Thermal and photochemical isomerization of heptafluorocyclohexadienes

Morland, John Beadling

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THERMAL AND PHOTOCHEMICAL ISOMERIZATION
OF HEPTAFLUOROCYCLOHEXADIENES

A thesis submitted for the degree of Master of Science
by
John Beadling Morland, C. Chem., M.R.I.C.
(Unattached)

UNIVERSITY OF DURHAM
1977

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SUMMARY

Thermal and Photochemical Isomerization of Heptafluorocyclohexadienes

In this work the starting materials, namely the heptafluorocyclohexadienes, were prepared by the dehydrofluorination of nonafluorocyclohexanes partially separated from the products of the fluorination of benzene using a cobalt fluoride fluid bed system.

Initial pyrolysis of the isomers of heptafluorocyclohexadienes indicated they were capable of interconversion and under more controlled conditions, using flow vacuum pyrolysis, the interconversion was quantified. That the mechanism for these thermal isomerizations involved catalysis by fluoride ion at a surface was discounted on the grounds that: vacuum pyrolysis of 1H-heptafluorocyclohexa-1,3-diene in the presence of sodium fluoride pellets gave a pattern of products which was both qualitatively and quantitatively different to a similar pyrolysis in the presence of silica wool, whereas pyrolysis of the same diene in a large bulb at a low pressure gave a similar pattern of products to that obtained from thermolysis in the presence of silica wool.

Photolysis of 1H-heptafluorocyclohexa-1,3-diene gave the expected 2,3,4,5,5,6,6-heptafluorobicyclo[2,2,0]hex-2-ene quantitatively. The reverse thermal reaction occurred at 350°C.
I would like to thank Dr. W.J. Feast for his encouragement and unfailing support throughout the supervision of this work and Professor W.K.R. Musgrave for his initial help and encouragement.

I am indebted to all the technical and laboratory staff for their constructive advice and assistance especially Mr. D. Hunter and Mr. R. Hart.
MEMORANDUM

The work of this thesis was carried out in the Chemistry Laboratories of the University of Durham between April 1973, and March 1977, on a part-time basis. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.
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<td>REFERENCES</td>
<td>89</td>
</tr>
</tbody>
</table>
Part I

General Background and Synthesis of Starting Materials
1. 1(a) Introduction

The first major study of fluorocarbons began at the end of the nineteenth century and owes much to Swarts, a Belgian Chemist, who was the major worker in this field. Fluorocarbon chemistry received its next significant stimulus in 1930 when Midgely and Henne discovered a commercial outlet for the chlorofluoromethanes and ethanes as refrigerants. The major step forward was made over the period 1939 - 1946 when it was recognised that compounds such as $\text{CF}_4$, $\text{C}_2\text{F}_6$, $\text{C}_4\text{F}_{10}$ were thermally stable and chemically inert, particularly towards reactions with $\text{UF}_6$. Intense work in developing suitable fluorinated lubricants, sealants and coatings for use on the $^{235}\text{UF}_6/^{238}\text{UF}_6$ diffusion separation plants resulted in a rapid expansion of fluorine chemistry. After the second World War the study of fluorine chemistry expanded and developed; intense activity in synthesis of functionalized fluorocarbons was followed by a study of the properties and applications of the new compounds which had become available. This activity continues to the present in industrial and academic laboratories on a worldwide basis.

1. 1(b) Comparison of Fluorine Compounds with their Hydrocarbon Analogues

Organofluoro compounds are usually prepared from their hydrocarbon counterparts by substituting some or all of the hydrogen atoms with fluorine, very few occur naturally. Highly fluorinated compounds are often much more thermally stable than their hydrocarbon analogues, just as easy to handle but their physiological effects are not so well understood. Since both $^1\text{H}$ and $^{19}\text{F}$ have a nuclear spin quantum number of $\frac{1}{2}$, n.m.r. techniques can be applied. However, as a result of significant long range $\text{F-F}$ and $\text{H-F}$ spin-spin interactions the spectrum of an organofluoro compound is often complex and consequently may be
difficult to interpret in detail, although the large chemical shifts observed can sometimes simplify the problem.

A Comparison of the Reactivity of Hydro- and Fluorocarbon Compounds

The electronegativity of fluorine and hydrogen are 4.0 and 2.1 respectively on the Pauling Scale, hence the electronic environment in organofluorocarbon compounds is very different to that of the corresponding hydrocarbon ones. This is illustrated very clearly when one compares the type of reagent which attacks both unsaturated and aromatic hydrocarbon and fluorocarbon compounds. Typical reactions are summarized in Figure 1.

![Chemical reactions](image)

Figure 1
The hydrocarbon analogue is susceptible to attack by electrophilic reagents leading to an intermediate carbonium ion, whereas an organofluoro compound is susceptible to nucleophiles and yields carbanion intermediates. The electronic effects of fluorine provide us with a dichotomy of behaviour. Being a highly electronegative atom fluorine extensively polarises any carbon-fluorine bond, this phenomenon being referred to as the sigma inductive effect (-I_σ). Thus, where a single fluorine is attached to a carbon framework a drift of electron density towards fluorine, through the σ bond framework is predicted, and this is expected to polarize electrons associated with the carbon framework. The effect is illustrated below in Figure 2.

\[ \sigma^+ \quad \sigma^- \]

Saturated System

\[ \sigma^+ \quad \sigma^- \]

Unsaturated System

\[ \sigma^+ \quad \sigma^- \]

Figure 2

However, there is a further factor to consider in relation to the effect of fluorine attached to an unsaturated system in that there are electrons in the p-atomic orbitals on fluorine with the appropriate symmetry and position in space to interact with the π molecular orbitals on the carbon framework (i.e., a mesomeric effect). However a strong interaction requires that not only must the symmetry and spatial match be good but also the energies, this latter requirement is not fulfilled in this case since the electrons on fluorine are much more tightly bound than the π electrons on the carbon framework.
Nevertheless, since the p-atomic orbitals on fluorine and the molecular orbitals on the carbon framework occupy the same element of space, there is a repulsive interaction resulting in a polarisation in the opposite direction to that predicted by the $-\text{I}_\sigma$, known as the $\Pi$inductive effect ($+\text{I}_{\Pi}$), as illustrated in Figure 3. In practice this means that the presence of fluorine in a compound tends to destabilize carbonium ions by the $-\text{I}_\sigma$ effect but stabilize them by the $+\text{I}_{\Pi}$ effect. The converse will be true for carbanions and both effects are shown in Figure 4.
The experimental evidence indicates that where the fluorine is directly attached to the charged centre the $+I_{\pi}$ effect is more predominant than that of the $-I_{\sigma}$ effect.

**Nomenclature**

In the naming of highly fluorinated compounds essentially two systems are used. In the first, the number of fluorine atoms is shown in the name and the positions are indicated by numerals or Greek letters, thus for example:

- $\text{CF}_3\text{COOH}$  
  Trifluoroethanoic acid
- $\text{CH}_2\text{OH}$
- $\text{(CF}_2\text{)}_2$
- $\text{CH}_2\text{OH}$  
  $2,2,3,3$ - tetrafluorobutan - $1,4$-diol

When the number of hydrogen atoms in a molecule is four or less and the hydrogen to halogen ratio is equal to or less than 1:3, then the position of the hydrogen atom is indicated thus, for example:

$$\begin{align*}
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{H}
\end{align*}$$

$1H$ - heptafluorocyclohexa-$1,3$-diene

Geometrical isomers can be indicated by means of an oblique line, thus

$$\begin{align*}
\text{H} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{H}
\end{align*}$$

$1H,4H/2H$ - nonafluorocyclohexane
In the second system the prefix 'perfluoro' is used before the name of the corresponding hydrocarbon analogue, for example:

\[
\text{perfluorobenzene} \quad \text{perfluorocyclopentene}
\]

Another system has been proposed which revises the nomenclature for highly fluorinated organic compounds and which has been adopted by the American Chemical Society. The new system replaces 'perfluoro' with 'F', and replaces 'H' with 'hydryl', a collective prefix which can be applied in conjunction with 'F' to functional compounds. For example:

\[
\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{F} = \text{CP}_2 \quad \text{F-1-Heptene}
\]

\[
\text{F-Benzene} \quad \text{F-Cyclopentene}
\]

\[
\text{1- Hydryl-F- cyclohexa-1,3-diene}
\]

I. 2(a) Review of Synthetic Methods for the Preparation of Fluorinated Cyclohexadienes

The basic material for the production of the compounds is benzene. Fluorination is effected by passing its vapour over an agitated bed of cobalt trifluoride at temperatures in the region of 100-200°C and collecting the resulting complex mixture in a cooled trap, see Figure 5.
Figure 5

From this mixture the twenty-two components listed below have been separated and identified.

Products of the Cobaltic Fluoride Fluorination of Benzene

\[
\begin{align*}
\text{I} & \quad 1H/2H- \\
\text{II} & \quad 1H/3H- \\
\text{III} & \quad 1H/4H \\
\text{IV} & \quad 1H, 2H-/ \\
\text{V} & \quad 1H, 3H-/ \\
\text{VI} & \quad 1H, 3H-/ \\
\text{VII} & \quad 1H, 4H-/ \\
\end{align*}
\]
The composition of the mixture depends upon conditions, but generally the products which are present in the greatest amounts are: \( \text{II, V, VII, VIII, IX, X, XI, XIII, XVI} \), whilst, \( \text{IV, VI, XII,} \) and \( \text{(XVII \text{ - XXII})} \) were present in only small amounts.

For separation diethyl ether and benzene are added to the mixture.
which is then fractionally distilled, many fractions being obtained as azeotropes: in the absence of added solvents the fractional distillation is difficult since the fluorohydrocyclohexanes have small liquid ranges and frequently solidify to transparent glasses. The fractions obtained are listed in Table 1, below:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>b.p. °C</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27</td>
<td>C_{6}F_{12}/Et,O azeotrope</td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>Et,O</td>
</tr>
<tr>
<td>3</td>
<td>60-61</td>
<td>C_{6}F_{11}H/C_{6}H azeotrope</td>
</tr>
<tr>
<td>4</td>
<td>approx. 67</td>
<td>C_{6}H_{6} azeotrope</td>
</tr>
<tr>
<td>5</td>
<td>73</td>
<td>C_{6}F_{11}/C_{6}F_{11} azeotrope</td>
</tr>
</tbody>
</table>

Table 1

The higher boiling materials are not easily obtained as pure compounds or simple mixtures by fractional distillation; however, the next fraction (Number 6 boiling range 80-90°C) is rich in 1H,2H,4H-nonafluorocyclohexanes

This fluorohydrocarbon mixture is isolated from its solution in benzene by sulphonating the benzene, using a mixture of concentrated sulphuric acid and oleum, the fluorocarbon being immiscible with the resulting
sulphuric, benzene sulphonie acid mixture. After separation the fluorohydrocarbon mixture is well washed with water.

**Dehydrofluorination of Polyfluorocyclohexanes**

The major factors which appear to determine the products, rates and stereochemistry of dehydrofluorination reactions of fluorohydrocyclohexanes are summarized below:

(i) The relative acidities of the hydrogens is the first factor determining the ease with which they will be removed by the base. The relative acidities are indicated below as a function of their environment.

(ii) Dehydrofluorination by a trans-coplanar $E_2$ process occurs where this is possible; thus cyclohexanes which can easily assume a conformation having H and F in a trans-diaxial disposition will be readily dehydrofluorinated compared with electronically equivalent cases where this is not possible.

Thus the chair forms of 1H,2H/-decafluorocyclohexane...
as illustrated in Figure 6, having H and F in a trans-diaxial arrangement dehydrofluorinate much more easily than the chair forms of 1H/2H-decafluorocyclohexane, which do not contain H and F in a trans-diaxial disposition as shown in Figure 7.

