The synthesis and reactions of some fluorinated polycyclic polyenes

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THE SYNTHESIS AND REACTIONS OF SOME FLUORINATED POLYCYCLIC POLYENES

A thesis submitted for the degree of Doctor of Philosophy

by

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ABSTRACT

The Synthesis and Reactions of Some Fluorinated Polycyclic Polyenes

Perfluorocyclohexa-1,3-diene gave the expected 1,4-adducts with cyclohexene, cyclopentene, 1H,2H-octafluorocyclohexene, 1H,2H-hexafluorocyclopentene and 1H,2H-tetrafluorocyclobutene; reaction with 1H,2H-tetrafluorocyclobutene also yielded two 2,2-difluorovinyldecafluorobicyclo[4,2,0]oct-2-enes and the dimer 3,3,4,4,7,7,8,8-octafluorotricyclo[3,3,0,$0^{2,4}$]octane. Dehydrofluorination of the adducts from 1H,2H-octafluorocyclohexene and 1H,2H-hexafluorocyclopentene gave the trienes, perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene and perfluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene respectively.

Perfluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene reacted as a diene in Diels-Alder reactions with ethylene, propyne and but-2-yne. The 1,4-adducts with alkynes could be pyrolysed selectively to either polyfluorobenzobicyclo-[2,2,2]octa-2,5-dienes or 2,3-disubstituted hexafluoronaphthalenes.

Irradiation of perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene and perfluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene in the vapour phase with UV radiation resulted in their isomerisation to perfluorotetracyclo[6,2,2,$0^{2,7}0^{5,7}$]-dodeca-2,9-dienes and perfluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,3,8-triene respectively. Arguments presented support the latter isomerisation being a photochemical 1,5-sigmatropic migration of a fluorine atom. Vacuum pyrolysis of perfluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene provides perfluoroindene in good yield. Irradiation of 2H-heptafluorocyclohexa-1,3-diene in the vapour phase with UV radiation yielded 2H-heptafluorobicyclo[2,2,0]hex-2-ene, the isomerisation proceeding in the reverse direction on pyrolysis; the photo-isomer was of the same order of dienophilicity as perfluorobicyclo[2,2,0]-hex-2-ene towards furan.

Perfluoroindene reacted readily with the nucleophiles sodium borohydride, sodium methoxide and lithium methyl replacing initially one of the vinylic fluorines in the five-membered ring. Its olefinic character was evident from the formation of a mixture of hydrazones on reaction with hydrazine hydrate and the isolation of 1,1,3,4,5,6,7-heptafluoroindan-2-one from its reaction with oleum; intermediate unstable compounds formed in the latter transformation suggest that the initial stage in the reaction is the formation of the β sultone of perfluoroindene.

ACKNOWLEDGEMENTS

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Assistance from the technical and laboratory staff is greatly appreciated; in particular thanks are due to Mr. D. Hunter for some practical assistance.

Finally I am grateful to the Imperial Smelting Corporation for the award of a maintainance grant.

MEMORANDUM

The work in this thesis was carried out in the Chemistry Laboratories of the University of Durham between September 1969 and September 1972. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has been the subject of the following publications.

1. Diels-Alder Reactions of Polyfluorocyclohexa-1,3-dienes. Part V, Addition of Cycloalkenes to Octafluorocyclohexa-1,3-diene and Dehydrofluorination of Some of the Adducts by W.J. Feast, W.K.R. Musgrave and W.E. Preston, J. Chem. Soc. Perkin I, 1972, 1527.

2. Diels-Alder Reactions of Polyfluorocyclohexa-1,3-dienes. Part VI, Reactions of Dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene with Ethylene and Alkynes. A Synthesis of Polyfluoro tricyclo[6,2,2,$0^{2,7}$]dodeca-2,4,6,9-tetraenes and 2,3-Di-substituted Hexafluoronaphthalenes by W.J. Feast, W.K.R. Musgrave and W.E. Preston, J. Chem. Soc., Perkin I, 1972, 1830.

3. The Photochemical Isomerization of Some Fluorinated Polycyclicpolyenes. A Possible Photochemical 1,5-Sigmatropic Migration of a Fluorine Atom by W.J. Feast and W.E. Preston, Tetrahedron, 1972, 28, 2805.

4. Charge Distributions in Dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene and Tetradecafluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene As Determined by ESCA by D.B. Adams, D.T. Clark, W.J. Feast, W.K.R. Musgrave and W.E. Preston, J. Fluorine Chemistry, 1972, 2, 207.

5. Application of ESCA to Structural Problems in Organic Chemistry; the Orientation of Nucleophilic Substitution in Perfluoroindene by D.B. Adams, D.T. Clark, W.J. Feast, W.K.R. Musgrave and W.E. Preston, Nature Physical Science, in the press.

CONTENTS

CHAPTER 3. The Photochemical Isomerisation of Tetradecafluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene, dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene and 2H-heptafluorocyclohexa-1,3-diene. Some Reactions of the Photoisomers including a Synthesis of Perfluoroindene

Introduction

Discussion

Experimental

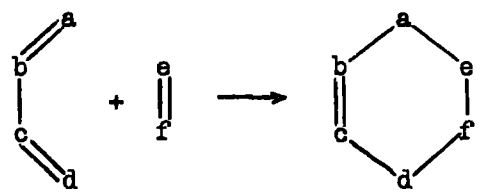
CHAPTER 1

ADDITION OF CYCLOALKENES TO OCTAFLUOROCYCLOHEXA-1,3-DIENE AND DEHYDROFLUORINATION OF SOME OF THE ADDUCTS

INTRODUCTION

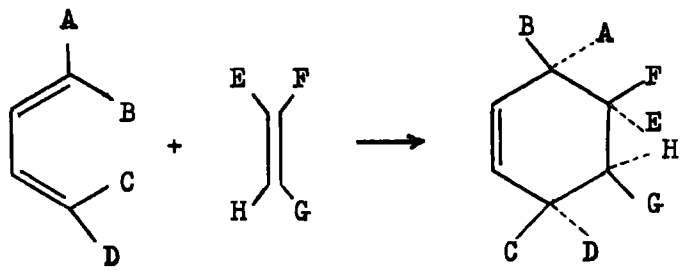
The Diels-Alder Reaction[1,2]

The formation of a six-membered ring by the 1,4-addition of an unsaturated system to a conjugated diene, discovered by Diels and Alder,[3] is one of the most versatile reactions of organic chemistry. The synthetic utility of the reaction is due to the range of dienes (abcd) and dienophiles (ef) which can combine together; interest in its mechanism has stemmed from the often strict stereochemical requirements of the process.



1.1 The Stereochemistry and Mechanism of the Diels-Alder Reaction

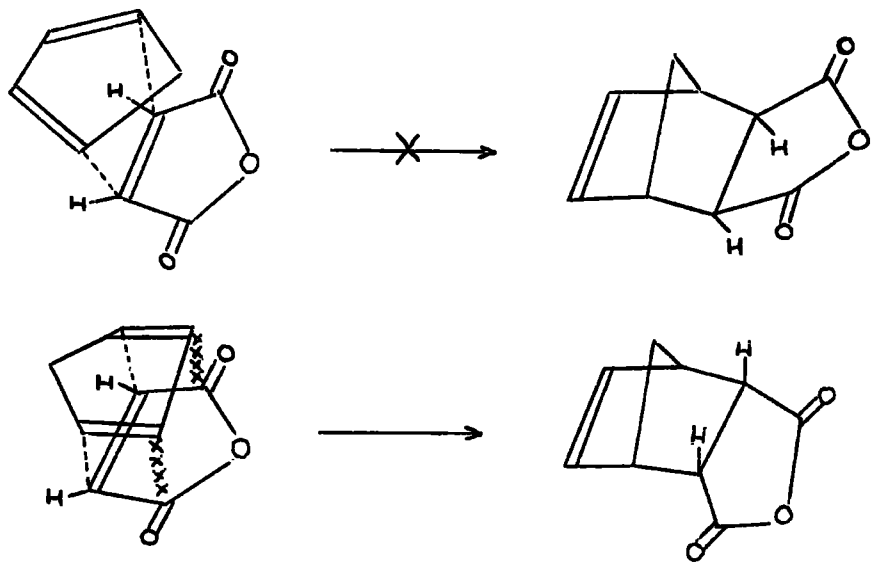
Only nine years after the first Diels-Alder reaction had been reported sufficient experimental data was available for Alder and Stein to formulate the "CIS" principle,[4] which states that the configurational relationship of the diene and dienophile is retained in the adduct. The consequences of this rule are shown for the general case below. The absence of evidence of free rotation



about the dienophile double or triple bond in the overwhelming majority of examples studied suggests a concerted rather than a two-step cycloaddition.

An essential requirement of Diels-Alder addition is that the diene must be cisoid and planar and the reactivity of a diene is drastically reduced when

these two conditions are not realisable (see section 1.2). Cyclic dienes with near planar rings satisfy these requirements. Such cyclic dienes may react with non-centrosymmetric dienophiles to give two possible stereoisomeric products, endo and exo isomers, although generally the isomer with endo configuration predominates. An example of a reaction of this type is the formation of the endo adduct in the Diels-Alder reaction of cyclopentadiene with maleic anhydride,[1] see below.



exo adduct

endo adduct

-------- primary interaction ×××××× secondary interaction

Alder and Stein rationalised the predominance of endo isomers in reactions of this type on the assumption that the reactants arrange themselves in parallel planes and that addition proceeds from the orientation with the "maximum accumulation" of double-bonds in the transition state, this secondary interaction being assumed to extend to π-bonds not directly involved in the cycloaddition.[4]

Apart from a few isolated examples[5] the Diels-Alder reaction can only be regarded as a concerted process and as such the orbitals of the reactants must be transformed into those of the product in a continuous manner. Woodward and

Hoffmann,[6] using the Principle of Conservation of Orbital Symmetry have derived a set of selection rules for the concerted terminal cycloaddition of an m π-electron system to an n π-electron system in both the ground and the excited states. These are tabulated below.

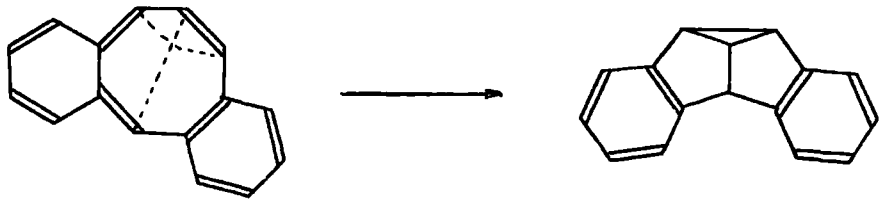
Table 1. Woodward-Hoffmann Selection Rules for m + n Cycloadditions

m + n	Allowed in Ground State Forbidden in Excited State	Allowed in Excited State Forbidden in Ground State
4q	$m_s + n_a$ $m_a + n_s$	$m_s + n_s$ $m_a + n_a$
4q + 2	$m_s + n_s$ $m_a + n_a$	$m_s + n_a$ $m_a + n_s$

q is an integer.

The subscripts s and a refer to suprafacial and antarafacial processes, the former where bonds are made or broken on the same face of the system undergoing reaction and the latter where newly formed or broken bonds lie on opposite faces of the reacting system.

The "CIS" principle means that the Diels-Alder reaction is the $[\pi 4_s + \pi 2_s]$ process; however the sterically much less favourable $[\pi 4_a + \pi 2_a]$ process, predicted to be an allowed thermal process by Woodward and Hoffmann, has been observed to occur when the reacting π-systems are suitably constrained, as in the example below.

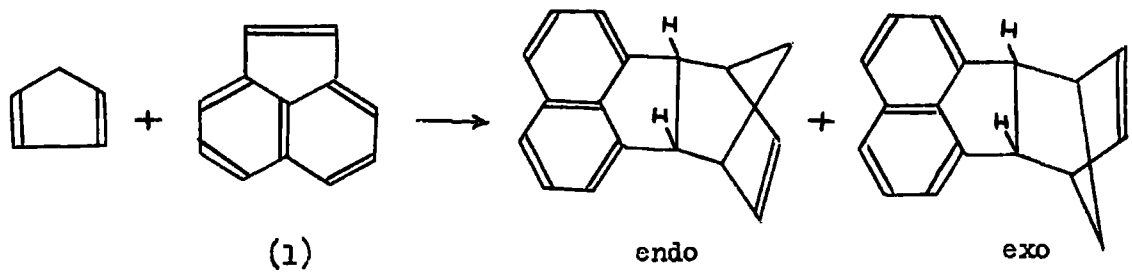


Photochemical 1,4-cycloadditions between dienes and dienophiles are also known, the stereochemical consequences of the $[\pi 4_s + \pi 2_a]$ concerted process being evident in the conversion of cis hexatrienes to bicyclo[3,1,0] hexenes (see Chapter 3).[6]

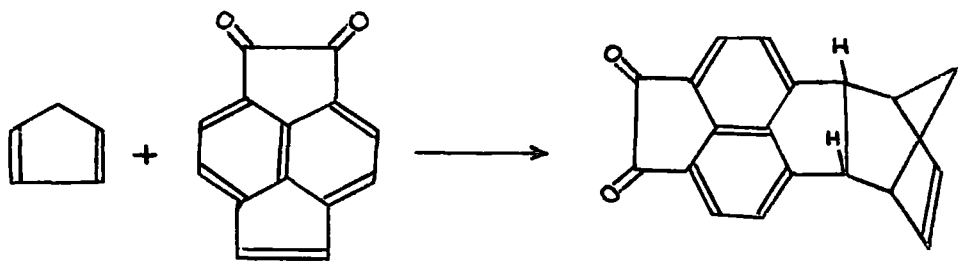
Orbital symmetry arguments have been extended to explain the predominance of endo isomers in Diels-Alder reactions of cyclic dienes by invoking secondary orbital interactions,[7,8] evidence of interactions of this type being provided by extended Hückel calculations.[9] However, like the explanation of Alder and Stein,[4] these arguments are unable to account for predominant endo addition of monoolefinic dienophiles such as cyclopropene, cyclopentene and norbornene to cyclic dienes. The relative importance of secondary orbital interactions is questionable. Calculations by Herndon and Hall have suggested that the stabilities of endo and exo transition states are governed mainly by the overlap of the π-orbitals at the primary centres where bonds are actually developing. They calculated that over 90% of the difference in the stabilisation energies for the exo and endo transition states for dicyclopentadiene could be accounted for by these primary interactions, and that there was no need to invoke secondary orbital interactions.[10]

Secondary orbital interaction, if it is important, will be a function of both the difference in energy between the highest occupied molecular orbital of

the diene and the lowest vacant molecular orbital of the dienophile and the symmetry of these two orbitals, the smaller the energy difference between the two orbitals the more favourable will be the interaction, as an energetically favourable interaction between two molecular orbitals requires that they have appropriate symmetries and similar energies. The reaction between cyclopentadiene and acenaphthylene (1) yields endo and exo adducts in the ratio of 3:1 respectively,[11] whereas pyracycloquinone (2) and cyclopentadiene produce only the endo isomer,[12] see below. This supports the secondary orbital interaction theory, as the energy gap between the relevant occupied and vacant molecular



(1) endo exo



endo

(2)

orbitals will be greater for acenaphthylene than for pyracycloquinone, resulting in greater secondary orbital interaction for the latter and hence a predominance of the endo isomer.[11] In contrast Trost found that in the reaction of pyracycloquinone (2) with diphenylisobenzofuran the high endo stereospecificity was no longer apparent and both endo and exo isomers were formed in the ratio of 3:1 respectively, a result which he interpreted as contrary to the secondary orbital interaction theory.[12]

Although the endo adduct is generally the major reaction product, there are instances in which the exo adduct is the predominant isomer, for example 3-chlorocyclopropene, 1,3-dichlorocyclopropene and 1,2,3-trichlorocyclopropene produce mainly or exclusively the exo adducts with diphenylisobenzofuran,[13] and cyclopropene itself yields both endo and exo adducts in equal amount on reaction with furan. However, cyclopropene and cyclopentadiene yield predominantly the endo Diels-Alder adduct. The ratio of endo and exo isomers produced with these two dienes has been attributed to steric hindrance to the dienophile on replacing an oxygen atom by a methylene bridge.[14] The prediction of endo/exo isomer ratios is somewhat hazardous as it is known that small changes in the energetics of a reaction may result in large variations in isomer distribution, a 99/1 isomer ratio corresponding to less than 3 kcals $mole^{-1}$ difference in the activation energies of the two competing reactions.[15]

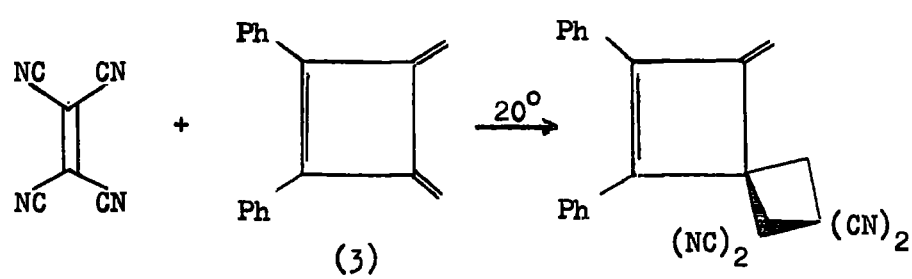
Reaction of an unsymmetrical diene with an unsymmetrical dienophile often tends to produce one of the possible adducts in major amount.[15] The preferred orientation of addition of some substituted butadienes with unsymmetrical dienophiles has been accurately predicted by Herndon and Hall by using a full perturbation calculation or by considering the interaction of the highest occupied molecular orbital of the diene with the lowest vacant molecular orbital of the dienophile.[16]

1.2 Factors Governing the Rates of Diels-Alder Reactions[1,2]

A surprising number of compounds undergo the Diels-Alder reaction.[1,2,15] Dienes can be cyclic or acyclic, "electron-poor" as in hexafluorocyclopentadiene or "electron-rich" as in cyclopentadiene, may contain heteroatoms as in α, β-unsaturated ketones and furan or may be aromatic, when particularly active dienophiles are needed to compensate for the loss of aromaticity which must result. Similarly a vast range of dienophiles are available, both cyclic and

acyclic, for example alkenes, alkynes, allenes, maleic anhydride and cyclobutenes, as well as those containing heteroatoms such as Schiff's bases, azodicarboxylic ester, nitriles, cyclic azo compounds, ketones and sulphur trioxide; they may be "electron-poor" as for tetracyanoethylene or "electron-rich" as for ethylene.[1,2,15]

As mentioned in section 1.1, the Diels-Alder reaction requires the diene to adopt a cis-coplanar configuration. In open-chain dienes bulky substituents can displace the conformational equilibrium either towards the cisoid form, increasing reactivity, or towards the transoid form, reducing reactivity. In 1,2-bismethylenecycloalkenes the double bonds are necessarily cis oriented and coplanar making these exocyclic 1,3-dienes extremely reactive in 1,4-cycloadditions. An interesting exception to this generalisation is 1,2-bismethylene-3,4-diphenylcyclobut-3-ene (3) which reacts with the powerful dienophile tetracyanoethylene in 1,2-fashion thus avoiding the formation of a cyclobutadiene system.



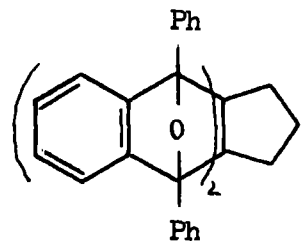
Some cyclic-1,3-dienes are also good dienes in the Diels-Alder reaction due to their cisoid configuration. Both cyclopentadiene[1,2] and hexafluorocyclopentadiene[17] dimerise very readily (one molecule acting as the diene and the other as the dienophile in a 1,4-cycloaddition), and form 1,4-adducts with a variety of dienophiles. Perchlorocyclopentadiene which is stable as a monomer because of the steric effect of the bulky chlorine atoms on the double bond which would act as the dienophile, readily forms 1,4-adducts with a large

number of dienophiles. As ring size increases the reactivity of a cyclic-1,3-diene falls, cyclohexa-1,3-diene is much less reactive than cyclopentadiene and cycloocta-1,3-diene is comparatively inert towards dienophiles; an increase in reactivity occurs again with cyclic 1,3-dienes containing 14- and 15-membered rings. The drop in reactivity on going from cyclopentadiene to cyclohexa-1,3-diene is probably mainly accounted for by an increase in the distance between the termini of the respective π-systems, for larger rings ring conformation affecting coplanarity and conjugation of the π-system in addition to hindering the approach of the dienophile will be more important.[1,2]

In his pioneering work Alder recognised that the presence of electron-donating substituents in the diene [$N(CH_3)_2$, OCH_3, CH_3, etc.] and electron-withdrawing substituents in the dienophile [CN, CO_2CH_3, CHO, NO, etc.] increased the rate of the Diels-Alder reaction;[18] kinetic measurements have since verified the so-called 'Alder rule'.[1] For example the order of reactivity of cyanoethylenes towards cyclopentadiene and 9,10-dimethylanthracene is $(NC)_2{=}C(CN)_2 > (NC)_2C{=}CH(CN) > (NC)_2C{=}CH_2 > CH_2{=}CH(CN)$, and the order of reactivity of butadienes towards tetracyanoethylene and maleic anhydride is 2,3-dimethylbutadiene > 2-methylbutadiene > butadiene.[1] It is possible to draw up a table of the dienophilicity of unsaturated compounds towards dienes such as cyclopentadiene and 9,10-dimethylanthracene based on rate measurements, the order of dienophilic properties varying little from one diene to another and the most powerful dienophile appearing to be tetracyanoethylene. However, although hexachlorocyclopentadiene due to its "electron-poor" nature would be expected to be a poor diene according to the 'Alder rule', it reacts quite readily with a large number of simple hydrocarbon olefins and acetylenes but not at all with tetracyanoethylene. The unusual behaviour of hexachlorocyclopentadiene led to the concept of the Diels-Alder reaction "with inverse electron demand", the diene acting as an "electron-poor" compound and

reacting with relatively "electron-rich" dienophiles, a reversal of the 'normal' Diels-Alder reaction discussed above. Kinetic measurements have verified that the reactivity of a dienophile towards hexachlorocyclopentadiene is enhanced by the presence of electron-donating substituents as is seen from the order of reactivity of a series of styrenes towards this diene, p-methoxystyrene > styrene > p-nitrostyrene.[19] It is now recognised that the Diels-Alder reaction "with inverse electron demand" is almost as general as the 'normal' Diels Alder reaction. Reaction in which both the diene and dienophile are of similar character, either both "electron-rich" or "electron-poor", are not very successful in contrast to the case of dienes and dienophiles of opposite character, which undergo rapid reaction.[1,2] Recently Eisenstein and Anh have shown that the 'Alder rule' and its inverse can be rationalised by considering the interactions between the frontier orbitals of the diene and the dienophile. They found that the interaction energy of the frontier orbitals of a diene and dienophile undergoing reaction increased when both reactants contained substituents of opposite electronic character, "electron-releasing" or "electron-withdrawing", relative to the unsubstituted reactants. By calculating the interaction energies for two series of Diels-Alder reactions they found that their calculated energies fitted in well with rate constants previously measured by Sauer.[20]

Ring strain and steric effects can also markedly influence the facility of Diels-Alder reactions. The sp hybridisation of acetylenes prevents strain-free inclusion of a triple bond in rings of less than nine-members. Lower cycloalkynes have however been trapped as their Diels-Alder adducts, the angle deformation making these compounds powerful dienophiles. An example is the trapping of cyclopentyne to form a bis adduct (4) with diphenylisobenzofuran.

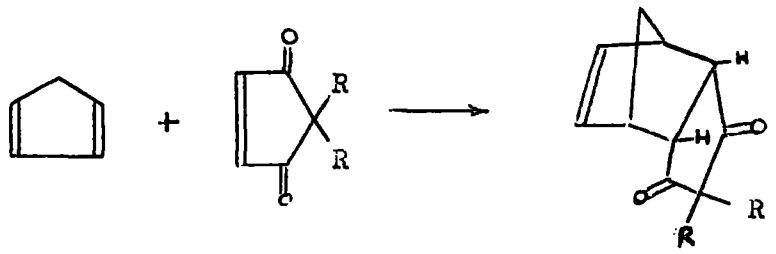


(4)

Arynes are of the same order of reactivity and they will combine with aromatic compounds under very mild conditions. Both tetrafluorobenzyne[21] and benzyne act as dienophiles towards benzene under very similar conditions. Electronic factors are less important than ring strain and both these benzynes have a similar high reactivity and lack of selectivity in their reactions. Similarly cyclopropenes and to a lesser extent cyclobutenes are reactive dienophiles due to ring strain, reacting readily with both "electron-poor" and "electron-rich" dienes. Norbornene is a more powerful dienophile than cyclopentene and octafluorobicyclo[2,2,0]hex-2-ene and hexafluorobicyclo[2,2,0]hexa-2,5-diene are far more dienophilic than perfluorocyclobutene, the fusion of an extra small ring to a cycloalkene increasing ring strain (see section 1.7).

The Diels-Alder reaction is particularly sensitive to steric effects and these may often override electronic factors. Volume activation studies on some Diels-Alder reactions of maleic anhydride have shown that the transition states were actually smaller in volume than the corresponding adducts, a result consistent with secondary interactions in the transition states of the type proposed by Woodward and Hoffmann to account for the predominance of endo isomers in reactions with cyclic dienes, and suggesting that steric effects should be of great influence in these reactions.[22] A steric effect of this type accounts for the low reactivity of 2,2-dimethylcyclopent-4-ene-1,3-dione (5,R=CH_3) as a dienophile compared with cyclopentenedione (5,R=H), the former

yielding the adduct (6,R=CH_3) in 48% yield on refluxing with cyclopentadiene in benzene for 16 hours whereas the latter reacted readily with the same diene at room temperature yielding (6,R=H). Similarly both maleic anhydride and

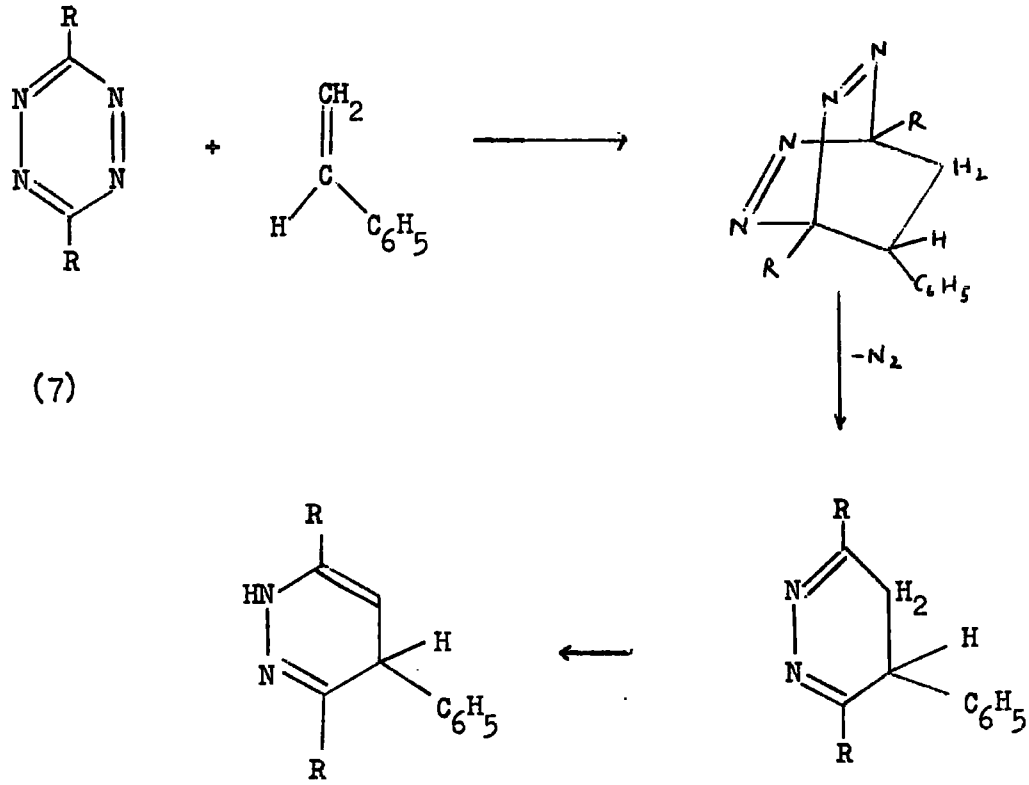


(5) R = H,CH_3 (6) R = H,CH_3

(5,R=H) react readily with trans-penta-2,4-dien-1-ol at room temperature whereas (5,R=CH_3) failed to react with this diene on refluxing in benzene or toluene. The lower dienophilicity of (5,R=CH_3) as against (5,R=H) results from the steric hindrance caused by the gem dimethyl system.[23]

1.3 "Electron-poor" Dienes

Since Diels-Alder reactions "with inverse electron demand" were first recognised there has been considerable interest in the reactions of "electron-poor" dienes with suitably chosen dienophiles. In hydrocarbon dienes activation towards attack by relatively "electron-rich" dienophiles is achieved by the carbonyl groups in orthoquinones, also 1,2,4,5-tetrazines (7) undergo Diels-Alder reactions "with inverse electron demand" with olefins forming eventually 1,4-dihydropyridazines by the sequence shown below, the rate of reaction being increased on substituting the molecule with electron-attracting groups R.[15] There are many other examples of "electron-poor" dienes in the literature some recent ones being the 1,2,4-triazines (8),[24] and tropone (9) which undergoes reaction with ethylene and other unsaturated hydrocarbons,[25] see below.


R
N
N
N
N
R
+
CH2
C
H
C6H5
N
N
N
R
N
R
H2
H
C6H5
-N2
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H2
H
N
C6H5
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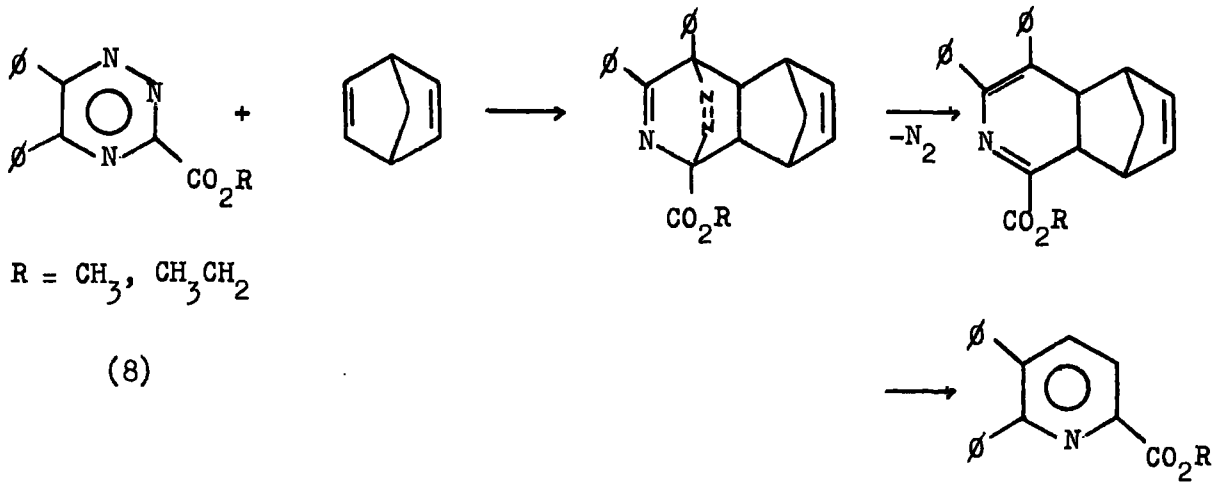
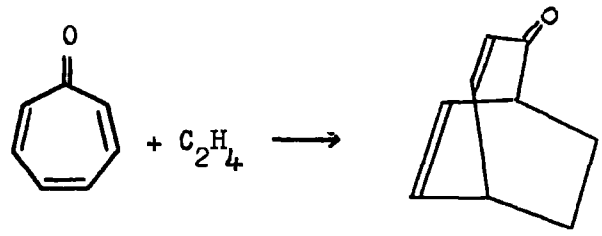
R
HN
N
H
C6H5
R

(7)



R = CH_3, CH_3CH_2

(8)



(9)

The most extensively studied "electron-poor" dienes have been highly halogenated systems. A great many Diels-Alder reactions of hexachlorocyclopentadiene and its derivatives are known and the work has been extensively reviewed.[26,27] In addition to their intrinsic chemical interest these Diels-Alder adducts and/or derived compounds are used as fungicides, plant-growth regulators and insecticides.[26] The Diels-Alder reactions of hexachlorocyclopentadiene take place between 20° and 200° with "electron-rich" dienophiles, simple hydrocarbon alkenes and alkynes, and polynuclear aromatic hydrocarbons.[25,26] Recent work with 1,3-alkadienes has shown that hexachlorocyclopentadiene is more reactive towards conjugated rather than isolated olefins and towards terminal rather than internal olefins, also alkyl substitution does not increase the reactivity of these dienophiles as steric

factors are more important than electronic factors. As conjugation of the dienophilic double bond will decrease electron density this might have been expected to reduce reactivity, the observed increase in reactivity is attributed to an increase in polarizability due to conjugation, resulting in stabilization of the polar transition state.[28]

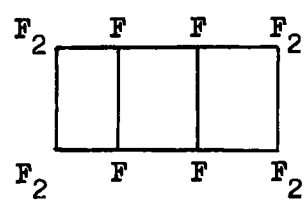
Whereas hexachlorocyclopentadiene is stable as the monomer at room temperature compounds such as 1,2,3,4,5-pentachlorocyclopentadiene and 1,2,3,4-tetrachlorocyclopentadiene dimerise on standing or gentle warming; they can however be regenerated on heating the dimer, as is the case for cyclopentadiene. 1,2,3,4-tetrachloro-5,5-difluorocyclopentadiene dimerises even more readily than its gem dihydro analogue. The ease of dimerisation varies with the 5-substituents in the order $F_2 > H_2 > HCl$, an explanation of this observation would probably involve an interplay of both steric and electronic factors.[29] Recently an elegant investigation of the Diels-Alder reactions of 1,2,3,4,5-pentachlorocyclopentadiene has been disclosed. The relative amounts of syn and anti, and exo and endo isomers were recorded for reactions with a large number of dienophiles, and on the basis of these results it has been proposed that syn-anti isomerisation is controlled by interactions of the van der Waal's-London type, whereas endo-exo isomerisation is determined by secondary orbital interactions.[30]

1.4 Fluorinated Acyclic Dienes

Unlike butadiene perfluorobutadiene shows little tendency to partake in the Diels-Alder reaction,[31] the only substantiated Diels-Alder adduct being formed with trifluoronitrosomethane.[32] With butadiene and acrylonitrile compounds believed to be cyclobutane derivatives were isolated[31] suggesting that the double-bonds act in isolation; acyclic fluoroolefins containing the $>C=CF_2$ group are known to readily form four-membered ring compounds when

heated alone or with other unsaturated compounds.[33,34] A rationalisation of the low reactivity of the molecule towards 1,4-cycloaddition has been offered in terms of "the inductive effect of the fluorines tending to localise the double-bonds, thus inhibiting conjugation", or a "loss of planar cisoid conformation due to steric interaction between fluorine atoms at C-1 and C-4."[35,36] The molecule has recently been shown to be non-planar by photoelectron and optical spectroscopy, a cis-bent geometry being in agreement with unpublished electron-diffraction data.[37]

On heating perfluorobutadiene to temperatures of between 150° and 180° in a steel bomb for up to 44 hours the isolated products were hexafluorocyclobutene, and dimers, trimers and polymers of the reactant.[38] The dimer fraction was not characterised but formed a hexabromide and on heating yielded a saturated dimer (m.p. 40°, b.p.80°) which was originally assigned structure (10) in agreement with preliminary X-ray studies,[38] later X-ray work assigned the more symmetrical structure (11) to this compound.[39]



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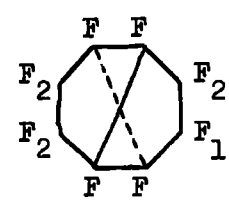


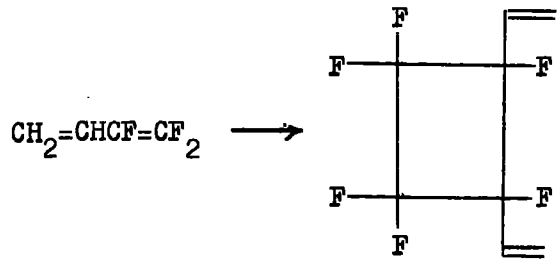
(11)

On increasing the reaction temperature the amount of hexafluorocyclobutene produced increased considerably, quantitative conversion of hexafluorobutadiene to hexafluorocyclobutene being achieved at 500° under atmospheric pressure.[38]

On heating 2,3-dichloroperfluoro-1,3-butadiene in a closed steel bomb at 170° for 44 hours a saturated dimer $C_8Cl_4F_8$, assumed to have a structure like (11), was obtained together with several unsaturated dimers. It was also

noted that this butadiene when heated for 89 hours at 176° led to 1,2-dichloro-perfluoro-1-cyclobutene (no yield quoted).[40]

1,1,2-Trifluoro-1,3-butadiene dimerises at temperatures between 150° and 200° yielding (12) and (13), and reacts readily with fluoroolefins,[41] the products being consistent with the formation of a bifunctional diradical intermediate as the first step in the cycloaddition process.[5]



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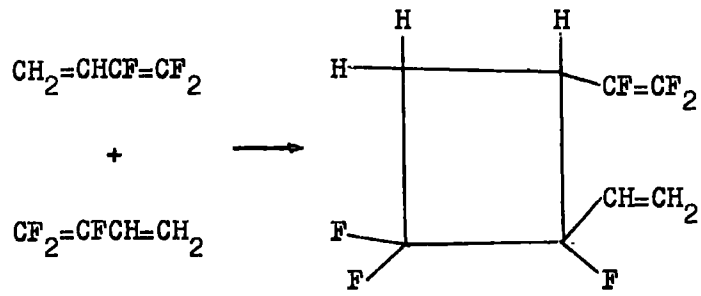
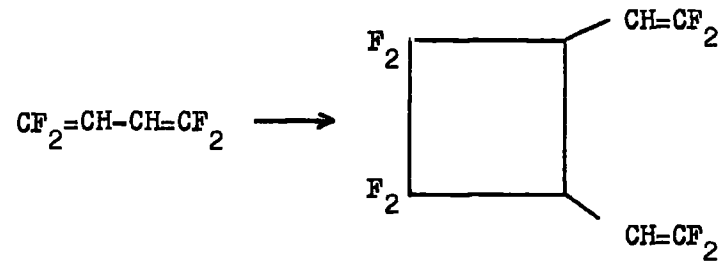


(13)

Like perfluorobutadiene 1,1,4,4-tetrafluorobutadiene is unreactive in the Diels-Alder reaction. It produced a formal Diels-Alder adduct with trifluoronitrosomethane but attempts to add dienophiles such as maleic anhydride were unsuccessful and with acrylonitrile, azodiformic ester and tetrafluoroethylene only cyclobutane derivatives were formed.[42] On heating to 178° it yielded a single dimer, identified as a divinylcyclobutane (14), optical isomers of a single trimer and higher polymers; no tetrafluorocyclobutene was recorded.[43]



(14)

The monofluorinated diene fluoroprene (2-fluorobuta-1,3-diene) forms Diels-Alder adducts with "electron-rich" and "electron-poor" dienophiles.[42,44]

1.5 Fluorinated Cyclopentadienes

Perfluorocyclopentadiene is a very reactive "electron-poor" diene. Like cyclopentadiene it undergoes dimerisation in 1,4-fashion extremely readily (9% dimerisation in 24 hours even at -22°) although it can be stored as the monomer at liquid nitrogen temperatures. This behaviour is in marked contrast to its perchloro analogue. Unlike dicyclopentadiene the dimer of perfluorocyclopentadiene is very thermally stable, but on heating to temperatures as high as 680° under vacuum the monomer is regenerated in 22% yield, the major product resulting from expulsion of difluorocarbene.[17] The high reactivity of perfluorocyclopentadiene towards "electron-rich" dienophiles enables the isolation of 1,4-adducts formed from a wide range of olefins and acetylenes under the mild conditions essential if dimerisation is to be kept to a minimum. The reported Diels-Alder reactions are tabulated below.

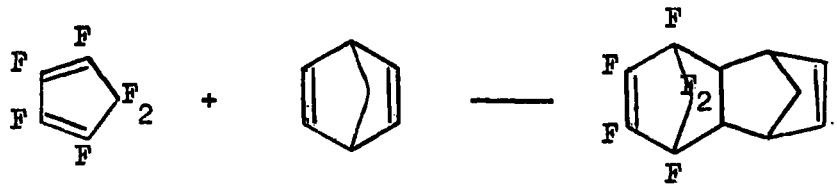
With "electron-poor" dienophiles, tetrafluoroethylene, tetracyanoethylene, perfluorobutadiene, perchlorobutadiene, perchlorocyclopentadiene[36] and perfluorocyclohexa-1,3-diene[45] no reaction was observed, as expected for Diels-Alder reactions with "inverse electron demand." Perfluorocyclopentadiene reacted as a dienophile with anthracene,[36] in contrast to perchlorocyclopentadiene

Table 2. Thermal Diels-Alder Reactions of Perfluorocyclopentadiene

Reactant	% Yield of Dimer	% Yield of 1:1 Adduct	Reaction Conditions	Reference
$H_3CO_2C{\equiv}CCO_2CH_3$	50	22	133°, 3d.	36
$HC{\equiv}CH$	22	42	115°, 65h.	36
diethyl maleate	34	66	110°, 3d.	47
diethyl fumarate	50	50	110°, 3d.	47
N-allyltrifluoroacetamide	c.70	30	50°, 64h.	50
$H_2C{=}CH_2$	41	51	106°, 8d.	36
maleic anhydride	53	41	110°, 2d.	36
butadiene	25	64	110°,4-5d.	36
norbornadiene	0	99	100°, 6d.	36
anthracene	-	27	120°, 5d.	36
cyclopentadiene	0	98	120-125°,4d.	36
CF_3NO	0	98	room temp., overnight	36

for which no dienophilic properties have been observed,[46] as both a diene and a dienophile with cyclopentadiene[45] and as a diene with the other reactants in Table 2. The reactions with diethyl maleate and diethyl fumarate show that the "cis" principle is applicable to this diene and the adduct with diethyl maleate was assigned the endo configuration from n.m.r. evidence.[47] A detailed investigation of the n.m.r. spectrum of perfluorocyclopentadiene dimer suggests that this compound also has the endo configuration;[48] support for this assignment is found in the fact that this dimer and endo-dicyclopentadiene give the same product on fluorination with cobalt trifluoride.[49] The reaction with norbornadiene produced two stereoisomeric 1:1 adducts (15)[36] whereas perchlorocyclopentadiene only produced one.[26] Irradiation of the endo-endo isomer (16)

would have been expected to yield the cage compound shown below; one of the isomeric adducts (15) did undergo reaction on irradiation but the resulting product could not be characterised.[36]



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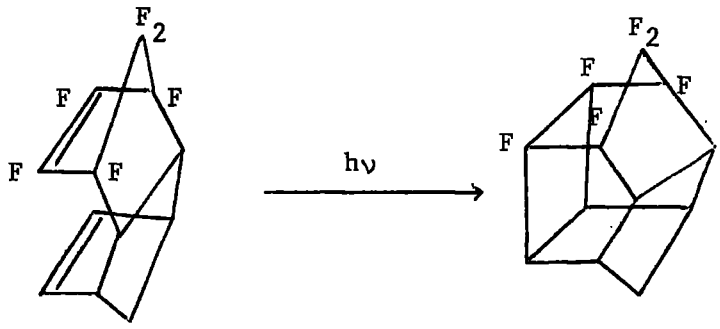
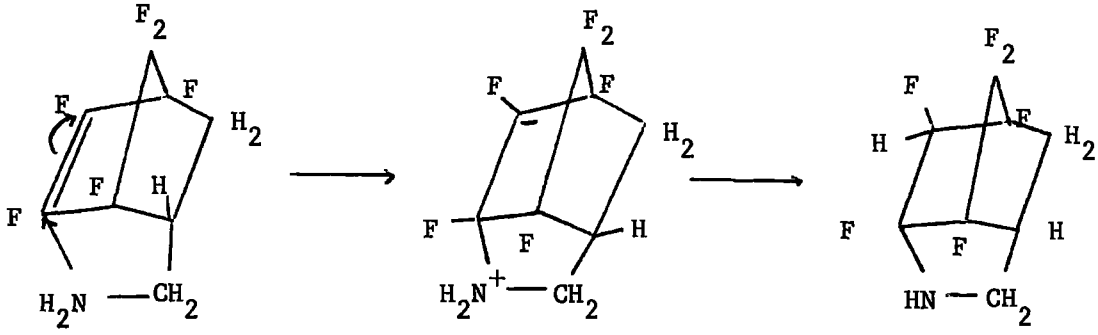


(16)

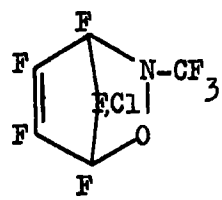
A further attempt to apply the photocyclisation technique to determine the stereochemistry of the Diels-Alder adduct of perfluorocyclopentadiene with p-benzoquinone was not possible as the isolated adduct possessed the enol form.

By reacting perfluorocyclopentadiene with N-allyltrifluoroacetamide and then releasing the free amine intramolecular cyclisation took place proving the endo nature of this adduct, see below. An exo adduct would have been expected to undergo intermolecular nucleophilic attack leading to a polymeric product.[50]



Perfluorocyclopentadiene reacted with cyclopentadiene[36] and cyclohexa-1,3-diene[51] to yield two 1,4- adducts in each case, one in which the fluorodiene acted as the diene and the other in which it acted as the dienophile, the relative amount of these 1,4-adducts being independent of reaction conditions. This led to the conclusion that a concerted but non-synchronous mechanism of the type proposed by Woodward and Katz[52] was operating, involving a single transition state leading to a common transient intermediate which collapses in steps of low activation energy to the products.[53]

The 1- and 5-chloropentafluorocyclopentadienes have recently been prepared, the 1-chloro compound dimerising more readily than its 5-chloro isomer at room temperature; the order of stability of these cyclopentadienes parallels that for perchlorocyclopentadienes substituted in the geminal positions. Pyrolysis of the dimer of 1-chloropentafluorocyclopentadiene at 600° resulted in monomerisation. 5-chloropentafluorocyclopentadiene readily reacted with trifluoronitrosomethane to produce two isomeric 1,4-adducts of structure (17) in the ratio of 1:7; the major product isolated when trifluoronitrosomethane reacted with the 1-chloro diene was (18). Reaction of 5-chloropentafluorocyclopentadiene with dimethylacetylenedicarboxylate at 135° produced two isomeric 1,4-adduct (19) in the ratio of 4:1.[54]



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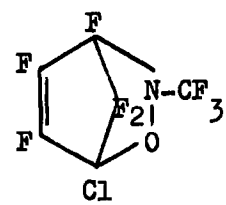

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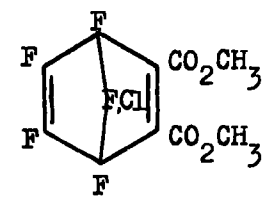
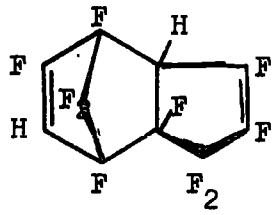


(19)

Some pentafluorocyclopentadienes are also known. 2H-pentafluorocyclopentadiene[55,56] dimerises extremely rapidly to yield one main dimer (20), assigned the endo configuration on the basis of its ^{19}F n.m.r. spectrum.[48]

Reaction of 2H-pentafluorocyclopentadiene containing some of its 5H-isomer as impurity with trifluoronitrosomethane at -78° led to adducts (21), (22) and (23), the latter being formed from the 5H-diene.[56]



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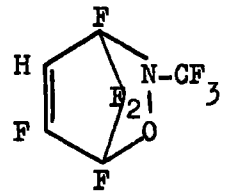

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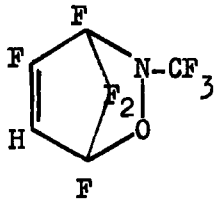

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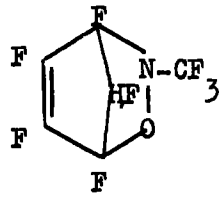
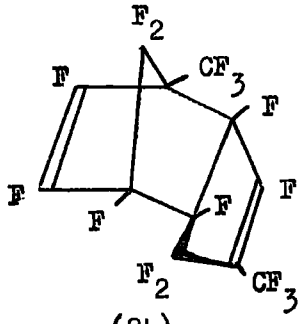


(23)

1H-pentafluorocyclopentadiene is more stable to dimerisation than its 2H-isomer, gives no 1,4-adducts with tetracyanoethylene or ethyl vinylether as expected, and yields one main dimer whose structure is not known.[55]

Perfluoro-(2-methylcyclopentadiene) on standing at 80° for 2 days yields a mixture of dimeric products (60%) and is partly transformed to the isomeric 1-perfluoromethyl diene. Perfluoro-(1-methylcyclopentadiene) under the same conditions yielded dimer (24) in 40% yield; (24) was assigned the endo configuration on the basis of its ^{19}F n.m.r. spectrum.[57]

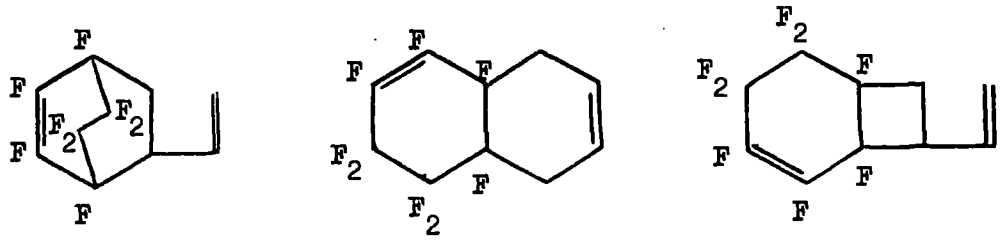


(24)

1.6 Fluorinated Cyclohexa-1,3-dienes

Like perfluorocyclopentadiene, perfluorocyclohexa-1,3-diene reacts with "electron-rich" dienophiles to produce 1,4-adducts. Reactions proceed smoothly with olefins and acetylenes and the diene shows a markedly reduced tendency to dimerise as compared with perfluorocyclopentadiene, consequently forcing conditions may be used to effect reaction with unreactive dienophiles. The reported Diels-Alder reactions with alkynes and alkenes are tabulated below. (Table 3). As can be seen from the table, the more "electron-rich" the dienophile the more readily will it react with perfluorocyclohexa-1,3-diene, in accord with the concept of Diels-Alder reactions with "inverse electron demand". Thus but-2-yne produces a higher yield of 1,4-adduct and under milder conditions than 1,1,1-trifluorobut-2-yne or perfluorobut-2-yne.[58]

The reaction with butadiene produced three major products (25), (26) and (27). Both (25) and (26) are 1,4-adducts, in the former the fluorinated compound behaves as the diene and in the latter as the dienophile. (27) is a 1.2-adduct of perfluorocyclohexa-1,3-diene and butadiene,[59,60] the only other example of perfluorocyclohexa-1,3-diene forming a 1,2-adduct is in its reaction with tetrafluoroethylene.[61]



(25) (26) (27)

Perfluorocyclohexa-1,3-diene resembles perfluorocyclopentadiene in behaving as a dienophile in its reaction with anthracene,[59,60] and as both a diene and a dienophile in its reaction with both cyclopentadiene and cyclohexa-1,3-diene. In the major adduct from reaction with cyclopentadiene, the fluorocarbon behaved

Table 3. Thermal Diels-Alder Reactions of Perfluorocyclohexa-1,3-diene with Alkynes and Alkenes

Reactant	% Yield of 1:1 Adduct	Reaction Conditions	Reference
$H_2C{=}CH_2$	80	200°, 4.5h.	66
$H_2C{=}CHCOCH_3$	73	114°, 2.5h.	59,60
$H_2C{=}CHOEt$	78	114°, 2.5h.	59,60
$H_2C{=}CHPh$	94	97°, 7h.	59,60
$H_2C{=}CHCO_2CH_3$	34	100°, 6h.	59,60
$H_2C{=}CHCN$	65	170°, 5h.	59,60
maleic anhydride	68	190°, 7h.	59,60
* butadiene	90	100°, 8h.	59,60
anthracene	7	99°, 48h.	59,60
N-allyltrifluoroacetamide	54	110°, 48h.	45
* cyclopentadiene	86	75°, 24h.	45
* cyclohexa-1,3-diene	61	60°, -	45
$H_2C{=}C{=}CH_2$	57	190°, 14h.	66
$HC{\equiv}CCH_3$	94	180°, 40h.	61
$HC{\equiv}CCF_3$	92	200°, 100h.	61
$HC{\equiv}CCH_2Cl$	88	180°, 17h.	61
$H_3CC{\equiv}CCH_3$	71	200°, 19h.	61
$ClH_2CC{\equiv}CCH_2Cl$	62	200°, 40h.	61
$HC{\equiv}CPh$	54	175°, 20h	61
$H_3CC{\equiv}CCF_3$	49	220°, 63h	61
$EtO_2CC{\equiv}CCO_2Et$	47	215°, 18h	61
$F_3CC{\equiv}CCF_3$	36(90)	225°, 18h. (264°, 22h.)	61(67)

* more than one adduct was isolated.

as the dienophile whereas reaction with cyclohexa-1,3-diene yielded predominantly the adduct in which the fluorocarbon behaved as the diene. As for perfluorocyclopentadiene the reaction of perfluorocyclohexa-1,3-diene with N-allyltrifluoroacetamide produced the endo 1,4-adduct for on releasing the free amine intramolecular nucleophilic attack took place. No reaction occurred with perfluorocyclopentadiene due to its ready dimerisation.[45]

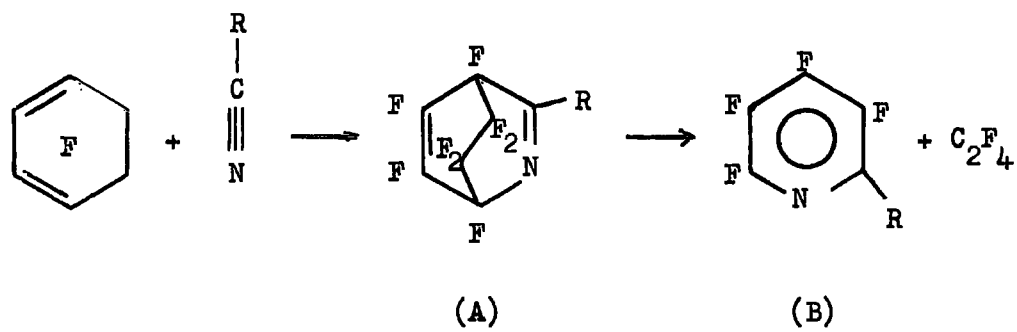
Under the conditions necessary for 1,4-cycloaddition to alkenes and alkynes perfluorocyclohexa-1,3-diene shows no tendency to dimerise. On heating at 390° for 144 hours however a 40% yield of a mixture of two compounds was formed these were deduced to be endo and exo dimers and were formed in the ratio of 9:1 respectively.[61]

Nitriles, which are generally regarded as unreactive dienophiles, will react with perfluorocyclohexa-1,3-diene at temperatures of around 400° producing 2-substituted pyridines together with diene dimers. The intermediate Diels-Alder adducts have been isolated in two instances using less drastic conditions, and although nitriles must be of high thermal stability and the pyridines are formed in low yield,this route allows access to 2-substituted pyridines, which are not readily available by other routes.[62,63] The results are tabulated in Table 4.

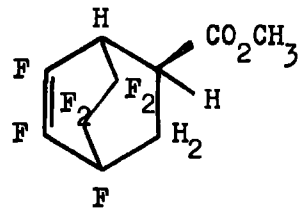
1H-heptafluorocyclohexa-1,3-diene when heated at 130° for 15 hours with methyl acrylate forms two isomeric products in 68% yield; these were assigned the endo structures (28) and (29).[64] Ethylene forms the expected 1,4-adducts with 2-methyl- and 2-methoxyheptafluorocyclohexa-1,3-dienes when heated to 250° for 42 hours,[65] and also with 2,3-dimethylhexafluorocyclohexa-1,3-diene at 216°.[66] An attempt to prepare the ethylene adduct of 2,3-dimethoxyhexafluorocyclohexa-1,3-diene by reaction at 200° for 16 hours was unsuccessful due to the thermal instability of this diene.[67]

Table 4. Thermal Diels-Alder Reactions of Perfluorocyclohexa-1,3-diene with nitriles[62,63]

Nitrile	Molar Ratio Diene:Nitrile	Reaction Conditions	% Yield (A)	(B)
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
$NC(CF_2)_3CN$	1:2	350°, 16h.	4	1
	1:2	350°, 64h.		10



Several Diels-Alder adducts have been prepared from 2H,3H-hexafluorocyclohexa-1,3-diene. The 1:1 adducts of this diene are formed in lower yields than the corresponding adducts of perfluorocyclohexa-1,3-diene, when reactions are carried out under similar conditions. This is ascribed to the formation of polyaddition products reducing yields, as the primary Diels-Alder adduct possesses a dienophilic -CH=CH- double bond which can compete with the initial dienophile for the remaining diene. In the reaction of 2H,3H-hexafluorocyclohexa-1,3-diene with but-2-yne a mixture of 2:1 adducts was isolated and



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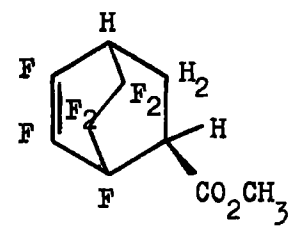
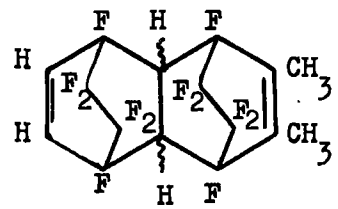


(29)

characterised as isomers (30). 2H,3H-hexafluorocyclohexa-1,3-diene is stable indefinitely in the dark at room temperature; its Diels-Alder reactions are tabulated below.[66,67] (Table 5).

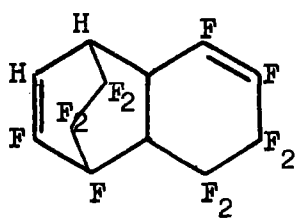


(30)

In contrast to its 2H,3H-isomer, 1H,2H-hexafluorocyclohexa-1,3-diene dimerises at room temperature to the extent of 66% after 3 months and is transformed to a single dimer of structure (31) or (32). It forms a single 1,4-adduct on reaction with 3,3,3-trifluoropropyne at 200° for 1 day and also forms an adduct with perfluorobut-2-yne. The unsymmetrical adduct formed from 3,3,3-trifluoropropyne was shown to have structure (33) by pyrolytic elimination of tetrafluoroethylene to give 3,4-difluorobenzotrifluoride which was identical with a sample prepared by an alternative unambiguous synthesis. The stereospecific outcome of this Diels-Alder reaction was accounted for in terms of a preferred orientation of the diene and dienophile prior to reaction.[67,68]

Table 5. Thermal Diels-Alder Reactions of 2H,3H-hexafluorocyclohexa-1,3-diene[66]

Dienophile	Reaction Conditions	% 1:1 Adduct
$CH_2=CH_2$	200°, 14.5h.	91
$CH_2=C=CH_2$	196°, 47.5h.	50
$CH_3C\equiv CCH_3$	200°, 22.5h.	30
$CH_3C\equiv CH$	212°, 19h.	58
$CF_3C\equiv CCF_3$	175°, 41h.	31
$CF_3C\equiv CCH_3$	210°, 14h.	37
$CF_3C\equiv CH$	208°, 18h.	75



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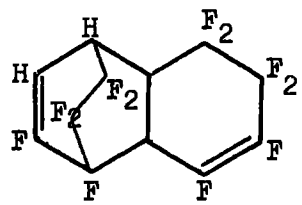

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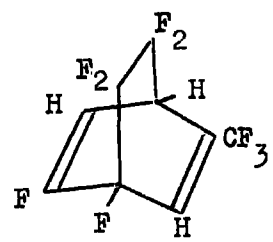


(33)

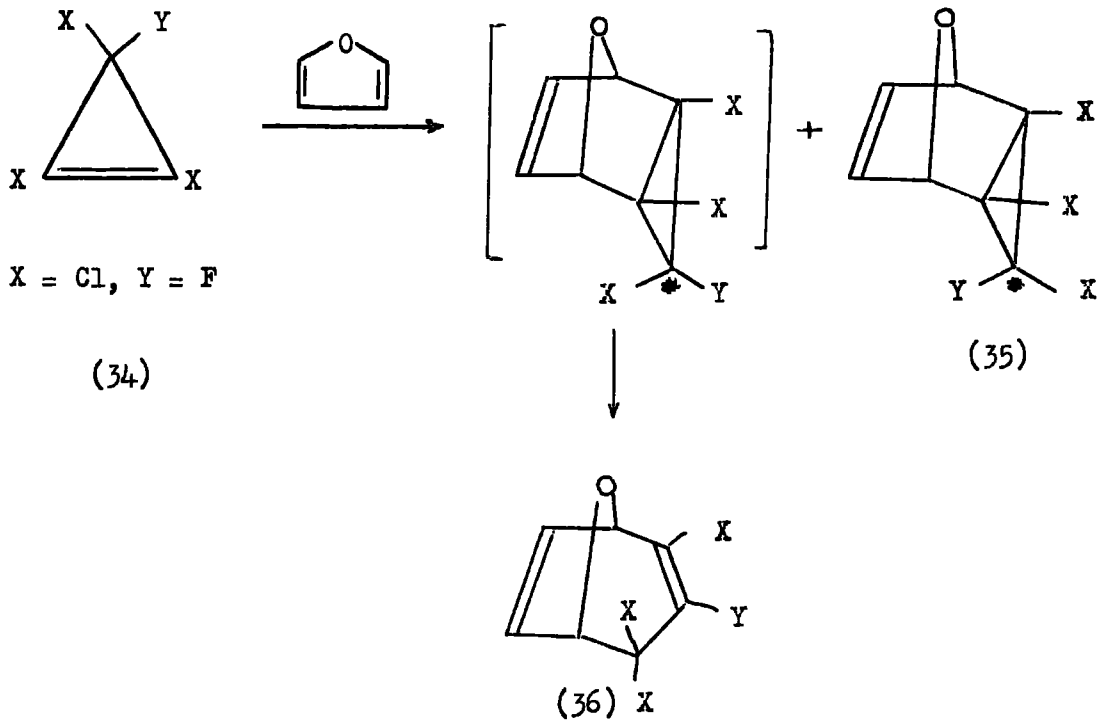
There have been no publications on the Diels-Alder reactions of perfluorocycloalka-1,3-dienes containing rings of greater than six-members. It would be expected that trends in reactivity would parallel those of hydrocarbon dienes, and perfluorocyclohepta-[69] and perfluorocycloocta-1,3-diene should partake in the Diels-Alder reaction with greater difficulty than perfluorocyclohexa-1,3-diene.

1.7 Cycloolefins as Dienophiles

A large number of small-ring cycloalkenes have been extensively used as dienophiles. They possess high reactivity because the reduction of angular deformation in the transition state compared with the free dienophile acts as the driving force for the reaction. In the case of cyclopropenes reactivity depends almost solely on ring-strain as a particular cyclopropene is often equally reactive towards 'normal' dienes and dienes which usually exercise "inverse electron demand", and the effect of substituents on the reactivity of a cyclopropene cannot be rationalised in terms of electronic effects. Cyclobutenes are also good dienophiles but the practically strain-free cyclopentenes and cyclohexenes are much less reactive.

Both cyclopropene[70] and perfluorocyclopropene[71] react readily with cyclopentadiene giving the endo 1,4-adducts at 0° and room temperature, respectively. The effect of ring-strain on the dienophilicity of the double bond in cyclopropene is evident from a comparison of the reactivities of ethylene and cyclopropene in 1,4-addition with butadiene, the former giving an 18% yield of the Diels-Alder adduct at 200°[72] whilst the latter gave a 37% yield of 1,4-adduct at 0°.[70]

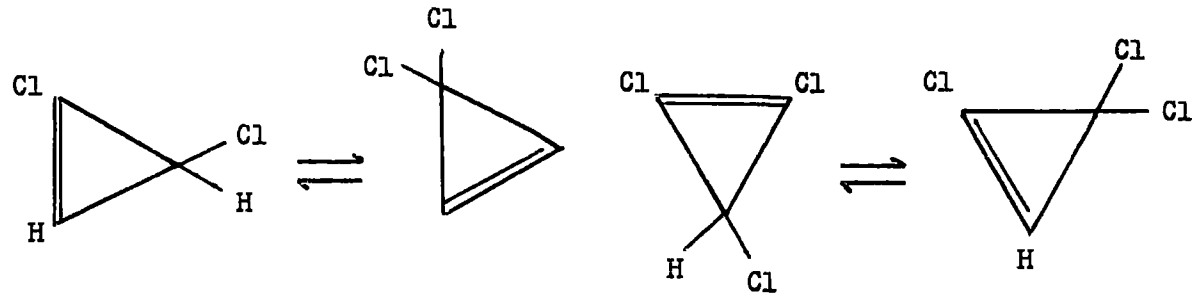
Law and Tobey have recently investigated the reactions of six fully halogenated cyclopropenes with cyclopentadiene, furan and butadiene. The isolated products were either the endo Diels-Alder adducts or compounds derived from them. In some cases the initial Diels-Alder adducts were thermally unstable and isomerised to ring-opened compounds by a mechanism involving stereospecific ionisation of the labile halide and disrotatory ring-opening of the resulting cyclopropyl cation to the corresponding allyl cation which then yielded the final product. The observed stereochemical results of this process are in agreement with the prediction of Woodward and Hoffmann for such a concerted electrocyclic reaction, illustrated below for the reaction of furan with compound (34).



The rearrangement involves disrotatory ring-opening together with ionisation of the halogen at carbon* syn to the double bond. In the reaction above the isolated products were the adduct (35) and the rearranged compound (36); (35) did not rearrange due to the strength of the C-F bond which would have to be broken in the ionisation process, the C-Cl bond is far more easily cleaved.[73] An alternative mechanism which would also account for Law and Tobey's observation, recently suggested by Magid and Wilson, involves ionisation of the cyclopropene prior to its Diels-Alder addition. An investigation of the validity of this mechanism was undertaken for cyclopentadiene as the 4π-system and it was concluded that the results obtained were more consistent with the simple direct cycloaddition mechanism.[74]

The exclusive formation of endo adducts or compounds derived from these adducts in reactions of fully halogenated cyclopropenes has been mentioned above; in some chlorocyclopropenes reaction with diphenylisobenzofuran produced

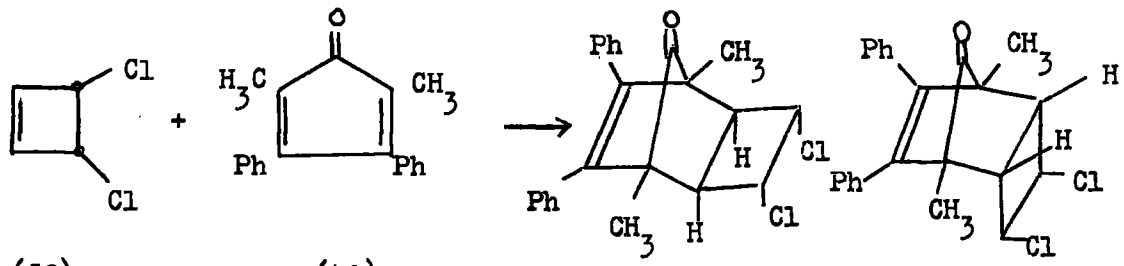
mainly the exo adducts. 3-chlorocyclopropene yielded exo and endo adducts in the ratio of 4.5:1 respectively whereas the equilibrating dichlorocyclopropenes (37) and trichlorocyclopropenes (38) yielded only the exo adducts of the cyclopropene containing no gem dichloro group.[13]



(37) (38)

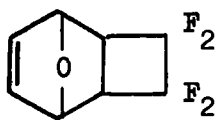
The reduction in ring strain makes cyclobutenes markedly less dienophilic than cyclopropenes, although they are still more reactive than simple olefins towards 1,4-cycloaddition. Cyclobutene itself forms endo and exo 1,4-adducts with diphenylisobenzofuran on reaction at room temperature (60% yield)[75] and cis 3,4-dichlorocyclobutene (39) forms 1,4-adducts with both "electron-rich" and "electron-poor" dienes examples being with cyclopentadiene (73% yield at 140°),[76] furan (10% yield at 120°),[76] diphenylisobenzofuran (83% yield at 100°),[77] anthracene and 9,10-dimethylanthracene (yields of 74% and 90% respectively at 150°),[78] tetraphenylcyclopentadienone (80% yield at 140°)[79] and hexachlorocyclopentadiene (33% yield at 140°).[76] Cis 3,4-dichlorocyclobutene (39) reacted with 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (40) at 60° to give an 85% yield of a 4:1 mixture of the exo anti- (41) and endo anti- (42) 1,4-adducts.

These 1,4-adducts possess the anti-structures due to attack taking place from the least hindered side of the dienophile, possible secondary orbital stabilization due to the lone-pairs of the chlorine atoms being insufficient to overcome the steric interaction of the 3,4-substituents in (40).[79]



(39) (40) (41) (42)

The reactions of a number of highly fluorinated cyclobutenes with "electron-rich" dienes have also been investigated.[80,81] 3,3,4,4-Tetrafluorocyclobutene has been found to be an active dienophile forming 1,4-adducts with butadiene (75% yield after 40 h. at 100-150°), 2,3-dimethylbutadiene (96% yield after 17h. at 100°) and cyclopentadiene (60% yield of an equimolar mixture of endo and exo adducts after 24 h. at 90°). Reaction with furan at 100° for 40 hours gave a 77% yield of a 1:1 adduct (43) together with a mixture of two compounds (44) which were 2:1 adducts, formed by the Diels-Alder reaction of furan with adduct (43). This was proved by heating furan and the 1:1 adduct (43) to 100° for 22 hours when the two 2:1 adducts were obtained in a yield of 40%; a similar reaction of adduct (43) with 2,3-dimethylbutadiene gave a 93% yield of the expected 1,4-adduct (45). When 3,3,4,4-tetrafluorocyclobutene was heated with 2,5-dimethylfuran at 100° for 49 hours the expected 1:1 adduct was isolated in a yield of only 40%, the poor yield being ascribed to steric interactions.[80] The greater yield of 1,4-adduct from reaction with 2,3-dimethylbutadiene compared with butadiene, even though milder conditions were used, is in agreement with the 'Alder rule', 3,3,4,4-tetrafluorocyclobutene, due to the allylic fluorines, behaves as a typical "electron-poor" dienophile reacting more readily with "electron-rich" dienes.



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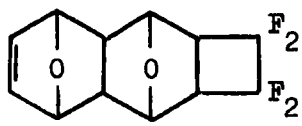

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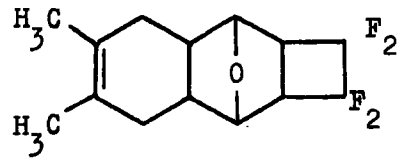
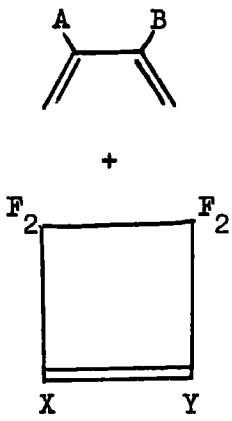


(45)

Link has studied the dienophilicities of a series of highly fluorinated cyclobutenes towards the "electron-rich" dienes butadiene, isoprene and 2,3-dimethylbutadiene. The cyclobutenes studied were fluorinated at the allyl positions and contained combinations of hydrogen, fluorine and chlorine atoms on the double bond. His results are tabulated below.

Table 6. Thermal Diels-Alder Reactions of Fluorinated Cyclobutenes with Butadienes[81]



A	B	X	Y	% Yield of 1,4-Adduct (after 48 h. at 170°)
H	H	F	Cl	3
		H	Cl	28
CH_3	H	F	Cl	20
		H	Cl	84
CH_3	CH_3	F	F	77
		Cl	Cl	2
		Cl	H	88
		F	Cl	89

The reactivities of all the cyclobutenes investigated were less than that of 3,3,4,4-tetrafluorocyclobutene and as all the compounds in the above table are more "electron-poor" than 3,3,4,4-tetrafluorocyclobutene electronic factors cannot be of prime importance. Yields are greater in reactions with more

"electron-rich" dienes in accord with the 'Alder rule' and the most reactive dienophiles are those containing a vinylic hydrogen. Steric effects are important as 1,2-dichlorotetrafluorocyclobutene is very unreactive towards the most "electron-rich" diene and they could also account for the greater reactivity of dienophiles containing a vinylic proton.[81]

Perfluorobicyclo[2,2,0]hexa-2,5-diene, the para-bonded valence isomer of hexafluorobenzene[82,83] and perfluorobicyclo[2,2,0]hex-2-ene[84] are far more powerful dienophiles than the cyclobutenes discussed above, due to the additional strain incorporated in their structures by the fusion of a second four-membered ring. Perfluorobicyclo[2,2,0]hexa-2,5-diene reacts at room temperature with a variety of "electron-rich" cyclic and acyclic dienes to yield both 1:1 and 2:1 Diels-Alder adducts, the latter where the second molecule of diene attacks the fluorinated double bond of the 1:1 adduct. The order of reactivity towards different dienes parallels that of maleic anhydride, as expected; the difficulty with this dienophile is that it rearomatises to hexafluorobenzene on standing and this tends to reduce yields. The stereochemistries of the 1,4-adducts have been assigned, on the basis of n.m.r. evidence, as resulting from exo attack on the dienophile and exo attack on the diene; this is the configuration which would lead to minimum steric interference in the transition state. The formation of a Diels-Alder adduct of perfluorobicyclo[2,2,0]hexa-2,5-diene with pyrrole was the first example of this heterocycle behaving as a diene in the Diels-Alder reaction.[82,83]

The dienophilic properties of perfluorobicyclo[2,2,0]hex-2-ene have been investigated as have those of its analogues in which the vinylic fluorines have been replaced by methyl or methoxyl groups or by hydrogen atoms. The parent compound is of the same order of reactivity as perfluorobicyclo[2,2,0]hexa-2,5-diene. The compounds in which both vinylic fluorines are replaced by methyl groups or one or both vinylic fluorines are replaced by methoxyl groups

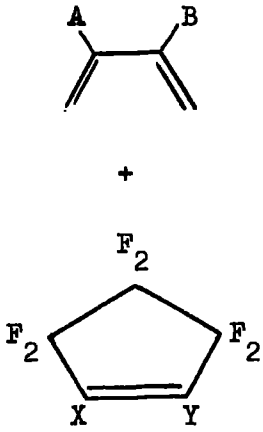
fail to form adducts with furan under conditions where the parent compound reacts readily. Deactivation towards 1,4-cycloaddition by the methyl group has been ascribed to the same type of hybridisation effect invoked to explain a similar deactivation of cyclopropenes containing this functional group whereas deactivation by the methoxyl group has been ascribed to a combination of steric and electronic effects.[67] Replacement of both vinylic fluorines by hydrogen resulted in a marked increase in reactivity, this activation paralleling the behaviour of simple fluorinated cyclobutenes[81] is no doubt also steric in origin.[84]

There are many other examples of strained cyclobutene moieties incorporated in polycyclic systems and like benzynes, these very reactive systems can be readily trapped as their Diels-Alder adducts.

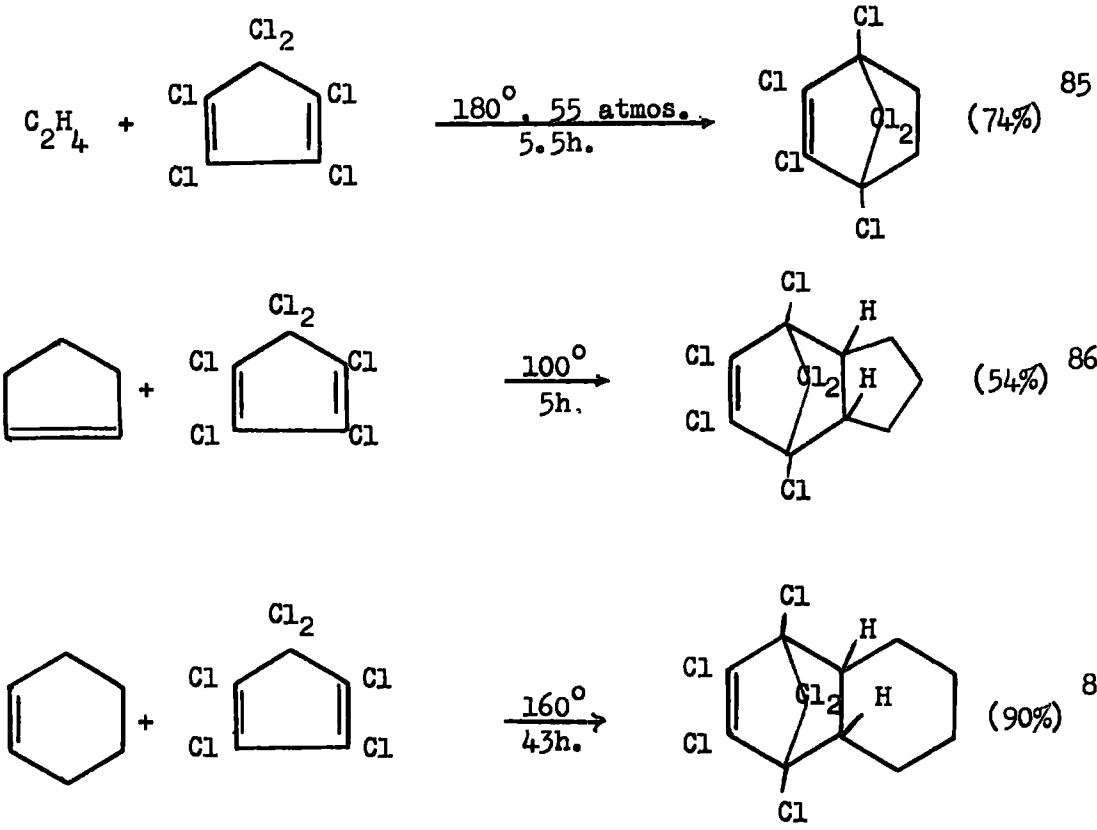
Cyclopentenes possess little inherent strain and are far less dienophilic than cyclobutenes. This is clearly evident if the yields of 1,4-adducts obtained from fluorinated cyclobutenes and butadienes in table 6 are compared with yields of similar adducts derived from their five-membered ring analogues shown in Table 7 (see below). The data recorded in Table 7 also shows that replacement of the vinylic fluorines of octafluorocyclopentene by halogens or hydrogen results in similar trends in reactivity to those observed previously for the analogous cyclobutenes, although for a specific Diels-Alder reaction reactivity of a cyclopentene is lower than that of the analogous cyclobutene.

The conditions necessary for 1,4-addition of cycloalkenes containing five and six-membered rings are generally similar to those required for 1,4-addition of open-chain alkenes, and there has been relatively little interest in using cyclohexenes and cyclopentenes as dienophiles. Examples of reactions of ethylene, cyclohexene and cyclopentene with perchlorocyclopentadiene are given below.

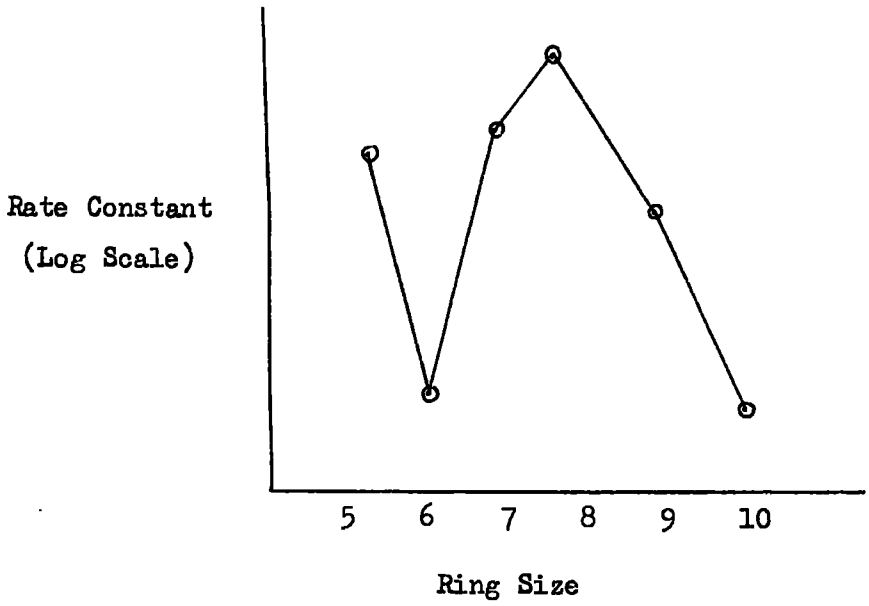
Table 7. Thermal Diels-Alder Reactions of Fluorinated Cyclopentenes with Butadienes[81]



A	B	X	Y	% Yield of 1,4-adduct (after 48h. at 170°)
H	H	F	Cl	3
		H	Cl	1
CH_3	H	F	F	21
		F	Cl	16
		H	F	28
		H	Cl	35
CH_3	CH_3	F	F	60
		F	Cl	84
		F	H	88
		Cl	H	76
		Cl	Cl	1



Ziegler has investigated the reactivities of all the cis cycloolefins, from cyclopentene to cis-cyclodecene, towards Diels-Alder addition with perchlorocyclopentadiene. His plot of rate constant against ring-size is shown below,[86] and follows the general pattern of reactivities of alicyclic compounds.[87] Conformational strain is the major factor governing the reactivities of the five and six-membered cycloolefins, the reactivities of the remaining cycloolefins are a consequence of the strain due to the crowded structure of their adopted configurations.[86]



Reaction is especially rapid for cis-cyclooctene and results in a 94% yield of 1,4-adduct after reaction at 100° for 4½ hours. Trans-cyclooctene is even more strained and reacts with perchlorocyclopentadiene in the cold to produce the expected 1,4-adduct.[88]

Similar trends in reactivity are observed when a series of cis-cycloolefins are allowed to react with diphenylisobenzofuran, cyclooctene reacting extremely readily[89] and reactivity decreasing from cyclopentene to cyclohexene and rising once more for cycloheptene, as indicated below.[90]

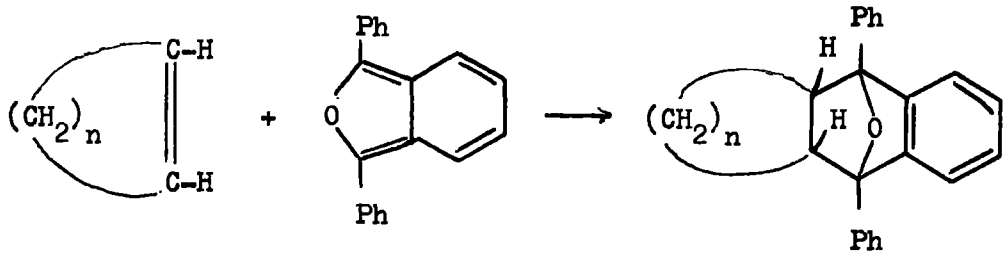


Table 8. Thermal Diels-Alder Reactions of Cycloolefins with Diphenylisobenzofuran[89,90]

n	reaction conditions	% 1,4-adduct
3	100°, 24 h.	75 (+ 16% dehydration product)
	80°, 12 h.	87
4	100°, 24 h.	60
5	100°, 24 h.	69
	80°, 12 h.	66

Dehydrofluorination of Fluorinated Cyclic Compounds

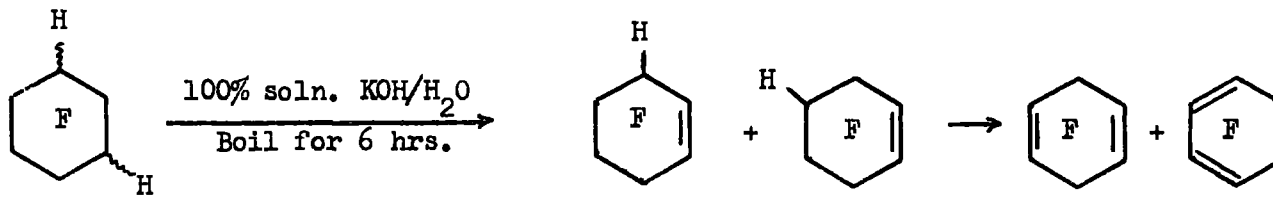
Vapour-phase fluorinations of benzene,[91,92] of cyclopentane[93] or cyclopentadiene,[94] and of cycloheptane or cycloheptatriene[69] using cobalt trifluoride lead to complex mixtures of polyfluorocyclohexanes, polyfluorocyclopentanes and polyfluorocycloheptanes respectively. These polyfluorocycloalkanes can be separated by distillation followed by gas-liquid chromatography.

Dehydrofluorination of suitable polyfluorocyclohexanes has afforded polyfluorobenzenes,[91,92] polyfluorocyclohexadienes and polyfluorocyclohexenes;[95] polyfluorocyclopentanes have been similarly dehydrofluorinated to polyfluorocyclopentenes and polyfluorocyclopentadienes,[96,55] and octafluorocyclohepta-1,3,5-triene and some polyfluorocycloheptadienes have been obtained by synthetic routes involving the dehydrofluorination of polyfluorocycloheptanes.[69]

Fluorinated cyclobutenes can be made by dehydrofluorination of the corresponding cyclobutanes although they are also accessible by other methods.[97]

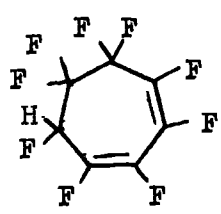
1.8 Methods of Dehydrofluorination

The most commonly used reagent for carrying out dehydrofluorination is aqueous potassium hydroxide. As the process is heterogeneous efficient stirring of the reactants is essential and both the concentration of the alkali and reaction temperature are varied depending upon the ease of elimination. An example of this method of dehydrofluorination is the formation of perfluorocyclohexa-1,3- and -1,4-dienes from a mixture of 1H,3H-decafluorocyclohexanes, see below.[95] The disadvantage of using aqueous potassium hydroxide is that use



of prolonged reaction times sometimes results in decomposition of reaction products giving water-soluble compounds and consequently low recoveries.

