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A Study of the Thermolyses of Polyfluoroaryl-Prop-2-ynyl  
Ethers in Inert Solvents and with Alkenes

By

Alan G. Morpeth, B.Sc., G.R.S.C.  
(Graduate Society)

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Undertaken to obtain an M.Sc. (part-time) at the University of Durham,  
Department of Chemistry from October 1981 until October 1983



P्रेस  
1983.10.12

To the memory of my parents and to my remaining  
family for their continuing support

'Spiritus intus alit, totamque infusa per artus  
Mens agitat molem et magno se copore miscet'

The spirit within nourishes, and mind instilled  
throughout the living parts activates the whole  
mass and mingles with the vast frame.

Virgil Aeneid. VI. 726.

## ACKNOWLEDGEMENTS

The author wishes note to be taken of the invaluable assistance given to him by the following people. Principally Dr. G.M. Brooke for his continued guidance and supervision. To Dr. I. Sadler, University of Edinburgh, for access to that Institute's n.m.r. analysis facilities and Dr. R.S. Matthews, University of Durham, for his assistance in the interpretation of  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. analysis.

Among the technical staff of the University of Durham, Messrs Ray Hart and Gordon Haswell, whose technical expertise in the art of Glassblowing was very much appreciated, must be given special mention. The assistance given by all the technical staff, both those operating analytical services and all others, was gratefully accepted and their contributions were invaluable.

Finally on a more personal note may the author extend his gratitude to Mrs. Eileen Duddy without whom this thesis could not have been presented, to Jenny and Phil who made the author's stay in Durham such a pleasure, to Niki and Dave for their gift of friendship, to Pam and Doug McCourt who made many an evening more bearable, lastly Dr. Ray Denman who generously accepted the task of proof-reader for this publication.

MEMORANDUM

Notes to the Reader.

Throughout this text a number of abbreviations are commonly used, these are:

n.m.r. Nuclear magnetic resonance spectroscopy

i.r. Infra-red spectroscopy

t.l.c. Thin layer chromatography

## ABSTRACT

In this research the thermal reactions of polyfluoroaryl prop-2-ynyl ethers in inert solvents and with alkenes was investigated.

Chapter 1 discusses the history of the Claisen and Cope rearrangements with particular reference to the scope, mechanism and stereochemistry of these reactions. Chapter 2 examines the behaviour of aryl prop-2-enyl and aryl prop-2-ynyl ethers when the ortho, para or both positions in the aromatic ring are substituted and illustrates the formation of both internal Diels-Alder adducts and cyclisation products.

Chapter 3 reports the behaviour of polyfluoroaryl prop-2-ynyl ethers and includes the first period of the author's own work. The thermolysis of these ethers was undertaken in a non-vitreous environment in both n-decane and 1,1,2-trichlorotrifluoroethane leading to large quantities of the cyclisation products: 2-fluoromethyl-4,5,6,7-tetrafluorobenzo[b]furan (117) from pentafluorophenyl prop-2-ynyl ether (115) and 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) from 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (120).

The final chapter describes the second period of the author's work in which the thermolyses of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (120) and 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) in the presence of (Z)-but-2-ene (120 only), 2,3-dimethylbut-2-ene and 3,3-dimethylbut-1-ene respectively were examined. The formation of the following novel alkenes is reported: 2-(2-methylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (137), 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138), 2-(2,2,3-trimethyl-

but-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139) and 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho-[1,2-b]furan (140). The latter's formation was attributed to the presence of 2,3,4,5,6,7,8-heptafluoro-1-naphthyl prop-2-ynyl ether (142) in the starting material, ether (120). The Chapter is concluded with a discussion of the mechanistic implications of the formation of compounds (138) and (139) from the two C<sub>6</sub> alkenes in reaction with the ether (120) and the 2-fluoromethyl derivative (126). The particular reactions of 3,3-dimethylbut-1-ene with (120) and with (126) are especially interesting. Three mechanistic routes have been submitted to account for the products formed in these reactions: (a) that the formation of (138) and (139) requires an initial anti-Markownikov addition of a carbocation, subsequent rearrangement and proton loss; (b) that the formation of (138) and (139) requires initial attack by F<sup>•</sup> followed by anti-Markownikov adduct formation, ionisation by loss of F<sup>-</sup> yielding a primary carbocation which rearranges and then loses a proton; and (c) that the formation of (138) and (139) really involves 2,3-dimethylbut-2-ene - formed by prior isomerisation of the terminal alkene by H<sup>+</sup>.

DECLARATION

I hereby declare that this work was undertaken in the Department of Chemistry, University of Durham between October 1st, 1981 and October 1st, 1983. Further, that this is the Author's own work except where acknowledged by reference, and that it has not been submitted for any other degree than the one stated.

A handwritten signature in cursive script, appearing to read 'A.G. Morpeth', written in black ink.

A.G. Morpeth

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## CHAPTER 1

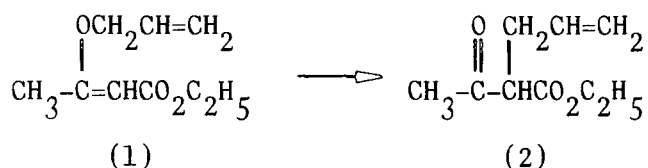
### The Claisen and Cope Rearrangements: Scope, Mechanism and Stereochemistry

#### 1.1. Introduction

The principal aim of this investigation is to examine the mechanism of cleavage of the  $sp^3$  carbon-fluorine bond in the Claisen rearrangement products obtained from the vapour and liquid phase thermolyses of polyfluoroaryl allyl ethers.

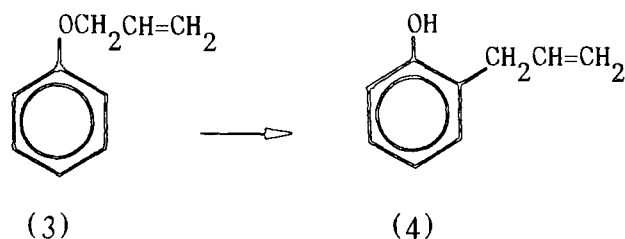
#### 1.2. The Claisen Rearrangement

Allyl ethers of enols and phenols undergo a skeletal rearrangement to C-allyl derivatives when heated at high temperatures. Claisen observed that compound (1), when distilled in the presence of ammonium chloride rearranged to isomer (2)<sup>1</sup> (Scheme 1).



Scheme 1

The Claisen rearrangement is better known for the rearrangement of allyl phenyl ethers to ortho allyl phenols as illustrated by (3) and (4)<sup>2</sup> (Scheme 2). When the ortho position is

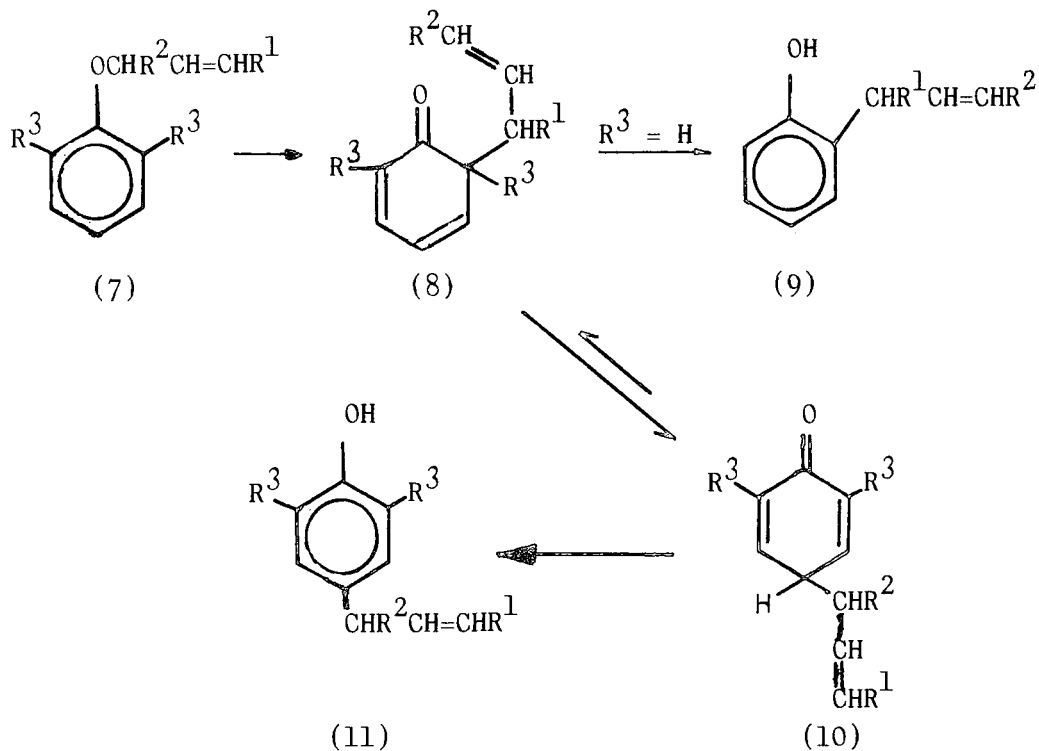


Scheme 2

substituted, the initial Claisen rearrangement may be followed by a Cope rearrangement which is the all carbon analogue of the Claisen, first observed in 1,5-hexadienes<sup>3</sup> to yield the para-allyl phenol



(11).<sup>4</sup> There are many examples of products from the Claisen rearrangement in the literature and the topic has been widely reviewed.<sup>4-12</sup> The behaviour of allylic phenyl ethers may be summarised by Scheme 3.<sup>9</sup> It can be seen that the thermal



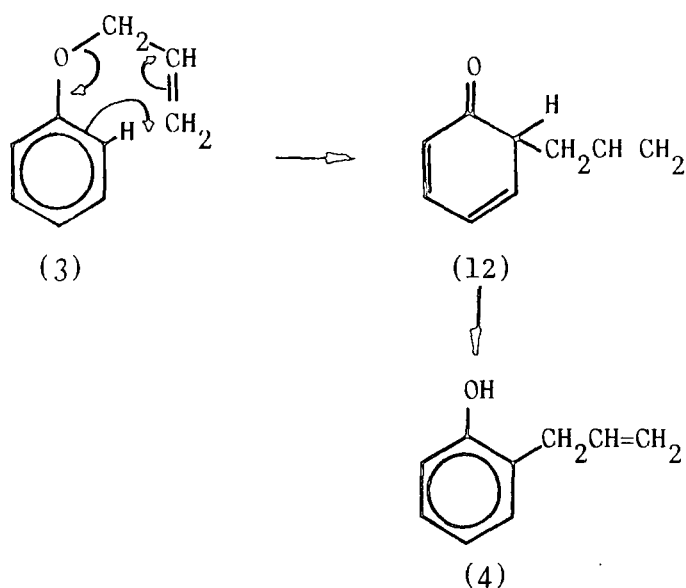
Scheme 3

rearrangement of ether (7) proceeds by an intramolecular pathway yielding an ortho dienone (8) which when  $R^3 = H$  rapidly enolises to the 2-(2,3-alkenyl)phenol (9). The result of this process is that the  $\gamma$ -carbon of (7) becomes directly attached to the ortho position of the benzene ring in phenol (9), a process referred to as inversion. If however the ortho-position is substituted i.e.  $R^3 \neq H$  then enolisation is not possible and a subsequent Cope rearrangement generates the para-dienone (10) which will enolise to yield the 4-(2,3-alkenyl)phenol (11); in this situation  $R^3 \neq H$  there are two reversals of ends of attachment and the carbon which was initially attached to oxygen in (7) is now directly attached to the benzene ring in (11).

### 1.3. The Mechanism of the Claisen Rearrangement

Although Claisen proposed an intramolecular mechanism involving the simultaneous making and breaking of a carbon bond coupled with the rearrangement of the double bond as early as 1925,<sup>13</sup> it was not until the 1960's that the intramolecular processes involved in the rearrangement were fully explained.

In early mechanistic work, the Claisen rearrangement to the ortho position was shown to be a first order reaction<sup>14,15</sup> which does not require catalysis by either acids or bases. The intramolecular nature of the reaction was illustrated by the absence of cross products in a number of rearrangements: e.g. the transformation of a mixture of allyl-2-naphthyl ether and cinnamyl phenyl ether<sup>16</sup>; or cinnamyl 4-methyl-phenyl ether and allyl-4-amino phenyl ether.<sup>17</sup> The conclusions drawn during this period suggested that the rearrangement was best explained by a cyclic mechanism<sup>4</sup> (Scheme 4), in which the cleavage of the carbon-



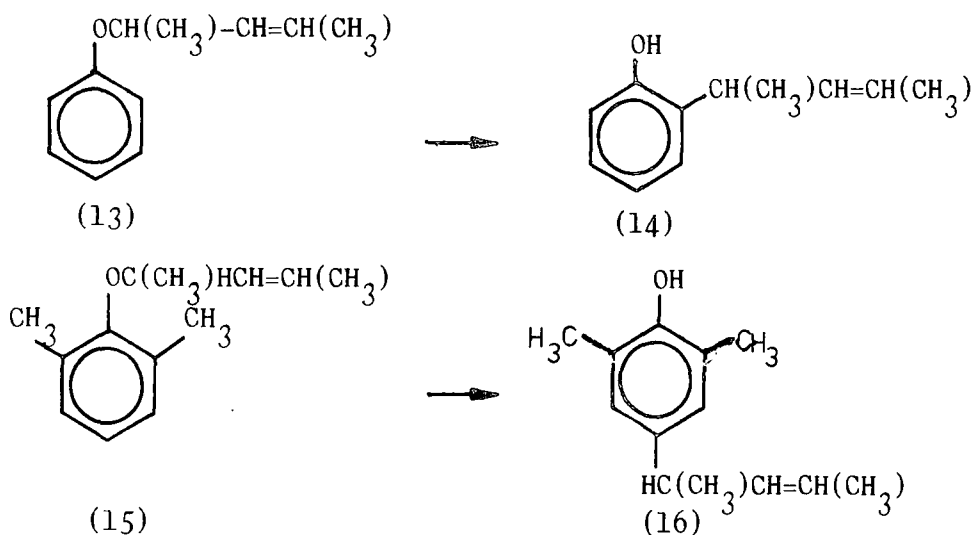
Scheme 4

oxygen bond occurs as the  $\gamma$ -carbon becomes attached to the ortho position in the benzene ring, and this step rather than

enolisation was rate determining.<sup>18</sup>

The rearrangement to the para-position was also shown to be first order<sup>19</sup> but at that time the atomic distances were believed to rule out the probability of a cyclic mechanism, and it was postulated that the para transformation was the result of either radical or ionic interactions.<sup>4</sup>

Throughout the 1950's a great deal of investigative work was undertaken to identify the nature of the mechanism of the Claisen rearrangement. Conroy and Firestone<sup>20,21</sup> first postulated, and later isolated the intermediate ortho-dienone, via a maleic anhydride adduct. Curtin *et al.*<sup>22-24</sup> isolated and rearranged 6-allyl-2,6-dimethyl-2,4-cyclohexadienone, and so illustrated the probability of an intermediate cyclohexadienone in the para-Claisen rearrangement. Schmid *et al.*<sup>25-28</sup> were able to show, using a  $\gamma$ -<sup>14</sup>C labelled compound, that both the ortho- and para-Claisen transformations required an intermediate cyclohexadienone. Finally Alexander and Kluiber<sup>29</sup> were able to confirm the cyclic mechanism of the rearrangement, when they observed retention of configuration in the rearrangements of optically active 1,3-dimethylallylphenyl ether (13) and 1,3-dimethylallyl(2,6-dimethyl)phenyl ether (15) (Scheme 5).



Scheme 5

Despite the work during the 1950's the rearrangement was still categorised as a 'No Mechanism' reaction<sup>11</sup> until 1965 when the Claisen rearrangement and other transformations of that type were defined by Woodward and Hoffmann as examples of sigmatropic rearrangements.<sup>30</sup>

#### 1.4. The Claisen Rearrangement as a Sigmatropic Transformation

Sigmatropic rearrangements are concerted reactions of the type shown (Figure 1). Group G migrates with its  $\sigma$ -bond in a  $\pi$ -framework, the reaction is accomplished by a shift in the  $\pi$ -bonds.

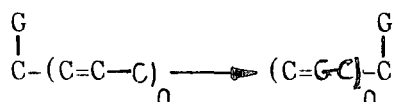
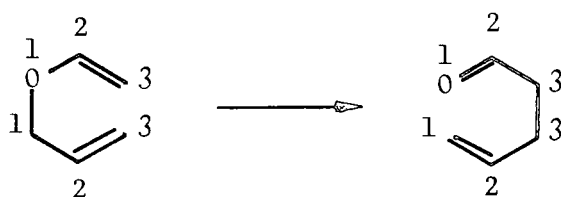


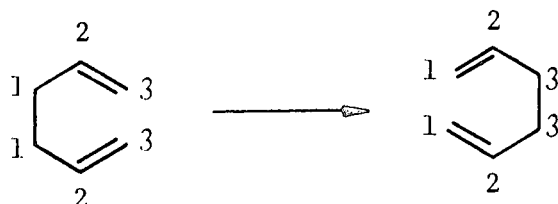
Fig. 1. General Example of a Sigmatropic Transformation

Woodward and Hoffmann define these shifts as a 'sigmatropic change of order [i,j]',<sup>30</sup> where i and j indicate the number of the atom to which each end of the migrating  $\sigma$ -bond goes, numbering from the original two atoms forming the original  $\sigma$ -bond. The  $\sigma$ -bond, which is flanked by one or more  $\pi$ -electron systems, migrates to its new position during a concerted reorganisation of the system.

Mechanistically the concerted nature of a sigmatropic rearrangement requires a cyclic transition state in which the migrating group is attached to both the source and the terminus of the migration. Bonding in the transition state can be seen as an overlap of an orbital lobe or lobes in migratory group G, with an orbital of an allylic system, i.e. the  $\pi$ -framework. The Claisen and Cope rearrangements may both be seen as [i = 3, j = 3] transformations (Figure 2); the bond which appears to connect two allyl systems at positions 1,1 rearranges via two  $\pi$ -electron systems to positions 3,3 producing the changes illustrated (Figure 2). In the transition state the Highest Occupied Molecular



Claisen Rearrangement of allyl vinyl ethers



Cope Rearrangement of 1,5-hexadienes

Fig. 2. Claisen and Cope Rearrangements as [3,3] Shifts

Orbital (HOMO) of one component overlaps with the HOMO of the other, each HOMO is singularly occupied and their combination yields an electron pair. The migrating group G passes from one end of the allylic system to the other and therefore the terminal carbons are of principal concern. In the HOMO of the  $\pi$ -framework the length of the chain dictates the phase of the terminal carbons. The symmetry of the HOMO in  $(C-G-C)_n$  alternates regularly and so the HOMO varies according to the number of carbons involved in the rearrangement (Figure 3).

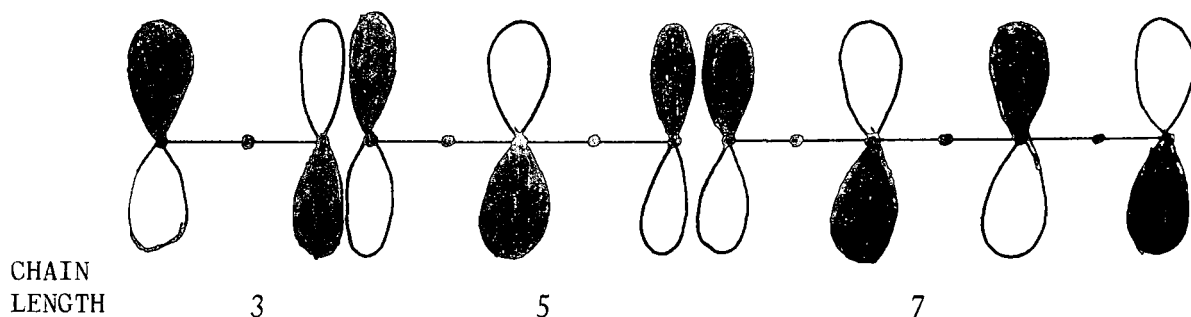


Fig. 3. HOMO of various carbon skeletons

In the Cope and Claisen rearrangements the migrating species is a 3-carbon chain and in carbon migrations there exist two possible bonding overlaps in the transition state of the sigmatropic

transformation. These are: (a) overlap of a single carbon orbital lobe with both ends of the  $\pi$ -framework, (b) overlap through two lobes on the migrating carbon.

Depending on the symmetry of the  $\pi$ -system, the symmetry-allowed migration may be suprafacial or antarafacial (Figure 4). By bonding through a single lobe on the migrating carbon the

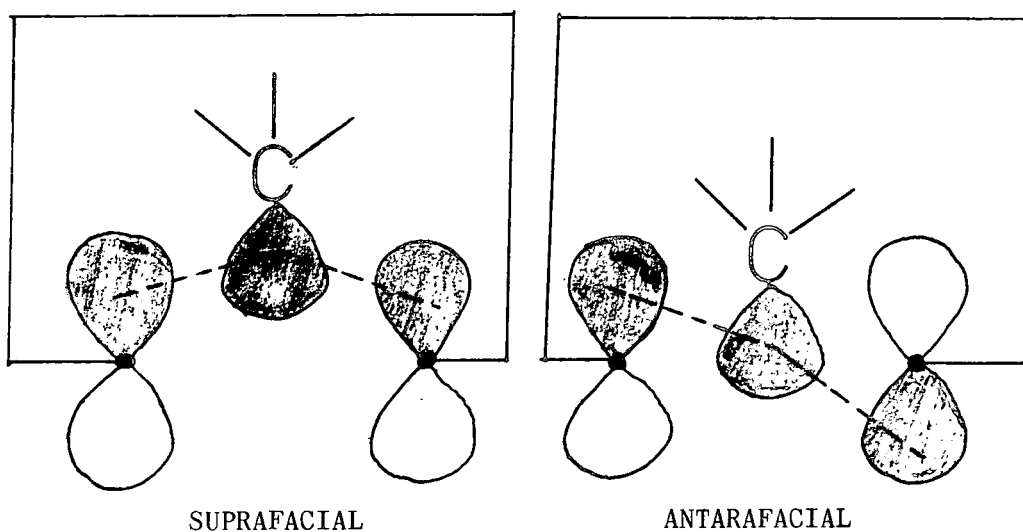


Fig. 4. Carbon Migration Single Lobe Overlap

stereochemical configuration of the migrating group is retained. The second possibility, overlap through two p-lobes will lead to inversion of configuration (Figure 5).

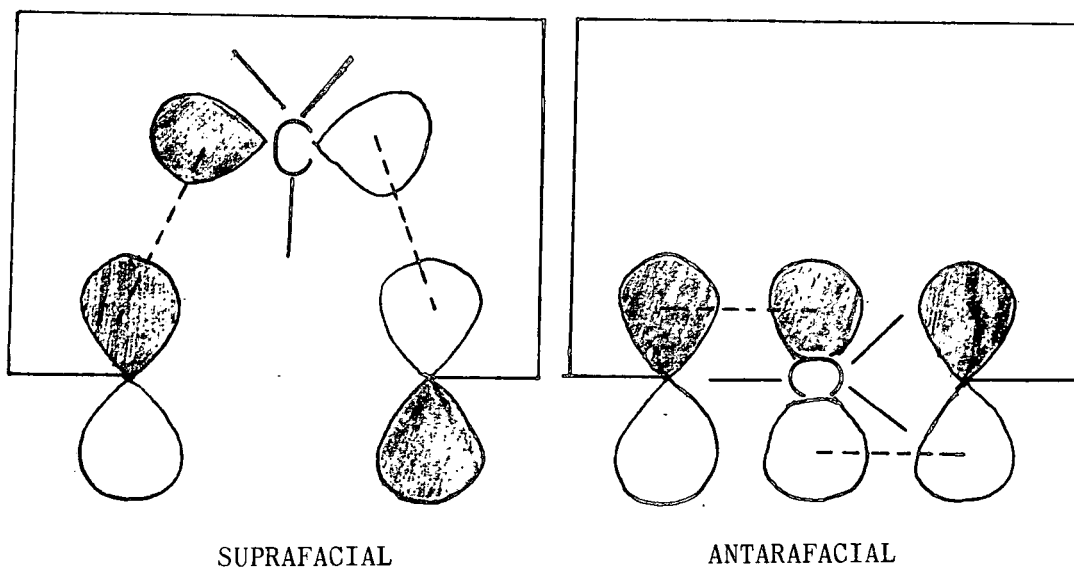


Fig. 5. Carbon Migration Overlap with Two P-Lobes

### 1.5. The Claisen Rearrangement - The Molecular Orbital Explanation

Both the Claisen and Cope rearrangements illustrated in Figure 2 have been categorised as [3,3] sigmatropic transformations. It is possible to show by use of the phase relationships of the Highest Occupied Molecular Orbital (HOMO), that for rearrangements of the order [i,j] in which both i and j are greater than one, thermal changes are symmetry allowed only when  $i + j = 4n + 2$  whilst a photochemically induced transformation requires  $i + j = 4n + 1$  where n is the number of electrons in the transition state. A pictorial representation of the [3,3] shifts may be devised by considering the  $\pi$ -electron system over the 3 carbons of the allyl group under Hückel Orbital Theory.<sup>31</sup> These can be described by three molecular orbitals  $\psi_1$ ,  $\psi_2$  and  $\psi_3$  which may be occupied by only two paired electrons (Figure 6). The three energy levels are defined as: bonding, non-bonding and anti-bonding. In Figure 6 each lobe of the wavefunctions has a phase (designated + or -), bonding can only occur between wavefunctions of the same phase.

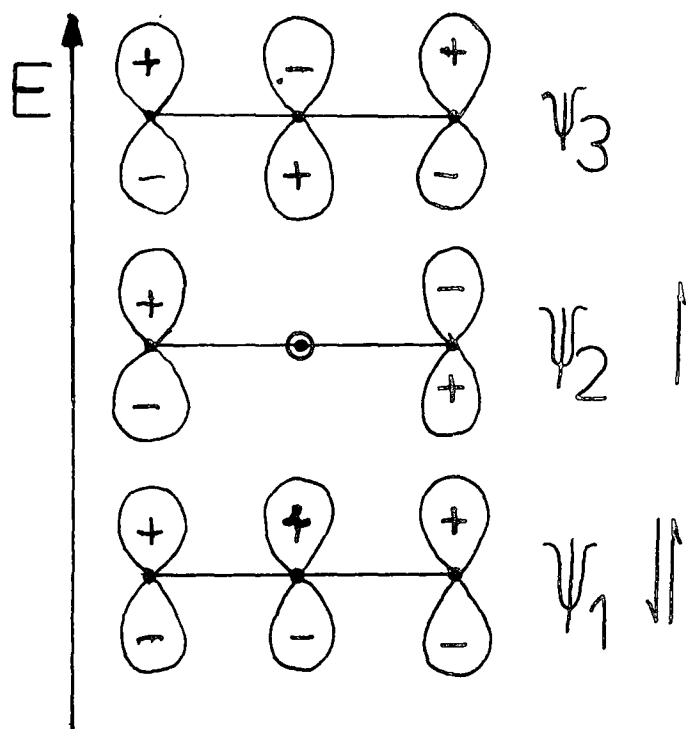


Fig. 6. Molecular Orbitals of the Allyl Group

In the allyl radical, which has three electrons as shown (Figure 6), the HOMO is represented by  $\psi_2$ . Given that both the Claisen and Cope rearrangements proceed via a concerted pathway involving the formation and overlap of allyl quasi radicals in the transition state it can be shown that with a HOMO of structure  $\psi_2$  the [3,3] rearrangement is allowed (Figure 7).

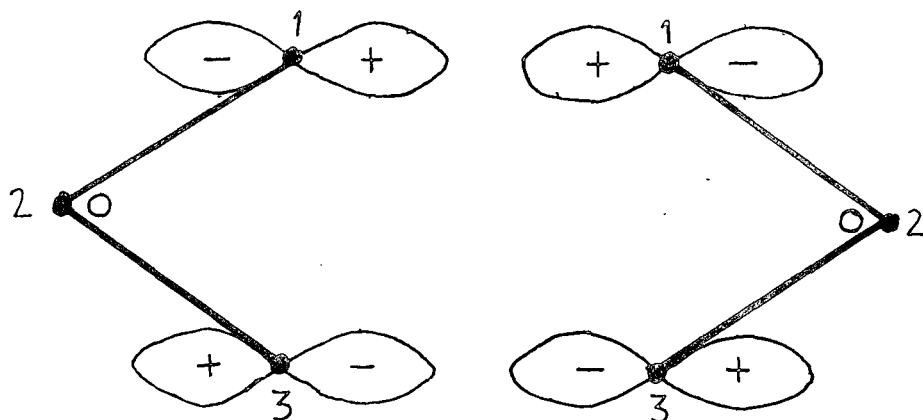


Fig. 7.  $\psi_2$  Orbital Symmetry Allows [3,3] Transformation

In this concept of the transition state atoms 1,1 and 3,3 are arranged so that the relative phases of the orbitals are maintained.<sup>9</sup> Further, this pictorial representation is consistent with the stereochemical requirement for intramolecular allylic transformations, which demands that bond breaking and bond formation both occur on the same side of the allyl group - a suprafacial migration.<sup>30</sup>

In the Claisen rearrangement of allyl phenyl ether and in the allyl migration shown by the all carbon analogue 4-phenylbut-1-ene, the highest occupied molecular orbital of the phenoxy and benzyl radicals is  $\psi_4$  (Figure 8).<sup>32</sup>

The HOMO for the benzyl and phenoxy radicals are very similar except in the position of the nodal planes with respect to the substituent. The diagram (Figure 8) illustrates how the phase of the wavefunction changes sign between the substituent and the ortho-

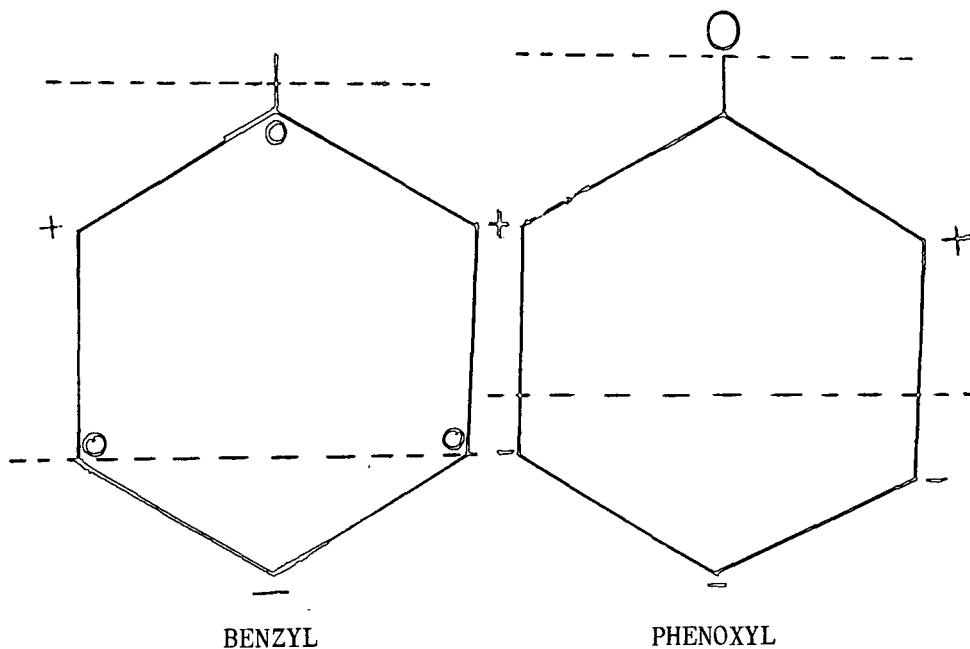


Fig. 8.  $\psi_4$  HOMO of Benzyl and Phenoxy Radicals position and again between the ortho- and para-positions.