(iii) In the elimination process, loss of fluoride ion from a difluoromethylene group (-CF₂⁻) appears to be more difficult than from a fluoromethylene group (-CHF⁻) reflecting the increased stability of fluorine in the former situation.

(iv) Cis-eliminations do proceed and may be faster than possible trans-eliminations in electronically favourable cases, that is, where the proton of the eliminated hydrogen fluoride is sufficiently acidic. In the light of points (i) to (iv) it is possible to rationalise the products formed by the dehydrofluorination of deca- and nonafluorocyclohexanes as listed in Table II.
<table>
<thead>
<tr>
<th>Decafluoro cyclohexanes</th>
<th>Monoene</th>
<th>Dienes</th>
<th>References</th>
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<tr>
<td><img src="image1" alt="Hexagon" /></td>
<td><img src="image2" alt="Hexagon with F" /></td>
<td><img src="image3" alt=" Pentagon" /></td>
<td>4</td>
</tr>
<tr>
<td><img src="image4" alt="Hexagon" /></td>
<td><img src="image5" alt="Hexagon with F" /></td>
<td><img src="image6" alt=" Pentagon" /></td>
<td>4</td>
</tr>
<tr>
<td><img src="image7" alt="Hexagon" /></td>
<td><img src="image8" alt="Hexagon with F" /></td>
<td><img src="image9" alt=" Pentagon" /></td>
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<tr>
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<td><img src="image11" alt="Hexagon with F" /></td>
<td><img src="image12" alt=" Pentagon" /></td>
<td>5</td>
</tr>
</tbody>
</table>

Table II
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<th>References</th>
<th>Other Products</th>
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</thead>
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<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>1,4</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Diene</td>
<td></td>
</tr>
<tr>
<td>1,4</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoene</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonfluoro- cyclohexane</td>
<td></td>
</tr>
</tbody>
</table>

Table II cont.
I. 2(b) Preparation of 1H- and 2H- Heptafluorocyclohexa-1,3-diene and 1H- Heptafluorocyclohexa-1,4-diene

From the preceding section it is clear that two possible approaches exist for the production of these isomers. One approach would involve separation of the crude mixture of nonafluorocyclohexanes by preparative g.l.c. to produce a more refined mixture containing only the nonafluorocyclohexane isomers. These, on controlled dehydrofluorination should yield a mixture of the isomers separable by preparative g.l.c. Alternatively dehydrofluorination of the crude mixture of di- and trihydropolyfluorocyclohexane from fraction 6 under controlled conditions followed by separation using preparative g.l.c. techniques, would also give the monohydroheptafluorocyclohexadienes.

The first method was attempted and met with only minimal success, this being primarily due to the fact that nonafluorocyclohexanes have long retention times and there were practical difficulties in detecting their emergence from the column with the equipment available. It was decided to dehydrofluorinate crude nonafluorocyclohexane mixture first and then attempt a separation since the dienes have much shorter retention times than the starting materials and thus should be detected more easily when they emerged from the column.

Dehydrofluorination of the mixture was carried out using a variety of techniques (see experimental), the most successful involved stirring it vigorously with an ice cooled mixture of potassium hydroxide and water in a 1:1:1 ratio by weight. When the reaction was quiescent the stirred mixture was heated, to obtain gentle reflux, for approximately three hours and periodically samples of the organic layer were removed for g.l.c. analysis. Under these controlled conditions it
was found possible to obtain the optimum yield of the diene isomers in the mixture and avoid excessive degradation. Separation of the dehydrofluorinated mixture by preparative g.l.c. although successful, proved to be very time consuming and not very productive since only about one third of the mixture consisted of the monohydroheptafluorocyclohexadienes. However by fractionally distilling the dehydrofluorinated mixture it was found possible to concentrate to the extent of 75% the required isomers in the fraction boiling over the range 71 - 78°C. This mixture when separated by preparative g.l.c. provided greater amounts of the required isomers in a shorter time. The perfluorocyclohexadienes and the monohydroheptafluorocyclohexadienes were identified by comparing their infrared, ultraviolet and mass spectrometric characteristics with known samples. The order of the g.l.c. retention times of the products agreed as expected with the results previously reported by Tatlow et.al.⁵,⁶ and are shown below in Figure 8.

Increasing order of retention time

![Figure 8](image-url)
PART I

EXPERIMENTAL
1. Source and Separation of the Fluorocarbon Mixture

The mixture of fluorocyclohexanes obtained from fluorination of benzene over cobaltic fluoride was purchased from the Imperial Smelting Corporation, Avonmouth. After addition of diethyl ether and benzene the mixture was fractionally distilled (122 cm x 2.5 cm vacuum jacketed column, packed with Dixon gauzes 0.15 cm x 0.15 cm), following the established procedures for this fractionation to yield a fraction (b.r. 80 - 90°C) known to contain primarily 1H,2H,4H-nonafluorocyclohexanes together with some decafluorocyclohexanes, benzene and minor amounts of other fluorohydrocarbons. The benzene was converted to benzene sulphonic acid by sulphonation at room temperature with a mixture of concentrated sulphuric acid and oleum, and the residual fluorohydrocarbon mixture was washed with water.

3(b) Dehydrofluorination of the Fluorohydrocarbon Mixture

(i) Using Molten Potassium Hydroxide

This experiment was carried out behind a safety screen in a fumecupboard using the apparatus shown in Figure 9.

Potassium hydroxide pellets (30g, B.D.H. Laboratory reagent grade) were placed in the flask and the apparatus purged with dry nitrogen while the oil bath was heated to 190°C and maintained at that temperature for the remainder of the experiment. When the potassium hydroxide was a mobile liquid the fluorohydrocarbon (29.2g) was added dropwise with caution. There was an immediate and violent reaction, the volatile product was trapped from the nitrogen stream in a glass trap cooled in liquid air. The material in the trap separated into two layers on warming to room temperature; the upper aqueous layer was discarded...
leaving a fluorohydrocarbon mixture (21.1 g). Analytical g.l.c. of the product showed it to be predominantly starting material with only limited amounts of the required dienes. This procedure was not pursued further, there was no attempt to optimise conversions.

(ii) Using Aqueous Potassium Hydroxide

The fluorohydrocyclohexane mixture (850 g) was slowly (2 hours) added to a solution of potassium hydroxide (500 g) in water (500 g) in a roundbottomed flask (2 litre) carrying an efficient reflux condenser (122 cm x 2.5 cm, water cooled), mechanical stirrer and dropping funnel. The flask and its contents were maintained at 0° C in an ice bath during the addition, on completion of the addition the flask was allowed to warm slowly to room temperature and then the flask was heated from an isomantle until gentle refluxing was maintained. During this heating process the mixture was continuously and efficiently stirred. The progress of the dehydrofluorination was monitored by analytical g.l.c. on samples of the organic layer periodically removed from the reaction flask. After refluxing for 3 hours the mixture was cooled to 0° C, the organic layer was separated, washed with water three times, dried \( \text{MgSO}_4 \) to give a fluorohydrocarbon mixture relatively rich in monohydroheptafluorocyclohexadienes (564 g).

3(c) Separation of the Dehydrofluorinated Mixture

The mixture of fluorohydrocyclohexadienes, hexenes and hexanes obtained above was fractionally distilled (air jacketed column, 50 cm x 1.8 cm, glass helices) to give: fraction I (111.2 g), b.r. 58-71°; fraction II (97.7 g), b.r. 71-78°. Analytical g.l.c. and comparison of retention volumes with those of authentic samples showed that both
fractions contained perfluorocyclohexa-1,3-diene, perfluorocyclohexa-1,4-diene, 1H-heptafluorocyclohexa-1,4-diene, 1H-heptafluorocyclohexa-1,3-diene and 2H-heptafluorocyclohexa-1,3-diene. Fraction I contained a much greater percentage of the perfluorocyclohexa-1,3- and 1,4-dienes than fraction II which also contained a small amount of longer retained material. Samples of fractions I and II were separated by preparative g.l.c. (Column A, ca. 90°C); the materials obtained were identified by comparison of their infrared spectra and g.l.c. retention volumes with those of authentic samples, typical results are shown in Tables III and IV.

Impure components were rechromatographed, and in this way pure samples of 1H-heptafluorocyclohexa-1,3-diene, 2H-heptafluorocyclohexa-1,3-diene and 1H-heptafluorocyclohexa-1,4 diene were obtained. Each compound was identified by comparison of its i.r., u.v., and mass spectra with those of authentic samples, there was complete agreement in each case. Each compound gave a single sharp peak on analytical g.l.c. and was pure within the limits of detection of spectroscopic and analytical techniques used (>99%).
The Separation of Fraction I by Preparative g.l.c.

Weight of mixture taken 64.5g
Total Weight of fractions recovered 50.7g, 78.6%

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight (g)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.7</td>
<td>( \text{F} : \text{F} ), 7:3 w/w</td>
</tr>
<tr>
<td>2</td>
<td>11.1</td>
<td>( \text{F} )</td>
</tr>
<tr>
<td>3</td>
<td>6.5</td>
<td>( \text{F}^\text{H} )</td>
</tr>
<tr>
<td>4</td>
<td>4.9</td>
<td>( \text{F}^\text{H} )</td>
</tr>
<tr>
<td>5</td>
<td>1.4</td>
<td>( \text{F}^\text{H} : \text{F}^\text{H} ), 1:9 w/w</td>
</tr>
<tr>
<td>6</td>
<td>2.8</td>
<td>( \text{H} )</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>( \text{F}^\text{H} : \text{F}^\text{H} ), 3:2 w/w</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
<td>( \text{F}^\text{H} )</td>
</tr>
</tbody>
</table>

*Table III*
The Separation of Fraction II by Preparative g.l.c.

Weight of mixture taken 59.4g
Total weight of fractions collected 48.5g, 81.7%

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight (g)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>F : [F] , 1:1 w/w</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
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<tr>
<td>3</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>9.3</td>
<td>[F]^H : [F]^H , 2:3 w/w</td>
</tr>
<tr>
<td>5</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3.5</td>
<td>[F]^H : [F]^H , 5:4 w/w</td>
</tr>
<tr>
<td>8</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>3.5</td>
<td>Longer retained material</td>
</tr>
</tbody>
</table>

Table IV
Part II

The Thermal and Photochemical Isomerizations of Heptafluorocyclohexadienes
II. 1 Introduction

Isomerization reactions have attracted the attention of chemists for many years and have been studied from various points of view. The first stage in studying isomerizations is, self evidently, that of establishing the structures of the interconverted isomers and the reaction conditions under which such isomerizations will occur. Subsequently kinetic and thermodynamic investigations have been undertaken to establish the rates of these processes, positions of equilibria and relative stabilities of the various isomers. The detailed mechanisms of such processes have attracted theoretical chemists, and particularly during the last ten to fifteen years, the interaction between theoreticians, kineticists and synthetic organic chemists has been very fruitful, both in rationalizing the large volume of data in the literature and in predicting the outcome of proposed reactions. It has been known for some years that highly fluorinated systems will undergo a variety of isomerization reactions, and this section of the thesis reports on an attempt to extend our understanding of the isomerization of the fluorinated cyclohexadiene system. Before discussing the work carried out, some of the recent developments in the theoretical rationalization of isomerization reactions are briefly reviewed. The published data on the isomerization of fluorinated polyenes is also considered in order to set the work in context.