This problem occurred in the attempted dehydrofluorination of 3H- and 4H-heptafluorocyclopentenes using refluxing aqueous alkali; only extensive decomposition of the olefin resulted and this was ascribed to nucleophilic attack by aqueous alkali on perfluorocyclopentadiene, the expected product, which was never isolated from this reaction.[96] Similarly dienes (46) and (47) yielded products which were labile to aqueous alkali.[69]



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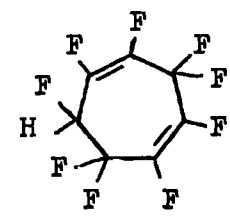
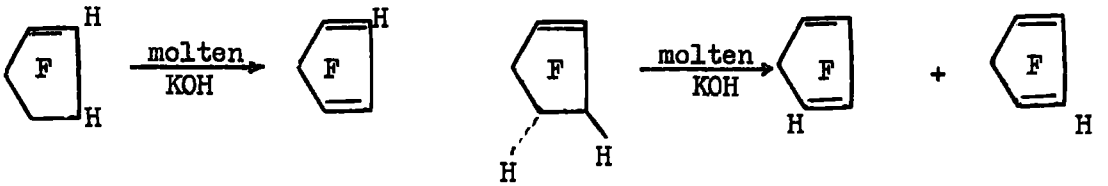


(47)

By introducing 3H- and 4H-heptafluorocyclopentenes below the surface of molten potassium hydroxide at 260°, a short contact time being essential to minimise decomposition, a 37% yield of perfluorocyclopentadiene was obtained,[96] and this process was also successfully applied to the preparation of 2H-pentafluorocyclopentadiene from 1H:5H-hexafluorocyclopentene and both 1H- and 2H-pentafluorocyclopentadienes from 3H/4H-hexafluorocyclopentene,[55] see below. Similarly dienes (46) and (47) were successfully dehydrofluorinated to octafluorocyclohepta-1,3,5-triene by rapid passage through molten potassium



hydroxide. An even better method for dehydrofluorinating dienes (46) and (47) involves powdered potassium hydroxide in benzene as the dehydrofluorinating agent and leads to high yields of octafluorocyclohepta-1,3,5-triene.[69]

Undecafluorocyclohexane, 1H:3H- and 1H:4H-decafluorocyclohexanes and 1H:2H:4H-nonafluorocyclohexanes were dehydrofluorinated to any required degree using strongly basic anion exchange resins. Only very mild conditions, usually 20°-60°, can be used so as not to denature the resin, however this technique does not appear to have been subsequently applied to other systems.[98]

Another dehydrofluorination method which would appear to be well-suited for large-scale experiments involves pyrolysis of the fluorocarbon in the presence of a metal fluoride. Although this technique has been successfully applied to the preparation of nonafluorocyclohexenes, hepta- and octafluorocyclohexadienes[99] and conjugated polyfluoroalicyclic compounds with exocyclic methylene groups,[100] it was unsuccessful for 4H-heptafluorocyclopentene. Pyrolysis of this compound

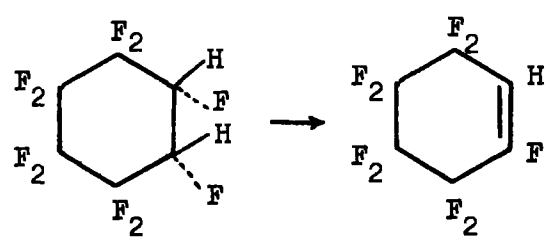
over sodium fluoride at 330° resulted in isomerisation to its 1H- and 3H-isomers rather than dehydrofluorination to perfluorocyclopentadiene.[96]

1.9 Mechanisms of Dehydrofluorination

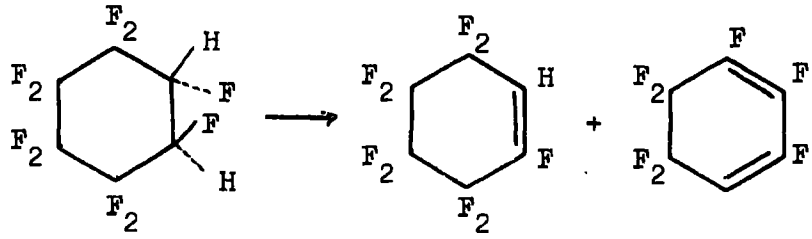
The dehydrofluorination of polyfluorocyclohexanes has been extensively studied and a number of factors have been recognised as determining which hydrogen and which fluorine are eliminated. They are listed below.

1. The most acidic hydrogen is preferentially eliminated, i.e. the one surrounded by most fluorines, and ease of dehydrofluorination parallels acidity.
2. Loss of fluorine from a CHF group is easier than from a CF_2 group.
3. Trans-elemination by an E2 trans-coplanar mechanism occurs whenever possible; cyclohexanes with substituents to be eliminated in trans and axial positions will be more readily dehydrofluorinated than their isomers in which this arrangement is not possible.
4. Cis-elimination can proceed when the proton to be eliminated is sufficiently acidic and may be faster than possible trans-eliminations.[101,102]

Some of these factors account for the products of dehydrofluorination of cis- and trans-1H,2H-decafluorocyclohexanes (48) and (49) respectively, shown below.



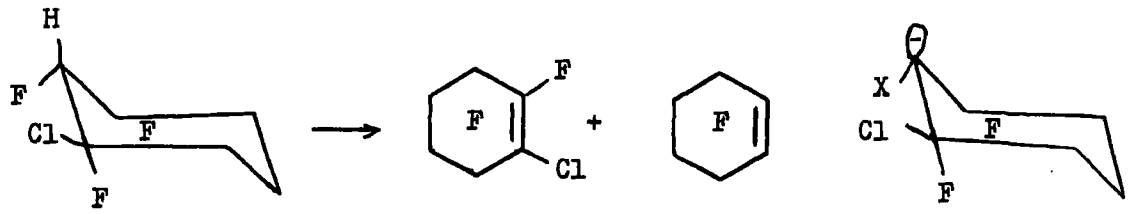
(48)



(49)

For the cis-isomer (48) an E2 process with loss of fluorine from the CFH group as against the CF_2 group accounts for the observed product, the hydrogen and fluorine eliminated being in a trans-axial arrangement in the reactant. Dehydrofluorination of (49) was more difficult than in the case of (48), the E2 process with loss of fluorine from the CFH group being impossible. An E2 process with loss of fluorine from both CF_2 groups accounts for formation of the diene, either a cis-elimination of hydrogen fluoride from the boat-form of (49)[101] or an Elcb mechanism involving elimination from the carbanion derived from (49) can account for the olefin formed. As (49) incorporates deuterium when shaken with potassium hydroxide in D_2O a carbanion mechanism seems more likely.[103]

The Elcb process has been suggested to account for the minor product of dehydrofluorination of 1H,2-chlorononafluorocyclohexane (50), see below.



(50) 86% 14% (51)

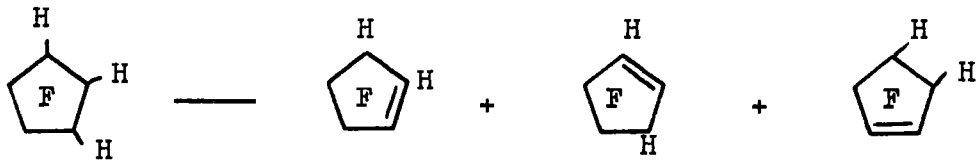
The major product can arise from dehydrofluorination via an E2 mechanism, as the hydrogen and fluorine eliminated are in a trans-axial arrangement. The

minor product could arise via a cis-coplanar elimination of hydrogen chloride from the boat form of (50), an E2 process, or by elimination from the carbanion (51). As (50) incorporated deuterium on shaking with potassium hydroxide in D_2O the latter mechanism is more likely.[103]

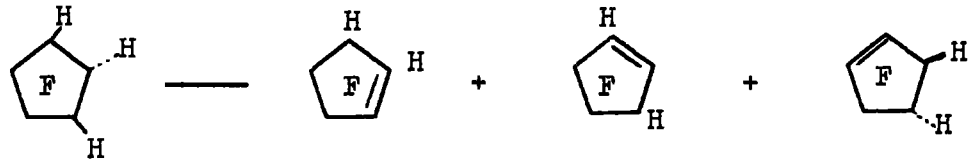
Another possible dehydrofluorination mechanism would be loss of hydrogen and fluorine from the same carbon atom to generate a carbene intermediate which could then rearrange to an olefin. This mechanism would not account for the large variations in reaction rate between steroisomers, also α-elimination has been proved not to take place when polyfluorocyclic olefins react with alcohols in the presence of potassium hydroxide, where reaction proceeds solely by β-elimination from the intermediate carbanion.[104]

The main difference between dehydrofluorinations in cyclopentane systems and in cyclohexanes is that as a consequence of the geometry of the cyclopentane ring the cis positions become coplanar and it is possible to have E2 cis-eliminations which are only slightly less favourable than the trans- possesses, in which a slight twisting of the molecule makes the trans positions coplanar. The groups which are to become vinylic are consequently also coplanar in a cis-elimination in a fluorinated cyclopentane and the relatively correct steric alignment of these potentially vinylic substituents may be an important feature of this coplanar reaction system. Rigid cis-elimination is only possible for a cyclohexane molecule fixed in a boat or a twist-boat configuration.

The operation of these considerations is evident from the products of dehydrofluorination of the two 1H,2H,3H-heptafluorocyclopentanes, the 1H,2H,3H/-isomer (52) and the 1H,3H/2H-isomer (53). The major product is the same for both isomers, the outside hydrogen flanked by a CF_2 group is the most acidic and the fluorine of the CHF group the easiest to remove; this is more marked when elimination is trans, in (52), than when it is cis, in (53); in the latter case more elimination takes place from the CF_2 group.[102] Also both 1H/2H- and



(52) (c.100%) trace trace



(53) (86%) (6%) (9%)

1H,2H/-octafluorocyclopentanes and 1H,2H/-decafluorocyclohexane lost hydrogen fluoride at approximately the same rate under identical conditions in aqueous alkali.[94]

Dehydrofluorination in cyclobutanes is similar to the situation in cyclo pentanes; both of the 1H,2H-hexafluorocyclobutanes lose hydrogen fluoride at approximately the same rate.[97]

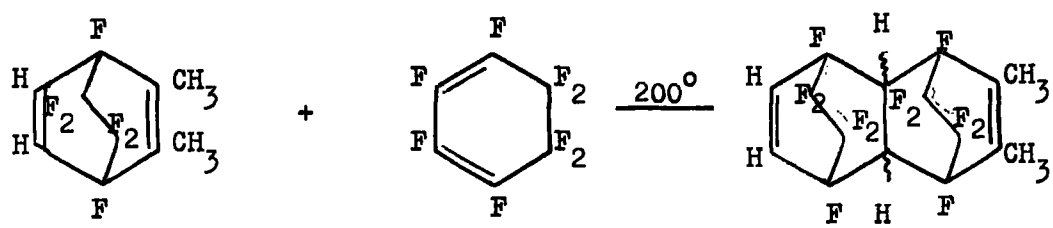
CHAPTER 1

DISCUSSION

1.10 Diels-Alder Reactions of Perfluorocyclohexa-1,3-diene with Cyclic Olefins

Although the Diels-Alder reactions of highly fluorinated cyclohexa-1,3-dienes have been extensively investigated, few examples have been reported involving simple cyclic dienophiles.[45,58,60,63,64,66,68] In this work it has been established that perfluorocyclohexa-1,3-diene (XII) undergoes thermal Diels-Alder reactions with five cyclic dienophiles, cyclohexene, cyclopentene, 1H,2H-octafluorocyclohexene, 1H,2H-hexafluorocyclopentene and 1H,2H-tetrafluorocyclobutene; in the latter case products other than the 1,4-addition product were also isolated (see Figure 1).

Severe conditions were required for reaction with the 1H,2H-perfluorocycloalkenes; in all three cases temperatures in excess of 300° were necessary to obtain reasonable yields of the 1,4-adducts. This is in marked contrast to the ready formation of a 2:1 adduct in the reaction between 2H,3H-hexafluorocyclohexa-1,3-diene and but-2-yne (41%, after 22.5 h. at 200°),[66] which must result from the relatively high dienophilic reactivity of the CH=CH double bond in the primary adduct.

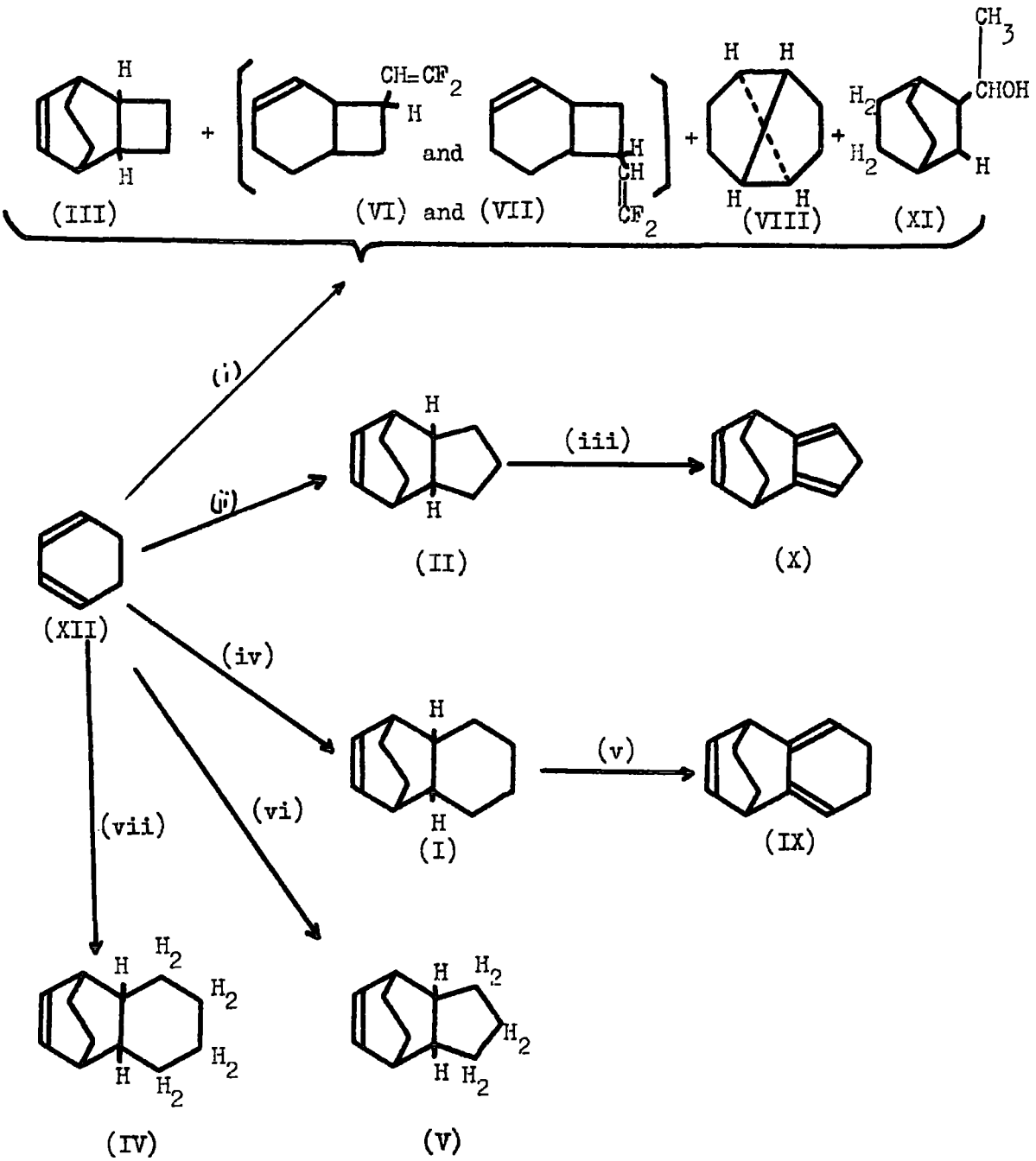


The evident difference between the reactivity of this CH=CH double bond and those in the 1H,2H-perfluorocycloalkenes investigated is probably best ascribed to the increased steric strain in the bicyclic as compared to the monocyclic dienophiles.

The n.m.r. spectra of the 1,4-adducts are tabulated below (Table 9). They all contain the octafluorobicyclo[2,2,2]oct-5-ene unit, and the fluorine resonances for tertiary, vinylic and bridging difluoromethylenes are similar in position to those previously reported for the Diels-Alder adducts of highly

FIGURE 1

Unmarked bonds are to fluorine



Key

(i) 1H,2H-tetrafluorocyclobutene/diethyl ether
(ii) 1H,2H-hexafluorocyclopentene
(iii) molten KOH
(iv) 1H,2H-octafluorocyclohexene
(v) aqueous KOH
(vi) cyclopentene
(vii) cyclohexene

Table 9. ^{19}F and ^{1}H n.m.r. Spectral Parameters[a]

Compound[b]	Tertiary F	Vinylic F	CF_2	Tertiary H	CH_2
(III)	202.4 (2)	149.7 (2)	127.2 (4)[c]	3.47	-
			δ_A 108.1 (2)		
			δ_B 123.6 (2)		
			J_{AB} 226		
(II)	205.7 (2)	150.2 (2)	128.0 (4)[c]	3.25	-
			δ_A 116.2 (2)		
			δ_B 124.1 (2)		
			J_{AB} 258		
			δ'_A 132.1 (1)		
			δ'_B 144.1 (1)		
			J_{AB} 258		
(I)	206.4 (2)	149.7 (2)	128.6 (4)[c]	3.2	-
			δ_A 122.9 (2)		
			δ_B 133.3 (2)		
			J_{AB} 270		
			δ'_A 111.9 (2)		
			δ'_B 120.3 (2)		
			J_{AB} 270		
(IV)[d]	208.1 (2)	151.5 (2)	128.5 (4)[c]	2.4 (2)	1.65 (8)
(V)	205.0 (2)	151.1 (2)	δ_A 125.3 (2)[c]	2.8 (2)	1.75 (6)
			δ_B 128.0 (2)[c]		
			J_{AB} 228		

a. Chemical shifts are in p.p.m. upfield from internal $CFCl_3$ or external Me_4Si and refer to centres of broad bands or unresolved multiplets, integrated intensities are in parentheses, coupling constants Hz;

b. Neat liquids; c. Bridging $-CF_2-CF_2-$; d. Solution in CCl_4.

fluorinated cyclohexa-1,3-dienes with alkenes and alkynes.[45,58,59,63] Tertiary fluorines are generally in the region (184-219 p.p.m.), vinylic fluorines in the region (150-163 p.p.m.) and bridging difluoromethylenes in the region (115-137 p.p.m.).[67] As can be seen the tertiary fluorines are all very similar in chemical shift (202-208 p.p.m.) and they are broadened as a result of extensive coupling with other nuclei; the vinylic fluorines produce sharp resonances at about the same shift (149.7-151.5 p.p.m.) and the bridging difluoromethylene resonances have been assigned on the basis of their position (125-128 p.p.m.) and the fact that the complex AA'BB' system in some instances simplifies to a pseudo AB system whose coupling constant in analogous systems has been found to be in the range 220-234 Hz, for compound (V) J_{AB} = 228 Hz. For compounds (I) and (II) the remaining difluoromethylenes formed AB systems with coupling constants of 270 and 258 Hz due to six and five-membered rings respectively, J_{AB} being much greater than expected for bridging difluoromethylenes of the octafluorobicyclo[2,2,2]oct-5-ene unit. For compound (III) the two difluoromethylene systems would be expected to have similar coupling constants; the bridging difluoromethylenes of the octafluorobicyclo[2,2,2]-oct-5-ene unit were assigned on the basis of shift by analogy with compounds (II) and (III), the J_{AB} of 226 Hz assigned to the cyclobutane CF_2 groups is compatible with literature values.[105] The proton n.m.r. resonances were very broad due to extensive long range coupling with both ^1H and ^{19}F nuclei, the chemical shifts observed for tertiary and methylene protons being as expected. Also consistent with the proposed structures are the infra-red CF=CF stretching frequencies which for the octafluorobicyclo[2,2,2]oct-5-ene unit are generally strong and in the region (1751-1772 cm^{-1}),[45,58,59,63] in these compounds a strong CF=CF stretch was observed in the region (1764-1776 cm^{-1}). Tertiary C-H stretch occurred in the region 2975-2994 cm^{-1} and methylene C-H stretch at slightly lower frequency 2890 cm^{-1}. All compounds had satisfactory elemental analyses.

The mass spectra were also consistent with these compounds being 1.4 cycloaddition products (see Appendix 2). They all showed parent peaks of moderate abundance (9-30% of base peak) and had breakdown patterns consistent with their structures. For compounds (I) and (II) the base peak was at m/e 199 corresponding to $C_7F_6H^+$, the stable hexafluorobenzyl or hexafluorotropylium ion, also the loss of tetrafluoroethylene from the parent peak lead to an abundant peak at P-100 which was of the same abundance as the base peak in the case of compound (II) and was 65% of the abundance of the base peak for compound (I). For the 1H,2H-tetrafluorocyclobutene adduct (III) the base peak corresponded to the formation of the tetrafluorobenzene cation, $C_6F_4H_2^+$ due to loss of C_4F_8 from the parent. In the case of the cyclohexene adduct (IV) loss of C_2F_4 from the parent peak produced a fragment whose abundance was 33% of the base peak, the base peak corresponding to $C_5H_7^+$; for the cyclopentene adduct (V) the base peak arose by loss of tetrafluoroethylene from the parent ion.

In each case only a single 1.4-adduct was isolated and this is assumed to be the ENDO adduct by analogy with the two examples where the stereochemistry of the Diels-Alder addition to perfluorocyclicdienes has been unambiguously established.[45,50] The inability to construct the Cortaulds space-filling molecular models of the exo isomers of compounds (I) and (II) due to steric interactions between the tetrafluoroethylene bridge of the octafluorobicyclo [2.2.2]oct-5-ene unit and the difluoromethylene groups of the five and six membered rings from the dienophile, whereas the endo isomers could be readily constructed, is also in agreement with endo stereochemistry being more favourable in these systems.

The hydrocarbon olefins reacted extremely readily with perfluorocyclohexa-1,3-diene at 208° for 21h. to give yields of 81% and 96% of the Diels-Alder adducts of cyclohexene and cyclopentene respectively, in contrast the fluorohydro carbon olefins were much less reactive. Adduct (III) from 1H,2H-tetrafluorocyclobutene was formed at the lowest temperature, the yield being reduced due

to competitive side reactions, and adduct (II) from 1H,2H-hexafluorocyclopentene was formed in higher yield and at lower temperatures than adduct (I) from 1H,2H-octafluorocyclohexene. The ready reactivity of the hydrocarbon olefins compared with the hydrofluorocarbons is what one would expect as perfluorocyclohexa-1,3-diene, an "electron-poor" diene, reacts more readily with "electron-rich" dienophiles.[2,15] Also the order of reactivity of the fluorohydrocarbon dienophiles is in accord with relief of ring strain in forming the adducts.[2] An examination of molecular ~~orbitals~~ models shows that there is little conformational strain introduced on forming the cyclopentene adducts (II and V) as the 5-membered ring can maintain its planarity in the adduct, however for adducts (I) and (IV) the cyclohexene reactant, presumably in a chair-like conformation,[106] has to assume the higher-energy skew-boat or boat form in the adduct, as the C-2 and C-7 substituents are fixed in an eclipsed conformation. The difference in yields between six-membered ring dienophiles and five-membered ring dienophiles is greater for the fluorohydrocarbons than for their hydrocarbon analogues and this can be ascribed to the more restricted conformational mobility and/or the greater steric strain in adduct (I) as compared with (II). That the low yield of (I) was not due to breakdown by the retro Diels-Alder reaction was shown by heating (I) for a considerable time at the temperature of its formation, a very slow retro Diels-Alder reaction occurred, similar treatment of (II) and (III) produced no detectable breakdown of the adducts, and these results are consistent with adduct (I) being more sterically strained than adduct (II).

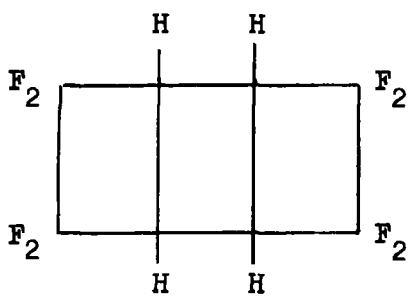
When 1H,2H-tetrafluorocyclobutene containing some diethyl ether was heated to 295° for 42 h. with a slight excess of perfluorocyclohexa-1,3-diene a complex product resulted which was separated by preparative g.l.c. The major product was the expected Diels-Alder adduct (III). The next most abundant products were also 1:1 adducts, shown by mass spectroscopy and chemical analysis, but

unlike the 1.4 adduct they had very low intensity parent ions (<1% of the base peak), and base peaks at m/e 126 ($C_4H_2F_4^+$), suggesting that the original tetrafluorocyclobutene moiety was retained intact in the adducts. The ^1H n.m.r. spectra of both of these adducts showed two distinct signals, one a doublet of sharp lines, and the other an extensively-coupled broad signal. The ^{19}F n.m.r. spectra of both isomers indicated a lack of symmetry and consisted of two low-field resonances coupling only with each other and with the lower field of the two proton signals, two tertiary and two vinylic fluorine resonances, and three difluoromethylene resonances. This data is thus consistent with 2,2-difluorovinyl-decafluorobicyclo[4,2,0]oct-2-ene structures for both isomers (VI) and (VII), but it is not possible to decide between a 7 or an 8-substituted difluorovinyl group or its stereochemical relationship to the rest of the molecule. The infra-red spectra of these isomers are also consistent with the proposed structures showing the two required olefinic absorptions at 1765 cm^{-1} (CF=CF) and 1755 cm^{-1} ($CH=CF_2$),[43] and the presence of hydrogen atoms at both saturated (2975 cm^{-1}) and unsaturated (3100 cm^{-1}) sites. Alternative structures such as 1,2-adducts of 1H,2H-tetrafluorocyclobutene and perfluorocyclohexa-1,3-diene can be ruled out. The presence of two double-bond stretching frequencies in the infra-red spectra and the two low field resonances in the ^{19}F n.m.r. spectra are inconsistent with 1,2-addition products, and it would be difficult to see how such products could be formed.

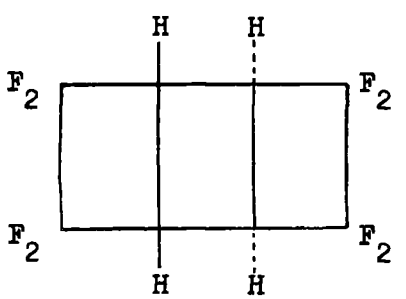
There are several possible mechanisms which could account for the formation of adducts (VI) and (VII). One mechanism would involve a [2 + 2] cycloaddition by a radical mechanism between perfluorocyclohexa-1,3-diene and 1,1,4,4-tetrafluorobuta-1,3-diene. This can be ruled out because the electrocyclic ring-opening of the cyclobutene to the butadiene requires high temperatures and a low pressure (550°-750° at 5.25 mm.Hg.) followed by immediate quenching of the product,[107] and under the reaction conditions employed the equilibrium

between fluorinated-1 3-dienes and cyclobutenes favours the cyclobutene.[108] For the butadiene to be an intermediate in the reaction some products of its ready thermal polymerisation would have been expected (see Introduction),[43] none were detected. Two alternative mechanisms (Figure 2) would involve the diradicals shown (Scheme 2a) or a concerted $[2\pi + 2\pi + 2\sigma]$cycloaddition[6] (Scheme 2b), possibly in a supra,supra,supra sense which is thermally allowed, involving one π-bond of the diene and the π-bond and a σ-bond of the cyclobutene.

The fourth product isolated from the reaction was a colourless solid, a volatile toxic compound with a fruity odour, readily sublimable, melting at 126°. The mass spectrum of this compound had a parent peak at m/e 252 ($C_8F_8H_4^+$) of high abundance (50% of base peak), an intense peak at m/e 126 ($C_4F_4H_2^+$), and a base peak at m/e 183 due to loss of CF_3 from the parent, (see Appendix 2), this together with the correct analysis identifies this compound as a dimer of the cyclobutene dienophile. The ^{19}F n.m.r. and ^{1}H n.m.r. spectra are both just a single sharp resonance and this together with the high melting point is suggestive of a highly symmetrical structure. Both the Raman* and the infra-red spectra of this compound showed no olefinic stretching vibrations and thus the compound must be saturated and therefore tricyclic. The assigned structure (VIII) is consistent with all these data, other structures (54) and (55) might



(54)

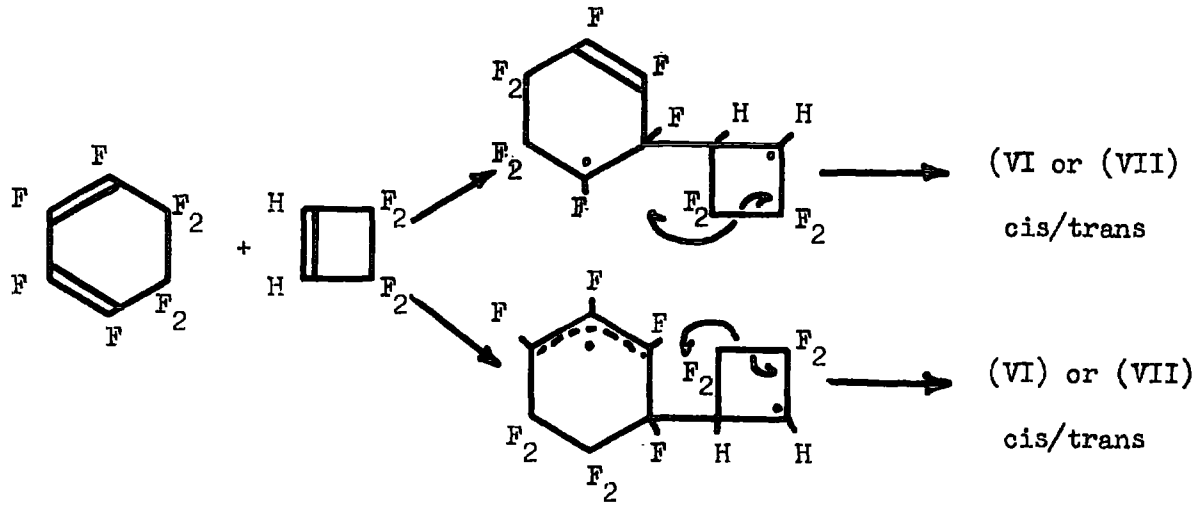


(55)

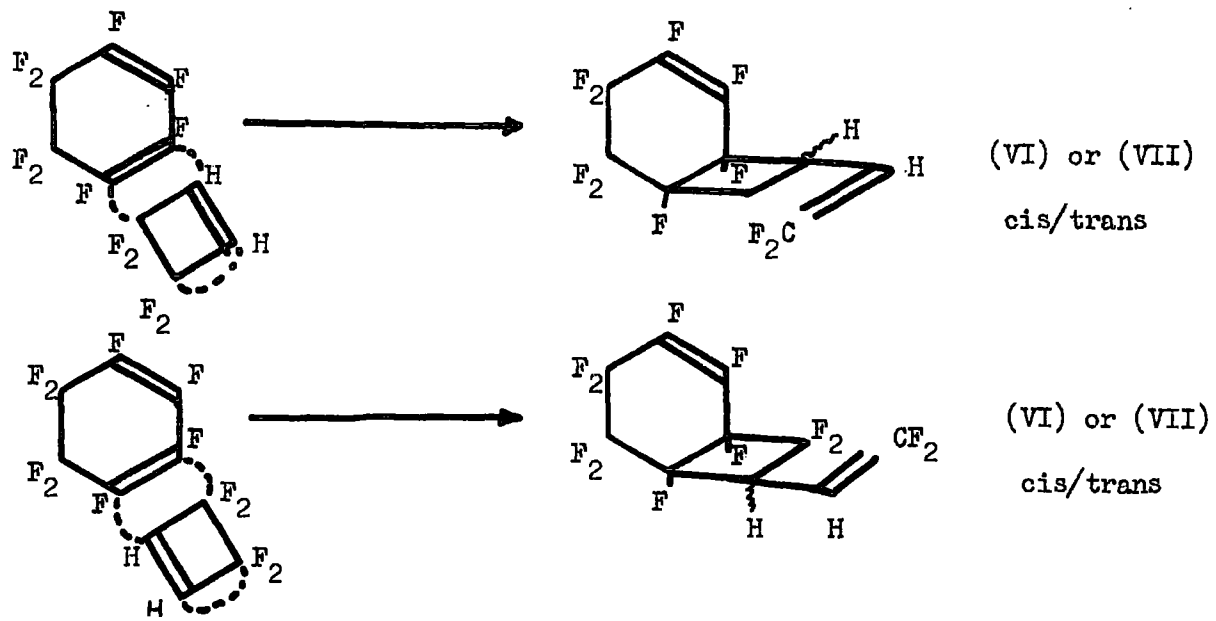
* Run on a Perkin-Elmer LR-1, Laser-Excited Raman Spectrometer using a Spectra-Physics 125 Laser; I am indebted to Dr. C.J. Ludman for this measurement.

FIGURE 2

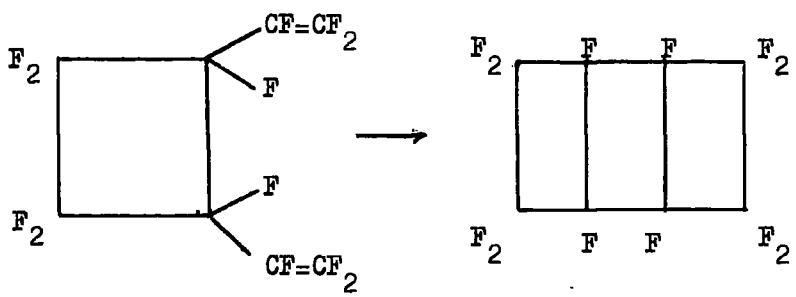
Scheme 2a. Radical Mechanism.



Scheme 2b. $\left[\pi 2_s + \pi 2_s + \sigma 2_s\right]$ cycloaddition

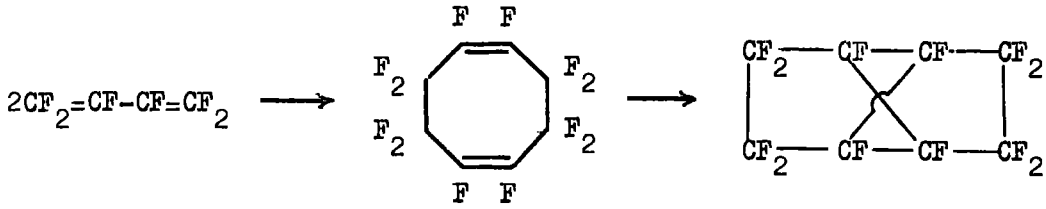


be expected to have fluorines in sufficiently different environments to give rise to separate resonances or at least line-broadening in the ^{19}F n.m.r. spectrum, also they might be expected to be formed together, an isomeric mixture in this case being unlikely on the basis of a sharp melting point and a clean n.m.r. spectrum. To confirm the mode of formation of (VIII) 1H,2H-tetrafluorocyclobutene containing some traces of diethyl ether was heated alone under the above conditions and (VIII) was obtained as the sole reaction product. There is a precedent for structure (VIII) (see Introduction); its completely fluorinated analogue, the structure of which has been determined by X-ray work,[39] was made by Miller by heating perfluorobuta-1,3-diene.[38] Initially, Miller assigned a tricyclic structure analogous to (54) and (55) to the saturated dimer and suggested a mechanism for its formation from an unsaturated dimer, see below.



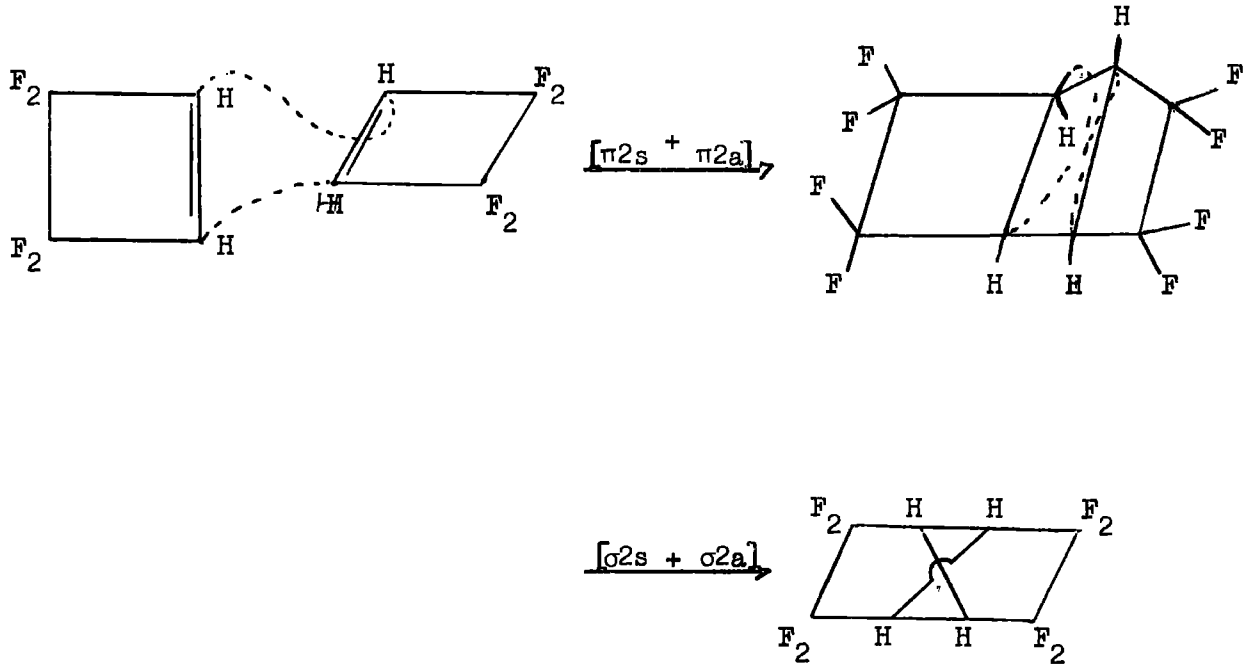
After the structure had been corrected an alternative mechanism was proposed by Karle[40] who assumed the intermediate dimer to be a cyclooctadiene presumably formed from diradicals of the butadiene, which then underwent a trans-annular addition to produce the required compound, see below.

There are several reasons for suggesting that these saturated dimers are formed from the corresponding cyclobutenes rather than the butadiene. When Putnam et al heated 1,1,4,4-tetrafluorobutadiene, the diene which would be formed by ring-opening of 1H,2H-tetrafluorocyclobutene, the products they isolated contained no saturated dimer neither did they report any cyclobutene.[43]



Miller recorded that the yield of the completely fluorinated saturated dimer increased with temperature as did that of perfluorocyclobutene which was always formed along with the saturated dimer.[38] Also the analogue of (VIII) formed by heating 1,3-dichloroperfluoro1,3-butadiene for 44 hours at 170° might also have been formed via the cyclobutene as it is stated that on heating at 176° for 89 hours 2,3-dichloroperfluoro-1,3-butadiene forms 1,2-dichloroperfluoro-1-cyclobutene.[40]

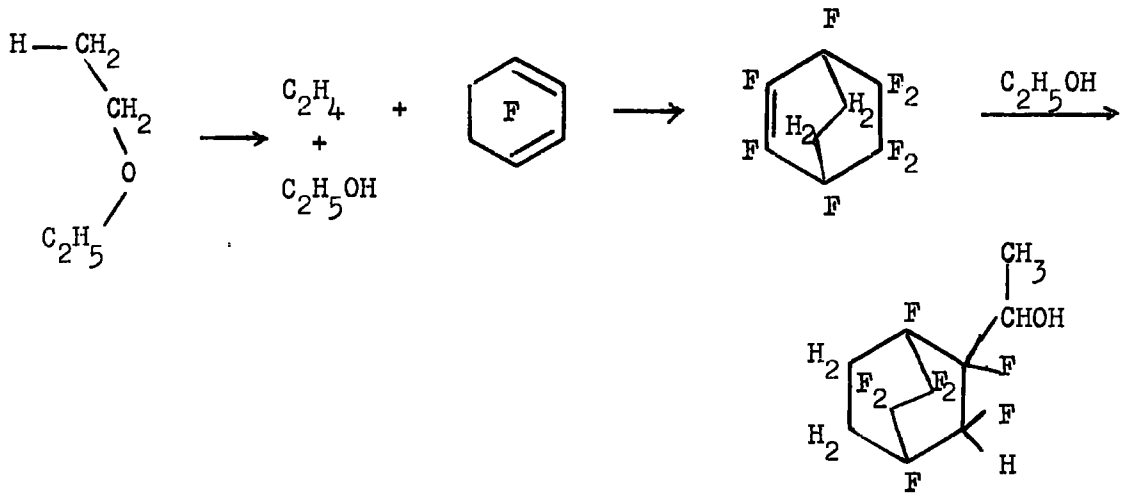
A concerted symmetry-allowed pathway could account for the formation of (VIII) from 1H,2H-tetrafluorocyclobutene, see below.



The initial [2+2]-cycloaddition, suprafacial on one π-system and antarafacial on the other leads to an unstable trans-fused cyclobutane moiety, which can undergo a symmetry allowed [σ_{2s} + σ_{2a}] process across the sigma bonds indicated to produce the required dimer.

In addition to the previously mentioned compounds four longer-retained compounds were obtained in small amount. Complete separation of the individual components by either distillation or gas liquid chromatography proved impossible, and they were examined as mixtures. By repeated g.l.c. separations it was possible to obtain a mixture containing the longest-retained compound as major constituent (> 90% by n.m.r. and g.l.c.) and another mixture containing the shortest-retained compound as major constituent (> 90% by g.l.c. and n.m.r.). Both these mixtures had quite similar infra-red spectra containing no CF=CF stretching vibration and the ^{19}F n.m.r. spectra of these particular mixtures contained in each case four fluorine resonances in the tertiary region integrating to four fluorines, the rest of the fluorine resonances lying in the saturated difluoromethylene region and integrating to four more fluorines, in one case being an AB system (corresponding to one CF_2) and a single broad peak (corresponding to the other CF_2), whereas for the other case a complex pattern of overlapping peaks was present (see experimental). The mass spectra of both these mixtures had a top mass peak at m/e 298 (corresponding to the 1:1 adduct of octafluorocyclohexa-1,3-diene and the elements of diethyl ether) and had similarities in their breakdown patterns (see experimental), the base peak at m/e 45 in both cases could be $CH_3\overset{+}{C}HOH$, and suggests a secondary alcohol. The infra-red spectrum of another mixture containing all four components in almost equal amount, by g.l.c., was very similar to those of the two mixtures above and also contained no evidence of a CF=CF. All the infra-red spectra contained absorptions due to C-H stretch and O-H stretch. The abundance of these compounds in the reaction product was dependent on the amount of diethyl ether

impurity present in the 1H,2H-tetrafluorocyclobutene used initially and it was considered that as minor products arising from impurities present in the starting material they did not merit more detailed investigation. The evidence obtained is consistent with these compounds being isomer mixtures of 1,2,3,4,5,5,6,6-octafluoro-2-(1-hydroxyethyl)-bicyclo[2,2,2]octane (XI) and they could be formed by pyrolytic elimination of ethylene from diethyl ether which could then react with perfluorocyclohexa-1,3-diene to form the 1,4-adduct, subsequent radical addition of ethanol to this compound would lead to compounds (XI), see below, of which there would be four possible geometric isomers.



(XI)

The ^{1}H n.m.r. spectra of the two mixtures containing a single major component were also consistent with structures (XI), the C_2H_4 bridge and CH_3 group forming one broadened resonance, the tertiary protons overlapping with one another to produce a second resonance and a third resonance broader than the others was ascribed to the hydroxyl proton.

The 1H,2H-perfluorocycloolefins used in the Diels-Alder reaction with perfluorocyclohexa-1,3-dienes were prepared by reduction of the corresponding perfluorocycloolefins using lithium aluminium hydride in diethyl ether.

Reduction of perfluorocyclohexene using the same ratio of reactants as in the literature method[109] produced the required olefin as the major product. For the preparation of 1H,2H-hexafluorocyclopentene the literature reduction[110] of perfluorocyclopentene was modified to produce reasonable yields of the required olefin (see experimental). 1H,2H-perfluorocyclohexene and 1H,2H-perfluorocyclopentene were obtained free of other fluorohydrocarbons by separation using preparative gas chromatography, their 1H,6H-and 1H,5H-isomers respectively, which had almost similar g.l.c. retention times were particularly difficult to remove. For the case of 1H,2H-tetrafluorocyclobutene the literature method[97] led to one product only, the 1H,2H-compound, which had very similar retention time to diethyl ether. Most of the diethyl ether was removed by careful distillation and the cycloolefin was then used in reactions without further purification.

Attempts were made to obtain high yields of adducts (I) and (II) in order to use these compounds for further synthetic work. It was found that essentially quantitative conversion of 1H,2H-hexafluorocyclopentene to adduct (II) could be achieved using an aged metal bomb and temperatures of about 340° with reaction time of about 16 hrs., by recycling unchanged starting materials - each reaction producing over 65% conversion. The starting materials were readily separable from adduct (II) by careful distillation and the reaction could be conveniently carried out on a scale of up to 100 g. of material; also the presence of small amounts of 1H,5H-hexafluorocyclopentene as a contaminant in the 1H,2H-isomer had little effect on the yield of adduct (II). Under the conditions for the formation of (II) in yields of over 65% (I) was obtainable only in yields of 10-17%. Reaction of 1H,2H-octafluorocyclohexene with perfluorocyclohexa-1,3-diene under more strenuous conditions than required for the formation of (II) for extended periods of time led to loss of material by the isomerisation of perfluorocyclohexa-1,3-diene to its 1,4-isomer and produced

no significant increase in the yield of (I). As mentioned previously (I) undergoes the retro Diels-Alder reaction slowly under the conditions of its formation, and this will no doubt becomes more important at higher temperatures.

In subsequent work emphasis was placed on the synthetic utility of the more readily available adduct (II).

1.11 Dehydrofluorination of 2H,7H-hexadecafluorotricyclo[6,2,2,$0^{2,7}$]dodec-4-ene(I) and 2H,6H-tetradecafluorotricyclo[5,2,2,$0^{2,6}$]undec-8-ene(II) and the attempted dehydrofluorination of 2H,5H-dodecafluorotricyclo[4,2,2,$0^{2,5}$]dec-7-ene(III)

Initially attempts were made to dehydrofluorinate adduct (I) by passage through molten potassium hydroxide in a stream of dry nitrogen. Varying both the temperature of the potassium hydroxide melt(from 200° to 360°)and the rate of flow of nitrogen had little effect on the resulting reaction, a black residue formed in the reaction vessel which tended to block the inlet and only traces of volatile materials were recovered from the liquid air trap at the exit of the apparatus. Dehydrofluorination was eventually satisfactorily achieved by heating and rapidly stirring the adduct with 50% aqueous potassium hydroxide until a vigorous exothermic reaction set in, leaving for a few minutes until the system became a deep brown colour and homogeneous and then immediately quenching the solution by rapid addition of a large excess of cold dilute hydrochloric acid. After separation of some residual starting material by preparative g.l.c. a single di-dehydrofluorination product (IX) was obtained in only moderate yield, (37%).

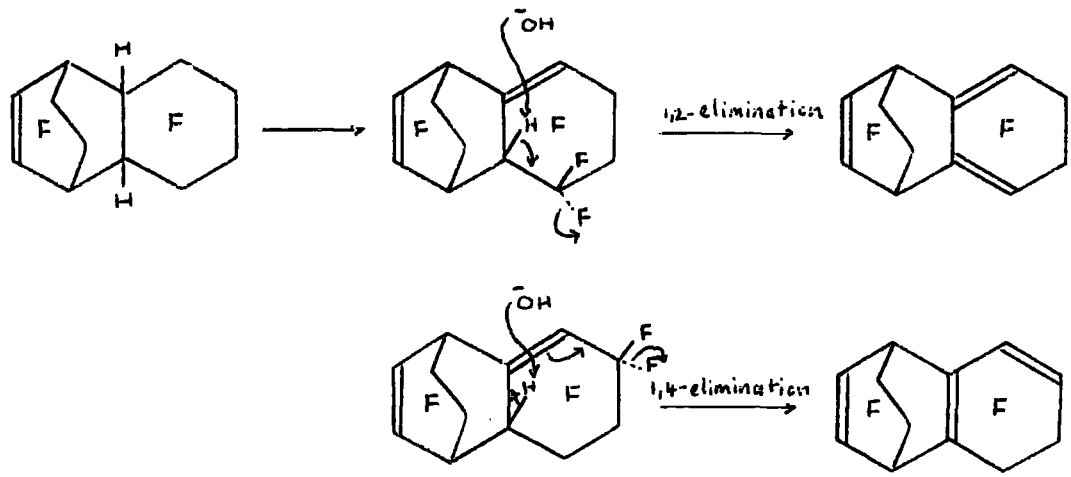
Adduct (II) could also be dehydrofluorinated using aqueous potassium hydroxide (100%), the product (X) resulting from loss of two moles of hydrogen fluoride was isolated in 33% yield after separation from residual starting material by preparative g.l.c. However slow passage of (II) through molten

potassium hydroxide (at around 200°) in a stream of dry nitrogen as carrier led to a 68% yield of (X); no more than a small amount of starting material remained in the recovered volatile material. This technique can be successfully used with quantities of (II) of the order of 10 gms, and the triene (X) can be obtained essentially pure by vacuum transfer as it has considerably higher volatility than residual (II). Thus (X) is much more accessible than (IX) as (II) is both easier to prepare and to dehydrofluorinate than (I).

All attempts to dehydrofluorinate adduct (III) were unsuccessful, resulting in either recovery or decomposition of (III), no tractable products being obtained in several attempts using a variety of conditions. The appropriate conditions for dehydrofluorination must depend on a variety of factors including the volatilities of the starting materials and the products, the stability of the products to the reagent used, side reactions of the starting material and the ease of loss of hydrogen fluoride. For adduct (III) the balance of these factors must have been particularly fine.

Examination of molecular models of adduct (I) in the boat conformation shows that a hydrogen atom and a fluorine of the adjacent difluoromethylene group are in a trans-coplanar configuration, the ideal situation for elimination of hydrogen fluoride[101] (see Introduction). For the alternative twist-boat conformation a cis-coplanar elimination is possible.[102] However, once the first molecule of hydrogen fluoride has been eliminated introduction of a double bond into the system ensures that the remaining hydrogen atom is rigidly fixed trans-coplanar to one fluorine of the adjacent difluoromethylene group, hence loss of a second molecule of hydrogen fluoride should occur readily to yield triene (IX). This may perhaps account for the lack of products of monodehydrofluorination of (I) in any of the reactions undertaken. Removal of the second molecule of hydrogen fluoride could theoretically lead to two triene systems, presumably 1,2-elimination is preferred over the alternative

1,4-elimination pathway due to the rigidly fixed trans-coplanar configuration of the 1 and 2 substituents.



For adduct (II) models indicate that a cis-coplanar elimination of hydrogen fluoride can occur, due to the planarity or near-planarity of the cyclopentane ring, and these processes are generally quite faile in hydrofluorocyclopentanes.[94,102] After loss of one molecule of hydrogen fluoride the olefin produced is fixed in a conformation offering an easy 1,2-trans near-coplanar elimination of hydrogen fluoride to give triene (X). Once more the product of the alternative 1,4-elimination was not isolated, neither were products due to loss of a single molecule of hydrogen fluoride from (II).

For adduct (III) the cis-elimination pathway would have been expected to produce the monodehydrofluorination product. Presumably this is further degraded to water soluble products or decomposes in molten potassium hydroxide.

Trienes (IX) and (X) were characterised by mass spectroscopy, n.m.r. spectroscopy, elemental analysis, ultra-violet and infra-red spectroscopy and

X-ray photoelectron spectroscopy. Their n.m.r. spectra are tabulated in Chapter 3. Both compounds possessed a single tertiary fluorine resonance, broadened by coupling, a sharp vinylic resonance, and bridging C_2F_4 resonances, characteristic of the octafluorobicyclo[2,2,2]-oct-5-ene unit. The remainder of the resonances were; for compound (X) an AB quartet with J_{AB} = 309 Hz, assigned to the difluoromethylene group in the cyclopentadiene ring, the limbs of this AB quartet being extensively coupled, and a multiplet integrating to two fluorines, assigned to the vinylic fluorines of the cyclopentadiene ring, to low field of the vinylic fluorine resonance of the octafluorobicyclo[2,2,2] oct-5-ene unit; for compound (IX) the difluoromethylenes of the cyclohexadiene ring overlapped with the bridging difluoromethylenes of the octafluorobicyclo [2,2,2]-oct-5-ene unit to produce a complex multiplet and the remaining resonance was a multiplet due to the vinylic fluorines of the cyclohexadiene ring, to low field of the resonance due to the vinylic fluorines of the octafluorobicyclo[2,2,2]oct-5-ene unit. Their infra-red spectra are also consistent with these structures, triene (IX) showing two infra-red absorptions at 1742 and 1703 cm^{-1} which can be assigned to the conjugated diene system (perfluorocyclohexa-1,3-diene absorbs at 1746 and 1712 cm^{-1} [95]) and a third at 1767 cm^{-1} which can be assigned to the isolated double band. Triene (X) also displayed three infra-red absorptions in the double band region, at 1765, 1755 and 1735 cm^{-1} (cf. perfluorocyclopentadiene, which absorbs at 1765 cm^{-1} [96]). The ultraviolet spectra of (IX) and (X) confirmed the presence of the conjugated diene systems, triene (IX) showing a broad absorption at 259 n.m. (ϵ 4,500), in cyclohexane solution, whereas perfluorocyclohexa-1,3-diene absorbs at 256 n.m. (ϵ 3,200) in diethyl ether solution, and triene (X) showing a broad absorption at 277 n.m. (ϵ 2800), in cyclohexane solution, as compared to perfluorocyclopentadiene which absorbs at 273 n.m. (ϵ 905) in the same solvent.[96] The mass spectra of (IX) and (X) were consistent with their

structures and will be discussed in Chapter 3. In addition trienes (IX) and (X) were used in an investigation of the applicability of X-ray photoelectron spectroscopy to structure determination in complex molecules; this work is discussed in Appendix 1.

The reduction of decafluorocyclohexene with lithium aluminium hydride in diethyl ether yielded a substantial amount of 1H,6H-octafluorocyclohexene in addition to its 1H,2H-isomer. Dehydrofluorination of 1H,6H-octafluorocyclohexene by molten potassium hydroxide yielded the known 2H-heptafluorocyclohexa-1,3-diene in 64% yield. Previous dehydrofluorination of this olefin using aqueous potassium hydroxide resulted in only a low yield of this diene.[109]

CHAPTER 1

EXPERIMENTAL

1.12 Reagents

Perfluorocyclohexa-1,3-diene was prepared as detailed in reference 58. 1H,2H-octafluorocyclohexene[109] and 1H,2H-tetrafluorocyclobutene[97] were prepared by published routes; cyclopentene and cyclohexene, purchased from Koch-Light Laboratories Ltd., puriss, were used without further purification. 1H,2H-hexafluorocyclopentene was prepared as the major product by modifying the conditions previously used[110] for the reduction of octafluorocyclopentene with lithium aluminium hydride in diethyl ether. Reagents were dried (phosphoric oxide) and degassed before being inserted in a Pyrex ampoule (Carius Tube) or an autoclave. N.m.r. references were internal $CFCl_3$ and external Me_4Si unless otherwise stated. Lithium aluminium hydride (LAH) was purchased from B.D.H. Chemicals Ltd.

1.13 Preparation of 1H,2H-hexafluorocyclopentene

In a typical experiment octafluorocyclopentene (100 g.) in diethyl ether (100 cc.) at -10° to -20° (acetone/CO_2) was added dropwise over 45 min. to a stirred suspension of LAH (11 g.) in diethyl ether (100 cc.) at 0°. After stirring at 0° for 5h. the mixture was stirred at room temperature overnight, then cooled to 0°, and water (100 cc.) was cautiously added followed by 50% v/v H_2SO_4 (400 cc.) followed by more water (ca.100 cc.) to dissolve all the inorganic salts. The ether layer and several ether extractions of the aqueous layer were combined, dried ($MgSO_4$) and distilled through a column (2' x $\frac{1}{2}$") packed with glass helices, the residue (69.2 g.) bp. > 34° was distilled in vacuo then separated by gas chromatography (column A, 98°) to give:-
(i) diethyl ether (6.9 g.), (ii) 1H,2H-hexafluorocyclopentene (32.2g, with correct i.r. spectrum[108]), (iii) 1H,2H-and 1H,5H-hexafluorocyclopentenes (12.5g, g.l.c. and i.r. consistent with a 1:1 mixture), (iv) longer retained material was not investigated.

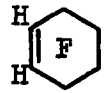
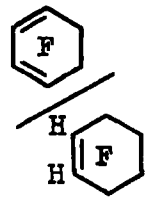
1.14 Cycloadditions of octafluorocyclohexa-1,3-diene (XII) with cycloalkenes

(a) With 1H,2H-octafluorocyclohexene. In a typical experiment octafluorocyclohexa-1,3-diene (XII) (7.54 g., 33.6 mmoles) and 1H,2H-octafluorocyclohexene (5.38 g., 23.8 mmoles) were heated at 330° for 31 hrs. in a 90 ml. Pyrex ampoule, which had been sealed *in vacuo*. The product mixture was separated by conventional vacuum line techniques to give: (i) a liquid mixture (7.08 g.), shown by analytical gas chromatography and i.r. spectroscopy to consist of perfluorocyclohexa-1,3-diene (XII) (ca.56%) and 1H,2H-octafluorocyclohexene (ca. 44%) with a trace of perfluorocyclohexa-1,4-diene; (ii) a liquid mixture (5.15 g.) which was separated (Column B, 120°) to give perfluorocyclohexa-1,3-diene (XII) (0.28 g.), 1H,2H-octafluorocyclohexene containing traces of perfluorocyclohexa-1,3-diene dimers (1.76 g.), and 2H,7H-hexadecafluorotricyclo[6,2,2,$0^{2,7}$]dodec-9-ene (I) (1.86 g., 4.13 mmoles, 17.3%) (Found: C,31.8; H,0.6; F,67.9; M (mass spectrometry), 450. $C_{12}H_2F_{16}$ requires C,32.0; H,0.5; F,67.5%; M,450) b.p. 174°, ν_{max} 2985 (>C-H) and 1776 cm^{-1} (-CF=CF-); and (iii) an involatile solid residue (ca. 0.1 g.).

Under more forcing conditions, for example 35 hrs. at 350°, a greater proportion of the recovered diene was isomerized to the 1,4-isomer but the yield of (I) was not improved. Milder reaction conditions, for example 24 hrs. at 234°, gave no detectable reaction. Table 10 summarises some of the reactions undertaken.

(b) With 1H,2H-hexafluorocyclopentene. By the same procedure as in (a), perfluorocyclohexa-1,3-diene (XII) (7.63 g., 34.0 mmoles) and 1H,2H-hexafluorocyclopentene (5.86 g., 33.3 mmoles) heated at 326° in an 80 ml. Pyrex ampoule for 43 hrs. gave: (i) a liquid mixture (2.79 g.), consisting of starting materials; (ii) 2H,6H-tetradecafluorotricyclo[5,2,2,$0^{2,6}$]undec-8-ene (II) (9.38 g., 23.4 mmoles, 70.2%) (Found: C,33.3; H,0.5; F,66.9; M (mass spectrometry), 400. $C_{11}H_2F_{14}$ requires C,33.0; H,0.5; F,66.5%; M, 400) b.p.153°,

Table 10

size of Carius tube			mole ratio 	reaction conditions	% conversion
75 ml.	2.85 g.(12.71 mmol)	2.79 g.(12.31 mmol)	1.17	234°/24h.	zero
90 ml.	7.36 g.(32.9 mmol)	7.95 g.(35.2 mmol)	0.93	350°/33h.	11.4
90 ml.	7.54 g.(33.6 mmol)	5.38 g.(23.8 mmol)	1.41	330°/31h.	17.4
70 ml.	4.90 g.(21.9 mmol)	4.81 g.(21.3 mmol)	1.03	330°/51h.	12.0
90 ml.	7.91 g.(35.3 mmol)	6.01 g.(26.6 mmol)	1.31	330°/40h.	12.0
90 ml.	7.38 g.(32.9 mmol)	3.96 g.(17.5 mmol)	1.88	335°/35h.	18.0

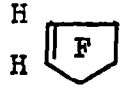
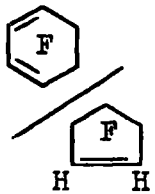
ν_{max} 2994 (>C-H) and 1773 cm^{-1} (-CF=CF-); and (iii) a trace of involatile black solid residue.

This addition was conveniently carried out on a larger scale using an aged stainless steel autoclave; for example, diene (XII) (22.06 g., 98.45 mmoles) and 1H,2H-hexafluorocyclopentene (17.82 g., 101.2 mmoles) heated in a 150 ml. autoclave at 340° for 16 hrs. gave (II) (26.39 g., 66.0 mmoles, 67%), a mixture of starting materials (8.23 g.) and an involatile residue (0.9 g.). Use of an autoclave with a clean metal surface results in a marginally lower yield of (II), together with good recoveries of unreacted olefin and hexafluorobenzene derived from (XII) by defluorination at the metal surface.

Milder reaction conditions gave low yields of (II); for example, an equimolar mixture of (XII) and 1H,2H-hexafluorocyclopentene heated at 280° for 21 hrs. gave only 14% of (II) together with unreacted starting materials. Table 11 summarises some of the reactions undertaken.

(c) <u>With 1H,2H-tetrafluorocyclobutene</u>. By the same procedure as in (a), perfluorocyclohexa-1,3-diene (XII) (3.57 g., 15.9 mmoles) and 1H,2H-tetrafluorocyclobutene containing traces of diethyl ether (1.75 g., < 13.9 mmoles) heated at 295° in a 130 ml. Pyrex ampoule for 42 hrs. gave: (i) a gaseous fraction which was discarded; (ii) a liquid mixture (3.76 g.); and (iii) an involatile yellow oil. Fraction (ii) was separated by preparative gas chromatography (Column G, 108°) to give in order of emergence from the column: (a) <u>cis</u> or <u>trans-7</u> or <u>8-(2',2'-difluorovinyl)-7</u> or <u>8H-decafluorobicyclo[4,2,0]oct-2-ene</u> <u>(VI)</u> (0.49 g., 1.4 mmoles, ca. 10%) (Found: C,34.0; H,0.6; F,65.1; M (mass spectrometry), 350. $C_{10}H_2F_{12}$ requires C,34.3; H,0.6; F,65.1%; M, 350), a colourless liquid b.p. 132°, ν_{max} 3100 (=CH-), 2975 (>C-H), 1765 (-CF=CF-) and 1755 cm^{-1} ($-CH=CF_2$), ^{19}F n.m.r. (ext. $CFCl_3$) resonances at 210.1 (1F,m) and 222.6 (1F,m) tertiary fluorines, 149.6 (1F,s) and 155.8 (1F,s) vinylic fluorines, 129.5 (2F,m), 127.4 (2F,m), 113.1 (2F,m), 80.0 (1F, d, J = 25) and

Table 11

Size of Carius tube or bomb			mole ratio 	Reaction Conditions	% Conversion
70 ml.	4.77g. (21.3 mmol)	3.45g. (19.6 mmol)	1.39	260-280°/24h.	14
95 ml.	6.02g. (26.9 mmol)	4.57g. (26.0 mmol)	1.32	308°/43h.	41
95 ml.	6.16g. (27.5 mmol)	4.82g. (27.4 mmol)	1.28	326°/43h.	59.8
80 ml.	7.63g. (34.0 mmol)	5.86g. (33.3 mmol)	1.31	326°/43h.	70.4
150 ml. (clean stainless steel bomb)	21.9g. (97.6 mmol)	17.4g. (98.6 mmol)	1.21	330°/27h.	66.7
150 ml. (aged stainless steel bomb)	22.0g. (98.5 mmol)	17.8g. (101.2 mmol)	1.24	340°/15½h.	67.0

85.4 (1F, d of d, J = 25 and 21) together assigned to $-CH=CF_2$; the ^1H n.m.r. consisted of a doublet of doublets of sharp lines (J = 21 and 10) overlapping with a broad poorly resolved band, the whole spectrum being centred at 3.75 p.p.m.; (b) cis or trans-7 or 8H-decafluorobicyclo[4,2,0]oct-2-ene (VII) (0.36 g., 1.03 mmoles, ca.8%) (Found: C,34.0; H,0.6; F,65.4; M(mass spectrometry),350. $C_{10}H_2F_{12}$ requires C,34.3; H,0.6; F,65.1%; M,350), a colourless liquid, ν_{max} 3100 (=CH-), 2975 (>C-H), 1765 (-CF=CF-), and 1755 cm^{-1} ($-CH=CF_2$), ^{19}F n.m.r. (ext. $CFCl_3$) resonances at 207.9 (1F,m) and 221.4 (1F,m) tertiary fluorines, 148.6 (1F,s) and 153.8 (1F,s) vinylic fluorines, 125.7 (2F,m), 123.1 (1F,m), 121.7 (1F,m), AB quartet (2F, δ_A=98.9, δ_B=118.3, J_{AB} = 244), 78.2 (1F, d, J = 25) and 85.3 (1F, d of d, J = 25 and 21) together assigned to $-CH=CF_2$; the ^1H n.m.r. spectrum showed an asymmetric poorly resolved multiplet centred at 4.0; (c) 3,3,4,4,7,7,8,8-octafluorotricyclo-[3,3,0,$0^{2,6}$]octane (VIII) (0.17 g., 0.67 mmoles), ca.5%) (Found: C,38.4; H,1.5; M (mass spectrometry), 252. $C_8H_4F_8$ requires C,38.1; H,1.6; M,252), a white solid m.p. 126°-127° (sealed tube) recryst. CCl_4. ^{19}F n.m.r. showed a sharp singlet at 119.6 and ^1H n.m.r. (internal T.M.S.) a sharp singlet at 3.0; (d) 2H,5H-dodecafluorotricyclo[4,2,2,$0^{2,5}$]dec-7-ene (III) (0.84 g., 2.4 mmoles, ca.18%) (Found: C,34.1; H,0.3; F,65.2; M (mass spectrometry), 350. $C_{10}H_2F_{12}$ requires C,34.3; H,0.6; F,65.1%; M,350), a colourless liquid b.p. 143°, ν_{max} 2975 (>C-H) and 1770 cm^{-1} (-CF=CF-); longer retained products were isolated in an impure state in trace amounts.

The abundance of the long retained products from this reaction varied with the amount of residual ether in the 1H,2H-tetrafluorocyclobutene used.

Analytical g.l.c. (co.0, col.A) showed four overlapping peaks and attempts to separate by preparative g.l.c. (col.F,140°) resulted in three fractions. Fraction 1 contained more than 90% of the first component of the mixture, fraction 2 was a mixture of all four components and fraction 3

contained more than 90% of the fourth component. The major peaks in the ^{19}F n.m.r. spectrum of fraction 1 were (solution in CCl_4/int $CFCl_3$), tertiary fluorines 232.7 (1F,broad), 224.5 (1F,broad), 194.0 (1F,broad), 178.3 (1F,broad); difluoromethylenes, complex system of overlapping bands between 112 and 150 (4F). The ^1H n.m.r. showed three groups of resonances tentatively assigned as follows. 1.31 (t, J= 5) ethylene bridge and CH_3, ca.4.35 (multiplet) tertiary protons, ca.5.45 (v.broad multiplet) hydroxyl proton. The major peaks in the mass spectrum were: (m/e (assignment, % base peak)) 298, (Parent, $C_{10}F_8H_{10}O$, 13%); 283 (p-CH_3, $C_9F_8H_7O$, 14%); 254 (p-C_3H_8, $C_7F_8H_2O$, 6%); 237 (p-C_3H_9O, C_7F_8H, 9%), 234 (11.4%); 171 (4.2%); 157 (4.5%); 139 (5.2%); 121 (10.3%); 109 (29%); 95 (10%); 91 (25%); 84 (6%); 77 (6%); 65 (8.7%); 59 (7.4%); 57 (9%); 51 (6.6%); 47 (10%); 45 (C_2H_5O, 100%); 43 (37%).

The major peaks in the ^{19}F n.m.r. spectrum of fraction 3 were (solution in CCl_4 (int.$CFCl_3$)), tertiary fluorines 227.9 (1F, dJ = 50), 207.9 (1F, d of d, J = 48 and 48), 188.2 (1F), 177.8 (1F); difluoromethylenes 121.8 (2F) and AB quartet (2F, δ_A 111.1, δ_B 126.9, J_{AB} = 280). The ^1H n.m.r. showed three groups of resonances tentatively assigned as follows. 1.45 (t,J = 5) ethylene bridge + CH_3 resonances, ca.3.8 (multiplet) tertiary protons, ca.4.9 (v.broad multiplet) hydroxyl proton. The principal peaks in the mass spectrum were (m/e (assignment, % base peak)). 298 (Parent, $C_{10}F_8H_{10}O$, 7%); 283 (p-CH_3, $C_9F_8H_2O$, 1.5%); 254 (p-C_3H_8, $C_7F_8H_2O$, 1.5%); 234 (6.9%); 207 (2.1%); 188 (2.4%); 157 (3.5%); 139 (4.3%); 121 (10%); 109 (22%); 95 (9.4%); 91 (20.3%); 84 (15.4%); 57 (24%); 45 (C_2H_5O, 100%); 43 (33%); 41 (16%); 39 (7.8%).

The infra-red spectra of all three fractions possessed the following absorptions, OH stretch 3,300 cm^{-1}, C-H stretch 3000, 2950 cm^{-1}, there was no evidence of CF=CF stretch. This data is consistent with these long-retained compounds being isomers of <u>1,2,3,4,5,5,6,6-octafluoro-2-(1-hydroxyethyl)-bicyclo[2,2,2]octane (XI)</u>

(d) With cyclohexene. By the same procedure as in (a) perfluorocyclohexa-1,3-diene (XII) (7.14 g., 31.9 mmoles) and cyclohexene (2.69 g., 32.8 mmoles) heated at 208° in a 75 ml. Pyrex ampoule for 24 hrs. gave: (i) a volatile liquid (0.39 g.) shown by analytical gas chromatography to be starting materials; (ii) a solid (8.96 g.), which was sublimed (60°/2 x 10^{-3} mm.Hg) yielding 1,8,9,10,11,11,12,12-octafluorotricyclo[6,2,2,$0^{2,7}$]dodec-9-ene (IV) (7.86 g., 25.7 mmoles, 81%) (Found: C,47.3; H,3.6; F,49.8; M (mass spectrometry), 306. $C_{12}H_{10}F_8$ requires C,47.1; H,3.3; F,49.6%; M,306), a white solid m.p. 55-56°, b.p. 215°, ν_{max} 2976 and 2890 (>C-H) and 1764 cm^{-1} (-CF=CF-); (iii) a brown involatile oil (ca.1.0 g.).

(e) With cyclopentene. By the same procedure as in (a), perfluorocyclohexa-1,3-diene (XII) (7.16 g., 31.9 mmoles) and cyclopentene (2.14g,31.4 mmoles) heated at 208° in a 70 ml. Pyrex ampoule for 24 hrs. gave: (i) starting materials (0.35 g.), (ii) 1,7,8,9,10,10,11,11-octafluorotricyclo[5,2,2,$0^{2,6}$]-undec-8-ene (V) (8.83 g., 30.2 mmoles, 96%) (Found: C,45.5; H,2.8; F,52.6; M (mass spectrometry), 292. $C_{11}H_8F_8$ requires C,45.2; H,2.8; F,52.0%; M,292) a colourless liquid b.p. 193°, ν_{max} 2976 and 2890 (>C-H) and 1767 cm^{-1} (-CF=CF-), (iii) residual brown oil, a trace.

1.15 Dimerisation of 1H,2H-tetrafluorocyclobutene

Heating 1H,2H-tetrafluorocyclobutene containing traces of diethyl ether in a Carius tube, which had been sealed *in vacuo*, for 60h. at 260° gave only 3,3,4,4,7,7,8,8-octafluorotricyclo[3,3,0,$0^{2,6}$]octane (VIII)

1.16 Dehydrofluorination of the Diels-Alder Adducts

(a) Dehydrofluorination of 2H,6H-tetradecafluorotricyclo[5,2,2,$0^{2,6}$]-undec-8-ene (II). Using molten KOH:- A thick-walled glass tube (ca.20 cm. x 3 cm. dia.) was fitted with an inlet tube reaching almost to the bottom of the tube through which dry nitrogen was passed, the exit from the tube was

connected in series with two glass traps cooled in liquid air. The tube was filled about $\frac{2}{3}$ full with potassium hydroxide (Hopkin and Williams Ltd., General Purpose Reagent Pellets) and heated in an oil bath at 150° for 2 hrs. with nitrogen passing, in order to remove the greater part of the absorbed water from the potassium hydroxide. The temperature of the bath was raised to 180° and olefin (II) (8.34 g., 20.9 mmoles) was introduced dropwise into the nitrogen stream, a vigorous reaction occurred and the volatile product collected in the glass traps. After drying by vacuum transfer from phosphoric oxide the product (5.14 g.) was shown to be essentially perfluorotricyclo $[5,2,2,0^{2,6}]$-undeca-2,5,8-triene (X) (14.28 mmoles, 68.3%), one component by analytical gas chromatography (>95%) the only impurity being a trace of starting material, a sample purified by chromatography (Col.B, 90°) for analysis gave (Found: C,36.8; F,63.6; M (mass spectrometry), 360. $C_{11}F_{12}$ requires C,36.7; F,63.3%; M,360), a colourless liquid b.p. 141°, ν_{max} 1765 (-CF=CF-), 1755 and 1735 cm^{-1} (diene system), λ_{max} 277 nm. (ε =2800), ^{19}F n.m.r. (ext. $CFCl_3$) resonances at 216.5 (2F,m, fluorines at C-1 and C-7), 152.8 (2F,s, fluorines at C-8 and C-9), 143.4 (2F,m, fluorines at C-3 and C-5), AB quartet (2F, δ_A = 132.2; δ_B = 139.2, J_{AB} = 309, fluorines at C-4), pseudo AB quartet (4F, δ_A = 127.7, δ_B = 129.5, J_{AB} = 228, fluorines at C-10 and C-11).

Using aqueous KOH:- Olefin (II) (3.15 g., 7.88 mmoles), potassium hydroxide (4g.) and water (4g.) were heated to 155° and stirred vigorously for 10 mins. The red-black homogeneous solution was quenched with 250 ml. of cold water, and the fluorocarbon layer was separated, distilled *in vacuo* off phosphoric oxide to yield a colourless liquid (1.48 g.). Separation by preparative gas chromatography (Col.B, 90°) gave:

(i) triene (X) (10.94 g., 2.61 mmoles, 33.1%) with correct i.r. spectrum and (ii) olefin (II) (0.23 g., 0.58 mmoles)

(b) Dehydrofluorination of 2H,7H-hexadecafluorotricyclo[6,2,2,$0^{2,7}$]-dodec-9-ene (I). Olefin (I) (4.98 g., 11.06 mmoles), potassium hydroxide (5 g.) and water (10 g.) were heated to 140° and stirred vigorously for 10 mins. At this point the reaction mixture was darkening rapidly and was quenched by rapid addition of cold dilute aqueous hydrochloric acid (ca. 200 ml.). Analytical gas chromatography of the fluorocarbon layer indicated that olefin (I) was the major component. The fluorocarbon was separated, mixed with further potassium hydroxide (3.0 g.) and water (6 g.) and heated to 150° and mixed for 10 mins. Quenching, as before, followed by vacuum transfer of the fluorocarbon layer from phosphoric oxide gave a two component product separated by gas chromatography (Col.B,110°) to give: (i) perfluorotricyclo[6,2,2,$0^{2,7}$]-dodeca-2,6,9-triene (IX) (1.67 g., 4.07 mmoles, 37%) (Found: C,35.4; M (mass spectroscopy), 410. $C_{12}F_{14}$ requires C,35.1%;M,410), a colourless liquid b.p. 159°, ν_{max} 1767 cm^{-1} (-CF=CF-), 1742 and 1703 cm^{-1} (diene system), λ_{max} 259 nm. (ϵ, 4500), ^{19}F n.m.r. resonances at 215.9 (2F,m, fluorines at C-1 and C-8), 152.4 (2F,s, fluorines at C-9 and C-10), 134.3 (2F,m, fluorines at C-3 and C-6), and 129.2 (8F, complex asymmetric multiplet, fluorines at C-4, 5, 11 and 12). (ii) olefin (I) (0.60 g., 1.33 mmoles).

(c) Attempted dehydrofluorination of 2H,5H-dodecafluorotricyclo[4,2,2,$0^{2,5}$]-dec-7-ene (III). (i) Using the technique successfully applied to (II), olefin (III) (0.235 g.) was introduced into molten potassium hydroxide at 180°. A vigorous reaction occurred and the initially colourless potassium hydroxide became yellow-brown. The volatile material which was collected (ca.0.1 g.) was shown by gas chromatography and infrared spectroscopy to be predominantly olefin (III) together with traces of four other compounds. (ii) Using the method successfully applied to (I), compound (III) (0.44 g.), potassium hydroxide (0.8 g.) and water (1 g.) were kept at 130° for 8 minutes. Quenching with dilute aqueous hydrochloric acid gave a fluorocarbon fraction

(ca. 0.2 g.), which was shown by infrared spectroscopy and analytical gas chromatography to be starting material containing only traces of the same four compounds formed in (i).

(iii) Repetition of the procedure in (ii) using olefin (III) (0.90 g.), potassium hydroxide (0.70 g.) and water (1.5 ml.) at 160° for 15 minutes gave essentially the same product as in (ii). Reheating at 170° for a further 15 minutes with additional potassium hydroxide (0.5 g.) gave a product mixture identical to that obtained before, however only ca. 0.1 g. of fluorocarbon was recovered.

(iv) Olefin (III) (0.44 g.) stirred at room temperature with water (1 ml.) and potassium hydroxide (0.8 g.) for 1 hour gave a fluorocarbon fraction shown by analytical gas chromatography and infrared spectroscopy to be unchanged starting material.

In cases (ii) and (iii) reaction did occur on heating since the mixture gradually became homogeneous and darkened to a deep brown/black. In case (iv) the initially colourless solution became deep red on standing, although there was no evidence of reaction in the isolated product.

1.17 Retrodiene reactions of the Diels-Alder adducts

Compound (I) (0.094 g.) was heated at 335° for 48 hrs. in a 12-ml. Pyrex ampoule sealed under vacuum to give a colourless liquid which was shown by gas chromatography and infrared spectroscopy to contain compound (I) (ca. 96%) and a mixture of perfluorocyclohexa-1,3-diene (XII) and 1H,2H-octafluorocyclohexene (ca. 4%).

Compound (II) (0.090 g.) under the same conditions as above gave a colourless liquid shown by infrared spectroscopy and gas chromatography to contain only compound (II).

Compound (III) (0.094 g.) under the same conditions as above gave a colourless liquid shown by infrared spectroscopy and gas chromatography to contain only compound (III).

1.18 Dehydrofluorination of 1H,6H-octafluorocyclohexene

Using the technique successfully applied to (II), 1H,6H-octafluorocyclohexene (2.62 g.) was introduced into molten potassium hydroxide, heated on a Wood's metal bath at 260°, on a stream of dry nitrogen over a period of 10 min. The initially colourless potassium hydroxide became yellow-brown and the volatile material collected was dried (P_2O_5) and distilled in vacuo to produce 2H-heptafluorocyclohexa-1,3-diene (1.52 g.) with correct infrared spectrum.[107] Yield = 64%.

CHAPTER 2

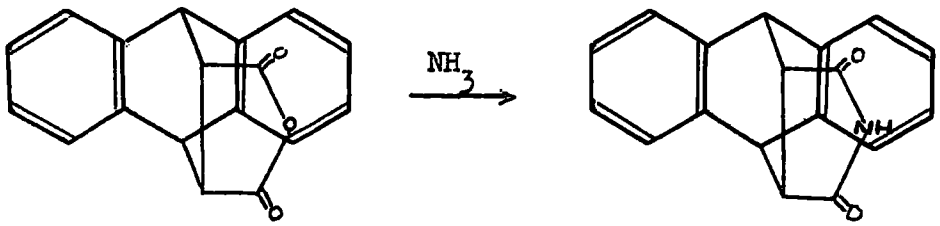
DIELS-ALDER REACTIONS OF DODECAFLUOROTRICYCLO[5,2,2,$0^{2,6}$]UNDECA-2,5,8-TRIENE WITH ETHYLENE AND ALKYNES. A SYNTHESIS OF POLYFLUOROBENZOBICYCLO[2,2,2]-OCTA-2,5-DIENES AND 2,3-DISUBSTITUTED HEXAFLUORONAPHTHALENES

INTRODUCTION

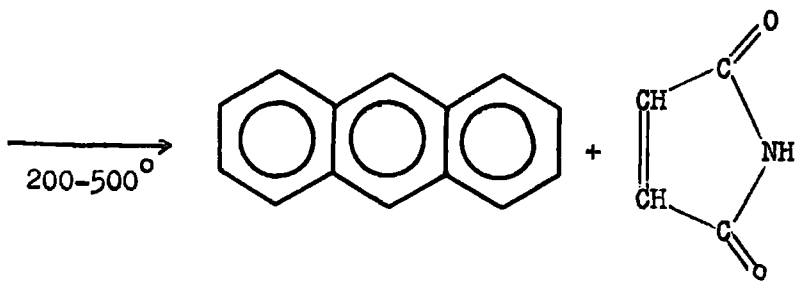
2.1 The Reverse Diels-Alder Reaction[111]

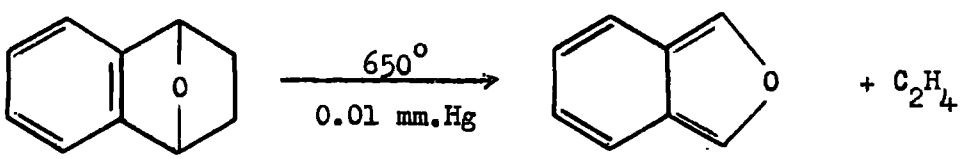
The reversibility of the Diels-Alder reaction was noted very soon after its discovery, Diels and Alder observing that the 1,4-adduct of furan and maleic anhydride dissociated at its melting point of 125°. There is a wide variation in the stabilities of 1,4-adducts towards dissociation to their addends but certain trends are evident; adducts of cyclic dienes are less stable than those of acyclic dienes, adducts of acetylenic dienophiles dissociate less readily than those of olefinic dienophiles and those of cyclopentadienes dissociate more readily than those of cyclohexa-1,3-dienes. In order to explain the observed stabilities of Diels-Alder adducts Schmidt formulated his "double bond" rule, which states that in any olefin pyrolysis it is the bond β to the double bond that cleaves.[112] It appears that the C-C bond in the β-position is weaker than a normal C-C single bond whereas that in the α-position is quite strong, also the lability of groups attached to allyl and benzyl systems show that this rule is not only applicable to C-C bonds. The ready dissociation of the 1,4-adduct of furan and maleic anhydride contrasts with the stability of the 1,4-adduct of furan and acetylenedicarboxylic acid; this observation is consistent with Schmidt's "double-bond" rule.