The consequences of these features in the Claisen rearrangement ensures that in the transition state the allyl radical may be represented by  $\psi_2$  (Figure 7) and the phenoxy radical by  $\psi_4$  (Figure 8). The nature of the phases of the wavefunctions results in the migration of the allyl group to both the ortho- and para-positions being thermally allowed by the symmetry of the molecular orbitals (Figure 9).

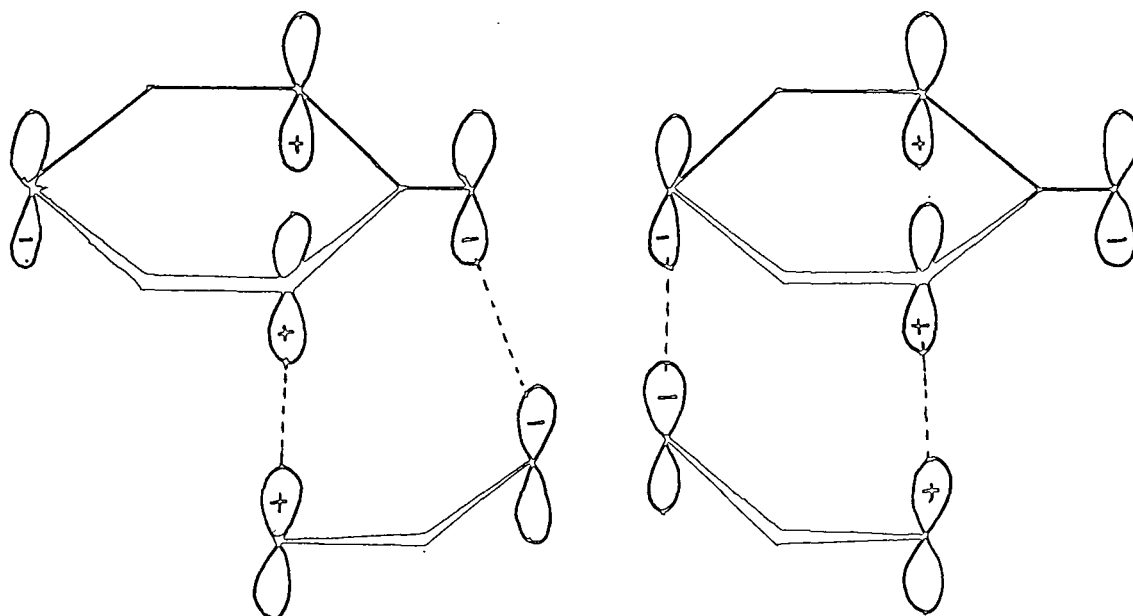


Fig. 9. Phase Relationships giving Thermally Allowed Migrations of the Allyl Group to both Ortho- and Para-Positions

Finally it should be noted that the migration of an allyl group to the ortho-position as observed in both the Claisen rearrangement of allyl phenyl ether, and the Cope transformation in 4-phenyl-but-1-ene, can be regarded either as a [3,3] or [3,7] sigmatropic shift depending on which direction the  $\sigma$ -bond migrates along the aromatic ring. Where there is a choice, Hoffmann recommends the assignment of minimum values to  $i$  and  $j$  to represent the shift.<sup>9</sup>

#### 1.6. The Stereochemistry of [3,3] Sigmatropic Transformations

In the preceding paragraphs the characterisation of both the Claisen and Cope rearrangements as suprafacial [3,3] sigmatropic shifts has been explained in mechanistic terms as requiring a cyclic transition state which may be seen as having two possible geometries: a chair-like arrangement (17), or a boat-like system (18) (Figure 10). For molecules which can adopt either system

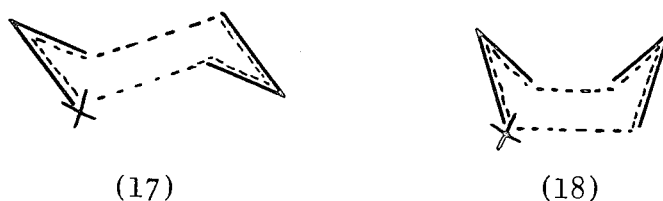
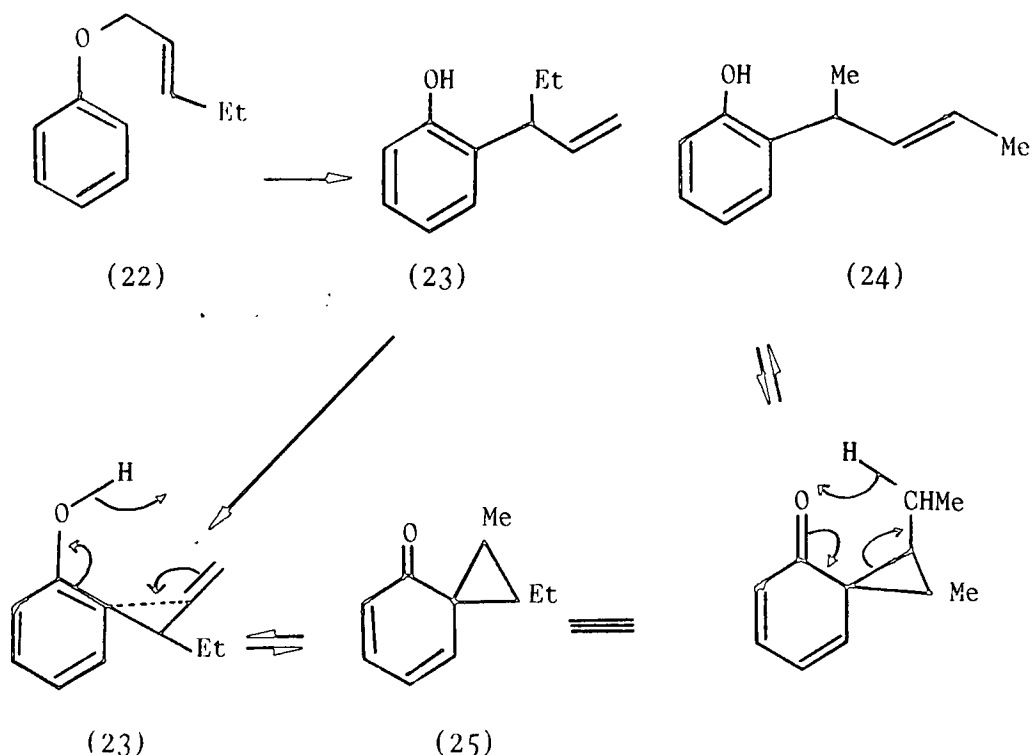


Fig. 10. Two Possible Geometries of Cyclic Transition State in [3,3] Suprafacial Migrations ( $X = O, C$ )

the chair (17) is strongly favoured.<sup>6</sup> Furthermore, of the two possible chair-like arrangements, the one which minimises diaxial interactions is preferred. These observations have been demonstrated for the Cope rearrangement of meso and racemic 3,4-dimethylhexa-1,5-diene,<sup>33</sup> in which the chair arrangement is favoured by a free energy of activation difference of 6 kcal/mol, whilst in the racemic mixture where two chair-like systems are available there is a free energy of activation difference of 2 kcal/mol (Scheme 6).

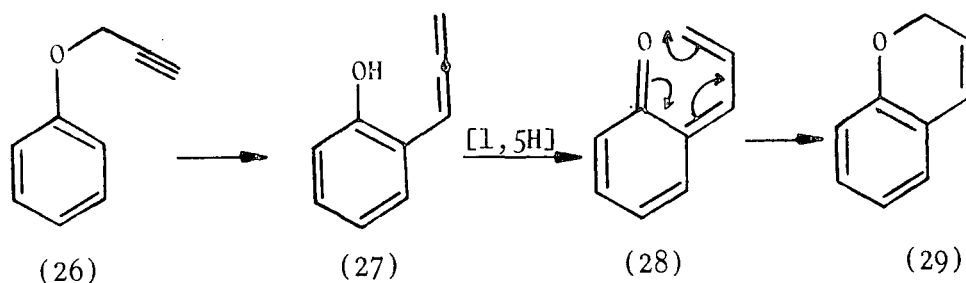


Claisen rearrangement, the original example of which was reported by Lauer and Filbert.<sup>39</sup> They observed that  $\gamma$ -ethyl-allyl phenyl ether (22) underwent a Claisen rearrangement to yield 2-( $\alpha,\gamma$ -dimethyl allyl)phenol (24) - not the expected 2-( $\alpha$ -ethyl-allyl)phenol (23). Later work showed that (23) was also present<sup>40</sup> (Scheme 7). The



Scheme 7

abnormal product is formed from the expected product<sup>40</sup> via two [1,5] homo-dienyl shifts. Equilibria of the type (23)  $\rightleftharpoons$  (25) may be set up in most Claisen rearrangements but they cannot lead to the formation of new products unless there is another alkyl group (Et above) on the side chain which is able to participate.<sup>41</sup> A reaction which is closely related to the abnormal Claisen rearrangement occurs when phenyl propynyl ether (26) is heated (Scheme 8). The product of the normal Claisen transformation  $\sigma$ -allenylphenol (27) is able to further rearrange by a [1,5]-H shift followed by electrocyclication to give the observed chromene (29).<sup>41</sup> The ortho-ortho Claisen



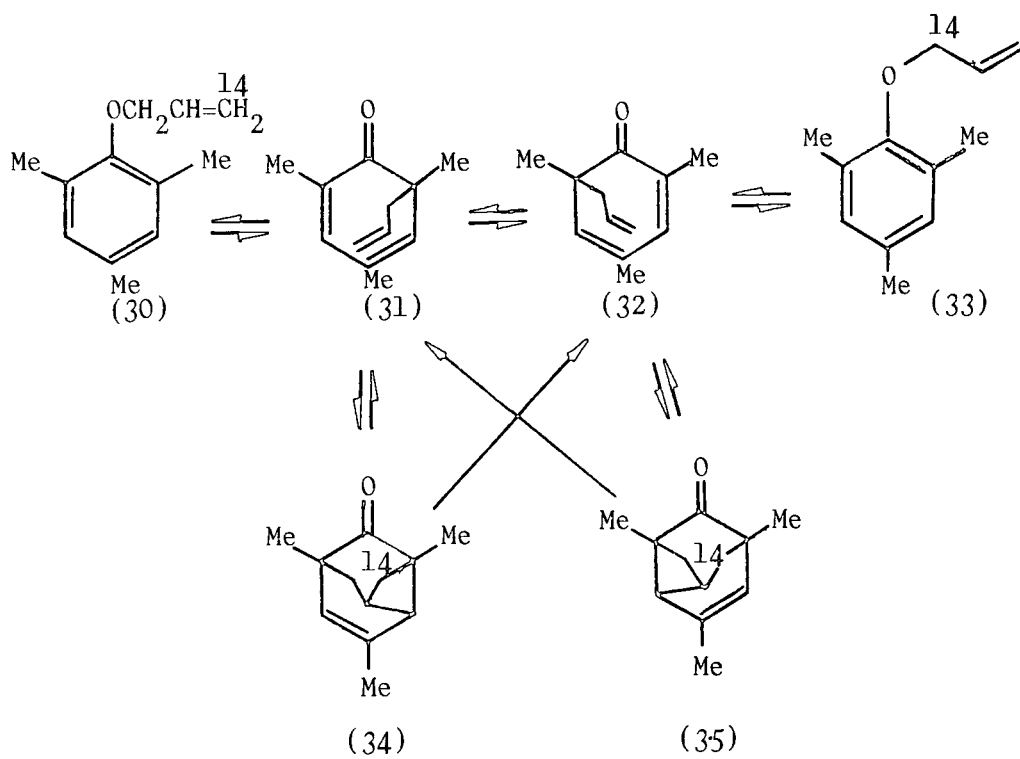
Scheme 8

transformation, which is also observed in aromatic systems like those already discussed, is not thermally allowed by Woodward-Hoffmann rules.<sup>30</sup> It has however been postulated by a number of workers to account for observed experimental results.<sup>42</sup>

If the rearrangement followed a concerted pathway through the  $\pi$ -system of the ring, it would be a [3,5] shift which is only thermally allowed via a suprafacial-antarafacial process, requiring a transition state whose geometry would be extremely difficult if not impossible to attain.

An alternative mechanism is a multi-stage process the first stage of which is the formation of an intramolecular Diels-Alder adduct derived from the addition of the allyl  $\pi$ -bond to the diene, the adduct then undergoes a stepwise fragmentation to yield the observed products. This pattern of reaction was first postulated by Schmid et al.<sup>42</sup> (Scheme 9).

The rearrangement was used to account for the distribution of radioactivity between  $\alpha$  and  $\gamma$  carbons observed when 2,4,6-trimethylphenyl allyl ether having  $\gamma$   $^{14}\text{C}$  (30) was heated. The radioactive distribution was accounted for by the occurrence of an ortho-ortho rearrangement ( $31 \rightleftharpoons 32$ ) with a reversal of ends of attachment. In the stepwise mechanism an internal Diels-Alder adduct (34, 35) is formed from the ortho-dienone (31, 32) and cleavage of the four membered ring completes the rearrangement.



Scheme 9

## CHAPTER 2

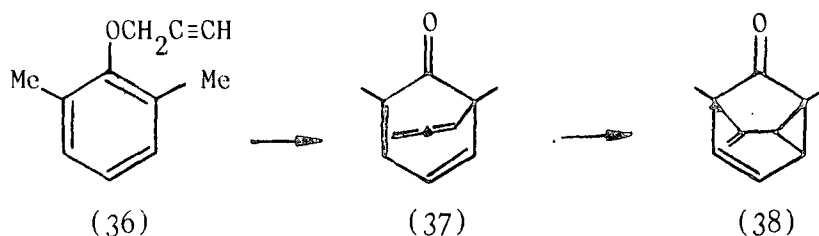
### Claisen Rearrangements Observed in Aryl Prop-2-ynyl and Aryl Prop-2-ynyl Ethers

#### 2.1. Introduction

In this chapter, an examination will be made of the important features of the behaviour of aryl allyl ethers when either the ortho, para or both positions are substituted, thus preventing enolisation to the 2-allyl phenol (9) or the 4-allyl phenol (11). One example of the remarkable behaviour of these substituted ethers is the ortho-ortho Claisen rearrangement discussed in detail in Chapter 1, Section 1.7.

#### 2.2. The Intramolecular Diels-Alder Addition

In Section 1.7 it was shown how Schmid *et al.*<sup>42</sup> postulated an intramolecular Diels-Alder adduct to account for observed results. Whilst the proposed Diels-Alder adducts (34, 35) were not isolated, in 1968 Schmid and co-workers<sup>43</sup> examined the thermolysis of 2,6-dimethylphenylprop-2-ynyl ether (36) and obtained adduct (38) (Scheme 10).



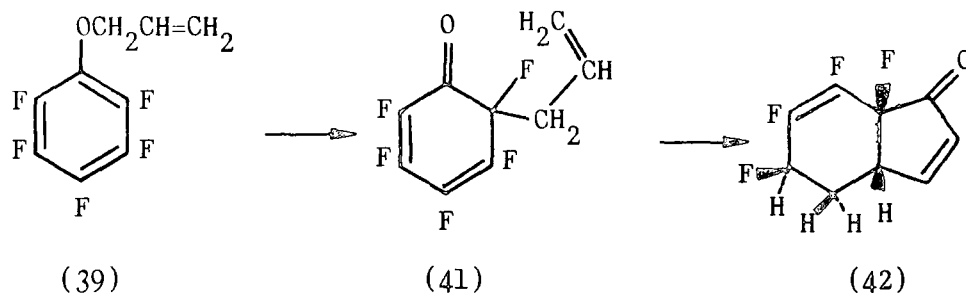
Scheme 10

The formation of the intramolecular adduct was rationalized in terms of a [3,3] sigmatropic rearrangement of the ether (36) to the ortho allenyl dienone (37), followed by ring closure to the tricyclic derivative (38).

In 1974 Brooke<sup>44</sup> also postulated the internal Diels-Alder

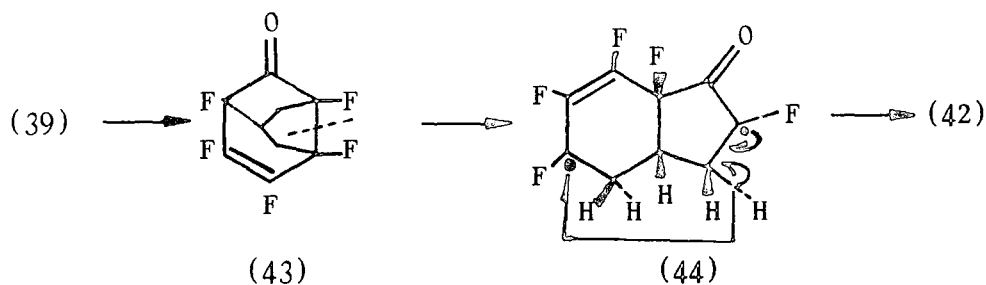
addition to account for the products formed when pentafluorophenyl prop-2-enyl ether (39), and [2,3,3-<sup>2</sup>H<sub>3</sub>]prop-2-enyl ether (40) were pyrolysed at 480° through a quartz tube packed with glass wool.

Pentafluorophenylprop-2-enyl ether (39) did not dehydrofluorinate on pyrolysis, as was expected, but instead isomerized to the bicyclic compound (42), via the Claisen intermediate ortho-dienone (41) (Scheme 11).



Scheme 11

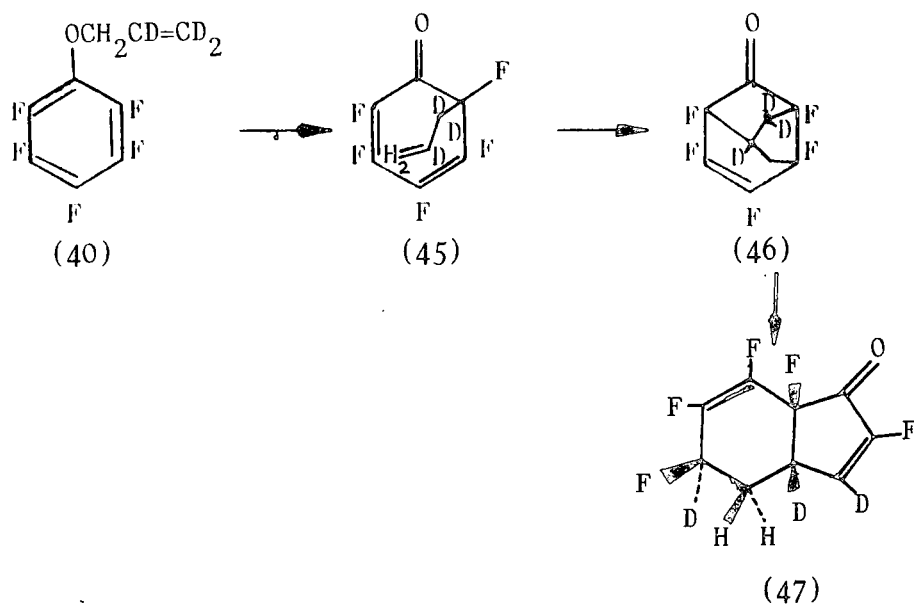
The formation of (42) requires that the adduct (43) be formed, followed by cleavage of a carbon-carbon bond to form the relatively stable diradical (44) which undergoes hydrogen abstraction to give (42) (Scheme 12).



Scheme 12

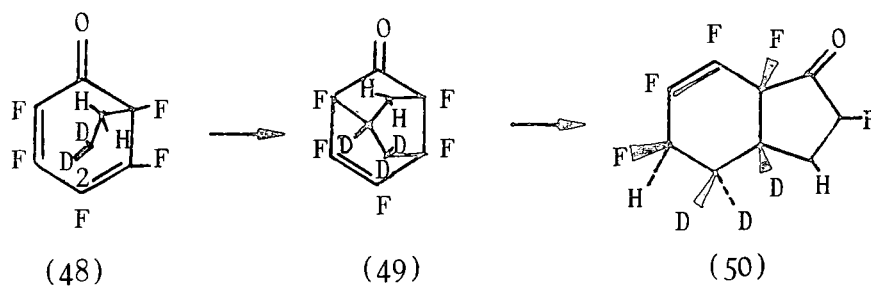
The described reaction sequence required that the hydrogen atoms on C<sub>3</sub> and C<sub>5</sub> in (42) were derived from the two terminal vinylic hydrogens in ether (39). To test this proposition the deuterated ether (40) was prepared, which was expected to undergo

the reaction sequence in Scheme 13.



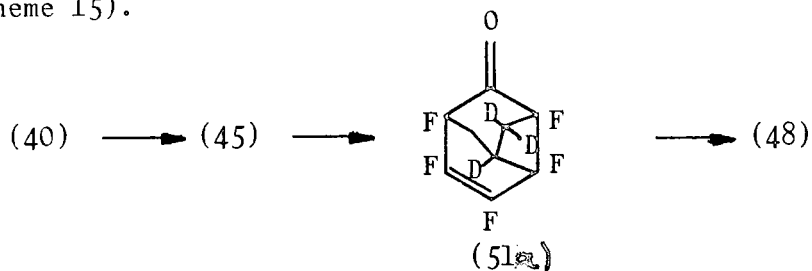
Scheme 13

On pyrolysis however the deuterated ether (40), did not give exclusively (47), but also produced an isomer (50) which required the precursor to (49) be obtained from (48) (Scheme 14).



Scheme 14

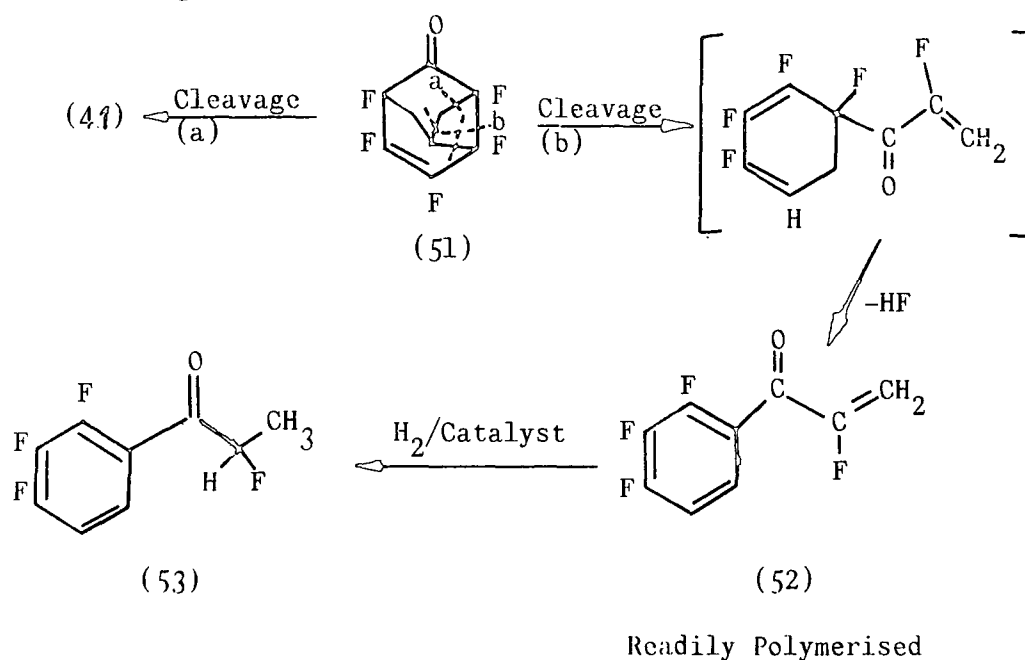
The most satisfactory explanation of this phenomenon was that the second possible Diels-Alder adduct (51a) was formed followed by a stepwise rearrangement as suggested by Schmid *et al.*<sup>42</sup> (Scheme 15).



Scheme 15

In a later paper, Brooke and Hall<sup>45</sup> showed how it was possible for the internal Diels-Alder adduct (51) to cleave in two ways:

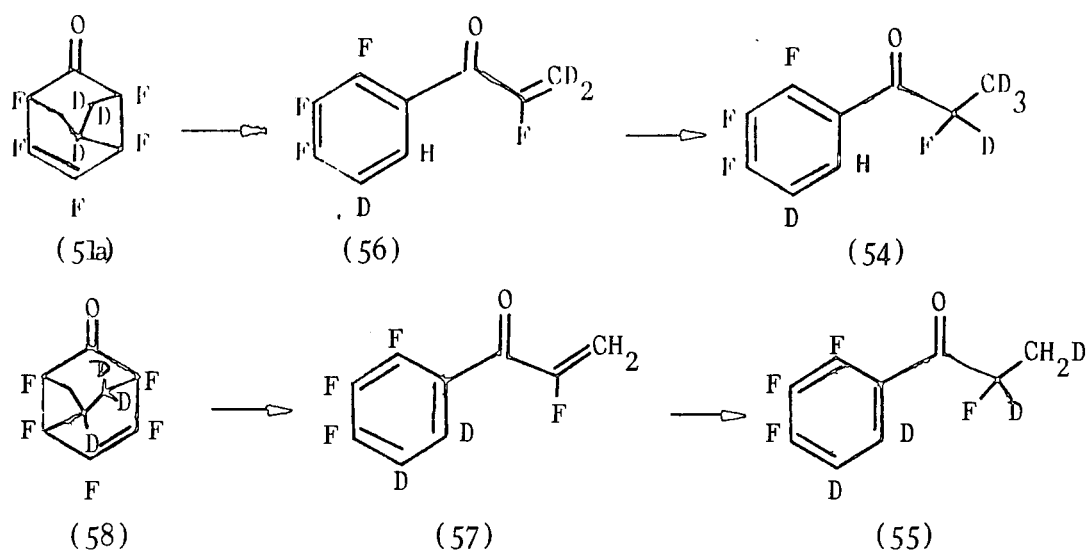
- (a) Cleavage leading to the initially formed Claisen rearrangement ortho-dienone (41) which could then produce the bicyclic derivative (42) (Scheme 11).
- (b) A cleavage which could produce 1-fluorovinyl-2,3,4-trifluorophenyl ketone (52) which readily polymerised in air and was therefore hydrogenated to prevent this occurring (53), (Scheme 16).



Scheme 16

The relative ease of cleavage was then determined by repeating the pyrolysis and immediately reducing the vinyl ketone (52) with deuterium in order once again to prevent polymerisation of (52). Two compounds were obtained (54, 55) in the ratio 1:1.1, these in turn indicated that the pyrolysis products were a ketone (56) obtained from (51a) and a second ketone (57) derived from Diels-Alder adduct (58) (Scheme 17).

It was concluded that cleavage of bonds (a) was easier than cleavage of bonds (b) in (51) (Scheme 16). This deduction was based



Scheme 17

upon the isolation of the bicyclic ketones (47, 50) in the same ratio as that of the unsaturated ketones (54, 55), which indicated common precursors, namely the 2,4-dienones (45, 48). Furthermore, the equilibrium between these compounds (45, 48) must be established quickly in comparison to reactions arising from Diels-Alder adducts (51, 58 and 46, 49).