II. 2. The Conservation of Orbital Symmetry

The concept that the stereochemical outcome of concerted isomerization processes could be rationalized by consideration of the symmetry of the orbitals undergoing change during the reaction was first put forward by Woodward and Hoffman in 1965. Its utility as a concept,
for rationalizing the large body of data already available in the literature, was rapidly seized upon and their approach was developed and applied widely. Although this topic is now a well established part of chemistry the nomenclature and generalized conclusions relating to the two areas in which we are particularly concerned, namely electrocyclic ring closures and sigmatropic migrations are briefly reviewed below.

II 2(a) The Nomenclature and Generalized Rules for Sigmatropic Migration

A number of processes have been observed in which isomerization proceeds via the migration of a sigma bond flanked by one or more π-electron systems, to a new position within the molecule, by an uncatalysed intramolecular process (Figure 10).

![Figure 10](image)

If the migrating centre Z is detached from $C_1$ and migrates to $C_j$ of the carbon framework, such that bonding is through the same atomic centre within Z, then the process is one of order $[1, j]$. Thus in the above example the order is $[1, 5]$, i.e., a 1,5 shift. Should the group Z also contain a π-system its point of detachment from $C_1$ in the carbon framework may not be the same as its point of reattachment at $C_j$ in the framework. In this case, if the centre attached is the $i$th carbon in Z, (where the numbering occurs from the original attachment point of Z to $C_1$), then the
sigmatropic change is of order $[i,j]$.

Figure 11

In Figure 11 the order is $[3,5]$, i.e., a $[3,5]$ shift.

When a shift occurs the migrating group can attach itself to the same face of the carbon framework - SUPRAFACIAL SHIFT, or the opposite face - ANTARAFACIAL SHIFT. The same nomenclature is used for the migrating group. This is illustrated diagrammatically in Figure 12.

Figure 12

Where $\square$ is $Z$ the migrating group and $S$ and $A$ represent suprafacial and antarafacial shifts respectively.

The orbital symmetry requirements may be deduced by assuming, that in a sigmatropic migration, interaction between the $Z$ radical and the framework radical takes place. For thermochemical processes the most important bonding interactions will be between the highest occupied
molecular orbital HOMO of Z and the framework radical, since these contain the unpaired electrons. (This is referred to as The Frontier Orbital Approach). This is the simplest theoretical approach, in the rigorous derivation of the symmetry rules all orbitals which change during the reaction are included in the analysis; both approaches lead to the same conclusions. For linear polyenes the framework radical will always possess an odd number of carbon atoms in conjugation and is therefore an odd-alternant radical. The HOMO of odd-alternants is non-bonding, the wave function being characterized by nodes at even-numbered carbon nuclei. This is illustrated in the π molecular orbital diagram for the pentadienyl system (Figure 13).

The First Three π - Molecular Orbitals of Pentadienyl

\[ \Psi_3 \quad - \quad - \quad + \quad + \quad H.O.M.O. \]

\[ \Psi_2 \quad - \quad - \quad - \quad + \quad + \quad Figure 13 \]

\[ \Psi_1 \quad - \quad - \quad - \quad - \quad - \quad + \quad + \quad + \quad + \quad + \quad + \quad + \]

The relationship between the signs of the π - molecular orbital at the termini of the HOMO of polyene radicals may be summarized thus:

\[ n-2 \]
For the case where \( n = 5 \) or 9, the signs are in phase, and for \( n = 3 \) or 7 the signs are out of phase. Thus a bonding interaction with one part filled s-orbital will involve suprafacial overlap for \( n = 5 \) or 9 and antarafacial overlap for \( n = 3 \) or 7, as illustrated in Figure 14 for the \( n = 3 \) and \( n = 5 \) cases.

![Figure 14](image)

The corresponding photochemically allowed sigmatropic migrations would be those shown in (Figure 15), in this case the interaction between the migrating radical and the lowest unoccupied molecular orbital (LUMO) of the framework radical is depicted.

![Figure 15](image)

The Woodward-Hoffmann rules for concerted sigmatropic migrations of order \([1,3]\) and \([i,j]\) are summarized over:
<table>
<thead>
<tr>
<th></th>
<th>[1,3]</th>
<th>Thermal</th>
<th>Photochemical</th>
<th>[i,3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4n</td>
<td>[1,3]</td>
<td>S-A</td>
<td>S-S</td>
<td>[3,5]</td>
</tr>
<tr>
<td></td>
<td>[1,7] etc.</td>
<td>A-S</td>
<td>A-S</td>
<td>[5,7]</td>
</tr>
<tr>
<td>4n + 2</td>
<td>[1,5]</td>
<td>S-S</td>
<td>S-A</td>
<td>[3,3]</td>
</tr>
<tr>
<td></td>
<td>[1,9]</td>
<td>A-A</td>
<td>A-S</td>
<td>[5,5]</td>
</tr>
</tbody>
</table>

Where n-No. of \(\pi\) electrons
II 2(b) The Nomenclature and Generalized Rules for Electrocyclic Ring Closure and Opening

Electrocyclic reactions are those in which a single bond is formed between the termini of a linear system containing $k$ electrons and the reverse processes (Figure 16).

![Figure 16](image)

This change may occur in either a conrotatory or a disrotatory fashion as shown in (Figure 17).

![Figure 17](image)

Not all of these modes of ring opening or closing will be distinguishable in a particular case. If A,B,C and D are identical, for example, there is only one possible product. If A,B, C and D are all different groups
there are four possible products. Basically, the theory distinguishes between disrotatory and conrotatory modes of ring opening and closing, it does not distinguish between the variations of a particular mode although one variation may be preferred on other grounds such as steric effects. The transition state in the conrotatory mode is characterized by a plane of symmetry while that of the disrotatory mode by a twofold axis of symmetry.

The predicted mode of electrocyclic ring opening or closure depends on the number of $\pi$ electrons in the open polyene. A conjugated linear polyene, whether neutral, positive or negatively charged, with $4n\pi$ electrons, has a HOMO with a twofold axis of symmetry in which the signs of the terminal lobes are out of phase (Figure 18).

Therefore the predicted thermal cyclization must take place by a conrotatory ring closure (Figure 19) in order to obtain a bonding interaction.

![Butadiene](image1)
![Allyl anion](image2)
![Pentadienyl cation](image3)

**Figure 18**

**Figure 19**
The stereochemical course of the photochemical ring closure of these systems can be regarded in this Frontier Orbital Approach, as being controlled by the symmetry of the lowest unoccupied molecular orbital (LUMO) of the framework radical. Since the symmetries of the LUMO and HOMO are different, the stereochemical course of the photochemically promoted ring closure will be different to the thermal one, in this case a disrotatory ring closure is allowed (Figure 20).

![Figure 20](image)

For \((4n + 2)\) \(\pi\) electron systems, the termini lobes in the HOMO are in phase (Figure 21). They are also characterized by having a plane of symmetry.

![Figure 21](image)
Predicted ring closure or ring opening in the disrotatory mode is thermally allowed, and by analogy with the earlier $4n \pi$ electron examples conrotatory ring closure will be observed for the photochemical process. Again it is worth mentioning that the use of the Frontier Orbital Approach is the simplest theoretical treatment, however a more rigorous derivation of the symmetry rules involving correlation diagrams gives the same answers. The above predictions may be summarized as follows:
<table>
<thead>
<tr>
<th>Number of electrons involved in ring closure</th>
<th>Thermal ring opening or closure</th>
<th>Photochemical ring opening or closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4n</td>
<td>Allowed</td>
<td>Disallowed</td>
</tr>
<tr>
<td>4n + 2</td>
<td>Disallowed</td>
<td>Allowed</td>
</tr>
</tbody>
</table>
II 3. The Dewar-Zimmermann Approach

Dewar and Zimmermann considered that concerted reactions occur via aromatic transition states. They related the facility of a pericyclic reaction to the stability of the cyclic transition state by analogy with cyclic polyenes. They then described the cyclic transition state as being aromatic, non-aromatic or antiaromatic, according to whether it was more stable than, as stable as, or less stable than the open chain analogue. The conclusions of this analysis are broadly in line with those of the Woodward-Hoffmann approach. Reviewed below are the nomenclature and general rules for the application of the Dewar-Zimmermann approach.

II 3(a) Nomenclature and Generalized Rules for the Dewar-Zimmermann Approach

The transition states in a pericyclic reaction can possess two possible arrays known as Hückel or Möbius arrays. In a Hückel type the number of sign discontinuities in the p-orbital array is zero or even, whereas in that of the Möbius it is odd. This is illustrated in Figure 22 for benzene and the transition state for the conrotatory ring closure of but-1,3-diene.

![Hückel and Möbius arrays](image)

**Hückel**  
No. of discontinuities 0

**Möbius**  
No. of discontinuities 1

Figure 22
The transition state is predicted to be aromatic when it either possesses \((4n + 2) \pi\) electrons in a Hückel array or \(4n \pi\) electrons in a Möbius array. In both cases the transition state is stabilized relative to its acyclic counterparts. The general rule for thermal pericyclic reactions can be stated as follows: Thermal pericyclic reactions take place via aromatic transition states. Predictions for thermal and photochemical pericyclic reactions are summarized overleaf.

The procedure for using it is as follows:

1. Draw a transition state as a series of overlapping s- and p-orbitals, putting in + and - signs so that they minimize the number of sign changes in the participating orbitals.

2. Count the number of sign inversions in the cyclic array and the number of electrons involved. If the cycle includes both lobes of a single p-orbital the necessary sign inversion across these two lobes is not counted.

3. Classify the transition state as being of the Hückel or Möbius type. From the number of electrons determine whether or not the transition state is aromatic.

At this stage it would seem advantageous to illustrate the use of this approach by examples. Consider the 1,5- sigmatropic migration of hydrogen in pent-1,3-diene, Figure 23.

![Figure 23](image-url)
<table>
<thead>
<tr>
<th>Number of ( \pi ) electrons in the transition state</th>
<th>THERMAL</th>
<th>PHOTOCHEMICAL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hückel</td>
<td>Möbius</td>
</tr>
<tr>
<td>4n</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>(4n + 2)</td>
<td>YES</td>
<td>NO</td>
</tr>
</tbody>
</table>

When \( n \) is 0,1,2 etc., and NO and YES refer to FORBIDDEN and ALLOWED processes respectively.
In the transition state (Figure 24) the terminal carbon atoms change hybridization from $sp^2$ to $sp^3$ and vice-versa.

The transition state contains 6 $\pi$-electrons and since the number of sign inversions is zero it is of the Hückel type. The theory predicts the sigmatropic migration should be thermally allowed but photochemically forbidden.

In the case of the electrocyclic ring closure of but-1,3-diene to cyclobutene, as shown in Figure 25, the transition state would show the terminal carbon atoms changing hybridization from $sp^2$ to $sp^3$ (Figure 26).

For a disrotatory ring closure the number of sign inversions in the transition state is zero and is of the Hückel type involving $4\pi$ electrons. The theory predicts this mode of ring closure should be thermally for-
bidden but photochemically allowed.