The reverse Diels-Alder reaction is often extremely valuable synthetically. In many instances adducts can be modified chemically and the addends may be regenerated by a reverse Diels-Alder reaction, reaction sequences which can be satisfactorily accomplished with the adduct being impossible for the free addend. An example is the preparation of maleimide which unlike succinimide cannot be prepared by fusion of the appropriate ammonium salt, a reaction which can be successfully carried out on its Diels-Alder adduct with anthracene (56), the pyrolysis of this adduct generating the required compound. Unstable compounds areoften accessible via a reverse Diels-Alder reaction, pyrolysis of 1,4-epoxy-1,2,3,4-tetrahydronaphthalene (57) leading to a quantitative yield of isobenzofuran (58),[113] ethylene being eliminated. Pyrolysis of a Diels-Alder



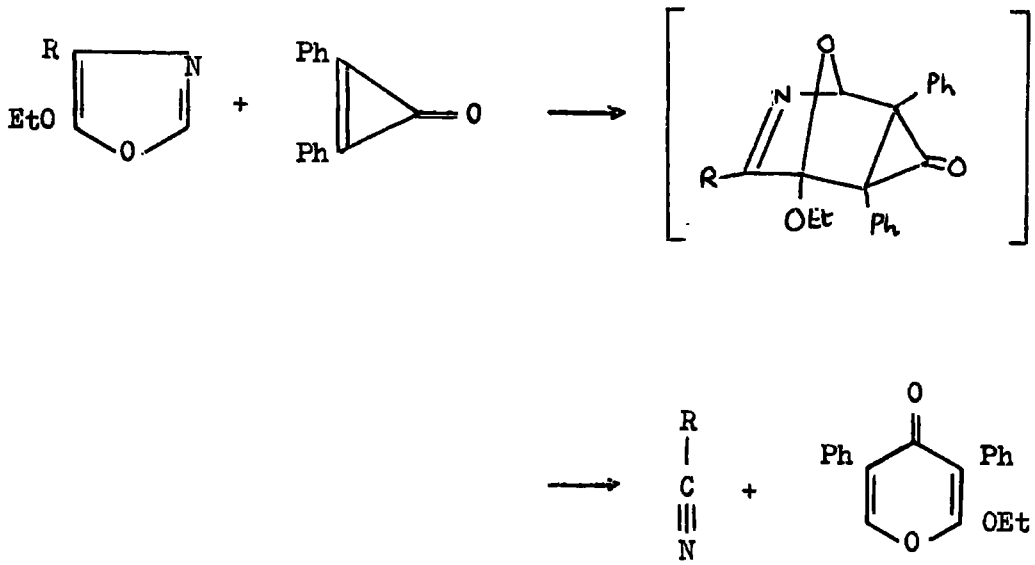
(56)



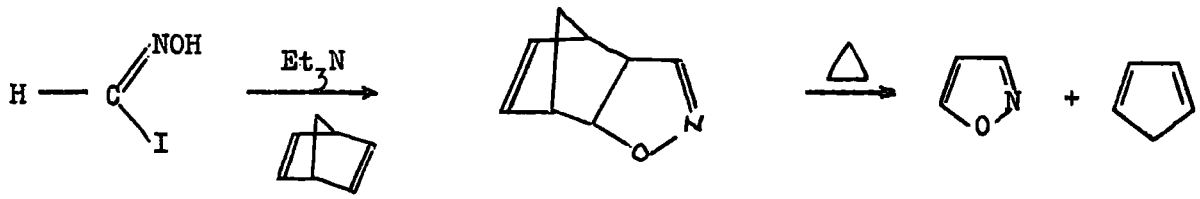


(57) (58)

adduct can lead to products other than the original addends, the formation of the most stable possible products being the driving force of the reaction. A recent example of this type of reaction is the elimination of a nitrile or hydrogen cyanide from the Diels-Alder adduct of an oxazole and diphenylcyclopropenone, to produce a γ-pyrone.[114] The compound undergoing reverse Diels-Alder reaction need not necessarily have been derived via a 1,4-cycloaddition. Isoxazole is formed by the reverse Diels-Alder reaction of compound (60)



originally formed by 1,3-dipolar addition of norbornadiene and fulminic acid, generated in situ by dehydroiodination of compound (59).[111]

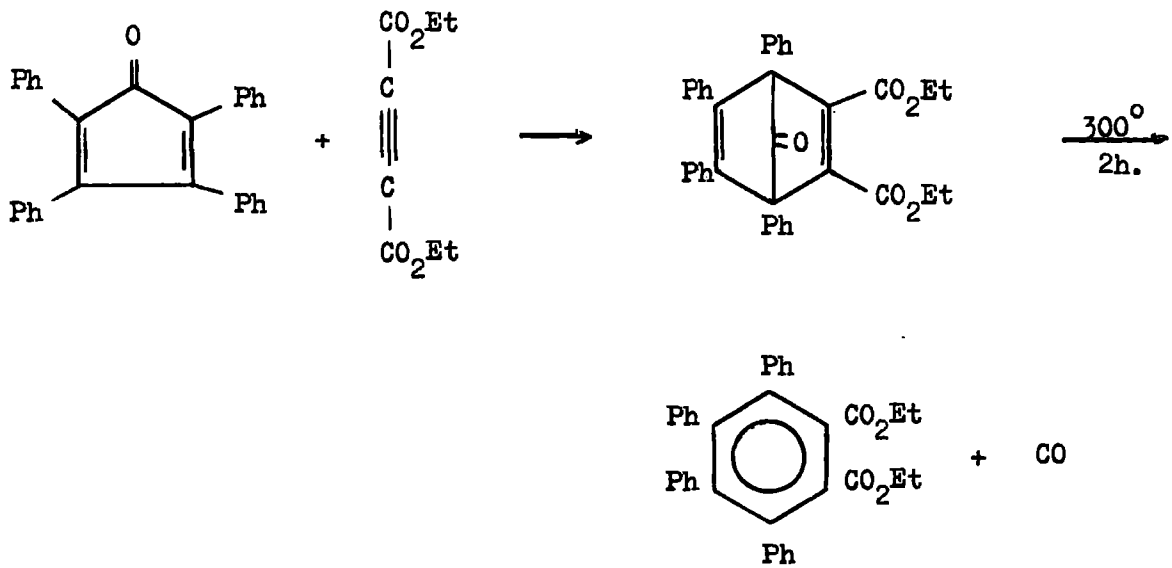


(59) (60)

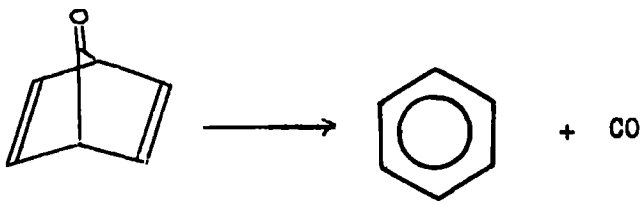
The reverse Diels-Alder reaction is classified as a 6 → 4 + 2 cyclo-elimination producing two relatively stable systems with saturated valencies. For some adducts of cyclopentadienes and related compounds cycloelimination can occur from the 5-membered ring to produce an odd fragment such as a carbene instead of dissociation to the original addends. This 5 → 4 + 1 cyclo-elimination can still be achieved under mild conditions providing that the

formation of the reactive intermediate carbene is balanced by the exothermic formation of a stable compound, usually an aromatic.[115]

The ready dimerisation of cyclopentadienones to produce Diels-Alder dimers is usually irreversible as on mild heating carbon monoxide, a stable carbene, is lost. Tetraphenylcyclopentadienone is stable as the monomer and readily forms 1,4-adducts with acetylenes and alkenes. Tetraphenylbenzenes result from reaction with alkynes, carbon monoxide being eliminated; the intermediate adduct is not isolable. A variety of cyclopentadienones generated in situ, due to ready dimerisation, react as above and provide a useful synthetic route to substituted benzenes. For example, diethylacetylenedicarboxylate reacts with tetraphenylcyclopentadienone:-[111]

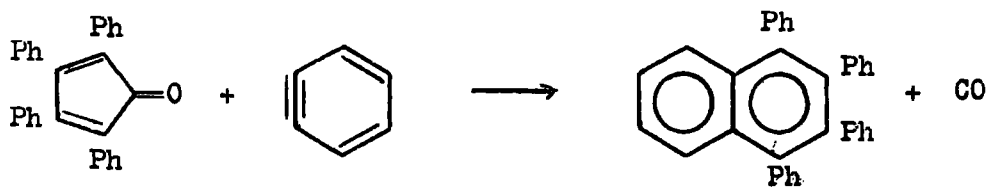


As expected all attempts to synthesise norbornadienone (61) have been unsuccessful due to ready loss of carbon monoxide to generate benzene.[115]



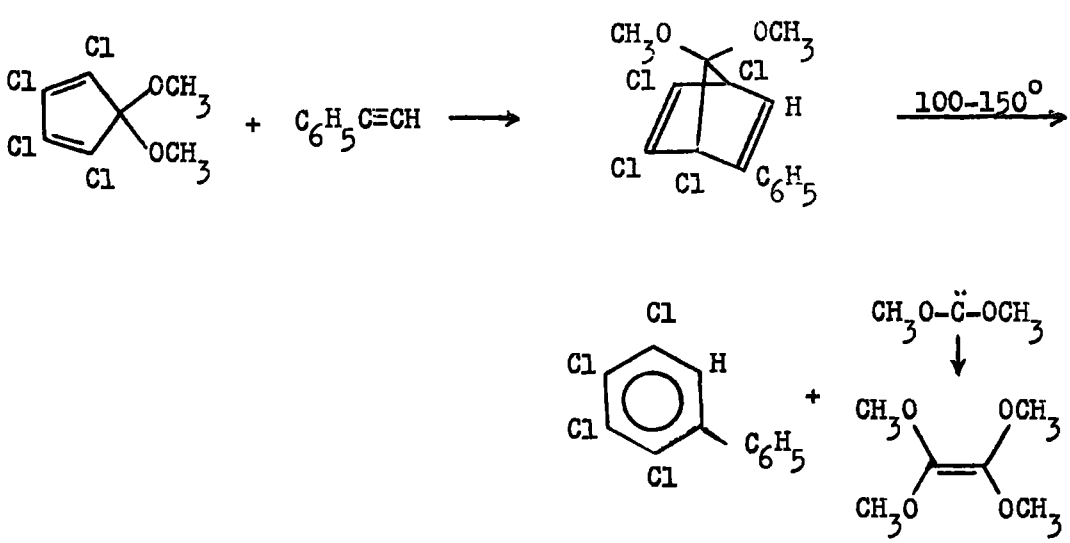
(61)

Cyclopentadienones can also be used in the synthesis of naphthalenes or other polycyclic systems using dehydroarenes. Tetraphenylcyclopentadienone and benzyne produce a high yield of the tetraphenylnaphthalene (62), 2,3-dehydronaphthalene leading to the corresponding tetraphenylanthracene.[116]

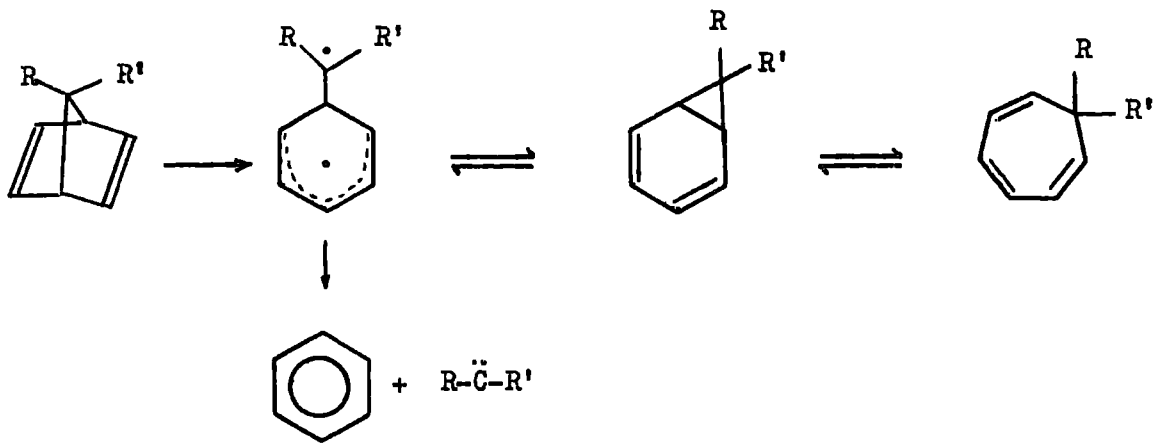


(62)

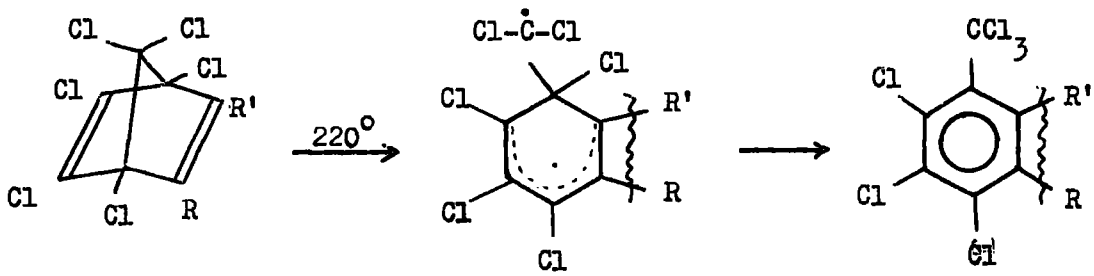
The elimination of methylene from cyclopentadiene adducts does not occur due to its high energy content, the normal mode of decomposition being to the original addends, however more stable carbenes, such as dialkoxycarbenes, can be eliminated on mild pyrolysis. A thorough study of the decomposition of 7,7-dialkoxynorbornadienes has been carried out and, as can be seen below, reaction with alkynes generates a benzene and a dialkoxy-carbene which undergoes dimerisation. Side reactions also occur, a competing reaction pathway involving



heterolytic breakage of the bridge is favoured by substituents on the cyclopentadiene system which will stabilise a negative charge and by polar solvents. Linear chelotropic 5 → 4 + 1 cycloeliminations are generally accepted as one-step processes if stereochemistry is the criterion, however cycloelimination of dialkoxycarbenes from systems such as the above is better explained by the multistep process shown below.[115]

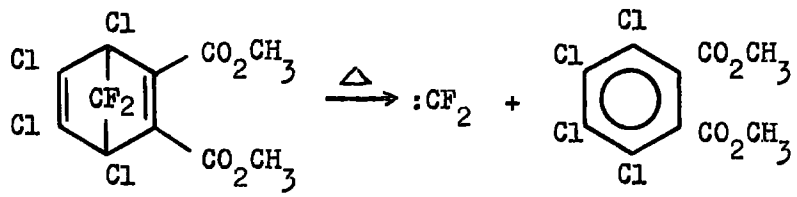


This scheme explains why no elimination of dichlorocarbene occurs on pyrolysis of (63), the products can easily be envisaged as arising via a radical mechanism.

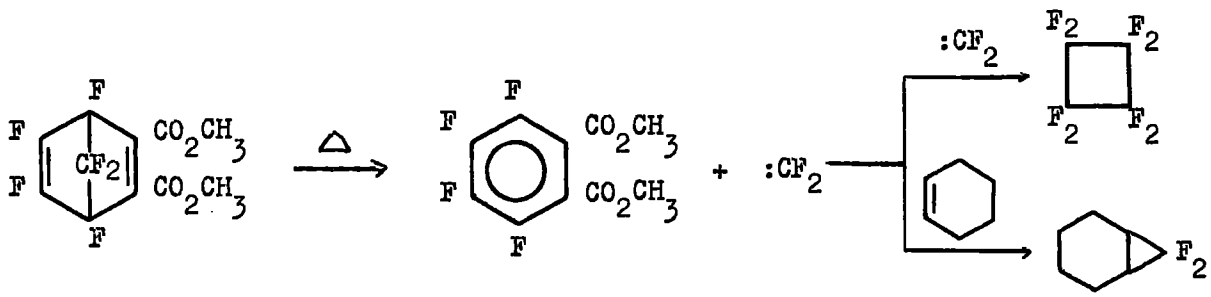


(63)

Elimination of difluorocarbene from (64) produces (65) in good yield at 480°.[115] Also the Diels-Alder adduct of hexafluorocyclopentadiene and dimethylacetylenedicarboxylate (66) on pyrolysis under similar conditions produced dimethylterephthalate (67) and perfluorocyclobutane; the eliminated difluorocarbene was trapped in a separate experiment by cyclohexene.[36] The higher temperatures required for these reactions has been ascribed to the lower stability of difluorocarbene compared with dimethoxycarbene.[115]

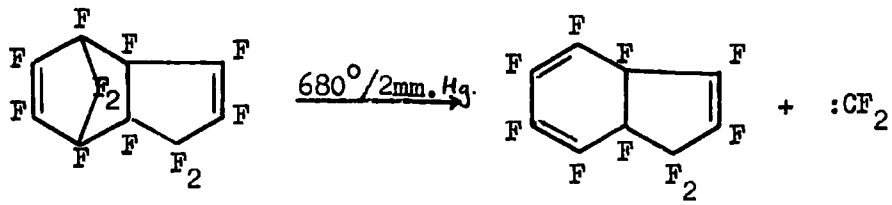


(64) (65)



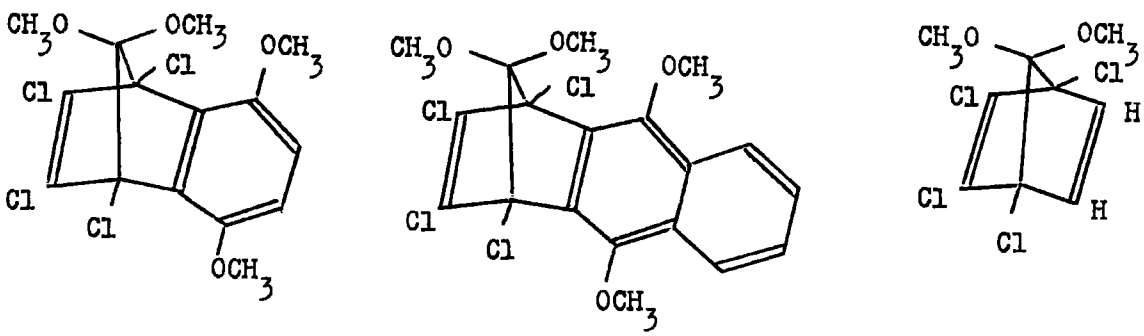
(66) (67)

Whereas cyclopentadiene dimer readily undergoes a reverse Diels-Alder reaction at 160° to produce the monomer, perfluorocyclopentadiene dimer is much more stable. At 680° and a low pressure (2 mm.Hg) with a contact time of 0.3 of a second pyrolysis of the dimer (68) produces as main product (69) by elimination of difluorocarbene from the dimer, some monomer is also formed by the reverse Diels-Alder reaction.[17]



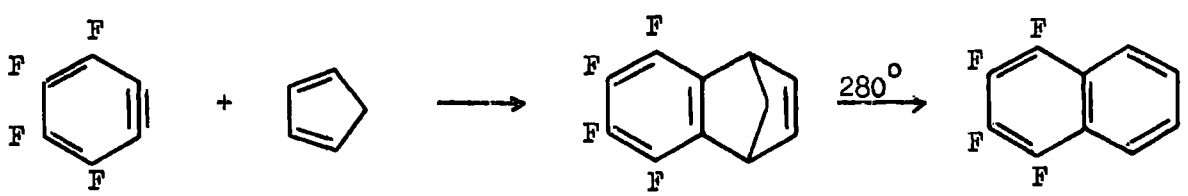
(68) (69)

Cycloelimination of a particular carbene becomes easier the greater the gain in stabilization on forming the aromatic species. Consequently compounds (70) and (71) undergo cycloelimination at temperatures about a hundred degrees higher than compound (72).[115]

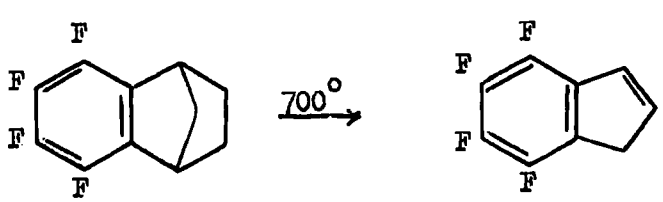


(70) (71) (72)

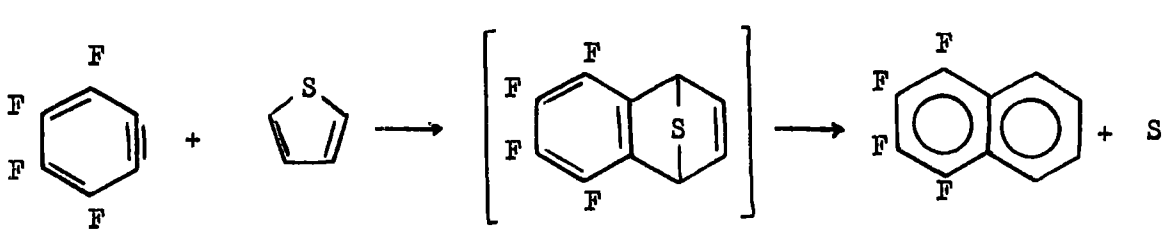
The 1,4-adduct of tetrafluorobenzyne and cyclopentadiene (73) produces an excellent yield of 1,2,3,4-tetrafluoronaphthalene on pyrolysis at 280° with no evidence of the formation of a benzocycloheptatriene, which is the product of pyrolysis of the corresponding hydrocarbon.[21] Reduction of the cyclopentadiene adduct (73) produces (74) in good yield, pyrolysis of this compound producing 4,5,6,7-tetrafluoroindene (75) by elimination of ethylene at 700°.[117] Also thiophenes react as dienes towards tetrafluorobenzyne to produce naphthalenes by desulphurisation of the initially formed 1,4-adduct, illustrated below for thiophene itself.[21]



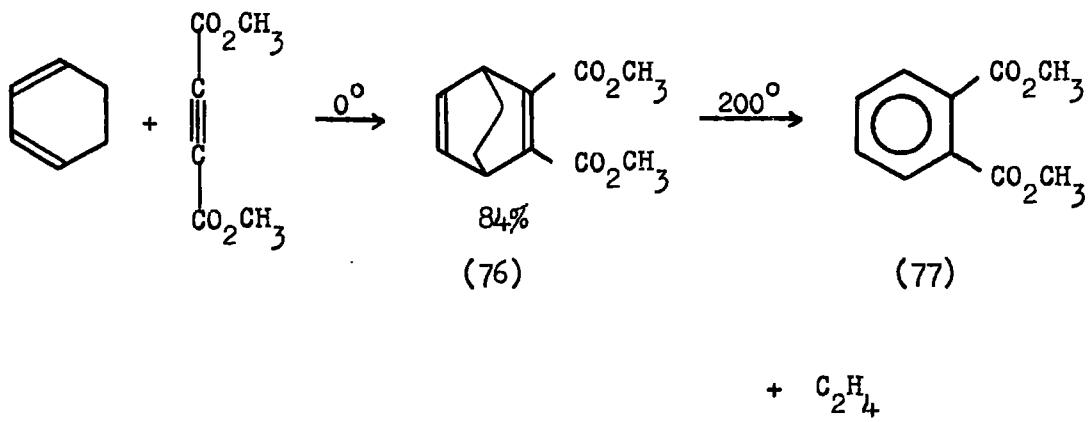
(73)



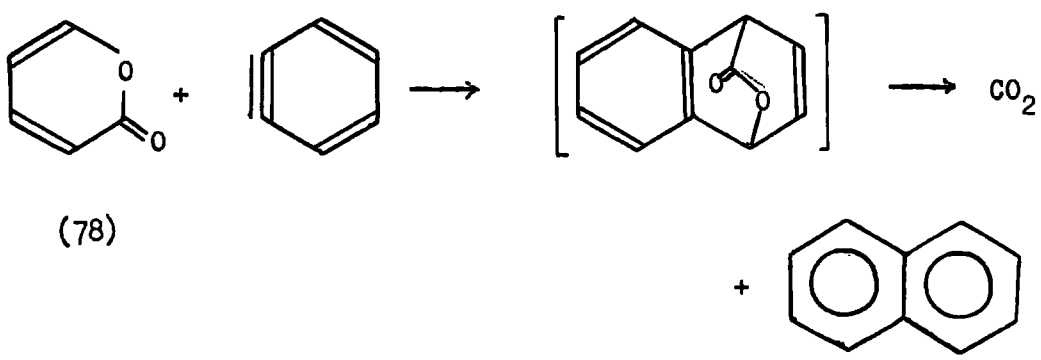
(74) (75)



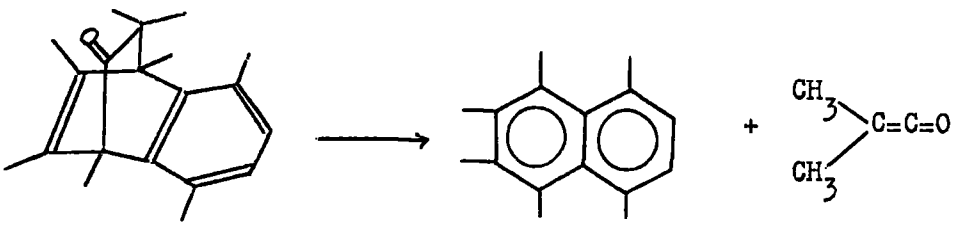
In contrast with cyclopentadiene the formal Diels-Alder adducts of cyclohexa-1,3-dienes and acetylenes tend to readily lose an olefin generating an aromatic system, and this has been suggested as a good diagnostic test for cyclohexa-1,3-dienes.[111] Often only mild conditions are required as is the case with the 1,4-adduct of cyclohexa-1,3-diene and dimethylacetylene dicarboxylate (76) formed at 0° in high yield, which eliminates ethylene on pyrolysis at 200° to produce dimethylphthalate, (77) see below.[118]



α-Pyrone (78) reacts extremely readily with alkynes, the 1,4-adduct being unstable to loss of carbon dioxide and generation of an aromatic,[118] with benzyne naphthalene is readily produced,[116] as below.

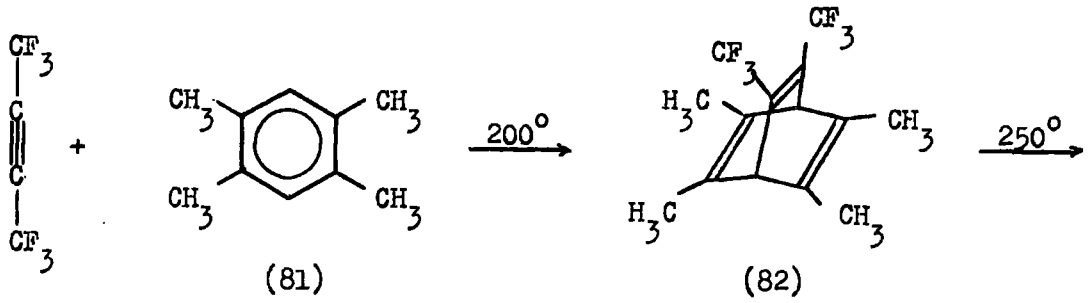


Another naphthalene synthesis based on pyrolysis of cyclohexadiene adducts with acetylenes involves cyclohexadienones and benzynes. Reaction of 3,6-dimethylbenzyne and hexamethyl-2,4-cyclohexadienone produces adduct (79) which on pyrolysis at 450° results in an 18% conversion to the hindered hexamethylnaphthalene, (80) dimethylketene being eliminated.[111]

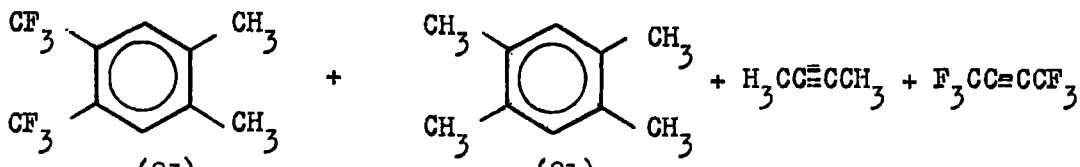


(79) (80)

The adducts of acetylenes and cyclohexa-1,3-dienes, bicyclo[2,2,2]octa-2,5-dienes are less stable to the reverse Diels-Alder reaction than are bicyclo[2,2,2]octa-2,5,7-trienes, which can be formed by the addition of acetylenes to aromatic systems. This is seen in the stability of the parent compounds; bicyclo[2,2,2]octa-2,5-diene eliminates ethylene at 200° to produce benzene[119] whereas bicyclo[2,2,2]octa-2,5,7-triene only loses acetylene at 250°.[120] The very reactive dienophile perfluorobut-2-yne reacts with durene (81) at 200° to produce the expected 1,4-adduct (82) which loses perfluorobut-2-yne to produce durene (81), and but-2-yne to produce 1,2-dimethyl-4,5-bis-(trifluoromethyl)benzene (83), at 250°.[111]

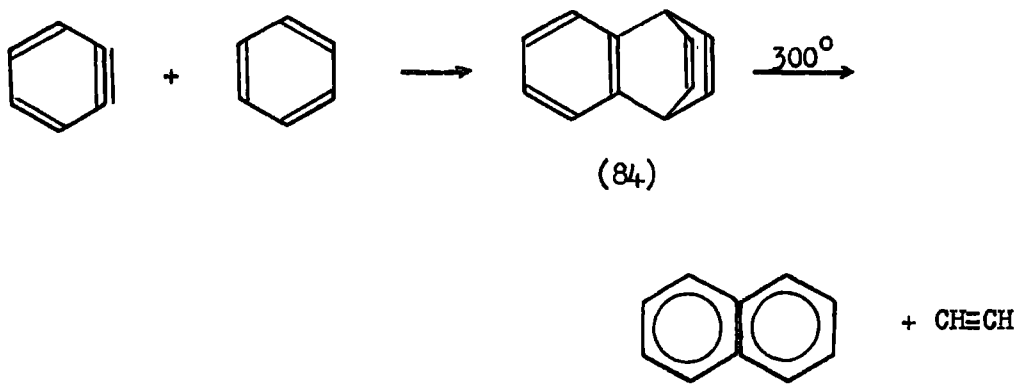


(81) (82)



(83) (81)

Similarly 1,4-adducts of benzynes and aromatic compounds can be pyrolysed to eliminate acetylenes producing the expected naphthalenes, the adduct of benzyne and benzene (84) losing acetylene at 300° to produce naphthalene.[116]

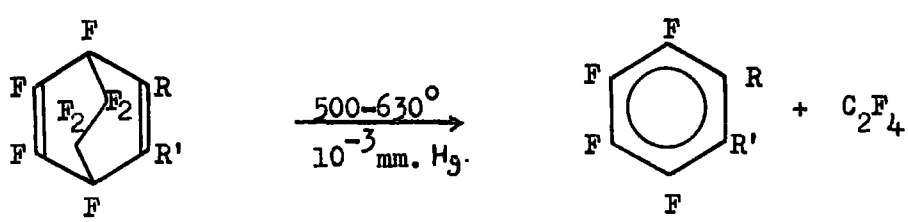


(84)

The bicyclo[2,2,2]octene system has greater thermal stability than the bicyclo[2,2,2]octa-2,5-diene system as the reverse Diels-Alder reaction of the former generates an olefin and cyclohexa-1,3-diene, a much less favourable process than formation of an aromatic system from the latter. Bicyclo[2,2,2]oct-2-ene decomposes to ethylene and cyclohexa-1,3-diene at temperatures of

376-445°, further disproportionation reactions leading to cyclohexene, benzene and hydrogen.[121]

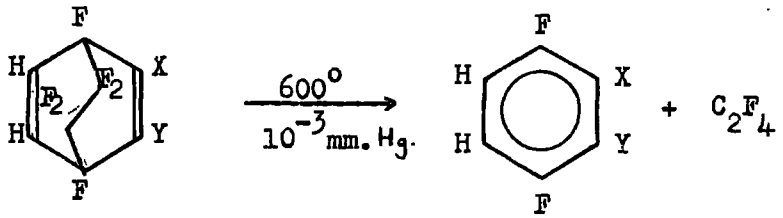
In highly fluorinated systems the same trends are evident but, as observed with the dimer of perfluorocyclopentadiene and its adduct with dimethylacetylene-dicarboxylate, the thermal stability of fluorocarbon systems is markedly greater than a corresponding hydrocarbon of similar structure. The adducts of perfluorocyclohexa-1,3-diene with acetylenes are stable up to at least 250° in contrast with those of cyclohexa-1,3-diene. Pyrolysis in a vacuum system, under a pressure of 10^{-3} mm.Hg., in the range of 500-630° results in the elimination of tetrafluoroethylene and the isolation of ortho disubstituted tetrafluorobenzenes in almost quantitative yield; this constitutes a very useful route to a class of compounds previously only accessible with difficulty. A prerequisite of pyrolyses under these vigorous conditions is thermal stability of the substituent in the adduct. When a CH_2Cl-substituent is present elimination of hydrogen chloride leaves a reactive carbene to undergo further reaction, also when the substituent is -COOEt elimination of ethylene and carbon dioxide can take place. The general scheme is shown below.[58,61]



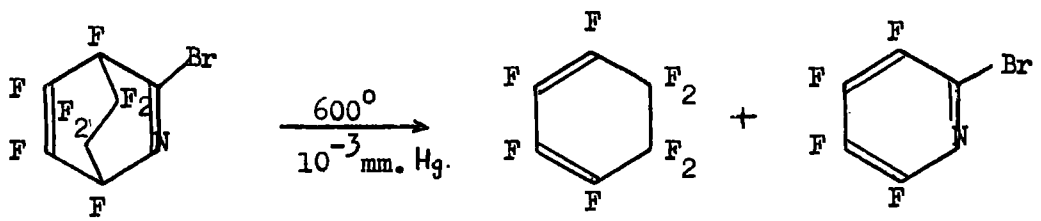
Similarly the Diels-Alder adducts of 2H,3H-hexafluorocyclohexa-1,3-diene with but-2-yne and propyne produced the expected benzenes under conditions similar to those used above, tetrafluoroethylene being eliminated.[66]

a. X = CH_3, Y = CH_3

b. X = CH_3, Y = H

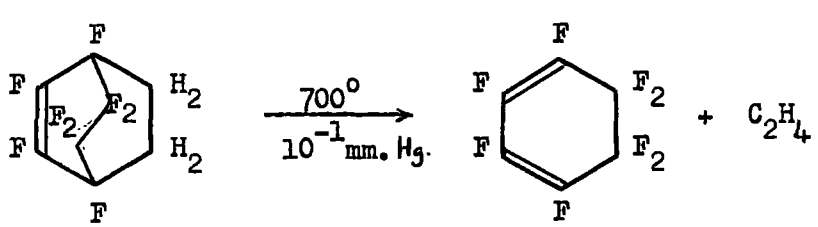


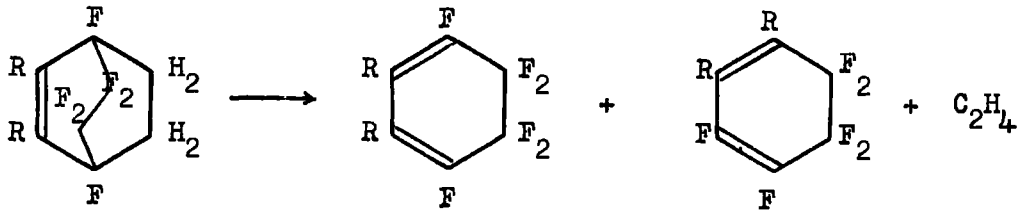
The reaction of perfluorocyclohexa-1,3-diene with thermally stable nitriles under vigorous conditions leads to only moderate yields of 2-substituted tetrafluoropyridines. In one instance the intermediate Diels-Alder adduct (85) was isolated and pyrolysis under the conditions used above led to elimination of tetrafluoroethylene and loss of the nitrile in about equal amounts.[63]



(85) 58% 42%

Pyrolysis of the ethylene adducts of highly fluorinated cyclohexa-1,3-dienes leads to loss of ethylene rather than tetrafluoroethylene and the formation of fluorinated cyclohexa-1,3-dienes. Conditions are more vigorous than those required for breakdown of the alkyne adducts, little breakdown occurring under milder conditions, a higher temperature and higher pressure, and hence longer contact time, being required, see below.



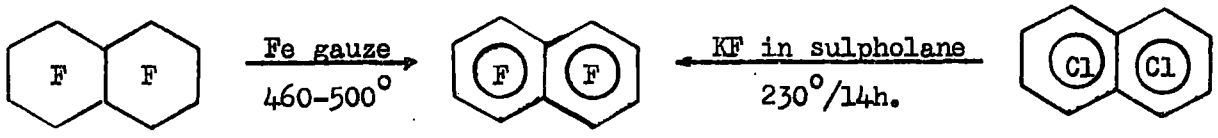


R = CH_3, H.

The initially formed 2,3-disubstituted dienes undergo thermal rearrangement to their 1,2-disubstituted isomers under these reaction conditions. The increased stability of the ethylene adducts of perfluorocyclohexa-1,3-diene over its alkyne adducts parallels the behaviour of analogous hydrocarbon systems and can be attributed to the more ready loss of an olefin in a reverse Diels-Alder reaction to generate an aromatic system than to generate a cyclohexa-1,3-diene. The exclusive loss of ethylene in the scheme above can be attributed to carbon-carbon σ-bond strengths, fluorine substituents increasing the stability of carbon-carbon σ-bonds compared with hydrogen.[66]

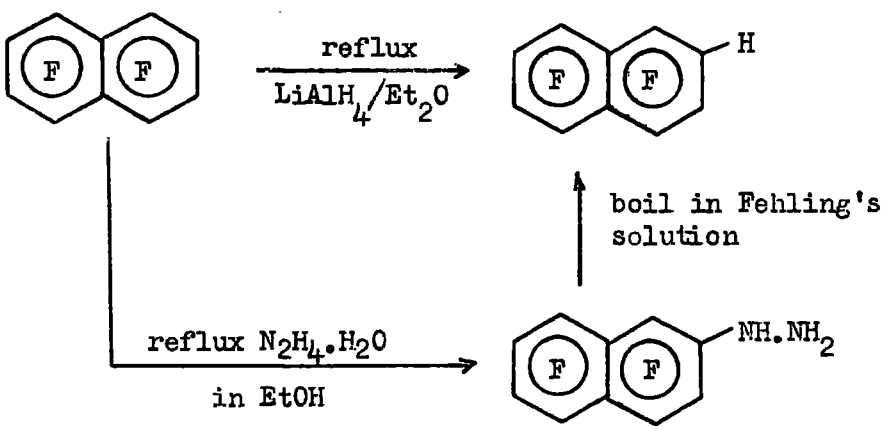
2.2 The Synthesis of Polyfluoronaphthalenes

Octafluoronaphthalene is readily obtained by defluorination of perfluorodecalin[122] over heated iron gauze, or by heating perchloronaphthalene with potassium fluoride in sulpholane.[123] The defluorination technique can be



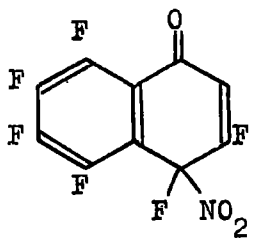
extended to the preparation of perfluoro(1-methylnaphthalene) and perfluoro (2-methylnaphthalene) from perfluoro(1-methyl-decalin) and perfluoro(2-methyl-decalin) respectively, although these naphthalenes are only obtained in poor yields.[124]

A range of β-substituted heptafluoronaphthalenes can be prepared by nucleophilic attack on octafluoronaphthalene. One of the most synthetically useful, 2H-heptafluoronaphthalene, can be obtained by either reduction of octafluoronaphthalene using lithium aluminium hydride in diethyl ether or by treating heptafluoro-2-naphthylhydrazine, formed by refluxing equimolar amounts of hydrazine hydrate and octafluoronaphthalene in solution in ethanol, with boiling Fehling's solution, see below.[125]

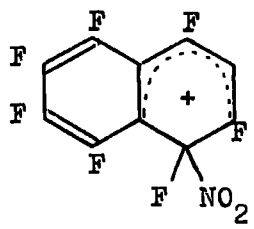


2H-heptafluoronaphthalene, like pentafluorobenzene, will undergo electrophilic substitution. Replacement of the hydrogen atom by $-SO_3H$, $-SO_2Cl$, $-Br$, $-CH_2Cl$, and $-CH_2.C_6F_5$ can be achieved using oleum, chlorosulphonic acid, bromine, bis(chloromethyl)ether and 2,3,4,5,6-pentafluorobenzyl chloride respectively. Reaction with fuming nitric acid does not produce the 2-nitro compound, obtainable by oxidation of 2-amino-heptafluoronaphthalene using peroxy-trifluoro acetic acid, but yields compound (86); a compound analogous to (86) can also be obtained from octafluoronaphthalene, and it has been suggested that

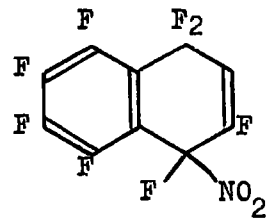
these compounds arise via an intermediate σ-complex which possesses structure (87) in the case of 2H-heptafluoronaphthalene. Nitric acid in hydrogen fluoride or nitric acid in sulpholane saturated with boron trifluoride yield (88) and (89), the former arising by fluorination of (86) and the latter by decomposition of (86) at the reaction temperature (40-50°).[126]



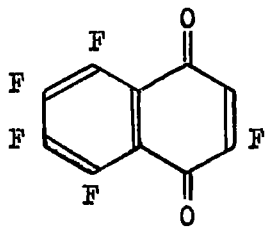
(86)



(87)

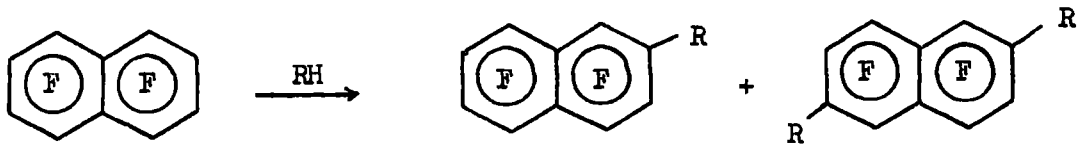


(88)



(89)

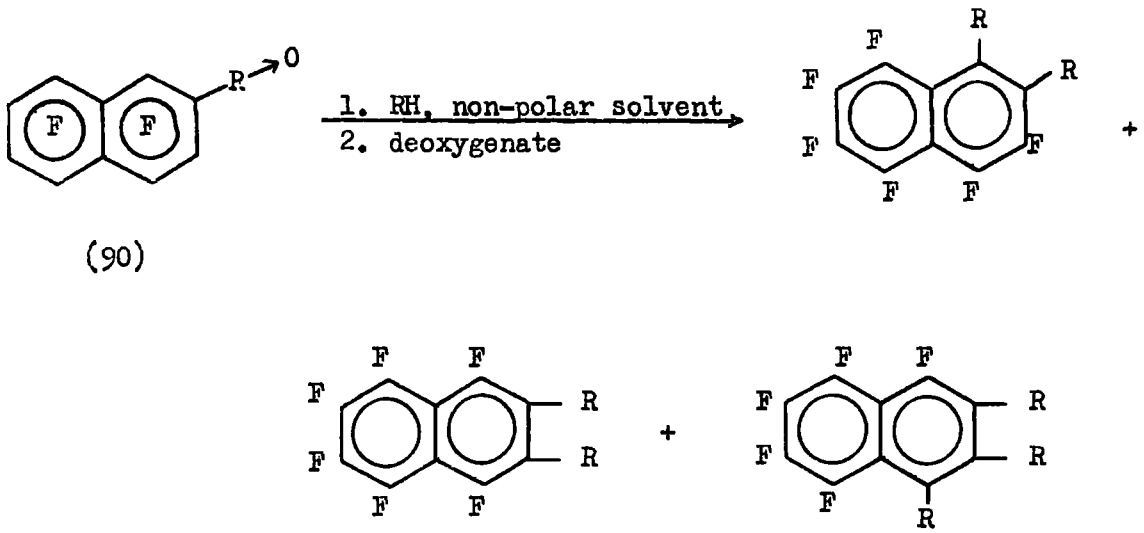
Octafluoronaphthalene reacts with secondary amines to yield both 2-monosubstituted and 2,6-disubstituted amino perfluoronaphthalenes, as below.



R = NN disubstituted amino

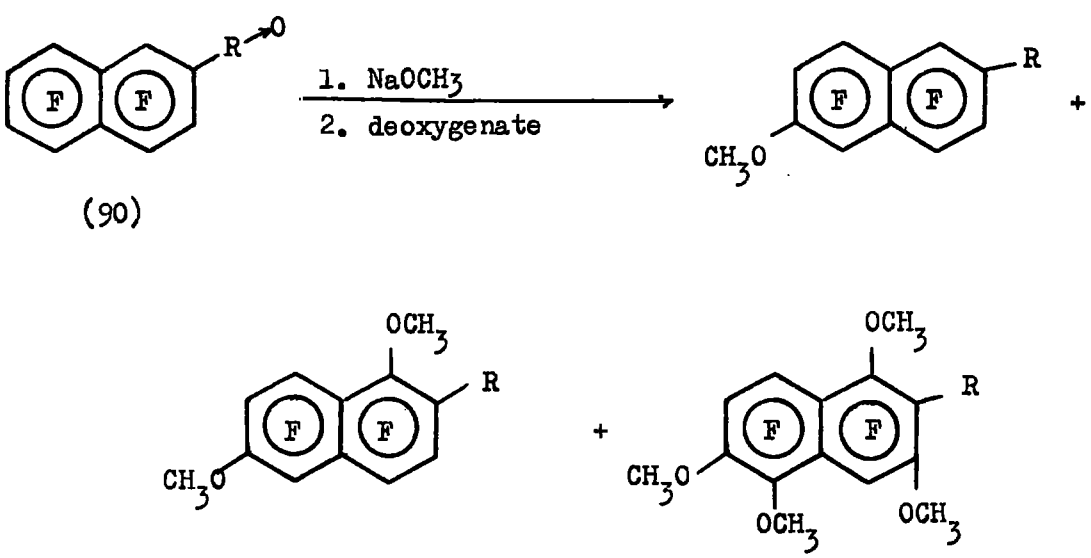
The amino substituent can be readily oxidies to its N-oxide using cold performic acid and when the 2-piperidinonaphthalene-N-oxide (90) was treated with piperidine in non-polar solvents the products after deoxygenation were

1,2- and 2,3-dipiperidino and 1,2,3-tripiperidinoperfluoronaphthalenes. This predominance of ortho substitution was not found in reactions in polar solvents such as methanol when 2,6-disubstituted products were obtained.



RH = piperidine

The reaction of (90) with sodium methoxide followed by deoxygenation of the products gave the compounds below.[127]

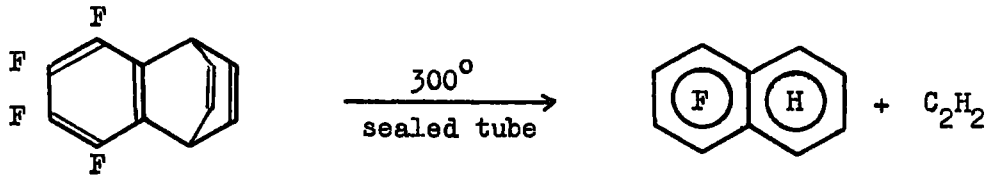


RH = piperidine

2-Trichloromethyl-heptafluoronaphthalene, prepared from perfluoro(2-methyl naphthalene) and aluminium trichloride, gave heptafluoro-2-naphthoic acid on hydrolysis with sulphuric acid. It was not possible to prepare 1-trichloromethyl-heptafluoronaphthalene or to hydrolyse perfluoro(1-methylnaphthalene) or perfluoro(2-methylnaphthalene).[124]

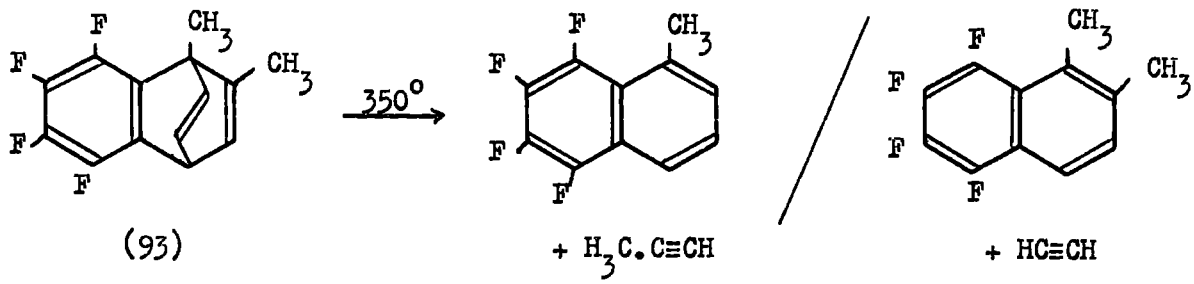
Although the preparations of specifically substituted highly-fluorinated naphthalenes appear to be restricted to defluorination of the corresponding saturated compounds, nucleophilic substitution in octafluoronaphthalene or its derivatives, or electrophilic substitution in 2H-heptafluoronaphthalene, a wide range of the less highly-fluorinated 1,2,3,4-tetrafluoronaphthalenes can be obtained by reaction sequences involving tetrafluorobenzyne.

Tetrafluorobenzyne reacts readily with benzenes, naphthalenes and other polycyclic aromatic compounds under mild conditions to give good yields of the Diels-Alder adducts. With a series of methyl substituted benzenes all possible isomeric products were obtained, except in the cases of p-xylene and durene where the adducts which would have contained bridgehead methyl groups were not isolated. The Diels-Alder adducts of tetrafluorobenzyne and benzenes can be pyrolysed at temperatures of 300-400° to give excellent yields of the corresponding naphthalenes by elimination of an acetylene, illustrated below for the formation of 1,2,3,4-tetrafluoronaphthalene (92) from the 1,4-adduct of tetrafluorobenzyne and benzene (91).[21,128] If there is the



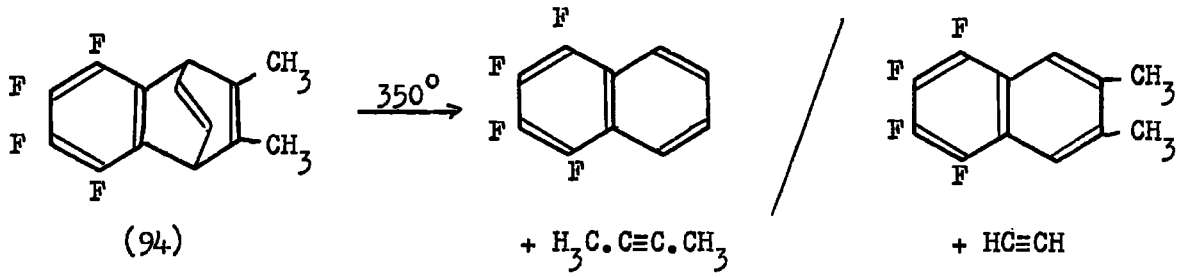
(91) (92)

possibility of eliminating either of two acetylenes the most-substituted acetylene is preferentially eliminated, as is the case in the pyrolyses of the two adducts of ortho-xylene, (93) and (94).



(93) + $H_3C.C{\equiv}CH$ + $HC{\equiv}CH$

5.2/4.8 ratio

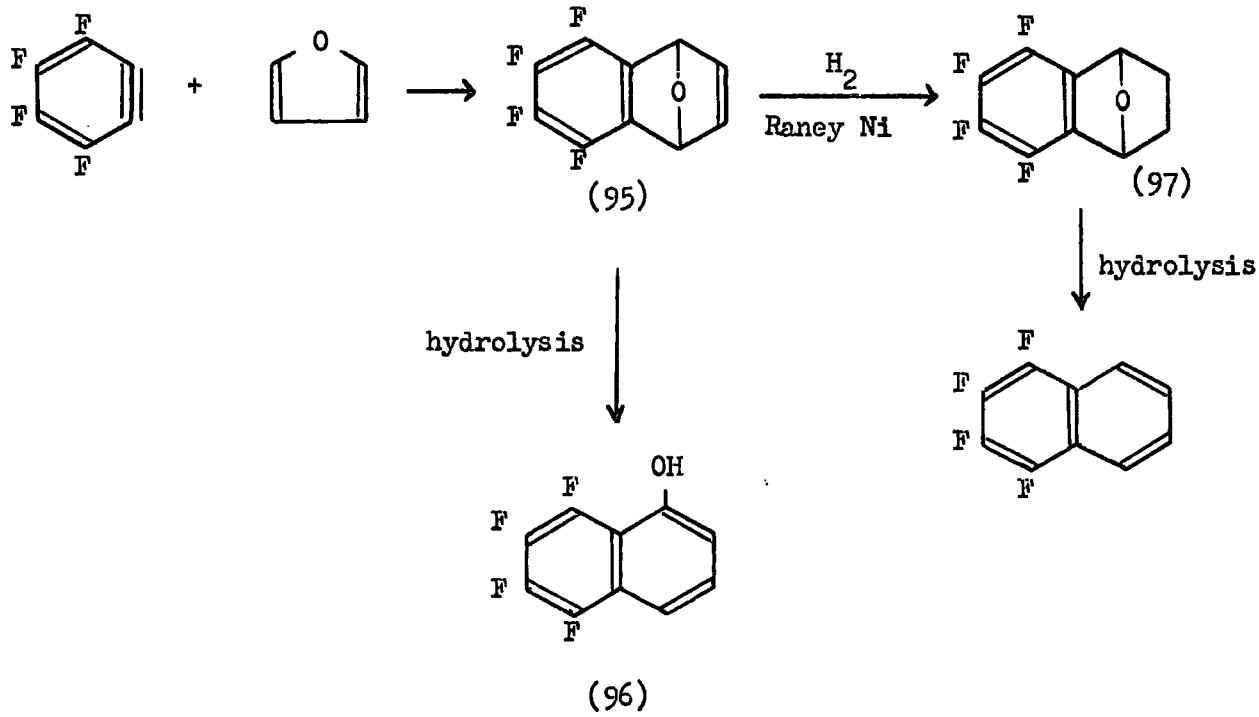


(94) + $H_3C.C{\equiv}C.CH_3$ + $HC{\equiv}CH$

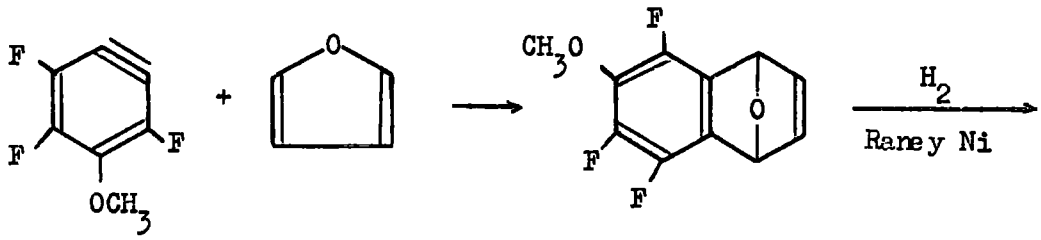
2/1 ratio

There are several other routes to 1,2,3,4-tetrafluoronaphthalene. As previously mentioned pyrolysis of the 1,4-adduct of cyclopentadiene and tetrafluorobenzyne under mild conditions leads to a good yield,[21] as does the facile pyrolysis of the 1,4-adduct of cyclohexa-1,3-diene and tetrafluorobenzyne at 300°.[129] The three adducts formed from the reaction of butadiene with perfluorocyclohexa-1,3-diene can be both defluorinated and dehydrofluorinated by passage over steel wool at 425° to give a 73% yield of this same compound.[60] Other methods of preparation of this compound are based on the reactions of tetrafluorobenzyne with thiophene[21] and furan.[130]

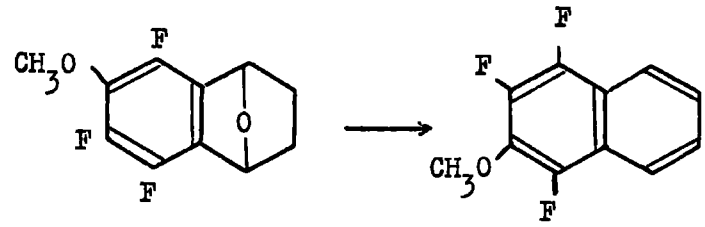
Tetrafluorobenzyne can be trapped as its 1,4-adduct by furan; the reaction of pentafluorophenylbromide and lithium amalgam in furan led to adduct (95) which gave 5,6,7,8-tetrafluoro-1-naphthol (96) on hydrolysis; hydrogenation of (95) gave (97), which was smoothly hydrolysed to 1,2,3,4-tetrafluoronaphthalene, see below.[130]



A monomethoxytrifluorobenzyne (98) has also been successfully trapped by furan yielding adduct (99), hydrogenation of (99) followed by hydrolysis of the resulting compound gave (100) in an unambiguous synthesis. This compound has also been prepared by the attack of methoxide ion on 1,2,3,4-tetrafluoronaphthalene.[131]

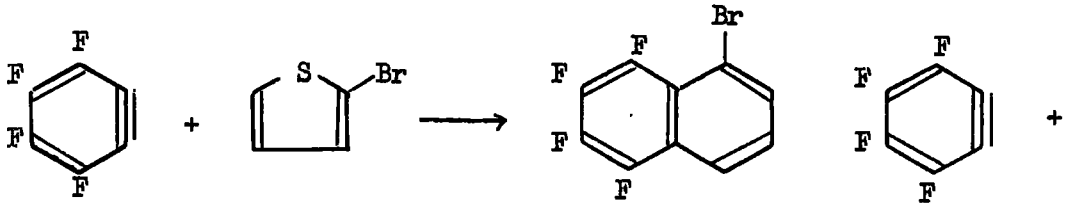


(98) (99)

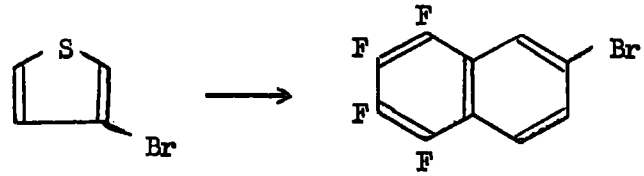


(100)

Thiophene, a very unreactive diene in the Diels-Alder reaction, reacts with tetrafluorobenzyne to give 1,2,3,4-tetrafluoronaphthalene; the 1,4-adduct is thought to be an intermediate but is desulphurised too readily to be isolated.[21] Substituted thiophenes also react with tetrafluorobenzyne and the two monobromotetrafluoronaphthalenes (101) and (102), formed by electrophilic bromination of 1,2,3,4-tetrafluoronaphthalene were unambiguously synthesised from tetrafluorobenzyne and 2-bromo and 3-bromothiophene respectively.[131] Tetrachlorothiophene reacts with tetrafluorobenzyne to give a poor yield of 1,2,3,4-tetrachlorotetrafluoronaphthalene.[21]

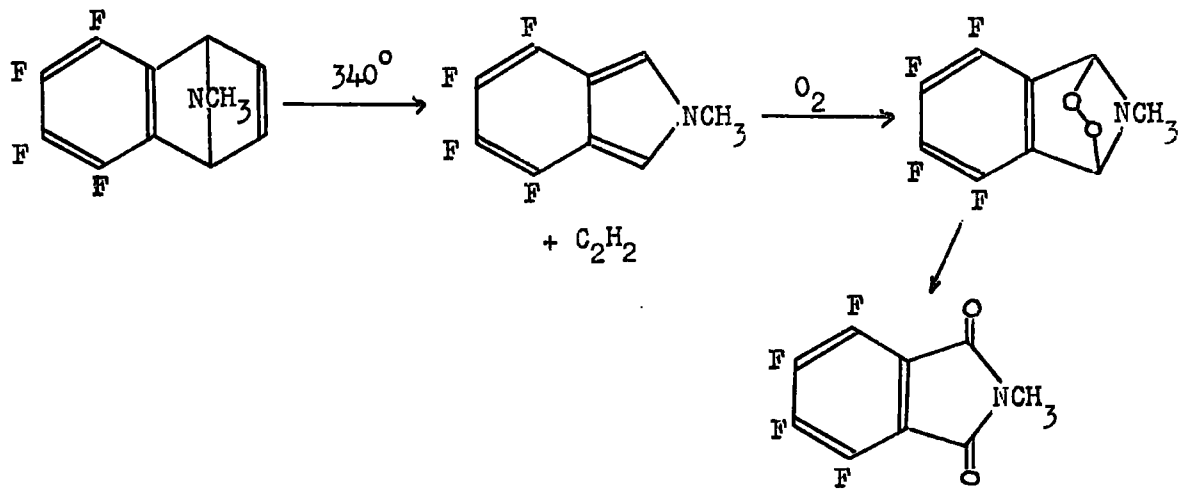


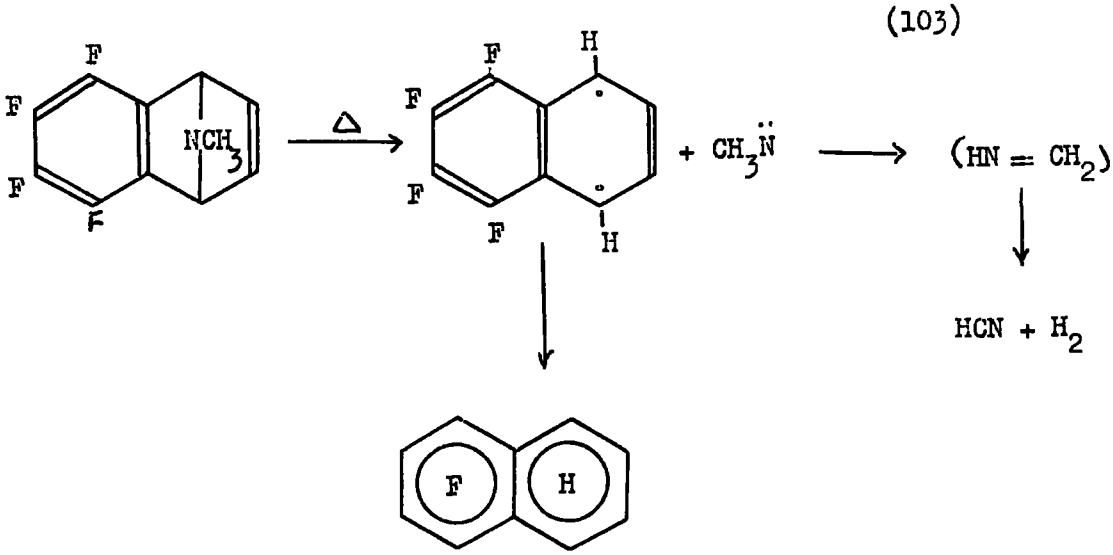
(101)



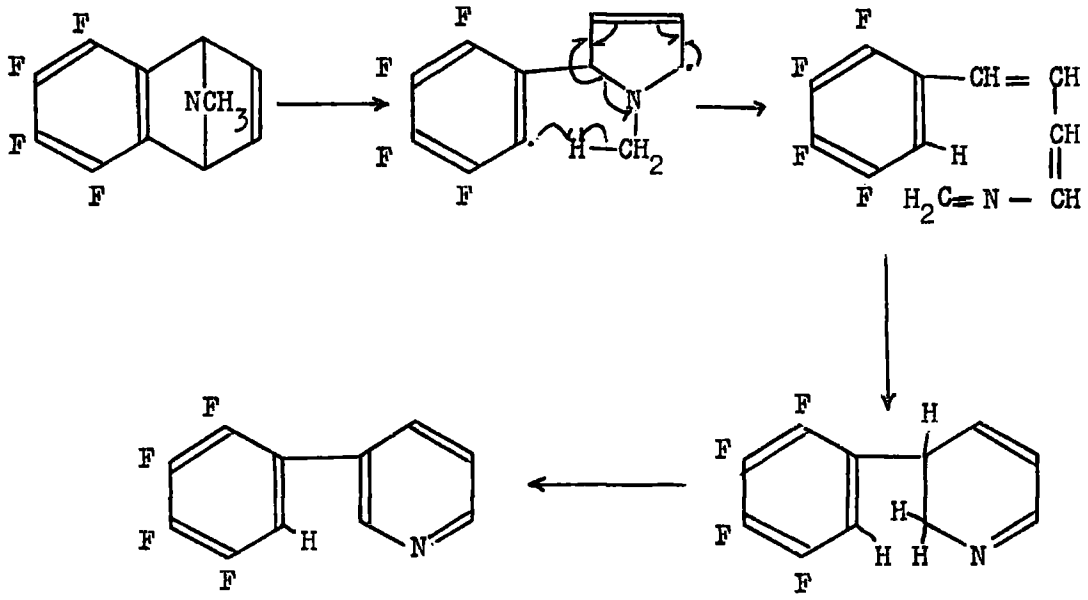
(102)

Tetrafluorobenzyne also forms a Diels-Alder adduct with N-methylpyrrole.[21] Pyrolysis of this adduct has been reported under a variety of conditions. At high temperatures there are a number of competing reaction pathways leading to compounds (92), (103) and (104). Loss of acetylene leads to an isoindole which on oxidation followed by thermal decomposition affords (103). 1,2,3,4-tetrafluoronaphthalene (92) is formed by elimination of the nitrene bridge, which is converted to hydrogen cyanide and hydrogen. The pyridine (104) may be formed by the scheme below; the thermal cyclization is symmetry-allowed and once the cyclic compound has been formed oxidation takes place to the required product.[132]



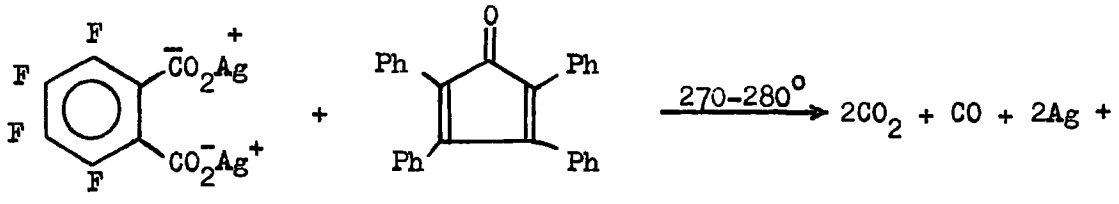


(92)

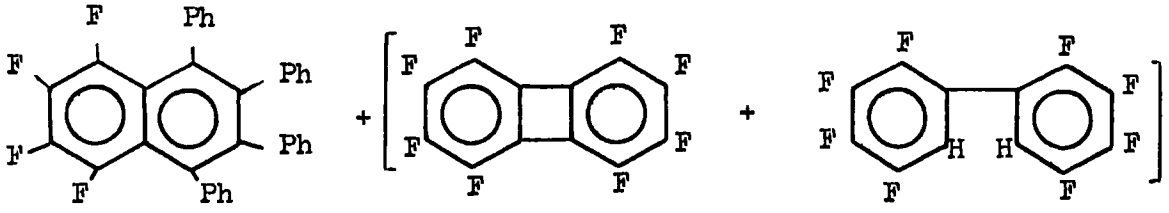


(104)

The pyrolysis of disilver tetrafluoronaphthalate (105) with tetraphenylcyclopentadienone at 270-280° yields 1,2,3,4-tetraphenyl-5,6,7,8-tetrafluoronaphthalene (106) as well as perfluorobiphenylene and 2,3,4,5,2',3',4',5'-octafluorobiphenyl, suggesting that the process involves the generation of tetrafluorobenzyne.[133]



(105)



(106)

1,2,3,4-tetrafluoronaphthalene undergoes both nucleophilic and electrophilic substitution, the former at the β-position with greater difficulty than octafluoronaphthalene and the latter at both α and β positions. This allows access to a range of fluorinated naphthalenes.[131]

CHAPTER 2

DISCUSSION

2.3 Diels-Alder Reactions of Dodecafluorotricyclo 5.2.2.$0^{2,6}$ undeca-2,5,8-triene with Ethylene and Alkynes

2-substituted tetrafluoropyridines and 1,2-disubstituted tetrafluorobenzenes have been unambiguously synthesised by the reaction of perfluorocyclohexa-1,3-diene with thermally-stable nitriles under drastic conditions, the intermediate Diels-Alder adduct losing tetrafluoroethylene under these conditions, and by forming the 1,4-adducts of perfluorocyclohexa-1,3-diene or perfluorocyclopentadiene with acetylenes followed by pyrolytic elimination of tetrafluoroethylene or difluorocarbene from these compounds.[63,58,66,67,36]

Prior to this work the use of the Diels-Alder reaction in the synthesis of fluorinated naphthalenes had been restricted to reaction sequences involving tetrafluorobenzyne, 1,2,3,4-tetrafluoronaphthalenes being obtained by synthetic routes involving reaction with cyclopentadiene,[21] cyclohexa-1,3-diene,[129] thiophenes,[21,131] furans[130] and tetraphenylcyclopentadienone.[133] (see introduction).

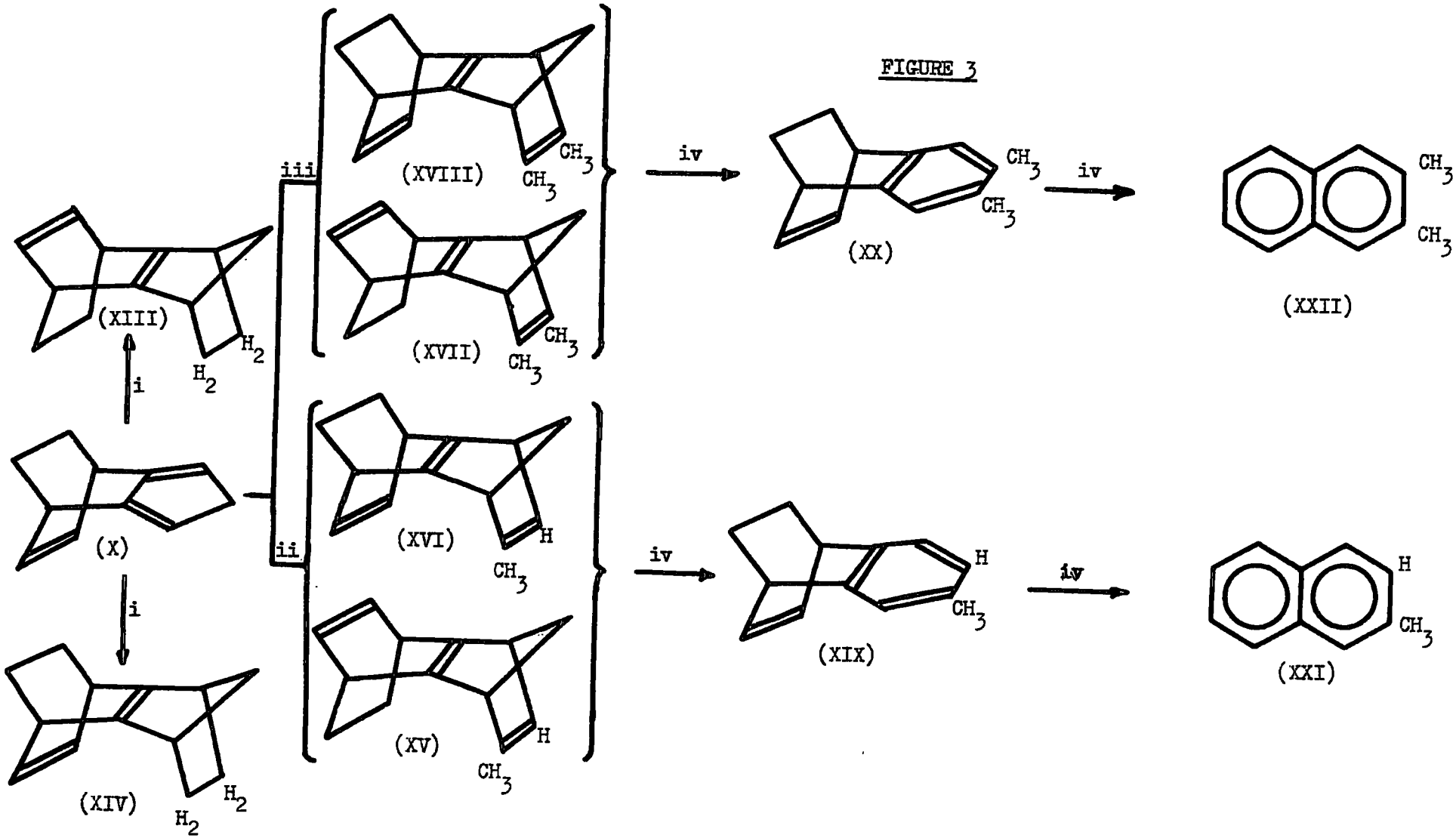
Trienes (IX) and (X), obtained by dehydrofluorination of the 1,4-adducts of perfluorocyclohexa-1,3-diene with 1H,2H-octafluorocyclohexene and 1H,2H-hexafluorocyclopentene respectively (see Chapter 1), both contain a cyclic conjugated diene system and would reasonably be expected to undergo Diels-Alder reactions. The 1,4-adducts of these trienes with acetylenes would be expected to undergo the reverse Diels-Alder reaction on pyrolysis to yield ββ-disubstituted hexafluoronaphthalenes by elimination of both the tetrafluoroethylene bridges from the 1,4-adducts of (IX) or the difluoromethylene and the tetrafluoroethylene bridge in the case of the 1,4-adducts of (X). The unambiguous synthesis of ββ-disubstituted hexafluoronaphthalenes was only investigated using triene (X) since this was far more readily available than triene (IX).

Unlike most other polyfluorocyclopentadienes described[36,54,55] compound (X) shows no tendency to undergo Diels-Alder dimerisation, having been recovered unchanged from reactions run at 200°, and this can be attributed to the steric restrictions imposed by the bulky substituents on the diene unit. It reacts very readily with ethylene, but-2-yne and propyne and it appears that its reactivity is qualitatively of the same order as that of perfluorocyclopentadiene[36] and greater than that of perfluorocyclohexa-1,3-diene,[58] although a detailed comparison of the reactivity of (X) and other fluorinated dienes has not been undertaken.

Reaction of (X) with ethylene, propyne and but-2-yne at temperatures of 192°, 115° and 120° respectively led to good yields of the expected 1,4-adducts (see Figure 3). As the substituents are not symmetrically disposed with respect to the plane of the pentadiene ring in structure (X) reaction with a simple acyclic dienophile can reasonably be expected to produce a pair of geometrically isomeric Diels-Alder adducts and this was observed in all three cases. The pairs of isomeric adducts were separated and purified using a combination of fractional sublimation and fractional crystallisation, the progress of the separation being followed by analytical g.l.c.

All six adducts, (XIII) to (XVIII), had elemental analyses and mass spectra consistent with their formulation as 1:1 adducts and each had a strong absorption in the infrared spectrum characteristic of a CF=CF. Of the two adducts obtained from each dienophile the ones with the shorter retention times on analytical g.l.c. crystallised as long needles, whereas their longer-retained isomers crystallised as platelets; in addition, except for the ethylene adducts which were both formed in equal proportion, there was a slight predominance of the longer-retained isomers, in the case of propyne the ratio of the two isomers being 45:55 whilst for but-2-yne it was 23:77.

FIGURE 3



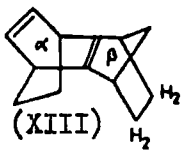
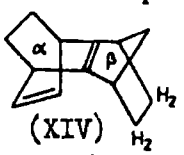
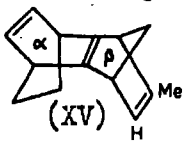
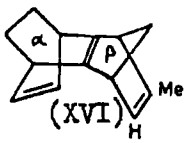
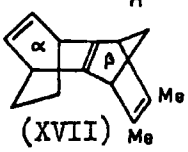
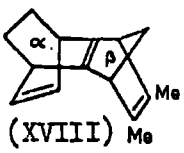
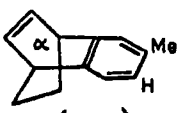
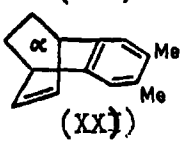
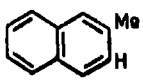
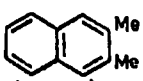
All unmarked bonds are to fluorine atoms

i. $CH_2{:}CH_2$ ii. $CH_3.C{:}CH$ iii. $CH_3.C{:}C.CH_3$ iv. vacuum pyrolysis

The structures and detailed stereochemistry of the six adducts can be assigned on the basis of their n.m.r. spectra (see Table 12). The gross structural features of all the adducts (XIII ⟶ XVIII) can be deduced from the chemical shifts and integrated intensities of the resonances. Thus, the bicyclo [2,2,2]unit, labelled α in the formulae (Table 12), present in the initial triene (X), is also present in the adducts and is readily identified by the characteristic tertiary, vinylic and bridging $-CF_2CF_2-$ resonances in the ^{19}F n.m.r. spectra.[58,63,66,68] The remaining resonances are the characteristic high field signals due to the two tertiary fluorines in the bicyclo [2,2,1]unit, labelled β (Table 12), and an AB quartet for the bridging difluoromethylene, the position of the tertiary fluorines and the position and observed coupling constant of the difluoromethylene being consistent with those reported previously for Diels-Alder adducts of perfluorocyclopentadiene[36,54] and dimers of highly fluorinated cyclopentadienes.[48,55] Assignment of the detailed stereochemistry is a question of deciding whether the bridging $-CF_2CF_2-$ of the bicyclic unit α and the bridging CF_2 of the other bicyclic unit β are on the same side or on opposite sides of the molecule. If they are both on the same side then molecular models indicate that one of the fluorines of the $-CF_2-$ will be in close proximity to two fluorines of the $-CF_2CF_2-$ bridge, and some evidence of spin-spin interaction would be expected. Evidence of an interaction of this type is clear from a comparison of the $-CF_2-$ and $-CF_2CF_2-$ resonances of the pairs of isomers (XV) and (XVI), and (XVII) and (XVIII). For compounds (XVI) and (XVIII), the longer-retained adducts, the components of one limb of the AB quartet due to the $-CF_2-$ are split into a seven-line multiplet and the signal due to the bridging $-CF_2CF_2-$ is broad and asymmetric. For the shorter-retained compounds, (XV) and (XVII), the components of both limbs of the $-CF_2-$ AB quartet are sharp single lines and the bridging $-CF_2CF_2-$ is a narrower symmetrical signal. Consistent with these observations is

TABLE 12

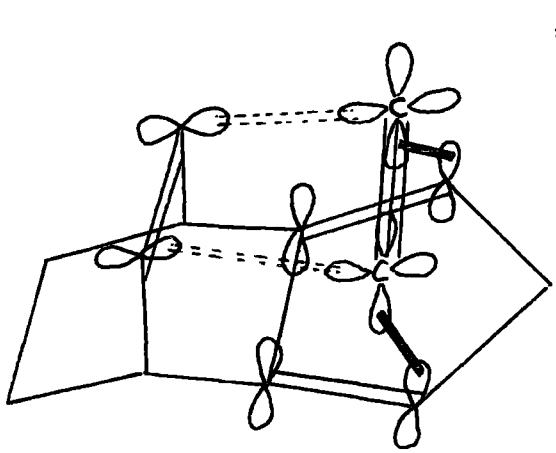
N.m.r. spectral parameters [a]

Compound [b]	α -C-F	α -C-F	α -CF_2CF_2-	β -C-F	β -CF_2-	Aromatic F	CH_2	H-	-CH_2CH_2-
 (XIII)	216·9(2)	153·1(2)	δ_A 123·9(2) [d] δ_B 118·8(2) J_{AB} 215	198·4(2)	δ_A 152·2(1) δ_B 140·6(1) J_{AB} 171				2·58(2) 2·92(2)
 (XIV)	217·2(2)	153·2(2)	δ_A 124·8(2) [d] δ_B 116·5(2) J_{AB} 215	200·0(2)	δ_A 153·1(1) δ_B 128·8(1) J_{AB} 171				2·47
 (XV)	216·9(2)	153·4(2)	122·0(4)	205·2(1) 199·9(1)	δ_A 137·3(1) δ_B 133·6(1) J_{AB} 146		1·97(3)	6·33(11)	
 (XVI)	217·6(2)	153·5(1) 152·1(1)	120·6(4)	205·0(1) 199·9(1)	δ_A 152·1(1) δ_B 125·7(1) J_{AB} 149		2·02(3)	6·42(1)	
 (XVII)	216·7(2)	153·1(2)	122·3(4)	205·7(2)	δ_A 136·3(1) δ_B 133·1(1) J_{AB} 152		1·87		
 (XVIII)	217·3(2)	153·0(2)	120·7(4)	206·4(2)	δ_A 134·1(1) δ_B 126·2(1) J_{AB} 144		1·85		
 (XIX)	216·4(2)	153·9(2)	δ_A 125·8(2) [d] δ_B 123·4(2) J_{AB} 221			125·6(1) 129·6(1)	2·38(3)	7·08(1)	
 (XX)	216·7(2)	153·9(2)	124·8(4)			127·8(2)	2·30		
 (XXI)						122·5(1) 126·5(1) 115·6(1) 146·8(1) 155·5(1) 157·7(1)	2·43(3)	7·08(1)	
 (XXII)						125·8(2) 147·1(2) 158·6(2)	2·30		

[a] Shifts are in p.p.m. with respect to internal $CFCl_3$ or Me_4Si as reference; integrated intensities in parentheses; coupling constants in Hz. [b] Unmarked valences to fluorine atoms. [c] Solution in acetone for ^{19}F, [$^2H_6$] acetone for ^1H. [d] Pseudo AB quartet. [e] Solution in CCl_4. [f] Neat liquid. External Me_4Si.

separation of the vinylic fluorines resonances in compound (XVI) to produce two discreet signals due to their close proximity to the asymmetrically substituted double bond; in the geometrical isomer (XV), when the vinylic fluorines are well-separated from the influence of the CH_3-C=C-H unit they appear as a single resonance. The n.m.r. spectra of isomers (XIII) and (XIV) were extremely complex and did not in themselves permit an assignment of stereochemistry, however structures (XIII) and (XIV) can be deduced from a comparison of the crystalline form, relative g.l.c. retention times and n.m.r. spectral parameters of this pair and the pairs (XV) and (XVI), and (XVII) and (XVIII).

There is a slight predominance of the longer-retained 1,4-adducts for the reactions of triene (X) with but-2-yne and propyne and as this is in marked contrast to the lack of selectivity for the addition of ethylene it perhaps merits brief consideration. The preferred geometry of approach of dienophiles to (X) will be parallel to the bridge systems and therefore substituents in the dienophile can exert little steric influence on the reaction. A possible explanation for the greater selectivity of acetylenes may lie in secondary orbital stabilisation of the transition state leading to the longer-retained isomers due to interaction of the π orbitals of the isolated double bond of the triene and the π orbitals of the dienophile at right angles to those involved in the cycloaddition, illustrated below.



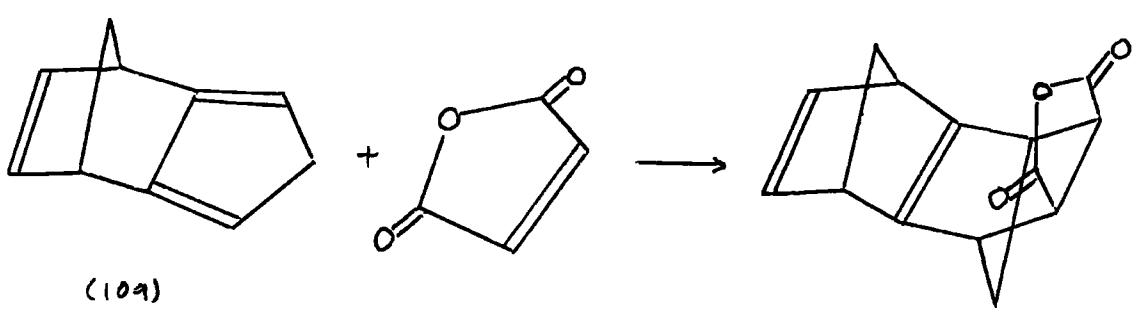
secondary interactions

primary interactions

The approaching acetylene will begin to bond to the cyclopentadiene system of triene (X) through one pair of π orbitals, the orbitals at right angles to this pair will be pointing towards the remaining double bond of the triene and secondary orbital interaction could occur stabilising approach of the dienophile from the side leading to the longer-retained isomer; no interaction of this type could occur with ethylene as the dienophile.

The selectivity is greater for but-2-yne than for propyne. This is not unreasonable as the former dienophile reacts somewhat more readily with fluorocarbon dienes than does propyne, the methyl groups enrich the π system and hence will also increase secondary as well as primary interactions and the geometry of approach leading to the longer-retained isomer will become even more preferable.

A hydrocarbon triene dehydroisodicyclopentadiene (109) possessing some of the structural features of triene (X) has been prepared by Alder et al. Unlike cyclopentadiene, but like (X), this compound shows no tendency to dimerise but undergoes Diels-Alder reactions with the same order of facility as cyclopentadiene, for instance it forms a single Diels-Alder adduct with maleic anhydride at room temperature. The structure proposed for this adduct is shown below and is the endo adduct in which the methylene bridges are on opposite sides of the molecule.[134]



(109)

2.4 Pyrolysis of the Diels-Alder Adduct of Dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene with alkynes. A Synthesis of Polyfluorobenzobicyclo[2,2,2]octa-2,5-dienes and 2,3-disubstituted hexafluoronaphthalenes.

Elimination of either the $-CF_2-$ or the $-CF_2CF_2-$bridges from adducts (XV) to (XVIII) leads to the formation of an aromatic ring and may be accomplished in a stepwise manner. Vacuum pyrolysis or pyrolysis in a sealed tube under mild conditions led to the exclusive loss of the CF_2 bridge and formation of a polyfluorobenzobicyclo[2,2,2]octa-2,5-diene whereas pyrolysis under more strenuous conditions led to the elimination of all bridges and the formation of ββ-disubstituted hexafluoronaphthalenes. Thus (XIX) is the major product when (XV) and (XVI) are heated to 200° in a sealed tube and (XX) is the only product when (XVIII) is pyrolysed in a flow system at 380° and 10^{-3} mm.Hg. pressure. By using reaction temperatures of over 600° in a flow system at 10^{-3}mm.Hg. pressure both bridges can be eliminated to produce the hexafluoronaphthalenes; (XV), (XVI) and (XIX) producing (XXI), and (XX) producing (XXII) under these conditions. The products of these pyrolysis reactions, the decafluorobenzobicyclo[2,2,2]octa-2,5-dienes (XIX) and (XX) and the 2,3disubstituted hexafluoronaphthalenes (XXI) and (XXII), are of kinds not previously available and it is to be expected that analogous structures with different substituents may be synthesised by the same route.

The facile loss of difluorocarbene from the 1,4-adducts of triene (X) with acetylenes at a temperature of only 200° may be partly due to the strain incorporated in compounds (XV)-(XVIII) as the Diels-Alder adduct of dimethylacetylene dicarboxylate and perfluorocyclopentadiene lost difluorocarbene on pyrolysis at 480°, although no mention was made in this publication of optimisation of conditions and it may be that the reaction would have been equally successful under milder conditions.[36] The loss of tetrafluoroethylene from the decafluorobenzobicyclo[2,2,2]octa-2,5-dienes (XIX) and (XX) to produce

the hexafluoronaphthalenes (XXI) and (XXII) is much less favourable than loss of difluorocarbene from adducts (XV)-(XVIII) due to the lower gain in stabilization energy on forming the pyrolysis products (XXI) and (XXII), compounds (XIX) and (XX) already possessing benzenoid aromaticity, and the initial loss of difluorocarbene having relieved considerable molecular strain. The conditions required for the elimination of tetrafluoroethylene from (XIX) and XX) are similar to those required for pyrolytic elimination of tetrafluoroethylene from the alkyne adducts of fluorinated cyclohexa-1,3-dienes.[58,66]

The structures of compounds (XIX)-(XXII) follow from their modes of preparation, elemental analyses and mass spectra, their infrared, ultraviolet and n.m.r. spectra confirming the assigned structures. The infrared spectra of (XIX) and (XX) are very similar showing a strong absorption due to a CF=CF double bond as well as an intense aromatic band not present in the initial adducts. Their ^{19}F n.m.r. spectra (Table 12) confirmed the presence of the bicyclo[2,2,2]unit, labelled α, the remaining resonances being due to the aromatic fluorines.

Although the ^{19}F n.m.r. spectra were very complex due to extensive coupling especially evident in the aromatic fluorine resonances, the ^{1}H n.m.r. spectra were more simple. The ^{1}H n.m.r. spectrum of (XIX) contained a doublet for the methyl resonance (J = 2.5 Hz) ascribed to coupling to the ortho fluorine, and a doublet of doublets (J = 11 Hz and 6Hz) for the aromatic proton, the larger coupling ascribed to coupling between this proton and the ortho fluorine and the smaller one to coupling to the meta fluorine; these coupling constants are compatible with values for analogous systems, thus for methylpentafluorobenzene $J(CH_3, F\text{-}2) = 2.2$ Hz and $J(CH_3, F\text{-}3) = 0$, and for pentafluorobenzene $J(H, F\text{-}2) = 11.3$ Hz and $J(H, F\text{-}3) = 8.0$ Hz.[135] The ^{1}H n.m.r. spectrum of (XX) was a single resonance 2Hz wide comprising three lines of equal intensity and equally spaced,

part of a complex spin-spin system which is not first order.

The naphthalenes (XXI) and (XXII) have infrared spectra which are clearly similar and display strong bands in the aromatic region. As expected their ^{19}F n.m.r. spectra are complex and although not first order it is clear that there is a large (c. 60 Hz) peri F-F coupling[127,136] present in the spectra of both compounds, the peri-fluorines being those at 145.6 and 146.8 p.p.m. for the aromatic ring carrying four fluorines in (XXI), and at 122.5 and 126.5 p.p.m. for those in the other ring, the analogous peri-fluorines in (XXII) being at 147.1 and 125.8 p.p.m. respectively. Again, the ^{1}H n.m.r. spectra were simple, the splitting patterns being identical with those observed for compounds (XIX) and (XX) respectively, suggesting that coupling between the substituents in the β position and aromatic fluorines is confined to the substituted ring.

As expected the ultra-violet spectra of (XXI) and (XXII) resembled those of naphthalene and octafluoronaphthalene (Table 13),[137] the bathochromic shift and intensification of the bands in (XXI) and (XXII) being qualitatively consistent with their structures. The spectra of all the dimethylnaphthalenes have been reported and possess the characteristic naphthalene absorptions with the expected bathochromic displacements and intensification of the bands due to hyperconjugation.[138]

TABLE 13

Ultra-Violet Spectra[a]

Compound	λ_{max}(log e ε)		
Naphthalene	275(3.75)	312(2.4)	
Octafluoronaphthalene	277(3.67)	308(3.22)	322.5(3.31)
(XXI)	283(3.64)	316(3.54)	330(3.69)
(XXII)	285(3.50)	315(3.40)	329(3.53)

a. in cyclohexane.

The aromaticity of compounds (XIX) and (XX) was similarly evident from strong absorptions in their ultra-violet spectra (see Experimental).