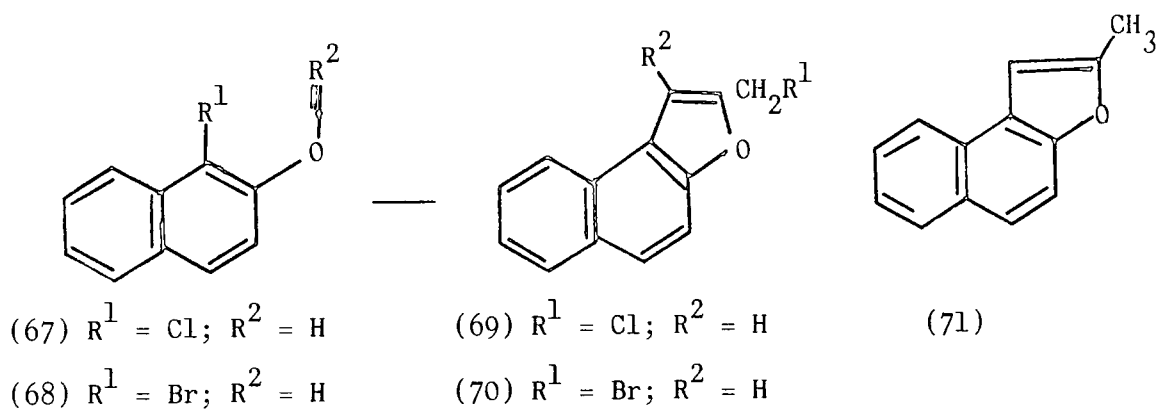
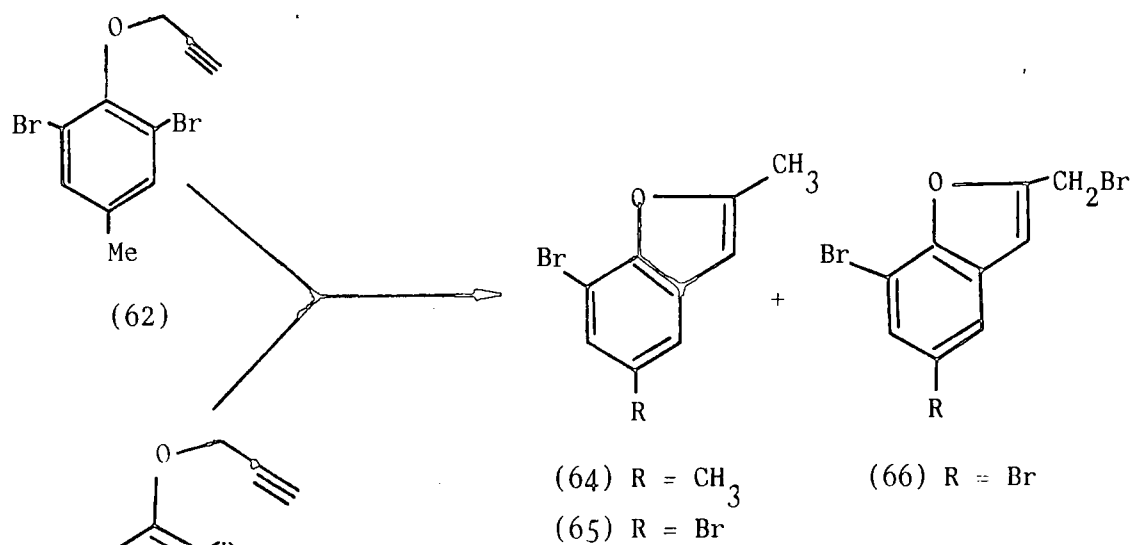
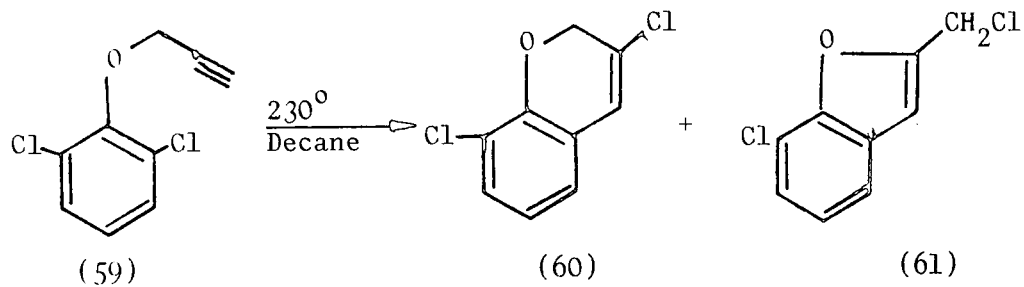
It is obvious therefore that the formation of an intramolecular Diels-Alder addition adduct is an important feature of the behaviour of 2,6-disubstituted aryl allyl ethers.

### 2.3. Cyclisations Following Initial Claisen Rearrangements

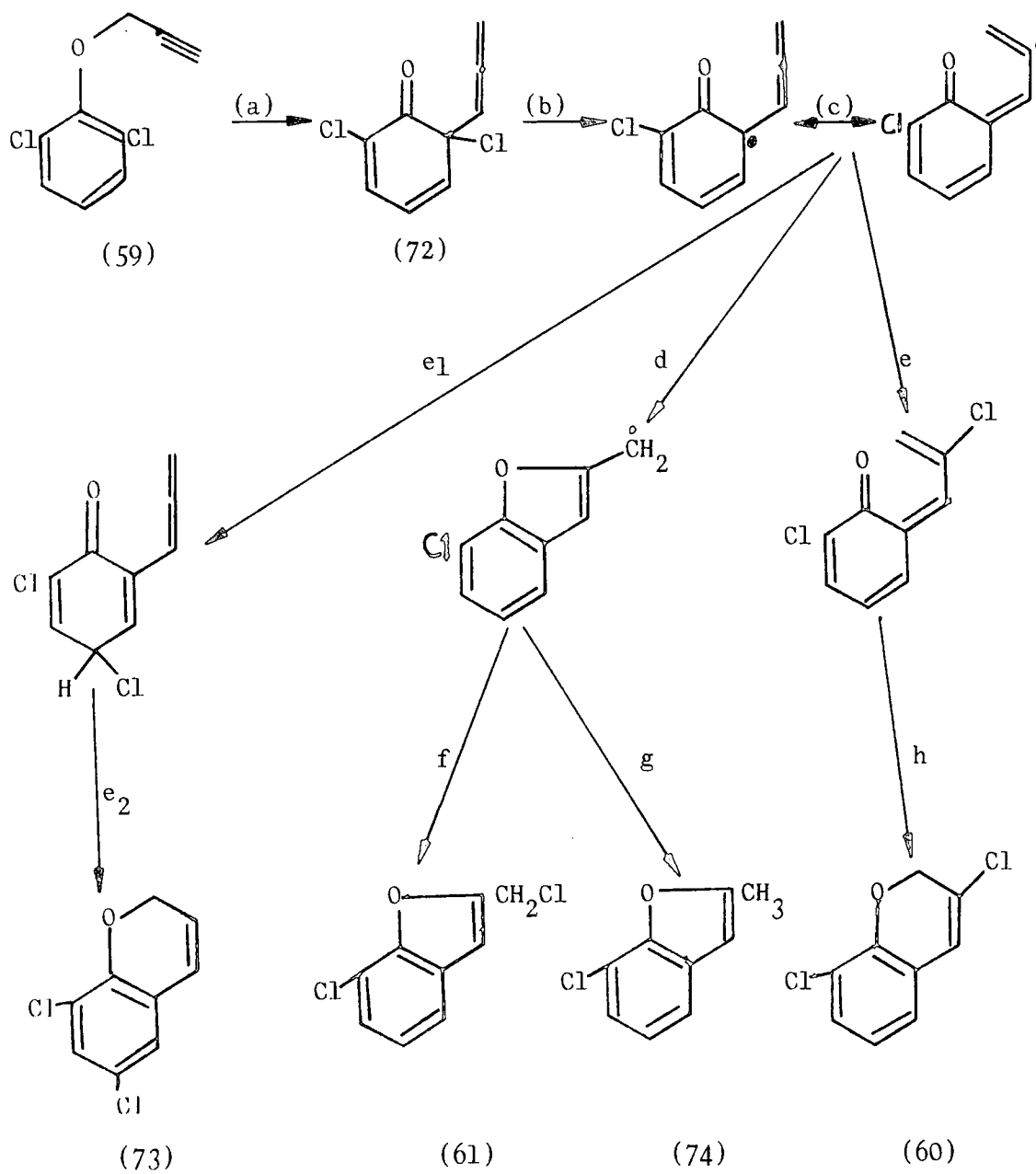
An alternative reaction, which Claisen intermediates such as the ortho allenyl dienones can undergo, is cyclisation.

In an extension of their earlier work<sup>42,43</sup> (cf. Section 2.2) Schmid *et al.*<sup>46</sup> investigated the thermal rearrangement of 2,6-dichlorophenyl prop-2-ynyl ether (59), which gave as its main products: 7-chloro-2-chloromethylbenzofuran (61) and 3,8-dichloro-2H-1-benzopyran (60). The bromo analogues (62), (63), showed one bromine atom less per molecule (64), (65) and (66). The corresponding naphthyl derivatives (67), (68) rearrange more readily to the halogeno-naphthofurans (69), (70), and the methyl furan (71). These reactions are illustrated in Scheme 18.

The reaction sequence suggested by Schmid required an initial



Scheme 18



(a) [3,3] Sigmatropic Shift.

(b) Homolysis of C-Cl.

(c) Resonance Stabilization.

(d) Ring Closure.

(e) Radical Recombination.

(e<sub>1</sub>) Radical Rearrangement/  
Recombination.

(e<sub>2</sub>) Radical Recombination/Ring  
Closure.

(f) Radical Recombination.

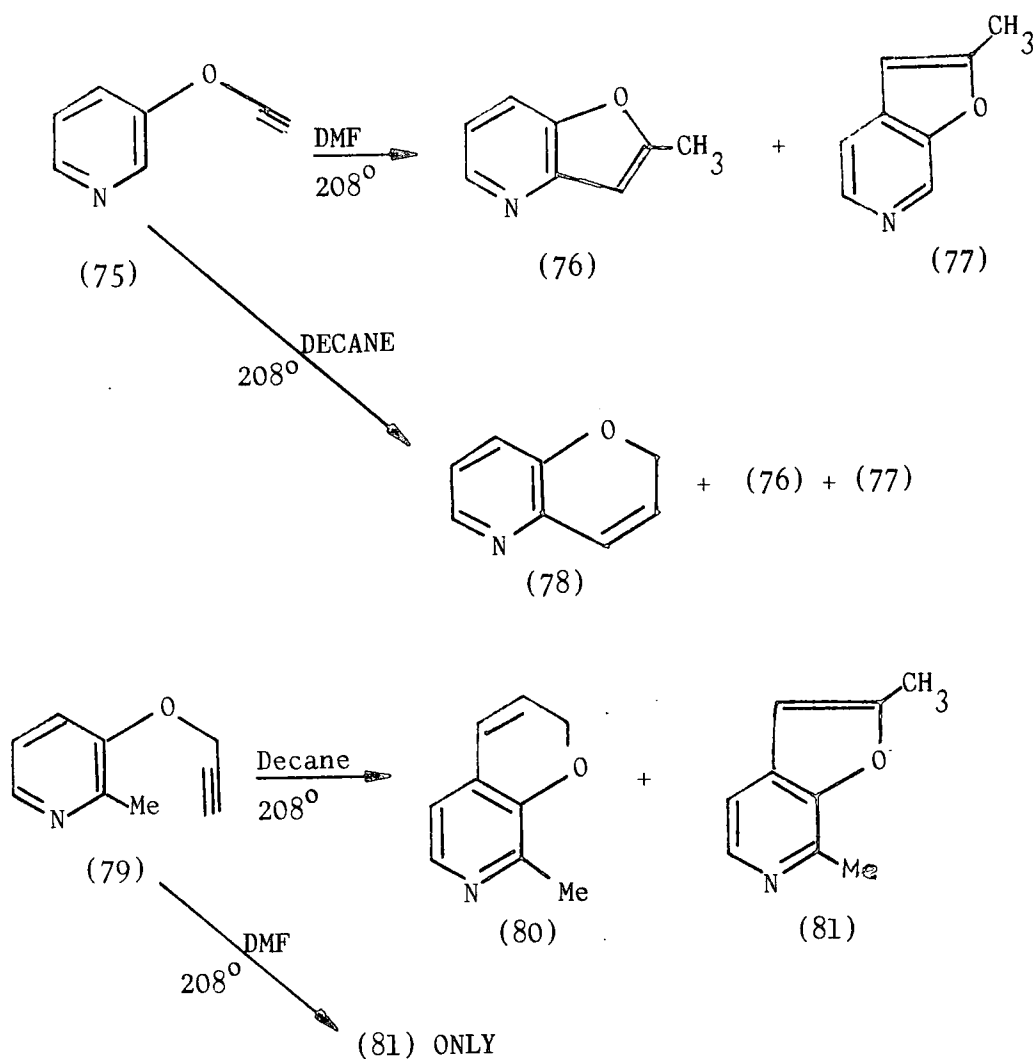
(g) Hydrogen Abstraction.

(h) Cyclisation.

Scheme 19

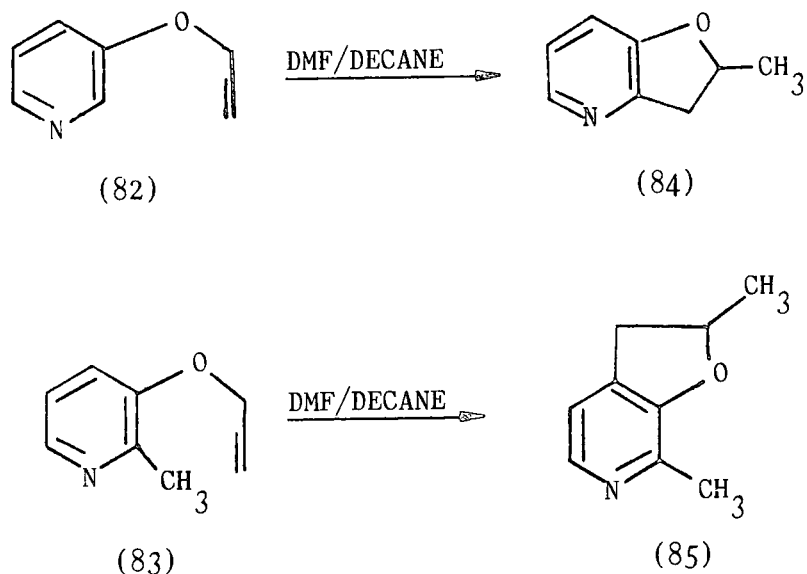
[3,3] sigmatropic shift to the 6-allyl-6-halogenocyclohexa-2,4-diene (72), this was followed by homolytic cleavage of the carbon-chlorine bond to give radicals, which then cyclised (Scheme 19).

In another paper published in 1978, Schmid *et al.*<sup>47</sup> investigated the behaviour of prop-2-ynyl (3-pyridyl)ether (75), when heated in a sealed tube with either n-decane or DMF at 208°. When DMF was used the furanopyridines were produced, whilst when the solvent was n-decane the products were the pyranopyridines. Similar behaviour was observed when the 2-methyl derivative (79) was used, the pyridine reacted in DMF to give one product (81) and in n-decane to generate two products (80, 81) (Scheme 20).



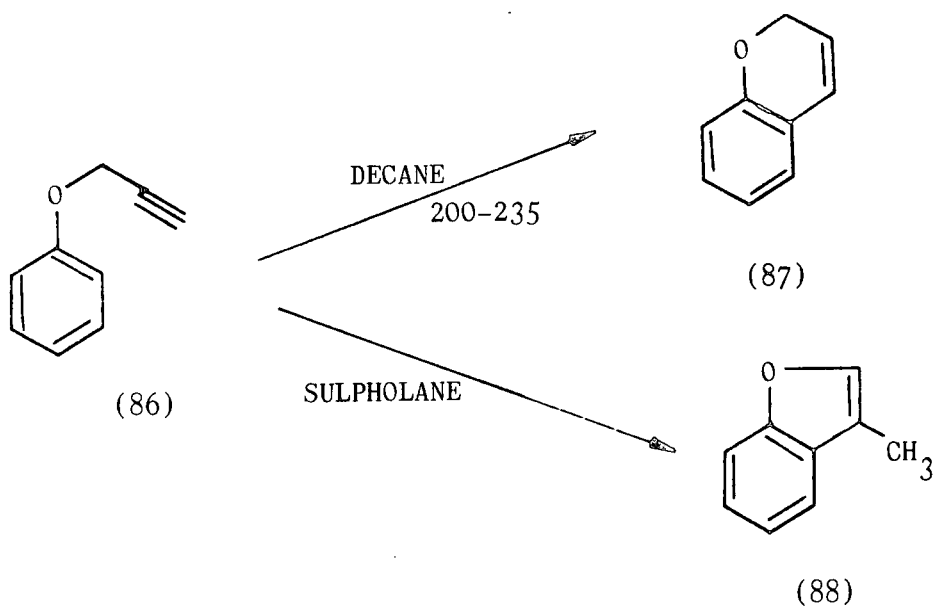
Scheme 20

The thermolysis of allyl-3-pyridyl ether (82) and 2-methyl-3-pyridyl allyl ether (83) gave rise to two different furanopyridines (84, 85) (Scheme 21).<sup>47</sup>

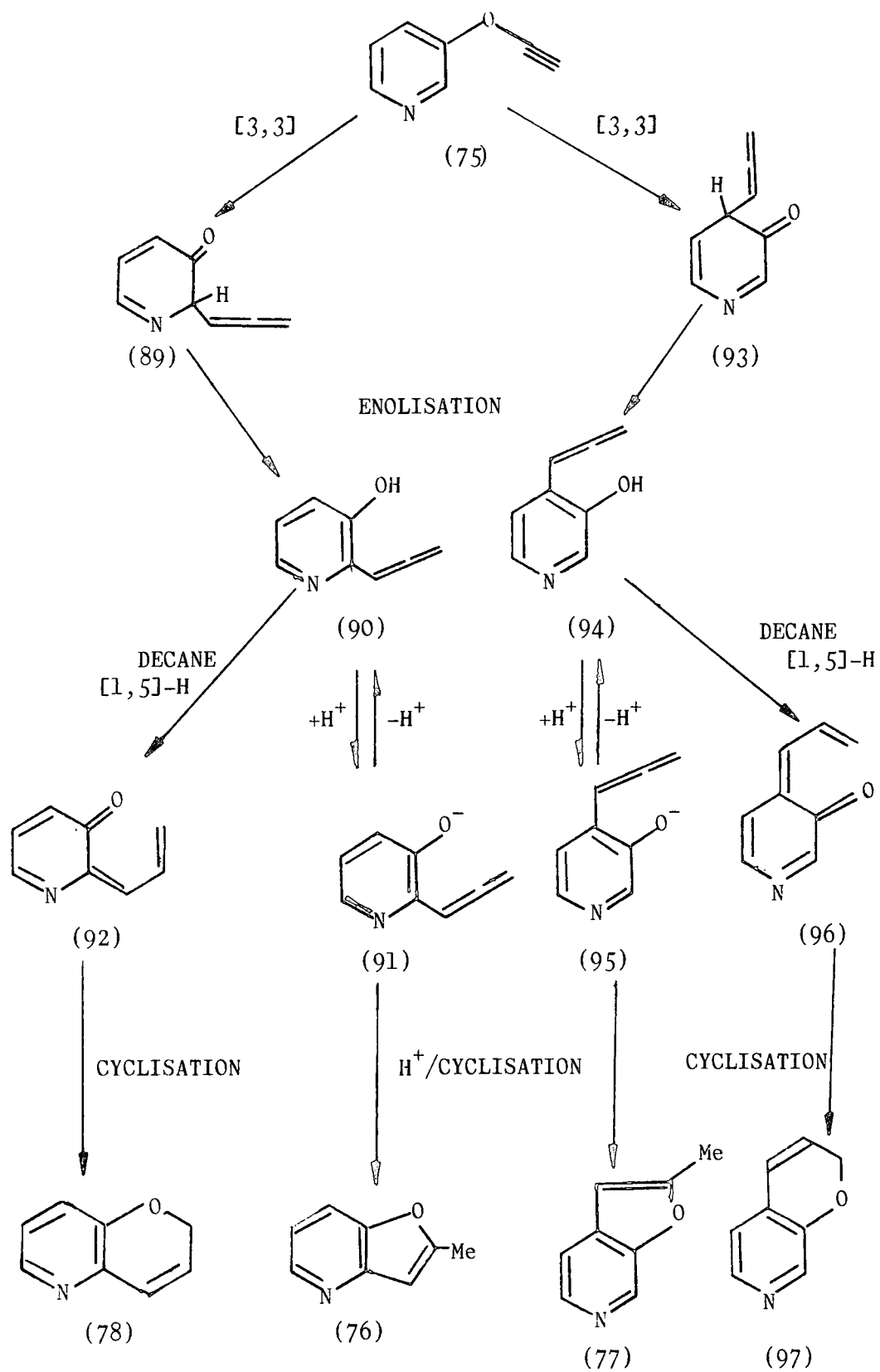


Scheme 21

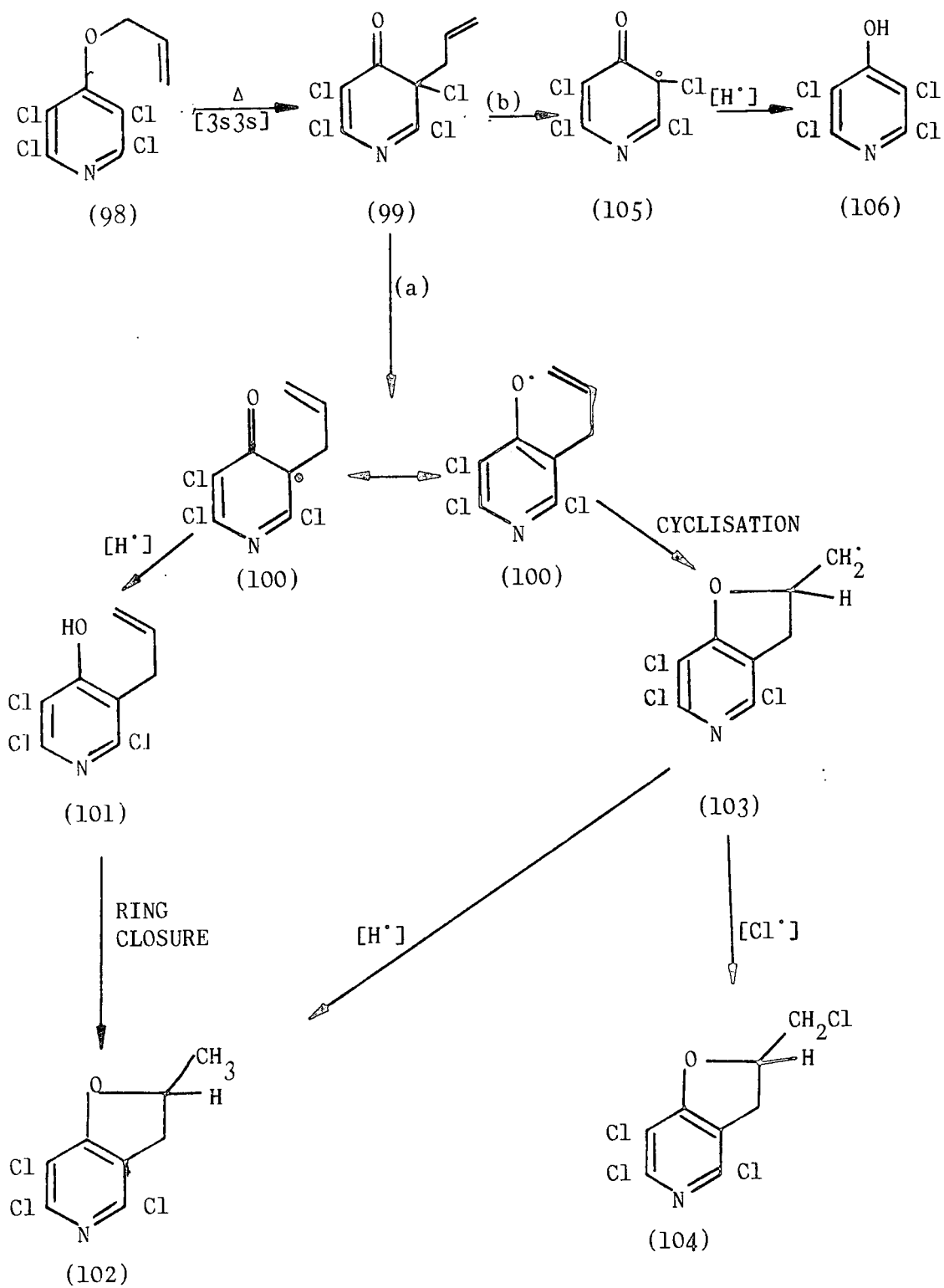
When a comparison of the unsubstituted pyridine derivative (75) with the unsubstituted phenyl prop-2-ynyl ether (86) was made, the behaviour of the aryl derivative was found to be similar to that of the pyridyl (75), yielding the benzopyran derivative (87) in decane and the benzofuran derivative (88) in sulpholane (Scheme 22).



Scheme 22



Scheme 23



(a) Homolytic Cleavage C-Cl

(b) Homolytic Cleavage C-C

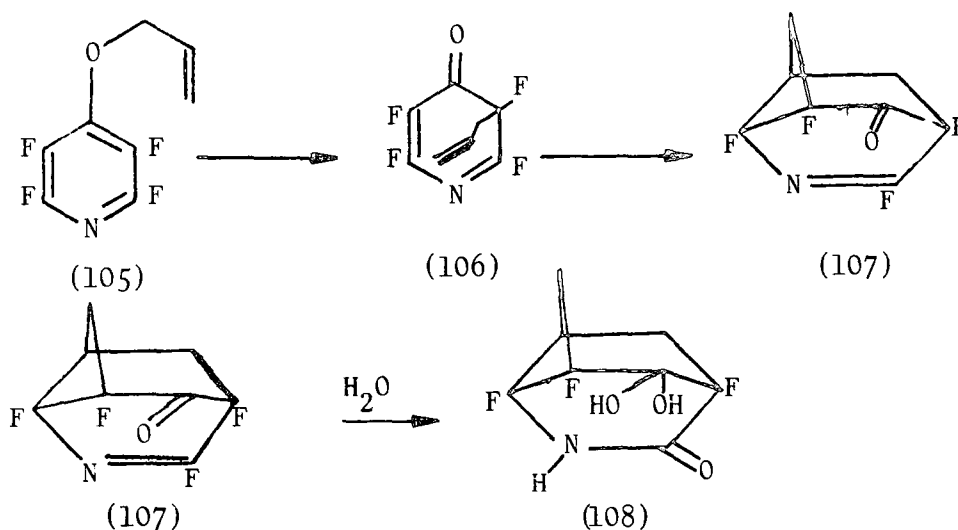
Scheme 24

The variation of products when the pyridine derivatives were reacted in either n-decane or DMF was explained by considering the pKa value of the intermediate allenyl hydroxy pyridines (90, 94). These hydroxy pyridines can only ionise in DMF which is able to accept protons, whilst n-decane cannot. In n-decane the hydroxy pyridines (90, 94) undergo [1,5] hydride shifts followed by cyclisation<sup>47</sup> (Scheme 23).

Iddon *et al.*<sup>48</sup> also examined the behaviour of related pyridyl ethers, in particular tetrachloropyridine derivatives, both the prop-2-enyl and prop-2-ynyl, to investigate the results of Claisen rearrangements in these fully substituted compounds. The reactions were undertaken at high temperature in sulfolane. Iddon *et al.* postulated the sequence of reactions shown (Scheme 24).

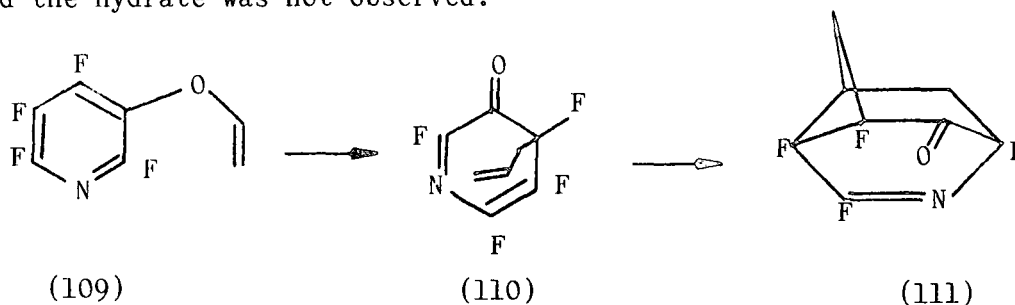
The free radical mechanism involving homolytic cleavage of a C-Cl bond, invoked to account for the experimental results, is similar to that of Schmid.<sup>46</sup>

Brooke and co-workers<sup>49</sup> investigated the behaviour of the tetrafluoropyridyl prop-2-enyl ethers when thermolysed at 140° for long periods (e.g. 10-13 days) in sealed flasks. Among the products when tetrafluoro-4-pyridyl prop-2-enyl ether (105) was heated in the vapour phase at 138° for 10 days, was a tetrafluorotricyclic compound (107) and the hydrated hydrolysis product (108) (Scheme 25).



Scheme 25

A second tricyclic compound (111) was isolated from the thermolysis of 2,4,5,6-tetrafluoro-3-pyridyl prop-2-enyl ether (109) (Scheme 26). This derivative (111) was less susceptible to hydrolysis and the hydrate was not observed.<sup>49</sup>



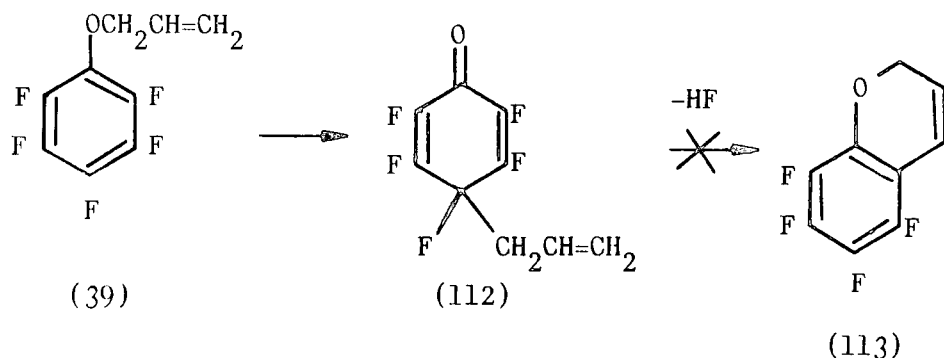
Scheme 26

The tetrafluoro-3- and tetrafluoro-4-prop-2-enyl ethers, (109) and (105), followed a reaction path which led to internal Diels-Alder adducts, similar to (43) in an analogous reaction to that of pentafluorophenyl-prop-2-enyl ether (39), rather than the cyclisation pathways observed in the more obvious counterpart tetrachloropyridyl prop-2-enyl ether (98). One possible explanation of these differences lies in the lower bond strength of C-Cl than C-F (78 kcal.mol.<sup>-1</sup>, 116 kcal.mol.<sup>-1</sup> respectively<sup>50</sup>) which would make the homolytic cleavage of C-Cl, postulated by Schmid *et al.*, and Iddon *et al.*,<sup>46,48</sup> somewhat easier than the homolytic cleavage of C-F. Furthermore, the two bond lengths of C-Cl and C-F (1.766 Å, 1.317 Å respectively<sup>50</sup>) indicate that the chlorine atom is not so strongly bound. These features would favour the homolytic cleavage mechanism shown in Scheme 24 and hence the observed cyclisation products (Schemes 20-24). These postulations however are qualified by the recorded behaviour of pentafluorophenyl-prop-2-enyl ether, and heptafluoro-2-naphthyl-prop-2-enyl ethers, which when thermolysed do give rise to recognisable electrocycloisatation products discussed in more detail in Chapter 3.