II 4. Limitations

It must be borne in mind that these are rationalizations applicable only to concerted processes. If steric or thermodynamic factors are favourable the theoretically predicted "allowed" pathway would be expected to be followed experimentally. However, a theoretically predicted "forbidden" pathway may actually be followed experimentally albeit with a somewhat higher activation energy than the analogous "allowed" process or by a nonconcerted mechanism. It is interesting to note that Woodward and Hoffmann suggest that the order of preference of transition states is:

\[
\text{ALLOWED} \succ \text{DIRADICAL} \succ \text{FORBIDDEN}
\]

however, Berson et al. claim this would mean orbitals at reactive sites in the diradical would overlap as little as possible and hence such reactions would be expected to result in stereorandomisation. They argue there is an underlying bias towards the following order of preference of transition states:

\[
\text{ALLOWED} \succ \text{FORBIDDEN} \succ \text{DIRADICAL}
\]

Consider a thermal suprafacial \([1,3]\) sigmatropic rearrangement of carbon, there are two possible transition states as shown:

\[
\begin{align*}
2s + 2a & \text{ Allowed} \\
2s + 2s & \text{ Forbidden}
\end{align*}
\]
The correlation diagrams for these two transition states and the

diradical are shown below in Figures 27 (a), 27 (b) and 27 (c).

\[ E = 4 \sqrt{2} \beta_0 \]

\[ E = 4 \beta_0 \]

\[ E = 2 \sqrt{2} \beta_0 \]

\( \psi_1^S \)

\( \psi_2^A \)

\( \psi_3^S \)

\( \psi_4^p \)

\( \psi_{\text{non-interacting}} \)

\( \text{diradical} \)

\( 2s + 2s \)

\( 2s + 2s \)

\( 2s + 2s \)

\( \text{Allowed} \)

\( \text{Forbidden} \)

\( \text{(a)} \)

\( \text{(b)} \)

\( \text{(c)} \)

Figure 27

Figure 27(b) illustrates the appreciable stabilization of the forbidden

state by interaction between a carbon p-orbital and a subjacent bonding

allyl orbital of the same symmetry. Two of the four electrons involved

can be accommodated in a more stable orbital than in the separate frag­

ments, see Figure 27(c). In this case there is not much difference

energetically between the allowed and forbidden processes. By restricting

the ability of the carbon to migrate antarafacially in selected compounds

they showed that the degree of retention and inversion in the products

could only be explained by assuming two concerted processes were op­

erating simultaneously, the allowed and forbidden. These alternatives

only assume importance when steric factors inhibit the allowed route.
II 5. Illustrative Examples of Sigmatropic Migrations and Their Rationalization

Thermal $[1,5]$ sigmatropic migration in cyclic systems has been observed in a wide variety of compounds. Sigmatropic $[1,3]$ and $[1,7]$ hydrogen migrations have not been observed in small or medium sized rings owing to the unattainable geometry requirements for antarafacial migration but $[1,3]$ migrations of carbon moieties are not uncommon.

In five membered ring dienes conformational effects are minimal but as the ring size increases the migrating group can take up two possible positions relative to the π electron system. Thus for example, in 1,3-cyclohexadiene and 1,3,5-cycloheptatriene, a migrating group can occupy either pseudo-axial or pseudo-equatorial positions. Kloosterziel et al. $^{19,20}$ first postulated that a group occupying a pseudo-axial position is more liable to participate in a concerted cyclic transition state than one occupying a pseudo-equatorial position. Spangler $^{21}$ has recently reported that migration of hydrogen from C$_5$ of a 5-substituted 1,3-cyclohexadiene may also be conformation dependant. In the range 300–350°C in a fast flow system, 5-tert-butyl 1,3-cyclohexadiene rearranges faster than does the corresponding 5-methyl compound to yield 1-alkyl-1,3-cyclohexadiene, as shown in Figure 28.

\[
\begin{align*}
\text{H} & \quad \text{R} \\
5 & \quad 4 \\
\text{R} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{R} \\
5 & \quad 4 \\
\text{R} & \quad \text{H} \\
\end{align*}
\]

Figure 28

These results indicate that ground state conformation may influence the relative migration rates, and migrating aptitudes of groups.

Isomerizations involving $[1,5]$ sigmatropic hydrogen migrations have been extensively studied. The suprafacial nature of the migration has been
demonstrated conclusively by Roth et al., who established that thermal migration in 1,3-cyclopentadiene and indene was a concerted \( [1,5] \) process; they used n.m.r. to follow the isomerization of appropriately deuterated compounds, for example, the deuteroidene shown in Figure 29.

![Figure 29](image)

Kinetic data for \( [1,5] \) hydrogen migrations in six, seven and eight membered cyclic dienes is sparse. Spangler reported that \( [1,5] \) hydrogen migration in the 1,3-cyclopentadiene systems was fairly slow below 300°C, but fast and reversible above 325°C. Van der Burg, Marvell et al., have all confirmed that \( [1,5] \) hydrogen migration is much slower in 1,3-cyclohexadiene systems than in those involving 1,3-cyclopentadiene. Activation energies for hydrogen migration in the 1,3-cyclohexadiene systems are about 13-15 K cal/mol higher than in the five-membered ring systems.

Looker first reported a \( [1,5] \) halogen migration in the dibenzotropylidene system where he found the gem-dichloro derivatives shown in Figure 30, isomerized to the 5,11-dichloro isomer at 180 to 200°C, the reaction being rationalized in terms of successive \( [1,5] \) chlorine and hydrogen shifts.
There have also been recent reports of both $[1,3]$ and $[1,5]$ chlorine migrations. Roedig et al. rationalized the observed rapid isomerizations of a tetrachloropentadienal in boiling carbon tetrachloride (Figure 31), in terms of a $[1,5]$ chlorine migration in an intermediate oxacyclohexa-1,3-diene as shown in Figure 31.
Strohmeier and Eden have interpreted the 3-chloro-1-butene to 1-chloro-2-butene isomerization in dioxan at 75°C as a \([1,3]\) sigmatropic chlorine migration, as shown in Figure 32.

**Figure 32**

II 6. Illustrative Examples of Electrocyclic Ring Opening and Closure

These intramolecular cycloadditions provided the initial stimuli for the study of molecular orbital symmetry and concerted reactions by Woodward and Hoffmann. Since 1965 application of their ideas have rationalized most of the numerous observed electrocyclic reactions, some illustrative examples relating to 1,3-hexadiene systems are presented in this section.

Irradiation of an ethereal solution of cyclohexa-1,3-diene in a quartz tube at 20°C gives primarily the linear triene presumably via the allowed conrotatory process as shown in Figure 33.

**Figure 33**

Photochemical conrotatory ring openings are illustrated in Figures 34 and 35 in which the stereochemical details are established.
In the example depicted in Figure 35 the photoisomer is unstable at room temperature and reverts to the more stable trans fused isomer by the allowed disrotatory thermal ring closure.

However, if cyclohexa-1,3-diene and \( \alpha \)-phellandrene are subjected to extended radiation, ring closure occurs as shown in Figures 36 and 37.
All of these products can be rationalized as arising from the initially formed triene via allowed processes, a $4\pi$ closure leading to 3-vinylcyclobutene and a $\pi^4_s + \pi^2_a$ (the so-called "Photochemical Diels-Alder Reaction") accounting for the other products depicted in Figures 36 and 37. Further evidence favouring this rationalization can be found in the photolysis of 1,5,6-triphenylcyclohexa-1,3-dienes, shown in Figures 38 and 39. Thus the 1,5,6-cis triphenyl isomer (Figure 38) was shown to give only exo,exo-3,4,6-triphenylbicyclo[3,1,0]hex-2-ene on irradiation, whereas the 1,5,6-trans isomer (Figure 39) gave only 4-exo,6-endo-3,4,6-triphenylbicyclo[3,1,0]hex-2-ene.

These observations can be rationalized in terms of an initial $6\pi$-conrotatory opening followed by a photochemically allowed $\pi^4_s + \pi^2_a$ cycloaddition process. In the first example there are two possible conrotatory modes, (i) and (ii) in Figure 40, however only mode (ii) leads to a triene which has favoured stereochemistry for the subsequent
$\pi^{4_s} + \pi^{2_s}$ closure mode, (i) would lead to an excessively crowded bicyclo [3,1,0] hexene derivative which is not observed in practice.

Figure 40

Thus we see where two allowed modes exist one may be preferred on stereochemical grounds. The rationalization of the observed isomerization of the trans -1,5,6,- triphenyl isomer (Figure 39 ), is analogous to that given for the cis.
Patrick et al. discovered that highly fluorinated cyclohexadienes isomerized when heated in the range 250-600°C in the absence of a reactive metal surface. Using a flow system through an unpacked "aged" nickel tube in the temperature range 400 - 600°C they found that both octafluorocyclohexa-1,4-diene and 1H-heptafluorocyclohexa-1,3,5-diene were isomerized (Figure 41).

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Reaction Conditions</th>
<th>Products (% composition)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>450°C Aged nickel tube</td>
<td>4QO</td>
</tr>
<tr>
<td>[F]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>260°C Aged nickel tube</td>
<td>12.9 41.3 6.8</td>
</tr>
</tbody>
</table>

Figure 41

Recently Patrick et al. have shown that the perfluoro-1,4-diene is slightly more stable than the 1,3-diene and that with rise in temperature, its relative stability decreases. Thus the equilibrium constant, \( K = \frac{[1,3\text{ diene}]}{[1,4\text{ diene}]} \), changes from 0.299 at 250°C to 0.405 at 450°C.

The equilibrium experiments were carried out in glass ampoules at low pressure, approximately \( 10^{-4}\text{ mm} \) and in the presence of a \( \text{NaF}^+ \) catalyst. Several other reactions have been reported which could plausibly be rationalized in terms of the migration of a fluorine atom.

Camaggi and Gozzo during their work on the photochemical isomerization derivatives of decafluorocyclohexene reported that perfluoro-
(-2-methylcyclopentadiene) isomerized to perfluoro(-1-methylcyclopentadiene) when heated at 80°C for two days (Figure 42).

\[ \text{CF}_3 \quad \xrightarrow{\Delta} \quad \text{CF}_3 \quad + \quad \text{Dimers} \]

Figure 42

Feast et al., while attempting to make polyfluorocyclohexa-1,3-dienes with specific substitution patterns prepared 1H,2H- and 2H,3H-hexafluorocyclohexa-1,3-dienes from bicyclo[2,2,2]-oct-2-ene, see Figure 43.

Figure 43

Subsequently, it was shown that either of the dihydrohexafluorocyclohexa-1,3-dienes was isomerized on pyrolysis to a mixture consisting predominantly of the two isomers shown in Figure 44.

Figure 44

It seemed unlikely that this isomerization was catalysed by traces of fluoride ion in a process analogous to that shown in Figure 45 for two reasons. In the first place the experimental conditions in the reaction
are unlikely to have resulted in the presence of significant quantities of fluoride ion and secondly, although the site of attack of \( F^\ominus \) is not readily predicted in this system, it would seem likely that such a process (see later) would lead to the production of large quantities of pentafluorobenzene rather than predominant interconversions between the 1,3-dienes as reported. They also found, while investigating the chemistry of some fluorinated polycyclic polyenes that dodecafluoro-\( \text{tricyclo}[5,2,2,0]_{\epsilon} \)-undeca-2,5,8-triene was isomerized photochemically to dodecafluorotricyclo[5,2,2,0]_\epsilon undeca-2,3,8-triene, see Figure 46.

Vacuum pyrolysis of the same compound yielded perfluoroindene in good yield as depicted in Figure 47.
They suggested that a plausible explanation for both observations could be provided by a $[1,5]$ sigmatropic migration of fluorine. Further work on perfluoroindene suggested that it was photochemically isomerized to perfluoroisoindene; the latter being postulated as an intermediate since irradiation of perfluoroindene in the presence of ethylene gives rise to the Diels-Alder adduct of perfluoroisoindene as shown in Figure 48.

This was considered to be an unambiguous example of a sigmatropic fluorine shift. Haszeldine et al. have reported fluorine shifts when highly fluorinated olefins are irradiated with ultra violet light. For example, Figure 49 shows the result of irradiating perfluoro-2,3-dimethylbut-2-ene for approximately seven days.

\[ \text{CF}_3 \quad \text{C} \quad \text{C} \quad \text{CF}_3 \]
\[ \text{CF}_3 \quad \text{C} \quad \text{C} \quad \text{CF}_3 \]
\[ \text{CF}_3 \quad \text{C} \quad \text{C} \quad \text{CF}_2 \]
\[ \text{CF}_3 \quad \text{C} \quad \text{C} \quad \text{CF}_3 \]
No rearrangement was detectable in the dark at temperatures up to 300°C. They suggest that the rearrangement is possibly a suprafacial[1,3] sigmatropic shift and state that this would be symmetry allowed, for the photochemically excited state.