It is of interest to compare the mass spectra of adducts (XV) and (XVI) with those of their pyrolysis products (XIX) and (XXI) and similarly to compare the mass spectra of (XVII) and (XVIII) with those of (XX) and (XXII). The breakdown of a molecular ion in the mass spectrometer often parallels the behaviour of the molecule on vigorous pyrolysis,[139] and it has often been observed that the pyrolysis products of the 1,4-adducts of perfluorocyclohexa-1,3-diene with alkynes have high abundances in the mass spectra of these compounds;[58,61] similar behaviour occurs with the 1,4-adducts of tetrafluorobenzyne with aromatic compounds; these compounds yield naphthalenes on pyrolysis by elimination of an acetylene; the ion due to loss of the acetylene from the parent ion has high abundance in their mass spectra.[128] For adducts (XV), (XVI), (XVII) and (XVIII), the expulsion of m/e 150 (C_3F_6) from the molecular ion is an ion of high abundance in their mass spectra, being the base peak in three cases; for compounds (XIX) and (XX) the base peak arises by loss of m/e 100 (C_2F_4) from the parent ion and for all these compounds (XV)-(XX) the mass spectral and pyrolytic fragmentations appear to follow similar paths. For the naphthalenes (XXI) and (XXII) the stability of these aromatic systems results in the parent ions also being the base peaks in their mass spectra (see Appendix 2).[140]

Pyrolysis of the Diels-Alder adducts of propyne and triene (X) in a flow system resulted in a clean reaction with the production of the pyrolysis product and tetrafluoroethylene. However a reaction between propyne and triene (X) at 200° in a sealed tube led to a reaction product containing unchanged (X) and three products. The major product was compound (XIX) obtained in 37% yield after separation; the other two compounds isolated by g.l.c. were identified as (XXIII), resulting from the addition of difluoromethylene to (XV)

and/or (XVI), and (XXIV) an isomerisation product of (XXIII). There was no evidence of (XV) or (XVI) when the reaction was carried out at this temperature.

Structures (XXIII) and (XXIV) (see Figure 4) were assigned on the basis of their mode of formation, elemental analysis and spectroscopic data. Both (XXIII) and (XXIV) had a strong CF=CF stretching frequency in their infrared spectra and a top mass peak in their mass spectra at m/e 450, corresponding to the molecular ion of a product arising from (XV) or (XVI) + CF_2 or (XIX) + C_2F_4, the latter possibility was excluded by heating compound (XIX) in a sealed tube with tetrafluoroethylene when no trace of (XXIII) or (XXIV) was observed, the reactants being recovered unchanged. Heating a mixture of the two Diels-Alder adducts (XV) and (XVI) in a sealed tube under the reaction conditions mentioned above led to a product which was shown by infrared spectroscopy and analytical g.l.c. to be a mixture containing (XIX) as major components, minor components having the same g.l.c. retention times as (XXIII) and (XXIV), no trace of (XV) or (XVI) being detectable. Thus it seems reasonable that (XXIII) has been produced by the addition of difluoromethylene to (XV) or (XVI). The bicyclo[2,2,2]octadiene unit in (XXIII) is indicated by the typical tertiary vinylic and bridging $-CF_2CF_2-$ resonances in the ^{19}F n.m.r. spectrum and by the base peak in the mass spectrum being formed from the parent ion by expulsion of m/e 100 (C_2F_4). The loss of C_2F_4 from the parent ion is a prominent feature of compounds containing the bicyclo[2,2,2]octadiene unit,[58,63,66,68] and can be rationalised by loss of the $-CF_2CF_2-$ bridge resulting in a stable aromatic cation. The remainder of the ^{19}F n.m.r. spectrum of (XXIII) consists of an AB quartet integrating to two fluorines and corresponding in shift and magnitude of the coupling constant (178 Hz) with a cyclopropyl/difluoromethylene group,[71] two more tertiary fluorines at very low field, and an AB quartet integrating to two fluorines and ascribed to the other difluoromethylene bridge.

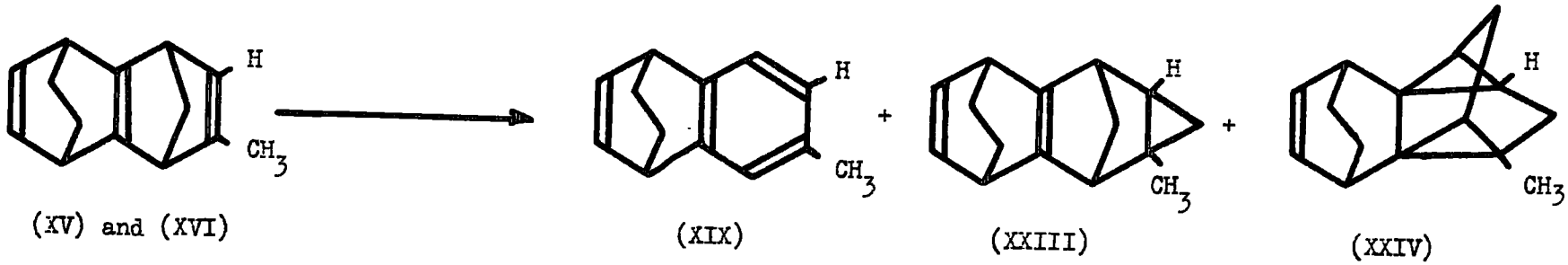
The proton n.m.r. indicates the presence of a tertiary proton and a methyl group, this data together being consistent with structure (XXIII).

Compound (XXIV) is isomeric with (XXIII) and their spectra are qualitatively similar, indicating a structural similarity; the two major differences between the spectra of (XXIII) and (XXIV) being that the base peak in the mass spectrum of (XXIV) does not arise by loss of m/e 100 from the molecular ion and that the low-field AB quartet in the ^{19}F n.m.r. spectrum of (XXIV) has a coupling constant of 250 Hz as opposed to 178 Hz for (XXIII). The reduced importance of the p-C_2F_4 ion is consistent with the structure proposed as is the magnitude of the coupling constant of the low-field AB quartet in the ^{19}F n.m.r. spectrum, which is compatible with a difluoromethylene in either of the environments present in (XXIV) but excludes a three-membered ring.[71] The remainder of the ^{19}F n.m.r. spectrum is complex but can be accommodated by the structure (XXIV). The proton n.m.r. again indicates the presence of a methyl group and a tertiary proton.

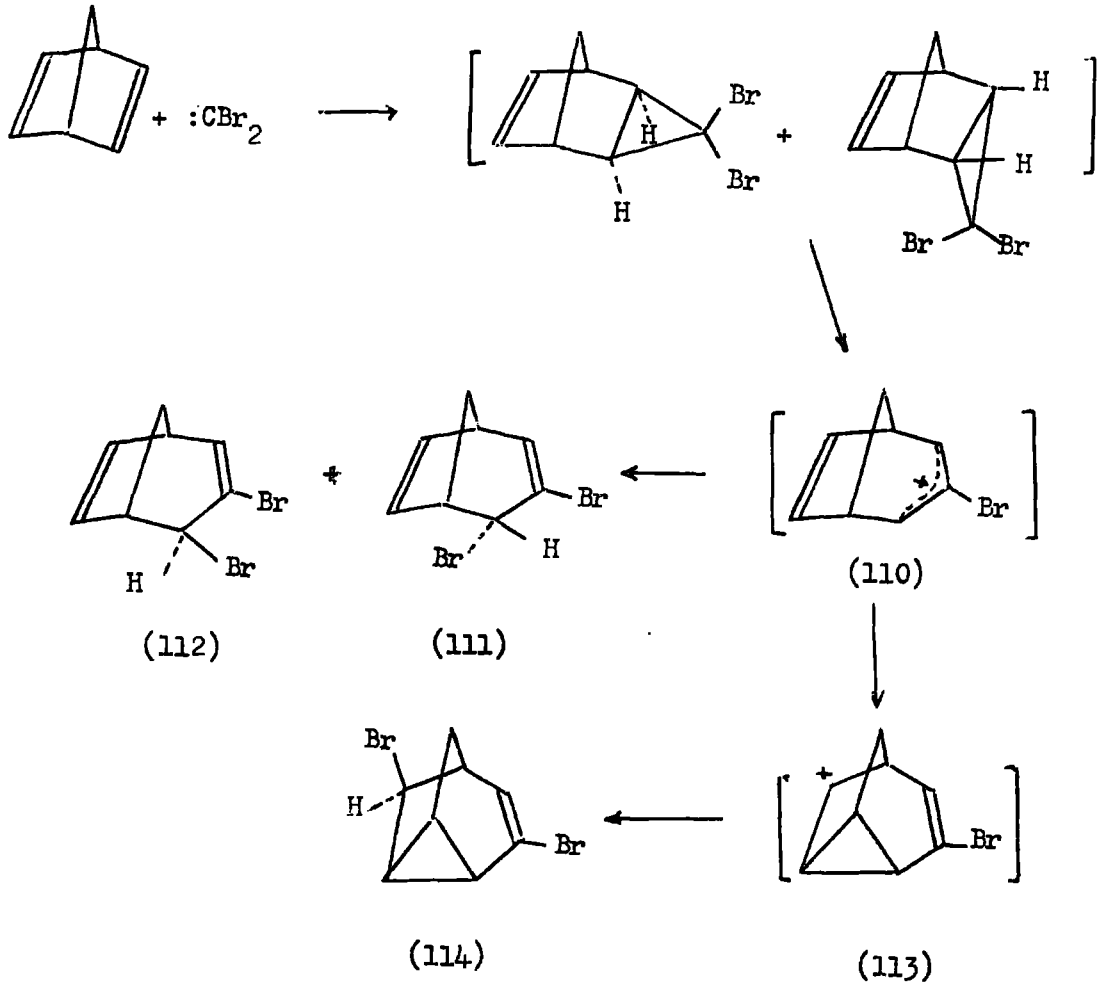
The addition of difluorocarbene to adducts (XV) or (XVI) would be expected to occur at the methyl substituted double bond to produce (XXIII), the ease of addition of electrophilic halocarbenes to double bonds being known to increase with increased alkyl substitution in the olefin.[141] Compound (XXIV) is most probably formed by thermal rearrangement of (XXIII); there are several examples of thermal processes of this type which have been rationalised as proceeding via ionic or free-radical mechanisms, as the $\pi^2_s + \sigma^2_s$ concerted process is only symmetry allowed in the excited state.[6]

The ionic mechanism has been successful in accounting for the products of the addition of dibromocarbene to bicyclo[2,2,1]heptadiene, a reaction somewhat related to the addition of difluorocarbene to (XV) or (XVI). The scheme is outlined below.

FIGURE 4



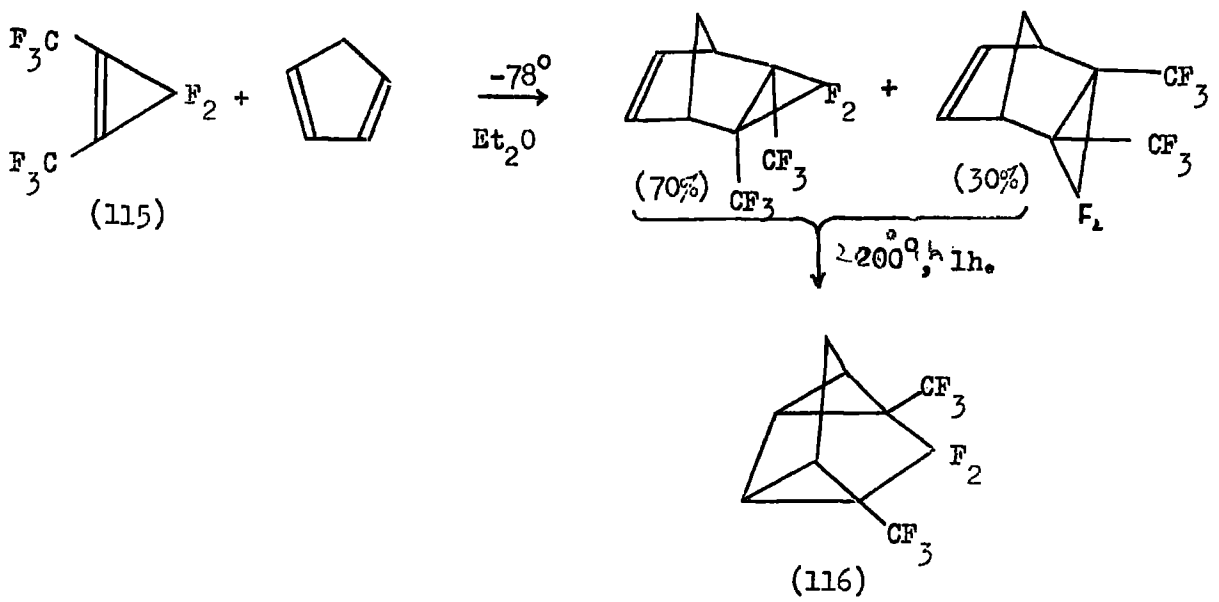
All unmarked bonds are to fluorine atoms



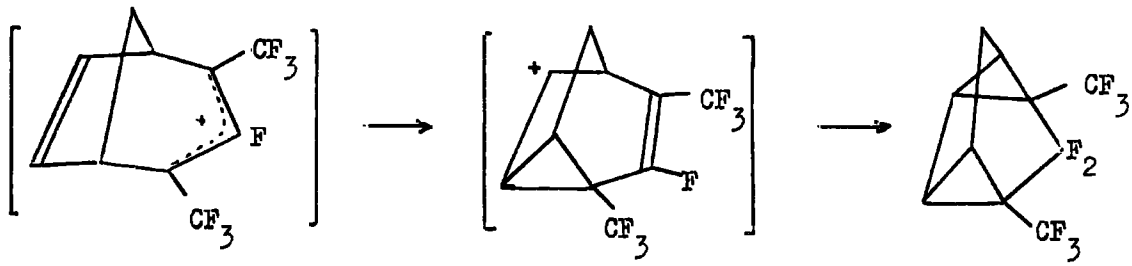
Compounds (111) and (112) are formed by collapse of the allyl carbonium ion (110); attack of the π bond of (110) on the allyl carbonium ion leads to a new carbonium ion (113) which can collapse to (114), the third reaction product. Heating or prolonged storage of (111) or (112) results in their conversion into (114). Compounds analogous to the initial unstable adducts above are also formed as intermediates in the 1,4-addition of halogenated cyclopropenes to cyclopentadiene, which rearrange by a similar mechanism (see Introduction, Chapter 1).[142]

1,2-Bis(trifluoromethyl)-3,3-difluorocyclopropene (115) reacts with cyclopentadiene at low temperatures to yield both the exo and the endo 1,4-adducts. Mild heating at 65° results in the conversion of the exo adduct to its more stable endo isomer and after 1 hour at 200° both 1,4-adducts

are quantitatively converted to tetracycle (116), see below.

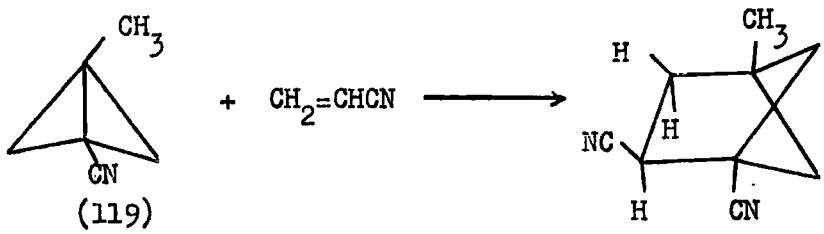


The rationalisation of these observations assumes that the initial steps in the isomerisation to (116) are analogous to those mentioned above. The allyl carbonium ion (117) is rearranged to carbonium ion (118) which is further converted to the required tetracycle (116); the driving force of the reaction is said to be the destabilisation of allyl carbonium ion (117) due to the electronegative trifluoromethyl groups. The exo-endo isomerisation of the initial adducts does not occur via a retro-Diels-Alder reaction but most probably proceeds via the allyl carbonium ion (117).[71] There are several examples of the formation of tetracycles analogous to (116) by the photochemical $[\pi 2_s + \sigma 2_s]$ concerted process,[143,144] however irradiation of the endo and exo 1,4-adducts of (115) and cyclopentadiene produced none of the desired tetracycle (116).[71]

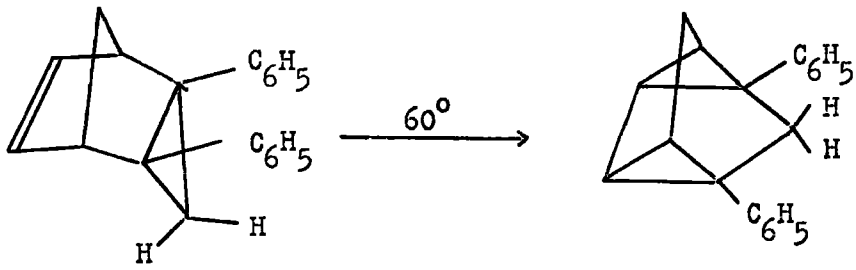


(117) (118) (116)

Although the ionic mechanism successfully rationalises the rearrangements above, the addition of highly-strained carbon-carbon σ-bonds and olefins, such as the reaction of 3-methylbicyclo[1,1,0]butanecarbonitrile (119) with acrylonitrile, below, has been shown to proceed via a diradical mechanism. This could also account for thermal intramolecular cycloaddition in the tricyclo [3,2,1,$0^{2,4}$]oct-6-ene skeleton, although strain is less, an example in the hydrocarbon field being the conversion of (120) to (121).[145]



(119)



(120) (121)

CHAPTER 2

EXPERIMENTAL

2.5 Diels-Alder Reactions of Perfluorotricyclo[5.2.2.$0^{2,6}$]undeca-2,5,8-triene(X)

General

Reagents were dried (phosphoric oxide) and degassed before insertion in a Pyrex ampoule. N.m.r. references were internal $CFCl_3$ and internal Me_4Si unless otherwise stated.

(a) With ethylene. A mixture of the triene (X) (1.66 g., 4.62 mmoles) and ethylene (4.78 mmoles) was sealed *in vacuo* in a Pyrex ampoule (130 ml.) which was heated at 192° for 16.5 hr. to give: (i) ethylene (1.67 mmoles); (ii) a colourless liquid (0.36 g.), shown by i.r. spectroscopy and analytical gas chromatography to be predominantly triene (X); (iii) a white solid (1.22 g.), shown by analytical gas chromatography to consist of two components in approximately equal proportions. This mixture was separated into two components by fractional sublimation (20°/10^{-3} mm.Hg) to give the two isomers of 4H,4H,5H,5H-dodecafluorotetracyclo[6.2.2.$1^{3,6}0^{2,7}$]trideca-2,9-diene (XIII) and (XIV). For the isomer with the shorter gas chromatographic retention time (XIII) (Found: C,40.0; H,1.15; F,59.0%; M (mass spectrometry), 388. $C_{13}H_4F_{12}$ requires C,40.2; H,1.0; F,58.7%; M, 388) recrystl. from acetone as fine needles m.p. 77-77.5°, ν_{max} 1754 (-CF=CF-) and 1623 cm^{-1} (>C=C<). For the isomer with the longer gas chromatographic retention time (XIV) (Found: C,40.0; H,1.2; F,59.1%; M (mass spectrometry), 388) recrystl. from acetone as platelets m.p. 126.5-127°, ν_{max} 1754 (-CF=CF-) and 1630 cm^{-1} (>C=C<).

(b) With propyne. Experiment 1. By the same procedure as in (a), triene (X) (2.56 g., 7.10 mmoles) and propyne (7.43 mmoles) were heated in a Pyrex ampoule (120 ml.) at 115° for 65 hr. to give (i) propyne (2.2 mmoles), with correct infrared spectrum; (ii) a colourless liquid (0.88 g.) shown by infrared spectroscopy and gas chromatography to be triene (X) containing < 10% of (XV) and (XVI); (iii) a white solid (1.88 g.) shown by analytical gas chromatography

to contain two components in the ratio 45:55. This mixture was separated by fractional sublimation (10^{-3} mm., 60°) followed by fractional crystallisation to give the two isomers of <u>4H-dodecafluoro-5-methyltetracyclo[6.2.2.1^{3,6}0^{2,7}]-trideca-2.4.9-triene</u> (XV) and (XVI). For the isomer with the shorter gas chromatographic retention time (XV) (Found: F,56.5%; M (mass spectrometry), 400. $C_{14}H_4F_{12}$ requires F,57.0%; M, 400) recrystl. from petroleum (60/80) as fine needles m.p. 81-82°, ν_{max} 1755 (-CF=CF-), 1640 and 1605 cm^{-1} (-CH=C(CH$_3$)- and >C=C<). For the isomer with the longer gas chromatographic retention time (XVI) (Found: F,56.9%; M (mass spectrometry), 400) recrystl. from petroleum (60/80) as platelets m.p. 63-64°, ν_{max} 1755 (-CF=CF-), 1640 and 1612cm^{-1} (-CH=C(CH$_3$)- and >C=C<).

Experiment 2. By the same procedure as in (a), triene (X) (2.0 g., 5.81 mmoles) and propyne (6.14 mmoles) were heated in a Pyrex ampoule (120 ml.) at 200° for 52 hr. to give a gas mixture (1.47 mmoles), shown by infrared spectroscopy to contain propyne, silicontetrafluoride and tetrafluoroethylene; and a liquid mixture (2.0 g.). The liquid mixture was shown to contain several components by analytical gas chromatography, of which the four major components were obtained pure by preparative gas chromatography (col.F; 150°), in order of emergence from the column they were (i) triene (X) (0.08 g., 0.22 mmoles), with correct infrared spectrum, (ii) <u>4H-tetradecafluoro-6-methyl-hexacyclo[7.2.2.1^{3,7}0^{2,4}0^{2,8}0^{6,8}]pentadec-10-ene (XXIV)</u> (0.06 g., 0.133 mmoles, 2.3%) (Found: F,59.6%; M (mass spectrometry), 450. $C_{15}H_4F_{14}$ requires F,59.1%; M, 450), a colourless solid, ν_{max} 1757 cm^{-1} (-CF=CF-). The ^{19}F n.m.r. spectrum showed resonances at 230.3 (1F), 222.8 (1F), 212.6 (1F) and 213.4 (1F) ascribed to fluorines at tertiary sites; 150.2 (1F) and 151.0 (1F), vinylic fluorines; 127.3 (4F), bridging $-CF_2CF_2-$; 121.2 (2F), difluoromethylene; and an AB quartet (2F, δ_A=100.1, δ_B=118.2, J_{AB} 250 Hz), difluoromethylene:

the ^{1}H n.m.r. spectrum showed two bands at 1.27 (3H) and 2.73 (1H, d, J = 15). (iii) 4H-tetradecafluoro-6-methylpentacyclo[$7,2,2,1^{3,7}0^{4,6}0^{2,8}$]deca-2,10-diene (XXIII) (0.19 g., 0.422 mmoles, 7.3%) (Found: F,58.5%, M (mass spectrometry) 450) a colourless solid, ν_{max} 1754 cm^{-1} (-CF=CF-). The ^{19}F n.m.r. spectrum showed resonances at 238.4 (1F), 219.6 (1F) and 212.7 (2F) assigned to fluorines at tertiary sites; 151.7 (1F) and 150.6 (1F), vinylic fluorines; a series of eight bands between 135.2 and 121.7 (6F) ascribed to the bridging $-CF_2CF_2-$ and the difluoromethylene bridge between C-3 and C-7; and an AB quartet (2F, δ_A=106.2, δ_B=125.7, J_{AB} = 178) assigned to the difluoromethylene of the three-membered ring: the ^{1}H n.m.r. spectrum showed two bands at 1.55 (3H, CH_3) and 3.12 (1H, tertiary proton). (iv) 4H-decafluoro-5-methyltricyclo[$6,2,2,0^{2,7}$]dodeca-2,4,6,9-tetraene (XIX) (0.75 g., 2.14 mmoles, 36.8%) (Found: C,44.8; H,1.2; F,53.8%; M (mass spectrometry), 350. $C_{13}H_4F_{10}$ requires C,44.6; H,1.2; F,54.3%; M,350) a colourless liquid, ν_{max} 1773 (-CF=CF-), λ_{max} 272 (ϵ, 1800) and 279 nm (ϵ,2160).

(c) With but-2-yne. By the same procedure as in (a) triene (X) (4.60 g., 12.8 mmoles) and but-2-yne (0.77 g., 14.3 mmoles) were heated in a Pyrex ampoule (100 ml.) at 120° for 64.5 hr. to give: (i) a volatile fraction (0.88 g.) shown by infrared spectroscopy to be a mixture of triene (X) and but-2-yne; (ii) a white solid (4.38 g.) shown by analytical gas chromatography to contain two components in the ratio 23:77. This mixture was separated by fractional sublimation (10^{-3} mm, 80°) followed by fractional crystallisation to give the two isomers of dodecafluoro-4,5-dimethyltetracyclo[$6,2,2,1^{3,6}0^{2,7}$]trideca-2,4,9-triene (XVII) and (XVIII). For the isomer with the shorter gas chromatographic retention time, the minor component, (XVII) (Found: C,43.9; H,1.2; F,55.2%; M (mass spectrometry) 414. $C_{15}H_6F_{12}$ requires C,43.5; H,1.5; F,55.0%; M, 414). Recrystl. from methanol as fine needles m.p. 64.5-65°,

ν_{max} 1760 (-CF=CF-) and 1620 cm^{-1} (-C(CH_3)=C(CH_3)- or $>$C=C$<$). For the isomer with the longer gas chromatographic retention time, the major component, (XVIII) (Found: C,43.2; H,1.2; F,54.6%; M (mass spectrometry), 414), recrystl. from petroleum (60/80) as platelets m.p. 82-82.5°, ν_{max} 1760 (-CF=CF-) and 1630 cm^{-1} (-C(CH_3)=C(CH_3)- or $>$C=C$<$).

2.6 Vacuum Pyrolyses

The apparatus consisted of a silica tube (62 cm x 1.2 cm int. diam.) lightly packed with silica wool. The middle 45 cm. were heated in an electric furnace and temperatures were measured at the outside surface of the pyrolysis tube, in the middle of the furnace, by a chrome-alumel thermocouple. A Pyrex reservoir containing the compound to be pyrolysed was attached to one end of the silica tube and a Pyrex trap was attached to the other end, the exit of the pyrolysis apparatus being connected to the vacuum system. The pyrolysis technique used involved cooling the reservoir and trap in liquid air, evacuating to the required pressure, and then allowing the reservoir to warm up to room temperature. When all the material to be pyrolysed had passed through the pyrolysis tube and the products had been collected in the liquid air trap, gaseous products were expanded into the calibrated gas measuring system, liquid products and solid products being recovered in the usual way.

(a) Compound (XIX). (0.27 g., 0.77 mmoles) was pyrolysed at 540°/10^{-3}mm followed by a further pyrolysis at 630°/10^{-3} mm to give: (i) a gas mixture (0.78 mmoles), shown by mass and infrared spectroscopy to be predominantly tetrafluoroethylene with a trace of silicon tetrafluoride; (ii) a yellow solid, sublimed (70°/10^{-3}mm) to give a colourless solid 2H-hexafluoro-3-methyl-naphthalene (XXI) (0.134 g., 0.54 mmoles, 70%) (Found: C,53.0; H,1.9; F,45.1%; M (mass spectrometry), 250. $C_{11}H_4F_6$ requires C,52.8; H,1.6; F,45.6%; M,250) m.p. *ca.* room temperature.

(b) Compounds (XV) and (XVI). An equimolar mixture of (XV) and (XVI) (0.207 g., 0.52 mmoles) was pyrolysed at $640^{o}/10^{-3}$ mm to give (i) a gas mixture (0.84 mmoles), shown by mass and infrared spectroscopy to be predominantly tetrafluoroethylene with a trace of silicon tetrafluoride; (ii) a yellow solid which gave as a colourless solid after sublimation ($70^{o}/10^{-3}$mm) 2H-hexafluoro-3-methylnaphthalene (XXI) (0.072 g., 0.283 mmoles, 55.4%), with correct infrared spectrum.

(c) Compound (XVIII). (0.813 g., 1.96 mmoles) was pyrolysed at $380^{o}/10^{-3}$mm to give (i) tetrafluoroethylene (0.995 mmoles), identified by infrared and mass spectroscopy; (ii) decafluoro-4,5-dimethyltricyclo[6,2,2,$0^{2,7}$]dodeca-2,4,6,9-tetraene (XX) (0.462 g., 1.27 mmoles, 64.8%) (Found: C,46.4; H,2.0; F,51.9%; M (mass spectroscopy), 364. $C_{14}H_6F_{10}$ requires C,46.2; H,1.7; F,52.2%; M, 364) recrystl. from petroleum (60/80) m.p. 66-67°, ν_{max} 1779 cm^{-1} (-CF=CF-), λ_{max} 272 (ϵ, 2680) and 279 nm (ϵ, 2850).

(d) Compound (XX). (0.245 g., 0.673 mmoles) was pyrolysed at $600^{o}/10^{-3}$mm to give (i) a gas mixture (0.363 mmoles) shown by mass and infrared spectroscopy to be predominantly tetrafluoroethylene with a trace of silicon tetrafluoride; (ii) a yellow solid (0.198 g.) recrystl. from petroleum (60/80) to give as a colourless solid in quantitative yield, 2,3-dimethylhexafluoronaphthalene (XXII) (Found: C,54.3; H,2.5%; M(mass spectrometry), 264. $C_{12}H_6F_6$ requires C,54.6; H,2.3%; M, 264) m.p. 120-121° (sealed tube).

2.7 Attempted reaction of βH,β-methyldecafluorobenzobicyclo[2,2,2]oct-2-ene (XIX) with tetrafluoroethylene.

A mixture of compound (XIX) (0.057 g., 0.163 mmoles) and tetrafluoroethylene (0.082 mmoles) was sealed under vacuum in a Pyrex ampoule (5 ml.) and

heated at 200° for 68 hr. to give (i) tetrafluoroethylene, with correct infrared spectrum and (ii) compound (XIX) (0.032 g.) with correct infrared spectrum.

2.8 Heating 4H,5-methyl-dodecafluorotetracyclo[6,2,2,1,^{3,6}0^{2,7}]tridec-2,4,9-trienes (XV) and (XVI).

An equimolar mixture of compound (XV) and (XVI) (0.10 g., 0.25 mmoles) was sealed under vacuum in a Pyrex ampoule (70 ml.) which was heated at 200° for 90 hr. to give (i) a gas (0.077 mmoles), discarded and (ii) a colourless liquid (0.076 g.). Analytical gas chromatography of this mixture and of the mixture enriched with authentic samples of compounds (XIX), (XXIII) and (XXIV) established that the mixture contained four components, the major component had a retention time identical with that of compound (XIX) and the two minor components had retention times identical with compounds (XXIII) and (XXIV), the fourth component was present in trace amounts only. The infrared spectrum of the mixture was entirely consistent with its being predominantly compound (XIX) with small concentrations of (XXIII) and (XXIV).

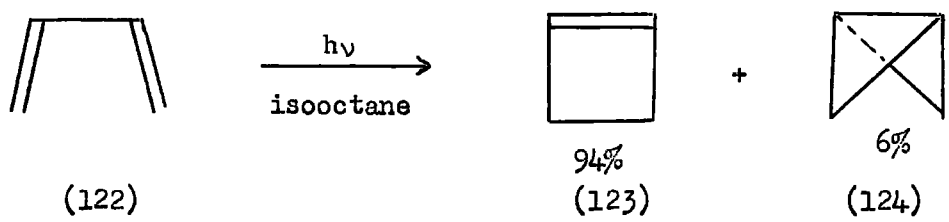
CHAPTER 3

THE PHOTOCHEMICAL ISOMERISATION OF TETRADECAFLUOROTRICYCLO[6,2,2,$0^{2,7}$]-DODECA-2,6,9-TRIENE, DODECAFLUOROTRICYCLO[5,2,2,$0^{2,6}$]UNDECA-2,5,8-TRIENE, AND 2H-HEPTAFLUOROCYCLOHEXA-1,3-DIENE. SOME REACTIONS OF THE PHOTO-ISOMERS INCLUDING A SYNTHESIS OF PERFLUOROINDENE

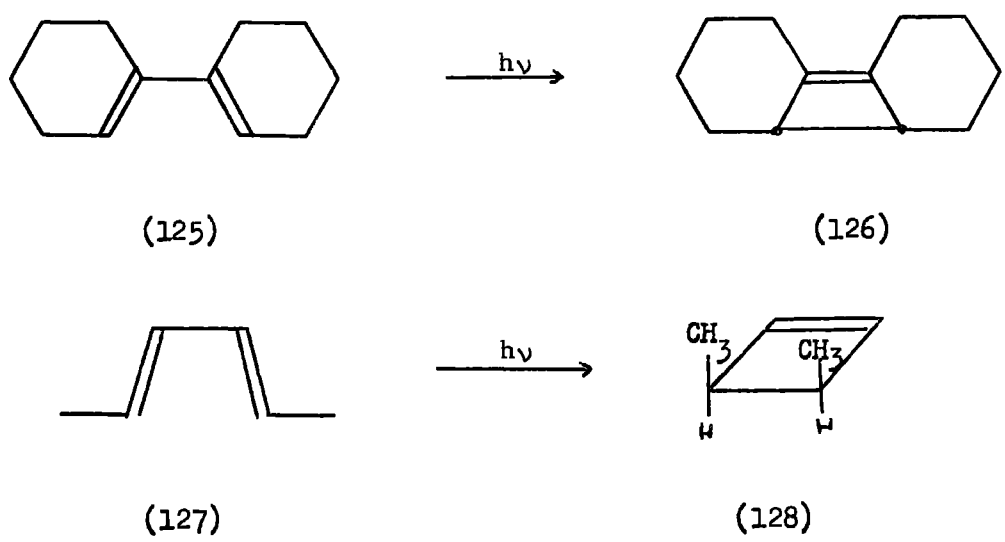
INTRODUCTION

3.1 Unsensitized Photoisomerisations of Cycloalka-1,3-dienes[146]

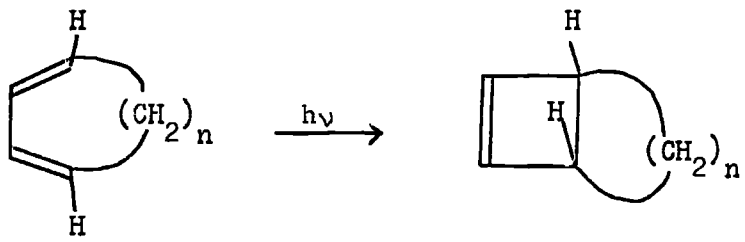
The development of the concept of orbital symmetry control of concerted reactions[6] has led to interest in a class of stereospecific intramolecular cycloadditions known as electrocyclic reactions. An electrocyclic reaction is defined as the interconversion of a conjugated polyene and the cyclic structural isomer formed by bonding between the terminal carbon atoms, and can be illustrated by the photoisomerisation of buta-1,3-diene (122) to cyclobutene (123); bicyclo[1,1,0]butane (124) is also formed as the minor product.



There are a large number of examples of the interconversions of buta-1,3-dienes and cyclobutenes, and these processes are predicted to be conrotatory in the ground state and disrotatory in the excited state, if concerted. In agreement with this proposition is the conversion of (125) to a single product (126) on irradiation and in similar fashion the formation of (128) from (127).



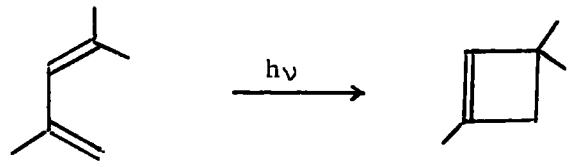
If the buta-1,3-diene moiety is incorporated in a ring system conrotatory ring closure now becomes impossible and the cycloalka-1,3-diene is instead ideally constrained to undergo photochemical ring-closure to a bicyclic cyclobutene derivative in a disrotatory process, as shown below. For values of n



other than n = 2 this is the only symmetry-allowed photochemical process, however for n = 2 there is an alternative symmetry-allowed process, conrotatory ring-opening to a hexa-1,3,5-triene, and the photochemistry of cyclohexa-1,3-dienes contains examples of both ring-opening and ring-closing processes, the former processes being more common in the absence of steric constraints. Apart from the exceptional behaviour of cyclohexa-1,3-dienes it is generally found in photochemical electrocyclic reactions that ring-closure reactions are more common, for example photochemical ring-opening of cyclobutenes to the corresponding buta-1,3-dienes is not normally significant, and this has been interpreted in terms of the ring-opened products having more extended chromophoric systems and being less transparent to ultra-violet light than their less-conjugated ring-closed isomers.

Formation of bicyclobutanes on irradiation of butadienes is not a common process, although due to the high reactivities of these compounds they may be lost before isolation. They have been formed in rigid molecules where the diene fragment is held in an S-trans configuration.

The course of a photochemical reaction may depend upon the conditions of irradiation. Thus cyclobutene (130) is prepared by irradiating the vapour of (129); it has not been obtained by irradiation in solution.[147]



(129) (130)

Only unsensitized photoisomerisations are considered in the following discussion; additional complications can arise in the presence of triplet sensitizers.

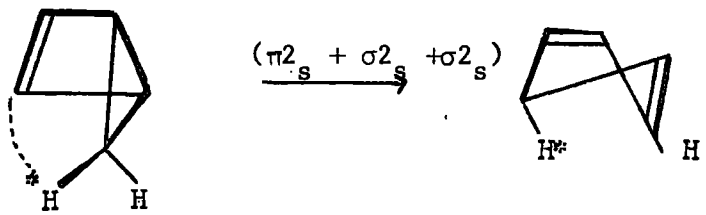
3.2 Irradiation of Cyclopentadienes

Bicyclo[2,1,0]pent-2-ene (131), previously postulated as an intermediate has recently been isolated as the product of irradiation of cyclopentadiene. By irradiating an ice-cold 0.3M solution of cyclopentadiene in ethanol yields of up to 15% were obtained.[148] The success of this photoisomerisation depends on the conditions of irradiation and isolation and although 2-methylbicyclo[2,1,0]pent-2-ene can be prepared by irradiating 2-methylcyclopentadiene, irradiation of 5,5-dimethylcyclopentadiene under similar conditions did not yield any isolable photoisomer.[149]

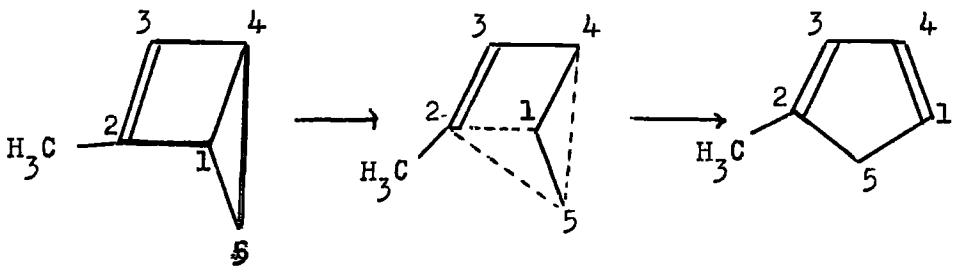
(131)

Bicyclic compounds analogous to (131) are extremely strained and decompose on standing to cyclopentadienes; 2-methylbicyclo[2,1,0]pent-2-ene and bicyclo[2,1,0]pent-2-ene (131) have half-lives of the same order, c. $4\frac{1}{2}$ hours at 47°.[149] The simplest explanation of their decomposition would be a disrotatory ring opening, a disallowed thermal process if concerted. The mechanism of this decomposition has been the subject of considerable investigation. Gas phase

kinetic work and deuterium labelling of the 5-positions of bicyclo[2,1,0]pent-2-ene (131) did not disprove a diradical process involving cleavage of the 1,4-bond, however the symmetry-allowed ($\pi 2_s + \sigma 2_s + \sigma 2_s$) process involving a [1,5]-sigmatropic hydrogen shift could not be the mechanism involved as the cyclopentadiene formed from thermal decomposition of bicyclo[2,1,0]pent-2-ene labelled in the 5-position was itself labelled only at the 5-position. The ($\pi 2_s + \sigma 2_s + \sigma 2_s$) process is illustrated below.



Further mechanistic data was obtained from the observation of Baldwin and Andrist that 2-methylbicyclo[2,1,0]pent-2-ene (132) rearranged to 1-methylcyclopentadiene (133), a rearrangement best explained in terms of a concerted ($\sigma 2_s + \sigma 2_a$) process which is symmetry-allowed in the ground state, see below.

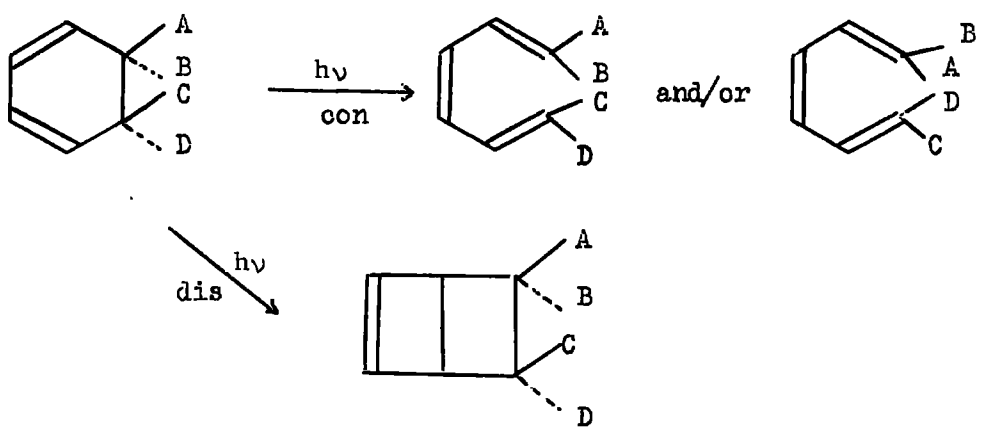


(132) (133)

A diradical mechanism must involve preliminary [1,3]-sigmatropic migration with inversion at C5 to produce 1-methylbicyclo[2,1,0]pent-2-ene followed by cleavage of the 1-4 bond. These two mechanistic possibilities would be distinguishable on rearrangement of 1,4- or 2,3-dideuterobicyclo[2,1,0]pent-2-ene.[150] As it appears that the impossibility of a normal conrotatory ring-opening enables the usually unimportant ($\sigma 2_s + \sigma 2_a$) process to occur, Baldwin et al. have examined other systems in which steric constraints make more usual processes impossible but have so far been unable to report any other examples of this process.[151]

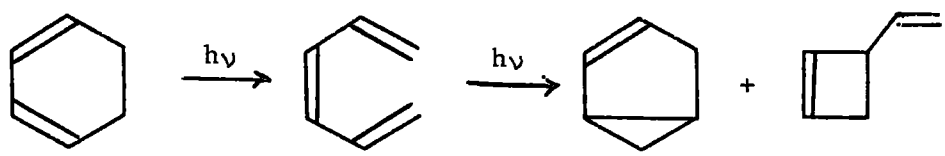
3.3 Irradiation of Cyclohexa-1,3-dienes[146]

The most usual reaction of a simple cyclohexa-1,3-diene on irradiation is the conrotatory ring-opening to a cis-cis hexa-1,3,5-triene, which can often undergo further photochemical reaction. Formation of bicyclo[2,2,0]hex-2-enes occurs in special circumstances; thus the electrocyclic ring closure of highly fluorinated cyclohexa-1,3-dienes may be attributed to the strength of C-C σ-bonds bearing fluorine as a substituent or the aversion of fluorine for vinylic sites, and in some complex molecules stereochemical restrictions can make the ring-opening process impossible. Both these processes are illustrated below.



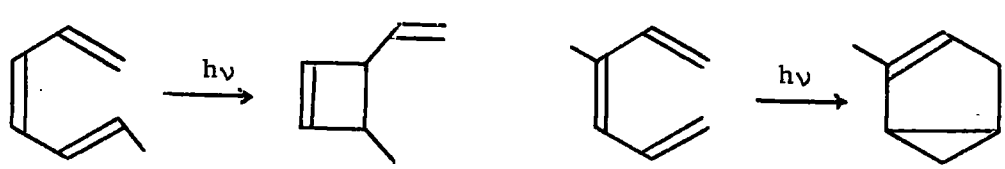
Formation of bicyclo[2,1,1]hex-2-enes has never been observed on irradiation of cyclohexa-1,3-dienes.[152]

Cyclohexa-1,3-diene (134), irradiated as a 1% ethereal solution, yields 1,3,5-hexatriene (135) initially, however prolonged irradiation leads to bicyclo[3,1,0]hexene (136) and 3-vinylcyclobutene (137) in equal amount.



(134) (135) (136) (137)

In contrast the 3-vinyl cyclobutene (139) and the bicyclo[3,1,0]hexene (141) are the major products formed on irradiation of 1-methylhexatriene (138) and 3-methyl hexatriene (140) respectively.

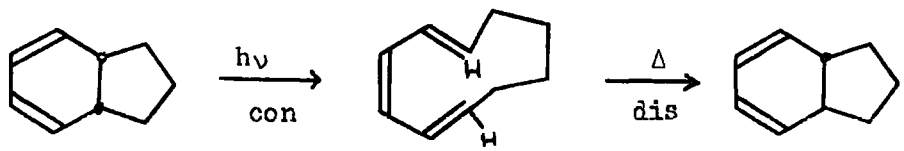


(138) (139) (140) (141)

Vinylcyclobutene formation is presumably an electrocyclic ring closure in which only two of the conjugated double bonds participate whereas bicyclo[3,1,0]hexenes are formed via a photochemical ($2_\pi + 4_\pi$) intramolecular Diels-Alder reaction.[146]

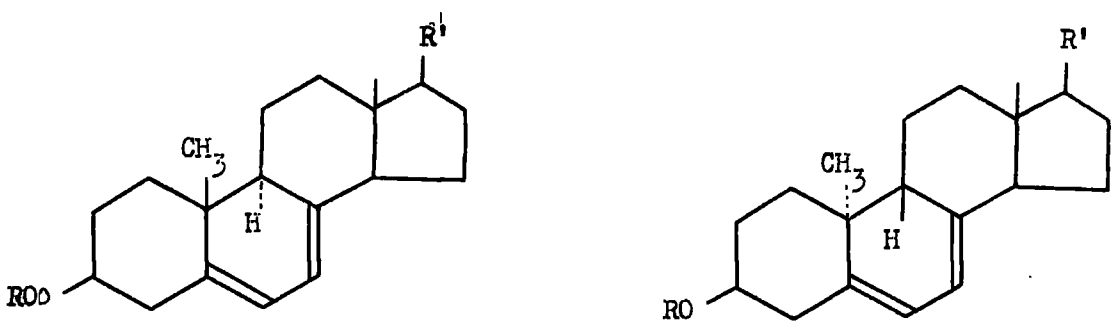
The conrotatory nature of the ring-opening of cyclohexa-1,3-dienes on irradiation is evident in the conversion of cis bicyclo[4,3,0]nona-2,4-diene

(142) to its trans isomer (144), the process involving the intermediacy of trans-cis-cis-cyclonona-1,3,5-triene (143), (144) being produced by thermal dis-rotatory ring-closure of (143).[153]

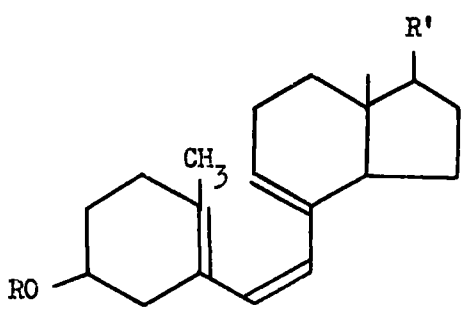


(142) (143) (144)

Several important isomerisations of this type have been observed in natural product chemistry, especially in the vitamin D field, see below.



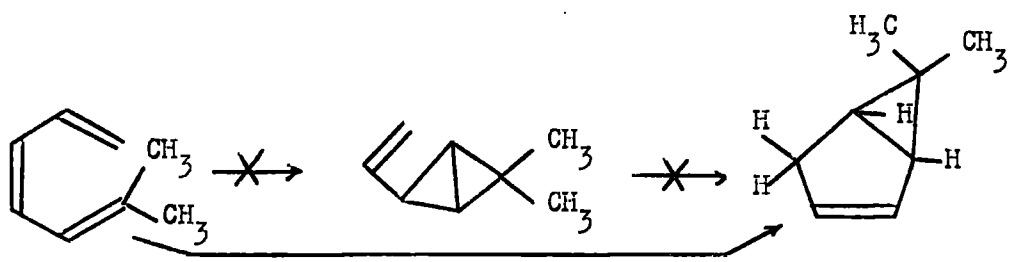
(145) (146)



(147)

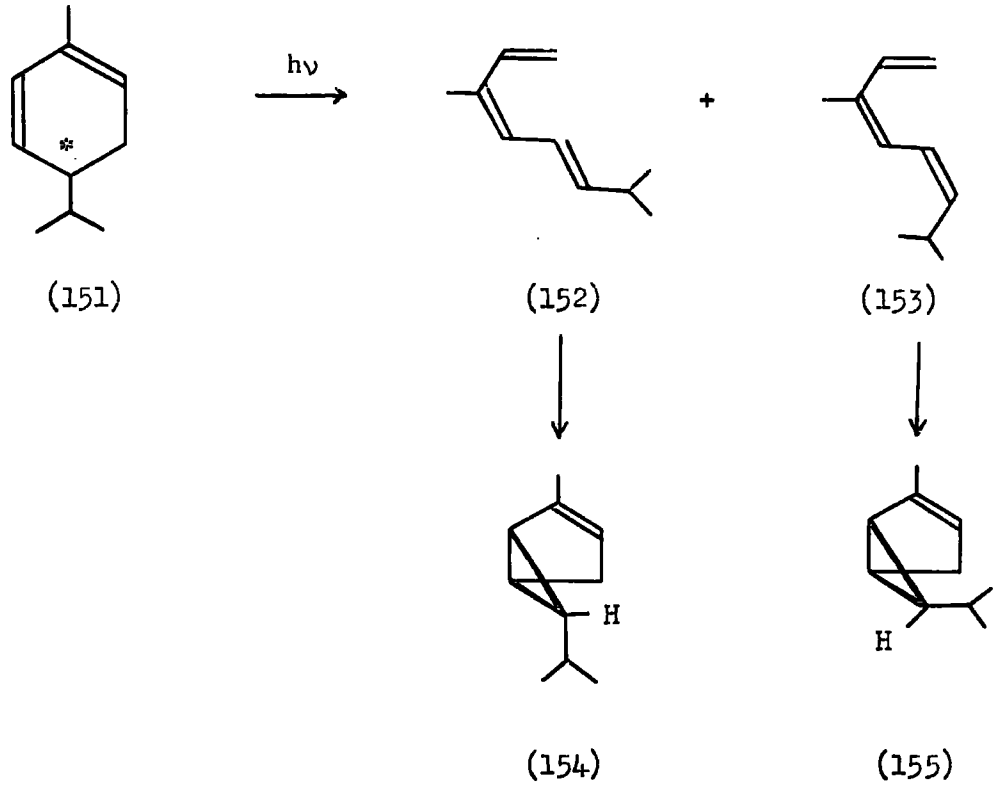
In these cases disrotatory ring-closure of (145) and (146) would be geometrically impossible, leading to a trans-fusion between the cyclohexane and cyclobutane rings.[6]

The formation of bicyclo[3,1,0]hexenes by the irradiation of cyclohexa-1,3-dienes and hexa-1,3,5-trienes has been extensively investigated. Some subtle experiments have been devised in order to clarify the exact nature of the precursors of these species. Deuteration studies have shown that 1,1-dimethylhexatriene (148) is photoisomerised to 6,6-dimethylbicyclo[3,1,0]hexene (150) without the intermediacy of the vinylbicyclobutane (149).[146] However as

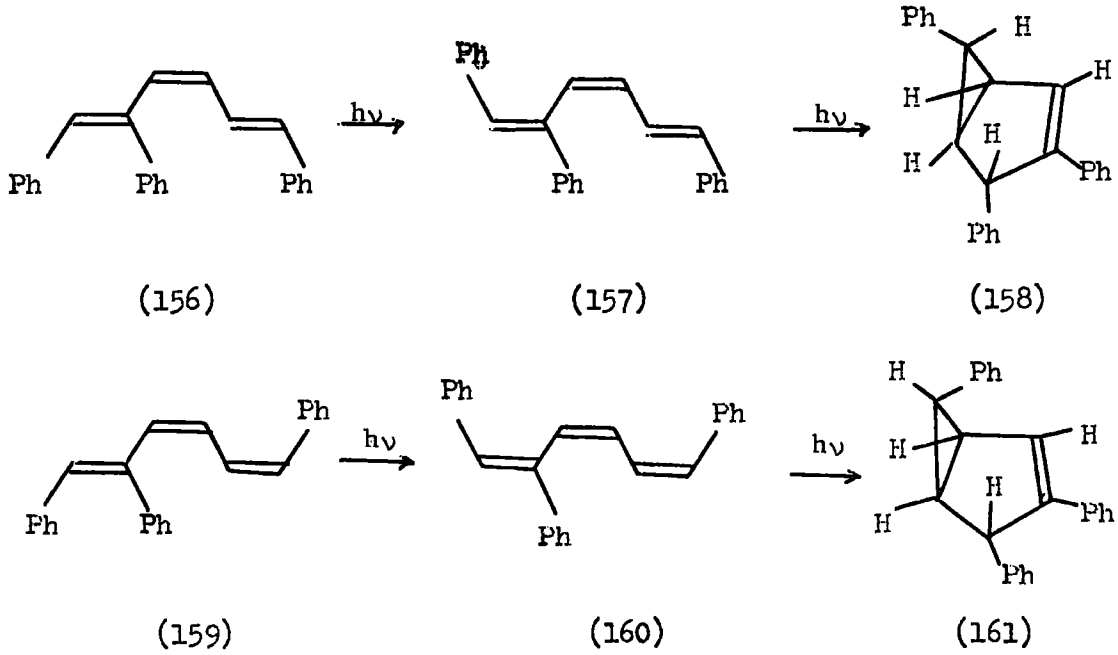


(148) (149) (150)

optically active α-phellandrene (151) yields an inactive product (154) we need to postulate an intermediate in which chirality is lost, the suggested reaction scheme involves trienes (152) and (153), the former which will predominate for steric reasons leads to the major product (154), a small amount of (155) is formed from the latter. It appears that in the majority of cases the initial process is formation of a hexa-1,3,5-triene by irradiation of a cyclohexa-1,3-diene, the bicyclo[3,1,0]hexene then being formed from the triene by a photochemical Diels-Alder reaction. Both ($\pi 4_s + \pi 2_a$) and ($\pi 2_s + \pi 4_a$) are symmetry-allowed processes,[6] irradiation of some 1,2,6-triphenyl-1,3,5-hexatrienes has shown that in these cases at least the former process only is followed. Thus irradiation of the Z,Z,E-triene (156) led to



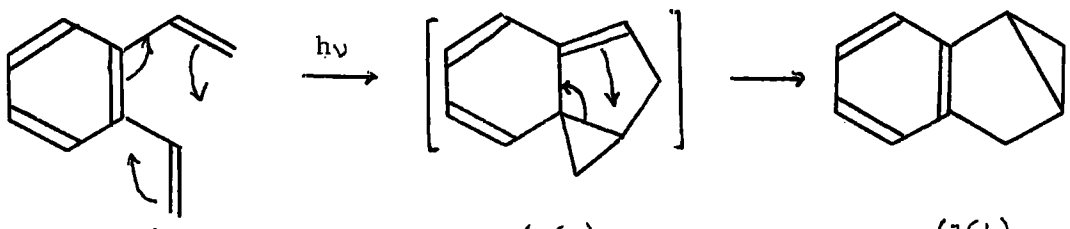
the bicyclo[3,1,0]hexene (158) via the rearranged triene (157) and similarly the Z,Z,Z-triene (159) photoisomerised to the bicyclo[3,1,0]hexene (161) via triene (160). The initial isomerisations about the 1,2-double bond relieve



cis-diphenyl non-bonded interactions and are fast relative to the ($\pi 4_s + \pi 2_a$) process. The ($\pi 4_s + \pi 2_a$) route would be expected to be more favourable than ($\pi 2_s + \pi 4_a$) both in terms of its lesser steric requirement and the nodal structure of the lowest antibonding level of the transoid conformer of the hexatriene.[154]

There is a single example in which formation of a bicyclo[3,1,0]hexene proceeds directly from the cyclohexa-1,3-diene without the intermediacy of the hexa-1,3,5-triene.[147]

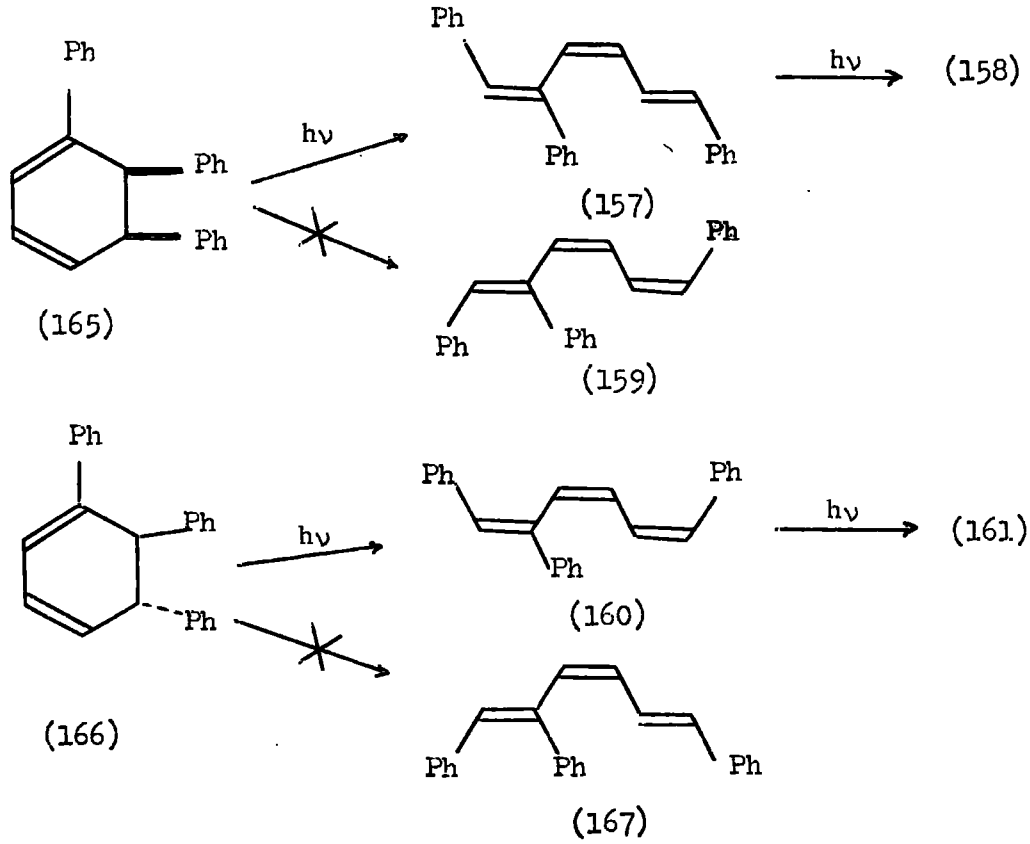
Although acyclic-1,3,5-trienes generally isomerise to bicyclo[3,1,0]hexenes on irradiation, other processes have been observed where the central double bond of the triene system is replaced by an aromatic ring. Thus irradiation of o-divinylbenzene (162) led to benzobicyclo[3,1,0]hex-2-ene (164), rationalised by the initial formation of the bicyclo[3,1,0]hexene (163) which is transformed to (164) via a vinylcyclopropane ⟶ cyclopentene rearrangement which restores aromaticity. Similar processes also occur in the photochemistry of divinyl naphthalenes.[155]



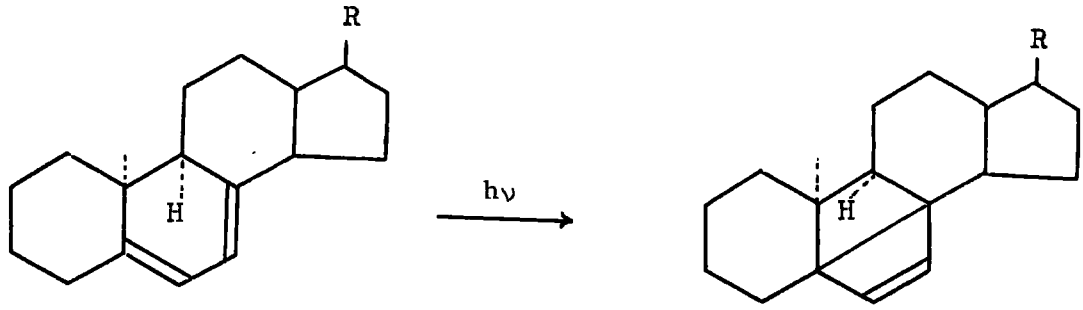
(162) (163) (164)

There are two possible modes of conrotatory ring-opening of a cyclohexa-1,3-diene and secondary steric forces can lead to the predominance of one of these processes. Irradiation of cis-1,5,6-triphenylcyclohexa-1,3-diene (165) and trans-1,5,6-triphenylcyclohexa-1,3-diene (166) produced products derived from trienes (157) and (160) respectively; there was no evidence of products which would have been derived from the alternative conrotatory modes via trienes (159)

and (167). The observed products are in agreement with the most favourable mode of ring opening minimising steric interaction between the bulky phenyl groups.[156]

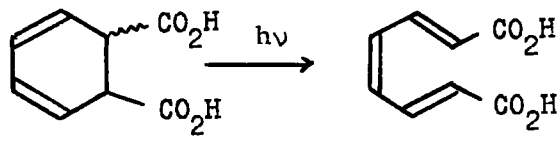


The first example of the formation of a bicyclic cyclobutene derivative by irradiation of a cyclohexa-1,3-diene was the irradiation of pyrocalciferol (168) to yield the pentacyclic isomer (169), the syn isomer of (168) behaving analogously and contrasting with the photochemical behaviour of the closely related anti structures (145) and (146) which ring-open to hexa-1,3,5-trienes.

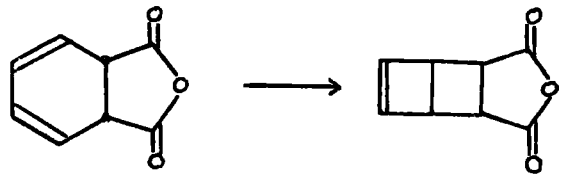


(168) (169)

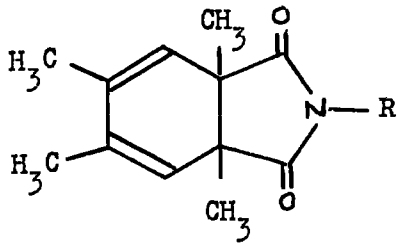
Ring-opening of (168) or its syn isomer in a conrotatory mode is impossible as the resulting product would contain a trans double-bond in a six-membered ring; thus the alternative allowed process is followed. Similarly irradiation of the cis and trans acids (170) leads to triene (171) whereas for the corresponding anhydride (172) the tricyclic compound (173) is formed in the alternative allowed process, as ring opening of (172) in conrotatory fashion would result in a strained 9-membered ring system. Compounds related to (172) in structure such as the imides (174) and (175) also produce bicyclo[2,2,0]-hex-2-enes on u.v. irradiation.[157]



(170) (171)

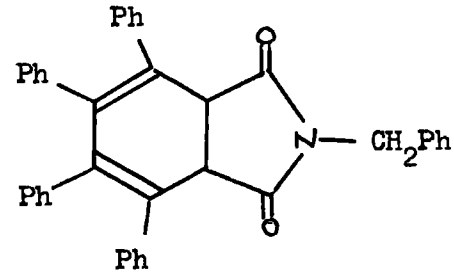


(172) (173)



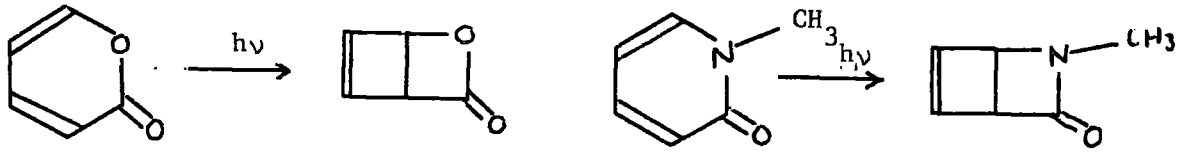
(174)

R = H,Ph,Bu



(175)

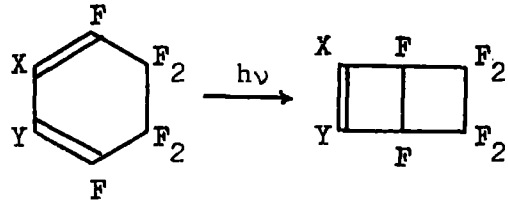
2-pyrone (176) is quantitatively converted to (177) on irradiation in ether, N-methyl-2-pyridone (178) isomerises to (179) in a 20% yield under similar conditions.



(176) (177) (178) (179)

Compounds (177) and (179) are of interest as they are formal 1,4-adducts of cyclobutadiene and the stable molecules carbon dioxide and methyl isocyanate respectively, this could account for their explosive decompositions on warming.[158]

Contrary to the behaviour of simple hydrocarbon cyclohexa-1,3-dienes the irradiation of the highly fluorinated cyclohexa-1,3-dienes (180) (X = Y = F; X = Y = H; X = Y = OCH_3; X = OCH_3, Y = F) leads to the corresponding bicyclo-[2,2,0]hex-2-enes (181) as the only photo products, yields being excellent except for irradiation of (180) (X = Y = OCH_3) when the yield was poor due to the instability of the diene.[84,159]



(180) (181)

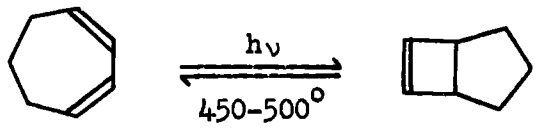
Although 2,3-dimethylhexafluorobicyclo[2,2,0]hex-2-ene (181) (X = Y = CH_3) was readily prepared by treatment of perfluorobicyclo[2,2,0]hex-2-ene (181) (X = Y = F) with methyl lithium it was not obtained on irradiating the corresponding diene (180) (X = Y = CH_3), only resin and silicon tetrafluoride being isolated.

It has been suggested that diene (180) (X = Y = CH_3) eliminates hydrogen fluoride on irradiation yielding a readily polymerisable triene. The explanation proposed for the difference between the products obtained on irradiation of (180) as against its hydrocarbon analogues was the differing strengths of the bonds which must be cleaved in forming the acyclic triene by conrotatory ring-opening; carbon-carbon sigma bonds bearing fluorine substituents being stronger than carbon-carbon sigma bonds in hydrocarbons.[67] Pyrolysis of the photoisomers (181) under a pressure of about 10^{-3} mm.Hg. at temperatures of 300-400° led to quantitative conversion back to the original dienes (180).[84,159]

3.4 Irradiation of Cycloalka-1,3-dienes containing Larger Rings

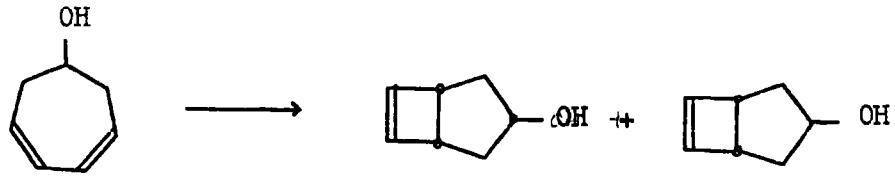
For cycloalka-1,3-dienes containing rings of more than six carbon atoms ring-closure to the corresponding bicycloalkene is the only photochemically-allowed concerted electrocyclic process.

Irradiation of a number of cyclohepta-1,3-dienes has resulted in their isomerisation to the corresponding bicyclo[3,2,0]heptenes. The parent compound (182) was smoothly converted to its photoisomer (183) in 60% yield on irradiation in diethyl ether, the process being reversed on heating the photoisomer to 450-500°.



(182) (183)

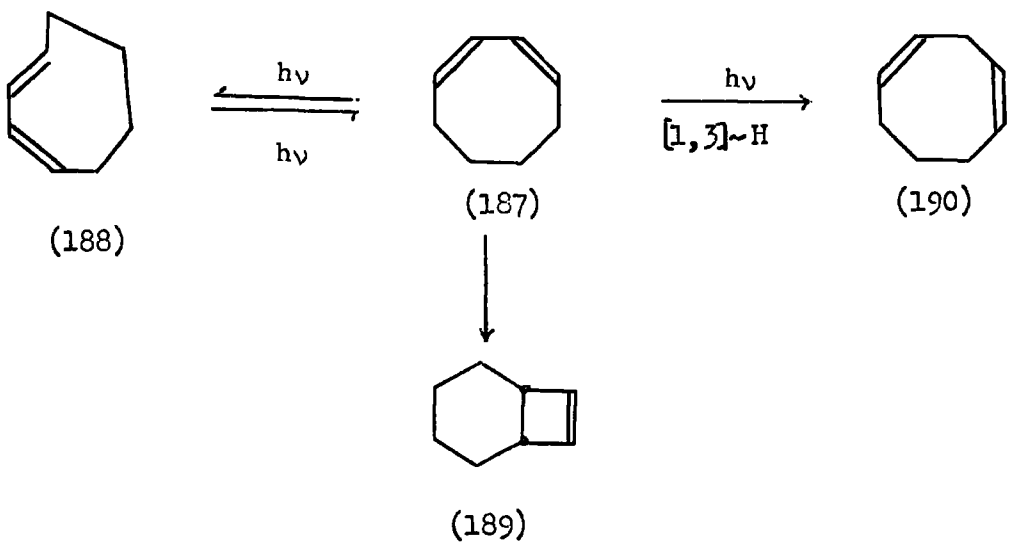
In the case of 3,5-cycloheptadienol (184) two photoisomers (185) and (186) were obtained in the ratio 3:1 respectively.[160]



(184) (185) (186)

Cycloalka-1,3-dienes containing rings of eight or more atoms can exist in both cis-cis and cis-trans forms and interconversion of these two isomers is the major photochemical process. The reaction is further complicated by the occurrence of sigmatropic migrations in addition to electrocyclic reactions.

The photochemical processes which occur on irradiation of cis-cis-cyclo octadiene (187) are shown below. Irradiation in a solvent results in the

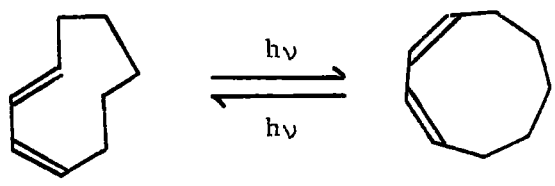


(188) (187) (190) (189)

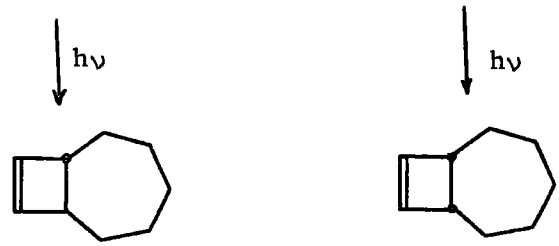
transformation of (187) to (188), its cis-trans isomer, the major photochemical process; competing processes are ring closure to bicyclo[4,2,0]oct-7-ene (189) and a photochemical [1,3]-sigmatropic hydrogen shift to cis,cis-1,4-cyclo-octadiene (190). Thermal isomerisation of (188) to (189), an allowed concerted

disrotatory process, occurs on heating to 80°.[161]

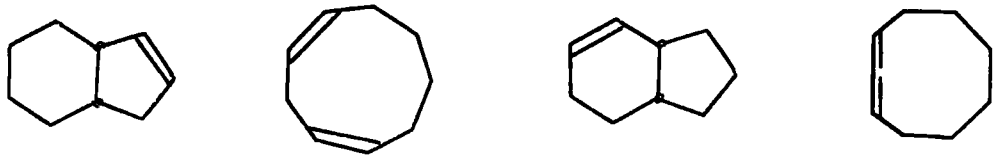
The complexity of photoproducts is much more marked for larger ring cycloalka-1,3-dienes although the transformations can all be assommodated in terms of orbital symmetry control, the stereochemistry of the processes being reversed on changing from the ground to the excited state. In the case of irradiation of ether solutions of cis,cis-1,3-cyclononadiene (191) or its cis-trans isomer (192) the products obtained are shown below. The major process once more is the interconversion of the cis-cis diene (191) and the cis-trans diene (192). Electrocyclic ring closure of (192) leads to (193) and that of (191) leads to (194) by a concerted disrotatory process, the other products (195)— (198) being formed by sigmatropic processes.[162]



(192) (191)



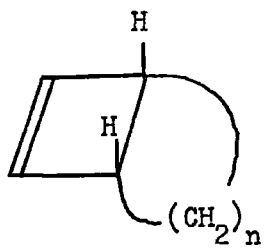
(193) (194)



(195) (196) (197) (198)

3.5 Thermal Stabilities of Bicyclo[n,2,0]alkenes (199)

The photoisomers of cycloalka-1,3-dienes formed by disrotatory ring closure, (199), have remarkably different stabilities. This is reflected in the temperature (T) at which the half-life of (199) is 2 hrs., see below.[6]



(199)

TABLE 14

Temperature (T) at which the half-life of (199) is 2h.[6]

n	1	2	3	4	5	6
T(°C)	< 100°	195°	> 380°	350°	335°	180°

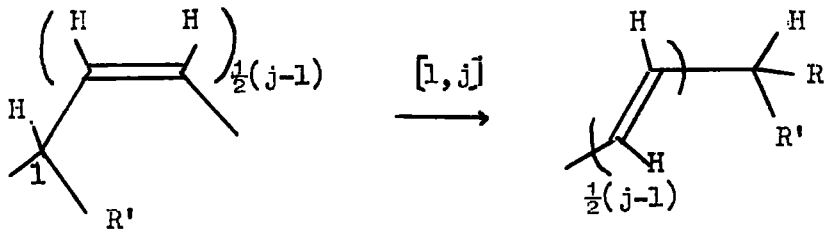
The symmetry-allowed mode of thermal ring opening of (199) in a concerted process is a conrotatory motion to produce a cis-trans diene. For n = 6 to n = 3 the stabilities of compounds (199) can be related to the ease of forming a trans double bond in a cycloalkene, a cis-trans diene being far easier to form in the case of n = 6 than for n = 3. Thus the order of stabilities appears to follow that expected for thermal decomposition in a concerted process. Although the product isolated from these thermal isomerisations is invariably a cis-cis diene, it has recently been shown that for the decomposition of (199) n = 4, the cis-trans diene is initially formed and rapidly isomerises,

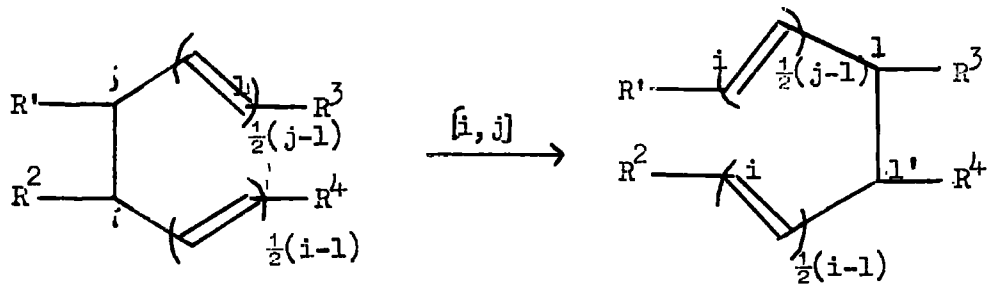
presumably via a [1,5]-hydrogen migration, and instead of an apparently disrotatory ring-opening we are observing two symmetry-allowed steps. This explanation appears to account for the cases of n = 3 to 6.[163]

For compounds (199) of n < 3 the trans double bond cannot be incorporated into the diene system expected from a thermal concerted process, and their stability appears to be more related to the strain inherent in the bicyclic compound (199). That these compounds exist at all must at least in part be due to the disrotatory ring opening to their decomposition products being disallowed as a concerted process. The decomposition of bicyclopentenes has been discussed previously and appears to be by an allowed concerted $[\sigma 2_s + \sigma 2_a]$ process; for the case of n = 2 there does not appear to be any compelling evidence to enable a distinction to be made between a disrotatory ring-opening or a diradical process.[164]

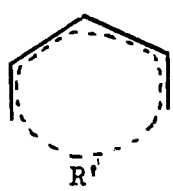
3.6 Sigmatropic Rearrangements[165]

A sigmatropic change is defined as the migration of a σ bond flanked by one or more π-electron systems to a new position within a molecule in an uncatalysed intramolecular process. The relationship of the σ-bond to the termini of the π-system(s) determines the reaction order of the rearrangement; thus migration of a σ-bonded atom or group R' from one end to the other of an allylic or polyenic chain is a sigmatropic change of order [1,j] where R' migrates from C(1) to C(j); and in a reaction of order [i,j] the σ-bond joining C(i) and C(j) is broken, the carbon framework being numbered from the terminus of each π-system, as below.

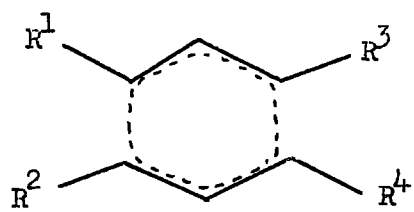




The transition state for a [1,5]-shift can be represented by (200) and that for a [3,3]-rearrangement by (201).



(200)



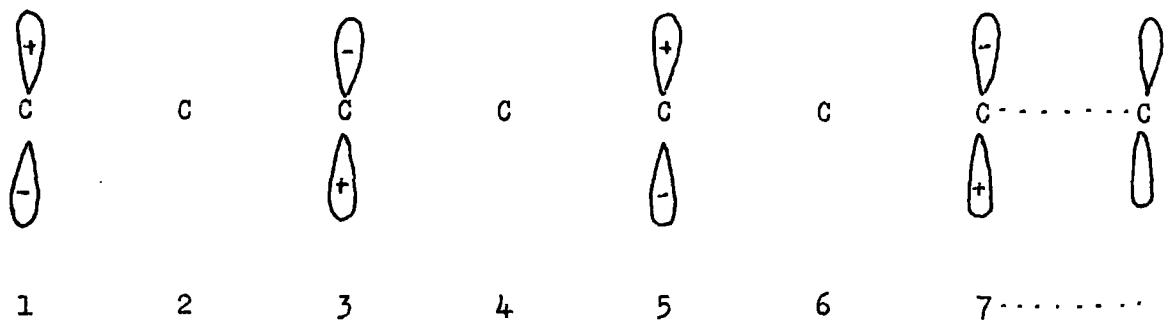
(201)

The following discussion is concerned solely with sigmatropic migrations of order [1,j] in neutral species.

3.7 Selection Rules for [1,j] Sigmatropic Migrations[165]

Orbital symmetry arguments of Woodward and Hoffmann have been applied to sigmatropic migrations by considering the process to involve two interacting radicals, the migrating group and the hydrocarbon 'framework' radical. The selection rules are derived by considering the symmetry of the highest occupied molecular orbital of the 'framework' radical and that of the

relevant orbital of the migrating group. In the case of thermal migrations in a linear polyene the odd electron is in the non-bonding electronic energy level shown below.



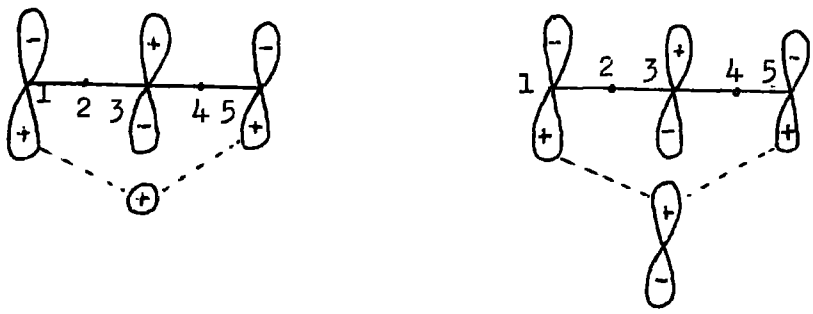
For [1,j]-sigmatropic migrations there are two different transition state geometries, corresponding to suprafacial and antarafacial processes; in a suprafacial process the migrating group is associated at all times with the same face of the π-system whereas in an antarafacial process the migrating group passes from the top face of one carbon terminus to the bottom face of the other. A further distinction is possible between sigmatropic migrations based on the symmetry of the orbital used by the migrating group in bonding to the unsaturated system; in a case I process the migrating group is bonded through a symmetric orbital or through one lobe of an antisymmetric orbital; in a case II process both lobes of an antisymmetric orbital are utilised in bonding to the unsaturated system.[166]

If we now consider thermal sigmatropic migration in a linear polyene, it is evident from the symmetry of the relevant orbital of the polyene, see above, and the migrating group, that [1,3]-sigmatropic migrations of case I, e.g. hydrogen migrations, will be antarafacial whereas [1,5]-sigmatropic hydrogen migrations will be suprafacial, hydrogen bonding to the polyene by its s orbital. For case II processes a [1,3]-thermal shift would be suprafacial

and a [1,5] thermal shift antarafacial; in addition bonding in a case II process takes place through opposite faces of the connecting atom, so rearrangement should invert the configuration of the migrating group. It is equally possible to consider higher sigmatropic migrations in the same way. The possible [1,3] and [1,5] thermal processes of cases I and II are shown below.

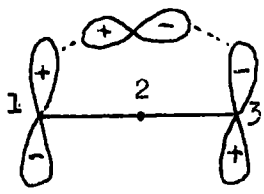
CASE I

[1,3] antarafacial shift
retention of configuration

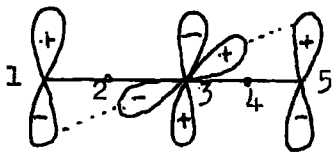


[1,5] suprafacial shift
retention of configuration

CASE II



[1,3] suprafacial shift
inversion of configuration



[1,5] antarafacial shift
inversion of configuration

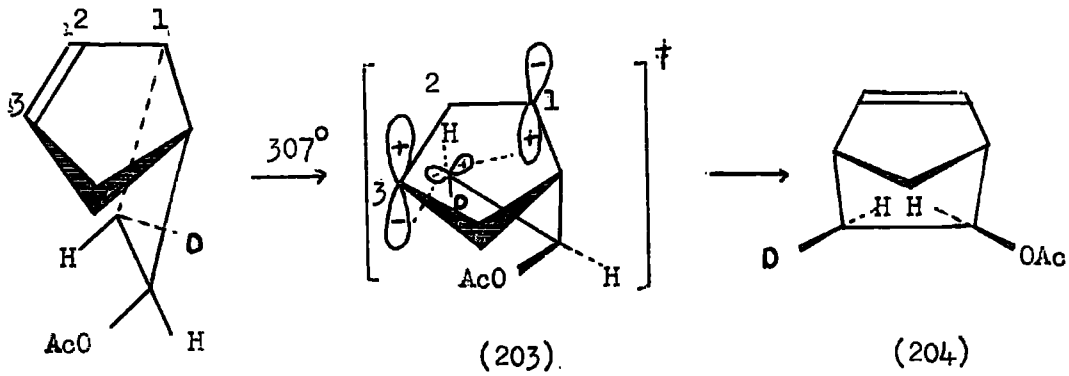
Rearrangements which involve the first-excited state and are concerted are governed by selection rules exactly the reverse of the above due to the differing symmetry of the lowest excited state energy levels of the polyenyl radical.

Steric factors reduce the possibility of certain sigmatropic migrations. In practice it is difficult to envisage structures which would permit [1,3]-antarafacial processes or even [1,5]-antarafacial processes as the allyl or pentadienyl systems need to retain approximate coplanarity to allow the application of the orbital symmetry rules, and thus [1,3]- and [1,5]-rearrangements are effectively restricted to the suprafacial class.[166]

The predictions of Woodward and Hoffmann, above, derived for an acyclic polyene, have been successfully applied to a large number of sigmatropic migrations involving cyclic polyenyl framework radicals. The molecular orbitals of a cyclic framework radical and its corresponding acyclic analogue differ considerably. For an odd-membered monocyclic C_nH_n π-system in a regular polygonal arrangement all molecular orbitals except for the molecular orbital of lowest energy occur in degenerate pairs. Selection rules are based on the symmetry of the highest occupied, or frontier, molecular orbital; in the case of a cyclopropenyl or cyclopentadienyl framework radical the highest occupied molecular orbital could be either of two orbitals of similar energy but differing symmetry. Anastassiou has reasoned that in these systems selectivity of migration will occur as the regular polygonal arrangement will be distorted and the degeneracies will be lifted. His predictions are in agreement with those derived for corresponding acyclic systems for migrations of case I except that for cycloheptatrienes, according to his model, all shifts should be allowed in the excited state; unfortunately only [1,7] photochemical migrations are known in these systems so the validity of this proposition cannot be ascertained.[167]

3.8 [1,3]-Shifts

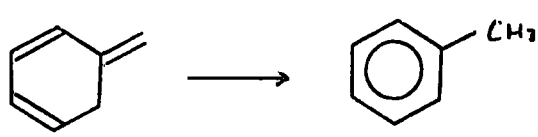
As expected, the only examples of thermal [1,3]-shifts are suprafacial shifts of case II. Berson and Nelson have examined the bicyclo[3,2,0]heptene → norbornene transformation of (202) to (204) and have shown it to be a concerted [1,3]-suprafacial migration with inversion of configuration at the migrating carbon. At the half-migrated stage (203) the hydrogens of the



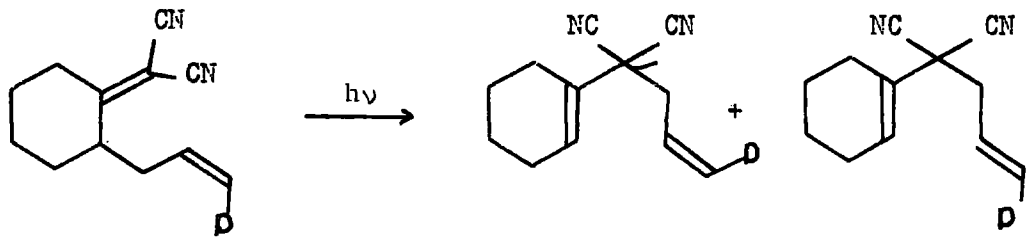
(202) (203) (204)

migrating carbon atom are in a plane perpendicular to the allyl plane and if the hydrogen atom H of the migrating carbon of (202) is replaced by a methyl group this group will be pointing inside towards the ring in a transition state analogous to (203) and this steric interaction results in a change of mechanism to a diradical process; whereas the analogous compound in which the deuterium atom D of the migrating carbon of (202) is replaced by a methyl group rearranges as above on pyrolysis. These results show clearly the value of orbital symmetry rules and strongly support the structure assigned to the transition state.[168]

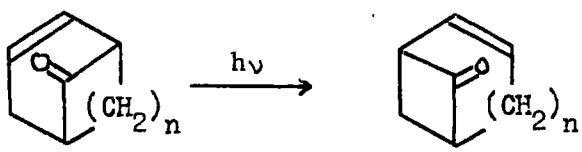
The triene below owes its stability to the fact that its thermal isomerisation to toluene involves a symmetry forbidden [1,3] hydrogen shift.[6]



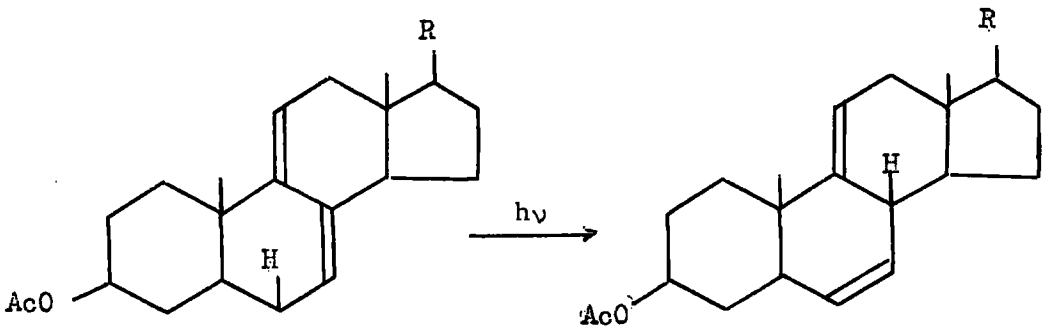
Photochemical [1,3]-shifts of case I are symmetry-allowed suprafacially and there are many examples of rearrangements of this type. An interesting migration of an allyl group is shown below, the cis-trans equilibration occurring during the migration.[169]



The photoisomerisation below is a general reaction which could also be a [1,3]-suprafacial process.[170]

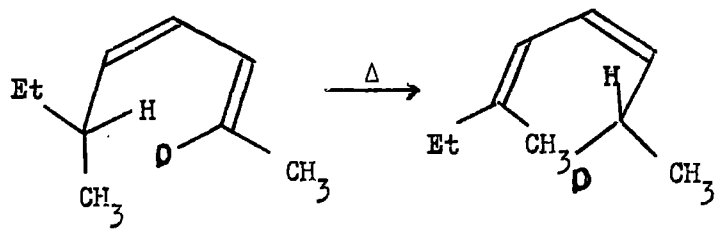


The [1,3]-hydrogen shift shown below also occurs photochemically.[171]

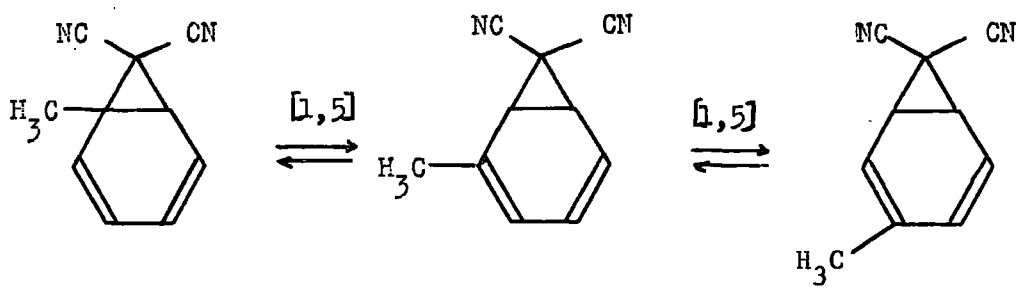


3.9 [1,5]-Shifts

Thermal [1,5]-hydrogen migrations are very common and the concerted suprafacial character of such a process has been demonstrated in the rearrangement below.[6]

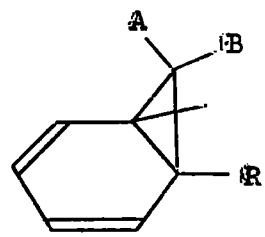


For a carbon migrating group it should also be possible to distinguish between inversion and retention of configuration and Berson has proposed an ingenious experiment based on the norcaradiene system to distinguish between these two possibilities. The methyl-7,7-dicyanonorcaradienes below equilibrate at 55° by [1,5]-shifts.