The Thermolysis of Polyfluoroaryl and Polyfluoropyridyl Prop-2-ynyl Ethers in the Liquid Phase

3.1. Introduction

The possibility of converting readily available pentafluorophenyl prop-2-enyl ether (39) into the partially fluorinated heterocyclic compound 5,6,7,8-tetrafluoro-2H-1-benzopyran (113) was originally proposed in 1974<sup>44</sup> (Scheme 27). However the vapour phase

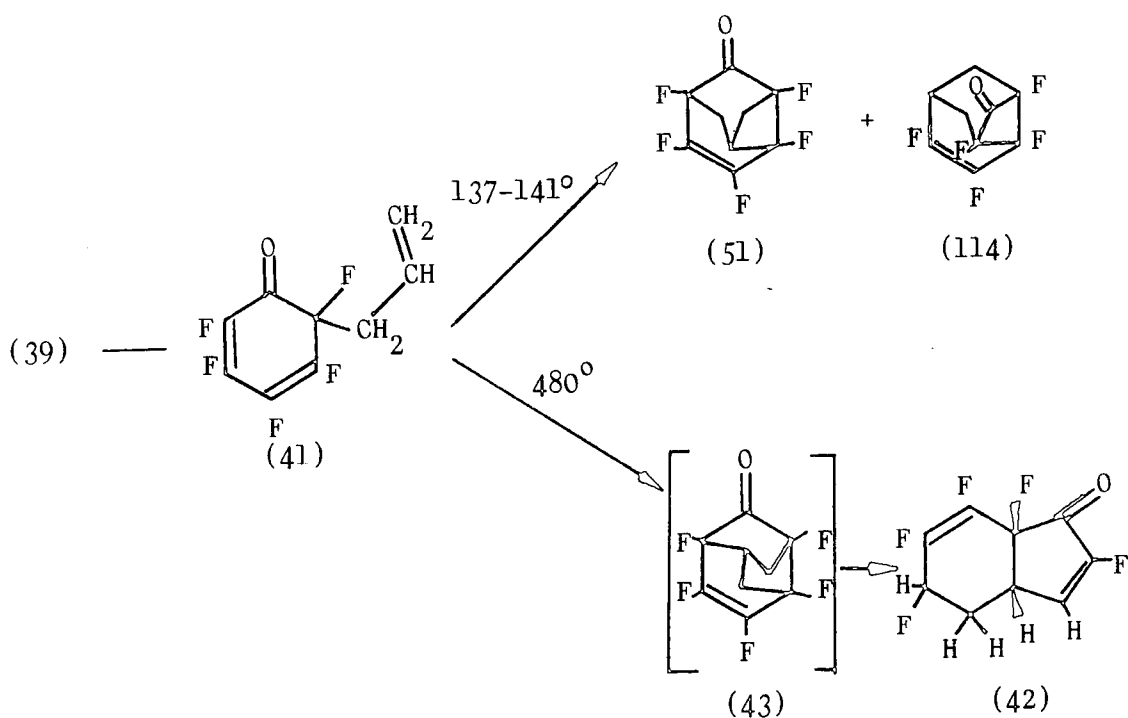


Scheme 27

pyrolysis of (39) gave a variety of products depending on the reaction temperature.

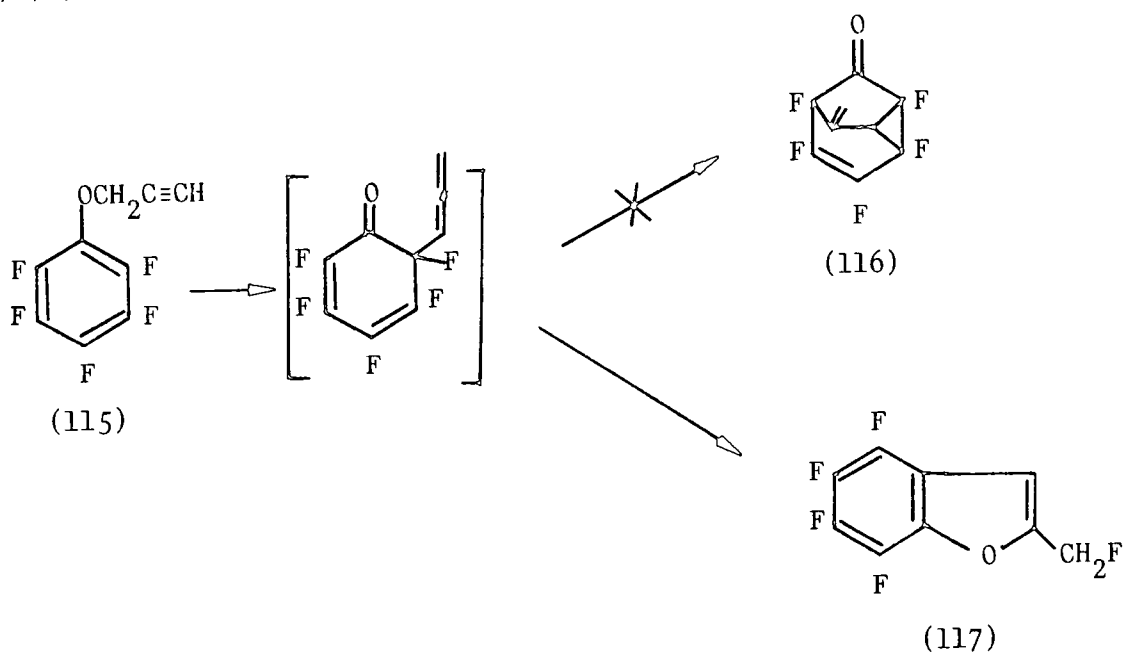
At 365° in a flow system the initial Claisen rearrangement was followed by a Cope rearrangement to give the dienone<sup>51</sup> (112). One of the two possible internal Diels-Alder adducts was formed in a static system at 137-141°C accompanied by an isomer. At 480° in a flow system a product (42) was isolated which resulted from the decomposition of a second possible Diels-Alder adduct of the Claisen rearrangement intermediate<sup>44</sup> (cf. Section 2.2) (Scheme 28).

The route was temporarily abandoned due to failure to obtain the 2-H-1-benzopyran derivative (113), and the search continued for other types of internal Diels-Alder adducts from pentafluorophenyl-prop-2-ynyl ether (115). A precedent for this reaction had been reported by Schmid<sup>43</sup> (Scheme 10, Section 2.2).



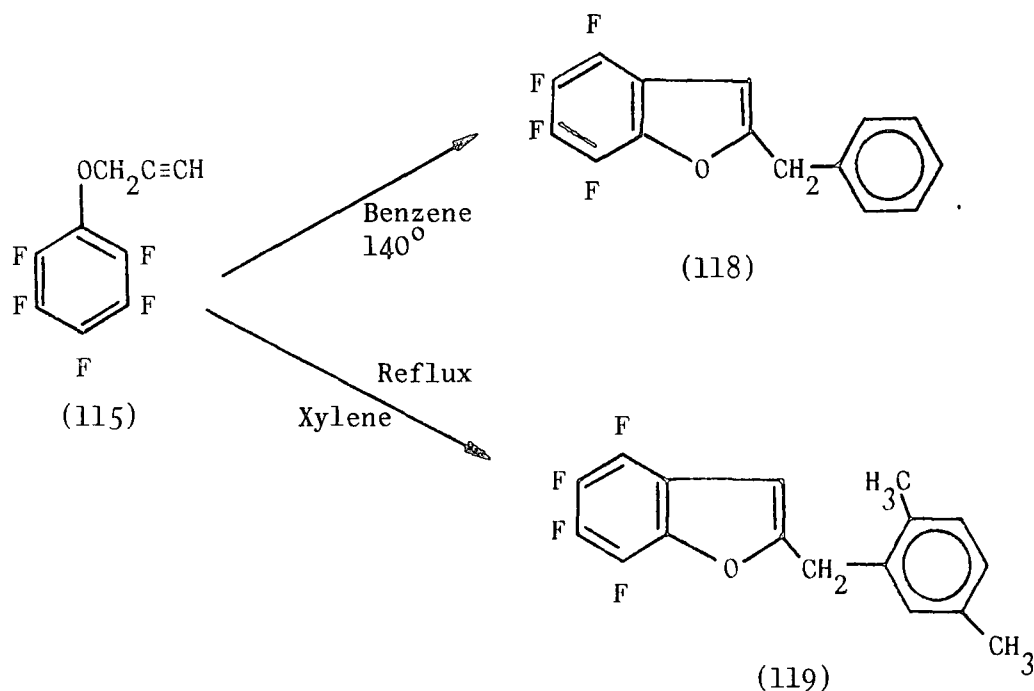
Scheme 28

When pentafluorophenyl prop-2-ynyl ether (115) was distilled through a silica tube packed with quartz wool at  $370^{\circ}$ , no Diels-Alder adduct (116) was formed, only the isomerisation product 2-fluoromethyl-4,5,6,7-tetrafluorobenzo[b]furan (117) (Scheme 29) was isolated.<sup>52</sup>



Scheme 29

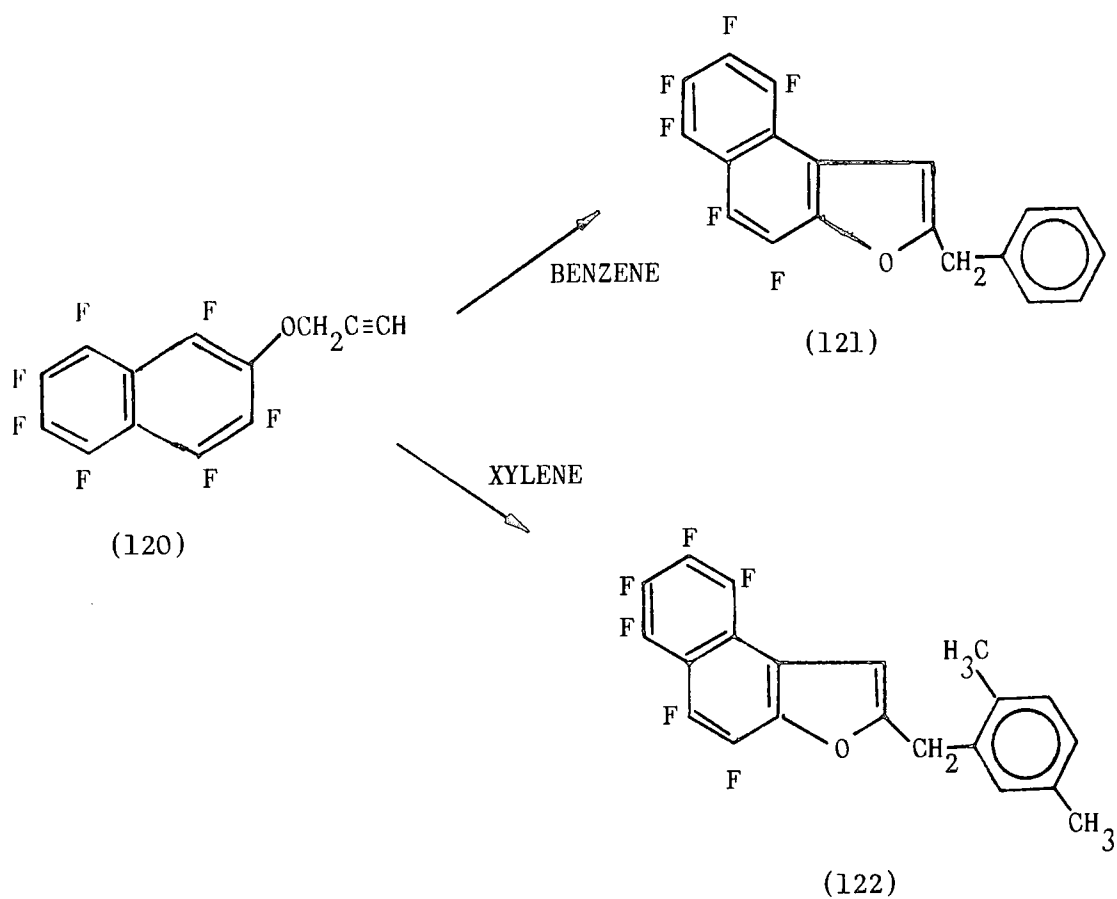
The liquid phase reaction of the ether (115) in benzene at 140° however gave 2-benzyl-4,5,6,7-tetrafluorobenzo[b]furan (118), and a similar reaction with p-xylene also led to substitution into the aromatic ring, giving 2-(2,5-dimethylbenzyl)-4,5,6,7-tetrafluorobenzo(b]furan (119) (Scheme 30).



Scheme 30

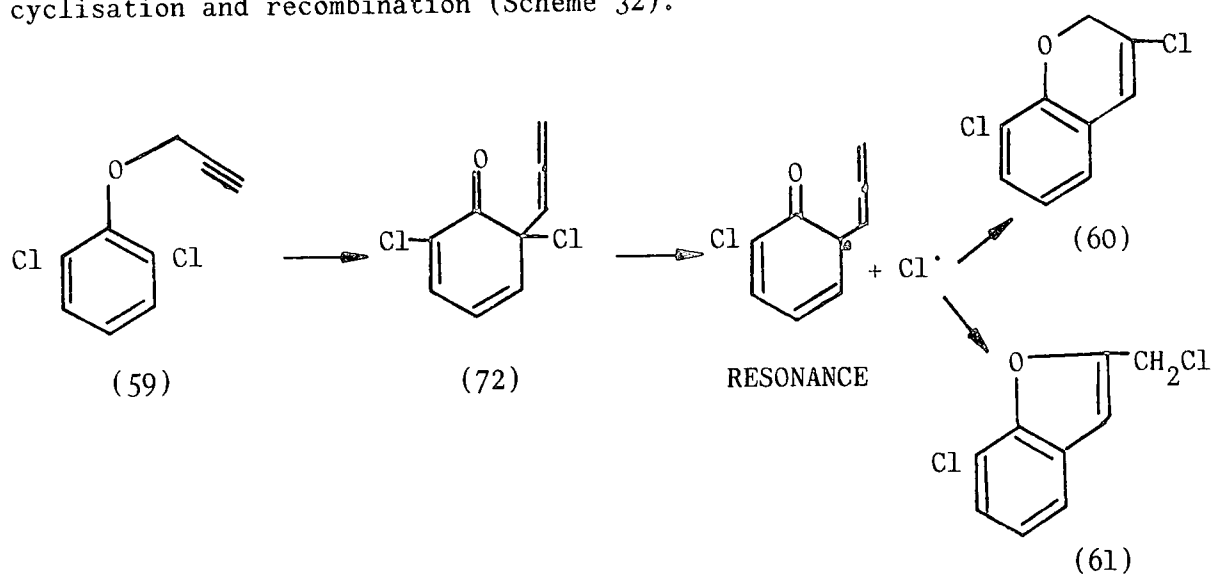
The liquid phase thermolysis of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (120) at 140° in the same aromatic solvents gave 2-benzyl and 2-(dimethylbenzyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (121) and (122) (Scheme 31).<sup>52</sup>

These experiments showed that the behaviour of the prop-2-ynyl ethers (115) and (120) was quite different from that of the prop-2-enyl ether (39). The work of Schmid *et al.*<sup>46</sup> had previously shown that aryl prop-2-ynyl ethers having ortho-halogens, when thermolysed in n-decane gave the 2-halomethylbenzo[b]furan derivatives. The 2,6-dichlorophenyl prop-2-ynyl ether (59) gave 3,8-dichloro-2H-1-benzopyran (60), and 2-chloromethyl-7-chlorobenzo[b]furan (61), whilst 1-chloro(bromo)-2-naphthyl prop-2-ynyl ethers (67, 68)



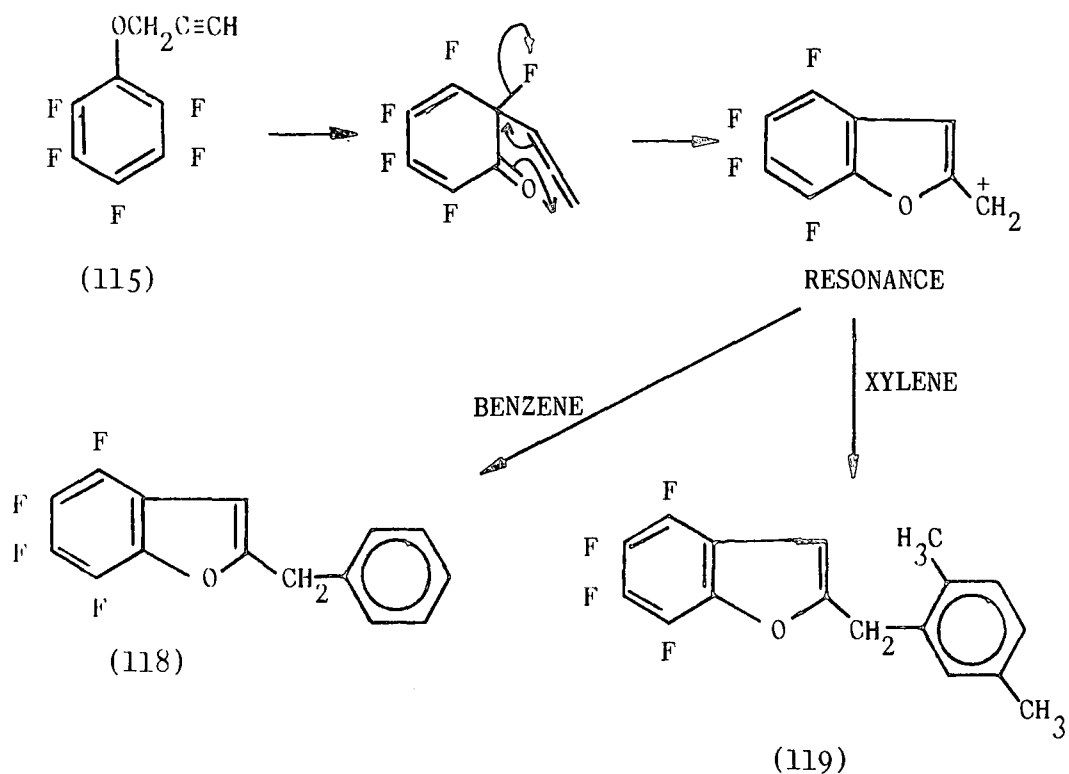
Scheme 31

produced 2-chloro(bromo)methylnaphtho[2,1-b]furan (69,70) and 2-methylnaphtho[2,1-b]furan (70) (Scheme 18, Section 2.3). To account for this behaviour Schmid postulated homolytic cleavage of the carbon-halogen bond in the initial Claisen rearrangement intermediate (72) followed by cyclisation and recombination (Scheme 32).



Scheme 32

The formation of the 2-fluoromethyl-4,5,6,7-tetrafluorobenzo[b]-furan (115) could also be accounted for by an analogous isomerisation mechanism, in which an  $sp^3$  C-F bond is cleaved homolytically, albeit at the remarkably low temperature of  $140^\circ$ . The formation of the 2-benzyl (118) and 2-(2,5-dimethylbenzyl) (119) derivatives is rationalized in terms of a homolytic substitution reaction of hydrogen in the ring. An alternative heterolytic mechanism can be invoked however to account for these reactions (Scheme 33).

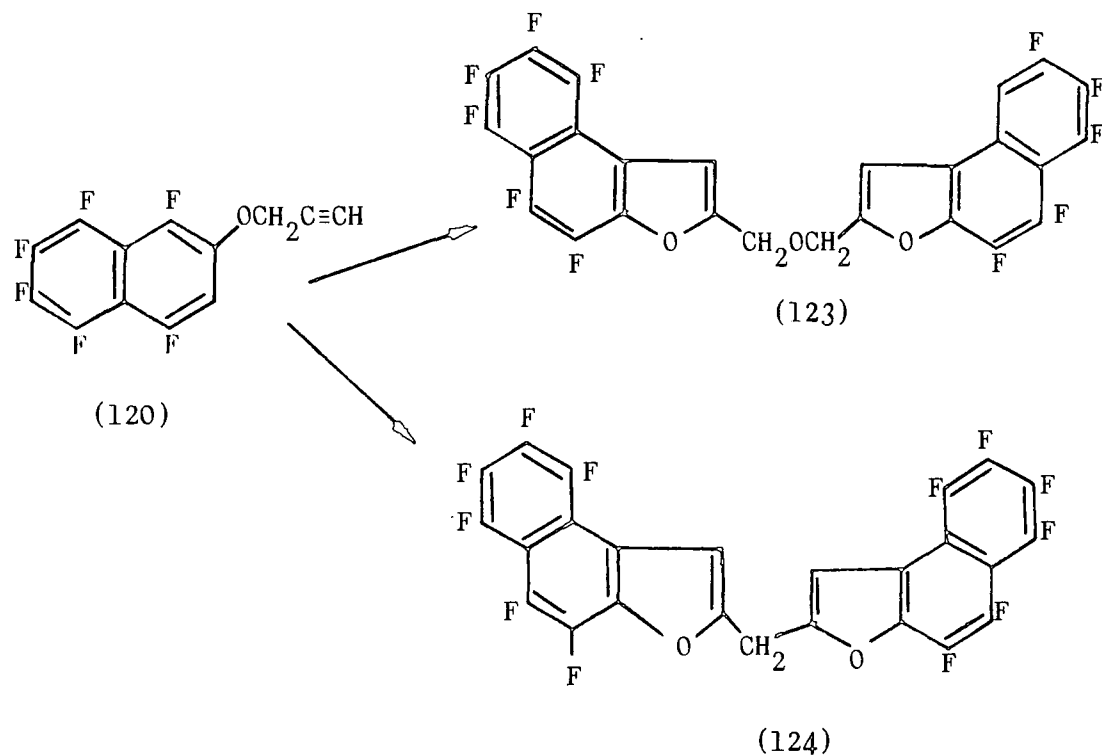


Scheme 33

A series of aromatic solvents: isopropylbenzene, nitrobenzene, benzylidene trifluoride and diethylaniline were examined in an attempt to distinguish between the two mechanisms by characterization of the substitution products; thus for example a carbocation mechanism in nitrobenzene should give meta-substitution, whilst a radical mechanism should give ortho, para and meta substitution. Unfortunately no definite conclusions could be reached.<sup>53,54</sup>

In view of the vapour phase isomerisation of pentafluoro-

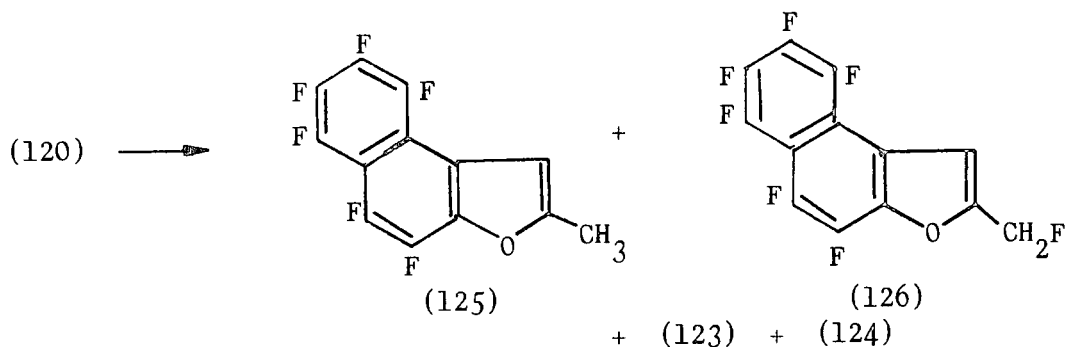
phenyl-prop-2-ynyl ether (115) to the 2-fluoromethyl derivative (117) at 370°, it was of interest to examine whether such an isomerisation process could be effected in the liquid phase at much lower temperatures used in the reactions with aromatic solvents (ca. 140°). The behaviour of the naphthyl prop-2-ynyl ether (120) in various solvents was examined since yields of products for the naphthalene derivatives, in general, are greater than those for the phenyl derivative. Thus the ether (120) was heated in a sealed glass tube with 1,1,2-trichlorotrifluoroethane to yield two products: di-(4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl methyl)ether (123) and bis-(4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl)methane (124), no fluoromethyl compound analogous to (117) was isolated (Scheme 34).



Scheme 34

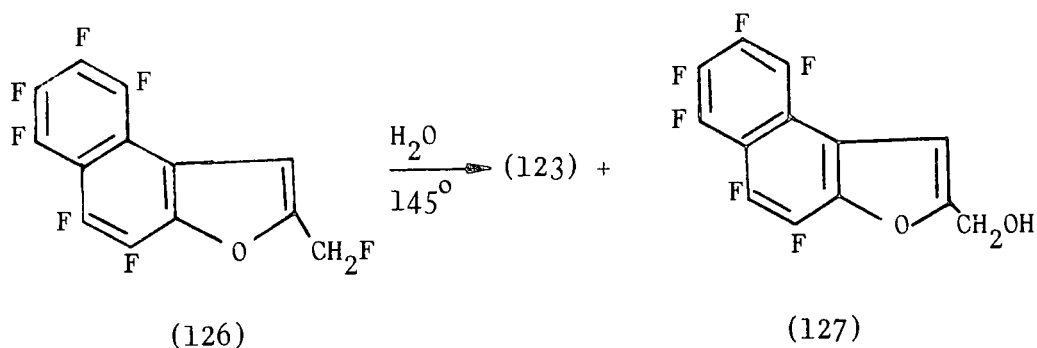
The reaction of the heptafluoro-2-naphthyl prop-2-ynyl ether (120) in N,N-diethylaniline gave, in addition to (123), (124), two other products which involved the formation of a furan ring without

the substitution reaction: 2-methyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (125) (1%), and 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) (2%) (Scheme 35).<sup>53,54</sup>



Scheme 35

The absence of the 2-fluoromethyl derivative (126) as a product in the thermal reaction of ether (120) in 1,1,2-trichlorotrifluoroethane was surprising in view of the observations made by Schmid *et al.* in their work with orthohalophenyl prop-2-ynyl ethers (67), (68)<sup>46</sup> (Scheme 32). The formation of the diether (123) indicated that water must have intervened in the reaction either within the reaction vessel or afterwards during the work-up procedures. The argument for hydrolysis was further supported by the reaction of (126) with water in a sealed tube, which gave the diether (123) (7%), and 4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl methyl alcohol (127) (Scheme 36).<sup>53</sup>

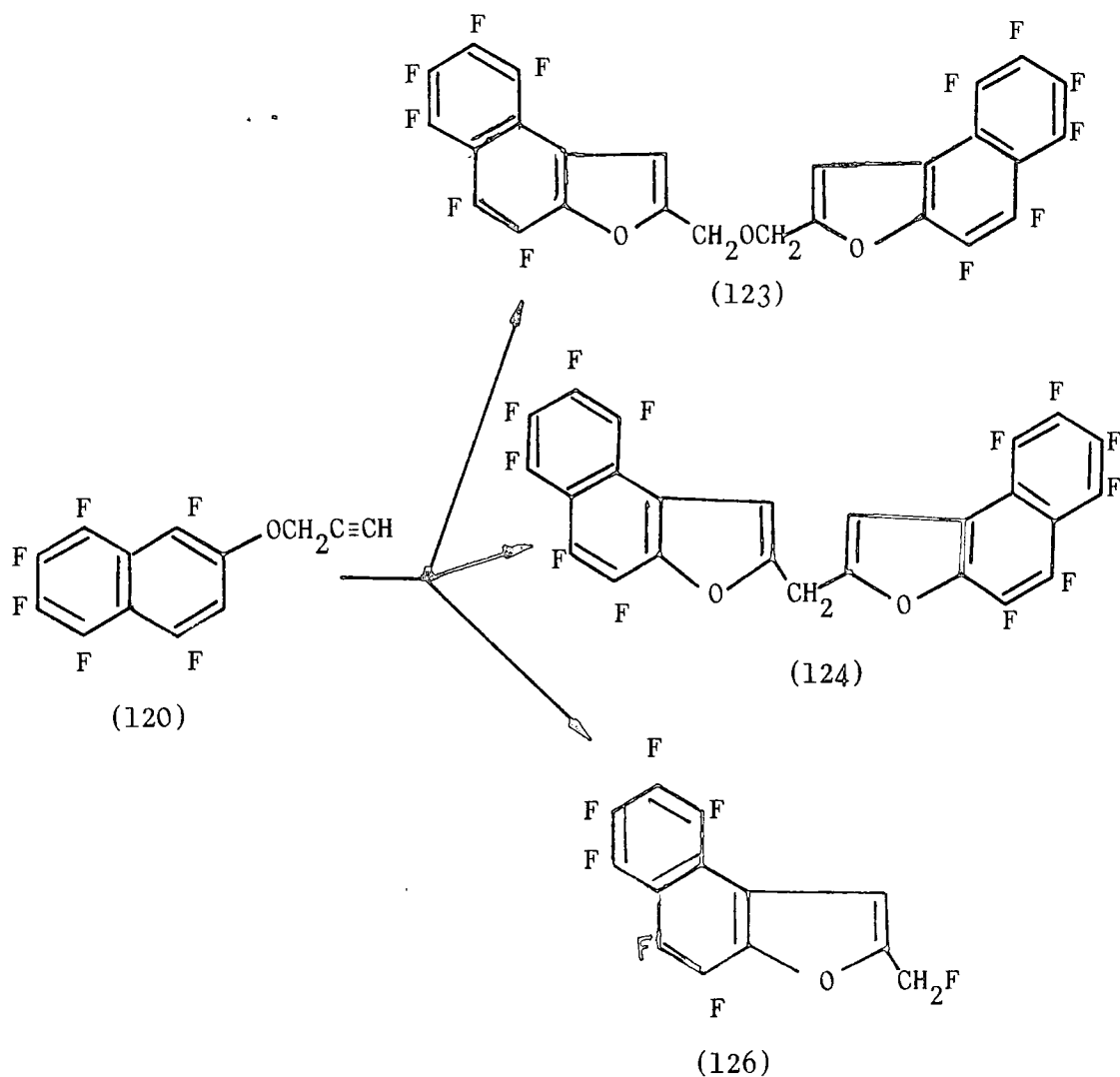


Scheme 36

It was finally concluded from work both with the pentafluorophenyl prop-2-ynyl ether (115) and the heptafluoro-2-naphthyl prop-2-ynyl ether (120), that the formation of the products (123) and (124) was ultimately attributable to the actual generation of water<sup>53</sup> within the reaction vessel via attack of hydrogen fluoride, formed during the decomposition of the reaction mixtures, on the glass walls of the reaction vessel.