The examples reported above can all be rationalized in terms of a process which involves the migration of a fluorine atom although in some cases alternative explanations are plausible, for example, fluoride ion catalysed processes.

Isomerizations of fluorinated systems catalysed by fluoride ions are well documented in the literature.

Camaggi et al. reported an interesting rearrangement in a fused ring system. Reaction of ethylene glycol with perfluorocyclohexene in the presence of potassium hydroxide led to isomeric 1,4-dioxanaphthalene structures (along with a 2-spirodioxolane), both of which were converted by potassium fluoride to a third structure in which the double bond was the most highly substituted, this is illustrated in Figure 50.

They suggest the mechanism follows the well known process in which a double bond migrates round a ring system by successive addition and eliminations of fluoride ion, as depicted in Figure 51, until the number of vinylic fluorine atoms is as small as possible.
Other rearrangements catalysed by fluoride ion are reported by Young and Chambers. The consensus of opinion favours an addition-elimination mechanism where CF$_2$=groups are particularly susceptible to fluoride ion attack. Consequently equilibration between isomers of fluoro-olefins frequently occurs in the presence of fluoride ion, giving the most stable isomer. Isomers with terminal CF$_2$= groups are readily isomerized, but internal olefins usually require much more vigorous conditions.

Attempts to construct a theoretical rationalization for isomerizations apparently involving fluorine shifts are frustrated by the fact that most of the systems for which observations are available involve cyclopentadienyl as the framework radical, and because of orbital degeneracy there is considerable ambiguity over defining the symmetries of the orbitals involved. A further complication exists in the nature of the migrating group in that the fluorine atom might conceivably use either one end of a p-atomic orbital or both ends. These points are elaborated in the discussion of Figures 52 and 53.
The odd electron may be assigned to either of the two degenerate orbitals $\Psi_2$ and $\Psi_3$. In the symmetric configuration of the five-membered ring, the odd electron has equal probability of going into $\Psi_2$ or $\Psi_3$, but according to the Jahn-Teller theorem, this is not the stable configuration for the system. A more stable state will be one in which distortion occurs and hence splitting of the degeneracy. The splitting of the degenerate molecular orbitals is quite small, approximately 1 kcal/mole. Anastassiou contends the magnitude of this split will be further increased by the presence of the migrating group, and he suggests that the frontier orbital of interest can be identified on the basis of first order perturbation theory. This requires that splitting of a pair of degenerate molecular orbitals upon partial bond fixation (distortion) occur in such a way as to increase the energy of the molecular orbital with the largest number of nodes crossing formal double bonds, and to decrease the energy of the alternate molecular orbital. Thus for the two initially degenerate molecular orbitals depicted in Figure 52, this approach predicts that $\Psi_3$ will move to higher energy than $\Psi_2$, and consequently, for the cyclopentadienyl radical $\Psi_3$ should be considered as the HOMO.
However, as already stated, even if the ambiguity over which orbital of the framework radical is to be considered as the HOMO can be resolved in this way, (Anastassiou also identifies the LUMO for cyclopentadienyl), there remains the ambiguity over how the migrating fluorine will interact with the relevant framework orbital. This latter point is illustrated in Figure 54. In the situation where fluorine uses one face of a p-atomic orbital to interact with the framework orbital we have an analogy with migration of carbon with retention of configuration, and in the case where both ends of the p-atomic orbital are used in the interaction we have an analogy with inversion at a migrating carbon centre. These terms are used below, although of course, there is no stereochemical significance attached to them in the case of fluorine migrations.

Figure 53

Fluorine Migration Possibilities

Using one end of a p-lobe Using both ends of p-lobes

Retention

Figure 54
At this point, it would be interesting to examine how the fluorine atom interacts with the framework radical in the previously reported fluorine isomerizations to see whether or not some pattern emerges with respect to retention or inversion. The results of previous investigations are summarized in Table V.

It can be seen that the migration of the fluorine atom with respect to inversion or retention occurs in a seemingly random manner, although some reservations should be made about placing too much reliance on the cyclopentadienyl assignments. Therefore, it was decided to attempt to examine the isomerization of cyclohexa-1,3-dienes, since in this case the ordering of the $\pi$ molecular orbitals in the framework radical is completely unambiguous. It might therefore be possible to establish whether the migrating fluorine atom displays a marked tendency to use one lobe or both lobes of the $p$-atomic orbitals.

In fact, all of the above arguments presuppose a concerted migration process. If a systematic rationalization in terms of orbital symmetry control emerged from this work, the observations could be taken as evidence supporting a concerted (or nearly concerted) fluorine migration; however, it was appreciated that the absence of a satisfactory theoretical rationalization in these terms leaves the mechanism of such migrations open to further question.

The system we chose to study was the monohydroheptafluorocyclohexa-1,3-dienes, since these are all relatively easily available, have quite distinct g.p.c. retention volumes, and mixtures could therefore be readily analysed. Furthermore, the likely products of reaction, other than those from isomerization, namely pentafluorobenzene and hexafluorobenzene (produced by defluorination and dehydrofluorination respectively), are also
<table>
<thead>
<tr>
<th>Ref.</th>
<th>Reaction</th>
<th>Interaction of the fluorine atom with the framework radical</th>
</tr>
</thead>
</table>
| 10   | \[
\begin{array}{c}
\text{CF}_3 \\
\text{F} \\
\hline
\text{CF}_3 \\
\text{F} \\
\end{array}
\xrightarrow{\Delta} 
\begin{array}{c}
\text{CF}_3 \\
\text{F} \\
\hline
\text{CF}_3 \\
\text{F} \\
\end{array}
\]
\[1,5\] shift with retention | \[
\begin{array}{c}
\text{H} \\
\text{F} \\
\hline
\text{H} \\
\text{F} \\
\end{array}
\xrightarrow{\Delta} 
\begin{array}{c}
\text{H} \\
\text{F} \\
\hline
\text{H} \\
\text{F} \\
\end{array}
\]
\[1,5\] shift with inversion |
| 12   | \[
\begin{array}{c}
\text{F} \\
\text{F} \\
\hline
\text{F} \\
\text{F} \\
\end{array}
\xrightarrow{h\nu} 
\begin{array}{c}
\text{F} \\
\text{F} \\
\hline
\text{F} \\
\text{F} \\
\end{array}
\]
\[1,5\] shift with inversion |
| 13   | \[
\begin{array}{c}
\text{CF}_3 \\
\text{C} \\
\hline
\text{CF}_3 \\
\text{C} \\
\end{array}
\xrightarrow{h\nu} 
\begin{array}{c}
\text{CF}_3 \\
\text{C} \\
\hline
\text{CF}_3 \\
\text{C} \\
\end{array}
\]
\[1,3\] shift with retention |

Table V
Ref. | Reaction | Interaction of the fluorine atom with the framework radical
--- | --- | ---
11 | \[
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{h} \rightarrow \\
\text{F} \\
\text{F} \\
\end{array}
\] | \[
\text{LUMO}
\]

\[1,5\] shift with inversion

--- | --- | ---
EITHER | \[
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\Delta \\
\text{F} \\
\text{F} \\
\end{array}
\] | \[
\text{HOMO of cyclopentadienyl}
\]

\[1,5\] shift with retention

--- | --- | ---
OR | \[
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\Delta \\
\text{F} \\
\text{F} \\
\end{array}
\] | \[
\text{HOMO of indenyl}
\]

\[1,5\] shift with either

In this case the mode is indeterminate since there is a node at one terminus

*Table V continued*
well known and characterized. The presence of the hydrogen atom allows one to detect isomerization processes and the early reports of Patrick et al. and Weston had already established that such processes do occur in analogous systems.

II 8 The Thermal Isomerization of Heptafluorocyclohexadienes

The objectives of the work to be described in this section were two-fold. In the first place it was expected, in the light of established results with closely analogous systems, that the heptafluorocyclohexadienes would interconvert thermally, hence to establish the interconversion pathways was the first objective. Since there are three isomers a number of possibilities exist as illustrated below, see Figure 55. If A, B, and C, are the three isomers, one or more of the processes (i) to (vi) could occur depending upon which isomer was initially taken and pyrolysed.

Secondly, it was important to establish whether we are observing a pure thermal isomerization or one involving another agent such as: a fluoride ion, a surface effect, or traces of hydrogen fluoride from the decomposition of the starting material.

Having established the isomerization processes which occur and their relative ease, assuming there is more than one observed process, it was
hoped a mechanistic rationalization might then be constructed.

Chromatographically pure samples of 1H- and 2H- heptafluorocyclo-
hexa -1,3-diene and 1H -heptafluorocyclohexa -1,4-diene were obtained
as described in Part I. The first attempts to study their thermal
isomerization were carried out by heating small amounts of thoroughly
degassed dry samples of the respective isomers in small, carefully
flamed out pyrex ampoules which had been sealed from a vacuum line.
This approach proved to be unsuitable since under conditions severe
enough to initiate any reaction there was always some decomposition of
the starting diene, except in the case of the 1,4 isomer. Thus on
opening the sealed tubes, after a period of heating, both those origi-

nally containing the 1,3-diene isomers contained hydrogen fluoride.
In the light of our stated objectives, the presence of hydrogen fluoride
in the product invalidated this experiment and hence this approach was
abandoned.

The next experimental procedure adopted was that of pyrolysis in
a flow system using the apparatus shown diagrammatically in Figure 56.

A weighed amount of starting material was placed in the reservoir
R along with some phosphorus pentoxide and it was cooled in liquid air.
The system was flushed out with dry nitrogen and then evacuated to a
pressure of approximately $10^{-3}$ mm, as measured on the Vacustat gauge on
the vacuum line. When conditions were stable, trap T was cooled in liquid
air, that surrounding R was removed and R was allowed to warm up to room
temperature. The contents of R passed through the hot zone and the
pyrolysis products were collected in the tared trap T. On completion
of the pyrolysis the tap to the vacuum line was closed and the system
was allowed to reach atmospheric pressure by bleeding in dry nitrogen.
T was removed, loosely stoppered, allowed to warm up to room temper­
ature, reweighed and finally its contents analysed by g.l.c. Where
pressures of above \(10^{-3}\) mm were used, dry nitrogen was allowed to
bleed into the system and the pressure was measured using either a
Vacustat gauge or the manometer. The results are recorded in Table VI,
and summarized graphically in Figures 57-62.