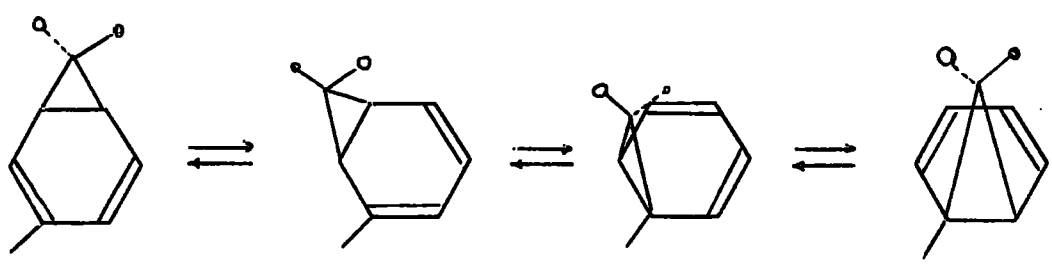
If these skeletal rearrangements are concerted the migrating carbon C-7 will begin to bond to C-5 before detaching itself from C-1 and, as orbital symmetry requirements for a thermal [1,5]-process of this type require the same face of C-7 to be involved in bonding to both the migration origin and terminus, configuration at C-7 should be retained. This means that in each

[1,5]-shift the substituents on the cyclopropane ring must pivot through 180°. For an optically-active system (205) this type of migration will preserve optical purity; in the forbidden process with C-7 bonded through opposite faces to C-1 and C-5 racemization should occur, as passage by back-side bonding over the site of a substituent interconverts two enantiomeric norcaradienes, see below. Unfortunately Berson has so far been unable to synthesise a suitable optically-active system.

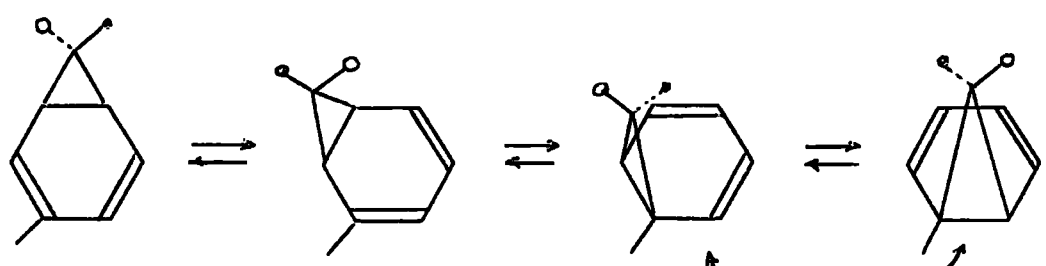


(205)

Case I [1,5]-shifts

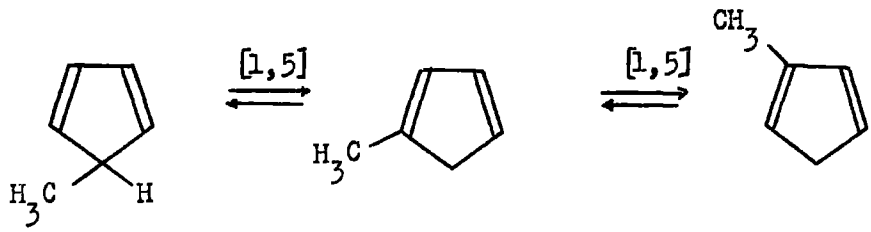


Allowed

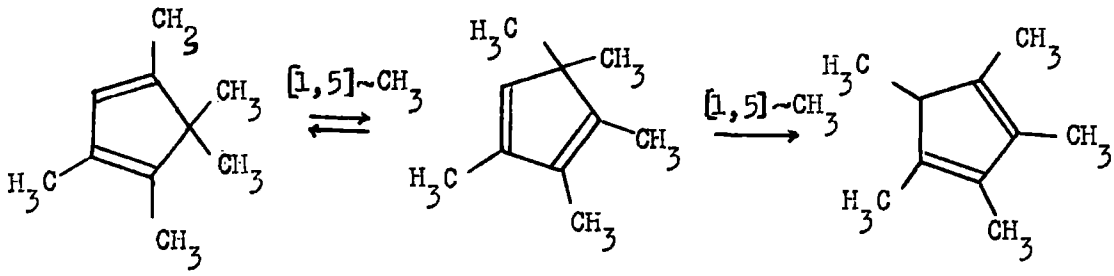


Forbidden enantiomers

[1,5]-shifts are common in systems with a cyclic polyenyl framework radical. The rearrangements of some substituted cyclopentadienes have been shown to occur by [1,5]-sigmatropic hydrogen shifts, the migrations below proceeding at room temperature.[172]

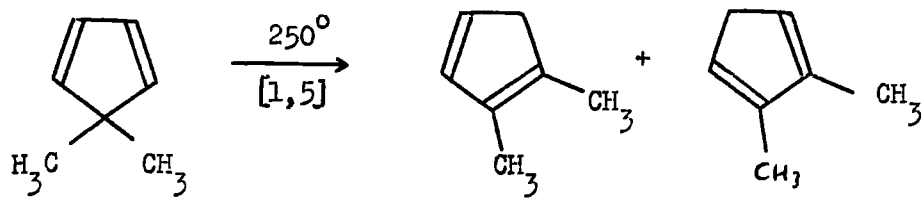


Under drastic conditions, pyrolysis at 450-490°, 1,2,4,5,5-pentamethylcyclopentadiene (206) is converted into 1,2,3,4,5-pentamethylcyclopentadiene (208); the process proceeds via two [1,5]-methyl migrations. The intermediate 1,2,3,5,5-pentamethylcyclopentadiene (207), was isolated and was shown to be formed in smaller amount for the higher temperature reactions.[173] 5,5-dimethylcyclopentadiene has also been shown to rearrange at temperatures of around 250° via

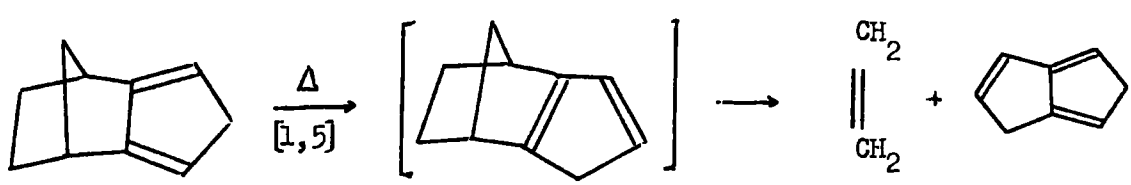


(206) (207) (208)

an initial [1,5]-methyl migration followed by rapid hydrogen migration. At higher temperatures the [1,5]-sigmatropic methyl shift competes with a radical process. This isomerisation is shown below.[149]

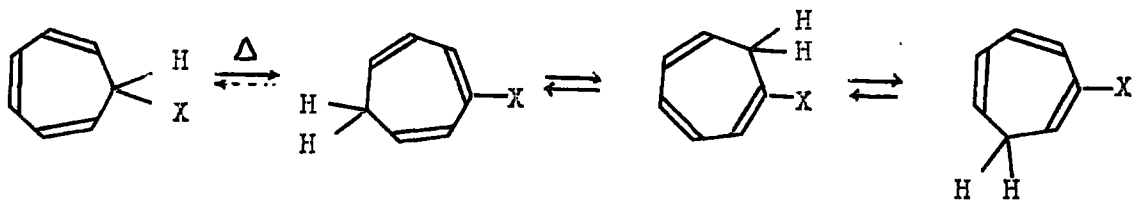


A more complex isomerisation occurs when dihydropentalene is prepared by pyrolysis of isodicyclopentadiene (209) at 575°/20 mm.Hg. in a stream of nitrogen. The process can be rationalised as double-bond isomerisation of the cyclopentadiene system via a thermal [1,5]-hydrogen shift, followed by a reverse Diels-Alder reaction eliminating ethylene.[174]

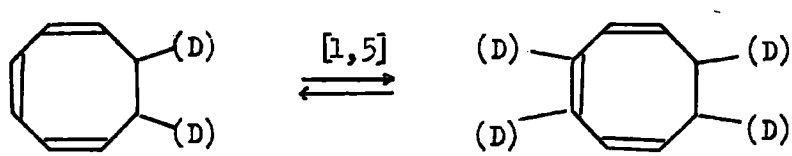


(209)

In cycloheptatrienes thermal [1,5]-sigmatropic hydrogen shifts occur in preference to the [1,3] and [1,7] processes & these are summarised below.[165]

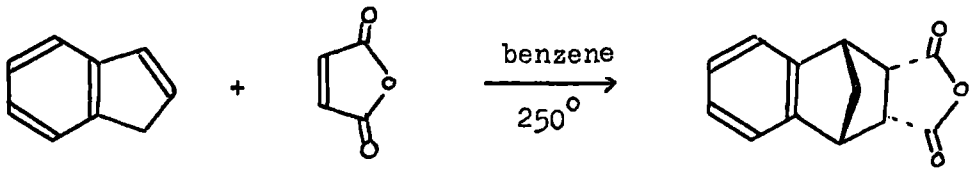


Roth showed that [1,5]-shifts scrambled the labelling in the cyclooctatriene (210) over the 3,4,7 and 8 positions whereas a sequence of [1,3]-shifts would have scrambled the deuterium overall ring positions.



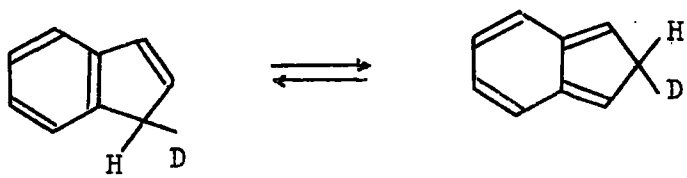
(210)

[1,5]-sigmatropic migrations also occur in the indene system. In 1942 Alder observed the indene and maleic anhydride reacted to produce the adduct (211),[175] this could be formed from isoindene in a 1,4-cycloaddition, the latter being the result of a [1,5]-hydrogen migration in indene. That this type of migration does occur is evident from the deuterium label in (212) being



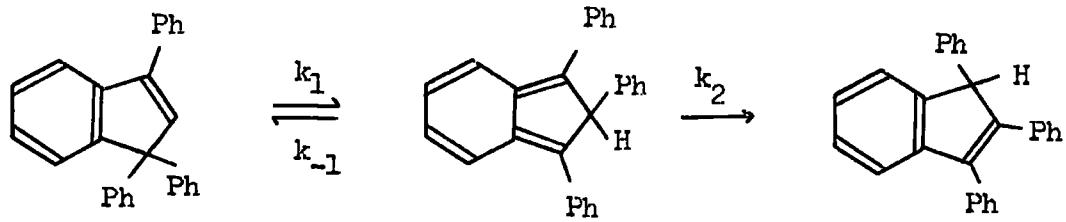
(211)

scrambled over all non-aromatic positions at elevated temperatures, via the isoindene (213).[176]



(212) (213)

The highest occupied molecular orbital of the indenyl radical for a thermal rearrangement will be Ψ_5. This molecular orbital, according to Huckel calculations possesses a positive or negative lobe at C-1 and a node at C-2 and is thus of correct symmetry for [1,5]-sigmatropic migrations of case I or case II. In a recent study of the thermolyses of substituted indenes it has been found that both phenyl and hydrogen shifts occur readily in the indene system; the general scheme is shown below for the thermal rearrangement of 1,1,3-triphenylindene to 1,2,3-triphenylindene.

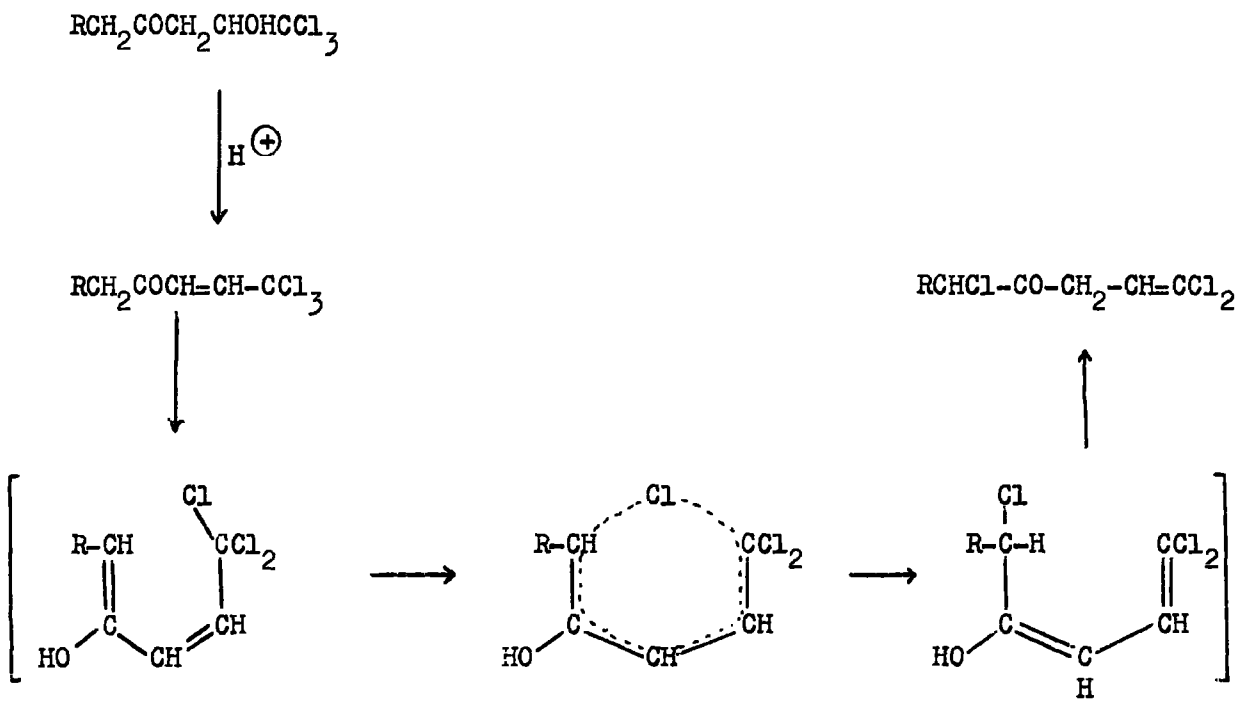


$k_{-1} > k_1$ but $k_2 > k_{-1}$, hydrogen migrations being much faster than phenyl migrations.

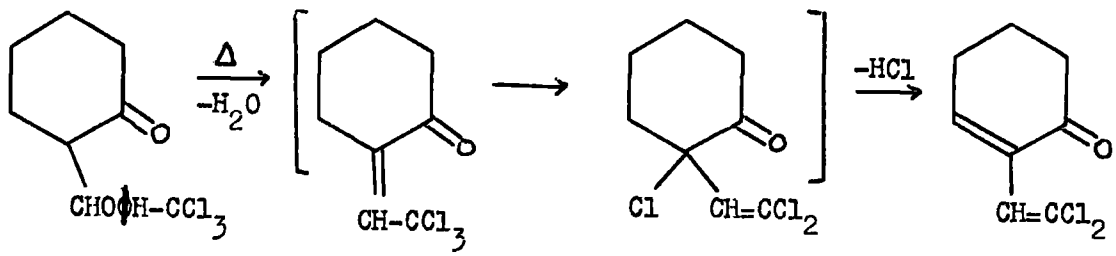
The drastic conditions required for migration of a methyl group in the cyclopentadiene system compared with those required for a hydrogen migration suggest that hydrogen atoms are much less reluctant to migrate than methyl groups in these systems. The low migratory aptitude of a methyl group is further evident from 7,7-dimethylcycloheptatrienes undergoing [1,5]-skeletal rearrangements in the norcaradiene form in preference to [1,5]-methyl shifts in the cycloheptatriene form. By comparing the rates of rearrangement of 1-phenyl indene and 1,1-diphenylindene, which possess the same non-migratory residue, it was found that hydrogen migration was much faster than phenyl migration in the indene system.

The relative ease of migration of a group can be ascribed to two main factors, the ability to form a bridged transition state and the nature of the highest occupied molecular orbital about which the group is migrating. Hydrogen bridges far more readily than carbon but a phenyl group overcomes the reluctance of carbon to bridge by attaining a transition state in which there is interaction with low-lying π-orbitals of the ring, a type of transition state not accessible for an alkyl group.[177]

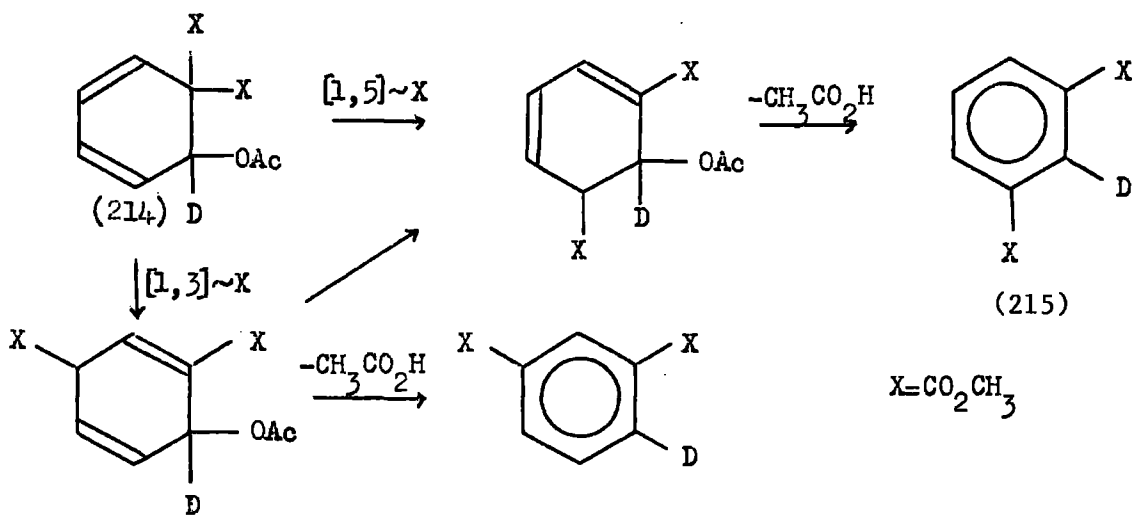
In addition to migrations of the hydrogen atom and phenyl and methyl groups, there are several examples of [1,5]-sigmatropic migrations of other species. The only recognised example of a sigmatropic halogen migration is the rearrangement scheme below.



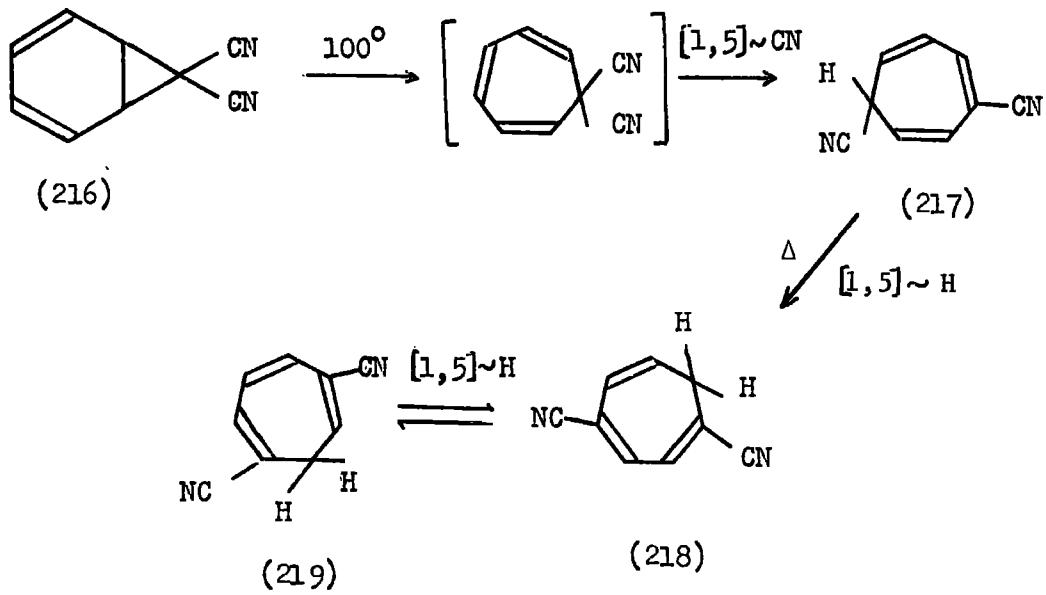
The closeness of the bulky trichloromethyl group to the α' methylene carbon in certain conformations of the enol/allylic chloride is said to be the major driving force for this [1,5]-sigmatropic thermal transfer of a chlorine atom. In the case of the reaction below, the CCl_3 of the initially-formed dehydration product cannot adopt a position for a [1,5]-chlorine shift of the above type, and the product is formed by allylic rearrangement and loss of hydrogen chloride.[178]



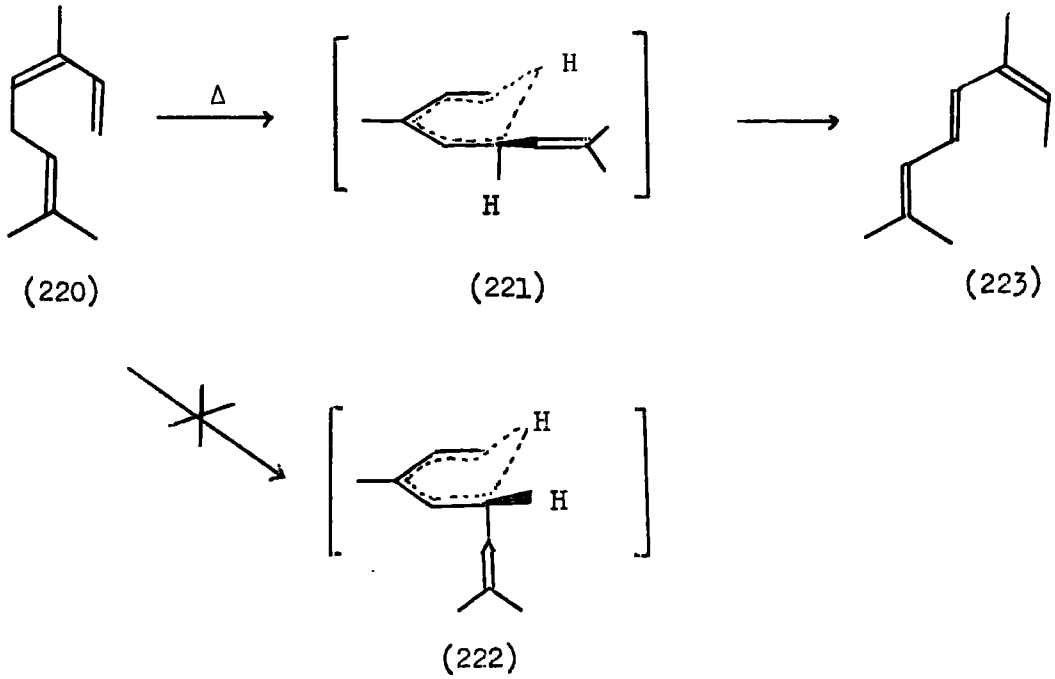
Recently Berson has recognised a [1,5]-thermal sigmatropic migration of a carboxymethyl group, proving the mechanism by deuterium labelling experiments. Only (215) is produced on heating (214), consistent with two [1,3]-migrations or a [1,5]-migration. The former can be discounted as methyl formate or acetic acid would have been expected to be lost after one migration, as deduced from experiments on model compounds. Berson has suggested that the [1,5]-shift should be preferred over the [1,3]-shift as rehybridisation would be necessary in order to use both lobes of an antisymmetric orbital in a case II process but not in a suprafacial [1,5]-shift of case I.[179] The scheme is shown below.



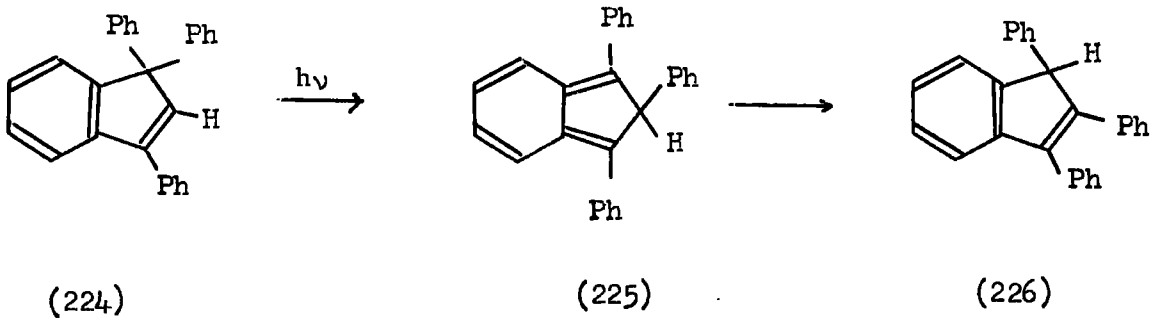
The isomerisation of 7,7-dicyanonorcaradiene (216) to 3,7-dicyanocycloheptatriene (217) is consistent with a [1,5]-cyano shift in the cycloheptatriene tautomer of (216). Further heating of (217) results in an equilibrium mixture of isomers of (217) thought to be (218) and (219) by a [1,5]-hydrogen shift in (217).[180]



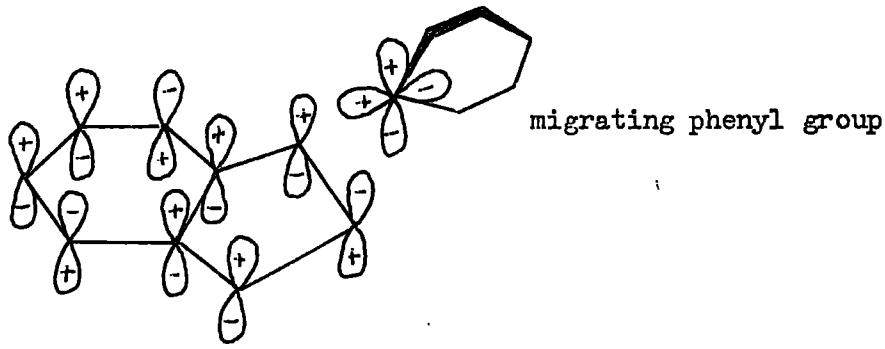
A recent study of the thermal [1,5]-sigmatropic hydrogen migration in cis-β-ocimene (220) has shown that the only product formed is (223). This suggests that transition state (221) is preferred over the alternative (222), explained by lesser steric repulsion of the isobutenyl group in the equatorial position, compared with the axial position.[181]



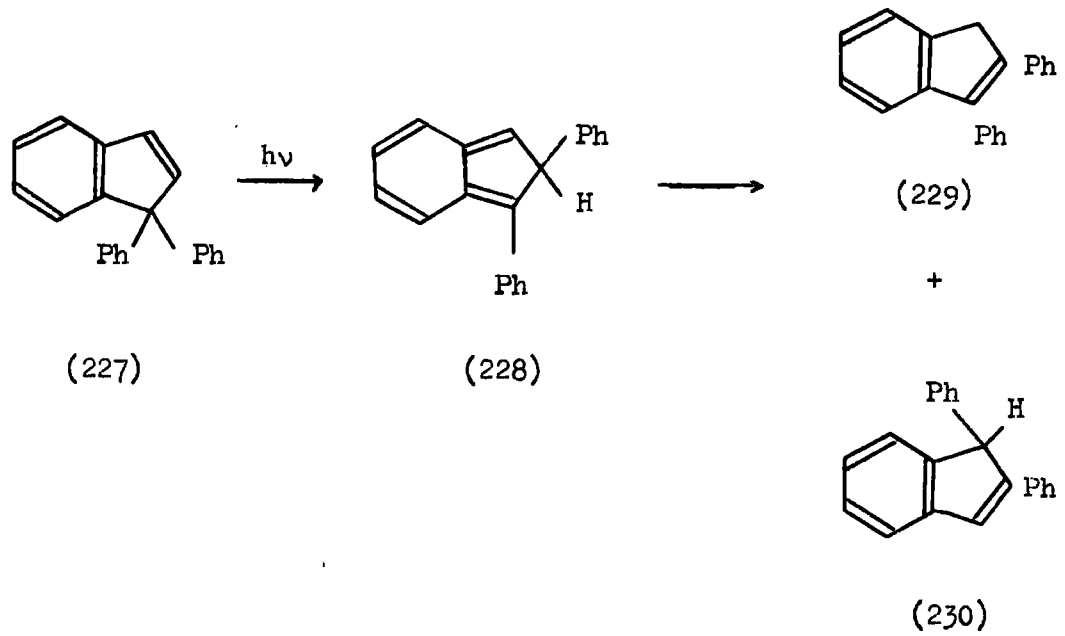
There are few examples of photochemical [1,5]-sigmatropic migrations.[165] According to orbital symmetry arguments suprafacial processes of this type would be expected to be of case II proceeding with inversion of the migrating group. The irradiation of substituted indenes has recently been investigated.[182] An earlier report of the photolytic rearrangement of 1,3,3-triphenylindene (224) to 1,2,3-triphenylindene (226) suggested the mechanism involved an initial photochemical [1,5]-phenyl migration to an isoindene intermediate,(225), which could then undergo a thermal [1,5]-hydrogen shift to the required product.[183]



Both 1,1-diphenylindene (227) and 1,1-dimethylindene have been irradiated with and without photosensitizers; for the former compound rearrangement occurred to 1,2-diphenylindene (230) and 2,3-diphenylindene (229), whereas the latter compound just dimerised. No photochemical hydrogen migration occurred on irradiating 1,1,3-trideuteroindene to 80% polymerisation, there being no change in the deuterium distribution of the recovered indene. These results can be readily explained using orbital symmetry considerations. The relevant indenyl radical orbital is Ψ_6 which possesses lobes of opposite sign at C_1 and C_2 so that a [1,5] suprafacial process will occur for a migrating radical using both lobes of an antisymmetric orbital, case II. A methyl group or a hydrogen atom migrate using a symmetric orbital or one lobe of an antisymmetric orbital respectively; however in the case of a phenyl group the p-orbitals of the π-system are of correct symmetry for overlap at C_1 and C_2 and the lowest anti-bonding orbitals of benzene have almost the same energy (-1.0β) as Ψ_6 of the indenyl radical (-0.9β) and overlap will result in stabilisation of the transition state and facile migration; see below. The isomerisation of 1,1-diphenylindene (227) can be represented as below.



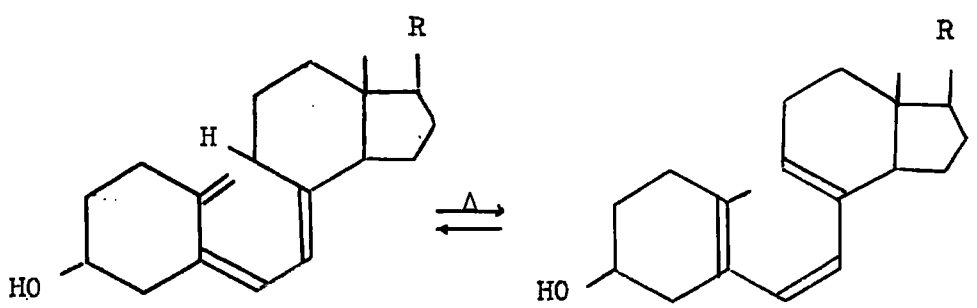
Ψ_6 indenyl radical



The isoindene (228) produced by the photochemical [1,5]-phenyl shift reacts to the final products by ground state [1,5]-hydrogen shifts. Products (229) and (230) are not interconcerted on irradiation.[184]

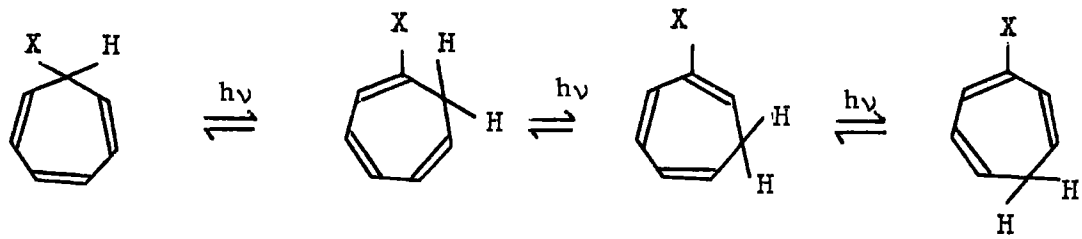
3.10 [1,7]-Shifts

[1,7]-thermal shifts in cyclic systems would be expected to proceed with inversion of configuration although there appear to be no examples known. In acyclic systems of correct configuration antarafacial [1,7]-shifts have been observed, for example in the thermal equilibration of vitamin D_2 and precalciferol, via a thermal [1,7]-antarafacial hydrogen shift, see below.



Apparently the heptatrienyl unit adopts a helical conformation in the transition state which is ideally geometrically disposed for the antarafacial hydrogen shift.

In cycloheptatrienes photochemical [1,7]-shifts are well-known and in 7-substituted cycloheptatrienes, [1,7]-photochemucal hydrogen shifts lead to a distribution of products shown below.



Other [1,j]-shifts

It is expected that migrations of order higher than [1,7] will be difficult due to the need for substantial through-conjugation of the framework radical and hence near planarity, although some have been observed in biochemical systems.[165]

CHAPTER 3

DISCUSSION

3.11 The Photochemical Isomerisation of Tetradecafluorotricyclo[6,2,2,$0^{2,7}$]-dodeca-2,6,9-triene and Dodecafluorotricyclo[5,2,2,$0^{2,6}$]-undeca-2,5,8-triene, and the preparation of Perfluoroindene

Perfluorocyclohexa-1,3-diene (XII) and simple substituted polyfluoro cyclohexa-1,3-dienes undergo disrotatory ring-closure to polyfluorobicyclo[2,2,0] hex-2-enes on irradiation with ultraviolet light[84,159] in contrast to hydrocarbon cyclohexa-1,3-dienes which in the absence of steric constraints form products derived from hexa-1,3,5-triene, the product of conrotatory ring opening.[6] Cyclopentadiene yields bicyclo[2,1,0]pent-2-ene on u.v. irradiation,[148] however the photochemical isomerisation of the fluorocarbon analogue, perfluorocyclopentadiene, has not been reported, possibly due to difficulties in handling this material which readily dimerises.[17] In the light of this information it was of interest to investigate the photochemical behaviour of tetradecafluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene (IX) and dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene (X), which are polyfluoropolycyclic compounds containing a cyclohexa-1,3-diene and a cyclopentadiene unit respectively and which are quite stable as monomers at room temperature (see Chapter 1). Both these compounds were irradiated in the vapour phase in silica tubes which had been sealed in vacuo.

Irradiation of triene (IX) with ultraviolet light of 2537Å led to a mixture of two products formed in roughly equal amounts which were both substantially more volatile than the initial triene; all (IX) was consumed. These compounds had very similar gas chromatographic retention times and were obtained pure in small amounts after repetition of the separation cycle. The separated products were single components on analytical g.l.c. (col.O and col.A) and were unambiguously characterised by spectroscopy and by vacuum pyrolysis.

The mass spectra of all three compounds, triene (IX) and products (XXV) and (XXVI), establish that they are isomeric, as they possess the same parent

peak and major fragment ions (see Appendix 2 and Figure 5). There is a major difference between the mass spectra of (XXV) and (XXVI) and that of (IX) as the former possess a fragmentation sequence involving an early expulsion of CF_2 which is not present in the latter. The loss of CF_2 from the parent ion leads to a fragment at m/e 360 present in (XXV) and (XXVI) but absent from (IX), and also the greater abundance of the ion at m/e 341 in (XXV) and (XXVI) as compared with (IX) and the presence of an ion at m/e 322 in (XXV) and (XXVI) but not in (IX) can be attributed to either an easy expulsion of CF_2 from P-F and P-2F or successive losses of one fluorine from m/e 360. A similar consideration of the relative abundances of ions at m/e 310 and m/e 260 is consistent with the presence of a CF_2 unit in (XXV) and (XXVI) which is relatively easily expelled.

The n.m.r. spectra of (XXV) and (XXVI) proved conclusive in assigning their gross structures (see Table 15). The bicyclo[2,2,2]oct-5-ene system (labelled in Table 15) is evident from the characteristic shift values of the vinylic, tertiary and bridging $-CF_2CF_2-$ [45,58,63,66,68] fluorines. Previously it has been found that where the substituents on this structure are sufficiently different the bridging $-CF_2CF_2-$ unit may be split into separate signals for each difluoromethylene.[66,68] Thus for the shorter-retained photoisomer (XXV), the $-CF_2CF_2-$ resonances are a quartet (integrated intensity 2F, J_{AB} 215 Hz) and a complex multiplet (integrated intensity 2F), whereas for the longer-retained photoisomer (XXVI), these fluorines form a system of two overlapping quartets ($J_{AB} \sim 230$ Hz); in the case of the symmetrical precursor (IX) all the difluoromethylene fluorines occur as a complex multiplet. The remaining resonances in the n.m.r. spectra of (XXV) and (XXVI) are two AB quartets, which from their chemical shifts and coupling constants are assigned to a CF_2 in a five-membered ring and adjacent to a double bond (J_{AB} 274 Hz for (XXV), and J_{AB} 273 Hz for (XXVI)),[37,50] and to a CF_2 in a three-membered ring (J_{AB} 173 Hz

FIGURE 5

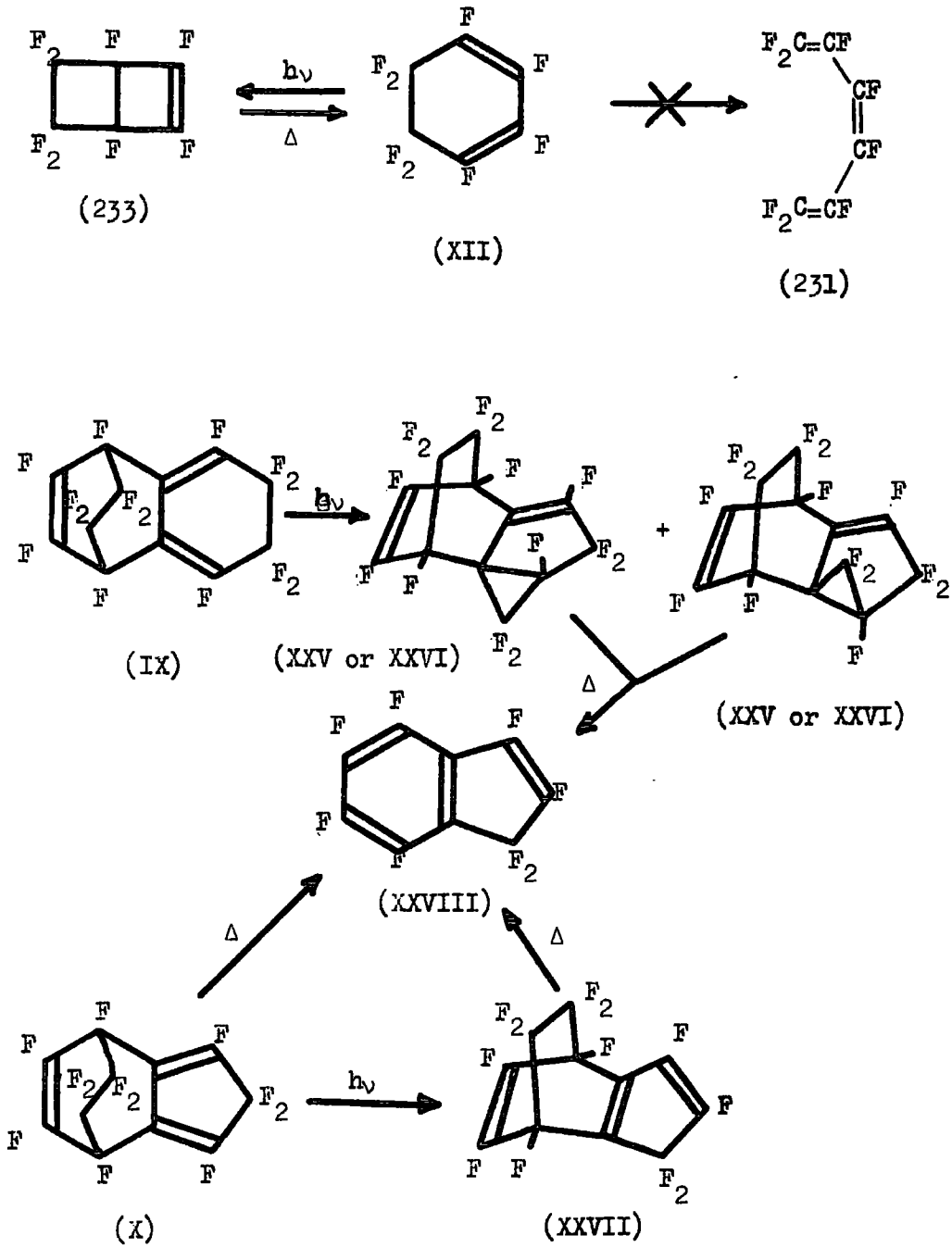
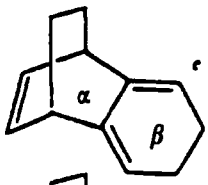
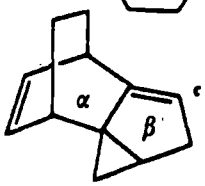
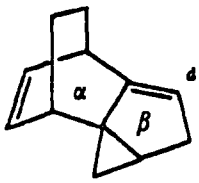
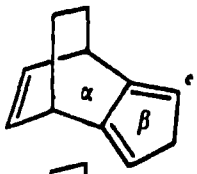
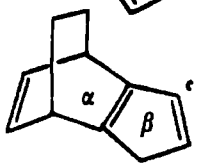


TABLE 15

^{19}F NMR SPECTRAL PARAMETERS[a]

Compound[b]	Tertiary F α	Tertiary F β	Vinylic F α	Vinylic F β	Difluoromethylene α	Difluoromethylene β
 [c]	215·9(2)	—	152·4(2)	134·3(2)	129·2(4)[e]	129·2(4)[e]
 [c]	214·5(1) 215·4(1)	229·6(1)	152·5(2)	131·5(1)	δ_A 125·0(1) δ_B 135·3(1) J_{AB} 215 133·0(2)	δ_A 105·4(1) δ_B 119·8(1) J_{AB} 274[f] δ'_A 143·4(1) δ'_B 150·3(1) J'_{AB} 173[g]
 [d]	213·4(1) 214·2(1)	229·9(1)	147·8(1) 148·5(1)	133·6(1)	δ_A ~ 110(1) δ_B ~ 133(1) J_{AB} ~ 230 δ'_A ~ 126(1) δ'_B ~ 132(1) J_{AB} ~ 230	δ_A 104·2(1) δ_B 124·2(1) J_{AB} 273[f] δ'_A 146·0(1) δ'_B 155·7(1) J_{AB} 176[g]
 [c]	216·5(2)	—	152·8(2)	143·4(2)	δ_A 127·7(2) δ_B 129·5(2) J_{AB} 228[h]	δ_A 132·2(1) δ_B 139·2(1) J_{AB} 309
 [c]	219·4(2)	—	154·9(1)[i] 156·0(1)[i]	151·5(1)[i] 152·4(1)[i]	133·2(4)[e]	δ_A 133·0 δ_B 137·6 J_{AB} 304

[a] Chemical shifts in p.p.m. upfield from external $CFCl_3$ (unless otherwise stated), integrated intensities in parentheses, coupling constants Hz; [b] unmarked valencies to F; [c] neat liquid; [d] solution in CCl_4 (internal $CFCl_3$); [e] complex multiplet; [f] five membered ring; [g] three membered ring; [h] pseudo AB; [i] assignment based on signal shape by analogy with related systems, vinylic F in α-rings are sharp singlets whereas in β-rings they are extensively coupled.

for (XXV) and J_{AB} 176 Hz for (XXVI));[70] a third tertiary fluorine resonance discreet from the tertiary fluorine signals of the α-unit is assigned to the cyclopropyl fluorine.[70] The fact that the tertiary fluorines of the bicyclic unit (α) are split into two separate signals for both (XXV) and (XXVI) whereas in the symmetrical precursor (IX) they give rise to a single resonance provides further evidence for the assigned structures.

Although the n.m.r. spectra of (XXV) and (XXVI) showed substantial differences they did not permit an unambiguous assignment of the relative stereochemistries of these two isomers.

The infra-red spectra of (XXV) and (XXVI), particularly the absorptions in the double bond region, are compatible with their assigned structures. Both photoisomers show two absorptions in this region; (XXV) possesses two distinct peaks at 1750 and 1738 cm^{-1} and (XXVI) a poorly-resolved pair at 1751 and 1747 cm^{-1}; the initial triene (IX) possesses three absorptions, one due to the isolated double bond at 1767 cm^{-1}, and two absorptions due to the conjugated diene system at 1742 and 1703 cm^{-1}.

Final confirmation of structure was obtained by vacuum pyrolysis of (XXV) and (XXVI). It was hoped that loss of difluorocarbene from the three-membered ring might result in their transformation to (X); however it was found that under relatively mild conditions ($340^{o}/10^{-3}$ mm.Hg) isomers (XXV) and (XXVI) were interconverted, whereas under most strenuous conditions ($600^{o}/10^{-3}$ mm.Hg) breakdown occurred with the expulsion of both CF_2 and C_2F_4 units to yield perfluoroindene (XXVIII), (see Figure 5). Insufficient material was available to optimise the conditions for expulsion of CF_2 only, although this has been achieved with other systems - loss of CF_2 or CF_2 and C_2F_4 can occur from the adducts of triene (X) and acetylenes (see Chapter 2).

Vapour phase irradiation of (X) under the same conditions as for the irradiation of (IX) led to only a single product (XXVII) (see Figure 5).

Elemental analysis and mass spectroscopy confirm that (X) and (XXVII) are isomers. The n.m.r. spectrum of (XXVII) was conclusive in assigning its structure (see Table 15). Asymmetry in compound (XXVII) is evident from the vinyl signals for the α and β rings. For compound (X) the vinyl fluorines for the α and β rings are single signals whereas for (XXVII) they become split into two resonances for the two different vinyl fluorines in each ring of (XXVII). As for trienes (IX) and (X) the vinyl fluorines of ring α are unsplit sharp singlets whereas those for ring β are extensively coupled. The remainder of the n.m.r. spectrum of (XXVII) contains a complex multiplet corresponding to the $-CF_2CF_2-$ system of ring α, a resonance due to the two tertiary fluorines of ring α and an AB quartet arising from the difluoromethylene of ring β. The chemical shifts, integrated intensities and the large coupling constant for the AB quartet arising from this difluoromethylene group are in very close agreement for compounds (XXVII) and (X), as expected for compounds with such close structural similarity.

Further evidence for structure (XXVII) is provided by a comparison of the infrared spectra of compounds (XXVII) and (X); whereas (X) has three bands in the double bond stretching region at 1765 cm^{-1} (isolated double bond) and 1755 and 1735 cm^{-1} (diene system), (XXVII) has absorptions at 1761, 1738 and 1629 cm^{-1}, the low frequency peak being assigned to the double bond at the ring junction. Evidence of the conjugated diene system is provided by the ultra-violet spectrum possessing a broad absorption at 305 nm (ε 1100, cyclohexane), cf. triene (X) with a broad absorption at 277 nm (ε 2800, cyclohexane).

On vacuum pyrolysis at $540^{\circ}/10^{-3}$ mm.Hg compound (XXVII) yielded tetrafluoroethylene and perfluoroindene (XXVIII) in good yield, in accord with the proposed structure; similarly triene (X) also yielded tetrafluoroethylene and perfluoroindene (XXVIII) in good yield on pyrolysis at $620^{\circ}/10^{-3}$ mm.Hg.

Perfluoroindene was characterised by elemental analysis and spectroscopy, its spectral parameters and those of some of its derivatives will be discussed in Chapter 4.

3.12 A Possible 1,5-Sigmatropic Migration of a Fluorine Atom

A comparison of the course of photochemical isomerisation of simple polyfluorocyclohexa-1,3-dienes and of the polycyclic fluorinated systems (IX) and (X) leads to some interesting conclusions. An explanation of the preferential ring-closure of simple polyfluorocyclohexa-1,3-dienes in preference to forming polyfluorohexa-1,3,5-trienes, e.g. (231), by conrotatory ring opening (see Figure 5) would be the well-known 'bond strengthening by fluorine substitution'[185] or the 'aversion of fluorine for vinylic sites'.[186]

The increase in strength of carbon-carbon bonds on substitution by fluorine is evident from the difference in the dissociation energies of the CF_3-CH_2Me and CF_3CH_2-Me bonds being 4.5 ± 0.4 kcals $mole^{-1}$, the former bond being stronger; this value was obtained by measuring the decomposition of chemically-activated 1,1,1-trifluoropropane.[185] The 'aversion of fluorine for vinylic sites' has been invoked to explain why addition reactions of fluoroolefins to form saturated compounds are more exothermic than the corresponding reactions of hydrocarbon olefins, for example hexafluorobuta-1,3-diene is quantitatively cyclized to hexafluorocyclobutene at 200° whereas the corresponding hydrocarbon reaction proceeds quantitatively in the opposite direction under similar conditions; however there is an alternative explanation that fluorine atoms attached to saturated carbon atoms are stabilized relative to their attachment to unsaturated carbon atoms. By measuring the kinetics of the cis-trans isomerisations of octafluorobut-2-ene and but-2-ene Schlag and Kaiser found that the activation energy for the fluorocarbon process was 6-8 kcals $mole^{-1}$ less than that for the hydrocarbon process; this is solely a measure of the

lowering of the π-uncoupling energy due to fluorine atom substitution and is in agreement with fluorine substitution on the unsaturated carbon atoms of an olefin leading to destabilisation and weakening the carbon-carbon double bond.[186]

These two factors must be overruled in the conversion of triene (IX) to the photoisomers (XXV) and (XXVI), as the most likely route which can account for these products is an initial ring-opening to the tetraene (232) followed by a photochemical Diels-Alder reaction, the allowed $[\pi 4_s + \pi 2_a]$ process (see Figure 6). Examination of molecular models clarifies the reasons for this difference in the preferred mode of allowed isomerisation of the analogous diene units in structures (IX) and (XII). It is clear from the models that during ring-closure in (XII) leading to (233) the C-F σ-bonds at C-2 and C-3 describe an outward rotary motion which would be sterically impossible for the analogous σ-bonds in (IX), consequently ruling out the 4_π electrocyclic ring closure for triene (IX).

This observation is also relevant to the isomerisation of (X) to (XXVII). A rationalisation of this transformation could involve an initial electrocyclic ring closure to (234), a photochemical process, followed by a thermally-allowed $[\sigma 2_s + \sigma 2_a]$ isomerisation (involving the bonds marked x of this highly strained intermediate), which is the most likely ring-opening mechanism for simple bicyclopentenes;[150] however the formation of (234) will be sterically more difficult than ring closure of triene (IX) and this route seems unlikely.

The only plausible alternative concerted mechanism is a [1,5]-sigmatropic migration of a fluorine atom, as shown in (235) (see Figure 7). Orbital symmetry arguments in cyclopentadienyl systems are ambiguous when based on the symmetry of the highest occupied orbital as the two antibonding and bonding orbitals of highest energy in the cyclopentadienyl radical occur as degenerate pairs possessing different symmetry characteristics. Attempts to resolve this ambiguity have been discussed in the introduction.[167] To investigate the feasibility of this process INDO SCF MO calculations were undertaken on the

FIGURE 6

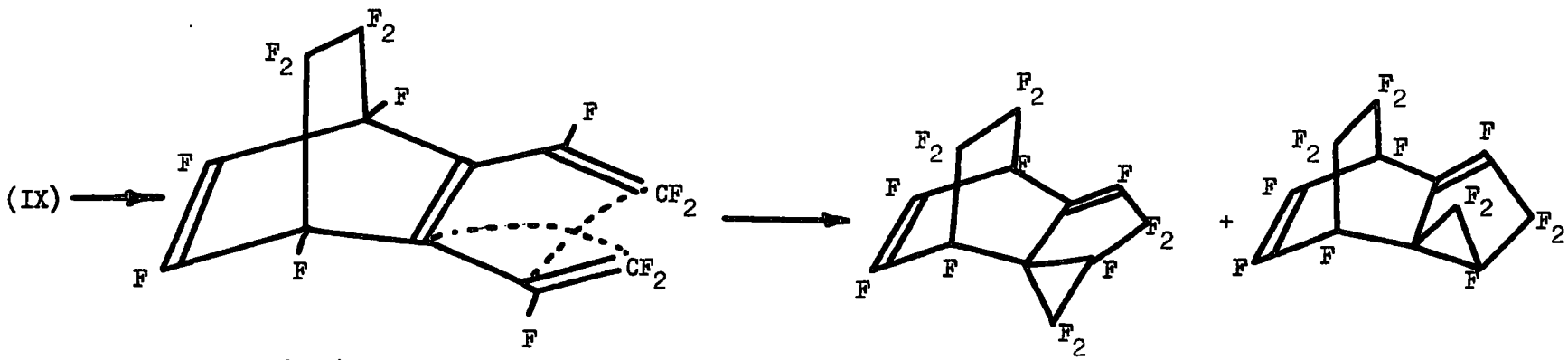
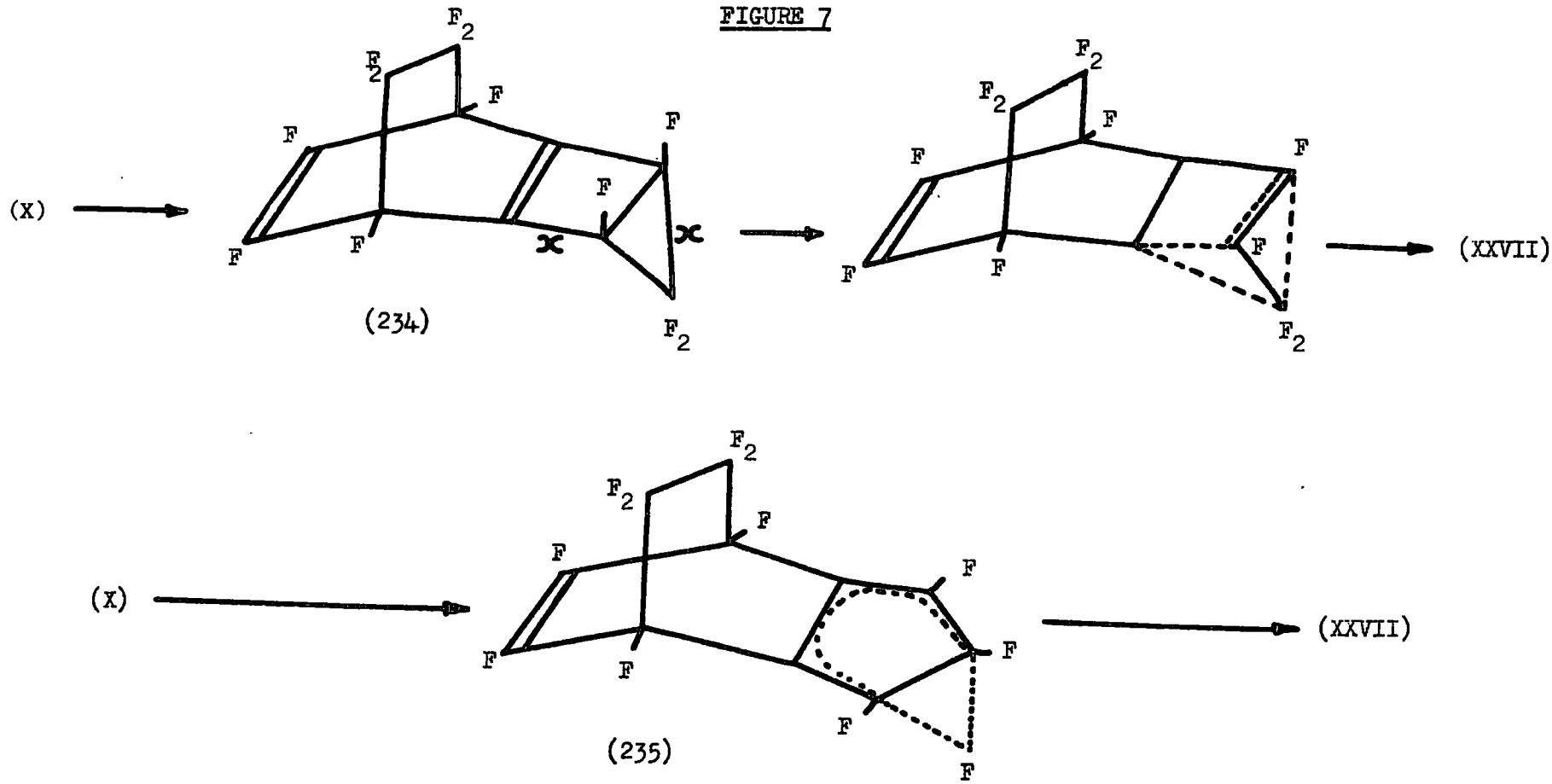
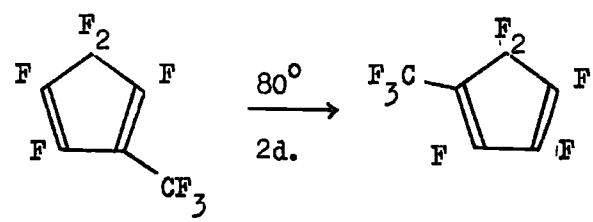


FIGURE 7



[1,5] suprafacial shift of a fluorine atom in hexafluorocyclopentadiene (taken as a model for this reaction) and indicated that there should be a considerable energy barrier to the ground state process whereas the excited state isomerisation should experience no energy barrier.[187] It might superficially have appeared that as [1,5] hydrogen migrations occur thermally in cyclopentadiene systems then case II migrations should be photochemically allowed, fluorine migrating using both lobes of an antisymmetric orbital.

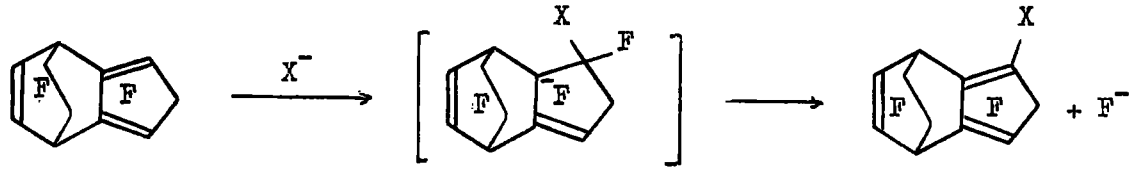
This appears to be the first recognised example of the sigmatropic migration of a fluorine atom; however Camaggi and Gozzo have reported that diene (236) when kept at 80° for 2 days isomerised to diene (237) in addition to dimerising.[57]



(236) (237)

As thermal [1,5]-fluorine shifts in cyclopentadienyl systems have been predicted to possess a substantial energy barrier,[187] further supported by triene (X) being recovered unchanged after being heated at 80° for 48 h. as above and also being recovered unchanged from reactions run at up to 200° (see Chapter 2), this rearrangement under mild conditions may be a [1,3]-thermal fluorine migration.

Although it has been argued that the isomerisation of (X) to (XXVII) is best interpreted as a [1,5]-sigmatropic migration of a fluorine atom it would clearly be more satisfactory if there was some method of unambiguously differentiating between this process and the alternative allowed two-step process involving a photochemical 4π electrocyclic reaction followed by a thermal $[\sigma 2_s + \sigma 2_a]$ process. One method of doing this would be to irradiate the vapour of a triene analogous to (X) but labelled in such a way that different products would result from the two mechanisms. The most convenient way of labelling (X) would be by replacing one of the fluorines of (X) by a nucleophile. Of the two possible positions of attack by a nucleophile, the isolated double bond and the conjugated diene system, the latter would be expected to be more reactive as nucleophilic attack in polyfluorocycloalka-1,3-dienes and polyfluorocyclo-alkenes follows an addition-elimination pathway, products being generally derived from the most stable intermediate carbanion. As shown below it should be possible by reacting (X) with an equimolar amount of nucleophile to obtain a compound (238) labelled at the terminus of the cyclopentadienyl system, although other products might also be expected by displacement of the fluoride ion from a different position.[188]



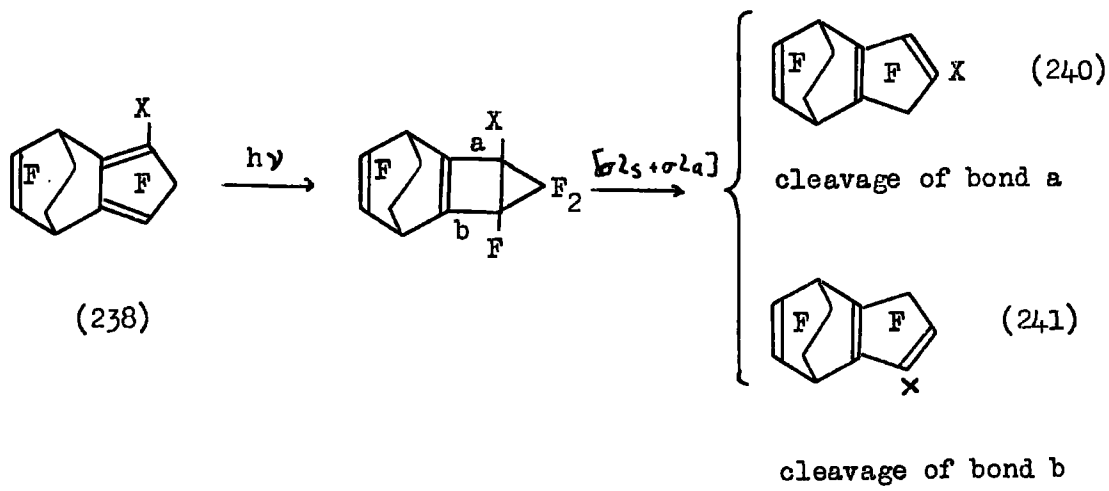
(X) (238)

+ other products

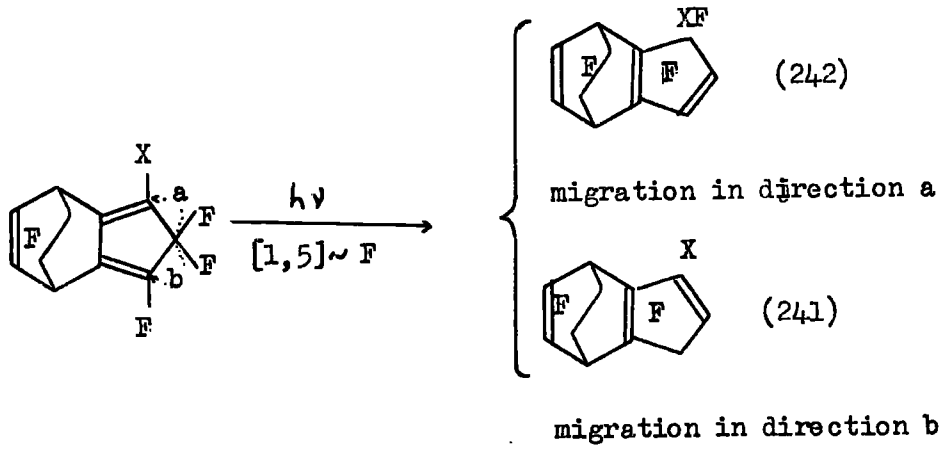
The substituent (X) needs to be photostable and compound (238) needs to be reasonably volatile for vapour phase irradiation. The best choice of (X) would probably be a perfluoroalkyl group, both from the point of view of the volatility and photostability of (238); (238) could be prepared by the reaction of (X) with a fluoroolefin and fluoride ion.

The expected products of irradiation of (238) for the two mechanisms are shown below.

1. 2-Stage Mechanism via Electrocyclic Ring Closure.



2. [1,5]-Sigmatropic Migration of a Fluorine Atom.



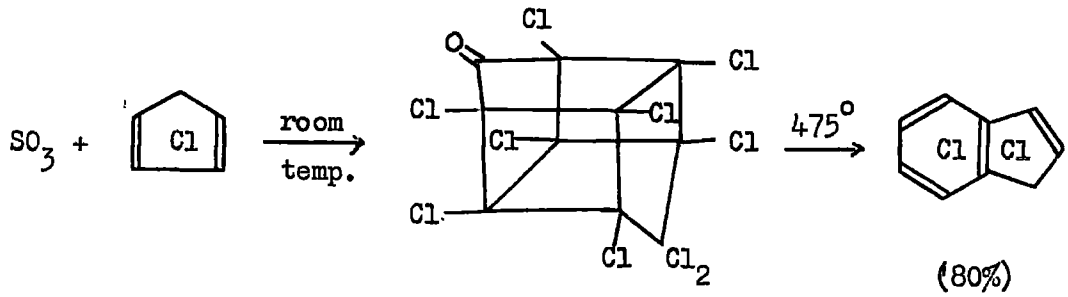
As can be seen, both mechanisms may lead to a mixture of isomers. If only (241) was produced it would be impossible to differentiate between these two mechanisms. Products (240)-(242) should be distinguishable by n.m.r. and i.r. spectroscopy.

If a compound analogous to (238) but substituted at both termini of the cyclopentadiene system was irradiated the 2-stage mechanism should lead to products with a CX=CX double bond, as the CF_2 group is transferred intact, whereas the products obtained via the fluorine migration mechanism should contain a CX=CF double bond and a geminal CXF system. In this case the photoproducts expected from the two mechanisms should be readily distinguishable simply by infrared spectroscopy.

Prior to the present work perfluorindene had proved an elusive compound. The general method of preparation of polycyclic fluoroaromatic compounds by exhaustive fluorination of the parent hydrocarbon in the vapour phase over a bed of cobaltic fluoride at temperatures of around 450-500°, followed by defluorination of the resulting fluorocarbon over a metal, usually nickel or iron heated to around 450°, could not be successfully applied to the preparation of perfluoroindene. Defluorination of perfluoroperhydroindane only went as far as perfluoroindane under a variety of reaction conditions and this is analogous to the difficult defluorination of decafluoroethylbenzene to octafluorostyrene and the resistance of octafluorocyclopentene to defluorination.[137]

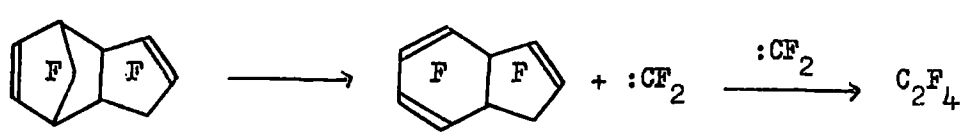
In marked contrast perchloroindene can be readily prepared in good yield by the pyrolytic dechlorination of perchloroindane at 200°,[189] and in lower yield by the pyrolysis of hexachlorocyclopentadiene.[190] The best preparation of this chlorocarbon is by pyrolysis of the cage ketone $C_{10}Cl_{10}O$ (243), formed by the reaction of hexachlorocyclopentadiene with sulphur trioxide, at temperatures of around 475°. Ketone (243) has a structure related to that of the saturated cage dimer of hexachlorocyclopentadiene although the inclusion

of a carbonyl group in the skeleton of the latter compound results in a reduction in its pyrolytic stability, see below.[191]



(243)

The pyrolysis of perfluorocyclopentadiene dimer has also been investigated. By pyrolysing this compound over sodium fluoride pellets and nickel in a nickel tube at 400-700° with varying contact times, perfluoroindane (43-52%) and perfluorostyrene (0.5-16%) were obtained.[192] Perfluorocyclopentadiene dimer displays marked thermal stability being unaffected by storage at 475° for 45 min. in a platinum thimble encased in silica. Pyrolysis in a silica flow system under a pressure of 2.3 mm.Hg. at 555° with a contact time of 2 secs. resulted in only 5% breakdown of the dimer yielding traces of tetrafluoroethylene and monomer. Under more drastic conditions at 630°/2 mm.Hg with a contact time of 0.3 sec. some monomer was formed but the major product was (244) produced by elimination of difluorocarbene from the dimer, see below.



(244)

A single attempt to defluorinate (244) by passage over mild steel at 490-495° gave perfluoroindane as the major product and a trace of a yellow liquid whose infrared and mass spectra were consistent with its formulation as perfluoroindene; insufficient material was obtained for complete characterisation of this compound.[45]

There appear to be no reports in the literature of attempts to prepare perfluoroindene by the exchange reaction between perchloroindene and potassium fluoride, a technique successfully applied to the synthesis of other fluorinated aromatic systems.[123]

The formation of perfluoroindene in excellent yield by the pyrolysis of triene (X) represents a good synthetic route to this new aromatic compound. Pyrolysis of (XXVII) to perfluoroindene can be interpreted as loss of tetrafluoroethylene in a reverse Diels-Alder reaction. The loss of tetrafluoroethylene from triene (X) to form perfluoroindene cannot be a one-step process. One possible mechanism would be an initial thermal [1,5]-sigmatropic fluorine migration in triene (X) to produce triene (XXVII) which could then lose tetrafluoroethylene yielding perfluoroindene; however even when conversion to perfluoroindene is incomplete at temperatures of less than 500° analytical g.l.c. indicates the formation of perfluoroindene and the presence of unchanged (X); no (XXVII) has been detected under these conditions, and as mentioned above calculations have predicted a substantial energy barrier for this thermal process. Although it is possible that at the temperatures required for the [1,5]-thermal fluorine shift to produce (XXVII) this compound will be unstable to the reverse Diels-Alder reaction and produce perfluoroindene immediately, a more likely explanation of this process is loss of tetrafluoroethylene from (X) to yield perfluoroisoindene in a reverse Diels-Alder reaction, a [1,5]-fluorine shift in this intermediate compound would then result in the formation of perfluoroindene. The latter migration is in accord

with orbital symmetry conservation, both case I and case II [1,5]-thermal sigmatropic migrations are allowed and occur in the indene system (see Introduction).

It is perhaps of interest that in the case of a [1,5]-migration of a fluorine atom, which uses both lobes of an antisymmetric orbital in migrating, in perfluoroindene, the generation of perfluoroisoindene should be allowed both in the ground and the excited states (see Introduction) due to the symmetry of Ψ_5 and Ψ_6 of the indenyl radical. Thus by suitable choice of a dienophile it may well be possible to trap this intermediate both in thermal and photochemical processes.

3.13 The Irradiation of 2H-heptafluorocyclohexa-1,3-diene and the reaction of its photoisomer with furan

A number of highly fluorinated cyclohexa-1,3-dienes have been smoothly concerted to bicyclo[2,2,0]hex-2-enes in high yield and the dienophilicity of these latter compounds has been investigated towards furan. Both octafluorobicyclo[2,2,0]hex-2-ene and 1,4,5,5,6,6-hexafluorobicyclo[2,2,0]hex-2-ene have been prepared by irradiation of octafluorocyclohexa-1,3-diene and 2H,3H-hexafluorocyclohexa-1,3-diene respectively and the former has been found to be at least twenty times less reactive than the latter by competition reaction with excess furan in carbon tetrachloride at room temperature.[67,84,159] As 2H-heptafluorocyclohexa-1,3-diene was available from the dehydrofluorination of 1H,6H-octafluorocyclohexene, formed in the reduction of decafluorocyclohexene with lithium aluminium hydride (Chapter 1), and its photoisomer formed by the analogous disrotatory ring-closure was unknown, it was decided to irradiate the former compound in order to prepare its photoisomer and investigate the dienophilicity of the latter compound towards furan.

Vapour phase irradiation of 2H-heptafluorocyclohexa-1,3-diene resulted in

the formation of a single product which was identified by elemental analysis and spectroscopy as 1,3,4,5,5,6,6-heptafluorobicyclo[2,2,0]hex-2-ene (XXIX). Like octafluorobicyclo[2,2,0]hex-2-ene and 1,4,5,5,6,6-hexafluorobicyclo[2,2,0]hex-2-ene, compound (XXIX) had a strong parent ion in the mass spectrum and a base peak corresponding to loss of CF_3 from the parent ion (see Appendix 2).[67] The infrared spectrum of (XXIX) showed a strong absorption assigned to the CH=CF bond at 1656 cm^{-1} and a vinylic C-H stretching frequency at 3125 cm^{-1}. Its n.m.r. spectra fully confirmed its structure as can be seen from Table 16 where the n.m.r. spectra of (XXIX) are compared with the n.m.r. spectra of the analogous compounds (233) and (245), containing CF=CF and CH=CH double bonds respectively. No attempt was made to completely interpret the n.m.r. spectra as all the bands were extensively coupled multiplets and the spectrum was not first order. Like other fluorinated bicyclo[2,2,0]hex-2-enes[84,159] compound (XXIX) under vacuum pyrolysis at 350° was quantitatively isomerised back to 2H-heptafluorocyclohexa-1,3-diene.

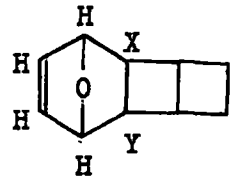
Like octafluorobicyclo[2,2,0]hex-2-ene and 1,4,5,5,6,6-hexafluorobicyclo-[2,2,0]hex-2-ene, olefin (XXIX) reacted with furan at room temperature to yield a single adduct, deduced from the sharpness of its melting point and simplicity of its n.m.r. spectra. This adduct (XXX) had the correct top mass peak for a 1:1 adduct and its infrared spectrum is similar to those of the furan adducts of the olefins (233) and (245), being transparent between 1400 and 1800 cm^{-1}, the CH=CH stretch presumably being extremely weak. As expected the parent peak in the mass spectrum was very weak and it contained two base peaks, corresponding to loss of furan from the parent at m/e 206 and to furan itself at m/e 68, as for the furan adducts of (233) and (245)[67] (see Appendix 2). The n.m.r. spectra of (XXX) are conclusive in assigning its gross structure as a Diels-Alder adduct of furan and (XXIX), as seen from Table 16 where the spectra of (XXX) are compared with those of the furan addents of (233) and (245).

TABLE 16

N.M.R. SPECTRAL PARAMETERS[b]

Compound[a]				^{19}F n.m.r.		^{1}H n.m.r.
	X	Y	$-CF_2CF_2-$	Tertiary F	Vinylic F	
(233)	F	F[b,c,f]	δ_A 119.4(2)			
			δ_B 130.0(2)	201.4(2)	122.0(2)	-
			J_{AB} 224[e]			
(245)	H	H[d,f]	δ_A 116.6(2)			
			δ_B 130.6(2)	191.4(2)	-	6.49
			J_{AB} 218[e]			
(XXIX)	H	F[b,c]	δ_A 117.9(1)			
			δ_B 130.8(1)	200.6(1)		
			J_{AB} 216	195.6(1)	91.8(1)	5.02
			δ_A 120.2(1)			
			δ_B 131.4(1)			
			J_{AB} 220			

Table 16 contd.



	X	Y	^{19}F n.m.r. $-CF_2CF_2-$	Tertiary F			^{1}H n.m.r. Vinylic H	Tertiary H	
	F	$F^{d,f}$	δ_A 118.8(2) δ_B 126.1(2) J_{AB} 226[e]	194.4(2)	187.0(2)		6.73(2)	5.33(2)	
	H	$H^{d,f}$	δ_A 123.6(2) δ_B 135.0(2) J_{AB} 226[e]	193.1(2)			6.40(2)	5.31(2)	2.47(2)
(XXX)	H	F^{d}	δ_A 122.9(1) δ_B 135.5(1) J_{AB} 220	200.7(1)	188.2(1)	182.5(1)	6.60(2)	5.30(2)	2.62(1)
			δ_A 122.8(1) δ_B 129.7(1) J_{AB} 225						

a. All unmarked valencies to fluorine. b. Chemical shifts in p.p.m. upfield from external $CFCl_3$ and external $(CH_3)_4Si$, unless otherwise stated, integrated intensities in parentheses, coupling constants Hz. c. neat liquid.
d. solution in CCl_4, references internal $CFCl_3$ and internal $(CH_3)_4Si$. e. 'pseudo' AB quartet. f. from reference 67.

Although a competition reaction between olefin (XXIX) and olefins (233) and (245) towards furan was not undertaken, it appears that the reactivity of (XXIX) is much less than that of (245) and probably close to that of(223), as (XXIX) had not undergone any detectable reaction after up to 60 minutes at room temperature whereas (245) with excess furan in carbon tetrachloride at room temperature had reacted to the extent of 90% after 45 minutes.[67] The difference in reactivity of these three olefins towards furan is presumably steric in origin and whereas replacement of two vinyl fluorines by hydrogens has a pronounced accelerating effect, the replacement of one vinylic fluorine by hydrogen makes little difference to the rate of reaction. A similar trend in reactivity has previously been observed in the Diels-Alder reactions of 3,3,4,4-tetrafluorocyclobutenes substituted in the vinyl positions, with electron-rich dienes.[81]

CHAPTER THREE

EXPERIMENTAL

3.14 Irradiations

Irradiations were carried out in a quartz ampoule, either 25 cm x 2.7 cm diam. (tube A) or 40 cm x 2.5 cm diam. (tube B). The top of the ampoule was connected via a graded seal to a pyrex constriction to enable it to be easily sealed under vacuum, and the ampoules were irradiated in a Rayonet 208 photochemical reactor at 25° using 253.7 nm lamps. The compound to be irradiated was introduced into the ampoule by vacuum transfer from phosphoric oxide, and the ampoule was then sealed under a pressure of 10^{-3} mm.Hg. The bottom 10 cm. of the sealed ampoule was covered with opaque paper to shield the liquid and the vapour was irradiated with the tube clamped vertically in the reactor. After a reaction the products were removed from the quartz tube by vacuum transfer.

(a) Tetradecafluorotricyclo[6.2.2.$0^{2,7}$]dodeca-2.6.9-triene (IX)

Triene (IX) (0.82 g., 2.0 mmoles) was irradiated for 120 hours (tube A). The volatile liquid recovered (0.69 g.) was shown by analytical gas chromatography (col A) to consist of two components of very similar retention time in approximately equal proportions; each component was obtained pure by repeated preparative g.l.c. (col D, 48°) giving the two isomers of tetradecafluorotetracyclo[6.2.2.$0^{2,7}0^{5,7}$]dodeca-2.9-diene (XXV) and (XXVI) (ca. 150 mg. and 100 mg.), single components on analytical g.l.c. (col A and col 0 over a range of temperatures. (Found: F,64.3%. $C_{12}F_{14}$ requires F,64.9% for the shorter retained isomer (XXV)).

(b) Dodecafluorotricyclo[5.2.2.$0^{2,6}$]undeca-2.5.8-triene (X)

Triene (X) (2.28 g., 6.33 mmoles) was irradiated for 160 hours (tube A), a volatile liquid (2.16 g.) was recovered leaving a trace of a viscous brown oil in the ampoule. Preparative g.l.c. (col B, 75°) gave (i) triene (X) (0.25 g.), identified by i.r. spectrum and (ii) dodecafluorotricyclo[5.2.2.$0^{2,6}$]-undeca-2.3.8-triene (XXVII) (1.0 g.). (Found: C,36.4; F,63.5%; M (mass spectroscopy) 360. $C_{11}F_{12}$ requires C,36.7; F,63.3%; M, 360).

(c) 2H-heptafluorocyclohexa-1,3-diene

2H-heptafluorocyclohexa-1,3-diene (1.2 g., 5.4 mmoles) was irradiated for 157 hours (tube B); the volatile liquid recovered (1.14 g.) was separated by preparative g.l.c. (col G, 100°) to give (i) 1,3,4,5,5,6,6-heptafluorobicyclo-[2,2,0]hex-2-ene (XXIX) (0.58 g., 2.6 mmoles, 48%) (Found: C,34.7%; H,0.5%; M (mass spectrometry), 206. C_6HF_7 requires C,35.0%; H,0.5%; M,206), a colourless liquid, ν_{max} 1656 cm^{-1} (CF=CH) and 3125 cm^{-1} (=C-H), (ii) 2H-heptafluorocyclohexa-1,3-diene (0.32 g.), identified by i.r. spectrum.

3.15 Vacuum Pyrolyses

The technique and pyrolysis apparatus have previously been described in the experimental section of Chapter 2.

(a) Dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene (X)

Triene (X) (12.0 g., 33.3 mmoles) was pyrolysed at 620°/10^{-3} mm.Hg. and yielded (i) tetrafluoroethylene, identified by its i.r. and mass spectra and (ii) a yellow liquid (9.28 g.) which was distilled to give a colourless liquid, perfluoroindene (XXVIII) (7.25 g., 27.9 mmoles, 84%) b.p. 149°. (Found: C,41.3; F,58.1%; M (mass spectroscopy), 260. C_9F_8 requires C,41.6; F,58.4%; M, 260); the ^{19}F n.m.r. showed six multiplets at 127.3 (2F), 141.3 (F), 148.2 (2F), 150.9 (F), 155.5 (F) and 162.0 (F) p.p.m. upfield from $CFCl_3$ external reference; the i.r. and mass spectra were substantially the same as reported previously,[45] ν_{max} 1754 cm^{-1} (CF=CF).

(b) Dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,3,8-triene (XXVII)

Triene (XXVII) (0.368 g., 1.02 mmoles) was pyrolysed at 540°/10^{-3} mm.Hg to give (i) tetrafluoroethylene and (ii) perfluoroindene (XXVIII) (0.231 g., 0.90 mmoles, 88%), with correct i.r. spectrum.

(c) Tetradecafluorotetracyclo[6.2.2.$0^{2,7}0^{5,7}$]dodeca-2,9-dienes (XXV) and (XXVI)

(i) The shorter retained isomer (XXV) (0.113 g.) was pyrolysed at 340°/ 10^{-3} mm.Hg; no gas was evolved and examination of the liquid product (0.110 g.) by analytical g.l.c. and i.r. spectroscopy showed it was a mixture of isomers (XXV) and (XXVI) in approximately 4:1 ratio with the shorter retained material predominating. This liquid mixture was repyrolysed at 600°/10^{-3} mm.Hg to give a gas (discarded) and perfluoroindene (0.062 g.) contaminated with an unidentified more volatile material (< 10%).

(ii) The longer retained isomer (XXVI) (0.057 g.) was pyrolysed at 600°/ 10^{-3} mm.Hg to give a gas (discarded) and perfluoroindene (XXVIII) (0.018 g.) containing approximately the same proportion of the same impurity as the product of pyrolysis c(i).

(d) 1,3,4,5,5,6,6-heptafluorobicyclo[2.2.0]hex-2-ene (XXIX)

Compound (XXIX) (0.032 g., 0.16 mmoles) was pyrolysed at 350°/10^{-3} mm.Hg, examination of the product (0.02 g., 0.10 mmoles) by infrared spectroscopy and analytical g.l.c., showed it was pure 2H-heptafluorocyclohexa-1,3-diene.

3.16 Reaction of 1,3,4,5,5,6,6-heptafluorobicyclo[2.2.0]hex-2-ene (XXIX) with furan

To 0.1 ml. of dry carbon tetrachloride was added 0.096 g. (4.66 mmoles) of compound (XXIX) through a serum cap. After running the g.l.c. of this mixture freshly distilled furan (0.074 g., 10.88 mmoles) was added through the serum cap. The reaction was followed by g.l.c. (col A, 60° and 150°) using carbon tetrachloride as an internal marker, and up to one hour after the commencement of reaction the decrease in furan or (XXIX) measured relative to carbon tetrachloride was negligible and there was no peak due to the expected furan adduct at this stage. After standing for 3.5 days at room temperature (col A, 60° and 150°) g.l.c. showed most of the furan and (XXIX) to have been

consumed and an additional peak due to the adduct was evident. Removal of the volatiles under vacuum left a residual white solid (0.098 g.) from which was sublimed 11-oxa-2,3,4,4,5,5,6-heptafluorotetracyclo[6,2,1,$0^{2,7}0^{3,6}$]undec-9-ene (0.063 g., 2.3 mmoles, 49.4%) (Found: F,48.0%, M (mass spectroscopy), 274. $C_{10}H_5F_7O$ requires F,48.5%; M,274) m.p. 57-57.5° (light petroleum 60/80).

3.17 Attempted Thermal Rearrangement of Dodecafluorotricyclo[5,2,2,$0^{2,6}$]-undeca-2,5,8-triene (X)

Triene (X) (0.63 g., 1.76 mmoles) was heated in a 12 ml. pyrex ampoule under vacuum, after drying over phosphoric oxide, for 2 days at 80°. Infra-red spectroscopy and analytical g.l.c. on the residual liquid showed it was unchanged (X).