3.2. Present Work: Thermal Reactions of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether in n-Decane and 1,1,2-Trichlorotrifluoroethane

The first phase of the experimental work was to investigate the behaviour of the 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (120) during thermolysis in a non-vitreous environment. A nickel lined stainless steel Carius tube was used to avoid the formation of water during the progress of reactions. Thermolysis of the ether (120) was carried out at 150° in both anhydrous n-decane (the solvent used by Schmid<sup>46</sup>), and anhydrous 1,1,2-trichlorotrifluoroethane. Every precaution was taken to exclude moisture from the reaction vessel by sealing the apparatus under an atmosphere of dry nitrogen. After work-up, involving sublimation and extensive dry silica column chromatography, three major products were obtained: 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) (24% in n-decane, 42% in 1,1,2-trichlorotrifluoroethane), di-(4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl methyl)ether (123) (2% in n-decane, approximately 6% in 1,1,2-trichlorotrifluoroethane), and bis-(4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl)methane (124) (1.5% in n-decane, approximately 3% in 1,1,2-trichlorotrifluoroethane) (Scheme 37).



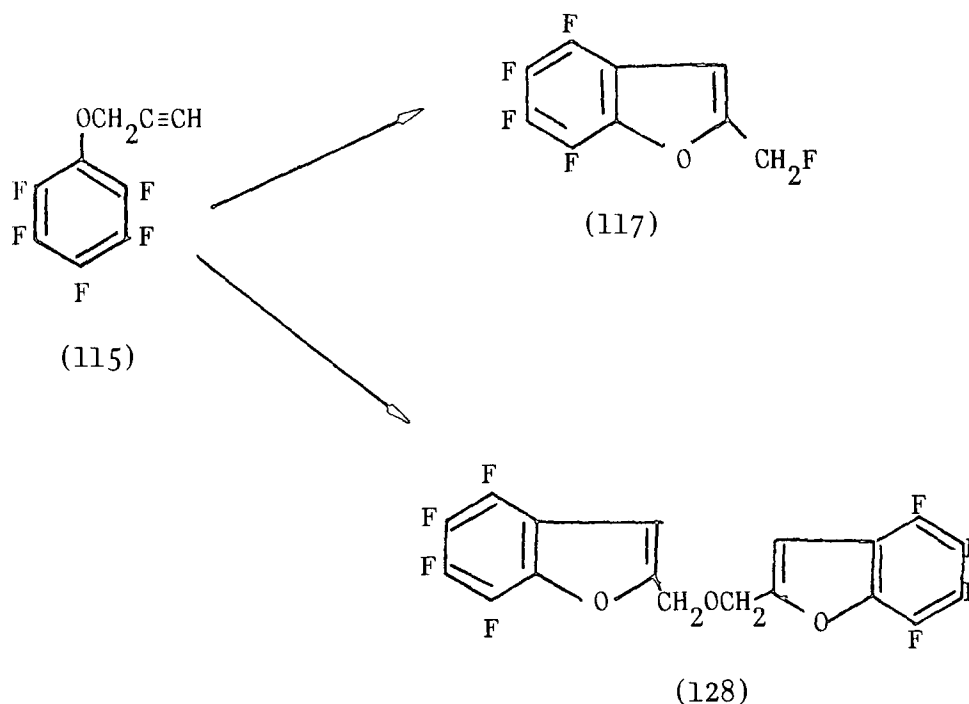
Scheme 37

The formation of the products (123) and (124) indicated that although the strictest precautions to maintain an anhydrous environment had been taken, water had still interacted with the reaction products to form the ether (123) and bis-methane (124) derivatives, presumably during the separation of products.

However the most significant result of these experiments was the fact that reasonably large quantities of the 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) could be obtained, and so showing that what Schmid had achieved with the chloro- and bromo-compounds (the formation of 2-halonaphthofuran derivatives),<sup>46</sup> could also be achieved with the fluoro compounds of the polyfluoro series.

### 3.3. Thermolysis of Pentafluorophenyl Prop-2-ynyl Ether in 1,1,2-Trichlorotrifluoroethane

The pentafluorophenyl prop-2-ynyl ether (115) was thermolysed as for the naphthalene derivative (120) at 150° for 5 days. Isolation of the major products from the reaction proved more difficult than before. Whilst the benzo analogues of naphthofurans, (123) and (126), have been identified by t.l.c. and i.r., pure samples were difficult to obtain. The two identified products from the thermolysis of the ether (115) were: 2-fluoromethyl-4,5,6,7-tetrafluorobenzo[b]furan (117) (19%), and di-(4,5,6,7-tetrafluorobenzo[b]furan-2-yl methyl)ether (128) (approximately 20%) (Scheme 38).

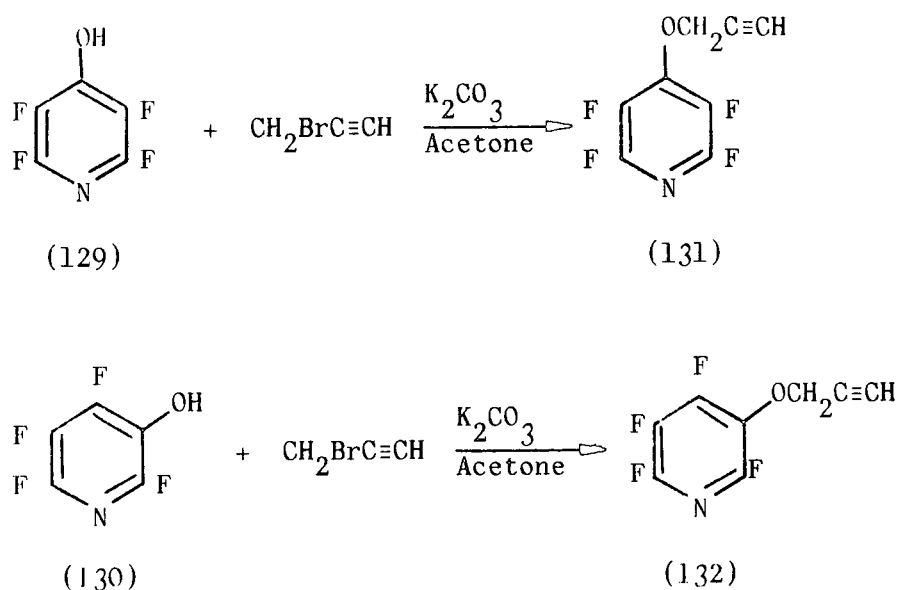


Scheme 38

### 3.4. Preparation of 2,3,5,6-Tetrafluoro-4-pyridyl and 2,4,5,6-Tetrafluoro-3-pyridyl Prop-2-ynyl Ethers and their Subsequent Thermolysis Reactions

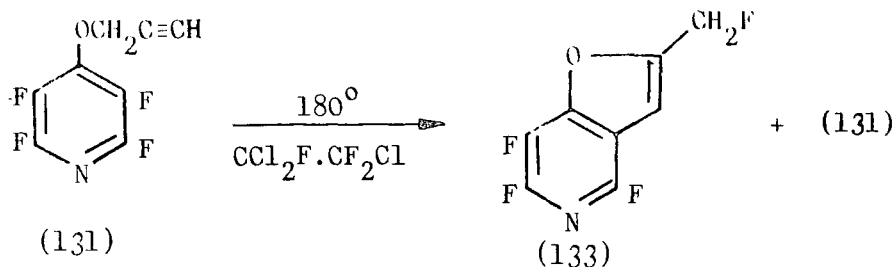
A further extension of the work involving the thermal behaviour of the polyfluoroaryl prop-2-ynyl ethers, led to an examination of the

behaviour of 2,3,5,6-tetrafluoro-4-pyridyl prop-2-ynyl ether (131), and 2,4,5,6-tetrafluoro-3-pyridyl prop-2-ynyl ether (132)<sup>55</sup> under thermolysis conditions in various solvents. Initially these compounds were prepared by reacting 2,3,5,6-tetrafluoro-4-hydroxypyridine (129) and 2,4,5,6-tetrafluoro-3-hydroxypyridine (130) respectively, with prop-2-ynyl bromide and anhydrous potassium carbonate in acetone under reflux (Scheme 39).



Scheme 39

The 3- and 4-pyridyl ethers (132) and (131) respectively, were thermolysed in a number of solvents: tetralin at 205° and under reflux; p-xylene and 1,1,2-trichlorotrifluoroethane at 150° and 180° in a nickel Carius tube. No viable products could be obtained from either ether with the aromatic hydrocarbons, or with the 3-pyridyl ether (132) in the freon solvent, tars were obtained. The 4-pyridyl ether (131) in 1,1,2-trichlorotrifluoroethane gave an amount of volatile material (22%), the <sup>19</sup>F n.m.r. of which showed it to contain mainly unreacted starting material ( $\delta_F$  CDCl<sub>3</sub> 92.8 p.p.m., and 164.5 p.p.m. above CFCl<sub>3</sub>), but there were four other signals one of which was a triplet at 213.4 p.p.m. due to a -CH<sub>2</sub>F presumably of compound (133) (Scheme 40).

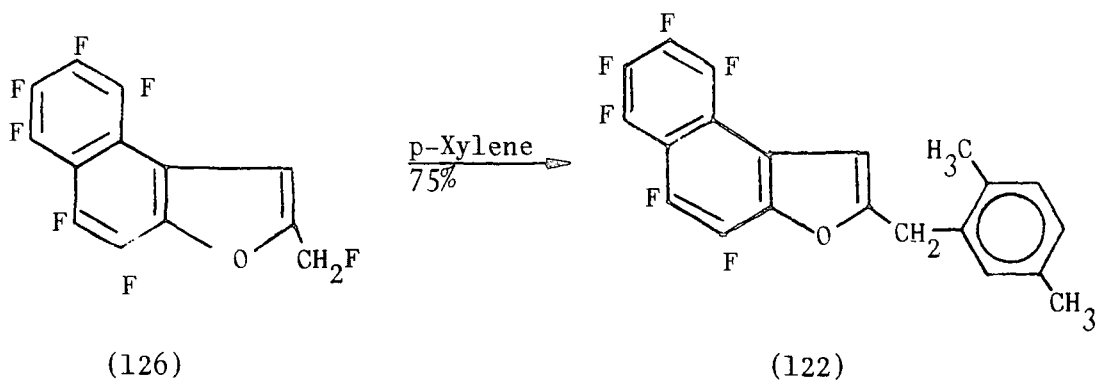


Scheme 40

### 3.5. Reaction of 2-Fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]-furan and p-Xylene

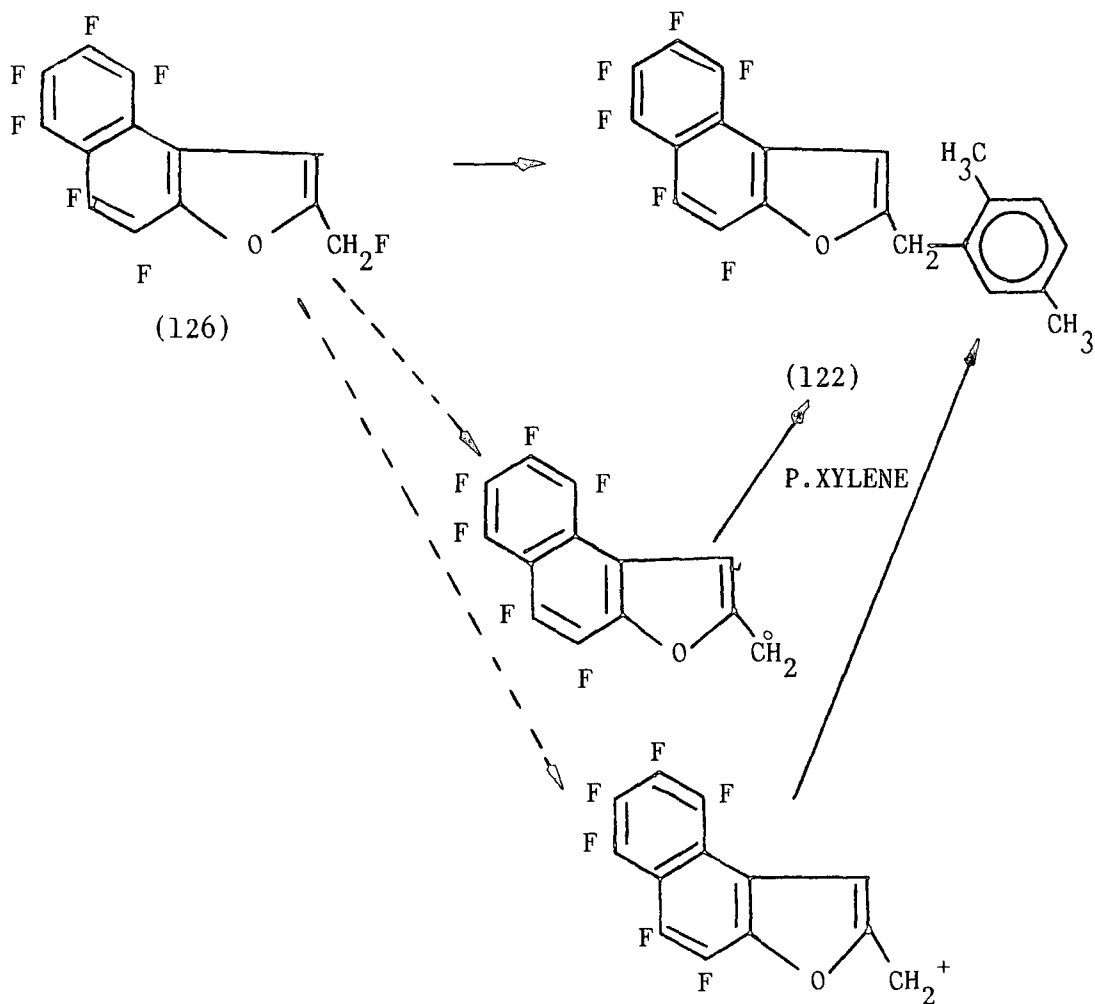
The successful synthesis of large quantities of 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) by the thermolysis of the 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (120) in 1,1,2-trichlorotrifluoroethane in sealed nickel Carius tubes, made it possible to investigate the reaction of the 2-fluoromethyl derivative (126) with aromatic hydrocarbons, to assess whether this compound could be an intermediate in the reactions of polyfluoroaryl-prop-2-ynyl ethers with aromatic solvents.

Compound (126) was heated with p-xylene under reflux for 20 hrs. during which time hydrogen fluoride was evolved, to give, 2-(2,5-dimethylbenzyl)4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (122) in 75% yield, along with some recovered starting material (17%) (Scheme 41).



Scheme 41

The result clearly indicated by the formation of the substitution product (122) that 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) could be an intermediate along the reaction path starting with the prop-2-ynyl ether (120). However it does not indicate the mode of fission of the  $\text{CH}_2\text{-F}$  bond (homolytic or heterolytic), which occurs readily at  $140^\circ$  or  $150^\circ$  (Scheme 42).



Scheme 42

### 3.6. Experimental

#### Thermolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (120)

##### (a) In n-Decane

The ether (120) (3.92 g.) and n-decane (15 ml.) (freshly distilled from  $\text{LiAlH}_4$ ), were sealed in a nickel Carius tube under

nitrogen and heated at 150° for 18 hrs. After cooling, the reaction product and washings (freshly distilled acetone, 150 ml.) were transferred to a flask, and the acetone removed on a rotary evaporator at reduced pressure. The n-decane was then distilled off at 30°/0.01 mm. Hg pressure to yield a brown solid which was separated on a dry silica column 72 x 3 cm. using CCl<sub>4</sub>:CHCl<sub>3</sub> 7:3 as eluant to give two fractions. Fraction (i) (1.15 g.) was sublimed to yield a white solid, 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) (0.966 g., 24%). The non-sublimable residue (0.18 g.) was triturated with diethyl ether to give a yellow solid, bis-(4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl)methane (124) (65 mg., 1.5%). Fraction (ii) (0.14 g.) was recrystallized from petroleum ether 100/120 to yield di-(4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl methyl)ether (123) (85 mg., 2%). All three compounds were characterised using i.r. and <sup>19</sup>F n.m.r. analysis by comparison with known samples.<sup>56</sup>

(b) In 1,1,2-Trichlorotrifluoroethane

The ether (120) (1.64 g.) and 1,1,2-trichlorotrifluoroethane (40 ml.) (freshly distilled from P<sub>2</sub>O<sub>5</sub>), were sealed in a nickel Carius tube under nitrogen and heated at 150° for 18 hrs. After cooling, the reaction product and washings (freshly distilled acetone 150 ml.) were transferred to a flask, and the solvent removed on a rotary evaporator under reduced pressure to yield a brown solid (1.58 g.) which was sublimed at 67°/0.01 mm. Hg pressure, to give 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) a white solid, which was recrystallized from petroleum ether 60/80 (0.69 g., 42%), characterization was completed by comparison of i.r. and <sup>1</sup>H n.m.r. analysis against known samples.<sup>56</sup>

The non-sublimable residue was shown to contain both di-(4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl methyl)ether (123) (approx. 6%) and bis-(4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl)-methane (124) (approx. 3%), by t.l.c. analysis on silica plates with  $\text{CCl}_4:\text{CHCl}_3$  7:3 as the developing solvent.

Thermolysis of Pentafluorophenyl Prop-2-ynyl Ether (115) in 1,1,2-Trichlorotrifluoroethane

The ether (115) (2.83 g.) and 1,1,2-trichlorotrifluoroethane (30 ml.), (freshly distilled from  $\text{P}_2\text{O}_5$ ), were sealed in a nickel Carius tube under nitrogen and heated at  $150^\circ$  for 5 days (116 hrs.). After cooling, the reaction product and washings (diethyl ether 150 ml.) were transferred to a flask and the solvent removed on a rotary evaporator under reduced pressure to yield a brown oil (2.6 g.) which was separated on a dry silica column using  $\text{CCl}_4$ : petroleum ether 30/40 2:1 as eluant to give three fractions. Fraction (i) (0.44 g.) a colourless oil identified as recovered starting material (115) (18%); fraction (ii) (0.48 g.) a colourless oil 2-fluoromethyl-4,5,6,7-tetrafluorobenzo[b]furan (117) (19%); and fraction (iii) (0.49 g.) identified as di-(4,5,6,7-tetrafluorobenzo[b]furan-2-yl methyl)ether (128) (20%). All compounds were characterized by t.l.c. and i.r. analysis against known samples.<sup>56</sup>

The Preparation of 2,3,5,6-Tetrafluoro-4-pyridyl Prop-2-ynyl Ether (131)

2,3,5,6-Tetrafluoro-4-hydroxypyridine (20.58 g., 0.123M) (131), prop-2-ynyl bromide 80% solution in toluene (20.42 g.  $\equiv$  16.34 g., 0.137 m.), and potassium carbonate (33.9 g.) were heated under reflux in freshly distilled acetone (400 ml.) for 18 hrs. After cooling the reaction product was filtered through a short column of  $\text{MgSO}_4$ , which in turn was washed with diethyl ether (300 ml.). The pale orange

solution was fractionally distilled through a column to low volume then distilled under reduced pressure. The 2,3,5,6-tetrafluoro-4-pyridyl prop-2-ynyl ether (131) was obtained as a colourless oil at 68-69°/8.6 mm. Hg (22.59 g., 89%) (Found: C, 46.71; H, 1.55; N, 6.53;  $C_8F_4H_3NO$  requires: C, 46.83; H, 1.46; N, 6.83%).  $\delta_H$  ( $CDCl_3$ ) 2.73 (multiplet  $\equiv C-H$ ) and 5.16 (multiplet  $OCH_2$ );  $\delta_F$  ( $CDCl_3$ ) 91.3 (multiplet  $F_2, F_6$ ) 159 (multiplet  $F_3, F_5$ ) p.p.m. upfield internal  $CFCl_3$ .

The Reaction of 2-Fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]-furan (126) with p-Xylene

The 2-fluoromethyl compound (126) (0.25 g.) and p-xylene (10 ml.) (freshly distilled from  $P_2O_5$ ), were refluxed for 20 hrs., during which time HF was evolved. After cooling the excess p-xylene was distilled off at 40°/0.01 mm. Hg to yield a brown-black solid which was separated into 3 bands by preparative t.l.c. on silica plates using  $CCl_4$  as eluant.

Band (i) contained residual p-xylene; band (ii) (0.24 g.) a white solid identified by i.r.,  $^1H$  and  $^{19}F$  n.m.r. as 2-(2,5-dimethylbenzyl)4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (122) (75%), three successive recrystallizations of which from ethanol gave (0.156 g.) (49%) pure material m.pt. 115.5-116°C. Band (iii) (55 mg.) contained recovered starting material (126) (17%).

The 2-(2,5-dimethylbenzyl) derivative (122) was characterised by comparison with the i.r.,  $^1H$  and  $^{19}F$  n.m.r. analyses of known samples.<sup>56</sup>

## CHAPTER 4

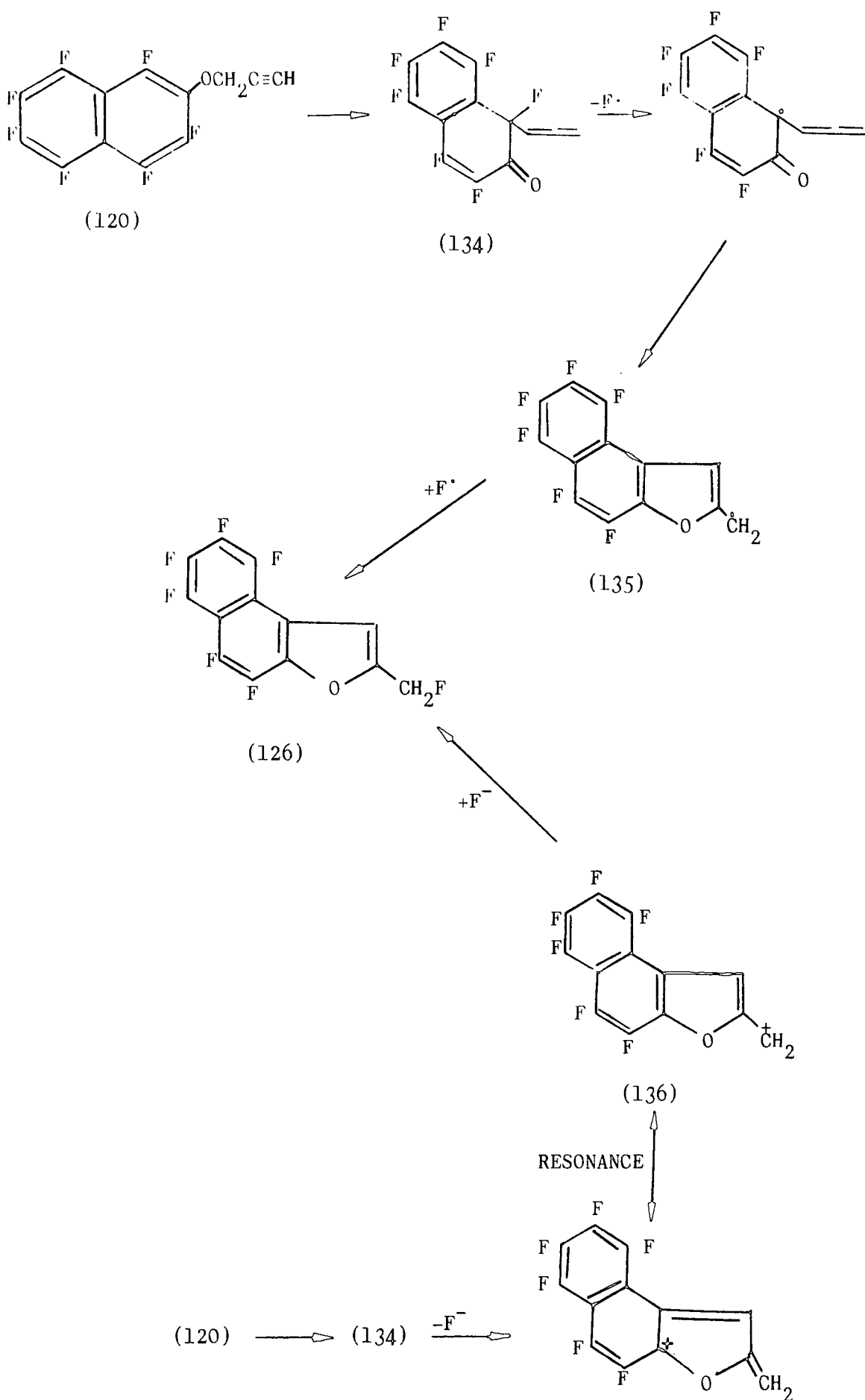
### The Thermolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether and 2-Fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan in the Presence of Alkenes

#### 4.1. Introduction

With the development of a general reaction procedure for the thermolysis of polyfluoroarylprop-2-ynyl ethers in a non-vitreous environment, as described in Chapter 3, attention was turned to the mechanism of these isomerisation reactions.

It has been shown how the formation of products of the type (117) and (126) can be rationalized via two possible reaction pathways:<sup>52,54</sup> (a) a [3,3] sigmatropic shift to form the Claisen rearrangement intermediate ortho-dienone (134) followed by homolytic cleavage of the  $sp^3$  carbon-fluorine bond, after which resonance can give intermediate (135), the reaction sequence is completed by radical recombination; (b) initial formation of the Claisen intermediate (134) followed by heterolytic cleavage of the  $sp^3$  carbon-fluorine bond, resonance then gives rise to intermediate (136) and reaction is completed by recombination of ions.

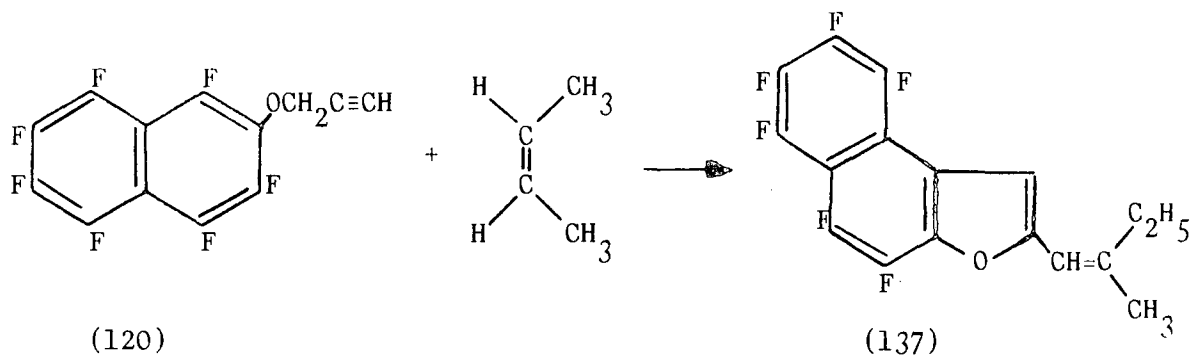
In an attempt to identify which of these two mechanisms operated, the reaction of (120), at  $150^\circ$  in the liquid phase, with alkenes was investigated. It was anticipated that because of the susceptibility of alkenes to electrophilic addition, the plausible reaction intermediates (135) and (136) would attack alkenes to give the overall addition of  $R^fCH_2-F$  to  $>C=C<$ , the orientation of the addition depending on the attacking species. With this aim in mind the naphthyl prop-2-ynyl ether (120) was thermolysed in the presence of a number of alkenes the first of which was (Z)-but-2-ene.



