHF$ as a ground state singlet.

The ground state of methylene has recently been confirmed experimentally

and theoretically to be the triplet $(^3B_1)$,[22a] which is 8 to 9 Kcals/mole lower

in energy than the singlet $(^1A_1)$. Uncertainty remains with regards to the

$(^1B_1) \longleftarrow (^1A_1)$ transition in methylene; experimentally it is considered

to be about 20 Kcals/mole whilst theoretically a value of 33 Kcals/mole is

suggested. The singlet/triplet energy difference in methylene is rather small

and the mode of production will be very important in determining the relative

amounts of singlet/triplet methylene. The difluorocarbene singlet $(^1A_1)$ is

computed to be 39 Kcals/mole lower in energy than the triplet $(^3B_1)$. The

$(^1B_1) \longleftarrow (^1A_1)$ transition is observed and corresponds to a 108 Kcal/mole

difference in energy. Hence the relatively low value of $(^1A_1)$ infers that

difluorocarbene will be a ground state singlet independent of the mode of

formation.

Experimentally it has been determined that the relative reactivities of

carbenes with different olefins is $CH_2 > CBr_2 > CCl_2 > CFCl > CF_2$ and that this

order coincides with the decrease in electrophilicity along the series.[24] The

rate of addition of dichlorocarbene to isobutylene is larger than that to

but-2-ene and this led Skell to propose that the approach of $:CCl_2$ to the olefin

is unsymmetrical with some carbonium ion character being developed in the

olefinic moiety. The reactivity of dichlorocarbene with olefin appears to be

primarily determined by the polarizability of the olefin along the π axis and

to a lesser extent by the ability of the olefins to form stabilized 'carbonium

ion' intermediates. The unsymmetrical transition state was also proposed by

Skell as early as 1956[25] from a consideration of dibromocarbene addition to

olefins. This transition state is essentially the same as that proposed from

a consideration of orbital symmetry.

The reaction of dichlorocarbene with 2,5-dihydrofuran gave both the

cyclopropane (12) and the allylic insertion product (13) in contrast to difluoro-

carbene which gave only the cyclopropane (14). The lower reactivity and hence

greater selectivity of difluorocarbene relative to dichlorocarbene is clearly

demonstrated.
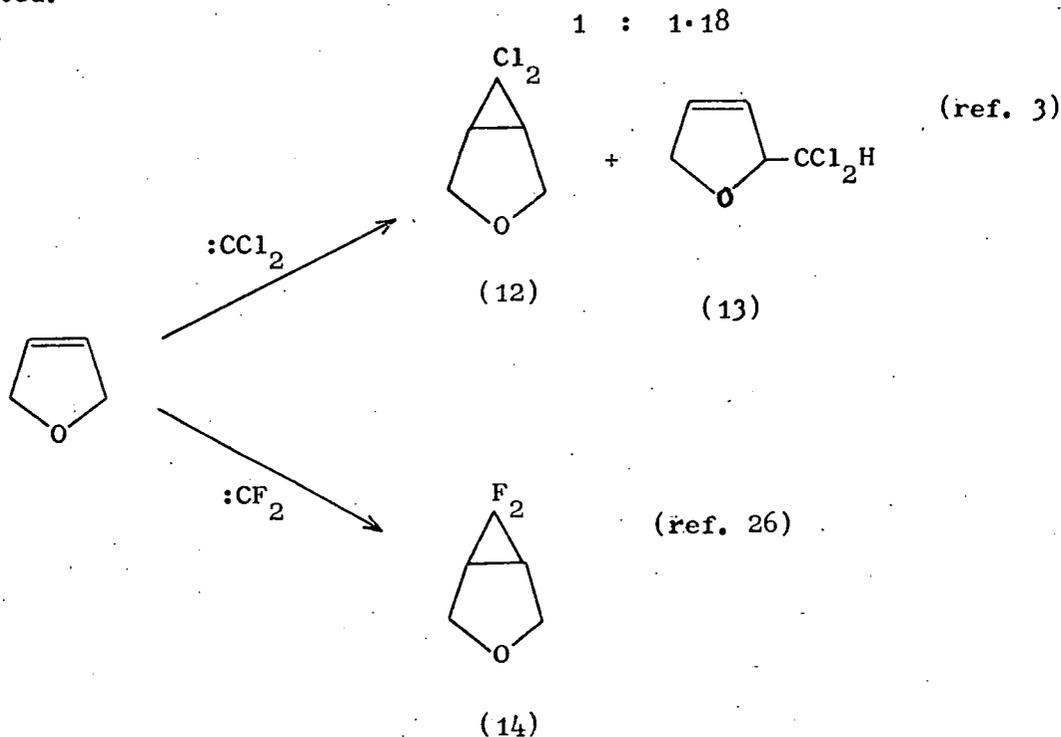
The stereospecific nature of $:CF_2$ addition has already been mentioned (1.3)

and is substantiated by two further examples:

$$\underline{\text{trans-n-C}_3\text{H}_7\text{CH=CHC}_2\text{H}_5} \xrightarrow[\text{NaI}]{\text{Me}_3\text{SnCF}_3}$$

C_2H_5 ... H / H ... C_3H_7 (cyclopropane with F_2) 74%   (ref. 3)

$$\underline{\text{trans-CH}_3\text{CH=CHCH}_3} + \text{CF}_2 \text{ (diazirine)} \xrightarrow{\text{u.v.}}$$

H ... CH_3 / CH_3 ... H (cyclopropane with F_2) 33%   (ref.9)
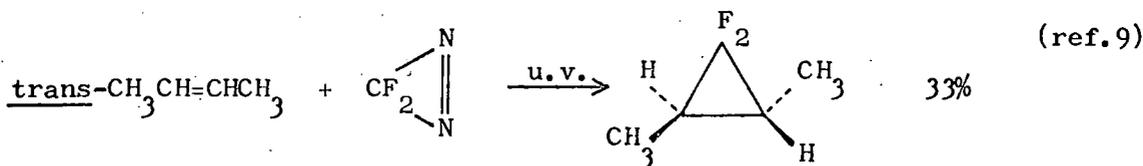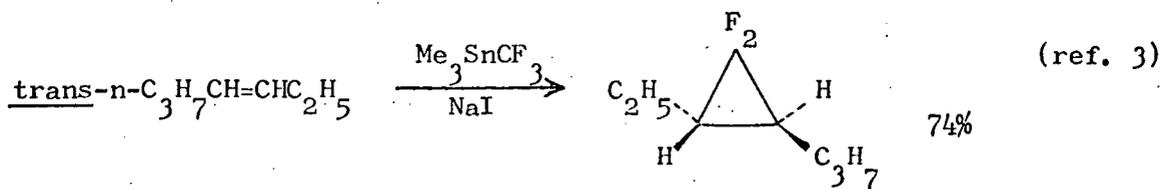
1.5 Structure and reactivity of perfluoroalkyl carbenes

Hoffmann[19] has predicted that bisperfluoromethylcarbene, $(\text{CF}_3)_2\text{C:}$, is a ground state singlet with a bond angle of $118°$. The presence of the CF_3 groups attached to the 'carbene carbon' means that the latter is much more electrophilic than $:\text{CF}_2$ especially as there is no possibility of compensation from π-bonding. Hence $(\text{CF}_3)_2\text{C:}$ should be much more reactive than $:\text{CF}_2$ and this is endorsed by the reaction of the diazirine (5) with cyclohexene at $165°\text{C}$ when the cyclopropane (15) and the C-H insertion products (16) and (17) were formed.[10] The reaction of difluorocarbene with cyclohexene gave no C-H insertion products and only the cyclopropane (1) in all reported cases.

cyclohexene $\xrightarrow{(\text{CF}_3)_2\text{C:}}$

44 : 44 : 11

(15)   (16)   (17)
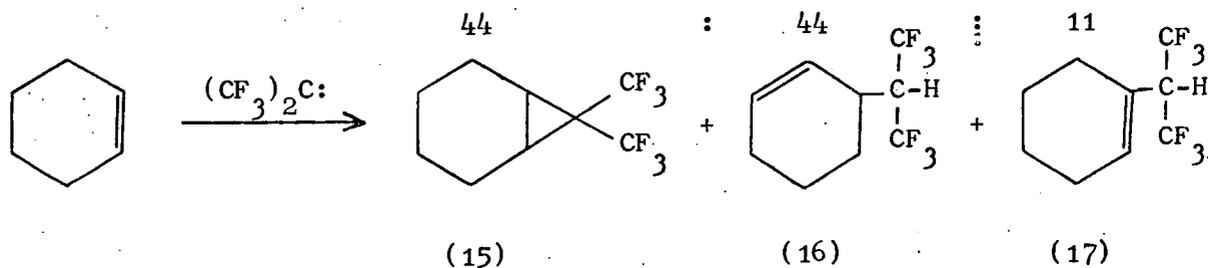
The extreme electrophilicity of $(\text{CF}_3)_2\text{C:}$ is confirmed by the reaction of the diazoalkane (4) with perfluorobenzene to give the cycloheptatriene (18) in 68% yield.[27]

(18)
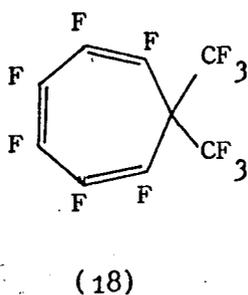
The heating of the diazirine (5) with <u>cis</u>-but-2-ene and <u>trans</u>-but-2-ene

at 165° led to a high degree of stereospecificity in the cyclopropanes formed.

In each case a number of C-H insertion products were formed.   However the

experimental results are consistent with $(CF_3)_2C$: having a ground state singlet

configuration.

1.6 Pyrolysis of highly fluorinated cyclopropanes

The usual mode of thermal decomposition of hydrocarbon and chlorinated

cyclopropanes is via isomerisation to olefins.   For instance, the unimolecular

rearrangement of methylcyclopropane (19) occurs to the largest extent via the

most stable diradical.[28]

(19)   (major)   (minor)

MeCH=CHMe + MeCH$_2$CH=CH$_2$ Me$_2$Ch=CH$_2$
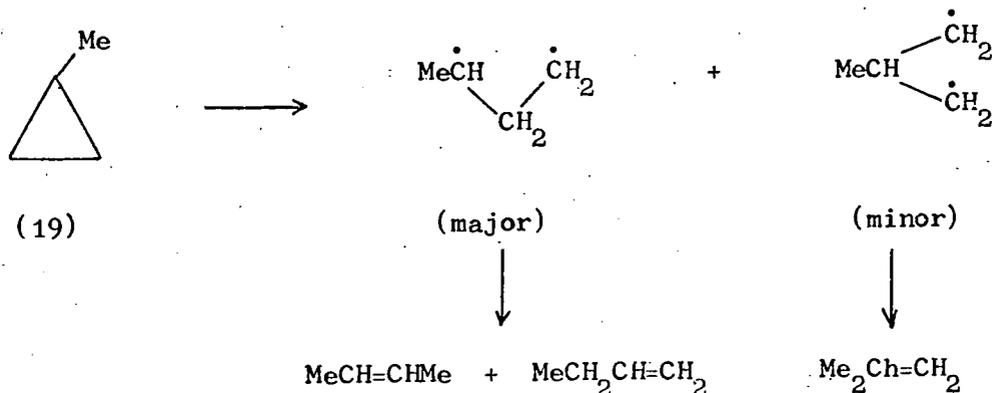
With chlorinated cyclopropanes the reaction mechanism on pyrolysis has not

been fully determined.   In a number of reactions the products can be explained

by a diradical intermediate that undergoes subsequent hydrogen migration

[e.g. (20)] or chlorine migration [e.g. (21)].[29]

(20)

(21)
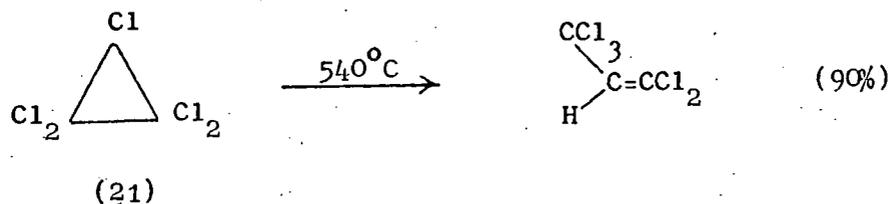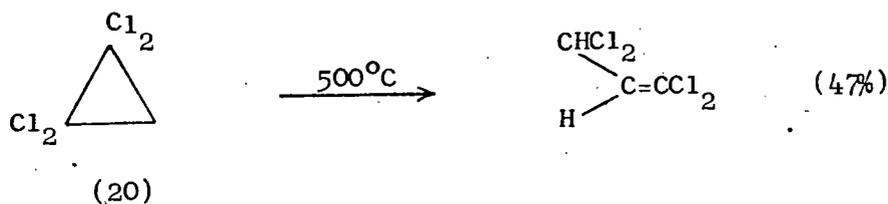
However, Haszeldine has also invoked a concerted chlorine migration to explain the formation of products that do not arise via the most stable radical.[29]　It is observed that $:CCl_2$ directs migration to the other carbon atom possibly through incipient stabilisation of the double bond [e.g. (22)].

(22)
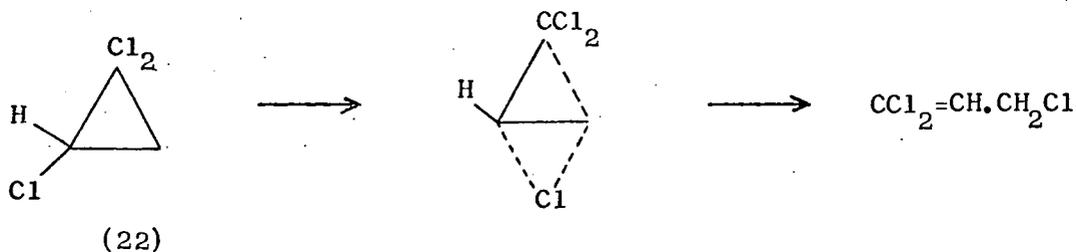
The normal mode of pyrolysis of highly fluorinated cyclopropanes is by the expulsion of difluorocarbene.[11]　For example the pyrolysis of perfluorocyclopropane at $165°C$ and 0.35 atm. gave a 50% yield of tetrafluoroethylene after 470 hours.　The kinetics of decomposition of perfluorocyclopropane are first order in the initial stages[30] and this is interpreted as involving free difluorocarbene:

$$CF_2=CF_2 \ + \ :CF_2$$
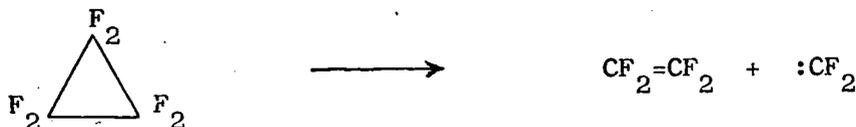
Haszeldine[11] has determined the order of stability of the highly fluorinated cyclopropanes, (23)-(28), by studying their thermal decomposition at 1.5 and 10 atm. at temperatures varying from 165 to $220°C$.　The order found, in decreasing stability, was:-
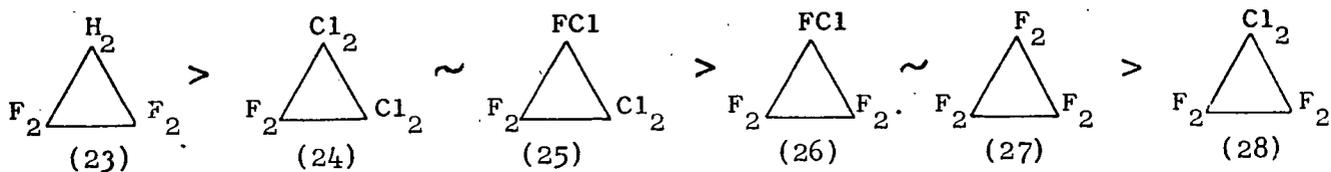
All of the above lost difluorocarbene on heating and formed the corresponding olefin [e.g. $Cl_2C=CCl_2$ in the case of (24)].　Elimination of $:CFCl$ did occur with (25) but the major product ($ClFC=CCl_2$) accrued from the elimination of $:CF_2$.

If the eliminated difluorocarbene does not dimerise or react with the olefin then the production of CO and SiF_4 occurs on the glass wall.

The thermal decomposition of cyclopropanes (29) and (30)[31] gives isomeric alkenes with the minor products arising from $:CF_2$ elimination and the major products arising from the migration of bromine and iodine respectively.

$$F_2 \bigtriangleup F_2 \quad (BrF) \quad \xrightarrow[\text{100 hr.}]{170^\circ C} \quad CF_2=CF.CF_2Br \;+\; CF_2=CFBr$$

(29) 69% 14%

$$F_2 \bigtriangleup F_2 \quad (FI) \quad \xrightarrow[\text{100 hr.}]{170^\circ C} \quad CF_2=CF.CF_2I \;+\; CF_2=CFI$$

(30) 79% 8%
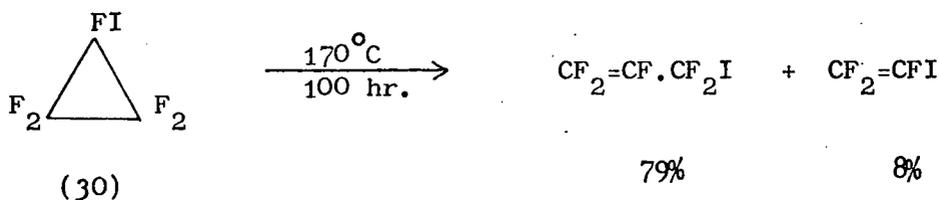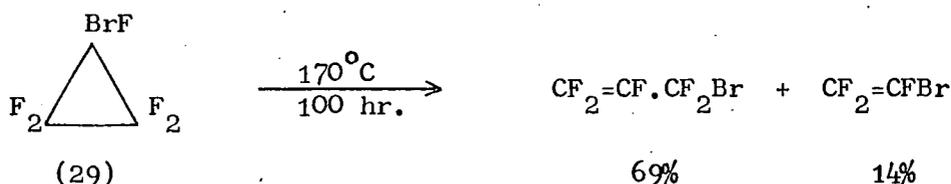
The factors determining the reaction path of some highly fluorinated cyclopropanes can occasionally be finely balanced. The decomposition of perfluoromethylcyclopropane is via elimination of $:CF_2$, yet (31) rearranges quantitatively to the isomeric alkene (32).[31]

$$\overset{F}{\underset{CF_3}{\bigtriangleup}} \overset{H_2}{} F_2 \quad \xrightarrow[\text{500 hr.}]{200^\circ C} \quad CF_3CF=CHCHF_2$$

(31) (32)
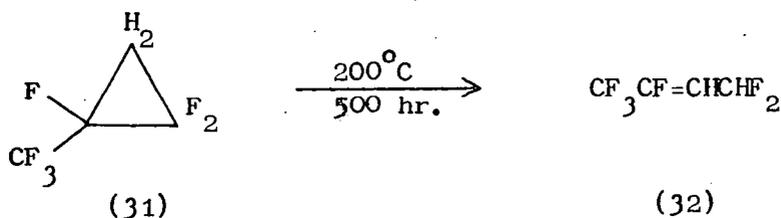
1.7 Cyclopropyl-allyl rearrangements

The reaction of tetrachlorocyclopropene or tetrabromocyclopropene with cyclopentadiene forms initially the Diels-Alder adduct (33) which subsequently undergoes a cyclopropyl-allyl rearrangement to give (35).[32]

(33)   (34)

(35)
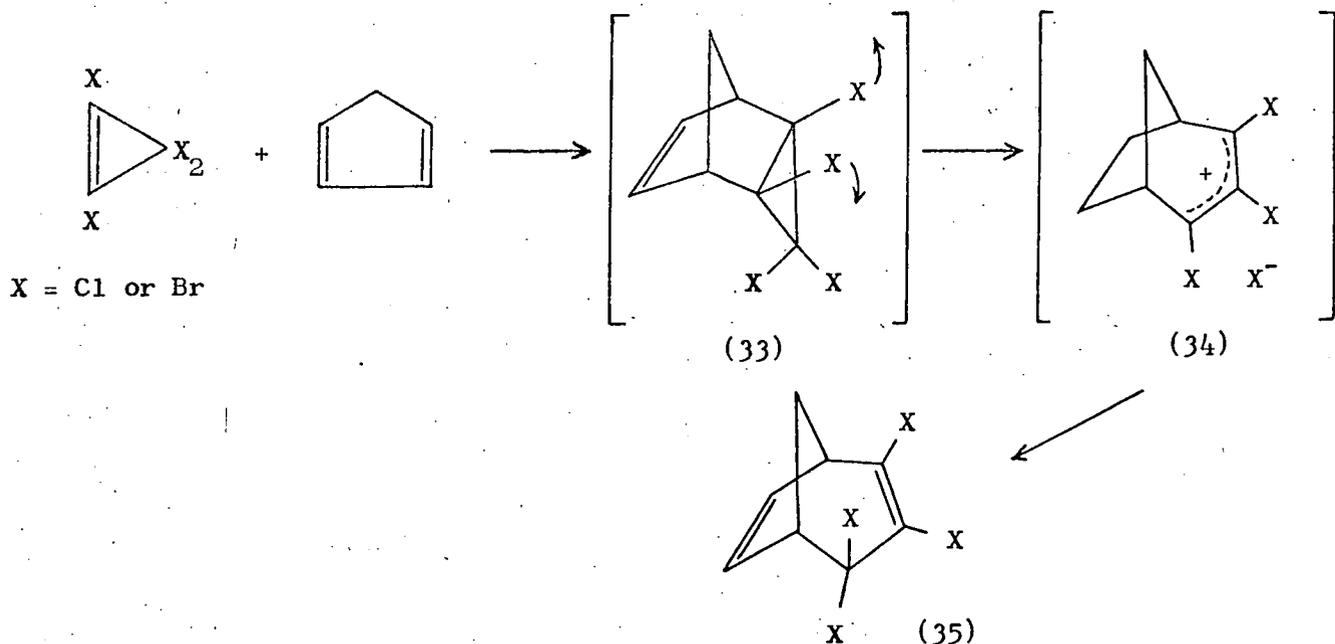
According to theoretical calculations[33] the rearrangement of (33) should involve

a disrotatory rotation of the halogen substituents at C_2 and C_4. The geometry

necessitates outward movement of X accompanied by the stereospecific ionisation

of the halogen atom at C_3, which is _syn_ to the double bond. The validity

of these predictions is found in the reaction products of furan with 1,2,3-

trichloro-3-fluorocyclopropene at $80^{\circ}C$ when after 16 hours products (36) and (37)

were obtained.[32]

(36)   (37)   (38)
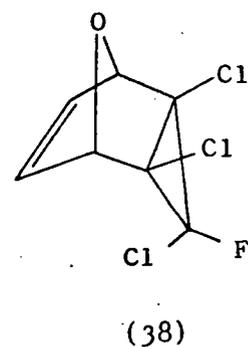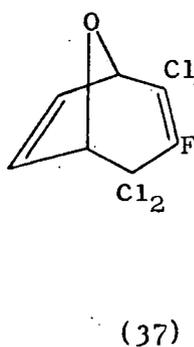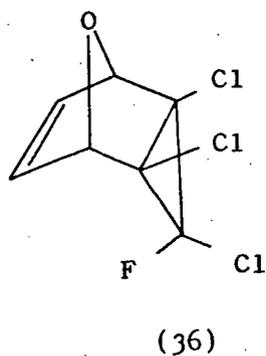
The cyclopropyl-allyl rearrangement of (38), which involves ionisation of the

C-Cl bond, led to the in situ production of (37). However, ring opening of

(36) did not occur as this requires ionisation of the much stronger C-F bond.

Further confirmation of the proposed mechanism came from the addition of :CFCl

to norbornene when (39) and (40) were obtained.   Rearrangement only occurred

where ionisation of the C-Cl bond was prerequisite.[34]

(39)   (41)

(39a)   (40)
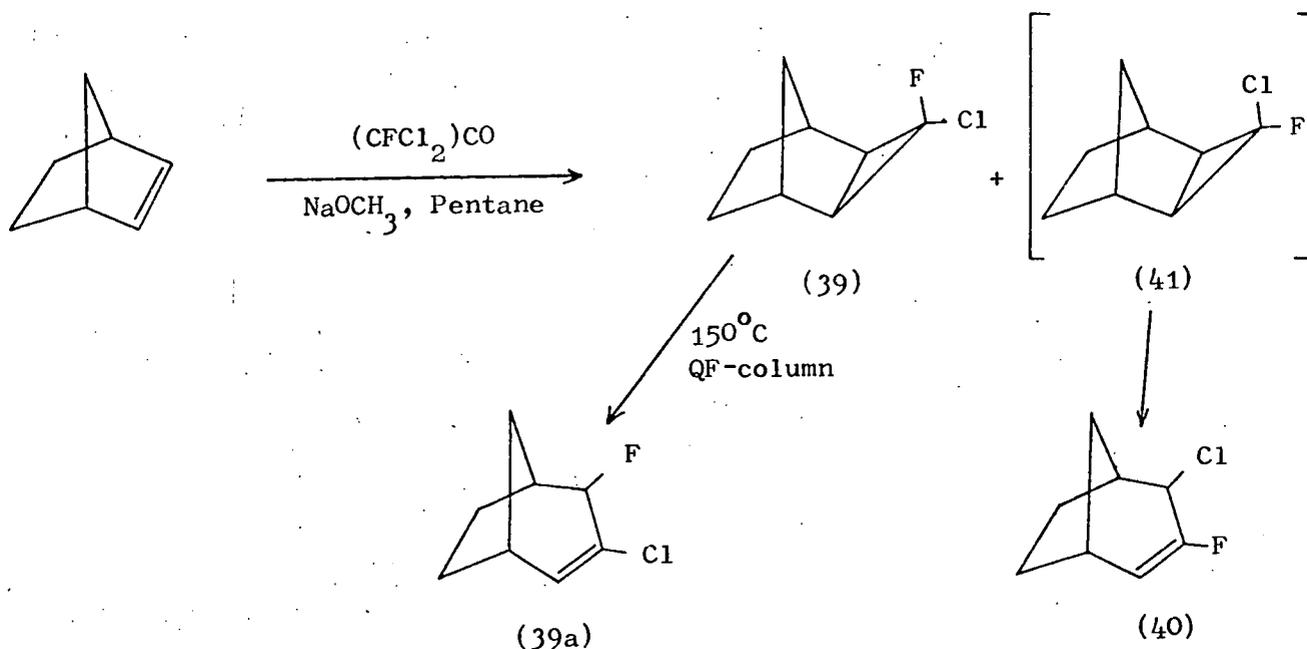
The addition of :CFCl to norbornene gave only the cyclopropanes with exo

configuration and the rearrangement of (41) to (40) gave specifically the

chlorine in the exo configuration.   The cyclopropyl-allyl rearrangement of

(39) to (39a), which requires the less favoured stereospecific ionisation of

the C-F bond, was efffected at $150^{\circ}C$ on a chromatographic column (QF-1 on

chromosorb W) and again produced only the isomer with fluorine in the exo

configuration.

The cyclopropyl-allyl rearrangement that involves ionisation of the C-F

bond is clearly rather unfavourable.   Nevertheless a number of examples have

been reported in the literature.   The cyclopropane (42) which has endo

configuration and is formed from the Diels-Alder reaction of cyclopentadiene

with perfluorocyclopropene readily undergoes a cyclopropyl-allyl rearrangement

to give a 50% yield of (43) after standing at room temperature for 2 months.[35]

(42)   (43)
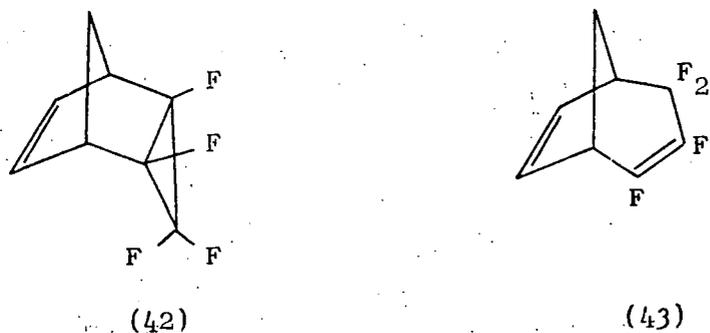
In a similar experiment the reaction of perfluorocyclopropene and norbornadiene at 90°C gave a 1,4-addition product (44), the majority of which rearranged in situ to give (45).

(44)   (45)
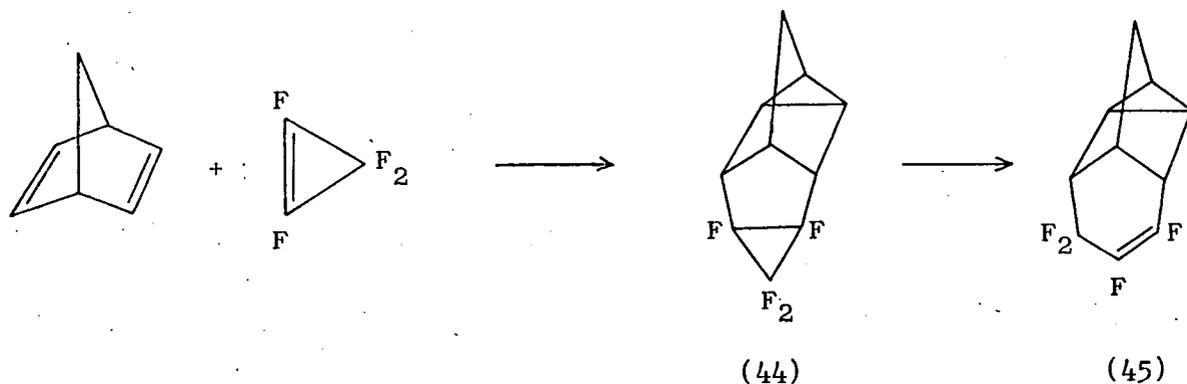
Perfluorocyclopropene and tetrafluoroethylene when heated at 135°C in a platinum lined autoclave gave a quantitative yield of perfluorocyclopentene presumably by a cyclopropyl-allyl rearrangement of (46).[36]

(46)
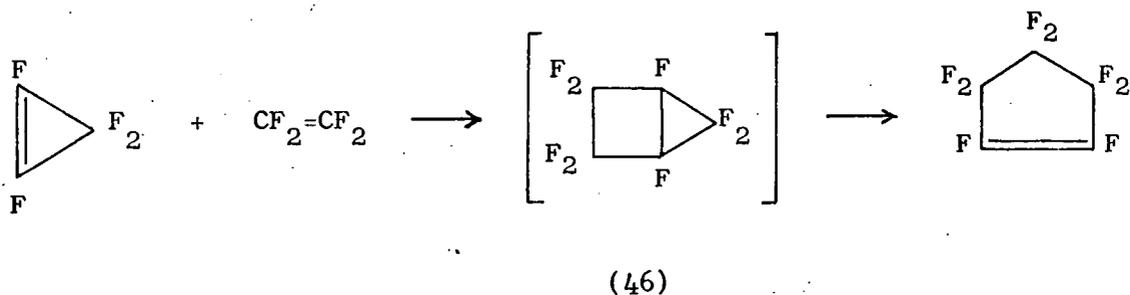
Sargent[35] has also reported the isomerisation of (47) to (49) at 200°C. The [π2s+σ2s] reaction is an allowed concerted reaction only in the excited state and for this reason a mechanism was postulated that initially followed the cyclopropyl-allyl rearrangement path to give (48).

(47)   (48)   (49)
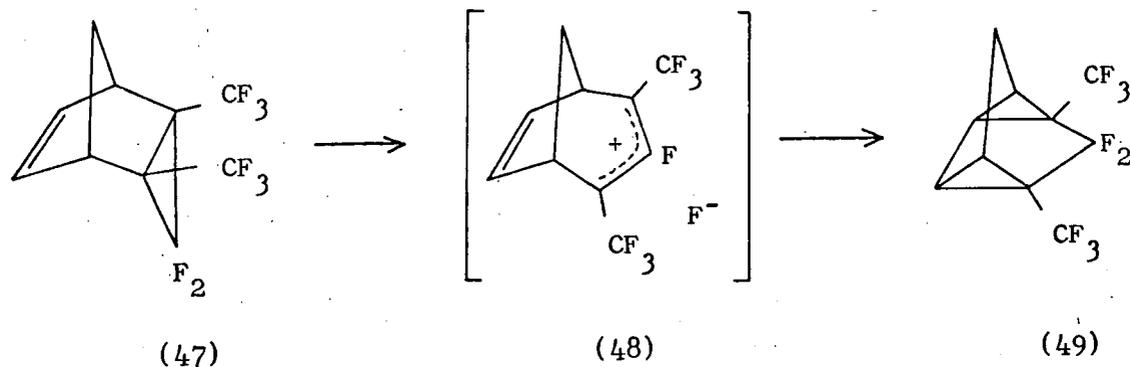
The addition of difluorocarbene to norbornadiene[37] gave a 1,4-addition product (50) and an exo 1,2-addition product (51)

(50)   (51)
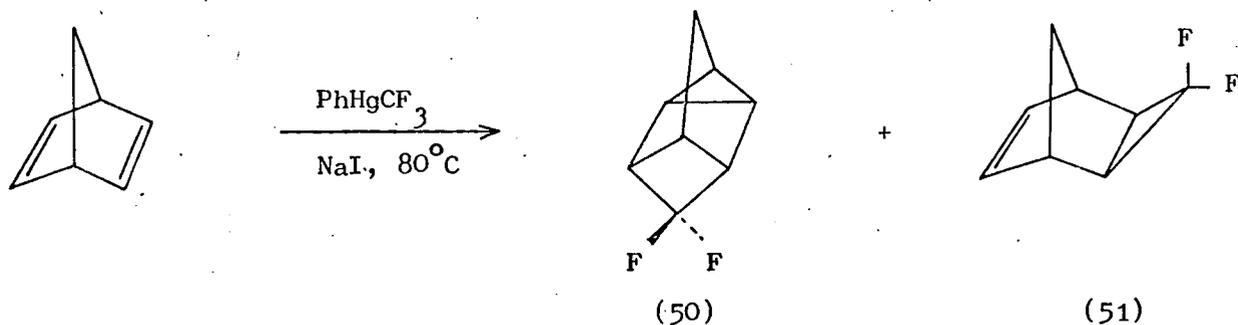
The cyclopropane (51) did not undergo a cyclopropyl-allyl rearrangement. This is the first recorded instance of a 1,4-addition product for a singlet carbene and has been achieved by virtue of the proximity of the ends of the polyene system.[37]

DISCUSSION

The original intention of this work was to obtain polyfluorinated cyclo-propanes by addition of difluorocarbene to a double bond contained either in a polyfluorinated six-membered ring or in a polyfluorinated bicyclic[2,2,2]octa-2,5-diene system. An envisaged cyclopropyl-allyl rearrangement could then yield highly fluorinated seven- and eight-membered ring systems which are rather difficult to obtain. Highly fluorinated products are obtained on the CoF_3 fluorination of cycloheptatriene.[55] However, highly fluorinated eight-membered ring compounds are less readily obtained: pentadecafluorocyclooctane and perfluorocyclooctane are obtained on direct fluorination of cyclooctane at $-78°C$.[56] Perfluorocyclooctane has also been prepared by the polymerisation of tetrafluoroethylene over charcoal at high temperatures and pressures,[57] whilst the dimerisation of perfluorobutadiene at $150°C$ gives perfluorocycloocta-1,5-diene.[58]

Moreover a synthesis of perfluoro-azulene that required the addition of difluorocarbene to a highly fluorinated system and subsequent rearrangement, was anticipated.

The reaction of HPE and cyclohexene gave the anticipated difluoronorcarane (1) which was identified by ^{19}F n.m.r. ($\delta_A = 125.9$, $\delta_B = 151.4$, $J_{AB} = 156$ Hz), i.r. spectroscopy, mass spectroscopy and boiling point. The i.r. and boiling point are recorded in the literature;[2] whilst the large J_{AB} of 156 Hz is a characteristic of gem cyclopropyl fluorines.

The preparation of HPE resulted in unavoidable contamination by hexafluoro-propene. It was possible to estimate the approximate amount of hexafluoro-propene impurity from an analysis of the infrared spectrum. (The absorption at 1800 cm^{-1} being attributable to hexafluoropropene ($-CF=CF_2$) and that at 1610 cm^{-1} to HPE). The hexafluoropropene, which may have reacted preferentially with difluorocarbene, was removed by bromination.

The attempted reaction of difluorocarbene with perfluorocyclopentene and perfluorocyclohexene at 180°C proved unsuccessful. When HPE and 1H,2H-octafluorocyclohexene were heated at 220°C for 4 hours no difluorocarbene addition product was observed. However, using identical conditions to the previous reaction a 12.1% yield of perfluorobicyclo[4,1,0]hept-3-ene (I) was obtained from difluorocarbene addition to perfluorocyclohexa-1,4-diene.

The evidence for the structure of (I) comes from the ^{19}F n.m.r.; two fluorines being in the characteristic tertiary region at 227 p.p.m. and the gem cyclopropyl fluorines having a coupling constant of 208 Hz, which is compatible with the values for other polyfluorinated cyclopropanes reported by Sargent.[35,36] The vinylic fluorines occur at 148.5 p.p.m. and the $-CF_2-$ fluorines form an AB system with J_{AB} = 280 Hz, which is compatible with values previously reported for five- and six-membered rings.[163] The elemental analysis for (I) is correct and the mass spectrum shows a small parent (9.4% of the base peak intensity) with the base peak arising from loss of CF_3. The infrared spectrum shows the expected (-CF=CF-) absorption at 1755 cm^{-1} and a broad absorption at 1480 cm^{-1} that is also present in other fluorinated cyclopropanes (e.g. refs. 8 and 11).

Unfortunately the cyclopropane (I) did not undergo a cyclopropyl-allyl rearrangement. The absence of a rearranged product from the initial reaction between difluorocarbene and perfluorocyclohexa-1,4-diene did not bode well and heating (I) at 165°C and 1 atm. pressure for 120 hours produced no change. Thermal decomposition of (I) did occur on pyrolysis at 220°C in a Carius tube (initial pressure ca. 1 atm.), and on vacuum pyrolysis at 450°C, with the result that difluorocarbene was eliminated and perfluorocyclohexa-1,4-diene formed. These results are consistent with the work published by Haszeldine[11] on the elimination of difluorocarbene from highly fluorinated cyclopropanes.

It is a little surprising that under comparable conditions difluorocarbene was found to add to a double bond in perfluorocyclohexa-1,4-diene yet not to

the CH=CH double bond of 1H,2H-octafluorocyclohexene (which might reasonably

be anticipated as more nucleophilic). From a study of the gas phase reaction

of dichlorocarbene with tetrafluoroethylene Haszeldine[11] has shown that the

cyclopropane (28a) is formed in an activated state and that unless deactivation

by collision occurs quickly then (28a) has sufficient vibrational energy to

eliminate difluorocarbene.

$$CCl_3SiF_3 \ + \ C_2F_4 \quad \xrightarrow[\substack{24 \ hrs. \\ 1 \ Atm. \\ pressure}]{140^\circ C} \quad \left[\overset{F_2}{\underset{Cl_2 \quad F_2}{\triangle}} \right]^* \xrightarrow{M} \overset{Cl_2}{\underset{F_2 \quad F_2}{\triangle}} \ + \ M$$

(28a)   (28)

                         59%

$$CF_2{:}CCl_2 \ + \ \overset{..}{CF_2} \quad \xrightarrow[Wall]{SiO_2} \quad CO \ + \ SiF_4$$

28%

|CCl_2 |C_2F_4

$$\overset{Cl_2}{\underset{F_2 \quad Cl_2}{\triangle}} \qquad \overset{F_2}{\underset{F_2 \quad F_2}{\triangle}}$$

(24)   (27)

12%   25%

The cyclopropane (28) is quite stable at this temperature and the yield of (24)

and (27) did not rise significantly with longer reaction times. This suggests

that (24) and (27) are formed from the vibrationally activated complex (28a).

Confirmation of this came with the marked improvement on the yield of (28) (82%)

when the reaction was performed at 10 atm. pressure.

An analogous situation can be envisaged for the addition of difluorocarbene

to perfluorocyclohexa-1,4-diene with the formation of the activated cyclopropane

of (I) requiring deactivation by collision.   However the reaction was carried

out at high pressure and this deactivation should have been fairly favourable.

The reactions of HPE with perfluorocyclohexa-1,4-diene and 1H,2H-octafluoro-

cyclohexene were carried out in the same autoclave with the same quantitites of

starting material and hence deactivation by collision should have had equal

opportunity in both reactions.   (N.B. If the critical pressure of HPE had not

been exceeded then the initial pressure for each reaction would have been about

60 atm.).

The crux of the situation must revolve around the fact that when heated at

$220^{\circ}C$ for 4 hours the cyclopropane (I) underwent an 80% decomposition by

elimination of difluorocarbene.   Hence the temperature required to produce the

cyclopropane (I) also causes the latter to decompose at an appreciable rate.

Only rapid cooling of the autoclave to room temperature enabled the rather

fortuitous preparation of the cyclopropane (I).   A similar predicament can be

envisaged for the addition of difluorocarbene to 1H, 2H-octafluorocyclohexene

with the cyclopropane being formed but also being unstable.   In this instance

the rate of formation and decomposition must have been very similar.

It would seem plausible to consider the addition of difluorocarbene to

perfluorocyclohexa-1,4-diene at $220^{\circ}C$ as a reversible reaction.
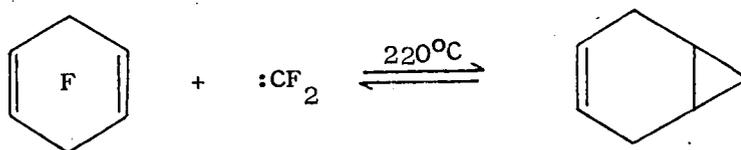
However a dynamic equilibrium is not achieved and the reaction is driven to the

left owing to the tendency of difluorocarbene to dimerise and also to react with

the vessel walls, particularly glass walls.   The principle of microscopic

reversibility demands that the transition state for the elimination of difluoro-

carbene from the cyclopropane (I) is non-symmetrical (cf. Introduction 1.4).
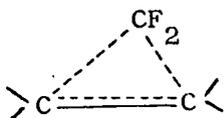
Haszeldine[11] has reported that decomposition of perfluorocyclopropane by elimination of difluorocarbene was 99% complete on heating in a sealed glass vessel at 160°C (initial pressure 0·35 atm.) for 352 hours. 92% decomposition occurred at 170°C after 255 hours when the initial pressure was 10 atm. Hence the cyclopropane (I) which did not decompose at 165°C is more stable than perfluorocyclopropane. The elimination of difluorocarbene is likely to proceed through transition states that are very similar energetically and it is assumed that the greater stability of the cyclopropane (I) arises from ground state stabilisation.

The ability of a fluorine substituent at C1 to stabilize the C1-C3 and C1-C2 bonds whilst destabilizing the C2-C3 bond in cyclopropane by interaction with the cyclopropane Walsh orbitals, is discussed in Chapter 2.5 (refs. 75-78).
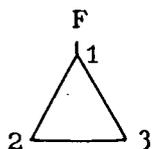
It has been considered for sometime that an α fluorine produces stabilization on the adjacent C-C bond and this has been confirmed from a gas kinetic study on radical recombinations.[100] The C-C bond α to fluorine in $CF_3CH_2CH_3$ was found to be 4·5 ± 0·4 Kcal/mole more stable than the β C-C bond. However it is not known if the α fluorine produces any stabilization on the β C-C bond.
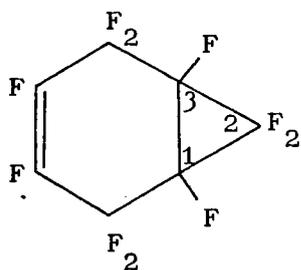
(I)
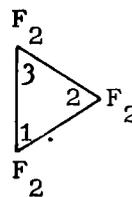
(52)

On changing from (I) to (52) the additional fluorine at C1 will destabilize the C2-C3 bond.

However, the change at C3 from a σ-bond to a difluoromethylene and one α carbon-fluorine bond in (I) to two α carbon-fluorine bonds in (52) may produce some increased stabilization of the C2-C3 bond. Depending on the relative magnitude of these effects it is possible that on changing from (I) to (52) the C2-C3 bond (and likewise the C1-C2 bond) will become weaker. Hence elimination of difluorocarbene would be easier for perfluorocyclopropane and would explain why the latter is less stable than (I). This argument is extremely speculative and with no molecular orbital calculation having been performed on highly fluorinated cyclopropanes a detailed insight into the situation is not available at present.

EXPERIMENTAL

1.8 Preparation of starting materials

Hexafluoropropene epoxide (HPE) (B.pt. -28°C) was prepared by reacting hexafluoropropene (B.pt. -29°C) with H_2O_2, in a water/methanol mixture containing KOH, at -50°C.[38] The HPE so formed contained about 10% of hexafluoropropene which was estimated from the relative intensities of the i.r. bands at 1800 cm^{-1} ($-CF=CF_2$) and 1610 cm^{-1} (HPE only). The hexafluoro-propene was removed by reaction with bromine in CCl_4 at -35°C to give $CF_3CFBrCF_2Br$ (B.pt. 70°C),[39] from which the HPE was easily separated by distillation.

Perfluorocyclopentene,[40] perfluorocyclohexa-1,4-diene[41] and 1H,2H-octafluoro-cyclohexene[42] were prepared by the published routes. All reagents were dried (P_2O_5) and degassed before use.

1.9 Reactions of hexafluoropropene epoxide (HPE)

(a) With perfluorocyclopentene

Perfluorocyclopentene (7·61g., 34·2 mmoles) and HPE (7·5g., 45·0 mmoles) were transferred by conventional vacuum line techniques into a 100 ml. Pyrex ampoule (Carius tube) which was sealed under vacuum and then heated at 185°C for 15 hours. The products were separated into: (i) a gaseous fraction shown by i.r. and m.s. to contain CF_3COF, SiF_4 and $CF_2=CF_2$ and (ii) a fraction shown by i.r., g.l.c. and m.s. to be primarily the unreacted perfluorocyclopentene (7·48g.) with a trace of the more volatile components previously identified in (i).

(b) With perfluorocyclohexene

Perfluorocyclohexene (5·13g., 18·3 mmoles) and HPE (8·00g., 48·1 mmoles) were transferred in vacuo into a stainless steel shaker tube (volume 20 ml. and length 22 cm.) and heated at 180°C for 14 hours to give: (i) a gaseous fraction shown by i.r. and m.s. to contain CF_3COF and $CF_2=CF_2$ and (ii) perfluorocyclo-

hexene (5·00g.), confirmed by n.m.r., i.r., g.l.c. and m.s.

(c) With cyclohexene

By using the same procedure as in (b), cyclohexene (1·6g., 19·5 mmoles) and HPE (7·0g., 42·1 mmoles) were heated at $185^{\circ}C$ for 4 hours to give: (i) a gaseous fraction shown by i.r. and m.s. to contain perfluoroacetyl fluoride and tetrafluoroethylene and (ii) a liquid fraction. Fraction (ii) was distilled to give cyclohexene (B.pt. $82^{\circ}C$, 0·85g.) and a liquid (B.pt. 121 to $123^{\circ}C$) identified as 7,7-difluorobicyclo[4,1,0]heptane (1) (1·6g., 61% yield) by comparison of i.r. and B.pt. with published data.[2] $C_7F_2H_{10}$ has a Mol. Wt. 132 (m.s.) and the ^{19}F n.m.r. showed two doublet resonances of equal intensity: δ_A = 125·9 p.p.m., δ_B = 151·4 p.p.m., J_{AB} = 156 Hz. (Int. $CFCl_3$, reference to centre of doublets, run as neat liquid).

(d) With 1H,2H-octafluorocyclohexene

(1) By using the same procedure as in (b), 1H,2H-octafluorocyclohexene (4·00g., 17·7 mmoles) and HPE (6·9g., 41·5 mmoles) were heated at $200^{\circ}C$ for 4 hours to give: (i) a gaseous fraction similar to that in (b) and (ii) 3·98g. of liquid shown by n.m.r., g.l.c. and i.r. to be unchanged 1H,2H-octafluorocyclo-hexene.

(2) 1H,2H-octafluorocyclohexene (36·1g., 159·7 mmoles) and pure HPE (43·7g., 263·1 mmoles) were transferred in vacuo into a stainless steel autoclave (volume 160 ml. and length 13·0 cm.) and heated at $220^{\circ}C$ for 4 hours. The autoclave was rapidly cooled and opened to give: (i) a gaseous fraction similar to that in (b)(i); (ii) a liquid fraction confirmed by n.m.r., g.l.c. and i.r. to be unreacted 1H,2H-octafluorocyclohexene (36·0g.) and (iii) a solid fraction (2·5g.) confirmed by i.r. to be polytetrafluoroethylene (PTFE).

(e) With perfluorocyclohexa-1,4-diene

By using the same procedure as in (d)(2), perfluorocyclohexa-1,4-diene (36·1g., 161·7 mmoles) and HPE (41·0g., 245·0 mmoles) were heated at $220^{\circ}C$ for

4 hours. The autoclave was rapidly cooled and opened to give: (i) a gaseous fraction (36.2g.) similar to that in (b)(i); (ii) a liquid fraction (36.6g.) and (iii) a solid (2.7g.) shown by i.r. to be (PTFE). The liquid fraction was separated (g.l.c. Col. F, 60°C) into the longer retained perfluorocyclohexa-1,4-diene (25.9g.) and perfluorobicyclo[4,1,0]hept-3-ene (I) (4.41g., 16.1 mmoles, a yield equivalent to 12.1% before separation). C_7F_{10}, which has a Mol. Wt. 274 (m.s.), requires C, 30.6% and F, 69.4%. Found: C, 30.4% and F, 69.6%. (I) is a colourless liquid B.pt 60.5°C. The ^{19}F n.m.r. of (I) shows tertiary fluorines at 226 (2), vinylic F at 148.5 (2), two F at C7 δ_A(1) 148.0 and δ_B(1) 145.5, J_{AB} = 208 Hz and four F at C2 and C5 $\delta_{A'}$ = 100.7 (2) and $\delta_{B'}$ = 109.6 (2) $J_{A'B'}$ = 280 Hz. (All resonances are at p.p.m. from int. $CFCl_3$ with integrated intensities in parentheses.) υ_{max} 1755 (-CF=CF-) and 1480 cm^{-1}.

1.10 Pyrolysis of perfluorobicyclo[4,1,0]hept-3-ene (I)

(a) Vacuum pyrolysis

Using the method outlined in section (2.9) 0.156g. (0.56 mmoles) of the olefin (I) was pyrolysed at 450°C and 2 x 10^{-2} mm. to give: (i) a gaseous fraction (0.66 mmoles) shown by i.r. and m.s. to be a mixture of C_2F_4, CO and SiF_4 and (ii) a liquid fraction (0.114g., 0.51 mmoles, ca. 90% yield) shown by g.l.c. and i.r. to consist only of perfluorocyclohexa-1,4-diene.

Vacuum pyrolysis at lower temperature resulted in incomplete decomposition of the olefin (I) to perfluorocyclohexa-1,4-diene.

(b) Pyrolysis at atmospheric pressure

The olefin (I) (0.061g.) was transferred (from P_2O_5) in vacuo, sealed in a 1 ml. Carius tube and heated at 220°C for 4 hours (initial pressure ca. 10 atm.) to give a liquid mixture that was analysed by i.r. and g.l.c. and shown to contain perfluorocyclohexa-1,4-diene and (I) in the ratio 4:1 respectively.

A similar experiment in which the olefin (I) was heated at 1 atm. pressure and 165°C for 12 hours showed no signs of decomposition and unchanged olefin (I) was obtained.

CHAPTER 2

The Photochemistry Of Polyfluorobicyclo[2,2,2]octa-2,5-dienes

INTRODUCTION

2.1 The photochemistry of norbornadienes

Irradiation of the norbornadiene dicarboxylic acid (56) in ether solution

gave the quadricyclane (57) which is a remarkably stable compound.[43] The

generality of this first recorded photochemical isomerisation of the norbornadiene

system was soon to be established.

(56)   (57)
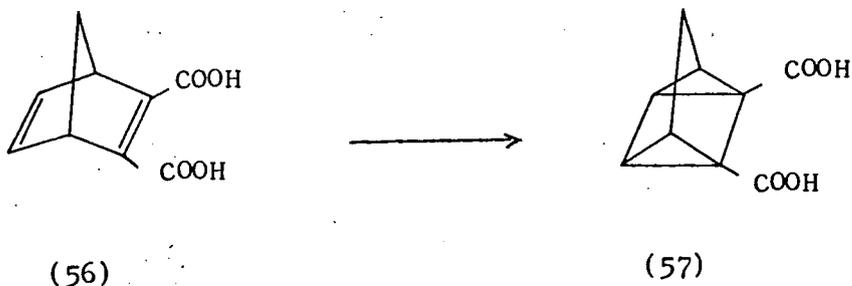
The photochemical isomerisation of bicyclo[2,2,1]hepta-2,5-diene (58) gave

tetracyclo[3,2,0,0^{2,7},0^{4,6}]heptane (59) which is quite thermally stable with a

half-life of about 3 mins. at 210°C.[44] This isomerisation may be photo-

sensitized and under these conditions becomes reversible leading to a photo-

stationary state, the composition of which depends upon the sensitizer.[45] The

low energy sensitizer fluorenone (E_T = 54 Kcals) gave a mixture containing 70%

of the quadricyclane (59) when equilibrium was approached from either side.

However, side reactions resulted in a change in the equilibrium position and

only 25% of the original C7 hydrocarbons remained after 63 hours.   Acetophenone

(E_T = 73·6) gave the quadricyclane (59) only and it did not appear to sensitize

the isomerisation of (59) to (58).   Benzophenone (E_T = 68·5) gave an

equilibrium mixture containing 88% of (59).   These observations suggest that

the isomerisation is not proceeding by the orbital symmetry allowed [π2s + π2s]

concerted pathway.

Hammond[45] postulated two possible mechanisms for the norbornadiene-quadricyclane isomerisation. The first involved the excitation of (58) or (59) to triplets having the same nuclear configuration in accord with the Franck-Condon principle. The intermediate (60) can be considered as arising from interaction between the π bonds in the excited state.
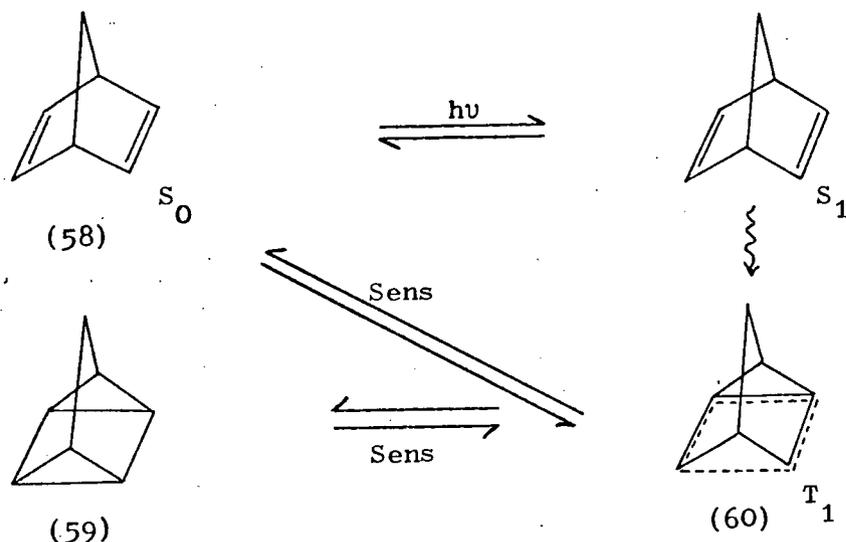
The second postulated mode of isomerisation involved the formation of a bi-radical (61).
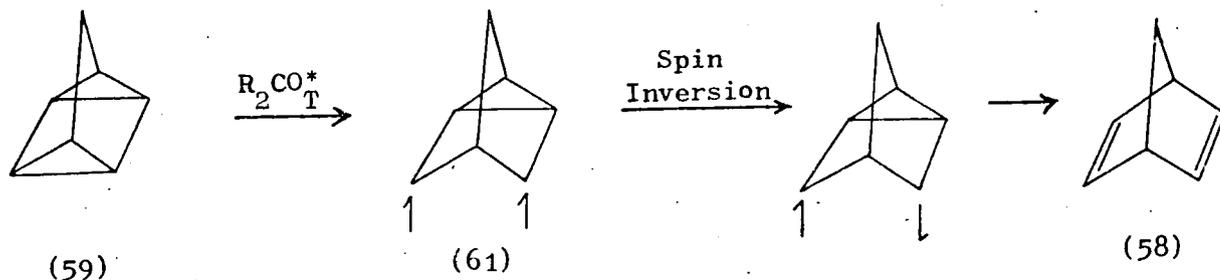
The reverse isomerisation (58) to (59) would require that the triplet formed from the diene and $R_2CO^*_T$ collapsed to the ground state of (59).

The vapour phase photolysis of norbornadiene in a mercury free system was not oxygen quenched and therefore the formation of cyclopentadiene, acetylene and toluene was presumed to proceed via the excited singlet state.[46] ($\Phi_{C_5H_6} = \Phi_{C_2H_2} = 10\ \Phi_{Toluene}$; where Φ = quantum yield). No quadricyclane was formed.

The substitution of electron withdrawing chlorine groups in the norbornadiene skeleton does not adversely affect quadricyclane formation.
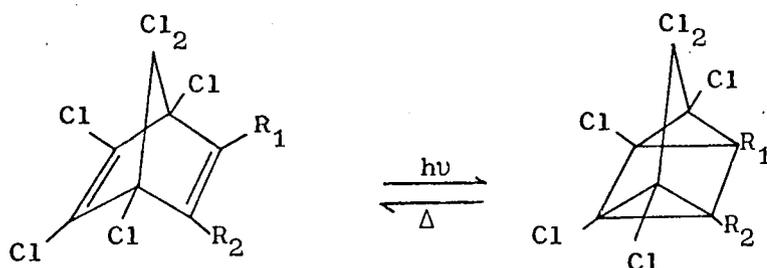
$R_1 = R_2 = H$, 76% yield of quadricyclane (Ref. 47)

$R_1 = H$, $R_2 = Me$; $R_1 = R_2 = SnMe_3$ (ref. 48)

The photochemical isomerisation of oxanorbornadiene (62) to oxaquadricyclane (63) has been extensively studied by Prinzbach.[49] The reactions when carried out in solution can be photosensitized with either acetone or benzophenone. However the reverse reaction is not photosensitized and heating the fairly stable oxaquadricyclanes (63) produced oxepines rather than the oxanorbornadienes. The oxygen bridge provides enough stabilization in the transition state to enhance cleavage of the cyclopropane σ bonds that are not formed in the initial photochemical change.
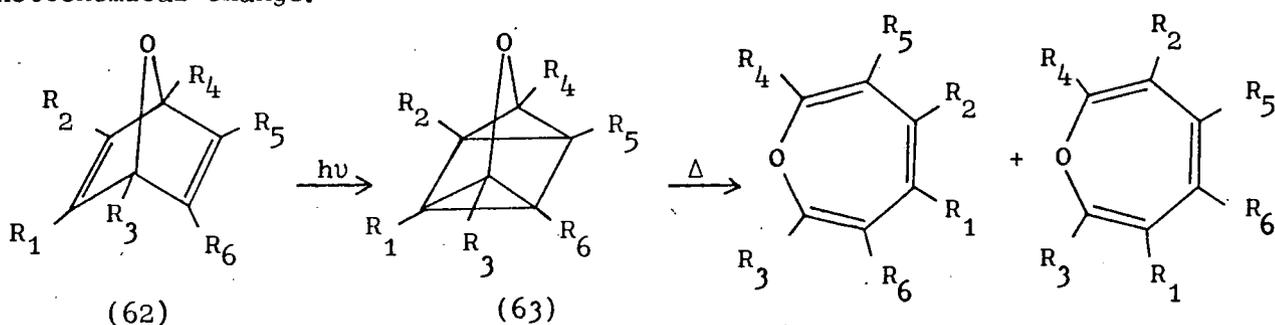
There is a noticeable bathochromic shift in the u.v. spectra of (64) relative to (65) and this presumably arises from the transannular interaction in the excited state of the former.
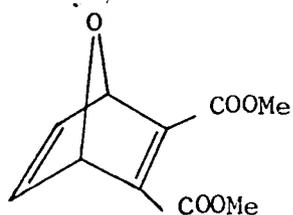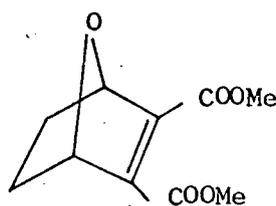
Prinzbach[49] has also converted a series of methylene-norbornadienes (e.g. 66) into the corresponding methylene-quadricyclanes (e.g. 67) by irradiation in solution. This isomerisation is reversed on heating. The pronounced bathochromic shift in the u.v. spectra of these compounds suggests that the sp^2 bridge carbon enables even more transannular interaction than in the parent norbornadienes. Predictably the photochemical isomerisation proceeds very smoothly and the forward reaction is photosensitized by fluorenone but (67) appears stable to energy transfer from this triplet sensitizer.
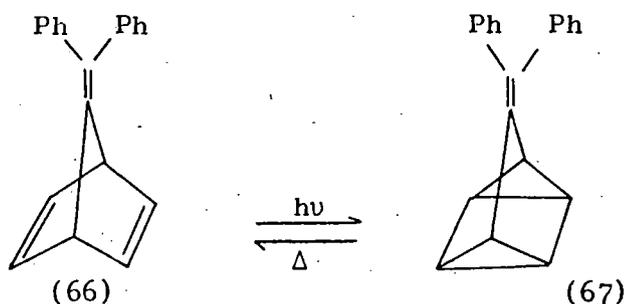
A kinetic model has recently been developed that in certain cases enables the differentiation between a concerted and two-step photochemical reaction.[50,51] In theory a reversible photochemical isomerisation proceeding via a common intermediate should give $\Phi_{AB} + \Phi_{BA} = 1$,[50] where Φ_{AB} is the quantum yield for the forward reaction and Φ_{BA} is the quantum yield for the reverse reaction, providing that no other photochemical process is proceeding simultaneously.

$$A \underset{k_1}{\overset{h\upsilon}{\rightleftharpoons}} X \underset{k_2}{\overset{h\upsilon}{\rightleftharpoons}} B$$
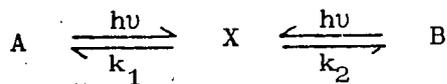
All quanta absorbed by A or B give the intermediate X which is deactivated to B and A in the ratio of $k_2 : k_1$. With a concerted reaction, and when the forward and reverse reactions proceed through different intermediates, $\Phi_{AB} + \Phi_{BA}$ could equal a maximum of two. (In practice no reversible reaction is known where the limiting value of one has been significantly exceeded[51]).
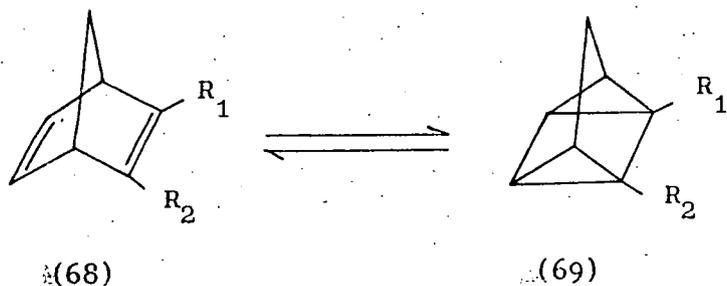
(a) $R_1 = R_2 = COOMe$

(b) $R_1 = Ph, R_2 = COOMe$

(c) $R_1 = H, R_2 = COOMe$

(68)   (69)

The isomerisations of compounds (68) and (69) are amenable to a mechanistic study of the norbornadiene-quadricyclane isomerisation since the reverse reaction can be followed directly on irradiation at 257 nm, whilst the forward reaction can be followed on irradiation at 300 nm. The presence of the ester and phenyl groups results in absorption of irradiation by the quadricyclanes so that the reverse reaction may be followed without triplet sensitization. For (68a) and (70) the sum of the quantum yields for the reversible isomerisations is about 1.[50] Irradiation of (68a) in acetonitrile gave a quantum yield of 0.47 for the forward reaction as opposed to a value of 0.52 for (70). Neither the presence of oxygen nor trans-piperylene altered the quantum yields for the forward reaction. Irradiation in ethyl bromide solution did not affect the quantum yield for the forward reaction. Hence Prinzbach and Kaupp[50] suggested that the photochemical isomerisation involves a singlet intermediate of the type (71).

(70)   (71)
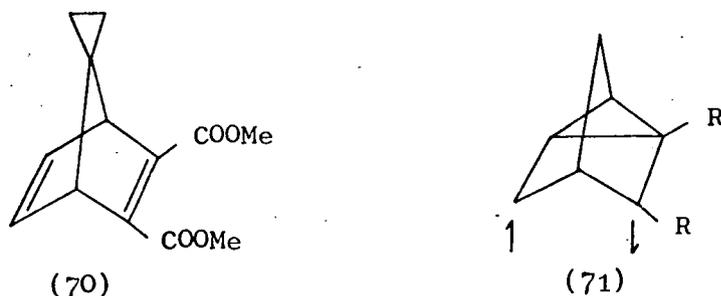
However the situation is lacking in lucidity as Kaupp has proffered evidence suggesting that the intermediate is of a triplet nature (73).[51] The study of the reversible isomerisation (72)-(74) gave $\Phi_{forward} + \Phi_{reverse} \simeq 1$, with no fluorescence and no detectable photochemical side reaction.

(72)   (73)   (74)
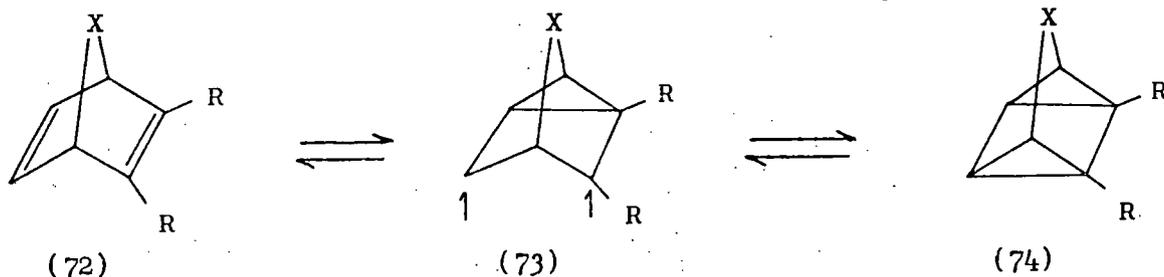
(a) X = CH_2, R = Ph

(b) X = O,   R = o, o'-$C_6H_4SO_2C_6H_4$

The mechanism of interaction of triplet benzophenone with norbornadienes and quadricyclanes has also been studied.[52] The irradiation of (75b) and benzophenone in a 1:10 molar ratio resulted in the formation of (76b) with zero-order kinetics. (76b) and benzophenone in a 1:10 molar ratio when irradiated in benzene formed the adducts (77b), (77c) and (78b) with first-order kinetics and 9% efficiency. From a kinetic and quantum mechanical study the authors

(75)

(a) R = H

(b) R = COOEt

(76)

(a) R = H

(b) R = COOEt

(77)

(a) R=R'=H

(b) R=COOEt, R'=H

(c) R=H, R'=COOEt

(78)

(a) R = H

(b) R = COOEt
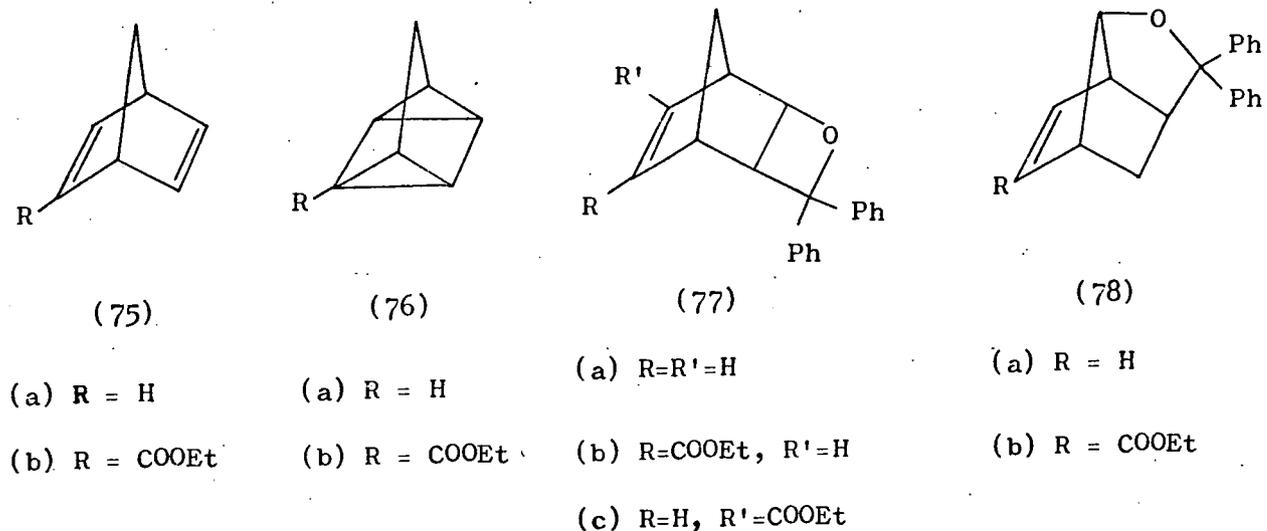
concluded that a collisional transfer mechanism is operative for the quenching of benzophenone by (75b). The position is less clear for the quenching of benzophenone by (75a) and (76a) where the mechanism involved could be considered as involving either a charge transfer or bi-radical intermediate. The bi-radical intermediate in the case of (75a) would be a triplet.[52]

Hence it would seem that the reversible norbornadiene-quadricyclane photochemical isomerisation can be achieved independently of the nature of the substituents on the carbon framework. It is also likely that the mechanism of this isomerisation is the same in all instances. All the examples to date that have been studied by quantitative photochemistry confirm that the reversible isomerisation proceeds through a common intermediate. Although the true nature of this intermediate is a little elusive it would appear to be bi-radical.

2.2 Photochemistry of bicyclo[2,2,2]octa-2,5-dienes

The photochemistry of these dienes is found to parallel that of the bicyclo[2,2,1]hepta-2,5-diene series with the main difference being that the tetracyclo[4,2,0,0^{2,8},0^{5,7}]octanes are much more unstable than the corresponding tetracyclo[3,2,0,0^{2,7},0^{4,6}]heptanes. The first isomerisations were reported by Prinzbach[53] who irradiated solutions of (79) and (81) in ether at -20°C to give the corresponding tetracyclic compounds (80) and (82). The solutions containing 100 mg. of compound in 300 ml. of ether were irradiated using a medium pressure mercury lamp of 70 watts output. The tetracyclic compounds were obtained in at least 95% purity by concentration at low temperature and recrystallization from ether at -60°C.

$t_{\frac{1}{2}}$ = 90 mins at 21°C

$t_{\frac{1}{2}}$ = 12 mins at 19°C
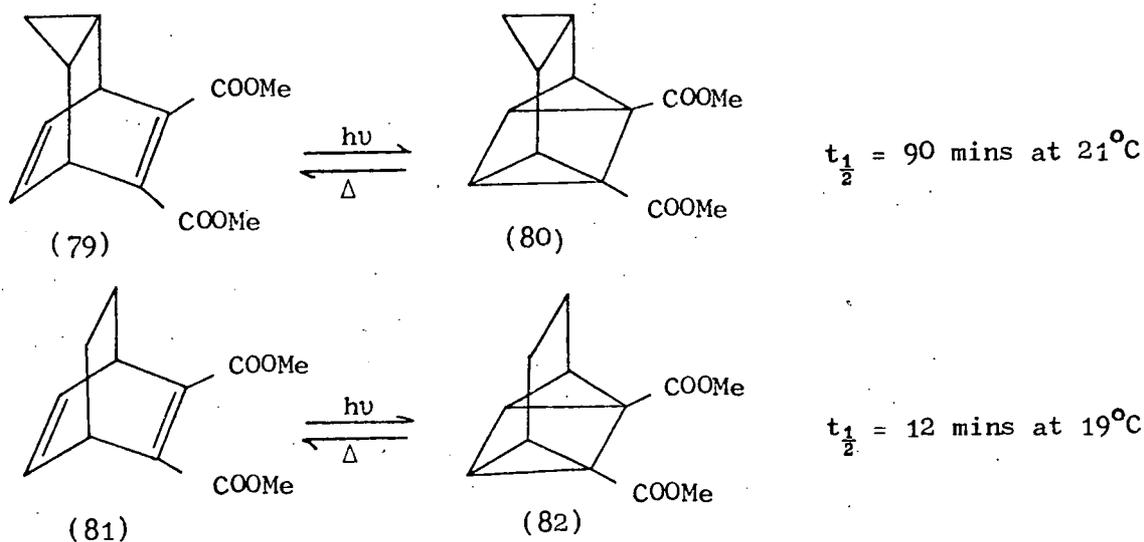
The photochemical isomerisation of (83) gave an 85% yield of (84) after 20 hours when a 25% solution was irradiated in acetonitrile with a low pressure mercury lamp.[54] In comparison with the tetracycles (80) and (82), (84) is fairly stable with a half-life of 5 mins. at 80.5°C.
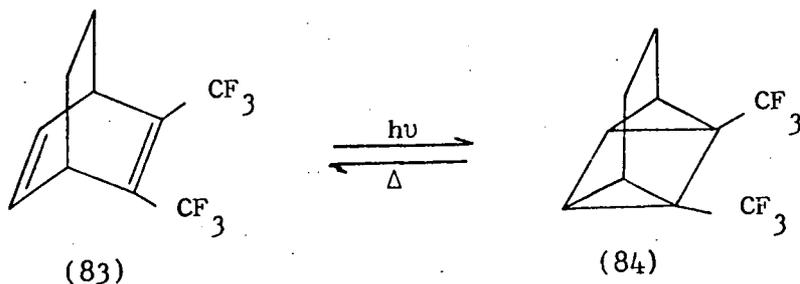
Two further $[2\pi + 2\pi]$ ring closure reactions have been reported by Nelsen and Gillespie who irradiated (85) and (86) at 313 nm in $CDCl_3$; the tetracyclic compounds so formed are very thermally unstable.

(Ref. 59)

$t_{\frac{1}{2}} = 3$ mins at $20^{\circ}C$

(85)

(86)

(Ref. 60)

$t_{\frac{1}{2}} = 16$ mins at $2^{\circ}C$
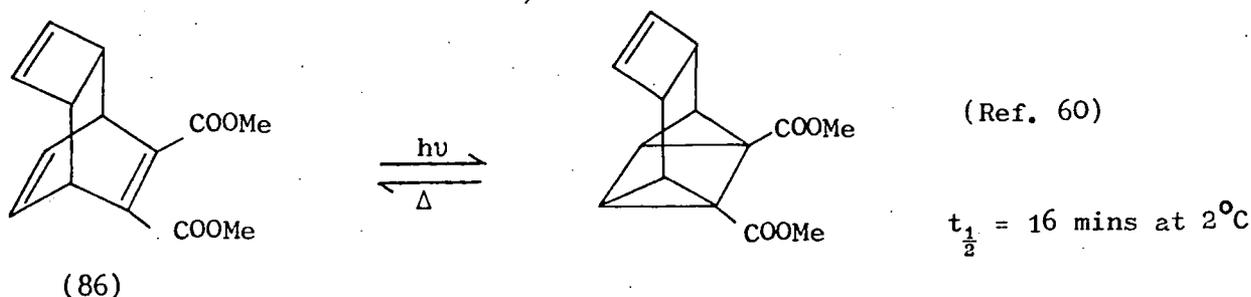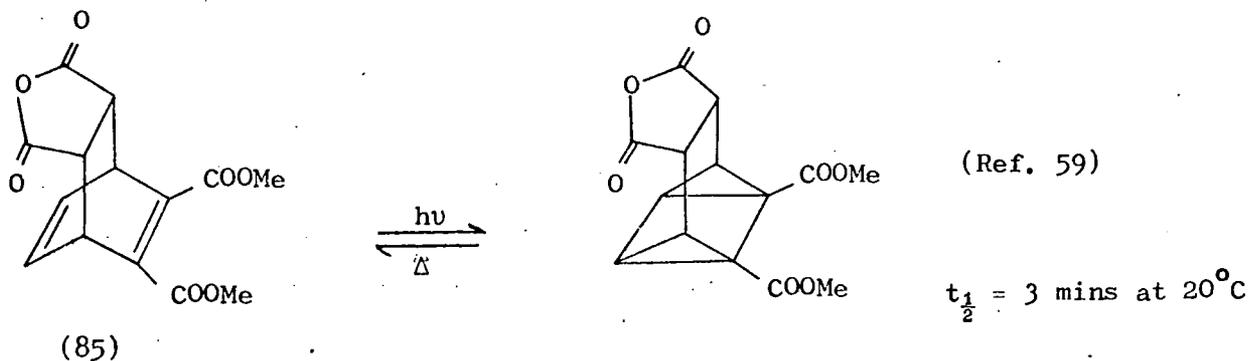
Prinzbach subsequently reported that the irradiation of (81) in ether solution (4×10^{-3} molar) at $-20^{\circ}C$ produced after 2 hours a mixture containing (81) and (82) in the ratio of 6:4.[61]   Also 1 or 2% of the decomposition product, dimethyl terephthalate was obtained.   Longer irradiation times produced more dimethyl terephthalate, hydrolysis, solvent addition and polymeric products. It was essential to perform the irradiation with $\lambda > 230$ nm (Vycorfilter) rather than with $\lambda > 280$ nm used for the irradiation of the norbornadiene homologue of (81), (i.e. 68a), as the extinction coefficient of (81) is a factor of 10 smaller than that of (68a) at 280 nm.   Unfortunately (82) also absorbs at $\lambda > 230$ nm and the reverse isomerisation proceeds simultaneously with the forward isomerisation.

None of the photochemical isomerisations of bicyclo[2,2,2]octa-2,5-dienes are triplet sensitized by acetophenone or benzophenone.   However, Prinzbach

claims that the evidence for this is not conclusive since the products are thermally labile and quantum yields are not reported for the photochemical reactions either in the presence or absence of a triplet sensitizer.[61]

Addition of HCl to the tetracycle (82) proceeded very readily at 0°C when the acid was added to a 6:4 mixture of (81) : (82) in dichloromethane.[61]   (87a) and (88a) were formed in the ratio of 9:1.   The photolysis of (81) at 0°C in acetonitrile that had been saturated with HCl also produced the same addition products (87a) and (88a) in the same ratio

(87)

(88)
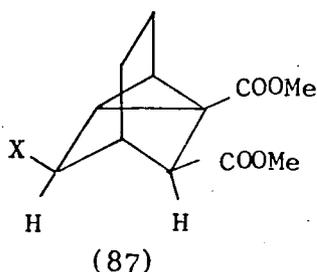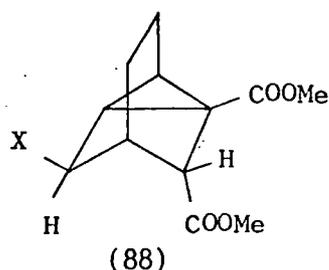
(a) X = Cl; (b) X = OCH_3

(a) X = Cl; (b) X = OCH_3

The photolysis of (81) in methanol containing 0·1M $HClO_4$ at 0°C produced the methanol addition tricycles (87b) and (88b), again in the ratio of 9:1. Likewise addition of a few drops of $HClO_4$ to a 6:4 mixture of (81):(82) in methanol at -20°C produced the same ratio of isomers (87b) and (88b).   The addition mechanism probably involves the protonated tetracycle (89) and always proceeds with the X group entering from the exo face.

(89)
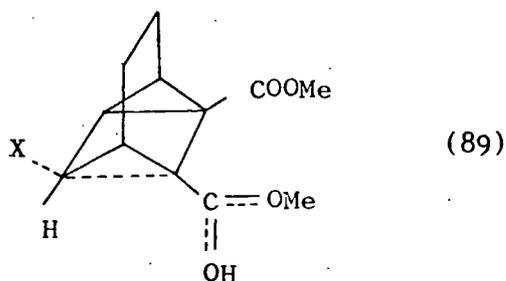
Prinzbach has also reported the unsensitized isomerisation of the dienes (90) to the pentacycles (91) which are thermally unstable.[62]

(90)   (91)
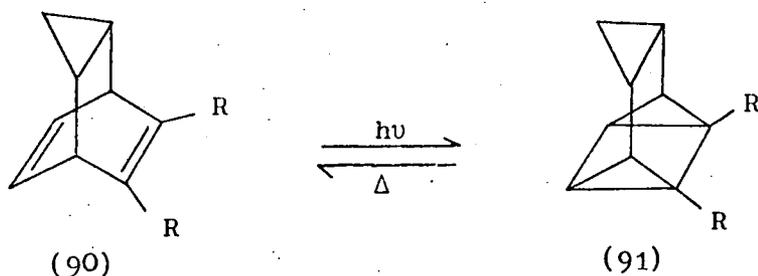
(a) R = COOMe;   (b) R = CF_3;   (c) R = COOH.

2.3   Photochemistry of bicyclo[2,2,0]hexa-2,5-dienes

The [$2\pi + 2\pi$] cycloaddition of these dienes appears energetically

unfavourable owing to the high level of strain associated with the prismane

structure.   The only successful formations of prismanes have occurred when

bulky groups are adjacent to one another in the diene system since the bulky

groups destabilize the ground state isomeric benzenes.