CHAPTER FOUR

SOME REACTIONS OF PERFLUOROINDENE

INTRODUCTION

4.1 Nucleophilic Substitution in Polyfluoroaromatic Compounds[193]

The parent perfluoroaromatic compound hexafluorobenzene was first synthesised in reasonable yield in 1955 by the pyrolysis of the readily-available compound tribromofluoromethane, as below.

$$CBr_4 \xrightarrow[120\text{-}130^{\circ}]{SbF_3 \text{ activated with } Br_2} CFBr_3 \ (75\%) \xrightarrow[\text{Pt. tube}]{630\text{-}640^{\circ}} C_6F_6 \ (45\%)$$

Since then better synthetic methods have been discovered for the preparation of this compound and the fully fluorinated analogues of many other aromatic compounds, both homocyclic and heterocyclic, have also been prepared.

Corresponding to the range of substituted benzenes and other hydrocarbon aromatics which are available by electrophilic attack on the parent hydrocarbons, an equally large number of fluoroaromatics are obtainable from the attack of nucleophiles on the parent perfluoroaromatic; elimination of a proton in the first instance changing to the elimination of fluoride ion in the second. Thus nucleophilic substitution in polyfluoroaromatic compounds is important synthetically and in addition it is also interesting theoretically for like electrophilic attack in aromatic hydrocarbons nucleophilic attack in polyfluoroaromatic compounds does not occur in a random manner but strict orientation rules are obeyed.

The following discussion is restricted to nucleophilic substitution in polyfluorohomoaromatic compounds, although the arguments advanced have been extended to include heteroaromatic compounds.

4.2 Nucleophilic Substitution in Fluorinated Benzenes[193,195]

Hexafluorobenzene reacts readily with a range of nucleophiles affording a good synthetic route to pentafluorophenyl compounds when the reactions are controlled to produce only monosubstitution. The increase in reactivity towards nucleophilic attack of hexafluorobenzene compared with fluorobenzene is

evident from the rate constants for reaction with sodium methoxide in methanol being in the ratio of 10^7:1. The reaction of sodium methoxide in methanol with hexafluorobenzene shows second order kinetics.[194] Examples of some typical reactions of hexafluorobenzene are shown below.

TABLE 17

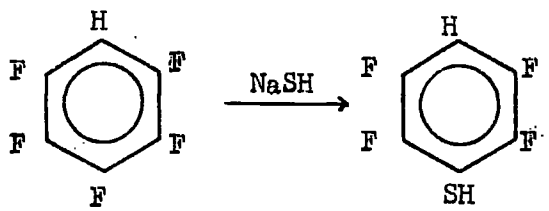
Nucleophilic Substitution Reactions of Hexafluorobenzenes[193]

Group Introduced	Reagent Used	Product
H	$LiAlH_4$ in Et_2O	C_6F_5H
NH_2	$NaNH_2$ or NH_3,H_2O/EtOH at 170°	$C_6F_5NH_2$
CH_3	CH_3Li in Et_2O	$C_6F_5CH_3$
OCH_3	$NaOCH_3$ in Et_2O	$C_6F_5OCH_3$
SH	NaSH/Pyridine/$(CH_2OH)_2$	C_6F_5SH
$NHCH_3$	CH_3NH_2 at 115°	$C_6F_5NHCH_3$
$NHNH_2$	$N_2H_4.H_2O$	$C_6F_5NHNH_2$
C_6H_5	C_6H_5Li in Et_2O	$C_6F_5C_6H_5$

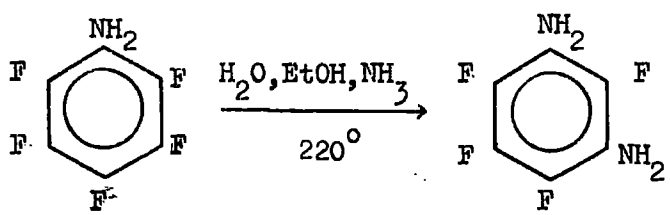
In addition to the formation of pentafluorophenyl compounds C_6F_5X further substitution often occurs to give compounds such as $C_6F_4X_2$ and $C_6F_3X_3$; derivatives such as C_6F_4XY, $C_6F_3XY_2$ and C_6F_3XYZ etc., can also be obtained by reaction of C_6F_5X or C_6F_4XY with other nucleophiles. The relative amounts of the isomeric products obtained when C_6F_5X undergoes nucleophilic attack and the rates of these reactions follow distinct trends where the nature of X is of prime importance and, except in a few special instances of pronounced ortho replacement in C_6F_5X, the nature of the nucleophile is of little significance. By considering the predominant isomers produced on monoreplacement in C_6F_5X it

is possible to divide these compounds into four main categories.

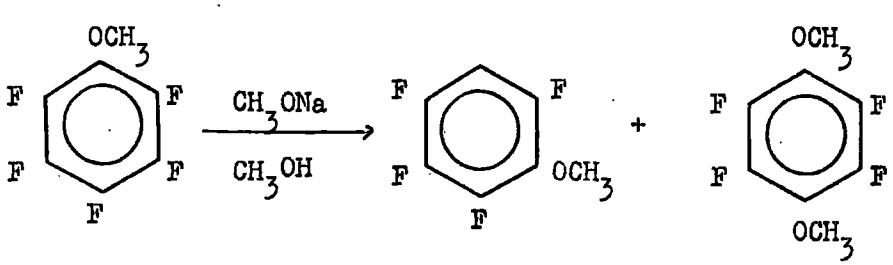
The most common reaction type is attack by nucleophiles almost exclusively at the fluorine atom <u>PARA</u> to X in C_6F_5X, and this occurs for X = H, C_6H_5, CH_3, CF_3, C_6H_5NH, OCH_2CH_2OH, N_2^+, Cl, Br, I, etc., for example.



When X = NH_2 or O^- attack by nucleophiles occurs almost exclusively at the fluorine atom <u>META</u> to X, for example.

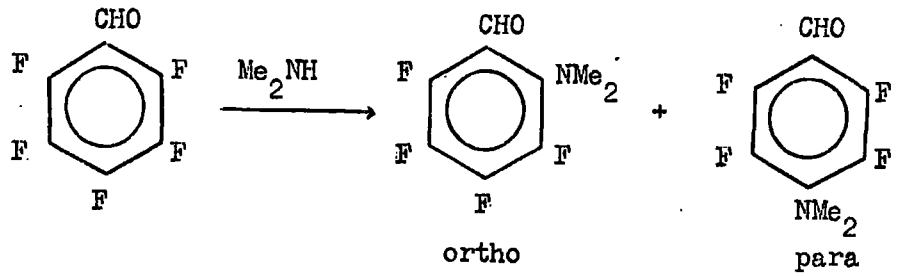


Attack at the fluorines <u>META</u> and <u>PARA</u> to X occurs when X = OCH_3 and $NHCH_3$, as below.



$$\frac{\text{meta}}{\text{para}} = \frac{7}{12}$$

Finally, when X = NO_2,[193,195] CO_2H,[205] CHO,[201] and NO[204] nucleophilic attack is para to X with most nucleophiles but anomalous high <u>ORTHO</u> replacement occurs with some amines, for example.

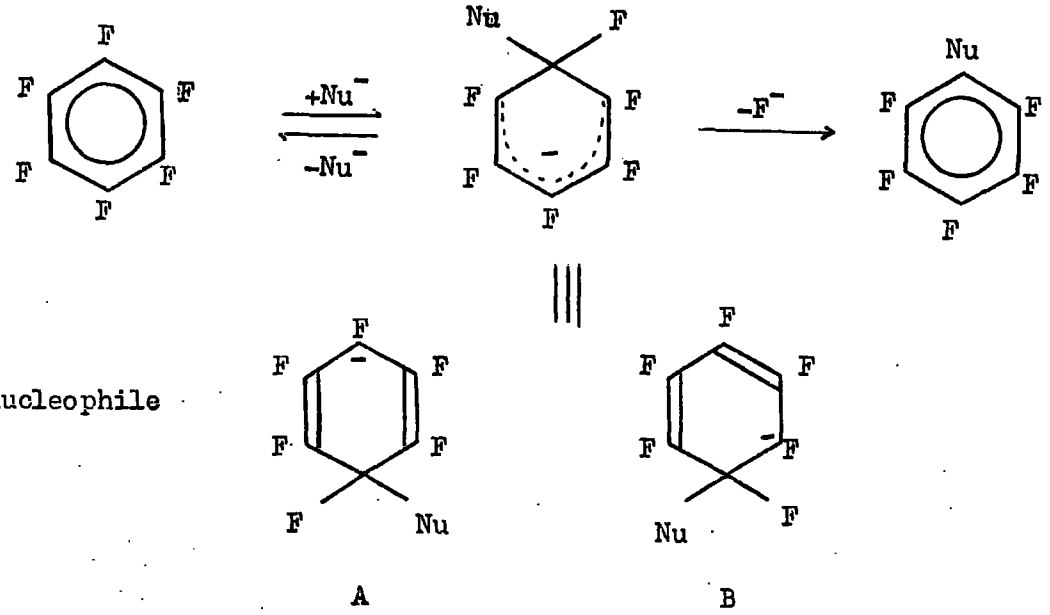


ortho/para = 3/2

In nearly all cases minor amounts of the non-predominant isomers are also obtained.

4.3 Rationalisation of the Orientation of Nucleophilic Substitution[195]

Burdon has successfully rationalised the direction and ease of nucleophilic substitution in simple fluorinated aromatic systems by considering the relative ground state and transition state stabilities of the reactions concerned. His model adopted for the transition state is the Wheland-type intermediate shown below, for the attack of a nucleophile on hexafluorobenzene, and it is assumed that resonance structure A makes a greater contribution to the intermediate than structure B; this assumption is supported by molecular orbital calculations which show a maximum density of negative charge para to the nucleophile.

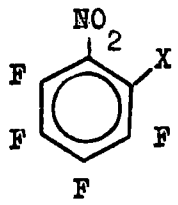


Nu^- = nucleophile

The ratio of isomeric products formed will depend on the stabilities of the transition states leading to the various isomers. For a pentafluorophenyl derivative C_6F_5X, where X has the same stabilising effect towards a negative charge on the carbon atom to which it is attached as does fluorine, the ratio of isomers obtained on monosubstitution, ortho/meta/para, should be the statistical 2/2/1, as the Wheland intermediates all have the same energy. If X tends to destabilise a negative charge on the adjacent carbon more than fluorine, attack by nucleophiles should be mainly at the position meta to X so that X will be attached to the carbon atom with the lowest electron density, and if X stabilises an adjacent negative charge more than fluorine, attack ought to be mainly at the para position (transition state A) with some slight attack at the ortho position (transition state B). Thus the nearer the stability of the transition state for nucleophilic attack in C_6F_5X is to that for attack in hexafluorobenzene the closer should the isomer distribution be to the statistical one; if the stability of the transition state is greater than that for the analogous reaction of hexafluorobenzene para replacement should predominate; if the opposite is true we should have predominant meta replacement.

A substituent can stabilise or destabilise an adjacent negative charge by inductive effects, as occurs with alkyl groups, or by delocalization effects, as for a nitro group. In the case of a halogen substituent the order of destabilisation is F > Cl > Br > I ~ H, the reverse of what is normally found for an inductive effect. The reason for this order of destabilization is that the negative charge is in a π-electron system and electron repulsion in π-systems (I_π - repulsion) follows the order F > Cl > Br > I, as deduced from spectroscopic measurements; the I_π -repulsive effects of oxygen and nitrogen are not derivable from spectroscopy but are assumed to be in the order N > O > F. Steric interactions can also affect the stabilising or destabilising ability of substituents X and are responsible for the I_π- repulsive effect of nitrogen being considerably reduced in pentafluoro-N,N-dimethylaniline and pentafluoro-N-methylaniline relative to pentafluoroaniline, and similarly account for the reduced I_π- repulsive effect of oxygen in pentafluoroanisole relative to pentafluorophenol. The substituents on the heteroatom are thought to interfere sterically with the orthofluorines, distorting the group X out of planarity with the ring, the p orbital of the heteroatom of the substituent is then no longer parallel to the π orbital of the ring and is unable to exercise its maximum I_π - repulsive effect. For X = O^- or NH_2 maximum I repulsion is realised and only meta substitution takes place; for X = $NHCH_3$ or OCH_3 distortion from coplanarity with the ring results in both para and meta substitution occurring to an equal extent; in the case of X = $N(CH_3)_2$ I_π- repulsion is so reduced that little or no meta substitution occurs. It has been suggested that the small amount of ortho replacement which occurs when pentafluoroanisole or pentafluoro-N-methylaniline react with nucleophiles is due to steric interaction between the incoming nucleophile and the methoxyl or N-methylamino group.[195] The tetrafluoronitrobenzenes (246) ,below, show a gradation in reactivity due to the group X adjacent to the nitro group

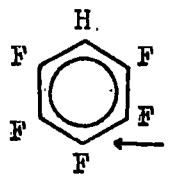
preventing the latter from achieving the coplanarity essential for full activation, the larger the group X the lower is the reactivity of the aromatic compound.[196]



(246)

Reactivity of $C_6F_5NO_2 \gg C_6F_4NH_2NO_2 > C_6F_4NHMeNO_2 \sim C_6F_4OCH_3NO_2 > C_6F_4NMe_2NO_2$

Burdon's theory has been extremely successful in predicting the sites of nucleophilic attack in simple halogenated benzenes. As an example pentafluorobenzene (247), pentachlorobenzene (248) and chloropentafluorobenzene (249) react with nucleophiles at the positions shown. This is in accord with Burdon's theory as the order of stability of the intermediate carbanions is $\overset{\ominus}{C}$-H > $\overset{\ominus}{C}$-Cl > $\overset{\ominus}{C}$-F.



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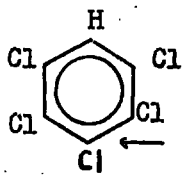
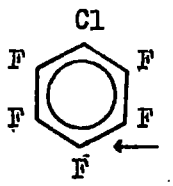
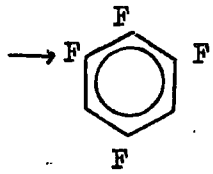


(248)



(249)

An even more illuminating example is the attack of nucleophiles on the three tetrafluorobenzenes. Attack at the arrowed positions once more leads to the most stable of the possible intermediates. Compounds (250) and (251) in reacting at the arrowed positions, enable the negative charge to be localised mainly on a hydrogen-bearing carbon in the transition state whereas this is not possible for (252); consequently (252) is 10^3 times less reactive than its isomers (250) and (251).[195]



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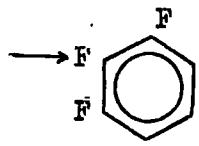

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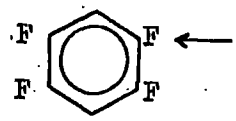
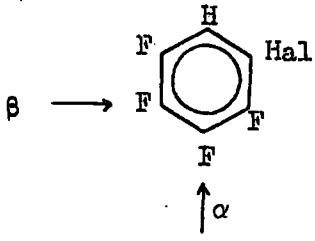
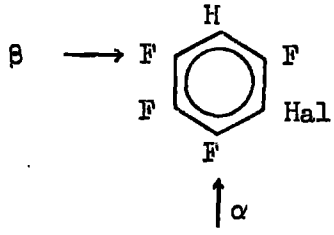


(252)

Although the two tetrafluorohalogenobenzene systems (253) and (254) had not been investigated when Burdon published his theory he was brave enough to predict that nucleophilic attack would take place mainly at positions, α, so that the negative charge of the intermediate would be mainly stabilised by the hydrogen atom; he also predicted that attack at position β would increase in the sequence Hal = I > Br > Cl as the I_{π} effect of the halogen approached that of hydrogen, the negative charge in this case being mainly stabilised by the halogen atom, see below. These predictions have since been verified experimentally, and for (254) it was further found that attack at position α could be subject to steric hindrance for a large halogen substituent; this was observed when dimethylamine attacked (254) with Hal = I.[197]





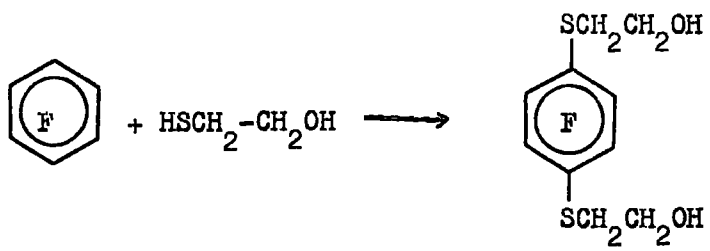
The order of the I_{π} repulsive effects of the halogens is evident from comparing the relative amounts of ortho and para substituted isomers formed when pentafluorohalobenzenes react with nucleophiles. Nucleophiles attack C_6F_5X, X = Cl, Br, I, H, mainly at the position para to X with some ortho attack and little meta attack; this is expected as the I_{π} repulsive effect of X is less than that of fluorine. The difference between the ortho and

para transition states should be less as the I_{π} repulsion effect of X nears that of fluorine and this is reflected in the percentage of ortho replacement varying from 25% (X = Cl) to 12% (X = Br) and less than 5% (X = I,H) in accord with I_{π} repulsion increasing from X = I up to X = F. Steric effects can be important in ortho substitution and the large nucleophile dimethylamine led to less ortho substitution in the pentafluorohalobenzenes than did the much smaller hydroxide ion; however the fact that pentafluorobenzene undergoes less ortho substitution than pentafluorobromobenzene or pentafluorochlorobenzene suggests that electronic factors play the major role in determining ortho/para ratio in nucleophilic substitution.[198]

It has been shown above that by considering the relative stabilities of possible transition states it is possible to predict the orientation of nucleophilic attack in a pentafluorophenyl derivative. It is also possible to assess the reactivity of a pentafluorophenyl derivative towards nucleophilic attack at a particular position by considering both the ground state and transition state energies. Substituents which tend to compensate for the electron-withdrawing fluorine atoms by electron-donation into the π system such as NH_2, OCH_3 and $N(CH_3)_2$ will have ground states of lower energy than that of hexafluorobenzene whereas substituents such as NO_2 which are electron-with drawing will have higher ground state energies. These considerations explain why pentafluoronitrobenzene reacts very readily with nucleophiles, pentafluoroaniline being quite unreactive in comparison, the difference in energy between the ground state and transition state for the reaction of pentafluoronitrobenzene with a nucleophile being far less than for the analogous reaction of pentafluoroaniline. There is also thermodynamic evidence that increase in fluorine substitution of a compound decreases its stability, and C_6F_5H is assumed to be of greater stability than C_6F_5X (where X is a halogen but not F) which is more stable than C_6F_6. The usefulness of this approach towards

predicting the relative reactivity of compounds is restricted because only qualitative estimates of the magnitudes of ground and transition state energies are possible.[195]

Nucleophiles also show marked variation in reactivity. Whereas methylamine and ammonia behave as nucleophiles towards hexafluorobenzene aniline only reacts as the anion $C_6H_5NH^{\ominus}$, generated by mixing sodium hydride with the amine.[199] Sulphur-containing nucleophiles react very readily with fluoroaromatics. Thus 2-mercaptoethanol yields no monosubstitution product with hexafluorobenzene, only the S-linked para-disubstituted product (255) is formed in good yield under mild conditions; under similar conditions the analogous bifunctional nucleophiles ethylene glycol and 2-aminoethanol yield monosubstituted products, see below.[200]



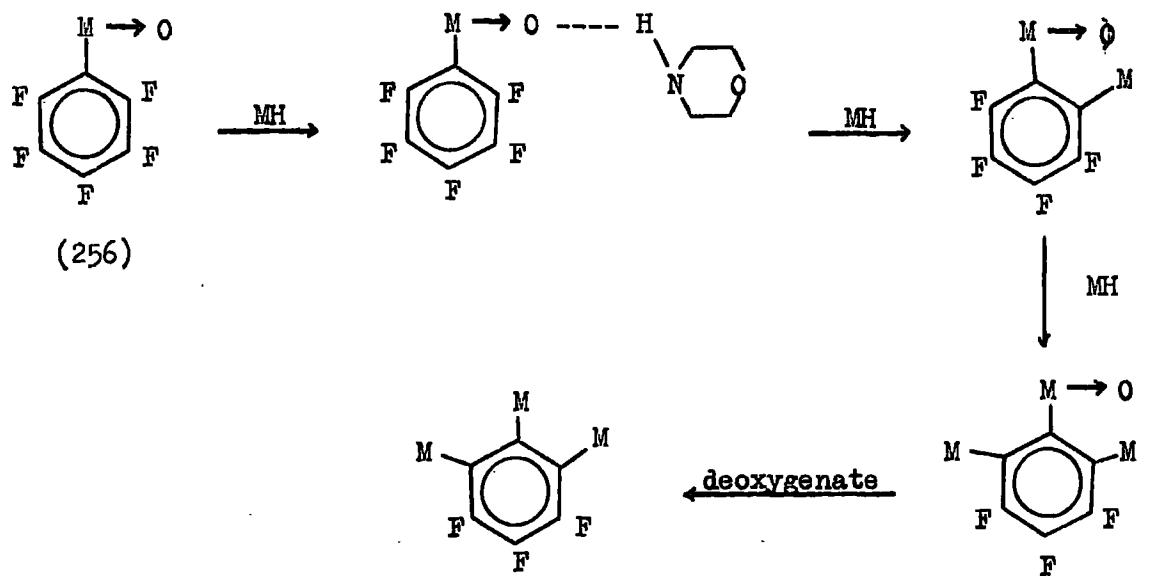
(255)

The above reaction suggests that the S-containing substituent activates the pentafluorophenyl ring towards further replacement. An extreme example of activation of this type is the replacement of all five fluorine atoms by the bulky thiophenyl group in reaction with pentafluorobenzaldehyde under very mild conditions, see below.

Sulphur activates by stabilising the negative charge of the intermediate using its vacant d orbitals.[201]

It was previously stated that certain pentafluorophenyl derivatives were attacked by most nucleophiles para to the substituent but that anomolous high ortho replacement occurred with certain amines. Compounds which behave in this way are pentafluoronitrobenzene, pentafluoronitrobenzene, pentafluorobenzoic acid, pentafluorobenzaldehyde and pentafluorophenyl-substituted-N-oxides.

An example is the reaction of the morpholino-N-oxide (256) with morpholine to give, after deoxygenation, compound (257) as the major product. Di-ortho substitution is said to be due to the inductive effect of the N-oxide substituent increasing the lability of the ortho fluorines and also the secondary amine forming a strong hydrogen bond to the N → O group which anchors the nucleophile in a position ideal for ortho attack as shown below. (257) is only formed in



(256)

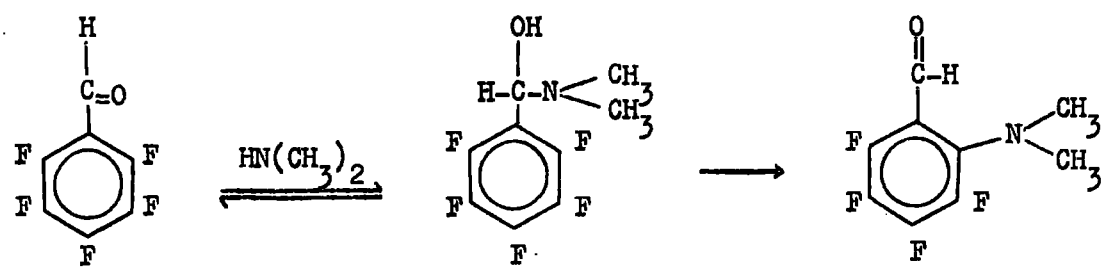
(257)

M = morpholino

non-hydroxylic solvents; reaction in water or alcohol led to the 1,4-disubstituted product as the N → O group hydrogen-bonded to the hydroxylic solvent in preference to the nucleophile.[202]

Similarly pentafluoronitrobenzene was attacked para to the nitro group by methoxide ion but underwent substantial ortho attack with amine nucleophiles. The percentage of substitution ortho to the nitro group decreased in the order $NH_3 > NH_2CH_3 > NH(CH_3)_2$ which is the order of decreasing strength of hydrogen-bonding, and solvent effects again had a marked effect on the amount of ortho substitution.[205] The high percentage of ortho substitution by amine nucleophiles in pentafluoronitrobenzene[204] and pentafluorobenzoic acid[205] has also been attributed to hydrogen-bonding between the nucleophile and the substituent.

Pentafluorobenzaldehyde reacted with dimethylamine to produce both the ortho and para replacement products in the ratio of 3:2 respectively. In this case reaction was said to proceed via an addition complex formed by nucleophilic attack at the carbonyl group, the nucleophilic NMe_2 group being released in an ideal position for attack at the ortho fluorine, as below.[201]



4.4 Nucleophilic Substitution in Polycyclic Fluoroaromatic Compounds

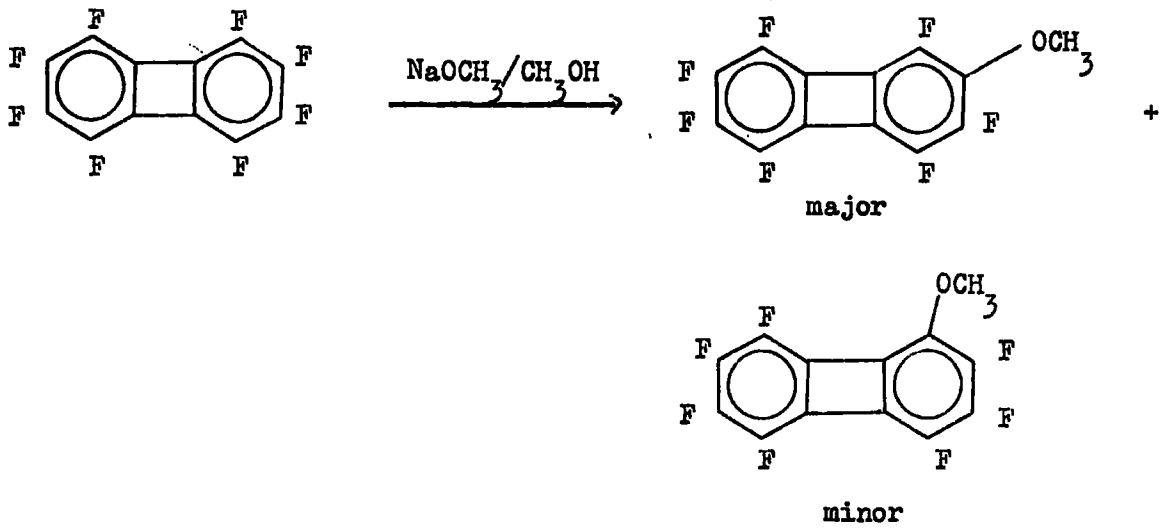
The method first used for the preparation of perfluoronaphthalene, by exhaustive vapour phase fluorination of the parent hydrocarbon using cobaltic fluoride followed by defluorination over a heated metal,[122] has been successfully applied to the preparation of perfluoroacenaphthylene, perfluoroacenaphthene, perfluoroindane, perfluoropyrene, and perfluoroanthracene.[137]

Perfluorophenanthrene has been prepared by the defluorination of perfluoroperhydrophenanthrene over diiron trioxide,[206] perfluorobiphenylene by the vacuum pyrolysis of tetrafluorophthalic anhydride in a silica tube at 750° [207] and 1,2,3,4-tetrafluoronaphthalene is readily available by a variety of routes (see introduction, Chapter 2). Like simple polyfluoro-benzenes, these fluorinated polynuclear aromatic systems are also susceptible to nucleophilic substitution and, to date, papers have been published on nucleophilic attack in perfluoronaphthalene,[125] 1,2,3,4-tetrafluoronaphthalene,[131] perfluoroacenaphthylene,[208] perfluorobiphenylene,[207] and perfluorophenanthrene.[206]

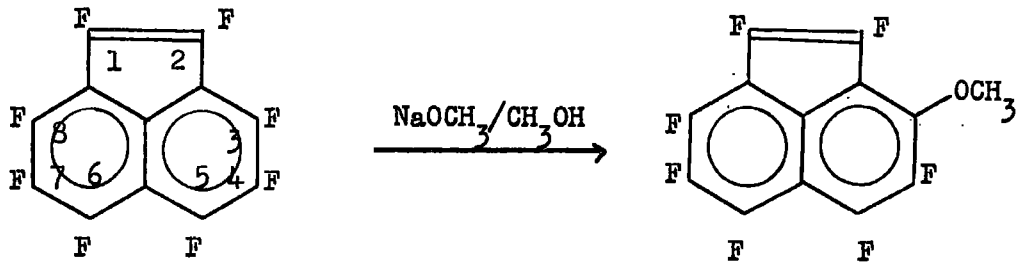
Of these compounds perfluoronaphthalene has been the most extensively investigated. Reaction with a variety of nucleophiles results in replacement of the β fluorine. Attack at the β position is in accord with Burdon's theory, as the negative charge on the intermediate will be mainly localised on a carbon atom involved in ring fusion rather than on carbons bearing a fluorine atom.[125,195] Also, attack of an amine nucleophile on the N-oxide of a β amino heptafluoronaphthalene occurs at the ortho positions in non-hydroxylic solvents, due to hydrogen-bonding; in hydroxylic solvents the 2,6-disubstituted compound is obtained; this is in accord with the results obtained for pentafluorophenyl substituted N-oxides.[127,202] (see introduction, Chapter 2).

1,2,3,4-Tetrafluoronaphthalene undergoes nucleophilic substitution in the fluorocarbon ring and electrophilic substitution in the hydrocarbon ring; the hydrocarbon ring is responsible for the low reactivity of this compound towards nucleophilic attack in comparison with perfluoronaphthalene; for example sodium methoxide will only react with the former compound if heated in a sealed tube to temperatures in excess of 100°, whilst the latter reacts readily under reflux. In agreement with Burdon's theory nucleophiles attack the 2-position of 1,2,3,4-tetrafluoronaphthalene.[131] (See Introduction, Chapter 2).

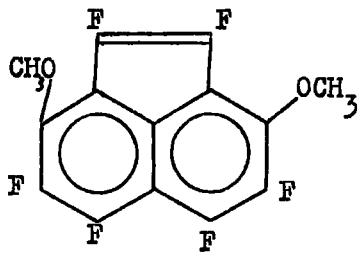
Perfluorobiphenylene reacts readily with sodium methoxide in methanol; under mild conditions the reaction can be controlled to produce mainly monosubstitution. Monosubstitution results in two isomeric products; the major isomer is 2-methoxyheptafluorobiphenylene, in accord with Burdon's theory, 1-methoxyheptafluorobiphenylene is produced in much smaller amount. The structures of these products were determined by n.m.r. spectroscopy. The reaction is shown below.[207]



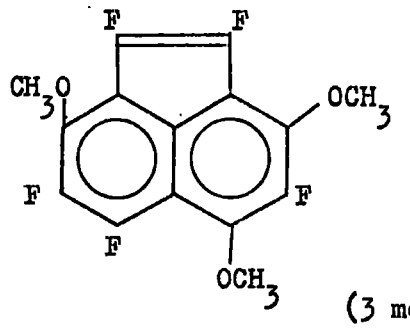
Perfluoroacenaphthylene, like acenaphthylene, possesses considerable double-bond character between C1 and C2; the C1-C2 bond is readily oxidised with potassium permanganate, can be catalytically hydrogenated and adds bromine. Reaction with sodium methoxide in methanol, hydrazine hydrate in ethanol, lithium aluminium hydride in diethyl ether and aqueous ammonia resulted in replacement of the 3-fluorine, the structure of the 3-methoxy compound was established by n.m.r. spectroscopy and all the compounds were interconvertible. Reaction with sodium methoxide could be controlled so that mono, di, tri or tetramethoxy-substituted polyfluoroacenaphthylenes were the major products by varying the mole ratio of nucleophile to fluorocarbon; the products obtained are shown below.



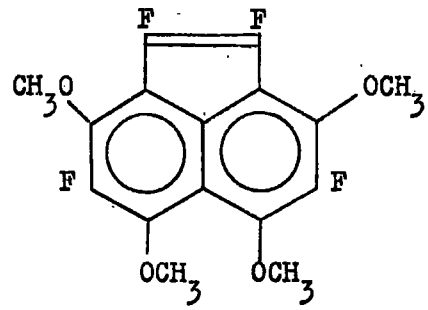
(1 mole) (1 mole of $\bar{O}CH_3$)



(2 moles of $\bar{O}CH_3$)



(3 moles of $^{-}OCH_3$)

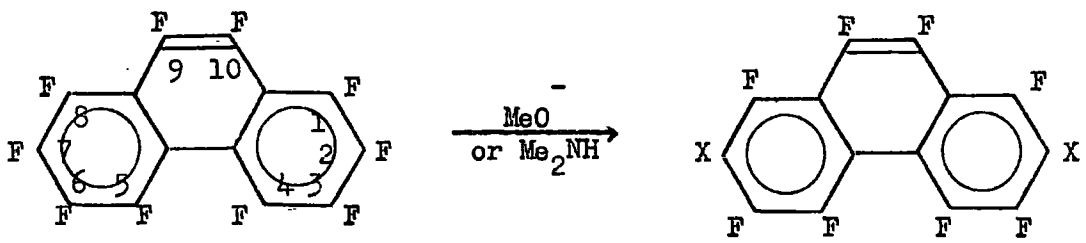


(4 moles of $\bar{O}CH_3$)

After one methoxyl group had been introduced the 8-position was then attacked, then the 5-position and finally the 6-position; replacement of the most-olefinic fluorines at C1 and C2 did not take place. It is not possible to compare the reactivities of the 1 and 2 positions with the remaining positions using Burdon's theory. If the 3,4 and 5 positions are considered it is reasonable to expect the 3 and 5 positions to be more susceptible to nucleophilic attack than the 4 position, for although all these positions possess a carbon atom in a para position which does not bear a fluorine atom, the

former positions have only one ortho-carbon bearing a fluorine atom whereas the latter possesses two; the theory does not explain why attack at C-3 is preferred over attack at C-5.[208]

Recent work on nucleophilic substitution in perfluorophenanthrene has established that the 2 and 7 fluorines are the most readily replaced. Reaction of perfluorophenanthrene with both sodium methoxide in methanol and dimethylamine in ethanol under conditions which led to the replacement of two fluorine atoms resulted in the isolation of the 2,7-disubstituted hexafluorophenanthrenes in both cases, the structures of these compounds being established by both n.m.r. spectroscopy and chemical means.



(X = MeO or Me_2N)

Burdon had tentatively predicted that attack by nucleophiles in perfluorophenanthrene should take place at positions 9 and 10, based on the stabilities of the Wheland-type intermediates. It has been suggested that the reactivity of these positions might be lowered due to the 9-10 bond being the most olefinic; an analogous explanation may also account for the low reactivity of the 1 and 2 position in perfluoroacenaphthylene towards nucleophilic attack.

If Burdon's theory is applied to the non-vinylic positions of perfluorophenanthrene then attack at positions 1 and 4 should be unfavourable, as attack at these positions would lead to intermediates in which the negative charge would be localized mainly on a carbon bearing a fluorine atom; this simple theory cannot however explain why the 2-position should be more reactive than the 3-position.[206]

CHAPTER FOUR

DISCUSSION

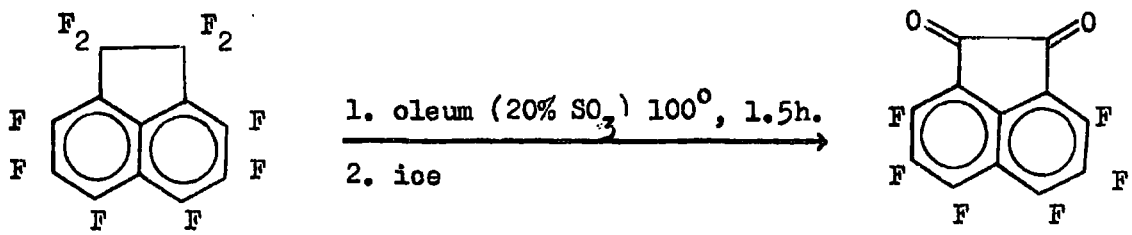
4.5 Some Reactions of Perfluoroindene

Perfluoroindene (XXVIII) can be conveniently prepared by the vacuum pyrolysis of dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene (X), almost quantitative conversion of (X) to (XXVIII) being achievable under optimum conditions and (XXVIII) can be obtained in quantities of the order of 10 grammes from a single experiment (see Chapter 3). The ready availability of perfluoroindene together with interest in the sites of nucleophilic substitution in polycyclic fluoroaromatic compounds stimulated interest in its chemical reactions.

Although Burdon has successfully rationalised the reactivity and orientation of nucleophilic substitution in both homocyclic mononuclear fluoroaromatic compounds,[195] and in the polycyclic fluoroaromatics per-fluoronaphthalene,[125] 1,2,3,4-tetrafluoronaphthalene[131] and perfluorobiphenylene,[207] difficulties arise in predicting the sites of nucleophilic substitution in perfluoroacenaphthylene[208] and perfluorophenanthrene.[206] In both these latter compounds the most olefinic fluorines were not replaced by nucleophiles although for perfluorophenanthrene these fluorines were predicted to be the most susceptible to nucleophilic substitution; for perfluoroacenaphthylene it was not possible to assess the reactivity of the most olefinic fluorines using Burdon's theory (see Introduction).[206,208] In the light of these results it is clearly of interest to investigate the reactions of perfluoroindene with nucleophiles to ascertain if it behaves like perfluoroacenaphthylene and perfluorophenanthrene undergoing substitution in the six-membered ring or if alternatively the olefinic fluorines of the five-membered ring are more readily replaced. The reactions of perfluoroindene with the nucleophiles sodium borohydride, sodium methoxide, hydrazine hydrate and lithium methyl were investigated.

Unsaturated fluorinated compounds often react with sulphuric acid or

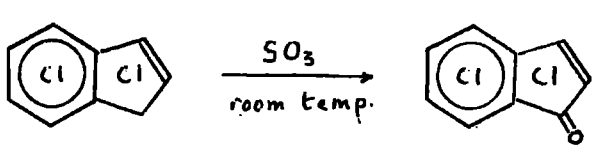
oleum to produce ketones. One of the most common reactions is the hydrolysis of a gem difluoro group to a keto group, the stability of the keto group depending on its position in the molecule.[209] This type of hydrolysis occurs in the transformation of perfluoroacenaphthene (258) to hexafluoroacenaphthene-1,2-quinine (259), using oleum containing 20% SO_3 at 100°, see below.[208]



(258) (259)

Ketone (259) is also formed from the reaction of perfluoroacenaphthylene with oleum containing 20% SO_3 at room temperature; this reaction is said to proceed via a mechanism related to that of the oxidation of 2,3-disubstituted hexafluorobutenes to perfluorobiacetyl using chromic oxide, which involves the intermediacy of a chromate ester.[208]

The reaction of perfluoroindene with oleum was undertaken to ascertain whether the allylic or vinylic fluorines of the five-membered ring would be attacked, the former appearing more likely as perchloroindene gave a quantitative yield of the hexachloroindene (260) on reaction with sulphur trioxide at room temperature, see below.[191]



4.6 Reactions of Perfluoroindene with Nucleophiles

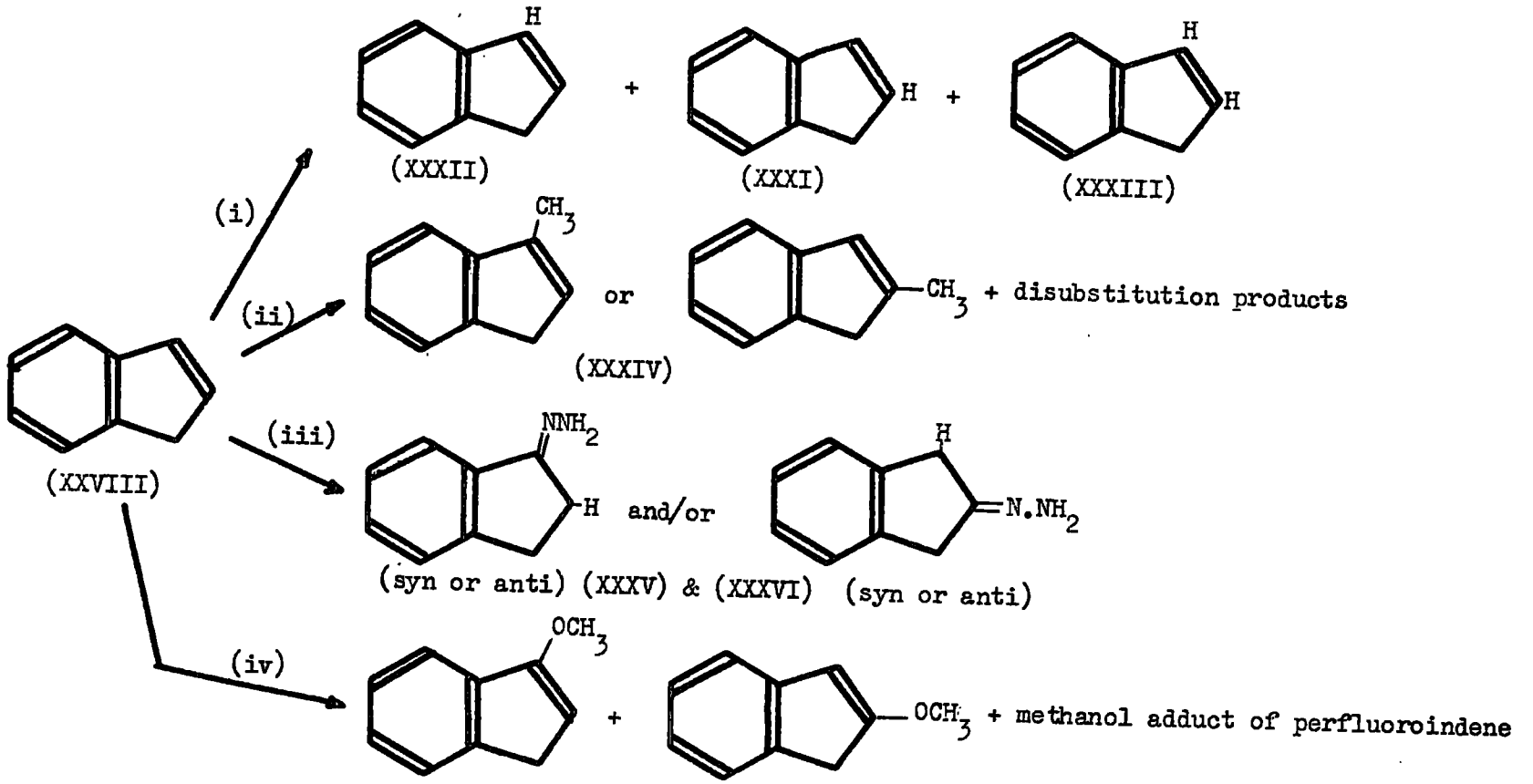
(a) Reaction with Sodium Borohydride in Diglyme

Both lithium aluminium hydride and sodium borohydride react as nucleophiles with fluorinated olefins and aromatic compounds, the nett result being the replacement of fluorine by hydrogen. Reaction with sodium borohydride was investigated in preference to the former reagent, as lithium aluminium hydride often leads to complex reaction products due to multiple substitution and rearrangement of initially-formed products, reactions being difficult to regulate; in contrast reactions with sodium borohydride usually proceed smoothly under mild conditions, substitution to any desired degree being possible.[210]

Reaction of perfluoroindene (XXVIII) with sodium borohydride at 0° could be regulated to give either the mono (C_9HF_7)- or di$(C_9H_2F_6)$- replacement products as major components of the product mixture. (See Figure 8). When perfluoroindene (XXVIII) (1 mole) reacted with sodium borohydride ($\frac{1}{2}$ mole) at 0° for 1 hour all the starting material was consumed and analytical g.l.c. of the product mixture indicated two new longer-retained peaks. Separation of these two peaks by preparative scale g.l.c. resulted in two fractions both of which were single peaks on analytical g.l.c. (col O and col A) over a variety of temperatures.

The shorter-retained fraction, the major product of reaction, had a parent ion in the mass spectrum at m/e 242 (C_9HF_7) with a breakdown pattern consistent with its formulation as heptafluoroindene, and successfully analysed as C_9HF_7. An examination of its ^{1}H and ^{19}F n.m.r. spectra however indicated that more than one product was present, in accord with monosubstitution at more than one position. The infrared spectrum of this mixture of heptafluoroindenes no longer possessed the intense absorption at 1754 cm^{-1} present in the spectrum of perfluoroindene and assigned to the CF=CF stretching frequency of the double bond in the five-membered ring, but contained instead

FIGURE 8



Key to Reagents

(i) $NaBH_4$/diglyme at 0°; (ii) $LiCH_3/Et_2O$ at -78°; (iii) $N_2H_4.H_2O$/EtOH at room temperature; (iv) $NaOCH_3/CH_3OH$ under reflux.

All unmarked bonds are to fluorine.

two bands at 1672 cm^{-1} and 1640 cm^{-1} and was otherwise transparent in the double-bond stretching region, suggesting monosubstitution at both vinylic positions in the five-membered ring, the replacement of the vinylic fluorine by hydrogen resulting in a reduction of the double-bond stretching frequency as also occurs for simple cyclic fluoroolefins.[211] The remainder of the infrared spectrum of these heptafluoroindenes resembled those of other fluorinated indenes prepared, in particular containing strong aromatic bands at close to 1510 cm^{-1}; the vinylic C-H stretch occured at 3130 cm^{-1}.

All the resonances in the n.m.r. spectra could be accounted for by assuming this fraction to be a 1:4 or 4:1 mixture of 1,1,3,4,5,6,7-heptafluoroindene (XXXI) and 1,1,2,4,5,6,7-heptafluoroindene (XXXII). The ^{1}H n.m.r. spectrum contained only two broad resonances due to vinylic protons (5.28 and 5.87δ) in the ratio of 4:1 respectively; the ^{19}F n.m.r. spectrum was more complex but could be interpreted as a 4:1 or 1:4 mixture of (XXXI) and (XXXII) with the aid of integrated intensities. The ^{19}F n.m.r. spectrum contained two low-field resonances in the ratio of 4:1 assigned to the CF_2 groups of compounds (XXXI) and (XXXII); the remaining resonances, ten in all, were assigned to the vinylic or aromatic fluorines of these compounds, each of these resonances integrating to half the intensity of the respective CF_2 resonance (see Table 18 and Figure 8).

The structure of the major isomer, (XXXI) or (XXXII), was determined by X-ray photoelectron spectroscopy (see Appendix 1). This technique convincingly established that fraction 1 was a 4:1 mixture of 1,1,2,4,5,6,7-heptafluoroindene (XXXII), the major component, and 1,1,3,4,5,6,7-heptafluoroindene (XXXI), the minor component. The ultra-violet spectrum of this mixture of isomeric heptafluoroindenes was also in agreement with a fluorinated indene structure (see Table 19).

TABLE 18

N.m.r. Spectral Parameters of Some Fluorinated Indenes[a]

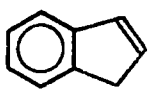
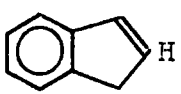
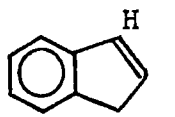
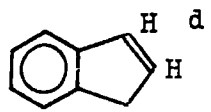
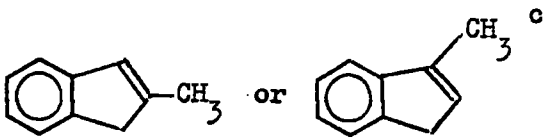
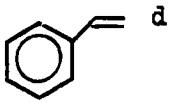
Compound[b]	Fluorines						Protons
	CF_2	Vinylic and/or Aromatic F					
 (XXVIII)	127.3(2)	141.3(1)	148.2(2)	150.9(1)	155.5(1)	162.0(1)	-
 (XXXI)	128.6(2)	136.1(1)	143.1(1)	148.4(1)	152.2(1)	158.7(1)	5.53
 (XXXII)	119.1(2)	120.8(1)	142.3(1)	147.0(1)	151.8(1)	154.4(1)	5.28
 (XXXIII)	121.5(2)	141.3(1)	145.6(1)	150.7(1)	154.9(1)		δ_A 6.03 δ_B 6.64 J_{AB} 6.4

Table 18 contd.

Compound[b]	Fluorines						Protons
	CF_2	Vinylic and/or Aromatic F					
 (XXXIV)	127.3(2)	143.7(1)	147.9(1)	150.5(1)	151.8(1)	158.5(1)	1.87
 (reference 224)		96.4(1)	112.7(1)	137.4(1)	149.7(1)	161.6(1)	171.0(1) -

a. Chemical shifts in p.p.m. upfield from external $CFCl_3$ and external $(CH_4)_4Si$ unless otherwise stated, coupling constants Hz, integrated intensities in parentheses; b. unmarked valencies to F; c. neat liquid; d. solution in CCl_4, ref. internal $CFCl_3$ and internal $(CH_3)_4Si$.

TABLE 19

Ultra-Violet Spectra of Some Indenes[a]

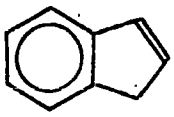
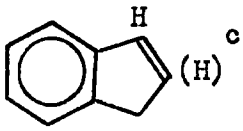
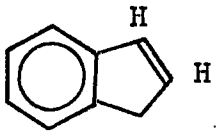
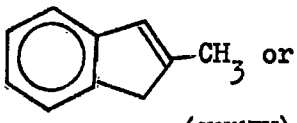
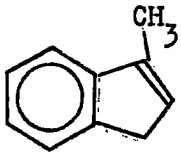
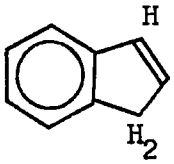
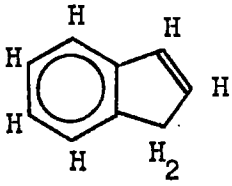
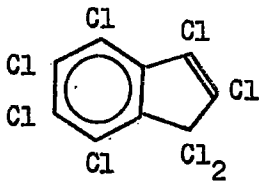
Compound[b]	λ_{max} f ($\log_{10}\varepsilon$)
 (XXVIII)	265^{s}, 272(3.24), 2.85(3.21), 302(3.28)
 (XXXI) and (XXXII)	262^{s}, 271(3.35), 283(3.31), 296(3.27)
 (XXXIII)	267^{s}, 274(3.10), 287^{s}, 300(3.12)
 or  (XXXIV)	265(3.15), 271(3.15), 285^{s}, 303(3.23)
 (reference 117)	248(4.03), 275^{s}, 278(3.03), 285(2.96), 289(2.96)
	223(4.06), 250^{e}(4.02), 281(2.75), 286(2.47), 291(2.20)

Table 19 contd.

Compound[b]		λ_{max}[f] ($\log_{10}\varepsilon$)
	(reference 191)	236(4.29), 242(4.32), 250(4.46), 259(4.49).

a. cyclohexane as solvent unless otherwise stated; b. all unmarked valencies to F; c. run as a 4:(1) mixture; d. ethanol as solvent; e. broad peak extending from 230 mμ to 270 mμ with several shoulders between 250 mμ and 270 mμ; f. in mμ; s. shoulder.

The longer-retained material was shown by mass spectroscopy to be a direplacement product, possessing a parent ion at m/e 224 ($C_9H_2F_6$) and a breakdown pattern consistent with its formulation as a hexafluoroindene. It was also formed as the sole volatile product when perfluoroindene (XXVIII) reacted with more than twice the amount of sodium borohydride used above, at 0° for 5 hours.

The n.m.r. and infra-red spectra of this compound were conclusive in assigning its structure as 1,1,4,5,6,7-hexafluoroindene (XXXIII). It possessed a single absorption in the double-bond stretching region of the infra-red spectrum at 1592 cm^{-1} (CH=CH) an aromatic band at 1517 cm^{-1} and a vinylic C-H stretch at 3125 cm^{-1}. The ^{19}F n.m.r. spectrum contained only five resonances. There was a reasonably sharp low-field resonance integrating to two fluorines and assigned to the CF_2 group, and four discreet multiplets which each integrated to one fluorine, in the aromatic region; these latter resonances were close in shift position to four of the resonances in the n.m.r. spectrum of perfluoroindene. The ^1H n.m.r. was a simple AB system (Table 18) and the ultra-violet spectrum (Table 19) was also consistent with this structural assignment. Recoveries in these reactions were generally poor and in addition to the mono- and di-replacement products isolated, involatile red tars were also formed but were not investigated.

(b) <u>Reaction with Lithium Methyl in Diethyl Ether</u>

The reaction of perfluoroindene (XXVIII) (1 mole) with lithium methyl in diethyl ether (1.6 moles) at -78° led to a product which was separated by preparative scale g.l.c. into two volatile fractions. The shorter-retained fraction, a colourless liquid, was a single pure product, evident from analytical g.l.c. and its spectra. It was characterised as a methylheptafluoroindene by analysis and mass spectroscopy, possessing a parent ion at m/e 256 ($C_{10}H_3F_7$) and a breakdown pattern consistent with this assignment.

Substitution had once more occurred in the five-membered ring as the double-bond stretching frequency of the parent compound at 1754 cm^{-1} was shifted to 1701 cm^{-1} ($H_3CC{=}CF$) in this methylheptafluoroindene (XXXIV); the aromatic stretching bands at approximately 1510 cm^{-1} were also consistent with the indene structure as was the ultra-violet spectrum (see Table 19 and Figure 8).

The ^{19}F n.m.r. spectrum of (XXXIV) contained a low field resonance, integrating to two fluorines and assigned to the CF_2 group, and five multiplets each integrating to a single fluorine in the aromatic or vinylic fluorine region (see Table 18); the ^{1}H n.m.r. spectrum contained a single resonance. As for perfluoroindene (XXVIII), 1,1,2,4,5,6,7-heptafluoroindene (XXXII), 1,1,3,4,5,6,7-heptafluoroindene (XXXI) and 1,1,4,5,6,7-hexafluoroindene (XXXIII) the n.m.r. spectra of compound (XXXIV) were not first-order; also the large peri-couplings observed for other fluorinated polycyclic aromatic compounds are not found in fluorinated indenes[136] and arguments based on the chemical shifts in (XXXIV) and those in compounds (XXVIII), (XXXI) and (XXXII) do not allow an unambiguous assignment of structure to compound (XXXIV), see Table 18.

In an attempt to differentiate between the two possible structures for (XXXIV) the carbon 1s X-ray photoelectron spectra of 2-methylheptafluoroindene and 3-methylheptafluoroindene were simulated theoretically and compared with the experimental spectrum obtained for compound (XXXIV). Unfortunately the experimental spectrum was not sufficiently similar to either of the predicted spectra to allow an unambiguous assignment of either of these structures to compound (XXXIV). The failure of this approach in resolving the structure of (XXXIV) contrasts with its success in the assignment of structures (XXXI) and (XXXII) to the minor and major monosubstitution products formed in the reaction of perfluoroindene with sodium borohydride. The most likely reason for this discrepancy is the well-known difficulty in the theoretical treatment of a methyl group, in contrast to the comparatively simple case of a hydrogen atom.[212]

No conclusion is possible at present as to the exact structure of (XXXIV) although a detailed investigation of the n.m.r. spectra of fluorinated indenes using decoupling techniques, which are not available at Durham, should enable an unambiguous assignment of structure to be made within the near future. (Work being undertaken by Dr. R.S. Matthews).

The longer-retained fraction from this experiment was not a pure compound but a mixture of compounds inseparable on available g.l.c. packings; this was evident from the complexity of its n.m.r. spectra. The mass spectrum of this mixture had a top mass peak at m/e 252 ($C_{11}H_6F_6$) corresponding to dimethyl-hexafluoroindene and a breakdown pattern consistent with this gross structure (see experimental section). If it is assumed that the components of this mixture are of similar volatility then the absence of peaks at m/e 248, 244, etc., and m/e 256 suggests that this fraction contains only or mainly disubstituted hexafluoroindenes.

The infrared spectrum of this mixture contained aromatic absorptions in the region 1520-1490 cm^{-1}, and the indene skeleton was indicated by the ultra-violet spectrum which possessed absorptions in the same regions as the other fluorinated indenes prepared, although of reduced intensity (cf. experimental section and Table 19). In addition to possessing C-H stretching vibrations at 2940 cm^{-1} the infra-red spectrum of this mixture also contained two absorptions in the double-bond region, at 1709 cm^{-1} and 1667 cm^{-1}. The band at 1709 cm^{-1} is at almost the same frequency as the double-bond absorption of the monosubstitution product (XXXIV) (1701 cm^{-1}) and may also be due to a ($H_3CC{=}CF$) double bond; the band at 1667 cm^{-1}, much weaker than the former band, can be assigned to a ($H_3CC{=}CCH_3$) double bond or to a ($H_3CC{=}CF$) double bond in which the methyl group is attached to the vinylic position other than the one to which it is bonded in (XXXIV); both the heptafluoroindenes (XXXI) and (XXXIII) had double bond absorptions at different frequencies. The presence

of a (H_3C=CF) double-bond in at least one of these products would indicate that if this is a dimethylhexafluoroindene one of the substituents must be in the six-membered ring.

The n.m.r. spectra of this disubstituted fraction were complex, as expected for an isomer mixture, it was, however, possible to deduct the major peaks from the ^{19}F n.m.r. spectrum and these are documented in the experimental section. The major peaks were a low-field resonance integrating to 2F and assigned to the CF_2 group and four multiplets integrating to 1F each in the aromatic or vinylic fluorine region, consistent with the major component of the mixture being a dimethylhexafluoroindene. The ^{1}H n.m.r. spectrum was more simple and contained only two resonances, both in the region expected for methyl protons (see experimental section).

(c) Reaction with Sodium Methoxide

Reaction of perfluoroindene (XXVIII) with sodium borohydride and with lithium methyl led to product mixtures from which it was possible to separate and identify individual components. The reaction of perfluoroindene (XXVIII) with methoxide ion was less satisfactory as it was not possible to obtain a pure product adopting the separation procedures successful in the other two cases, however tentative deductions have been made on the basis of spectroscopic data of the unseparated products.

Refluxing approximately equimolar amounts of perfluoroindene (XXVIII) and a solution of sodium methoxide in methanol for 18 hours gave a yellow fluorocarbon product in high yield. Analysis of this product by analytical g.l.c. showed that it contained no more than a trace of unchanged (XXVIII) and an additional volatile peak of longer retention time than perfluoroindene. Attempts were made to separate this product from perfluoroindene and possible involatile products by distillation and by preparative g.l.c.; both attempts were unsuccessful. In the former case the residue after distillation of

perfluoroindene from the product contained none of the initial volatile product, as shown by analytical g.l.c. and i.r. spectroscopy, but contained only more involatile materials whose infra-red spectrum contained several absorptions in the region 1800-1600 cm^{-1}, characteristic of carbonyl or fluorinated double-bond stretching frequencies, and a vast number of absorptions elsewhere. These results are not inconsistent with the initially-formed product decomposing to a mixture of ketones on heating. The attempted separation by preparative scale g.l.c. resulted in the recovery of only a trace of brown volatile material whose infra-red spectrum was identical to that of the product prior to separation; brown involatile tars were found in the manifold of the instrument.

The instability of the initial product was further evident from the yellow fluorocarbon darkening considerably on standing at room temperature for 24 hours in a stoppered tube; the pungent fumes were emitted on unstoppering the tube.

Examination of the product formed from the reaction of approximately equimolar amounts of the two reactants by infrared spectroscopy showed a single intense absorption in the region 1800-1517 cm^{-1}, at 1709 cm^{-1}. The stoichiometry of the reaction is in agreement with this being a ($FC{=}COCH_3$) stretching absorption consistent with substitution taking place in the five-membered ring; the rest of the infrared spectrum, which contained aromatic bands at about 1510 cm^{-1}, was consistent with a fluorinated indene structure.

The n.m.r. spectra of this product showed that it contained more than one compound. The ^{19}F n.m.r. spectrum contained three sets of resonances at low-field in the CF_2 region. An AB quartet, $J \sim 270$ Hz, of weak intensity (<10% of the product) centred at approximately 102 p.p.m. was assigned to the CF_2 group of a methanol adduct of perfluoroindene, the value of the coupling constant together with the shift of the fluorines indicating a CF_2 group in a fluorinated indane skeleton (see experimental section and Table 20).

TABLE 20

N.m.r. Spectral Parameters of Some Fluorinated Indane Derivatives[a]

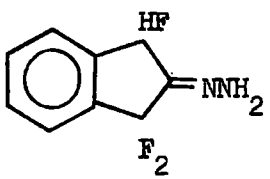
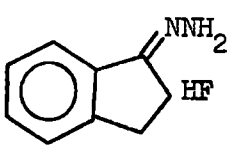
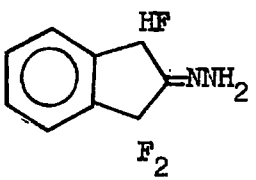
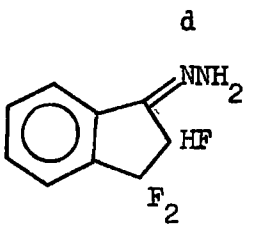
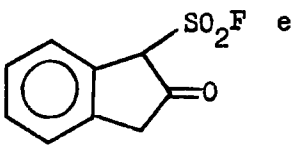
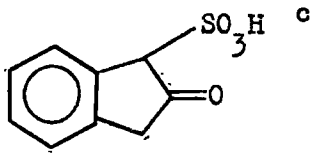
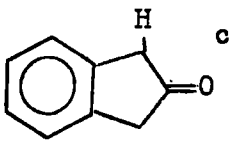
Compound[b]		Fluorines				Protons
 (XXXV) or  (syn and/or anti)	δ_A 94.0(1) δ_B 109.0(1) J_{AB} ~270	194.5(1) (d, J~50)	137.3(1)	142.2(1)	148.3(2)	
 (XXXVI) or  (syn and/or anti)	δ_A 94.0(1) δ_B 107.8(1) J_{AB} ~270	199.4(1) (d, J~50)	143.4(2)	149.6(1)	157.1(1)	
 (XXXVII)	δ_A 95.1(1) δ_B 105.7(1) J_{AB} 279	-42.0(1)	130.4(2)	135.6(1) 141.3(1)	164.2(1)	

Table 20 contd.

Compound[b]	Fluorines					Protons
 (XXXVIII)	δ_A 94.4 (1) δ_B 111.1(1) J_{AB} 271		136.8(1)	139.1(2)	145.5(1)	170.5(1)	8.27
 (XXXIX)	103.2(2)	208.6(1) (d.J = 48)	135.9(1)	139.1(2)	145.7(1)		5.42(d,J = 48)

a. Chemical shifts in p.p.m. upfield from internal $CFCl_3$ and internal $(CH_3)_4Si$; unless otherwise stated, integrated intensities in parentheses, coupling constants Hz; b. unmarked valencies to F; c. neat liquid or oil; d. solution in methanol; e. solution in oleum (20%, SO_3) ref external $CFCl_3$.

Two other resonances present in the ratio of 2:1 at similar chemical shift to the CF_2 resonances of other fluorinated indenes prepared (see Table 18 and experimental section) were assigned to the CF_2 resonances of 2-methoxyheptafluoroindene and 3-methoxyheptafluoroindene. A doublet of low intensity at 203 p.p.m., with J = 50 Hz was assigned to the fluorine of the geminal HF system in a methanol adduct of perfluoroindene, the position of this resonance and magnitude of the coupling constant being as expected for a fluorine of this type.[213] Two broad resonances to high-field of the remaining resonances, which were all sharp multiplets, integrated in the ratio of 2:1 and their combined areas were half the combined area of the resonances assigned to the CF_2 fluorines 2-methoxyheptafluoroindene and 3-methoxyheptafluorindene; these were assigned to the vinylic fluorines in the five-membered rings of these compounds, their broadness and highfield position being presumably attributable to the adjacent methoxyl group. The remaining resonances lay between 123.1 and 157.2 p.p.m. and together integrated to slightly more than twice the area of the three sets of CF_2 resonances. This is consistent with the above assignments as, in addition to the aromatic and vinylic fluorines, the fluorine geminal to the methoxyl group in a methanol adduct of perfluoroindene might also resonate in this region. It was not possible to make any meaningful assignments in this part of the spectrum due to its complexity caused by a large number of extensively overlapping multiplets.

The ^1H n.m.r. spectrum contained only two broad resonances at 3.15 and 3.9 δ, the correct region for methoxyl protons, in the ratio of 1:2 respectively. Presumably resonances due to the methanol adduct of perfluoroindene were either underlying these resonances or were very weak (see experimental section).

The mass spectrum of the crude product mixture provided further evidence for the above assignments. The top mass ion at m/e 292 ($C_{10}F_8H_4O$)

corresponded to the parent ion of a methanol adduct of perfluoroindene, and the most abundant ion in the mass spectrum was at m/e 272 ($C_{10}F_7H_3O$) due to either the parent ion of methoxyheptafluoroindene or loss of hydrogen fluoride from a methanol adduct of perfluoroindene. The breakdown pattern is not inconsistent with a mixture of 2-methoxyheptafluorindene and 3-methoxyheptafluoroindene containing a minor amount of a methanol adduct of perfluoroindene. If we assume all the products are of similar volatility the absence of ions at m/e 284, 296, 308, etc. suggests that further substitution has not occurred to any marked extent (see Figure 8).

Attempts to remove the methanol adduct from the product mixture after equimolar amounts of perfluoroindene and sodium methoxide in methanol had undergone reaction, by dehydrofluorination, were unsuccessful. Warming with aqueous potassium hydroxide resulted in some reaction, as the reactants darkened in colour and some fluorocarbon was consumed, however the infra-red and n.m.r. spectra of the recovered material and the material before dehydrofluorination were almost identical. It appears that dehydrofluorination of the methanol adduct of perfluoroindene and decomposition of the methoxy heptafluoroindenes must proceed at similar rates under these conditions.

A reaction was also undertaken between perfluoroindene and sodium methoxide in diglyme; the infra-red spectrum and analytical g.l.c. trace of the product was substantially the same as for reaction with sodium methoxide in methanol.

(d) Reaction with Hydrazine Hydrate in Ethanol

Refluxing hydrazine hydrate (2 moles) with perfluoroindene (1 mole) in ethanol led to a sticky black solid from which a small quantity of sublimable material was isolated, the residue being an involatile tar.

When equimolar proportions of perfluoroindene (XXVIII) and hydrazine hydrate, in solution in ethanol, were allowed to react at room temperature a

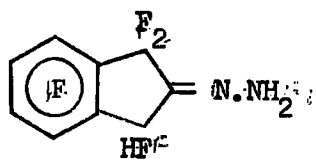
brown solid product was isolated. The ^{19}F n.m.r. spectrum of this product showed that it contained more than one compound and from repeated fractional crystallisations, monitored by ^{19}F n.m.r. spectroscopy, it became evident that the product was a mixture of two compounds whose ^{19}F n.m.r. spectral parameters were closely similar; although it was not possible to isolate either of these compounds in a pure form, some degree of concentration of one isomer was obtained by this means and the ^{19}F n.m.r. spectral parameters of each component were deduced from the ^{19}F n.m.r. spectra of several mixtures of these compounds. The two compounds (XXXV) and (XXXVI) were present in the reaction product in the ratio of 85:15 respectively.

The mass spectrum of this mixture of (XXXV) and (XXXVI) possessed a top mass ion at m/e 272 ($C_9F_7N_2H_3$) corresponding to the loss of one fluorine from perfluoroindene and the gain of $NHNH_2$, as might be expected for attack by NH_2NH_2 and loss of HF; it also analysed correctly for $C_9F_7N_2H_3$.

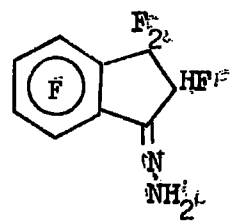
The spectral parameters of (XXXV) and (XXXVI) showed that the indene skeleton of the starting material was no longer present in these products. In particular the ^{19}F n.m.r. spectra of both compounds contained a low-field AB quartet with $J \sim 270$ Hz, (cf. the methanol adduct of perfluoroindene, previous section) integrating to two fluorines, assigned to the CF_2 group in a five-membered ring of an indane skeleton, and four other resonances together integrating to five fluorines. A high-field signal close to 200 p.p.m. from $CFCl_3$, a doublet with $J \sim 50$ Hz, is indicative of a fluorine geminal to a hydrogen in the five-membered ring of an indane skeleton[213] (cf. the methanol adduct of perfluoroindene, previous section) and integrated to a single fluorine. The remaining resonances were in the aromatic or vinylic fluorine region and consisted of three multiplets, two of which integrated to one fluorine, the third integrated to two fluorines (see Table 20).

The infra-red spectra of mixtures of (XXXV) and (XXXVI) contained two absorptions in the N-H stretching region at 3448 and 3333 cm^{-1} characteristic of $-NH_2$, an absorption at 1613 cm^{-1} in the N-H bending region and two absorptions at 1520 and 1513 cm^{-1} characteristic of a fluorinated benzene ring. A single intense absorption in the ultra-violet spectrum at 284 mμ ($\log_{10}\varepsilon$ = 4.33, $CHCl_3$ as solvent), indicates that the fluorinated indene structure is no longer present in these compounds. (cf. Table 19).

The spectral evidence above is consistent with (XXXV) and/or (XXXVI) possessing either of the gross structures (261) or (262) shown below (see Figure 8).



(261)



(262)

It appears to be quite general that the aromatic fluorines in fluorinated indane derivatives, as above, resonate as three signals, one due to two fluorine atoms the other two fluorines producing discreet resonances, in contrast to substituted polyfluoroindenes where all the aromatic and vinylic fluorines resonate at discreet positions (cf. Tables 18 and 20). Presumably the fluorines farthest from the ring junction are little influenced by the asymmetry in the five-membered ring and possess almost the same shift. There appears to have been little work done on the formation of fluorinated hydrazenes from the reaction of hydrazine with fluoroolefins.

Hexafluoropropene ($\frac{1}{2}$ mole) when heated in a silver-lined bomb at 60° for

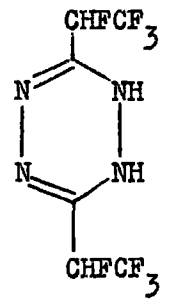
8 hours with hydrazine hydrate (1 mole) in relatively non-polar solvents such as dioxan or ether produced the α hydrazone (263, R=H) in 66% yield. Related products (263, R=C_6H_5, $CONH_2$) were formed when phenylhydrazine and semicarbazide reacted with this olefin, see below.

$$H_2N.NHR + F_3C\text{-}CF{=}CF_2 \longrightarrow F_3CCHF\text{-}CF{=}N\text{-}NHR \qquad R = H,\ C_6H_5,\ CONH_2$$

(263)

The α hydrazone (263, R=H) possessed infra-red absorptions at 3390, 3333, 3226 and 1626 cm^{-1} due to NH_2 (cf. compounds (XXXV) and (XXXVI)); it was also readily transformed into sym-tetrazines (264) on standing at room temperature, hydrogen fluoride being evolved. The sym-tetrazines (264) were the only products isolated when hexafluoropropene reacted with hydrazine hydrate in hydroxylic solvents at temperatures below 100°, see below.[214]

$$2CF_3CF{=}CF_2 + 2NH_2.NH_2.H_2O \longrightarrow$$

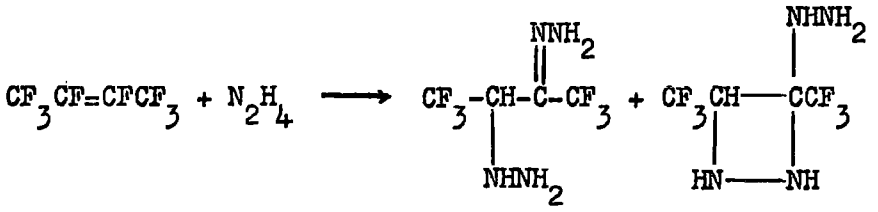


(264)

Although no mention was made of the observation of more than one isomer of compounds (263), geometric syn and anti isomers of some hydrazones are known and have been separated and identified, although they have closely similar physical characteristics.[215]

Reaction of anhydrous hydrazine (4 moles) with the internal fluorinated olefins octafluoro-2-butene or 2,3-dichlorohexafluoro-2-butene (1 mole) at 0° in ether or acetonitrile led to two isomeric disubstitution products in each

case. One of the products of reaction with octafluoro-2-butene was characterised as a 1,1,1,4,4,4-hexafluoro-3-hydrazino-2-butanone hydrazone (265) m.p. 124-125°, the other isomer (m.p. 54-55°) was thought to be either another form of this compound (syn or anti) or the cyclic structure (266) shown below.[216]



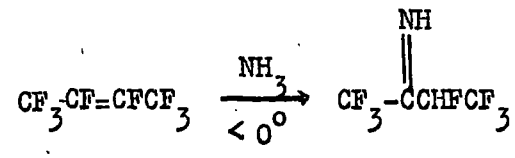
(265) (266)

On the basis of the evidence available and in the absence of compounds of structure similar to (261) or (262) it is not possible to make absolute assignments of structure to (XXXV) and (XXXVI). Clearly they could be either syn or anti isomers of either of the structures (261) or (262).

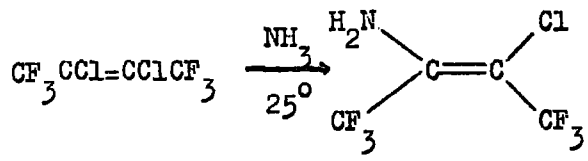
As attack of both sodium methoxide and sodium borohydride on perfluoroindene led to replacement of both the 2- and 3-fluorines, formation of both structures (261) and (262) is possible from reaction with hydrazine. Also the aromatic fluorine resonances of (XXXV) and (XXXVI) are at quite different shift positions and it is not obvious how syn and anti isomers of one of the gross structures above, (261) and (262), can account for this difference; the aromatic fluorine resonances of the positional isomers (261) and (262) however would intuitively be expected to occur at quite different shifts, but in the absence of n.m.r. data of analogous compounds it is not possible to come to any firm conclusion as to the exact nature of compounds (XXXV) and (XXXVI).

The formation of the hydrazones (XXXV) and (XXXVI) in preference to the hydrazine substitution product(s) can be explained by the destabilisation

of fluorine attached to sp^2 carbon relative to fluorine attached to sp^3 carbon. A similar explanation has been invoked to account for the products of reaction of ammonia with octafluoro-2-butene and 2,3-dichlorohexafluoro-2-butene. Reaction of the former compound with ammonia below 0° led to a good yield of the imine (267), whereas in the latter case reaction at 25° gave a low yield (2%) of the vinyl amine (268), the less electronegative chlorine atom being less destabilising towards a double bond than a fluorine atom.[216]



(267)



(268)

4.7 Reaction of Perfluoroindene with Fuming Sulphuric Acid

Perfluoroindene reacted extremely readily with oleum. Examination of the ^{19}F n.m.r. spectrum of a mixture of perfluoroindene and oleum containing 33% SO_3, which had stood at room temperature for 2 hours, indicated that all the initial perfluoroindene had undergone reaction. On pouring this reaction mixture onto packed ice the expected deposition of a fluorocarbon product did not occur but instead a pale yellow aqueous solution was obtained.

The aqueous solution was extracted with ether; the ether extracts were dried with magnesium sulphate and most of the ether was removed using a rotary

evaporator; when no more ether appeared to be evaporating the red-brown oily residue was warmed to $60^{o}/10$ mm.Hg for a further 30 minutes in an attempt to remove any final traces of solvent. The red-brown oily residue was insoluble in chloroform or cyclohexane but was very soluble in water to give a solution which was acid to litmus. Due to its ready thermal decomposition, discussed below, it could not be adequately purified, however its n.m.r. spectra were consistent with it being a single fluorocarbon (XXXVIII) containing a small amount of ether as a contaminant.

Distillation of this brown oil at $100^{o}/10^{-3}$ mm.Hg., resulted in its complete decomposition to a more volatile fraction, which will be discussed later, and a pale yellow liquid (XXXIX). Elemental analysis and mass spectroscopy confirm that this compound (XXXIX) has the molecular formula C_9HOF_7; evidence for its gross structure is provided by its infra-red, n.m.r. and ultra-violet spectra.

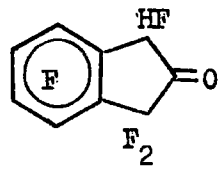
The ^{19}F n.m.r. spectrum of (XXXIX) contained four sets of resonances. A broad low-field resonance integrating to 2F is assigned to a CF_2 group; a high field resonance at 208.6 p.p.m. due to a single fluorine, a doublet with J = 48 Hz, is characteristic of a tertiary fluorine geminal to a hydrogen atom;[213] three remaining resonances, two of which integrate to a single fluorine, the third integrating to two fluorines, in the vinylic or aromatic fluorine region, can be assigned to the four aromatic fluorines of a fluorinated indane skeleton (see previous section and Table 20). The only resonance in the ^{1}H n.m.r. spectrum was a doublet, J = 48 Hz, due to the tertiary proton geminal to a fluorine atom.[213]

In the infra-red spectrum strong absorptions at 1771 and 1639 cm^{-1} were present, in the double bond or carbonyl stretching region; a third strong band at 1515 cm^{-1} can be attributed to the fluorinated benzene ring.

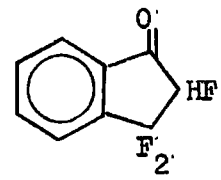
The loss of the fluorinated indene structure in (XXXIX) was indicated by the ultra-violet spectrum possessing strong absorptions at 240 and 246 mμ

with less-intense absorptions at 285 and 289 m (see experimental section and Table 19).

The above spectral data is consistent with (XXXIX) possessing either of the structures (269) or (270) shown below.



(269)



(270)

In particular the ^{19}F n.m.r. spectrum supports the fluorinated indanone structures. Ketones (269) and (270) are closely related to the fluorinated indanone hydrazones (XXXV) and (XXXVI) which may possess structures (261) and/or (262), discussed in the previous section, and this is evident from a comparison of the n.m.r. spectra, (Table 20), (XXXV), (XXXVI) and XXIX).

It might appear anomolous that ketone (XXXIX) possesses two strong absorptions in the carbonyl region; however both cyclopentanone and octafluorocyclopentanone also show this peculiarity. The second band is said to be a combination band; their four and six-membered ring anologues display a single carbonyl absorption.[211]

Infra-red or ultra-violet spectroscopy ought to be capable of distinguishing between structures (269) and (270) for compound (XXXIX), on the basis of the latter structure having more extended conjugation than the former, however there is a paucity of published spectral data for structures of this type. A distinction between these two structures is however possible from a detailed examination of the mass spectral fragmentation pattern of (XXXIX) (see Figure 9). All the major fragmentation pathways are readily accounted for

by structure (269); rearrangements need to be invoked if (XXXIX) has structure (270).

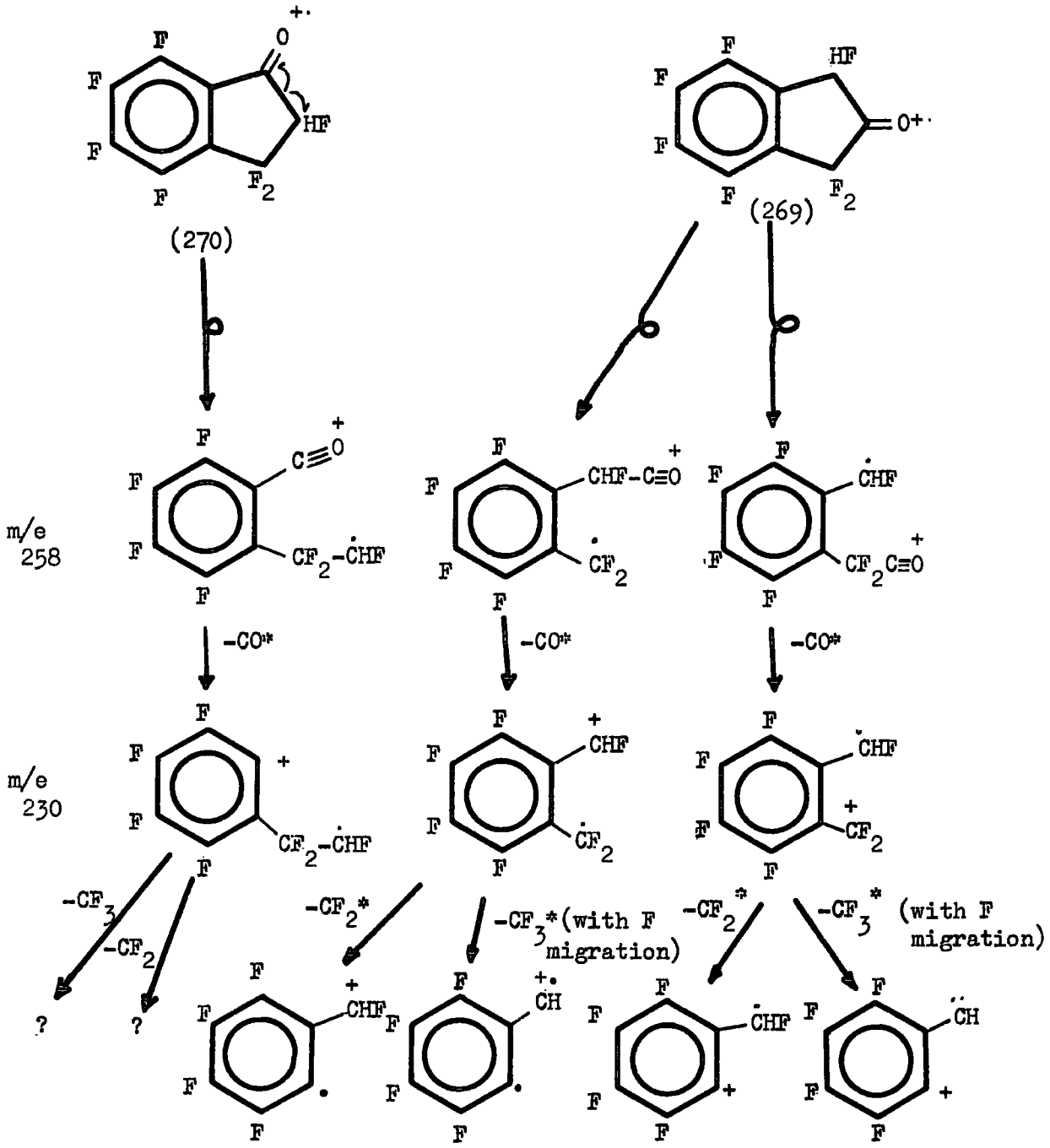
The major fragmentation ions are those at m/e 230 (70%, P-28), 180 (63%, P-78) and 161 (94%, P-97) and metastable ions are present identifying the fragmentation processes m/e 258 → m/e 230 with elimination of a unit of 28 a.m.u. (CO); m/e 230 → m/e 180 with elimination of 50 a.m.u. (CF_2) and m/e 230 → m/e 161 with elimination of 69 a.m.u. (CF_3). Initial ionization will remove an n electron from oxygen and subsequent fragmentation can be rationalised as shown in Figure 9.[217] In addition to the major fragmentation processes shown, which are supported by metastable transitions, the less important transitions can also be accounted for by structure (269) but not by (270). (see Appendix 2).

Having assigned structure (269) to compound (XXXIX) it is possible to speculate as to the nature of its precursor (XXXVIII) and attempt to elucidate the mechanism of the formation of this unexpected product.

The brown oil, precursor to (XXXIX), contained a small amount of ether and a single fluorocarbon (XXXVIII) as deduced from its spectra. The acidic nature of (XXXVIII) was evident from its insolubility in relatively non-polar solvents but ready solubility in water to give a solution acid to litmus, its infra-red spectrum contained a broad acid OH absorption which had a maximum at 3450 cm^{-1} and extended to 2500 cm^{-1} and its ^1H n.m.r. spectrum possessed a low-field resonance at 8.3 δ which can be assigned to an acidic proton.

A comparison of the spectra of (XXXVIII) and (XXXIX) indicates structural similarities. The infra-red spectrum of (XXXVIII), like that of (XXXIX), possesses two absorptions in the carbonyl region (1770 and 1645 cm^{-1}) at almost the same frequencies as the latter (1771 and 1639 cm^{-1}), and possesses a further strong absorption at 1515 cm^{-1} which can be attributed to a fluorinated benzene ring.

FIGURE 9

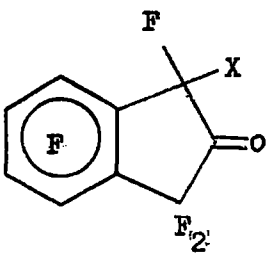


* transitionsalsupported by metastable ions.

The ^{19}F n.m.r. spectra of (XXXVIII) and (XXXIX) are also closely similar (see Table 20). In the aromatic fluorine region (XXXVIII), like (XXXIX), possesses three resonances two of which integrate to a single fluorine, the third integrating to two fluorines; these resonances are at approximately the same shift for both compounds. The low-field CF_2 resonance of (XXXVIII) is an AB system with J = 271 Hz, indicative of the coupling expected in a fluorinated indane skeleton (cf. compounds (XXXV) and (XXXVI) in Table 20), the AB system being centred at approximately the same shift as the broad CF_2 resonance of (XXXIX), and integrating to two fluorines. The remaining resonance in the ^{19}F n.m.r. spectrum of (XXXVIII) is a very sharp signal integrating to a single fluorine, to high field of the aromatic fluorines at 170.5 p.p.m., the position and sharpness of this fluorine suggesting a tertiary environment.

The ultra-violet spectrum of (XXXVIII) contained an intense absorption at 265 m and a weaker one at 290 mμ; (XXXIX) also possessed absorptions in the same region.

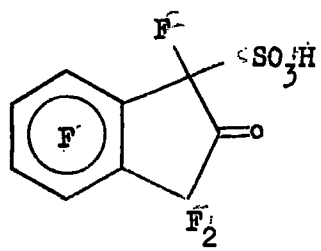
The above evidence suggests that (XXXVIII) has a structure related to that of (XXXIX) in which the hydrogen atom of (XXXIX) is replaced by some other group X which on pyrolysis becomes a hydrogen atom. Thus compound (XXXVIII) can be assigned structure (271).



(271)

The nature of the group is not easy to determine due to the ready decomposition and hence incomplete purification of (XXXVIII). An attempt to obtain a mass spectrum of (XXXVIII) was unsuccessful, only the spectrum of its decomposition product (XXXIX) was obtained. The presence of sulphur in X was indicated by analysis of (XXXVIII); after removing as much ether as possible without excessive decomposition to (XXXIX) the oil was found to contain 8.22% sulphur. Further evidence of the nature of X was obtained from a spectral investigation of the volatiles obtained when (XXXVIII) was completely decomposed to (XXXIX). The gas-phase infra-red spectrum of the volatiles was almost identical to that of pure ether, the contaminant of (XXXVIII); however the mass spectrum of the volatiles possessed ions due to the fragmentation of ether and in addition ions containing only one atom of sulphur, deduced from the ratio of the intensities of the parent ions to the parent +2 ions; parent + 4 ions were absent. Peaks at m/e 64 and m/e 48 were suggestive of SO_2^+ and SO^+ respectively, a peak at m/e 81 suggested SO_3H^+ and the top mass ion at m/e 155 was not inconsistent with $[HSO_3 + (C_2H_5)_2O]^+$.

The most likely structure for (XXXVIII), based on the above data, is (272) shown below.