From these results certain generalizations can be drawn. When
either 1H- or 2H-heptafluorocyclohexa -1,3-diene is pyrolysed in this
manner the concentration of the other 1,3-diene isomer first increases
and then decreases, in all cases, with rise in the pyrolysis temperature.
The other compounds in the product mixture, namely, 1H-heptafluoro-
cyclohexa -1,4-diene, hexafluorobenzene and pentafluorobenzene also
generally increase in concentration with temperature rise. On some
occasions there were some relatively small quantities of higher
molecular weight materials. Coupled gas chromatography mass spectrometric
analyses of these mixtures indicated that these products corresponded
to di and trimers of the starting material after elimination of some
hydrogen fluoride and fluorine; they were not present in appreciable
amounts in all the experiments and have not been properly characterized,
hence they are omitted from further consideration. The results of the
experiments outlined above are consistent with the hypothesis that the
first outcome of these pyrolyses is the interconversion of the two
conjugated isomers. Under only marginally more severe conditions both
of these are then further isomerized to the 1,4-diene and/or lose
either hydrogen fluoride or fluorine to yield hexa and pentfluorobenzene
respectively.
## ANALYSIS OF PRODUCTS FROM FLASH PYROLYSIS

### 1H-HEPTAFLUOROCYCLOHEXA-1,3-DIENE

<table>
<thead>
<tr>
<th>Press in mm</th>
<th>Temp °C</th>
<th>% Loss</th>
<th>[F]</th>
<th>[F]</th>
<th>[F]</th>
<th>% of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.7</td>
<td>5.7</td>
<td>69.1</td>
<td>13.4</td>
<td>1.0</td>
</tr>
<tr>
<td>10⁻³</td>
<td>550</td>
<td>6.5</td>
<td>Trace</td>
<td>0.1</td>
<td>1.0</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>17.7</td>
<td>1.0</td>
<td>2.2</td>
<td>18.7</td>
<td>33.6</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>17.2</td>
<td>0.6</td>
<td>2.2</td>
<td>18.7</td>
<td>33.6</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>46.7</td>
<td>1.2</td>
<td>3.7</td>
<td>17.0</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td>10⁻¹</td>
<td>550</td>
<td>10.9</td>
<td>0.1</td>
<td>0.5</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>11.3</td>
<td>0.2</td>
<td>1.0</td>
<td>2.2</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>14.2</td>
<td>0.4</td>
<td>1.6</td>
<td>17.8</td>
<td>32.6</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>47.6</td>
<td>1.2</td>
<td>3.1</td>
<td>14.8</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>10¹</td>
<td>550</td>
<td>38.2</td>
<td>0.1</td>
<td>0.5</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>42.3</td>
<td>0.2</td>
<td>0.6</td>
<td>5.9</td>
<td>55.0</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>52.8</td>
<td>0.3</td>
<td>1.4</td>
<td>12.4</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>62.7</td>
<td>0.6</td>
<td>2.6</td>
<td>17.7</td>
<td>21.0</td>
</tr>
</tbody>
</table>

**Table VI**
## ANALYSIS OF PRODUCTS FROM FLASH PYROLYSIS

### 2H-HEPTAFLUOROCYCLOHEX-1,3-DIENE

<table>
<thead>
<tr>
<th>Press in mm</th>
<th>Temp. °C</th>
<th>% Loss</th>
<th>% of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-3})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>4.6</td>
<td>4.3</td>
<td>29.0</td>
</tr>
<tr>
<td>600</td>
<td>16.5</td>
<td>7.7</td>
<td>40.1</td>
</tr>
<tr>
<td>650</td>
<td>21.6</td>
<td>1.4</td>
<td>23.0</td>
</tr>
<tr>
<td>700</td>
<td>42.6</td>
<td>3.8</td>
<td>19.2</td>
</tr>
<tr>
<td>(10^{-1})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>12.9</td>
<td>Trace</td>
<td>2.6</td>
</tr>
<tr>
<td>600</td>
<td>13.8</td>
<td>0.5</td>
<td>9.1</td>
</tr>
<tr>
<td>650</td>
<td>24.0</td>
<td>0.9</td>
<td>18.7</td>
</tr>
<tr>
<td>700</td>
<td>33.5</td>
<td>2.6</td>
<td>22.9</td>
</tr>
<tr>
<td>(10^1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>44.7</td>
<td>1.0</td>
<td>10.1</td>
</tr>
<tr>
<td>600</td>
<td>48.3</td>
<td>4.3</td>
<td>28.8</td>
</tr>
<tr>
<td>650</td>
<td>51.9</td>
<td>12.6</td>
<td>38.2</td>
</tr>
<tr>
<td>700</td>
<td>59.3</td>
<td>0.1</td>
<td>18.2</td>
</tr>
</tbody>
</table>

### 1H-HEPTAFLUOROCYCLOHEXA-1,4-DIENE

<table>
<thead>
<tr>
<th>% of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-1})</td>
</tr>
</tbody>
</table>

### INCREASING ORDER OF RETENTION TIME

---

TABLE VI (continued)
At this point in the research, the question arises as to whether these observations were the result of a thermal isomerization of the diene or an alternative process. One clear candidate for the alternative process was a catalysed isomerization by the presence of adventitious traces of fluoride ion; this could arise from the decomposition of some pyrolysed material on the silica wool or tube walls. To examine this possibility the dienes were submitted to pyrolysis in a flow system over sodium fluoride. The experimental procedure was similar to that used before except sodium fluoride pellets replaced silica wool in the pyrolysis tube. The products from the pyrolysis of 1H-heptafluorocyclohexa-1,3-diene contained starting material, 1H-heptafluorocyclohexa-1,4 diene and pentafluorobenzene but no 2H-heptafluorocyclohexa-1,3-diene or perfluorobenzene. In all previous pyrolyses of the 1H-1,3-diene the 2H-isomer was a major component in the product, and the perfluorobenzene content, although small, rose significantly with rise in pyrolysis temperature. Thus the composition of the products from the pyrolysis over sodium fluoride pellets differs both qualitatively and quantitatively from those obtained in the pyrolysis over silica wool, and is strong evidence that the processes observed in the latter case were not initiated by traces of adventitious fluoride ion. However, the question of a surface effect still remains and to examine this the thermal reactions in systems with a minimum surface area, were investigated. The experimental technique involved sealing under vacuum, a small dry sample of 1H-perfluorocyclohexa-1,3-diene in a ten litre, essentially spherical, pyrex flask (See Figure 63). The vessel was then heated for a set period in a thermostated oven, the products were recovered and analysed by g.l.c., as before. The results of these experiments are shown in Table VII, and graphically summarized.
Analysis of products from the Pyrolysis of 1H-heptafluorocyclohexa-1,3-diene at low pressure

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume bulb</td>
<td>10.1</td>
<td>10.1</td>
<td>10.1</td>
<td>10.1</td>
<td>10.1</td>
<td>10.1</td>
<td>10.1</td>
<td>10.1</td>
</tr>
<tr>
<td>Wt. material (g)</td>
<td>0.242</td>
<td>0.246</td>
<td>0.25</td>
<td>0.264</td>
<td>0.244</td>
<td>0.248</td>
<td>0.245</td>
<td>0.225</td>
</tr>
<tr>
<td>Press. in mm at temp °C</td>
<td>3.46</td>
<td>4.41</td>
<td>4.83</td>
<td>5.16</td>
<td>4.82</td>
<td>4.90</td>
<td>4.99</td>
<td>4.58</td>
</tr>
<tr>
<td>°C</td>
<td>200</td>
<td>320</td>
<td>365</td>
<td>380</td>
<td>380</td>
<td>380</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Time in hours</td>
<td>31</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>48</td>
<td>100</td>
<td>24</td>
<td>100</td>
</tr>
</tbody>
</table>

Analysis

<p>| | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{F}^H)</td>
<td>(\text{H})</td>
<td>(\text{F})</td>
<td>(\text{N}_2)</td>
<td>(\text{N}_2)</td>
<td>2.3</td>
<td>4.5</td>
<td>20.0</td>
<td>7.4</td>
</tr>
<tr>
<td>(\text{F}^H)</td>
<td>(\text{H})</td>
<td>(\text{F})</td>
<td>(\text{REACTION})</td>
<td>(\text{REACTION})</td>
<td>76.1</td>
<td>54.8</td>
<td>51.6</td>
<td>50.2</td>
</tr>
<tr>
<td>(\text{F}^H)</td>
<td>(\text{H})</td>
<td>(\text{F})</td>
<td>(\text{REACTION})</td>
<td>(\text{REACTION})</td>
<td>21.6</td>
<td>35.1</td>
<td>21.5</td>
<td>36.0</td>
</tr>
<tr>
<td>(\text{H})</td>
<td>(\text{F})</td>
<td>(\text{N}_2)</td>
<td>(\text{N}_2)</td>
<td>3.32</td>
<td>5.2</td>
<td>6.3</td>
<td>6.3</td>
<td></td>
</tr>
</tbody>
</table>

Table VII
Pyrolysis of 1H-heptafluorocyclohexa-1,3-diene
in a large bulb, at a low pressure and
at a temperature of 380°C

Figure 64
in Figure 64. Unfortunately, only a restricted series of experiments could be carried out using this technique since the only oven large enough to accommodate the ten litre flask was the glass blowers' annealing oven, and this was available on limited occasion only. Smaller flasks did not allow samples to be used of a size which would exert only a low pressure at the isomerization temperature and yet at the same time yield a sufficient amount of material for analysis by the available techniques. The results of these experiments supported the earlier conclusions drawn on the vacuum pyrolysis experiments in that the first process observed, and therefore the easiest accomplished, was the interconversions of the 1,3-isomers, subsequently, these isomerized to the 1,4-isomer. In this work no dehydrofluorinated product was detected and it seems possible that this reaction may be dependent upon surface effects.

It is of particular interest to note, that the interconversion of the conjugated dienes occurs before their conversion to the non-conjugated isomer. The results of Patrick,\textsuperscript{32} referred to earlier, indicate that for the perfluorocyclohexadiene case the non-conjugated isomer is the most stable, and it seems quite likely that the heptafluorocyclohexadiene
system will be more analogous to that of the perfluoro than to that of the hydrocarbon system, where the conjugated diene is the most stable.

The question to be considered at this point is whether or not these experimental results fit into a convenient theoretical rationale. In Figure 65 the possible processes which may be occurring during thermolysis of the heptafluoro-1,3-diene system are summarized schematically, the structures shown in parenthesis have not been isolated.

Since it has been shown that fluoride ion catalysed processes do not provide a satisfactory explanation of the thermal isomerization results, it seems reasonable to assume we have established the following:
(i) Thermal isomerizations occur in the cyclohexadiene series and these are most conveniently accounted for in terms of sigmatropic fluorine shifts.

(ii) The easiest process available is apparently that of a $[1,5]$ shift followed by a $[1,3]$ shift; of necessity, both of these processes must be suprafacial. Unfortunately, the difference in activation energy for the two processes cannot be estimated from these results, but it would appear that it is not particularly large.

It is apparent that if the observed migrations are concerted, a shift in which the fluorine migrates with retention, illustrated in Figure 66, is preferred over one involving inversion at the fluorine, as shown in Figure 67, although the degree of preference observed is not particularly marked.

![Figure 66](image)

![Figure 67](image)

This leaves the overall picture no clearer since the previous cases where the framework radicals $\pi$-molecular orbitals ordering is unambiguous are both photochemical isomerizations, one of which would appear to favour retention and the other inversion. What does emerge from this work is that thermal isomerizations of cyclohexadienes do occur and by a
mechanism which does not involve catalysis by fluoride ion at a surface. Whether the observed fluorine migrations are concerted sigmatropic shifts or whether alternative mechanisms involving discrete C-F bond homolysis or heterolysis and recombination of the resulting species occur cannot be ascertained. It will require more sophisticated studies to solve this particular problem.

II 9. The Photochemical Isomerization of 1H-heptafluorocyclohexa-1,3-diene

The object of the work described in this section was to extend the body of information already obtained from previous photolysis experiments on perfluorocyclohexa-1,3-diene, 2H-heptafluorocyclohexa-1,3-diene and 2H,3H-hexafluorocyclohexa-1,3-diene.

The photoisomerization of cyclohexa-1,3-diene and its derivatives has been studied in depth both for sensitized and unsensitized processes. The course taken by the rearrangement is not simple since the individual structures of reactants, intermediates and products can affect it to a greater or lesser extent. The work of Woodward and Hoffmann, and H.C. Longuet-Higgins and E.W. Abrahamson has provided a widely accepted basis for rationalizing these photochemical electrocyclic reactions. The photochemistry of cyclohexa-1,3-dienes is potentially more complicated than that of its immediate lower and higher homologues because ring closure and opening are both symmetry-allowed processes as shown in Figure 68.