(92)   (93)   (94)
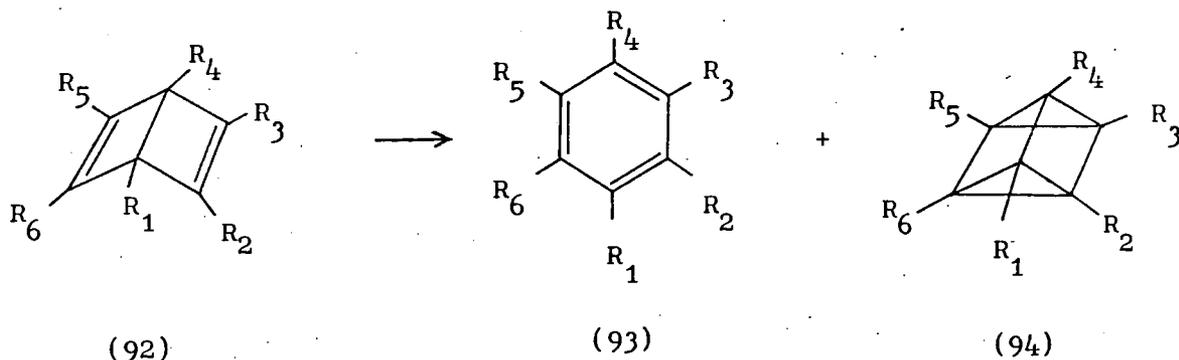
(a) $R_1 = R_2 = R_5 = \underline{t}$-Butyl, $R_3 = R_4 = R_6 = H$;

(b) $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = Me$;   (c) $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = CF_3$

The first reported isomerisation of a bicyclo[2,2,0]hexa-2,5-diene to a

prismane was by the irradiation of (92a) in isohexane with light of 253·7 nm when

(94a) was obtained in 65% yield and (93a) in 21% yield.[63]   Irradiation of (92b)

as a 1% solution in ether, with a low pressure mercury lamp produced after 3 hours

7% of (94b) and 45% of (93b).[64]   Irradiation of (93c) with u.v. light of $\lambda >$

200 nm produced (92c) and irradiation of (92c) in perfluoro-n-pentane gave

substantial yields of (94c).[65]   The prismane (94c) is a remarkably thermally stable

compound. The bicyclo[2,2,0]hexa-2,5-dienes (92b) and (92c) revert to the

benzenes (93b) and (93c) on heating. The half-life for (92c) is 135 hours at

$170^{\circ}C$[65] and the half-life for (92b) is 5·5 hours at $140^{\circ}C$.[68]

2.4 Photochemistry of bicyclo[3,2,2]nona-6,8-dienes

Recently Prinzbach[66] has reported that these dienes do not undergo the

$[2\pi + 2\pi]$ cycloaddition reaction either by direct or sensitized excitation.

Instead irradiation of (95a) in acetonitrile at $-30^{\circ}C$ with light of $\lambda > 230$ nm

formed (96) by a 1,3-alkyl shift and (98) by a di-π-methane rearrangement[67] from

the presumed bi-radical intermediate (97). Irradiation of (95b) gave only (99)

and this again can be rationalized by a di-π-methane rearrangement from (97).

(95) → [(97)] → (98)

(96)   (99)

Ratio

(96a) : (98a) $\cong$ 1:1
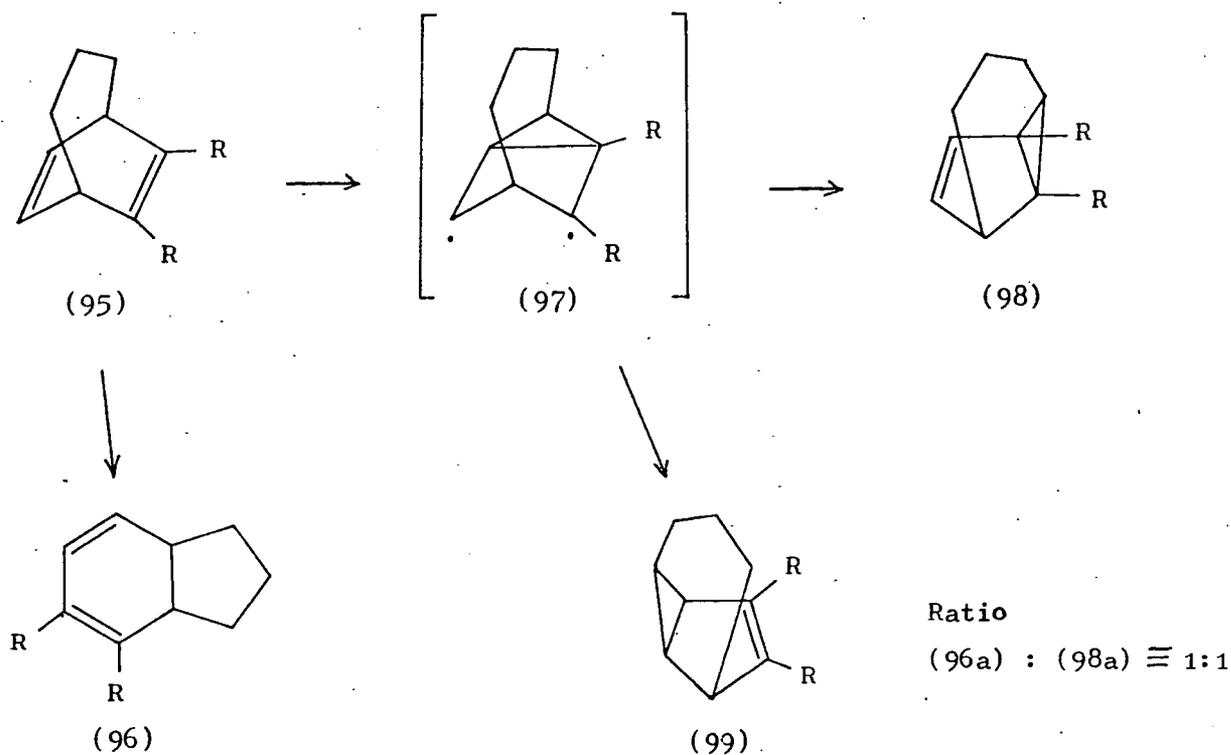
(a) R = COOMe;   (b) R = CF_3;   (c) R = COOH

Irradiation of the octadiene (100) in water produced the carbinol (101)

presumably via the intermediate tetracycle (102).[66] However irradiation of

(100)   (102)   (101)
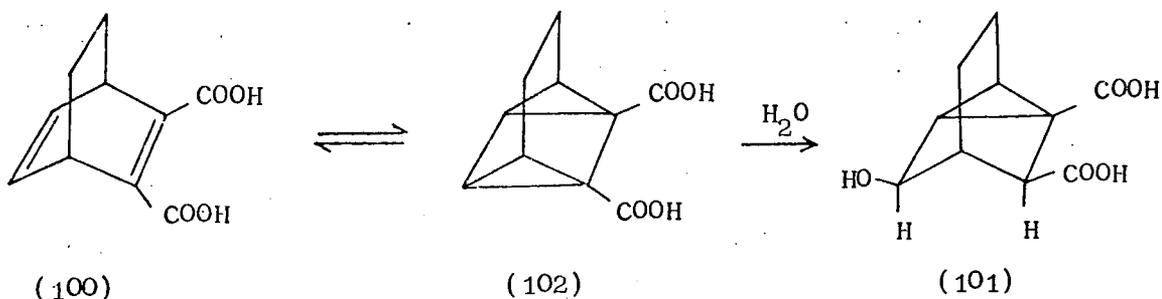
(95c) in water produced no analogous tricyclic compound and this is interpreted

as final confirmation that no [π2s + π2s] addition occurs on irradiation of the

bicyclo[3,2,2]nona-2,5-diene system.

2.5 The effect of fluorine on the stability of the cyclopropane ring

The half-lives for the tetracyclic compounds (103) and (104) are:

(103)
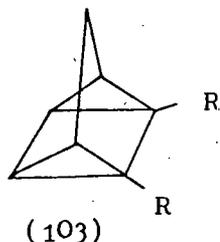
(a) R = CF$_3$ $t_{\frac{1}{2}}$ = 88.5 min. at 218°C   (ref. 61)

(b) R = COOMe $t_{\frac{1}{2}}$ = 3 min. at 132°C   (ref. 61)

(c) R = H $t_{\frac{1}{2}} \cong$ 3 min. at 210°C   (ref. 44)

(104)
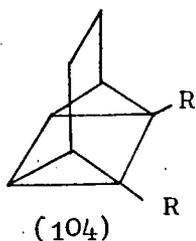
(a) R = CF$_3$ $t_{\frac{1}{2}}$ = ca. 5 min. at 80.5^{o}C.   (ref. 54)

(b) R = COOMe $t_{\frac{1}{2}}$ = 12 min. at 19°C   (ref. 61)

The stabilizing effect of the highly electron withdrawing CF$_3$ group on the

cyclopropane ring is well documented above and is also observed in hexakis-

(trifluoromethyl)prismane (94c) which is more stable than its hexamethyl analogue

(94b).

(94)   (92)   (93)
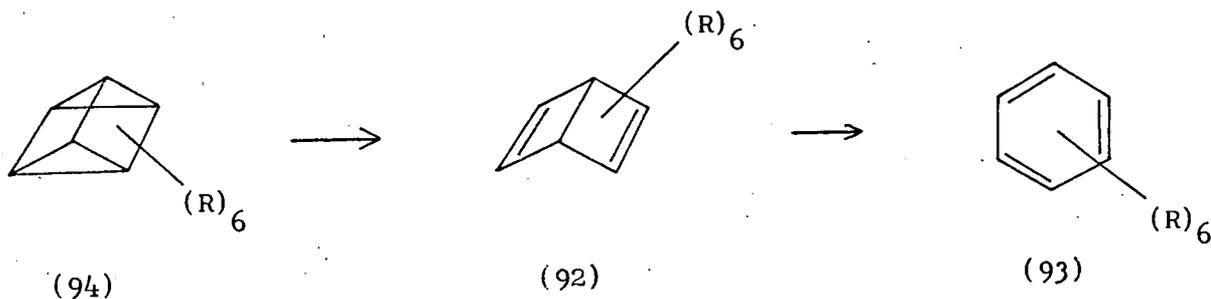
(b) R = CH$_3$ Kinetic data obtained from Direct Calorimetry[69]

(c) R = CF$_3$ Kinetic data obtained from Differential Scanning Calorimetry.[70]

	Temp. (°C)	k_1 sec^{-1}	ΔH Kcal/mole	AE Kcal/mole
94b ⟶ 92b	150	1×10^{-3}	-31.7	33.8
92b ⟶ 93b	150	6×10^{-5}	-59.5	37.2
94c ⟶ 93c	225	8×10^{-4}	-31.0	43.1
92c ⟶ 93c	225	1×10^{-4}	-28.0	38.4

The hexakis(trifluoromethyl) Dewar benzene (92c) is also more stable than (92b). Despite the large negative heats of reaction the isomerisations are protected by high activation energies which are not unreasonable since all of the reactions are orbital symmetry forbidden to occur in a concerted manner.[71] The non-bonded interactions of the substituents are only important in the benzenes (93) and the large difference in enthalpies of aromatization can be accounted for by the more unfavourable CF_3 interactions in (93c).[70] The greater stability of the Dewar benzene (92c) relative to (92b), in spite of their very similar activation energies for isomerisation to their respective benzenes, can be attributed to the low activation entropy (-1.9 eV) of (92c). However, the greater stability of the prismane (94c) relative to (94b) is accounted for by the higher activation energy barrier to reaction of the former. Hence the perfluoroalkyl groups destabilise the transition state by about 9 Kcals/mole and this is rationalized by the stabilising effect of CF_3 on the highly strained cyclopropane ring.

The bis(trifluoromethyl)acetolactone (105) is the only relatively stable α-lactone known and has a half-life of 8 hours at 24°C. The bismethyl analogue has only been observed in a glassy matrix at 77°K.[72]

(105)

Haszeldine has also reported the preparation of hexakis(pentafluoroethyl) prismane which again is remarkably stable though somewhat less so than the trifluoromethyl analogue.[73]   Hence the stabilising effect of perfluoroalkyl groups on the cyclopropane ring is well documented, although little is understood about the mechanism of this stabilisation.

A novel synthesis by Jefford has heralded the preparation of 7,7-difluoro-norbornadiene (109a) and its quadricyclane isomer (108a).[74]

(a) R = H;   (b) R = Ph

The quadricyclane (107a) was obtained by irradiating a pentane solution of (106a) for 15 hours at 15°C.   (107a) is thermally unstable and reverts to (106a) on heating at 130°C.   However (108a) can be prepared by reductive dechlorination of (107a) using lithium dissolved in t-butanol and tetrahydrofuran.   Jefford claims that (108a) is the most stable quadricyclane known but no half-life is given, though at 360°C quantitative isomerisation to (109a) occurs.   The fluorine (C-F) bond is parallel to the cyclopropane ring and Jefford claims that stabilisation of the cyclopropane ring arises in a manner analogous to that for hexakis(trifluoromethyl) prismane but no substantive account of the stabilisation mechanism has been published.[74]   In contrast the quadricyclane (108b) is very thermally labile and isomerises to (109b) at room temperature.

Analysis by n.m.r. of the sequential Cope rearrangements in fluorobullvalene ($C_{10}H_9F$) has revealed that 85% consists of (110) and the remaining 15% consists of a mixture of (111) and (112).[75]   The isomer (113) that has the fluorine on the cyclopropane ring was not observed.

(110)   (111)   (112)   (113)

In the cyclopropane ring a single π acceptor (e.g. CN) will weaken bonds 1-2 and 1-3 but strengthen the 2-3 bond.[76]   The important interaction of the

(114)
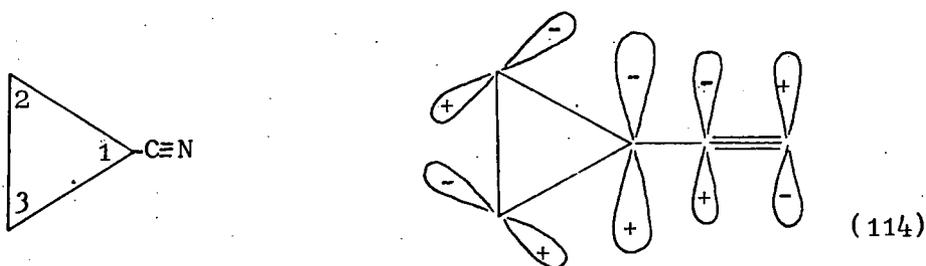
CN group with its low-lying unoccupied molecular orbitals, is the mixing of the acceptor orbital with the antisymmetric component of the occupied degenerate Walsh orbital pair in cyclopropane (cf. 114).[77]   The delocalization over the π system means that there is a net electron transfer from the cyclopropane with the consequence that the 2-3 bond is strengthened since electron density is removed from the MO antibonding in this region.   With a π donor like F that has a spherical π system and cannot therefore be out of conjugation with the cyclopropane Walsh orbitals, the interaction means that the 1-3 and 1-2 bonds are strengthened whilst the 2-3 bond is necessarily weakened.[78]

Hoffmann has calculated that the fluoro-semibullvalene (115) should be more stable than (116) owing to fluorine destabilization of the 2-8 bond in the latter.   Hence the absence of the fluorobullvalene (113) can be explained in terms of fluorine interaction with the Walsh orbital destabilizing the opposite carbon-carbon σ bond.

$$\Delta E = -0.66 \text{ eV}$$
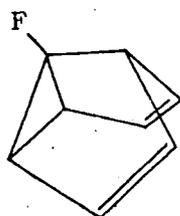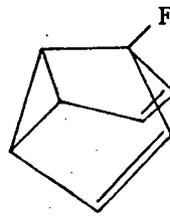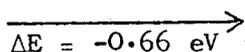
(116)   (115)

Hoffmann has confirmed by extended Hückel calculations that to a first approximation the effects of the CN group on the disubstituted cyclopropane (117) are additive.[78]

(117)
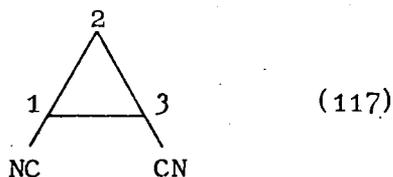
Thus the 1-3 bond is severely weakened in (117) whilst in the 1-2 and 2-3 bonds the bonding and anti-bonding effects should approximately cancel each other. A similar situation with difluorocyclopropane requires the greater stability of (118) over (119). Unfortunately neither a difluorobullvalene nor a difluoro-semibullvalene have been prepared and these predictions cannot be confirmed.

$$\Delta E = +0 \cdot 16 \text{ eV}$$

(118)   (119)
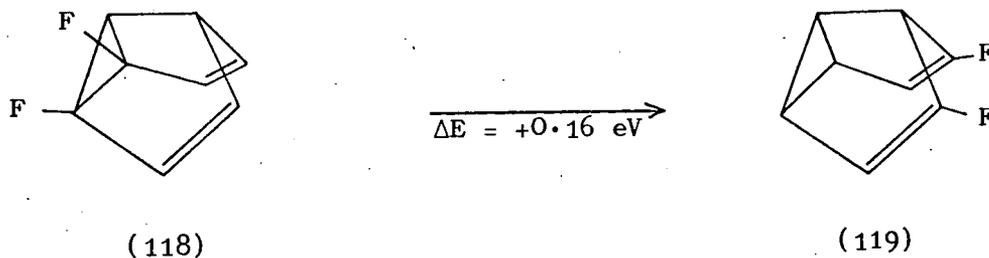
However the situation with more highly fluorinated systems is less clear. For instance Hoffmann's approximation would require that cyclopropane and 1,2,3-trifluorocyclopropane were of similar stability.

Haszeldine has recently prepared the prismane (122)[79] by the vapour phase irradiation of (120) with the isomerisation proceeding via the Dewar benzene (121).

(120)   (121)   (122)
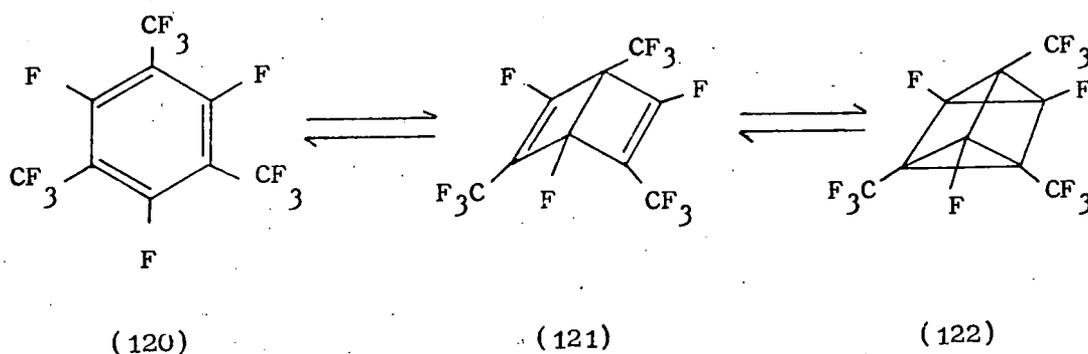
The prismane (122) is very unstable in comparison with the hexa(trifluoromethyl) prismane (94c) and has a half-life of 19 hours at 35°C. The isomerisation of (122) is readily catalyzed by any surface and the half-life quoted is that in solution. Again this is in contrast to (94c) which is quite stable to glass surfaces. Photolysis of hexafluorobenzene did not give the appropriate prismane and only perfluorobicyclo[2,2,0]hexa-2,5-diene was obtained.[80]

The ability of fluorine to stabilise cyclopropane rings is open to question and it would be pertinent to compare the stability of compounds like (123), (124) and (125) with quadricyclane and the stability of compound (126) with that of (122).
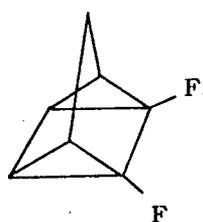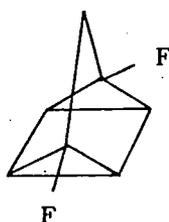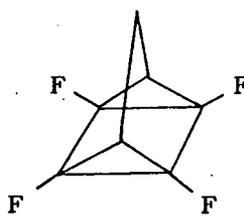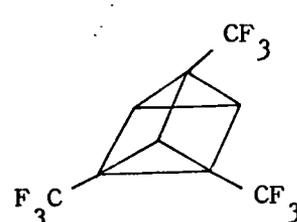
(123)   (124)   (125)   (126)

2.6 The interaction of π-orbitals in non-conjugated bicyclic dienes

The interaction of the π orbitals in the excited state of norbornadiene was proposed by Winstein in 1960,[81] from theoretical calculations which were performed in order to explain the bathochromic shift in the u.v. spectra of norbornadiene relative to norbornene. Prinzbach has also given an account of this bathochromic shift in terms of transannular interaction in the excited state.[49] (cf. Section 2.1). Analysis of the ionisation potentials, which have been determined by photoelectron spectroscopy (PES), revealed that for norbornadiene there is a ground state interaction of the π orbitals.[82,83] If norbornadiene, with its two mirror planes, is considered then some overlap of the π orbitals beneath the carbon skeleton may be expected. The delocalized combinations after interaction may be represented by their symmetry designations SS and SA with the latter having a nodal plane and being at higher energy. The

observed splitting is 0.85 eV.[84]   Likewise the π^* levels will mix to yield an

AS combination below AA.

SS   SA   AS   AA

$$\pi^* = \begin{array}{ll} AA & - \quad a_2 \\ AS & - \quad b_1 \end{array}$$

$$\pi = \begin{array}{ll} SA & - \quad b_2 \\ SS & - \quad a_1 \end{array}$$
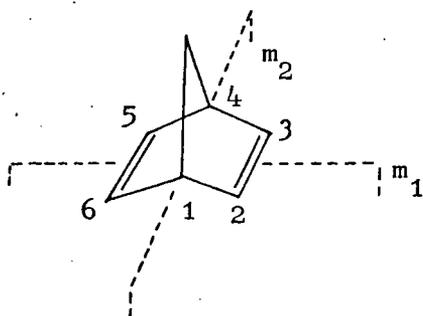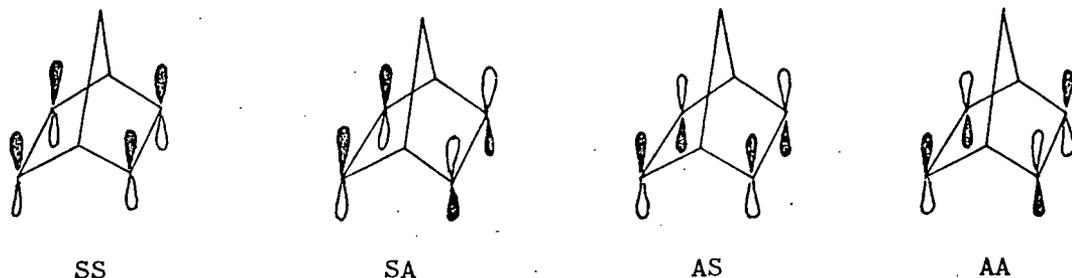
Two consequences of this interaction are the ionisation potential of

norbornadiene is less than that of norbornene and the $\pi \rightarrow \pi^*$ transition

(SA $\rightarrow$ AS) promotes an electron from an orbital which is 2-6 and 3-5 antibonding

to one that is bonding in the same regions.   Closure to quadricyclane is thus

promoted by the dominant 'through space' overlap between the π orbitals.

However, a second mode of interaction between the π bonds is the 'through

bond' or hyperconjugative interaction.[82,83]   Optimal 'through bond' interaction

occurs in 1,4-cyclohexadiene where the π orbitals interact with the CH_2 orbitals

that have π symmetry.   In this manner the SS π bonding combination is

destabilized by mixing with a CH_2 σ level.   Extended Hückel calculations confirm

that SS and SA levels are split by hyperconjugative interaction in the opposite

sense to that occurring by 'through space' interaction.   Hence in 1,4-cyclohexa-

diene the b_2 (SA) orbital is the one of lowest energy and the splitting is

1.0 eV.[84]

Norbornadiene has a PES measured π splitting of 0.85 eV.[84] (Extended Hückel

calculations gave a value of 0.43 eV).   The 'through space' splitting of the π

levels will be larger than 0.85 eV since the 'through bond' contribution must be accounted for.[85,86,99]   The observed splitting in bicyclo[2,2,2]octa-2,5-diene was 0.58 eV.[84]

The 'through space' interaction between the two π bonds decreases as n and therefore the angle w increases.   Consequently the orbital energy of a_1 (π) increases as that of b_2 (π) decreases along the series shown below.[87]

$--- \equiv a_1(\pi)$ $--- \equiv b_2(\pi)$
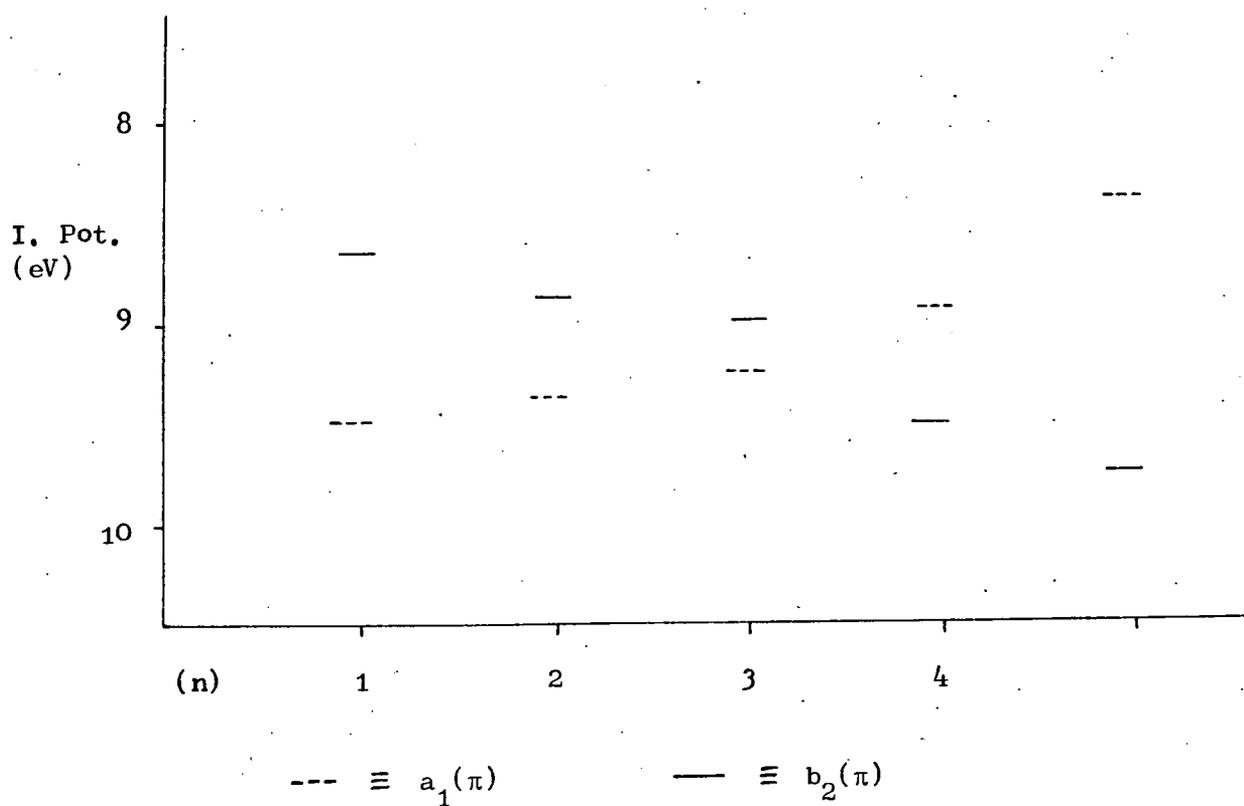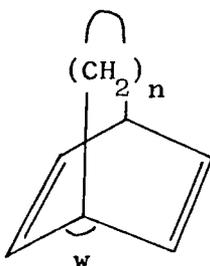
The 'through bond' interaction arising from the interaction of the a_1 (π) orbital with the high lying σ orbital on the polymethylene bridge results in b_2 (π) becoming the lower energy orbital when n > 2.   The π level splitting

of n = 3 is only 0·18 eV and thus the calculated assignment is a little
uncertain.[87]   In all cases where n > 3 and therefore w > 130° it is to be
expected that the 'through bond' interaction dominates and that b_2 (π) is the
lowest energy.

However, the recently reported photoelectron spectrum of Dewar benzene
(n = 0) reveals that the Ionisation Potentials from the π system are 9·40
and 9·70 eV.[88]   It has not been possible to assign the orbital sequence as the
calculations performed (Ab Initio and SPINDO) suggest degeneracy, thus the
behaviour of (n = 0) deviates from the pattern set by its higher homologues.

Heilbronner has shown that there is an interaction between the cyclopropyl
σ orbitals and the π orbital in (127) where the cyclopropane ring is exo but
not in the endo derivative (128).[89]

(128)   (127)   (129)
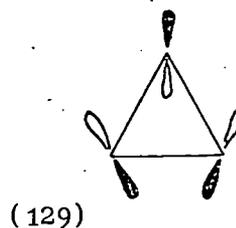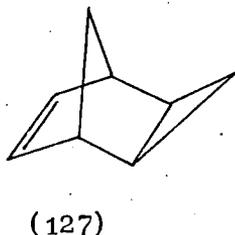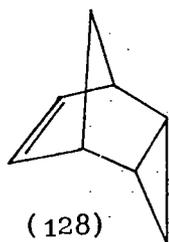
The interaction in (127) can be considered to arise from the symmetric Walsh
orbital (129) and the π orbital.   Obviously with (128) the lobes of this Walsh
orbital are pointing in the wrong direction to facilitate interaction.   The
extent of interaction is estimated at -0·3 eV, however this cannot be measured
directly.[89]   Analysis indicates that the 'through space' interaction dominates
the 'through bond'.

Many examples of photochemical [2π + 2σ] reactions involving derivatives of
(128) and (127) are known.[90]   These proceed very smoothly as anticipated from
the extent of 'through space' interaction (e.g. (130) → (131)).

(130)   (131)
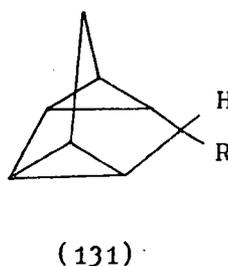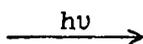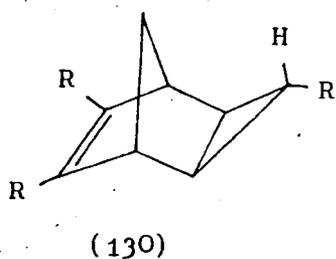
Justification of the results obtained by Heilbronner is manifested by the isomerisation of (132) to (133).[90] The dominant 'through space' interaction of the π orbitals with the exo cyclopropyl system means that (133) and not (134) is produced.[91]

$$ (133) \quad \xleftarrow{h\upsilon} \quad (132) \quad \xslashedrightarrow{} \quad (134) $$

R = COOMe
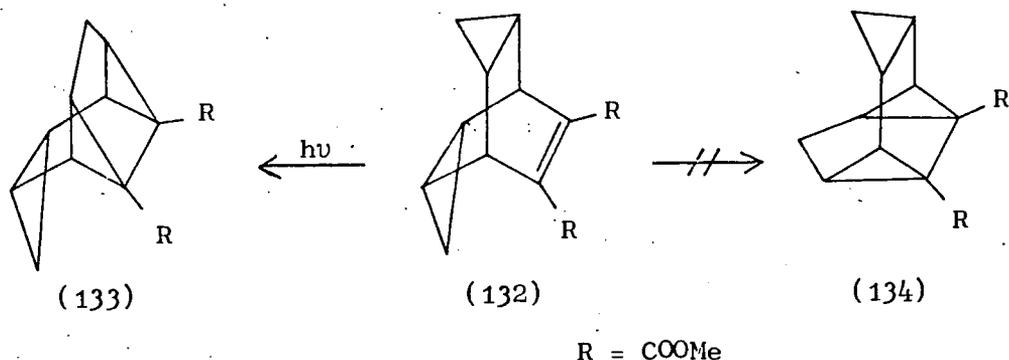
The isomerisation of (90) to (91) (cf. page 36) proceeds photochemically and here the [2π + 2π] interaction must exceed the [2π + 2σ] interaction with the cyclopropyl system. The 'through space' interaction in the bicyclo[2,2,2]-octa-2,5-diene system has a value of -0·29 eV estimated on the same basis as that of -0·3 eV in (127); however, the 'through bond' contribution is likely to be greater for the diene system and the value of -0·3 eV for (127) is only estimated.[89] Hence it would seem not unreasonable that the 'through space' interaction of the [2π + 2π] system exceeds that of the [2π + 2σ] and hence dictates the course of the photochemical reaction.

Heilbronner in a recent report has calculated the 'through space' interaction in norbornadiene from three different semi-empirical calculations and obtained widely differing results.[99] (The 'through space' interaction calculated from CNDO/2 was 4·04 eV). Heilbronner has suggested that a reassessment of the relay orbitals involved in 'through bond' interaction is required and that the contribution from direct 'through space' interaction may be less than at first thought. For instance the effect of σ/π interaction in 7,7-difluoronorbornadiene relative to norbornadiene has been found to shift the π bonds by equal amounts towards higher ionisation energies. However, each semi-empirical method confirms that the crossing of a_1 (π) and b_2 (π) occurs as described earlier (page 46) when w $\cong$ 130°.

DISCUSSION

2.7 Preparation of starting materials and spectral parameters of the Diels-Alder adducts of perfluorocyclohexa-1,3-diene

The general background to Diels-Alder reactions of polyfluorinated dienes is discussed in detail in Chapter 3 (Introduction); in this work the Diels-Alder reactions of perfluorocyclohexa-1,3-diene formed the basis for the preparation of the required bicyclo[2,2,2]octa-2,5-dienes. The reaction of vinyl bromide with perfluorocyclohexa-1,3-diene gave predominantly the oct-2-ene (II) which was dehydrobrominated by refluxing with aqueous potassium hydroxide to give the octa-2,5-diene (III). The bicyclo[2,2,2]octa-2,5-diene (IV) was formed directly by the Diels-Alder reaction of perfluorocyclohexa-1,3-diene with acetylene dicarboxylic acid dimethyl ester.

The structural assignments are based upon n.m.r. analysis, resonances are complex and broad owing to long range H-F and F-F coupling between many nuclei, however it is found that the chemical shifts of the tertiary bridgehead, bridging $-CF_2-CF_2-$ and vinylic fluorine resonances lie in characteristic regions. The Diels-Alder reaction of highly fluorinated cyclohexa-1,3-dienes with alkenes and alkynes is well documented[92,93,94] and the bicyclo[2,2,2] system obtained has the following characteristic resonances for fluorine: bridgehead (184-220 p.p.m.), $-CF_2-CF_2-$ (115-137 p.p.m.) and vinylic (150-163 p.p.m.).[95] The $-CF_2-CF_2-$ group in some instances forms a complex AA'BB' system in these compounds. However, in symmetrically substituted derivatives this often collapses to a pseudo AB system and shows a characteristic geminal coupling constant with J_{AB} in the range 215-235 Hz. The structures proposed in Table 1 are all consistent, on the basis of fluorine resonance and integration, with previously reported examples.

Another characteristic of the octafluorobicyclo[2,2,2]oct -2-ene unit is that the infrared stretching frequency of (-CF=CF-) is generally strong and

TABLE 1

N.m.r. data for starting materials

(Unmarked bonds are to fluorine)

Compound	-CF$_2$-CF$_2$-	$>$C-F	$>$C-F	H
(II) [structure with Br, H's]	124·0 (2) δ$_A$ 126·9 (1) δ$_B$ 128·0 (1) J$_{AB}$ 235	147·4 (1) 151·6 (1)	213 (1) 218 (1)	δ$_A$ 2·67 (1) CH$_2$ δ$_B$ 3·09 (1) J$_{AB}$ 8 CHBr 4·42 (1)
(III) [structure with H's]	δ$_A$ 125·6 (2) δ$_B$ 126·7 (2) J$_{AB}$ 225	163 (2)	215 (2)	$>$C-H 6·40
(IV) [structure with COOMe, COOMe]	δ$_A$ 123·2 (2) δ$_B$ 124·1 (2) J$_{AB}$ 216	153 (2)	218 (2)	-OMe 3·97
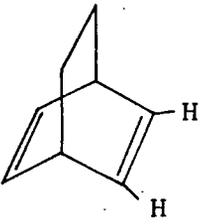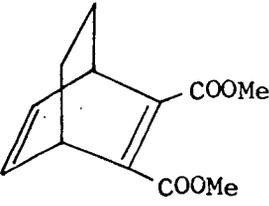
Chemical shifts are in p.p.m. upfield from internal CFCl$_3$ or external Me$_4$Si and refer to unresolved multiplets, integrated intensities are in parentheses, coupling constants in Hz.

II and III as neat liquids and IV in solution in CHCl$_3$

[All unmarked bonds to fluorine]

occurs in the region (1751-1772 cm^{-1}). Concomitant with this generalization, absorption bands are observed at 1760, 1760 and 1770 cm^{-1} for (II), (III) and (IV) respectively.

The mass spectra of the dienes (III) and (IV) show base peaks corresponding to the elimination of C_2F_4. The mass spectral fragmentation pattern observed for analogous dienes generally parallels their high temperature vacuum thermolysis,[96] thus tetrafluorobenzene derivatives are produced on pyrolysis by elimination of C_2F_4. In agreement with this the vacuum pyrolysis of (IV) gave dimethyl tetrafluorophthalate. This particular example is in contrast to the diethyl analogue of (IV) which decomposed on thermolysis by elimination of C_2F_4, C_2H_4 and CO_2 to give primarily 1,2,3,4-tetrafluorobenzene. The mass spectrum of (II) gave a base peak corresponding to the loss of Br.

The reaction of vinyl bromide with perfluorocyclohexa-1,3-diene produced two isomers in the ratio of 1:52, with the minor isomer having the shorter gas chromatographic retention time. Only sufficient of the minor isomer was separated for a mass spectrum to be obtained; this spectrum was almost identical to the one recorded for the major isomer (II). The major isomer (II) was characterised and the bromine was assumed to be in the endo configuration by analogy with the two examples where the stereochemistry of the Diels-Alder addition to perfluorocyclodienes has been unambiguously established.[92,97]

2.8 The photochemistry of polyfluorobicyclo[2,2,2]octa-2,5-dienes

[In this section the diagrams have unmarked bonds to fluorine unless otherwise stated].

The gas phase photolysis of perfluoro-2,3-dimethylbicyclo[2,2,2]octa-2,5-diene (135) resembled that of norbornadiene in that a reverse Diels-Alder reaction occurred, the perfluorocyclohexa-1,3-diene formed initially undergoes further photochemical reaction to give perfluorobicyclo[2,2,0]hex-2-ene.[98]

(135)
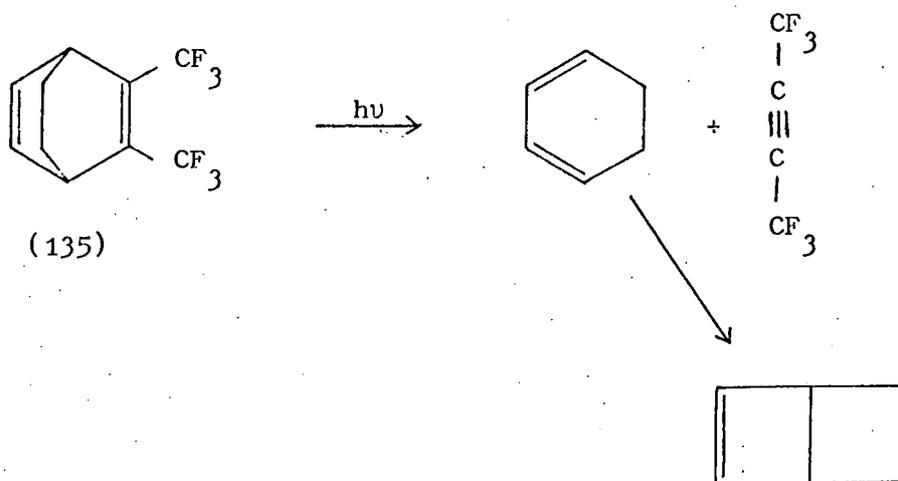
The diene (III) did not undergo a reverse Diels-Alder reaction on gas phase irradiation.

Hence it appeared that the gas phase photolysis of (135) resulted in the molecules having so much excess vibrational energy that only dissociation occurred. To establish if polyfluorobicyclo[2,2,2]octa-2,5-dienes, like their hydrocarbon analogues, undergo ring closure to tetracyclic compounds it seemed pertinent to attempt the reactions in solution. The attempted isomerisation of the diester (IV) to the tetracyclic compound (136) was the principal system investigated.

(IV)   (136)
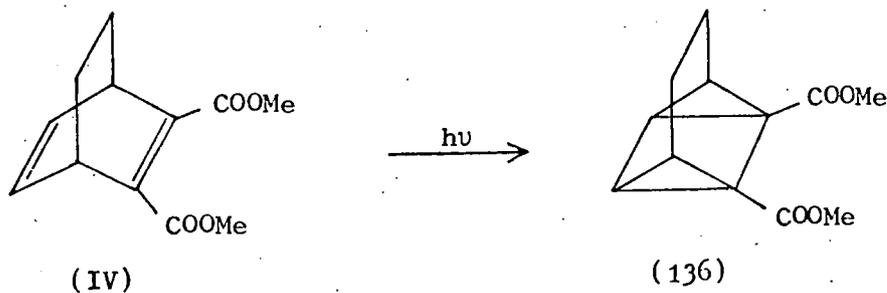
The diester (IV) by virtue of its conjugated chromophore has an extinction coefficient of 600 at 254 nm and this made it ideal for use with a medium pressure mercury lamp having a fairly high (70 watts) radiative output. From the outset it was assumed that, vis a vis the hydrocarbon analogue, the tetracyclic compound (136) would be thermally labile. Hence the procedure adopted for the irradiation of (IV) in solution was based on that reported by Prinzbach et al.[61] The solutions were extensively nitrogen streamed both before and during the irradiation in order to remove any dissolved oxygen. This seemed

desirable as the norbornadiene/quadricyclane isomerisation has been shown to proceed through a biradicaloid intermediate, although the presence of oxygen did not adversely affect the quantum yield.[50,51]   The solutions were irradiated for 2/3 hours between -20 and -30°C (apart from the benzene solution which was irradiated between 5 and 10°C) and the solvent was removed immediately by vacuum transfer at low temperature.   A low temperature (-30°C) ^{19}F n.m.r. and i.r. of the solid residue were then recorded.

The diester (IV) was first irradiated in diethyl ether and the low temperature ^{19}F n.m.r. of the residue showed that 95% of the starting material had reacted to give a new compound with the vinylic fluorines being removed to the tertiary fluorine region.   The i.r. confirmed that both of the C=C bonds had disappeared.   The ^{19}F n.m.r. of the product did not change on standing in ether solution at room temperature ($\simeq$ 20°C) overnight and the residue appeared to be thermally stable.   The residue was recrystallised from a number of hydrocarbon solvents and was eventually purified by column chromatography ($CHCl_3$ eluant) to give a white solid (V) whose ^{19}F n.m.r. was the same as that previously recorded.

Elemental analysis of (V) indicated that it was a diethyl ether addition product of the diester (IV).   The mass spectrum of (V) showed the required parent peak at 440[101] an assignment that was confirmed by a metastable peak at 400.6 arising from the loss of HF from the parent ion.   The major fragment peaks arose from the loss of CH_3OH (40.8% of the base peak) and C_2H_5O (30.9%) from the parent ion;   with CO_2 (m/e 44) forming the base peak.   The i.r. and u.v. confirmed that both of the olefinic bonds present in (IV) were absent in (V).   The ^{19}F n.m.r. indicated that the $-CF_2-CF_2-$ bridge was still present and that otherwise only tertiary fluorines were to be found.   However, a more detailed analysis of the ^{19}F and ^{1}H n.m.r. reveals that more than one isomer was present.   The isomers could not be separated either by recrystallisation from hydrocarbon solvents or by column chromatography.   G.l.c. analysis (Col.B, 220°C)

of (V) after a retention time of half an hour revealed two components in the ratio of 5:6 (in order of increasing retention time). On the other hand, integration of the non-coincident ^{19}F n.m.r. tertiary fluorine resonances suggests an isomer ratio of 4:3. A more detailed analysis of the/the ^{19}F n.m.r. -CF$_2$-CF$_2$- *spectrum in* bridge region (118-123 p.p.m.) suggests that two major components are present in a 1:1 ratio with about 5% of a third minor isomer. It has proved impossible to completely identify these products, however the i.r. and u.v. data limit the possible structural assignments and a detailed analysis of the ^{1}H and ^{19}F n.m.r. spectra suggests that the major components are isomers of the tricycle (137)

(137)
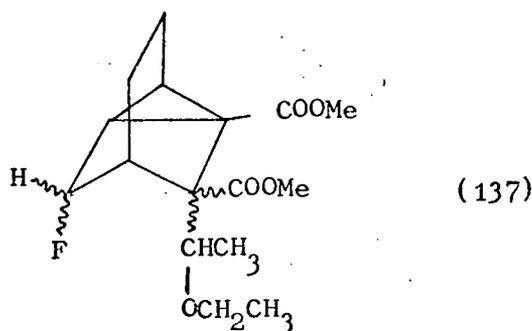
In theory there are four possible isomers of (137) (excluding optical isomers) depending upon the detailed stereochemistry at C2 and C6.

The ^{19}F n.m.r. signals of (V) in the tertiary region occur at: 169·1 (2), 194·7 (2), 198·9 (1·2) and 201·1 (0·9), 216·2 (0·9) and 217·1 (1·2). (The integrated intensities are in parentheses). The ^{1}H n.m.r. signals can be assigned and occur at 1·32 (1·5) and 1·40 (4·5) -CH$_3$; 3·68 (6) -OCH$_3$; a broad resonance centred at 4·3 (3·0) -OCH$_2$ and -CH; and a resonance centred at 5·3 (1·0), which contains four equal signals all separated by 25 Hz (-CHF groups). It would appear from this data that the structure of the major isomers is rather similar and the ^{19}F resonance at 169·1 which was unresolved (110 Hz broad) suggests the presence of CHF because of its chemical shift position.[176] The other coincident tertiary fluorine (194·7) resonance was 80 Hz broad whilst the non-coincident resonances were all about 65 Hz in breadth. The J_{HF} coupling constant observable in the proton spectra could be 25 or 50 Hz. However a value of 50 Hz would be consistent with previously reported examples.[102,103,176] For instance (138)

has a J_{HF} gem coupling constant of 52 Hz.[103]

(138)
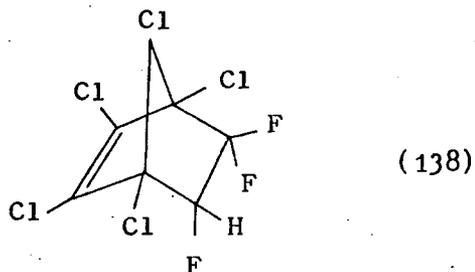
It may be rather fortuitous that four peaks of equal intensity occur at

5·3 p.p.m. in the proton spectra and that a quarter of the CH_3 protons occur as

a doublet at 1·32 p.p.m. but the evidence would seem to suggest that two major

components are present. However a small side peak on the OCH_3 signal suggests

the presence of a minor isomer. The presence of the $CH_3CHOCH_2CH_3$ moiety is

implicit from the proton n.m.r. integration and was further substantiated by

proton homonuclear decoupling. (The author wishes to thank Dr. R.S. Matthews

for this work). Broad band decoupling of the CH_3 resonance signals caused the

profile of the OCH_2 to become much sharper. Decoupling of the OCH_2 at 4·3 p.p.m.

resulted in the resonance at 1·40 p.p.m. changing from a multiplet 12 Hz in

width to a broad resonance of 9 Hz width whilst that at 1·32 p.p.m. remained

unchanged. A 7 Hz doublet at 1·32 collapsed on decoupling at 4·4.

Some analysis of the $-CF_2-CF_2-$ bridge region is possible with the aid of

integration and J_{AB} assignments. The ester (IV) has very weak outer limbs in

its pseudo AB pattern and the weak intensity was likewise found for the mixture

of isomers (V). However the intensity of the outer limbs was enhanced by means

of the CAT technique. Unfortunately only two coupling constants of 252 Hz and

258 Hz could be unambiguously assigned, though evidence for a further two

coupling constants of similar magnitude could be found. The fluorine resonances

were found in two main blocks that were separated by 260 Hz and the consequent

overlapping of the pseudo AB systems made complete interpretation impossible;

the situation was further confused by the presence of 5% of a minor isomer.

As previously mentioned the $-CF_2-CF_2-$ bridge resonances could be assigned to two

major isomers formed in a 1:1 ratio. One isomer showed resonances at 118·8 (2)

and 121·8 (2) with no assignment of J_{AB}'s being possible. The other isomer gave: δ_A 120·4 (1), δ_B 119·1 (1), J_{AB} = 258 Hz and δ_A 121·5 (1), δ_B 122·5 (1), J_{AB} = 252 Hz.

Hence, it would appear that (V) is formed via an intermediate like (139), which abstracts hydrogen from the α-methylene of the solvent ether. Hydrogen abstraction thus proceeds from the CF radical centre and this is reasonable since the C-COOMe radical should be the more stable.

(139)
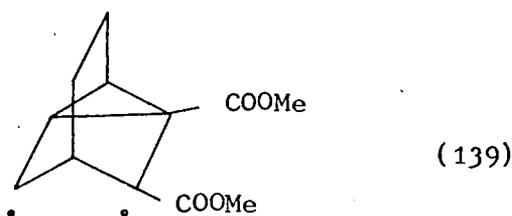
The biradical (139) is analogous to the intermediate through which the norbornadiene/quadricyclane isomerisation proceeds (cf. Introduction). Prinzbach has recently reported that the bicyclo[3,2,2]nona-6,8-dienes do not undergo ring closure to tetracyclic compounds on irradiation (cf. Introduction); however, the photochemical reactions of these nonadienes also appears to proceed through a biradicaloid intermediate analogus to (139).[66]

The most obvious proceeding step was to irradiate the diester (IV) in solvents that do not have an easily abstractable hydrogen atom in the hope that the biradicaloid (139) would form the desired tetracycle (136). Unfortunately the irradiation of (IV) in acetonitrile, benzene and perfluoromethylcyclohexane produced only unchanged starting material. Irradiation of the same solution for much longer periods of time at room temperature (ca. 20°C) also gave unchanged starting material only.

The final proposition to consider was that the tetracycle (136) was formed at -20/-30°C but was so unstable that it reverted back to the ester (IV) in the time (ca. 1 hour) required to vacuum transfer the solvent at 10°C. Prinzbach had reported that with the tetracycle (82), the hydrocarbon analogue of (136),

HCl addition occurred very readily to one cyclopropane ring to give the tricycles (87a) and (88a) (cf. Introduction, page 35). Prinzbach seemed convinced that HCl addition occurred only to the tetracycle (82) and not to any biradicaloid intermediate. Analogous experiments to those reported by Prinzbach were performed in the hope that if the tetracycle (136) was formed it could be trapped in situ as its HCl adduct. In the first experiment the acetonitrile solution of (IV) was saturated with HCl at 0°C and irradiated for 3 hours at $-20/-30^{\circ}$C and in the second experiment the acetonitrile solution of (IV) was irradiated for 3 hours at $-20/-30^{\circ}$C and then saturated with HCl at this low temperature and allowed to warm to room temperature over a 24 hour period. However, in each case only unchanged starting material (IV) was obtained along with some hydrolysis products.

Prinzbach also achieved the addition of methanol to the tetracycle (82) to form the tricycles (87b) and (88b) by irradiation of the diene (81) in methanol containing $0.1N$ H_3PO_4. In view of the previous results ring closure of (IV) to (136) did not seem to occur and the author hoped that the irradiation of (IV) in methanol only would give rise to compounds derived from solvent abstraction by the biradical (139). However, only products arising from the addition of methanol across the conjugated double bond were obtained. The three major products were confirmed as methanol addition products by g.l.c./m.s. (Col.M, 220°C). The ^{19}F n.m.r. revealed that the ratio of $-CF_2-CF_2-$: vinylic : tertiary fluorine was still 2:1:1. The small amount of starting material was removed from the residue by recrystallisation from acetone and pet. ether. The i.r. and u.v. on the recrystallised material confirmed that the conjugated double bond characteristic of (IV) was absent. The i.r. confirmed that $-CF=CF-$ was still present from the absorption at 1780 cm^{-1}. However, no attempt was made to isolate and further characterise the methanol addition products.

The ability of the CF_3 group to stabilize the cyclopropane was elaborated in the Introduction (Section 2.5). Hence perfluoro-2,3-dimethylbicyclo[2,2,2]octa-

2,5-diene (135) was irradiated in solution in the hope that ring closure to the desired tetracycle would occur. The diene (135) has an end absorption in the u.v. (CH_3CN solvent) that extends down to 253 nm where the extinction coefficient is 25. (At 227 nm, $\epsilon \simeq 45$). The u.v. spectrum of norbornadiene in cyclohexane shows the following charactersitcs λ_{max} 189·5 nm (log ϵ = 3·78), 202 nm (3·41), 213 nm (3·24), 219 (3·01), 227 (2·41).[104]

Unfortunately the volatility of the diene (135), which has a B.Pt. of 40°/ 50 mm,[96] would make the separation from acetonitrile in vacuo impossible. The irradiation of (135) in a perfluorocarbon solvent with a B.Pt. of about 0°C would have been ideal since no solvent abstraction by any biradical derived from (135) should have proceeded and separation in vacuo should have been possible. Unfortunately no exceptionally volatile perfluorocarbon solvent was available for use and consequently the irradiation was performed in $CFCl_3$ at -25/-35°C using the medium pressure mercury lamp. (The diene (135) has a small end absorption that extends down to 253 nm ($\epsilon \simeq 15$) in $CFCl_2CF_2Cl$). However this reaction produced primarily chlorine addition products. The addition products seemed to have occurred via direct addition across the double bonds and there was no evidence for any tricycle or tetracycle. The addition products were not purified and completely characterised.

The irradiation of pure $CFCl_3$ did not yield an e.s.r. spectrum.[105] However, the photolysis of $CFCl_3$ in the presence of ketone triplets does generate radicals derived from $CFCl_3$, ($\cdot CCl_2F$ being identified by its e.s.r. spectrum), presumably by exciplex formation.[105] It would seem likely that irradiation of the diene (135) generates a radical species that abstracts from the solvent.

It seems likely that the irradiation of (IV) in contrast to the analogous hydrocarbon compound (81) does not result in formation of a tetracyclic compound. An explanation may be forthcoming from a consideration of the more extensively investigated hydrocarbon systems. Electron diffraction studies have been used to obtain the geometry of norbornadiene[106] and bicyclo[2,2,2]octa-2,5-diene.[107]

In both electron diffraction studies it is necessary to assume $C_{2\upsilon}$ symmetry and a number of other constraints (bond lengths and bond angles) had to be applied such that different workers have reported the C1-C7 bond length in norbornadiene varying between the extremes of 1·514Å and 1·573Å.[108] The value of w in norbornadiene has been variously reported between the extremes of $103·4 \pm 0·4°$ and $106·8 \pm 0·8°$.[106] Prinzbach has constructed models for the bicyclic dienes shown below.[66] The values of w and d for n = 1 and n = 2 are in approximate agreement with the results obtained from electron diffraction studies.
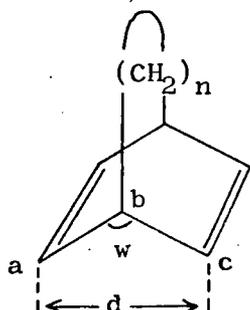
w = bond angle a$\hat{b}$c

d = distance between carbon atoms a and c in Å

[unmarked bonds to hydrogen]

n	1	2	3	4
d	2·36	2·42	2·45	2·45
w	112	117	130	135

With w and d increasing along the series then the $[2\pi + 2\pi]$ ring closure to tetracyclic compounds will be less favoured since the conditions for π interaction become less favourable and the tetracyclic compounds will be more strained. This expectation is confirmed since quadricyclane compounds are more stable than their tetracyclooctane analogues (cf. Introduction). Ring closure does not occur with the dienes n = 3 and this is explicable since w and d are much larger than for n = 2. (Prinzbach's measurements for n = 3 and n = 4 seem a little incompatible since the same value of d is reported as making w $5°$ larger for n = 4. In spite of this the general trends along the series are as anticipated).

An alternative explanation for the photochemistry of these dienes can be obtained from a consideration of 'through space' interaction. When n = 1 and n = 2 the 'through space' interaction dominates the 'through bond' and the

unsymmetrical b_1 is the HOMO. Although for $n \geqslant 4$ the symmetrical a_1 is the HOMO, the HOMO for $n = 3$ is rather uncertain. It may well be that b_1 the HOMO for $n = 1$ and $n = 2$ dictates the course of the photochemical reactions by promoting an electron from a situation where it is C2-C6 and C3-C5 antibonding in b_1 to a situation where it is bonding in the same region in b_2 and so favours ring closure. This would require that a_1 is the HOMO for the diene $n = 3$.[66] A similar explanation for the photochemistry of cyclohexa-1,4-diene, which does not undergo the $[2\pi + 2\pi]$ ring closure, has been put forward.[109] The 'through bond' interaction dominates in cyclohexa-1,4-diene and a_1 is therefore the HOMO.

However, Heilbronner has very recently struck a note of warning with regards to the interpretation of PES and to the inadequacies of the semi-empirical calculations.[99] The 'through space' interaction in norbornadiene, which was calculated by CNDO/2 as $4 \cdot 02$ eV and by MINDO/2 as $2 \cdot 1$ eV (1 eV = $23 \cdot 06$ Kcals/mole), seems far too large. Obviously there is an interaction between the π orbitals and Heilbronner has suggested that the important part played by relay orbitals in this interaction has been underestimated whilst the direct 'through space' mechanism has been overestimated, nevertheless the semi-empirical calculations suggest that b_1 becomes the lower energy orbital between $n = 2$ and $n = 3$ (i.e. when $w \simeq 130°$).[99] Hence, although the mechanism of interaction in the bicyclic dienes may be less dependent upon direct 'through space' interaction it may still be that the b_1 HOMO of $n = 1$ and $n = 2$ favours the photochemical ring closure reaction.

With polyfluorobicyclo[2,2,2]octa-2,5-dienes then the pertinent questions to consider in view of their inability to undergo ring closure are what effect does fluorine have on the shape of the carbocyclic framework and what effect does fluorine have on the PES. If the fluorines of the $-CF_2-CF_2-$ bridge are not eclipsed then the molecule will be twisted such that w and d may be larger and hence ring closure will be less favoured. However, the analysis of the electron diffraction pattern for bicyclo[2,2,2]octa-2,5-diene requires that C_{2v} symmetry

is assumed and hence the hydrogens of the $-CH_2-CH_2-$ bridge are assumed to be eclipsed.[107]   No data is available for the analogous perfluorodienes.

X-ray diffraction measurements of perfluorocetane $(n-C_{16}F_{34})$ and polytetrafluoroethylene reveal interaction between fluorines on adjacent carbon atoms since the zigzag carbon chains are twisted.[110]   In contrast normal paraffins and polyethylene have planar zigzag carbon chains.   Polytetrafluoroethylene has a helical carbon chain that undergoes a full 360° twist after 26 carbon atoms. This could perhaps lead one to conclude that the $-CF_2-CF_2-$ bridge fluorines in bicyclo[2,2,2]octa-2,5-dienes may be more staggered than hydrogens in the same position.   However, a comparison of the electron diffraction data for cyclobutane[111] and perfluorocyclobutane,[112] and cyclopentene[113] and perfluorocyclopentene[114] reveals that the fluorines of adjacent CF_2 groups tend to be less staggered than hydrogens of adjacent CH_2 groups.   In all cases it was necessary to assume C_{2v} symmetry for interpretation of the electron diffraction data.
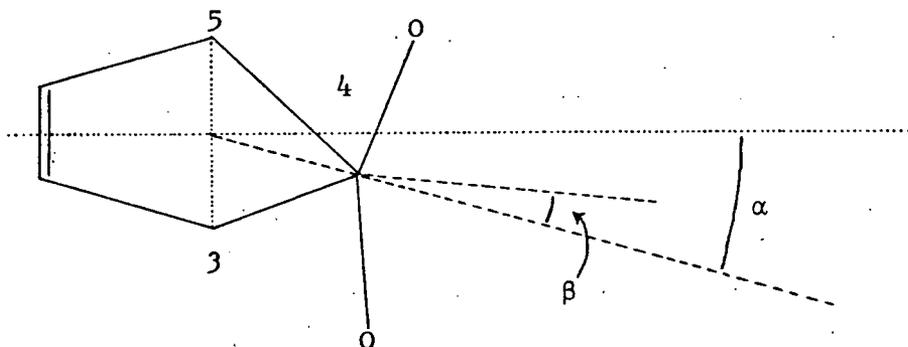
For perfluorocyclopentene the angle of pucker (α) is 20.8° whereas for cyclopentene $\alpha = 28.8^\circ$.   The FC_4F bond angle is not bisected by the $C_3C_4C_5$ plane and the upwards tilt angle β represents the discrepancy between the two. β is 3.5° for perfluorocyclopentene and 0 for cyclopentene.   Hence the overall effect is for the fluorines to be more eclipsed than hydrogen.   A similar situation arises with perfluorocyclobutane ($\alpha = 17.5^\circ$, $\beta = 5.4^\circ$) and cyclobutane ($\alpha = 27^\circ$, $\beta = 4.0^\circ$). Hence it is impossible at present to assess the importance of staggering of adjacent fluorines and adjacent hydrogens in the bicyclo[2,2,2]octa-2,5-diene series.

The lower energy of the C-F as compared with the C-H σ orbitals should reduce the amount of 'through bond' interaction between the π orbitals.[109] The influence of fluorine substitution on the interaction of π orbitals in the cyclohexa-1,4-diene series has been investigated by Ahlgren,[109] who calculated that fluorine substitution at C3 and C6 did reduce the amount of 'through bond' interaction. However these calculations were not supported by PES data and this approach probably needs revising in the light of Heilbronner's recent paper.[99] If Ahlgren's approach was applied to polyfluorobicyclo[2,2,2]octa-2,5-dienes then the 'through bond' interaction in these compounds should be less than with their hydrocarbon analogues and the 'through space' interaction should be still more dominant. This would leave the b_1 as the HOMO and thus ring closure should still be favourable.

Heilbronner and co-workers have obtained the PES spectra for a number of polyfluorobicyclo[2,2,2]octa-2,5-dienes supplied from this department. In general, compared with bicyclo[2,2,2]octa-2,5-diene, these dienes show a shift to higher energies in the π ionisation potentials of about 2.0 eV. (This shift to higher energies is analogous to that reported for 7,7-difluorobicyclo[2,2,2]-octa-2,5-diene although the magnitude of this shift has not been reported by Heilbronner[99]). The data for ionisation potentials from the π levels of a number of dienes is recorded below. Generally there is a splitting in the π levels ranging from 0.4 to 0.8 eV, although in the last recorded example no splitting is observed. With the diester (IV) ionisation from the carbonyl group does not make assignment possible. At the time of writing a detailed analysis and interpretation of the data is not available. However, it is hoped that Heilbronner will perform a more detailed analysis of these polyfluorinated dienes as this may give insight into the photochemistry of these dienes and clarify the situation vis a vis 'though space' and 'through bond' interaction.
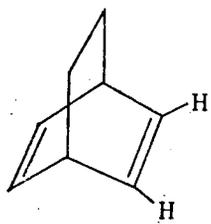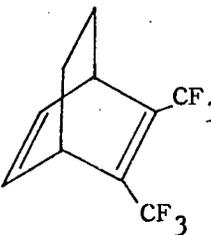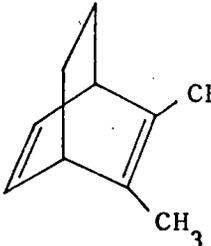
	Ionisation Potentials from π Levels (eV)		π Split (eV)
Bicyclo[2,2,2]octa-2,5-diene	ca. 8·9	9·5	0·56
(III)	10·39	11·19	0·80
(135)	10·95	11·80	0·85
	9·78	10·20	0·42
	11·25		0
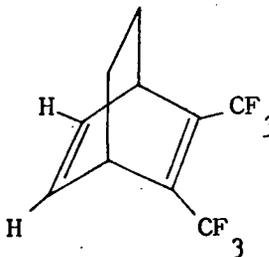
EXPERIMENTAL

2.9 Preparation of starting materials

(a) <u>Preparation of 5-bromo-1,2,3,4,7,7,8,8-octafluorobicyclo[2,2,2]oct-2-ene (II)</u>

Perfluorocyclohexa-1,3-diene (14·7g., 66·2 mmoles) and vinyl bromide (4·79g., 45·0 mmoles) were dried (P_2O_5) and degassed.   Conventional vacuum line techniques were used to transfer these reagents into a 100 ml. Pyrex ampoule (Carius tube) which was sealed under vacuum and subsequently heated at $200^{\circ}C$ for 14 hours.   The products were separated into (i) a gaseous fraction (ca. 0·9 mmoles) shown by i.r. and m.s. to contain primarily HBr, (ii) a gaseous fraction (0·19 mmoles) shown by i.r. to be vinyl bromide with a trace of perfluorocyclo-hexa-1,3-diene and (iii) a liquid mixture (17·20g.).   Distillation of fraction (iii) gave perfluorocyclohexa-1,3-diene (8·20g.) and a higher boiling fraction (9·00g., 54% yield) part of which was separated by preparative gas chromatography (Col.F, $120^{\circ}C$) to give in order of emergence from the column: (a) a trace of a compound assumed to be exo-5-bromo-1,2,3,4,7,7,8,8-octafluorobicyclo[2,2,2]oct-2-ene (IIa) on the basis of its m.s., and (b) endo-5-bromo-1,2,3,4,7,7,8,8-octa-fluorobicyclo[2,2,2]oct-2-ene (II), M.pt. $19^{\circ}C$. $C_8F_8H_3{}^{79}Br$ has a Mol. Wt. of 330 (m.s.) and $C_8F_8H_3Br$ requires: C, 29·01;   H, 0·9;   F, 45·9;   Br, 24·2%. Found: C, 29·3;   H, 1·2;   F, 45·5;   Br, 23·9%.   (II) has υ_{max} 3000 ($>CH_2$) and 1760 cm^{-1} (-CF=CF-).   The ratio of (II):(IIa) determined by analytical g.l.c. (Col.C, $120^{\circ}C$) was approximately 52:1.

(b) <u>Preparation of dimethyl 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate (IV)</u>

Using the same procedure as in (a), perfluorocyclohexa-1,3-diene (13·52g., 60·2 mmoles) and acetylene dicarboxylic acid dimethyl ester (9·0g., 63·4 mmoles) were heated at $250^{\circ}C$ in a 100 ml. Carius tube for 17 hours to give: (i) perfluoro-cyclohexa-1,3-diene (1·6g.) and (ii) a badly charred product that was purified by column chromatography (Silica gel/CT, $CHCl_3$ eluant) and finally recrystallised

from 40/60 pet. ether to give dimethyl 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]-octa-2,5-diene-2,3-dicarboxylate (IV) (10·11g.; 45% yield). $C_{12}F_8O_4H_6$ has a Mol. Wt. of 366 (m.s.) and requires C, 39·3; H, 1·7; F, 41·5%. Found: C, 39·6; H, 1·7; F, 41·1%. (IV) has a M.pt of 84-85°C and υ_{max} 2962 (-CH$_3$), 1770 (-CF=CF-), 1725 and 1750 ($>$C=O) and 1655 cm^{-1} ($>$C=C$<$).

(c) **Preparation of 1,2,3,4,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (III)**

The mixture of isomers (II) and (IIa) formed in preparation (a) (25·4g., 76·6 mmoles) were refluxed with potassium hydroxide (33g.) and water (30g.) for 6 hours. The organic product (10·8g.) was dried and fractionally distilled to give two fractions: (i) 1,2,3,4,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (III) (4·5g., 17·2 mmoles, 22·4% yield). $C_8F_8H_2$, which has a Mol. Wt. of 250 (m.s.), requires: C, 38·4; H, 0·8. Found: C, 38·2; H, 0·8. (III) has a M.pt. 32-32·5°C, a B.pt. 88°C and υ_{max} 3110 ($>$C-H) and 1760 cm^{-1} (CF=CF). The second fraction (ii) was starting material (6·3g., 18·6 mmoles), which had a B.pt. of 160°C.

(d) **Pyrolysis of dimethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate**

The diester (IV) (1·51g., 4·11 mmoles) was pyrolysed at 630°C and 10^{-3} mm pressure, by passage through a silica tube (45 cm in length, 1·5 cm internal diameter) that was lightly packed with silica wool. The products consisted of (i) a gas, shown by i.r. to be tetrafluoroethylene (3·95 mmoles) and (ii) a solid (1·05g.) shown by g.l.c. (Col.B, 250°C) to consist of a trace of starting material and one other compound which after purification by recrystallisation from 40/60 pet. ether was confirmed by n.m.r., i.r. and m.s. to be dimethyl tetrafluorophthalate, (Mol. Wt. 266), by comparison with published data.[127]

2.10 Photochemical reactors

A Hanovia low pressure mercury lamp (6LQ) of radiative output 3·2 watts, 90% of which is between 185 nm and 254 nm (0·04 watts at 185 nm), was used for gas phase irradiations. The lamp was fitted into a double-walled Hanovia quartz immersion well ($7\frac{1}{4}$" in length), that enabled nitrogen streaming. The outer well was inserted through a B45/40 joint into a spherical 3 litre Pyrex vessel so that the lamp was in the centre of the vessel. Liquid was allowed to evaporate into the evacuated vessel from a small removable 25 ml. flask attached to a side arm. The position of the side arm enabled shielding of the liquid from radiation.

Irradiations in solution utilized the Hanovia (100LW) medium pressure mercury lamp, (total radiative power 25 watts with 0·55 watts at 254 nm) inserted into a double-walled quartz well, which enabled water cooling for reactions carried out at room temperature. The cylindrical quartz wells were inserted into a cylindrical Pyrex vessel to give a reactant capacity of 300 ml. Two side arms, one for a nitrogen inlet tube that extended down to the bottom of the apparatus and the other for a reflux condenser, were fitted to the top of the Pyrex vessel. During irradiations and for 3 hours before, nitrogen was bubbled through the solution and the apparatus was completely dry-sealed with conc. H_2SO_4 bubblers.

2.11 Irradiation of polyfluorinated bicyclo[2,2,2]octa-2,5-diene systems

(a)   Gas phase irradiation of 1,2,3,4,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (III)

The diene (III) (0·5g., 2·0 mmoles) was irradiated for 24 hours to give a viscous residue (0·48g.) whose i.r. was substantially the same as that of (III) though the presence of aliphatic $\geq$C-H bonds at 2980 cm^{-1} indicated slight decomposition. G.l.c. analysis (Col.A, 70°C) confirmed that (III) was the only volatile material present.

(b) <u>Gas phase photolysis of perfluoro-2,3-dimethylbicyclo[2,2,2]octa-2,5-diene (135)</u>

The diene (135) (0·94g., 2·43 mmoles) was irradiated for 13 days to give a liquid mixture (0·72g.) shown by g.l.c. analysis (Col.C, 90°C) to be perfluorobicyclo[2,2,0]hex-2-ene (21%), perfluorocyclohexa-1,4-diene (8%), perfluorocyclohexa-1,3-diene (28%), (135) (38%) and a trace of two other components more volatile than the diene (135).

(c) <u>Irradiation of dimethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate in solution</u>

(i) <u>In ether</u>

The diester (IV) (1·89g., 5·16 mmoles) was dissolved in 300 ml. of diethyl ether (Na dried) and irradiated for 3 hours at a temperature between -25°C and -20°C. The ether was then immediately vacuum transferred at 0°C to leave a viscous residue, whose n.m.r. was recorded in ether solution at -40°C. The ^{19}F n.m.r. spectrum integrated to eight fluorine atoms and was consistent with the anticipated tetracyclic structure as the two vinylic fluorines of (IV) were replaced by two signals in the tertiary fluorine region. The ^{19}F n.m.r. spectrum did not change with time and 1·85g. of residue were recovered. This residue would not recrystallise from any of the common hydrocarbon solvents and purification was effected using column chromatography (Silica gel/CT, $CHCl_3$ eluant). A trace of (IV) was firstly obtained, followed by a white solid (1·45g.) which was recrystallised from 40/60 pet. ether to give (V) whose ^{19}F n.m.r. spectrum was identical to that initially run at -40°C.

Elemental analysis and m.s. indicated that (V) was a 1:1 adduct of the ester (IV) and diethyl ether. $C_{16}F_8O_5H_{16}$, which has a Mol. Wt. of 440 (m.s.), requires: C, 43·6; H, 3·6; F, 28·9%. Found: C, 43·7; H, 3·5 and F, 28·6%. The Mol. Wt. of (V) in solution (Perkin-Elmer molecular weight apparatus 115, benzene solvent) gave a value of 420. (V) has a υ_{max} 2982 (-CH_3), 1745 and

1768 cm^{-1} ($>$C=O). However, (V) was resolved by g.l.c. analysis (Col.B, 230°C) after being retained on the column for 30 minutes. Two peaks were obtained in the ratio of 5:6 in order of increasing retention time.

(ii) In acetonitrile

The diester (IV) (2·05g., 5·63 mmoles) was dissolved in 300 ml. of acetonitrile (P$_2$O$_5$ dried) and irradiated for 4 hours between -30 and -20°C. The acetonitrile from 100 ml. of solution was vacuum transferred at 10°C to give a solid residue whose ^{19}F n.m.r.,in CHCl$_3$ at -35°C,and i.r. confirmed the presence of (IV) only. This material was redissolved in 100 ml. of acetonitrile and returned to the reactor. The solution was then irradiated again for 8 hours at 20°C to give 1·90g. of unchanged starting material.

(iii) In benzene

The diester (IV) (2·10g., 5·74 mmoles) was dissolved in 300 ml. of benzene (Na dried) and irradiated for 3 hours between 5 and 10°C. Vacuum transfer of C$_6$H$_6$ at 10°C gave a solid whose ^{19}F n.m.r.,at 10°C,and i.r. confirmed the presence of (IV) only.

Irradiation of this solution for 24 hours at 20°C gave 1·98g. of unchanged starting material.

(iv) In perfluoromethylcyclohexane

The procedure as in (ii) was followed except only (0·57g., 1·56 mmoles) of the diester (IV) were used owing to its low solubility in this solvent. At each stage only unchanged (IV) was observed.

(v) In methanol

The diester (IV) (3·00g., 8·14 mmoles) was dissolved in 300 ml. of dry methanol and irradiated for 3 hours between -30 and -20°C. The methanol was distilled to give (3·18g.) of solid which was shown by g.l.c./m.s. (Col.J, 200°C) to consist of a trace of starting material (IV) (ca. 8%) and three major components, which formed about 80% of the mixture, and a number of minor components. The

major components all had a Mol. Wt. of 398 and were formed in the ratio of

1:1:2 in order of increasing retention time ((i):(ii):(iii)). The breakdown

patterns of the top mass peaks are analysed in the table below:

m/e	Assignment	Origin	(i)	(ii)	(iii)
398	$C_{13}F_8O_5H_{10}$	Parent	1·4	9·1	8·1
396	$C_{13}F_8O_5H_8$	P-H_2	4·3	-	-
383	$C_{12}F_8O_5H_5$	P-CH_3	9·2	2·0	1·4
381	$C_{13}F_8O_4H_9$	P-OH	-	1·8	3·2
380	$C_{13}F_8O_4H_8$	P-OH_2	-	3·2	3·2
379	$C_{13}F_8O_4H_7$	P-OH_3	-	3·6	4·0
378	$C_{13}F_8O_4H_6$	P-OH_4	2·2	0·9	-
368	$C_{12}F_8O_4H_8$	P-CH_2O	10·0	-	-
367	$C_{12}F_8O_4H_7$	P-CH_3O	-	100	100
366	$C_{12}F_8O_4H_6$	P-CH_3OH	21·0	26·3	10·8
337	$C_{11}F_8O_3H_5$	P-$C_2H_5O_2$	100	81·8	61·9

The ^{19}F n.m.r. on the mixture of isomers showed that the ratio of

(-CF_2-CF_2-) : (vinylic F) : (tertiary F) was the same as that of the starting

material namely 2:1:1. However, six resonances for vinylic fluorine were

observed with the three major ones comprising 35, 30 and 15% of the total. No

attempt was made to purify and fully characterise the products though the small

amount of starting material (IV) was removed by recrystallisation from acetone

and pet. ether (60/80) to leave a white solid residue whose i.r. and u.v.

confirmed the absence of the conjugated C=C found in (IV). The i.r. of the

recrystallised solid showed ν_{max} 3500 (-OH), 2980 (-CH_3), 1780 (-CF=CF-) and

1750 cm^{-1} ($>$C=O). The above data is consistent with the formation of methanol

adducts at the conjugated C=C bond of the ester (IV).

(vi) <u>With acetonitrile and HCl</u>

The diester (IV) (1·39g., 3·71 mmoles) was dissolved in 300 ml. of dry

acetonitrile which was saturated with HCl gas at $0^{\circ}C$, and then irradiated for

3 hours at between -20 and $-30^{\circ}C$. N_2 was then bubbled through the acetonitrile

solution for 20 hours in order to remove the bulk of the HCl, however on distillation

down to 50 ml. (23·0g.) of predominantly solvent derived material was

precipitated and filtered.   A small amount of this solid (ca. 0·1g.) was

shaken with 0·5 ml. acetone and g.l.c./m.s. analysis (Col.K, $180^{\circ}C$) of the

acetone soluble compounds indicated in order of emergence from the column:

(i) a product $(C_{13}F_8O_4H_4)$ obtained from hydrolysis of one of the ester groups

of (IV);   (ii) $(C_{12}F_8O_4H_2)$ from the hydrolysis of both ester groups of (IV);

and (iii) a trace of (IV).   The remaining 50 ml. of CH_3CN solution was

distilled to give a viscous residue (ca. 2·4g.) which together with the (23·0g.)

of solid was shaken with 300 ml. of water.   (IV) (1·05g., 2·85 mmoles) was

precipitated and confirmed by n.m.r. and i.r.   The aqueous solution (pH 2) was

ether extracted for 2 days.   The ethereal layer was dried $(MgSO_4)$ and distilled

to give a viscous residue (ca. 1·1g.).   However, isolation of the mono- and di-

acids of the diester (IV) was not possible as ether extraction of some of the

assumed polymeric acetonitrile residue had also occurred.   The acids could not

be purified by sublimation.

(0·778g., 2·12 mmoles) of the diester (IV) were dissolved in 300 ml. of

dry acetonitrile and photolysed between -30 and $-20^{\circ}C$ for 3 hours.   Then the

acetonitrile was saturated with dry HCl at $-20^{\circ}C$ and was allowed to stand for

18 hours by which time the temperature had increased to $0^{\circ}C$.   A white solid

(35·0g.), formed on standing, evolved HCl on warming and gave an acetonitrile

solution that was shown by g.l.c./m.s. to contain the diester (IV) and the mono-

and di-acids obtained by hydrolysis of this ester.   The bulk of the acetonitrile

was distilled and by an analogous method to that previously used (0·650g.) of

unreacted (IV) were recovered.

(d) <u>The photolysis of perfluoro-2,3-dimethylbicyclo[2,2,2]octa-2,5,diene (135)</u>

<u>in CFCl$_3$</u>

The diene (135) (0·74g., 1·91 mmoles) was dissolved in 300 ml. of dry CFCl$_3$

and irradiated for 6 hours at temperatures between -35 and -25°C. The CFCl$_3$

was distilled at 50 mm and -15°C to ~~give~~ leave a viscous liquid residue (1·02g.)

which was analysed by g.l.c./m.s. (Col.J, 200°C) and shown to consist of four

major components.   The major components, which comprised 95% of the liquid

mixture, were addition products to the diene (135) and in order of increasing

g.l.c. retention time these corresponded to: (i) addition of Cl$_2$ (C$_{10}$F$_{10}$^{35}Cl$_2$;

456), (ii) addition of Cl$_2$, (iii) addition of FCl$_3$ (C$_{10}$F$_{11}$^{35}Cl$_3$; 510) and (iv)

addition of at least FCl$_4$, though the top mass peak must have been absent.

(N.B. The top mass peak for CF^{35}Cl$_3$ was at CF^{35}Cl$_2$).   No attempt was made to

further identify or purify the products.   The ^{19}F n.m.r. indicated that the

majority of resonances occurred between 55 and 65 p.p.m., although a small

percentage of the resonances occurred in the region 110-130 p.p.m.   The diene

(135) has υ_{max} 1760 (-CF=CF-) and 1660 cm^{-1} ($>$C=C$<$)[96] and the i.r. of the viscous

residue indicated that weak absorptions occurred at these positions and this

suggests that (i) and (ii) probably arise via Cl$_2$ addition to one or other of

the double bonds.

CHAPTER 3

The Diels Alder Reactions Of Perfluorotricyclo[6,2,2,0^{2,7}]-2,6,9-triene

INTRODUCTION - The Diels Alder Reaction

3.1 Stereochemistry and mechanism

The formation of a six-membered ring by 1,4-addition of an unsaturated

system (dienophile) to a conjugated diene, which was first discovered by Diels

and Alder in 1928[115], is one of the most versatile reactions in organic chemistry.