Scheme 43

#### 4.2. Thermolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether in the Presence of (Z)-But-2-ene

In a short period of early work the behaviour of the naphthyl ether (120) in the presence of (Z)-but-2-ene was examined. The ether (120) was sealed in a steel autoclave and an excess of (Z)-but-2-ene was introduced using vacuum transfer techniques. The mixture was then heated at 150° for 20 hrs. The reaction product which appeared to be very simple when examined by t.l.c. was shown by <sup>1</sup>H n.m.r. to be extremely complex. Extensive column and preparative thin layer chromatography using principally 30/40 petroleum ether as an eluant, followed by successive recrystallizations from 60/80 petroleum ether isolated 2-(2-methylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]-furan (137) (Scheme 44). The structure of (137) was identified

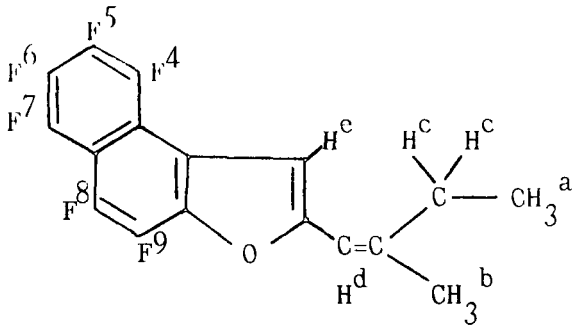


Scheme 44

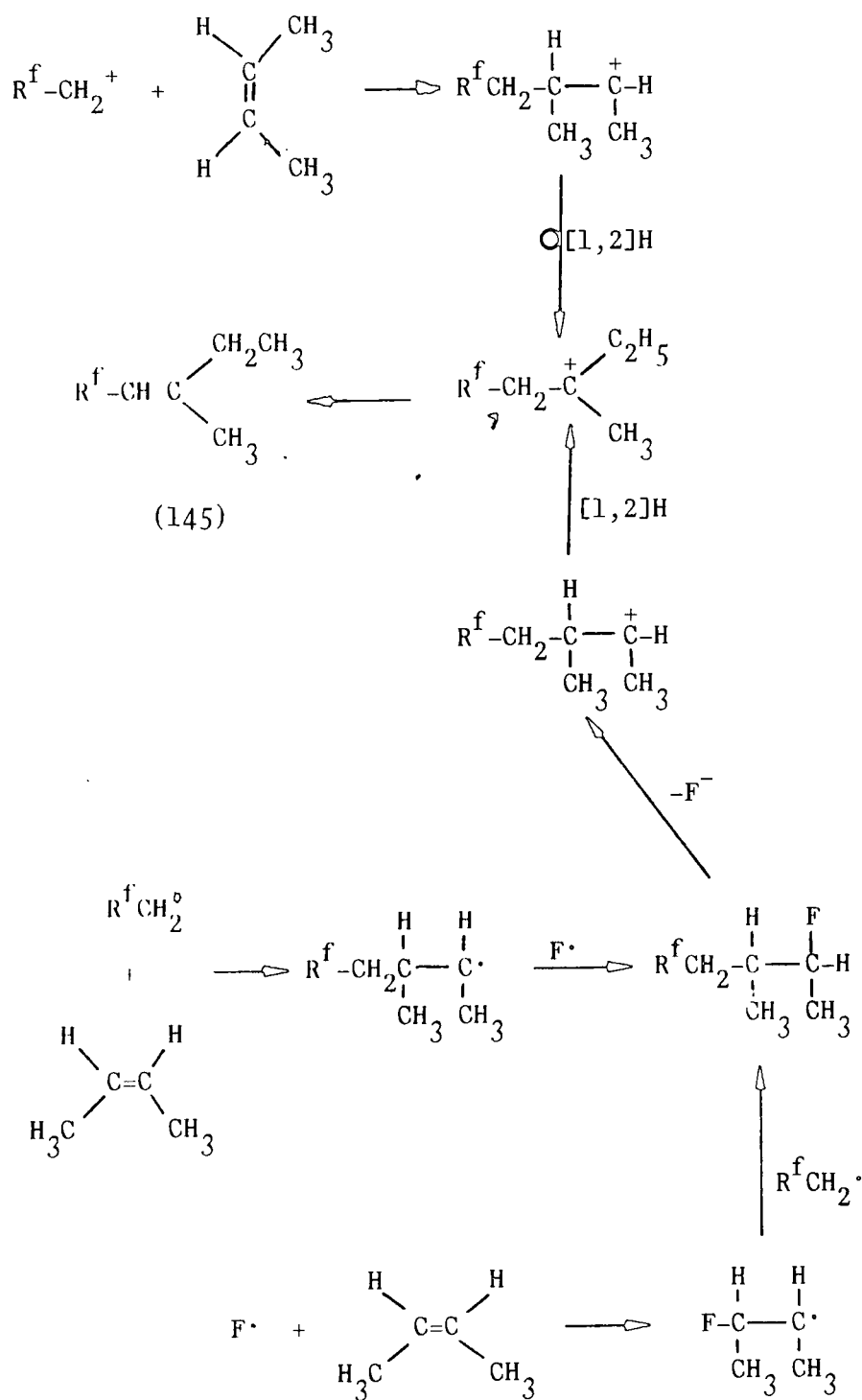
by <sup>1</sup>H and <sup>19</sup>F n.m.r. using accurate integration, the splitting pattern of the proton spectra, and the existence of only one peri  $J_{F-F}$  coupling constant; the mass spectrum was entirely consistent with the formulation C<sub>17</sub>H<sub>10</sub>F<sub>6</sub>O (Table 1).

The formation of alkene (137) could involve initial attack by carbocation (136) followed by a [1,2] hydride shift and subsequent proton loss. Alternatively (137) could be formed via initial attack by either F<sup>•</sup> or R<sup>f</sup>CH<sub>2</sub> adduct formation, then ionisation to yield a carbocation which could then rearrange (Scheme 45). No adduct was

Table 1: Data characterising 2-(2-methylbut-1-enyl)4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan

 <p style="text-align: center;">(137)</p>		
M.pt.	83-84°	
M <sup>+</sup>	344	
C	59.00% requires 59.3%	
H	3.00% requires 2.9%	
		REL. INT.
H <sup>a</sup>	1.13 - 1.17δ (t-CH <sub>3</sub> )	3
H <sup>b</sup>	2.15δ (d-CH <sub>3</sub> )	3
H <sup>c</sup>	2.25 - 2.32δ (qd CH <sub>2</sub> <sup>c</sup> -CH <sub>3</sub> <sup>a</sup> )	2
H <sup>d</sup>	6.26δ (sex. vinylic =CH-)	1
H <sup>e</sup>	7.07 - 7.09δ (dd 3-furanyl CH)	1
F <sup>4</sup> , F <sup>7</sup>	145 - 146 (b.m)	2
F <sup>8</sup>	151 - 152 (b.m) peri J <sub>F-F</sub> 66.5 Hz	1
F <sup>5</sup> , F <sup>6</sup> , F <sup>9</sup>	158 - 159 (b.m)	3

$R^f = 4,5,6,7,8,9\text{-hexafluoronaphtho}[2,1\text{-}b]\text{furan}.$



Scheme 45

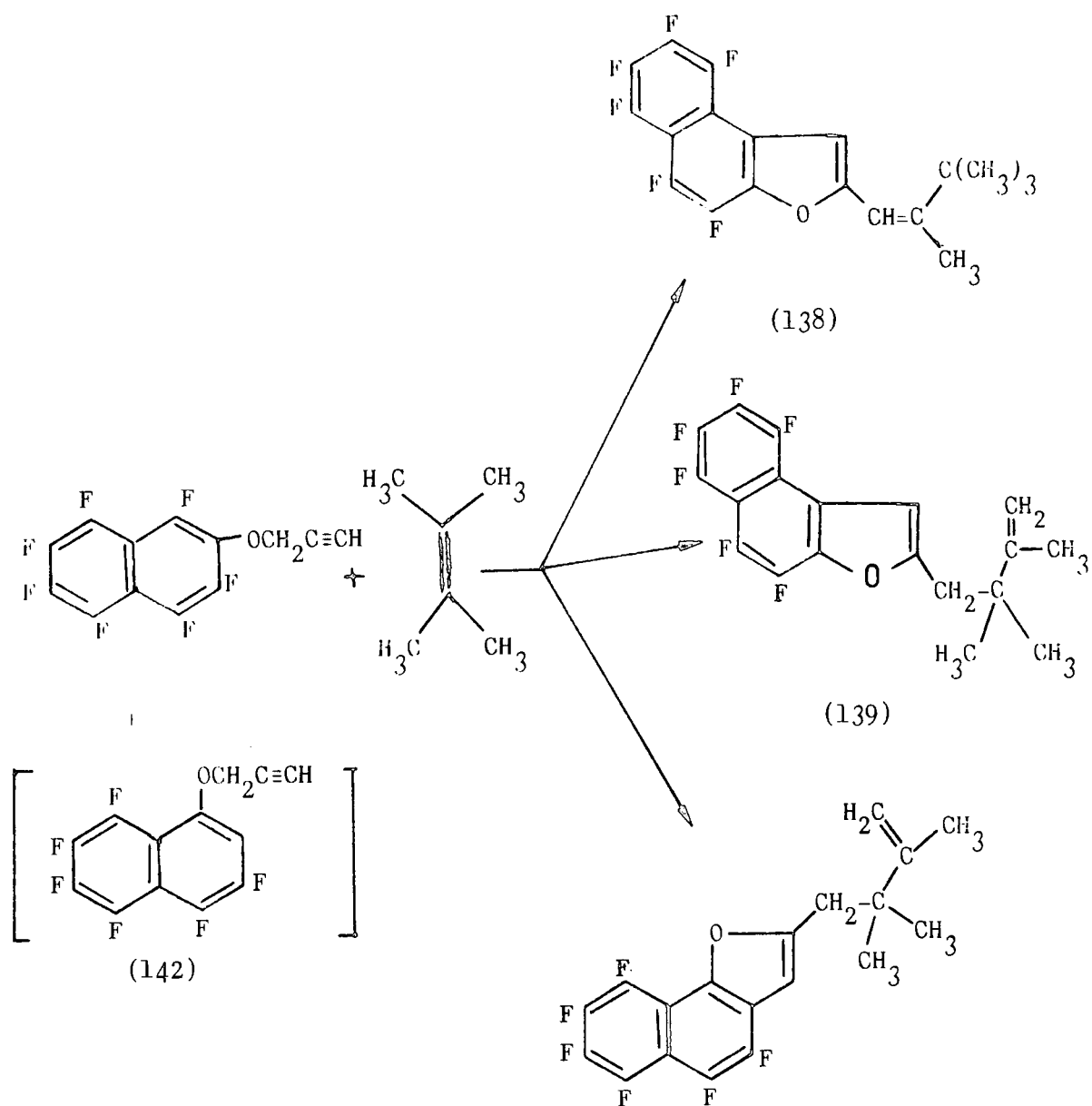
observed, and the reaction only served to illustrate the viability of the reaction of heptafluoro-2-naphthyl prop-2-ynyl ether (120) with alkenes leading to substitution products. Finally note should be made that during the work undertaken to isolate alkene (137) a degradation product 4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl aldehyde was observed<sup>by H.M.R.</sup>, formed presumably by aerial oxidation of the carbon to carbon double bond.

#### 4.3. Thermolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl-Prop-2-ynyl Ether in the Presence of 2,3-Dimethylbut-2-ene

A second alkene investigated to assess whether a simple adduct could be obtained was 2,3-dimethylbut-2-ene. The ether (120) was thermolysed in a nickel lined Carius tube in the presence of a large excess of 2,3-dimethylbut-2-ene at 150° for 20 hrs. The excess alkene was largely to ensure a liquid phase via condensation under pressure throughout the reaction period.

Work-up of the reaction products using extensive column chromatography and recrystallization gave three new compounds ( $\Delta R_f$  (30/40 petroleum ether)  $\sim$  0.1): 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138), 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139), and 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoro[1,2-b]furan (140) (Scheme 46). Identification of these three compounds was made principally by  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r., and final characterization was completed by mass spectroscopy.

The direction of the [3,3] sigmatropic shift towards the C-1 position in the naphthalene ring, shown in Scheme 46, was derived from the existence of only one large peri  $J_{\text{F-F}}$  coupling constant in the  $^{19}\text{F}$  n.m.r. spectrum of each compound, and the chemical shifts



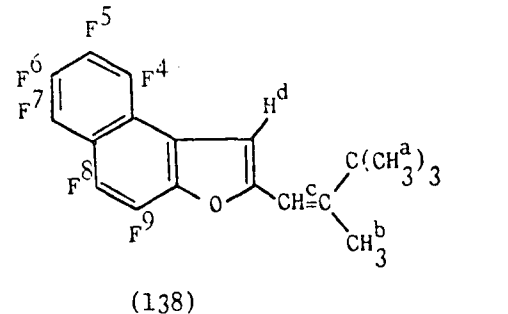
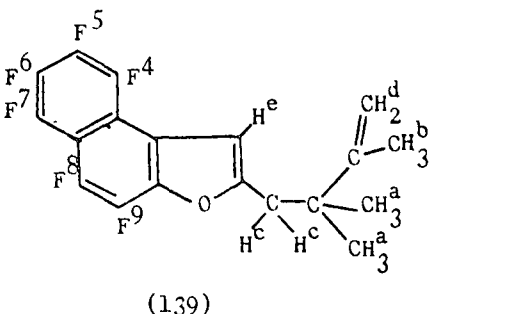
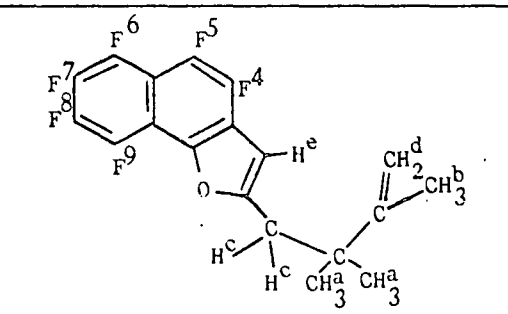
[(140) Due to presence of  $\alpha$ -ether in (120)]

Scheme 46

and accurate integration of the signals in the proton spectra (Table 2); the stereochemistry of the alkene (138) could not be determined. No adduct was observed, instead an addition-elimination reaction had occurred, leading to overall substitution of  $R^fCH_2-$  into the alkene.

The two compounds of most interest were the t-butyl derivative (138) and the terminal alkene (139). The formation of compound (139) can be rationalized via an initial attack by the carbocation species (136) followed by proton loss. Alternatively an initial radical attack

Table 2: Analytical results for the isolated products from the thermolysis of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl-prop-2-ynyl ether with 2,3-dimethylbut-2-ene

	M.Pt.	M <sup>+</sup>	Elemental Analysis	<sup>1</sup> H n.m.r.	Rel. Inten.	<sup>19</sup> F n.m.r.	Rel. Inten.
 <p>(138)</p>	153-4°	372	C, 61.53; (61.3) H, 3.81; (3.76)	H <sup>a</sup> 1.19δ (s) H <sup>b</sup> 2.13δ (d) H <sup>c</sup> 6.38δ (s) H <sup>d</sup> 7.12 (t)	9 3 1 1	145-6.5 (b.m.) F <sup>4</sup> ; F <sup>7</sup> 150.9 (b.m.) F <sup>8</sup> 158.2-.9 (b.m.) F <sup>5</sup> ; F <sup>6</sup> ; F <sup>9</sup> Peri J <sub>F-F</sub> 76 Hz	2 1 3
 <p>(139)</p>	45-6°	372	C, 61.17; (61.3) H, 3.82; (3.76)	H <sup>a</sup> 1.19δ (s) H <sup>b</sup> 1.86δ (d of d) H <sup>c</sup> 2.95δ (s) H <sup>d</sup> 4.72-4.77 (d) H <sup>e</sup> 6.96 (dd)	6 3 2 2 1	145.7-146.7 (b.m.) F <sup>4</sup> ; F <sup>7</sup> 151.9-152.4 (b.m.) F <sup>8</sup> 158.2-159.4 (b.m.) F <sup>5</sup> ; F <sup>6</sup> ; F <sup>9</sup> Peri J <sub>F-F</sub> 50 Hz	2 1 3
 <p>(140)</p>	34.5-6.5	372	C, 61.29; (61.3) H, 3.80; (3.76)	H <sup>a</sup> 1.19δ H <sup>b</sup> 1.88δ (d of d) H <sup>c</sup> 2.96δ (s) H <sup>d</sup> 4.69-4.75 (d) H <sup>e</sup> 6.66 (s)	6 3 2 2 1	143.9 (b.m.) F <sup>9</sup> 146.8 (b.m.) F <sup>5</sup> ; F <sup>6</sup> 154.5-155.2 (b.m.) F <sup>8</sup> 158.2-158.9 (b.m.) F <sup>4</sup> ; F <sup>7</sup> Peri J <sub>F,F</sub> 68 Hz	1 2 1 2

by either  $F\cdot$  or  $R^f-CH_2\cdot$  (135) and subsequent adduct formation is followed by ionization through loss of  $F$ , and the carbocation then loses a proton to generate the alkene. To produce compound (138) however requires a [1,2] migration of a methyl group, such rearrangements are well known for reactions proceeding via carbocations. When considering radical rearrangements, Sharp stated<sup>57</sup> 'the most marked contrast with carbenium ions is the absence of 1,2-shifts of hydrogen and alkyl groups'. Consequently radical rearrangements will not be countenanced.<sup>57,58,59</sup> The formation of compounds (138) and (139) via the described routes is illustrated in Scheme 47.

The formation of the isomer (140) was due to the presence of 2,3,4,5,6,7,8-heptafluoro-1-naphthyl prop-2-ynyl ether (142) in the starting material (120).

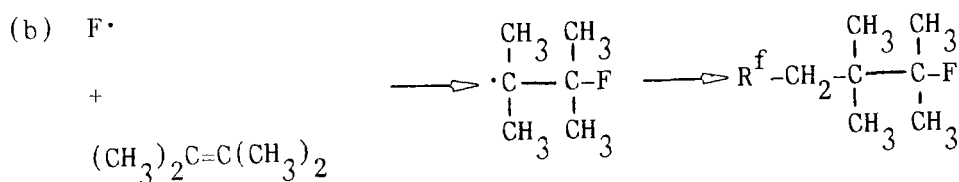
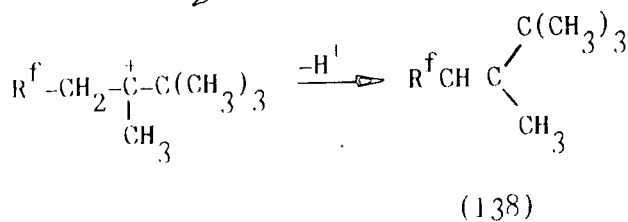
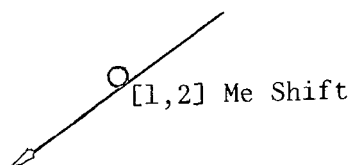
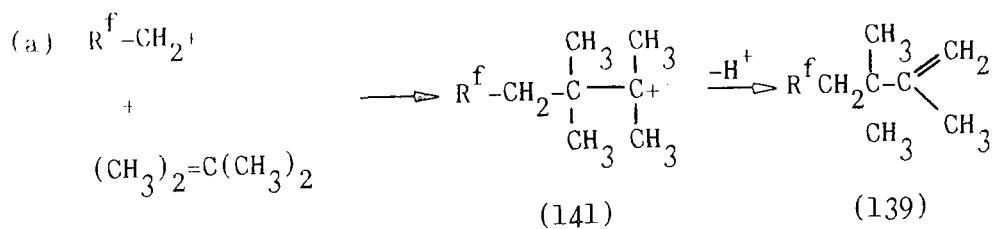
The isolation and characterisation of viable substitution products from the reaction of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (120) with 2,3-dimethylbut-2-ene under thermolysis conditions led to an examination of the isomer ratios of (138), (139) and (140). Two further reactions involving (120) and 2,3-dimethylbut-2-ene were undertaken and the substitution products (138), (139) and (140) were isolated as a mixture. This mixture was extensively analysed by  $^1H$  n.m.r. and from a comparison of the relative intensities of appropriate proton signals the ratio of isomers were determined. The results of the analyses are shown in Table 3.

#### 4.4. Thermolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether in the Presence of 3,3-Dimethylbut-1-ene

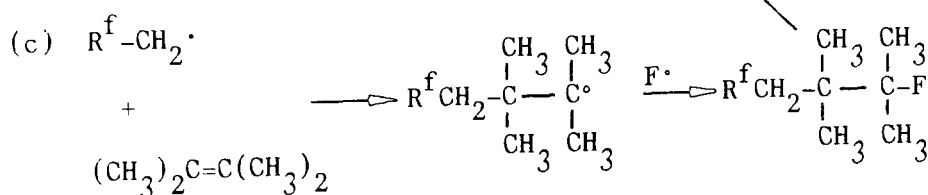
##### 4.4.1. Introduction

The formation of the substitution products (138), (139) and (140) from the reaction of heptafluoro-2-naphthylprop-2-ynyl ether (120) with 2,3-dimethylbut-2-ene clearly demonstrated the viability of the

R<sup>f</sup> 4,5,6,7,8,9 hexafluoronaphtho[2,1-b]furan.



As above  $\longleftarrow$  (141)

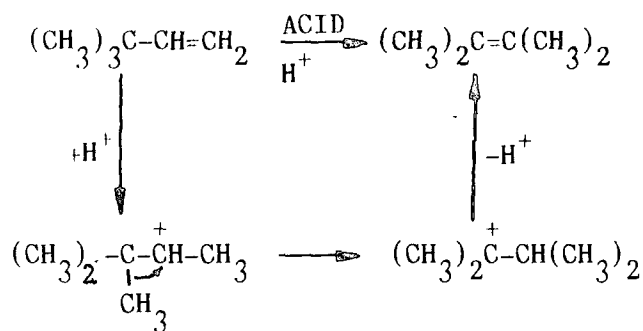


Scheme 47

Table 3: Isomer ratios of products observed in the thermolysis of  
(120) in the presence of 2,3-dimethylbut-2-ene

Experiment	1	2
	Isomer Ratios	Isomer Ratios
Reaction Yield	45%	54%
(138)	1 Part	1 Part
(139)	95 Parts	95 Parts
(140)	4 Parts	4 Parts

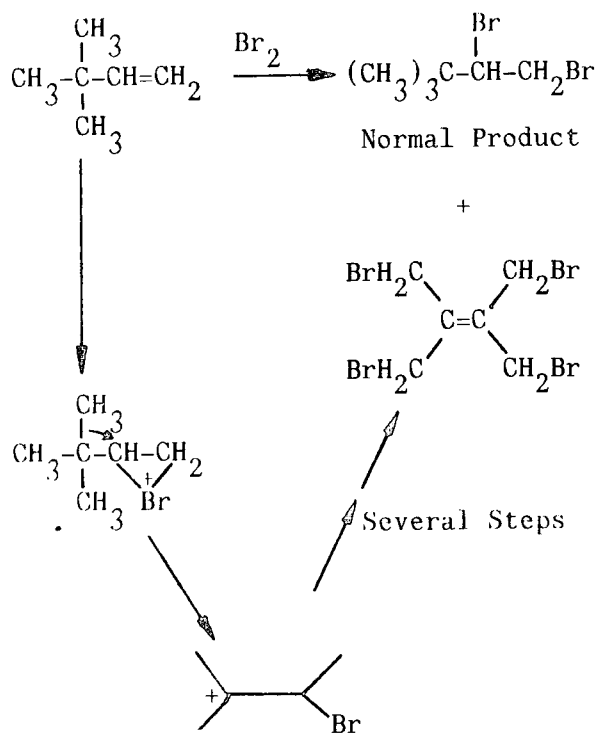
reaction of (120) with alkenes. To provide further information about the mechanism of formation of these substitution products the thermolysis procedure was repeated using 3,3-dimethylbut-1-ene. Reactions involving rearrangement of the carbon skeleton of this reagent are well known, and an example is shown (Scheme 48).<sup>60</sup>



Scheme 48

When 3,3-dimethylbut-1-ene was chlorinated, as a probe for Wagner-Meerwein rearrangements,<sup>61</sup> the major product was formed without rearrangement. A minor product was formed however; the result of a methyl shift followed by proton loss to give 4-chloro-2,3-dimethylbut-1-ene. Similarly when 3,3-dimethylbut-1-ene was brominated at room temperature,<sup>62</sup> the expected 1,2-dibromide was obtained, along with a minor component 2,3-dibromomethyl-1,4-dibromo-

but-2-ene, as a result of a methyl shift in the carbon skeleton (Scheme 49).

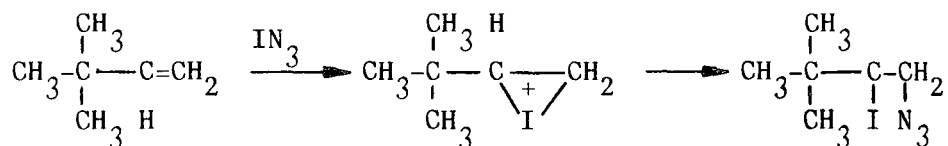


Scheme 49

Pocker and Stevens<sup>63</sup> examined the reaction of hydrogen chloride with 3,3-dimethylbut-1-ene using preparative gas-liquid chromatography and found that using nitromethane as a solvent 83% of the rearranged product 2-chloro-2,3-dimethylbutane was obtained, whilst reaction of HCl with alkene in the absence of solvent gave 50% of the rearranged product.

Interesting steric factors were observed in the reactions of 3,3-dimethylbut-1-ene with certain iodine compounds. Hassner and Fowler<sup>64</sup> examined the addition of iodine azide to a number of alkenes. Regiospecific addition was observed and accounted for by a bridging iodinium ion, which opened at the more substituted carbon atom for electronic reasons. When the iodine azide was reacted with 3,3-dimethylbut-1-ene, however, a reversal of regiospecificity was observed; Hassner and Fowler<sup>64</sup> believed this was due to steric

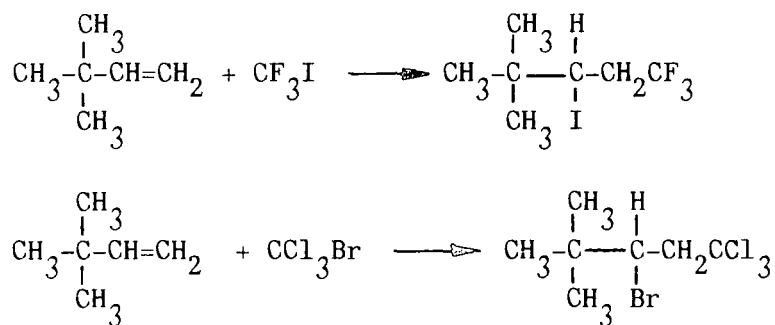
factors (Scheme 50). Hassner *et al.*<sup>65</sup> recorded similar behaviour



Scheme 50

when examining the addition of iodine isocyanate to 3,3-dimethylbut-1-ene, which yielded (3,3-dimethyl-2-iodo)butyl isocyanate. Diner and Lown<sup>66</sup> investigated the reaction of iodine nitrate with 3,3-dimethylbut-1-ene and once again steric hindrance was invoked to account for the formation of the (3,3-dimethyl-2-iodo)butyl nitrate. In 3,3-dimethylbut-1-ene therefore the bulky *t*-butyl group allows steric factors to have a strong influence in certain addition reactions.

There are surprisingly few examples of reactions between 3,3-dimethylbut-1-ene and radicals: the reaction of the alkene with substituted bromosuccinimides<sup>67</sup> gave no rearrangement products, whilst the reaction of  $\text{CF}_3\text{I}$  and  $\text{CCl}_3\text{Br}$  with 3,3-dimethylbut-1-ene<sup>68</sup> gave the Markownikov products: 1,1,1-trifluoro-3-iodo-4,4-dimethylpentane, and 1,1,1-trichloro-3-bromo-4,4-dimethylpentane (Scheme 51).

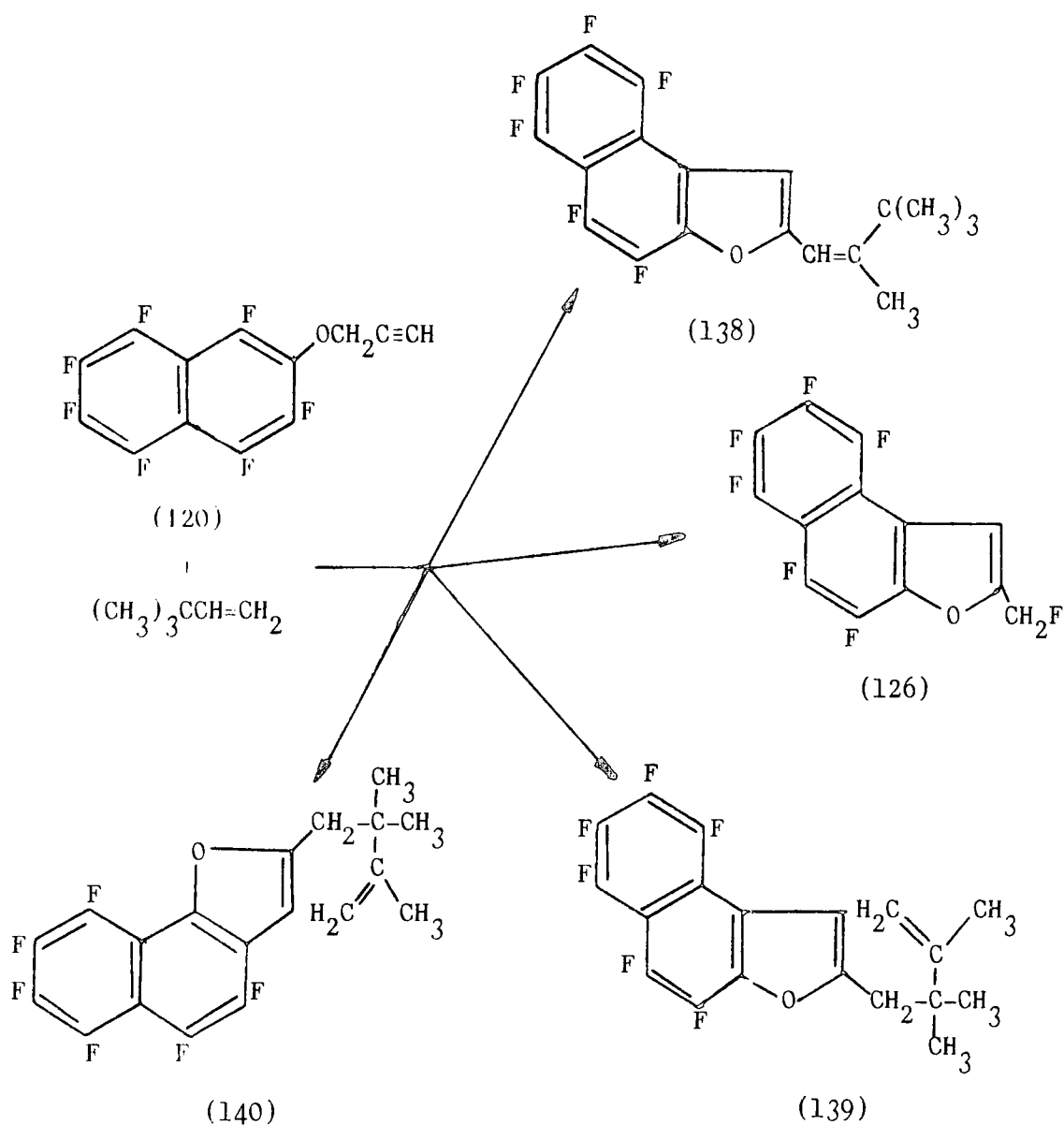


Scheme 51

#### 4.4.2. Current Work

The ether (120) was thermolysed as previously in the presence of 3,3-dimethylbut-1-ene at 150° for 20 hrs. Three products were again identified by <sup>1</sup>H n.m.r.: 2-(2,3,3-trimethylbut-1-enyl)-

4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138), 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139), and 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[1,2-b]furan (140), i.e. the same materials observed as products in the thermolysis of (120) with 2,3-dimethylbut-2-ene (cf. Section 4.3). Along with these three substitution products a small amount of 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) was formed, which was identified by i.r. analysis (Scheme 52).