The hydrocarbon analogue favours initially the photochemical 6 \( \pi \) conrotatory ring opening, whereas the perfluorocyclohexa-1,3-diene favours the photochemical 4 \( \pi \) disrotatory ring closure, shown in Figure 69, which is essentially quantitative. The bicyclo [2,2,0]
compound formed is found to have a relatively high degree of thermal stability.

Similarly 2H-heptafluorocyclohexa-1,3-diene\(^1\) and 2H,3H-hexafluorocyclohexa-1,3-diene\(^2\) yield 1,3,4,5,5,6,6-heptafluorobicyclo[2,2,0]hex-2-ene and 1,4,5,5,6,6-hexafluorobicyclo[2,2,0]hex-2-ene respectively, as shown in Figure 70.
Both of these compounds are relatively thermally stable, however, they quantitatively revert back to the parent dienes when pyrolysed at reduced pressure at 300-350°C. Why fluorinated dienes should favour 4 π ring closure in preference to 6 π ring opening is still open to question. The fact that it does happen only serves to emphasize the information already accumulated which can be summarized by saying that reactions which result in reducing the number of fluorines at vinylic sites and consequently increasing the number at saturated sites appear to be favoured.

It should be noted that not all fluorinated cyclohexa-1,3-diene systems isomerize via the 4 π ring closure route, for example, the perfluorotricyclo [6,2,2,0] undeca-2,6,9-triene shown in Figure 71.

![Diagram](image)

Figure 71
gives on irradiation the pair of isomers shown on the right hand side of the figure. This isomerization presumably proceeding via an initial 6 π opening to the tetraene shown in square brackets which was not isolated but would be expected to undergo a 4 π + 2 π closure to the observed products. This result demonstrates that the 6 π ring opening is
not prohibited although all other things being equal the 4π ring closure is preferred; in this case the 4π ring closure is sterically prevented as becomes evident from the examination of molecular models.

**Irradiation of 1H-heptafluorocyclohexa-1,3-diene**

Direct irradiation at 253.7 nm of 1H-heptafluorocyclohexa-1,3-diene in the vapour phase in a quartz ampoule gave as the only photoproduction 2,3,4,5,5,6,6-heptafluorobicyclo[2,2,0]hex-2-ene. Irradiation of the vapour above the liquid diene was achieved by shielding the liquid from the radiation with black paper.

Like the polyfluorobicyclo[2,2,0]hexenes prepared previously this photoisomer showed a strong parent ion in the mass spectrum and a base peak corresponding to loss of $-\text{CF}_3$ from the parent ion; its infrared spectrum showed a strong absorption $1770 \text{ cm}^{-1}$ assigned to the $\text{CF}=\text{CF}$ bond and a very weak tertiary C-H stretching frequency at $3000 \text{ cm}^{-1}$.

The n.m.r. spectra were complex but compatible with the spectra of the previously characterized polyfluorobicyclo[2,2,0]hex-2-ene. The $^1\text{H}$ spectrum showed a broad band at $6.17 \text{ ppm}$ with evidence of extensive spin-spin coupling. On examination of the $^{19}\text{F}$ n.m.r. spectrum it was possible to pick out a tertiary fluorine at $197.5 \text{ ppm (IF)}$, a clearly defined AB system, $\delta_A 112.5 \text{ ppm (IF)}, \delta_B 133.2 \text{ ppm (IF)}, J_{AB} 220\text{Hz}$, in which the downfield limb displayed extensive spin-spin coupling being a multiplet of at least nine lines. From the remaining absorptions the two vinylic fluorines were assigned to the relatively narrow absorptions at $119.9 \text{ ppm (IF)}$ and $120.8 \text{ ppm (IF)}$ by comparison with the shift and peak shape of the more easily assigned spectra of the known perfluorobicyclo[2,2,0]hex-2-ene. The remaining $-\text{CF}_2$ group constitutes the rest of the integrated intensity of the $^{19}\text{F}$ spectrum, however it consists of a complex
non-first order set of bands with peaks of greatest intensity at 118.5 ppm and 124.2 ppm. Spectral parameters of this and related compounds are summarized in Table VIII.

2,3,4,5,5,6,6-Heptafluorobicyclo[2,2,0]hex-2-ene remained unchanged for a period of three years when stored at 0°C and like similar bicyclo products reverted back almost quantitatively to the parent diene on vacuum pyrolysis at 350°C. The pyrolysis product contained some 2H-heptafluorocyclohexa-1,3-diene as would be expected from the earlier discussion of the thermal isomerization of heptafluorocyclohexa-1,3-dienes.

This result adds one more example to the data on photoisomerization of fluorinated dienes. More varied substitution patterns require investigation before conclusions can be drawn about why the 4 π ring closure is the apparently preferred mode of isomerization for these systems.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{19}\text{F N.M.R.} \text{ Shifts in ppm from CFCl}_3$</th>
<th>$^1\text{H N.M.R. (c)}$</th>
<th>i.r. cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[F, F]</td>
<td>$\delta_A$ 119(2) $\delta_B$ 130(2) $J_{AB}$ 224 Hz</td>
<td>201.4 (2) 122.0 (2) (X$\equiv$F)</td>
<td>$\equiv\text{C}=$ 1764 (s)</td>
</tr>
<tr>
<td>[H, F, F]</td>
<td>$\delta_A$ 116.6 (2) $\delta_B$ 130.6 (2) $J_{AB}$ 218 Hz</td>
<td>191.4 (2) -</td>
<td>-</td>
</tr>
<tr>
<td>[H, F, F]</td>
<td>$\delta_A$ 117.9 (1) $\delta_B$ 130.8 (1) $J_{AB}$ 216 Hz $\delta_A$ 120.2 (1) $\delta_B$ 131.4 (1) $J_{AB}$ 220 Hz</td>
<td>200.6 (1) 91.8 (1) (X$\equiv$H)</td>
<td>$\equiv\text{C}=$ 1656 (s) C-H stretch 3125</td>
</tr>
<tr>
<td>[H, F, F]</td>
<td>$\delta_A$ 112.5 (1) $\delta_B$ 133.2 (1) $J_{AB}$ 220 Hz Complex multiplet (non-first order) centred at 118.5(1) &amp; 124.2(1)</td>
<td>197.5 (1) 119.9 (1) 120.8 (1)</td>
<td>$\equiv\text{C}=$ 1770 (s) $\equiv\text{C}=$ C-H stretch 3000 (vw)</td>
</tr>
</tbody>
</table>

Table VIII
EXPERIMENTAL

PART II
II. 10(a) Flash Vacuum Pyrolysis of 1H-heptafluorocyclohexa-1,3-
and-1,4-diene and 2H-heptafluorocyclohexa-1,3-diene

The apparatus used in these experiments is shown diagrammatically
on page 59 , it consisted of a silica tube, 1.4cm int. diam. x 59cm
lightly packed with silica wool to one end of which a pyrex reservoir
(R) containing the compound to be pyrolysed was attached, with a pyrex
trap T at the other end. Both reservoir and trap could be cooled in
liquid air and all connections were through ground glass joints. The
inlet to the reservoir was connected via a needle valve and a Dreschel
bottle-containing-concentrated-sulphuric-acid-to-a-nitrogen-supply, and
the outlet from the trap was connected to a vacuum system incorporating
a mercury manometer. The middle 44cm of the silica tube was heated in
a tubular electric furnace, the latter being insulated with a surrounding
pyrex glass tube packed with Vermiculite. The temperature at the outer
surface of the silica tube was measured using a Chromel-Alumel thermo­
couple. The sample to be pyrolysed was weighed into the reservoir,
approximately 1g of P₂O₅ was added, the reservoir was then connected
to the pyrolysis apparatus and cooled in liquid air. The apparatus
was evacuated (approximately 10⁻³ mm Hg) and the tared trap was cooled
in liquid air whilst the reservoir was allowed to warm up to room
temperature. When all the material had evaporated from the reservoir
the contents of the trap were allowed to reach atmospheric pressure,
by bleeding in dry nitrogen, and then to warm up. Finally the trap
was weighed and the contents analysed by g.l.c. (Column A, 125⁰,GDB
detector). For pyrolyses carried out above a pressure of 10⁻³ mm dry
nitrogen was bled into the system to the required pressure, the pressure
being measured by the mercury manometer or Vacustat gauge at a point
close to the outlet of the trap.
II. 10(b) Flash Vacuum Pyrolysis of 1H-heptafluorocyclohexa-1,3-diene
Over Sodium Fluoride Pellets

The apparatus was identical to that used in II.10(a) with sodium fluoride pellets (Thompson and Capper, Liverpool, cylindrical pellets, 0.3 cm x 1 cm diam., 0.5g) replacing silica wool. Before use the tube was heated to 400°C and purged with dry nitrogen to remove absorbed water and any volatile materials derived from the pellet binder. Since the packing in the pyrolysis tube was much denser than that used in II.10(a) dry nitrogen was used as a carrier gas. The results of three runs are summarized in Table IX over.

II. 10(c) Extended pyrolysis of 1H-heptafluorocyclohexa-1,3-diene
at Low Pressure

The bulb shown diagrammatically above was connected to a vacuum line and evacuated to $10^{-3}$ mm Hg. A tared sample of the degassed compound, was vacuum transferred from $\text{P}_2\text{O}_5$ into the flask, which was sealed at the constriction, enclosed in a metal cage, and placed in a thermostatically controlled air oven and heated to the required
Analysis of Products from the Flash Pyrolysis of 1H-heptafluorocyclohexa-1,3-diene over Sodium Fluoride

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>% Recovery</th>
<th>Nitrogen Flow Rate cm³/min</th>
<th>Product (% Composition)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>81.9</td>
<td>5.5</td>
<td>F H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>300</td>
<td>56.4</td>
<td>7.0</td>
<td>F H 7.4</td>
</tr>
<tr>
<td>360</td>
<td>72.7</td>
<td>7.0</td>
<td>F H 9.6 63.9 0</td>
</tr>
</tbody>
</table>

In each case 0.5 g of diene were pyrolysed for approximately 3 hours.

Table IX
temperature for the required period. After cooling the finger was placed in liquid air, the bulb opened at A by hot spotting and the whole allowed to warm up to room temperature. The condensation of atmospheric water vapour in the cold finger and the small amount of sample used made the weight determination of the product impracticable. The product was analysed by g.l.c. (Column A, 125°C, GDB detector). The results of these experiments are recorded in Table VII page 65.

II. 10(d) Other Pyrolysis Experiments

(i) About 0.3g of each isomer was degassed and vacuum transferred from \( \text{P}_2 \text{O}_5 \) into a small evacuated Carius tube (1cm int. diam. x 5cm) and the latter sealed. They were heated in a boiling ethylene glycol bath at 220°C ± 10°C for approximately 100 hours. All three isomers are colourless liquids. After heating 1H-heptafluorocyclohexa-1,3-diene was pale yellow, 2H-heptafluorocyclohexa-1,3-diene was brown with a brown deposit and 1H-heptafluorocyclohexa-1,4-diene remained colourless. The tubes were frozen in liquid air, opened by hot spotting, vacuum transferred into tared tubes and the latter weighed. Each sample was analysed as in II.10(a).

1H-heptafluorocyclohexa-1,3-diene (0.67g) gave a mixture (0.56g, 84%) consisting of starting material (98.8%) 1H-heptafluorocyclohexa-1,4-diene (1.2%) and traces of hydrogen fluoride.