(Reviews of the Diels Alder reaction are found in references 116, 117, 118). In

1937 Alder and Stein formulated the 'Cis Principle' which states that the

configurational relationships of the diene and the dienophile are retained in

the adduct.[119]
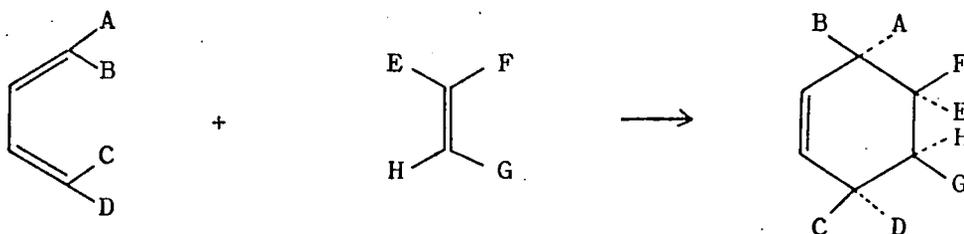
The diene must be cisoid and planar whilst the absence of free rotation about the

double bond of the dienophile suggests that the mechanism is concerted.

The concerted Diels Alder reaction is a [π4s + π2s] orbital symmetry allowed

ground state reaction.[71] The [π4a + π2a] is also a thermally allowed process

but the transition state for this is much less sterically favourable, though in

suitably constrained systems this mode of cycloaddition has been observed. Apart

from a few examples[120], the Diels Alder reaction can only be regarded as a

concerted process. Attempts to show the involvement of free radicals and

biradical intermediates have not been successful. Similarly, the kinetic effects

of para substituents in 1-phenylbutadiene are considered too small for a rate-

determining transition state that involves zwitterionic character.[117]

Cyclic dienes with near planar rings are particularly effective dienes and

may react with non-centrosymmetric dienophiles to give the endo or exo isomer, although the former generally predominates.   The reaction of cyclopentadiene with maleic anhydride gives the endo adduct with less than 1.5% of the exo isomer.[121]

Exo Adduct

Endo Adduct

----- primary interaction   ·········· secondary interaction
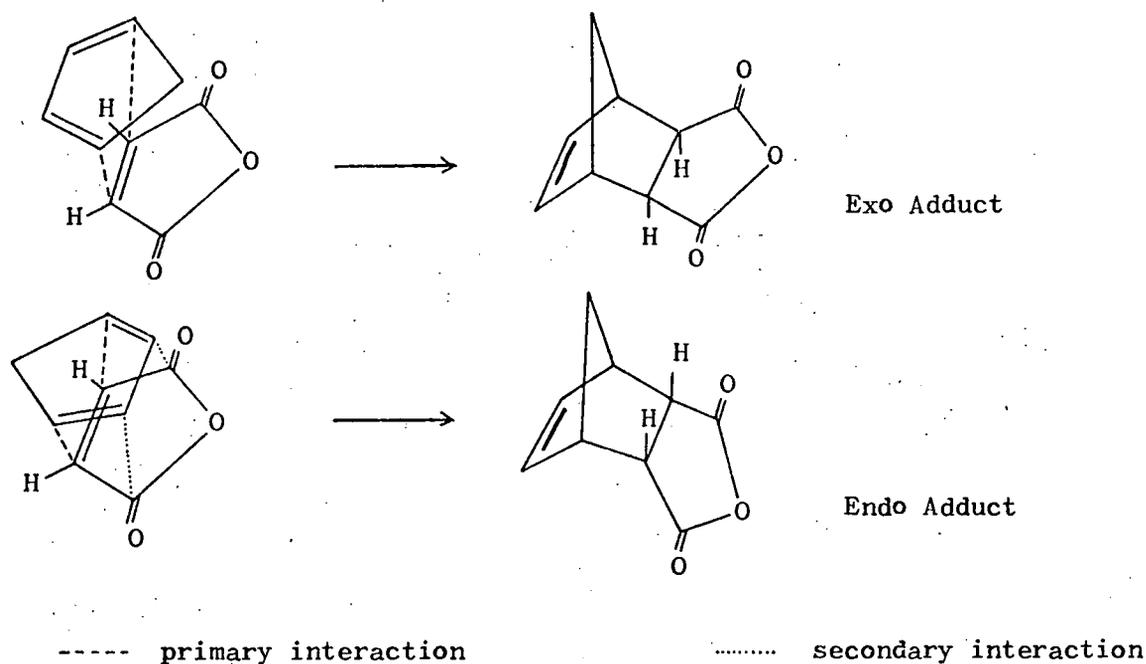
Alder and Stein assumed that the reactants arranged themselves in parallel planes and that orientation of addition proceeds from the transition state in which there is 'maximum accumulation' of double bonds.[119]   This secondary interaction extends to the π bonds not directly involved in the cycloaddition and would explain the predominance of the endo adduct even though the exo adduct is thermodynamically more stable.   Woodward and Hoffmann have predicted that the Diels Alder dimerisation of butadiene will proceed through the endo rather than the exo approach of the two butadiene molecules.[71]   Only the endo approach generates favourable interaction in the transition state arising from symmetry allowed mixing of the unoccupied and occupied molecular orbitals.   Volume activation studies on some Diels Alder reactions of maleic anhydride have shown that the transition state volume was actually smaller than that for the final adduct.[122]   This result is consistent with secondary interactions playing an important role in the transition state.

However, secondary interactions cannot be invoked to explain the high endo stereoselectivity observed in the reaction of cyclopendadiene with cyclopentene. In fact many cyclic dienes when reacting with cyclic dienophiles give mainly the endo isomers. Calculations by Hendon and Hall indicate that the stereo-selectivity is controlled by the difference in activation energies which in turn depend upon the overlap of π orbitals at the primary centres where new bonds are developing.[123] These primary interactions could account for 90% of the difference in the stabilisation energies between the endo and exo transition states for dicyclopentadiene and hence, Hendon and Hall claimed that there was no need to invoke secondary interactions. However, the predictions of endo:exo isomer ratios is somewhat difficult as an activation energy difference of only 3 Kcals/mole can result in an isomer ratio of 99:1.[124] The transition state is affected by subtle electronic, steric and non-bonding interactions and the importance of each will depend upon the particular reaction under consideration.

The reaction of an unsymmetrical diene with an unsymmetrical dienophile often selectively produces one of the possible adducts.

Ph + CO_2CH_3 $\longrightarrow$ Ph CO_2CH_3 + Ph CO_2CH_3

Ph CO_2CH_3 + CO_2CH_3 $\longrightarrow$ Ph CO_2CH_3 + Ph CO_2CH_3
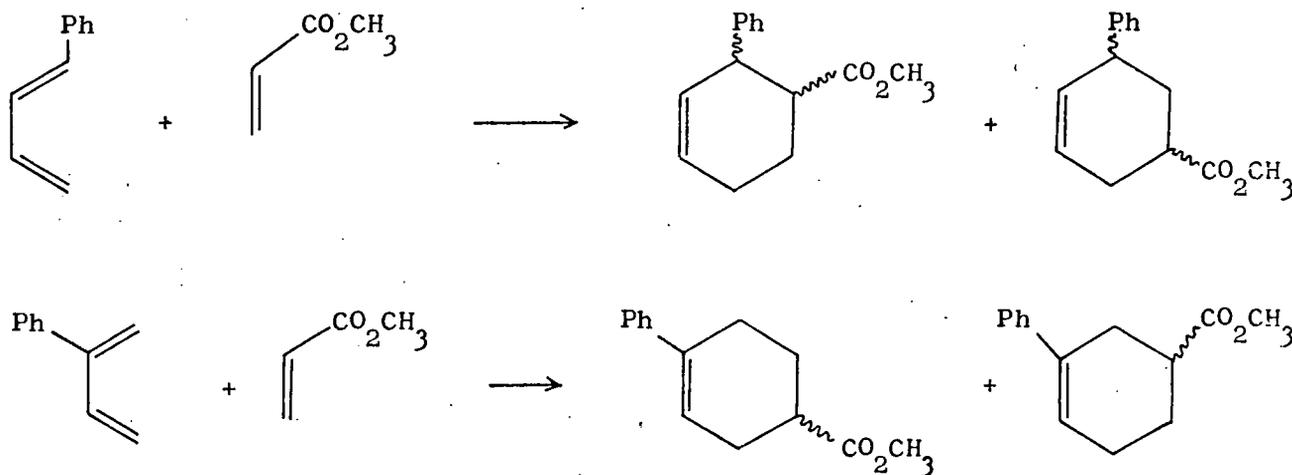
The above reactions are highly selective with trans-1-phenylbutadiene giving over 97% of the 3,4-disubstituted isomer whilst 2-phenylbutadiene gives approximately 80% of the 1,4-disubstituted isomer.[125] The preferred orientation of addition of some substituted butadienes with unsymmetrical dienophiles (acrylonitrile, methyl acrylate and styrene) has been accurately predicted by Hendon and Hall

from a full perturbation calculation and from a consideration of the frontier orbital interaction between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO).[126]

An example of the importance of HOMO (diene)/LUMO (dienophile) interaction is discerned from the fact that (140) reacts instantaneously with tetracyano- ethylene in chloroform at room temperature whereas (141) reacts only slowly on refluxing.[128]

(140)   (140a)   (141)   (141a)
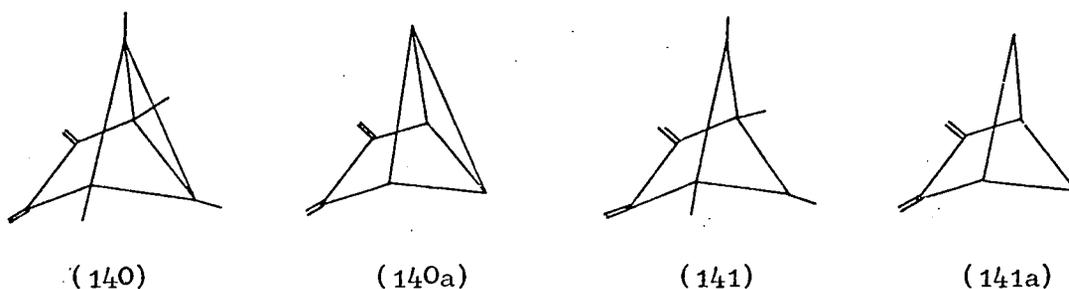
Ab initio calculations have shown that the HOMO of (140a) lies about 25 Kcals/mole above that of (141a) and since the HOMO's of (140) and (141) have the required symmetry to interact with the LUMO (dienophile), the more favourable interaction with (140) may explain its greater Diels Alder reactivity.   The difference in Diels Alder reactivity had already been predicted from extended Huckel calculations.[129]

(140b)   (141b)

The difference in Diels Alder reactivity between (140) and (141) can also be rationalised from another standpoint.   The HOMO/LUMO interactions between the butadiene moiety and the cyclobutane Walsh orbitals in (141a) is stabilizing (π bond order + 0.078).   However, a similar calculation for (141b) indicates that in this case these interactions are destabilizing (π bond order - 0.007). The HOMO/LUMO interaction between the olefin moiety and the bicyclobutane

orbitals in (140a) and (140b) are both stabilizing with the respective π bond

order being (+0·121) and (+0·085).   Thus the conversion of (141a) to (141b) is

far less favoured than that of (140a) to (140b) on the basis of orbital

interactions.

(142)   (143)   (144)
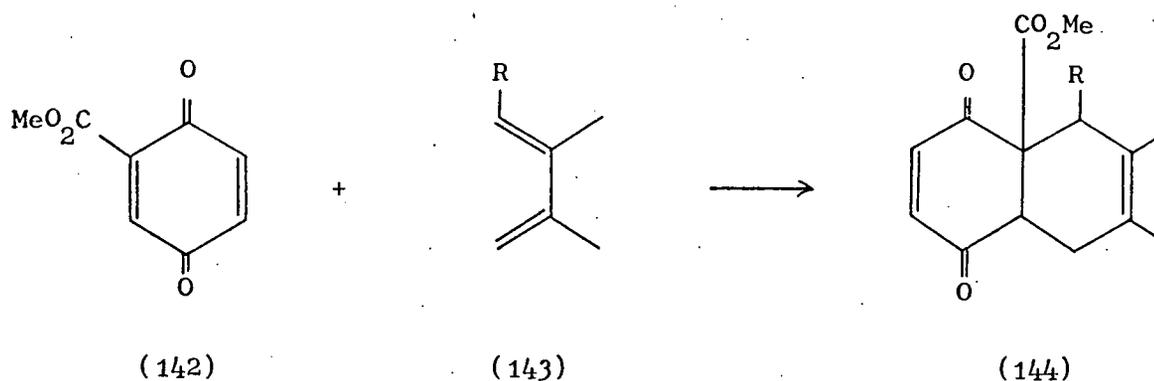
The Diels Alder reaction between the substituted butadienes (R = Ph,

pMeO.C_6H_4, pNO$_2$.C_6H_4) (143) and the p-benzoquinone (142) gave the adducts (144)

as the major products.[130]   It has been shown that the relative orientation of

the quinone and the diene substituent in the product is not affected by the

electronic nature of R or the substituent in the quinone.   This has lead the

authors to speculate that if a concerted mechanism operates, such that both

bonds are not equally developed, then the transition state is likely to have

some diradical rather than zwitterionic character.

Many Diels Alder reactions are exothermic.[118]   In particular for the

reaction of ethylene with butadiene ΔH = -30 Kcals/mole[118] and for the reaction

of cyclopentadiene with maleic anhydride ΔH = -25 Kcals/mole.[131]   The Diels

Alder reaction is often reversible, particularly with adducts derived from cyclic

dienes and cyclic dienophiles when reversibility becomes more favourable at

higher temperature.

Although a concerted mechanism for the Diels Alder reaction is now accepted

it is an open question whether the new bonds are formed to the same extent in the

transition state.   If a non-concerted mechanism operates the experimental results

available seem to be consistent only with a 'biradical' transition state.   A

recent study of the transition state by MINDO/3 suggested asymmetry and

biradicaloid presence for the addition of ethylene to butadiene.[132]   The

authors found the asymmetry so large that it was necessary to postulate that the

Diels Alder was not a concerted pericyclic reaction.   However, such theoretical

calculations on the transition state have been rather unreliable in the past.[132]

Certainly molecular orbital calculations in the past decade have helped

considerably in the understanding of the mechanism involved in the Diels Alder

reaction.   The HOMO/LUMO interactions between the diene and dienophile being

particularly pertinent to the rationalisation of reactivity differences between

superficially similar reactants.   As a consequence of the immense scope of the

Diels Alder reaction, the importance of frontier orbital, secondary orbital,

steric and electronic factors will depend upon the specific reaction under

consideration.

3.2   Reactivities in the Diels Alder reaction

The kinetic studies of Sauer have done much to elucidate the nature of the

Diels Alder reaction.[124,133]   Two reaction types are exemplified: the normal

Diels Alder reaction and the Diels Alder reaction with inverse electron demand.

In the normal reaction the diene is an electron rich species whilst the

dienophile is electron poor.   Hence the empirical Alder Rule[134] recognised that

the reaction rate is increased by electron donating substituents in the diene

and by electron attracting substituents in the dienophile.   The reaction with

inverse electron demand involves an electron poor diene and an electron rich

dienophile.

Sauer has measured the rates of reaction of many electron rich dienes with

the electron poor maleic anhydride.[133]   It was found that the order of increasing

reactivity was butadiene $<$ cyclohexa-1,3-diene $<$ cyclopentadiene.   The higher

reactivity of the cyclic dienes arises from their fixed cisoid conformation

whilst the higher reactivity of cyclopentadiene relative to cyclohexa-1,3-diene

arises because the terminii of the π system are closer together in the former and

the latter is also slightly distorted from a planar configuration. Electron poor alkynes were found to be slightly less reactive than corresponding alkenes, in which one of the double bonds had been replaced with hydrogen, in the reaction with 9,10 dimethylanthracene.

The rates of addition of various dienophiles to hexachlorocyclopentadiene and 9,10-dimethylanthracene have been measured by Sauer.[124] The results are presented in Table 2 and illustrate clearly the phenomenon of inverse electron demand.

TABLE 2

Kinetics of the reaction of hexachlorocyclopentadiene and

9,10-dimethylanthracene with dienophiles in dioxan at $130^{\circ}C$

Dienophile	Rate x 10^6 l.mole^{-1}sec^{-1}	
	Hexachlorocyclopentadiene	9,10-Dimethylanthracene
p-methoxystyrene	1580	50
styrene	793	70
p-nitrostyrene	558	602
norbornene	72	36
cyclopentene	59	7.8
maleic anhydride	29	1,410,000

3.3 Electron poor dienes in the Diels Alder reaction

The most extensively studied electron poor dienes have been the highly halogenated systems. A great many Diels Alder reactions of hexachlorocyclo-pentadiene and its derivatives are known;[135,136] some of these adducts being used as fungicides, plant growth regulators and insecticides. The insecticide Aldrin is the adduct of hexachlorocyclopentadiene with norbornene. The reaction of hexachlorocyclopentadiene with dienophiles takes place between 20 and $200^{\circ}C$, for

example the reaction with ethylene at 200°C gave (145) and with allene at

150-200°C gave (146).

(145)

(146)
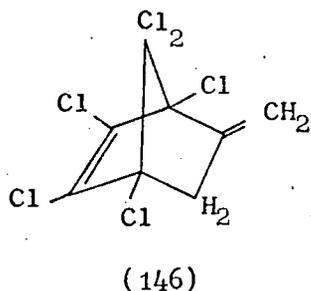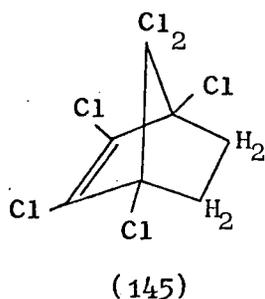
The reaction of hexachlorocyclopentadiene with 1,3-alkadienes has shown

that the former is more reactive towards conjugated rather than isolated

olefins and towards terminal rather than non-terminal olefins. Alkyl

substitution of these dienophiles did not increase the reactivity, presumably

steric inhibition becomes more important than electronic factors. Conjugation

of the dienophilic double bond will decrease the electron density and this

would be expected to reduce reactivity. The observed increase in reactivity

has been attributed to stabilisation of the polar transition state arising from

the increased polarizability of the π bond.[137]

Hexachlorocyclopentadiene shows no tendency to dimerise but a change in

substituent at the 5-position causes unanticipated changes in the ease of

dimerisation in the order of $F_2 > H_2 > HCl$.[135]   1,2,3,4-Tetrachloro-5,5-

difluorocyclopentadiene dimerises very rapidly and also forms Diels Alder

adducts at room temperature. The dimers formed when the five-substituents

are changed to F_2, H_2 and HCl all disassociate at higher temperatures.

The Diels Alder reactions of 1,2,3,4,5-pentachlorocyclopentadiene with

maleic anhydride and p-benzoquinone generated a larger amount of the anti-endo

isomers (147) than the syn-endo isomers (148).[138]

(147)

(148)
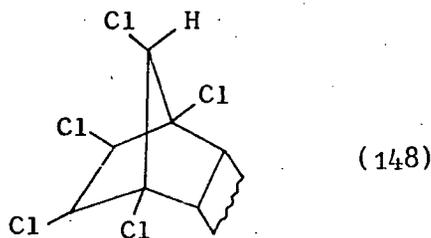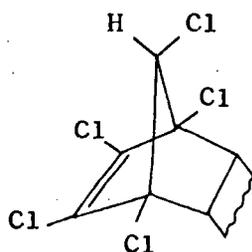
This led the authors to postulate that interactions of the van der Waals-London type were important in the transition state with the more polarizable chlorine atom, in spite of its larger size, being found adjacent to the dienophile.

3.4 Fluorinated dienes in the Diels Alder reaction

(a) Acyclic dienes

In general these dienes do not undergo the Diels Alder reaction and acyclic fluoro-olefins containing the $>C=CF_2$ group readily form 4-membered ring compounds when heated alone or with other unsaturated compounds. The dimerisation of tetrafluoroethylene to perfluorocyclobutane proceeds readily at $200°C$ and is exothermic by 50 Kcals/mole[139], with the driving force being the removal of the repulsive interaction between the π bond and the fluorine lone pairs. Also the F atoms are mutually bond strengthening in the cyclobutane.[141] It seems likely that these dimerisations involve a radical process rather than the thermally allowed $[\pi2a + \pi2s]$.[71] This accounts for the often observed 'head to head' dimerisation of substituted fluoro-olefins since the greater stability of (149a) over (149b) would account for the cyclobutane obtained (149) on dimerisation of 1,1-dichlorodifluoroethylene.[141]

$$CCl_2-\overset{\bullet}{C}F_2$$
$$CF_2-\overset{\bullet}{C}Cl_2$$

(149b)

$$2CF_2=CCl_2$$

$$\overset{\bullet}{C}F_2-\overset{\bullet}{C}Cl_2$$
$$CF_2-\overset{\bullet}{C}Cl_2$$

(149a)

$$F_2\,\square\,Cl_2$$
$$F_2\quad Cl_2$$

(149)
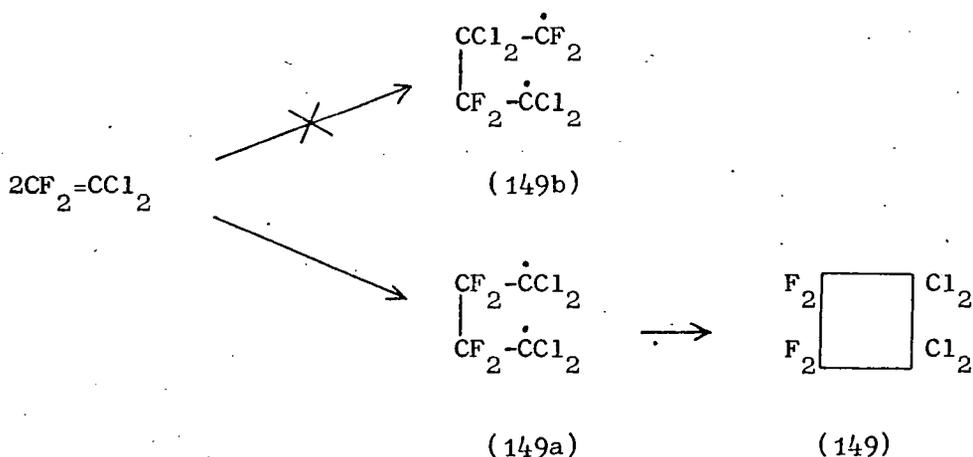
However the Diels Alder reaction of tetrafluoroethylene with cyclopentadiene competes with the 1,2-addition at $475°C$ and 1 atm. (Perfluorocyclobutane dissociates to tetrafluoroethylene at this temperature).[140]
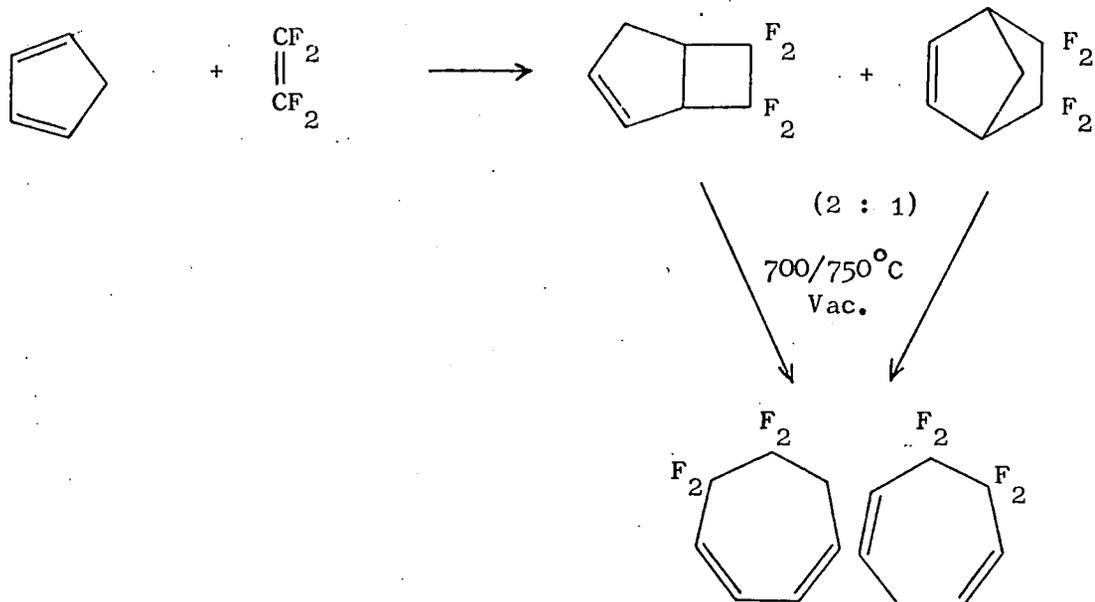
Perfluorobutadiene undergoes intermolecular dimersation to the diene (150) at 150°C, whilst the intramolecular cyclisation product, perfluorocyclobutene, is formed at 450°C.[55] The diene (150) isomerises to the tricyclic compound (151) at 200°C.[142]
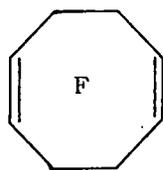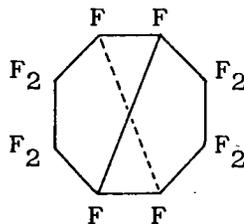
(150)   (151)

Thus perfluoro-acyclic dienes cannot be used in Diels Alder reactions because of this remarkable tendency to cyclise and dimerise. The ground state of perfluorobutadiene in the gas phase has recently been determined by photo-electron and optical spectroscopy to be cisoid and to differ substantially from planarity.[143] This is also in agreement with unpublished electron diffraction data.[143] This non-planarity presumably arises from the steric interaction of the C_1 and C_4 fluorines and has been previously postulated to explain the lack of Diels Alder reactivity.[144]

(b) Polyfluorocyclopentadienes

Perfluorocyclopentadiene dimerises readily at room temperature and slowly, even at -22°C, to give the Diels Alder dimer (152),[145] which has been assigned the endo-configuration on the basis of a detailed analysis of its ^{19}F n.m.r. spectrum.[146] Further confirmation for this assignment is that (152) and endo-dicyclopentadiene give the same product on fluorination with CoF_3.[147]

(152)
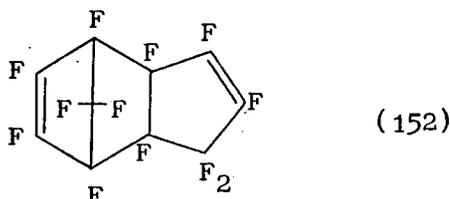
The thermal stability of the dimer (152) is very much greater than that of dicyclopentadiene: (152) remained unchanged after heating at 475°C for 45 mins. whereas dicyclopentadiene breaks down quantitatively at 160°C.

Like perchlorocyclopentadiene, perfluorocyclopentadiene is a reactive electron poor diene, however formation of the dimer reduces the yields of the adducts obtained in the Diels Alder reaction[145,146] (cf. Table 3). Perfluorocyclo-pentadiene reacted as a dienophile with anthracene, as both a diene and a dienophile with cyclopentadiene and as a diene with the other reactants in Table 3. The reaction with electron rich dienophiles occurs fairly readily whilst electron poor dienes like maleic anhydride also give reasonable yields. In accord with the 'Cis Principle', diethyl fumarate and diethyl maleate retain their configuration in their adducts, whose structures have been assigned from their n.m.r. spectra.[148] The yield of adduct (153) from the trifluoronitroso-methane reaction is quantitative in contrast to perchlorocyclopentadiene which did not react even at 100°C. Like perchlorocyclopentadiene, perfluorocyclo-pentadiene shows no reactivity towards tetracyanoethylene, tetrafluoroethylene or perfluorocyclohexa-1,3-diene.

Chemical methods have shown that N-allyltrifluoroacetamide reacts to give the adduct (154) which is predominantly or even exclusively the endo isomer.

TABLE 3

The Diels Alder reactions of perfluorocyclopentadiene

Reactant	% Yield Dimer	% Yield 1:1 Adduct	Reaction Conditions
$H_3CO_2C\equiv CCO_2CH_3$	50	22	133°, 3d
$HC\equiv CH$	22	42	115°, 65h
Diethyl fumarate	55	50	110°, 3d
Diethyl maleate	34	66	110°, 3d
N-allyltrifluoroacetamide	70	30	50°, 64h
$H_2C=CH_2$	41	51	106°, 8d
Maleic anhydride	53	41	110°, 2d
Butadiene	25	64	110°, 4-5d
Norbornadiene	0	99	110°, 6d
Anthracene	-	27	120°, 5d
Cyclopentadiene	0	98	$120-125^\circ$, 4d
CF_3NO	0	98	20°, overnight

The hydrolysis of (154) gave the free amine which cyclised to the tricyclic amine (155).[97]
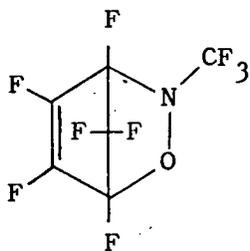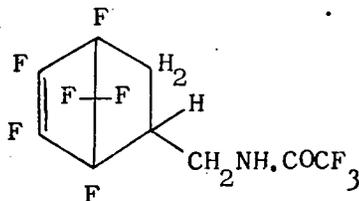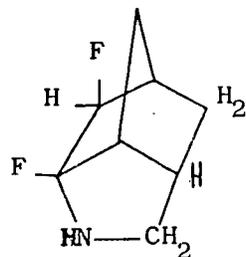
(153) (154) (155)

The exo isomer would not undergo such an intramolecular cyclisation and would probably have reacted by intermolecular nucleophilic attack. Hence it appears that the Diels Alder reaction adducts of perfluorocyclopentadiene had primarily endo configuration.

It has also been found that 2H-pentafluorocyclopentadiene dimerises by the Diels Alder reaction to give the endo isomer (156).[146] Perfluoro-1-methyl-cyclopentadiene is much more stable, being only 40% converted to the dimer (157) after 50 hours at 80°C . (157) was assigned the endo configuration on the basis of its ^{19}F n.m.r. spectrum.[149]

(157)   (156)
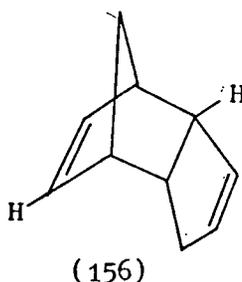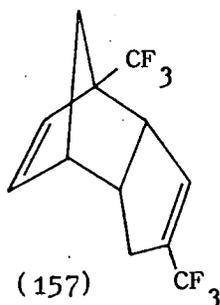
[Unmarked bonds to fluorine]

(c) Polyfluorocyclohexa-1,3-dienes

Perfluorocyclohexa-1,3-diene is stable to dimerisation up to 250°C but when heated at 390°C for 144 hours a 40% yield of endo and exo Diels Alder dimers (158) are produced in the ratio of 9:1 respectively.[96] This dimerisation proceeds readily at 340°C and is reversible (cf. Discussion). Thus in contrast to perfluorocyclopentadiene, more forcing conditions may be employed to effect the Diels Alder reaction of perfluorocyclohexa-1,3-diene with unreactive dienophiles

(158)   (159)
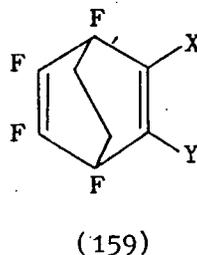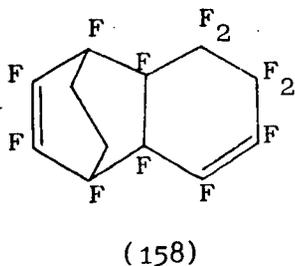
[Unmarked bonds to fluorine]

Perfluorocyclohexa-1,3-diene was the first polyfluorinated diene reported to undergo the Diels Alder addition[150] and the reactions with electron rich olefins and acetylenes proceed readily (cf. Table 4). The reaction with acetylenes gives polyfluorobicyclo[2,2,2]octa-2,5-dienes (e.g. 159).[93]

TABLE 4

The Diels Alder reactions of perfluorocyclohexa-1,3-diene

Reactant	% Yield of 1:1 Adduct	Reaction Conditions	Reference
$CH_2=CHCOCH_3$	73	$114°$, 2.5h	150
$CH_2=CH_2$	80	$200°$, 4.5h	151
$CH_2=CHPh$	94	$97°$, 7h	150
$CH_2=CHCN$	65	$170°$, 5h	150
Maleic anhydride	68	$190°$, 7h	150
Anthracene	7	$99°$, 48h	150
N-allyltrifluoroacetamide	54	$110°$, 48h	92
Cyclohexa-1,3-diene	61	$60°$, -	92
$HC\equiv CCH_3$	94	$180°$, 40h	96
$HC\equiv CPh$	54	$175°$, 20h	96
$F_3C\equiv CCF_3$	36	$225°$, 18h	96
$HC\equiv CCF_3$	92	$180°$, 100h	96
$EtO_2CC\equiv CCO_2Et$	47	$215°$, 18h	96

Table 4 illustrates that perfluorocyclohexa-1,3-diene reacts with 'inverse electron demand' and hence the order of reactivity in the Diels Alder reaction is

$CF_3C{\equiv}CCF_3 < HC{\equiv}CF_3 < HC{\equiv}CH_3$. Perfluorocyclohexa-1,3-diene resembles perfluoro-cyclopentadiene in behaving as a dienophile with anthracene and as both a diene and a dienophile with cyclopentadiene and cyclohexa-1,3-diene. The adduct from the reaction with N-allyltrifluoroacetamide was shown to be predominantly or even exclusively the endo isomer by the method described earlier for the analogous perfluorocyclopentadiene adduct (154). In this case the free amine group was slower to cyclise than the corresponding perfluorocyclopentadiene derivative. The slower rate of cyclisation being attributed to the lower reactivity of the less strained -CF=CF- double bond in the bicyclo[2,2,2] system and the larger distance between the $-NH_2$ group and the proximate -CF=.[92] Hence. it would seem reasonable to anticipate that the reaction of non-centrosymmetric dienophiles with perfluorocyclohexa-1,3-diene produces predominantly endo configuration adducts.

When heated with tetrafluoroethylene at $400^{\circ}C$, perfluorocyclohexa-1,3-diene gave a [2 + 2] adduct (160).[96]
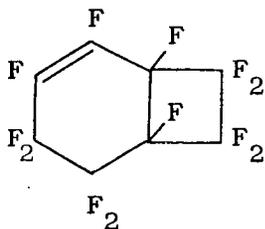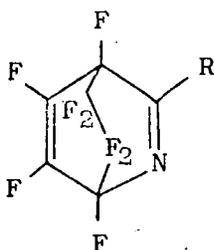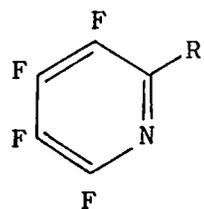
(160)   (161)   (162)

Under forcing conditions ($400^{\circ}C$) perfluorocyclohexa-1,3-diene will react with nitriles, $R-C{\equiv}N$ (Cf. Table 5). The low dienophilic reactivity of the $-C{\equiv}N$ group necessitates the high reaction temperature and limits the synthetic utility to nitriles of high thermal stability. In only two instances ($R = C_6F_5$ and R = Br) were the intermediate adducts (161) isolated, since elimination of tetrafluoro-ethylene generally occurred to give the 2-substituted pyridines (162), which are not readily available by other routes.[152]

TABLE 5

The Diels Alder reactions of perfluorocyclohexa-1,3-diene with nitriles.

Nitriles	Mole Ratio Diene : Nitrile	Reaction Conditions	% Yield	% Yield
CF_3CN	1 : 1	$400°$, 16h	-	40
BrCN	1 : 3	$400°$, 15h	-	40
	2 : 3	$380°$, 12h	9	18
C_6F_5CN	1 : 1	$390°$, 64h	-	4
NC$(CF_2)_3$CN	1 : 2	$350°$, 16h	4	1
	1 : 2	$350°$, 64h	-	10

The Diels Alder reaction of perfluorocyclohexa-1,3-diene with 1H,2H-tetrafluorocyclobutene occurs at $295°C$.[94] A similar reaction with 1H,2H-hexafluorocyclopentene at $326°C$ gave a 70% yield of the assumed endo adduct (163) whilst the reaction of 1H,2H-octafluorocyclohexene at $330°C$ gave a 17% yield of the assumed endo adduct (164).[94] The decreasing reactivity of the dienophile
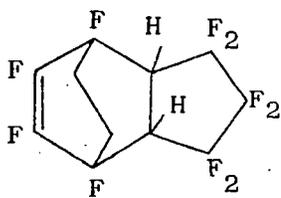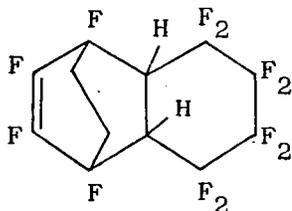
(163)   (164)

[Unmarked bonds to fluorine]

with increasing ring size parallels and possibly arises from the decrease in ring strain in the dienophile. A similar ring size effect is found in the reaction of perfluorocyclohexa-1,3-diene with cyclopentene and cyclohexene, with the latter being the less reactive.[163]

2H,3H-Hexafluorocyclohexa-1,3-diene also undergoes the Diels Alder reaction under similar condition and with the same reagents that undergo successful reaction with the perfluorodiene.   However, the adduct formed with but-2-yne (165) has a reactive -CH=CH- dienophilic bond and this results in further reaction with the diene to give (166).[151]

(165)   (166)
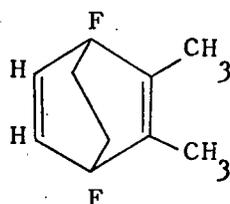
[Unmarked bonds to fluorine]
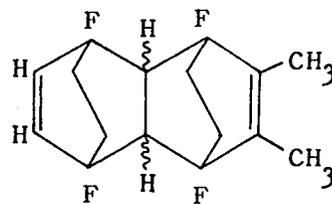
In contrast, 1H,2H-hexafluorocyclohexa-1,3-diene dimerises on standing at room temperature with the -CH=CH- being the dienophilic moiety.[154]

INTRODUCTION - Dehydrofluorination of Fluorinated Cyclic Compounds

3.5 Methods of dehydrofluorination

A heterogeneous reaction between the fluorohydrocarbon and aqueous potassium hydroxide is the most commonly used dehydrofluorination method.   For instance perfluorocyclohexa-1,3- and -1,4-dienes are obtained by refluxing a mixture of 1H,3H-decafluorocyclohexanes and aqueous KOH (50% w/w) for several hours.[155]
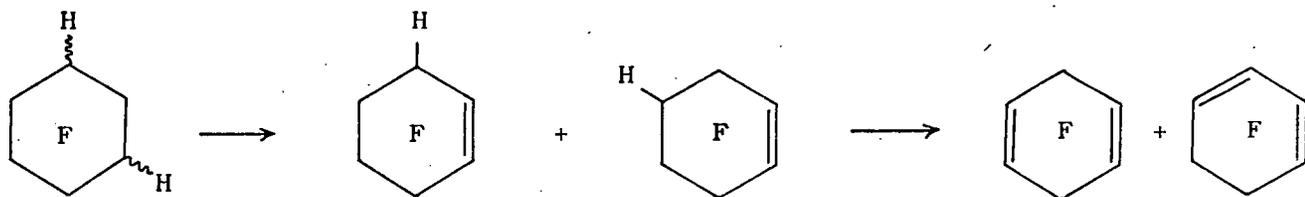
The disadvantage with this method is that prolonged reaction times can result in hydroxide ion attack on the olefins and dienes formed with subsequent decomposition to water soluble compounds.

Octafluorocycloheptatriene was found to be very labile to aqueous alkali

and could not be prepared from (167) or (168) by the above method, though
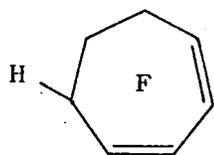
(167)   (168)

dehydrofluorination was achieved by using powdered KOH in benzene.[55]

Short contact times are achieved by passing compounds into and below the

surface of molten potassium hydroxide at $200/260^{\circ}$C. In this manner decomposition

is minimised and a 37% yield of perfluorocyclopentadiene was obtained from 3H-

and 4H-heptafluorocyclopentenes.[147]

Undecafluorocyclohexane, 1H,3H- and 1H,4H-decafluorocyclohexanes and

1H,2H,4H-nonafluorocyclohexanes were dehydrofluorinated using a strongly basic

anionic exchange resin at 60°C.[156] However this method is limited as the resin

denatures above 60°C.

Passing hydro-fluorocarbons over heated sodium fluoride pellets produces

dehydrofluorination products. This technique has been successfully applied to

the preparation of nonafluorocyclohexenes, hepta- and octa-fluorocyclohexadienes[157]

and to conjugated polyfluoroalicyclic compounds with exocyclic methylene groups.[158]

However pyrolysis over NaF can also produce isomerisation of the olefins. 4H-

Heptafluorocyclopentene gave its 1H and 3H isomers when passed over NaF and

no dehydrofluorination product.[147]

3.6 Mechanisms of dehydrofluorination

The dehydrofluorination of polyfluorocyclohexanes has been extensively

studied[159] and the salient features are:

(a) Elimination of the most acidic hydrogen occurs (i.e. the one flanked

     by the most fluorines).

(b) Loss of fluorine is easier from CHF than from CF_2.

(c) A trans-coplanar E2 mechanism is favoured and dehydrofluorination proceeds more readily when the cyclohexane can adopt the conformation in which H and F are trans and diaxial.

(d) Cis eliminations do proceed when the proton is sufficiently acidic and may be faster than possible trans-non coplanar eliminations.[160,161]

(169)
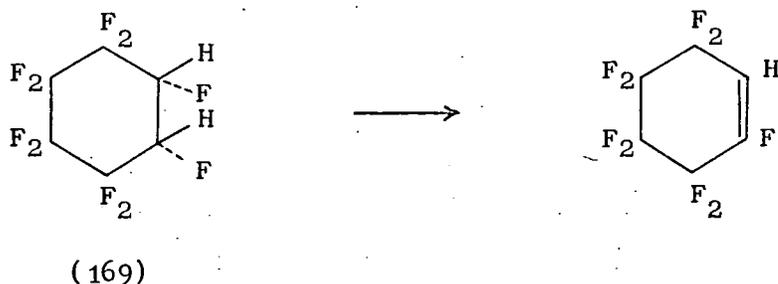
Factors (b) and (c) are dominant in the dehydrofluorination of (169). However the trans isomer (170) cannot react via a trans-coplanar E2 mechanism with loss of fluorine from CHF. Dehydrofluorination of (170) was found to be more difficult than for (169) and proceeded via an E2 process with loss of fluorine from the CF_2 group to give the diene and either by a cis elimination of HF[161] or by an Elcb mechanism which involves a carbanion[162], to give an olefin from which further dehydrofluorination is not possible.

(170)
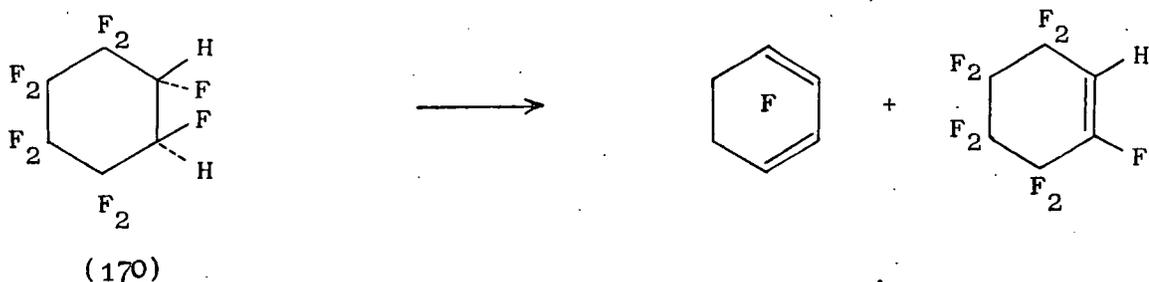
As (170) incorporates deuterium when shaken with KOH and D_2O then the Elcb mechanism seems more likely.[162]

That electronic factors dominate reactivity is confirmed by the fact that (171) is dehydrofluorinated much more readily than (172) to give primarily (173).[42]
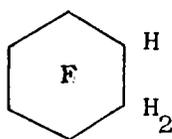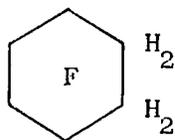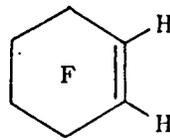
(171)   (172)   (173)

The main factor here appears to be the C-F bond strength with elimination of fluorine occurring preferentially from CHF and this necessitates proton abstraction from the least acidic hydrogen (CH_2).

In the cyclopentane series the electronic factors remain unchanged but the geometry of the ring causes the cis E2 elimination to become coplanar. It is now possible to have a cis E2 coplanar elimination which is only slightly less favourable than trans elimination in the fluorinated cyclopentane ring.[162]
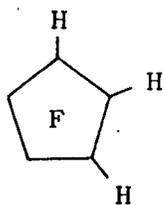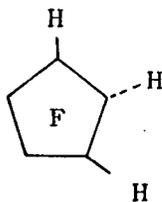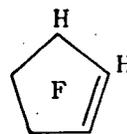
(174)   (175)   (176)

With (174) and (175) the major product obtained on dehydrofluorination is (176) and this arises respectively from a trans- and cis-coplanar mechanism. The cis-coplanar mechanism is slightly less favoured than the trans-elimination. Dehydrofluorination of (174) gave at least 99% of (176) whereas dehydrofluorination of (175) gave 86% of (176) and 9% of the isomer arising from elimination of a CF_2 fluorine.

DISCUSSION

[In this discussion the diagrams have unmarked bonds to fluorine unless otherwise stated].

3.7 The preparation of starting materials

(a) 2H,7H-Hexadecafluorotricyclo[6,2,2,0^{2,7}]dodeca-9-ene (164)

The Diels Alder reaction between perfluorocyclohexa-1,3-diene and 1H,2H-octafluorocyclohexene to give the adduct (164) has been reported previously.[163]

(164)   (158)
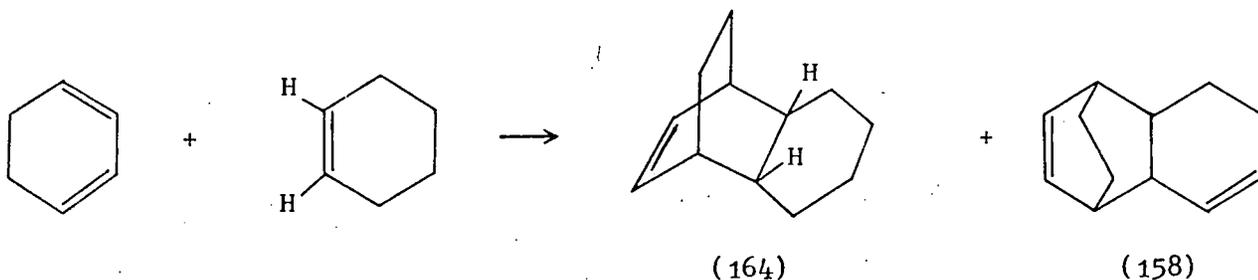
Only one isomer of (164) was obtained and this was assumed to have the _endo_ configuration. Forcing conditions are required to ensure the production of (164) with optimum yields being obtained at temperatures and pressures not too far removed from those at which reactant and products decompose. This is in marked contrast to the dimerisation of 1H,2H-hexafluorocyclohexa-1,3-diene which occurs at room temperature with -CH=CH- being the dienophilic moiety.[154]

(181)
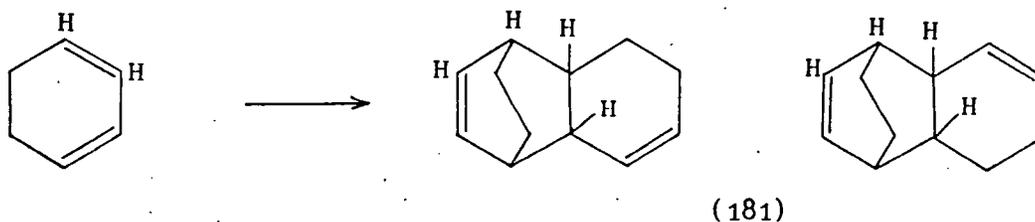
The dimer (181) appeared to be one compound though the structure could be either of the alternatives shown.

The optimum conditions for the production of adduct (164) also produced the perfluorocyclohexa-1,3-diene dimers (158);[93] the respective ratio of (164) : (158) being 3:2 at 345°C. At 335°C this ratio became nearly unity whilst milder conditions gave negligible yields of the adduct (164), (cf. Table 12, Experimental

Section 3.9]. The dimers (158) readily undergo a retro Diels Alder reaction at 345°C to give perfluorocyclohexa-1,3-diene whilst the adduct (164) underwent a rather slow retro Diels Alder reaction. Bearing in mind these results and the experimental data in Table 12, the formation of adduct (164) and dimers (158) is consistent with an equilibrium situation.

The reaction temperature was found to be very critical and a temperature of 355°C, though giving slightly better yields of the adduct (164), produced extensive decomposition and partial isomerisation of the diene. The adduct (164) when heated in a sealed tube at 355°C also underwent some decomposition. Decomposition may have arisen through isomerisation of the 1H,2H-octafluoro-cyclohexane to the 1H,6H-isomer and subsequent dehydrofluorination to 2H-heptafluorocyclohexa-1,3-diene, which is unstable at this temperature.[166] Thus the attempted Diels Alder reaction between perfluorocyclohexa-1,3-diene and 1H,6H-octafluorocyclohexene, under analogous conditions to those employed for the reaction with 1H,2H-octafluorocyclohexene, was unsuccessful and resulted in extensive decomposition.

The synthesis of the adduct (164) was performed in Pyrex Carius tubes and the percentage yield of products at a particular temperature did not vary with increasing amounts of starting material. It is assumed that the critical pressures of the starting materials were exceeded otherwise in the last example quoted in Table 12 (Experimental Section) the calculated pressure would have been about 75 atm. The reaction when performed in a stainless steel autoclave at 335°C gave a very low yield of the adduct (164) with products mainly accruing from defluorination. In contrast the reaction with perfluorocyclohexa-1,3-diene and 1H,2H-hexafluorocyclopentene proceeded readily in a stainless steel autoclave at 335°C to give a 66% yield of the Diels Alder adduct after 27 hours.[163]

The reason why it is so much more difficult to form the Diels Alder adduct of 1H,2H-octafluorocyclohexene with perfluorocyclohexa-1,3-diene than that with

1H,2H-hexafluorocyclopentene probably lies in the conformational requirements

imposed by the cyclohexane ring in the adduct (164). Examination of molecular

models suggests that the normally favoured chair conformation is prohibited.

(b) Methods of dehydrofluorination of 2H,7H-hexadecafluorotricyclo[6,2,2,0^{2,7}]-

dodeca-9-ene (164)

The most successful method of dehydrofluorination, as previously reported,[163]

was achieved with a 60% aqueous KOH solution. The olefin (164; B.Pt. 174°C)

and the aqueous KOH solution were heated to 160°C whereupon a vigorous exothermic

reaction proceeded to give the triene (178; B.Pt. 159°C), which tended to form

droplets on the surface of the reactant mixture. The reaction, as illustrated

by the data in Table 13 (Experimental Section), was a little difficult to control

with the triene (178) being labile to hydroxide ion and degrading to water

soluble compounds. The extent of reaction was gauged from the reflux rate and

at the appropriate time the mixture was rapidly cooled and quenched with dilute

HCl whereupon the fluorocarbon layer separated out. In a typical experiment a

25% yield of the triene (178) was obtained with a 20% loss in weight through

degradation.

  (164)   (179)   (178)
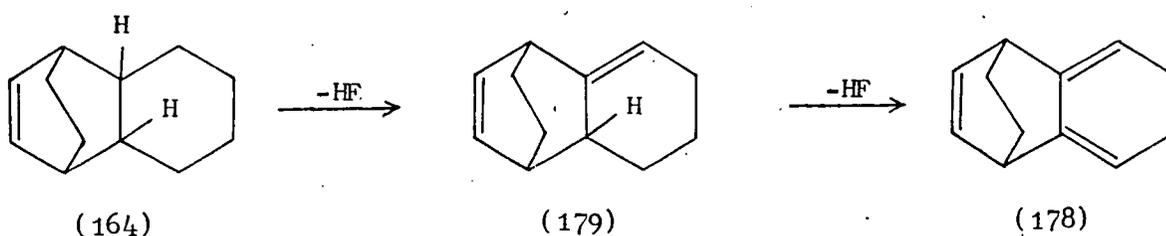
The reaction is extremely sensitive to changes in conditions: either increased

alkali concentration[165] or increased temperature results in greater degradation.

In the olefin (164) the hydrogen atoms and a fluorine of the adjacent CF_2

groups are in a trans coplanar configuration when the cyclohexane moiety is in

what appears (on the basis of Dreiding Molecule models) to be the most likely

boat conformation and this is an ideal situation for the elimination of HF. For

the alternative boat conformation, in which the fluorines at C4 and C5 are only

about 2·0Å from the vinylic fluorines, the CH bond lies in the plane which

bisects the F-C-F angle.   A skew-boat conformation would give one trans

coplanar and one cis HF dispostion.   However, once the diene (179) has been

formed the structure becomes locked in a rigid conformation with a fixed trans

coplanar HF arrangement.   The absence of the diene (179) in the reaction

products may be attributable to the ready loss of HF from this structure.

Dehydrofluorination of (179) proceeded exclusively by the 1,2 rather than the

alternative 1,4 elimination pathway.   The 1,4 elimination pathway is observed

in hydrofluorocyclohexanes;   for example 1H,6H,6H-heptafluorocyclohexene gives

both 1H,2H- and 2H,3H-hexafluorocyclohexa-1,3-dienes on dehydrofluorination.

The 1,2 specificity is also attributable to the favoured conformation for

elimination of HF imposed on (179).

     An attempt to dehydrofluorinate the olefin (164) by passing it in a stream

of dry nitrogen at 200°C into molten KOH at 260°C was unsuccessful and led to

almost complete degradation of the olefin (164) with no triene (178) being

recovered.   An analogous experiment with the olefin (163) gave a 60% yield of

the triene (180).[165]

        (163)   (180)
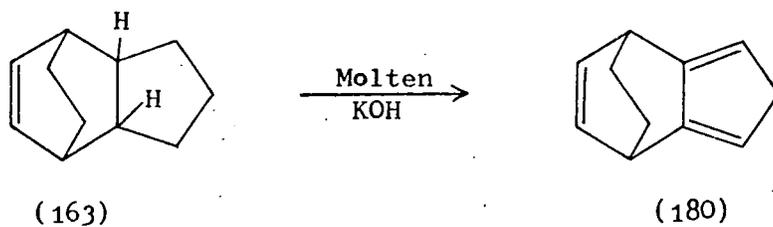
When a mixture of olefin (164), potassium hydroxide and benzene were

refluxed together the potassium hydroxide became black and no fluorocarbon was

recovered.   When used in excess   the olefin (164) was recovered and no

triene was observed.   The attempted dehydrofluorination of the olefin (164), by

utilizing anionic exchange resin, proved unsuccessful.   The low temperature

(60°C), which was necessary to ensure that the resin did not denature, precluded

dehydrofluorination of (164) by this technique.   Dehydrofluorination was readily

achieved with methyl lithium in ether (cf. Chapter 4).   However, methyl

substitution of the conjugated double bond of the triene (178) occurred more readily than dehydrofluorination and consequently this method was impracticable for the production of (178).

Dehydrofluorination of the olefin (164) was also successfully achieved using sodium fluoride. No reaction was observed when the olefin was refluxed over powdered sodium fluoride, although heating the olefin and powdered sodium fluoride in a sealed ampoule at 275°C resulted in degradation of the fluorocarbon. Dehydrofluorination was achieved by passing the olefin in a stream of dry nitrogen over sodium fluoride pellets. In spite of a 20% yield of the triene (178) the total recovery was low presumably because of degradation processes which led rapidly to a carbon covering of the NaF pellets. Hence, the reaction was soon rendered ineffective. No isomerisation of the triene (178) occurred though defluorination to give (VI) occurred quite readily.
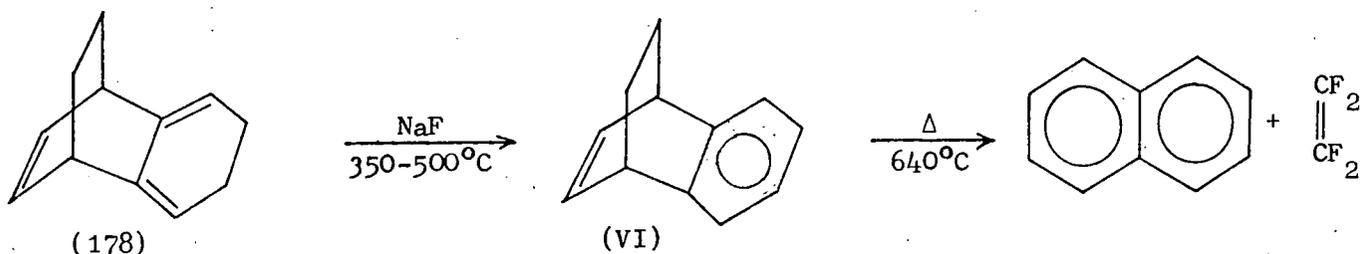
The tetraene (VI), a colourless solid M.Pt. 30/31°C, gave the ^{19}F n.m.r. resonances anticipated for the octafluorobicyclo[2,2,2]oct-2-ene unit with the bridging CF_2 groups giving a 'pseudo AB' coupling constant of 214 Hz. The aromatic fluorines could be assigned by virtue of the large 'through space' coupling between the tertiary fluorines and the respective 'peri' fluorines (at C3 and C6); $J_{F_1F_3} = J_{F_8F_6} = 36$ Hz. An examination of 'Prentice-Hall' molecular models using 'normal' bond lengths and bond angles suggests that the two C-F bonds at C1 and C3 are parallel and that the F internuclear distance is about 2·7Å. The peri-peri F coupling constant in fluorinated naphthalenes is generally about 60/65 Hz[169,170] with the F internuclear distance being 2·5Å. The smaller coupling constant of (VI) is appropriate for the slightly larger internuclear distance and the magnitude of the 'through space' coupling is known to depend

on the separation of the fluorine nuclei.[170]   Confirmation of the structure

assigned to (VI) arises from the i.r. spectrum with -CF=CF- at 1765 cm^{-1} and the

fluorinated benzene ring at 1515 cm^{-1}; from the u.v. with λ_{max} at 267 nm

(ϵ = 800); and from the m.s. where the base peak arises from the loss of tetra-

fluoroethylene.   Finally the structure was confirmed by vacuum pyrolysis at 640°C

whereupon tetrafluoroethylene was produced along with perfluoronaphthalene.

Defluorination of highly fluorinated compounds over NaF has previously been

reported in the literature.[171]   The diene (187) remained largely unchanged on

passage over NaF pellets at 410/530°C though a small amount (ca. 10%) of

isomerisation and defluorination products were obtained.

(187)

Similarly the author has found that perfluoro-1,2-dihydronaphthalene (XXI)

defluorinates over KF at 350°C to give after 40 hours a 26% yield of perfluoro-

naphthalene with only a 13% loss through decomposition; 17% of perfluoro-1,4-

dihydronaphthalene (XIX) was also obtained in this experiment.

(XXI) (3.57g.)   (XIX)

The normal method used for defluorination of perfluorocyclic compounds

involves the use of iron gauze or nickel at high temperatures 400-600°C.[172]   The

metal is regenerated from the metal fluoride by passing hydrogen through the

tube.   However the yields obtained by this method are generally low and a

considerable amount of decomposition occurs.   For instance perfluoromethylcyclo-

hexane (17.6g.) was passed in a stream of dry nitrogen over iron gauze at 500°C to

give (11·6g.) of a liquid mixture that contained (3·0g.) of perfluorotoluene.

The use of smaller amounts of starting material produced a higher percentage of

degradation.   Thus it could possibly be the metal fluoride that is the 'active'

defluorinating agent.   Certainly alkali fluorides (NaF and KF) have been

demonstrated to be 'active' defluorinating agents and in particular only a small

amount of decomposition was observed on defluorination of perfluoro-1,2-

dihydronaphthalene.   However the author has not investigated this proposal.

3.8   The Diels Alder reactions of tetradecafluorotricyclo[6,2,2,0^{2,7}]dodeca-

2,6,9-triene (178)

The conjugated diene system of the triene (178) was expected to undergo the

Diels Alder reaction with electron rich dienophiles.   Two possible isomers were

anticipated as the dienophile may approach the diene system from either the

same or opposite side to the -CF$_2$-CF$_2$- bridge.   Furthermore on vacuum pyrolysis

the Diels Alder adducts of (178) with alkynes should eliminate two moles of

tetrafluoroethylene to give 2,3-disubstituted hexafluoronaphthalenes.

The Diels Alder reactivity of the triene (180) with alkynes had been

reported and the isomers (190) and (191) were obtained.[173]   Pyrolysis of these

Diels Alder adducts resulted in the elimination of difluorocarbene and tetra-

fluoroethylene to give the naphthalenes (192).
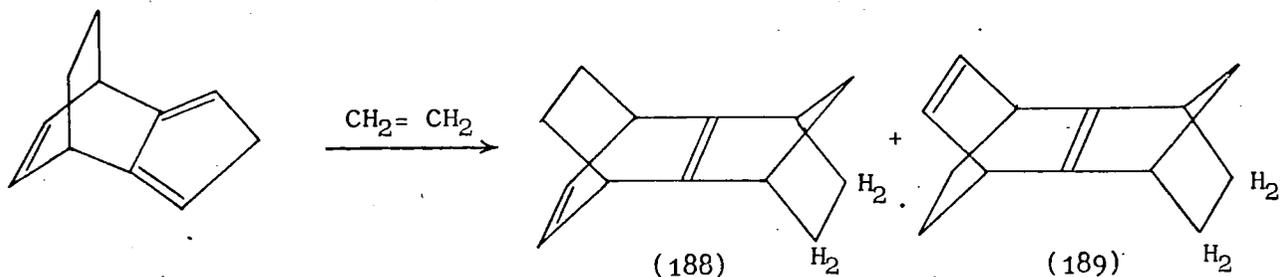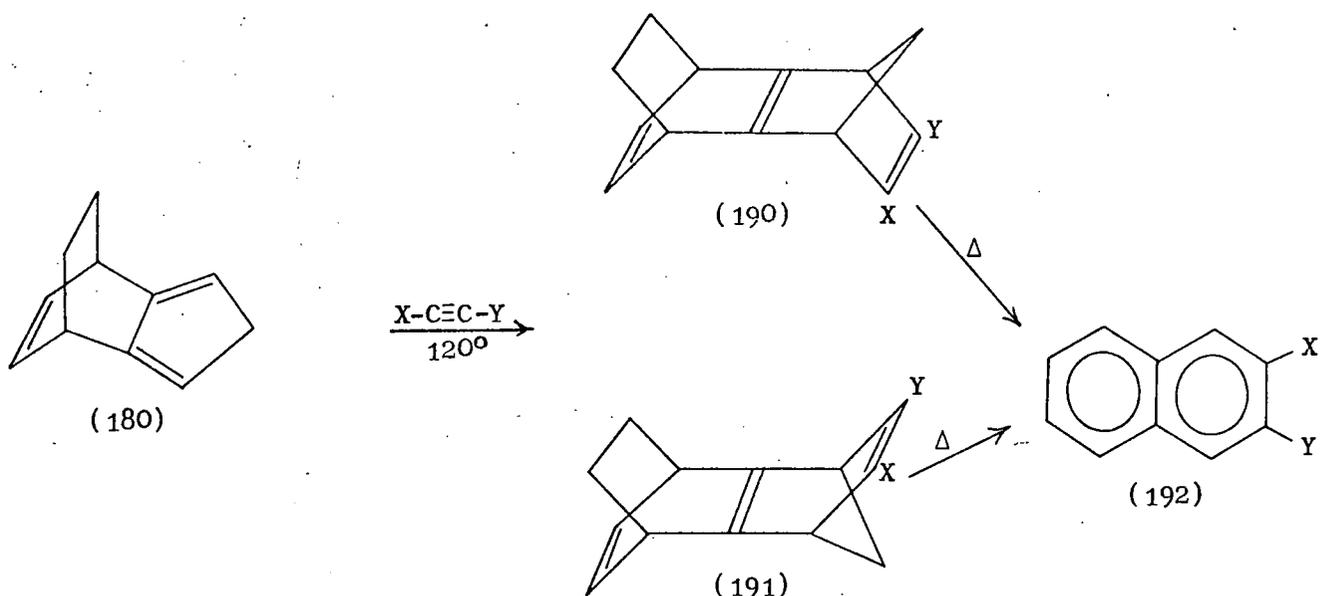
Ratio (190) : (191)

(a) X = H, Y = CH_3 55   45

(b) X = Y = CH_3 77   23

The Diels Alder reaction of the triene (180) with ethylene at $200°C$

produced the two geometrical isomers (188) and (189) in equal amounts. The

stereochemistry of the ethylene and propyne adducts was assigned on the basis

of their ^{19}F n.m.r. spectra.[173] The adducts with the C_2F_4 and CF_2 moieties

on the same side of the molecule [(188) and 190a)] and hence in close proximity

produce a 'through space' spin-spin coupling interaction. This results in

one limb of the $-CF_2-$ 'AB' being split into a 7 line multiplet whilst the

bridging $-CF_2-CF_2-$ resonance signals become broad and asymmetric. In contrast

the adducts with the C_2F_4 and CF_2 moities on opposite sides [(189) and (191a)]

have much sharper resonance signals. However, the ^{19}F n.m.r. spectra of (190b)

and (191b) were too complex for analysis. Instead the assignment of the

stereochemistry was based on the well defined trends in crystallinity and g.l.c.

retention time (Col.A) observed for the previous isomeric pairs. Thus isomers

with the $-CF_2-CF_2-$ and $-CF_2-$ bridges on the same side (190) had the longer g.l.c.

retention times and crystallised as platelets; whereas the isomers (191)

crystallised as needles.

Thus, in view of the previously reported Diels Alder reactivity of the

triene (180), it is not surprising that the triene (178) did indeed undergo

the Diels Alder reaction quite readily with electron rich dienophiles. The

reaction with: (a) ethylene at 200°C gave an 88% yield of (VII) and (VIII),

(b) but-2-yne at 125°C gave a 95% yield of (IX) and (X), and (c) with acetylene

dicarboxylic acid dimethyl ester (200) at 125°C gave a 90% yield of (XI) and

(XII) (cf. Table 9, for the assigned structures). The triene (178) appeared

to be of a similar order of reactivity as the triene (180). The temperatures

required for triene (178) to form adducts with alkynes were much lower than

temperatures reported for the Diels Alder addition of the same alkynes to

perfluorocyclohexa-1,3-diene.[96] Thus the reaction of acetylene dicarboxylic

acid diethyl ester with perfluorocyclohexa-1,3-diene gave a 47% yield of adduct

after 18 hours at 215°C,[96] whilst the reaction with the dimethyl ester gave a

45% yield after 17 hours at 250°C (cf. Chapter 2). Though no direct comparison

was made it would seem likely that the triene (180) is more reactive than

perfluorocyclohexa-1,3-diene in the Diels Alder reaction.

The pairs of isomers were separated and purified by fractional crystallisation,

though the small quantity of (XI) necessitated the use of column chromatography.

All the isomers, (VII) → (XII) showed the characteristic octafluorobicyclo[2,2,2]-

oct-2-ene [19]F n.m.r. resonance signals (cf. Table 9) and confirmed that this

structural unit had remained intact. Furthermore the gross structure was

consistent with the presence of a new $-CF_2-CF_2-$ bridge and two new tertiary

fluorines. The elemental analyses and mass spectra confirmed the formation of

1:1 adducts. The mass spectra all had base peaks corresponding to the loss of

two moles of tetrafluoroethylene. All of the adducts gave a fairly strong i.r.

$-CF=CF-$ absorption between 1755-1770 cm^{-1}. The very weak non-conjugated $\diagup C=C \diagdown$

absorptions occur between 1635-1650 cm^{-1} whilst the conjugated $\diagup C=C \diagdown$ absorption

TABLE 9

N.m.r. spectral parameters for Diels Alder adducts (VII) → (XII)

Compound	$-CF_2-CF_2-$ bridges	$\overset{\backslash}{/}C-F$	$\overset{\backslash}{/}C-F$	Proton
(VII)	$\delta_A = 120 \cdot 7$ (2) $\delta_B = 122 \cdot 8$ (2) $J_{AB} = 225$ Hz $\delta_{A'} = 125 \cdot 3$ (2) $\delta_{B'} = 128 \cdot 3$ (2) $J_{A'B'} = 230$ Hz	$152 \cdot 9$ (2)	$218 \cdot 1$ (2) $197 \cdot 6$ (2) $J_{F_1 F_3} = 32$ Hz	$1 \cdot 4$
(VIII)	$\delta_A = 123 \cdot 4$ (2) $\delta_B = 124 \cdot 8$ (2) $J_{AB} = 215$ Hz $\delta_{A'} = 131 \cdot 6$ (2) $\delta_{B'} = 133 \cdot 5$ (2) $J_{A'B'} = 240$ Hz $J_{F_C F_D} = 37$ Hz	$153 \cdot 1$ (2)	$218 \cdot 3$ (2) $198 \cdot 6$ (2) $J_{F_1 F_3} = 30$ Hz	$1 \cdot 6$
(IX)	$\delta_A = 120 \cdot 9$ (2) $\delta_B = 124 \cdot 2$ (2) $J_{AB} = 225$ Hz $\delta_{A'} = 121 \cdot 7$ (2) $\delta_{B'} = 122 \cdot 9$ (2) $J_{A'B'} = 220$ Hz	$153 \cdot 4$ (2)	$218 \cdot 5$ (2) $208 \cdot 9$ (2) $J_{F_1 F_3} = 28$ Hz	$2 \cdot 0$
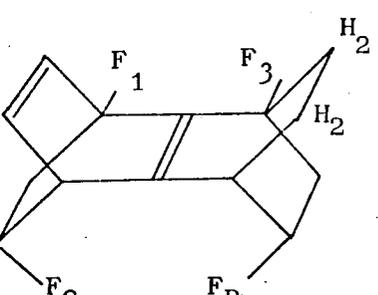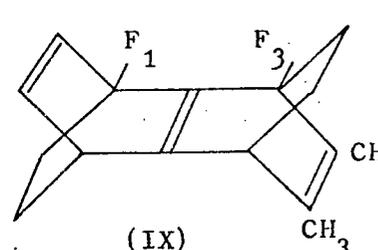
TABLE 9 (continued
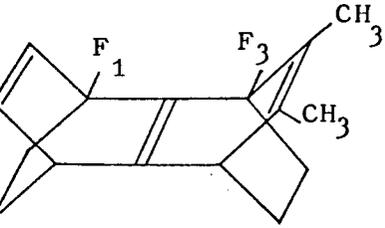
Compound	-CF_2-CF_2- bridges	C-F	$\geq$C-F	Proton
(X)	Complex unresolved multiplet centred at 123·0 (8)	153·5 (2)	218·0 (2) 209·0 (2) $J_{F_1F_3}$ = 28 Hz	2·0
(XI)	δ_A = 122·5 (2) δ_B = 120·9 (2) J_{AB} = 230 Hz 120·7 (4)	152·1 (2)	218·1 (2) 208·2 (2) $J_{F_1F_3}$ = 30 Hz	3·9
(XII)	Complex unresolved multiplet centred at 120·0 (8)	150·2 (2)	218·5 (2) 207·8 (2) $J_{F_1F_3}$ = 30 Hz	3·9
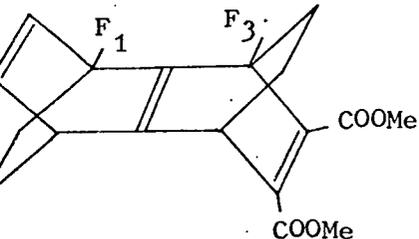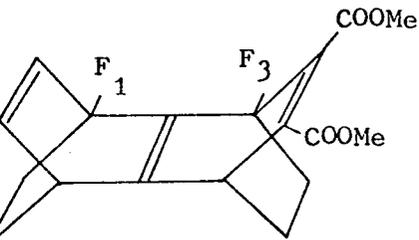
[All spectra were recorded in CD_3COCD_3 solutions]
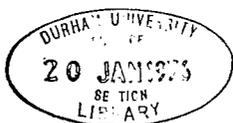
occurs at 1660-1670 cm^{-1} for the ester adducts (XI) and (XII)

The 1:1 nature of the Diels Alder adducts of the alkynes was further confirmed as on pyrolyses at $650°C$ and 10^{-3} mm. they eliminated two moles of tetrafluoroethylene to form the appropriate 2,3-disubstituted hexafluoro-naphthalenes (cf. Chapter 4.4). In contrast the ethylene adducts (VII) and (VIII) only eliminated one mole of tetrafluoroethylene on pyrolysis.

Further analysis of the ^{19}F n.m.r. data for the compounds (VII) → (XII) reveals that the chemical shift position of one set of tertiary fluorines is immutable for all the adducts and occurs at 218 p.p.m. It would seem consistent to assign these tertiary fluorines to the fully fluorinated bicyclo[2,2,2]oct-2-ene unit.[93] This would mean that the remaining set of tertiary fluorines occurred downfield from 218 p.p.m. and this is consistent with previously reported examples.[163] The tertiary fluorines show a large 'through space' coupling of 28-32 Hz. 'Through space' coupling of fluorines has been mentioned in Chapter 3.7(b) and the most generally accepted rationalisation is that it arises through lone pair interactions between fluorines.[170] An examination of molecular models using approximate bond lengths and bond angles suggests that the F-F internuclear distance for (VII) → (XII) is 2·85Å. Thus the decreasing coupling constant with increasing internuclear distance is admirably demonstrated by the series

|←2·5Å→| |←~ 2·7Å→| |←~ 2·85Å→|
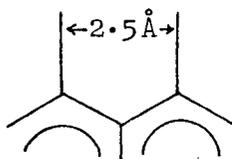
J_{FF} ~ 60/70 Hz   (VI) J_{FF} = 36 Hz   (VII) → (XII)
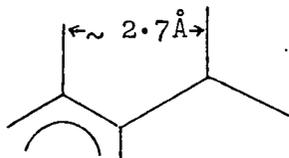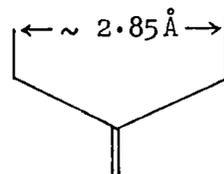
(Ref. 159 and 160)   (cf. Section 3·7(b)) J_{FF} = 28/32 Hz

However only the fluorines in the naphthalene system are rigidly fixed in the same plane and the tertiary fluorines may be eclipsed depending upon the bond angle adopted at the carbon atom bearing the tertiary fluorine. Any eclipsing

of the fluorines may affect the magnitude of the 'through space' coupling.

The stereochemistry of the ethylene adducts (VII) and (VIII) could be unambiguously assigned on the basis of their ^{19}F and ^{1}H n.m.r. spectra. The ^{19}F n.m.r. spectra for the $-CF_2-CF_2-$ bridge regions (120 → 135 p.p.m.) of isomers (VII) and (VIII) are informative. With (VIII) a coupling constant of 37 Hz is observed in one limb of both of the pseudo AB systems. This large coupling is assigned to the 'through space' interaction between adjacent fluorines (cf. Table 9).[174] The construction of an approximated model for the isomer (VIII) suggests that the adjacent fluorines are separated by about 3·1Å. To complement this assignment it is found that the resonance in the ^{1}H spectra of (VIII) is relatively sharp (12·5 Hz) whilst that of (VII) is rather broad (50 Hz).

'Through space' H-F couplings are known, though they are much smaller than F-F coupling constants. The most well documented 'through space' J_{HF} coupling constants occur in compounds of the type shown below where J_{HF} varies from 11·9 → 3·7 Hz with the maximum HF separation being about 1·0Å.[182]
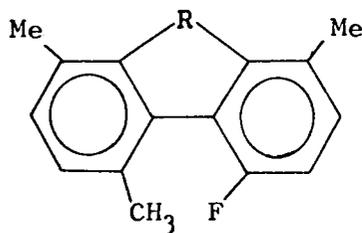
R = (-CH=CH-) J_{HF} = 11·9 Hz

R = (-CO-CO-) J_{HF} = 8·1 Hz

Hence the large 37 Hz coupling constant in (VIII) must arise via a F-F 'through space' interaction and this enables unambiguous structural assignment of the isomers (VII) and (VIII).

The relative g.l.c. retention time (Col.A) of (VII) and (VIII) is 1:4·7. It is informative to compare the Diels Alder ethylene adducts of the triene (178) and the triene (180). The adducts, (VIII) and (188), that have respectively the two $-CF_2-CF_2-$ bridges and the $-CF_2-CF_2-$ and $-CF_2-$ bridges adjacent, have the longer retention times. (VIII) and (188) crystallise as needles whereas the other isomers (VII) and (189) crystallise as platelets.

The stereochemistry of the but-2-yne adducts (IX) and (X) cannot be assigned on the basis of their ^{19}F n.m.r. as most of the $-CF_2-CF_2-$ bridge resonances overlap. However the relative g.l.c. retention time of (IX) to (X) is 1:4·9. Both the isomers appeared to crystallise as needles but a more detailed x-ray analysis revealed that isomer (IX) was a twinned crystal.[175] The structures of isomers (X) and (XII) are at present being investigated by x-ray analysis and it is hoped that information may be forthcoming, though none is available to date. The similarities in g.l.c. retention time (Col.A) for the ethylene and but-2-yne adducts suggest the tenuous stereochemical assignment proposed in Table 9, where (X) is the isomer with the $-CF_2-CF_2-$ bridges adjacent. The ratio of (IX) to (X) formed was 2·8 : 1·0.

A similar situation to that with the but-2-yne adducts is found for the diester adducts (XI) and (XII) with no stereochemical assignment being possible from the ^{19}F n.m.r. Both the diester adducts appeared to crystallise in the same form and the tenuous structural assignment is based upon the relative g.l.c. retention time of (XI):(XII) being 1·0:2·7.

Ethylene does not discriminate on reaction with the diene moiety of (178) between approach from the same and opposite sides of the $-CF_2-CF_2$ bridge with the consequence being that (VII) and (VIII) are formed in equal amounts. With but-2-yne the major isomer (IX) is formed by approach from the same side as the $-CF_2-CF_2-$ bridge whereas with the ester (200) the major isomer (XII) is formed by approach from the opposite side of the bridge. The ratio of (XI) to (XII) formed was 1·0 : 5·3.

$\longleftarrow$ 3·7Å $\longrightarrow$
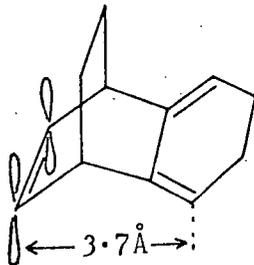
The isomer ratios observed for the Diels Alder reaction of (178) with alkynes precludes steric control via secondary orbital interaction between the alkyne p orbitals not directly involved in bond formation and the olefinic p orbitals at C9-C10. (N.B. diagram above). As the 'thickness' of the π cloud of a typical aromatic molecule is 1·7Å,[183] then the 'bulk' of the π bond above the carbon framework of an olefinic moiety will be about 0·8Å. From a model constructed using 'normal' bond lengths and bond angles the C7/C9 (and C3/C10) distances are about 3·7Å and hence, it is not surprising that no secondary orbital interaction is observed between the alkyne and olefinic C9-C10 bond.

The observations on the stereochemistry of the Diels Alder additions to the triene (178) are in broad agreement with those reported by Jacobson on the Diels Alder addition of olefins to the cis polyhydronaphthalenes (197-199).[184]
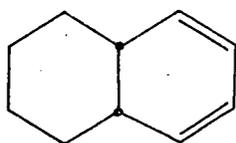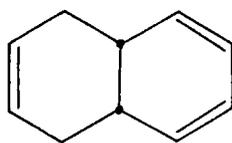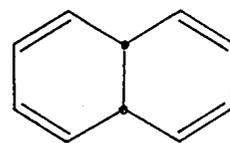
(197)   (193)   (199)

[For (197) → (199) all unmarked bonds are to hydrogen]

Secondary orbital interaction involving the polarizable π bonds not directly involved at the reaction centre was not consistent with the products formed.[184]

Perfluorocyclohexa-1,3-diene undergoes the Diels Alder reaction with a number of nitriles, in spite of the latter being unreactive dienophiles (cf. Section 3.4 (c) and Table 5). For instance the reaction with perfluoroacetonitrile proceeds at 400°C to give an intermediate adduct which loses tetrafluoroethylene in situ and gives a 40% yield of perfluoro-2-methylpyridine.[152] The triene (178) appeared a sufficiently reactive diene to attempt a Diels Alder reaction with perfluoroacetonitrile. The only forseeable problem was that the triene might lose tetrafluoroethylene at 400°C. (Pyrolysis of the triene (178) over NaF at 400°C had given a small percentage of products arising from the elimination of tetrafluoroethylene). However, an excess of perfluoroacetonitrile was used in

an attempt to suppress this reaction by maintaining a high pressure throughout

(ca. 14 atmospheres, providing the critical pressure for perfluoroacetonitrile

had not been exceeded). A 55% yield of products derived from Diels Alder

addition was obtained. In spite of the high pressure the initial adduct (192),

which was not isolated, lost tetrafluoroethylene readily to give (XIV) in 17%

yield. The corresponding isomer to (XIV), (193), which would arise by tetra-

fluoroethylene elimination from the aza-bicyclic[2,2,2] unit was not isolated.