Scheme 52

The formation of the substitution products depends on the reaction of intermediates (135) and (136) (Scheme 43) with the double bond of the alkene. The occurrence of isomer (140) was once again due to the presence of heptafluoro-1-naphthyl ether (142) in the starting material heptafluoro-2-naphthyl ether (120). When the ether (120) was purified by successive sublimations ( $50^{\circ}$ , 0.01 mm. Hg) and recrystallizations (30/40 petroleum ether), the pure material (120) gave only 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138) and 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139). The product mixture was partially separated using extensive column and preparative thin layer chromatography to yield pure 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138) which was identified by melting point and i.r. analysis.

The appearance of the same two products (138) and (139) in the reaction of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (120) with both 2,3-dimethylbut-2-ene and 3,3-dimethylbut-1-ene was a surprising result. The formation of (138) and (139) from 3,3-dimethylbut-1-ene and the ether (120) required either anti-Markownikov attack by carbocation (136) and subsequent skeletal rearrangement, or initial attack by  $F^{\cdot}$  followed by anti-Markownikov adduct formation, the adduct must then ionize via loss of  $F^{-}$  to give a carbocation which rearranges. The significance of the observed results are discussed in more detail in Section 4.6.

The isomer ratios for the reaction of (120) with 3,3-dimethylbut-1-ene were determined by accurate integration of  $^1H$  n.m.r. spectra. The results are shown in Table 4. Although similar procedures were used to separate the isomer mixtures in the reactions of (120) with both alkenes, the mixtures from the thermolyses of (120) in 2,3-

Table 4: Isomer ratios of products from the thermolysis of (120) in the presence of 3,3-dimethylbut-1-ene

	1	2
	Isomer Ratios	Isomer Ratios
Reaction Yield	33%	43%
(138)	7 Parts	7 Parts
(139)	91 Parts	93 Parts
(140)	2 Parts	-
Unidentified	Not examined	33 Parts

dimethylbut-2-ene were much cleaner than those observed with 3,3-dimethylbut-1-ene and up to 25% of the isomer mixture remained unidentified when 3,3-dimethylbut-1-ene was used. Further the complexity of the  $^1\text{H}$  n.m.r. of the unknown portion suggested a complex mixture. A second observation which can be made is the variation in the percentage of 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138) obtained from 2,3-dimethylbut-2-ene and 3,3-dimethylbut-1-ene. The reaction of (120) with 3,3-dimethylbut-1-ene yields approximately five times as much of (138) as the thermolysis of (120) in 2,3-dimethylbut-2-ene.

4.5. Reaction of 2-Fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]-furan with 2,3-Dimethylbut-2-ene and 3,3-Dimethylbut-1-ene

Since reasonable quantities of the 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) were available, the reaction of (126) with 2,3-dimethylbut-2-ene and 3,3-dimethylbut-1-ene was investigated. Furthermore, it had been shown to react with p-xylene

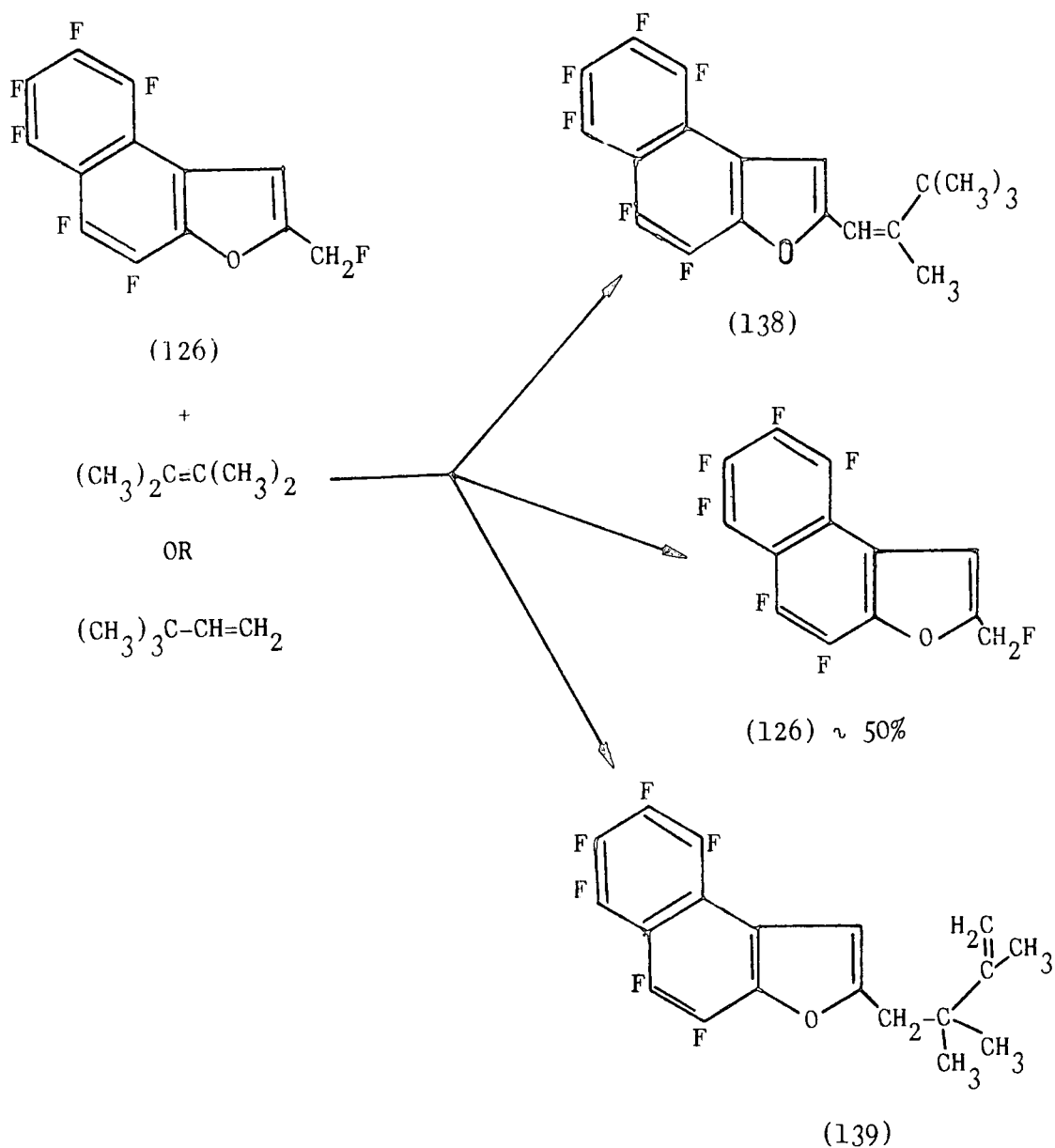
(see Chapter 3, Section 3.5) presumably after heterolytic cleavage of the  $R^fCH_2-F$  bond yielded the reactive intermediate  $R^fCH_2^+$  (136), a stabilized benzylic-type intermediate, although electrophilic substitution into the aromatic ring could be via a carbocation or a radical. The 2-fluoromethyl compound (126) therefore was reacted with the same two alkenes.

(a) The 2-fluoromethyl compound (126) and 2,3-dimethylbut-2-ene were sealed in a nickel-lined Carius tube and heated at  $150^\circ$  for 3 days. The fastest moving components, by t.l.c., were isolated and analysed by  $^1H$  n.m.r. The spectra indicated that the main products were: 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]-furan (138) and 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139). Extensive column chromatography and successive recrystallization allowed pure (138) to be isolated and characterized by melting point and i.r. analysis.

(b) The 2-fluoromethyl compound (126) was sealed in a nickel-lined Carius tube with 3,3-dimethylbut-1-ene and heated for either 20 hrs. or 3 days. In the initial experiments a time period of 20 hrs. was used; however the conversion of 2-fluoromethyl derivative (126) into viable products was of the order 20-30%, so that in an attempt to improve the conversion the reaction time was increased to 3 days. Unfortunately this produced no improvement in the yield of products.

The fastest moving components, by t.l.c., from the reaction of (126) with 3,3-dimethylbut-1-ene were separated and analysed by  $^1H$  n.m.r., which showed that this reaction also gave the two alkenes

(138) and (139). Both compounds were later isolated and characterised by i.r. analysis. In both groups of reactions between the 2-fluoromethyl compound (126) and the two alkenes, recovered starting material accounted for up to 50% of the product mixture (Scheme 53).



Scheme 53

Isomer ratios were examined and the results are shown in Table 5. The most noteworthy feature of the values obtained is the large increase in the formation of the 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138). The increase is even

Table 5: The isomer ratios of products observed in the thermolysis of (126) in the presence of 2,3-dimethylbut-2-ene and 3,3-dimethylbut-1-ene

	Isomer Ratios			
	(A)	(B)	(C)	(D) <sup>69</sup>
Alkene	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	3,3-Dimethylbut-1-ene		
	72 hrs.	20 hrs.	68 hrs.	20 hrs.
Yields	58%	33%	20%	21%
(138)	8 Parts	8 Parts	20 Parts	30 Parts
(139)	92 Parts	92 Parts	80 Parts	70 Parts
(Unknown)	48 Parts	16 Parts	40 Parts	48 Parts

more marked at the longer reaction time (68 hrs.), though the actual percentage yields of substitution products were significantly lower, particularly in reactions involving 3,3-dimethylbut-1-ene. The third set of figures (D) were obtained for a thermolysis of 20 hrs. duration and were inconsistent with the other two sets of data. One factor which may have been partly responsible for these discrepancies was that the time lapse between the separation of the isomeric mixtures and the actual analysis was significantly longer for determination (B) than for either (C) or (D) (Table 5). Consequently it is possible that some degradation of the t-butyl derivative (138) may have occurred in the interim period. Close examination of the spectra revealed no evidence of the aldehydic proton of 4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl aldehyde, a compound already observed as the oxidation product of the analogous alkene 2-(2-methylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (137).

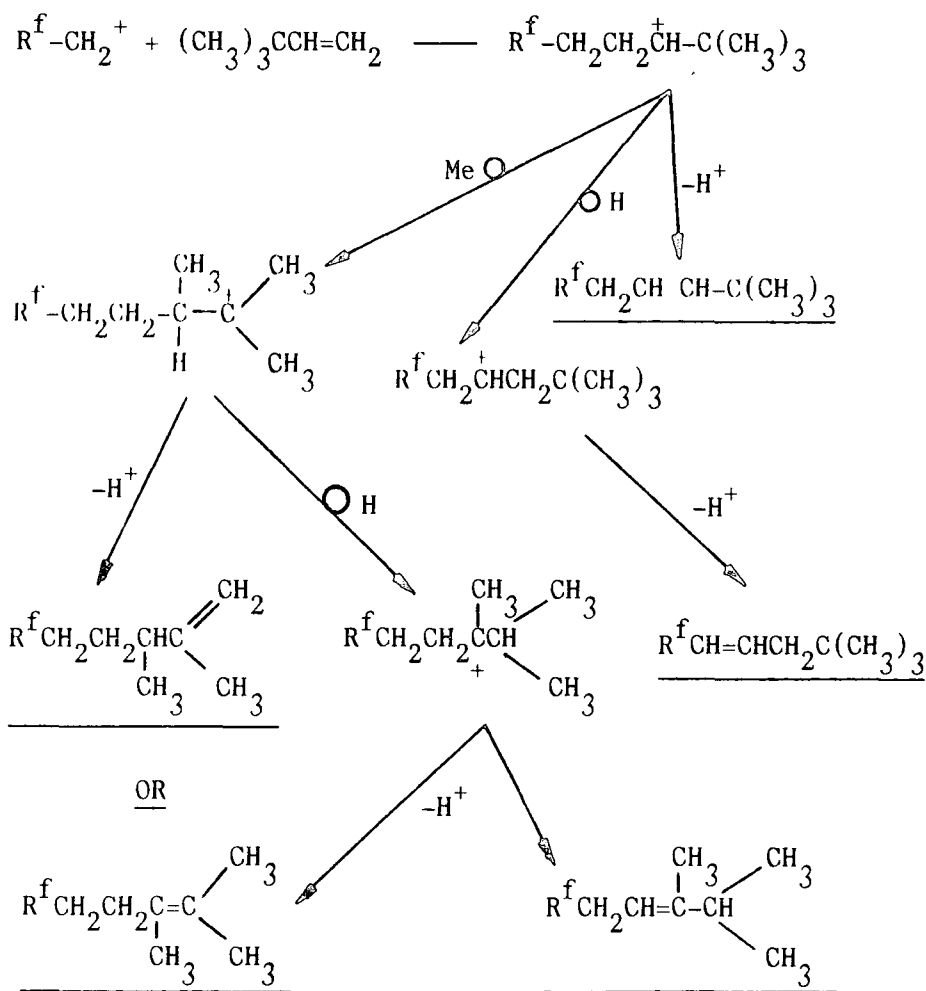
Interestingly the unidentified portions of the  $^1\text{H}$  n.m.r. spectra observed in the reactions of both (120) and (126) with 3,3-dimethylbut-1-ene were identical in almost every detail, whilst the  $^1\text{H}$  n.m.r. spectra of the reaction products from both (120) and (126) with 2,3-dimethylbut-2-ene were different, and also different to those involving 3,3-dimethylbut-1-ene.

Finally it should be noted that in all analyses for isomer ratios, (Tables 3, 4 and 5), the reaction yields were low and this obviously places some doubt on the reliability of the determined ratios.

#### 4.6. Mechanistic Aspects of the Reaction of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether and 2-Fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan with 2,3-Dimethylbut-2-ene and 3,3-Dimethylbut-1-ene

The reaction of (120) and (126) with 2,3-dimethylbut-2-ene to

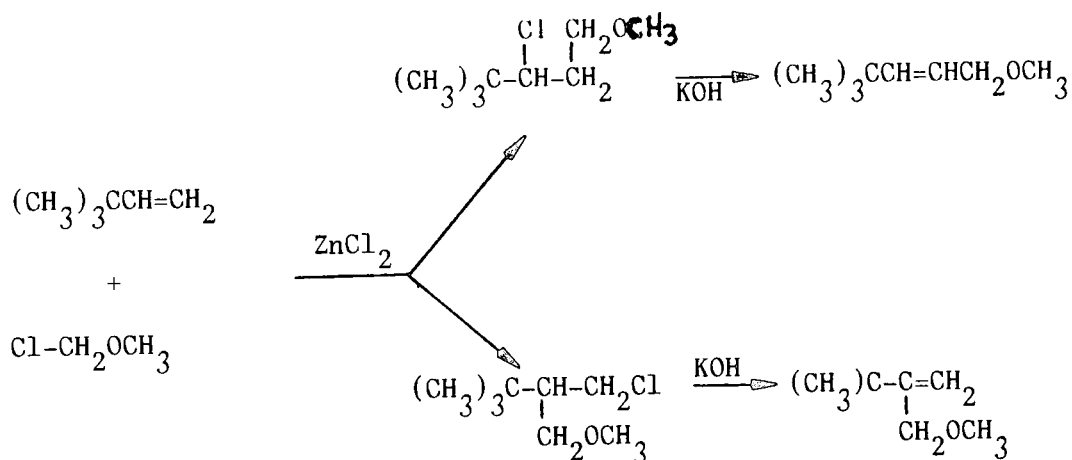
yield 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138) and 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139) has been readily rationalized in terms of an intermediate cationic species. This species was derived from either initial carbocation attack by  $R^fCH_2^+$  (136), or addition adduct formation after attack of the alkene by either  $F\cdot$  or  $R^fCH_2\cdot$  (135) followed by ionization through loss of  $F^-$  to yield a carbocation and subsequent formation of the alkenes (138), (139) (Section 4.3, Scheme 47). However, when the action of a cationic intermediate such as (136) derived from either (120) or (126), on 3,3-dimethylbut-1-ene was examined, the alkenes (13g) and (13q) should not have been among the five possible products which could arise via an initial Markownikov addition (Scheme 54). When, however,



Scheme 54

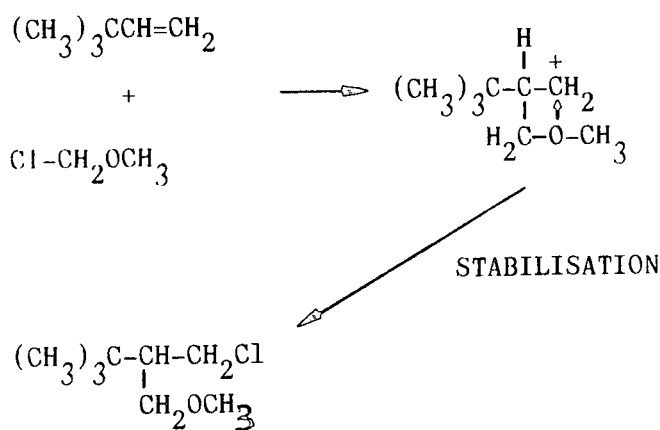






Scheme 58

the reaction, illustrated in Scheme 58, which could be seen as a form of bridging intermediate<sup>71</sup> (Scheme 59). The argument could be extended to the present work suggesting a transition state of even more favourable geometry (Scheme 60). Models of the proposed bridged anti-Markownikov adducts have been made which show that the



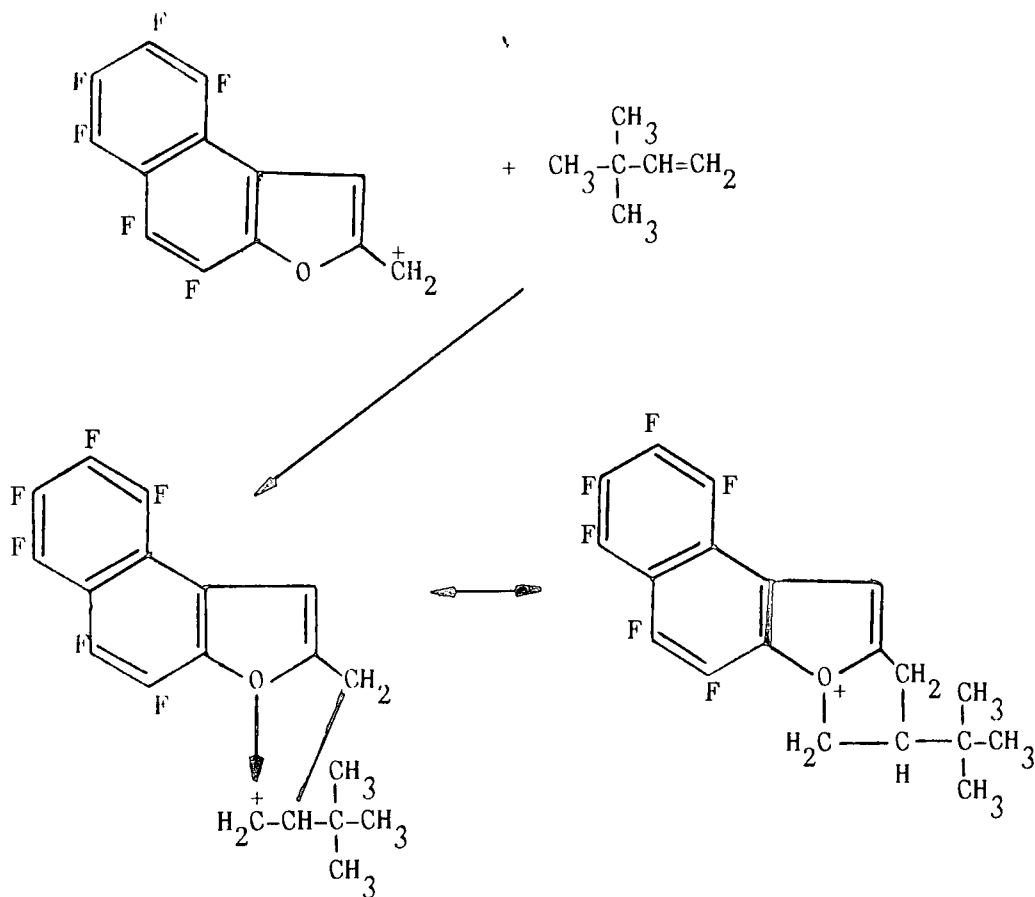
Anti-Markownikov addition

Scheme 59

anti-Markownikov structures are sterically more stable than the conventional Markownikov adducts with analogous bridging.

#### 4.7. Concluding Remarks

The most important feature of the formation of the two substitution products (138) and (139) in all the experiments



Scheme 60

described in this Chapter involving 3,3-dimethylbut-1-ene, is the need at some point for the carbon skeleton to rearrange by a [1,2]-methyl shift. Radicals do not show this type of rearrangement,<sup>57-59</sup> which therefore allows only two mechanisms to be postulated:

(a) initial anti-Markownikov addition of a carbocation moiety of the type  $R^f-CH_2^+$  (136) to the alkene (Scheme 55); or (b) initial attack on the alkene by  $F\cdot$  followed by formation of the adduct (144) which must then ionise by loss of  $F^-$  (Scheme 56).

The formation of (138) and (139) from 2,3-dimethylbut-2-ene and naphthyl prop-2-ynyl ether (120) is readily explained via a carbocation mechanism which involves some rearrangement (Scheme 47a);

if a radical mechanism is invoked then there can be initial attack by either  $F\cdot$  or  $R^fCH_2\cdot$  (135) followed by adduct formation, then ionisation and subsequent cation rearrangement (Scheme 47b,c). However, the formation of (138) and (139) from the reaction of heptafluoro-2-naphthyl prop-2-ynyl ether (120) and 3,3-dimethylbut-1-ene involving initial carbocation attack requires anti-Markownikov addition of  $R^fCH_2^+$  (136) (Scheme 55) for which there is only one literature example,<sup>70</sup> but which may be accounted for by a bridged intermediate of the type shown in Scheme 59. Alternatively the formation of (138) and (139) from reaction of (120) and 3,3-dimethylbut-1-ene involving a radical mechanism requires initial attack by  $F\cdot$  followed by adduct formation then loss of  $F^-$  to yield a primary cation (143) which will undergo rearrangement (Scheme 55). It is not possible therefore to state from the present data, whether the mechanism involved in the intramolecular rearrangement of polyfluoroarylprop-2-ynyl ethers involves either heterolytic or homolytic fission of the  $sp^3$  carbon-fluorine bond in the intermediate (134), illustrated in Scheme 43.

If one considers the behaviour of the 2-fluoromethylhexafluoro-naphtho[2,1-b]furan (126) with 2,3-dimethylbut-2-ene and 3,3-dimethylbut-1-ene respectively, in which both reactions yield (138) and (139), it is reasonable to suggest that the initial cleavage of the aliphatic C-F bond is a heterolytic process since  $R^fCH_2^+$  [(136) Scheme 43] is a stabilized benzylic-type cation. The reaction of this cation with 3,3-dimethylbut-1-ene must then proceed via an anti-Markownikov addition possibly through a stabilized cyclic transition state of the type (145) (Scheme 60).

There remains however the possibility of a very much simpler explanation. The formation of the very first  $H^+$  ion in the

reaction mixture could bring about the complete isomerisation of 3,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene (Scheme 48). The reaction would then simply be between the naphthyl ether (120) and 2,3-dimethylbut-2-ene. While this is a genuine possibility it is difficult to see why  $R^f-CH_2^+$  should not react directly with 3,3-dimethylbut-1-ene to some extent.

#### 4.8. Experimental

##### Reaction of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (120) and (Z)-But-2-ene

The ether (120) (3.23 g.) was sealed in a steel autoclave, Z-but-2-ene (2.89 g.) was transferred in vacuo into the autoclave and the combined reactants heated at  $150^{\circ}$  for 18 hrs. After cooling, the residual Z-but-2-ene was removed by venting the apparatus. The reaction products and washings (diethyl ether 150 ml.) were combined and the ether removed under reduced pressure. The residue was chromatographed on a dry silica column using 30/40 petroleum ether as an eluant. The fastest moving components were separated as one main fraction (0.80 g.) which had a very complex  $^1H$  n.m.r. spectrum. By a combination of column chromatography and preparative t.l.c. using 30/40 petroleum ether, and successive recrystallization from 60/80 petroleum ether 2-(2-methylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (137) was isolated. M.pt.  $83-84^{\circ}$ ; (Found: C, 59.00; H, 3.00;  $C_{17}H_{10}F_6O$  requires C, 59.30; H, 2.9%);  $M^+$  344 a.m.u.;  $\delta_H$   $CDCl_3$  1.17 - 1.13 (t.  $\underline{CH_2-CH_3}$ ), 2.15 (s.  $\underline{-CH_3}$ ), 2.32 - 2.25 (q.  $\underline{-CH_2-CH_3}$ ), 6.26 (s. vinylic  $\underline{CH}$ ), 7.07 - 7.09 (t. 3-furanyl  $\underline{CH}$ );  $\delta_F$   $CDCl_3$  145 - 146 (b.m.), 151 - 152 (b.m.), 158 - 159 (b.m.), (p.p.m. upfield from internal  $CFCl_3$ ) in the ratio 2:1:3 respectively; single peri  $J_{F-F}$  66.5 Hz.

Reaction of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether  
(120) and 2,3-Dimethylbut-2-ene

The ether (120) (5.98 g.) and 2,3-dimethylbut-2-ene (11.0 ml.  $\equiv$  7.8 g.) were sealed in a nickel lined Carius tube and heated at 150<sup>o</sup> for 20 hrs. After cooling, the excess alkene was removed by distillation. The residue was chromatographed on a dry silica column using 30/40 petroleum ether as an eluant. The main products were collected as the fastest moving components total weight 3.89 g., three compounds were later isolated using a combination of column chromatography and recrystallisation. The fastest moving component was 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]-furan (138) m.pt. 153 - 154<sup>o</sup> (Found: C, 61.53; H, 3.81; C<sub>19</sub>H<sub>14</sub>F<sub>6</sub>O requires C, 61.30; H, 3.76%); M<sup>+</sup> 372 a.m.u.;  $\delta_{\text{H}}$  CDCl<sub>3</sub> 1.19 (s. 3 x CH<sub>3</sub>), 2.13 (d. CH<sub>3</sub>), 6.38 (s. vinylic CH), 7.12 (t. 3-furanyl CH);  $\delta_{\text{F}}$  CDCl<sub>3</sub> 145 - 146.5 (b.m.), 150.9(m), 158.2 - 158.9 (b.m.) (p.p.m. upfield from internal CFCl<sub>3</sub>) in the ratio 2:1:3 respectively; single peri J<sub>F-F</sub> 76 Hz. The second fastest moving component was 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]-furan (139) m.pt. 45 - 46<sup>o</sup> (Found: C, 61.17; H, 3.82; C<sub>19</sub>H<sub>14</sub>F<sub>6</sub>O requires C, 61.30; H, 3.76%), M<sup>+</sup> 372 a.m.u.;  $\delta_{\text{H}}$  CDCl<sub>3</sub> 1.19 (s. 2 x CH<sub>3</sub>), 1.86 (d of d CH<sub>3</sub>), 2.95 (s. -CH<sub>2</sub>-), 4.72, 4.77 (d. = CH<sub>2</sub>), 6.96 (t. 3-furanyl CH);  $\delta_{\text{F}}$  CDCl<sub>3</sub> 145.7 - 146.7 (b.m.), 151.9 - 152.4 (b.m.), 158.2 - 159.4 (b.m.), (p.p.m. upfield from internal CFCl<sub>3</sub>) in the ratio 2:1:3 respectively; single peri J<sub>F-F</sub> 50 Hz. The slowest of the faster moving components was 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[1,2-b]furan (140) m.pt. 34.5 - 36.5 (Found: C, 61.29; H, 3.80; C<sub>19</sub>H<sub>14</sub>F<sub>6</sub>O requires C, 61.30; H, 3.76%); M<sup>+</sup> 372 a.m.u.;  $\delta_{\text{H}}$  CDCl<sub>3</sub> 1.19 (s. 2 x CH<sub>3</sub>), 1.88 (d of d CH<sub>3</sub>), 2.96 (s. -CH<sub>2</sub>-), 4.69, 4.75 (d. = CH<sub>2</sub>), 6.66

(s. 3-furanyl  $\underline{\text{CH}}$ );  $\delta_{\text{F}}$ ,  $\text{CDCl}_3$  143.9 (b.m.), 146.8 (b.m.), 154.5 - 155.2 (b.m.), 158.2 - 158.9 (b.m.), (p.p.m. upfield from internal  $\text{CFCl}_3$ ) in the ratio 1:2:1:2 respectively; single peri  $J_{\text{F-F}}$  68 Hz.

#### Determination of Isomer Ratios

Two further experiments were undertaken to calculate yields of materials and determine (as calculated by  $^1\text{H}$  n.m.r.) isomer ratios. In each case the thermolyses were carried out as previously described and all three isomers were separated by elution of the reaction products through dry silica columns with 30/40 petroleum ether.

Experiment 1: The ether (120) (1.63 g.) and 2,3-dimethylbut-2-ene (10 ml.  $\equiv$  7.09 g.) were thermolysed. The main products (0.894 g., 45%) were collected and the mixture analysed by  $^1\text{H}$  n.m.r. to determine the isomer ratios of (138), (139) and (140).

Experiment 2: The ether (120) (4.27 g.) and 2,3-dimethylbut-2-ene (10 ml.  $\equiv$  7.09 g.) were thermolysed. The main products (2.78 g., 54%) were collected and the mixture analysed by  $^1\text{H}$  n.m.r. to determine the isomer ratios of (138), (139) and (140). The results obtained in both experiments are shown in Table 3 (Section 4.3).

#### Reaction of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (120) and 3,3-Dimethylbut-1-ene

The ether (120) (2.05 g.) and 3,3-dimethylbut-1-ene (12 ml.  $\equiv$  7.8 g.) were sealed in a nickel lined Carius tube and heated at  $150^\circ$  for 20 hrs. After cooling, the products and washings (diethyl ether 150 ml.) were combined and the solvent removed under reduced pressure. The residue was chromatographed on a dry silica column using 30/40 petroleum ether as an eluant, two fractions were obtained. Fraction (i) (1.07 g., 43%) comprised the faster moving components and was shown by  $^1\text{H}$  n.m.r. to contain 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-

hexafluoronaphtho[2,1-b]furan (138), and 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139), using the same  $^1\text{H}$  n.m.r. analysis the isomer ratios of (138) and (139) were determined. Recrystallization of fraction (i) from 60/80 petroleum ether at  $-14^\circ$  gave a small amount of a white solid which i.r. analysis identified as (138). Fraction (ii) was sublimed to yield 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) (75 mg. 3.5%) identified by i.r. analysis.