2H-heptafluorocyclohexa-1,3-diene (0.34g) gave a mixture (0.28g, 82.4%) consisting of starting material (91.9%) 1H-heptafluorocyclohexa-1,3-diene (1.4%), 1H-heptafluorocyclohexa-1,4-diene (6.7%) and traces of hydrogen fluoride.

1H-heptafluorocyclohexa-1,4-diene (0.38g) remained unchanged.
(ii) About 0.4g of each isomer was introduced into separate small evacuated Carius tubes (1cm int.diam. x 11cm) as in (i). They were heated in a nitrogen gas fluidised sand bath for three weeks at 300°C ± 5°C. The cooled tubes were opened and analysed as in (i). 1H- and 2H-heptafluorocyclohexa-1,3-diene had both charred considerably, 1H-heptafluorocyclohexa-1,4-diene was pale brown.

1H-heptafluorocyclohexa-1,3-diene (0.43g) gave a mixture (0.37g, 86%) containing seven components including starting material. g.l.c. coupled with mass spectroscopic analysis was complex and inconclusive but it did indicate the longer retained components had molecular weight at least twice that of the starting material.

2H-heptafluorocyclohexa-1,3-diene (0.40g) gave a complex mixture (0.34g, 85%) containing at least ten components. g.l.c. coupled with mass spectroscopic analysis indicated most of these had molecular weights greater than 206.

1H-heptafluorocyclohexa-1,4-diene (0.32g) remained unchanged.

(iii) About 7.0g of 1H-heptafluorocyclohexa-1,3-diene was vacuum transferred into an evacuated 100cm³ pyrex ampoule as in (i). The sealed ampoule was placed in a steel tube inside a Carius furnace and heated for 22 hours at 300°C, after which it was opened and the product vacuum transferred into a tared tube; product reluctant to transfer was pumped over. It was analysed as in (i).

1H-heptafluorocyclohexa-1,3-diene (7.3g) gave a complex mixture (6.7g, 92%) containing at least eight components of which two, with the shortest g.l.c. retention times, were starting material and 1H-heptafluorocyclohexa-1,4-diene.
II. Irradiations

Irradiations were carried out in a quartz ampoule (40 cm x 2.5 cm diameter). 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 RPR 204 photochemical reactor using 253.7 nm lamps. The reactor was placed over a powerful fan to maintain the temperature below 25°C. 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 the reaction the products were removed from the quartz tube by vacuum transfer.

1H-heptafluorocyclohexa-1,3-diene (4.4g, 21.6mmoles) was irradiated for 14 days. The volatile liquid recovered (4.26g, 96.8%) was shown by analytical gas chromatography (Col.A, 40°C) to be a pure compound, 2,3,4,5,5,6,6 heptafluorobicyclo [2,2,0] hex-2-ene (Found: C, 34.5%; H, 0.5%; F, 64.6%; M (mass spectrometry), 206. C$_6$F$_7$H requires C, 34.7%; H, 0.5%; F, 64.8%; M, 206), a colourless liquid, ν max.1770 cm$^{-1}$(CF=CF), and 3,000 cm$^{-1}$(C-H).
APPENDIX A

APPARATUS AND INSTRUMENTS
Vacuum System

Volatile compounds were handled in a conventional vacuum system incorporating a mercury diffusion pump and rotary oil pump.

Mass Spectra were measured with an A.E.I. spectrometer at an ionizing beam energy of 70 eV.

Combined g.l.c./mass spectra - V.G. Micromass 12B coupled to a Pye 104 Gas Chromatograph.

Infrared Spectra were recorded with both a Perkin-Elmer 457 and 557 Grating Infrared Spectrophotometer.

Ultraviolet Spectra were recorded with a Unicam SP800 spectrophotometer.

N.M.R. Spectra were measured with either a Bruker Spectrospin HX 90E High Resolution N.M.R. Spectrometer (operating at 84.67 MHz for $^{19}$F and 90.0 MHz for $^1$H spectra), or a Varian A56/60 spectrometer (operating at 56.40 MHz for $^{19}$F and 60.0 MHz $^1$H, operating temperature 40°C); unless otherwise stated. $^{19}$F chemical shifts are in p.p.m. from external fluorotrichloromethane (positive upfield) and $^1$H shifts are measured on the $^*$ scale relative to external tetramethylsilane.

Analytical Gas Liquid Chromatography (g.l.c.)

A Perkin-Elmer 452 gas chromatograph using hydrogen as carrier gas and a hot wire detector were used and also a Griffin Gas Density Balance (GDB) Chromatograph using nitrogen as carrier gas and a gas density balance detector.
Column designations were:

452 Column A; 2.2m x 7 mm diameter, with a stationary phase of di-n-decylphthalate/Celite 1:2.

GDB Column A: 2.0m x 5mm diam., with a stationary phase of di-n-decylphthalate/Celite 1:2.

Preparative g.l.c. - The chromatograph, not of commercial origin, used white spot nitrogen as the carrier gas and a hot wire detector.

Column A: 4.9m x 75mm diam., dinonylphthalate/Celite 1:2.

The carrier gas flow rate was approximately 60l/hr.

Carbon and Hydrogen Analysis were carried out with a Perkin-Elmer 240 CHN Analyser.
APPENDIX B

MASS SPECTRA
The mass spectra of compounds produced in the course of this work are tabulated below. Ions are tabulated in the form:

187(10%, C₆F₆H, P-F)

In this example the ion has a mass number 187, its intensity is 70% of the intensity of the base peak of the spectrum, it has been provisionally assigned the formula C₆F₆H⁺ (the + being understood), and its supposed origin is loss of a fluorine from the parent ion (P). The base peak is designated B.

Metastable ion Peaks where observed, are tabulated underneath the main spectrum in the form M* (M₁-Fr → M₂), where the metastable ion is understood to have been observed at.

\[ M^* = \frac{M_2^+}{M_1^+} \]

for the loss of neutral fragment Fr⁺ from ion M₁⁺ to give M₂⁺.

1H-heptafluorocyclohexa-1,3-diene

\[
\begin{array}{c}
\text{H} \\
\text{F}
\end{array}
\]

206 (32.1%, C₆F₇H₁, PARENT), 187 (26.1%, C₆F₆H, P-F), 168 (9.7%, C₆F₅H, P-F₂), 156 (19.4%, C₅F₅H, P-CF₂), 149 (10.5%, C₆F₄H, P-F₃), 137 (100%, C₅F₄H, BASE PEAK, P-CF₃), 119 (15.7%), 106 (22.4%, C₄F₃H, P-C₂F₄), 69 (20.9%, CF₃)

Metastable ions: 206→ 137 (-CF₃) at 91.1, 187→ 137 (-CF₂) at 100.4, 156→ 137 (-F) at 120.3, 156→ 106 (-CF₂) at 72
2H-heptafluorocyclohexa-1,3-diene

\[
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.5\textwidth]{cyclohexa_diene.png}};
\end{tikzpicture}
\]

206 (34%, \(C_6F_7H\), PARENT), 187 (27%, \(C_6F_6H\), P-F), 186 (28%, \(C_6F_6\), P-HF)
169 (18%), 168 (14%, \(C_6F_5H\), P-F₂), 156 (20%, \(C_5F_5H\), P-CF₂)
150 (12%, \(C_3F_6\), P-C₃F₄), 149 (28%, \(C_6F_4H\), P-F₃), 138 (17%)
137 (100%, \(C_5F_4\), BASE PEAK, P-CF₃), 119 (82%, \(C_2F_5\))
106 (22%, \(C_4F_3H\), P-C₂F₄), 99 (12%, \(C_5F_2H\), P-CF₅)
93 (10%), 88 (17%), 75 (14%), 69 (32%, CF₃)

Metastable Ions: 206 \(\rightarrow\) 137 (CF₃) at 91.1, 187 \(\rightarrow\) 137 (CF₂) at 100.4

Perfluorocyclohexa-1,3-diene

\[
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.5\textwidth]{cyclohexa_diene.png}};
\end{tikzpicture}
\]

224 (46%, \(C_6F_8\), PARENT), 205 (40%, \(C_6F_7\), P-F), 186 (12%, \(C_6F_6\), P-F₂)
174 (31%, \(C_5F_6\), P-CF₂), 155 (100%, \(C_5F_5\), BASE PEAK, P-CF₃),
124 (46%, \(C_4F_4\), P-C₂F₄), 117 (21%, \(C_5F_3\), 105 (13%, \(C_4F_3\))

1,2,3,4,5,5,6,6,-octafluorobicyclo [2,2,0] hex-2-ene

\[
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.5\textwidth]{bicyclo.png}};
\end{tikzpicture}
\]

224 (23.5%, \(C_6F_8\), PARENT), 205 (18%, \(C_6F_7\), P-F), 186 (4%, \(C_6F_6\), P-F₂)
174 (27%, \(C_5F_6\), P-CF₂), 155 (100%, \(C_5F_5\), BASE PEAK, P-CF₃),
124 (71%, \(C_4F_4\), P-C₂F₄), 117 (12%), 105 (12%, \(C_4F_3\)).
1,3,4,5,5,6,6-heptafluorobicyclo[2,2,0]hex-2-ene

\[
\begin{array}{c|c|c}
\text{H} & \text{F} & \text{F} \\
\end{array}
\]

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-CF_4), 99 (5.8\%), 93 (11.1\%, C_3F_3),
87 (44\%), 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

2,3,4,5,5,6,6-heptafluorobicyclo[2,2,0]hex-2-ene

\[
\begin{array}{c|c|c}
\text{H} & \text{F} & \text{F} \\
\end{array}
\]

206 (37.4\%, C_6F_7H, PARENT), 187 (15.2\%, C_6F_6H, P-F)
156 (23.2\%, C_5F_5H, P-CF_2), 137 (100\%, C_5F_4H, BASE PEAK, P-CF_3),
106 (48.5\%, C_4F_3H, P-CF_4), 93 (12.1\%, C_3F_3), 75 (20.2\%),
69 (26.3\%, CF_3).

Metastable ions: 156→137 (-F) at 120.3, 187→137 (-CF_2) at 100.4,
206→137 (-CF_3) at 91.1
APPENDIX C

INFRARED SPECTRA
Infrared spectra are given in the order (I), (II), ..., (L).

All spectra were measured using KBr cells, and were run under conditions designated by

- (A) - KBr disc
- (B) - Nujol. mull: Nujol bands are marked 'n' on the spectra
- (C) - thin liquid film

<table>
<thead>
<tr>
<th>Compound Number</th>
<th>Name of Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Perfluorocyclohexa-1,4-diene (c)</td>
</tr>
<tr>
<td>II</td>
<td>Perfluorocyclohexa-1,3-diene (c)</td>
</tr>
<tr>
<td>III</td>
<td>1H-heptafluorocyclohexa-1,4-diene (c)</td>
</tr>
<tr>
<td>IV</td>
<td>1H-heptafluorocyclohexa-1,3-diene (c)</td>
</tr>
<tr>
<td>V</td>
<td>2H-heptafluorocyclohexa-1,3-diene (c)</td>
</tr>
<tr>
<td>VI</td>
<td>Pentafluorobenzene (c)</td>
</tr>
<tr>
<td>VII</td>
<td>Hexafluorobenzene (c)</td>
</tr>
<tr>
<td>VIII</td>
<td>1,2,3,4,5,5,6,6-octahydrobicyclo[2,2,0] hex-2-ene (c)</td>
</tr>
<tr>
<td>IX</td>
<td>2,3,4,5,5,6,6-heptafluorobicyclo[2,2,0] hex-2-ene (c)</td>
</tr>
</tbody>
</table>
REFERENCES
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