Hence tetrafluoroethylene elimination must occur more readily from the octafluoro-

bicyclo[2,2,2]oct-2-ene unit than from the aza-bicyclo[2,2,2] unit. The major

product perfluoro-3-methylisoquinoline was obtained in 38% yield.
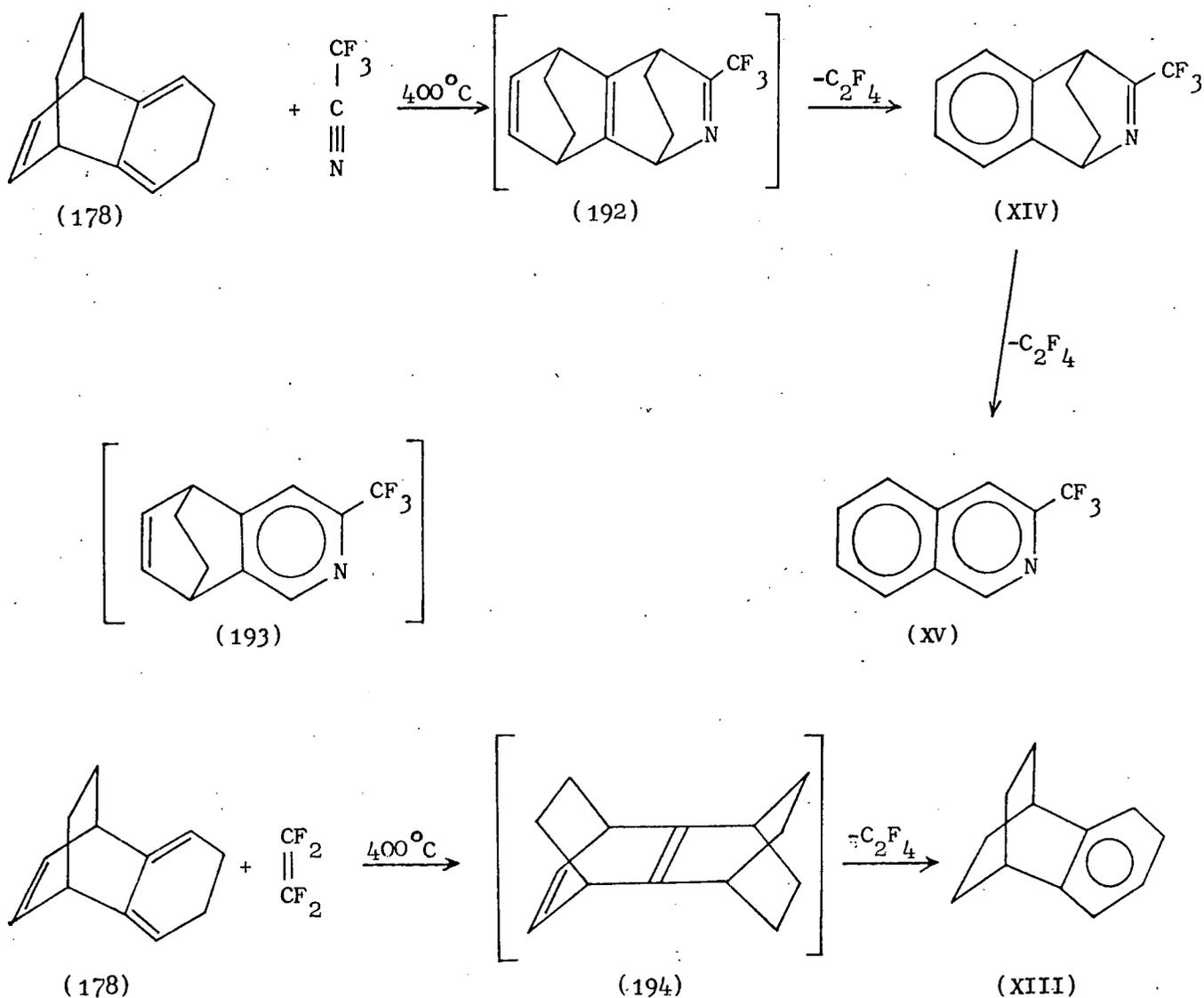
(Compounds in square brackets not isolated).

TABLE 10

N.m.r. spectral parameters for the products from the reaction of CF_3CN with
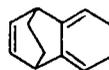
Compound	CF_3 and $-CF_2-CF_2-$ bridge	Aromatic C-F	$\geq$C-F
(XIII)	$\delta_A = 125\cdot3$ (4) $\delta_B = 127\cdot6$ (4) $J_{AB} = 250$ Hz	$145\cdot0$ (2) at C3/C6 $147\cdot9$ (2) at C4/C5	$219\cdot6$ (2) $J_{F_1F_3} \simeq 38$ Hz
(XIV)	$\delta_A = 125\cdot0$ (1) $\delta_B = 129\cdot4$ (1) $J_{AB} = 230$ Hz $\delta_{A'} = 126\cdot2$ (1) $\delta_{B'} = 127\cdot7$ (1) $J_{A'B'} = 235$ Hz CF_3 at $73\cdot9$ (3)	$151\cdot3$ (2) $145\cdot8$ (2)	$173\cdot1$ (1) at C8 $213\cdot2$ (1) at C1
(XV)	CF_3 at $66\cdot3$ (3)	$148\cdot5$ (1) and $145\cdot7$ (1) at C6/C7 $132\cdot6$ (1) at C4 $143\cdot3$ (1) at C5 $J_{F_4F_5} = 60$ Hz $61\cdot2$ (1) at C1 $134\cdot4$ (1) at C8 $J_{F_1F_8} = 66$ Hz	

[(XIII) run in CD_3COCD_3 solution and, (XIV) and (XV) as neat liquids]

The ^{19}F n.m.r. of (XIV) was a little complex to analyse.   The aromatic

fluorine resonances must have been partially superimposed as one resonance

position, which integrated to two fluorines, at 145·8 p.p.m. was over 230 Hz wide.

The tertiary fluorines are broad unresolved multiplets that are probably

extensively coupled to the CF_3 fluorines.   Both tertiary resonances are over

120 Hz in width and broad enough to encompass the envisaged 'through space'

coupling with 'peri' fluorines of the aromatic ring.   The tertiary fluorines can

be assigned, as nitrogen attached to a C-F bond will move the resonance position

downfield.[176]   The mass spectrum of (XIV) has a base peak that corresponds to

the loss of tetrafluoroethylene and the i.r. shows an intense absorption at

1510 cm^{-1} that probably arises from the $>C=N$ and/or fluorinated benzene ring

absorptions.   The u.v. spectrum is consistent with the presence of a benzene

ring, having λ_{max} at 275 nm ($\epsilon \doteqdot 1,400$).   Final confirmation of the structure of

(XIV) was ascertained from pyrolysis at $660°C$ and 10^{-3} mm when (XV) and

tetrafluoroethylene were formed.

The ^{19}F n.m.r. structural assignment of compound (XV) is based upon that

reported for other polyfluoroquinolines and polyfluoroisoquinolines.[177,178]   The

two salient features being that the fluorine aromatic resonance when adjacent to

the ring nitrogen is moved considerably downfield (e.g. the F resonance at C1 in

perfluoroisoquinoline occurs at 61·0 p.p.m.) and the 'peri' fluorines have a

'through space' coupling of 60-65 Hz.   This information enabled the assignment

of the ^{19}F n.m.r. for (XV) apart from the C6 and C7 fluorines.   One aromatic

fluorine resonance was very broad (180 Hz) and unresolved.   This was assigned

to the fluorine at C4 and the breadth must arise from extensive coupling with the

CF_3 fluorines.[179]   The remaining fluorine resonances could be assigned as the

$J_{F_4F_5}$ was 60 Hz and $J_{F_1F_8}$ was 66 Hz.   The C1 fluorine resonance occurred at

61·0 p.p.m. and this is very similar to that reported for other polyfluoroiso-

quinolines.   The fluorine at C1 occurs as a quartet with coupling constants of

66 Hz ($J_{F_1F_8}$) and 30 Hz, the latter of which unfortunately was not resolved in

any other part of the ^{19}F n.m.r. spectrum.   The u.v. spectra of perfluoroiso-
quinoline[180] and perfluoro-3-methylisoquinoline are compatible (cf. Table 10a).

TABLE 10a

	Perfluoroisoquinoline		Perfluoro-3-methylisoquinoline	
λ_{max} (ϵ)	260·0 (sh)	(5660)	260 (sh)	(3600)
	271·5	(6650)	273	(5100)
(sh) = shoulder	282·0 (sh)	(5660)	283	(4600)
			298	(2900)
			311	(5300)
	323·0 (sh)	(5660)	322 (sh)	(6600)
	332·0	(5940)	325	(6900)

Pentafluoropyridine is more reactive towards nucleophilic aromatic
substitution than hexafluorobenzene.   Hence nucleophilic substitution in
perfluoroquinoline and perfluoroisoquinoline occurs preferentially in the activated
nitrogen heterocyclic ring.[181]   The reaction of perfluoroisoquinoline with
nucleophiles produces C1 substitution products.

(a)   X = H

(b)   X = NH$_2$
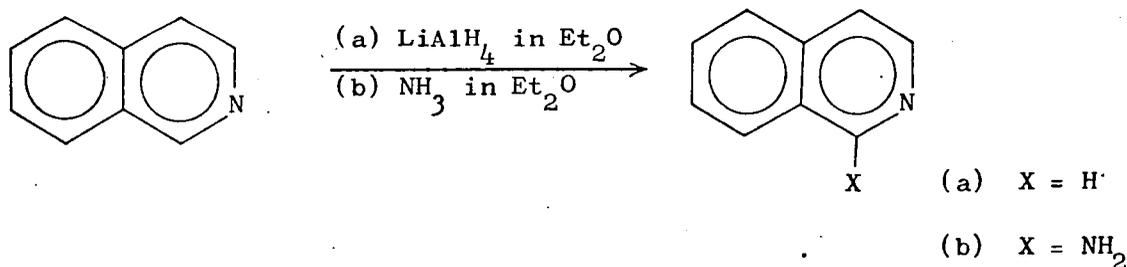
Perfluoroisoquinoline with sodium methoxide in methanol gave initially the C1
substitution product whilst the disubstitution product derived from further
substitution at C6.
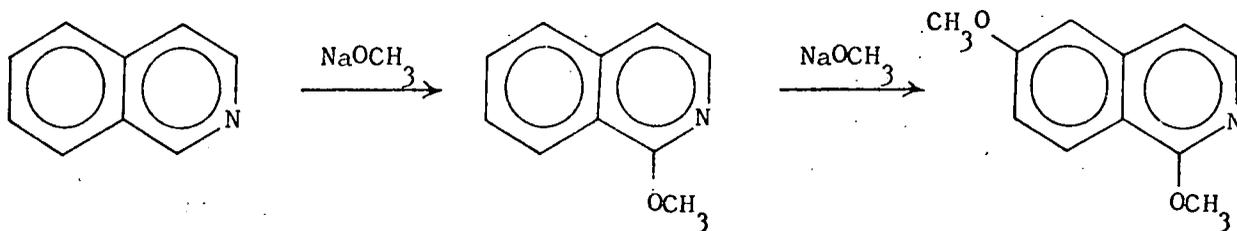
It is probable that the triene (178), like perfluorocyclohexa-1,3-diene, would undergo a Diels Alder reaction with cyanogen bromide at 380/400°C. Loss of tetrafluoroethylene from the adduct (195) on pyrolysis should give the 3-bromohexafluoroisoquinoline (196), from which a number of 3-substituted hexafluoroisoquinolines could be prepared. The triene (178) provides a synthetic route to the hitherto unavailable 3-substituted hexafluoroisoquinolines and is analogous to a synthetic route available for 2-substituted tetrafluoropyridines.[152]
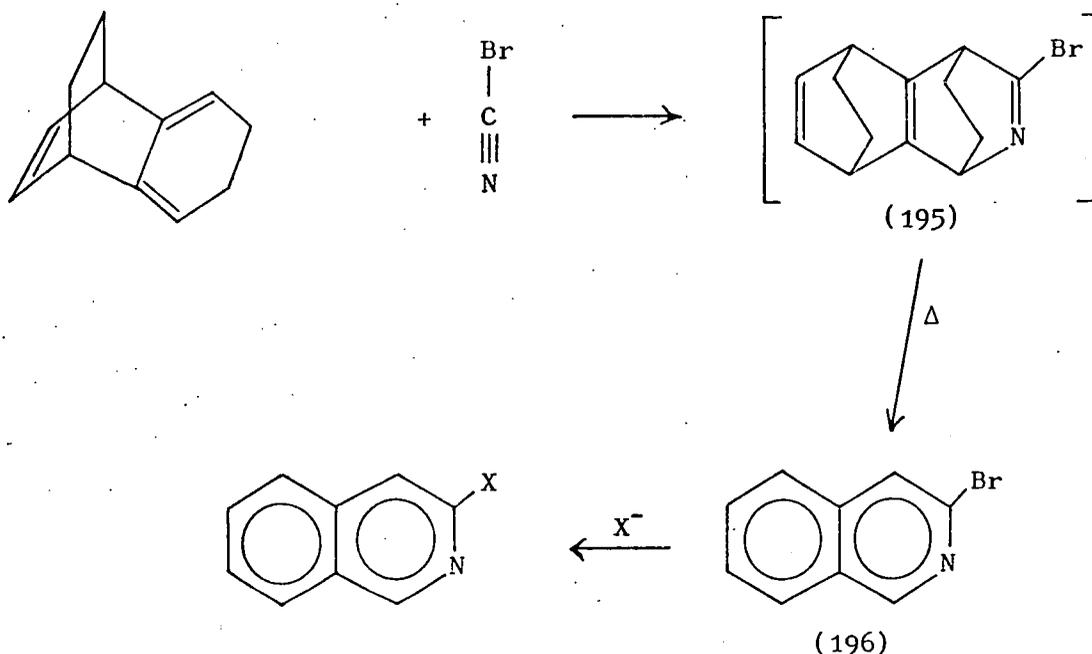
A small amount of (XIII) was also isolated. Tetrafluoroethylene eliminated from the adduct (192) underwent a Diels Alder reaction with the triene (178) to give (194), which subsequently eliminated tetrafluoroethylene by a reverse Diels Alder reaction to give the isolated product (XIII).

The structural assignment of compound (XIII) is primarily based upon the ^{19}F n.m.r. data. The $-CF_2-CF_2-$ bridges are found to be equivalent and they give

a pseudo AB; J_{AB} = 250 Hz. The large 'through space' coupling between the tertiary fluorines and the fluorines in the 'peri' position in the aromatic ring (at C3 and C6) is again found ($J_{F_1 F_3}$ = $J_{F_6 F_8}$ $\simeq$ 38 Hz). The value of this 'through space' coupling constant is similar to that found for the tetraene (VI) which has a similar carbon framework to (XIII). However, this coupling constant can be measured directly only from the aromatic fluorines because the tertiary fluorine couples extensively with the bridge $-CF_2-CF_2-$ fluorines to give a broad unresolved band of 120 Hz width. Obviously the 'through space' coupling enables assignment of the aromatic fluorines. The i.r. spectrum of (XIII) shows an absorption at 1510 cm^{-1} as expected for a fluorinated benzene ring. Again the u.v. spectrum of (XIII) is as anticipated with λ_{max} at 267 nm (ϵ = 1,200); whilst the m.s. indicates a base peak corresponding to the loss of $C_3F_7 \cdot$ from the parent ion.

Tetrafluoroethylene was found to add to the triene (178) even at 335°C. A small amount of (XIII) was obtained via the reaction of 1H,2H-hexafluorocyclopentene with the triene (178) at 335°C as the initial Diels Alder adduct formed between these two reactants [(XXXVII) see Table 11] readily lost tetrafluoroethylene. Support for the presumed mode of formation of (XIII) arises from the fact that heating the triene (178) at 350°C for 30 hours in the presence of a small amount of potassium fluoride gave primarily unchanged triene (178) with none of (XIII) being formed.

This represents one of the few reported Diels Alder additions of tetrafluoroethylene to a perfluorodiene since the normal mode of addition is [2+2]. Thus the reaction of tetrafluoroethylene with perfluorocyclohexa-1,3-diene gave the [2+2] addition product, perfluorobicyclo[4,2,0]oct-2-ene and only in one unreproducible reaction was the [4+2] addition product obtained.[96] This again highlights that the triene (178) tends to be a more reactive diene in the Diels Alder reaction than perfluorocyclohexa-1,3-diene, although a 2+2 addition to the diene moiety of the triene (178) is unfavourable as it would create a rather

strained molecule.

The triene (178) also underwent the Diels Alder reaction with 1H,2H-hexa-
fluorocyclopentene and this firmly substantiates the reactivity of the diene in
the [4+2] addition.   The reaction was performed at 335°C in a Carius tube, and
in order that some of the reactants remained in the same phase it was essential
to use an excess of the olefin and ensure that the reactants occupied half of
the volume of the ampoule.   Under these conditions some decomposition occurred
and the initially formed 1:1 adduct readily lost tetrafluoroethylene to give
(XXXVIII), which was the major product (cf. Table 11 for structures of compounds).
By using an excess of the dienophile 95% of the triene was consumed after 25 hours
at 335°C and an 84% yield of products derived from Diels Alder addition was
obtained.   In contrast the reaction with perfluorocyclohexa-1,3-diene and 1H,2H-
hexafluorocyclopentene gave a 70% conversion to the Diels Alder adduct after 43
hours at 326°C.

In view of the previous results it may have been expected that the Diels
Alder addition of 1H,2H-hexafluorocyclopentene to the triene (178) would have
given two isomeric adducts.   Although only one product was isolated, it is
difficult to ascertain whether both adducts were formed since the major product
(XXXVIII), which comprised 88% of the products, arose from tetrafluoroethylene
elimination from the adduct.   It may well be that tetrafluoroethylene elimination
is slightly more favourable for one of the adducts and hence the isolation of both
adducts may have been precluded.   An examination of molecular models confirms
that endo approach by the cyclopentene moiety is prohibited by the carbocyclic
framework.   Hence, this Diels Alder addition should give the exo product and this
itself is unusual for a highly fluorinated diene.

An analysis of the ^{19}F n.m.r. spectrum of (XXXVII) in the CF_2 region
(117 ⟶ 124 p.p.m.) suggests that only one isomer is present as the resonances
are relatively sharp and coupling constants for the AB systems are measurable.
The ^{19}F n.m.r. spectrum is consistent with the formation of another bicyclo[2,2,2]-

TABLE 11

N.m.r. data for (XXXVII) and (XXXVIII
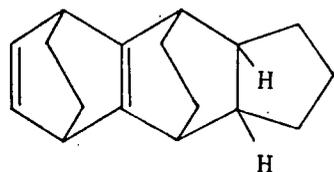
(XXXVII)

Tertiary fluorines

at C1 and C11   216·8 (2)

at C3 and C9   201·4 (2)

Vinylic fluorines   153·0 (2)

CF_2- cyclopentane ring fluorines

at C5 and C7, $\delta_A = 117·0$ (2), $\delta_B = 119·7$ (2)

$J_{AB} = 256$ Hz

at C6, $\delta_{A'} = 132·6$ (1); $\delta_{B'} = 142·7$ (1)

$J_{A'B'} = 254$ Hz

CF_2-CF_2 bridge fluorines

$\delta_{A''} = 121·3$ (2), $\delta_{B''} = 122·3$ (2)

and 124·3 (4) $J_{A''B''} = 218$ Hz

$\geq$CH at 3·8 (ext. T.M.S.)
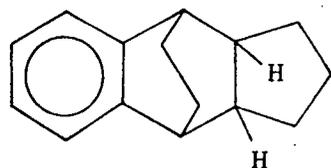
(XXXVIII)

Tertiary fluorines   199·1 (2)

$J_{F_1F_3} = J_{F_6F_8} = 40$ Hz

Aromatic fluorines

at C3 and C6   145·2 (2)

at C4 and C5   150·1 (2)

CF_2- cyclopentane ring fluorines

at C10 and C12, $\delta_A = 116·3$ (2), $\delta_B = 121·4$ (2)

$J_{AB} = 254$ Hz

at C6 $\delta_{A'} = 133·9$ (1), $\delta_{B'} = 142·9$ (1)

$J_{A'B'} = 252$ Hz

CF_2-CF_2 bridge fluorines   126·8 (4)

$\geq$C-H at 3·9 (ext. T.M.S.)

[Spectra recorded in acetone solutions]

oct-2-ene unit. The partial assignment of the resonances is made possible by the occurrance of the characteristic AB coupling constants for the fluorines in the cyclopentane ring. The tertiary fluorines are assigned as previously described and although the characteristic 'through space' coupling constant is not determinable, the tertiary fluorine resonances are broad enough to encompass the anticipated value of about 30 Hz.

The structure of compound (XXXVIII) was primarily interpreted from its ^{19}F n.m.r. spectrum. A 'though space' coupling constant of 40 Hz between the tertiary and 'peri' fluorines enabled assignment of the aromatic fluorines. The presence of a fluorinated benzene ring was confirmed by the i.r. absorption at 1510 cm^{-1} and the u.v. spectra (λ_{max} 265 nm; $\epsilon = 850$).

Hence the triene (178) is rather versatile in the Diels Alder reaction and enables the ready preparation of some hitherto unobtainable compounds. The triene (178) is probably more versatile than the triene (180), in spite of the latter having a diene system in which the π terminii are closer together, since the loss of difluorocarbene from the adducts of the latter can sometimes lead to complicated side products and rearrangements. (For instance the reaction of propyne with the triene (180) at 200°C gave only a 37% yield of products directly attributable to Diels Alder addition[163]). The triene (178) appears to be more reactive in the Diels Alder reaction than perfluorocyclohexa-1,3-diene and this is probably a consequence of the diene moiety being rigidly fixed in a planar cisoid conformation which is a result of the restrictions imposed by the bicyclic unit.

EXPERIMENTAL

3.9 Preparation of starting materials

(a) Diels Alder reaction between perfluorocyclohexa-1,3-diene and 1H,2H-
octafluorocyclohexene

The method used was based on that described previously[163] except that it was
found possible to modify the conditions in order to increase the yield from the
reported 17% to an average of 30%. In a typical experiment perfluorocyclohexa-
1,3-diene (30.0g., 133.9 mmoles) and 1H,2H-octafluorocyclohexene (22.5g., 99.5
mmoles) were dried (P_2O_5), degassed and sealed in vacuo in a 150 ml. Carius tube
which was heated at 345°C for 72 hours. Under these conditions there was some
decomposition and the small quantities of HF and SiF_4 formed were removed by
shaking the product mixture with water. Analysis by g.l.c. (Col.B, 125°C) showed
the presence of unreacted starting materials, perfluorocyclohexa-1,4-diene (ca. 4%),
perfluorocyclohexa-1,3-diene dimers (158) (21.0% yield based on initial amount of
diene) and 2H,7H-hexadecafluorotricyclo[6,2,2,0^{2,7}]dodeca-9-ene (164) (30.2% yield).
After removal of the more volatile components by distillation, (158) and (164) were
separated by fractional distillation under reduced pressure (Concentric tubes
Column, Fischer 'Spaltrohr-system', Buchi Model MMS 200 having 35 theoretical
plates at a throughput of 1 ml/hour). At 10 mm pressure (158) has a B.Pt. of
53°C and (164) a B.Pt. of 58°C.

Table 12 lists some of the experiments performed that led to the
optimization of conditions.

The reaction was also carried out in a stainless steel autoclave at 335°C
for 18 hours but the main products were hexafluoro- and 1,2,3,4-tetrafluorobenzene
arising from defluorination of the starting materials on the metal surface.
The yield of (164) was low (ca. 6%).

TABLE 12
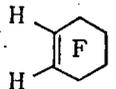
Weight of F (g.)	Weight of H...F (g.)	Size of Carius tube (ml.)	Reaction Time (Hrs.)	Temp. (°C)	% Yield Dimer (158)	% Yield Adduct (164)	Comment
6·1	6·1	100	35	335	14·0	12·5	Full recovery
6·7	5·8	100	59	340	17·5	22·0	Slight decomposition
7·8	6·7	100	80	345	11·5	27·0	Slight decomposition
8·0	6·4	100	112	355	12·0	33·0	Extensive charring and decomposition
18·7	13·1	150	70	345	22·5	30·5	Slight decomposition
30·1	22·5	150	74	345	21·0	30·0	Slight decomposition

(b) Dehydrofluorination of 2H,7H-hexadecafluorotricyclo[6,2,2,0^{2,7}]dodeca-9-ene (164)

(i) With aqueous potassium hydroxide

This was the most successful method for the dehydrofluorination of olefin (164) and corresponds to the method previously reported.[163]   In a typical experiment the olefin (164) (13·5g.), potassium hydroxide (45g.) and water (80g.) were heated at 160°C for 15 mins.   A vigorous reaction occurred and the reaction mixture darkened.   The mixture was heated for about 15 mins. and after rapid cooling and addition of dilute HCl, the fluorocarbon layer (10·8g.) was separated and analysed by g.l.c. (Col.A, 125°C) which indicated that perfluorotricyclo-[6,2,2,0^{2,7}]dodeca-2,6,9-triene (178) (3·1g.) had been formed in 25% yield, leaving (7·7g.) of unreacted (164).   The triene (178), B.Pt. 53°C at 10 mm, was separated from the unreacted (164) by reduced pressure distillation using the concentric tubes apparatus.

Table 13 lists a few of the experiments performed.

TABLE 13

Weight of (164) (g.)	Weight of KOH (g.)	Weight of H_2O (g.)	Time of reflux (mins.)	Weight on recovery (g.)	% Yield (178)	Comment
14·1	48	85	8	12·5	5	Reaction time too short
16·6	60	100	5	0·3	< 2	Violent reaction
13·5	45	80	15	10·8	25	Typical
13·3	55	85	10	10·8	21	Typical
14·5	56	100	20	11·1	48	Exceptional

(ii) <u>With molten potassium hydroxide</u>

The olefin (164) (10·71g.) was injected over a 15 min. period into a heated chamber at 200°C and was swept from there by a stream of dry nitrogen into 300g. of fluid potassium hydroxide at 260°C. Only (0·25g.) of unreacted olefin was collected on passing the nitrogen stream into a flask cooled by liquid air and no triene (178) was observed.

(iii) <u>With powdered potassium hydroxide in benzene</u>

Following the published method,[55] the olefin (164) (0·2g.) was added to benzene (2·1g.) and powdered potassium hydroxide (0·05g.), which became deep brown on standing. The mixture was refluxed whereupon the potassium hydroxide became black and g.l.c. analysis (Col.B, 120°C and Col.A, 120°C) on the benzene solution indicated that the olefin (164) had been consumed with no formation of the triene (178).

A similar experiment with less potassium hydroxide and prolonged refluxing, again resulted in the potassium hydroxide becoming black. No triene (178) was formed though some of the olefin (164) was not degraded.

(iv) With an anionic exchange-resin

This method for dehydrofluorination is based on published data.[156]

Amberlite I.R.A. 400 (OH) was dried by vacuum pumping (10^{-3} mm) at 60°C for 10 hours. (The quaternary ammonium salt based resin denatures at 66°C). (0.40g.) of this resin (60% excess) and olefin (164) (0.10g.) were sealed in vacuo in a 3 ml. Carius tube and heated at 60°C for 4 hours. The olefin (164) (0.10g.) was recovered unchanged.

In another experiment (0.4g.) of resin, olefin (164) (0.1g.) and benzene (1.0g.) were sealed in vacuo in a 3 ml. Carius tube and heated at 60°C for 4 hours. G.l.c. analysis of the benzene solution showed the presence of olefin (164) but no triene (178).

(v) With sodium fluoride pellets

These experiments were performed by injecting the olefin (164), through a serum cap, into a heating chamber at 220°C. A stream of dry nitrogen carried the olefin vapour over sodium fluoride pellets (1g. size) which were packed into a silica tube (55 cms. long and 2.0 cms. internal diameter) that was heated in an electric furnace. The products were collected in receivers cooled by liquid air.

The results shown in Table 13a were obtained with a nitrogen flow-rate of 1 litre/hour and a furnace temperature of 365°C. Analysis by g.l.c. (Col.E, 100°C).

TABLE 13a

Experiment	g./hour	Weight of (164) (g.)	Weight recovered (g.)	% Yield (178)	% Yield (VI)
a	0.7	2.00	0.85	20	15
b	1.2	2.15	1.17	28	18
c	2.0	2.19	1.35	24	12
d	1.5	2.05	1.45	12	4

The combined products from experiments (a) $\longrightarrow$ (d) were fractionally distilled (Concentric tubes column) at 10 mm. to give in order of increasing B.Pt. (178), (164) and perfluorotricyclo[6,2,2,0^{2,7}]tetradeca-2,4,6,9-tetraene (VI) (B.Pt. 63°C/ 10 mm.) containing about 2% of perfluoro-1,2-dihydronaphthalene (XXI) (cf. Chapter 4); the pot residue consisted of (VI) with about 10% of perfluoronaphthalene. The tetraene (VI) was purified by recrystallisation at -20°C from petroleum ether (40/60) to give a colourless solid M.Pt. 30/31°C. $C_{12}F_{12}$, which has a Mol. Wt. of 372 (m.s.), requires: C, 38·7 and F, 61·3%. Found F, 61·1%. (VI) has λ_{max} 267 nm (ϵ = 800); υ_{max} 1765 (-CF=CF-) and 1515 cm^{-1} (aromatic C-F); and ^{19}F n.m.r. resonances from internal CFCl$_3$ at:- δ_A (2) 124·4 and δ_B (2) 125·0 J_{AB} = 215 Hz (CF$_2$-CF$_2$ bridge), 158·0 (2) (vinylic fluorines), 154·8 (2) (aromatic fluorines at C4 and C5), 146·0 (2) (aromatic fluorines at C3 and C6) and 218·2 (2) (tertiary fluorines). $J_{F_1F_3}$ = $J_{F_6F_8}$ = 36 Hz. The ^{19}F n.m.r. spectra were obtained on the neat liquid and integrated intensities are in parentheses.

The low percentage conversion for experiment (d) is attributed to a black deposit on the sodium fluoride pellets primarily arising from fluorocarbon degradation. New pellets were packed in the tube and a series of reactions run at higher temperatures (400 to 500°C) and higher olefin and nitrogen flow rates (up to 8g. and 10 litres/hour, respectively). However analysis of the product mixture became complicated as the triene (178) and (VI) eliminated tetrafluoro-ethylene at these temperatures to form relatively large amounts of (XXI) and perfluoronaphthalene, respectively. Analysis was further complicated as (VI) and (XXI) had the same B.Pts. at 10 mm. and had almost the same g.l.c. retention time on all available columns. The products from a number of experiments run at higher temperatures were distilled at reduced pressure (Concentric tubes column 10 mm) and the volatile products being removed to leave a pot residue consisting of perfluoronaphthalene, which was identified by comparison of its g.l.c. (Col.A, 150°C), i.r., m.s., and n.m.r. with those of an authentic sample.

(vi) With powdered sodium fluoride

Olefin (164) (1·00g.) was heated under reflux (B.Pt. 174°C) with dry sodium fluoride (0·55g.) for one hour. No reaction occurred and the olefin (1·00g.) was recovered by distillation.

The olefin (164) (0·820g.) and dry powdered sodium fluoride (0·40g.) were sealed in vacuo in a Carius tube and heated at 275°C for one hour. Only a trace of (164) (< 0·01g.) was recovered along with a very fine water insoluble powder.

(c) The attempted Diels Alder reaction between perfluorocyclohexa-1,3-diene and 1H,6H-octafluorocyclohexene

Perfluorocyclohexa-1,3-diene (8·35g., 37·3 mmoles) and 1H,6H-octafluorocyclo-hexene (6·37g., 28·1 mmoles) were transferred in vacuo from P_2O_5, sealed in a 100 ml. Carius tube and heated at 335°C for 37 hours to give 11·21g., of a liquid mixture that was shown by g.l.c. analysis to consist of starting materials with a small amount of the perfluorocyclohexa-1,3-diene dimers (158). G.l.c. analysis also confirmed that the considerable decomposition was attributable to the 1H,6H-octafluorocyclohexene.

3.10 The Diels Alder reactions of perfluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (178)

(a) With ethylene

A mixture of the triene (178) (1·52g., 3·71 mmoles) and ethylene (5·88 mmoles) were sealed in vacuo in a 100 ml. Carius tube and heated at 210°C for 34 hours. (The reagents were dried (P_2O_5) and degassed before use). Three fractions were obtained: (i) ethylene (2·34 mmoles); (ii) a colourless liquid (0·08g., 0·19 mmoles), shown by i.r. and g.l.c. to be unreacted (178) and (iii) a white solid (1·42g., 3·26 mmoles, 88% yield) shown by (Col.A, 150°C) analytical g.l.c. to consist of two components in equal proportions. The two components were separated by fractional recrystallisation from petroleum ether (60/80) and shown to be the two isomers of 4H,4H,5H,5H-tetradecafluorotetracyclo[6,2,2,2^{3,6}0^{2,7}]-

tetradeca-2,9-diene.   The isomer (VIII) with the longer g.l.c. retention time

crystallised first as long white needles and (0·35g.) were obtained pure.

$C_{14}F_{14}H_4$, which has a Mol. Wt. of 438 (m.s.), requires: C, 38·4;   F, 60·7 and

H, 0·9%.   Found: C, 38·1;   F, 61·0 and H, 1·0%.   (VIII) has a M.Pt. of 135/

136°C., υ_{max} 2930 (-CH$_2$), 1755 (-CF=CF-) and 1650 cm^{-1} (very weak, >C=C<).   The

isomer with the shorter g.l.c. retention time (VII), which has a Mol. Wt. of 438

(m.s.), crystallised as platelets that had a M.Pt. of 92-93°C.   Found: C, 38·1;

F, 61·0 and H, 0·9%.   (VII) has υ_{max} 2920 (-CH$_2$), 1765 (-CF=CF-) and 1645 cm^{-1}

(very weak >C=C<).

(b)   With but-2-yne

By the same procedure as in (a), the triene (178) (1·82g., 4·54 mmoles) and

but-2-yne (0·326g., 5·53 mmoles) were heated in a Carius tube (100 ml.) at 125°C

for 68 hours to give: (i) unreacted but-2-yne, (ii) a liquid fraction (0·039g.)

shown by i.r. and g.l.c. to be (178) and (iii) a white solid (1·93g., 4·31 mmoles,

95% yield) shown by analytical g.l.c. (Col.A, 150°C) to consist of two components

in the ratio 2·8 : 1·0.   The major component was obtained pure by recrystallisation

from petroleum ether (60/80) whilst fractional recrystallisation from acetone and

petroleum ether gave a pure sample of the minor component.   The components were

shown to be the isomers of 4,5-dimethyltetradecafluorotetracyclo[6,2,2,2^{3,6}0^{2,7}]-

tetradeca-2,4,9-triene.

The isomer (IX), the major component, had the shorter g.l.c. retention time

and crystallised as needles. $C_{16}F_{14}H_6$, which has a Mol.Wt. of 464 (m.s.),

requires: C, 41·4; F, 57·3 and H, 1·3%.   Found: C, 41·1;   H, 1·5 and F, 57·1%.

(IX) has a M.Pt. 127·5°C, υ_{max} 1763 (-CF=CF-) and 1640 cm^{-1} (>C=C<).

The isomer (X) with the longer g.l.c. retention time crystallised as needles,

M.Pt. 118·5°C.   Found: C, 41·1;   F, 57·0 and H, 1·6%.   (X) has a Mol.Wt. of

464 (m.s.), υ_{max} 1760 (-CF=CF-) and 1640 cm^{-1} (>C=C<).

(c)   With acetylene dicarboxylic acid dimethyl ester (200)

By using the same method as in (a), the triene (178) (2·20g., 5·37 mmoles)

and the ester (200) (5·60 mmoles) were heated at 125°C for 72 hours in a 100 ml.

Carius tube to give: (i) unreacted triene (0.20g.) and (ii) a solid (2.65g.),

slight decomposition had occurred. G.l.c. analysis (Col.A, 150°C; Col.B, 250°C;

Col.L, 250°C) of the solid indicated a slight trace of the ester (200) (ca. 5%

by mole ratio) and two components in the ratio of 1.0 : 5.3 with the major

isomer being the longer retained on all columns. The two components were shown

to be the isomers of dimethyl tetradecafluorotetracyclo$[6,2,2,2^{3,6}0^{2,7}]$tetradeca-

2,4,9-triene-4,5-dicarboxylate (ca. 90% yield). The major isomer (XII) was

obtained pure by recrystallisation from chloroform at -20°C. The isomer ratio

had now become 4:1 and final purification involved silica column chromatography

(CHCl$_3$ eluant), which gave in order of emergence from the column: (i) a trace

of ester (200) and other impurities; (ii) (XI) and (iii) (XII). (XI) (0.23g.)

was obtained pure after recrystallisation from 8 ml. of petroleum ether (60/80)

at -20°C.

(XI), the isomer with the shorter g.l.c. retention time has a M.Pt. of 148°C.

$C_{18}F_{14}H_6O_4$, which has a Mol.Wt. of 552 (m.s.), requires: C, 39.1; F, 48.2 and

H, 1.1%. Found C, 39.4; F, 48.6 and H, 0.9%. (XI) has υ_{max} 2970 (-CH$_3$),

1765 (-CF=CF-), 1745 ($>$C=O) 1660 and 1640 cm^{-1} ($>$C=C$<$).

The isomer (XII) has a M.Pt. 185°C and a Mol.Wt. of 552 (m.s.). Found:

C, 38.8; F, 48.4 and H, 0.9%. (XII) has υ_{max} 2975 (-CH$_3$), 1770 (-CF=CF-),

1750 and 1730 ($>$C=O), 1670 and 1635 cm^{-1} ($>$C=C$<$) and the u.v. spectra

(methanol reference) is that anticipated for an extended conjugated system

involving ($>$C=C$<$) with two adjacent carbonyl groups, (ϵ_{254} = 1030).

(d) With perfluoroacetonitrile

Perfluoroacetonitrile was prepared by heating perfluoroacetamide with P$_2$O$_5$,

as in reference 215. The triene (178) (2.20g., 5.37 mmoles) and perfluoro-

acetonitrile (10.92 mmoles) were heated at 400°C for 14 hours in a 35 ml. Carius

tube to give: (i) a gaseous fraction (15.21 mmoles) shown by i.r. and m.s. to

consist of perfluoroacetonitrile and tetrafluoroethylene, and (ii) a liquid

fraction that was separated by preparative g.l.c. (Col.H, 150°C) into (a) a liquid

fraction (iii) and (iv) a solid that was recrystallised from petroleum ether (40/60) at $-20^{\circ}C$ to give white crystals of perfluoro-3-methylisoquinoline (XV) (0.51g., 1.64 mmoles, 38% yield before separation). $C_{10}F_9N$, Mol.Wt. (m.s.) 305, requires F, 56.1%. Found F, 55.9%. (XV) has a M.Pt. of $30^{\circ}C$, λ_{max} 268 nm (shoulder, ϵ = 3600), 273 nm (ϵ = 5100), 283 nm (ϵ = 4600), 311 nm (ϵ = 5300), 322 nm (shoulder ϵ = 6600) and 325 nm (ϵ = 6900); υ_{max} 1658, 1628, 1533, 1490 and 1475 cm^{-1}.

The liquid fraction (iii) was separated by preparative g.l.c. (Col.G, $125^{\circ}C$) to give in order of emergence: (a) unreacted triene (178) (ca. 0.009g.) whose (m.s.) indicated the presence of a compound of Mol.Wt. 505; (b) perfluorotricyclo-$[6,2,2,0^{2,7}]$dodeca-2,4,6-triene (XIII), (0.032g., 0.08 mmoles). $C_{12}F_{14}$ has a Mol.Wt. of 410 (m.s.); (XIII) has a M.Pt. of $59^{\circ}C$; λ_{max} 267 nm (ϵ = 1200) and υ_{max} 1510 cm^{-1}; (c) a colourless liquid, perfluoro-9-aza-10-methyltricyclo-$[6,2,2,0^{2,7}]$dodeca-2,4,6,9-tetraene; (XIV) (0.25g., 0.62 mmoles, 17% yield before separation). $C_{12}F_{13}N$, Mol.Wt. 405 (m.s.), requires: F, 61.0%. Found F, 61.0%. (XIV) has λ_{max} 275 nm (ϵ = 1400) and υ_{max} 1510 cm^{-1} (broad and intense), and (d) perfluoro-1,2-dihydronaphthalene (XXI) (ca. 0.1g.).

(e) With 1H,2H-hexafluorocyclopentene

The triene (178) (0743g., 1.05 mmoles) and 1H,2H-hexafluorocyclopentene (0.40g., 2.21 mmoles) were transferred in vacuo into a small Pyrex Carius tube, (of volume ca. 0.8 ml.), which was heated at $335^{\circ}C$ for 25 hours. The contents of the tube showed signs of decomposition and were therefore shaken with water. The fluorocarbon layer was separated and transferred in vacuo from P_2O_5 to give (0.71g.) of a liquid mixture that was partly separated by transfer under a partial vacuum of 2 cms. Hg into: (i) a volatile fraction (0.18g.) shown by i.r. and g.l.c. to be primarily 1H,2H-hexafluorocyclopentene and (ii) a liquid fraction (0.53g.). The fraction (ii) was shown by g.l.c. (Col.C, $150^{\circ}C$) and g.l.c./m.s. (Col.N, $170^{\circ}C$) to consist of, in order of increasing g.l.c. retention time, (percentage analysis

by weight): (iii) 1H,2H-hexafluorocyclopentene, Mol.Wt. 186, (8%); (iv) triene (178), Mol.Wt. 410, (5%); (v) a compound of Mol.Wt. 410, (XIII) (3%, ca. 3% yield); (vi) perfluoro-1,2-dihydronaphthalene, Mol.Wt. 310, (3%); (vii) a compound of Mol.Wt. 586, (XXXVII), (8% ca. 7% yield); and (viii) a compound of Mol.Wt. 486, (XXXVIII), (70% ca. 74% yield).

The liquid fraction (ii) was separated by preparative g.l.c. (Col.G, $120^{\circ}C$) to give a trace of (XIII) which was identified by its i.r. spectrum, (XXXVII) (ca. 0.010g.) and (XXXVIII) (0.211g., 0.43 mmoles). (XXXVII), 4H,8H-eicosa fluoropentacyclo$[9,2,2,2^{3,9},0^{2,10},0^{4,8}]$heptadeca-2,12-diene, $C_{17}F_{20}H_2$, has a Mol.Wt. of 586 (m.s.), υ_{max} 1768 cm^{-1} (-CF=CF-) and is a white solid with a M.Pt. of $86^{\circ}C$.

(XXXVIII), 9H,13H-hexadecafluorotetracyclo$[6,5,2,0^{2,7},0^{9,13}]$pentadeca-2,4,6-triene, $C_{15}F_{16}H_2$, has a Mol.Wt. of 486 (m.s.) and requires F, 62.5%. Found: F, 62.3%. (XXXVIII) has υ_{max} 1505 cm^{-1} (fluorinated benzene ring), λ_{max} 265 nm (ϵ = 850) and is a white solid with a M.Pt. of $84^{\circ}C$.

CHAPTER 4

Vacuum pyrolyses of the Diels Alder adducts of tetradecafluorotricyclo-[6,2,2,0^{2,7}]dodeca-2,6,9-triene and an investigation into the mechanism of pyrolysis of tetradecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene

INTRODUCTION

### 4.1 The retro Diels Alder Reaction

[For a general review consult Reference 185]

The reversibility of the Diels Alder reaction was noted very soon after its discovery. There is a wide variation in the stabilities of the Diels Alder adducts towards dissociation; adducts of acyclic dienes are more stable than those of cyclic dienes; adducts of alkynes are more stable than those of alkenes and adducts of cyclohexa-1,3-dienes are more stable than those of cyclopentadienes. Thus the adduct of furan and maleic anhydride dissociates at its melting point (125°C), whereas the adduct of furan and diethyl acetylene dicarboxylic ester is much more stable. The adduct of maleic anhydride and cyclopentadiene dissociates at 200°C whereas the corresponding adduct of cyclohexa-1,3-diene does not start to dissociate until 310°C. These results are embodied in the general empirical rule of Schmidt, which states that on olefin pyrolysis the bond β to the double bond cleaves.[186] The C-C bond in the β position appears to be weaker than the normal C-C single bond whereas that in the α position appears to be stronger. The lability of groups attached to allyl systems suggests that this effect is not confined to C-C bonds.

The reverse Diels Alder reaction is often extremely valuable for the synthesis of compounds that cannot be prepared by other routes. The reaction of ammonia on the adduct of maleic anhydride and anthracene produces an adduct that when pyrolysed at 200°C yields maleimide. Benzoquinone and its derivatives cannot be oxidised directly to epoxides with alkaline hydrogen peroxide because

of the sensitivity of the quinone ring to alkaline conditions. However the action of alkaline hydrogen peroxide on the cyclopentadiene adduct of para benzoquinone and subsequent pyrolysis gives the epoxide (198) in high yield.[107]

(198)
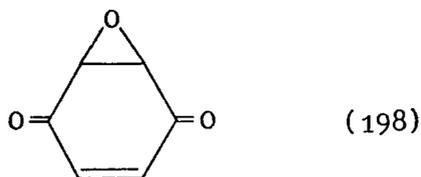
Unstable and interesting compounds are often obtained via a reverse Diels Alder reaction: the pyrolysis of (199) giving isobenzofuran (200) in a quantitative yield.[187]
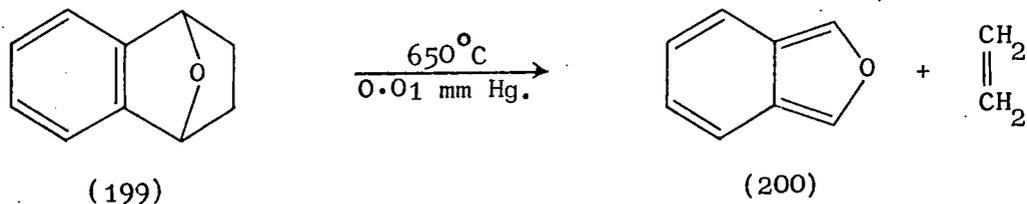

The flash vacuum pyrolysis of (201) gave tetrafluoroisoindole which is surprisingly stable when compared to isoindole.[188]
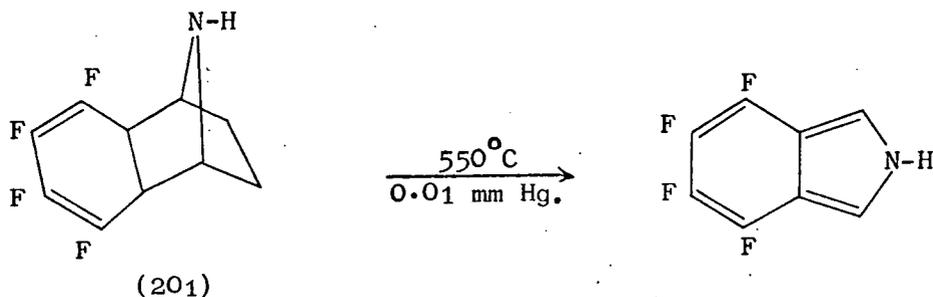

The pyrolysis of bicyclic adducts often occurs to give products other than the original addends with the driving force being the formation of more stable products. Decomposition to aromatic compounds occurring particularly readily. Thus the highly strained adducts of tetracyclones with acetylenes (202) are not normally isolable and lose the stable carbene, CO, very readily to give the aromatic (203). The adducts of tetracyclones with alkenes are more stable and (204) does not start to decompose until 130°C. The greater stability of (204) relative to (202) reflects the fact that 1,3 dienes are less energetically favoured

than aromatics although elimination from (202) is favoured also by the doubly allylic β C-C bond.


(202)　　　　(203)

(204)
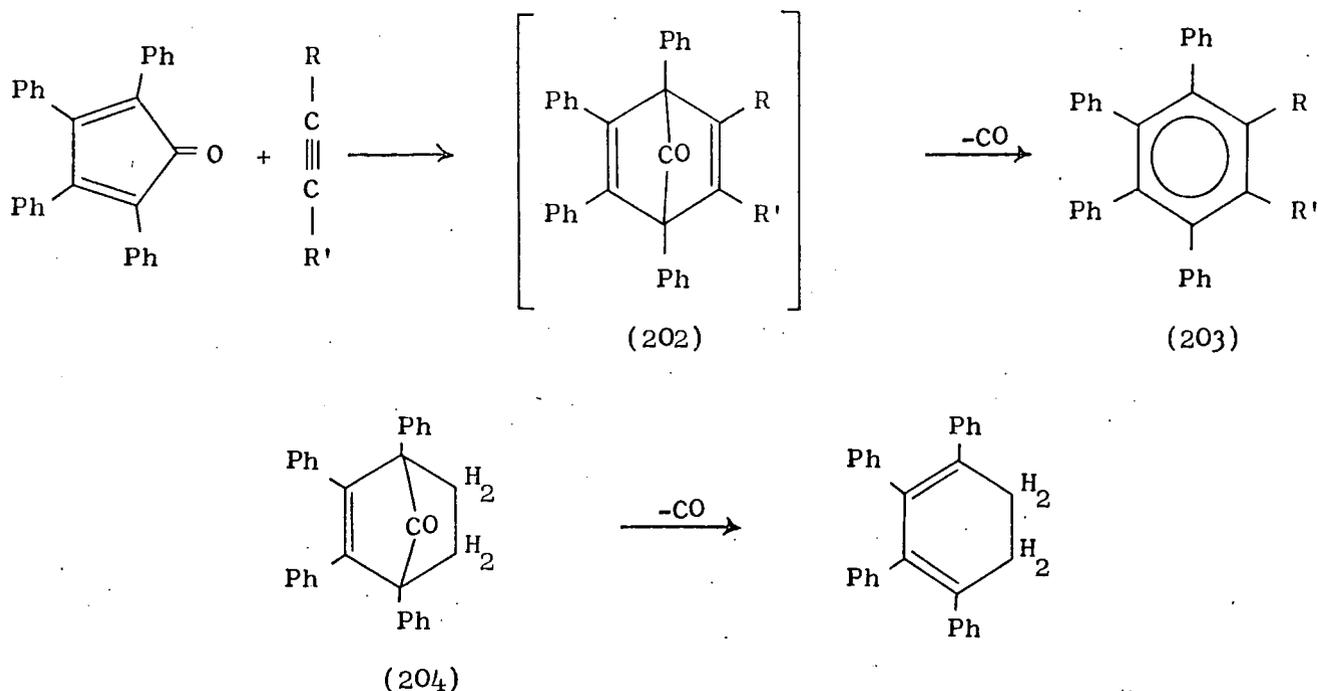
The elimination of methylene from cyclopentadiene adducts does not usually occur, presumably because of the high energy content of the methylene, and the normal mode of decomposition is to the original addends. However (205), which is formed from the Diels Alder addition of tetrafluorobenzyne to cyclopentadiene, does lose methylene on pyrolysis at 280°C to give 1,2,3,4,-tetrafluoronaphthalene in excellent yield.[189]


(205)
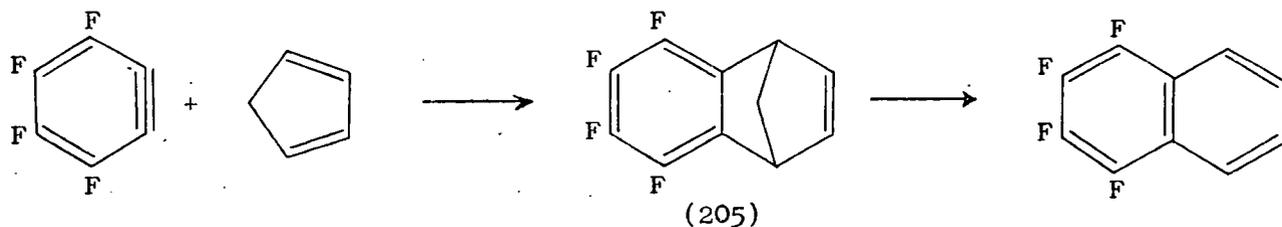
The pyrolysis of the 7,7-dialkoxynorbornadiene (206) at $100-150^{\circ}$C causes the ready elimination of the dialkoxycarbene, which subsequently dimerises, and the formation of (207) by reaction path (a). However a competing pathway (b) produces (208) and (209) by homolytic cleavage of the bridge.[190]

(206) → (a) → (207) + $(MeO)_2C=C(OMe)_2$

(206) → (b) → (208) + (209) + CH_3Cl
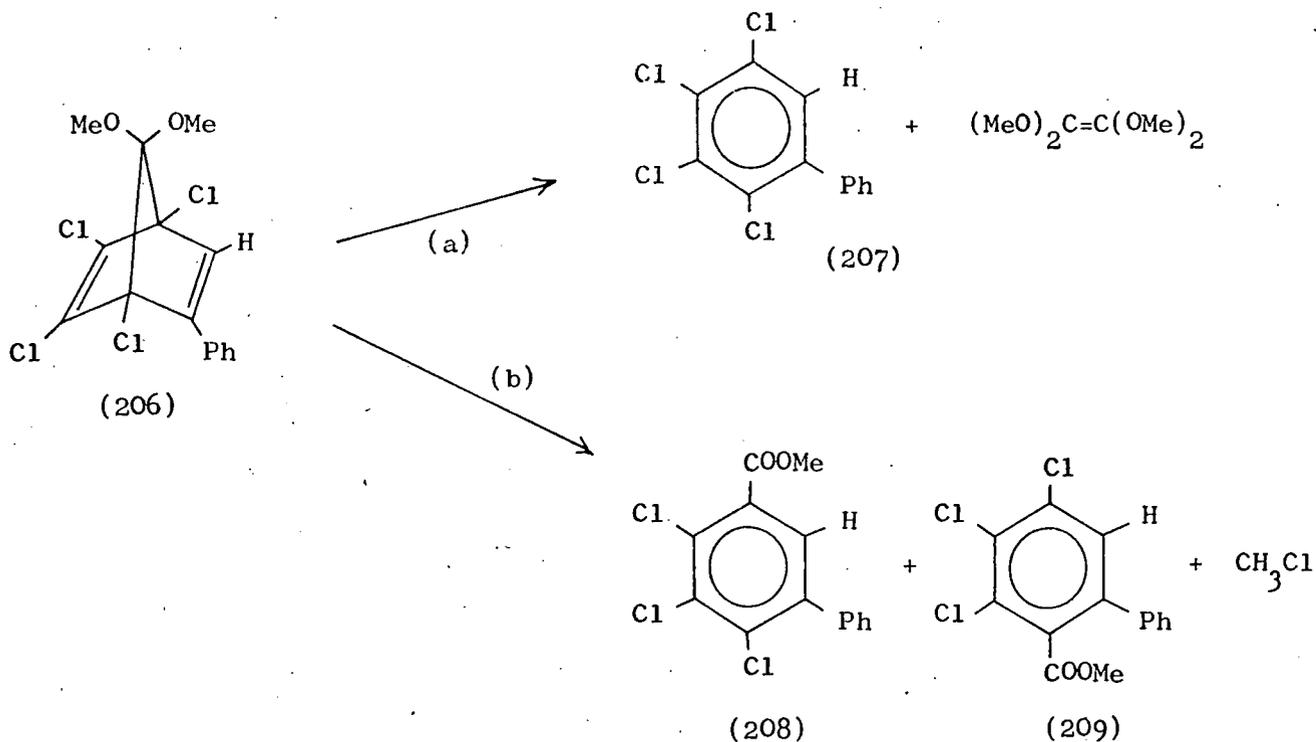
The cycloelimination of a singlet carbene from norbornadiene may proceed in a concerted symmetry allowed manner. However in instances like those with 7,7-dialkoxy- and 7,7-dichloro-norbornadienes the products are perhaps better rationalised by a non concerted process involving cleavage of the bridge.[190]
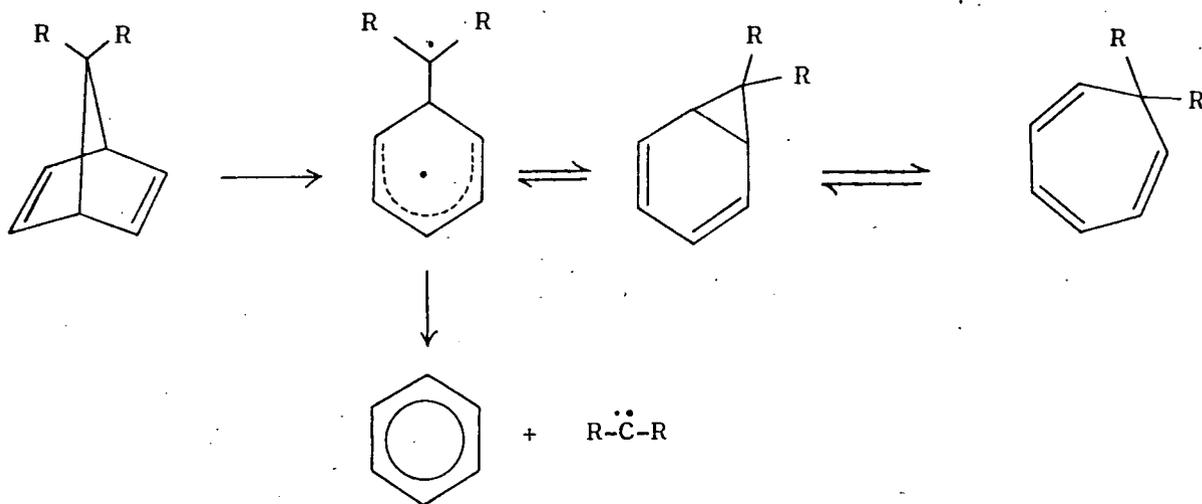

The isomerisation of norbornadiene to cycloheptatriene on heating is thought to occur via the above mechanism.[191,192] The elimination of dichlorocarbene does not occur on pyrolysis of adducts (210) derived from hexachlorocyclopentadiene but rearrangement occurs presumably by the radical pathway.

(210)
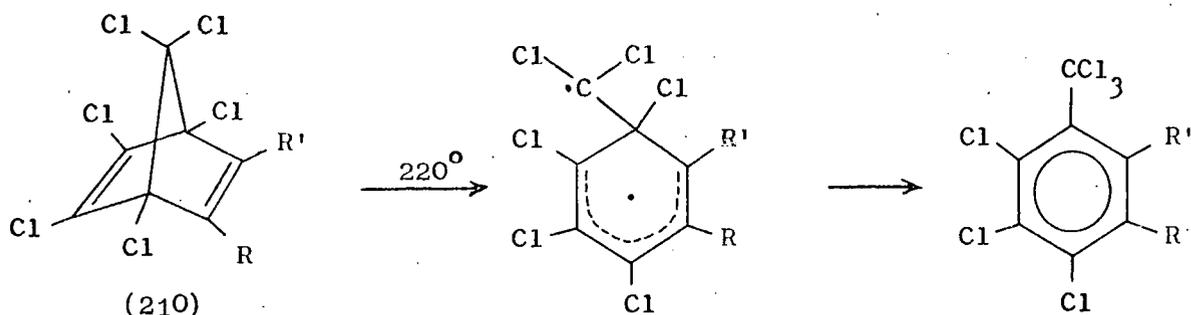
Difluorocarbene is eliminated when adducts (211) are pyrolysed at 480°C to give the corresponding aromatics. In the case of (211b) the intermediacy of difluorocarbene was demonstrated by trapping with cyclohexene to give the 7,7-difluoronorcarane.

(211)

(a) X = Cl (Ref. 135)

(b) X = F (Ref. 127)
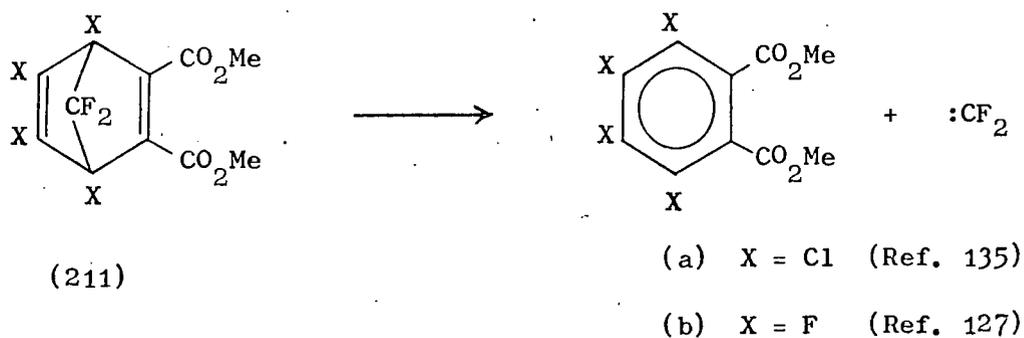
The high thermal stability of the polyhalogenated adducts (211) with respect to dissociation into their respective addends is very remarkable. In particular fluorine substitution greatly increases the stability of the carbocyclic system. Thus perfluorocyclopentadiene dimer (152) in contrast to dicyclopentadiene is exceedingly stable though at 680°C it does eliminate difluorocarbene to give (212) and also form a small amount of monomer.


(152)   (212)
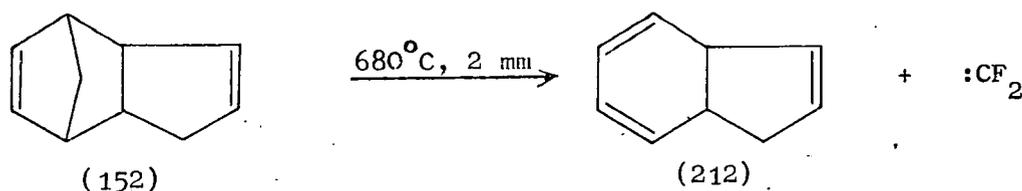
[All unmarked bonds to fluorine]

The elimination of difluorocarbene from (211) probably occurs via a concerted cheletropic reaction since this is a symmetry allowed process in the ground state and the singlet energy of difluorocarbene is about 39 Kcals below

that of the triplet. The elimination of difluorocarbene from (211) contrasts with the reaction of 7,7-dichloronorbornadienes (210) on pyrolysis. Similarities are found in the behaviour of cyclopropanes and norbornadienes on pyrolysis. Highly fluorinated cyclopropanes readily lose difluorocarbene on heating whereas highly chlorinated cyclopropanes readily undergo isomerisation to alkenes either via a radical process or via chlorine migration, (cf. Chapter 1).

The loss of an olefin from the bicyclo[2,2,2]octa-2,5-diene system occurs very readily and the adduct (213) decomposes at 200°C to give dimethyl phthalate (214) and ethylene.[193]

that of the triplet. The elimination of difluorocarbene from (211) contrasts

(213)   (214)
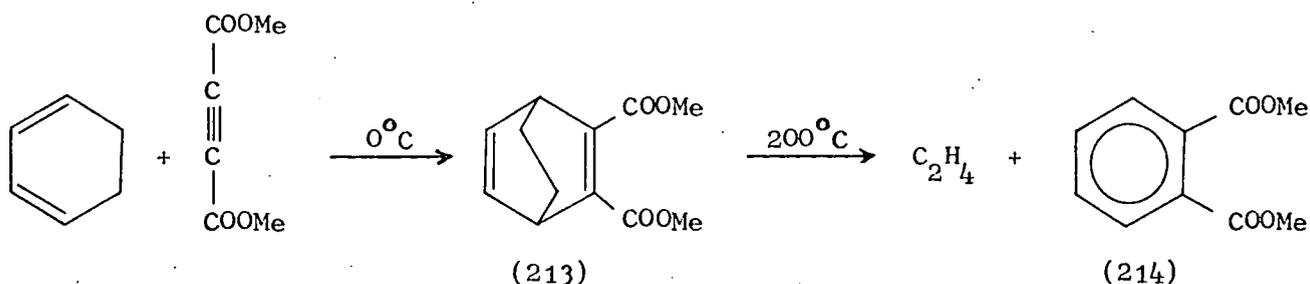
Similarly the 1,4 adducts of benzynes and aromatic compounds can be pyrolysed to eliminate acetylenes and produce the expected naphthalene. The adduct (215) loses acetylene at 300°C.[194]


(215)
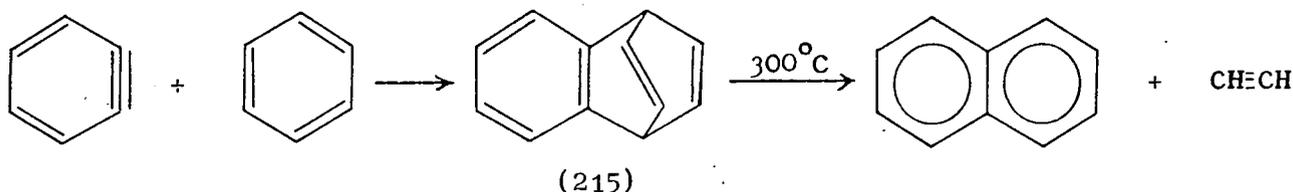
The bicyclo[2,2,2]oct-2-ene system has greater thermal stability than the bicyclo[2,2,2]octa-2,5-diene system as the former generates the energetically less favoured diene. Bicyclo[2,2,2]oct-2-ene decomposes to ethylene and cyclohexa-1,3-diene at 376°C.[195]

The thermal stability of fluorocarbon systems is markedly greater than the corresponding hydrocarbon ones. The adducts of perfluorocyclohexa-1,3-diene with acetylenes are stable up to 250°C at least and pyrolysis of these adducts at 10^{-3} mm

in a vacuum system in the range 500-630°C results in the elimination of

tetrafluoroethylene and the formation of ortho disubstituted tetrafluorobenzenes

in almost quantitative yield.[93]   This constitutes a useful route to ortho

disubstituted tetrafluorobenzenes which were previously prepared only with

difficulty.
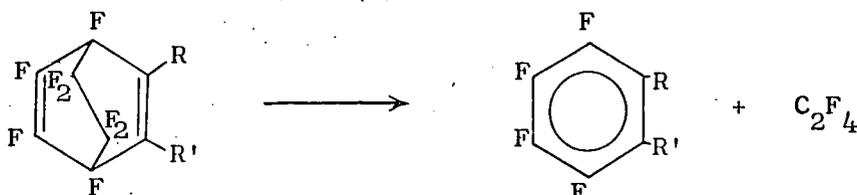
The reaction of perfluorocyclohexa-1,3-diene with nitriles has previously

been mentioned (cf. Section 3.3(c)) and loss of tetrafluoroethylene occurs

readily in situ to give the 2-substituted pyridines (162).
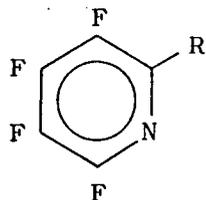
(a)   X = Y = CH$_3$

(b)   X = H. Y = CH$_3$

(162)   (216)
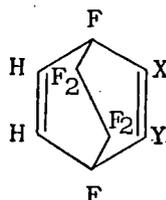
Vacuum pyrolysis of the adducts (216) at 600°C also results in the expulsion

of tetrafluoroethylene.[151]   By analogy with the hydrocarbon systems it is found

that the fluorinated bicyclo[2,2,2]oct-2-ene derivatives break down on pyrolysis

at higher temperatures (ca. 700°C) than bicyclo[2,2,2]octa-2,5-diene derivatives.

For instance, adducts (217) and (218) decompose at 700°C by the elimination of

ethylene only.[95]

(217)

(218)   (218a)   (218b)
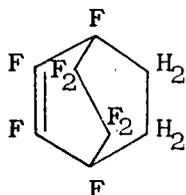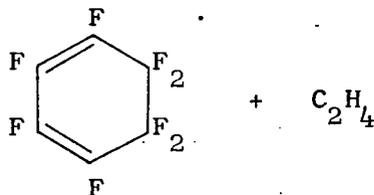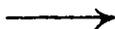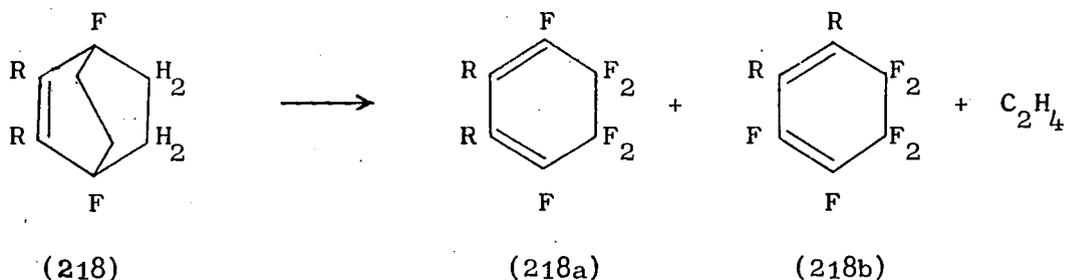
(a) R = CH$_3$

[All unmarked bonds to fluorine]

(b) R = H

The initially formed 2,3-disubstituted dienes (218a) undergo thermal

rearrangement to their 1,2-disubstituted dienes (218b) under these reaction

conditions.   This isomerisation superficially represents a 1,5-fluorine migration.

4.2 The reaction of cyclic fluoro-olefins with nucleophiles

In acyclic systems nucleophilic attack usually occurs at the terminal

difluoromethylene such that the reactivity in the series is: $CF_2=CF_2$ <

$CF_2=CF \cdot CF_3$ < $CF_2=C \cdot (CF_3)_2$.[196,197] The order in this series reflecting the

ability of CF_3 to stabilise the carbanion formed on nucleophilic attack.   The

reaction of hexafluoropropene with methanolic potassium hydroxide gave primarily

the addition product (219).

$$CF_2=CF-CF_3 \xrightarrow[60°C]{CH_3OH/KOH} CH_3OCF_2 \cdot CHF \cdot CF_3 + CH_3OCF=CF \cdot CF_3$$

(219) (83%)
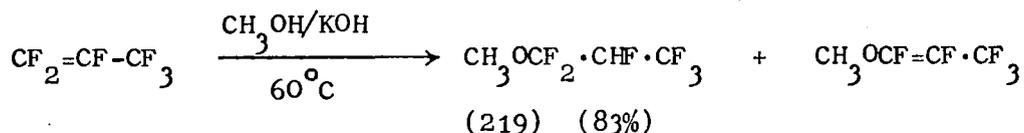
In general the reactions of acyclic olefin with alcohols in the presence of base

give mainly addition products though the amount of unsaturated product depends

upon the nature of the substituents and reaction conditions.

In contrast the reaction of cyclic olefins with methanolic potassium

hydroxide produces products by the displacement of fluoride ion.   The reaction of

perfluorocyclohexene gave (221) and (222) in the ratio of 1:3;   presumably via

the common carbanionic intermediate (220).[198]

(221)

(220)

(222)

(a) = 'inwards' elimination of F⁻

(b) = 'outwards' elimination of .F⁻
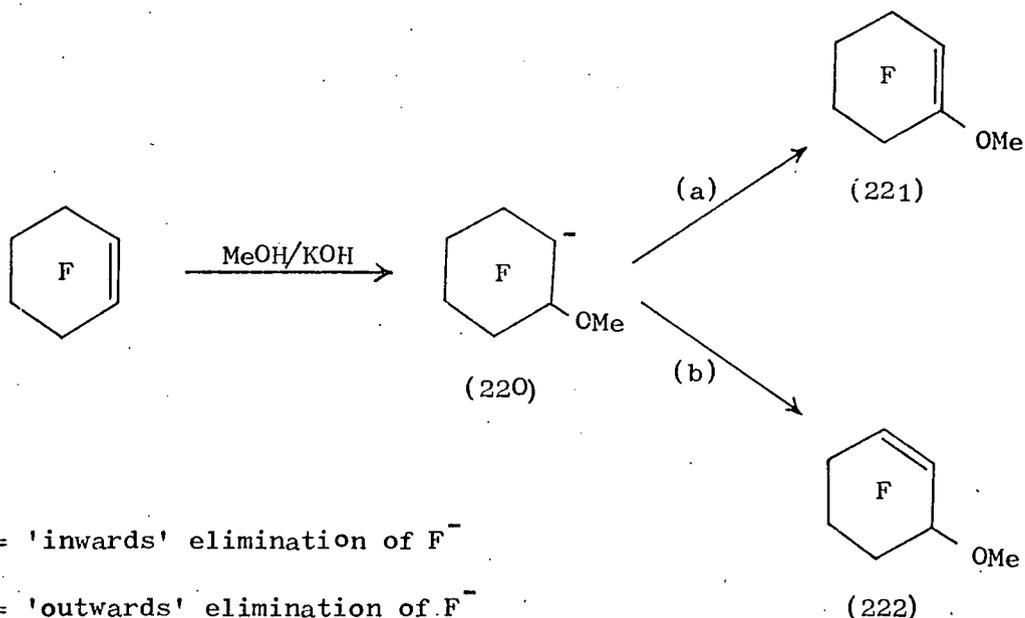
The reactions of cyclic fluoro-olefins with methyl lithium and lithium

aluminium hydride give products primarily derived from the inwards elimination of

fluoride. The reaction of perfluorocyclohexene with methyl lithium in ether

gave primarily the 1-methyl- and 1,2-dimethyl-cyclohexenes, (223) and (224).[199]

However a small amount of 3-methyleneoctafluorocyclohexene (225) was also formed

either by 1,4-dehydrofluorination of (223) with methyl lithium or by 1,2-

dehydrofluorination of (226). However no evidence for (226) was found.

(223)   (224)   (225)   (226)
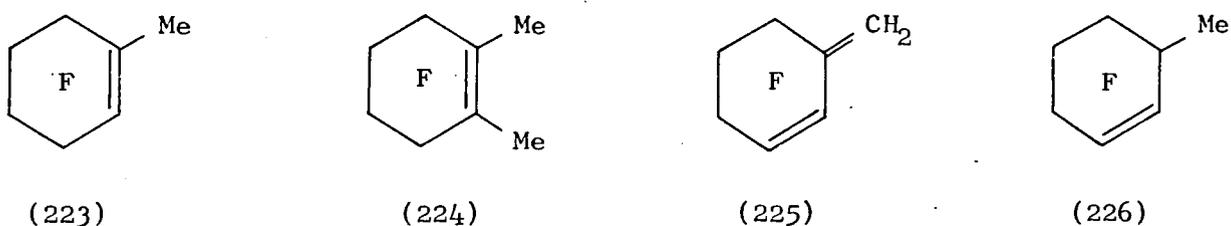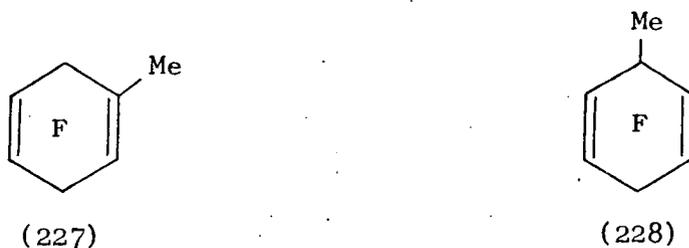
Only in one instance has unambiguous direct allylic substitution of fluorine

been observed.[171] The reaction of perfluorocyclohexa-1,4-diene with methyl

lithium produced the anticipated 1-methyl-heptafluorocyclohexa-1,4-diene (227)

and 3-methyl-heptafluorocyclohexa-1,4-diene (228) in the ratio of 38:1 respectively.

(227)   (228)

This allylic replacement is explained by the abnormally high reactivity of the fluorine atoms in the CF_2 group of perfluorocyclohexa-1,4-diene. With the weaker nucleophilic reagent methanolic potassium hydroxide no allylic substitution occurred.

With an equimolar quantity of methyl lithium in ether, substitution in perfluorocyclohexa-1,3-diene occurs predominantly in the 2-position giving the products (229), (230), (231) and (232) in the ratio of 90 : 3 : 2 : 1.[171]

(229)   (230)   (231)   (232)
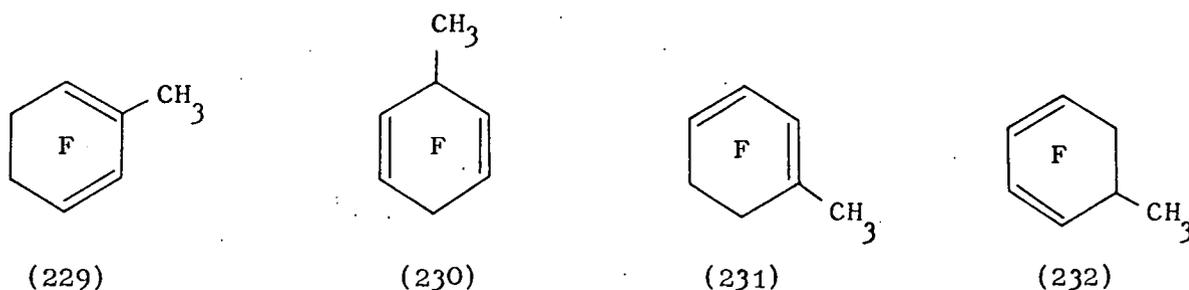
All the products can be explained by an addition-elimination mechanism. Likewise with methanolic potassium hydroxide the 2-methoxy-heptafluorocyclohexa-1,3-diene is the major product.

The reactions of cyclic fluoro-olefins with lithium aluminium hydride resemble those with methyl lithium.[197] Fluorine atoms on saturated, non allylic carbon are in general inert to attack but fluorine atoms attached to unsaturated carbon are readily replaced by an addition-elimination process with H^- acting as the effective nucleophile.

The reaction of perfluorocyclopentene with $LiAlH_4$ gave a complex mixture of polysubstituted fluoro-olefins that were initially derived from 1H- and 3H-heptafluorocyclopentene.[159] The further reduction of 1H- and 1-chlorocyclopentene produced compounds derived from exclusive attack at the olefin C2 position and it would appear, that provided the inductive effects of the groups in positions allylic to the double bond are similar the reduction of unsymmetrical polyhalo-olefins proceeds through the most stable carbanion. The ability of substituents to stabilize the negative charge on the carbanion being Cl > H > F.[159]

4.3 1,3-Alkyl migrations

The [1,3] sigmatropic process (233) → (234) can be considered as a [σ2+π2] reaction.

(233)   (234)
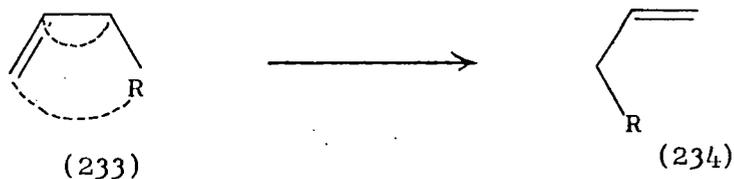
The concerted symmetry allowed process must therefore be [σ2s+π2a] or [σ2a+π2s] in the ground state.[71]

[σ2s+π2a]

Suprafacial [1,3] shift with inversion at R,

[σ2a+π2s]

Suprafacial [1,3]shift with inversion at R

[σ2s+π2a]

Antarafacial with retention at R
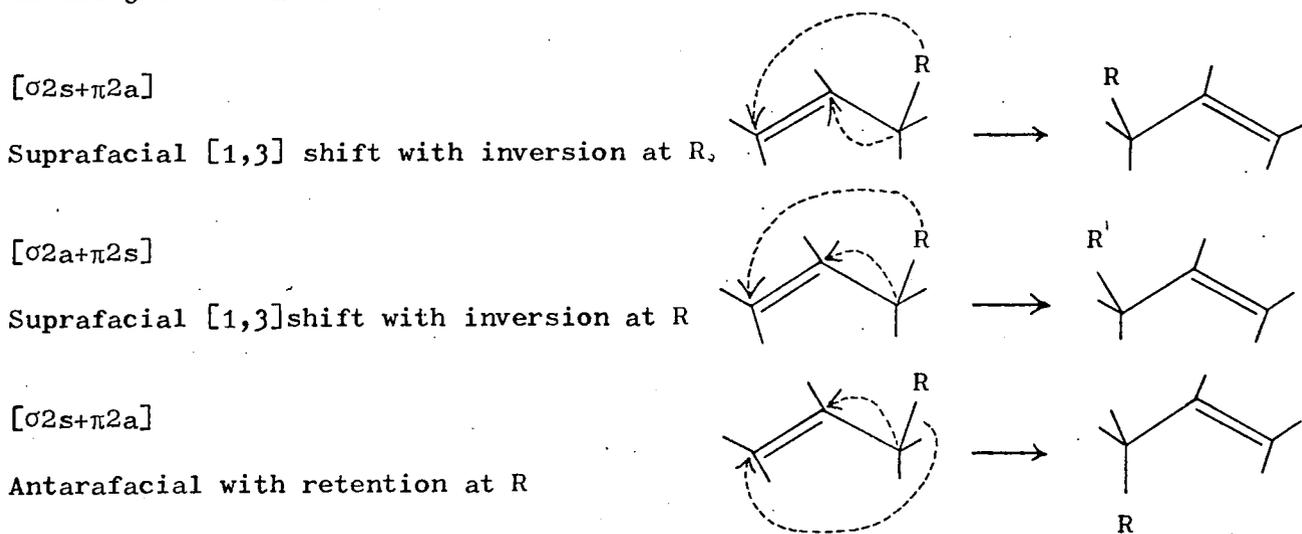
Obviously the suprafacial processes will be indistinguishable as they relate to the same physical process.