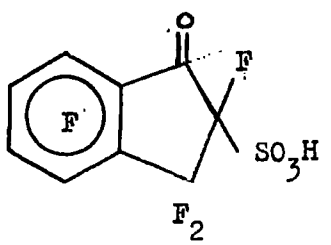


(272)

A number of perfluoroalkane-sulphonic acids have been prepared and their infrared spectra, particularly the asymmetrica and symmetric stretching frequencies of the $-SO_2-$ group, have been recorded. It appears that the symmetric stretching frequency of the $-SO_2-$ system is little influenced by the

presence of fluorine in a molecule whereas the asymmetric stretching vibration is shifted to higher frequency, being at 1260 cm^{-1} for CF_3SO_3-systems as against 1190-1160 cm^{-1} for analogous hydrocarbon systems.[218] Compound (XXXVIII) possesses a strong band at 1266 cm^{-1} which may be assignable to the asymmetric stretching vibration of the SO_2 group. (XXXVIII) is also very corrosive and after running its infra-red spectrum the potassium bromide plates were found to be badly etched; this is consistent with the behaviour of a fluorinated sulphonic acid.[218] The sulphur content of $C_9HF_7SO_3$ is 9.95%; the value of 8.22% obtained above is not unreasonable both in terms of (XXXVIII) not being analytically pure, still containing some ether, and also as fluorinated sulphonic acids are known to readily absorb water.

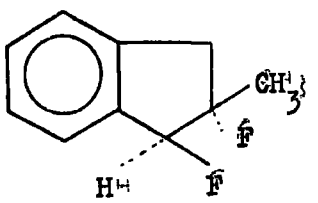
Ketone (XXXIX), the decomposition product of (XXXVIII), has been assigned structure (269) in preference to the alternative structure (270) on the basis of its mass spectral fragmentation pattern. As (XXXVIII) and (XXXIX) are structurally related then if it can be shown that (XXXVIII) does not possess structure (273) below, this will provide further evidence for the assignment of structure (269) to ketone (XXXIX).



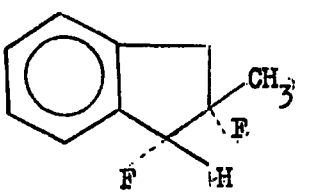
(273)

Structure (273) is most probably ruled out on the basis of the sharpness of the tertiary fluorine resonance in the ^{19}F n.m.r. spectrum of (XXXVIII). The ^{19}F n.m.r. spectra of the products of fluorination of 2-methyl indene and indene, compounds (274), (275) and (276) respectively, see below, contain a

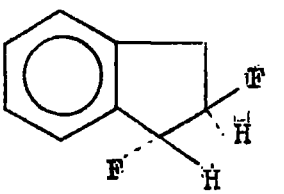
vicinal FF coupling of approximately 8 Hz, where $\angle FF_{vic} = 0^{o}$ and a viccinal FF coupling of approximately 4 Hz where $\angle FF_{vic} \sim 90^{o}$. The tertiary fluorine in compound (272) might also be expected to contain some evidence of couplings of this type, however the tertiary fluorine of (XXXVIII) is a sharp resonance only 2 Hz wide at half-height. This supports the assignment of structure (272)



(274)



(275)



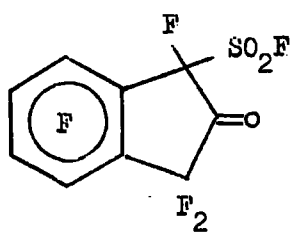
(276)

to compound (XXXVIII) and hence that of (269) to compound (XXXIX).[213]

The sulphonic acid (XXXVIII) was obtained when a mixture of perfluoroindene (XXVIII) and oleum, which had been standing for two hours at room temperature, was poured onto ice. The ^{19}F n.m.r. spectrum of the reaction mixture prior to its addition to water closely resembled that of the sulphonic acid (XXXVIII) (see Table 20). It contained resonances integrating to eight fluorines; as for (XXXVIII) there was an AB quartet in the CF_2 region integrating to two fluorines, three resonances in the aromatic fluorine region, two of which integrated to a single fluorine, the third integrating to two fluorines, and the distinctive sharp resonance due to a tertiary fluorine which integrated to one fluorine; in addition, to very low field, below $CFCl_3$, an extremely sharp resonance was present which also integrated to a single fluorine.

The loss of a fluorine atom in forming the sulphonic acid (XXXVIII) from perfluoroindene (XXVIII) must occur either in solution in oleum or on

adding the reaction mixture to water. If the former is true then the ^{19}F n.m.r. spectrum of the mixture of perfluoroindene and oleum, prior to its addition to water, must be that of a mixture of the sulphonic acid (XXXVIII) and some other species containing a single fluorine, which must account for the very low-field signal. Although marked solvent shifts might occur in oleum solution it is considered more likely that the considerable shift differences in the ^{19}F n.m.r. spectra of (XXXVIII) and the mixture of perfluoroindene and oleum prior to the addition of water are due to the presence of the sulphonyl fluoride (XXXVII) in the latter solution. In addition, the most plausible mechanism for the transformation of perfluoroindene (XXVIII) to ketone (XXXIX) would involve the intermediacy of (XXXVII), and also the very low-field signal present in the ^{19}F n.m.r. spectrum of the reaction mixture prior to its addition to water is consistent with the S-F signal of a sulphonyl fluoride;[105] however, loss of fluorine from perfluoroindene (XXVIII) in the oleum solution would no doubt result in its displacement as F^- which would then attack some species in oleum with the formation of an S-F bond, sulphur being the most electrophilic centre; this might also account for the low-field signal. Sulphonyl fluoride (XXXVII) would possess structure (277) below.

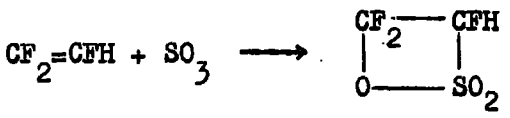


(277)

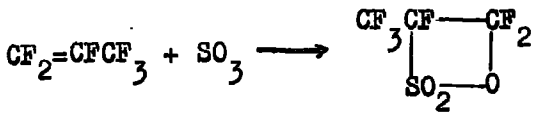
The mechanism for the conversion of perfluoroindene (XXVIII) to 1,1,3,4,5,6,7-heptafluoroindan-2-one (XXXIX) via the intermediate compounds 1,1,3,4,5,6,7-heptafluoroindan-2-one-3-sulphonyl fluoride (XXXVII) and 1,1,3,4,5,6,7-

heptafluoroindan-2-one-3-sulphonic acid (XXXVIII) (see Figure 10) can be best rationalised as proceeding initially from the β sultone of perfluoroindene.

In marked contrast to hydrocarbon olefins, fluoroolefins readily add sulphur trioxide forming β sultones. Many of these compounds have been prepared and it appears that the initial stage of reaction is attack at the double-bond by the electrophilic sulphur atom; reactions with unsymmetrical fluoroolefins proceed in accord with the polarity of the double bond and there is a decreasing tendency towards sultone formation with increasing hydrogen substitution in the fluoroolefin, see below.



(60%)

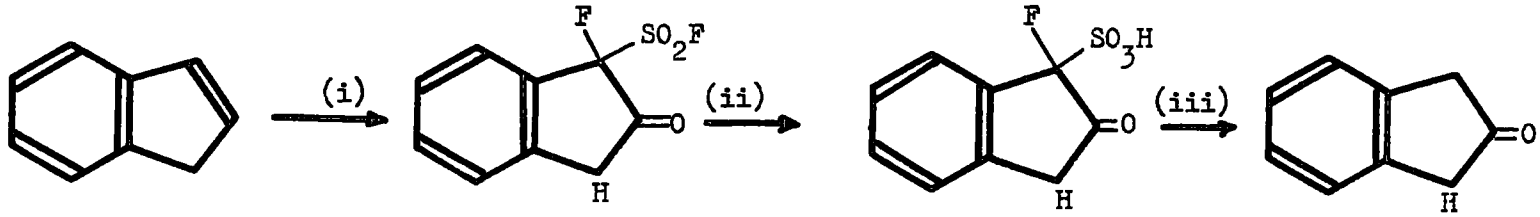


(85%)

A catalytic amount of a nucleophilic reagent is sufficient to completely decompose the sultone; the sultone ring is cleaved to yield initially a sulphonic-carboxylic acid halide. An example of a process of this type is the addition of a few drops of triethylamine to 2-hydroxytetrafluoroethane-sulphonic acid sultone (278) at 0°, fluorosulphonyldifluoroacetylfluoride (279) is formed exothermically in 90% yield by the mechanism below.[219]

FIGURE 10

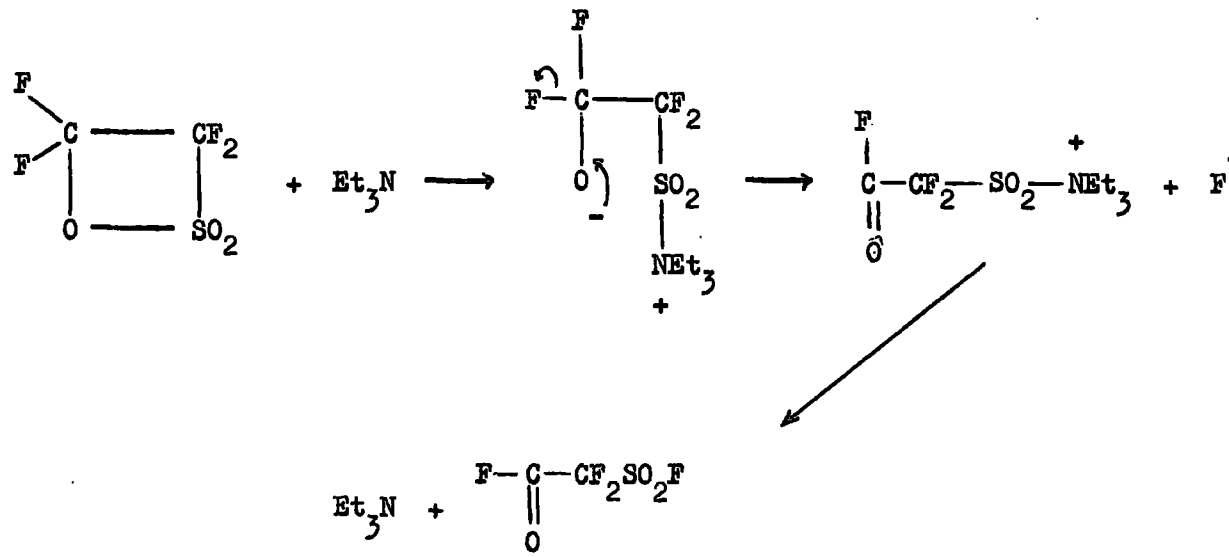
(All unmarked bonds are to fluorine)



(XXVIII) (XXXVII) (XXXVIII) (XXXIX)

Key to Reagents

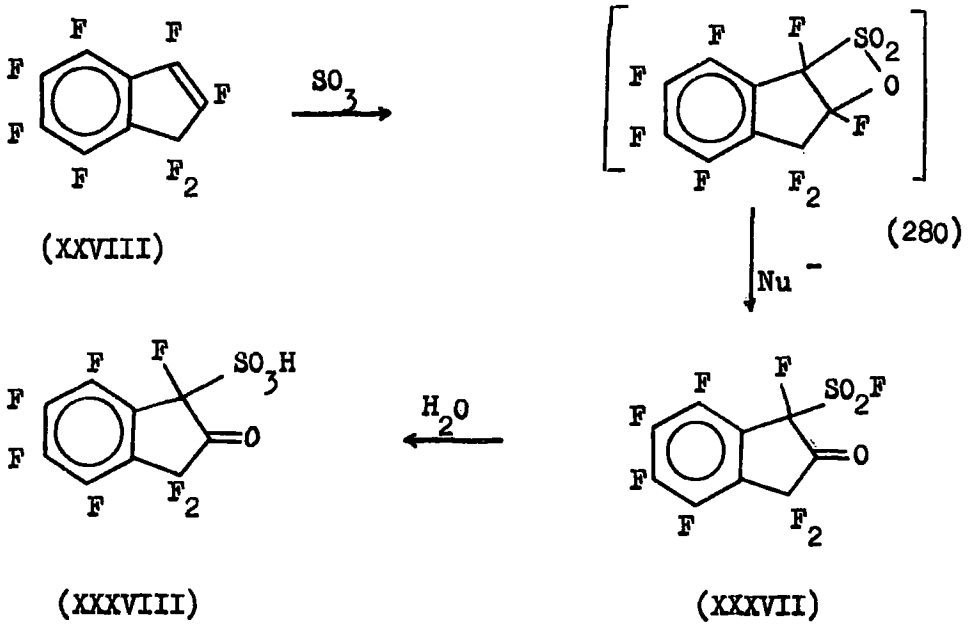
i. SO_3/H_2SO_4 ii. H_2O iii. Δ



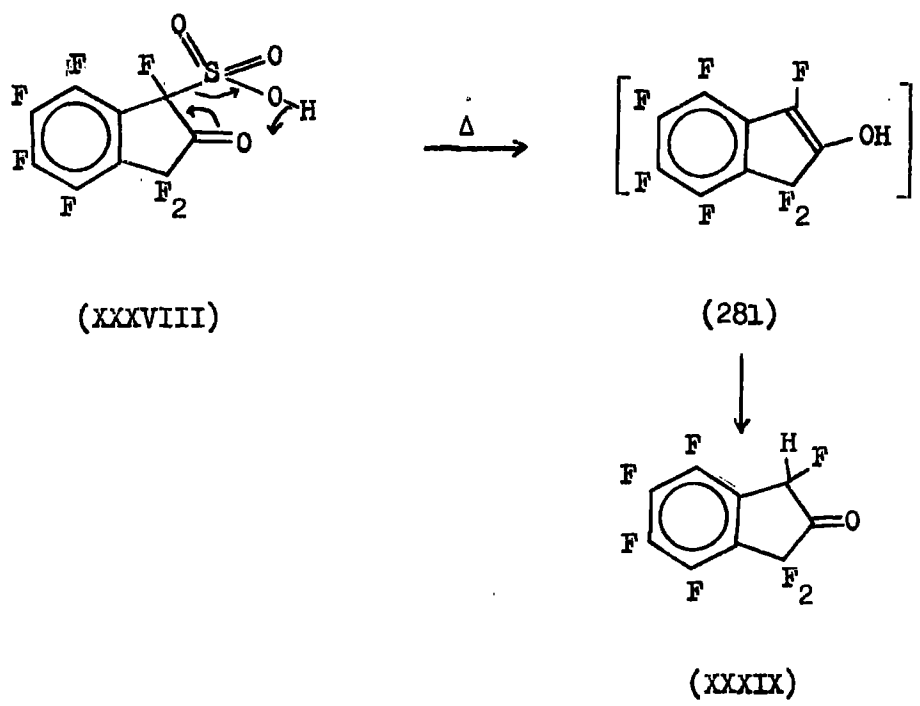
(279)

The double bond in the five-membered ring of perfluoroindene has previously displayed olefinic charcter in forming a methanol adduct (in the reaction with sodium methoxide in methanol) in forming a hydrazone (in the reaction with hydrazine hydrate in ethanol) and it is not unreasonable to postulate the addition of sulphur trioxide to form (280) as the first stage in its reaction with oleum; as only one compound appears to be present at each stage in the mechanism it is assumed that the 3-position of perfluoroindene is more electron-rich than the 2-position and is attacked exclusively by the electrophilic sulphur atom of sulphur-trioxide.

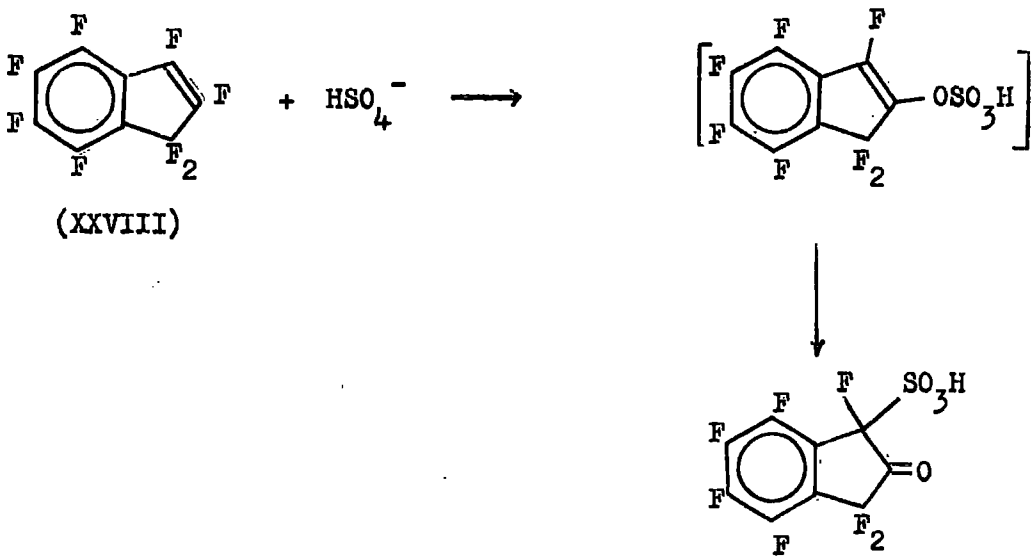
Once the sultone (280) has been formed nucleophilic species in the oleum, such as SO_4^{2-} or HSO_4^- etc., will be responsible for its decomposition to the sulphonyl fluoride (XXXVII). Sulphonyl fluorides of this type, for example (279), are readily hydrolysed to the corresponding sulphonic acids by water at room temperature, hence (XXXVIII) will be obtained by hydrolysis of (XXXVII). The reaction scheme is outlined below.[219]



The pyrolytic elimination of sulphur-trioxide from (XXXVIII) may proceed via the cyclic transition state shown below to yield initially the enol (281) which then tautomerises to the final product (XXXIX).



An alternative mechanism for the formation of (XXXVIII) from perfluoroindene (XXVIII) would be nucleophilic replacement of the 2-fluorine by HSO_4^- followed by tautomerism of the substitution product to the sulphonic acid (XXXVIII), see below.



(XXVIII)

(XXXVIII)

The former mechanism is considered more likely as the major species present in oleum is sulphur trioxide; HSO_4^- is only present in quite small amount.[202]

4.8 Spectral Parameters of Perfluoroindene and Derived Compounds

(a) Mass Spectra

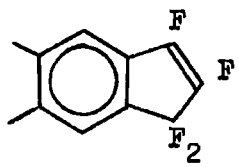
As is generally the case for fluorinated aromatic systems, the parent ions of perfluoroindene and the highly fluorinated indenes and indanes prepared during this work are in high abundance in their mass spectra.[140] For perfluoroindene (XXVIII), the mixture of heptafluoroindenes (XXXI) and (XXXII), the hexafluoroindene (XXXIII) and 4,5,6,7-tetrafluoroindene,[117] the base peaks in their mass spectra correspond to the loss of a fluorine atom from the

molecular ion, a transition supported by a metastable ion. For the methylheptafluoroindene (XXXIV), the mixture of dimethylhexafluoroindenes (section 4.6(b)) and the mixture of methoxyheptafluoroindenes containing some methanol adduct of perfluoroindene (section 4.6(c)), the molecular ion is the base peak and the ion corresponding to the loss of a fluorine atom from the molecular ion is less abundant than that corresponding to the loss of a methyl group from the molecular ion, the latter being the second most abundant ion in the mass spectrum. Ions due to loss of a difluoromethylene group from the molecular ion are abundant in the mass spectra of perfluoroindene (XXVIII), the mixture of heptafluoroindenes (XXXI) and (XXXII), the hexafluorindene (XXXIII), the methylheptafluoroindene (XXXIV) and the mixture of dimethylhexafluoroindenes (section 4.6(b)) but absent from the mass spectrum of the mixture of methoxyheptafluoroindenes containing some methanol adduct of perfluoroindene (section 4.6(c)).

In both the mass spectrum of the mixture of hydrazones (XXXV) and (XXXVI) and that of the ketone (XXXIX), which possess indane skeletons, the molecular ion is also the base peak. The mass spectrum of (XXXIX) has been discussed in detail in section 4.7

(b) Infra-Red Spectra

The infra-red spectra of all the substituted fluorinated indenes prepared in this work possess absorptions characteristic of the fluorinated aromatic nucleus and an absorption due to the double-bond in the five-membered ring. Absorptions at approximately 1515 cm^{-1} are characteristic of the aromatic ring in all the fluorinated indenes and indanes. The frequency of absorption of the double bond in the five-membered ring depends upon the substituents in the vinylic positions. For perfluoroindene the double bond absorbs at 1754 cm^{-1}; the indene (282) which also possesses a CF=CF bond in the five-membered ring absorbs at 1740 cm^{-1}.[81]



(282)

As expected replacement of a vinylic fluorine by CH_3, H or OCH_3 causes a reduction in the frequency of the double-bond absorption, the CH=CF stretching frequencies of (XXXI) and (XXXII) being lower in frequency than the $CF=CCH_3$ stretching frequency of (XXXIV) which is in turn slightly lower than the CF=$COCH_3$ stretching frequencies of the 2- and 3-methoxyheptafluoroindenes.[211] It is of interest that the two polyfluoroindenes substituted at a single vinylic position by hydrogen, (XXXI) and (XXXII), have quite different double-bond stretching frequencies whereas a mixture of the analogous methoxy-substituted heptafluoroindenes possesses a single broadened double-bond absorption. The CH=CH stretching frequency of (XXXIII) is lower than those of the mono-substituted compounds (XXXI) and (XXXII).

(c) Ultra-Violet Spectra

It has previously been found that the ultra-violet spectra of fully fluorinated carbocyclic polynuclear aromatic compounds closely resemble those of their hydrocarbon analogues both in the positions and in the intensities of their absorptions; this is true for the fully fluorinated analogues of indane, acenaphthene, pyrene, phenanthrene, acenaphthylene[137] and biphenylene.[207]

In contrast the ultra-violet spectra of highly chlorinated carbocyclic polynuclear aromatics often differ considerably from those of their hydrocarbon and fluorocarbon analogues. Thus in octachloronaphthalene some absorptions are considerably broadened and the whole spectrum experiences a bathochromic shift relative to naphthalene and the ultra-violet spectrum of decachloropyrene is

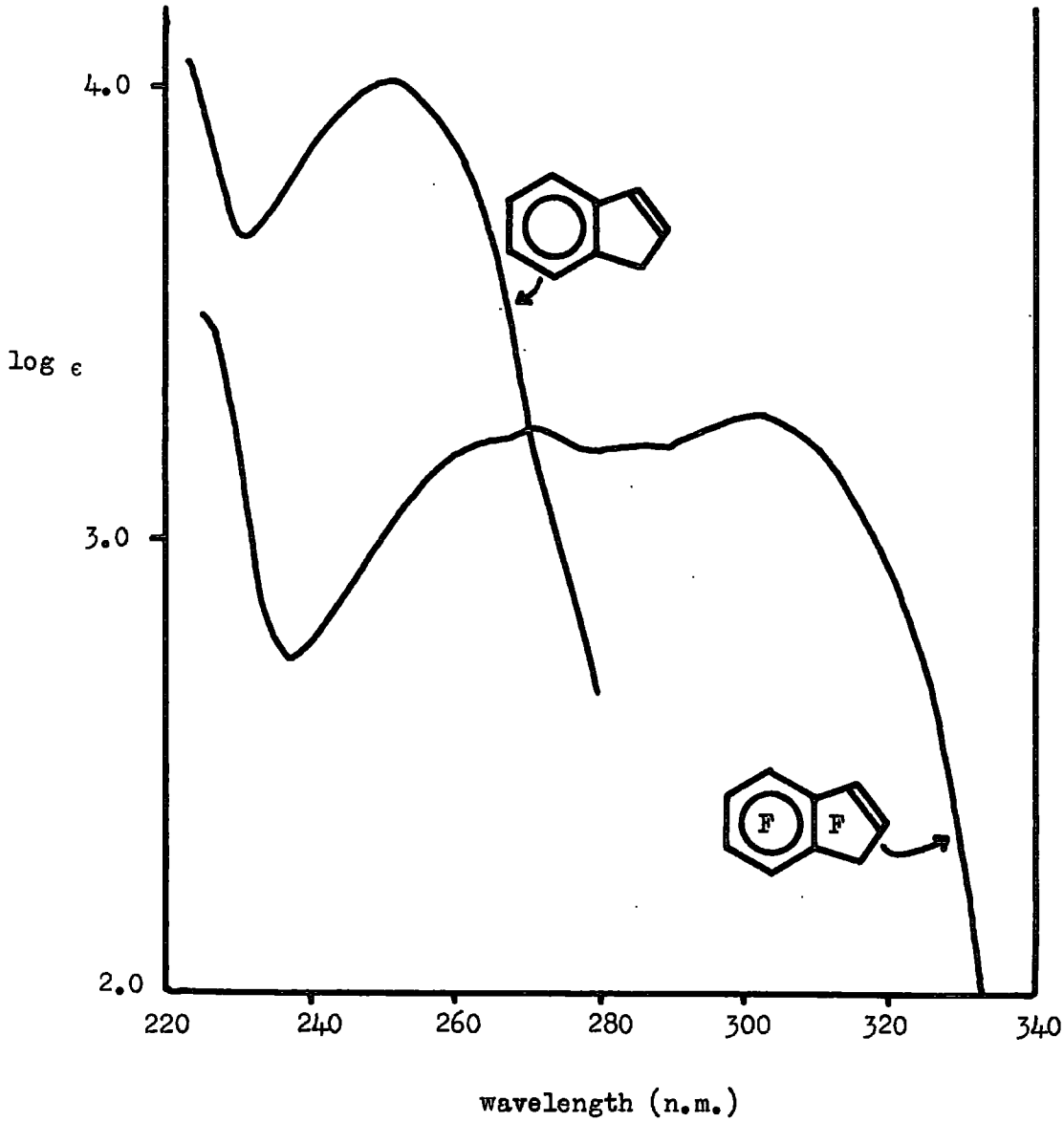
hardly recognisable as that of a pyrene derivative, there being a pronounced bathochromic shift with modification of all the absorptions relative to those of less highly chlorinated pyrenes. The anomolous spectra of these chlorocarbons can be explained by the steric size of the chlorine atoms preventing the molecules from achieving full coplanarity and consequently reducing conjugation. In the case of the fluorocarbons, fluorine must exert little or no steric effect, and will therefore not inhibit conjugation in this way.[221]

A comparison of the ultra-violet spectrum of perfluoroindene (XXVIII) with that of indene, similar to the previously reported spectrum,[222] shows marked differences (Figure 11). The main absorption in the spectrum of indene is on the short wavelength side of 270 mμ, the extinction coefficient attaining a maximum value of the order of 10,000 at 246 mμ; in the spectrum of perfluoroindene four broad absorptions are present with extinction coefficients of between 1620 and 2130 at longer wavelength, 265,272,285 and 302 mμ; in addition there are no analogues of the weaker well-resolved peaks on the long wavelength side of the broad maximum of indene in the spectrum of perfluoroindene. It is also of interest that the ultra-violet spectra of indene and styrene are very similar; the latter also possesses a broad intense maximum at 246 mμ ($\epsilon \sim 10,000$) with two weak maxima at 291 and 282 mμ; this suggests that the absorption of the C_6H_5-C=C- system is little influenced by ring-closure.[222] In contrast the ultra-violet spectrum of perfluorostyrene possesses strong absorptions in the region 225-280 mμ with maxima at 235 mμ ($\epsilon = 5754$) and 265 mμ ($\epsilon = 1413$) and therefore differs considerably from the ultra-violet spectra of both styrene and perfluoroindene.[223] Perchloroindene has a strong absorption in its ultra-violet spectrum in the same region as indene[191] (see Table 19).

It appears from the above data that perfluoroindene and perfluorostyrene both possess anomolous ultra-violet spectra in contrast to the closely-related

FIGURE 11

Ultra-Violet Spectra of Indene
and Octafluoroindene



perfluoroacenaphthylene which, although a non-alternant like perfluoroindene, has a spectrum resembling that of acenaphthylene. Replacement of the 2- or 3-substituents of perfluoroindene by a hydrogen atom or a methyl group has little influence on the form of the ultra-violet spectrum, which closely resembles that of perfluoroindene; however replacing the difluoromethylene group of 1,1,4,5,6,7-hexafluoroindene (XXXIII) by a methylene group in 4,5,6,7-tetrafluoroindene results in a major change in the ultra-violet absorptions, the u.v. spectrum of (XXXIII) closely resembling that of perfluoroindene whereas that of 4,5,6,7-tetrafluorindene is like the spectrum of indene, with an intense absorption at 250 mμ (ϵ ~10,000) & with well-resolved absorptions of reduced intensity at longer wavelengths.[117] (see Table 19). This suggests that the difluoromethylene group in perfluoroindene and highly-fluorinated indenes may have a major influence on the form of their ultra-violet spectra.

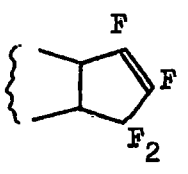
(d) N.m.r. Spectra

As might be expected the ^{19}F n.m.r. spectra of the fluorinated indenes prepared in this work are extremely complex and not first-order; consequently it has not been possible to completely analyse the spectra of any of these compounds. Attempts are at present being made to analyse some of these spectra with the help of decoupling techniques (work being undertaken by Dr. R.S. Matthews).

The ^{19}F n.m.r. spectra of all these compounds possessed certain features in common. The resonance to lowest field in all cases integrated to two fluorine atoms and was assigned to the CF_2 group; it contained no large couplings and was sharper than the other resonances in the spectrum. The aromatic and vinylic fluorines occur in the same region to high field of the CF_2 resonance. Apart from perfluoroindene, in which two fluorines resonate at about the same shift, these aromatic and vinylic fluorines resonate at discrete positions, each resonance being a complex multiplet.

It has not been possible to distinguish between the vinylic and aromatic fluorines in these compounds, a distinction which would be helpful in determining the sites of nucleophilic substitution. The large easily-identified peri F-F coupling which has been observed in other polycyclic fluoroaromatics[136] is not found in the n.m.r. spectra of fluorinated indenes and arguments based on chemical shift correlations with nearly analogous structures are not rigorous. Thus, if the n.m.r. spectra of perfluoroindene (XXVIII), the heptafluoroindenes (XXXI) and (XXXII), and the hexafluoroindene (XXXIII) are compared it might appear that the highest field resonance at 158.7 p.p.m. in (XXXI) is due to the 3-fluorine and that the 2-fluorine in (XXXII) is at 120.8 p.p.m.; the presence of an high field fluorine at 158.5 p.p.m. in the methylheptafluoroindene (XXXIV) might then suggest that this compound is 3-methyl heptafluoroindene (see Table 18). However the two methoxyheptafluoroindenes substituted in the five-membered ring, both have high-field resonances at about the same chemical shift which are most logically assignable to the vinylic fluorines in these compounds (see section 4.6(c)). There is also no obvious correlation between the spectra of these fluorinated indenes and the spectra of fluorinated styrenes.[224]

In the fluorinated indane systems (XXXV)-(XXXIX), in which an aromatic six-membered ring is fused to a saturated five-membered ring, the CF_2 system is to low-field of the CF_2 system in fluorinated indenes and apart from (XXXIX), in which this resonance is a single broad peak, is an AB quartet with a coupling constant of the order of 270 Hz. This is comparable to the coupling constant of 260 Hz for the CF_2 group of the dienophilic residue (283) of the Diels-Alder dimer of perfluorocyclopentadiene.[17]



(283)

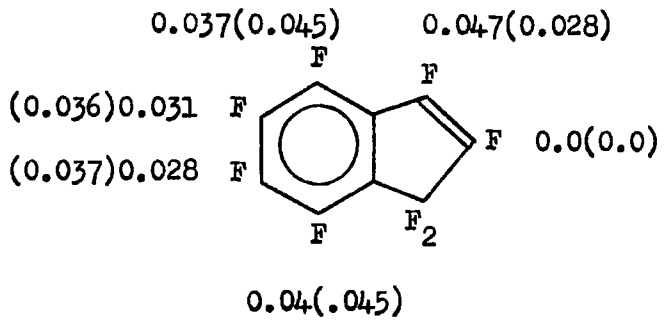
The aromatic fluorines in all these fluorinated indane skeletons are present as three resonances; the two fluorines farthest from the ring junction presumably having almost the same chemical shift.

4.9 The Chemical Reactions of Perfluoroindene

Perfluoroindene reacts readily with nucleophiles displacing initially one of the vinylic fluorines in the five-membered ring; in contrast perfluoroacenaphthylene and perfluorophenanthrene were attacked by nucleophiles exclusively at the non-vinylic sites.[208,206]

Monosubstitution products were obtained from replacement of both vinylic fluorines when perfluoroindene reacted with sodium borohydride and sodium methoxide; reaction with methyl lithium yielded only one product, the substituent again being introduced into the five-membered ring. Attack by hydrazine also occurred in the five-membered ring but it has not been unambiguously determined whether both or only one position are attacked.

Clearly Burdon's theory[195] is inapplicable to predicting the sites of nucleophilic substitution in perfluoroindene. In an attempt to rationalise the relative reactivities of the various sites in this system towards attack by nucleophiles CNDO/2 MO calculations have been used. The results obtained by Kilcast and Clark for nucleophilic substitution by H^- are shown below. The numbers adjacent to each position indicate the reactivity of that position relative to the most reactive position taken as zero, the greater the number the lower is the reactivity of the position. The units used are a.u. and the number is the amount by which the activation energy for the reaction exceeds the value of the activation energy for the most reactive site. Values in brackets also account for solvation of the intermediate anion whereas the other values are based on the isolated molecule model.



The model which includes solvation is closest to experiment in predicting the vinylic sites to be more reactive than the aromatic ones, although both models predict the 2-position to be the most reactive site. Solvation would be expected to be important in this system as attack at position-2 leads to the highly delocalised benzyl anion whereas in position-3 the charge is completely localised at C-2. This approach succeeds in predicting that vinylic replacement should take place in preference to aromatic although the predicted order of reactivity is incorrect.[212]

Perfluoroindene displays olefinic character in forming a methanol adduct on reaction with sodium methoxide in methanol and in forming a hydrazone on reaction with hydrazine in ethanol. The reaction with oleum, which might have been expected to form hexafluoroindone by attack of the allylic fluorines or hexafluoroindan-2,3-dione by attack of the vinylic fluorines, resulted in the isolation of 1,1,3,4,5,6,7-heptafluoroindan-2-one (XXXIX). The formation of this product is best rationalised as proceeding via the β sultone of perfluoroindene, another example of perfluoroindene displaying the properties of a typical fluoroolefin.

CHAPTER FOUR

EXPERIMENTAL

4.10 Reagents

Sodium borohydride was purchased from B.D.H. Chemicals Ltd. and oleum from Hopkin and Williams Ltd. Di(2-methoxyethyl)ether, diglyme, was dried over sodium and distilled off sodium wire under nitrogen, b.p. 163°, and stored over molecular sieve. Lithium methyl was prepared from lithium metal and methyl iodide as in reference 225.

4.11 Reactions of Octafluoroindene (XXVIII) with Nucleophiles

(a) With Sodium Borohydride in Diglyme

Experiment 1. Sodium borohydride (0.185 g., 4.89 mmoles) was dissolved in the minimum of diglyme (7 ml.) and added dropwise over 35 mins to a solution of perfluoroindene (XXVIII) (2.43 g., 9.34 mmoles) in diglyme (3 ml.) at 0° (ice-bath). After stirring at 0° for 1 hr. the deep-red solution was poured into ice-cold HCl (250 ml., 0.2N). The lower red fluorocarbon layer which separated (1.7 g.) was distilled in vacuo off phosphoricoxide to yield a yellow liquid (1.3 g.) and a red residue. Separation of this liquid (col B; 95° for (i) raised to 120° for collection of (ii)) gave: (i) 1,1,3,4,5,6,7- and 1,1,2,4,5,6,7-heptafluoroindenes (XXXI) and (XXXII) respectively (0.41 g., 1.69 mmoles, 18.1%) (Found: C,44.6; H,0.4; F,54.5; M (mass spectrometry), 242. C_9HF_7 requires C,44.7; H,0.4; F,54.9; M,242) a liquid mixture of (XXXI) and (XXXII) in the ratio of 1:4 respectively (see Appendix 1), ν_{max} 1672 and 1640 cm^{-1} (CH=CF), 1510 and 1500 cm^{-1} (fluorinated benzene ring), 3130 cm^{-1} (=$\overset{|}{C}$-H); (ii) 1,1,4,5,6,7-hexafluoroindene (XXXIII) (0.15 g., 0.67 mmoles, 7.2%) (Found M (mass spectrometry) 224. $C_9H_2F_6$ requires M 224); colourless liquid, ν_{max} 1592 cm^{-1} (CH=CH), 1517 cm^{-1} (fluorinated benzene ring) 3125 cm^{-1} (=$\overset{|}{C}$-H).

Experiment 2. Perfluoroindene (XXVIII) (1.89 g., 7.27 mmoles) was rapidly added to a solution of sodium borohydride (0.35 g., 9.24 mmoles) in

diglyme (30 ml.) at room temperature. The cherry-red reaction mixture was cooled to 0° for 10 mins. and was then stirred at room temperature for 4h. Excess sodium borohydride was destroyed by HCl (200 ml., N) and a lower red layer which separated (1.1 g.) was shown by analytical g.l.c. and i.r. to consist of two volatile components, 1,1,4,5,6,7-hexafluoroindene (XXXIII) and diglyme. Further washing with a large volume of water followed by separation by preparative g.l.c. (col B; 110°) led to 1,1,4,5,6,7-hexafluoroindene (XXXIII) (c. 0.3 g., 1.3 mmoles, 18%), with correct i.r. spectrum.

(b) With Lithium Methyl in Ether

A solution of lithium methyl in diethyl ether[225] (2M, 9 ml., 18 mmoles) was added over 15 mins. to perfluoroindene (XXXVIII) (3.0 g., 11.5 mmoles) in diethyl ether (15 ml.) which was being rapidly stirred at -70° (acetone/CO_2) The brown reaction mixture was stirred at -70° for 30 mins. and was then allowed to warm up to room temperature over 30 mins. HCl (20 ml., 2N) was added and the ether layer separated; the residual red liquid, after removing the ether, was distilled under vacuum (10^{-3} mm up to 100°) off phosphoric oxide to yield a yellow liquid (2.3 g.) and a red residue. Separation of this yellow liquid by preparative g.l.c. (col E, 140° for (i) raised to 150° for collection of (ii)) gave: (i) 1,1,3,4,5,6,7-heptafluoro-2-methylindene or 1,1,2,4,5,6,7-heptafluoro-3-methylindene (XXXIV) (0.51 g., 1.99 mmoles, 17.3%) (Found: C,46.8%; H,1.3%; M (mass spectrometry), 256. $C_{10}H_3F_7$ requires C,46.9%; H,1.2%; M, 256), colourless liquid b.p. 188°, ν_{max} 1701 cm^{-1} ($CH{=}CCH_3$), 1515, 1508 1497 cm^{-1} (fluorinated benzene ring), 2940 cm^{-1} (-C-H). (ii) a mixture of dimethylhexafluoroindenes (0.84 g., 3.33 mmoles, 29%), three overlapping broad peaks on analytical col A and col O inseparable on available g.l.c. packings, one component appeared to be present in major amount, c.70%. Major peaks in the mass spectrum were: m/e(origin of ion, assignment, % base peak) 252 (Parent and Base Peak, $C_{11}H_6F_6$, 100%); 251 (P-H, $C_{11}H_5F_6$, 21.3%);

238 (P-CH_2, $C_{10}H_4F_6$, 6.7%); 237 (P-CH_3, $C_{10}H_3F_6$, 58.1%); 236 (P-CH_4, $C_{10}H_2F_6$, 9.3%); 233 (P-F, $C_{11}H_6F_5$, 18.7%); 232 (P-HF, $C_{11}H_5F_5$; 23.6%); 231 (P-HF-H, $C_{11}H_4F_5$, 16.7%); 219 (P-F-CH_2, $C_{10}H_4F_5$, 5.9%); 218 (P-F-CH_3, $C_{10}H_3F_5$, 13.8%); 213 (P-F-HF, $C_{11}H_5F_4$, 6.9%); 202 (p-CF_2, $C_{10}H_6F_4$, 15.5%); 201 (P-CF_2H, $C_{10}H_5F_4$, 16.3%); 200 (P-CF_2H_2, $C_{10}H_4F_4$, 6.3%); 187 (P-CF_2-CH_3, $C_9H_3F_4$, 22.4%); 183 (P-CF_3, $C_{10}H_6F_3$, 9.6%); 182 (P-CF_3H, $C_{10}H_5F_3$, 7.9%); 151 (P-C_2F_4H, $C_9H_5F_2$, 3.9%); 100 (C_2F_4, 4.9%) ..... Metastable ions. 252 → 237 (-CH_3) at 222.9, 252 — 232 (-HF) and 252 — 233 (-F) broad metastable at 212-215, 252 — 202 (-CF_2) at 161.9, 237 — 187 (-CF_2) at 147.6, 202 — 187 (-CH_3) at 173.1. The ^1H n.m.r. showed a complex resonance at 1.90δ and a single resonance at 1.62δ, (CH_3 groups) in ratio of c.5:1 respectively (ref. ext. $(CH_3)_4Si$). The ^{19}F n.m.r. spectrum was complex, all resonances occurring between 123.2 and 154.6 p.p.m. (ref. ext. $CFCl_3$). The major peaks were at: 126.8 p.p.m. (2F) CF_2 group; 131.2 p.p.m. (1F), 138.6 p.p.m. (1F), 147.5 p.p.m. (1F) and 150.5p.p.m. (1F). Vinylic or aromatic Fluorines. Less intense resonances were present in agreement with a mixture of products. The i.r. spectrum had absorptions at 2940 cm^{-1} (C-H), 1709 cm^{-1} ($CF=CCH_3$), 1667 cm^{-1} ($CCH_3=CCH_3$), 1517, 1513 and 1493 cm^{-1} (fluorinated benzene ring). The u.v. spectrum (cyclohexane as solvent) had absorptions at $265^s m$ (ϵ = 316), 272 (ϵ = 339), 288^s (ϵ =339) 305 (ϵ = 427).

(d) With Hydrazine Hydrate in Ethanol

Experiment 1. Hydrazine hydrate (100%, 1.2 g., 24 mmoles) was added rapidly to a mixture of perfluoroindene (XXVIII) (2.8 g., 10.8 mmoles) and absolute ethanol (5 ml.). An immediate red colouration developed and a further 10 ml. of absolute ethanol were added. After heating under reflux for 17 h. the reaction mixture, now black in colour, was poured into water (150 ml.) and a black sticky solid separated, which was washed with more water. Several extractions with hexane followed by sublimation (10^{-3} mm.Hg pressure at 100°)

led to the isolation of 0.2 g. of pale yellow crystals, from $CHCl_3$, with an involatile intractable black tar remaining.

Experiment 2. Hydrazine hydrate (100%, 0.54 g., 10.79 mmoles) in absolute ethanol (1 ml.) was added dropwise to perfluoroindene (2.61 g., 10.04 mmoles) in absolute ethanol (6 ml.), whilst being stirred at room temperature. On the addition of the hydrazine an immediate red colouration was evident, and after stirring at room temperature for 4 h. the reaction mixture was poured into water (500 ml.), releasing a brown solid (1.53 g.). After thoroughly washing with water the solid was recrystallised from chloroform yielding 0.89 g. of fawn crystals. N.m.r. and i.r. spectroscopy indicated this solid to be a mixture of two isomeric compounds and repeated recrystallisations from chloroform and other solvents failed to completely separate these compounds pure and they were examined as mixtures. The initial product contained 85% (XXXV) and 15% (XXXVI) syn and/or anti 1,1,3,4,5,6,7-heptafluoroindan-2-one hydrazone or 1,1,2,4,5,6,7-heptafluoroindan-3-one hydrazone (0.89 g., 3.27 mmoles, 33%)(Found: C,39.4%; H, 1.3%; N,10.0%; M (mass spectrometry) 272. $C_9H_3N_2F_7$ requires C,39.7%; H,1.1%; N,10.3%; M, 272) pale fawn crystals, ν_{max} 1613 cm^{-1} (N-H bend), 3448 and 3333 cm^{-1} (N-H stretch), 1520 and 1513 cm^{-1} (fluorinated benzene ring). ν_{max} ($CHCl_3$) 284 mμ ($\log_{10}\varepsilon$ 4.33)

(c) With Sodium Methoxide

Experiment 1. A solution of sodium methoxide in methanol (5 ml., 0.452N, 2.26mmoles) was added over 5 mins. to perfluoroindene (XXVIII) (0.525 g., 2.02 mmoles). The reaction mixture was heated under reflux for 18 h. and was then shaken with HCl (2N, 50 ml.); the lower yellow fluorocarbon layer was separated (0.5 g.). Analytical g.l.c. of the fluorocarbon showed a trace of perfluoroindene and only a single less volatile peak (col A, 150°). The infra-red spectrum of this liquid had bands at 1709 cm^{-1} ($CF{=}COCH_3$), 2963 and 2857 cm^{-1} (C-H) and 1517, 1504 cm^{-1} (fluorinated benzene ring). The ^1H

n.m.r. (ref. ext. $(CH_3)_4Si$) contained broad absorptions at 3.15δ and 3.9δ in the ratio of 1:2 respectively, assigned to methoxyl protons of 2- and 3-methoxy-heptafluoroindene. The ^{19}F n.m.r. (ref. ext. $CFCl_3$) contained a weak intensity low-field AB system $J_{AB}\sim270$ at 102 p.p.m., assigned to the CF_2 group of a methanol adduct of perfluoroindene, two resonances at 123.1 and 122.4 p.p.m. in the ratio of 2:1 respectively assigned to the CF_2 groups of 2- and 3-methoxy-heptafluoroindene. Between 123.1 and 157.2 p.p.m. a series of extensively coupled resonances were assigned to aromatic fluorines. Two broad resonances at 173.3 and 174.7 p.p.m. in the ratio of 2:1 respectively were assigned to the vinylic fluorines in the five-membered ring of 2- and 3-methoxyheptafluoroindene; these resonances together integrated to half the area of the two resonances at 123.1 and 122.4 p.p.m. Integration of the resonances between 123.1 and 157.2 p.p.m. and comparison with the area beneath the CF_2 systems gave a ratio of slightly greater than 2:1 but less than 5:2 for these two areas; this suggests that the fluorine geminal to a methoxyl group in the methanol adduct of perfluoroindene also resonates in this region. It was not possible to assign the aromatic resonances of the two substitution products due to extensive overlap of resonances in this region.

The mass spectrum of this mixture was also run: m/e(assignment, origin of ion % base peak): 292 ($C_{10}F_8OH_4$, Parent, 13.5%); 277 (C_9F_8OH, P-CH_3, 2.5%); 272 ($C_{10}F_7OH_3$, Parent', 100%); 258 (C_9F_7OH, 10.3%); 257 (C_9F_7O, P'-CH_3, 80%); 253 ($C_{10}F_6OH_3$, P'-F, 13.5%); 242 (C_9F_7H, P'-OCH_2, 5.6%); 241 (C_9F_7, P'-OCH_3, 19.0%); 238 (C_9F_6O, P'-CH_3F, 14.7%); 230 (C_8F_7H, P'-OC_2H_2, 8%); 229 (C_8F_7, P'-OC_2H_3, 69.5%) 223 (C_9F_6H, P'-OCH_2F, 8.4%); 210 (C_8F_6, P'-OC_2H_3F, 17.2%); 179 (C_7F_5, 42.1%); 160 (C_7F_4, 10.5%); 141 (C_7F_3, 15%); 117 (C_5F_3, 6%); 93 (C_3F_3, 5.5%); 69 (CF_3, 4%).

After standing for 24 hours at room temperature this yellow liquid blackened and on opening a stoppered sample of the liquid pungent fumes were

emitted. The n.m.r., i.r. and g.l.c. of this liquid however were identical with the previous yellow liquid.

On warming with potassium hydroxide solution (1 gm. in 1 ml.) the solution rapidly darkened in colour, and acidification released a yellow fluorocarbon c. 0.2 g. with n.m.r., i.r. and g.l.c. not significantly different from the previous samples above. It thus appears that dehydrofluorination competes unsuccessfully with decomposition of the substituted compounds.

Experiment 2. As for experimentl, perfluoroindene (XXVIII) (2.05 g., 7.84 mmoles) and a solution of sodium methoxide in methanol (18 ml., 0.452N, 8.13 mmoles) were refluxed for 4h. Work up as above led to 1.72 g. of a yellow fluorocarbon whose g.l.c., i.r. and n.m.r. spectra were essentially the same as above. Attempted separation by g.l.c. (col B, 150°) resulted in only a trace of brown volatile material being recovered, whose infrared spectrum was the same as the material before separation. Brown involatile oils collected in the manifold of the instrument.

Experiment 3. Sodium methoxide, prepared from 0.286 g. of sodium (12.44 mmoles) and 25 ml. of dry methanol after removing all the solvent by vacuum distillation followed by warming at $100^{\circ}/10^{-3}$ mm.Hg. for 24 h., was suspended in dry diglyme (c. 20 ml.) and stirred vigorously. Perfluoroindene (XXVIII) (3.36 g., 12.92 mmoles) in dry diglyme (5 ml.) was rapidly added to the methoxide suspension at 0° (ice bath) and the reaction was kept at 0° for 1h, was allowed to warm up to room temperature and was kept at this temperature for 3h. and was finally heated at 92° for 14h. Work up, as above, led to a fluorocarbon layer (3.3 g.) whose i.r. spectrum and g.l.c. showed the presence of unchanged perfluoroindene and a product or products of similar infrared spectrum and g.l.c. retention time to the products of experiments 1 and 2. Distillation of this liquid product led to perfluoroindene (1.1 g.) and a red residue, which on distillation at $100^{\circ}/10^{-3}$ mm gave a yellow liquid (c. 1.5 g.) Examination by g.l.c. and infrared spectroscopy showed the absence of any

of the initially formed product.. The infrared spectrum showed aromatic bands at ~1520 cm^{-1} and strong bands at 1780, 1740, 1710, 1680 and 1640 cm^{-1}, and a weak C-H stretch at 2950 cm^{-1}, there was no volatile material evident from g.l.c. (col A, 150°), and this material was not further investigated.

4.12 Reaction of Perfluoroindene (XXVIII) with Fuming Sulphuric Acid

Experiment 1.

(a) Perfluoroindene (XXVIII) (3.0 g., 11.53 mmoles) and fuming sulphuric acid (33% SO_3, 20 ml.) were mixed at room temperature and allowed to stand for 2 hrs. At the end of this time a small amount of the reaction mixture was withdrawn and sealed in an n.m.r. tube; the ^{19}F n.m.r. spectrum of this mixture (Table 20) is consistent with it being a solution of 1,1,3,4,5,6,7-heptafluoroindan-2-one-3-sulphonyl fluoride (XXXVII) in oleum; the remainder of the homogeneous yellow solution was poured onto packed ice (c. 50 g.) and a further 200 ml. of water were then added. The pale yellow aqueous solution was extracted with c.100 ml. of diethyl ether (twice); the ethereal solution was dried ($MgSO_4$) and the ether was removed on a rotary evaporator connected to a water pump/ 10 mm.Hg. After all the ether appeared to have been removed the residual brown oil was warmed to c. 60° for 15 mins. The brown oil (substantially 1,1,3,4,5,6,7-heptafluoroindan-2-one-3-sulphonic acid (XXXVIII) was soluble in water, insoluble in hexane and chloroform and the aqueous solution was acid to litmus. An analysis of the red oil indicated 8.2% sulphur.

In the infrared spectrum there was a broad band stretching from maximum intensity at 3450 cm^{-1} down to 2500 cm^{-1} assigned to an acid O-H stretch, a sharp band at 1770 cm^{-1} and a less intense sharp band at 1645 cm^{-1} (C=O), a broader band at 1515 cm^{-1} (fluorinated benzene ring), and a broad band at 1266 cm^{-1} ($-SO_2-$). The ultra violet spectrum (H_2O) possessed an intense absorption at 256 mμ and a weak shoulder at 290 mμ. Due to ready decomposition it was not possible to obtain a meaningful mass spectrum.

(b) Distillation of the brown oil (XXXVIII) formed as above (from 1.4 g., 5.38 mmoles of perfluoroindene (XXVIII)) under 10^{-3} mm.Hg pressure up to 100° yielded a pale yellow liquid, which was further distilled off phosphoric acid to give 1,1,3,4,5,6,7-heptafluoroindan-2-one, (XXXIX) (0.36 g., 1.40 mmoles, 26.0%) (Found: C,42.2%; H,0.8%; F,51.3%; M (mass spectrometry) 258. C_9HOF_7 requires C,41.9%; H,0.4%; F,51.5%; M 258), pale yellow liquid b.p. 213°, ν_{max} 1771, 1717^{w} and 1639 cm^{-1} (C=O), 1515 cm^{-1} (fluorinated benzene ring). ν_{max} (cyclohexane), 246 mμ ($\log_{10}\epsilon$ = 4.06), 240^{s} mμ ($\log_{10}\epsilon$ = 4.02), 285^{s} mμ and 289 mμ ($\log_{10}\epsilon$ = 3.15); chloroform) 287.5 mμ ($\log_{10}\epsilon$ = 2.83).

Experiment 2. As in experiment 1, perfluoroindene (XXVIII) (2.16 g., 8.31 mmoles) and fuming sulphuric acid (33% SO_3, 20 ml.), led to 1.0 g. of a brown oil (XXXVIII). This was decomposed as before at 10^{-3} mm.Hg. pressure up to 150°, to produce (i) a very volatile fraction (0.23 g.); the mass spectrum of this gaseous product contained peaks at m/e 64, 48, 81 and 155 (top mass peak) whose P/P+2 ratios were consistent with the prescence of a single sulphur atom in these ions, peaks assigned to SO_2, SO, HSO_3, $C_4H_{11}SO_3$; in addition peaks at m/e 29, 45, and 74 contained no sulphur and are consistent with the breakdown peaks of Et_2O, i.e. C_2H_5, C_2H_5O and $C_2H_5OC_2H_5$ respectively. These were the only main peaks in the mass spectrum. The infra-red spectrum was almost identical to that of diethyl ether. (ii) a pale yellow liquid (XXXIX) (0.509 g., 1.97 mmoles, 24%), identified by infra-red and n.m.r. spectroscopy. (iii) an involatile black residue (trace).

APPENDIX 1

X-RAY PHOTOELECTRON SPECTRA

Photoelectron Spectroscopy[226]

There are two types of photoelectron spectroscopy, X-Ray Photoelectron Spectroscopy (XPS), sometimes referred to as Electron Spectroscopy for Chemical Analysis (ESCA), and Ultra-Violet Photoelectron Spectroscopy (UPS); both techniques involve irradiating a sample and accurately measuring the kinetic energy of the emitted photoelectrons; in the former case irradiation is accomplished by X-rays, whereas the latter technique uses vacuum ultraviolet photons. The measured kinetic energy of the emitted electron is related to its binding energy and is a function of the element irradiated and its electronic environment. In ESCA we are concerned with emission of electrons from one of the lower energy levels whereas for UPS only valence electrons are ejected; this is a consequence of the energy of the exciting irradiation. Although UPS is capable of much better peak resolution than ESCA its spectra are normally quite complex and difficult to interpret; in contrast X-ray photoelectron spectra are simpler and have proved useful in structure determinations in quite complex systems.

Experimental Applications of ESCA[226]

ESCA has been widely used throughout the field of chemistry and it possesses certain inherent advantages over other spectroscopic techniques.

It is applicable to the study of solids, liquids or gases. Gases are studied at low pressure ($< 10^{-3}$ torr); solid samples can be investigated as a crushed powder adhering to conducting tape or as a flat plate or wafer; liquids at room temperature are either frozen or vapourised before examination. Very little material is required to obtain a spectrum and in most cases the technique is non-destructive; it is also possible to obtain photoelectron spectra of all elements apart from hydrogen.

As ESCA is a surface technique, the escape depth of electrons in the X-ray photoelectron emission process being < 100Å, it has been much used in

investigations of catalysis; in order to ensure no surface contamination care needs to be exercised in sample preparation.

Some of the general uses of ESCA are in chemical analysis, investigations of bonding, and the determination of structures.

Use of ESCA in Structure Determination[226]

In ESCA the kinetic energy (E_k) of the electron emitted after irradiating a sample is the observable and depends on the incident X-ray energy ($h\nu$) and the binding energy (E_B) of the electron in the element. The equation relating these quantities is, $E_k = h\nu - E_B$.

The binding energy is the parameter of interest and it is found, for instance in the carbon 1s ESCA of ethylchloroformate, that all three carbon atoms in different electronic environments have different carbon 1s electron binding energies. Although these "chemical shifts" in electron spectra, caused by differences in the electronic structure of atoms, are small compared with changes in binding energy on going from one element to another, they provide insight into the bonding of the atom. The conventional X-ray sources ($MgK\alpha_{1,2}$, $AlK\alpha_{1,2}$) for carbon 1s levels have linewidths of the same order of magnitude as chemical shifts in most organic systems, and hence ESCA has been little used as a routine structural tool in organic chemistry. When highly electronegative substituents are attached to carbon there is a range of ~10 eV in carbon 1s levels and as linewidths are of the order of 1.2 eV (the inherent width of the X-radiation) ESCA becomes a useful structural tool in these circumstances.

Theoretical explanations for chemical shifts vary in sophistication. For the examples to be discussed below their complexity precludes a rigorous approach but analysis of experimental spectra has been helped by CNDO/2-SCF-MO calculations. CNDO/2 calculations produce molecular charge distributions from which binding energies E_i can be obtained using the charge potential model of Siegbahn from the equation below.

$$E_i = E_o + kq_i + \sum_{j \neq i} \frac{q_j}{r_{ij}}$$

E_o is a reference level; kq_i is the contribution from the charge on the atom in question; the third term is an intramolecular Madelung potential. The values of $E_i - E_o$ calculated as above give a theoretical estimate of the relative binding energies. The value of k, which depends on the definition of atomic charge, and in an SCF-MO treatment on the basis set, may be equated approximately to the one-centre Coulomb repulsion integral between a core and a valence electron.[227]

The Orientation of Nucleophilic Substitution in Perfluoroindene

The reaction of perfluoroindene with sodium borohydride gave 1,1,4,5,6,7-hexafluoroindene (XXXIII) and a 4:1 mixture of two heptafluoroindenes which were inseparable on available g.l.c. packings but from the n.m.r. and i.r. spectra of the mixture were assigned the structures 1,1,2,4,5,6,7-heptafluoroindene (XXXII) and 1,1,3,4,5,6,7-heptafluoroindene (XXXI); it was not possible to determine which was the major isomer using these spectroscopic techniques (see Chapter 4).

As it had previously been found that charge distributions in perfluoroindene as determined by CNDO/2 SCF MO calculations were in close agreement with experimental charges obtained from experimental binding energies and known parameters using Siegbahn's charge-potential model, it was decided to calculate the spectra expected for 1:4 and 4:1 mixtures of (XXXI) and (XXXII) and, if these spectra were sufficiently different to allow a distinction between the two mixtures, to compare the experimental spectrum with these predicted spectra.[228]

Firstly theoretical carbon 1s spectra of the two isomers were determined by using charge distribution calculations for (XXXI) and (XXXII) by the CNDO/2 method and previously established values of E_o and k, in conjunction with the charge potential model. The carbon 1s spectra were then computed using a Du Pont 310 Anologue Computer and linewidths previously derived from a study of perfluoroindene (see Figure 12).[228] The carbon 1s spectra of 1:4 and 4:1 mixtures of the two isomers were also computed and were compared with the experimental carbon 1s spectrum for the 1:4 mixture of the two isomeric heptafluoroindenes (see Figure 13). The experimental spectrum matches the theoretical spectrum of a 4:1 mixture of (XXXII) and (XXXI) respectively. The theoretical spectrum of the other possible mixture has a totally different appearance to this spectrum, possessing two distinct peaks at low binding energy; this conclusively proves the mixture to be 80% (XXXII) and 20% (XXXI).

<u>Charge Distributions in Dodecafluorotricyclo[5,2,2,$o^{2,6}$]undeca-2,5,8-triene (X) and Tetradecafluorotricyclo[6,2,2,$o^{2,7}$]dodeca-2,6,9-triene (IX)</u>

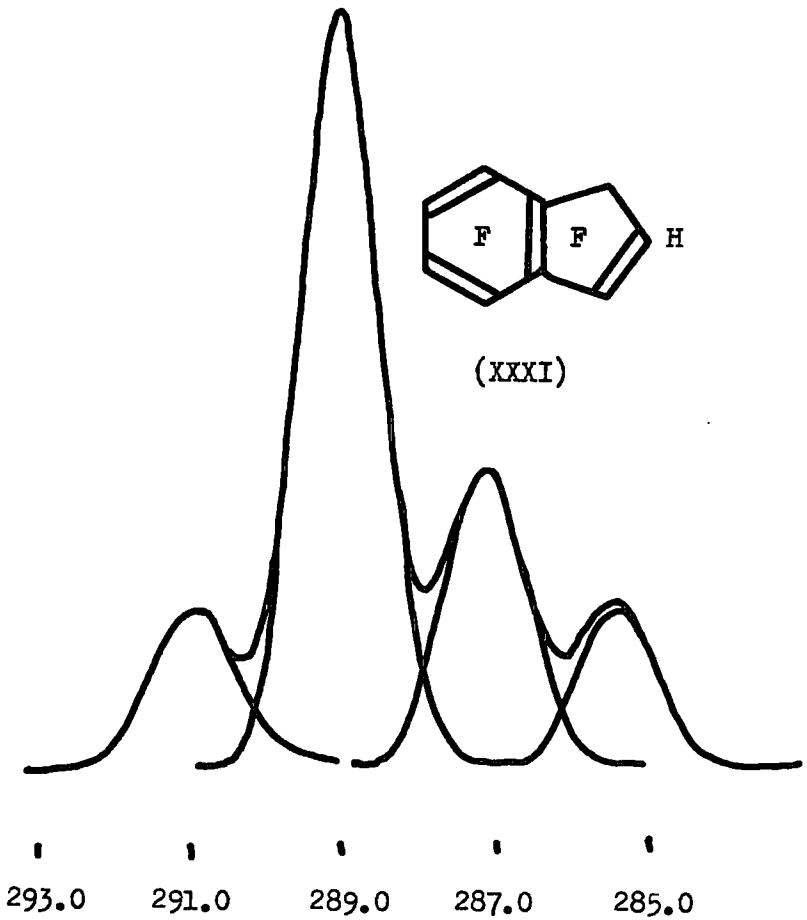
In the above example molecular core binding energies were assigned on the basis of CNDO/2 SCF MO calculations using the charge potential model of Siegbahn. Using experimental values of E_i and suitable values of E_o and k it is also possible to set up a series of simultaneous equations which can be solved uniquely to give charge distributions within a molecule, the reverse of the above process. This is useful for molecules which are too large to accommodate using conventional molecular orbital calculations; a crude idea of charge distribution is often useful in understanding the chemistry of such complex systems.

Trienes (IX) and (X) were considered to be sufficiently complex systems on which to test the feasibility of this approach. The carbon 1s spectra of these trienes are shown in Figure 14 together with the deconvolution into their component peaks.

FIGURE 12

Computer Simulated theoretical C_{1s} spectra

(Binding Energies are in eV)



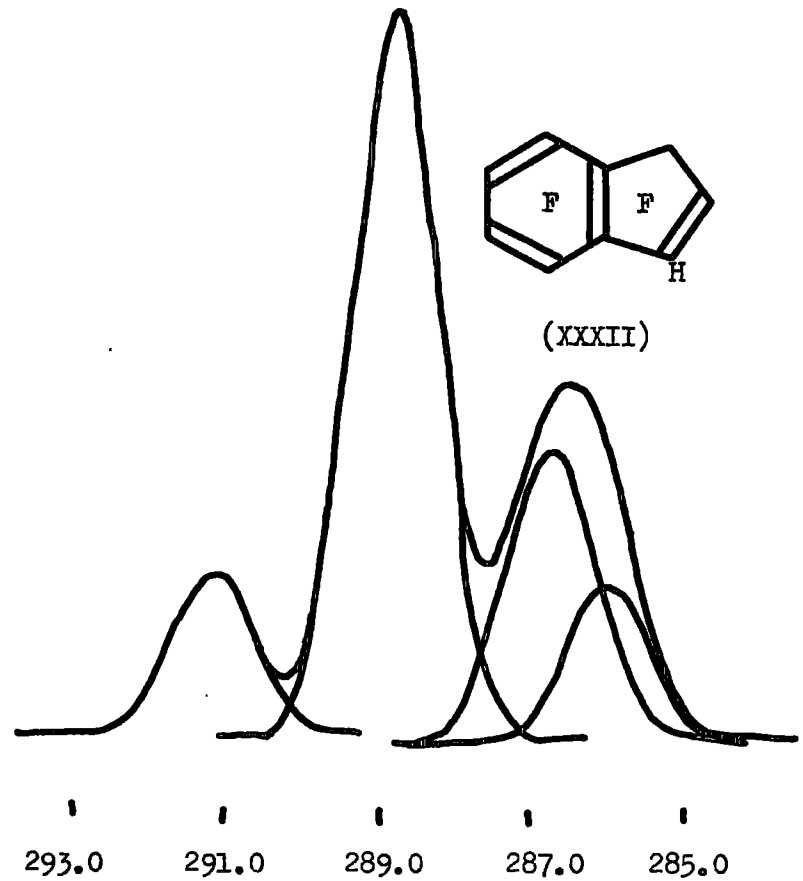
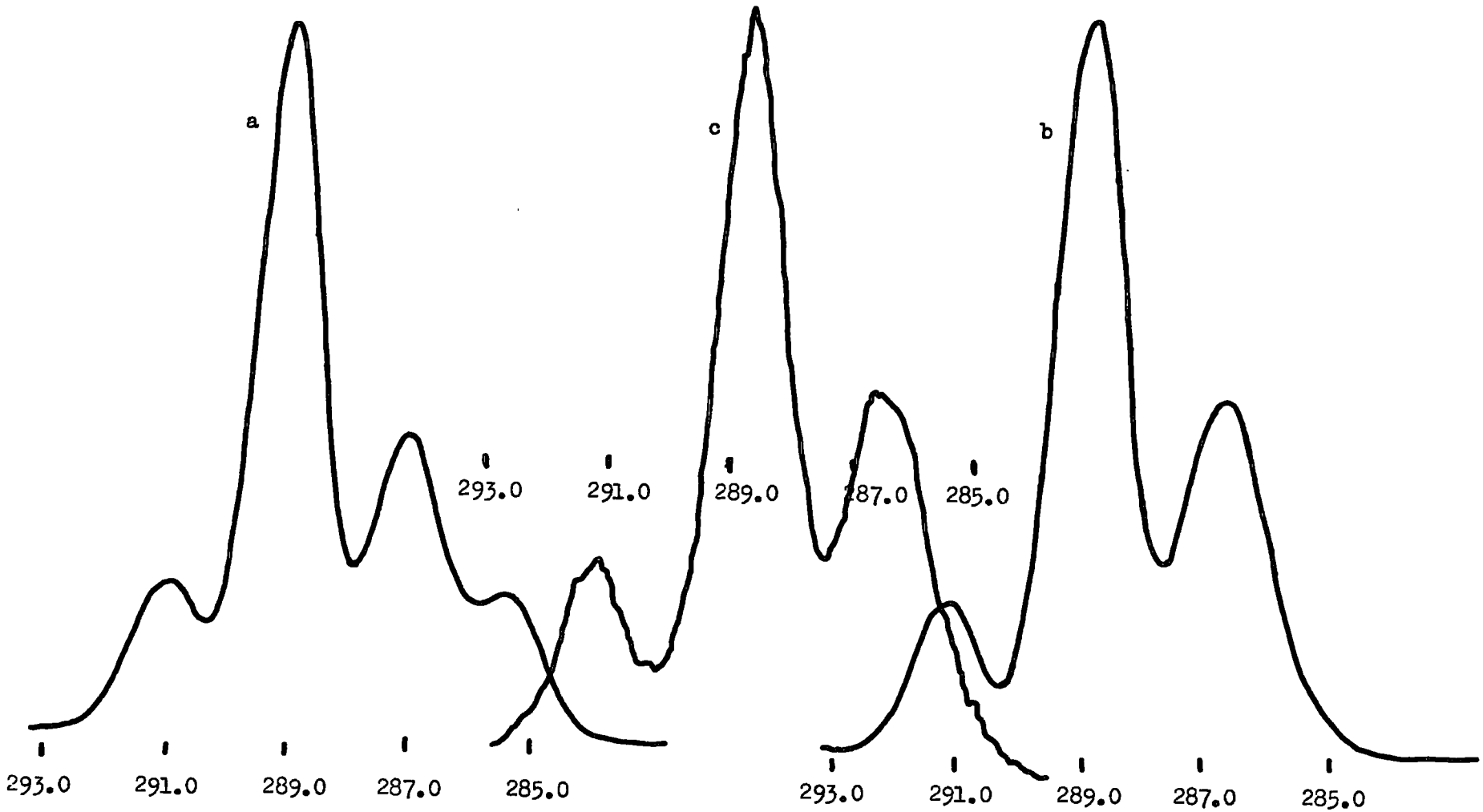


FIGURE 13

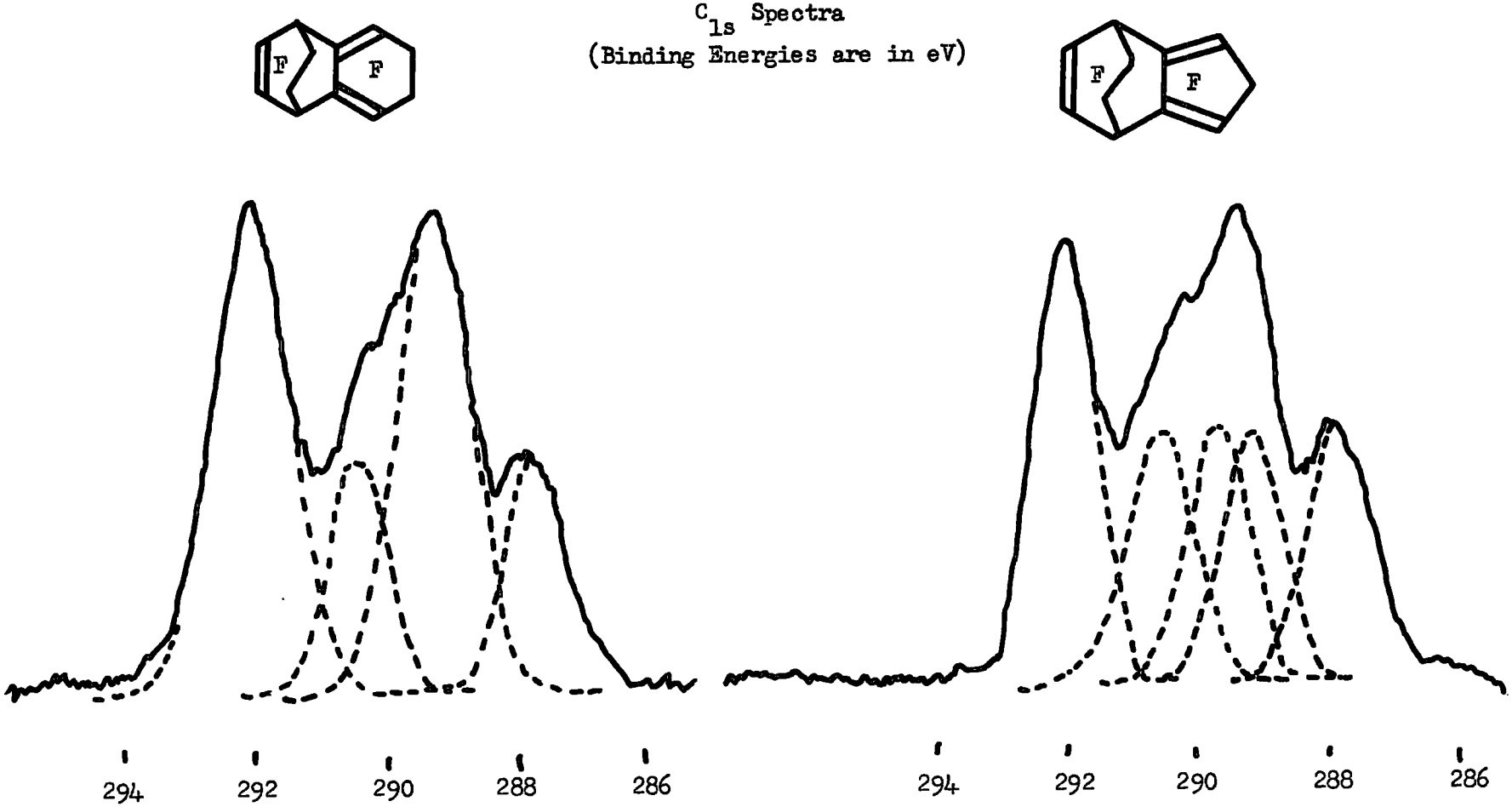
(Binding Energies are in eV)



a. Computer simulated theoretical C_{1s} spectrum of (XXXI):(XXXII), 4:1. b. Computer simulated theoretical C_{1s} spectrum of (XXXI):(XXXII), 1:4. c. Experimental C_{1s} spectrum of the mixture of heptafluoroindenes.

FIGURE 14

C_{1s} Spectra
(Binding Energies are in eV)



Triene (IX) has four component peaks with area ratios, in order of decreasing binding energy, (4:2:4:2), assigned to the ($>CF_2$) carbons, the tertiary ($-C-F$) carbons, the vinylic ($>C-F$) carbons and the bridgehead ($-C=$) carbons, respectively. Triene (X) has five component peaks in the area ratio (3:2:2:2:2). The two types of vinylic ($>CF$) carbons, which have slightly different binding energies (289.9 and 289.4 eV), are still readily distinguished from the tertiary ($-C-F$) carbons (290.9 eV). The experimental binding energies and assignments are tabulated below.

TABLE 21

Binding Energies and Their Assignments

	COMPOUND (X)		COMPOUND (IX)	
Environment of Atom	Binding Energy (eV)	Area Ratio	Binding Energy (eV)	Area Ratio
	C_{1s}		C_{1s}	
$>CF_2$	292.3	3	292.3	4
$-CF$	290.9	2	290.6	2
$>CF$	289.9 289.4 289.65 (Av.)	2	289.4	4
$-C=$	288.0	2	287.8	2
	F_{1s}		F_{1s}	
All F atoms	690.9		691.0	

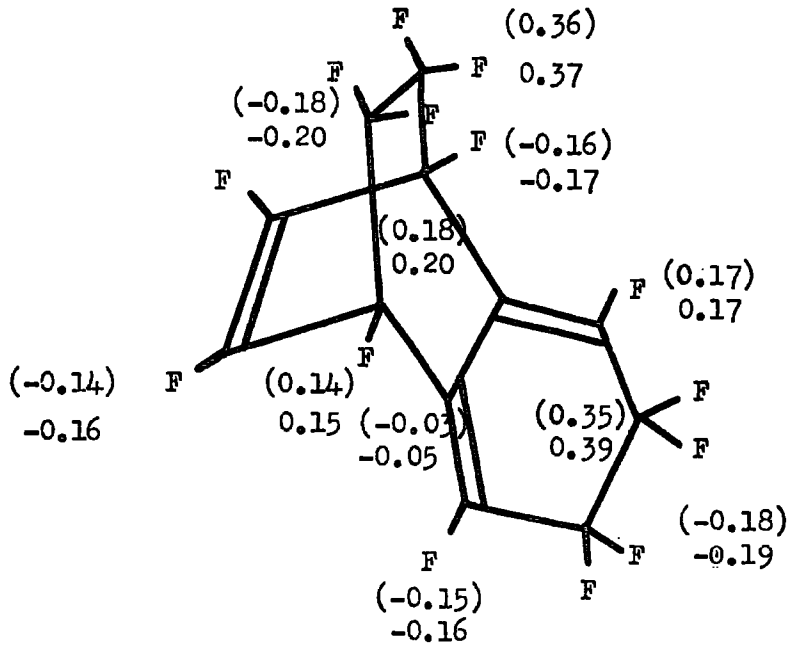
These binding energies and assignments were used with the values of k and E_o for carbon and fluorine obtained from the perfluoroindene study[228] to calculate the experimental charge distributions (Figure 15). Theoretical charge distributions in these molecules are determined by CNDO/2 SCF MO calculations are also shown in Figure 15, and the excellent agreement evident from these figures was confirmed by least squares analysis.

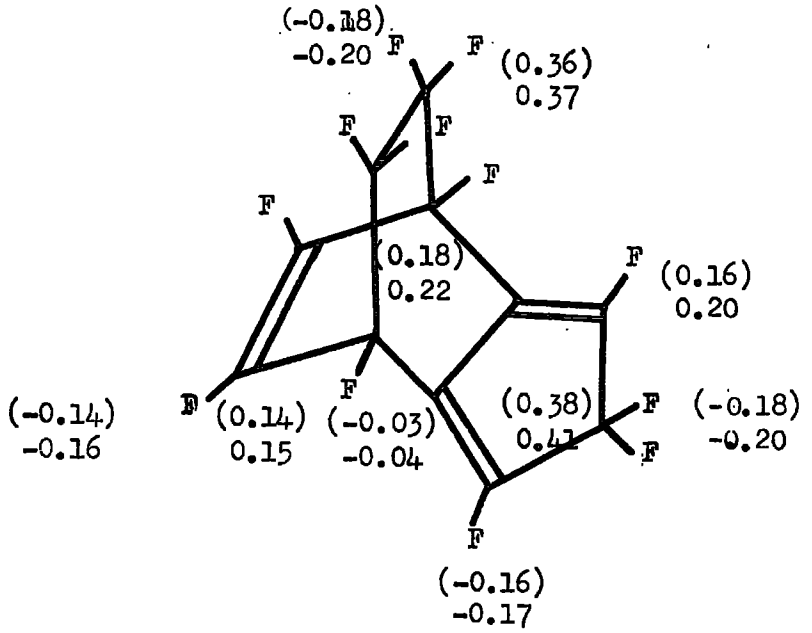
The calculations in the above discussion and the running and interpretation of the X-ray photoelectron spectra were undertaken by Mr. D. Adams, Dr. D.T. Clark and Dr. D. Kilcast in this department.

Spectra were recorded on an A.E.I. ES100 electron spectrometer using $MgK\alpha_{1,2}$ radiation and under the conditions used the Au $4f_{7/2}$ level at 84 eV (used as a standard) had a half-width of 1.15 eV. The samples were introduced via a heated reservoir shaft, leaked through a metrosil plug and were condensed as a thin film on gold on a cooled probe. Partially resolved spectra were deconvoluted using a Du Pont 310 curve resolver.

FIGURE 15

Experimental and CNDO/2 charge distributions



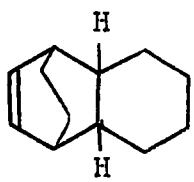


Theoretical CNDO/2 charges are in parentheses

APPENDIX 2

MASS SPECTRA

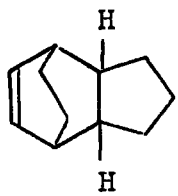
The mass spectra of compounds prepared during this work are tabulated below. Ions are tabulated in the form: mass number (intensity as % of base peak , assignment, proposed origin of the ion); charges on ions are omitted. Base peaks and parent ions (parent abbreviated to P in assignments) are indicated, and where observed, metastable ions are tabulated below the mass spectrum in the form: A $\rightarrow$ B (-C) at D, the metastable ion being observed at m/e D, $D = B^2/A$, A^+ giving B^+ by the loss of the neutral fragment C. In the structural formulae all unmarked bonds are to fluorine.



(I)

450 (7.4%, $C_{12}F_{16}H_2$, <u>PARENT</u>), 431 (3.3%, $C_{12}F_{15}H_2$, P-F), 351 (7.0%), 350 (65.2%, $C_{10}F_{12}H_2$, P-C_2F_4), 349 (3.5%, $C_{10}F_{12}H$, P-C_2F_4H), 299 (26.1%, $C_9F_{10}H$, P-C_3F_6H), 224 (8.4%, C_6F_8, P-$C_6F_8H_2$) 207 (20.9%, $C_6F_7H_2$, P-C_6F_9), 205 (3.8%, C_6F_7, P-$C_6F_9H_2$), 200 (8.4%, C_4F_8, P-$C_8F_8H_2$), 199 (100%, C_7F_6H, <u>BASE PEAK</u>, P-$C_5F_{10}H$), 181 (10.4%, C_4F_7, P-$C_8F_9H_2$), 155 (4.6% C_5F_4, P-$C_7F_{11}H_2$), 150 (11.4%, C_3F_6, P-$C_9F_{10}H_2$), 131 (5.0%, C_3F_5, P-$C_9F_{11}H_2$), 100 (9.9%, C_2F_4), 69 (6.9%, CF_3).

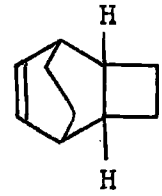
<u>Metastable ions</u>: 450 $\rightarrow$ 350 (-C_2F_4) at 272.2. 350 $\rightarrow$ 199 (-C_3F_6H) at 113.2



(II)

400 (16.7%, $C_{11}F_{14}H_2$, PARENT), 381 (11.5%, $C_{11}F_{13}H_2$, P-F), 310 (6.5%, $C_{10}F_{10}$, P-CF_2-2HF), 300 (100%, $C_9F_{10}H_2$, BASE PEAK, P-C_2F_4), 241 (15.2%, C_9F_7, P-C_2F_5-2HF), 200 (27.2%, $C_7F_6H_2$, P-C_4F_8), 199 (100%, C_7F_6H, BASE PEAK, P-C_4F_8H), 181 (20.9%, $C_7F_5H_2$, P-C_4F_9), 157 (22.5%, $C_5F_5H_2$, P-C_6F_9), 149 (21.7%, C_6F_4H, P-$C_5F_{10}H$), 100 (19.6%, C_2F_4), 69 (16.2%, CF_3).

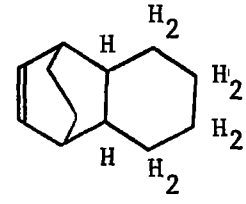
Metastable ions: 300 → 199 (-C_3F_6H) at 132.0



(III)

350 (9.7%, $C_{10}F_{12}H_2$, PARENT), 331 (4.6%, $C_{10}F_{11}H_2$, P-F), 311 (0.9%, $C_{10}F_{10}H$, P-F-HF), 281 (2.1%, $C_9F_9H_2$, P-CF_3), 250 (14.2%, $C_8F_8H_2$, P-C_2F_4), 231 (3.0%, $C_8F_7H_2$, P-C_2F_5), 212 (2.6%, $C_8F_6H_2$, P-C_2F_6), 206 (5.5%, C_6F_7H, P-C_4F_5H), 181 (13.3%, $C_7F_5H_2$, P-C_3F_7), 150 (100%, $C_6F_4H_2$, BASE PEAK, P-C_4F_8), 126 (4.6%, $C_4F_4H_2$, P-C_6F_8), 113 (6.7%, C_3F_4H, P-C_7F_8H), 108 (19.7%), 100 (3.8%, C_2F_4), 99 (3.6%. C_5F_2H), 69 (11.8%, CF_3).

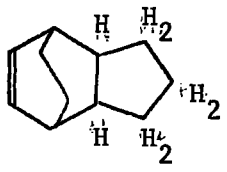
Metastable ions: 250 → 150 (-C_2F_4) at 90.0.



(IV)

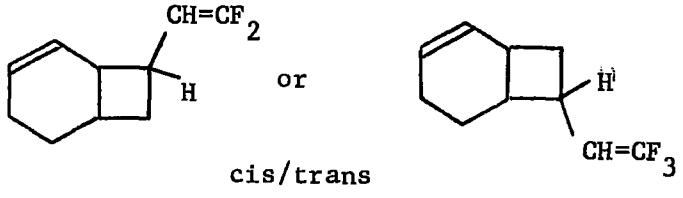
306 (29.4%, $C_{12}F_8H_{10}$, PARENT), 242 (11.6%, $C_{10}F_6H_8$, P-CH_2-CF_2), 219 (9.6%, $C_7F_7H_2$, P-C_5FH_8), 206 (33.1%, $C_{10}F_4H_{10}$, P-C_2F_4), 205 (15.4%, $C_{10}F_4H_9$, P-C_2F_4H),

187 (5.8%, $C_{10}F_3H_{10}$, P-C_2F_5), 181 (6.4%, $C_8F_4H_9$, P-C_4F_4H), 164 (13.4%, $C_7F_4H_4$, P-C_2F_4-C_3H_6), 163 (38.5%, $C_7F_4H_3$, P-C_2F_4-C_3H_7), 155 (11.4%, $C_9F_2H_9$, P-C_3F_6H), 150 (19.2%, C_3F_6), 145 (14.9%, $C_4H_2F_5$, P-$C_8F_5H_6$), 131 (10.1%, C_3F_5), 104 (21.6%), 100 (31.6%, C_2F_4), 99 (9.2%, C_6H_8F, P-$C_6F_6H_2$), 82 (48.5%, C_6H_{10}), 81 (78.2%, C_6H_9), 80 (19.2%, C_6H_8), 79 (16.4%), 77 (15.8%), 75 (8.6%), 69 (35.5%), 67 (100%, C_5H_7, <u>BASE PEAK</u>, P-$C_7F_8H_3$), 55 (17.8%), 54 (34.1%), 53 (15.4%), 51 (16.4%), 41 (66.5%), 39 (45%).



(V)

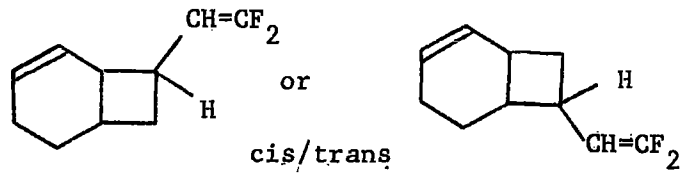
292 (18.9%, $C_{11}F_8H_8$, <u>PARENT</u>), 193 (11.5%), 192 (100%, $C_9F_4H_8$, <u>BASE PEAK</u>, P-C_2F_4), 163 (25.5%, $C_7F_4H_3$, P-C_2F_4-C_2H_5), 150 (21.4%, C_3F_6), 86 (26.3%, C_5H_7F, P-C_6F_7H), 68 (43.5%, C_5H_8, P-C_6F_8), 67 (35.7%, C_5H_7, P-C_6F_8H), 42 (14.8%, C_3H_6), 41 (15.6%, C_3H_5).



(VI)

350 (0.35%, $C_{10}F_{12}H_2$, <u>PARENT</u>), 331 (1.4%, $C_{10}F_{11}H_2$, P-F), 311 (0.52%, $C_{10}F_{10}H$, P-F-HF), 281 (1.6%, $C_9F_9H_2$, P-CF_3), 262 (1.1%, $C_9F_8H_2$, P-CF_4), 231 (1.6%, $C_8F_7H_2$, P-C_2F_5), 225 (1.1%), 212 (1.1%), 205 (6,3%, C_6F_7, P-$C_4F_5H_2$), 200 (1.0%, C_4F_8), 199 (2.7%, C_7F_6H, P-C_3F_6H), 181 (6.0%, C_4F_7, P-$C_6F_5H_2$),

161 (2.3%), 155 (4.7%), 150 (1.8%, C_3F_6), 145 (5.0%, $C_4F_5H_2$, P-C_6F_7), 131 (2.7%, C_3F_5), 127 (6.7%), 126 (100%, $C_4F_4H_2$ BASE PEAK, P-C_6F_8) 124 (2.7%, C_4F_4), 117 (2.8%, C_5F_3), 113 (2.9%, C_3F_5H), 100 (2.3%, C_2F_4) .....