The conversion of the bicyclo[3,2,0]heptane (235) to the norbornadiene (236) is a suprafacial [1,3] shift with inversion at the migrating centre (*).[200]

(235)

(237)

(236)

(238)

(a) R_1=H, R_2=Me

(b) R_2=H, R_1=Me
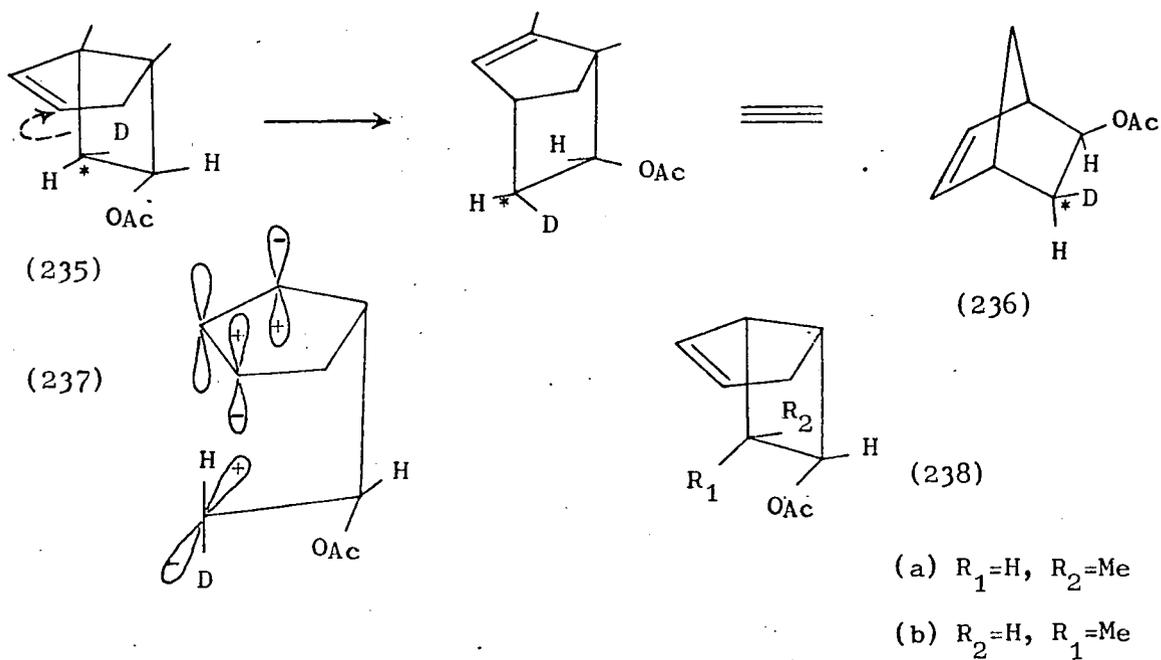
At the half-migrated stage (237) the hydrogen atom on the migrating carbon is in a plane perpendicular to the allyl plane. If the H atom on the migrating carbon of (235) replaced by CH_3 (238b) then this CH_3 group will be pointing inwards towards the ring and unfavourable steric interaction arises. Hence (238b) migrates by a diradical mechanism. In contrast (238a) where the D atom on the migrating carbon of (235) is replaced by CH_3 then unfavourable steric interaction will not arise in the transition state and it is found that (238a) migrates in a concerted manner.[201]

(239)   (240)

(a) R = H;   (b) R = Me

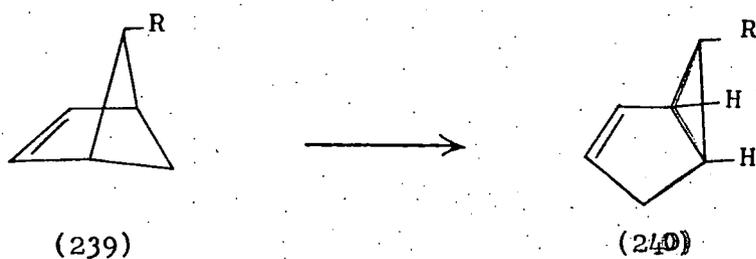Bicyclo[2,1,1]hexene (239a) rearranges at 150-200°C to give bicyclo[3,1,0]-hexene (240a).[202] The concerted suprafacial [1,3] alkyl migration was confirmed with the isomerisation of syn- and anti-5-methylbicyclo[2,1,1]hexene.[203] The anti isomer (239b) rearranged with complete inversion of configuration at C5 to give (240b).[203]

Thermal isomerisation of the propane (241) gives the products (242) and (243), both of which arise from the allowed suprafacial 1,3 alkyl migration with inversion at the migrating centre.[71]

(241)   (242)   (243)
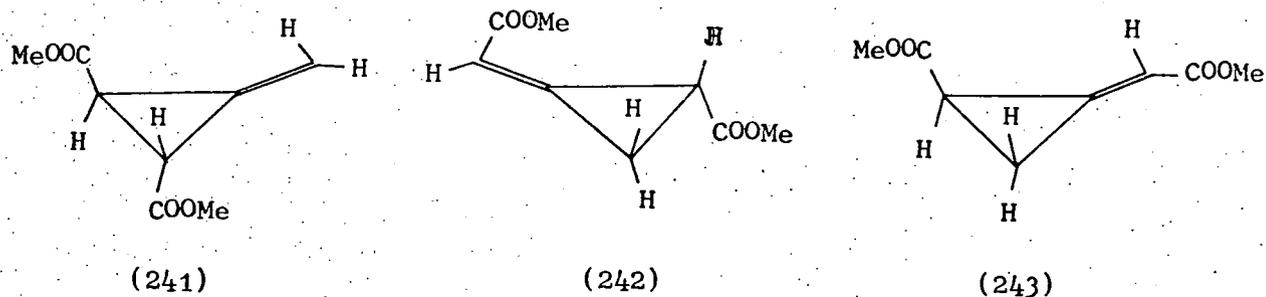
The activation energy for the two vinylcyclopropane $\longrightarrow$ cyclopentene rearrangements (244) $\longrightarrow$ (245) and (245) $\longrightarrow$ (246) is about 50 Kcals/mole.[204]

(244)   (245)   (246)
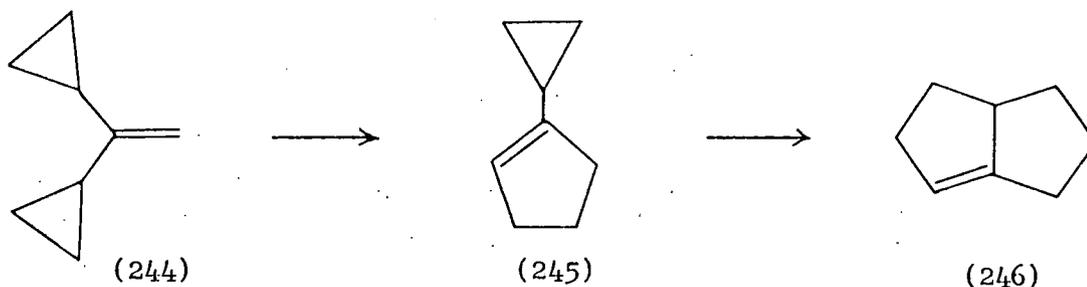
Both of these isomerisations are symmetry allowed [1,3] alkyl shifts. However it must be remembered that the bond breaking process in cyclopropane requires an activation energy of 63 Kcals/mole[205] whilst allylic stabilization of radicals has been estimated at about 13 Kcals/mole,[206] thus in certain instances the energy difference between the allowed concerted process and the diradical mechanism may be so small that the stereochemical integrity implicit in the symmetry controlled process is not maintained.

(247)   (248)   (249)
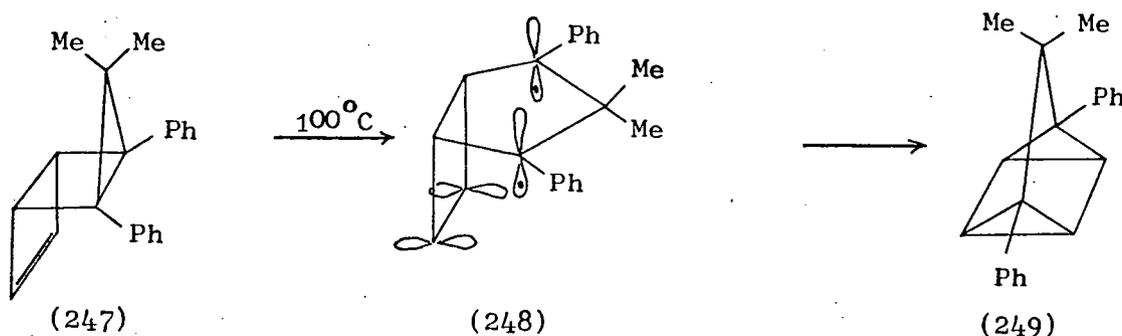
The quantitative conversion of (247) to (249) is formally a [σ2s+π2s] cycloaddition but this is orbital symmetry forbidden in the ground state and the reaction is thought to proceed through (248) which is a 1,3 diradical formed on homolytic rupture of the cyclopropane C2-C4 bond.

The photochemical [1,3] alkyl shift is suprafacially allowed with retention of configuration at the migrating centre. Many examples are known particularly where a ring system is involved (eg. (250) $\longrightarrow$ (251)).[208]

(250)   (251)

(Ref. 66)
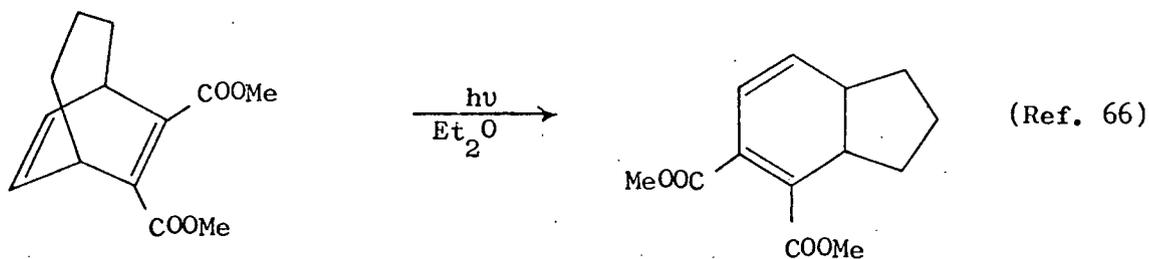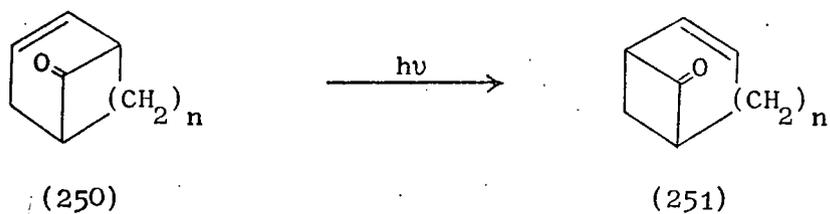
The unsensitized photochemical isomerization of (252) to (253) has recently

been reported and this presumably arises via a [1,3] alkyl shift.[209]

(252)   (253)
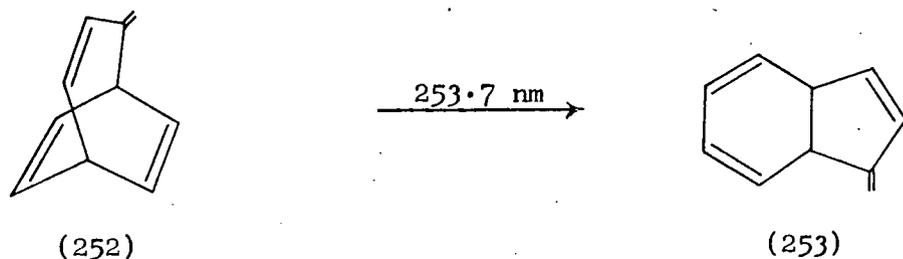
[1,5] Sigmatropic alkyl migration should proceed thermally with retention

of configuration at the migrating centre.[71]   Berson and Wilcott[210] have observed

the thermal isomerisation at $300^{\circ}C$ of 1,5-dideuterio-3,7,7-trimethyltropilidene

(254).   The initial process is thought to involve a cycloheptatriene-norcaradiene

equilibrium which is an established process.[211]   Subsequently [1,5] alkyl shifts

and rearrangement of the norcardienes rationalises the formation of the cyclo-

heptatrienes (255) and (256).   All the cycloheptatrienes were interconvertible on

thermolysis.

(254)   (255)   (256)

1,5   1,5
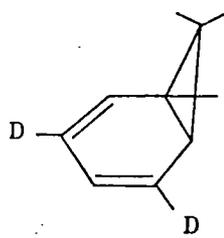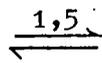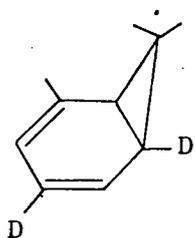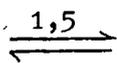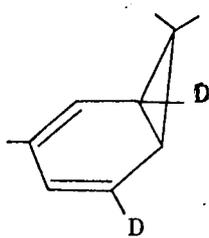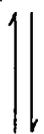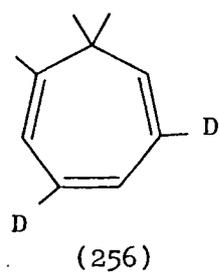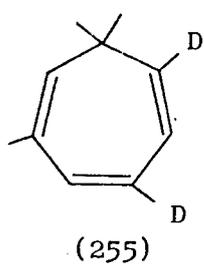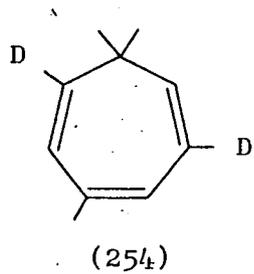
DISCUSSION

The greater part of this chapter is concerned with the pyrolysis and mechanism of pyrolysis of the triene (178).   This necessitated the preparation of methyl substituted trienes which were obtained by the reaction of lithium methyl on the triene (178).   The Diels Alder adducts of the triene (178) which were reported in Chapter 3 were also pyrolysed.   [In the discussion diagrams have unmarked bonds to fluorine unless otherwise stated].

4.4 Vacuum pyrolyses of the Diels Alder adducts of tetradecafluorotricyclo-
$[6,2,2,0^{2,7}]$dodeca-2,6,9-triene (178)

A synthesis of 2,3-disubstituted hexafluoronaphthalenes

The elimination of tetrafluoroethylene from the but-2-yne adducts (IX) and (X) and from the diester adduct (XII) occurred readily on pyrolysis at 660°C and 10^{-3} mm to give the expected 2,3-disubstituted hexafluoronaphthalenes.   The conditions employed were similar to those required for tetrafluoroethylene elimination from the alkyne adducts of perfluorocyclohexa-1,3-diene[93] and from the alkyne adducts of dodecafluorotricyclo$[5,2,2,0^{2,6}]$undeca-2,5,8-triene (180).[173] The latter pyrolyses also generate 2,3-disubstituted hexafluoronaphthalenes[173] and in particular 2,3-dimethylhexafluoronaphthalene was prepared by this route, (cf. Discussion, Chapter 3.8).

The pyrolysis of the diester (XII) gave dimethyl hexafluoronaphthalene-2,3-dicarboxylate (XVII) which had the anticipated mass spectrum and correct elemental analysis.   The ^{19}F n.m.r. spectrum of (XVII) is shown in Table 14. The resonances can be assigned as there is a large 'through space' coupling constant between the 'peri' fluorines and the ortho fluorines in dimethyl tetrafluorophthalate are shifted downfield by 25·5 p.p.m.   The ^{19}F n.m.r. spectrum of dimethyl tetrafluorophthalate was recorded by the author from a sample prepared in Chapter 2 and was in agreement with that recorded by Spring.[216] The chemical shift positions being at -25·5 and -13·1 p.p.m. from hexafluorobenzene.

TABLE 14

N.m.r. spectral parameters for (XVI) and (XVII)

$-CF_2-CF_2-$ δ_A 129·6 (2)	
δ_B 127·5 (2)	J_{AB} = 232 Hz
$\gtrless C-F$ 193·4 (2)	$J_{F_1F_3} = J_{F_6F_8} \simeq$ 46 Hz
Aromatic F 146·6 (2) at C3 and C6	
153·1 (2) at C4 and C5	
Proton ($\gtrless CH_2$) at 1·5	
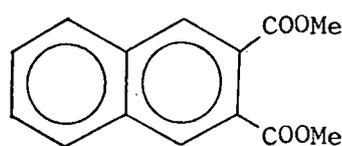
(XVI)

Aromatic F 119·5 (2) at C1 and C4	
	$J_{F_1F_8} = J_{F_4F_5} \simeq$ 70 Hz
141·3 (2) at C5 and C8	
151·2 (2) at C6 and C7	
Proton (-OMe) at 3·9	

(XVII)

Pyrolysis of an equimolar mixture of the ethylene adducts (VII) and (VIII) at 600°C resulted in the elimination of one molecule of tetrafluoroethylene and the formation of (XVI). The lower temperature was used to ensure that elimination of ethylene did not occur. The reverse Diels Alder reaction with elimination of tetrafluoroethylene from polyfluorobicyclo[2,2,2]octa-2,5-dienes occurs at 600°C, however, elimination of ethylene from 1,2,3,4,5,5,6,6-octafluoro-bicyclo[2,2,2]oct-2-ene occurs only at 700°C.[95] Presumably the driving force for the more ready elimination from the bicyclo[2,2,2]octa-2,5-dienes arises from the stabilization associated with aromatization.

Compound (XVI) had correct elemental analyses and mass spectrum. The presence of a fluorinated benzene ring was confirmed by u.v. and i.r., whilst the

^{19}F n.m.r. and ^{1}H n.m.r. spectra confirmed the structure of (XVI). Again a

large 'through space' coupling of 46 Hz is observed between the tertiary

fluorines and the 'peri' fluorines of the benzene ring; allowing unambiguous

assignment of the aromatic fluorines.

4.5 Vacuum pyrolysis of tetradecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (178)

The vacuum pyrolysis of the triene (178) proceeded through an intermediate

(XVIII), which was isolated and characterised, to give perfluoroindene, perfluoro-

1,4-dihydronaphthalene (XIX), either perfluoro-2 or -3-methylindene (XX) and

perfluoro-1,2-dihydronaphthalene (XXI).

(178) (XVIII) (XX) (XIX) (XXI)
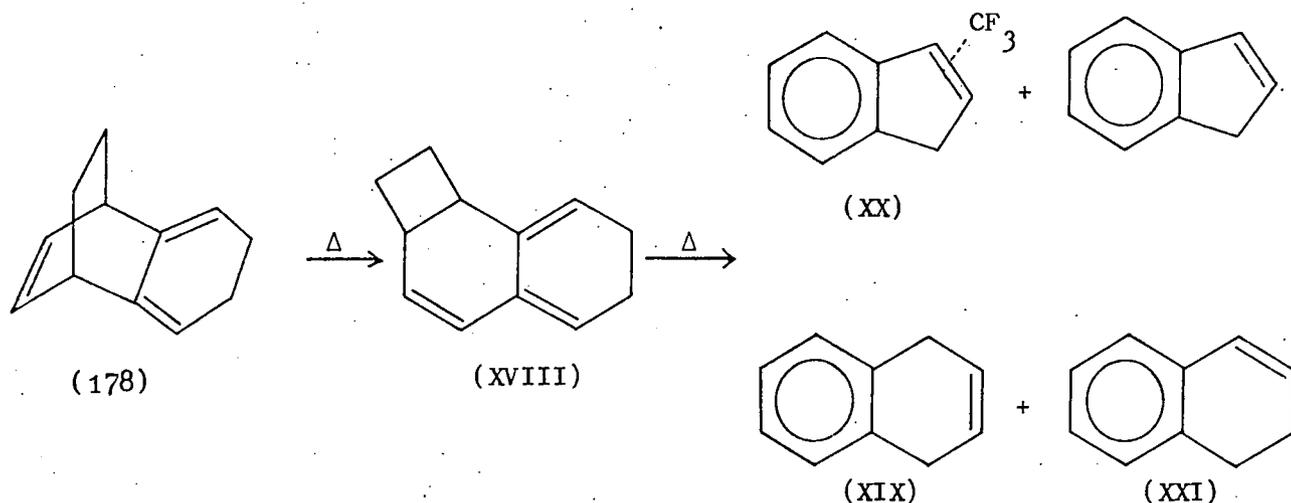
At a pyrolysis temperature of 680°C (XVIII) was not observed in the products,

however, at 580°C this intermediate compound formed about 30% of the products,

(cf. Table 18, Experimental section 4.10).

The ratio of perfluorindene : (XIX) : (XX) : (XXI) formed on pyrolysis

over the temperature range 580-680°C was analyzed by g.l.c. and found to be

constant within the limits of measurement at 6·2 : 2 : 1 : 14. (Each component

was determined by area measurement with a confidence level of ± 3% for each

value). Vacuum pyrolysis of (XVIII) at 680°C also gave the same ratio of

products and this confirms that all the products of pyrolysis are derived from

this intermediate. None of the final products were interconvertible on

repyrolysis at 680°C, although (XIX) did isomerise to give a trace (ca. 1%) of

(XXI).

The elemental analysis of (XVIII) together with the mass spectral data confirmed that the molecular formula was $C_{12}F_{14}$. However, the structure of (XVIII) could not be unambiguously assigned on the basis of other spectral data. The u.v. spectrum was indicative of an extensively conjugated system, e.g. 325 nm ($\epsilon = 200$), 250 nm ($\epsilon = 3000$) and 230 nm ($\epsilon = 7400$). The i.r. spectrum showed absorptions at 1710 and 1645 cm^{-1} with no absorption characteristics of the fluorinated benzene ring. These i.r. absorptions are compatible with those occurring at 1700 and 1650 cm^{-1} in perfluoro-7,7-dimethylcycloheptatriene.[27] Hence it seemed that (XVIII) contained an extensively conjugated but non-aromatic π system. This intermediate compound hydrolysed on exposure to moist air eliminating HF to give a white solid whose i.r. spectrum showed absorptions at 3500 (-OH) and 1750 ($>C=O$) cm^{-1}. However, the presence of three smaller absorptions in the carbonyl region suggested that more than one compound was present. This fairly rapid hydrolysis of (XVIII) is in marked contrast to the stability of the triene (178).

Unfortunately the ^{19}F n.m.r. spectrum of (XVIII) was difficult to interpret as all the $-CF_2-$ resonances and one vinylic fluorine resonance lie very close together at about 123 p.p.m. A large 'through space' coupling constant of 57 Hz is observed for the vinylic fluorines at C6 and C8. This is similar to the values found for the 'peri' couplings in polyfluoronaphthalenes. The value of this coupling constant could not be measured exactly from the resonance at 117.6 as it overlapped with one limb of an AB system. The resonances at 120.8 and 122.3 have definite outer limbs corresponding to J_{AB} values of 220 Hz; likewise the resonances at 125.6 (1) and 127.3 (1) could have outer limbs of 220 Hz assigned to them, although the spectrum in these regions is less distinct. The AB coupling constants of 220 Hz are assigned to the difluoromethylenes at C11 and C12, since they are similar to those reported for a series of tetrafluoro-cyclobutanes[176] and are too small for those characteristic of the cyclohexadiene moiety, (see Sec. 4.11). The last significant feature of the ^{19}F n.m.r. spectrum

TABLE 15

^{19}F n.m.r. spectral parameters for (XVIII) and (XXII)
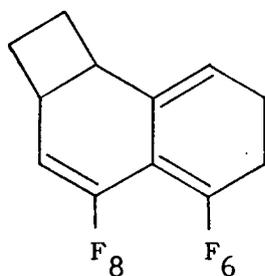
(XVIII)

Vinylic Fluorines

at C6 and C8 117·6 (1)/134·6 (1) $J_{F_6F_8} \simeq$ 57 Hz

129·0 (1) a doublet of 16 Hz

143·2 (1)

Tertiary Fluorines

at C1 and C10 185·4 (1)/182·3 (1) $J_{F_1F_{10}}$ = 25 Hz

CF$_2$ Fluorines

at C4 and C5 127·3 (4)

at C11 and C12 120·8 (1), 122·3 (1)

$J_{AB's} \simeq$ 220 Hz

125·6 (1), 127·3 (1)
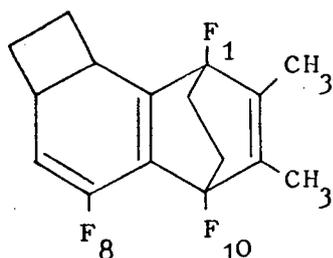
(XXII)

Tertiary Fluorines

at C1 and C10 205·0 ($\frac{1}{2}$) and 205·5 ($1\frac{1}{2}$)

at C3 and C6 176·0 (1) and 189·7 (1)

Vinylic Fluorine 151·1 (1)

CF$_2$ and one vinylic fluorine centred at

120·9 (3) and 123·8 (6)

CH$_3$ at 2·0

is that the tertiary fluorines have a mutual coupling constant of 25 Hz and this

enables the <u>cis</u> stereochemistry of the cyclobutane ring to be ascertained.

Neither the cyclobutane CF$_2$ resonances nor the vinylic fluorine resonances were

broad enough to encompass this 25 Hz coupling. The tertiary fluorines occur at

182·3 and 185·4 which is rather similar to the values of 187·6 and 198·0 recorded

for perfluorobicyclo[4,2,0]oct-2-ene (257).[96]
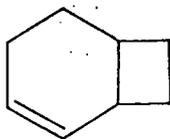
(257)

It is also worth mentioning that the double bond i.r. absorption of (257) occurs

at 1740 cm^{-1},[96] which is a little low for that usually found for the CF=CF in

fluorinated cyclohexenes.   The vacuum pyrolysis of a sample of (257) at 640°C

and 10^{-3} mm has been shown by the author to give primarily perfluorocyclohexa-

1,3- and -1,4-diene, in the ratio of 3 : 2, by elimination of tetrafluoroethylene.

Hence a precedent is available for tetrafluoroethylene elimination from a polycyclic

system containing a tetrafluorobutane moiety similar to that in (XVIII).   In

order to confirm the spectroscopic analysis and preclude the possibility of the

intermediate being the conjugated triene (258) a Diels Alder reaction with but-2-

yne was performed under analogous conditions to those employed for the triene (178).

(258)   But-2-yne →   (259)   CH$_3$ CH$_3$ Δ →   CH$_3$ CH$_3$

CH$_3$ CH$_3$ Δ →   ?
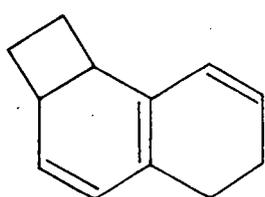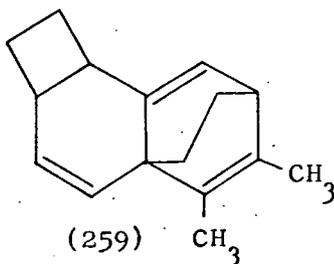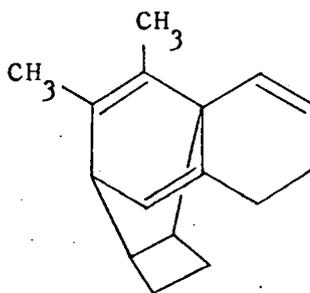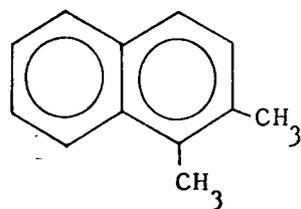
(260)

If the intermediate was (258) and underwent the Diels Alder reaction with but-2-yne then two possible products could be obtained, (259) and (260), depending upon which six membered ring provided the diene moiety.   Obviously two isomers could be envisaged for both (259) and (260);   nevertheless the overall effect will be to form a product that has an isolated CF=CF double bond, that has no conjugation and whose gross structural ^{19}F n.m.r. reveals the formation of one tertiary fluorine resonance.   Vacuum pyrolysis of (259) would be expected to yield the unknown 1,2-dimethylhexafluoronaphthalene, although the results on pyrolysis of (260) are less easily predicted.

If the intermediate is (XVIII), as predicted, then a Diels Alder reaction with but-2-yne should give the adduct (XXII). Again there are two possible isomers for (XXII) depending upon the stereochemical arrangement of the two -CF$_2$-CF$_2$- bridges.

(XVIII)   (XXII)
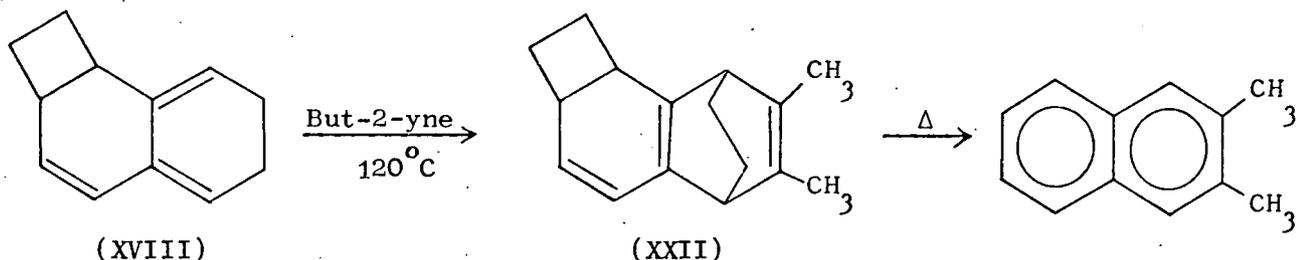
The adduct (XXII) has a conjugated diene system and two tertiary fluorines. Hence it should be readily distinguishable from (259) and (260).   (XXII) was in fact obtained from the reaction of (XVIII) with but-2-yne at 120°C and pyrolysis of (XXII) gave the known 2,3-dimethylhexafluoronaphthalene.   Hence the structure of (XVIII) is confirmed.

The adduct (XXII) had correct elemental analysis and mass spectrum.   The u.v. λ_{max} 263 nm (ϵ = 4500) was consistent with the presence of a conjugated cyclohexadiene unit and the i.r. absorption bands for the conjugated diene moiety were at 1710 and 1620 cm^{-1}.   Absorption bands of 1720 and 1630 cm^{-1} were observed in the i.r. spectrum of (XXVI) which has a similar diene moiety (cf. Section 4.6).   Although (XXII) was purified by preparative g.l.c. and appeared

to be only one component, a detailed analysis of the ^{19}F n.m.r. spectrum revealed that more than one isomer was present. The CF_2 resonances and one vinylic fluorine resonance occurred between 120 and 124 p.p.m. However, the resonance positions of the isomers could not have been coincident as the resonances were very broad and no analysis was possible from this region of the spectrum. The tertiary fluorines of the cyclobutane ring are found at 176.0 (85 Hz broad), and 189.7 (an apparent triplet of 25 Hz). This triplet is probably fortuitous and is more likely to arise from the overlapping resonances of the two isomers of (XXII). A coupling constant of 25 Hz is anticipated to occur between these tertiary fluorines, since it is present in the parent compound (XVIII). The remaining tertiary fluorines are found further upfield and are assigned to the C1 and C10 fluorines (see Table 15). A 'through space' coupling constant of about 35 Hz is anticipated between the C10 tertiary and C8 vinylic fluorines. With 25% of these tertiary fluorine resonances occurring at 205.0 and 75% occurring at 205.5 (a separation of ca. 28 Hz) then the anticipated 'through space' coupling is present only if the tertiary fluorines at C1 and C10 are coincident for each isomer and if each isomer is present in equal amounts. The resonance at 205.0 would then represent one limb of the expected 35 Hz doublet. This analysis concomitant with the information from the resonance at 189.7 suggests that (XXII) is a 50:50 mixture of the two anticipated isomers. The indisputable evidence from the ^{19}F n.m.r. spectrum is that on Diels Alder addition of but-2-yne two vinylic fluorines of (XVIII) become displaced to the tertiary fluorine region of (XXII). (XXII) also retains the cyclobutane ring. This is only consistent with the assigned structure (XVIII) and rules out the alternative (258).

To return to a consideration of the end products of pyrolysis of the triene (178), the perfluoro-1,4- and -1,2-dihydronaphthalenes, (XIX) and (XXI), have been reported previously in the Russian literature by Shteingarts and coworkers.[233,235] (The alternative mode of preparation of these compounds is discussed in Chapter 5.1).

All the end products of the pyrolysis, (XIX), (XX) and (XXI) had correct

elemental analyses and mass spectra.

The non-conjugated perfluorodihydronaphthalene (XIX) gave an i.r.

absorption of 1770 cm^{-1} for the CF=CF stretch and had a u.v. absorption

characteristic of a fluorinated benzene ring (λ_{max} 275 nm and $\epsilon = 1700$). The

vinylic and aromatic ^{19}F n.m.r. signals of (XIX) could not be assigned by the

author, however, the chemical shift pattern of these signals in monosubstituted

derivatives, which were obtained from nucleophilic substitution of (XIX), have

enabled Shteingarts to assign the spectra of (XIX). This assignment is based

on the assumption that the ortho, meta and para shifts in the benzene ring of

(XIX) would be similar in magnitude to those occurring in the corresponding

pentafluorophenyl derivatives. The author agrees with the assignment proposed

by Shteingarts and has quoted this in Table 16.

TABLE 16

 (XIX)	$>CF_2$ at 99·5 (4); vinylic F at 155·5 (2) Aromatic F at C5 and C8, 137·2 (2) at C6 and C7, 147·7 (2)
 (XXI)	$>CF_2$ at C1 116·9 (2) $J_{F_1F_8} \simeq 31$ Hz $>CF_2$ at C2, 125·8 (2) F at C4 and C5, 139·6(1)/140·6(1) $J_{F_4F_5} = 65$ Hz F at C8, 136·1 (1) and 3 F's 147·1 (1), 149·2 (1) and 159·3 (1)
 or (XX)	-CF$_3$ at 67·7 (3) $>CF_2$ at 117·3 (2) Vinylic and/or Aromatic F 112·9 (1), 145·5 (1), 147·7 (1), 154·3 (2)
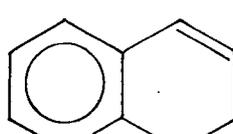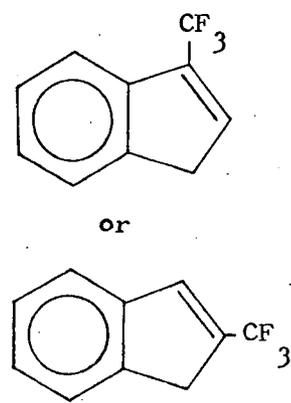
In the conjugated perfluorodihydronaphthalene (XXI) the i.r. absorption of CF=CF is moved down to 1730 cm^{-1}. The u.v. spectrum of (XXI) shows extensive conjugation and will be discussed in Chapter 5. Shteingart claims to have completely assigned the ^{19}F n.m.r. signals of (XXI),[234] however the chemical shift positions are inaccurately recorded (e.g. two fluorines were reported to occur at 150) and the assignment of the C3, C6 and C7 fluorines is completely guess work. Similarly in 1966 Shteingarts had made a guess at the ^{19}F n.m.r. assignment of (XIX),[233] only to revoke this a few years later.[235] However, the author agrees with the major assignments proposed by Shteingarts (cf. Table 16). The ^{19}F n.m.r. spectrum of (XXI) can be partly assigned as there is a large 'through space' coupling constant of 65 Hz between the 'peri' fluorines at C4 and C5. One of the CF_2 resonances is a doublet of 31 Hz and this almost certainly arises via the C1 fluorines coupling with the unresolved C8 aromatic fluorine since the latter being 120 Hz broad is the only resonance capable of embracing this large coupling constant.

The i.r. spectrum of (XX) shows a fairly strong absorption band at 1695 cm^{-1} and this is consistent with a -CF=C- moiety. The presence of a CF_3 group can be ascertained from the ^{19}F n.m.r. spectrum, which apart from the -CF_2- group remains unassigned. This is primarily a consequence of the vinylic and aromatic resonance signals of perfluoroindene and its monosubstituted derivatives remaining unassigned.[163,174] In spite of this it is known that perfluoroindene, its monosubstituted derivatives and its disubstituted derivatives all have characteristic u.v. spectra.[163] The u.v. spectra of (XX) and perfluoroindene are compared below (Figure 1) and are found to be very similar, confirming the presence of an indene skeleton in (XX).

The i.r. and ^{19}F n.m.r. spectra seemed to indicate that (XX) was one compound and hence it is assigned as either the perfluoro-2- or -3-methylindene. A reacton sequence was devised that should have enabled differentiation between the two structural possibilities:
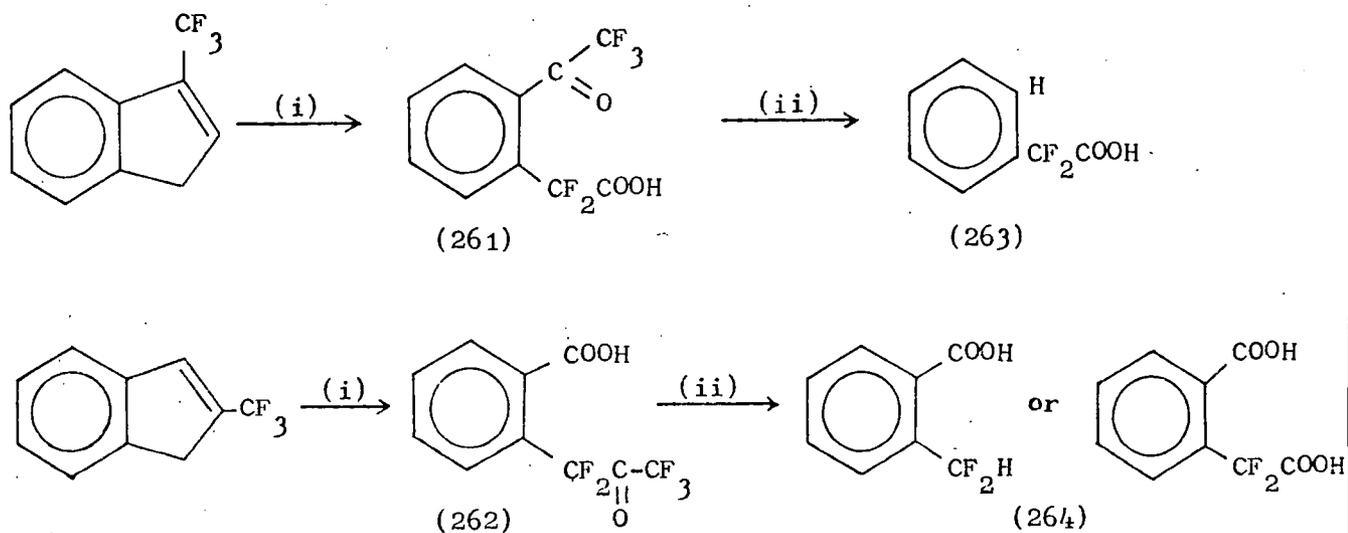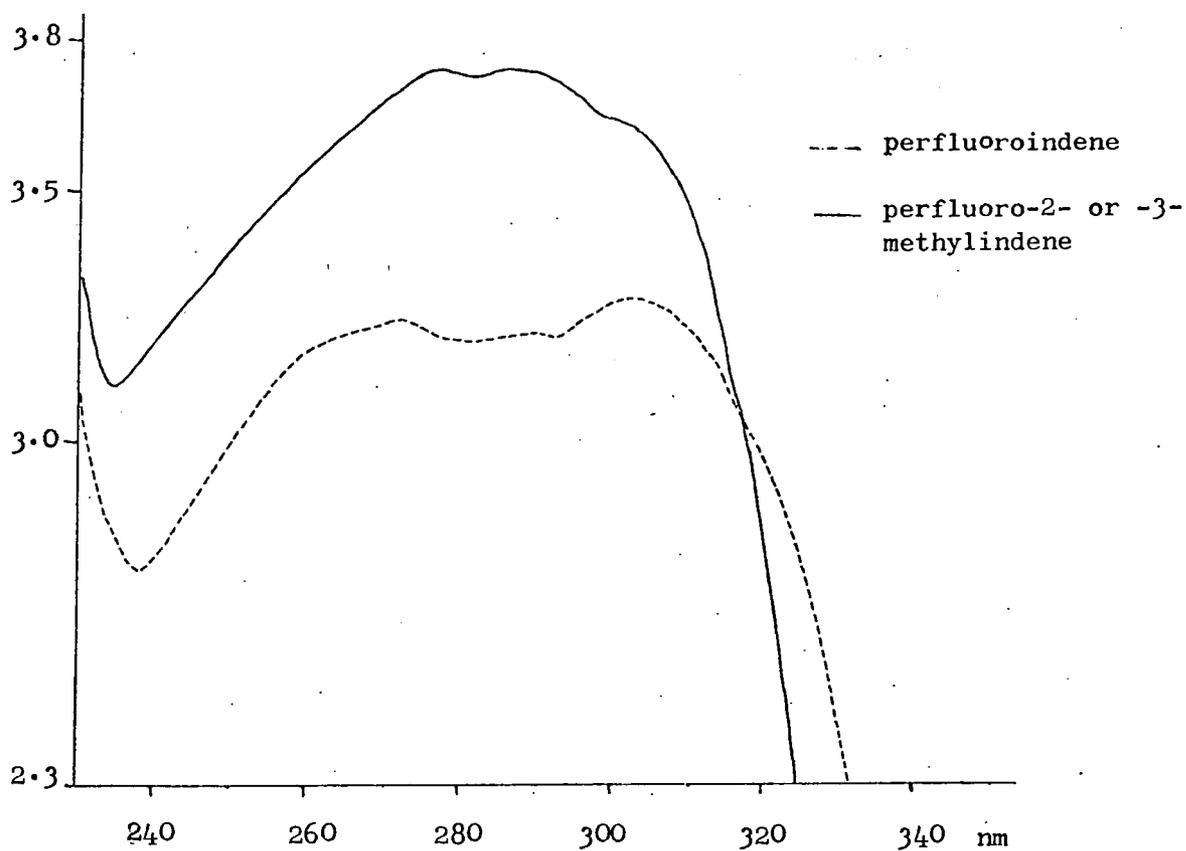
(i) = $KMnO_4$/Acetone; (ii) = 2N.NaOH

Although differentiation between (261) and (262) would have been difficult,

(263) and (264) should have very different n.m.r. characteristics. The second

reaction sequence involving reflux with sodium hydroxide solution is a haloform

cleavage reaction and is based upon the following reported example:[212]
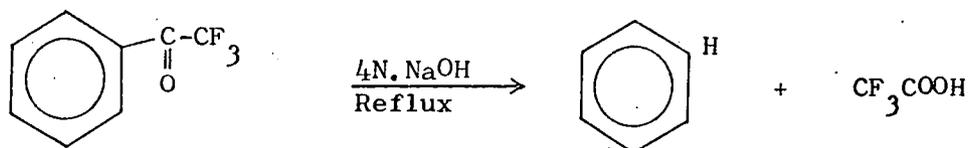
The cleavage of the aryl-carbon bond indicates a greater stability for a pentafluorophenyl than for a trifluoromethyl anion, if the reaction involves an anionic intermediate.[212]

The ^{19}F n.m.r. and i.r. spectra of the initial oxidation product (261) or (262) was consistent with the keto-acid having been formed. However, on refluxing this keto-acid with 2N.NaOH for two hours only degraded material was obtained. Unfortunately only 0·2g. of pure (XX) were available for this reaction sequence. All the material was used in one reaction and none was available for a repeat experiment. For instance it may have been possible to effect the 'haloform' cleavage reaction at room temperature merely by shaking the mixture. Hence it has not been possible to completely determine the structure of (XX).

A discussion of the mechanism of pyrolysis of the triene (178) is presented in Section 4.8.

4.6 The preparation of methylpolyfluorotricyclo[6,2,2,0^{2,7}]dodecatrienes

A number of methyl derivatives of the triene (178) were prepared in the hope that their pyrolysis would give insight into the mechanism involved. These trienes were chosen as pyrolysis of the monomethyl compounds was anticipated to give monomethyl derivatives of (XXI), four of which had been prepared by the reaction of lithium methyl with (XXI) (cf. Chapter 5). Hence, analysis of the pyrolysis products was facilitated. A mixture of 6- and 7-monomethyl derivatives of (XXI) that were produced in the substitution reaction proved to be inseparable and analysis by ^{19}F n.m.r. was rather difficult owing to coincident resonances. It was hoped to synthesise a similar mixture with a different ratio of components by pyrolysis of the 9-methyl substituted triene in order to confirm the previous ^{19}F n.m.r. assignments.

Lithium methyl in ether was added dropwise to the triene (178) in ether at

-78°C. A number of reactions were performed with the conditions being optimized

for the production of monomethyl, dimethyl and trimethyl substitution products.

Three monomethyl products (XXIII), (XXIV) and (XXVI) were obtained in the ratio

of about 8 : 1 : 8 (cf. Table 17 for structures). The substitution occurs

preferentially at the conjugated diene moiety and no monomethyl product was

obtained from replacement at the C9 olefinic position. An analysis of the

experimental results in Table 18 (4.11) is consistent with the conjugated dienes

(XXIII) and (XXVI) readily forming the major disubstitution product, which is the

non-conjugated (XXVII). A small amount of the symmetrically substituted (XXV)

was also formed. Only when conjugation had been removed from the diene moiety

did substitution take place at the olefinic position of the bicyclo[2,2,2]oct-2-

ene unit. An analysis of the ^{19}F n.m.r. spectra of the two major trimethyl

substituted products revealed that replacement of the C9 or C10 vinylic fluorine

of (XXVII) had occurred. Although two trimethyl substituted products were

prepared only sufficient of the major component (XXVIII) could be obtained pure

for characterisation.

All the compounds (XXIII) ⟶ (XXVIII) had correct elemental analyses and

mass spectra. The compounds were assigned on the basis of their i.r. and u.v.

spectra which are recorded in Table 19 (experimental section 4.11), and on the

basis of their n.m.r. spectra which are recorded in Table 17. All the compounds

except (XXVIII) had a strong i.r. absorption between 1767 and 1772 cm^{-1} that is

a characteristic of the CF=CF in the bicyclo[2,2,2]oct-2-ene unit. The u.v.

spectra depicted the lack of conjugation in (XXIV), (XXVII) and (XXVIII) and this

data was consistent with increase in the CF=CF i.r. absorption to 1750/1755 cm^{-1}.

Otherwise conjugation resulted in a lowering of the CF=CF i.r. absorption

frequency; for instance to 1720 cm^{-1} in (XXVI) which also showed the $>C=C<$

absorption at 1630 cm^{-1}. Only one double bond stretching frequency was observed

for (XXV) and this was very weak. Along the series (178), (XXIII) and (XXV),

TABLE 17

N.m.r. spectral parameters for the methylpolyfluorotricyclo[6,2,2,0^{2,7}]dodecatrienes

[All unmarked bonds to fluorine]
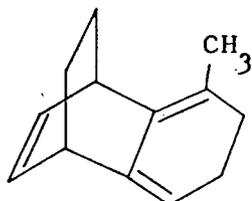
  (XXIII)	Tertiary fluorines: at C1 208·2 (1) and at C8 216·6 (1); $J_{F_6F_8}$ = 40 Hz. Vinylic fluorines: at C9 and C10 150·7 (1)/151·1 (1) at C6 133·4 (1); $J_{F_5F_6} \simeq$ 15 Hz. CF$_2$ fluorines: at C4 123·5 (2) and C5 130·0 (2) Bridging CF$_2$-CF$_2$: at 127·5 (4) CH$_3$ at C3 2·2
  (XXIV)	Tertiary fluorines: at C1 and C8 209·5 (1) a doublet of ca. 40 Hz/212·9 (1) a doublet of ca. 42 Hz. Vinylic fluorines: at C9 and C10 147·2 (1)/152·1 (1) at C3 and C6 one at about 124·0 (1)/135·6 (1) a doublet of 42 Hz. at C5 160·5 [$J_{F_4F_5} \simeq$ 18 Hz]. CF$_2$ fluorines: at C4 δ_A 102·3 (1), δ_B 109·4 (1) J_{AB} = 300 Hz Bridging CF$_2$-CF$_2$: $\delta_{A'}$ 124·2 (1), $\delta_{B'}$ 125·0 (1) $J_{A'B'}$ = 236 Hz. $\delta_{A''}$ 127·9 (1), $\delta_{B''}$ 132·5 (1), $J_{A''B''} \simeq$ 210 Hz CH$_3$ at C7 1·8
  (XXV)	Tertiary fluorines: 210·1 (2) Vinylic fluorines: 152·0 (2) CF$_2$ fluorines: 127·4 (4), 128·1 (2) and 128·3 (2) CH$_3$ at 2·2
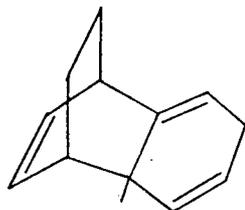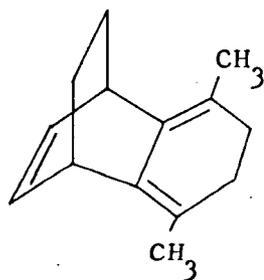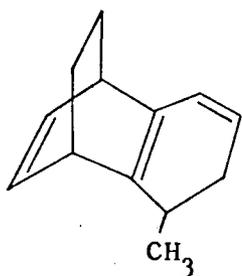
Tertiary fluorines: at C8 214·4 (1), at C1 216·1 (1)

$J_{F_1F_3}$ = 52 Hz and at C6 171·3 (1)

Vinylic fluorines: at C9 and C10 152·6 (2), at C3

148·3 (1), $J_{F_3F_5}$ 18 Hz and at C_4 154·3 (1),

$J_{F_4F_5}$ ≃ 18 Hz.

CF_2 fluorines: at C5 120·4 (2)

Bridging CF_2-CF_2: 122·6 (2), δ_A 122·6 (1),

δ_B 123·5 (1), J_{AB} = 220 Hz.

CH_3 at C6 1·7, J_{HF} = 22·5 Hz.
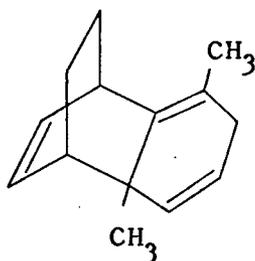
Tertiary fluorines: at C1 204·1 (1) and at C8 213·1 (1),

$J_{F_6F_8}$ = 44 Hz

Vinylic fluorines: at C9 and C10 148·4 (1)/153·3 (1),

at C6 138·5 (1) and at C5 146·1 (1), [$J_{F_4F_5}$ ≃ 18 Hz].

CF_2 fluorines: at C4 δ_A 97·7 (1), δ_B 102·5 (1),

J_{AB} = 300 Hz.

Bridging CF_2-CF_2: $\delta_{A'}$ 124·1 (1), $\delta_{B'}$ 125·1 (1),

$J_{A'B'}$ = 236 Hz.

$\delta_{A''}$ 127·5 (1), $\delta_{B''}$ 131·9 (1), $J_{A''B''}$ = 220 Hz.

CH_3 at C7 1·7 and CH_3 at C3 2·2
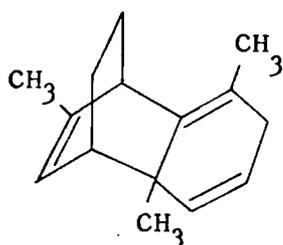
Tertiary fluorines: at C1 (195·6 (1) and at C8 213·2 (1),

$J_{F_6F_8}$ = 45 Hz.

Vinylic fluorines: at C9 129·4 (1), at C6 139·0 (1),

and at C5 164·6 (1), $J_{F_4F_5}$ ≃ 18 Hz.

CF_2 fluorines: at C4 δ_A 98·7 (1), δ_B 102·8 (1),

J_{AB} = 302 Hz.

Bridging CF_2-CF_2: $\delta_{A'}$ 125·7 (1), $\delta_{B'}$ 127·3 (1),

$J_{A'B'}$ = 242 Hz.

$\delta_{A''}$ 129·1 (1), $\delta_{B''}$ 131·4 (1), $J_{A''B''}$ = 220 Hz.

CH_3 (1) at 1·75, CH_3 (1) at 2·0 and CH_3 (1) at 2·2.

(XXVI)

(XXVII)

(XXVIII)

all of which have the conjugated double bonds in the same skeletal position, the increasing methyl substitution is reflected in their u.v. spectra by the increased extinction coefficient and movement in the absorption maxima from 259 to 262 to 269 nm. This is anticipated since hyperconjugation of the CH_3 group results in bathochromic shifts and intensification of bands.[213]

The ^1H and ^{19}F n.m.r. data for compounds (XXIII) → (XXVIII) are recorded in detail in Table 17 and only the general trends in the series will be discussed. The proton n.m.r. reveals that a $-CH_3$ occurs at 1·7/1·8 p.p.m. when attached to a tertiary carbon and at 2·0/2·2 p.p.m. when attached to a carbon at a vinylic site. The partial assignment of the fluorine n.m.r. spectra was aided by four characteristic coupling constants. In all the compounds a large 'through space' coupling of 40-44 Hz was observed between the tertiary fluorines and the vinylic fluorines at C3 and C6. This coupling constant was found even when the intermediate carbon atom had a CH_3 group attached (e.g. XXIV); although for (XXVI) the magnitude was an exceptional 52 Hz. The bridging difluoromethylenes give AB coupling constants of 210-242 Hz whilst the CF_2 of the cyclohexadiene moiety gives AB's of 300-302 Hz. It is curious that in the parent triene (178) and in the methyl substituted trienes that have the same position for the conjugated diene moiety (XXIII and XXV) no pseudo AB coupling is observed for any of the difluoromethylene groups. The last coupling constant found to be of value was that between the vinylic fluorine and adjacent difluoromethylene in the cyclohexadiene moiety. This is of the order of 15 to 18 Hz. In compound (XXIII) this was clearly visible in both the difluoromethylene and vinylic fluorines. However in instances where the difluoromethylene showed an AB pattern (e.g. XXIV, XXVII) the coupling constant was measurable only from the vinylic fluorine. Coupling constants for these systems where the assignment is only tentative are denoted by square brackets. One anomalous situation is found with (XXVI), here the CF_2 resonance is a triplet of 18 Hz and the CF_2 is found to have equal coupling constants with both vinylic fluorines ($J_{F_3F_5}$ =

$J_{F_4 F_5} \simeq 18$ Hz). The complex nature of the ^{19}F n.m.r. spin-spin couplings makes the assignments somewhat tentative, especially as the magnitude will depend upon conformational requirements imposed on the cyclohexadiene moiety, however, they are generally supported by the coupling constants found on analysis of the perfluorocyclohexa-1,3-diene ^{19}F n.m.r. spectra, in which $J_{F_1 F_6} = 15$ Hz and $J_{F_2 F_6} \simeq 10$ Hz.[214] The vinylic fluorines of the perfluorobicyclo[2,2,2]oct-2-ene unit are as expected, essential uncoupled sharp resonances that occur in a very narrow and well defined range, 147-154. Comparing the tertiary resonances of (XXVII) and (XXVIII) reveals that in the latter the C8 fluorine resonance moves 8.6 p.p.m. downfield whilst the C1 fluorine resonance is found at virtually the same position, suggesting that methyl substitution is at the C10 position in the trimethyl substituted (XXVIII).

Nothing can be ascertained from the ^{19}F n.m.r. spectra with regards to the detailed stereochemistry of (XXIV), (XXVII) and (XXVIII) all of which appear to be one isomer. Two isomers are possible since the CH_3 group at C2 can be disposed above or below the plane containing the CF_2-CF_2 bridge. However, an examination of molecular models suggests that the approach of a CH_3 group to the C2 position from the same side as the CF_2-CF_2 will result in 'steric interaction' if the C2 carbon is 'sp^2 hybridised'. This interaction constraint is removed as soon as the carbon becomes 'sp^3 hybridised'. Thus a cogent argument is available for the assertion that the CH_3 group at C2 in all of the compounds (XXIV), (XXVII) and (XXVIII) is to be found on the opposite side of the molecule to the CF_2-CF_2 bridge. Little can be said about the stereochemistry of (XXVI), though again only one isomer appears to be present on the basis of the ^{19}F n.m.r. spectra.

Of the two major monomethyl products, (XXIII) arose via inwards 1,2-elimination of fluorine whereas (XXVI) arose via outwards 1,4-elimination of fluorine. The minor monomethyl product (XXIV) arises from attack at the C2 position of the conjugated diene moiety. This is in marked contrast to the reaction of methyl lithium with perfluorocyclohexa-1,3-diene when attack at the

C2 position gave a 90% yield of the product derived from inwards elimination.

The nucleophilic substitution reactions of polyfluorocyclic dienes and olefins have been interpreted in terms of intermediate carbanion stability and relative ease of loss of fluoride ion.[171,159,199] In particular substitution at the C2 position of perfluorocyclohexa-1,3-diene is probably favoured as there is evidence that an α fluorine substituent may destabilize a conjugated planar anion more than a non-conjugated pyramidal anion.[171] Hence attack at C2 is favoured especially as the assumed carbanionic intermediate is additionally favoured by the presence of an adjacent CF_2 group. With the triene (178) attack by CH_3^- at C1 of the diene moiety generates a conjugated carbanion without an α fluorine substituent (265) whilst attack at C2 would lead to a pyramidal carbanion with an α fluorine (266).

(265)   (266)
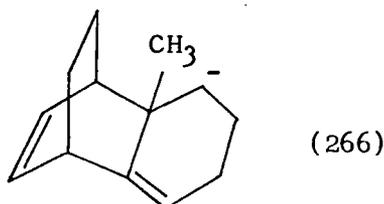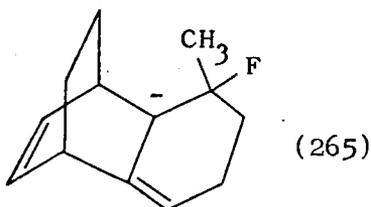
On the basis of previous reasoning it is the intermediate carbanionic stability that dictates reactivity, hence (265) should be more stable than (266) as the ratio of products derived from these carbanions is 16:1 respectively.

It would seem from a comparison of the relative proportions of products in experiments 1 and 2 (Table 19, Experimental Section) that the major monomethyl compounds (XXIII) and (XXVI) undergo further nucleophilic substitution almost exclusively at the C2 position of the conjugated diene moiety and that (XXIII) does so more readily than (XXVI). Thus nucleophilic attack by CH_3^- generates the carbanions (267) from (XXIII) and (268) from (XXVI).
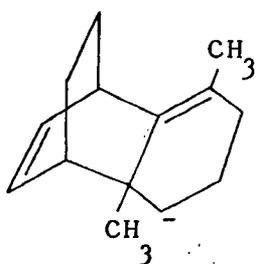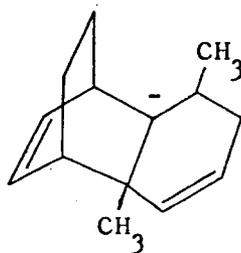
(267)   (268)

The intermediate carbanion (268) appears the most stable obtainable from compound (XXVI) but the generation of (267) from (XXIII) is somewhat surprising. Nucleophilic attack on (XXIII) would, on the basis of carbanion stability and by comparison with the initial attack at C1 on the triene (178), have been anticipated to generate the conjugated anion. However, very little of the conjugated product (XXV) is obtained by substitution of the C1 position of (XXIII). An analysis based exclusively on carbanion stability leads to the conclusion that (267) is more stable than (268), i.e. the tertiary pyramidal carbanion appears to be less stable than the secondary pyramidal carbanion with one α C-F bond.

Other information that emerged from work in this area was that nucleophilic substitution by CH_3^- occurred more readily with the perfluorocyclohexa-1,3-diene dimers (158) than with the triene (178), suggesting that the carbanion (269) is more favourable than (265) and (266).

(269)
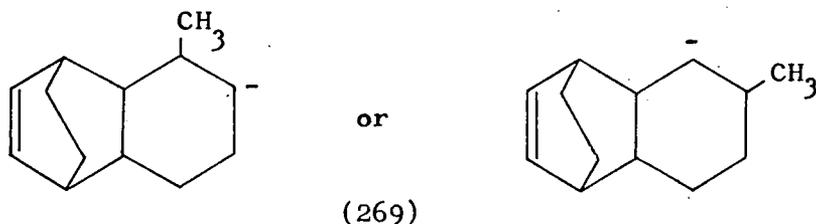
The reaction with lithium methyl was carried out on a mixture of the endo and exo isomers of (158), which were assumed to be present in a 9:1 ratio.[96] However, a complete analysis of the products was not achieved as mixtures of isomers having the same g.l.c. retention time were produced. The only unequivocal conclusion was that nucleophilic substitution occurred in the six membered ring since the spectral characteristics associated with the octafluoro-bicyclo[2,2,2]oct-2-ene unit were still present in the products. Fortunately both the monomethyl and dimethyl derivatives of (158) had retention times differing from the substituted derivatives of (178) and hence the order of reactivity was ascertained from a competition experiment.

Clearly the order of reactivity, of the dimers (158) and the triene (178), and the monomethyl substituted trienes (XXIII) and (XXVI), together with the preferred site of attack in (XXIII) cannot be rationalised solely in terms of the relative stability of the carbanionic intermediates. Other important factors are likely to be the ease of approach of tetrameric lithium methyl, solvation of the carbanion and the relative ground state energies of the products and starting materials. To assert the dominance of any one of these factors in a particular reaction would be highly speculative at present. The aim of this work was to provide suitably labelled triene derivatives for pyrolysis and consequently these other aspects have not been investigated in any depth.

The problem with the synthesis of labelled trienes revolved around the fact that the desired monomethyl substituted trienes readily formed the dimethyl products and only small quantities of the former were isolated. Unfortunately none of the desired C9 monomethyl triene was obtained and an alternative route to this compound also proved unsuccessful. The treatment of the olefin (164), which is the precursor to the triene [(178) cf. Chapter 3.9], with lithium methyl in ether gave no evidence for methyl substitution at the olefinic moiety and instead the major products arose from dehydrofluorination of (164) to the triene (178). At any one time the amount of triene (178) present was rather small, since substitution into the conjugated diene system was more favourable than dehydro-fluorination. Thus the products obtained on distillation were those previously reported for the reaction of lithium methyl with the triene (178). However, in this manner sufficient quantities of (XXIV) and (XXV) were obtained to enable their complete characterisation. In the reaction of lithium methyl with the triene (178) only small amounts of (XXIV) and (XXV) were formed and separation of sufficient quantities by preparative g.l.c. would have been impractical, however, sufficient of each compound was separated and identified by its i.r. spectrum.

The acidity of bridgehead protons in fluorinated systems is well known and when treated with lithium methyl in ether at -50°C the polyfluorobicyclo[2,2,1]-

heptane (183) forms the anion (184), which slowly decomposes at room temperature with precipitation of lithium fluoride.[167]   Decomposition of (184) in the presence of: (a) excess methyl lithium gave the olefin (185), (b) lithium iodide gave the olefin (185a) and (c) furan produced the adducts(186) presumably via the unstable bridgehead olefin (186a).
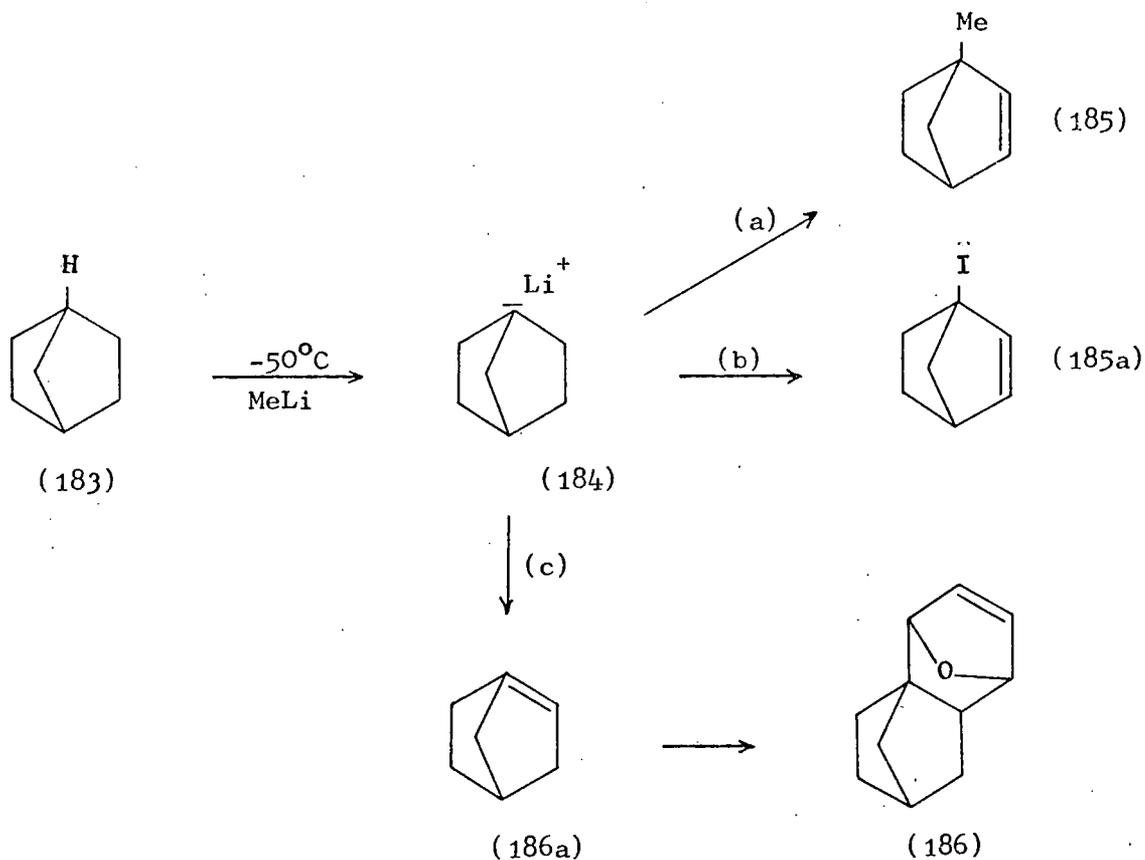
The acidity of (183) is so pronounced that the base catalysed exchange of hydrogen for tritium in (183) was found to be five times faster than that in $(CF_3)_3CH$.[168]

Hence the dehydrofluorination of (164) with lithium methyl is not without precedent and like the bridgehead proton of (183), the tertiary proton of (164) is anticipated to be acidic.   When only a small amount of lithium methyl was added to the olefin (164) at -78°C, the triene (178) and its methyl substituted derivatives were formed whilst the majority of the olefin remained unreacted. It seems likely that dehydrofluorination proceeds more readily and at a lower temperature with (164) than with (183) and this must be a consequence of the highly unfavoured stereochemical requirements of the bridgehead olefin (186a).

4.7 Vacuum pyrolyses of the monomethyltridecafluorotricyclo[6,2,2,0^{2,7}]dodecatrienes

Owing to the difficulties associated with preparation of these compounds only small quantities were available for pyrolysis. The monomethyl trienes (XXIII) and (XXVI) were pyrolysed at 640°C and 10^{-3} mm to give the major products shown below:

(XXVI)	77%	10%
	(XXX)	(XXXIV)

(XXIII)	8%	71%
	(XXX)	(XXXIV)
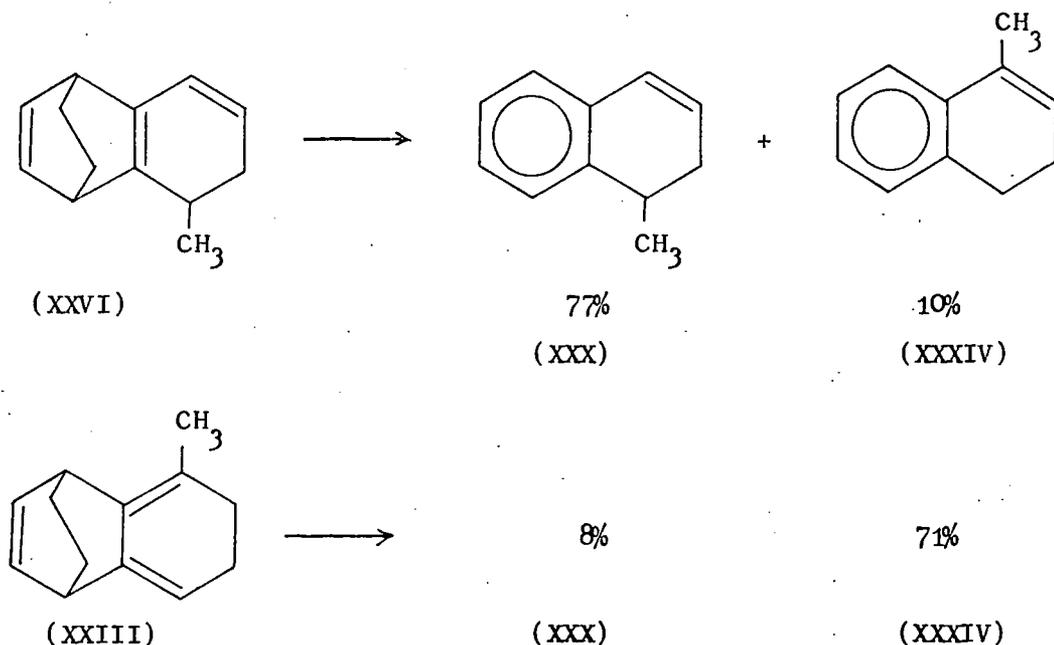
The spectroscopic evidence for (XXX) and the preparation of (XXXIV) are discussed in Chapter 5. Repyrolysis confirmed that (XXXIV) and (XXX) were not inter-convertible. Both pyrolyses also resulted in the formation of a small quantity of perfluoronaphthalene (ca. 2%) by elimination of methyl fluoride and both pyrolyses gave small quantities of two compounds which had molecular weights of 406 (m.s.) and hence were isomers of the starting materials. These minor components had the same g.l.c. retention times but unfortunately were not formed in either pyrolysis in sufficient quantity to allow isolation and identification. Sufficient quantities of material were available for qualitative u.v. spectra to be obtained. These spectra were very similar for the two shorter retained isomers and different for the two longer retained isomers; all four spectra were not inconsistent with extensively conjugated trienes and rule out simple conjugated 1,3-dienes. The relative g.l.c. retention time of triene (178) to that of compound (XVIII) is 1:1·7; for compound (XXVI) and the unknown compounds formed

on pyrolysis the ratios are 1:2·5 and 1:3·0, and for compound (XXIII) 1:2·7 and

1:3·2. It is possible then that the pyrolyses of the methyl labelled compounds

proceed through intermediate compounds which like (XVIII) are formed by 1,3-alkyl

migrations. Obviously with monomethyl labelling two isomers are possible as a

result of 1,3-alkyl migration of the bridging tetrafluoroethylene unit.

Methyl groups do have a propensity to migrate in hydrocarbon systems and

the 1,5 migrations depicted below were observed at 450-490°C.[217]

$$\xrightarrow{1,5} \qquad \xleftarrow{\quad} \qquad \xrightarrow{1,5} \qquad \xleftarrow{\quad}$$
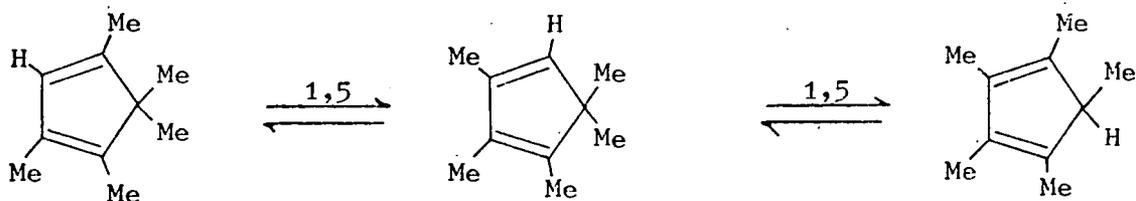
The position of methyl migrations in fluorocarbon systems is less clear. Methyl

migration was not observed in any of the aromatic compounds, which were the

final pyrolysis products, and it is therefore unlikely that methyl migration can

account for the formation of the small amounts of isomeric monomethyl trienes.

Furthermore in another experiment 50 mg. of compound (XXVI) were pyrolyzed at a

higher temperature and in this instance much smaller percentages of the unidentified

isomers were obtained, suggesting that perhaps they are intermediate compounds en

route to the major products and are analogous to the intermediate (XVIII) formed

on pyrolysis of (178).

4.8 Possible reaction pathways in the pyrolysis of polyfluorotricyclo[6.2.2,0^{2,7}]-dodecatrienes

The initial step in the pyrolysis of the triene (178) results in the formation

of (XVIII) which can proceed as a suprafacial concerted 1,3 migration providing

that inversion proceeds at the migrating centre.[71] Equally satisfactorily the

migration could be considered as an allylic C-C homolysis followed by a 1,3 radical

recombination. [The average C-C bond energy is about 84 Kcals; however,

homolysis of this bond would be more favourable as allylic stabilization of

radicals is about 13 Kcals/mole[206]]. It is then possible that (XVIII) could

eliminate tetrafluoroethylene to form the tetraene (285) by a diradical process, as the concerted elimination is symmetry forbidden:

(178)　　　　　　　　　　(XVIII)　　　　　　　　　　(285)
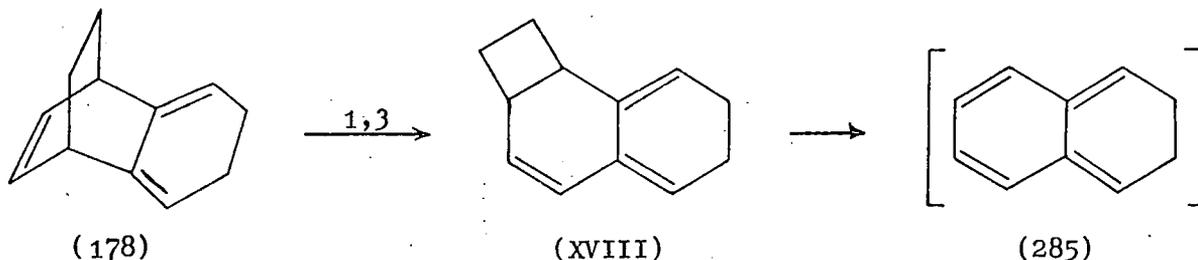
A full correlation diagram for the cheleotropic reaction involving the elimination of tetrafluoroethylene from the triene (178) cannot be constructed as the symmetry element does not bisect the bonds made or broken during the course of the reaction. However a consideration of the HOMO/LUMO interactions reveals that symmetry allowed mixing can occur and the concerted elimination should be allowed.[218] The π energies of the tetraene have been obtained from M.O. calculations.[219]
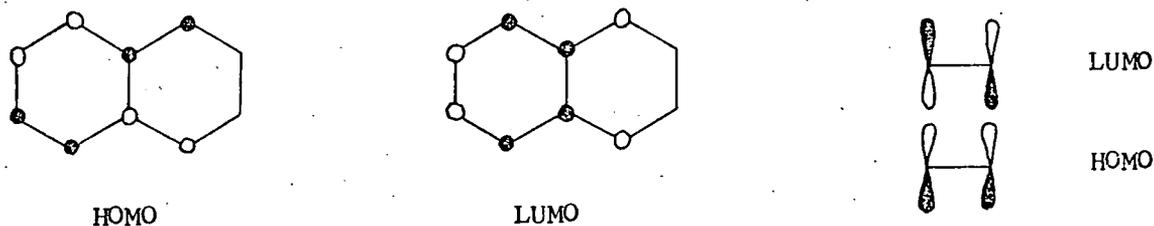
HOMO　　　　　　　　　　LUMO　　　　　　　　　　LUMO
　　　　　　　　　　　　　　　　　　　　　　　　　　HOMO

Thus, although the concerted elimination of tetrafluoroethylene from the triene (178) is symmetry allowed, an alternative mode appears to be chosen. It is interesting to note that a similar HOMO/LUMO treatment for the elimination of ethylene from the bicyclo[2,2,2]octa-2,5-diene system also reveals that the reaction is allowed in a concerted fashion. Elimination of tetrafluoroethylene proceeds much more readily from the bicyclo[2,2,2] unit of (XXXVII) than from the triene (178). The former almost completely eliminated tetrafluoroethylene at 335°C whereas the triene (178) was essentially stable even at 400°C (cf. Chapter 3.10). It may well be that concerted elimination from (XXXVII) does occur.

A number of structures similar to the tetraene have been prepared; isobenzo-furan[187] and tetrafluoroisoindole[188] being obtained on flash vacuum pyrolysis at

650°C and 550°C respectively (see Introduction 4.1, page 126). However,
attempts to isolate orthoxylylenes have proved unsuccessful even though they
have often been posultated as reaction intermediates.[237] A solution of (286)
when heated at 60-80°C in the presence of diethyl fumarate forms the adduct (287),
which presumably arises via Diels Alder addition to the orthoxylylene (288)
since stereochemical integrity is maintained.[237] The activation energy for the
ring opening of (286) to orthoxylylene has been calculated at 17 Kcals. The
disrotatory opening is required from symmetry considerations to proceed in a
non-concerted manner.

(286) (288) (287)
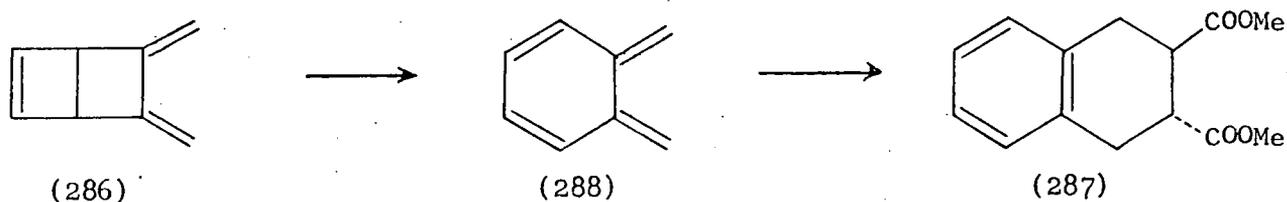
The only M.O. calculations performed suggest that the orthoxylylene (288) has a
fairly high energy HOMO with the HOMO/LUMO separation being 1.3 eV.[238] This may
explain the high reactivity of isobenzofuran, tetrafluoroisoindole and all the
known orthoxylylenes.

Hence it is not too surprising that the tetraene (285) was not obtained on
pyrolysis of the triene (178). Pyrolysis of this triene gives a good mass
balance (> 98%) and the same four non-interconvertible products in the same ratio
over a temperature range of 100°C. This would tend to suggest that only one
transition state is involved and it could possibly be that the tetraene (285) is
formed with such a high energy content that decay to the four products requires no
further input of energy. This may explain the constancy of the product ratio.
However, unless the reaction is proceeding through a complex 'surface rearrangement'
it becomes necessary to postulate two simultaneous mechanisms for the formation
of products.

The pyrolysis of the monomethyl substituted trienes confirms that the
aromatic ring is formed from the moiety that previously contained the CF_2-CF_2

bridge. Hence it would seem reasonable to propose that the rearrangement occurs

in the other 6-membered ring. Examination of models demonstrates that the

tetraene (285) is obliged to deviate from planarity. As shown in the diagram

the suprafacial 1,5 transannular shift of F_a or F_b can account for the formation

of the major product, perfluoro-1,2-dihydronaphthalene, whilst the simultaneous

1,5 shift of F_a and F_b accounts for the formation of perfluoro-1,4-dihydronaphthalene.

(XXI)   (XIX)
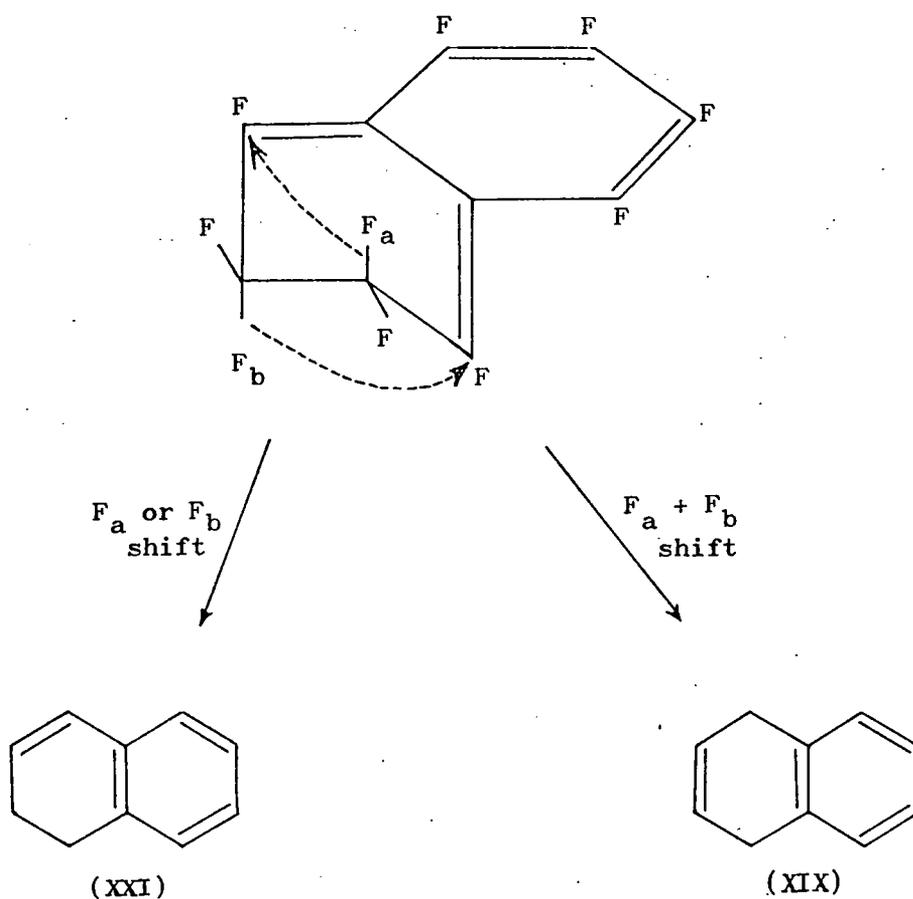
Similar 1,5-fluorine migrations have been observed on pyrolysis of 2H,3H-

and 2,3-dimethylhexafluorocyclohexa-1,3-diene at 700°C.[95]   1H-Heptafluorocyclo-

hexa-1,3-diene also undergoes a 1,5-fluorine shift on pyrolysis at 600°C,[166]

whilst the formation of perfluoro-1-methylcyclopentadiene from perfluoro-2-

methylcyclopentadiene on heating at 80°C for 2 days can also be considered

formally as a 1,5-fluorine shift.[139]   This does not imply that a theoretical

pronouncement is being made on an allowed concerted 1,5-fluorine migration, since

it is impossible to establish a priori, the 'allowed' or 'forbidden' nature of

fluorine shifts. However, 1,5-fluorine shifts do explain the observations in certain instances and are postulated in the formation of perfluorodihydro-naphthalenes from the proposed intermediate tetraene (285).

The formation of perfluoroindene and perfluoro-2- or -3-methylindene can only be accounted for in terms of a radical sequence initiated either by a σ-allylic shift (Scheme A) or by homolysis of the CF_2-CF_2 to give a diradical, which will obtain double allylic stabilisation (Scheme B).

Scheme A
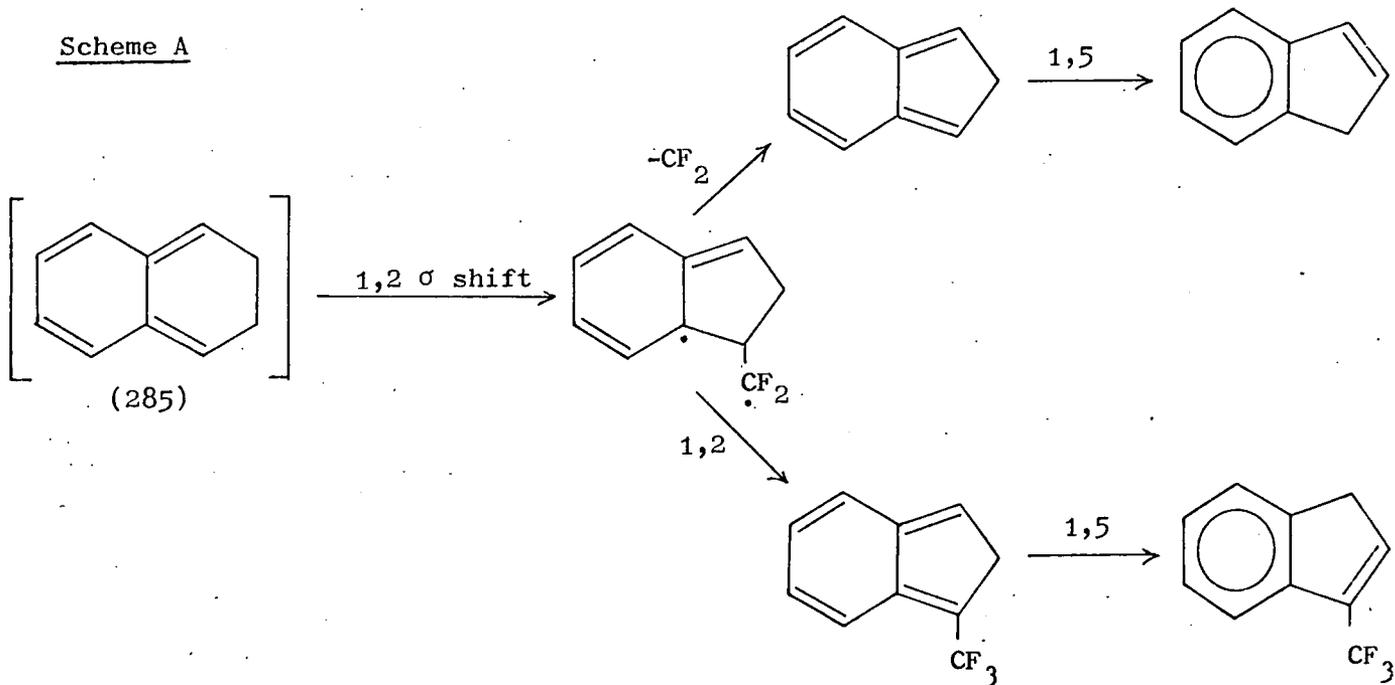
Scheme B
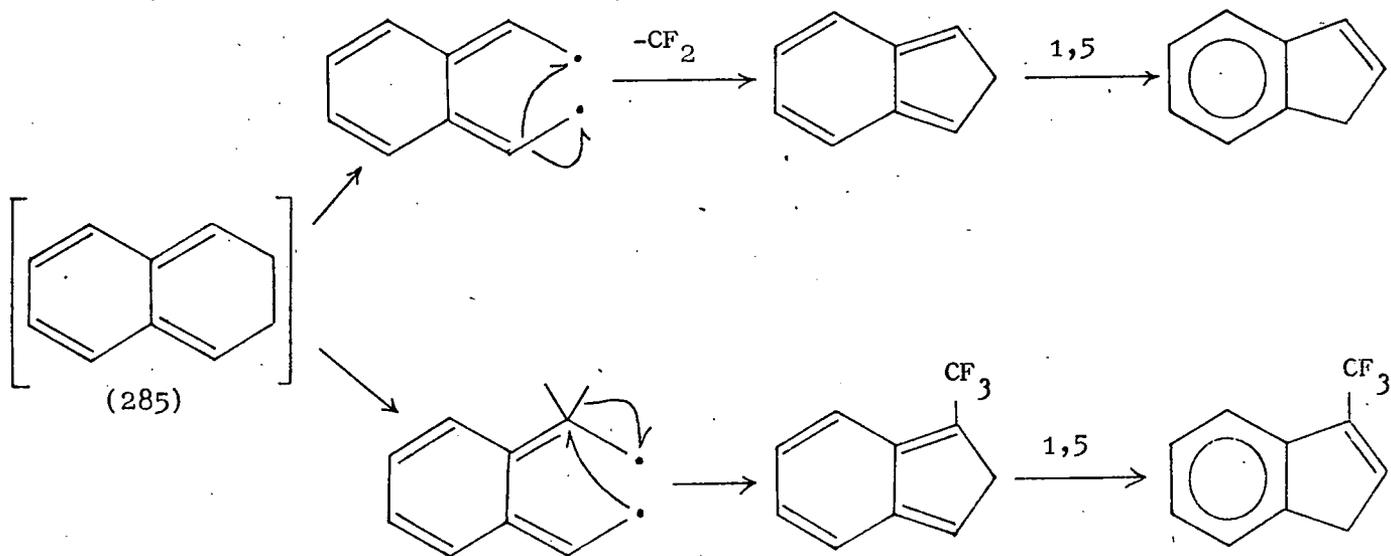
The above analysis presupposes the formation of the tetraene (285), although it is equally possible that the rearrangements and migrations could take place in the intermediate triene (XVIII). The products from the pyrolysis of the monomethyl triene (XXIII) can be accounted for in terms of 1,5-fluorine migrations from the presumed intermediate tetraene (289).
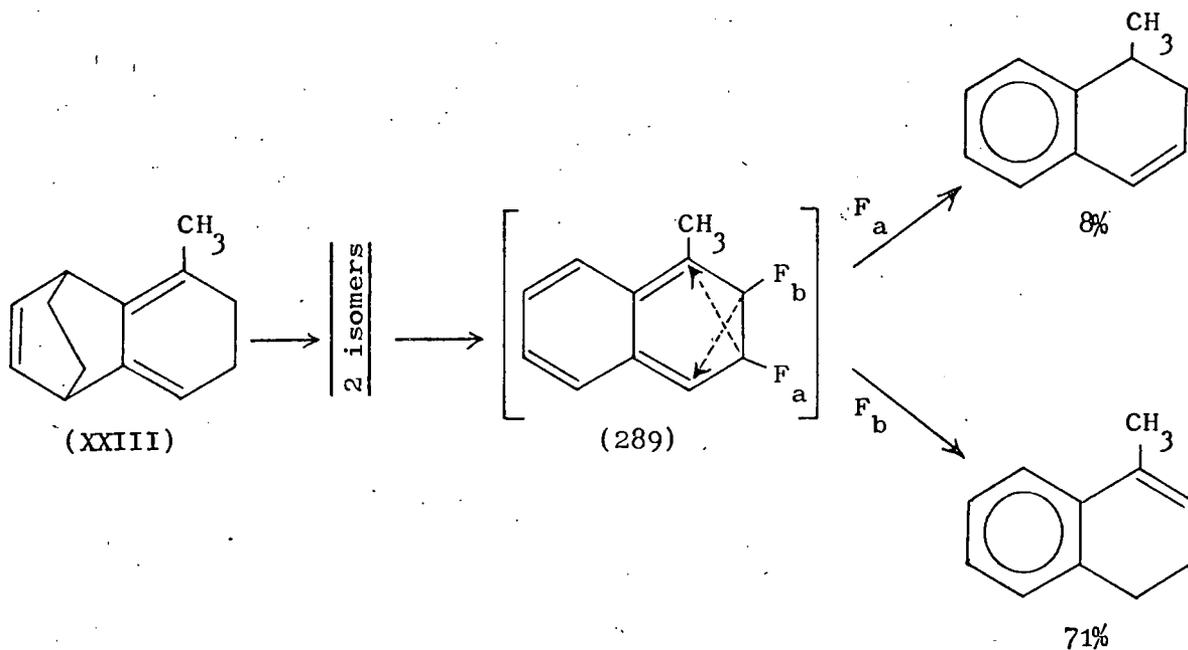
However, the intermediacy of a tetraene in the pyrolysis of (XXVI) cannot be posulated, since elimination of tetrafluoroethylene would lead to the stable aromatic (XXX) from which no further rearrangement proceeds. Hence it must be asserted that the formation of (XXXIV) occurs via a fluorine migration in one of the apparent and unknown intermediates (see Discusion 4.7).
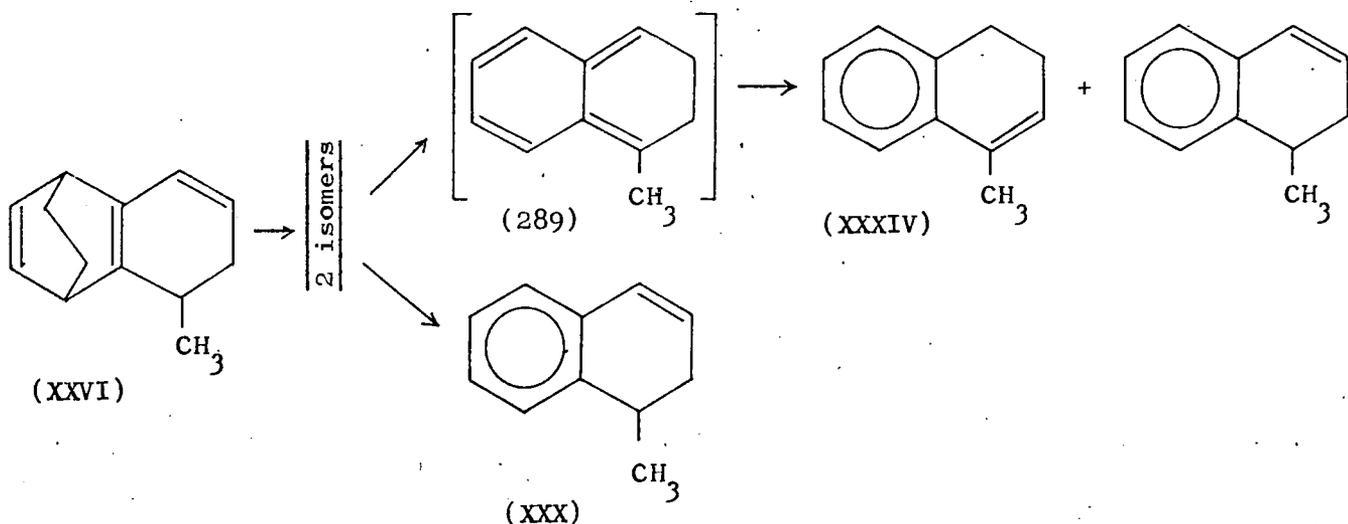
The ratio of (XXX) : (XXXIV) is 77 : 10.   The generation of the tetraene (289)

from (XXVI) would require the same intermediate as that obtained from (XXIII).

This is plausible on the basis of the qualitative u.v. spectra obtained, however

it remains speculative.

The reaction schemes outlined above are by no means certain.   It is possible

that the tetraenes (285) and (289) do not have a finite existence and that the

migrations and rearrangements involve the intermediate trienes.   An attempt

to generate the tetraene (285) by pyrolysis of (XVI) at 750°C proved unsuccessful

and the starting material was recovered unchanged.

(XVI)
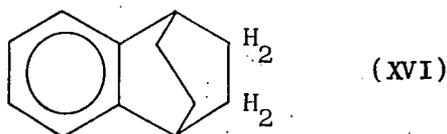
Preferential elimination of ethylene was anticipated though this did not occur

in spite of the reaction being, from a consideration of HOMO/LUMO interaction,

symmetry allowed.

EXPERIMENTAL

4.9 Vacuum pyrolyses of the Diels Alder adducts of tetradecafluorotricyclo-[6,2,2,0^{2,7}]dodeca-2,6,9-triene

The apparatus consisted of a silica tube (45 cm. in length and 1·2 cm. in internal diameter)which was lightly packed with silica wool and heated in an electric furnace. Any gaseous products formed were expanded into a calibrated measuring bulb.

(a) The ethylene adducts (VII) and (VIII)

An equimolar mixture of (VII) and (VIII) (0·679g., 1·59 mmoles) was pyrolysed at 620°C/10^{-3} mm to give (i) a gas shown by i.r. and m.s. to be tetrafluoroethylene (1·36 mmoles) and (ii) (0·488g.) of solid shown by g.l.c. (Col.A, 150°C) to consist of one new component with a small amount of starting material. Recrystallisation from petroleum ether (60/80) afforded (0·259g., 0·79 mmoles) of pure 9H,9H,10H,10H-decafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,4,6-triene (XVI). C$_{12}$F$_{10}$H$_4$, which has a Mol.Wt. of 338 (m.s.), requires: C, 42·6; H, 1·2; F, 56·3%. Found: C, 42·8; H, 1·4; F, 56·5%. (XVI) has a M.Pt. of 89°C, λ_{max} 263 nm (ϵ = 850), υ_{max} 2920 ($>$CH$_2$) and 1510 cm^{-1} (fluorinated benzene ring).

(b) The but-2-yne adducts (IX) and (X)

An equimolar mixture of (IX) and (X) (0·058g., 0·126 mmoles) was pyrolysed at 650°C/10^{-3} mm to give (0·028g., 0·106 mmoles) of 2,3-dimethylhexafluoro-naphthalene, which was identified by comparison of i.r., m.s. and M.Pt. with published data.[163]

(c) The diester adduct (XII)

(0·540g., 0·98 mmoles) of (XII) were pyrolysed at 650°C/10^{-3} mm but g.l.c. analysis (Col.B, 250°C) and tetrafluoroethylene elimination indicated only 70% of (XII) had reacted. The mixture was then repyrolysed at 650°C/10^{-3} mm to give (i) a gaseous fraction (1·05 mmoles) consisting of tetrafluoroethylene with a trace of SiF$_4$ and (ii) (0·260g., 0·74 mmoles, 76% yield) of a yellow solid, which

was recrystallised from petroleum ether (60/80) to give white crystals of dimethyl hexafluoronaphthalene-2,3-dicarboxylate (XVII). $C_{14}F_6H_6O_4$, which has a Mol.Wt. of 352 (m.s.), requires: C, 47·7; F, 32·4; H, 1·8%. Found: C, 47·9; F, 32·7; H, 2·0%. (XVII) has a M.Pt. of 107/108°C, v_{max} 2970 (-CH$_3$), 1745 and 1728 (>C=O), and 1530 cm^{-1} (fluorinated benzene ring); λ_{max} 340 nm (ϵ = 3900), 327 nm (ϵ = 2900), 295 nm (ϵ = 1900), 283 nm (ϵ = 2500) and 273 nm (ϵ = 2300).

(d) Compound (XIV)

(0·051g., 0·125 mmoles) of (XIV) was pyrolysed at 660°C/10^{-3} mm to give (i) tetrafluoroethylene (0·12 mmoles) with correct i.r. and (ii) a liquid fraction (0·039g.) shown by i.r. to be perfluoro-3-methylisoquinoline (XV). G.l.c. analysis (Col.A, 150°C) confirmed the presence of (XV) with a trace (ca. 3%) of unreacted (XIV).

(e) Compound (XVI)

(0·035g., ca. 0·1 mmoles) of (XVI) was pyrolysed at 750°C/10^{-3} mm to give (0·035g.) of white solid that was shown by i.r. and g.l.c. to be unchanged (XVI).

4.10

(a) Pyrolyses of perfluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (178)

Using the apparatus described previously (Section 4.9) the triene (178) (1·430g., 3·49 mmoles) was pyrolysed at 620°C/5x10^{-3} mm to give (i) tetrafluoro-ethylene (0·320g., 3·20 mmoles) and (ii) (1·098g.) of a liquid fraction which was analysed by g.l.c. (Col.E, 100°C) and was shown to be in order of increasing retention time unreacted triene (19% by wt., 0·54 mmoles), perfluorotricyclo-[8,2,0,0^{2,7}]dodeca-2,6,8-triene (XVIII) (7% by wt., 0·20mmoles); perfluoroindene (17% by wt., 0·64 mmoles); perfluoro-1,4-dihydronaphthalene (XIX) (6·5% by wt., 0·24 mmoles); perfluoro-2-methylindene or perfluoro-3-methylindene (XX) (3·2% by wt., 0·12 mmoles) and perfluoro-1,2-dihydronaphthalene (XXI) (47% by wt., 1·67 mmoles).

The results obtained for a series of experiments at varying temperatures are given in Table 18.

TABLE 18

Expt.	Pyrolysis Rate (g./hr.)	Temp. $^\circ$C	Triene	XVIII	Perfluoroindene	XIX + XX	XXI
(1)	8	580	65	11	5·7	3·2	15·0
(2)	8	620	19	7	17·0	9·7	47
(3)	6	650	9	2	19·9	12·3	56
(4)	15	650	17	8	17·1	10·1	48
(5)	4	680	ca. 1	0	22·4	13·2	63

[Analysis is by weight only and quoted with a confidence level of ±3% for each value]

The mole ratio of (XIX) : (XX) : (XXI) remained constant (to the limits of measurement) at all temperatures and was 2 : 1 : 14. Also the mole ratio of perfluoroindene to (XXI) remained, apart from experiment (i), constant to within the limits of experimental measurement, the ratio being 1 : 2·27.

Fractions from experiments (1) to (5) inclusive were combined and distilled on the concentric tubes apparatus at 10 mm to give in order of increasing B.Pt. (i) perfluoroindene B.Pt. 45°C which was confirmed by comparison of u.v., g.l.c. and i.r. with an authentic sample[165]; (ii) unchanged triene B.Pt. 53°C; (iii) a fraction (B.Pt. 58 $\rightarrow$ 60°C) containing approximately 25% of (XIX) and 25% of (XX) together with several other components; and (iv) a fraction (B.Pt. 61 $\rightarrow$ 62°C) containing 10% (XVIII) and 90% (XXI).

Fraction (iii) was separated by preparative g.l.c. (Col.F, 125°C) to give: (a) (XIX) (ca. 0·2g.). $C_{10}F_{10}$, Mol.Wt. 310 (m.s.), requires: F, 61·3%. Found: F, 61·3%. (XIX) is a colourless solid that has a M.Pt. of 34°C, (Lit. 30/31°C [233]); λ_{max} 275 nm (ϵ = 1,700) and 270 nm (shoulder, ϵ = 1600) and υ_{max} 1770 (-CF=CF-), 1505 and 1535 cm^{-1} (fluorinated benzene ring)

and (b) (XX), a colourless liquid (ca. 0·2g.). $C_{10}F_{10}$, Mol.Wt. 310 (m.s.); Found: F, 61·2%. (XX) has λ_{max} 285 nm (ϵ = 5500), 275 nm (ϵ = 5400), 305 nm (shoulder ϵ = 4000) and 295 nm (shoulder ϵ = 5000); and υ_{max} 1695 (>C=C-CF$_3$) and 1510 cm^{-1} (fluorinated benzene ring).

Fraction (iv) was separated by preparative g.l.c. (Col.G, 150°C) to give:

(a) (XVIII), a colourless liquid (ca. 1·5g.), $C_{12}F_{14}$, Mol.Wt. 410 (m.s.) requires: F, 64·9%. Found: F, 65·3%. (XVIII) has λ 325 nm (ϵ = 200), 300 nm (ϵ = 800), 280 nm (ϵ = 1900), 250 nm (ϵ = 3000) and 230 nm (ϵ = 7400) and υ_{max} 1710 and 1645 cm^{-1};

and (b) (XXI), $C_{10}F_{10}$, Mol.Wt. 310 (m.s.) requires: F, 61·3%. Found: F, 61·5%. (XXI) has a B.Pt. of 168°C, λ_{max} 260 nm (ϵ = 8300), 267 nm (shoulder, ϵ = 7200), 293 nm (ϵ = 6300) and 301 nm (shoulder, ϵ = 5300) and υ_{max} 1730 (-CF=CF-), 1522 and 1495 cm^{-1} (fluorinated benzene ring).

(b) **Pyrolyses of products obtained from reaction 4.10(a)**

(i) Perfluoro-1,2-dihydronaphthalene (XXI) (0·062g.) was pyrolysed at 640°C/ 5x10^{-3} mm to give (0·060g.) of unreacted (XXI), confirmed by i.r. and g.l.c.

(ii) Perfluoro-1,4-dihydronaphthalene (XIX) (0·070g.) was pyrolysed at 640°C/ 5x10^{-3} mm to give (0·069g.) of (XIX) by i.r., but this was shown by g.l.c. to contain a trace (ca. 1%) of perfluoro-1,2-dihydronaphthalene.

(iii) Compound (XX) (0·0356g.) was pyrolysed at 640°C/5x10^{-3} mm to give unchanged (XX) (0·0350g.), confirmed by i.r. and g.l.c.

(iv) Perfluorotricyclo[8,2,0,0^{2,7}]dodeca-2,6,8-triene (XVIII) (0·0540g., 0·135 mmoles) was pyrolysed at 680°C/5x10^{-3} mm to give: (i) a gas fraction (0·184 mmoles) shown by i.r. and m.s. to be tetrafluoroethylene with a trace of SiF$_4$ and (ii) a liquid fraction (0·0350g.) shown by g.l.c. analysis (Col.E, 100°C) to be a mixture of perfluoroindene, (XIX and XX) and (XXI) in the ratio of 22:13:63 respectively. (Analysis by weight).

(c) (i) **The formation of (XXII) by the Diels Alder reaction of perfluorotricyclo-**
    [8,2,0,0^{2,7}]dodeca-2,6,8-triene (XVIII) with but-2-yne

(XVIII) (0·50g., 1·22 mmoles) and but-2-yne (0·071g., 1·29 mmoles) were sealed in vacuo in a 70 ml. Carius tube and heated at 120°C for 72 hours. The products in the tube showed signs of decomposition though g.l.c. analysis (Col.A,

150°C) indicated that 80% of the mixture consisted of a new long retained
compound. Purification by preparative g.l.c. (Col.H, 150°C), gave 11,12-
dimethyltetradecafluorotetracyclo[8,2,2,0^{3,6},0^{2,9}]tetradeca-2,7,11-triene (XXII)
(0.22g., 0.47 mmoles, 49% yield before separation). $C_{16}F_{14}H_6$, which has a Mol.Wt.
464 (m.s.), requires C, 41.4 and H, 1.3%. Found: C, 41.3 and H, 1.5%.
(XXII) was a white solid whose M.Pt. (65/72°C) was not sharp. (XXII) has υ_{max}
2940 (-CH$_3$), 1710 and 1620 (conjugated -CF=CF- and $>$C=C$<$) and 1680 cm^{-1}
(CH$_3$-$\overset{|}{C}$=$\overset{|}{C}$-CH$_3$) and λ_{max} 263 nm (4500).

(ii) Pyrolysis of compound (XXII)

(XXII) (0.200g., 0.430 mmoles) was pyrolysed at 680°C/5x10^{-3} mm to give: (i)
tetrafluoroethylene (0.80 mmoles) and (ii) a solid mixture (0.115g.) analysed
by g.l.c./m.s. (Col.L, 150°C) and shown to consist of, in order of emergence from
the column, a component (ca. 8%), Mol.Wt. 364 and a component (ca. 92%), Mol.Wt.264.
The solid was recrystallised from petroleum ether (40/60) and the major compound
shown to be 2,3-dimethylhexafluoronaphthalene, by comparison of its n.m.r., i.r.,
and m.s. with published data.[163]

4. Oxidation of compound (XX)

(XX) (0.200g., 0.488 mmoles) was added to 30 ml. of dry acetone and potassium
permanganate (0.4g.) and stirred at room temperature for one hour. 60 ml. of
water were added and SO$_2$ bubbled in until decolourisation occurred. The
acetone was removed by distillation under reduced pressure and the aqueous
solution ether extracted continuously for 17 hours. The ether solution was
dried with MgSO$_4$ and distilled to give a solid (0.18g.) whose i.r. confirmed the
presence of a carboxylic acid and whose ^{19}F n.m.r. indicated that the product
contained one fluorine atom less than the starting material and that the CF$_3$
resonance remained.

This solid was then refluxed with a solution of sodium hydroxide (20 ml. of
2N) for 2 hours. The resulting solution was acidified and continuously ether
extracted for 24 hours but only degraded fluorocarbon was obtained.

4.11 <u>The preparation of methylpolyfluorotricyclo[6,2,2,0^{2,7}]dodecatrienes</u>

(a) <u>The reaction of perfluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (178) with</u>

<u>lithium methyl in diethyl ether</u>

Three experiments were performed to regulate the ratio of monomethyl,

dimethyl and trimethyl substituted trienes in the product.   In each experiment

the lithium methyl in diethyl ether (1·0M) was added drop by drop over 10 mins.,

to the triene (178) in 20 ml. of diethyl ether at -78°C.   This mixture was then

stirred at -78°C for half an hour and allowed to warm to 20°C over 15 mins.   The

reaction was monitored by g.l.c. (Col.A, 150°C) and if required the mixture was

again cooled to -78°C and more lithium methyl added.   When the reaction was

complete, 50 ml. of water were added.   The ether layer was separated, dried

(MgSO$_4$) and distilled to leave a fluorohydrocarbon residue which was vacuum

transferred from P$_2$O$_5$.   In experiment 1 the triene (178) (2·7g., 6·6 mmoles)

reacted with lithium methyl (ca. 12·0 mmoles) to give a liquid fluorohydrocarbon

mixture (2·2g.).   In experiment 2 the triene (2·5g., 6·1 mmoles) with lithium

methyl (ca. 4 mmoles) gave (2·2g.) of fluorohydrocarbon and in experiment 3

the triene (4·8g., 11·7 mmoles) with lithium methyl (ca. 30 mmoles) gave (3·5g.)

of fluorohydrocarbon.

The fluorocarbon mixture from experiments 1 and 2 was separated by

preparative g.l.c. (Col.G, 140°C) to give in order of increasing retention time:

(i) 3-methyltridecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (XXIII), a

white solid with a M.Pt. of 37/38°C.   C$_{13}$F$_{13}$H$_3$, which has a Mol.Wt. of 406 (m.s.),

requires: C, 38·4 and H, 0·7%.   Found: C, 38·1 and H, 0·6%.

(ii) 7-Methyltridecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,5,9-triene (XXIV), a

white solid with a M.Pt. 85/86°C and a Mol.Wt. of 406 (m.s.).   Found: C, 38·2

and H, 0·4%.

(iii) 3,6-Dimethyldodecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (XXV) a

white solid with a M.Pt. of 52/53°C.   C$_{14}$F$_{12}$H$_6$, which has a Mol.Wt. of 402 (m.s.)

requires: C, 41·8 and H, 1·5%.   Found: C, 41·6 and H, 1·4%.

(iv) 6-Methyltridecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,3,9-triene (XXVI), a white solid with a M.Pt. of 55/56°C and a Mol.Wt. 406 (m.s.). Found: C, 38·1 and H, 0·4%.

(v) 3,7-Dimethyldodecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,5,9-triene (XXVII), a white solid with a M.Pt. of 78·5°C and a Mol.Wt. 402 (m.s.). Found: C, 41·6; H, 1·8 and F, 57·0%. C$_{14}$F$_{12}$H$_6$ requires F, 56·7%.

Only sufficient of compounds (XXIV) and (XXV) were obtained to compare i.r. and g.l.c. with authentic samples obtained from experiment 4.11(b). An analysis of percentage yields is given in Table 19, along with i.r. and u.v. data.
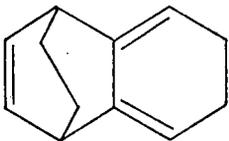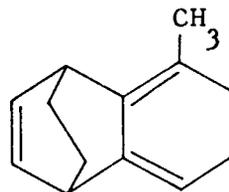
The mixture from experiment 3 was separated initially by g.l.c. (Col.H, 150°C) to give in order of emergence (i) (XXVII) and (ii) a mixture of trimethyl substituted trienes. The latter were further separated (Col.G, 150°C) to give a mixture of the 3,7,9 (and 10)-trimethylundecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,5,9-trienes, from which the 10-methyl isomer (XXVIII) was obtained pure by recrystallisation from petroleum ether 40/60. (XXVIII) is a white solid M.Pt. 88°C. C$_{15}$F$_{11}$H$_9$, which has a Mol.Wt. of 398 (m.s.) requires C, 45·2; H, 2·26 and F, 52·5%. Found: C, 45·5 and H, 2·5%. None of the other trimethyl substituted trienes were obtained in a pure state.

The percentage yield data from Table 19 have been calculated by analytical g.l.c. using (Col.A, 150°C) and (Col.E, 150°C).

(b) The reaction of 2H,7H-hexadecafluorotricyclo[6,2,2,0^{2,7}]dodeca-9-ene (164) with ∴ lithium methyl in diethyl ether

The olefin (164) (12·5g., 27·8 mmoles) in 40 ml. of diethyl ether was kept at -78°C whilst lithium methyl in diethyl ether (20 ml. of 2M, 40 mmoles) was added drop by drop over 15 mins. The mixture was stirred at -78°C for 30 mins., and then allowed to warm to 20°C over 15 mins. G.l.c. analysis (Col.A, 150°C) indicated the presence of triene (178) and unreacted olefin (164) but no longer retained material. A further 100 mmoles of lithium methyl were added (at -78°C)

TABLE 19

		% Yields			u.v. λ_{max} (ϵ)	i.r. ($>$C=C$<$)
		Expt.1	Expt.2	Expt.3		
	(178)	13	58	-	259 nm (4500) Ref. 163	1767 1742 1703
	XXIII	10	16	-	262 nm (4900)	1767 1725 1660
	XXIV	6	ca.2	-	-	1770 1750 1710
	XXV	1·5	-	-	267 nm (5900)	1767 1690 (weak)
	XXVI	24	17	-	269 nm (4600)	1768 1720 1630
	XXVII	30	5	24	-	1772 1755 1665
	XXVIII	-	-	49	-	1755 1730 1665
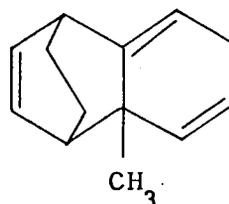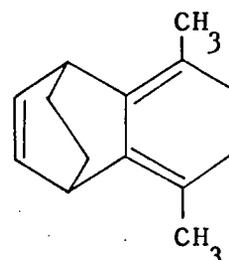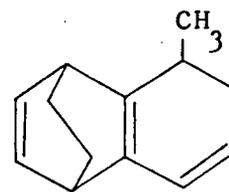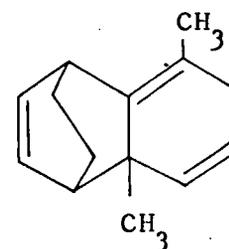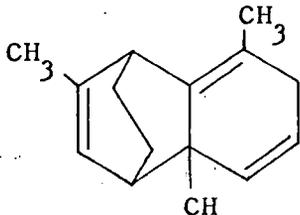
in order to produce a substantial amount of longer retained material. Using the same procedure as in (a) (9·3g.) of a fluorohydrocarbon liquid mixture was recovered. This fluorocarbon liquid mixture was distilled on the concentric tubes apparatus (10 mm) to give: (i) B.Pt. 53 → 58°C a liquid mixture (ca. 0·31g.) shown by i.r. and g.l.c./m.s. (Col.E, 135°C) to consist of 20% triene (178) and 80% olefin (164); (ii) B.Pt. 77 → 81°C a liquid mixture (0·8g.) containing 40% of (XXIV); (iii) B.Pt. 81 → 87°C a liquid mixture (1·0g.) containing 20% of (XXIV) and 60% of (XXV); (iv) B.Pt. 92 → 93°C a mixture that solidified on standing and consisted of 95% of (XXVII) (1·9g.) and (v) a pot residue (5·3g.). Compound (XXVII) was purified by recrystallisation from petroleum ether (40/60). Compounds (XXIV) and (XXV) were partially separated by preparative g.l.c. (Col.G, 135°C) and finally purified on (Col.H, 135°C) to give approximately (0·25g.) of each compound. Analysis by g.l.c./m.s. (Col.J, 230°C) of the pot residue confirmed that the ratio of products in order of emergence was (XXVII): (an unidentified trimethyl substituted triene): (XXVIII): (a trimethyl substituted triene) respectively.

(c) The reaction of perfluorocyclohexa-1,3-diene dimers (158) with lithium methyl in diethyl ether and a competition reaction between the dimers (158) and the triene (178) for lithium methyl

Lithium methyl in diethyl ether (2 cc's of a 2M solution) was added slowly to the dimers (158) (0·73g., 1·6 mmoles) in 10 cc's of diethyl ether at -78°C over a 10 minute period. Using the same procedure as in (a) 0·65g. of a fluorohydrocarbon mixture was obtained and analysis by g.l.c./m.s. (Col.N, 140°C) revealed two major peaks; the first peak (a) was barely resolved and analysis of each side of the peak was consistent with the presence of isomers of Mol.Wt. 444; the second peak (b) was not resolved but analysis of the mass spectral breakdown pattern implied the presence of compounds of Mol.Wt. 440 and of Mol.Wt. 424.

The fluorohydrocarbon mixture was separated by preparative g.l.c. (Col.G, 120°C) into the fractions (a) and (b). Fraction (a) (0·36g.) was a liquid

mixture whose ^{19}F n.m.r. spectrum indicated the presence of two major and some minor components. The ^{19}F n.m.r. spectrum could not be completely interpreted, however, the ratio of tertiary bridgehead fluorines (210 $\rightarrow$ 216 p.p.m.) to sharp vinylic fluorine resonances (150 $\rightarrow$ 153 p.p.m.) was 1:1. The ^1H n.m.r. showed a single peak at 2·0 p.p.m. The i.r. of the liquid mixture revealed υ_{max} 2980 ($-CH_3$), 1765 (CF=CF) and 1725 cm^{-1} (CF=C.CH_3). Hence the products in (a) are consistent with monomethyl substitution at the olefinic moiety of the six membered ring since the spectral characteristics associated with the octafluoro-[2,2,2]oct-2-ene unit are still present.

The second fraction (b) (0·20g.) was also a liquid and analysis by ^{19}F n.m.r. revealed a number of components, nevertheless the presence of the octafluoro-bicyclo[2,2,2]oct-2-ene unit was discernable from the i.r. and ^{19}F n.m.r. data. The u.v. spectrum of (b) suggested the presence of a conjugated diene moiety (λ_{max} 268 nm) and this with the m.s. and ^1H n.m.r. (protons at 4·2 p.p.m.) data infers that some dehydrofluorination of the monosubstituted products (a) had occurred. However, the main products appeared to be the dimethyl substituted dimers (υ_{max} 1675 cm^{-1} CH_3-C=C-CH_3). Integration of the proton n.m.r. signals indicated that the ratio of the dimethyl substituted dimers (CH_3 at 1·9) to the dehydrofluorinated products (CH_2 at 4·2) was 7 : 6.

The competition reaction was performed by the addition of 0·5 cc's of a 1M solution of lithium methyl in diethyl ether to 10 cc's of an ether solution which was at -78°C and contained the dimers (158) (0·32g., 0·71 mmoles) and the triene (178) (1·41g., 3·43 mmoles). Using the same procedure as in (a), the fluorohydrocarbon mixture was obtained and g.l.c. analysis of the products showed that the ratio of monomethyl substituted dimers to monomethyl substituted trienes was 47 : 2 respectively.

4.12 <u>The vacuum pyrolyses of monomethyltridecafluorotricyclo[6,2,2,0^{2,7}]dodeca-</u>

     <u>trienes</u>

(a) <u>6-Methyltridecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,3,9-triene (XXVI)</u>

     The triene (XXVI) (0.440g., 1.08 mmoles) was pyrolysed at 10^{-3} mm and 640°C

to give: (i) a gaseous fraction (1.01 mmoles) shown by i.r. and m.s. to consist

of tetrafluoroethylene and a trace of fluoromethane and (ii) a liquid fraction

(0.339g.) that was shown by g.l.c. (Col.C, 150°C) and g.l.c./m.s. (Col.N, 150°C)

analysis to contain the following components in order of increasing retention time:

(percentages being derived from areas on the g.l.c. trace and being accurate to

within ± 3% of each value).

	Percentage
Starting material, (XXVI), Mol.Wt. 406	ca. 4
An unknown compound of Mol.Wt. 406	ca. 3
An unknown compound of Mol.Wt. 406	ca. 3
1,1,2,2,3,5,6,7,8-nonafluoro-4-methyl-1,2-dihydronaphthalene, (XXXIV), Mol.Wt. 306	10
1,2,2,3,4,5,6,7,8-nonafluoro-1-methyl-1,2-dihydronaphthalene, (XXX), Mol.Wt. 306	77
Perfluoronaphthalene, Mol.Wt. 272	ca. 3

     The liquid fraction (ii) was then separated by preparative g.l.c. (Col.G,

120°C) to give in order of increasing retention time: (iii) (XXXIV) confirmed by

comparison of its i.r. with an authentic sample and (iv) the hitherto unknown

(XXX) which showed the anticipated u.v. and ^{19}F n.m.r.   (The ^{19}F n.m.r. and u.v.

of (XXX) and (XXXIV) are recorded and discussed in Chapter 5).   (XXX) has ν_{max}

1730 (-CF=CF-), 1635 and 1620, and 1515 and 1490 cm^{-1} (fluorinated benzene ring)

and is a white solid M.Pt. 43°C.

(b) <u>3-Methyltridecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (XXIII)</u>

     The triene (XXIII) (0.261g., 0.65 mmoles) was pyrolysed at 10^{-3} mm and 640°C

to give: (i) a gaseous fraction (0.60 mmoles) that was shown by i.r. and m.s. to

consist primarily of tetrafluoroethylene with a trace of fluoromethane and (ii) a liquid fraction (0·195g.) which was shown by g.l.c. (Col.C, 150°C) and g.l.c./m.s. (Col.N, 150°C) analysis to contain the following components in order of increasing retention time (percentages being derived as in 4.12(a)).

	Percentage
Starting material, (XXIII), Mol.Wt. 406	ca. 6·0
An unknown compound of Mol.Wt. 406	ca. 7·0
An unknown compound of Mol.Wt. 406	ca. 7·0
(XXIV), Mol.Wt. 306	71·0
(XXX), Mol.Wt. 306	8·1
Perfluoronaphthalene	ca. 2·0

[The unknown compounds of Mol.Wt. 406 corresponded in g.l.c. retention time to those reported in 4.12(a)]

The liquid fraction (ii) was separated by preparative g.l.c. (Col.C, 120°C) and (XXX) and (XXXIV) were identified by i.r.

(c) Pyrolysis of (XXX)

(0·025g., 0·081 mmoles) of (XXX) was pyrolysed at 640°C and 10^{-3} mm to give a liquid (0·025g.) that was shown by g.l.c. and i.r. to consist of 96% of unchanged (XXX) with a number of more volatile components and a trace of perfluoronaphthalene.

(d) Pyrolysis of (XXXIV)

(0·021g., 0·068 mmoles) of (XXXIV) was pyrolysed at 640°C and 10^{-3} mm to give a liquid (0·021g.) that was shown by g.l.c. and i.r. to be 98% of unchanged (XXXIV) with a number of more volatile components.

CHAPTER 5

## Some Reactions Of Perfluoro-1,2-dihydronaphthalene

INTRODUCTION

5.1 **Orientation and reactivity in nucleophilic substitution in fluorinated benzenes**

Nucleophilic substitution in pentafluorophenyl derivatives C_6F_5X produces in most instances products arising from the displacement of the fluorine atom para to the substituent group X (where X = H, CH_3, SCH_3, CF_3, $N(CH_3)_2$, NO_2, C_6F_5, OC_6F_5 etc.).[220,221,181] When X = NH_2 or O^- substitution occurs almost exclusively at the meta position whilst in a few cases (X = OCH_3 and $NHCH_3$) comparable amounts of meta and para replacement occur. Finally when X = NO_2,[220,221] CO_2H,[223] CHO[222] and NO[224] nucleophilic attack is para to X with most nucleophiles but high ortho replacement occurs with some amines.

Nucleophilic substitution in highly fluorinated systems is considered to be a two step process with the rate determining step, in general, not involving much C-F breaking. The mobility of halogens in displacement from polyfluoro-aromatic compounds is F > Cl > Br and this is consistent with a two step mechanism.[225] In order to account for the orientation of substitution Burdon has proposed that the charge density in the Wheland-type intermediate is greatest at the para position (i.e. (270) makes a larger contribution than (271)).[221]
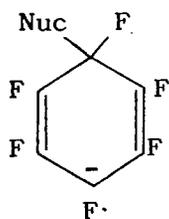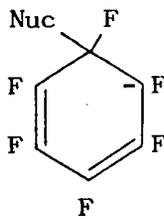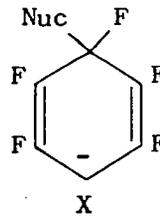
(270)   (271)   (272)

The assumption above has the support of molecular orbital calculations.[226] The rationale for Burdon's argument is that providing electron pair repulsions involving X in (272) are not greater than those involving fluorine in (270) then

para substitution in C_6F_5X will be preferred, even though X may be electron donating and therefore, deactivating as in the case of CH_3. When the substituent X is NH_2 or O^- then electron pair repulsion involving the substituent are more important and the nucleophile enters meta to the substituent.

The ability of the halogen to stabilize an adjacent negative charge is $F < Cl < Br < I \sim H$. The inductive effect of the halogens is much smaller than the I_π repulsive effect and hence $\overline{C}$-F is the least stable arrangement. The generalisation that nucleophilic attack in polyfluorinated benzene occurs in positions that are not para to a fluorine is confirmed by the position of attack (arrowed) in a number of systems.
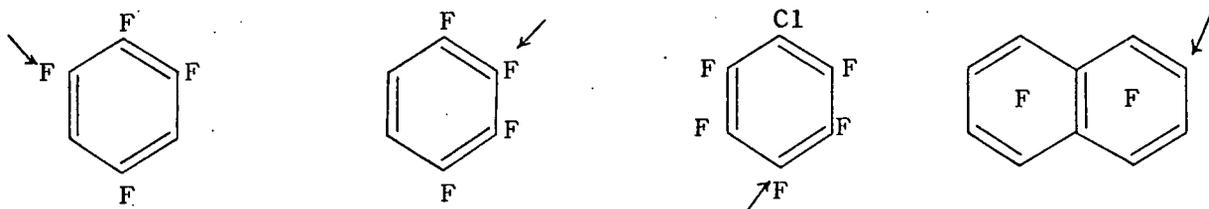
The formation of ortho products occurs only when the nucleophilic amine group has a free N-H bond and when the X substituent of C_6F_5X contains an oxygen atom. Hence high ortho product formation has been attributed to hydrogen bonding in the transition state with a subsequent lowering of activation energy.

The effect of substituents on the rate of attack is that anticipated for nucleophilic aromatic substitution. Electron donating groups deactivate whilst electron withdrawing groups activate. The relative reactivities of $C_6F_5CH_3$, C_6F_5H and $C_6F_5CF_3$ being $0.63 : 1 : 4.5 \times 10^3$, respectively, towards methoxide ion at $60°C$.[227] The relative rates of substitution of $C_6F_5O^-$ in C_6F_5X at $106°C$ in dimethylacetamide are:[225]

X	Relative Rate
CF_3	2.4×10^4
$CO_2C_2H_5$	2.9×10^3
C_6F_5	7.3×10^2
Br	39
Cl	32
H	1
F	0.9

5.2 Preparation and nucleophilic substitution in polycyclic fluoroaromatic

compounds

Perfluoronaphthalene was first prepared by exhaustive fluorination of the

parent hydrocarbon using CoF_3, followed by dehydrofluorination over heated iron

gauze at $500°C$.[172]   Nucleophilic attack by CH_3^-, CH_3O^- and lithium aluminimum

hydride occurs at the β position, in accord with Burdon's hypothesis, whereby

the negative charge on the intermediate will be mainly localised on a carbon

atom involved in ring fusion rather than on carbon bearing fluorine.[228]
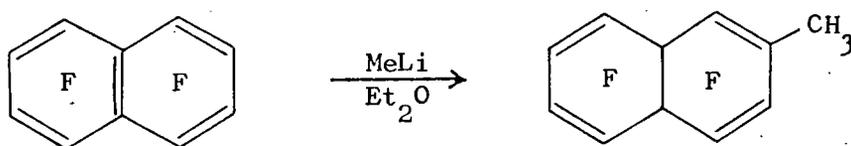
Perfluorobiphenylene is prepared by vacuum pyrolysis of tetrafluorophthalic

anhydride in a silica tube at $750°C$.[229]   The reaction of perfluorobiphenylene

(273) with sodium methoxide in methanol gave primarily 2-methoxyheptafluoro-

biphenylene with a trace of 1-methoxyheptafluorobiphenylene.   The structures

of the products were determined by n.m.r. spectroscopy.
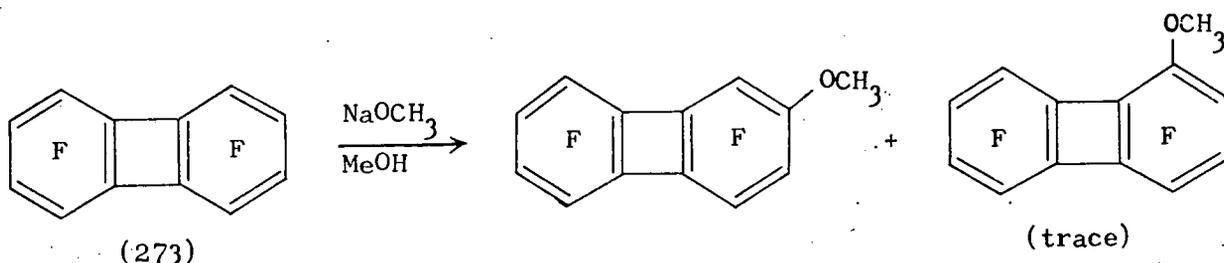
Perfluoroacenaphthylene is prepared in an analogous manner to perfluoro-

naphthalene.[230]   Perfluoroacenaphthylene (274), like acenaphthylene, possesses

considerable double bond character between C1 and C2.   Thus the C1-C2 bond

readily adds bromine and hydrogen and can also be oxidised with potassium

permanganage to give the appropriate diacid.[231]   The reaction of perfluoroace-

naphthylene with sodium methoxide in methanol, hydrazine hydrate in ethanol,

lithium aluminium hydride in ether and aqueous ammonia resulted in replacement

of the 3-fluorine.   The structure of (275), the 3-methoxy compound, was

established by n.m.r. spectroscopy.
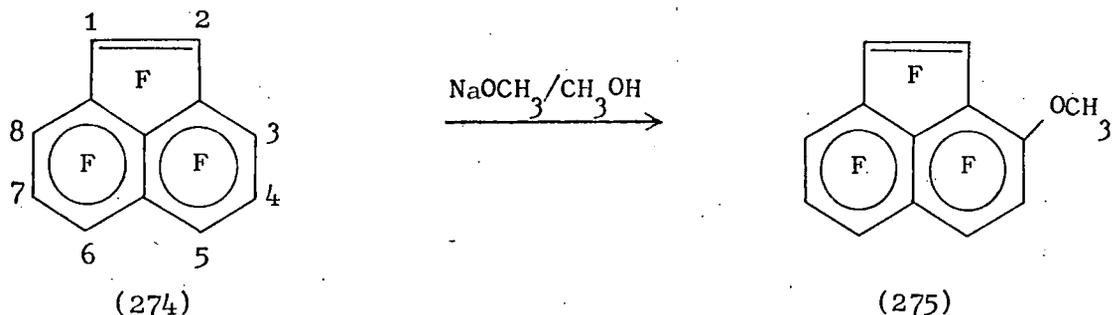
Subsequent addition of methoxide to (275) occurs at the 8 position to give the dimethoxy compound, to which methoxide adds at the 5 position. Finally the 3,5,6,8-tetramethoxytetrafluoroacenaphthylene is obtained.

Perfluorophenanthrene is prepared by defluorination of perfluoroperhydro-phenanthrene over Fe_2O_3.[232] The nucleophilic substitution pattern proceeds by the replacement of the 2- and 7-fluorines with the structures being confirmed by n.m.r. spectroscopy and chemical means.

X = MeO or Me_2N
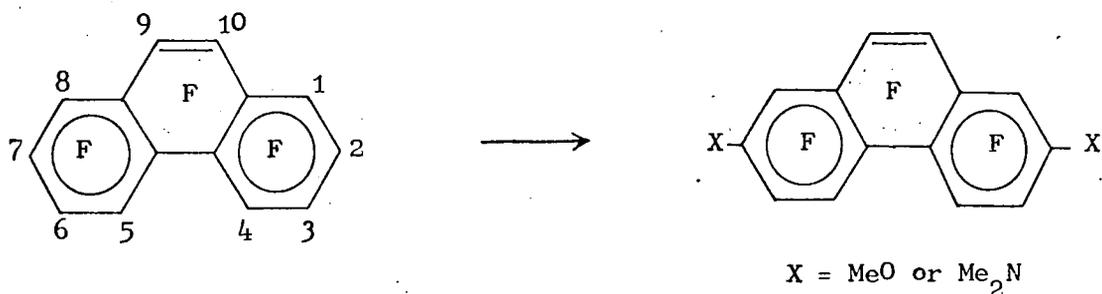
Apart from methods developed in this work (cf. Experimental Sections: Chapters 4 and 5) the preparation of 1,2- and 1,4-perfluorodihydronaphthalenes has been reported by Shteingarts and co-workers and the intial step involves electrophilic attack by the nitronium ion on perfluoronaphthalene. A 61% yield of the nitrofluorination product (277) is obtained when the reaction is performed in conc. HNO_3 (11 mole %) and HF, along with a 13% yield of the isomeric hexa-fluoronaphthoquinones (278) and (279).[233] The participation of NO_2^+ is confirmed by the formation of (277) when perfluoronaphthalene is heated with NO_2BF_4 in sulpholane. The hexafluoronaphthoquinones are thought to arise from the attack by water on the nucleophilic intermediate (276).

(276)   (277)

(278)   +   (279)
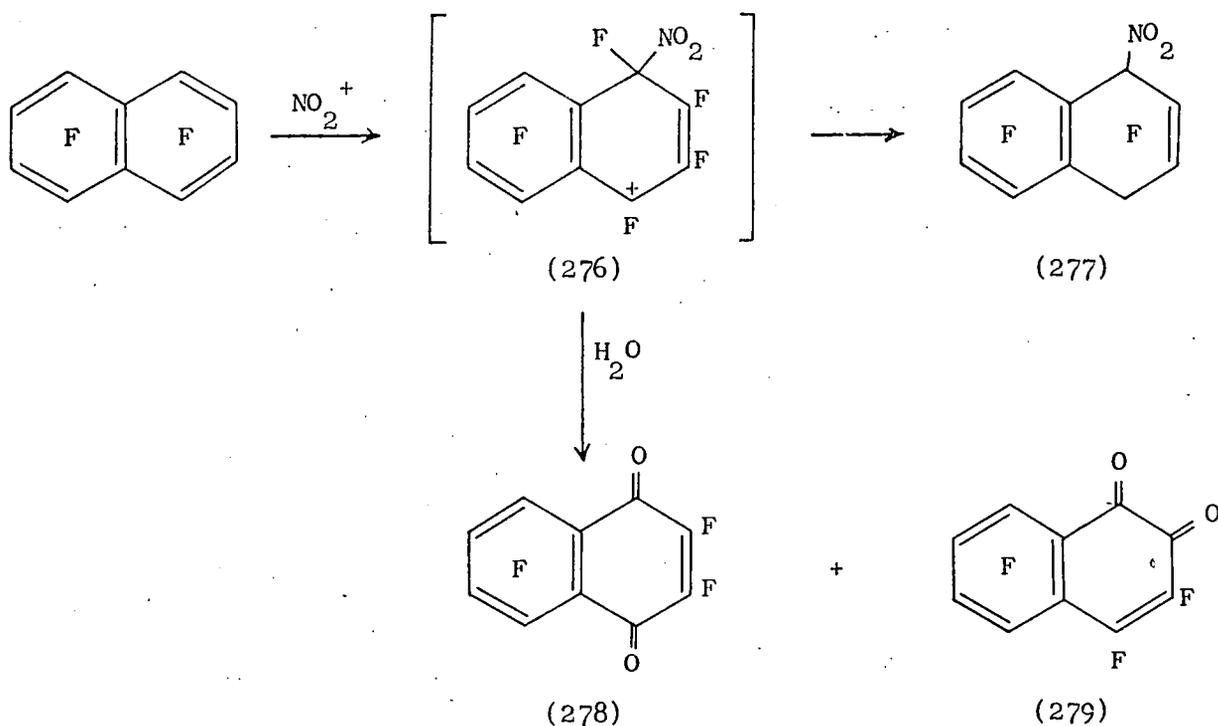
The required perfluorodihydronaphthalenes are obtained by the reaction of SF$_4$ in the presence of HF catalyst on the quinones (278) and (279).[234]   At 140°C, hexafluoro-1,2-naphthoquinone (279) is converted into a mixture of perfluoro-1,2-dihydronaphthalene (XXI, 43%) and perfluoro-1,4-dihydronaphthalene (XIX, 35%). At 75-140°C, hexafluoro-1,4-naphthoquinone is converted into (XIX, 56%) and (XXI, 6%).

The nucleophilic substitution pattern for perfluoro-1,4-dihydronaphthalene involves the initial replacement of the C6 fluorine in the benzene ring.[235]

(280)   (281)
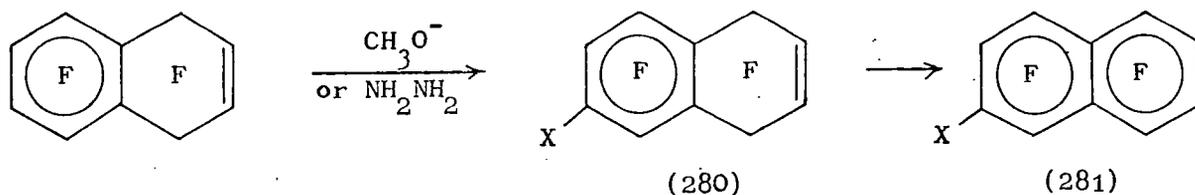
(a)   X = OCH$_3$;   (b)   X = NHNH$_2$

The position of substitution was confirmed by chemical means.   Defluorination of (280a) using Mg in C$_2$H$_4$Br$_2$ gave the known 2-methoxyheptafluoronaphthalene (281a). The action of HI on (280b) gave the known 2-aminohexafluoronaphthalene (281b).

Nucleophilic attack by $C_6F_5^-$, piperidine and ammonia on perfluoro-1,4-dihydronaphthalene also gave the monosubstituted product derived from the replacement of the C6 fluorine.[235]   The position of substitution was ascertained by comparison of the ^{19}F n.m.r. chemical shifts with those produced by the corresponding substituent in C_6F_5X.   This substituent shielding effect has been used with remarkable success to predict the chemical shifts in ortho-disubstituted tetrafluorobenzenes[93] and in other tetra- and tri-fluorobenzenes.[232,236]   Thus if substitution occurred at C5 one ortho substituent shift would be observed, whereas substitution at C6 would give two ortho shifts.   Shteingarts claims that nucleophilic substitution by CH_3^- occurs preferentially at the C6 position, whilst the disubstitution product arises from subsequent attack at a vinylic position.[235]   However, Shteingarts could not analyse the monosubstitution product and in view of the poor separation technique employed (distillation in vacuo) it is thought by the author that the monosubstitution product may well have been a mixture of vinylic and C6 substitution products.   (A critique of Shteingart's work and in particular the inaccuracy of one reported reaction is given in the Discussion).   The disubstitution product with pentafluorophenyl lithium arises from replacement of the C6 and C7 aromatic fluorines.[235]

Perfluoroindene has been prepared by the pyrolysis of perfluorotricyclo-[5,2,2,0^{2,6}]dodeca-2,5,8-triene, which eliminates tetrafluoroethylene at 620°C/ 10^{-3} mm.[153]   Nucleophilic substitution in perfluoroindene occurs preferentially at the vinylic sites, both monosubstitution products were obtained with sodium borohydride and sodium methoxide, whilst attack by CH_3^- occurred at only one vinylic site.[153]

DISCUSSION

5.3 Nucleophilic substitution in perfluoro-1,2-dihydronaphthalene

Two nucleophilic substitution reactions of perfluoro-1,2-dihydronaphthalene were investigated and the site of attack was found to be dependent upon the nucleophile. Only one monosubstituted product, (XXXI), was obtained from the reaction with sodium borohydride and this resulted from the replacement of the vinylic fluorine at C3. A small quantity of the dihydro-substituted product, (XXXII), was also obtained, presumably by attack at the C7 position of (XXXI).

(XXXI)   (XXXII)
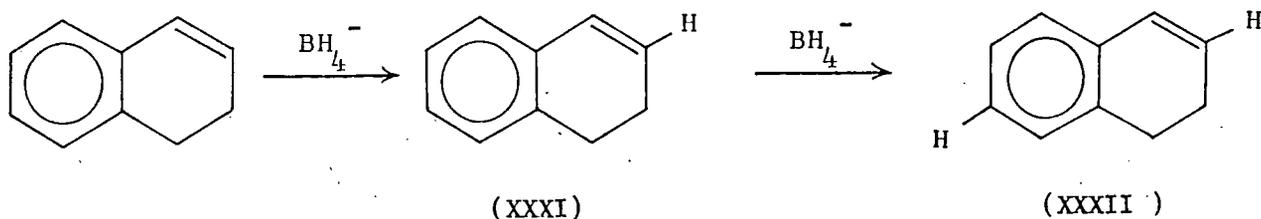
The reaction of lithium methyl with perfluoro-1,2-dihydronaphthalene gave four monosubstituted products, the major of which occurred from nucleophilic attack at the C6 and C7 positions in the aromatic ring.

(XXXIII)   (XXXIV)

1   1

(XXXV)   (XXXVI)

4·4   2·2
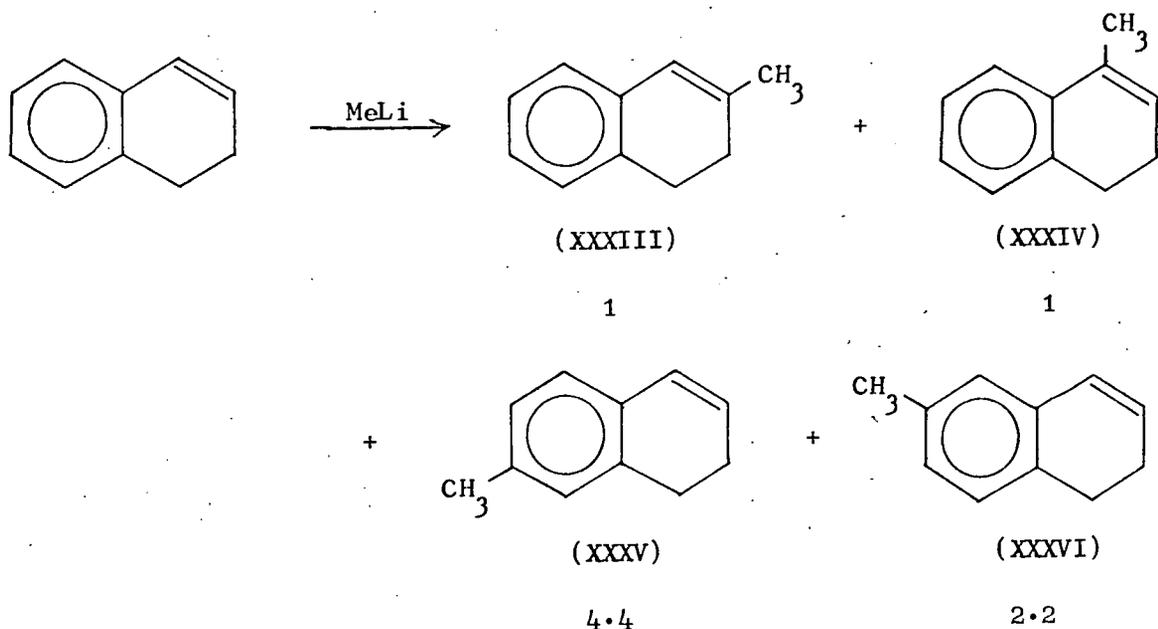
Analysis of the i.r. spectrum of the mixture of dimethyl substituted products indicated that about 95% of the isomers had one substituent in the vinylic position and one substituent in the aromatic ring, presumably at the C6 or C7

position.   The remaining 5% had both methyl substituents in the aromatic ring.

The mass spectra of compounds (XXXI) $\longrightarrow$ (XXXVI) were consistent with the

assigned structures and the mass spectral fragmentation pattern was supported by

metastable ions.   Unfortunately difficulty was obtained with C and H analyses of

these compounds as for all compounds the presence of nitrogen was indicated.

This suggests that the compounds were not completely breaking down during the

combustion stage but this problem was not resolved in spite of efforts by the

technical staff.   In most instances only small amounts of pure material were

obtained and fluorine analysis was only carried out on (XXXI), the inseparable

mixture of (XXXV) and (XXXVI), and the mixture of dimethyl substituted products

all of which gave the correct values.

The i.r. spectra of these compounds contained pertinent information.   The

conjugated perfluorodihydronaphthalene (XXI) has the CF=CF absorption at 1730 cm^{-1};

however, substitution by H at the vinylic site causes a lowering of this

frequency to 1682 cm^{-1} in (XXXI) and to 1687 cm^{-1} in (XXXII); whilst substitution

by CH$_3$ at the vinylic site results in the CF=C.CH$_3$ absorption occurring at

1695 cm^{-1}.   Concomitant with this information, it was observed that substitution

at the vinylic position caused no change in the fluorinated benzene ring

absorption at 1520 cm^{-1}, whereas substitution in the aromatic ring resulted in

the highest aromatic ring absorption frequency occurring 25 cm^{-1} lower at 1495

cm^{-1}.   All the compounds have two absorptions between 1600 and 1640 cm^{-1} and

these are presumably overtone and/or combination modes.   These absorptions occur

at 1620 and 1635 cm^{-1} for (XXI); whereas for compounds with substituents in the

aromatic ring these occur at slightly lower values (e.g. at 1600 and 1620 cm^{-1}

in the mixture of (XXXV) and (XXXVI)).

As mentioned in Chapter 4.7 the u.v. and ^{19}F n.m.r. spectra of (XXX) will

be discussed along with those belonging to the nucleophilic substitution products.

All the compounds (XXX) $\longrightarrow$ (XXXVI) and the parent compound (XXI) possess very

similar and characteristic u.v. spectra (cf. Table 20).   In general most of these

TABLE 20

U.v. spectral data for perfluoro-1,2-dihydronaphthalene and
its substituted derivatives (XXX) $\longrightarrow$ (XXXVI)

The data in this table is tabulated in the form: 268 (8000) $\equiv \lambda_{max}$ 268 nm (ϵ = 8000)

A superscript 's' after the wavelength denotes a shoulder.
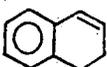
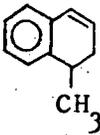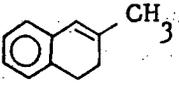| Structure					
(naphthalene-type)		260 (8300)	267^{s} (7200)	293 (6300)	301 (5300)
(H substituted)	252^{s} (6100)	260 (6800)	270^{s} (5200)	291 (4300)	301 (3900)
(H, H substituted)		261 (6700)		295 (4000)	303 (3800)
(CH_3 substituted)	252^{s} (6100)	260 (7000)	269^{s} (5500)	290 (3100)	295 (3000)
(CH_3 substituted)	254^{s} (6600)	262 (7900)	271^{s} (6600)	294 (5100)	303 (5000)
(CH_3 substituted)	253^{s} (7100)	260 (7700)		294 (6100)	303 (5200)
A mixture of (CH_3, 66%) + (CH_3, 33%)		263.5 (5700)		297.5 (4400)	306 (4000)
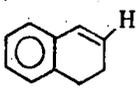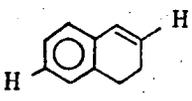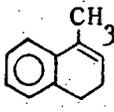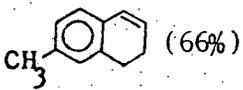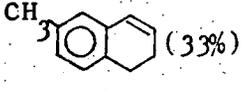
spectra have maxima between 260 and 264 nm (5700-8300); 291 and 298 nm (3000-6300);
and 301-306 nm (3900-5300). Also most of the spectra show shoulders at 252-254 nm
and 267-271 nm.

The u.v. spectra of 1,2-dihydronaphthalene and its perfluoro-analogue are not too dissimilar. The spectrum of 1,2-dihydronaphthalene consists essentially of one broad absorption with a maxima at 262 nm (ϵ = 10200), however, an inflexiom occurs at 273 nm (ϵ = 1000) and there is a narrow band between 290 and 300 nm (λ_{max} 296 nm; ϵ = 470).[240] The spectrum of perfluoro-1,2-dihydronaphthalene shows four distinct absorption bands at 260 nm (ϵ = 8300), 267 nm (ϵ = 7200), 293 nm (ϵ = 6300) and 301 nm (ϵ = 5300); there is also a weak inflexion at 252 nm (ϵ = 6800). Hence the main difference between the two spectra lies within the extinction coefficients although absorption by the perfluorocarbon does extend to slightly longer wavelengths (e.g. at 315 nm; ϵ = 800). Very similar trends are found on comparing the u.v. spectra of naphthalene[102] with that of perfluoro-naphthalene.[228]

The n.m.r. spectral data for the parent compounds and its substituted derivatives (XXX) $\longrightarrow$ (XXXVI) are recorded in Table 21. As previously asserted in Chapter 4.6 partial assignment of the resonances in the perfluorodihydro-naphthalene (XXI) is made possible by the two large coupling constants, $J_{F_4F_5}$ = 65 Hz and $J_{F_1F_8}$ = 31 Hz. Without the presence of these two large coupling constants it would have been impossible to accurately assign the position of substitution. That these coupling constants are accurately assigned can be assessed from compound (XXXIV) where methyl substitution at C4 results in the loss of the 65 Hz coupling constant and from compound (XXX) where methyl substitution at C1 causes the collapse of the well defined doublet of the CF_2 fluorines. (The additional J_{HF} coupling constant of 22 Hz results in the C1 fluorine resonance in (XXX) becoming a broad unresolved band 60 Hz in width).

Further information that was required for the assignment of the site of substitution in the aromatic ring was the shift positions occurring in the pentafluorophenyl derivatives C_6F_5X; these are tabluated below with respect to the resonance signal of hexafluorobenzene.[236]

	ortho	meta	para
X = H	-23.7	-0.2	-8.4
X = CH$_3$	-18.8	+1.5	-3.2

TABLE 21

N.m.r. spectral parameters for perfluoro-1,2-dihydronaphthalene
and its substituted derivatives (XXX) → (XXXVI)

	CF_2 at C1	CF_2 at C2	Aromatic/Vinylic Fluorines	Protons Coupling Constants
(XXI)	116·9	125·8	C4 and C5 at 139·6(1)/140·6 (1) C8 at 136·1 (1) 147·1 (1), 149·2 (1) and 159·3 (1)	$J_{F_4F_5}$ = 65 Hz $J_{F_1F_8}$ = 31 Hz
(XXXI)	117·6	113·4	C4 at 107·6 (1) C5 at 137·4 (1) C8 at 136·6 (1) C6 and C7 at 148·2 (2)	H at 5·5 (ext. T.M.S.) $J_{F_4F_5}$ = 67 Hz $J_{F_1F_8}$ = 31 Hz
(XXXII)	121·6	113·9	C4 at 106·9 (1) C5 at 141·6 (1) C8 at 112·3 (1) C6 at 125·0 (1)	H at 6·4 (1) and 7·7 (1) $J_{F_4F_5}$ = 68 Hz $J_{F_1F_8}$ = 32 Hz
(XXX)	180·8 (1) J_{HF} = 22 Hz	δ_A 115·8 (1) δ_B 125·8 (1) J_{AB} = 264 Hz	C4 and C5 at 141·8 (1)/142·5 (1) C8 at 138·6 (1) 151·2 (1), 153·6 (1) and 162·5 (1)	CH_3 at 2·0 $J_{F_4F_5}$ ≃ 65 Hz
(XXXIII)	120·7	121·8	C4 at 114·5 (1) C5 at 138·8 (1) C8 at 136·8 (1) C6 and C7 at 148·7 (1)/149·9 (1)	CH_3 at 1·8 (ext T.M.S.) $J_{F_4F_5}$ = 65 Hz $J_{F_1F_8}$ = 32 Hz
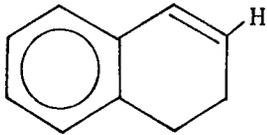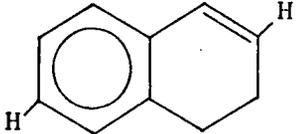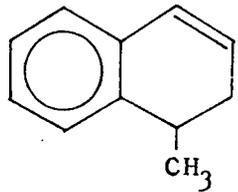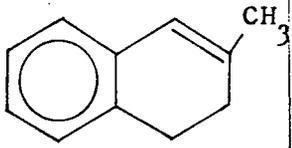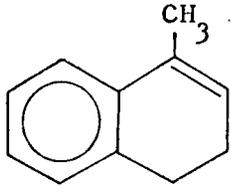
	CF_2 at C1	CF_2 at C2	Aromatic/Vinylic Fluorines	Protons Coupling Constants
(XXXIV)	120.7	129.9	C3 and C5 at 134.1 (1)/136.8 (1) C8 at 136.8 (1) C6 and C7 at 148.7 (1)/154.3 (1)	CH_3 at 1.9 $J_{F_1F_8} \simeq$ 30 Hz
(XXXV)	125	116.0	C3 at 161.0 (1) C4 and C5 at 141.2 (1)/143.1 (1) C6 at 128.4 (1) C8 at 125 (1)	CH_3 at 2.7 $J_{F_4F_5}$ = 67 Hz
(XXXVI)	116.4	116.0	C3 at 162.9 (1) C4 at 139.8 (1) C5 at 117.6 (1) C7 at 130.1 (1) C8 at 142.2 (1)	CH_3 at 2.7 $J_{F_4F_5}$ = 68 Hz $J_{F_1F_8} \simeq$ 32 Hz
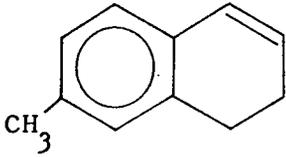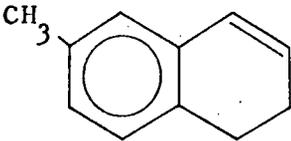
[All spectra recorded in CD_3COCD_3 solution apart from (XXI) and (XXXI) which were recorded as neat liquids]

It can be seen that the largest shifts occur for the fluorines ortho to the substituent.

Hence the site of substitution in the aromatic ring can be determined since substitution at C5 would lead to a loss of the 65 Hz coupling constant; substitution at C6 should cause a movement of about 20 p.p.m. downfield for one of the aromatic and the C5 doublet resonances; substitution at C7 should cause a movement of about 20 p.p.m. downfield for one of the aromatic and the broad C8 resonances; whilst substitution at C8 would cause a collapse of the C1 31 Hz doublet. A change in the width of the C8 fluorine resonance is also anticipated on substitution at C7. Ortho fluorines in polyfluorobenzenes have coupling

constants of about 20-24 $Hz^{236,241}$ and hence substitution of CH_3 at C7 should result in a reduction of at least 20 Hz in the C8 fluorine resonance width. (In $C_6F_5CH_3$, $J_{F_2F_6}$ = 1.9 Hz and $J_{F_2F_5}$ = 8.0 Hz).[241] Substitution of H at C7 should not result in such a large reduction in the width of the C8 fluorine resonance as the ortho J_{HF} coupling constant in C_6F_5H is about 11 Hz.[236]

The assignment of resonances for compound (XXXI) was straightforward apart from the fact that half of the limb of the C5 doublet at 137.4 was obscured by the C8 resonance at 136.6. Thus the coupling constant could be measured accurately only from the C4 resonance. Comparing (XXXII) with (XXXI), substitution in the aromatic ring causes an ortho shift of one resonance by -23.2 whilst the C8 resonance moves by -24.3. That the site of substitution in (XXXII) is at C7 is confirmed by the anticipated reduction in the width of the C8 fluorine resonance to about 100 Hz.

The assignment of resonances and the determination of the site of substitution in compounds (XXX), (XXXIII) and (XXXIV) posed no difficulties. However, analysis of the inseparable mixture of (XXXV) and (XXXVI) was very difficult owing to the overlapping of non-coincident resonances and was further complicated by the ratio being 2:1 respectively. The correct ratio for the mixture was ascertained by integration from the well separated vinylic resonances at C3 and aromatic resonances in the 128-130 region. It was impossible to completely assign the resonances of both isomers from the 56.4 MHz spectrum and successful analysis was only achieved from the higher resolution and better integration of the 84.7 MHz spectrum. For both isomers the CF_2 fluorine resonances at C2 overlap exactly at 116.0 and this signal is only 30 Hz in width. The minor isomer (XXXVI) has a 30 Hz doublet for the CF_2 resonance at C1 and this is clearly visible at 116.4. However, the corresponding doublet for (XXXV) cannot be measured as the CF_2 absorption is coincident with that for the C8 absorption of (XXXV) at 125. The site of substitution in (XXXVI) is established firmly from the shift of the C5 resonance, which is the expected 68 Hz doublet, being -22 or -23 and in

agreement with this the C8 fluorine width remained at about 120 Hz. The other ortho fluorine shift for (XXXVI) is -17 or -19 and the large 68 Hz coupling constant could be measured accurately only from the C5 absorption at 117·6. For compound (XXXV) the C6 ortho shift is -19 or -21 whilst the C8 ortho shift is -15 or -16. The assignments for (XXXV) are unambiguously confirmed by the reduction in the width of the C8 fluorine resonance at 125 to about 90 Hz. The C8 absorption for (XXXV) must occur at 125 since the C6 absorption at 128·4 is a broad unresolved resonance of only 50 Hz width. The large 67 Hz coupling constant of (XXXV) was measurable from both the C4 and C5 absorptions. In order to confirm the assignments attempts were made to develop an alternative synthesis in the hope that the mixture would contain a different ratio of (XXXV):(XXXVI). Unfortunately the two different approaches chosen were unsuccessful [cf. Chapter 4.12(a) and 4.12(b)].

The ^{19}F n.m.r. assignments for the compounds (XXI) and (XXX)→(XXXVI) are in mutual agreement. It is worth noting that substitution in the non-aromatic ring has little effect on the chemical shift position of the C8 fluorine resonance which is found between 136·1 and 138·8, whilst two unassigned resonances are always found between 147 and 154. It may well be that the latter resonances belong to aromatic fluorines and hence that the C3 vinylic resonance in (XXI) occurs at 159·3. This assertion finds support from the chemical shift positions of the C3 vinylic fluorines in (XXXV) and (XXXVI) which unambiguously occur at 161·0 and 162·9 respectively.

The statement by Shteingarts that CH_3^- attack on perfluoro-1,2-dihydro-naphthalene occurs only in the aromatic ring is incorrect.[235] Shteingarts has given no validity for this statement although more information was promised in 1970. At this point it was essential to consider why Shteingarts had incorrectly reported this reaction and why he could not analyse the monomethyl substitution product of perfluoro-1,4-dihydronaphthalene (cf. Introduction). Although Shteingarts has only given a preliminary report on these reactions it is likely that his separation

technique involved distillation in vacuo since this is the only reported technique employed in the paper published on the orientation of nucleophilic substitution in perfluorodihydronaphthalenes.[235]   This method would not separate the vinylic and aromatic substituted monomethyl perfluoro-1,2-dihydronaphthalenes as they are all of similar volatility.   Indeed it is doubtful if this technique could even separate the monomethyl compounds from either the starting materials or the dimethyl substituted compounds.   It would appear that Shteingarts has not obtained many of these compounds in a pure state;   in this manner it would be possible to ignore the effects of minor components in the i.r. and n.m.r. spectra.   Thus knowing that the major dimethyl substituted product for perfluoro-1,2-dihydronaphthalene arises from replacement of one aromatic and one vinylic fluorine resonance, any i.r. band at 1695 cm^{-1} in the monomethyl products would be merely dismissed as a consequence of contamination by dimethyl substituted compound.

Shteingarts also claims that the nucleophilic substitution reaction of perfluoro-1,2-dihydronaphthalene with sodium methoxide and piperidine gives rise to only C6 and C7 substitution products.[235]   Again the mixture of components were obtained by distillation in vacuo and the claim that the position of substitution can be determined from ^{19}F n.m.r. chemical shift data seems very dubious.   The ^{19}F n.m.r. data were recorded on a Varian machine operating at 56·4 MHz but no measurements of the large 65-68 Hz 'peri' fluorine coupling constants were reported.   (This is particularly surprising since in the nine spin system of the monosubstituted perfluoro-1,4-dihydronaphthalenes Shteingarts claims to have assigned in general five and in one extreme case nine coupling constants all of of which are 15-22 Hz in magnitude.   Although these values are in agreement with ones recorded in the literature it seems unlikely that any could have been unambiguously established).   The chemical shifts of these monosubstituted perfluoro-1,2-dihydronaphthalenes are not accurately recorded (e.g. for one compound the C8 fluorine is reported at -40 to -44, with respect to C_6F_6) and no

ratio of the C6:C7 substitution products is given.   It may well be that

Shteingarts, largely by intuitive guesswork, has once again assessed correctly

the major sites of substitution for both nucleophiles but on the basis of the

unreliability of his previous work and the inadequacy of his separation

technique, nucleophilic attack by sodium methoxide and piperidine at the vinylic

sites cannot be totally ruled out.

Obviously Shteingarts claims that nucleophilic substitution in perfluoro-1,4-

dihydronaphthalene occurs only in the C6 position requires treating with a certain

amount of circumspection and in particular it seems likely that with CH_3^- a

certain amount of vinylic replacement occurs.   It may well be that the major

product does arise from C6 replacement but these reactions require reinvestigation

with more sophisticated separation techniques in order to unambiguously establish

the nucleophilic substitution pattern.

5.4   Nucleophilic substitution in polyfluoroaromatics

Burdon's theory successfully rationalises the reactions of polyfluorobenzenes

with nucleophiles[221] and has been extended successfully to explain nucleophilic

substitution in perfluoronaphthalene[228] and perfluorobiphenylene.[229]   Essentially

the theory is founded upon a consideration of the energy of the proposed 'Wheland-

type' carbanion intermediates (cf. Introduction).   The activation energy for

attack at the various positions is assumed to be primarily dependent upon the

more unfavourable I_π repulsive interaction generated by the presence of a fluorine

para to the position of attack.   Although this approach cannot be the whole

story it works particularly well for polyfluorobenzenes.   However, Burdon's

theory is not sufficiently sophisticated to explain the orientation of substitution

in perfluoroacenaphthylene[231], perfluorophenanthrene[232], perfluorostyrene[239],

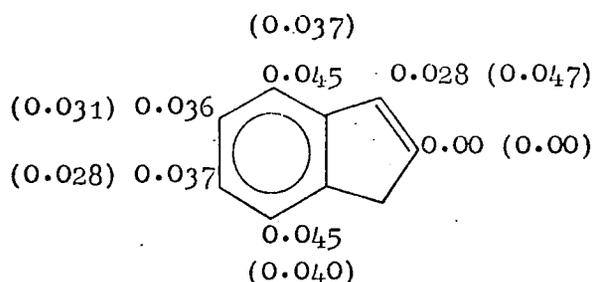perfluoroindene[163] and perfluoro-1,2-dihydronaphthalene.

In a recent paper by Chambers et al the relative reactivity of a number of

polyfluorobenzenes towards methoxide ion have been reported.[242]   These are

quoted overleaf:

Rate: 1   ~ 1 2.35×10^{-2} 8×10^{-3} ~ 10^{-4}
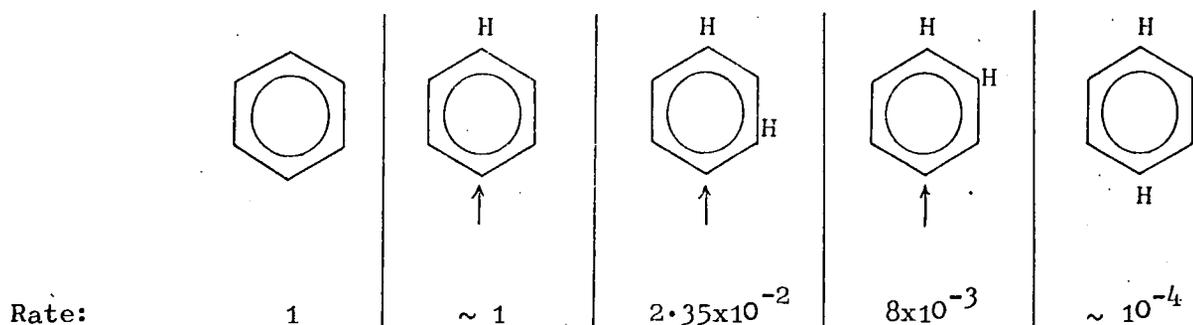
The nucleophilic replacement by methoxide occurs at the arrowed positions and this

is in accord with Burdon's hypothesis.   Chambers et al conclude from the rate

data that there is an activating influence by fluorine in the order of meta >

ortho > > para and propound that a reappraisal of the Burdon theory is warranted.