(VII)

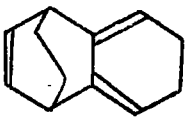
350 (0.38%, $C_{10}F_{12}H_2$, PARENT), 331 (1.1%, $C_{10}F_{11}H_2$, P-F), 311 (0.52%, $C_{10}F_{10}H$, P-F-HF), 281 (1.2%, $C_9F_9H_2$, P-CF_3), 262 (0.9%, $C_9F_8H_2$, P-CF_4), 231 (1.6%, $C_8F_7H_2$, P-C_2F_5), 224 (1.3%, C_6F_8, P-$C_4F_4H_2$), 205 (5.2%, C_6F_7, P-$C_4F_5H_2$), 199 (1.8%, C_7F_6H, P-C_3F_6H), 181 (3.9%, C_4F_7, P-$C_6F_5H_2$), 161 (1.6%), 158 (3.3%), 155 (3.6%), 150 (1.6%, C_3F_6), 145 (4.0%, $C_4F_5H_2$, P-C_6F_7), 144 (2.0%), 143 (1.1%), 131 (1.8%, C_3F_5), 127 (5.8%), 126 (100%, $C_4F_4H_2$, BASE PEAK, P-C_6F_8), 124 (1.9%, C_4F_4), 117 (2.0%, C_5F_3), 113 (2.7%, C_3F_5H), 100 (1.6%, C_2F_4).....

(VIII)

252 (49.5%, $C_8F_8H_4$, PARENT), 233 (17.2%, $C_8F_7H_4$, P-F), 213 (9.1%, $C_8F_6H_3$, P-F-HF), 202 (9.1%, $C_8F_6H_4$, P-CF_2), 201 (8.1%, $C_8F_6H_3$, P-CHF_2), 188 (12.6%), 183 (100%, $C_7F_5H_4$, BASE PEAK, P-CF_3), 163 (41.4%, $C_7F_4H_3$, P-CF_3-HF), 152 (32.3%, $C_7F_4H_4$, P-C_2F_4), 151 (33.3%, $C_7F_4H_3$, P-C_2F_4H), 133 (86.9%, $C_6F_3H_4$,

P-C_2F_5), 132 (20.2%, $C_6F_3H_3$, P-C_2F_5H), 126 (88.9%, $C_4F_4H_2$, P-$C_4F_4H_2$), 120 (37.4%, C_2F_5H), 119 (15.7%, C_2F_5), 114 (14.7%, $C_3F_4H_2$), 113 (59.1%, C_3F_4H), 101 (19.2%, C_2F_4H), ... 69 (44.4%, CF_3).

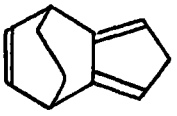
Metastable ions: 183 → 163 (-HF) at 145.2



(IX)

410 (9.4%, $C_{12}F_{14}$, PARENT), 391 (4.0%, $C_{12}F_{13}$, P-F), 341 (4.7%, $C_{11}F_{11}$, P-CF_3), 310 (45%, $C_{10}F_{10}$, P-C_2F_4), 291 (19.0%, $C_{10}F_9$, P-C_2F_5), 272 (9.9%, $C_{10}F_8$, P-C_2F_6), 260 (11.0%, C_9F_8, P-C_3F_6), 241 (100%, C_9F_7, BASE PEAK, P-C_3F_7), 222 (4.1%, C_9F_6, P-C_3F_8), 210 (5.5%, C_8F_6, P-C_4F_8), 203 (3.6%), 141 (4.6%), 117 (5.0%), 93 (3.6%, C_3F_3), 69 (3.6%, CF_3).

Metastable ions; 410 → 310 (-C_2F_4) at 234.4, 310 → 241 (-CF_3) at 187.4, 291 → 241 (-CF_2) at 199.6, 260 → 241 (-F) at 223.4.

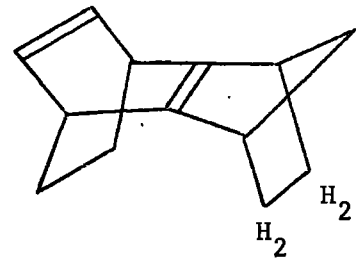


(X)

360 (18.0%, $C_{11}F_{12}$, PARENT), 341 (2.5%, $C_{11}F_{11}$, P-F), 291 (11.8%, $C_{10}F_9$, P-CF_3), 272 (4.9%, $C_{10}F_8$, P-CF_4), 261 (9.8%), 260 (100%, C_9F_8, BASE PEAK, P-C_2F_4), 242 (6.5%), 241 (61.2%, C_9F_7, P-C_2F_5), 222 (3.1%, C_9F_6, P-C_2F_6), 210 (21.2%, C_8F_6, P-C_3F_6), 203 (2.7%), 168 (7.8%), 141 (8.6%), 117 (8.5%), 93 (5.9%, C_3F_3),

69 (3.9%, CF_3).

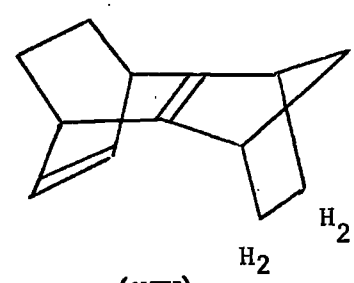
<u>Metastable ions</u>: 360 → 260 ($-C_2F_4$) at 187.8, 341 → 241 ($-C_2F_4$) at 170.3, 260 → 241 (-F) at 223.4



(XIII)

388 (11.5%, $C_{13}F_{12}H_4$, <u>PARENT</u>), 369 (4.9%, $C_{13}F_{11}H_4$, P-F), 338 (10.9%, $C_{12}F_{10}H_4$, P-CF_2), 319 (8.5%, $C_{12}F_9H_4$, P-CF_3), 288 (100%, $C_{11}F_8H_4$, <u>BASE PEAK</u>, P-C_2F_4), 273 (7%, $C_{10}F_8H$, P-C_2F_4-CH_3), 269 (8.5%, $C_{11}F_7H_4$, P-C_2F_5), 268 (5.5%), 267 (4.2%), 260 (48.5%, C_9F_8, P-C_2F_4-C_2H_4), 255 (7.3%, $C_{10}F_7H_2$, P-$C_3F_5H_2$), 249 (7.9%), 241 (18.8%, C_9F_7, P-C_2F_5-C_2H_4), 238 (73.3%, $C_{10}F_6H_4$, P-C_3F_6), 237 (86.7%, $C_{10}F_6H_3$, P-C_3F_6H), 236 (8.5%), 224 (15.8%, $C_9F_6H_2$, P-C_3F_6-CH_2), 223 (14.6%, C_9F_6H, P-C_3F_6-CH_3), 220 (9.7%, C_4F_9H), 219 (73.3%, $C_{10}H_4F_5$, P-C_3F_7), 218 (29.7%, $C_{10}H_3F_5$, P-C_3F_7H), 210 (7.3%), 205 (23.6%, C_6F_7), 200 (7.6%, C_4F_8), 187 (26.7%), 169 (20%, C_3F_7), 100 (7.6%, C_2F_4), 69 (9.7%, CF_3), 65 (9.1%, $C_2F_2H_3$)

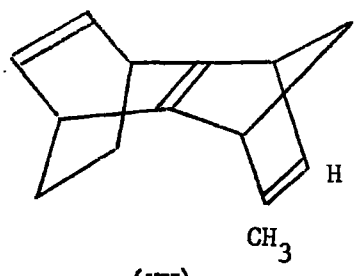
<u>Metastable ions</u>: 388 → 288 ($-C_2F_4$) at 213.8, 288 → 238 ($-CF_2$) at 196.7, 237 → 187 ($-CF_2$) at 147.6, 219 → 169 ($-CF_2$) at 130.4



(XIV)

388 (4.4%, $C_{13}F_{12}H_4$, PARENT), 369 (4.4%, $C_{13}F_{11}H_4$, P-F), 338 (5.9%, $C_{12}F_{10}H_4$, P-CF_2), 319 (7.7%, $C_{12}F_9H_4$, P-CF_3), 288 (94.1%, $C_{11}F_8H_4$, P-C_2F_4), 273 (6.9%, $C_{10}F_8H$, P-C_2F_4-CH_3), 269 (7.8%, $C_{11}F_7H_4$, P-C_2F_5), 268 (1.6%), 267 (4.1%), 260 (61.8%, C_9F_8, P-C_2F_4-C_2H_4), 255 (6.9%, $C_{10}F_7H_2$, P-$C_3F_5H_2$), 249 (7.7%), 241 (24.7%, C_9F_7, P-C_2F_5-C_2H_4), 238 (64.7%, $C_{10}F_6H_4$, P-C_3F_6), 237 (100%, $C_{10}F_6H_3$, BASE PEAK, P-C_3F_6H), 236 (7.9%), 224 (15%, $C_9F_6H_2$, P-C_3F_6-CH_2), 223 (14.4%, C_9F_6H, P-C_3F_6-CH_3), 220 (9.4%, C_4F_9H), 219 (88.2%, $C_{10}H_4F_5$, P-C_3F_7), 218 (29.7%, $C_{10}H_3F_5$, P-C_3F_7H), 210 (9.1%), 205 (22.4%, C_6F_7), 200 (6.3%, C_4F_8), 187 (27.1%), 169 (22.4%, C_3F_7), 100 (15.3%, C_2F_4), 69 (11.2%, CF_3) 65 (7.1%, $C_2F_2H_3$).

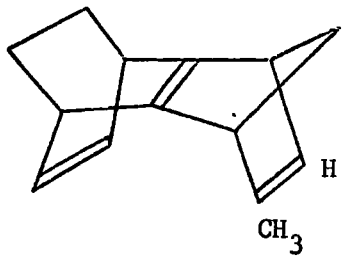
Metastable ions: 388 → 288 (-C_2F_4) at 213.8, 288 → 238 (-CF_2) at 196.7, 237 → 187 (-CF_2) at 147.6



(XV)

400 (5.3%, $C_{14}F_{12}H_4$, PARENT), 385 (0.5%, $C_{13}F_{12}H$, P-CH_3), 381 (0.6%, $C_{14}F_{11}H_4$, P-F), 350 (11.1%, $C_{13}F_{10}H_4$, P-CF_2), 331 (5.5%, $C_{13}F_9H_4$, P-CF_3), 300 (3.9% $C_{12}F_8H_4$, P-C_2F_4), 281 (3.6%, $C_{12}F_7H_4$, P-C_2F_5), 251 (13.5%), 250 (100%, $C_{11}F_6H_4$, BASE PEAK, P-C_3F_6), 249 (20.7%, $C_{11}F_6H_3$, P-C_3F_6H), 231 (10%, $C_{11}F_5H_4$, P-C_3F_7), 229 (4%, $C_{11}F_5H_2$, P-$C_3F_7H_2$), 223 (4.9%), 211 (2.7%), 205 (2.4%, C_6F_7), 200 (5.2%, C_4F_8), 100 (2.8%, C_2F_4), 81 (1.4%, C_2F_3), 44 (11.8%, C_2HF).

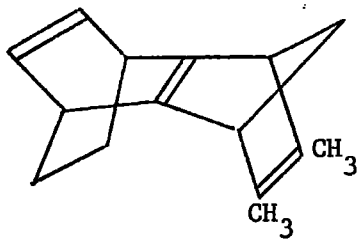
Metastable ions: 400 → 331 (-CF_3) at 273.9, 250 → 231 (-F) at 213.4, 350 → 250 (-C_2F_4) at 178.6, 250 → 200 (-CF_2) at 160.0.



(XVI)

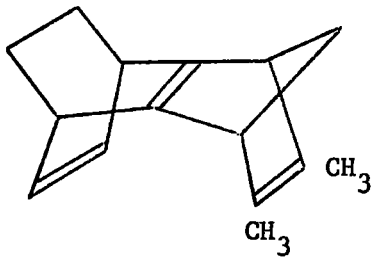
400 (3.5%, $C_{14}F_{12}H_4$, PARENT), 385 (0.4%, $C_{13}F_{12}H$, P-CH_3), 381 (0.7%, $C_{14}F_{11}H_4$, P-F), 350 (10.2%, $C_{13}F_{10}H_4$, P-CF_2), 331 (4.8%, $C_{13}F_9H_4$, P-CF_3), 300 (4.3%. $C_{12}F_8H_4$, P-C_2F_4), 281 (3.7%, $C_{12}F_7H_4$, P-C_2F_5), 251 (13.1%), 250 (100%, $C_{11}F_6H_4$, BASE PEAK, P-C_3F_6), 249 (22.5%, $C_{11}F_6H_3$, P-C_3F_6H), 231 (10.4%, $C_{11}F_5H_4$, P-C_3F_7), 229 (4.1%, $C_{11}F_5H_2$, P-$C_3F_7H_2$), 223 (4.6%), 211 (2.9%), 205 (2.1%, C_6F_7), 200 (5.4%, C_4F_8), 100 (6.8%, C_2F_4), 81 (5.9%, C_2F_3), 44 (8.3%, C_2F_3).

Metastable ions: 250 → 231 (-F) at 213.4, 350 → 250 (-C_2F_4) at 178.6, 250 → 200 (-CF_2) at 160.0.



(XVII)

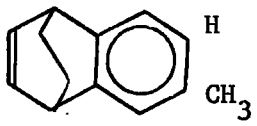
414 (100%, $C_{15}F_{12}H_6$, PARENT and BASE PEAK), 264 (52%, $C_{12}F_6H_6$, P-C_3F_6), 249 (8.4%, $C_{11}F_6H_3$, P-C_3F_6-CH_3), 236 (12%), 234 (18%), 219 (5%), 205 (6.5%, C_6F_7), 199 (5.8%, C_7F_6H), 156 (7.7%), 149 (9.4%, C_6F_3H), 115 (20%), 105 (10.7%, C_4F_3) ..... 69 (20%, CF_3).



(XVIII)

414 (10.6%, $C_{15}F_{12}H_6$, PARENT), 399 (0.9%, $C_{14}F_{12}H_3$, P-CH_3), 395 (1.6%, $C_{15}F_{11}H_6$, P-F), 364 (4.6%, $C_{14}F_{10}H_6$, P-CF_2), 345 (14.3%, $C_{14}F_9H_6$, P-CF_3), 314 (7.5%, $C_{13}F_8H_6$, P-C_2F_4), 299 (8%, $C_{12}F_8H_3$, P-C_2F_4-CH_3), 295 (7.5%, $C_{13}F_7H_6$, P-C_2F_5), 265 (13.1%), 264 (100%, $C_{12}F_6H_6$, BASE PEAK, P-C_3F_6), 263 (9%), 250 (7.2%), 249 (54%, $C_{11}F_6H_3$, P-C_3F_6-CH_3), 245 (9.4%, $C_{12}F_5H_6$, P-C_3F_7), 242 (9.2%), 241 (9.6%), ... 205 (6.6%), ... 69 (4%, CF_3).

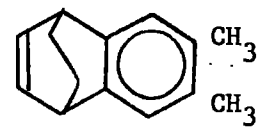
Metastable ions: 414 → 345 (-CF_3) at 287.5, 364 → 264 (-C_2F_4) at 191.5, 264 → 249 (-CH_3) at 234.9.



(XIX)

350 (7.5%, $C_{13}F_{10}H_4$, PARENT), 331 (3.7%, $C_{13}F_9H_4$, P-F), 300 (4.4%, $C_{12}F_8H_4$, P-CF_2), 281 (3.6%, $C_{12}F_7H_4$, P-CF_3), 251 (14.5%), 250 (100%, $C_{11}F_6H_4$, BASE PEAK, P-C_2F_4), 249 (27.5%, $C_{11}F_6H_3$, P-C_2F_4H), 231 (12.3%, $C_{11}F_5H_4$, P-C_2F_5), 229 (5.1%),223 (6.7%), 211 (3.8%), 205 (3%, C_6F_7), 200 (7.1%, C_4F_8), 100 (4.2%, C_2F_4), 99 (2.1%), ... 69 (1.9%, CF_3) .....

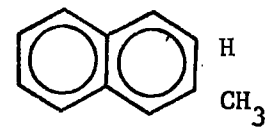
Metastable ions: 350 → 250 ($-C_2F_4$) at 178.6, 250 → 231 (-F) at 213.4, 250 → 200 ($-CF_2$) at 160



(XX)

364 (13.5%, $C_{14}F_{10}H_6$, PARENT), 345 (3.6%, $C_{14}F_9H_6$, P-F), 295 (2.1%, $C_{13}F_7H_6$, P-CF_3), 265 (13.8%), 264 (100%, $C_{12}F_6H_6$, BASE PEAK, P-C_2F_4), 263 (13%), 249 (23.7%, $C_{11}F_6H_3$, P-C_2F_4-CH_3), 245 (2.8%, $C_{12}F_5H_6$, P-C_2F_5), 242 (3.2%), 236 (2.8%), 231 (2.0%), 229 (2.2%), 224 (3.0%), 223 (3.4%), 205 (2.8%, C_6F_7), 193 (1.8%), 187 (2.3%), 118 (1.5%), 100 (1.6%, C_2F_4), 99 (1.1%), 81 (1.5%) .....

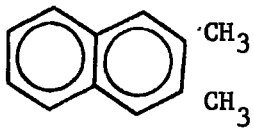
Metastable ions: 364 → 264 ($-C_2F_4$) at 191.5, 264 → 249 ($-CH_3$) at 234.9.



(XXI)

250 (100%, $C_{11}F_6H_4$, PARENT and BASE PEAK), 249 (73%, $C_{11}F_6H_3$, P-H), 231 (33%, $C_{11}F_5H_4$, P-F), 229 (14%, $C_{11}F_5H_2$, P-F-H_2), 223 (20%, C_9F_6H, P-C_2H_3), 218 (4%, $C_{10}F_5H_3$, P-CHF), 211 (7%, $C_{11}F_4H_3$, P-HF_2), 205 (8.1%, $C_9F_5H_2$, P-C_2FH_2), 200 (19%, $C_{10}F_4H_4$, P-CF_2) ..... 100 (7.3%), 99 (4.2%) .....

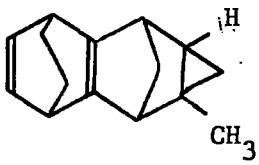
Metastable ions: 250 → 231 (-F) at 213.4, 250 → 200 ($-C_2F_4$) at 160.



(XXII)

264 (100%, $C_{12}F_6H_6$, PARENT and BASE PEAK), 263 (27%, $C_{12}F_6H_5$, P-H), 250 (7.5%, $C_{11}F_6H_4$, P-CH_2), 249 (50.2%, $C_{11}F_6H_3$, P-CH_3), 245 (6.5%, $C_{12}F_5H_6$, P-F), 242 (5.8%), 236 (4.7%, $C_{10}F_6H_2$, P-C_2H_4), 231 (4.2%, $C_{11}F_5H_4$, P-CH_2F), 229 (3.7%), 223 (5.8%), 205 (4.4%, $C_9F_5H_2$, P-C_2H_4-CF), 193 (2%), 187 (2.9%), 132 (3.4%), 118 (3.2%) .....

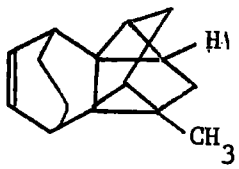
Metastable ions: 264 → 249 (-CH_3) at 234.9.



(XXIII)

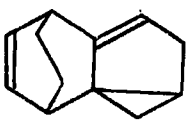
450 (11.9%, $C_{15}F_{14}H_4$, PARENT), 431 (4.8%, $C_{15}F_{13}H_4$, P-F), 381 (13.1%, $C_{14}F_{11}H_4$, P-CF_3), 350 (100%, $C_{13}F_{10}H_4$, BASE PEAK, P-C_2F_4), 335 (52.4%, $C_{12}F_{10}H$, P-C_2F_4-CH_3), 331 (19.1%, $C_{13}F_9H_4$, P-C_2F_5), 300 (14.3%, $C_{12}F_8H_4$, P-C_3F_6), 299 (14.3%, $C_{12}F_8H_3$, P-C_3F_6H), 285 (33.3%, $C_{11}F_8H$, P-C_3F_6-CH_3), 281 (81%, $C_{12}F_7H_4$, P-C_3F_7), 250 (45.2%, $C_{11}F_6H_4$, P-C_4F_8), 249 (21.4%, $C_{11}F_6H_3$, P-C_4F_8H), 231 (33.3%, $C_{11}F_5H_4$, P-C_4F_9), 113 (31.0%, C_3F_4H), 109 (19.1%), 100 (15.5%), 69 (21.4%, CF_3).

Metastable ion: 450 → 350 (-C_2F_4) at 272.2



(XXIV)

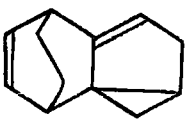
450 (19.0%, $C_{15}F_{14}H_4$, PARENT), 431 (6.9%, $C_{15}F_{13}H_4$, P-F), 400 (3.5%, $C_{14}F_{12}H_4$, P-CF_2), 381 (10.3%, $C_{14}F_{11}H_4$, P-CF_3), 350 (37.9%, $C_{13}F_{10}H_4$, P-C_2F_4), 335 (6.9%, $C_{12}F_{10}H$, P-C_2F_4-CH_3), 331 (10.3%, $C_{13}F_9H_4$, P-C_2F_5), 300 (12.1%, $C_{12}F_8H_4$, P-C_3F_6), 299 (3.5%, $C_{12}F_8H_3$, P-C_3F_6H), 285 (12.1%, $C_{11}F_8H$, P-C_3F_6-CH_3), 281 (69%, $C_{12}F_7H_4$, P-C_3F_7), 250 (56.9%, $C_{11}F_6H_4$, P-C_4F_8), 249 (16.6%, $C_{11}F_6H_3$, P-C_4F_8H), 231 (22.4%, $C_{11}F_5H_4$, P-C_4F_9), 219 (20.7%, $C_{10}F_5H_4$, P-C_5F_9), ... 127 (100%, $C_4F_4H_3$, BASE PEAK), 113 (8.6%, C_3F_4H, 127 -CH_3), 100 (5.2%, C_2F_4), ... 69 (10.3%, CF_3).



(XXV)

410 (1.2%, $C_{12}F_{14}$, PARENT), 391 (2.4%, $C_{12}F_{13}$P-F), 360 (0.9%, $C_{11}F_{12}$, P-CF_2), 341 (10.1%, $C_{11}F_{11}$, P-CF_3), 322 (4.0%, $C_{11}F_{10}$, P-CF_4), 310 (26.9%, $C_{10}F_{10}$, P-C_2F_4), 291 (18.9%, $C_{10}F_9$, P-C_2F_5), 272 (9.9%, $C_{10}F_8$, P-C_2F_6), 260 (21.7%, C_9F_8, P-C_3F_6), 241 (100%, C_9F_7, BASE PEAK, P-C_3F_7), 222 (4.6%, C_9F_6, P-C_3F_8), 210 (11.1%, C_8F_6, P-C_4F_8), 141 (9.1%), 117 (9.3%), 93 (6.5%, C_3F_3), 69 (7.6%, CF_3).

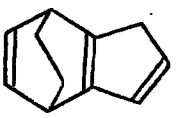
Metastable ions: 310 → 241 ($-CF_3$) at 187.4, 291 → 241 ($-CF_2$) at 199.6, 260 → 241 (-F) at 223.4.



(XXVI)

410 (2.7%, $C_{12}F_{14}$, PARENT), 391 (2.5%, $C_{12}F_{13}$, P-F), 360 (1.2%, $C_{11}F_{12}$, P-CF_2), 341 (7.5%, $C_{11}F_{11}$, P-CF_3), 322 (2.8%, $C_{11}F_{10}$, P-CF_4), 310 (28.7%, $C_{10}F_{10}$, P-C_2F_4), 291 (15.5%, $C_{10}F_9$, P-C_2F_5), 272 (16.8%, $C_{10}F_8$, P-C_2F_6), 260 (19.9%, C_9F_8, P-C_3F_6), 241 (100%, C_9F_7, BASE PEAK, P-C_3F_7), 222 (4.9%, C_9F_6, P-C_3F_8), 210 (10%, C_8F_6, P-C_4F_8), 141 (7.3%), 117 (7.7%), 93 (5.8%, C_3F_3), 69 (6.6%, CF_3).

Metastable ions: 310 → 241 ($-CF_3$) at 187.4, 291 → 241 ($-CF_2$) at 199.6, 260 → 241 (-F) at 223.4

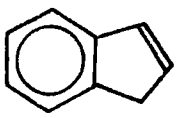


(XXVII)

360 (11.3%, $C_{11}F_{12}$, PARENT), 341 (4.7%, $C_{11}F_{11}$, P-F), 291 (10.0%, $C_{10}F_9$, P-CF_3), 272 (6.0%, $C_{10}F_8$, P-CF_4), 260 (100%, C_9F_8, BASE PEAK, P-C_2F_4), 241 (66.7%, C_9F_7, P-C_2F_5), 222 (4.7%, C_9F_6, P-C_2F_6), 210 (27.3%, C_8F_6, P-C_3F_6),

203 (4.0%, C_9F_5), 191 (4.7%, C_8F_5, P-C_3F_7), 179 (4.7%, C_7F_5), 172 (4.0%, C_8F_4), 160 (6.0%, C_7F_4), 141 (12.0%), 122 (4.3%), 117 (8.0%), 100 (7.3%, C_2F_4), 93 (7.3%, C_3F_3), 81 (4.0%, C_2F_3), 69 (6.0%, CF_3).

Metastable ions: 260 → 241 (-F) at 223.4, 360 → 260 (-C_2F_4) at 187.8, 341 → 241 (-C_2F_4) at 170.3.



*

(XXVIII)

260 (64%, C_9F_8, PARENT), 241 (100%, C_9F_7, BASE PEAK, P-F), 210 (44%, C_8F_6, P-CF_2), 191 (6.9%, C_8F_5, P-CF_3), 160 (9.4%, C_7F_4, P-C_2F_4), 141 (20%, C_7F_3, P-C_2F_5), 122 (6.3%), 117 (8.1%, C_3F_4), 93 (6.5%, C_3F_3).

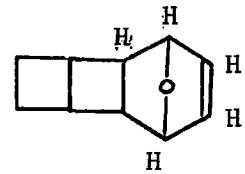
Metastable ions: 260 → 241 (-F) at 223.4, 260 → 210 (-CF_2) at 169.6, 241 → 191 (-CF_2) at 151.4.

* previously obtained in impure form.[45]

(XXIX)

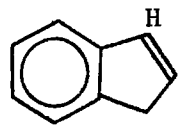
206 (26.4%, C_6F_7H, PARENT), 187 (15.3%, C_6F_6H, P-F), 168 (3.6%, C_6F_5H, P-2F), 156 (25.2%, C_5F_5H, P-CF_2), 137 (100%, C_5F_4H, BASE PEAK, P-CF_3), 117 (4.4%), 106 (41.5%, C_4F_3H, P-C_2F_4), 99 (5.8%), 93 (11.1%, C_3F_3), 87 (4.4%), 75 (17.1%), 69 (29.3%, CF_3).

Metastable ions: 206 → 187 (-F) at 169.8, 187 → 137 (-CF_2) at 100.4, 206 → 137 (-CF_3) at 91.1, 156 → 106 (-CF_2) at 72.0.



(XXX)

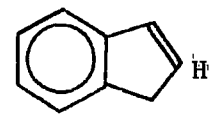
274 (v. weak, $C_{10}F_7H_5O$, PARENT), 206 (16%, C_6F_7H, P-C_4H_4O), 187 (28%, C_6F_6H, P-C_4H_4O-F), 156 (23.3%, C_5F_5H, P-C_4H_4O-CF_2), 137 (100%, C_5F_4H, BASE PEAK, P-C_4H_4O-CF_3), 106 (50%, C_9F_3H, P-C_4H_4O-C_2F_4), 99 (13%), 93 (18%), 75 (28%), 69 (37%, CF_3), 68 (100%, C_4H_4O, BASE PEAK), 40 (21%), 39 (64%), 31 (18%, CF), 29 (14%, C_2H_5) .....



(XXXII)

80%

+

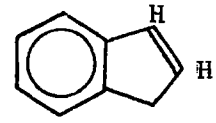


(XXXI)

20%

242 (51.5%, C_9F_7H, PARENT), 241 (7.4%, C_9F_7, P-H), 223 (100%, C_9F_6H, BASE PEAK, P-F), 192 (33.2%, C_8F_5H, P-CF_2), 161 (6.6%, C_7F_4H, P-C_2F_3), 142 (6.1%, C_7F_3H, P-C_2F_4), 141 (6.6%, C_7F_3, P-C_2F_4H), 123 (16.2%), 117 (6.6%, C_5F_3), 104 (5.2%), 99 (6.1%), 93 (7.4%, C_3F_3).

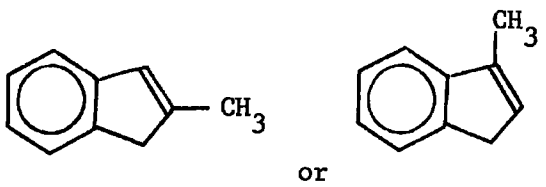
Metastable ions: 242 → 223 (-F) at 205.5, 242 → 192 (-CF_2) at 152.3.



(XXXIII)

224 (72.7%, $C_9F_6H_2$, PARENT), 223 (38.7%, C_9F_6H, P-H), 205 (100%, $C_9F_5H_2$, BASE PEAK, P-F), 174 (24.7%, $C_8F_4H_2$, P-CF_2), 124 (3.3%, $C_7F_2H_2$, P-C_2F_4), 123 (6.7%, C_7F_2H, P-C_2F_4H), 117 (4.0%, C_5F_3), 112 (4.0%, C_3F_4), 104 (4%), 99 (5.3%), 93 (5.0%, C_3F_3).

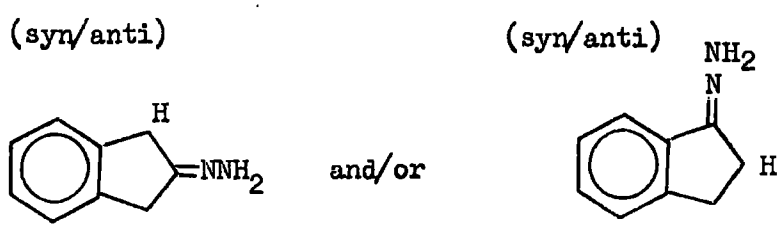
Metastable ions: 224 → 205 (-F) at 187.6



(XXXIV)

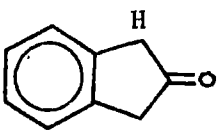
256 (100%, $C_{10}F_7H_3$, PARENT and BASE PEAK), 255 (15.4%, $C_{10}F_7H_2$, P-H), 241 (48.5%, C_9F_7, P-CH_3), 237 (25.4%, $C_{10}F_6H_3$, P-F), 236 (39.1%, $C_{10}F_6H_2$, P-HF), 223 (9.2%, C_9F_6H, P-CH_2F), 206 (30.8%, $C_9F_5H_3$, P-CF_2), 205 (49.4%, $C_9F_5H_2$, P-CF_2H), 187 (46.2%, $C_9F_4H_3$, P-CF_3) .....

Metastable ions: 256 → 237 or 236, 255 → 236, 235 (-HF, -F) broad metastable at 216-219, 206 → 187 (-F) at 169.8, 256, 255 → 205 (-CF_2, -CF_2H) broad metastable at 164-166, 237 → 187 (-CF_2) at 147.6, 256 → 187 (-CF_3) at 136.6.



(XXXV) (85%) + (XXXVI) (15%)

272 (100%, $C_9F_7N_2H_3$, PARENT and BASE PEAK), 253 (11.1%, $C_9F_6N_2H_3$, P-F), 252 (28.9%, $C_9F_6N_2H_2$, P-HF), 234 (8.2%, $C_9F_5N_2H_3$, P-2F), 225 (24.4%, $C_9F_6H_3$ or C_8F_6NH, P-F-N_2 or P-$CFNH_2$) 224 (23.7%), 223 (77.8%, C_9F_6H, P-F-N_2H_2), 206 (44.4%, 225-F), 205 (75.6%, 224-F), 204 (27.0%, 223-F), 192 (8.9%, C_8F_4H, P-CF_2-N_2H_2), 179 (11.9%, C_7F_4, P-$C_2F_3N_2H_3$), 174 (13.3%, C_8F_3H, P-CF_3-N_2H), 154 (7.4%, C_8F_2H, P-CF_4-N_2H_2), 148 (8.2%, C_7F_2H, 174-CF), 123 (13.7%), 120 (17.0%), 104 (21.1%), 103 (17.0%), 99 (7.4%), 93 (9.6%, C_3F_3), 77 (9.6%), 69 (6.7%, CF_3), 51 (7.4%, CHF_2), 48 (13.0%, $CHFNH_2$), 31 (7.4%, CF), 29 (8.5%).



(XXXIX)

258 (100%, C_9F_7OH, PARENT and BASE PEAK), 239 (17.4%, C_9F_6OH, P-F), 238 (18.8%, C_9F_6O, P-HF), 230 (69.6%, C_8F_7H, P-CO), 211 (13.0%, C_8F_6H, P-COF), 210 (18.8%, C_8F_6, P-CO-HF), 180 (63.0%, C_7F_5H, P-CO-CF_2), 179 (29.0%, C_7F_5, P-CO-CF_2H), 161 (94.2%, C_7F_4H, P-CO-CF_3), 148 (39.1%, C_6F_4, P-CO-C_2F_3H), 141 (18.1% C_7F_3), 117 (17.4%, C_5F_3), 104 (17.4%), 98 (16.7%), 93 (17.4%), 79 (18.8%), 58 (29.0%).

Metastable ions: 258 → 230 (-CO) at 205.0, 258 → 238 (-HF) at 219.6, 230 → 161 (-CF_3) at 112.7, 238 → 210 (-CO) at 185.3, 180 → 161 (-F) at 144.0, 230 → 180 (-CF_2) at 140.9.

APPENDIX 3

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 stored in 3 l. storage bulbs and measured by noting the pressure on a wide-bore manometer connected to one of two standard volume bulbs (672 ml. and 4040 ml.). The smaller bulb was used for quantities of gas less than 10 mmoles, the larger one for quantities up to 50 mmoles.

Infrared Spectra were recorded on a Perkin-Elmer 137 (sodium chloride) spectrometer and a Grubb Parson Spectromaster. High resolution work was done on either the Grubb-Parsons Spectromaster or on a Perkin-Elmer 457 Grating Infrared Spectrophotometer.

Ultra-violet Spectra were recorded on a Unicam SP800 Spectrophotometer.

Mass Spectra were measured with an A.E.I. MS9 spectrometer at an ionising beam energy of 70 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 spectra, operating temperature 40°. ^{19}F chemical shifts are in p.p.m. from fluorotrichloromethane (positive upfield) and ^{1}H chemical shifts are measured on the δ scale relative to tetramethyl silane. Wherever possible internal references were used on either neat liquids or solutions in carbon tetrachloride.

Analytical Gas Liquid Chromatography (g.l.c.)

A Perkin-Elmer 452 using hydrogen as carrier gas and a hot wire detector was used for analytical work. The stationery phases used were:

Column A: 2.2m x 7 mm. diam., di-n-decylphthalate/Celite

Column O: 2.2m x 7 mm. diam., silicone grease/Celite

Preparative g.l.c. All instruments used nitrogen carrier gas.

Column A: 4.9m x 75 mm diam., dinonylphthalate-Celite 1:2, N_2 carrier (1100 ml/min)

Column B: Perkin-Elmer F.21. Präparativer Gaschromatograph, 4.5m x 0.95 cm. diam., di-n-decylphthalate-Chromosorb P (1:4); N_2 carrier (ca. 0.8-1.5 atmos).

Column C: As for Column B but with silicone oil-Chromosorb P (1:4) as stationery phase.

Column D: Perkin Elmer F.21. Präparativer Gaschromatograph, 7.7m x 0.95 cm. diam., di-n-decylphthalate-Chromosorb P (1:4); N_2 carrier (ca. 0.8-1.5 atmos).

Column E: As for Column D but with silicone oil-Chromosorb P (1:4) as stationery phase.

Column F: Varian "Autoprep". 6.1m x 13 mm diam., silicone elastomer-Celite (1:2), ca. 10 l./hr.

Column G: As for Column F with di-n-decylphthalate-Celite, (1:2)

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.

APPENDIX 4

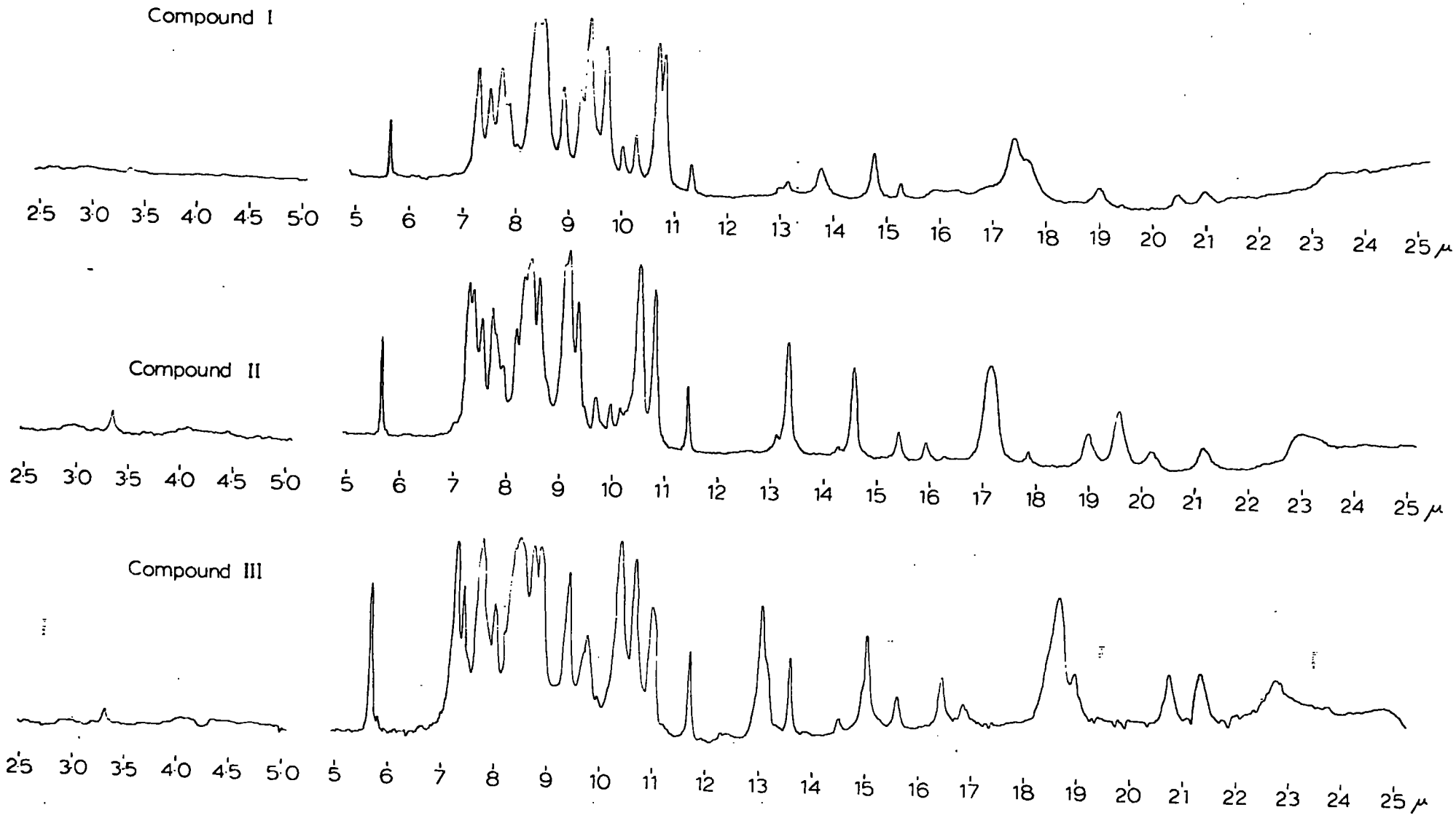
INFRA-RED SPECTRA

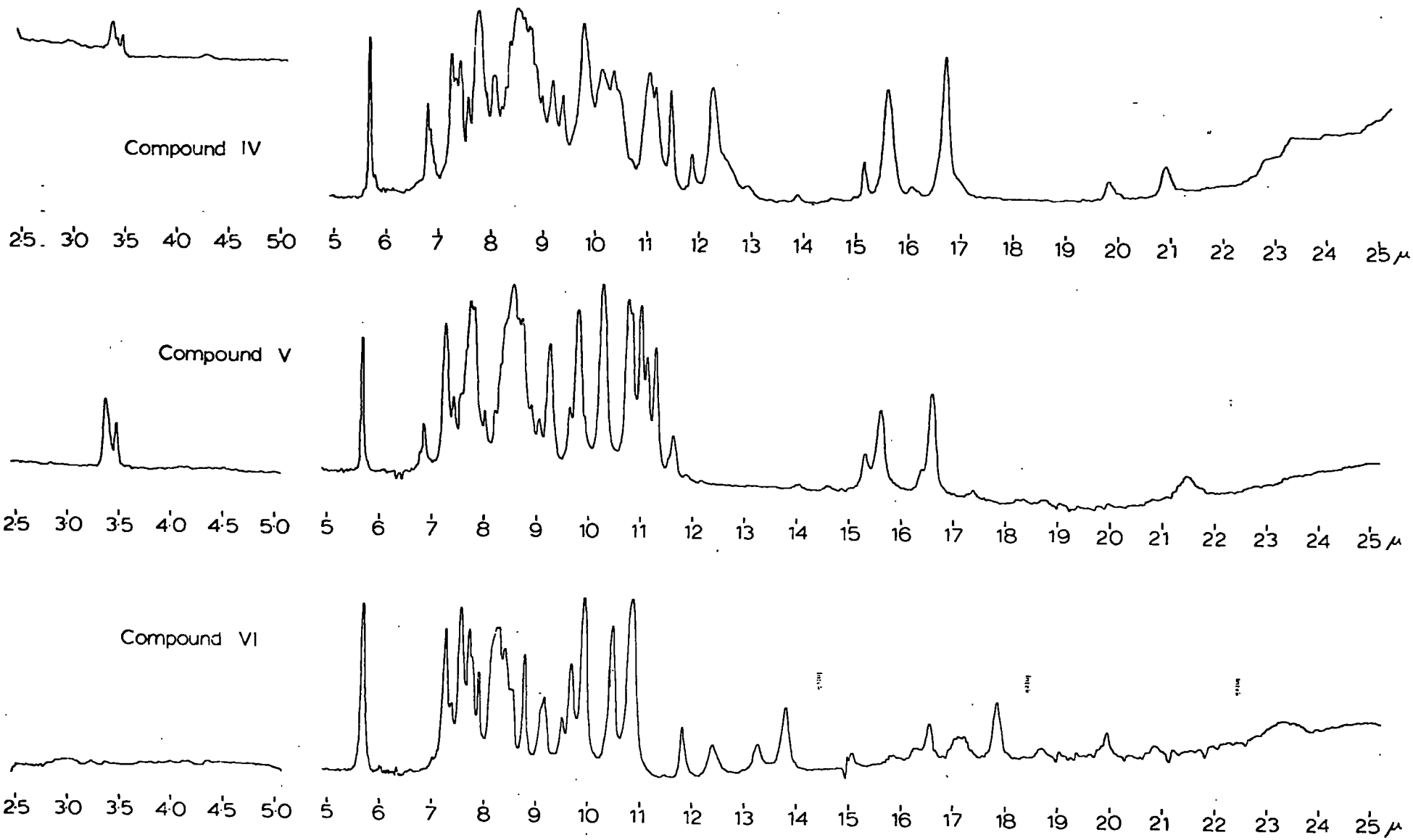
The infra-red spectra below were run on a Grubb-Parsons Spectromaster. All spectra were run using KBr cells under the following conditions.

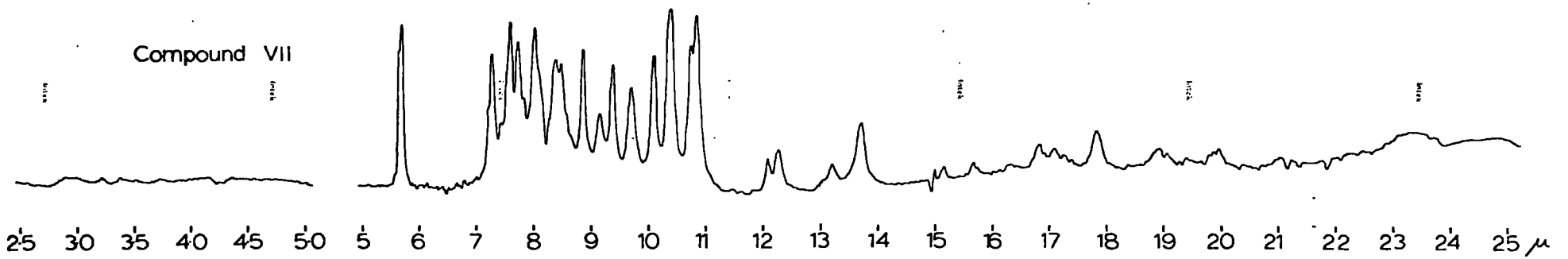
(A) Liquid film
(B) KBr disc
(C) Nujol mull - nujol bands marked 'n' in the spectrum
(D) Thin contact film produced by melting a solid between the infra-red plates.

Compound Number	Name of Compound	
(I)	2H,7H-hexadecafluorotricyclo[6,2,2,$0^{2,7}$]dodec-9- ene	(A)
(II)	2H,6H-tetradecafluorotricyclo[5,2,2,$0^{2,6}$]undec-8-ene	(A)
(III)	2H,5H-dodecafluorotricyclo[4,2,2,$0^{2,5}$]dec-7-ene	(A)
(IV)	1,8,9,10,11,11,12,12-octafluorotricyclo[6,2,2,$0^{2,7}$]-dodec-9-ene	(B)
(V)	1,7,8,9,10,10,11,11-octafluorotricyclo[5,2,2,$0^{2,6}$]-undec-8-ene	(A)
(VI)	cis- or trans-7H or 8H-decafluorotricyclo[4,2,0]-oct-2-ene	(A)
(VII)	" " " " "	(A)
(VIII)	3,3,4,4,7,7,8,8-octafluorotricyclo[3,3,0,$0^{2,6}$]octane	(C)
(IX)	perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6-9-triene	(A)
(X)	perfluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene	(A)
(XIII)	4H,4H,5H,5H-dodecafluorotetracyclo[6,2,2,$1^{3,6}0^{2,7}$]-trideca-2(7),9-diene	(D)
(XIV)	" " " " "	(B)
(XV)	4H-dodecafluoro-5-methyltetracyclo[6,2,2,$1^{3,6}0^{2,7}$]-trideca-2(7),4,9-triene	(B)
(XVI)	" " " " "	(B)
(XVII)	dodecafluoro-4,5-dimethyltetracyclo[6,2,2,$1^{3,6}0^{2,7}$]-trideca-2(7),4,9-triene	(B)
(XVIII)	" " " " "	(B)

Compound Number	Name of Compound	
(XIX)	4H-decafluoro-5-methyltricyclo[6,2,2,$0^{2,7}$]-dodeca-2,4,6,9-triene	(A)
(XX)	decafluoro-4,5-dimethyltricyclo[6,2,2,$0^{2,7}$]-dodeca-2,4,6,9-tetraene	(B)
(XXI)	2H-hexafluoro-3-methylnaphthalene	(D)
(XXII)	2,3-dimethylhexafluoronaphthalene	(B)
(XXIII)	4H-tetradecafluoro-6-methylpentacyclo[7,2,2,$1^{3,7}0^{4,6}$-$0^{2,8}$]tetradeca-2(8),10-diene	(B)
(XXIV)	4H-tetradecafluoro-6-methylhexacyclo[7,2,2,$1^{3,7}0^{2,4}$-$0^{2,8}0^{6,8}$]tetradec-10-ene	(B)
(XXV)	perfluorotetracyclo[6,2,2,$0^{2,7}0^{5,7}$]dodeca-2,9-diene	(A)
(XXVI)	" " " " " "	(A)
(XXVII)	perfluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,3,8-triene	(A)
(XXVIII)	perfluoroindene	(A)
(XXIX)	1,3,4,5,5,6,6-heptafluorobicyclo[2,2,0]hex-2-ene	(A)
(XXX)	11-oxa-3,4,4,5,5,6,7-heptafluorotetracyclo[6,2,1,-$0^{2,7}0^{3,6}$]undec-9-ene	(B)
20% (XXXI)	1,1,3,4,5,6,7- and 80% (XXXII) 1,1,2,4,5,6,7-heptafluoroindenes	(A)
(XXXIII)	1,1,4,5,6,7-hexafluoroindene	(A)
(XXXIV)	1,1,3,4,5,6,7-heptafluoro-2-methyl-indene or 1,1,2,4,5,6,7-heptafluoro-3-methyl-indene	(A)
85% (XXXV) and 15% (XXXVI)	syn and/or anti 1,1,3,4,5,6,7-heptafluoroindan-2-one hydrazone or 1,1,2,4,5,6,7-heptafluoroindan-3-one hydrazone	(B)
(XXXVIII)	1,1,3,4,5,6,7-heptafluoroindan-2-one-3-sulphonic acid	(A)
(XXXIX)	1,1,3,4,5,6,7-heptafluoroindan-2-one	(A)


Compound I
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ
Compound II
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ
Compound III
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ


Compound IV
Compound V
Compound VI
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ


Compound VII
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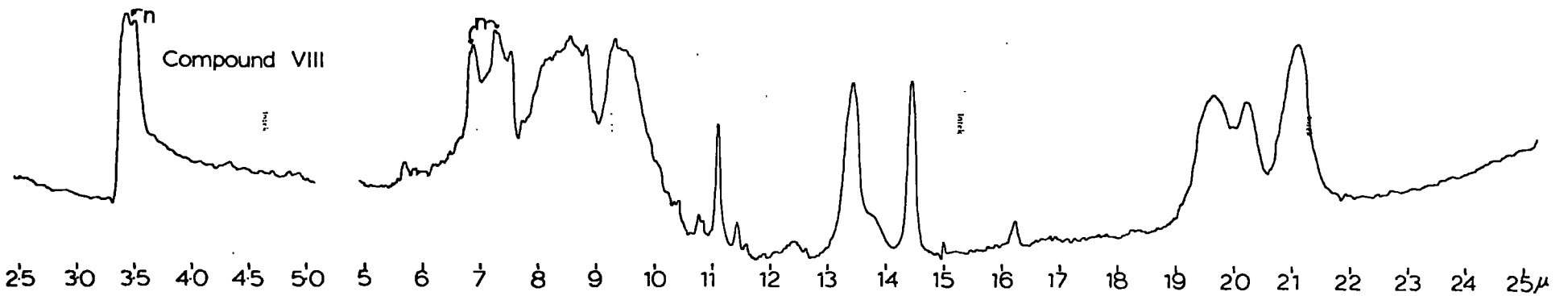
n
m
Compound VIII
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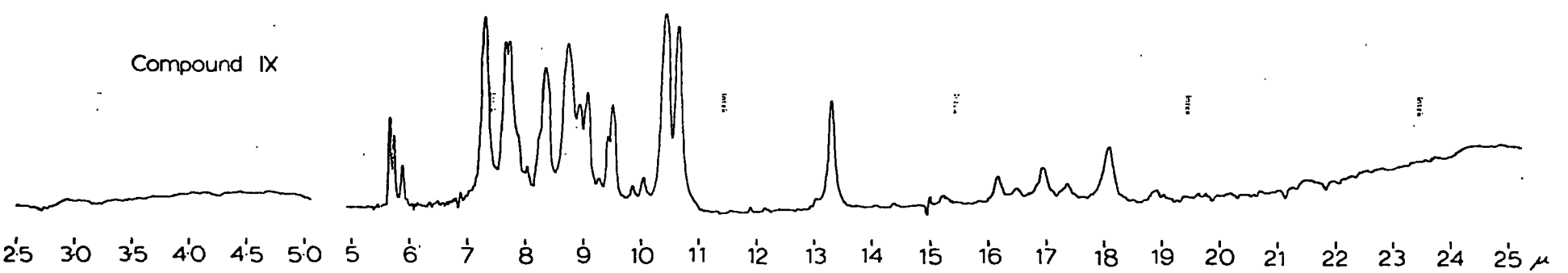
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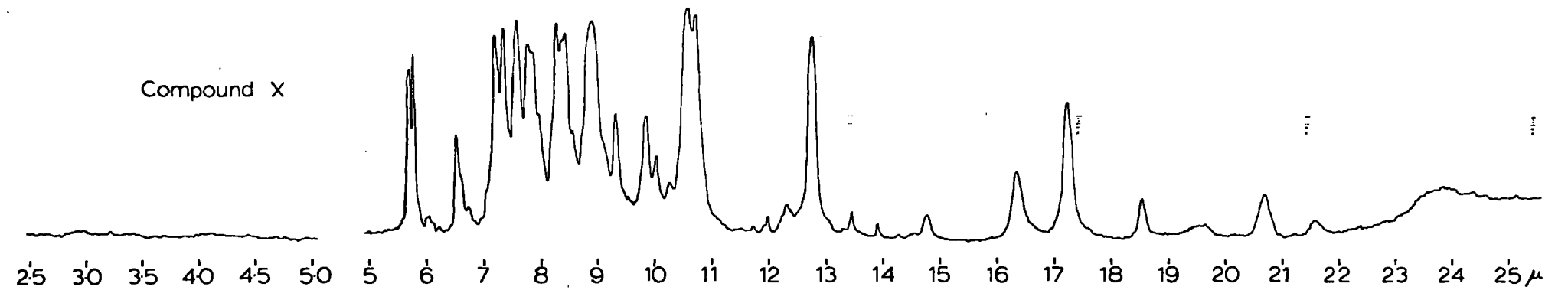
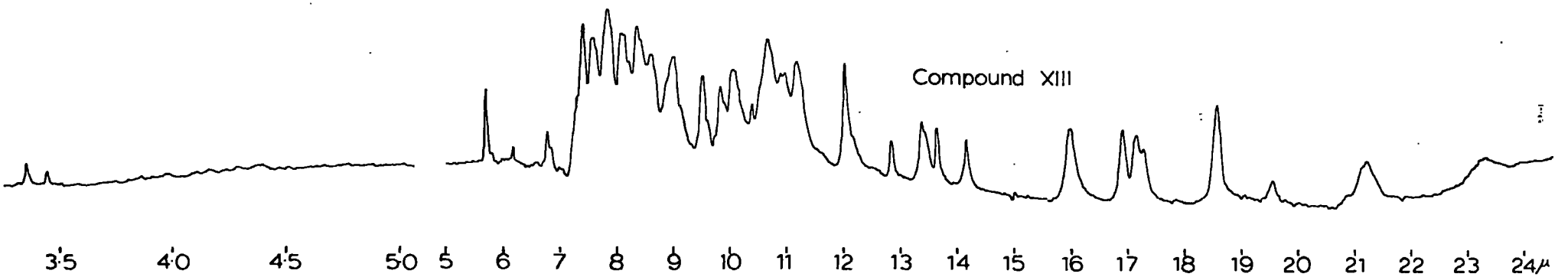
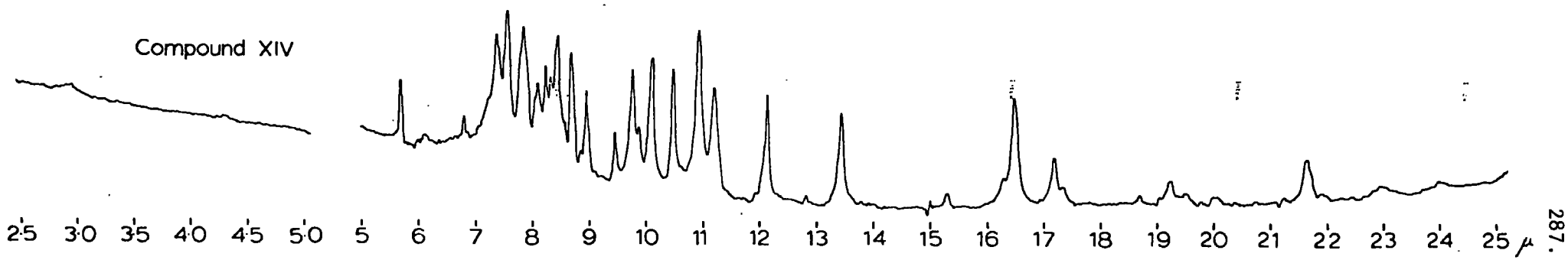

Compound X
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ


Compound XIII
3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 μ


Compound XIV
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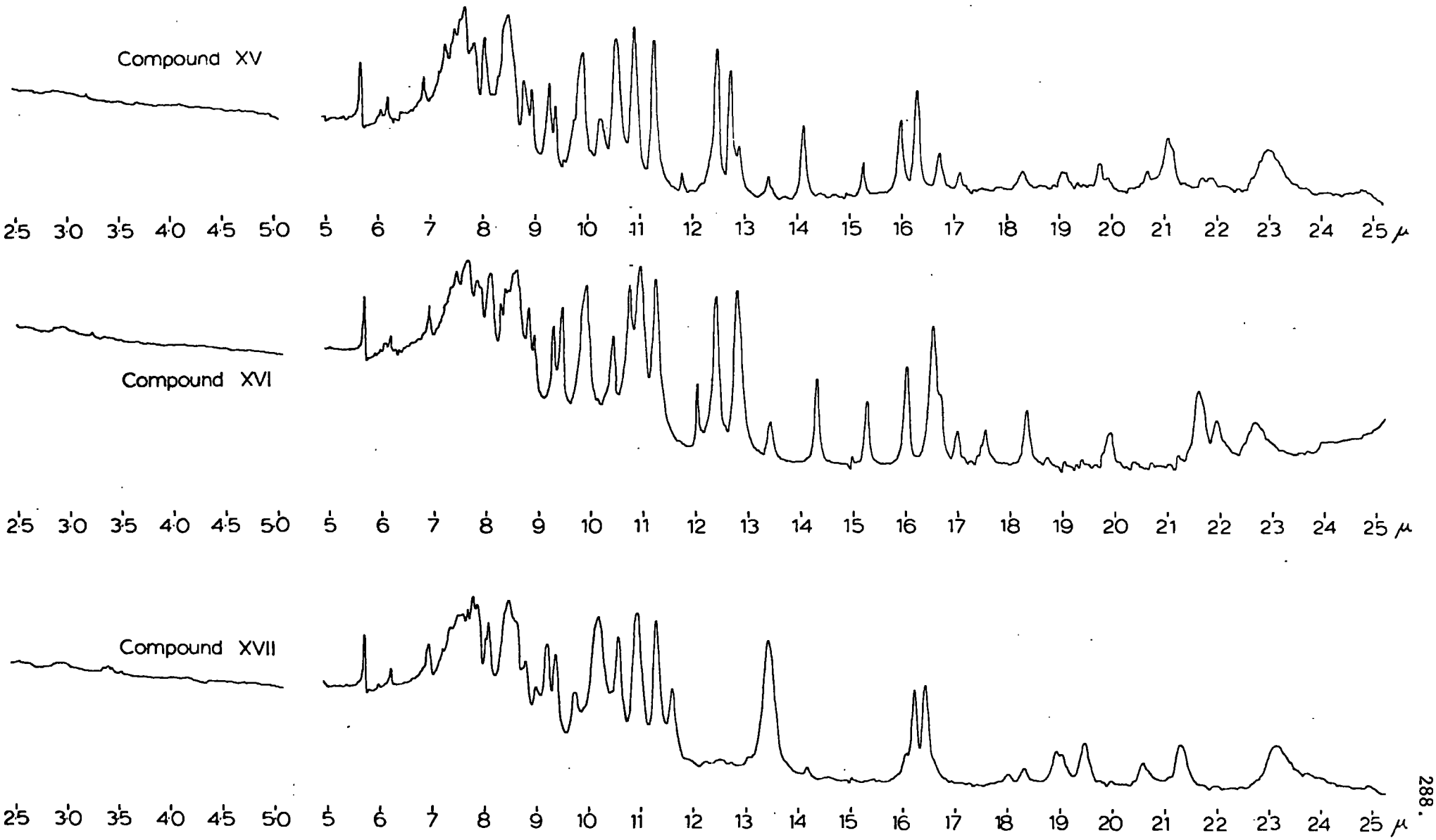
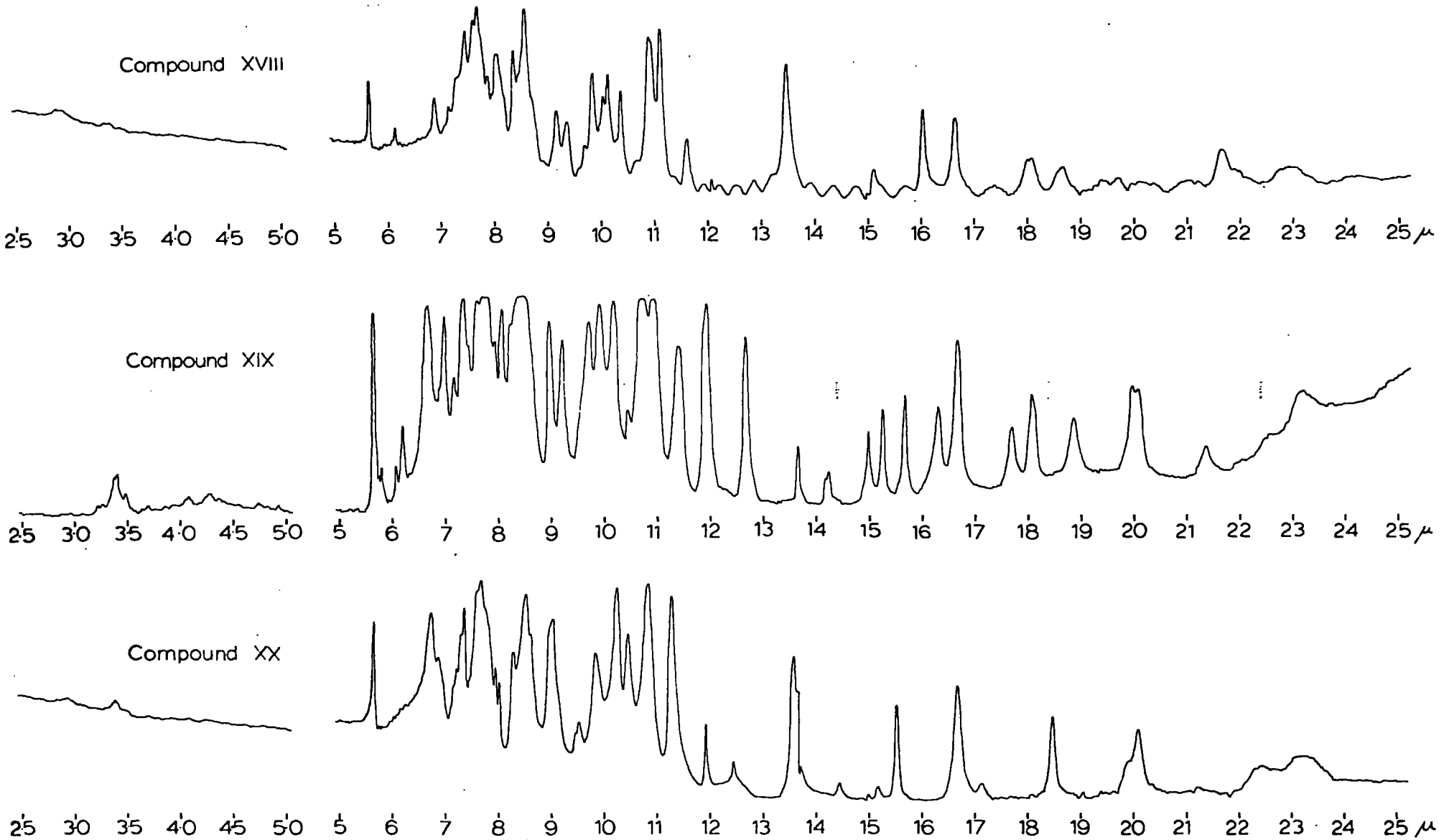

Compound XV
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ
Compound XVI
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ
Compound XVII
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ


Compound XVIII
Compound XIX
Compound XX
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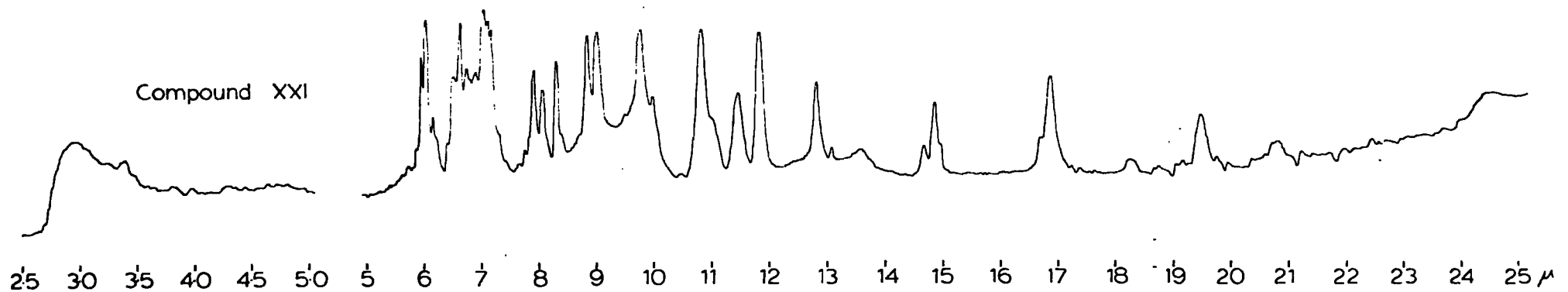
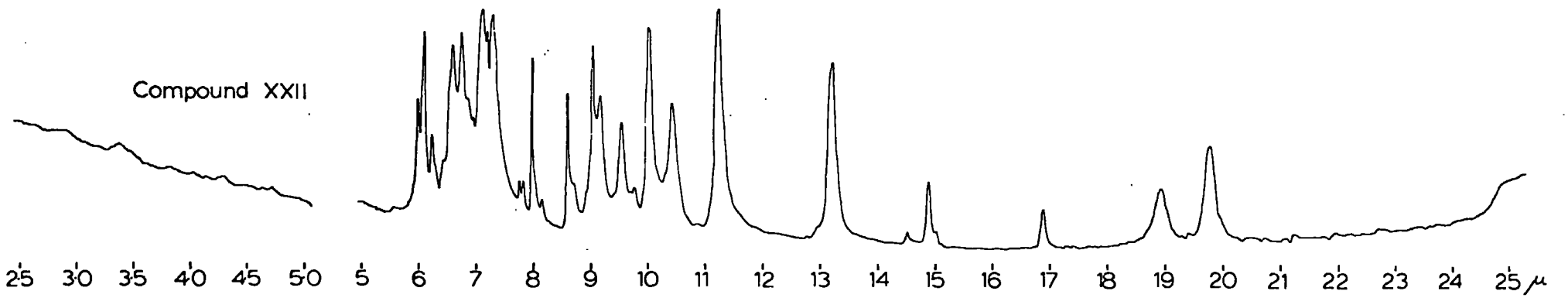

Compound XXI
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ


Compound XXII
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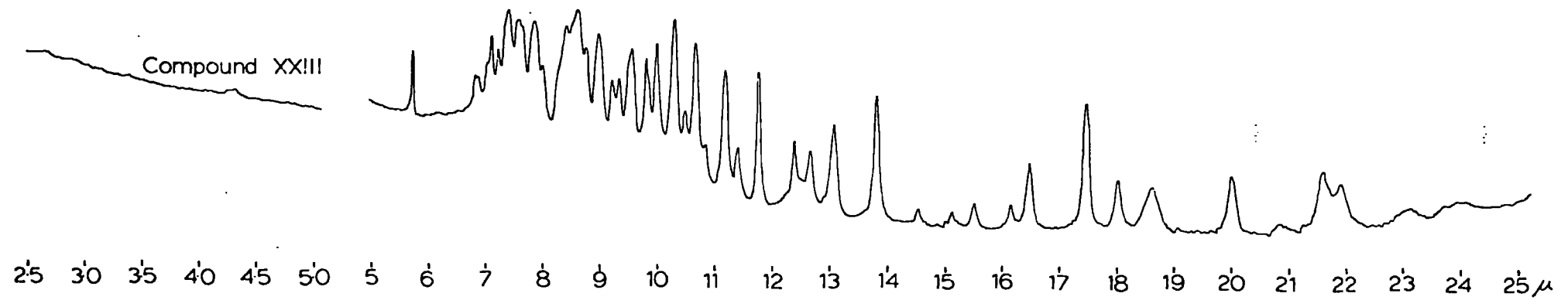
Compound XXIII
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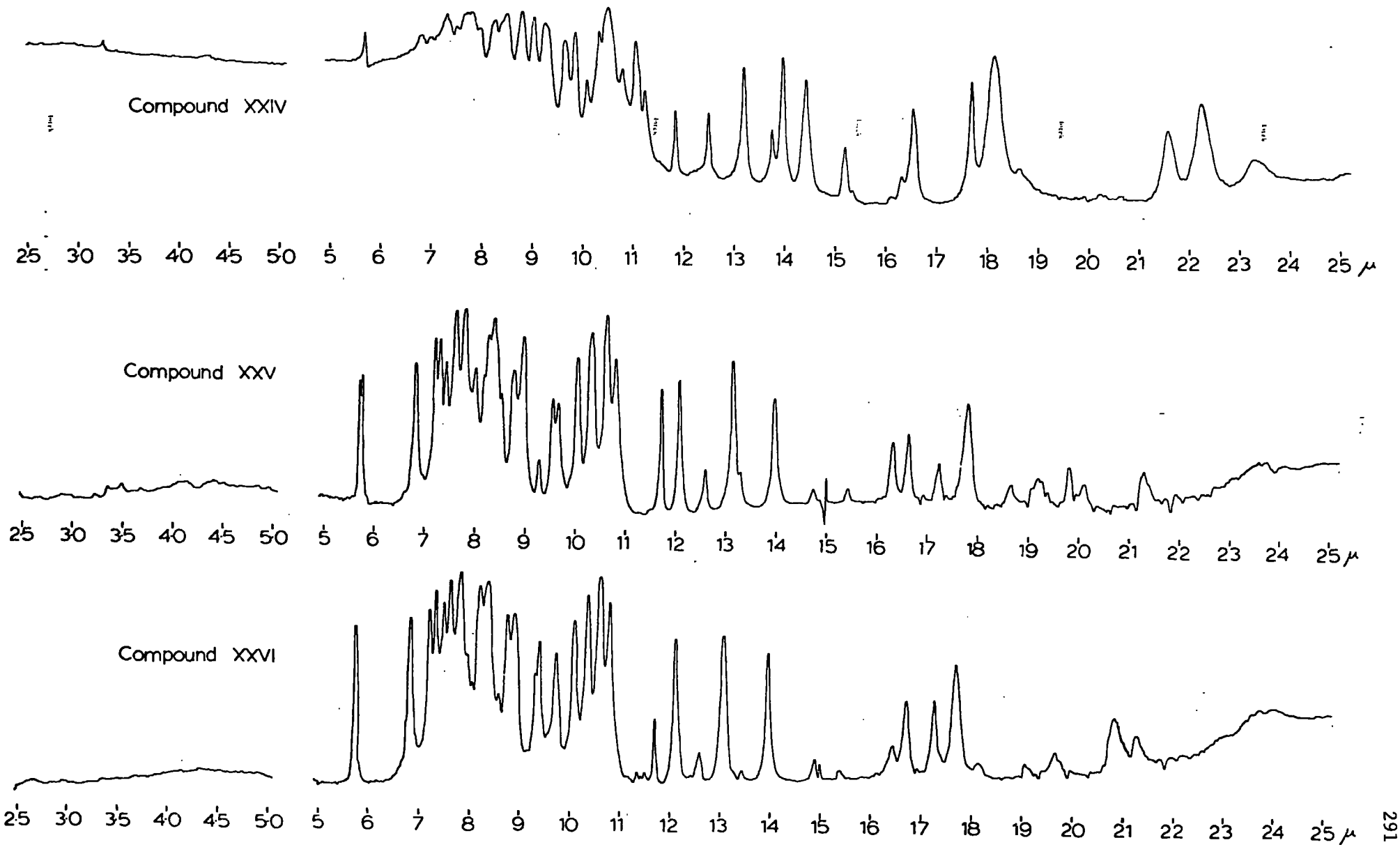
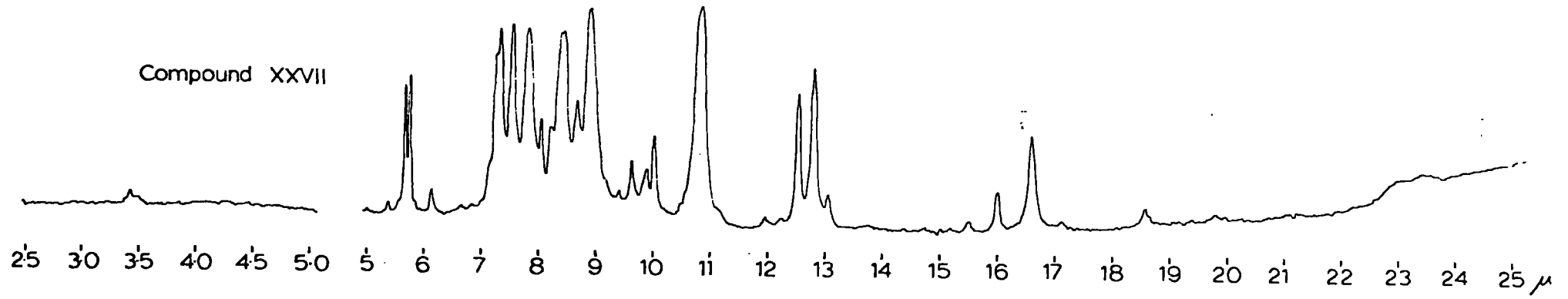
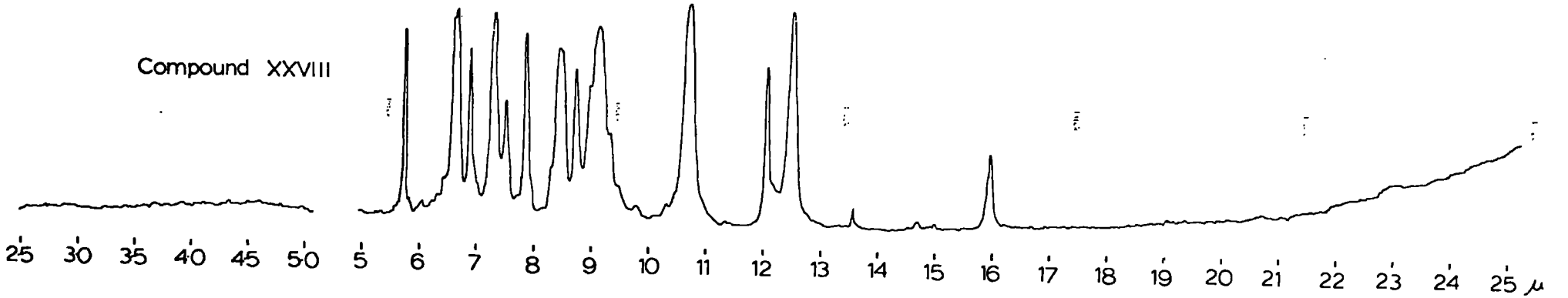
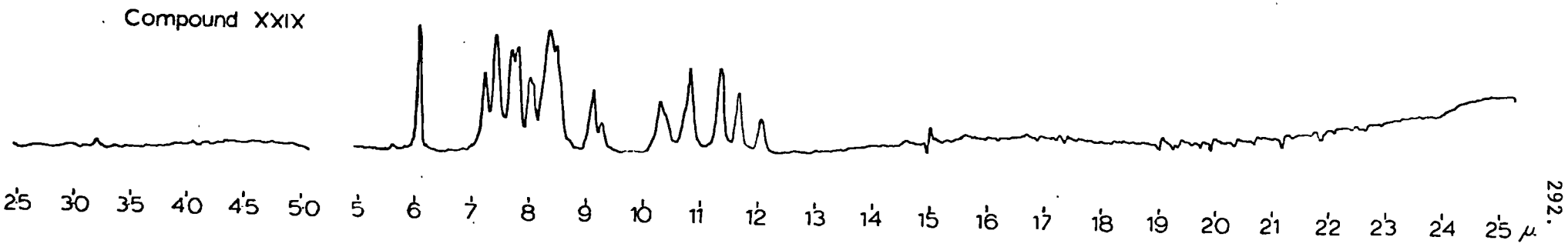
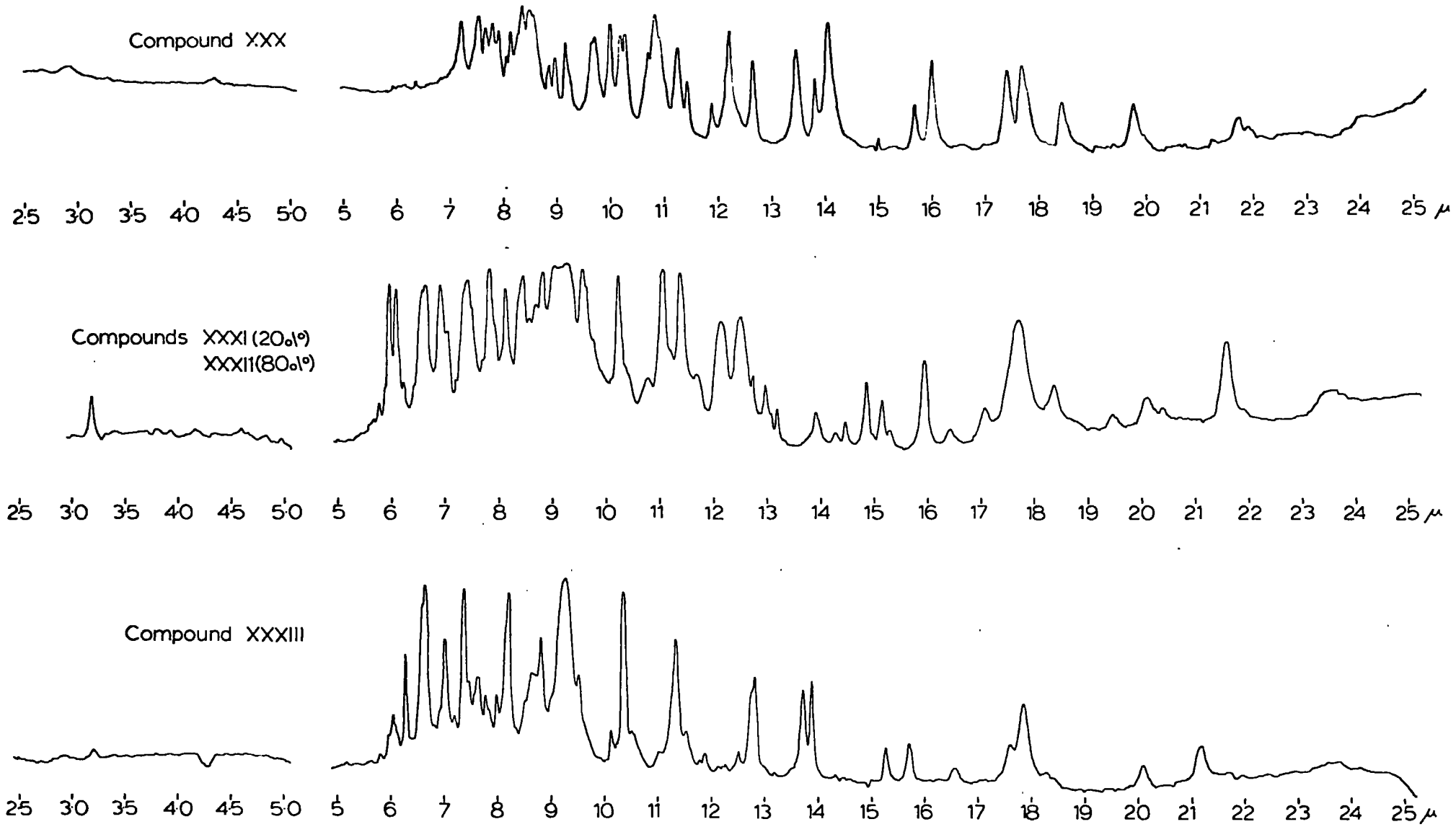
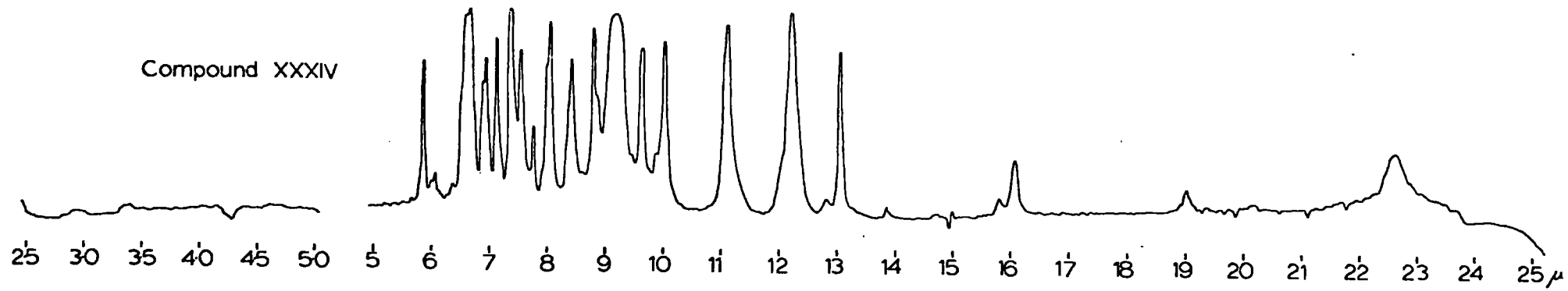

Compound XXIV
Compound XXV
Compound XXVI
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ

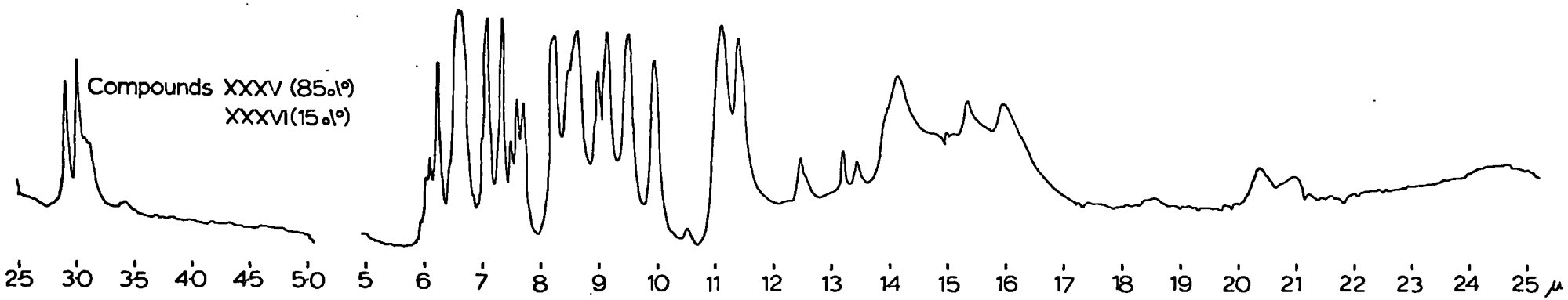

Compound XXVII
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ

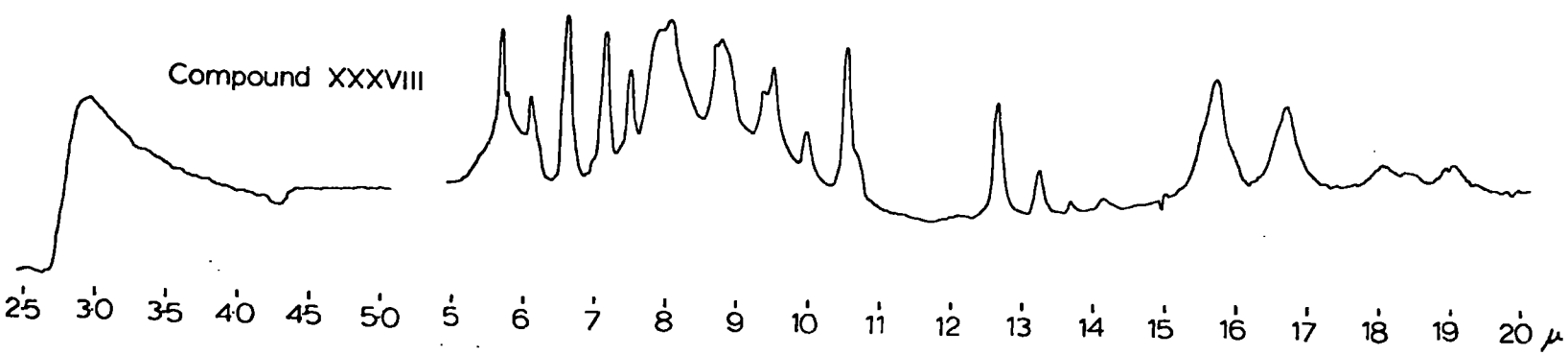

Compound XXVIII
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ

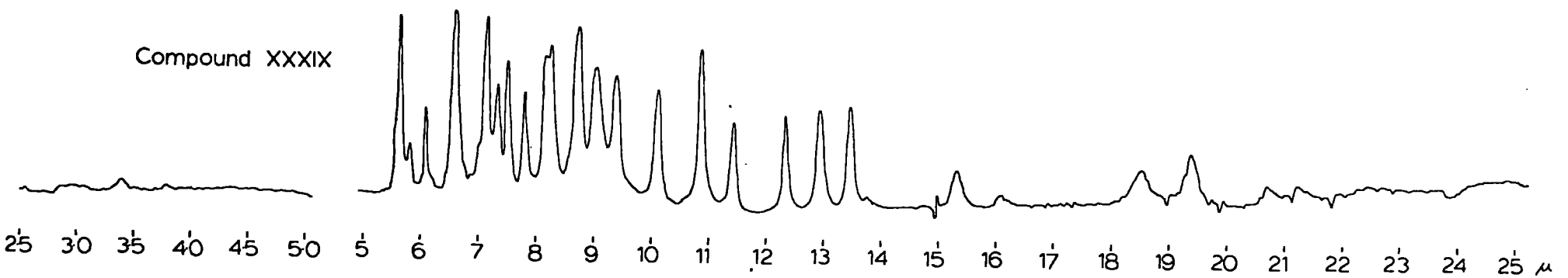

Compound XXIX
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ


Compound XXX
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ
Compounds XXXI (20%)
XXXII (80%)
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ
Compound XXXIII
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ


Compound XXXIV
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ


Compounds XXXV (85·1%)
XXXVI (15·1%)
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ


Compound XXXVIII
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 μ


Compound XXXIX
2·5 3·0 3·5 4·0 4·5 5·0 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 μ

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