However, this argument seems unfounded to the author since no assessment of the

factors affecting the relative activation energies is presented and this must

surely be the major consideration in a discussion on relative rates.   The

important factors, which determine the activation energies and relative rates,

are the energies of the intermediate carbanions and ground state energies of the

reactants.   [An activation energy difference of only 3 Kcals/mole can result in

a specificity of at least 99:1].[124]   In spite of the claims by Chambers et al

to the contrary,[242] it seems to the author that the rate data gives very little

further insight into nucleophilic substitution in polyfluorobenzenes.

It would seem that a simple qualitative generalisation for nucleophilic

substitution in polyfluoroaromatics is not available.   The substitution pattern

in a particular polycyclic fluoroaromatic appears to be rather specific for that

compound.   However, molecular orbital calculations CNDO/2 of localization

energies (i.e. the energy difference between the starting materials and Wheland

intermediates) have been used to give insight into the substitution pattern in

perfluoroindene.[243]   After the solvation energy factors for the intermediate

anions had been included in the theoretical computation, the model for H^-

substitution in perfluoroindene was found to predict that the reactivity of the

vinylic sites was greater than that of the aromatic sites.   The calculations

obtained for nucleophilic attack by H^- at a particular site in perfluoroindene

are shown below. The localization energies are given in atomic units (a.u.) and the values represent the difference in activation energy for substitution at a particular site with the most reactive site being at C2 (0.00).

$$(0.037)$$
$$0.045 \quad 0.028 \quad (0.047)$$
$$(0.031) \quad 0.036$$
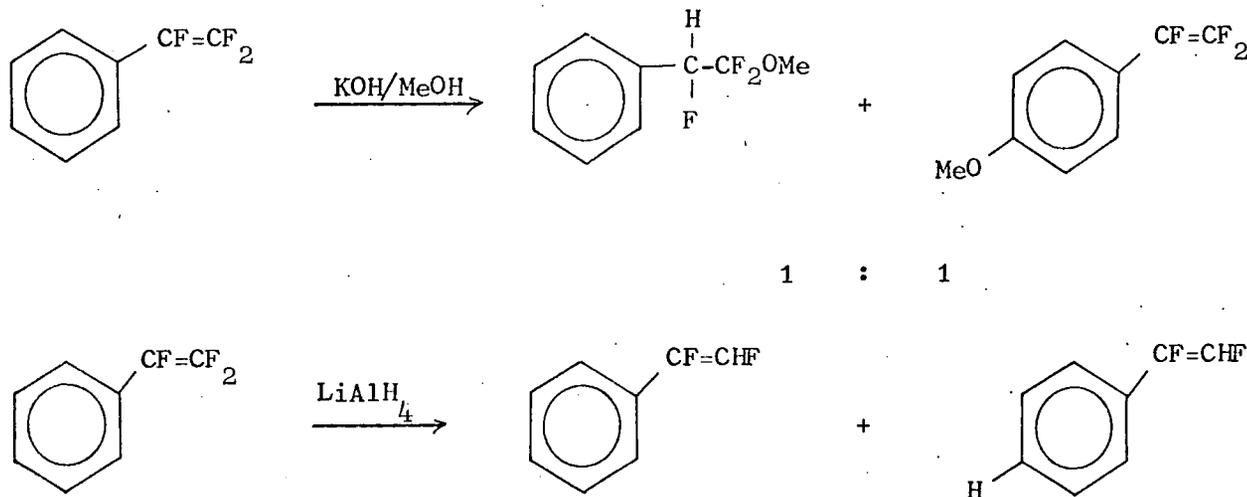$$(0.028) \quad 0.037 \qquad 0.00 \quad (0.00)$$
$$0.045$$
$$(0.040)$$

The values in brackets are those obtained before solvation factors were considered. Attack at C3 has the largest compensation from solvation owing to the development of a highly localised charge at the C2 position of the intermediate carbanion. The vinylic site at C3 is predicted to be only slightly more reactive than the C5 and C6 aromatic positions, however, in reality the vinylic positions are of similar reactivity towards attack by H^-.[165]

The initial attack by H^- on perfluoro-1,2-dihydronaphthalene occurs only at the C3 position and it would be of interest to ascertain whether MO calculations are capable of predicting this site of attack. However, in view of the calculations performed with perfluoroindene, it is perhaps not surprising that the homologue (XXI) undergoes nucleophilic substitution with CH_3^- both at the vinylic and aromatic positions, since the more reactive nucleophile will be less discriminating between sites of similar localization energy.

The CNDO/2 MO calculations also correctly predict the site of nucleophilic substitution in perfluorobiphenylene and perfluoroacenaphthalene, however, with perfluoronaphthalene the α position is predicted to be marginally more reactive than the β position and although substitution in the aromatic ring was predicted for perfluorophenanthrene, the actual site was incorrect.[243] Clearly this approach to an understanding of nucleophilic substitution in perfluoropolycyclic aromatics is a step in the right direction but a more satisfactory solution will probably be only forthcoming when less approximate MO methods can be applied to molecules of this complexity.

The dependence of the site of substitution upon the nucleophile being used
is not a new phenomenon with perfluoroaromatics and has been previously reported
for perfluorostyrene.[239]

$$\text{Ph–CF=CF}_2 \xrightarrow{\text{KOH/MeOH}} \text{Ph–CHF–CF}_2\text{OMe} \; + \; \text{MeO–C}_6\text{H}_4\text{–CF=CF}_2$$

1 : 1

$$\text{Ph–CF=CF}_2 \xrightarrow{\text{LiAlH}_4} \text{Ph–CF=CHF} \; + \; \text{H–C}_6\text{H}_4\text{–CF=CHF}$$

<u>cis</u> and <u>trans</u> isomers

Hence the nucleophilic substitution pattern of perfluorostyrene is very similar
to that of perfluoro-1,2-dihydronaphthalene. In both cases attack by H^- occurs
solely at the vinylic position of the perfluorocarbon with the disubstituted
product arising via attack in the aromatic ring at the position para to the
olefinic moiety. Again it is the vinylic position more remote from the aromatic
ring that is the more reactive site to attack by H^-; presumably because of the
stabilization associated with the delocalised benzyl anion. The attack by MeO^-
on perfluorostyrene parallels that of CH_3^- on (XXI) in so much as substitution
occurs both at the vinylic and aromatic positions.

Finally a competition reaction between perfluorobenzene and perfluoro-1,2-
dihydronaphthalene (XXI) for lithium methyl was performed at -78°C. The latter
was so reactive that even when perfluorobenzene was present in a ten fold excess
no reliable competition data could be obtained. The dimethyl substituted
products of (XXI) are formed preferentially to methylpentafluorobenzene. These
results are not surprising in the light of the calculations performed on the
homologue of (XXI), perfluoroindene, which was predicted to undergo nucleophilic
substitution more readily than perfluorobenzene.[243]

5.5 Oxidation of perfluoro-1,2-dihydronaphthalene and the mixture of monomethyl substituted derivatives (XXXV) and (XXXVI). The relative stability of the conjugated and non-conjugated perfluorodihydronaphthalenes

Perfluoro-1,2-dihydronaphthalene was oxidised by potassium permanganate in acetone solution at room temperature to give the diacid (XXXXII), which was not hygroscopic and was obtained pure by sublimation. The ^{19}F n.m.r. of (XXXXII) is recorded in Table 22. The elemental analysis of (XXXXII) was correct whilst m.s. gave a top mass peak at 292 (P-CH_2O_2) and the i.r. spectrum showed a carbonyl absorption at 1745 cm^{-1}, whilst the highest absorption corresponding to the fluorinated benzene ring was at 1525 cm^{-1}.
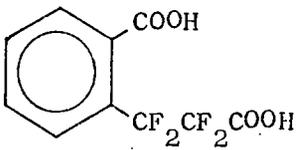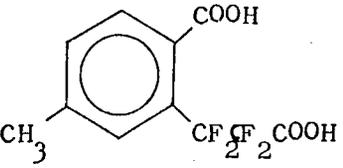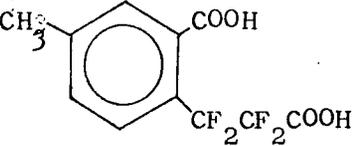
A small amount (0.42g.) of the 2:1 mixture of (XXXV) and (XXXVI) was also oxidised by the same procedure. However, in this instance a small quantity (ca. 0.05g.) of unidentified oxidation product was also formed, presumably being derived from oxidation of the CH_3 group. This minor oxidation product, which had an i.r. spectrum not inconsistent with an aromatic fluorocarbon acid, could be removed by preferential recrystallisation from water. The ^{19}F n.m.r. of the residue remaining after recrystallisation was consistent with a mixture of two products in the ratio of 2:1 and since the starting material was a 2:1 mixture of (XXXV) and (XXXVI), the corresponding diacids (XXXXIII) and (XXXXIV) were assumed to be present in a 2:1 ratio.

Sublimation of the residue and then recrystallisation from dry benzene afforded a very small amount of white solid (0.05g.). The elemental analysis, m.s. and i.r. of this white solid was consistent with (XXXXIII) and/or (XXXXIV). The m.s. showed the parent peak at 334 and the i.r. showed a carbonyl absorption at 1740 cm^{-1} with the absorption of the fluorinated benzene ring occurring at 1490 cm^{-1}.

As pointed out earlier (page 186) substituent shielding effects in C_6F_5X have been accumulated to accurately predict the chemical shift position in some disubstituted tetrafluorobenzenes. However, with 2,3,4,5-tetrafluorobenzoic acid there was a discrepancy of 6 p.p.m. for one resonance.[96] A similar treatment

TABLE 22

^{19}F N.m.r. data for the acids (XXXXII) $\rightarrow$ (XXXXIV)

	CF$_2$	Aromatic Fluorines
(structure) COOH / CF$_2$CF$_2$COOH (XXXXII)	104·6 (2) 117·2 (2)	133·9 (1) 140·6 (1) 151·4 (1) 156·7 (1)
(structure) CH$_3$ / COOH / CF$_2$CF$_2$COOH (XXXXIII)	107·2 (2) 119·9 (2)	114·5 (1) 131·9 (1) 147·2 (1)
(structure) CH$_3$ / COOH / CF$_2$CF$_2$COOH (XXXXIV)	107·2 (2) 119·9 (2)	122·5 (1) 132·6 (1) 136·5 (1)

[All spectra recorded in aqueous solution]

treatment for (XXXXIII) and (XXXXIV), which was based on the assumption that the substituent shielding effect of CF$_2$CF$_2$COOH would be similar to that of CF$_3$ in C$_6$F$_5$X, requires that the ^{19}F n.m.r. signals of (XXXXIII) to occur at 139·9 (F$_3$), 129·3 (F$_4$) and 121·8 (F$_6$), and those of (XXXXIV) to occur at 119·0 (F$_3$), 113·6 (F$_5$) and 140·6 (F$_6$). The inadequacies of this additive shielding parameter approach, particularly for acid derivatives, are clearly highlighted by the experimental values recorded in Table 22.

The oxidation of the mixture of (XXXV) and (XXXVI) unambiguously confirms that methyl substitution was in the aromatic ring.

When heated at 350°C, in the presence of potassium fluoride, perfluoro-1,2-dihydronaphthalene primarily underwent a defluorination reaction to give perfluoronaphthalene (see page 96 and Experimental Section), however a 17% yield

of perfluoro-1,4-dihydronaphthalene (XIX) was also obtained. The small amount

of potassium fluoride became black and it is unlikely that an equilibrium

situation between the two perfluorodihydronaphthalenes was achieved; however,

Shteingarts has studied this equilibrium at $100^{\circ}C$ in a solvent in the presence

of potassium fluoride and has found that the ratio of (XIX) : (XXI) is 3 : 7.

Hence the conjugated perfluorodihydronaphthalene appears to be the more stable

and this is in contrast to the stability of perfluorocyclohexa-1,3-diene being

less than that of the non-conjugated perfluorocyclohexa-1,4-diene.[248]

5.6 Photochemical reactions of perfluoro-1,2-dihydronaphthalene

The gas phase irradiation of a mixture of perfluoro-1,2-dihydronaphthalene

and ethylene gave (XXXXI), the 2+2 adduct in 82% yield (cf. Table 23 for structure).

The assignment of the structure of (XXXXI) was straightforward since the i.r.

spectrum confirmed the absence of an olefinic moiety whilst the absorption at

1526 cm^{-1} together with the u.v. data (λ_{max}, 268 nm ϵ = 1900) confirmed the presence

of a fluorinated benzene ring. The ^{19}F n.m.r. spectrum of (XXXXI) revealed that

the CF_2 groups formed AB systems with coupling constants typical for those found

in a cyclohexane ring. The tertiary fluorines are broad unresolved resonances

90 Hz in width whereas the non superimposed aromatic resonances at 148.8 and 151.4

are 20 Hz triplets. The compound (XXXXI) formed white crystals on

recrystallisation which gave the correct elemental analyses and mass spectrum.

In contrast to perfluoro-1,2-dihydronaphthalene, perfluoroindene undergoes

a different gas phase photochemical reaction with ethylene to give the adduct
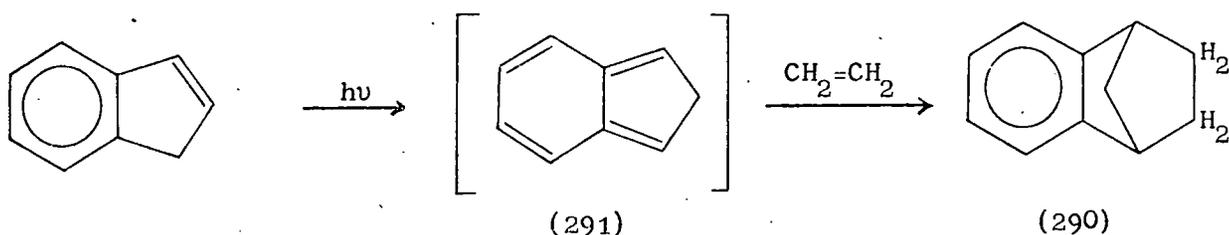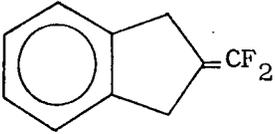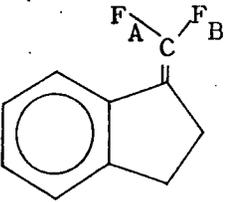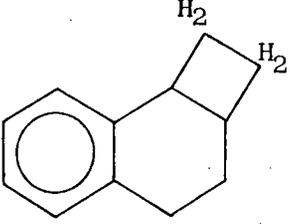
(290).[244]

(291)   (290)

TABLE 23

N.m.r. spectral parameters for the photochemical products (XXXIX) → (XXXXI)

	$-CF_2-$	Aromatic F	
(XXXIX)	86·8 (4)	138·3 (2) 145·0 (2)	Vinylic F 64·8 (2)
(XXXX)	107·1 (2) 112·1 (2)	At C7 134·4 (1) $J_{F_A F_7} = 70$ Hz 139·2 (1) 145·6 (1) 149·6 (1)	Vinylic F F_A at 63·5 F_B at 70·6
(XXXXI)	δ_A 107·3 (1) δ_B 110·6 (1) J_{AB} = 292 Hz δ_A 132·7 (1) δ_B 133·7 (1) J_{AB} = 272 Hz	138·9 (2) 148·8 (1) 151·4 (1)	Tertiary F 155·4 (1) 182·4 (1) Proton 2·2

[(XXXIX) and (XXXXI) run as a solution in CD_3COCD_3 and (XXXX) as a neat liquid]

The percentage yield of (290) has not been quoted but the reaction is thought to proceed via a 1,5 sigmatropic fluorine migration to give the intermediate tetraene (291);[244] however, a radical process involving a 1,2 fluorine shift would be an equally satisfactory interpretation. Another contrast between perfluoro-1,2-dihydronaphthalene and perfluoroindene is that the olefinic moiety of the latter undergoes the 2+2 addition reaction with ethylene at 200°C.[244]

Perfluoro-1,2-dihydronaphthalene on irradiation in the gas phase with light

of 253·7 nm also undergoes a photochemical reaction; the main product was a

viscous liquid, which was shown by g.l.c. analysis to contain a large number of

components. The i.r. spectrum of the viscous liquid suggested that very few

of the components contained an olefinic moiety, the u.v. spectrum was consistent

with a fluorinated benzene ring (λ_{max} 264 nm), whilst the ^{19}F n.m.r. spectrum

was consistent with the presence of $-CF_2-$ moieties. Hence it appears that

polymerisation of the starting material had occurred and only 50% of volatile

liquid remained; however, this contained primarily starting material and only

very small yields of the previously unknown perfluoromethyleneindanes (XXXIX) and

(XXXX), and the previously prepared perfluoro-2 or 3-methylindene (XX).

(XXI)	(XXXIX)	(XXXX)	(XX)
	3%	8%	2%

(XXXIX) was readily separated from the mixture by preparative g.l.c. but (XXXX)

and (XX) were separated only after being recycled through a different column.

The presence of (XX) was established from the ^{19}F n.m.r. data on the mixture of

(XXXX) and (XX), and by i.r. and qualitative u.v. on the pure material. The

structures of compounds (XXXIX) and (XXXX) were determined from their i.r.,

n.m.r., m.s., and u.v. data.

The sample of perfluoro-1,2-dihydronaphthalene that was irradiated

contained a trace of mercury and consequently the possibility exists that the

photoreaction may be mercury sensitized. In the reaction with ethylene the

mercury diffusion pump was not used and all taps to the mercury manometers were

closed, however, the excess perfluorocarbon liquid still contained some of the

photoisomerisation products. Obviously it would have been pertinent to perform

an analytical scale reaction on a mercury free vacuum line. Perfluoro-1,2-

dihydronaphthalene was also irradiated in a solution of perfluoromethylcyclohexane for five hours. A photochemical reaction did occur but only 2% of product was formed and this corresponded in g.l.c. retention time to either (XXXX) or (XX). Although the solution reaction was not further investigated, it seems that the photochemical isomerisation of perfluoro-1,2-dihydronaphthalene does proceed in the absence of mercury vapour.

The determination of the structures for the perfluoromethyleneindanes would not have been possible without prior knowledge of the spectroscopic data for perfluorostyrene which has an i.r. absorption at 1780 cm^{-1} (CF=CF)[245] and u.v. absorption maxima at 235 nm (ϵ = 5700) and 265 nm (ϵ = 1400).[246] The ^{19}F n.m.r. data for perfluorostyrene is recorded below:[247]

X : 171·0	J_{XZ} =	118·8 Hz
Y : 96·4	J_{XY} =	35 Hz
Z : 112·7	J_{YZ} =	61 Hz
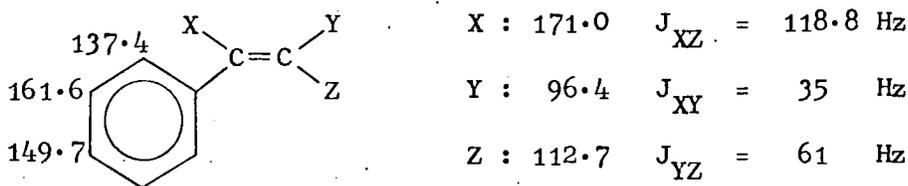
The other imperative information was that the exocyclic ($>$C=CF$_2$) i.r. absorption in perfluoromethylenecyclopentane occurs at 1757 cm^{-1}.

Compound (XXXIX) had a very intense i.r. absorption at 1758 cm^{-1} which is attributable to a fluorinated double bond and absorptions at 1525 and 1510 cm^{-1} which are typical for a fluorinated benzene ring. The u.v. spectra revealed a maximum at 268 nm (ϵ = 800) as expected for a fluorinated benzene ring but the absorption at 313 nm (ϵ = 175) was somewhat surprising. Thus before the ^{19}F n.m.r. spectral data was considered the spectroscopic information was consistent for either (XXXIX) or the ortho-divinylbenzene (292).
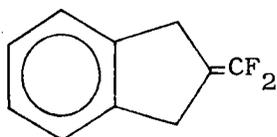

(XXXIX)
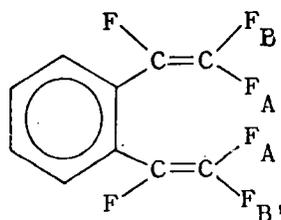
(292)

Steric interaction between F_A and $F_{A'}$ in (292) would cause the vinylic carbons to twist out of planarity with the benzene ring and hence conjugation would be reduced. This would go some way towards an explanation of the u.v. data, although the i.r. absorption at 1758 cm^{-1} is possibly a little low for a $CF=CF_2$. However, a comparison of the ^{19}F n.m.r. data for (XXXIX) (cf. Table 23) with that of perfluorostyrene reveals that the structure cannot possibly be (292). For instance the vinylic fluorine -CF= in perfluorostyrene occurs at 171, whereas for the similar environment in (292) it would be necessary to assert that it occurred below 72. More important is the fact that large coupling constants analogous to those in perfluorostyrene are not found, the resonance corresponding to four fluorines at 86.8 is only 20 Hz broad. Aromatic fluorine resonances do have coupling constants of about 12 Hz but coupling constants of this magnitude can be found for 'meta' fluorines in aromatic rings.[241,255] The ^{19}F n.m.r. assignments for (XXXIX) are also in broad agreement with the chemical shift data published for perfluoromethylenecyclopentane in which the vinylic fluorines occur at 59 p.p.m. and the allylic difluoromethylenes at 111 p.p.m.[139] Hence the spectroscopic data is only consistent with structure (XXXIX) and the u.v. absorption at 313 nm possibly arises as a result of 'through space' conjugation of the benzene ring with the olefinic moiety.

The assignment of structure (XXXX) was far more straightforward with the very intense exocyclic $C=CF_2$ occurring lower down at 1743 cm^{-1}, as a result of conjugation. The u.v. spectral characteristics of (XXXX), λ_{max} 252 nm (ϵ = 10500) and 281 nm (ϵ = 160) are not too dissimilar from those of perfluorostyrene (cf. page 205). It seems highly improbable that the C7 aromatic fluorine resonance in (XXXX) would occur at 63.5 and therefore the large 70 Hz coupling constant which is observable in the resonances at 63.5 and 134.4 is assigned to the 'through space' coupling between the F7 and vinylic F_A fluorines, which appear from molecular models to be separated by about 2.7Å.

The results obtained on the gas phase irradiation of perfluoro-1,2-dihydronaphthalene parallel those reported for the gas phase irradiation of decafluorocyclohexene:[139]
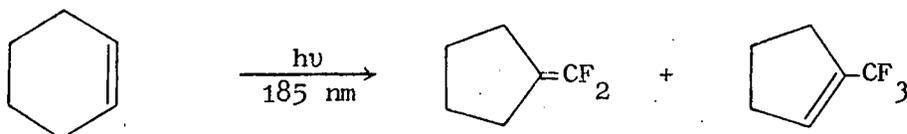
This isomerisation gave optimum yields when approximately 20% of air was present but the authors did not specify whether the isomerisation occurred in the absence of air. It could possibly be that the function of the air is merely to quench the excess vibrational energy obtained on excitation at 185 nm.

It was considered that the photochemistry of 1,2-dihydronaphthalene might give some insight into the mechanism of isomerisation occurring in the perfluoro analogue. The first reported mechanism for the photochemical rearrangement of 1,2-dihydronaphthalene was in 1969 and was established from the irradiation of the deuterium compounds (294) and (295), which formed the benzobicyclo[3.1.0]-hexanes (296) and (297).[249]
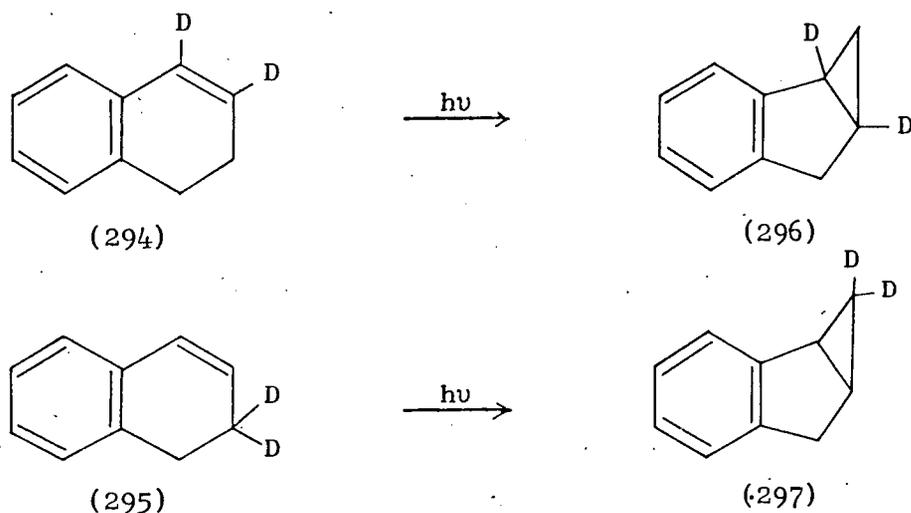
[Unmarked bonds to hydrogen]

The irradiations were performed in ether solutions (0.35%) for about 3 hours whereupon only one third of the product was volatile material and of this over 90% consisted of the benzobicyclohexanes. The mechanism for the isomerisation

was interpreted as proceeding via ring opening of the C1-C2 bond to give the

vinyl-o-quinodimethanes with the new bonds C3-C1 and C2-C4 subsequently being

formed.[249]   In this manner there was no need to invoke H migrations.
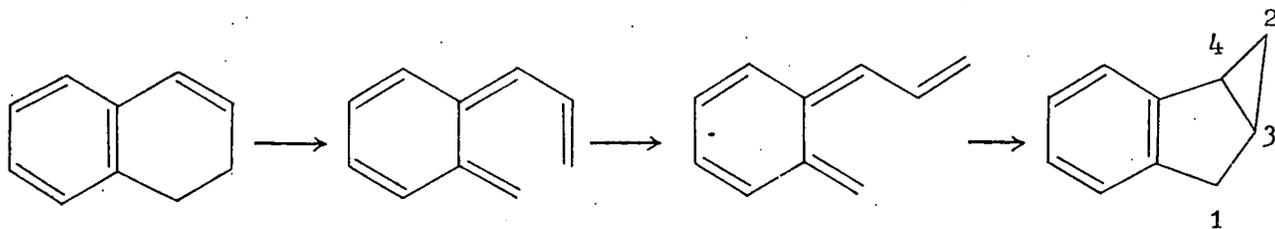
[Unmarked bonds to hydrogen]

It has subsequently been shown that the formation of the benzobicyclohexanes

involves two photochemical processes, the ring opening to the pentaenes occur

at 280 nm whilst ring closure to the benzobicyclohexanes proceeds on irradiation

at 400 nm.[250]

The irradiation of the substituted 1,2-dihydronaphthalene (298) resulted in

the formation of the ring opened product (300), which was presumed to arise via

a 1,7 H shift from the intermediate vinyl-o-quinodimethane (299).[251]

(298)   (299)   (300)
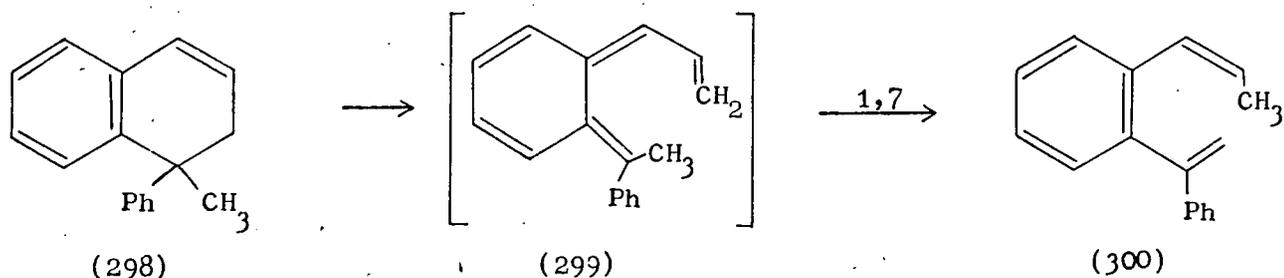
[Unmarked bonds to hydrogen]

In a series of very elegant experiments it has been shown that these observed

1,7 H migrations are temperature dependent and do not occur at -100°C.[252]   The

irradiation of (301) in dimethylbutane/pentane solutions at -100°C resulted in the

formation of three products all arising from the intermediate vinyl-o-quinodimethane

(302).   The substituted allene being formed via a 1,5 H migration from (302).

The initial isomerisation of the substituted 1,2-dihydronaphthalenes to the

intermediate pentaenes has also been confirmed as proceeding via an allowed

conrotatory path.[252]

(301) → (302) →
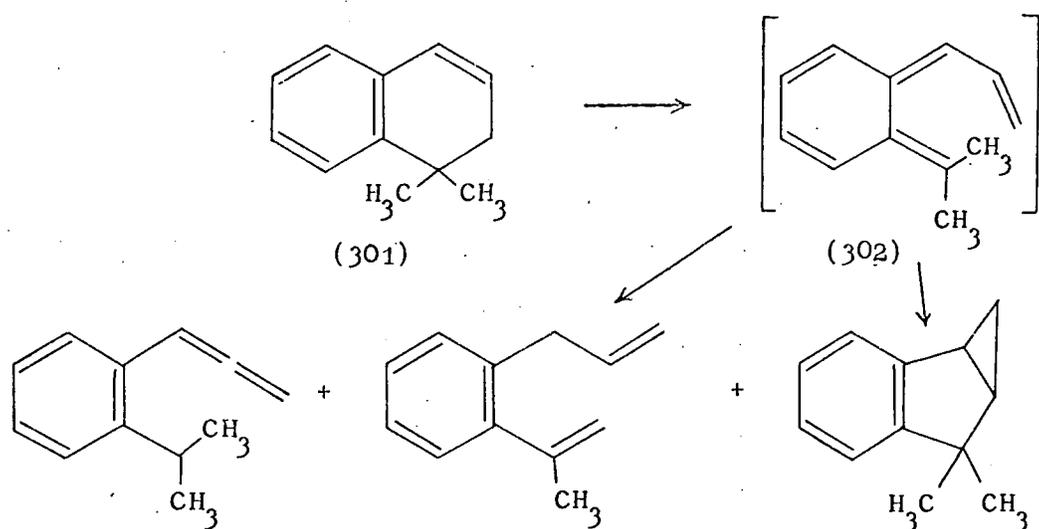
[Unmarked bonds to hydrogen]

A rather similar photochemical transformation occurs when benzobicyclo-hexanes are formed on irradiation of o-divinylbenzenes. The irradiation of the deuterium labelled compound (303) gave rise solely to (304) and this led the author to suggest that the transformation involved one of the two possible radical mechanisms postulated below.[253]
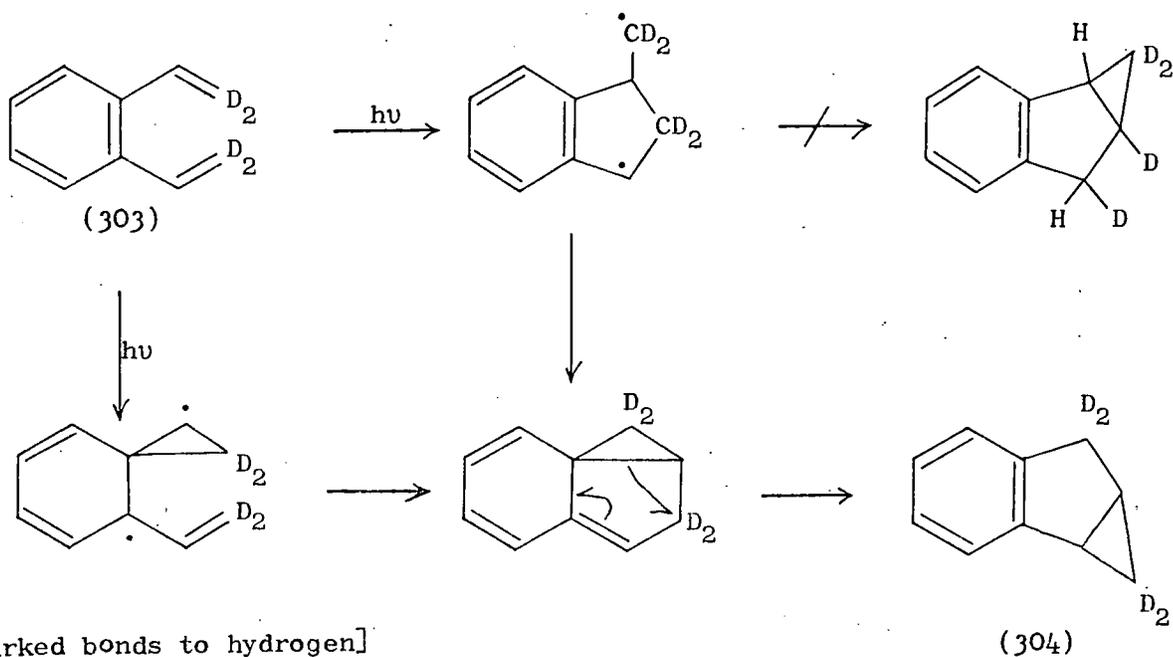

[Unmarked bonds to hydrogen]   (304)

The only theoretical study (CNDO/C1) on the ground and excited states of 1,2-dihydronaphthalene suggests that the four lowest singlet transitions are

$\pi \longrightarrow \pi^*$ and that four triplet states lie at lower energy than the first singlet.[254]

However, the authors also claim that the $S_0 \longrightarrow S_1$ transition results in a

weakening of the C3-C4 bond.   In view of this and the previous experimental

results it would seem relevant to consider the photochemical transformation of

perfluoro-1,2-dihydronaphthalene as proceeding through an allowed conrotary ring

opening to give the intermediate pentaene (305).   The anticipated high

reactivity of (305) would explain the high percentage of polymeric products.

However, for the formation of the perfluoromethyleneindanes from (305) it seems

necessary to propose a radical mechanism, one possible scheme (A) is that

outlined below:

Scheme A

(305)   (XXXIX)

(305)   1,2σ   (307)   F shift   (XXXX)
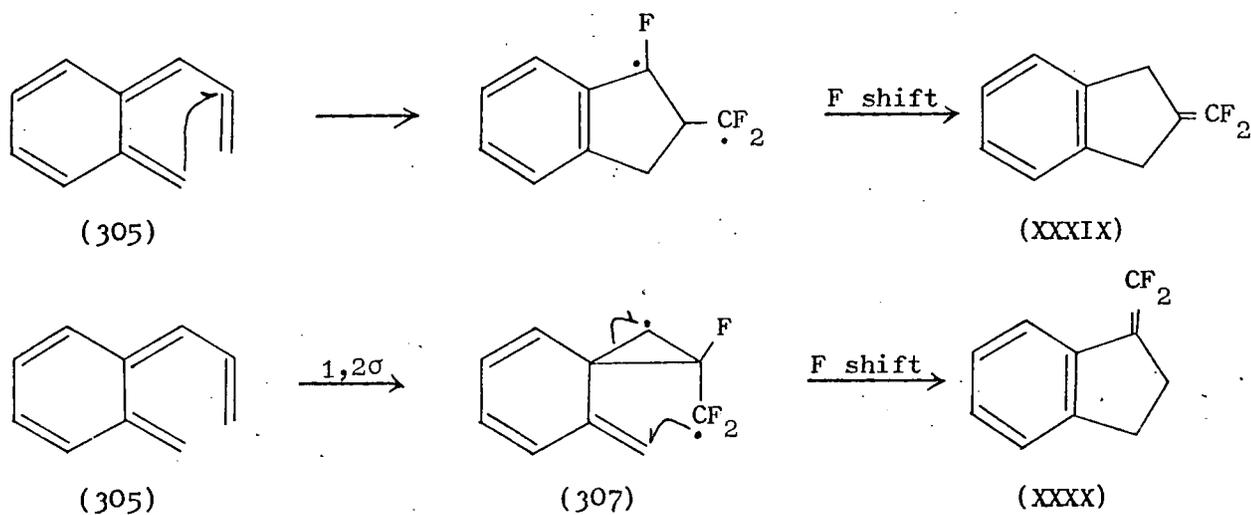
Equally plausible is the alternative scheme (B) where by analogy with

previous results the perfluorobenzobicyclohexane (306) is formed.

Scheme B

(XXI)   (305)   (306)
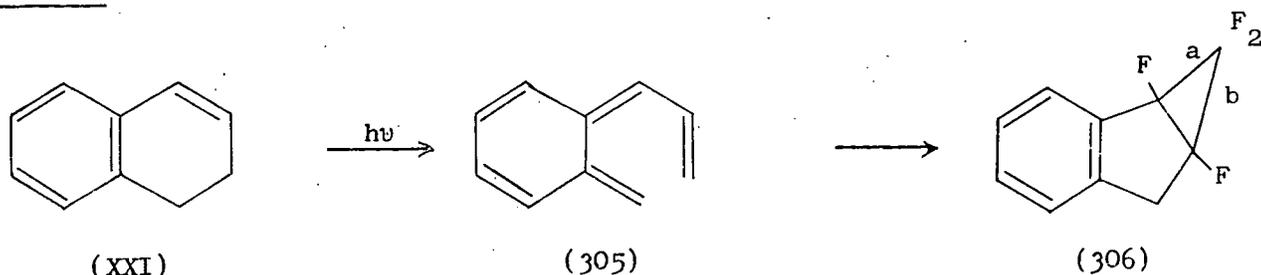
Cleavage of bond (a) with subsequent fluorine migration could lead to the

nonconjugated perfluoromethyleneindane, whilst cleavage of bond (b) with subsequent fluorine migration could lead to the conjugated perfluoromethyleneindane. The fluorine migrations would necessarily involve radical systems. However, if the photochemical isomerisation proceeds via (306) it is a little difficult to understand why none of this benzobicyclohexane (306) was isolated.

The formation of the perfluoro-2 or -3-methylindene (XX) could proceed via a 1,3 fluorine migration from either (XXXIX) or (XXXX) respectively. Unfortunately Camaggi and Gozzo did not establish whether perfluoromethylene-cyclopentane underwent isomerisation to perfluoromethylcyclopentane.[139] else evidence to support the suggestion of a 1,3 fluorine migration may have been available. It is equally possible that for (306) cleavage of the cyclopropane bonds (a) and (b) with subsequent 1,2 fluorine migrations could explain the formation of perfluoro-2 and -3-methylindene respectively, whilst isomerisation of (307) in scheme A could with subsequent fluorine migrations be developed such that the formation of the 'required' indene occurs. However the radical schemes are only proposed as tentative possibilities but it would seem likely that the perfluoro-1,2-dihydronaphthalene parallels the photochemical reaction of 1,2-dihydronaphthalene in initially undergoing a conrotatory ring opening to give the very reactive vinyl-o-quinodimethane intermediate.

EXPERIMENTAL

5.7   Reactions of perfluoro-1,2-dihydronaphthalene with nucleophiles

(a)   With sodium borohydride

Sodium borohydride (3·09 mmoles) was dissolved in 6 ml. of dry tetraglyme and added dropwise over 15 mins. to a solution of perfluoro-1,2-dihydronaphthalene (2·50g., 8·07 mmoles) in 6 ml. of dry tetraglyme at 0°C.   After stirring at 0°C for one hour the solution was poured into dilute HCL (100 ml., 0·1N) and the lower fluorocarbon layer, which separated, was distilled in vacuo from P_2O_5 to give a colourless liquid (1·48g.).   This liquid was separated by preparative g.l.c. (Col.G, 145°C) to give in order of emergence: (i) perfluoro-1,2-dihydro-naphthalene (0·07g.), (ii) 1,1,2,2,4,5,6,7,8-nonafluoro-1,2-dihydronaphthalene (XXXI) (0·88g., 3·03 mmoles, 52% yield before separation), a colourless liquid of B.Pt. 173°C. $C_{10}F_9H$, which has a Mol.Wt. of 292 (m.s.), requires: F, 58·6%. Found: F, 58·2%.   (XXXI) has ν_{max} 3100 (vinylic H), 1687 (-CH=CF-), 1520 and 1495 cm^{-1} (fluorinated benzene ring).   The final fraction (iii) was 1,1,2,2,4,5,6,8-octafluoro-1,2-dihydronaphthalene (XXXII) (0·091g., 0·33 mmoles). $C_{10}F_8H_2$ has a Mol.Wt. of 274 (m.s.).   (XXXII) is a colourless liquid and has ν_{max} 3100 (vinylic and aromatic C-H), 1682 (-CH=CF-) and 1495 cm^{-1} (fluorinated benzene ring).

(b)   With lithium methyl

A solution of lithium methyl in diethyl ether (1M, 22 ml., 22 mmoles) was added over 10 mins. to a solution of perfluoro-1,2-dihydronaphthalene (3·00g., 9·68 mmoles) in diethyl ether (20 ml.) at -78°C.   The mixture was stirred at -78°C for 15 mins. and then slowly allowed to warm to room temperature.   Any excess lithium methyl was destroyed by addition of 20 ml. of dilute HCl.   The ether layer was separated, dried and distilled leaving a fluorocarbon mixture which was distilled in vacuo from P_2O_5 to give a colourless liquid (2·25g.) which was separated by preparative g.l.c. (Col.G, 150°C) to give in order of emergence:

(i) unchanged perfluoro-1,2-dihydronaphthalene (0·12g.); (ii) a mixture of

1,1,2,2,4,5,6,7,8-nonafluoro-3-methyl-1,2-dihydronaphthalene (XXXIII) and

1,1,2,2,3,5,6,7,8-nonafluoro-4-methyl-1,2-dihydronaphthalene (XXXIV) (0·25g.);

(iii) a colourless liquid mixture (1·18g., 4·86 mmoles, 57% yield before

separation) that contained 1,1,2,2,3,4,5,6,8-nonafluoro-7-methyl-1,2-dihydro-

naphthalene (XXXV) and 1,1,2,2,3,4,5,7,8-nonafluoro-6-methyl-1,2-dihydro-

naphthalene (XXXVI) in the ratio of 2:1 respectively. The fraction (iii) was

not separated by any available g.l.c. column packing and hence analysis was

carried out on the mixture. $C_{10}F_9H_3$, which has a Mol.Wt. of 306 (m.s.) requires:

F, 55·9%. Found: F, 55·5%. The i.r. of the mixture gave υ_{max} 1728 (-CF=CF-),

1480 and 1490 cm^{-1} (fluorinated benzene ring).

The last fraction (iv) was a liquid (ca. 0·22g.) that consisted of a mixture

of octafluorodimethyl-1,2-dihydronaphthalenes. $C_{12}F_8H_6$, which has a Mol.Wt. of

402 (m.s.), requires: F, 50·3%. Found: F, 49·9%. The i.r. of the liquid

mixture gave υ_{max} 2940 (-CH$_3$), 1695 (-CF=C-CH$_3$), and 1490 and 1480 cm^{-1}

(fluorinated benzene ring). The i.r. also shows a slight absorption at 1720 cm^{-1}

(-CF=CF-, ca. 5% of the intensity of absorption at 1695 cm^{-1}) attributed to the

isomer having both methyl groups in the benzene ring. Major peaks in the mass

spectrum were: m/e (origin of ion, assignment, % base peak). 302 (Parent,

$C_{12}F_8H_6$, 81·6); 287 (P-CH$_3$, $C_{11}F_8H_3$, 48·0); 283 (P-F, $C_{12}F_7H_6$, 21·8); 268

(P-CH$_3$F, $C_{11}F_7H_3$, 6·1); 264 (P-F$_2$, $C_{12}F_6H_6$, 10·0); 254 (P-C$_2$H$_5$F, $C_{10}F_7H$, 19·8);

253 (P-C$_2$H$_6$F, $C_{10}F_7$, 18·8); 234 (P-C$_2$H$_6$F$_2$, $C_{10}F_6$, 100); 203 (P-C$_3$H$_6$F$_3$, C_9F_5,

27·3); 185 (P-C$_3$H$_5$F$_4$, C_9F_4H, 39·4). Metastable ion 302 → 234 (P-C$_2$H$_6$F$_2$) at

181·3.

It was not possible to separate either fraction (iii) or fraction (iv) on

any available g.l.c. packing. However fraction (ii) was separated (Col.G, 115°C)

to give in order of increasing retention time: (v) (XXXIII) (ca. 0·06g.), which

has a Mol.Wt. of 306 (m.s.) and υ_{max} 2945 (-CH$_3$), 1695 (-CF=C-), 1520 and 1490

cm^{-1} (fluorinated benzene ring); and (vi) (XXXIV) (ca. 0·06g.), which has a

Mol.Wt. of 306 (m.s.) and υ_{max} 2940 (-CH$_3$), 1695 (-CF=C-), 1520 and 1490 cm^{-1}

(fluorinated benzene ring). (XXXIII) and (XXXIV) are colourless liquids.

The ratio of $C_{11}F_9H_3$ isomers formed, analysed by (Col.C, 150°C) and ^{19}F

n.m.r. was (XXXIII) : (XXXIV) : (XXXV) : (XXXVI) $\equiv$ 1 : 1 : 4·4 : 2·2.

(c) Competition of perfluoro-1,2-dihydronaphthalene and perfluorobenzene for

lithium methyl in ether

Lithium methyl (0·30 mmoles) in 2 ml. of diethyl ether was added dropwise

to a solution of (XXI) (0·076g., 0·245 mmoles) and perfluorobenzene (0·429g.,

2·31 mmoles) in 5 ml. of diethyl ether at -78°C. The reactants were stirred

at -78°C for 30 mins. and then allowed to warm to 20°C over 30 mins. G.l.c.

analysis (Col.A, 150°C) indicated that the ratio of (XXI) : (monomethyl

substituted XXI) : (dimethyl substituted XXI) was respectively 32 : 46 : 21.

Less than 0·5% of the perfluorobenzene had reacted to give methylpentafluorobenzene.

A further (0·20 mmoles) of lithium methyl in 1·3 ml. of diethyl ether was

added to the above solution at -78°C. After 1 hour analysis indicated that no

(XXI) remained and that the ratio of (monomethyl substituted XXI) : (dimethyl

substituted XXI) was respectively 1 : 9. Only 3% of methyl pentafluorobenzene

had been formed.

Hence dimethyl substituted perfluoro-1,2-dihydronaphthalenes, 95% of which

consist of isomers having a methyl substituent on the double bond at positions

3 or 4, are formed much more readily than methylpentafluorobenzene.

5.8 Reaction of perfluoro-1,2-dihydronaphthalene (XXI) with potassium fluoride

(XXI) (3·57g., 11·56 mmoles) and dry KF (0·41g., 7·1 mmoles) were sealed in

vacuo in a 10 ml. Carius tube and heated at 350°C for 40 hours to give a liquid

mixture (2·98g.) that was distilled into three fractions on the concentric

tubes apparatus at 10 mms: to give fraction (i) B.Pt. 59°C, consisting mainly of

perfluoro-1,4-dihydronaphthalene (XIX); fraction (ii) B.Pt. 62°C, mainly (XXI)

and fraction (iii) a pot residue consisting of perfluoronaphthalene (0·81g.,

2·98 mmoles, 26% yield) which was recrystallised from petroleum ether (40/60)

and identified by comparison of i.r., m.s. and n.m.r. with an authentic sample.

Fraction (i) was purified by preparative g.l.c. (Col.G, 120°C) to give (XIX)

(0·50g., 1·61 mmoles, 17% yield before separation) which was identified by i.r.,

m.s. and g.l.c.

In another experiment (XXI) (0·190g.) and dry KF (0·03g.) were sealed in

vacuo in a 6 ml. Carius tube and heated at 250°C for 40 hours to give unchanged

(XXI) (0·185g.).

5.9 Photochemical reactions of perfluoro-1,2-dihydronaphthalene

Irradiations (a) and (b) were carried out in a quartz ampoule (50 cm. x

2·5 cm. diameter), the top of which was connected via a graded seal to a Pyrex

constriction.   Compounds were transferred in vacuo from P_2O_5, sealed in the

ampoule (10^{-3} mm), and irradiated with medium pressure mercury lamps (253·7 nm).

The ampoule was placed in the centre of a Rayonet 208 photochemical reactor

after the bottom 10 cm. had been covered with opaque paper to ensure that only

the vapour was irradiated.   The products were removed from the quartz tube by

vacuum transfer.

(a) Vapour phase

Perfluoro-1,2-dihydronaphthalene (XXI) (1·32g., 4·36 mmoles) was irradiated

for seven days in the presence of a trace of mercury vapour to give: (i) a

volatile liquid fraction (0·66g.) and (ii) an involatile viscous residue that was

removed from the ampoule through the agency of benzene.   The benzene was

distilled from the mixture and g.l.c. analysis (Col.B, 250°C) of the viscous

residue (ii) indicated a number of unresolved components.   The ^{19}F n.m.r.

spectra of (ii) showed broad unresolved absorptions centred at 110-120 p.p.m.

and 150-160 p.p.m.; whilst the i.r. indicated that no -CF=CF- was present.

The volatile liquid fraction (i) was separated by preparative g.l.c. (Col.G,

120°C) into fractions (iii), (iv) and (v) in order of increasing retention time.

Fraction (iii) was perfluoro-2-methyleneindane (XXXIX) (ca. 0·008g., 0·003 mmoles,

ca. 3% yield before separation).   (XXXIX), $C_{10}F_{10}$, has a Mol.Wt. of 310 (m.s.),

υ_{max} 1758 ($>$C=CF$_2$), 1633 and 1650, 1525 and 1510 cm^{-1} (fluorinated benzene ring);

λ_{max} 269 nm (ϵ = 800) and 313 nm (ϵ = 300), and is a colourless liquid.

The liquid fraction (iv) (0·088g., ca. 10% yield before separation) was

shown by g.l.c./m.s. (Col.M, 100°C) to contain two compounds of Mol.Wt. 310.

The ^{19}F n.m.r. of the mixture confirmed the presence of two isomers in the ratio

of 4 : 1. Fraction (v) (0·34g.) was shown by g.l.c. and i.r. to be the starting

material (XXI).

The fraction (iv) was then separated by preparative g.l.c. (Col.H, 100°C) to

give in order of increasing retention time: (vi) a trace of a liquid that was shown

by i.r. and u.v. (and by ^{19}F n.m.r. and g.l.c./m.s. analysis of the mixture (iv))

to be the previously prepared perfluoro-2 or 3-methylindene (XX); and (vii)

perfluoro-1-methyleneindane (XXXX) (ca. 0·040g.). (XXXX), C$_{10}$F$_{10}$, has a Mol.Wt.

of 310 (m.s.); υ_{max} 1743 ($>$C=CF$_2$), 1645 and 1620, and 1520 and 1500 cm^{-1}

(fluorinated benzene ring); and λ_{max} 252 nm (ϵ = 15,000), 281 nm (ϵ = 160) and a

shoulder at 289 nm (ϵ = 140).

(b) Vapour phase with ethylene

Perfluoro-1,2-dihydronaphthalene (XXI) (1·35g., 4·35 mmoles) was irradiated

in the presence of ethylene (2·5 mmoles) for 14 days to give: (i) ethylene

(0·45 mmoles); (ii) a liquid mixture (0·55g.) consisting of 80% (XXI) and 20%

of products obtained in the previous experiment (a); and (iii) a solid (0·69g.,

2·05 mmoles, 82% yield) that was recrystallised from petroleum ether (60/80) to

give white crystals of 11H,11H,12H,12H-decafluorotricyclo[8,2,0,0^{2,7}]dodeca-2,4,6-

triene (XXXXI). C$_{12}$F$_{10}$H$_4$, which has a Mol.Wt. of 338 (m.s.) requires: C, 42·6

and H, 1·2%. Found: C, 42·5 and H, 1·4%. (XXXXI) has υ_{max} 1526 and 1498

cm^{-1} (fluorinated benzene ring); λ_{max} 268 nm (ϵ = 1,900) and a M.Pt. of 61/62°C.

(c) Irradiation in solution

(The medium pressure mercury lamp was used in the apparatus previously

described in Chapter 2.10).

Perfluoro-1,2-dihydronaphthalene (XXI) (0·45g., 1·45 mmoles) was dissolved

in 300 ml. of dry perfluoromethylcyclohexane. The solution was nitrogen

streamed for 3 hours and then irradiated for 5 hours. The bulk of the solvent

was removed by distillation apart from the last 5 ml. which was removed by

transfer in a partial vacuum of 1 cm., to give a liquid (0·42g.) that was shown

by i.r. and g.l.c. (Col.A, 125°C) to be primarily unchanged (XXI) (ca. 98%) with

a trace of a compound that had a slightly shorter retention time and was probably

an isomer of (XXI).

5.10 Oxidation of perfluoro-1,2-dihydronaphthalene with potassium permanganate

By using an analogous method to that previously described (Chapter 4.10(4))

(XXI) (1·00g., 3·30 mmoles) was added to $KMnO_4$ (1·00g.) in 60 ml. of dry acetone

and stirred at 20°C for one hour. The white solid obtained after ether

extraction was sublimed (10^{-3} mm., 130°C) to give 3-(2-carboxy-3,4,5,6-tetrafluoro-

phenyl)perfluoropropionic acid (XXXXII) (0·78g., 2·31 mmoles, 71·5% yield), a

white solid M.Pt. 165/170°C (with decomposition). $C_{10}F_8O_4H_2$, which has a Mol.Wt.

of 338 (m.s. gave top mass peak of 291, i.e. $P-CH_2O_2$), requires: C, 35·5%;

H, 0·6% and F, 44·9%. Found: C, 35·2; H, 0·9 and F, 44·5%. The i.r. spectrum

of (XXXXII) showed υ_{max} broad intense absorption $3700 \rightarrow 2400$ (-COOH), 1745

(>C=O), 1525 and 1485 cm^{-1} (fluorinated benzene ring).

5.11 Oxidation of compounds (XXXV) and (XXXVI)

(0·42g., 1·39 mmoles) of 2:1 mixture of (XXXV) and (XXXVI) respectively,

was added to potassium permanganate (0·24g.) in 20 ml. of dry acetone and stirred

at 20°C for one hour. The residue remaining after ether extraction was dissolved

in a small amount of water and the ^{19}F n.m.r. of this solution was consistent

with a 2 : 1 mixture of 3-(2-carboxy, 5-methyl, 3,4,6-trifluorophenyl)perfluoro-

propionic acid (XXXXIII) and 3-(2-carboxy, 4-methyl, 2,5,6-trifluorophenyl)-

perfluoropropionic acid (XXXXIV). This residue was then sublimed (120°C, 10^{-3}mm.)

and recrystallised from dry benzene to give an off white solid (ca. 0·05g.)

$C_{11}F_5O_4H_5$, which has a Mol.Wt. of 334 (m.s.) requires: C, 39·5 and H, 1·5%.
Found: C, 39·1 and H, 1·6%. The i.r. spectrum of the recrystallised solid
showed v_{max} broad absorption 3700 ⟶ 2400 (-COOH), 1740 (>C=O), 1490 and 1460
cm^{-1} (fluorinated benzene ring).

APPENDIX A

Apparatus and Instruments

Vacuum system

A conventional vacuum system incorporating a rotary oil pump and a mercury diffusion pump was used for handling volatile compounds. Gases were measured by noting the pressure on a wide-bore manometer that was connected to a storage bulb of volume 510 ± 10 ml.

Infra-red spectra were recorded on a Perkin-Elmer 457 Grating Infra-red Spectrophotometer.

Ultra-violet spectra were recorded on a Unicam SP800 Spectrophotometer.

Carbon and hydrogen analyses were carried out with a Perkin-Elmer 240 CHN Analyser.

Melting points and boiling points are uncorrected. The boiling points were measured by Sivoloboff's method.

Mass spectra were measured with an A.E.I. MS9 spectrometer at an ionising beam energy of 70 eV or with a V.G. Micromass 12b that incorporates gas liquid chromatography and has an ionising beam energy of about 30 eV.

N.m.r. spectra were measured with a Varian A56/60 spectrometer, operating at 56.46 MHz for ^{19}F and 60.0 MHz for ^{1}H. High resolution spectra when required were measured on a Bruker HX 90E operating at 84.67 MHz for ^{19}F and 90 MHz for ^{1}H.

Gas liquid chromatography

The instruments and stationery phases used for analytical and preparative separations are recorded below. The stationery phases incorporated in the V.G. micromass 12b (g.l.c./m.s.) are also recorded.

(i) **Analytical**

Column A: Perkin-Elmer 452 (hot wire detector);   di-n-decylphthalate/Celite

$[H_2$ carrier gas, 6' x $\frac{1}{4}$" diam.].

Column B: Pye 104 (flame ionisation detector); silicone oil (30%)/ Chromosorb P $[N_2$ carrier gas, 12' x $\frac{1}{4}$" diam.].

Column C: Griffin Gas Density Balance; di-n-decylphthalate/Chromosorb P $[N_2$ carrier gas 6' x $\frac{1}{4}$" diam.].

Column D: As for C except silicone oil (30%).

Column E: As for C except 2-cyanoethylmethylsilicone (17%).

(ii) Preparative

Column F: Perkin-Elmer Praparativer Gaschromatograph; di-n-decylphthalate/ Chromosorb P $[N_2$ carrier gas, 15' x $^3/8$" diam.].

Column G: Varian Autoprep; di-n-decylphthalate/Chromosorb P $[H_2$ carrier gas, 20' x $^3/8$" diam.].

Column H: As for G but with silicone oil (30%).

Column I: As for G but with 2-cyanoethylmethylsilicone (17%).

(iii) G.l.c./m.s. - all columns were fitted to the Pye 104 (flame ionisation detector) and N_2 carrier gas was used [12' x $\frac{1}{4}$" diam.].

Column J: Stationery phase was silicone oil (30%) on Chromosorb P.

Column K: As for J but with silicone oil ($2\frac{1}{2}$%).

Column M: As for J but with silicone oil (15%).

Column N: Stationery phase was 2-cyanoethylmethylsilicone (17%)/Chromosorb P.

APPENDIX B

Mass Spectra

The mass spectra of compounds prepared during this work are tabulated below. Compounds marked with an asterisk were measured on the V.G. Micromass 12b (g.l.c./m.s.) whilst the majority were recorded on the A.E.I. MS9 Spectrometer. Ions are tabulated in the form:

$$231 \ (P-F, \ C_8F_7H_2, \ 4\cdot2)$$
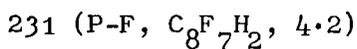
In this example the ion has a mass number of 231, its supposed origin is the loss of a fluorine atom from the parent ion (P), it has been assigned the formula $C_8F_7H_2^+$ (the + being understood) and its intensity is $4\cdot2\%$ of the intensity of the base peak (B).

Metastable ion peaks, where observed, are tabulated underneath the main spectrum in the form $M_1 \rightarrow M_2 \ (-F_r)$ at M* where the metastable ion occurs at

$$M^* = \frac{M_2^{\ 2}}{M_1^{\ 2}}$$ for the loss of F_r the neutral fragment.

[In this Appendix all diagrams have unmarked bonds to fluorine].
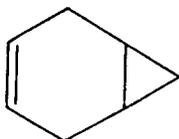
(I)

$274 \ (P, \ C_7F_{10}, \ 9\cdot4)$, $224 \ (P-CF_2, \ C_6F_8, \ 20\cdot3)$, $205 \ (P-CF_3, \ C_6F_7, \ 93\cdot9)$, $186 \ (P-CF_4, \ C_6F_6, \ 23\cdot5)$, $174 \ (P-C_2F_4, \ C_5F_6, \ 26\cdot3)$, $155 \ (P-C_2F_5, \ C_5F_5, \ 62\cdot4)$, $131 \ (P-C_4F_5, \ C_3F_5, \ 10\cdot5)$, $124 \ (P-C_3F_6, \ C_4F_4, \ 22\cdot0)$, $117 \ (P-C_2F_7, \ C_5F_3, \ 18\cdot8)$, $112 \ (P-C_4F_6, \ C_3F_4, \ 8\cdot3)$, $93 \ (P-C_4F_7, \ C_3F_3, \ 30\cdot3)$, $69 \ (P-C_7F_7, \ CF_3, \ 100, \ B)$.

Metastable ions: $274 \rightarrow 205 \ (-CF_3)$ at $153\cdot5$, $205 \rightarrow 155 \ (-CF_2)$ at $117\cdot1$, $224 \rightarrow 155 \ (-CF_3)$ at $107\cdot3$ and $274 \rightarrow 155 \ (-C_2F_4)$ at $87\cdot7$.

(II)
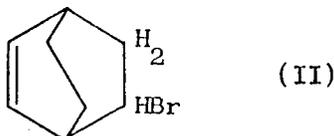
332, (P, $C_8F_8H_3Br$, 18·3), 330 (P, $C_8F_8H_3Br$, 19·6), 251 (P-Br, $C_8F_8H_3$, 100, B), 224 (P-C_2H_3Br, C_6F_8, 57·1), 205 (P-C_2FH_3Br, C_6F_7, 17·0), 181 (P-CF_3H_2Br, $C_7F_5H_2$, 22·3), 180 (P-CF_3H_2Br, C_7F_5H, 24·1), 174 (P-$C_4F_2H_3Br$, C_4F_6, 17·3), 155 (P-$C_4F_3H_3Br$, C_4F_5, 31·5), 151 (P-$C_5F_2H_2Br$, C_3F_6H, 89·9), 150 (P-$C_5F_2H_3Br$, C_3F_6, 24·4), 108 (P-C_6F_8, C_2H_3Br, 97·5), 106 (P-C_6F_8, C_2H_3Br, 93·2), 101 (P-$C_6F_6H_2Br$, C_2F_2H, 25·0) and 69 (P-$C_7F_5H_3Br$, CF_3, 25·0).

Metastable ions: 332 → 251 (-Br) at 189·9, 330 → 251 (-Br) at 191·0.

(III)
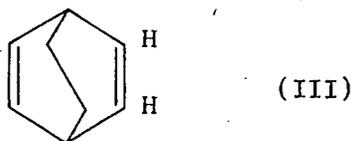
250 (P, $C_8F_8H_2$, 3·3), 231 (P-F, $C_8F_7H_2$, 4·2), 181 (P-CF_3, $C_7F_5H_2$, 16·0), 150 (P-C_2F_4, $C_6F_4H_2$, 100, B), 100 (C_2F_4, 8·4), 81 (C_2F_3, 16·0) and 69 (CF_3, 4·5).

(IV)
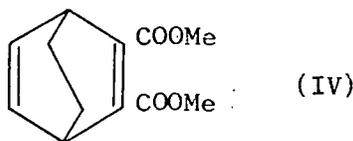
366 (P, $C_{10}F_8H_6O_4$, 2·8), 347 (P-F, $C_{10}F_7H_6O_4$, 1·5), 335 (P-OMe, $C_9F_8H_3O_3$, 15·3), 307 (P-COOMe, $C_8F_8H_3O_2$, 5·2), 266 (P-C_2F_4, $C_8F_4H_6O_4$, 23·8), 235 (P-$C_3F_4H_3O$, $C_7F_4H_3O_3$, 100, B), 205 (P-$C_4F_4H_5O_2$, $C_6F_4HO_2$, 6·1), 179 (P-$C_5F_4H_3O_3$, $C_5F_4H_3O$, 5·2), 177 (P-$C_5F_4H_5O_3$, C_5F_4HO, 8·3), 148 (P-$C_6F_5H_3O_3$, $C_4F_5H_3O$, 8·3), 69 (CF_3, 8·4), 59 (COOMe, 16·3) and 44 (CO_2, 50).

Metastable ions: 366 → 266 (-C_2F_4) at 193·2, 335 → 307 (-CO) at 207·6 and 266 → 235 (-OMe) at 193·2.
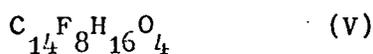
$$C_{14}F_8H_{16}O_4 \qquad (V)$$

440 (P, $C_{14}F_8H_{16}O_4$, 5·6), 424 (P-CH$_4$, $C_{13}F_8H_{12}O_4$, 1·4), 420 (P-HF, $C_{14}F_7H_{15}O_4$, 3·7), 419 (P-H$_2$F, $C_{14}F_7H_{14}O_4$, 3·7), 408 (P-CH$_3$OH, $C_{13}F_8H_{12}O_3$, 40·8), 395 (P-C$_2$H$_5$O, $C_{12}F_8H_{11}O_3$, 30·9), 387 (P-CFH$_5$O, $C_{13}F_7H_{11}O_3$, 8·9), 380 (P-C$_2$H$_4$O$_2$, $C_{12}F_8H_{12}O_2$, 3·4), 379 (P-C$_2$H$_5$O$_2$, $C_{12}F_8H_{11}O_2$, 2·8), 375 (P-C$_2$FH$_6$O, $C_{12}F_7H_{10}O_3$, 3·7), 364 (P-C$_3$H$_8$O$_2$, $C_{11}F_8H_8O_2$, 10·4), 363 (P-C$_3$H$_9$O$_2$, $C_{11}F_8H_7O_2$, 5·1), 336 (P-C$_4$H$_8$O$_3$, $C_{10}F_8H_8O_2$, 16·2), 331 (7·4), 316 (4·7), 304 (5·2), 284 (9·4), 272 (5·8), 260 (6·0), 170 (5·8), 100 (5·4), 59 (COOMe, 37·2), 58 (C_3H_6O or COOCH$_2$, 35·4) and 44 (CO$_2$, 100, B).

Metastable ions: 440 → 420 (-HF) at 400·6 and 419 → 387 (-CH$_3$OH) at 357·5.
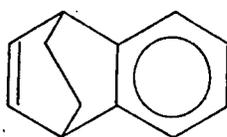
(VI)

372 (P, $C_{12}F_{12}$, 7·9), 353 (P-F, $C_{12}F_{11}$, 6·8), 303 (P-CF$_3$, $C_{11}F_9$, 7·7), 272 (P-C$_2$F$_4$, $C_{10}F_8$, 100, B), 253 (P-C$_2$F$_5$, $C_{10}F_7$, 4·5), 241 (P-C$_3$F$_5$, C_9F_7, 18·6), 222 (P-C$_3$F$_6$, C_9F_6, 7·9) and 203 (P-C$_3$F$_7$, C_9F_5, 8·7).

Metastable ions: 372 → 272 (-C$_2$F$_4$) at 198·9, 272 → 241 (-CF) at 213·5 and 272 → 222 (-CF$_2$) at 182·2.
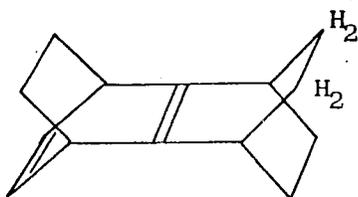
(VII)

438 (P, $C_{14}F_{14}H_4$, 8·1), 419 (P-F, $C_{14}F_{13}H_4$, 5·1), 369 (P-CF$_3$, $C_{13}F_{11}H_4$, 3·4), 338 (P-C$_2$F$_4$, $C_{12}F_{10}H_4$, 39·7), 319 (P-C$_2$F$_5$, $C_{12}F_9H_4$, 3·4), 238 (P-C$_4$F$_8$, $C_{10}F_6H_4$, 100, B), 219 (P-C$_4$F$_9$, $C_{10}F_5H_4$, 10·2), 220 (P-C$_2$F$_{10}H_4$, $C_{12}F_4$, 6·1), 206 (P-C$_5$F$_9$H, $C_9F_5H_3$, 8·5), 188 (P-C$_5$F$_{10}$, $C_9F_4H_4$, 11·3), 100 (C_2F_4, 4·1) and 69 (CF$_3$, 4·7).

Metastable ions: 438 → 338 (-C$_2$F$_4$) at 262·0 and 338 → 238 (-C$_2$F$_4$) at 167·6.

(VIII)
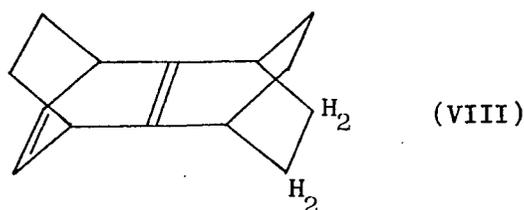
438 (P, $C_{14}F_{14}H_4$, 6·8), 419 (P-F, $C_{14}F_{13}H_4$, 8·6), 369 (P-CF$_3$, $C_{13}F_{11}H_4$, 6·4), 338 (P-C_2F_4, $C_{12}F_{10}H_4$, 43·3), 319 (P-C_2F_5, $C_{12}F_9H_4$, 9·0), 238 (P-C_4F_8, $C_{10}F_6H_4$, 100, B), 220 (P-$C_2F_{10}H_4$, $C_{12}F_4$, 8·1), 219 (P-C_4F_9, $C_{10}F_5H_4$, 13·2), 206 (P-$C_5F_9H_3$, C_9F_5H, 10·0), 188 (P-C_5F_{10}, $C_9F_4H_4$, 13·4), 100 (C_2F_4, 13·2), 83 ($C_2F_3H_2$, 18·2) and 69 (CF$_3$, 22·8).

Metastable ion: 338 → 238 (-C_2F_4) at 167·6

(IX)
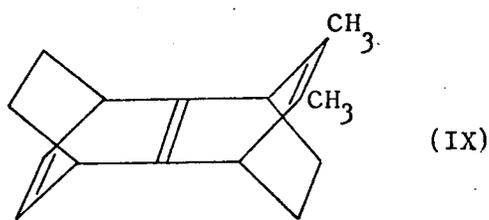
464 (P, $C_{16}F_{14}H_6$, 23·0), 445 (P-F, $C_{16}F_{13}H_6$, 7·6), 364 (P-C_2F_4, $C_{14}F_{10}H_6$, 9·7), 345 (P-C_2F_5, $C_{14}F_9H_6$, 4·2), 264 (P-C_4F_8, $C_{12}F_6H_6$, 100, B), 249 (P-$C_5F_8H_3$, $C_{11}F_6H_3$, 9·7), 237 (P-$C_6F_8H_3$, $C_{10}F_6H_3$, 5·2) and 69 (CF$_3$, 4·2).

Metastable ions: 464 → 364 (-C_2F_4) at 285·6, 264 → 249 (-CH$_3$) at 234·9.

(X)
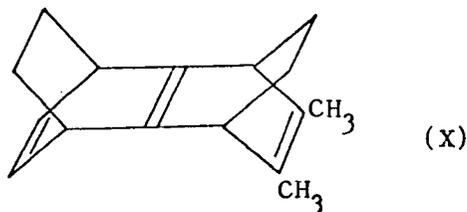
464 (P, $C_{16}F_{14}H_6$, 18·8), 445 (P-F, $C_{16}F_{13}H_6$, 9·1), 364 (P-C_2F_4, $C_{14}F_{10}H_6$, 17·5), 345 (P-C_2F_5, $C_{14}F_9H_6$, 5·0), 264 (P-C_4F_8, $C_{12}F_6H_6$, 100, B), 249 (P-$C_5F_8H_3$, $C_{11}F_6H_3$, 12·5) and 100 (C_2F_4, 2·5).

Metastable ions: 464 → 364 (-C_2F_4) at 285·6, 364 → 264 (-C_2F_4) at 191·4 and 264 → 249 (-CH$_3$) at 234·9.
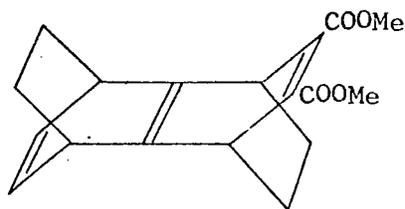
(XI)

552 (P, $C_{18}F_{14}O_4H_6$, 7·5), 533 (P-F, $C_{18}F_{13}O_4H_6$, 5·2), 521 (P-OMe, $C_{17}F_{14}O_3H_3$, 36·2), 452 (P-C_2F_4, $C_{16}F_{10}O_4H_6$, 28·0), 421 (P-$C_3F_4OH_3$, $C_{15}F_{10}O_3H_3$, 18·3), 393 (P-$C_4F_4O_2H_3$, $C_{14}F_{10}O_2H_3$, 9·1), 377 (P-$C_4F_4O_3H_3$, $C_{14}F_{10}OH_3$, 10·4), 352 (P-C_4F_8, $C_{14}F_6O_4H_6$, 100, B), 321 (P-$C_5F_8OH_3$, $C_9F_6O_3H$, 79·9), 265 (8·4), 235 (8·6), 234 (10·0), 196 (17·2), 194 (16·0), 153 (7·0), 151 (12·4), 126 (6·8), 124 (7·6) and 59 (COOMe, 21·6).
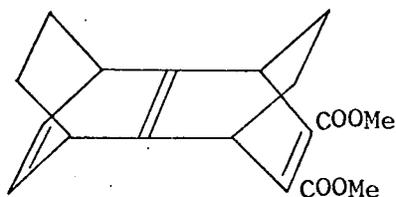
(XII)

552 (P, $C_{18}F_{14}O_4H_6$, 10·5), 533 (P-F, $C_{18}F_{13}O_4H_6$, 10·0), 521 (P-OMe, $C_{17}F_{14}O_3H_6$, 41·8), 452 (P-C_2F_4, $C_{16}F_{10}O_4H_6$, 31·4), 421 (P-$C_3F_4OH_3$, $C_{15}F_{10}O_3H_3$, 20·2), 393 (P-$C_4F_4O_2H_3$, $C_{14}F_{10}O_2H_3$, 10·7), 377 (P-$C_4F_4O_3H_3$, $C_{14}F_{10}OH_3$, 11·7), 352 (P-C_4F_8, $C_{14}F_6O_4H_6$, 100, B), 321 (P-$C_5F_8OH_3$, $C_{13}F_6OH_3$, 76·8), 265 (6·4), 235 (6·8), 234 (10·0), 196 (11·2), 194 (13·3), 153 (6·0), 151 (8·2), 126 (5·3), 124 (7·4) and 59 (COOMe, 8·2).
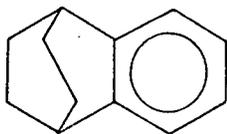
(XIII)[*]

410 (P, $C_{12}F_{14}$, 20·1), 391 (P-F, $C_{12}F_{13}$, 11·1), 341 (P-CF_3, $C_{11}F_{11}$, 13·2), 310 (P-C_2F_4, $C_{10}F_{10}$, 15·3), 291 (P-C_2F_5, $C_{10}F_9$, 41·6), 272 (P-C_2F_6, $C_{10}F_8$, 24·6) 241 (P-C_3F_7, C_9F_7, 100, B) and 141 (P-C_5F_{11}, C_7F_3, 15·3).

Metastable ions: 310 → 241 (-CF_3) at 187·4 and 291 → 241 (-CF_2) at 199·5

(XIV)*
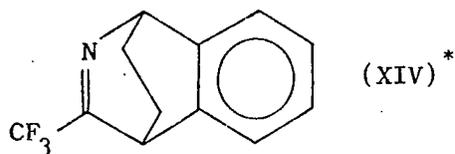
405 (P, $C_{12}F_{13}N$, 19·3), 386 (P-F, $C_{12}F_{12}N$, 4·5), 336 (P-CF$_3$, $C_{11}F_{10}N$, 3·9), 305 (P-C$_2$F$_4$, $C_{10}F_9N$, 100, B), 286 (P-C$_2$F$_5$, $C_{10}F_8N$, 30·0), 255 (P-C$_3$F$_6$, C_9F_7N, 59·8), 241 (P-C$_3$F$_6$N, C_9F_7, 59·8), 236 (P-C$_3$F$_7$, C_9F_6N, 10·8), 186 (P-C$_4$F$_9$, C_8F_4N, 15·1) and 141 (P-C$_5$F$_{10}$N, C_7F_3, 6·5).

Metastable ion: 305 → 255 (-CF$_2$) at 213·2

(XV)
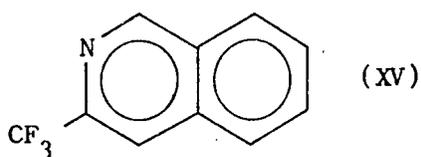
305 (P, $C_{10}F_9N$, 100, B), 286 (P-F, $C_{10}F_8N$, 56·2), 255 (P-CF$_2$, C_9F_7N, 98·6)
236 (P-CF$_3$, C_9F_6N, 15·8), 224 (P C$_2$F$_3$, C_8F_6N, 6·8), 217 (P-CF$_4$, C_9F_5N, 7·9)
186 (P-C$_2$F$_5$, C_8F_4N, 28·1), 148 (P-C$_2$F$_7$, C_8F_2N, 6·8), 141 (P-C$_3$F$_6$N, C_7F_3, 7·5)
117 (P-C$_3$F$_8$, C_7F_2N, 6·3), 93 (C_3F_3, 6·6) and 69 (CF$_3$, 9·6).

Metastable ions: 305 → 286 (-F) at 268·1, 305 → 255 (-CF$_2$) at 213·5, 255 → 224 (-CF) at 196·7, 286 → 236 (-CF$_2$) at 194·7 and 236 → 186 (CF$_2$) at 146·5.

(XVI)
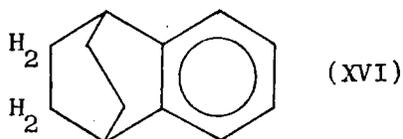
338 (P, $C_{12}F_{10}H_4$, 29·2), 319 (P-F, $C_{12}F_9H_4$, 7·0), 238 (P-C$_2$F$_4$, $C_{10}F_6H_4$, 100, B), 219 (P-C$_2$F$_5$, $C_{10}F_5H_4$, 23·6), 206 (P-C$_3$F$_5$H, $C_9F_5H_3$, 19·1), 188 (P-C$_3$F$_6$, $C_9F_4H_4$, 30·6) and 169 (P-C$_3$F$_7$, $C_9F_3H_4$, 8·3).

Metastable ion: 238 → 188 (-C$_2$F$_4$) at 148·5.

(XVII)
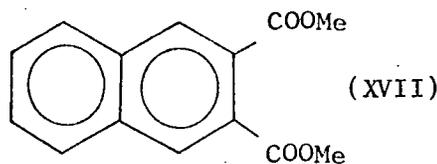
352 (P, $C_{14}F_6O_4H_6$, 55.0), 321 (P-OMe, $C_{13}F_6O_3H_3$, 100, B), 290 (P-$C_2O_2H_6$, $C_{12}F_6O_2$, 6.3), 263 (P-$C_3O_3H_5$, $C_{11}F_6OH$, 6.3), 262 (P-$C_3O_3H_6$, $C_{11}F_6O$, 5.7), 235 (P-$C_4O_4H_5$, $C_{10}F_6H$, 27.5), 234 (P-$C_4O_4H_6$, $C_{10}F_6$, 35.6), 222 (P-$C_5O_4H_6$, C_9F_6, 8.1), (P-$C_5FO_4H_6$, C_9F_5, 5.0) and 184 (P-$C_5F_2O_4H_6$, C_9F_4, 10.0).

Metastable ion: 352 → 321 (-OMe) at 292.7.

(XVIII)
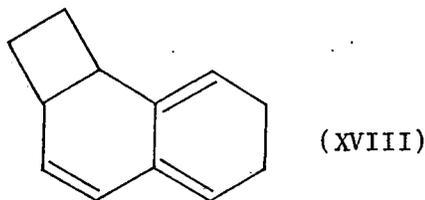
410 (P, $C_{12}F_{14}$, 15.4), 391 (P-F, $C_{12}F_{13}$, 5.3), 341 (P-CF_3, $C_{11}F_{11}$, 12.0), 322 (P-CF_4, $C_{11}F_{10}$, 3.25), 310 (P-C_2F_4, $C_{10}F_{10}$, 60.9), 291 (P-C_2F_5, $C_{10}F_9$, 18.1), 272 (P-C_2F_6, $C_{10}F_8$, 11.5), 260 (P-C_3F_6, C_9F_8, 9.9), 241 (P-C_3F_7, C_9F_7, 100, B) and 210 (P-C_4F_8, C_8F_6, 4.0).

Metastable ions: 410 → 310 (-C_2F_4) at 234.4, 391 → 341 (-CF_2) at 297.3, 310 → 241 (-CF_3) at 187.9, 291 → 241 (-CF_2) at 199.5 and 260 → 241 (-F) at 223.5.

(XIX)
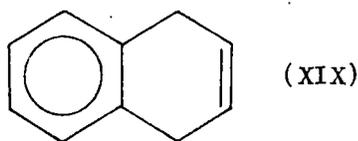
310 (P, $C_{10}F_{10}$, 42.8), 291 (P-F, $C_{10}F_9$, 26.6), 272 (P-F_2, $C_{10}F_8$, 11.3), 260 (P-CF_2, C_9F_8, 22.3), 241 (P-CF_3, C_9F_7, 100, B), 222 (P-CF_4, C_9F_6, 6.0), 210 (P-C_2F_4, C_8F_6, 9.2), 191 (P-C_2F_5, C_8F_5, 4.0) and 148 (P-C_4F_6, C_6F_4, 18.4).

Metastable ions: 310 → 241 (-CF_3) at 187.9, 291 → 241 (-CF_2) at 199.5, 291 → 210 (-C_2F_3) at 151.6 and 260 → 241 (-F) at 223.5.

(XX)
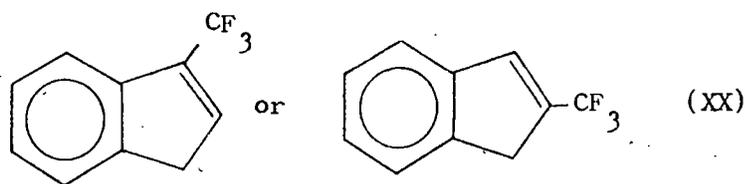
310 (P, $C_{10}F_{10}$, 63·8), 291 (P-F, $C_{10}F_9$, 47·8), 272 (P-F_2, $C_{10}F_8$, 12·4), 260 (P-CF_2, C_9F_8, 7·0), 241 (P-CF_3, C_9F_7, 100, B), 222 (P-CF_4, C_9F_6, 11·4), 210 (P-C_2F_4, C_8F_6, 5·4), 203 (P-CF_5, C_9F_5, 3·3), 191 (P-C_2F_5, C_8F_5, 4·3), 141 (P-C_3F_7, C_7F_3, 3·1) and 69 (CF_3, 1·9).

Metastable ions: 310 → 241 (-CF_3) at 187·9, 291 → 272 (-F) at 254·3, 291 → 241 (-CF_2) at 199·5, 291 → 210 (-C_2F_3) at 151·6 and 272 → 222 (-CF_2) at 181·2.

(XXI)
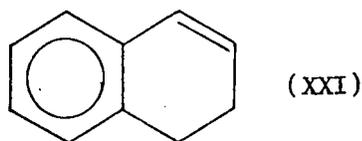
310 (P. $C_{10}F_{10}$, 55·9), 291 (P-F, $C_{10}F_9$, 33·9), 272 (P-F_2, $C_{10}F_8$, 9·3), 260 (P-CF_2, C_9F_8, 24·9), 241 (P-CF_3, C_9F_7, 100, B), 222 (P-CF_4, C_9F_6, 5·0), 210 (P-C_2F_4, C_8F_6, 10·0), 203 (P-CF_5, C_9F_5, 4·2), 191 (P-C_2F_5, C_8F_5, 4·2) and 141 (P-C_3F_7, C_7F_3, 7·5).

Metastable ions: 310 → 241 (-CF_3) at 187·9, 291 → 241 (-CF_2) at 199·5, 291 → 210 (-C_2F_3) at 151·6, 260 → 241 (-F) at 223·5 and 260 → 210 (-CF_2) at 169·0.

(XXII)
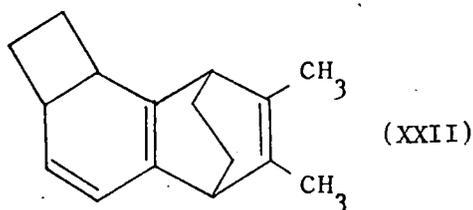
464 (P, $C_{16}F_{14}H_6$, 13·0), 445 (P-F, $C_{16}F_{13}H_6$, 2·9), 364 (P-C_2F_4, $C_{14}F_{10}H_6$, 6·3), 264 (P-C_4F_8, $C_{12}F_6H_6$, 100, B), 249 (P-$C_5F_8H_3$, $C_{11}F_6H_3$, 7·8) and 100 (C_2F_4, 2·1).

Metastable ions: 464 → 364 (-C_2F_4) at 285·6, 364 → 264 (-C_2F_4) at 191·5 and 264 → 249 (-CH_3) at 234·9.

(XXIII)
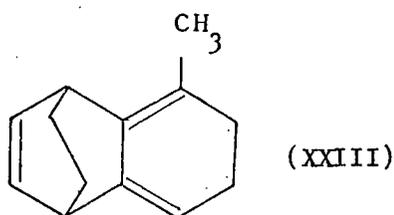
406 (P, $C_{13}F_{13}H_3$, 31·6), 387 (P-F, $C_{13}F_{12}H_3$, 8·4), 306 (P-C_2F_4, $C_{11}F_9H_3$, 69·5), 291 (P-$C_3F_4H_3$, $C_{10}F_9$, 13·1), 287 (P-C_2F_5, $C_{11}F_8H_3$, 10·1), 268 (P-C_2F_6, $C_{11}F_7H_3$, 8·4), 256 (P-C_3F_6, $C_{10}F_7H_3$, 8·4), 237 (P-C_3F_7, $C_{10}F_6H_3$, 100, B), 218 (P-C_3F_8, $C_{10}F_5H_3$, 10·5), 206 (P-C_4F_8, $C_9F_3H_3$, 14·7) and 187 (P-C_4F_9, $C_9F_4H_3$, 27·4).

Metastable ions: 406 → 306 (-C_2F_4) at 230·6, 306 → 237 (-CF_3) at 183·5 and 237 → 187 (-CF_2) at 147·4.

(XXIV)
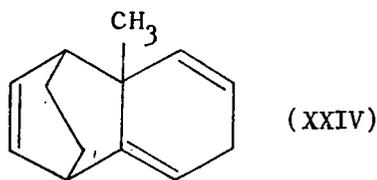
406 (P, $C_{13}F_{13}H_3$, 70·0), 391 (P-CH_3, $C_{12}F_{13}$, 17·0), 387 (P-F, $C_{13}F_{12}H_3$, 9·5), 356 (P-CF_2, $C_{12}F_{11}H_3$, 26·2), 306 (P-C_2F_4, $C_{10}F_9H_3$, 31·0), 291 (P-$C_3F_4H_3$, $C_{10}F_9$, 100, B), 287 (P-C_2F_5, $C_{11}F_8H_3$, 24·8), 272 (P-$C_3F_5H_3$, $C_{10}F_8$, 28·5), 241 (P-$C_4F_8H_3$, C_9F_7, 65·1) and 237 (P-C_3F_7, $C_{10}F_6H_3$, 30·0).

(XXV)
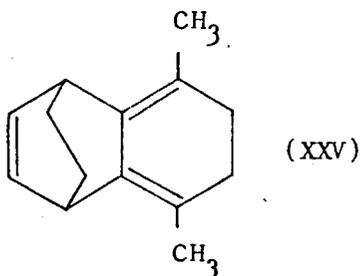
402 (P, $C_{14}F_{12}H_6$, 34·9), 383 (P-F, $C_{14}F_{11}H_6$, 9·3), 302 (P-C_2F_4, $C_{12}F_8H_6$, 58·1), 287 (P-$C_3F_4H_3$, $C_{11}F_8H_3$, 11·6), 233 (P-C_3F_7, $C_{11}F_5H_6$, 100, B), 218 (P-$C_4F_7H_3$, $C_{10}F_5H_3$, 18·6) and 187 (P-$C_5F_8H_3$, $C_9F_4H_3$, 9·3).

Metastable ions: 402 → 302 (-C_2F_4) at 226·9 and 302 → 233 (-CF_3) at 180·2.
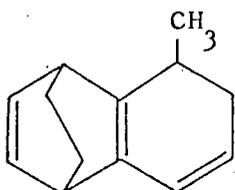
(XXVI)

406 (P, $C_{13}F_{13}H_3$, 22·2), 387 (P-F, $C_{13}F_{12}H_3$, 4·6), 337 (P-CF$_3$, $C_{12}F_{10}H_3$, 4·0), 336 (P-CHF$_3$, $C_{12}F_{10}H_2$, 4·0), 310 (P-C$_3$F$_3$H$_3$, $C_{10}F_{10}$, 24·2), 306 (P-C$_2$F$_4$, $C_{11}F_9H_3$, 71·7), 291 (P-C$_3$F$_4$H$_3$, $C_{10}F_9$, 33·3), 287 (P-C$_2$F$_5$, $C_{11}F_8H_3$, 8·0), 272 (P-C$_3$F$_5$H$_3$, $C_{10}F_8$, 10·1), 268 (P-C$_2$F$_6$, $C_{11}F_7H_3$, 15·1), 267 (P-C$_2$F$_6$H, $C_{11}F_7H_2$, 11·0), 241 (P-C$_4$F$_6$H$_3$, C_9F_7, 35·3), 237 (P-C$_3$F$_7$, $C_{10}F_6H_3$, 100, B), 223 (P-C$_4$F$_7$H$_2$, C_9F_6H, 12·1), 218 (P-C$_3$F$_8$, $C_{10}F_5H_3$, 9·0), 205 (P-C$_4$F$_8$H, $C_9F_5H_3$, 13·1) and 187 (P-C$_4$F$_9$, $C_9F_4H_3$, 22·2).

Metastable ion: 306 $\rightarrow$ 237 (-CF$_3$) at 183·6
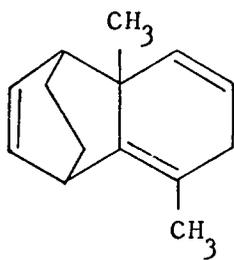
(XXVII)

402 (P, $C_{14}F_{12}H_6$, 80·0), 387 (P-CH$_3$, $C_{13}F_{12}H_3$, 27·2), 383 (P-F, $C_{14}F_{11}H_6$, 12·0), 352 (P-CF$_2$, $C_{13}F_{10}H_6$, 40·0), 333 (P-CF$_3$, $C_{13}F_9H_6$, 12·0), 302 (P-C$_2$F$_4$, $C_{12}F_8H_6$, 19·2), 287 (P-C$_3$F$_4$H$_3$, $C_{11}F_8H_3$, 100, B), 268 (P-C$_3$F$_5$H$_3$, $C_{11}F_7H_3$, 60·0), 252 (P-C$_3$F$_6$, $C_{11}F_6H_6$, 14·4), 249 (P-C$_3$F$_6$H$_3$, $C_{11}F_6H_3$, 16·0), 237 (P-C$_4$F$_6$H$_3$, $C_{10}F_6H_3$, 37·2), 233 (P-C$_3$F$_7$, $C_{11}F_5H_6$, 32·0), 218 (P-C$_4$F$_7$H$_3$, $C_{10}F_5H_3$, 32·0), 205 (P-C$_5$F$_7$H$_4$, $C_9F_5H_2$, 12·0) and 187 (P-C$_5$F$_8$H$_3$, $C_9F_4H_3$, 22·3).
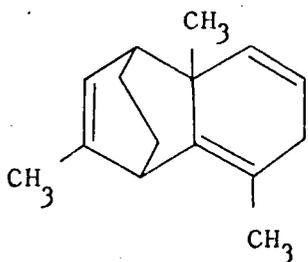
(XXVIII)

398 (P, $C_{15}F_{11}H_9$, 52·6), 383 (P-CH$_3$, $C_{14}F_{11}H_6$, 14·3), 379 (P-F, $C_{15}F_{10}H_9$, 4·5),

348 (P-CF$_2$, C$_{14}$F$_9$H$_9$, 37·8), 333 (P-C$_2$F$_2$H$_3$, C$_{13}$F$_9$H$_6$, 4·2), 298 (P-C$_2$F$_4$, C$_{13}$F$_7$H$_9$, 21·5), 283 (P-C$_3$F$_4$H$_3$, C$_{12}$F$_7$H$_6$, 100, B), 268 (P-C$_4$F$_4$H$_6$, C$_{11}$F$_7$H$_3$, 11·6), 264 (P-C$_3$F$_5$H$_3$, C$_{12}$F$_6$H$_6$, 15·7), 263 (P-C$_3$F$_5$H$_4$, C$_{12}$F$_6$H$_2$, 10·4), 248 (P-C$_3$F$_6$, C$_{12}$F$_5$H$_9$, 8·2), 233 (P-C$_4$F$_6$H$_3$, C$_{11}$F$_5$H$_6$, 18·3), 229 (P-C$_3$F$_7$, C$_{12}$F$_4$H$_9$, 27·3), 218 (P-C$_5$F$_6$H$_6$, C$_{10}$F$_5$H$_3$, 6·8), 214 (P-C$_4$F$_7$H$_3$, C$_{11}$F$_4$H$_6$, 8·2), 213 (P-C$_4$F$_7$H$_4$, C$_{11}$F$_4$H$_5$, 6·5), 169 (C$_3$F$_7$, 6·6), 131 (C$_3$F$_5$, 7·1) and 69 (CF$_3$, 7·9).
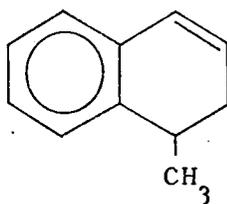
(XXX)

306 (P, C$_{11}$F$_9$H$_3$, 70·3), 291 (P-CH$_3$, C$_{10}$F$_9$, 35·1), 287 (P-F, C$_{11}$F$_8$H$_3$, 11·0), 272 (P-CFH$_3$, C$_{10}$F$_8$, 12·5), 267 (P-F$_2$H, C$_{11}$F$_7$H$_2$, 12·0), 253 (P-CF$_2$H$_3$, C$_{10}$F$_7$, 9·5) 241 (P-C$_2$F$_2$H$_3$, C$_9$F$_8$, 37·1), 237 (P-CF$_3$, C$_{10}$F$_6$H$_3$, 100, B), 236 (P-CF$_3$H, C$_{10}$F$_6$H$_2$, 28·6), 223 (P-C$_2$F$_3$H$_2$, C$_9$F$_6$H, 11·8), 205 (P-C$_2$F$_4$H, C$_9$F$_5$H$_2$, 26·0) and 187 (P-C$_2$F$_5$, C$_9$F$_4$H$_3$, 54·8).

Metastable ions: 306 ⟶ 237 (-CF$_3$) at 184·0 and 237 ⟶ 187 (-CF$_2$) at 147·5.
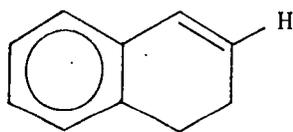
(XXXI) *

292 (P, C$_{10}$F$_9$H, 47·0), 273 (P-F, C$_{10}$F$_8$H, 18·0), 272 (P-HF, C$_{10}$F$_8$, 18·0), 254 (P-F$_2$, C$_{10}$F$_7$H, 4·5), 253 (P-HF$_2$, C$_{10}$F$_7$, 11·9), 242 (P-CF$_2$, C$_9$F$_7$H, 19·9), 241 (P-CHF$_2$, C$_9$F$_7$, 6·9), 223 (P-CF$_3$, C$_9$F$_6$H, 7·9), 222 (P-CHF$_3$, C$_9$F$_6$, 100, B), 203 (P-CHF$_4$, C$_9$F$_5$, 35·4) and 192 (P-C$_2$F$_4$, C$_8$F$_5$H, 8·4).

Metastable ions: 292 ⟶ 222 (-CHF$_3$) at 168·9, 273 ⟶ 223 (-CF$_2$) at 182·2, 272 ⟶ 222 (-CF$_2$) at 182·2 and 222 ⟶ 203 (-F) at 185·7.

(XXXII) *
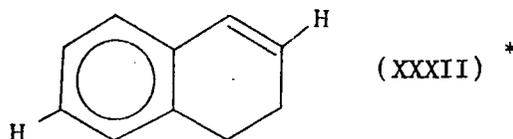
274 (P, $C_{10}F_8H_2$, 62·6), 273 (P-H, $C_{10}F_8H$, 4·5), 255 (P-F, $C_{10}F_7H_2$, 15·3), 254 (P-HF, $C_{10}F_7H$, 17·5), 236 (P-F_2, $C_{10}F_6H_2$, 10·8), 224 (P-CF_2, C_9F_6H, 18·6), 223 (P-CHF_2, C_9F_6H, 15·0), 205 (P-CF_3, $C_9F_5H_2$, 16·6), 204 (P-CHF_3, C_9F_5H, 100, B), 187 (P-CF_4, $C_9F_4H_2$, 4·8), 186 (P-CHF_4, C_9F_4H, 5·6) and 174 (P-C_2F_4, $C_8F_4H_2$, 6·8).

Metastable ions: 274 → 205 (-CF_3) at 153·4, 273 → 204 (-CF_2) at 152·4, 255 → 205 (-CF_2) at 164·9, 254 → 204 (-CF_2) at 163·9, 224 → 205 (-F) at 187·7 and 223 → 204 (-F) at 186·6.

(XXXIII)
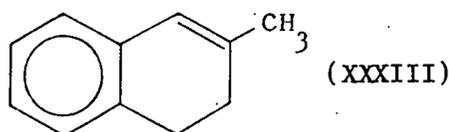
306 (P, $C_{11}F_9H_3$, 69·0), 291 (P-CH_3, $C_{10}F_9$, 43·2), 287 (P-F, $C_{11}F_8H_3$, 20·1), 272 (P-CFH_3, $C_{10}F_8$, 6·2), 268 (P-F_2, $C_{11}F_7H_3$, 11·7), 256 (P-CF_2, $C_{10}F_7H_3$, 15·9), 255 (P-CHF_2, $C_{10}F_7H_2$, 16·6), 241 (P-$C_2F_2H_3$, C_9F_7, 17·2), 237 (P-CF_3, $C_{10}F_6H_3$, 100, B), 236 (P-CF_3H, $C_{10}F_6H_2$, 59·3), 225 (P-C_2F_3, $C_9F_6H_3$, 13·8), 206 (P-C_2F_4, $C_9F_5H_3$, 35·8) and 187 (P-C_2F_5, $C_9F_4H_3$, 48·3).

Metastable ions: 306 → 237 (-CF_3) at 183·5 and 237 → 187 (-CF_2) at 147·5.

(XXXIV)
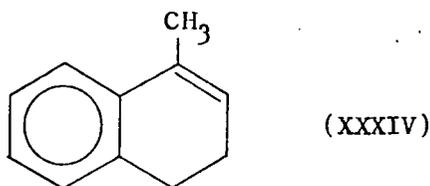
306 (P, $C_{11}F_9H_3$, 63·0), 291 (P-CH_3, $C_{10}F_9$, 15·8), 287 (P-F, $C_{11}F_8H_3$, 17·6), 268 (P-F_2, $C_{11}F_7H_3$, 11·7), 256 (P-CF_2, $C_{10}F_7H_3$, 18·1), 241 (P-$C_2F_2H_3$, C_9F_7, 19·0), 237 (P-CF_3, $C_{10}F_6H_3$, 80·5), 236 (P-CF_3H, $C_{10}F_6H_2$, 53·3), 223 (P-$C_2F_3H_2$, C_9F_6H, 13·6), 218 (P-CF_4, $C_{10}F_5H_3$, 29·0), 206 (P-C_2F_4, $C_9F_5H_3$, 36·2) and 187 (P-C_2F_5, $C_9F_4H_3$, 100, B).

Metastable ions: 306 → 237 (-CF_3) at 183·5 and 237 → 187 (-CF_2) at 147·5.
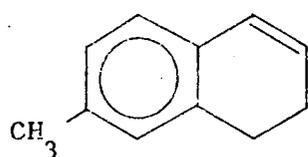
(XXXV)   and   (XXXVI)
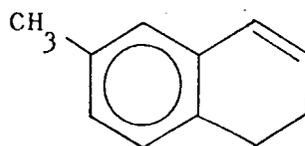
306 (P, $C_{11}F_9H_3$, 28·4), 287 (P-F, $C_{11}F_8H_3$, 18·9), 256 (P-CF$_2$, $C_{10}F_7H_3$, 18·9), 255 (P-CHF$_2$, $C_{10}F_7H_2$, 9·4), 237 (P-CF$_3$, $C_{10}F_6H_3$, 100, B), 236 (P-CHF$_3$, $C_{10}F_6H_2$, 19·6), 217 (P-CF$_4$H, $C_{10}F_5H$, 9·4), 203 (P-$C_2F_4H_3$, C_9F_5, 12·2) and 187 (P-C_2F_5, $C_9F_4H_3$, 31·0).

Metastable ions: 306 → 237 (-CF$_3$) at 183·5 and 237 → 187 (-CF$_2$) at 147·5.
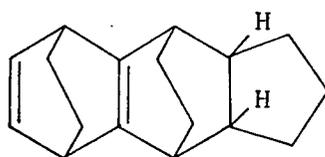
(XXXVII)

586 (P, $C_{17}F_{20}H_2$, 1·6), 567 (P-F, $C_{17}F_{19}H_2$, 9·1), 548 (P-F$_2$, $C_{17}F_{18}H_2$, 3·7), 507 (P-CF$_3$, $C_{16}F_{17}H_2$, 5·5), 486 (P-C_2F_4, $C_{15}F_{17}H_2$, 100, B), 467 (P-C_2F_5, $C_{15}F_{16}H_2$, 18·2), 386 (P-C_4F_8, $C_{13}F_{12}H_2$, 100, B), 385 (P-C_4F_8H, $C_{13}F_{12}H$, 4·5), 367 (P-C_4F_9, $C_{13}F_{11}H_2$, 45·4), 366 (P-C_4F_9H, $C_{13}F_{11}H$, 9·1), 348 (P-C_4F_{10}, $C_{13}F_{10}H_2$, 13·5), 347 (P-C_4F_{10}H, $C_{13}F_{10}H$, 4·8), 316 (P-C_5F_{11}H, $C_{12}F_9H$, 15·9), 286 (P-C_6F_{12}, $C_{11}F_8H_2$, 35·2), 268 (P-C_6F_{14}, $C_{11}F_6H_2$, 12·9), 241 (C_9F_7, 14·7), 236 (C_7F_8, 28·7), 157 (C_5F_5, 13·6), 100 (C_2F_4, 37·8) and 69 (CF$_3$, 20·5).

Metastable ions: 486 → 386 (-C_2F_4) at 306·5 and 386 → 286 (-C_2F_4) at 211·9.
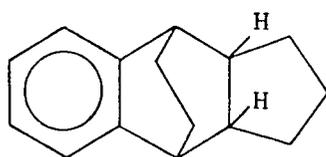
(XXXVIII)

486 (P, $C_{15}F_{16}H_2$, 77·6), 467 (P-F, $C_{15}F_{15}H_2$, 18·9). 386 (P-C_2F_4, $C_{13}F_{12}H_2$, 100, B), 385 (P-C_2F_4H, $C_{13}F_{12}H$, 11·2), 365 (P-$C_2F_5H_2$, $C_{13}F_{11}$, 6·0), 355 (P-C_3F_5, $C_{12}F_{11}H_2$, 46·6), 286 (P-C_4F_8, $C_{11}F_8H_2$, 32·8), 285 (P-C_4F_8H, $C_{11}F_8H$, 69·0), 284 (P-$C_4F_8H_2$, $C_{11}F_8$, 13·8), 267 (P-C_4F_9, $C_{11}F_7H_2$, 17·3), 241 (C_9F_7, 20·7), 236 (C_7F_8, 50·0) and 69 (CF$_3$, 33·0).

Metastable ions: 486 → 386 (-C_2F_4) at 306·5, 386 → 286 (-C_2F_4) at 211·9 and 386 → 285 (-C_2F_4H) at 210·4

(XXXIX) *
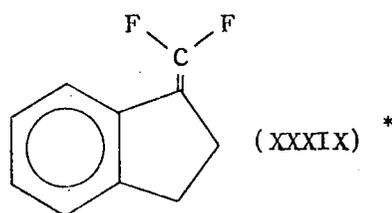
310 (P, $C_{10}F_{10}$, 39.3), 291 (P-F, $C_{10}F_9$, 17.8), 292 (P-F$_2$, $C_{10}F_8$, 5.7), 260 (P-CF$_2$, C_9F_8, 9.0), 241 (P-CF$_3$, C_9F_7, 100, B), 222 (P-CF$_4$, C_9F_6, 6.9), 210 (P-C$_2$F$_4$, C_8F_6, 11.8), 203 (P-CF$_5$, C_9F_5, 4.3), 191 (P-C$_2$F$_5$, C_8F_5, 5.5), 172 (P-C$_2$F$_6$, C_8F_4, 5.0), 160 (P-C$_3$F$_6$, C_7F_4, 4.0) and 141 (P-C$_3$F$_7$, C_7F_3, 9.6).

Metastable ions: 310 $\rightarrow$ 241 (-CF$_3$) at 187.9, 291 $\rightarrow$ 241 (-CF$_2$) at 199.5 and 241 $\rightarrow$ 191 (-CF$_2$) at 151.4.

(XXXX) *
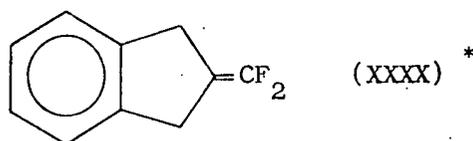
310 (P, $C_{10}F_{10}$, 64.6), 291 (P-F, $C_{10}F_9$, 100, B), 272 (P-F$_2$, $C_{10}F_8$, 14.9), 260 (P-CF$_2$, C_9F_8, 9.6), 241 (P-CF$_3$, C_9F_7, 88.5), 222 (P-CF$_4$, C_9F_6, 10.7), 210 (P-C$_2$F$_4$, C_8F_6, 4.6), 203 (P-CF$_5$, C_9F_5, 3.2), 191 (P-C$_2$F$_5$, C_8F_5, 3.4), 172 (P-C$_2$F$_6$, C_8F_4, 3.0) and 141 (P-C$_3$F$_7$, C_7F_3, 3.5).

Metastable ions: 310 $\rightarrow$ 241 (-CF$_3$) at 187.9, 291 $\rightarrow$ 241 (-CF$_2$) at 199.5 and 291 $\rightarrow$ 272 (-F) at 254.2.

(XXXXI)
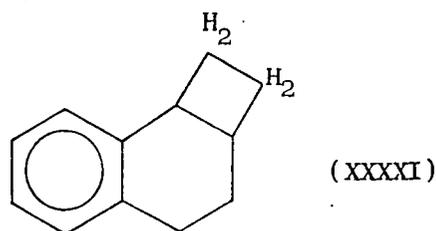
338 (P, $C_{12}F_{10}H_4$, 16.0), 323 (P-CH$_3$, $C_{11}F_{10}H$, 3.0), 319 (P-F, $C_{12}F_9H_4$, 6.2), 310 (P-C$_2$H$_4$, $C_{10}F_{10}$, 100, B), 291 (P-C$_2$FH$_4$, $C_{10}F_9$, 15.4), 260 (P-C$_3$F$_2$H$_4$, C_9F_8, 21.4), 241 (P-C$_3$F$_3$H$_4$, C_9F_7, 83.1), 238 (P-C$_2$F$_4$, $C_{10}F_6H_4$, 12.0), 237 (P-C$_2$F$_4$H, $C_{10}F_6H_3$, 16.8) 223 (P-C$_3$F$_3$H$_3$, C_9F_7H, 40.7), 210 (P-C$_4$F$_4$H$_4$, C_8F_6, 5.8) and 205 (P-C$_3$F$_5$, $C_9F_7H_4$, 7.5).

Metastable ion: 310 $\rightarrow$ 241 (-CF$_3$) at 187.4.
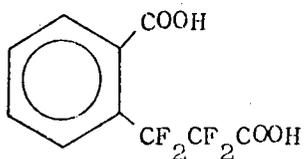
(XXXXII)

292 (P-CH_2O_2, $C_9F_8O_2$, 68.3), 273 (P-CFH_2O_2, $C_9F_7O_2$, 18.3), 264 (P-$C_2H_2O_3$, C_8F_8O, 83.4), 245 (P-$C_2FH_2O_3$, C_8F_7O, 15.7), 214 (P-$C_3F_2H_2O_3$, C_7F_6O, 100, B), 195 (P-$C_3F_3H_2O_3$, C_7F_5O, 73.3), 164 (P-$C_4F_4H_2O_3$, C_6F_4O, 29.0), 157 (P-$C_3F_5H_2O_3$, C_7F_3O, 15.7), 133 (P-$C_5F_5H_2O_3$, C_5F_3O, 16.2), 109 (13.9) and 44 (CO_2, 100, B).

Metastable ions: 292 $\rightarrow$ 264 (-CO) at 238.7, 264 $\rightarrow$ 214 (-CF_2) at 173.5, 264 $\rightarrow$ 195 (-CF_3) at 144.1 and 214 $\rightarrow$ 195 (-F) at 177.8.

(XXXXIII)   and
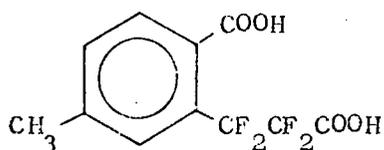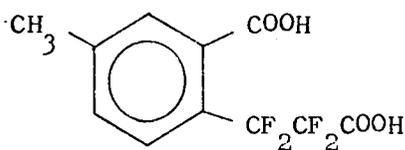
(XXXXIV)

334 (P, $C_{11}F_7O_4H_5$, 20.1), 317 (P-OH, $C_{11}F_7O_3H_4$, 4.0), 239 (P-$C_2FO_3H_4$, C_9F_6OH, 9.3), 219 (P-$C_2F_2O_3H_5$, C_9F_5O, 100, B), 195 (P-$C_4F_2O_3H_5$, C_7F_5O, 8.0), 194 (P-$C_3F_2O_4H_2$, $C_8F_5H_3$, 8.0), 164 (P-$C_5F_3O_3H_5$, C_6F_4O, 10.7), 143 (7.6) and 44 (CO_2, 6.7).

Metastable ion: 239 $\rightarrow$ 219 (-HF) at 200.7.

APPENDIX C

Infra-red Spectra

The infra-red spectra are given in the order (I), (II) .... (XXXXIV). The spectra ($2 \cdot 5 \longrightarrow 25\mu$) were obtained using KBr cells and were run as liquids, unless denoted by (D) which designates that the spectrum was obtained from a KBr disc. [The exception being compound (I) whose spectrum was obtained in the gas phase].
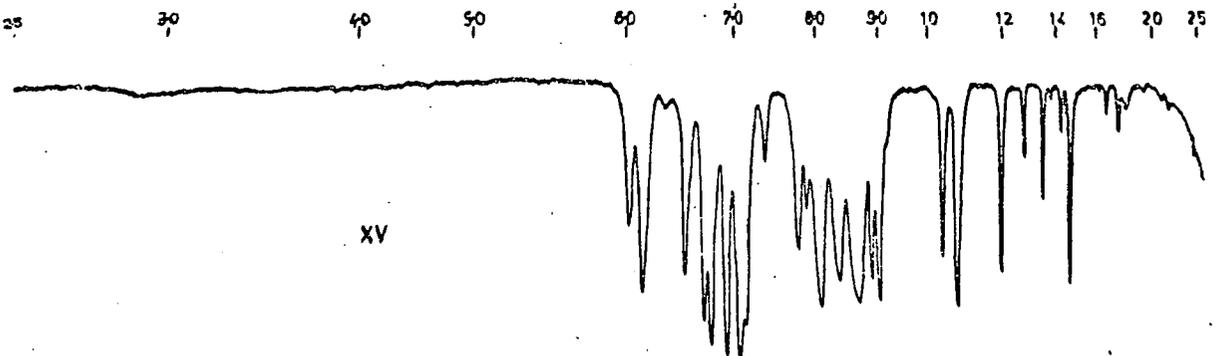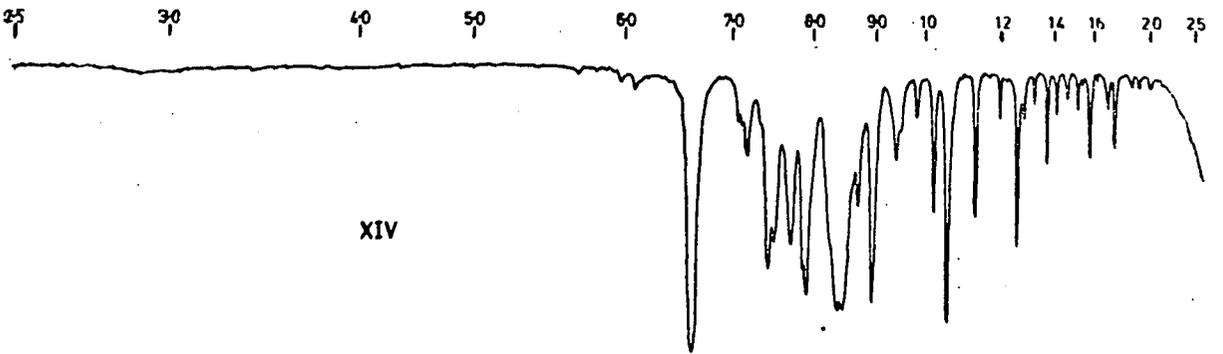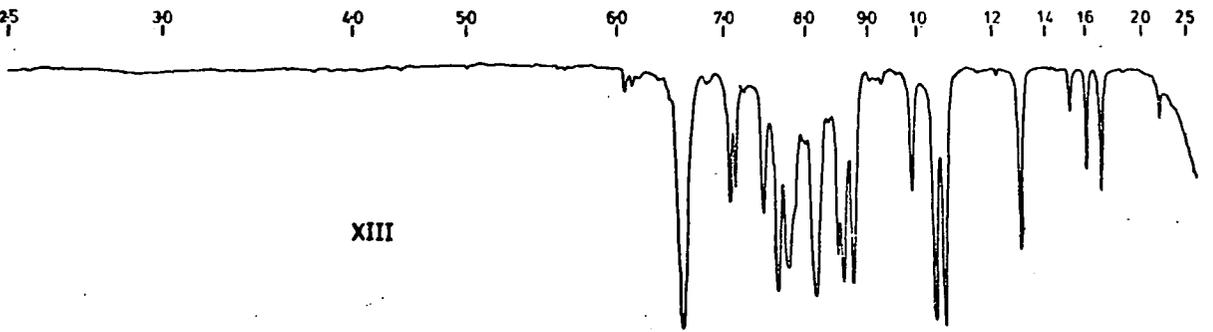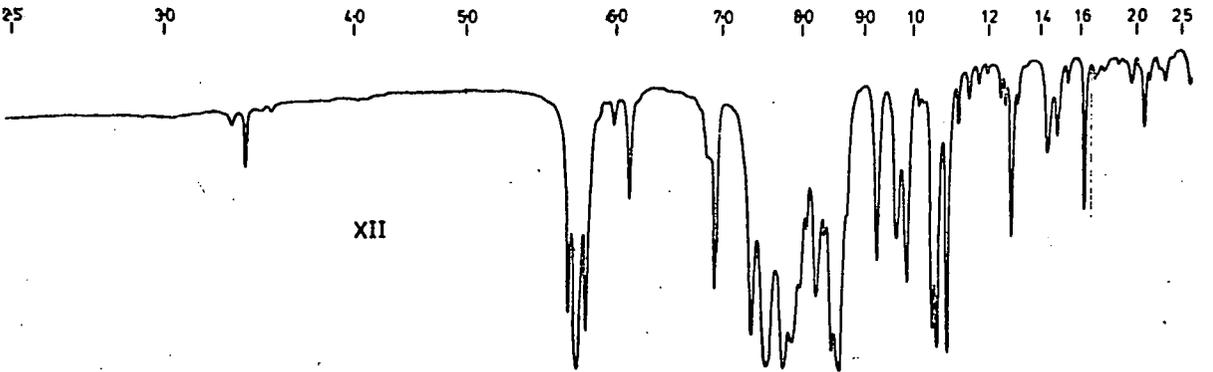
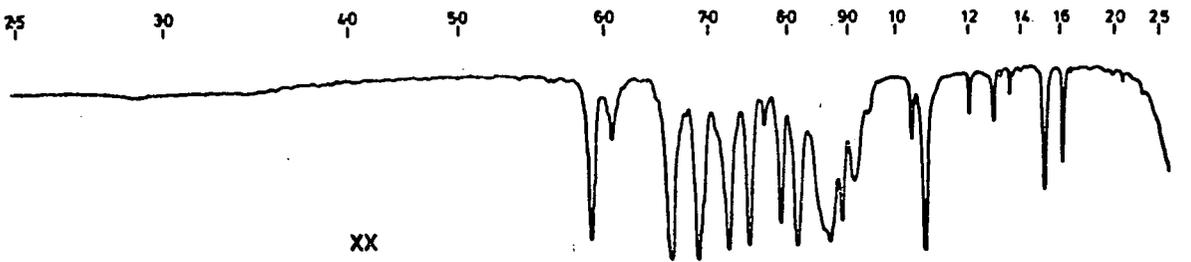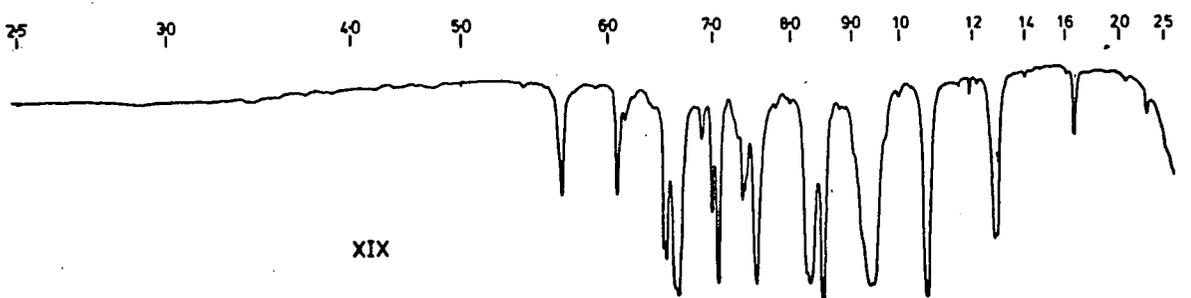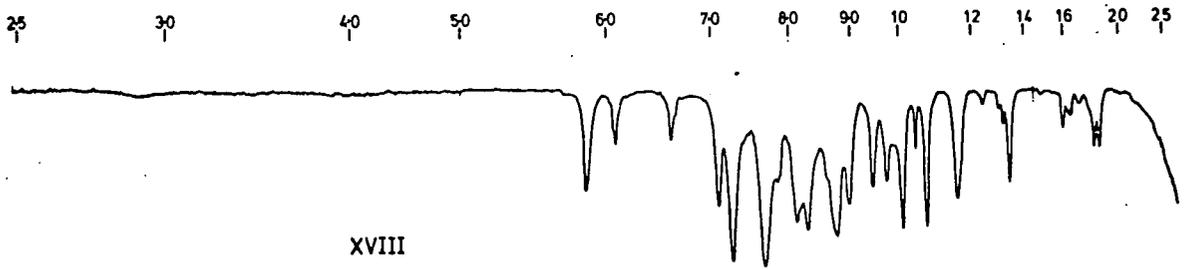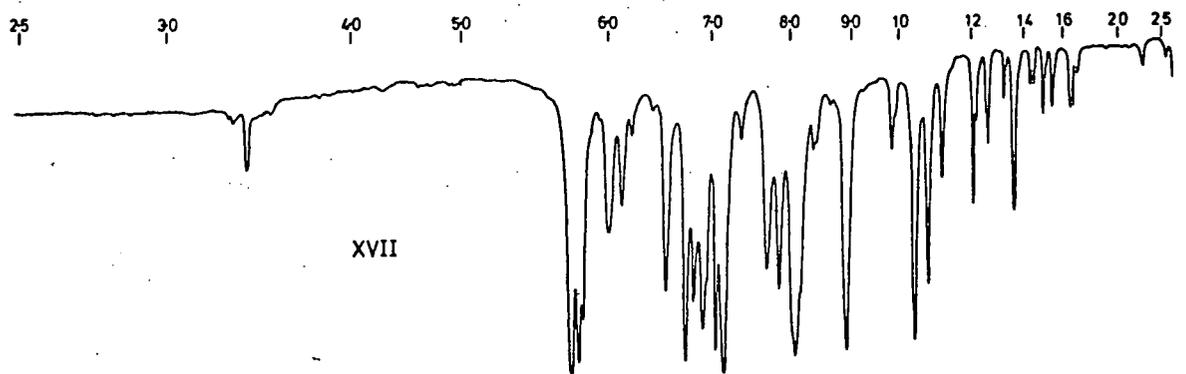| Compound Number	Name of Compound	
(I)	perfluorobicyclo[4,1,0]hept-3-ene	
(II)	endo-5-bromo-1,2,3,4,7,7,8,8-octafluorobicyclo[2,2,2]-oct-2-ene	
(III)	1,2,3,4,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene	
(IV)	dimethyl 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate	(D)
(V)	isomers of dimethyl 2-(3'-oxa-2'-pentyl)-1,4,5,6,7,7,8,8-octafluorotricyclo[2,2,2,0^{3,5}]octane-2,3-dicarboxylate	(D)
(VI)	perfluorotricyclo[6,2,2,0^{2,7}]tetradeca-2,4,6,9-tetraene	
(VII)	4H,4H,5H,5H-tetradecafluorotetracyclo[6,2,2,2^{3,6},0^{2,7}]-tetradeca-2,9-diene	(D)
(VIII)	4H,4H,5H,5H-tetradecafluorotetracyclo[6,2,2,2^{3,6},0^{2,7}]-tetradeca-2,9-diene	(D)
(IX)	4,5-dimethyltetradecafluorotetracyclo[6,2,2,2^{3,6},0^{2,7}]-tetradeca-2,4,9-triene	(D)
(X)	4,5-dimethyltetradecafluorotetracyclo[6,2,2,2^{3,6},0^{2,7}]-tetradeca-2,4,9-triene	(D)
(XI)	dimethyl tetradecafluorotetracyclo[6,2,2,2^{3,6},0^{2,7}]-tetradeca-2,4,9-triene-4,5-dicarboxylate	(D)
(XII)	dimethyl tetradecafluorotetracyclo[6,2,2,2^{3,6},0^{2,7}]-tetradeca-2,4,9-triene-4,5-dicarboxylate	(D)

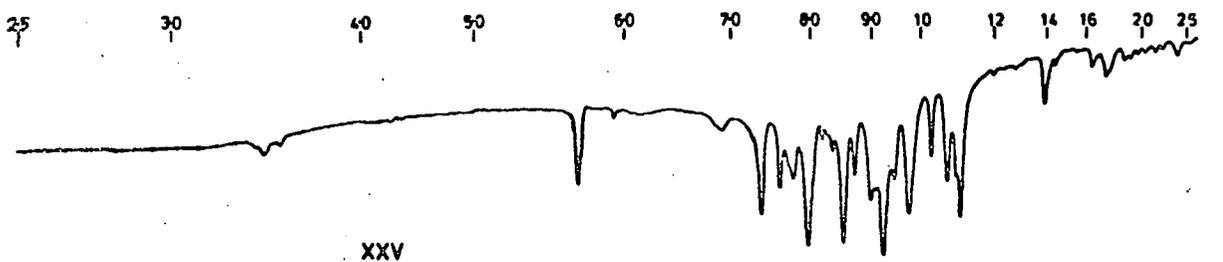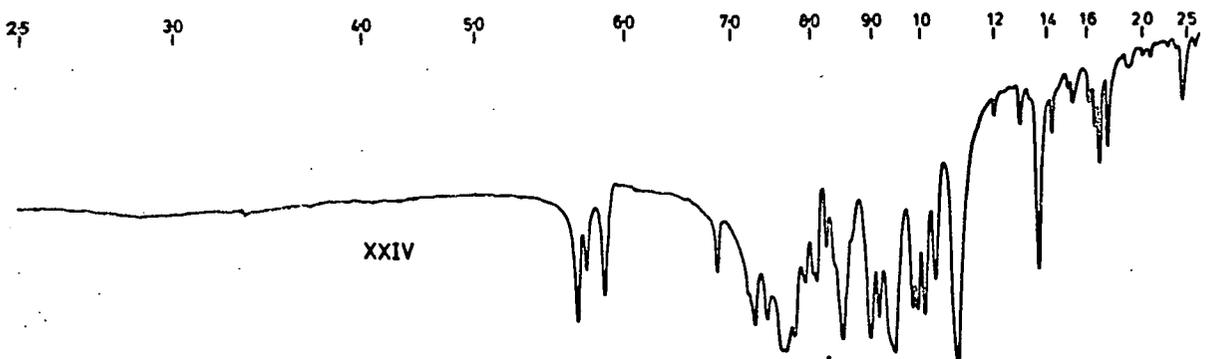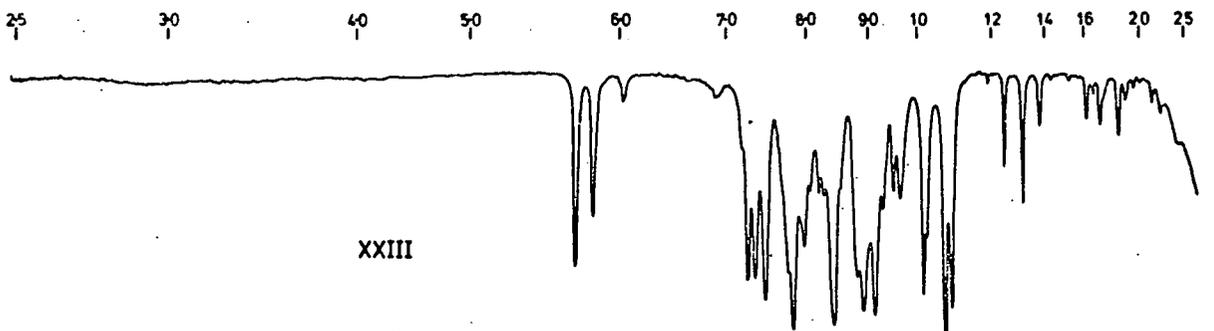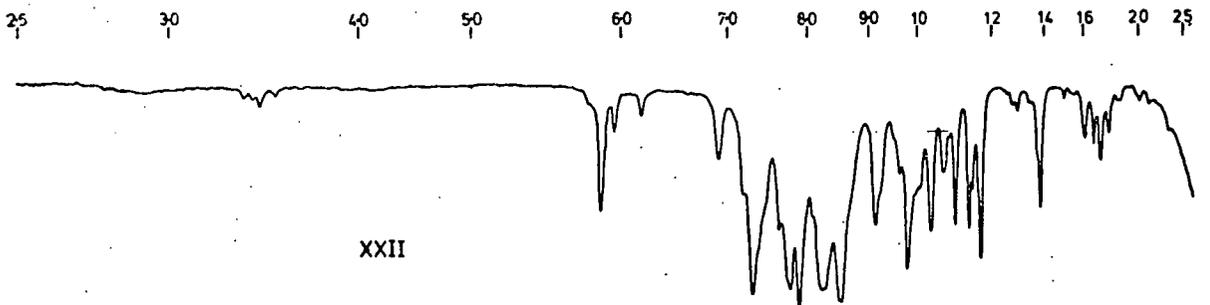| Compound Number	Name of Compound	
(XIII)	perfluorotricyclo[6,2,2,0^{2,7}]dodeca-2,4,6-triene	(D)
(XIV)	perfluoro-9-aza-10-methyltricyclo[6,2,2,0^{2,7}]-dodeca-2,4,6,9-tetraene	
(XV)	perfluoro-3-methylisoquinoline	
(XVI)	9H,9H,10H,10H-decafluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,4,6-triene	(D)
(XVII)	dimethyl hexafluoronaphthalene-2,3-dicarboxylate	(D)
(XVIII)	perfluorotricyclo[8,2,0,0^{2,7}]dodeca-2,6,8-triene	
(XIX)	perfluoro-1,4-dihydronaphthalene	
(XX)	perfluoro-2 or -3-methylindene	
(XXI)	perfluoro-1,2-dihydronaphthalene	
(XXII)	11,12-dimethyltetradecafluorotetracyclo-[8,2,2,0^{3,6},0^{2,9}]tetradeca-2,7,11-triene	(D)
(XXIII)	3-methyltridecafluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,6,9-triene	
(XXIV)	7-methyltridecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,5,9-triene	(D)
(XXV)	3,6-dimethyldodecafluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,6,9-triene	(D)
(XXVI)	6-methyltridecafluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,3,9-triene	(D)
(XXVII)	3,7-dimethyldodecafluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,5,9-triene	(D)
(XXVIII)	3,7,10-trimethylundecafluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,5,9-triene	(D)
(XXX)	1,2,2,3,4,5,6,7,8-nonafluoro-1-methyl-1,2-dihydronaphthalene	
(XXXI)	1,1,2,2,4,5,6,7,8-nonafluoro-1,2-dihydronaphthalene	
(XXXII)	1,1,2,2,4,5,6,8-octafluoro-1,2-dihydronaphthalene	

Compound Number	Name of Compound	
(XXXIII)	1,1,2,2,4,5,6,7,8-nonafluoro-3-methyl-1,2-dihydronaphthalene	
(XXXIV)	1,1,2,2,3,5,6,7,8-nonafluoro-4-methyl-1,2-dihydronaphthalene	
(XXXV) 66%	1,1,2,2,3,4,5,6,8-nonafluoro-7-methyl-1,2-dihydronaphthalene, and	
(XXXVI) 33%	1,1,2,2,3,4,5,7,8-nonafluoro-6-methyl-1,2-dihydronaphthalene	
(XXXVII)	4H,8H-eicosafluoropentacyclo$[9,2,2,2^{3,9},0^{2,10},0^{4,8}]$-heptadeca-2,12-diene	(D)
(XXXVIII)	9H,13H-hexadecafluorotetracyclo$[6,5,2,0^{2,7},0^{9,13}]$-pentadeca-2,4,6-triene	(D)
(XXXIX)	perfluoro-2-methyleneindane	
(XXXX)	perfluoro-1-methyleneindane	
(XXXXI)	11H,11H,12H,12H-decafluorotricyclo$[8,2,0,0^{2,7}]$-dodeca-2,4,6-triene	(D)
(XXXXII)	3-(2-carboxy,3,4,5,6-tetrafluorophenyl)-perfluoropropionic acid	(D)
(XXXXIII) 66%	3-(2-carboxy,5-methyl,3,4,6-trifluorophenyl)-perfluoropropionic acid and	
(XXXXIV) 33%	3-(2-carboxy,4-methyl,2,5,6-trifluorophenyl)-perfluoropropionic acid	(D)
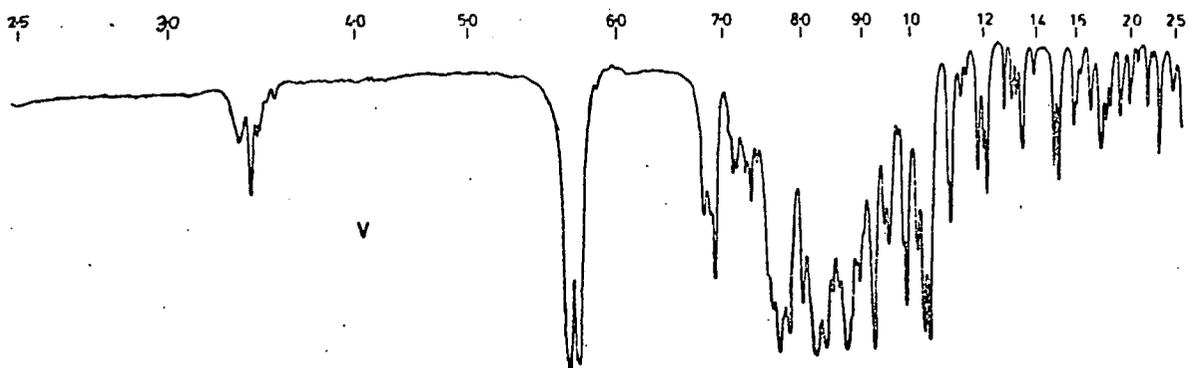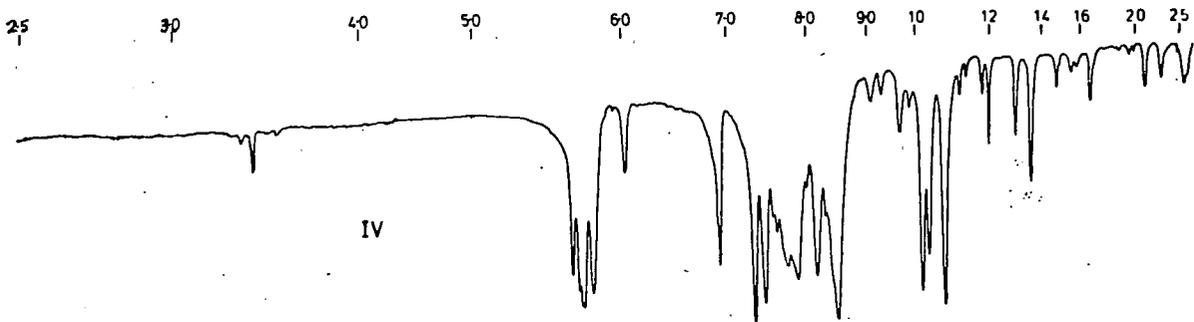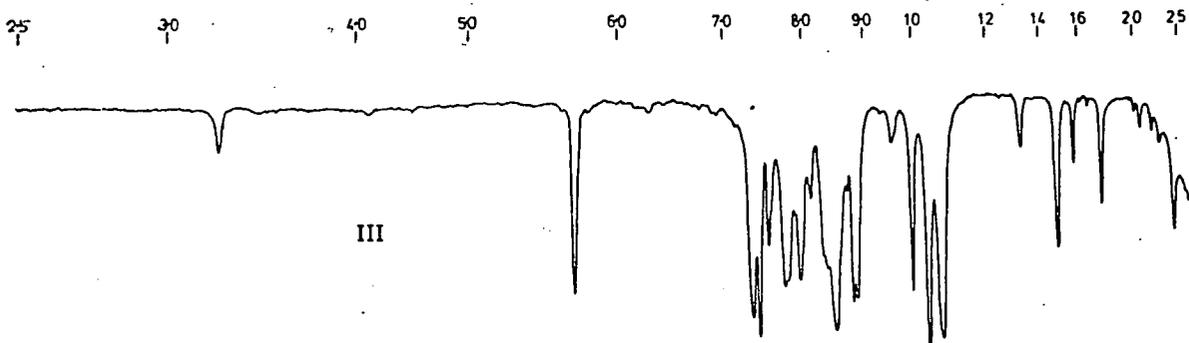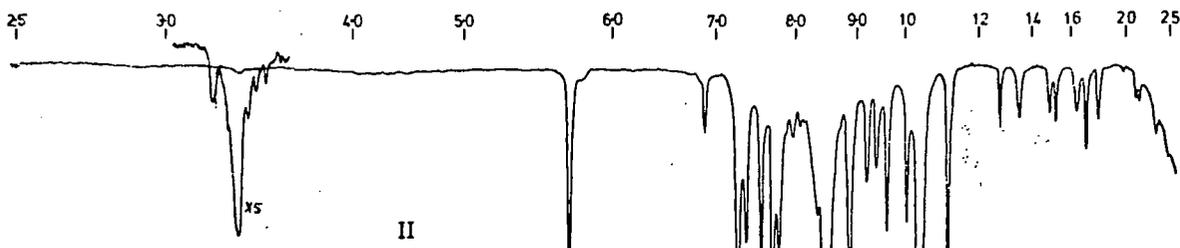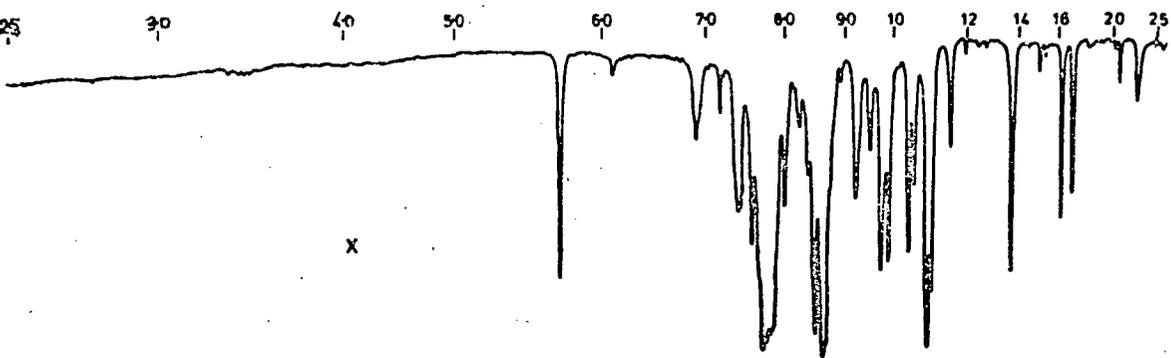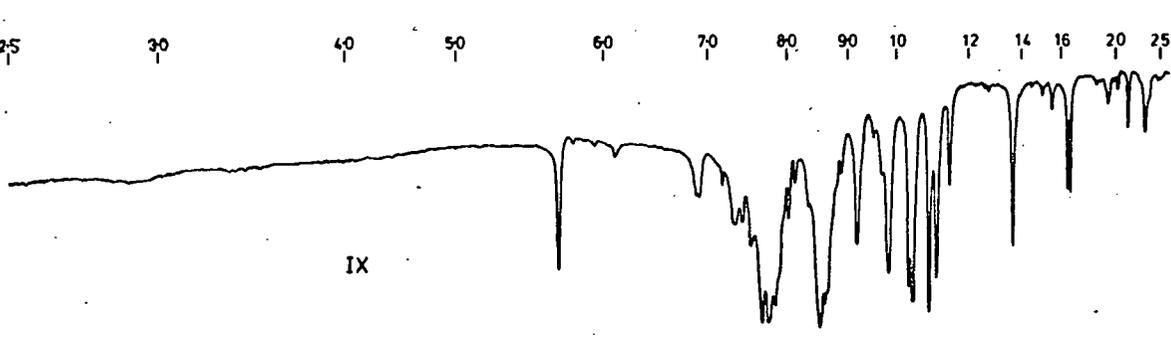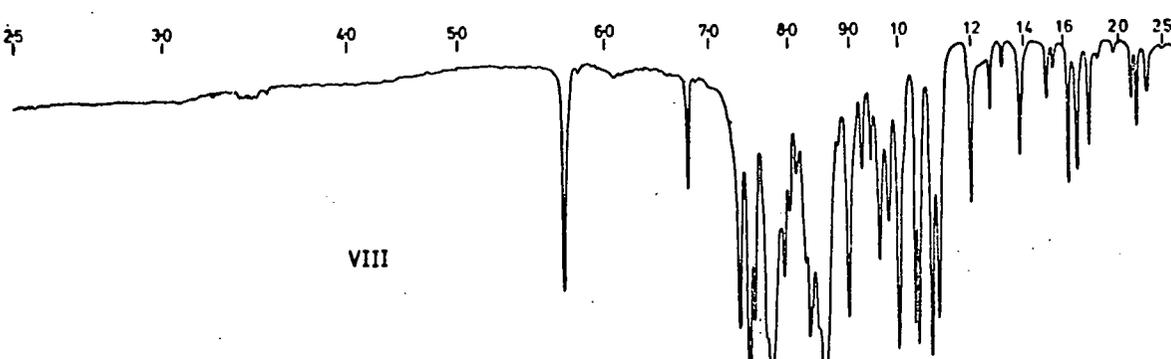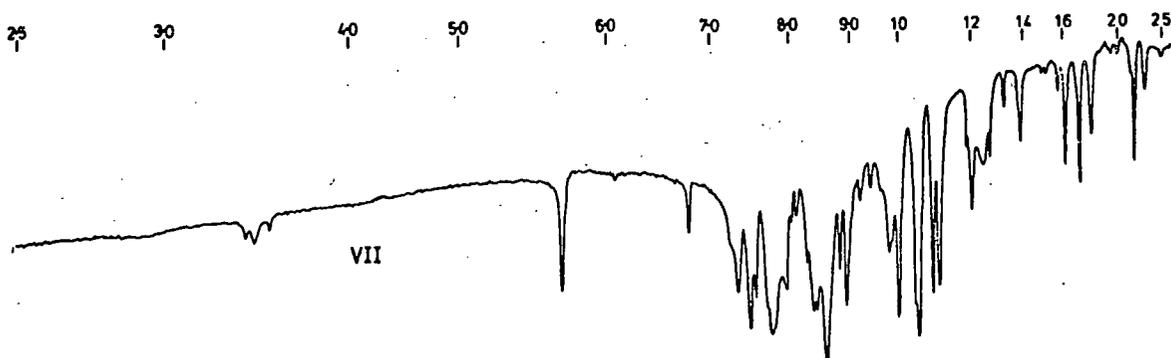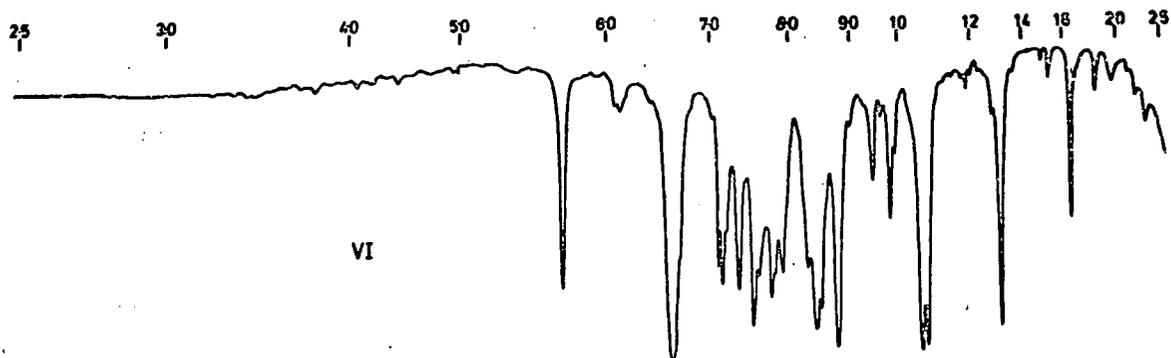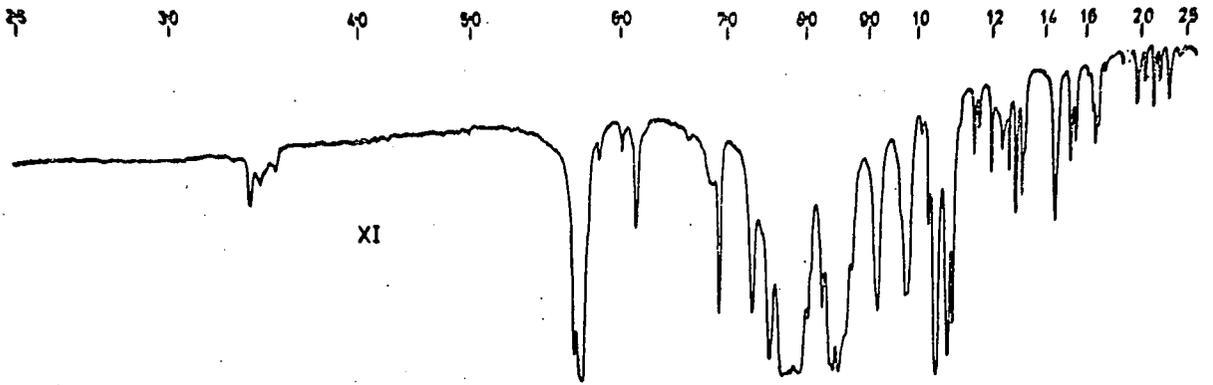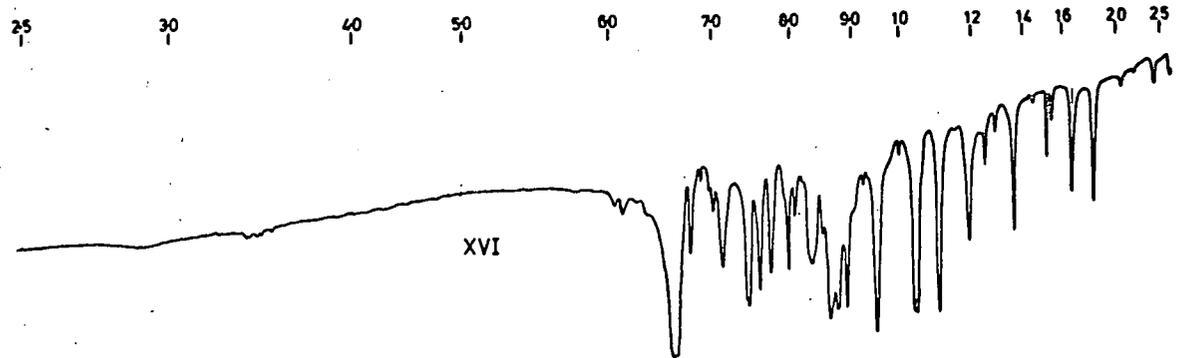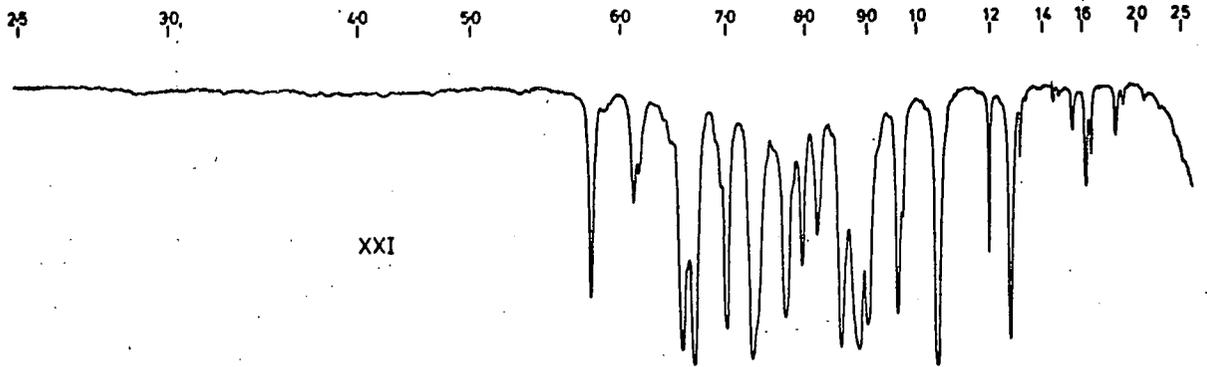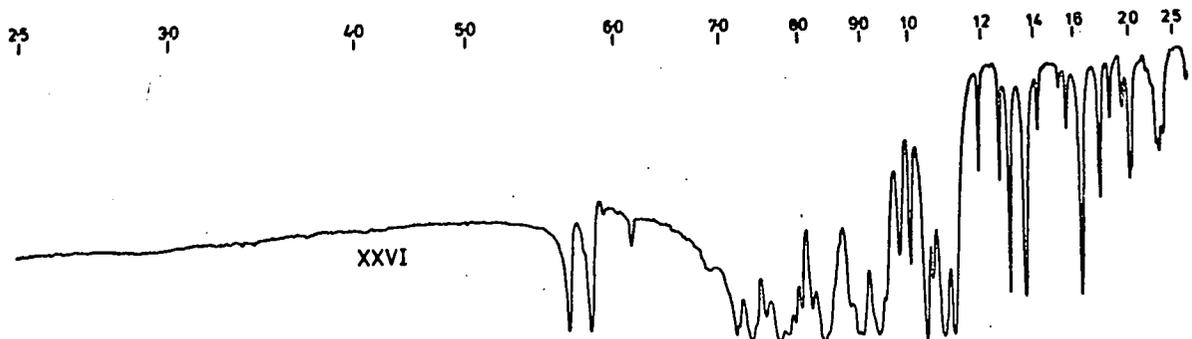
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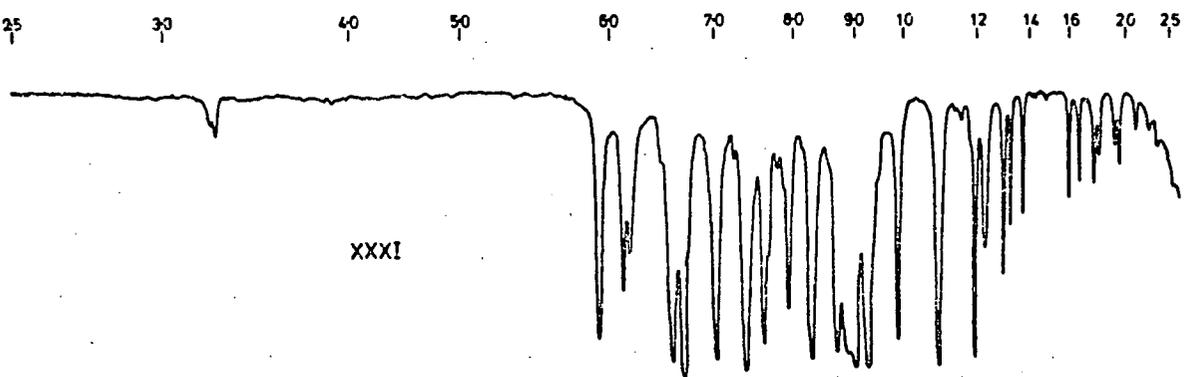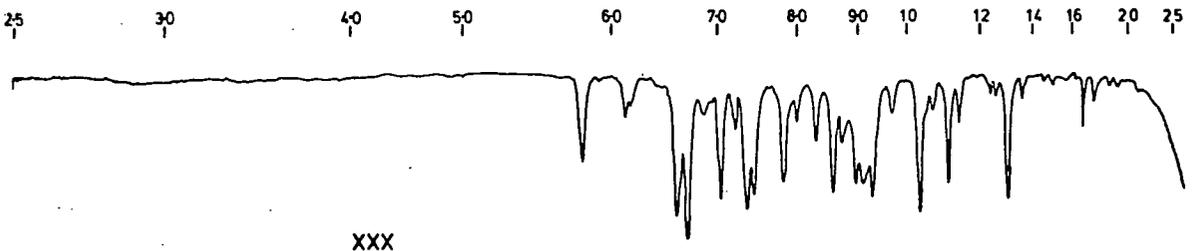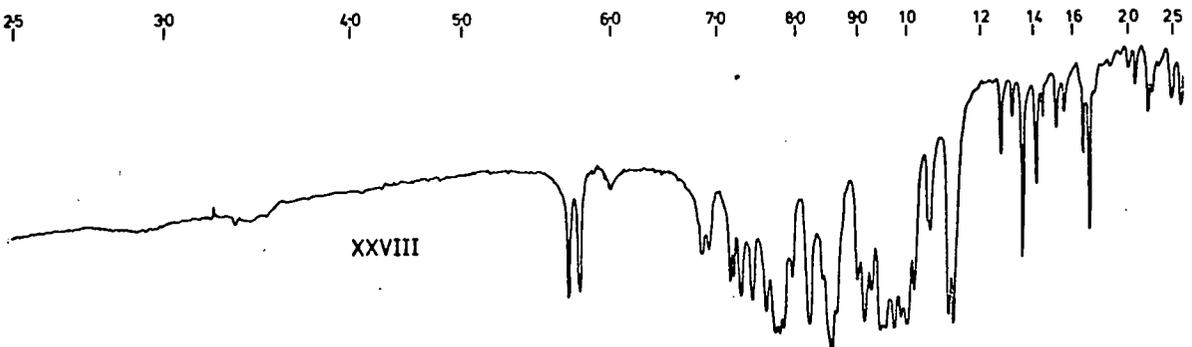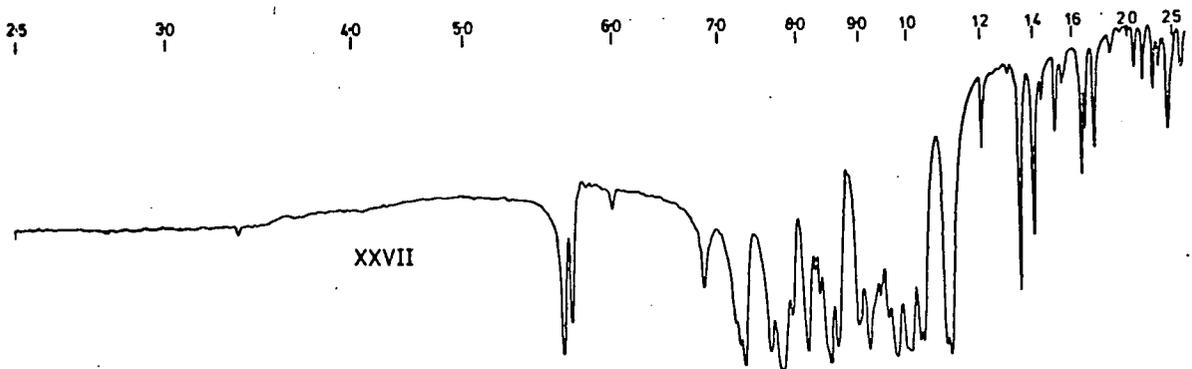
IX

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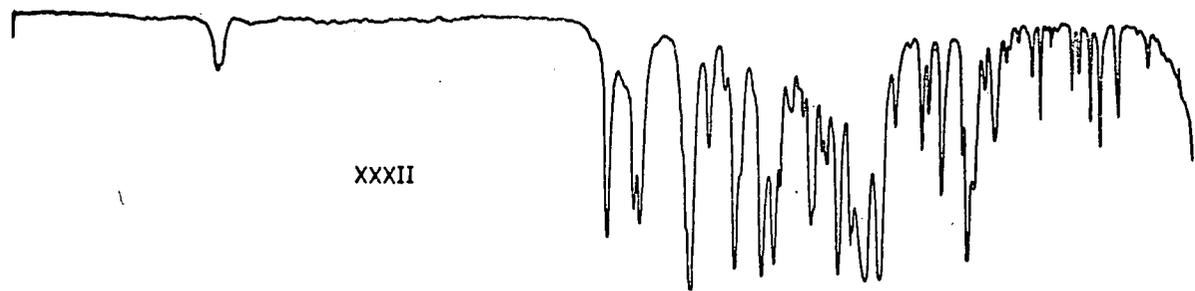
XXXI

XXXII

XXXIII

XXXIV

XXXV (66%)
and
XXXVI (33%)

XXXVII

XXXVIII

XXXIX

XXXX

XXXXI

XXXXII

XXXXIII (66%)
and
XXXXIV (33%)
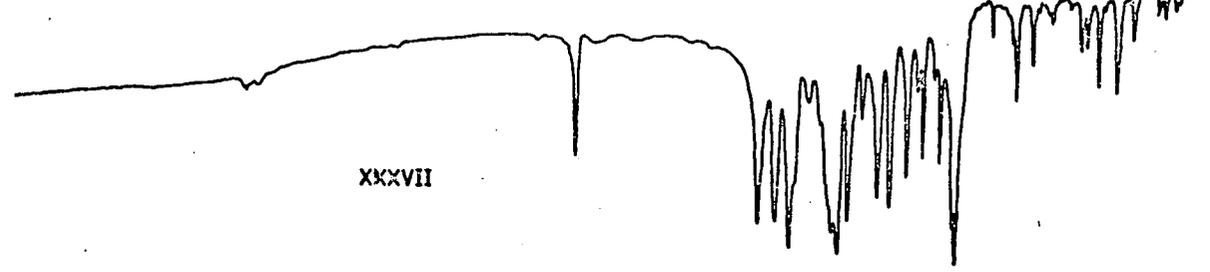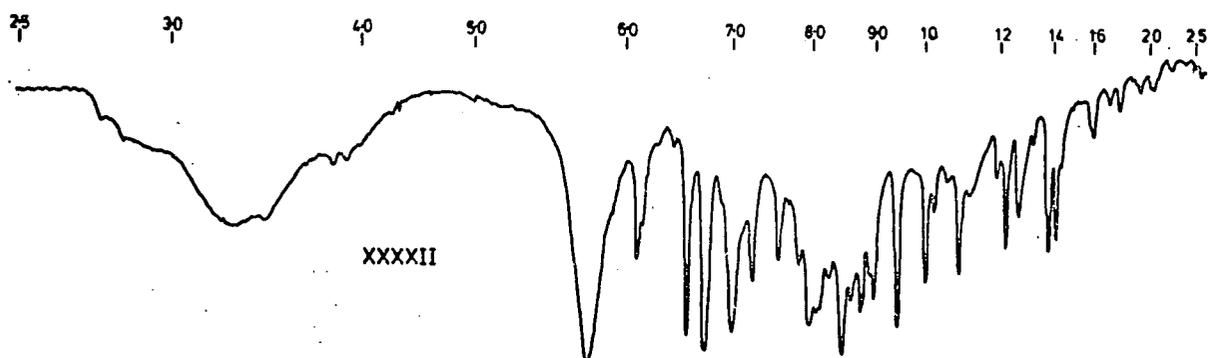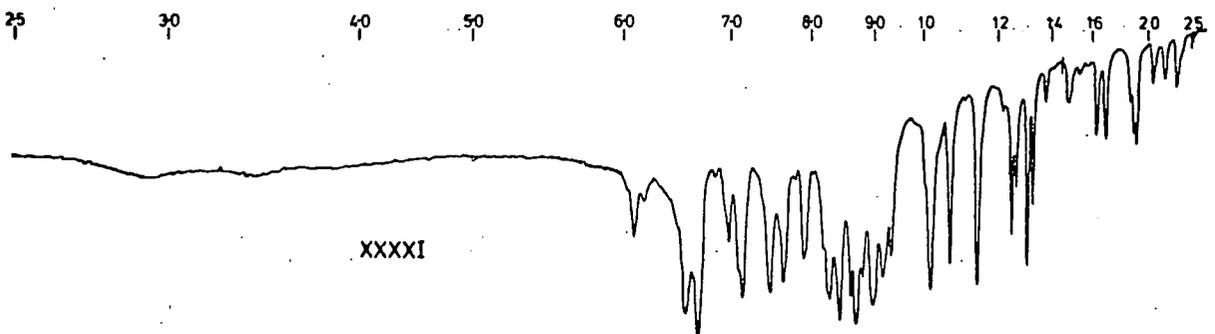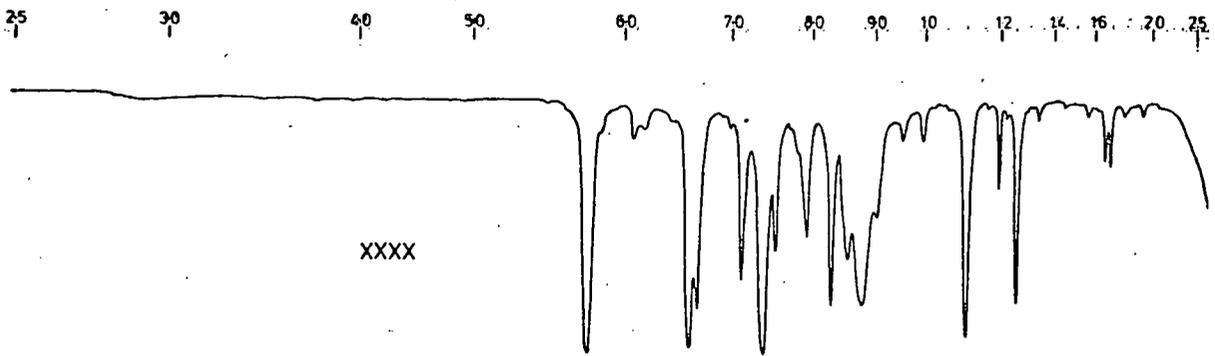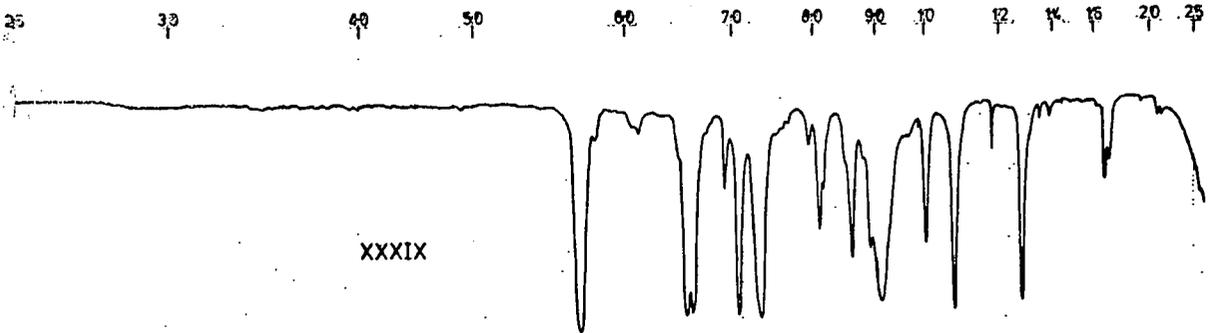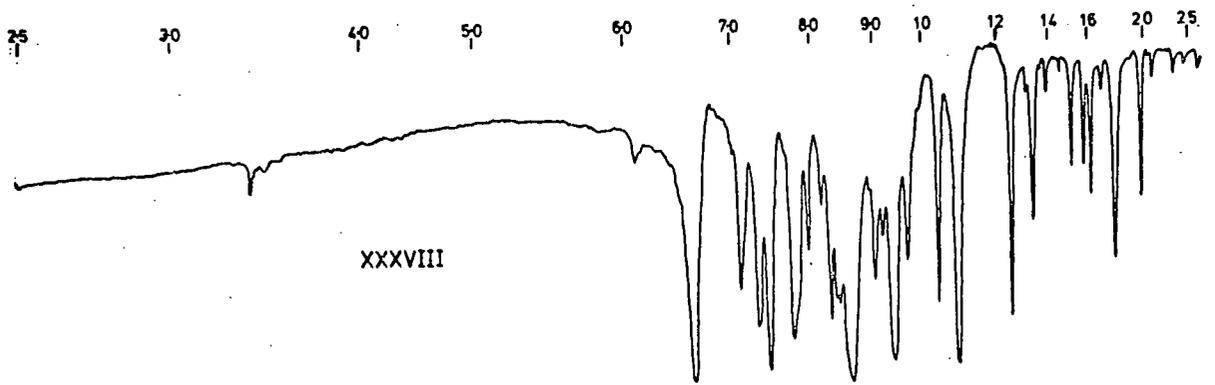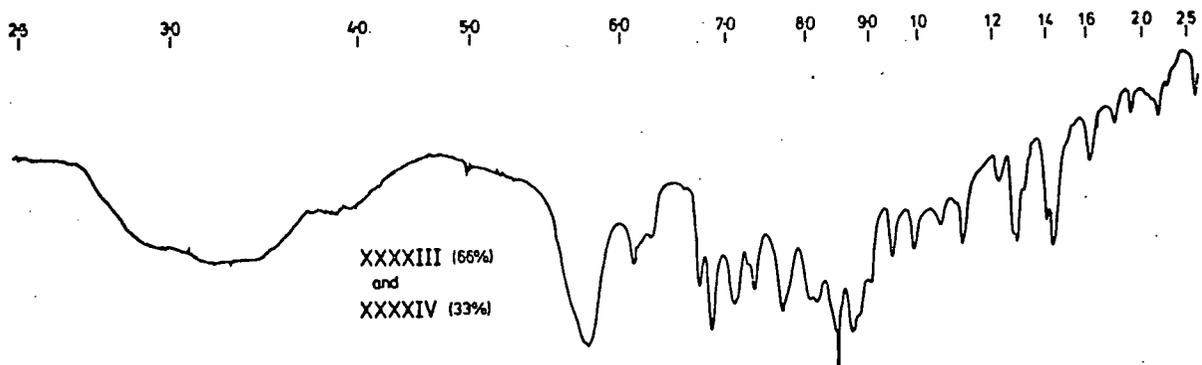
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