#### Determination of Isomer Ratios

The ether (120) (2.53 g.) and 3,3-dimethylbut-1-ene (12 ml.  $\equiv$  7.8 g.) were thermolysed as previously described. The main products, collected as one fraction by elution down a dry silica column with 30/40 petroleum ether, were analysed by  $^1\text{H}$  n.m.r. to determine the isomer ratios of (138) and (139). The results from this and the preceding experiment are shown in Table 4 (Section 4.4.2).

#### Reaction of 2-Fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) and 2,3-Dimethylbut-2-ene

The 2-fluoromethyl compound (126) (0.463 g.) and 2,3-dimethylbut-2-ene (10 ml.  $\equiv$  7.09 g.) were sealed in a nickel lined Carius tube and heated at  $150^\circ$  for 3 days. After cooling, the reaction products and washings (diethyl ether 150 ml.) were combined and the solvent removed under reduced pressure. The residue was chromatographed on a flash column<sup>72</sup> of silica using 30/40 petroleum ether as an eluant. One main fraction of faster moving components (0.325, 58%) was obtained,  $^1\text{H}$  n.m.r. analysis showed it to contain: 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138) and 2-(2,3,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139). The same  $^1\text{H}$  n.m.r. analysis was used to determine the isomer ratios of (138) and (139) (Table 5, Section 4.5).

Preparative t.l.c. (developed with 30/40 petroleum ether), successive recrystallizations (60/80 petroleum ether) and finally sublimation 100°/0.01 mm. Hg gave pure (138) identified by i.r. spectroscopy. The second isomer (139) was not separated.

Reaction of 2-Fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126) and 3,3-Dimethylbut-1-ene

The 2-fluoromethyl compound (126) (0.449 g.) and 3,3-dimethylbut-1-ene (12 ml.  $\equiv$  7.8 g.) were sealed in a nickel lined Carius tube and heated at 150° for 68 hrs. After cooling, the reaction products and washings (diethyl ether 150 ml.) were combined and the solvent removed under reduced pressure. The residue was chromatographed through a flash column<sup>72</sup> of silica using 30/40 petroleum ether as an eluant, two main fractions were obtained. Fraction (i) (0.108 g., 20%) was separated into two components by preparative t.l.c. developed using 30/40 petroleum ether: (a) 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138) (12 mg., 2%), and (b) 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139) (35 mg., 6%), each compound was characterised by i.r. analysis. Prior to separation <sup>1</sup>H n.m.r. analysis of the mixture allowed the isomer ratios of (138) and (139) to be calculated, Fraction (ii) was sublimed to yield 2-fluoromethyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (126), recovered started material (0.25 g., 55%) as identified by i.r. analysis.

Determination of Isomer Ratios

The 2-fluoromethyl compound (126) (1.177 g.) and 3,3-dimethylbut-1-ene (12 ml.  $\equiv$  7.8 g.) were thermolysed as previously but for only 20 hrs. The main products were collected as one fraction by elution of a flash chromatography column<sup>72</sup> of silica with 30/40 petroleum ether. The mixture was analysed by <sup>1</sup>H n.m.r. and the isomer ratios of (138)

and (139) were determined. The results from this and the preceding experiment are shown in Table 5 (Section 4.5), as are the results from a third experiment which were supplied via a private communication.<sup>69</sup>

## APPENDIX 1

### Analytical Instrumentation

The following instrumentation was used in the analysis of the compounds described in this thesis.

- I.r.: Perkin-Elmer 597 infra-red spectrophotometer scanning range  $4000 - 200 \text{ cm.}^{-1}$  (2.5 - 50 microns).
- N.m.r.: Varian EM360 nuclear magnetic resonance spectrometer ( $^1\text{H}$  60 MHz,  $^{19}\text{F}$  56.46 MHz).  
Bruker WX90E nuclear magnetic resonance spectrometer modified for Fourier transform pulsed operation ( $^1\text{H}$  90 MHz,  $^{19}\text{F}$  84.68 MHz).  
Bruker WH360 nuclear magnetic resonance spectrometer ( $^1\text{H}$  360 MHz).
- Mass spectroscopy: AEI MS9 mass spectrometer with data system.
- Elemental analysis: Perkin-Elmer 240 C,H,N elemental analyser.

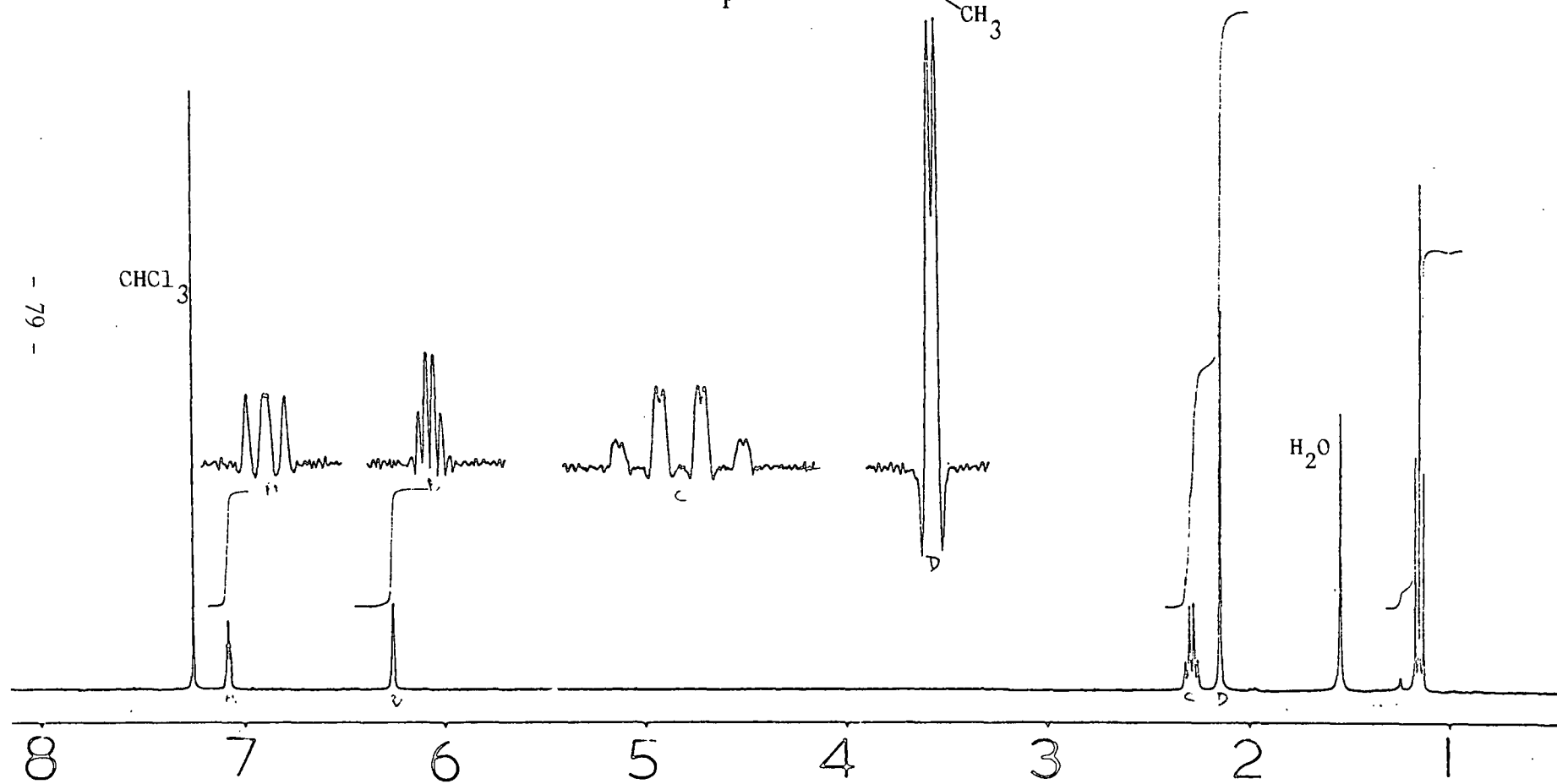
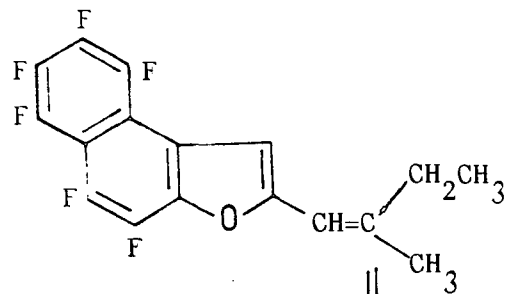
## APPENDIX II

Proton n.m.r. spectra used in the identification of the alkenes (137 - 140) and the determination of isomer ratios tabulated in

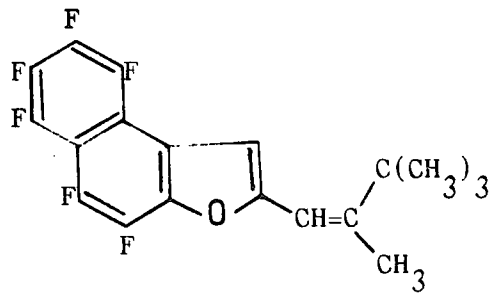
### Tables 3 - 5

- Spectrum I: 2-(2-methylbut-1-enyl)-4,5,6,7,8,9-hexafluoro-naphtho[2,1-b]furan (137).
- Spectrum II: 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138).
- Spectrum III: 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[1,2-b]furan (140).
- Spectrum IV: 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139).
- Spectrum V: Isomer ratio calculation spectrum for the reaction of 2,3-dimethylbut-2-ene and the ether (120).
- Spectrum VI: Isomer ratio calculation spectrum for the reaction of 3,3-dimethylbut-1-ene and the ether (120).
- Spectrum VII: Isomer ratio calculation spectrum for the reaction of 2,3-dimethylbut-2-ene and the 2-fluoromethyl derivative (126).
- Spectrum VIII: Isomer ratio calculation spectrum for the reaction of 3,3-dimethylbut-1-ene and the 2-fluoromethyl derivative (126).

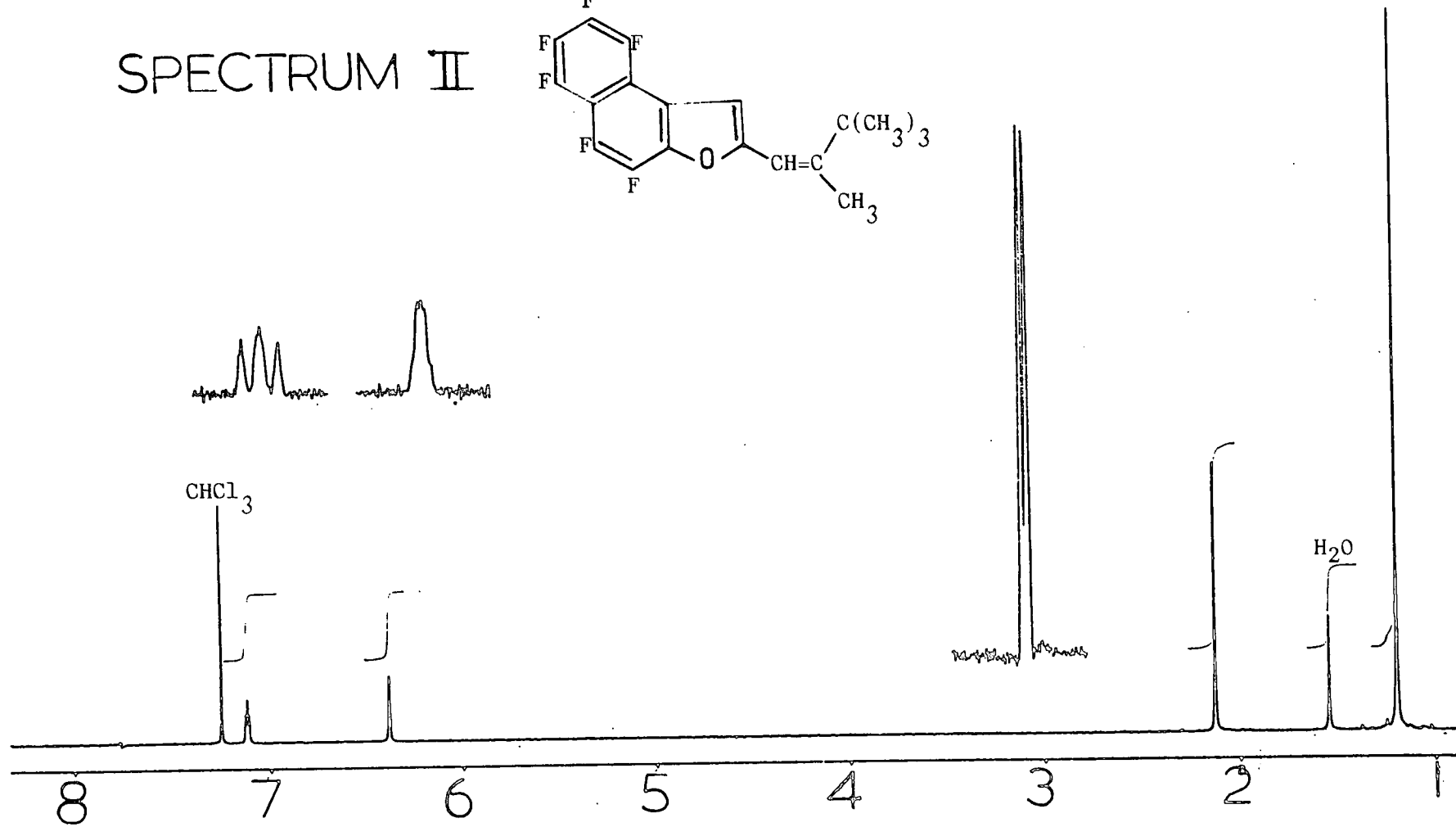
# SPECTRUM I



# SPECTRUM II

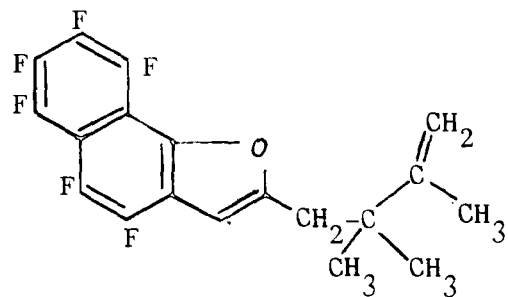


- 08 -

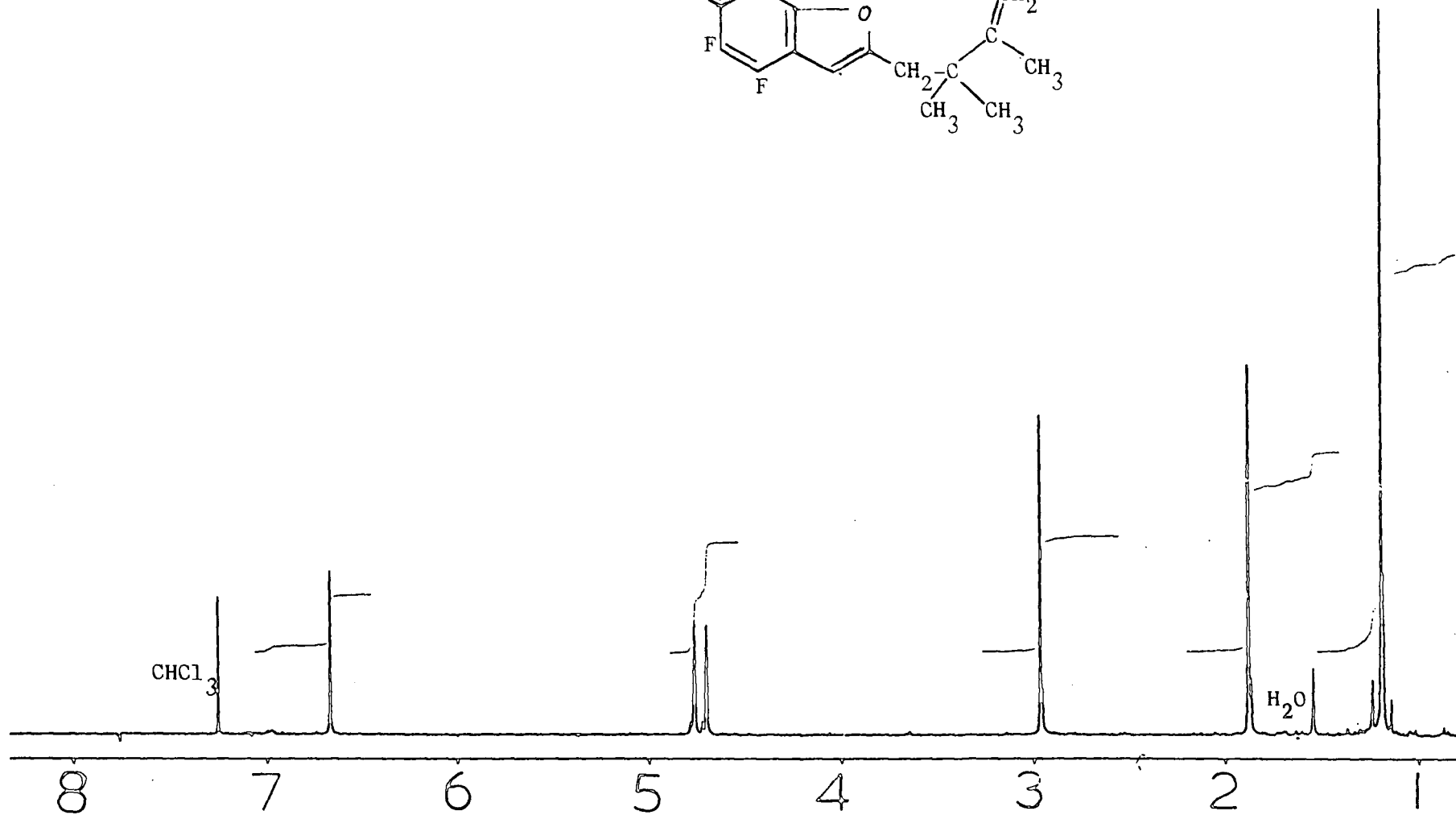


SPECTRUM

III

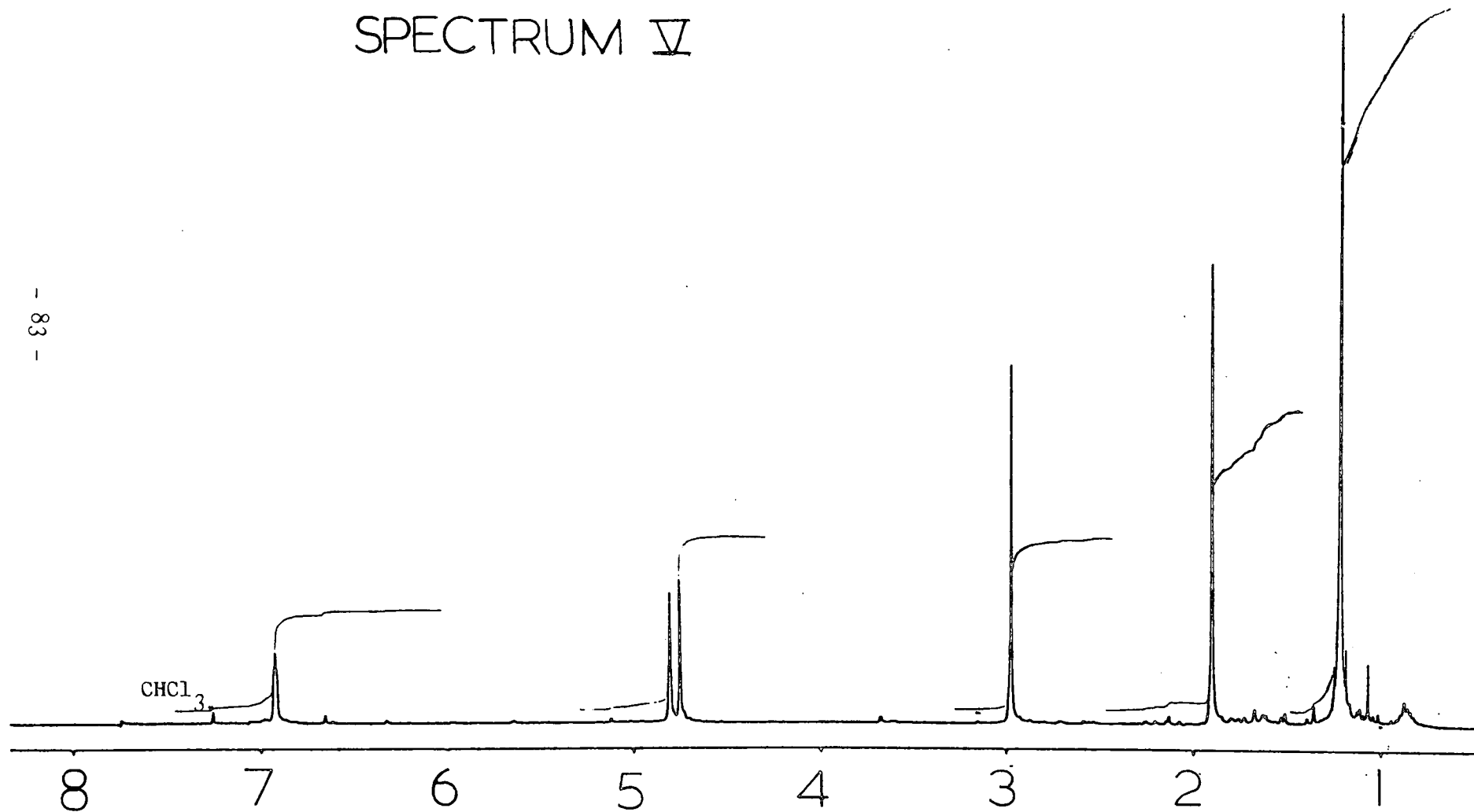


- 18 -

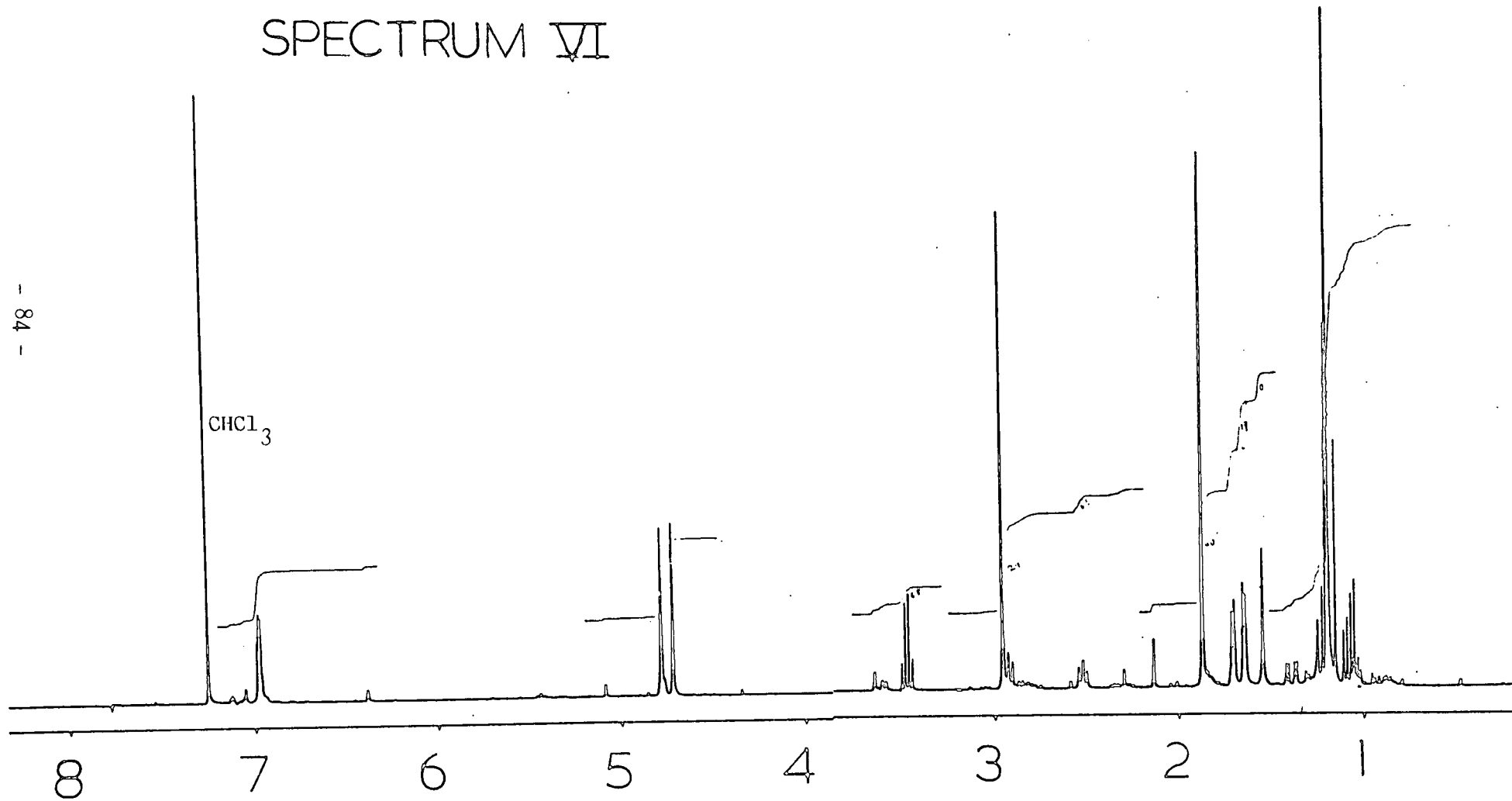




# SPECTRUM V

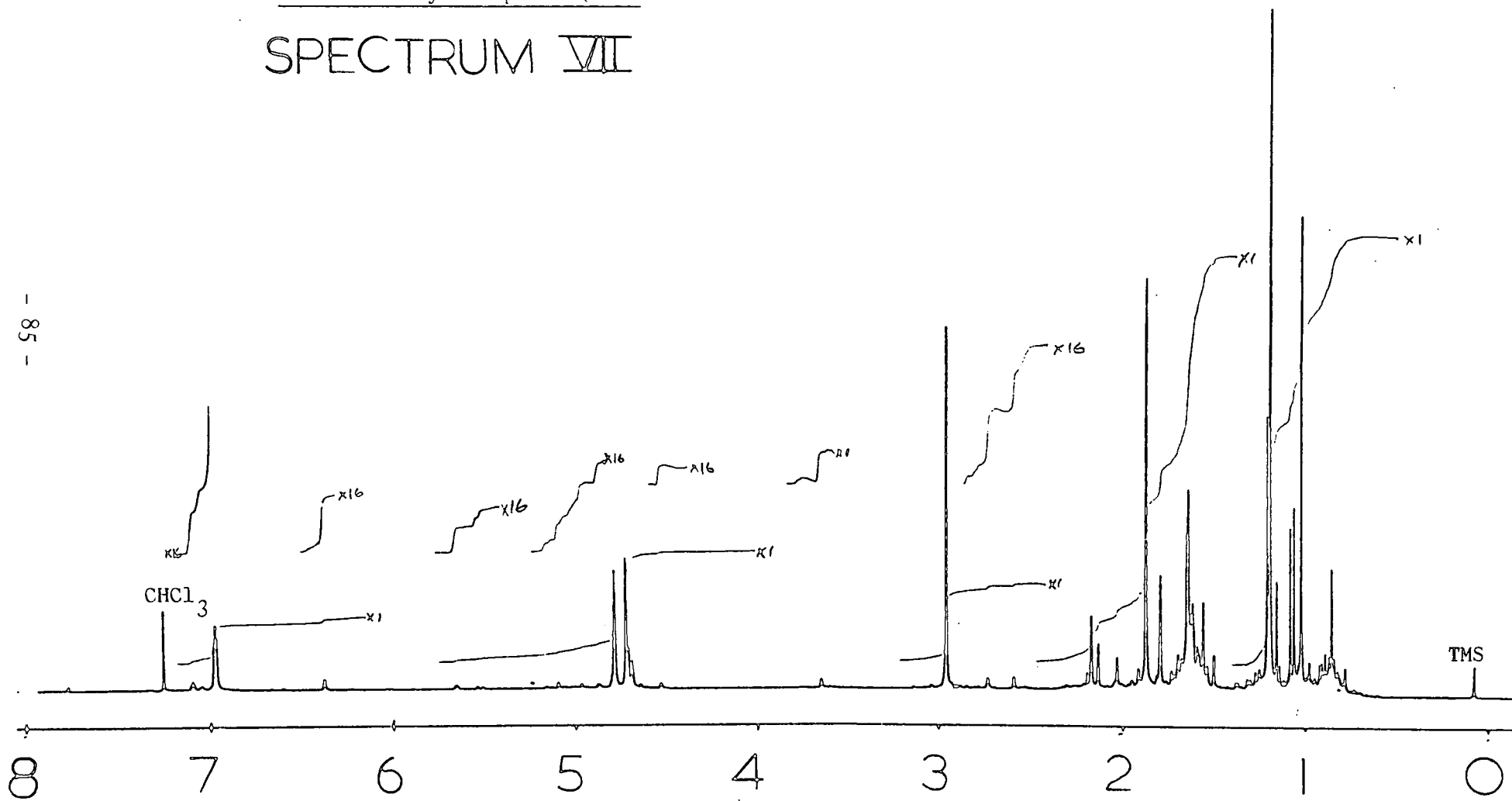


# SPECTRUM VI



The Isomer Ratio Calculation Spectrum for the Reaction of 2,3-Dimethylbut-2-ene and the  
2-Fluoromethyl Compound (120)

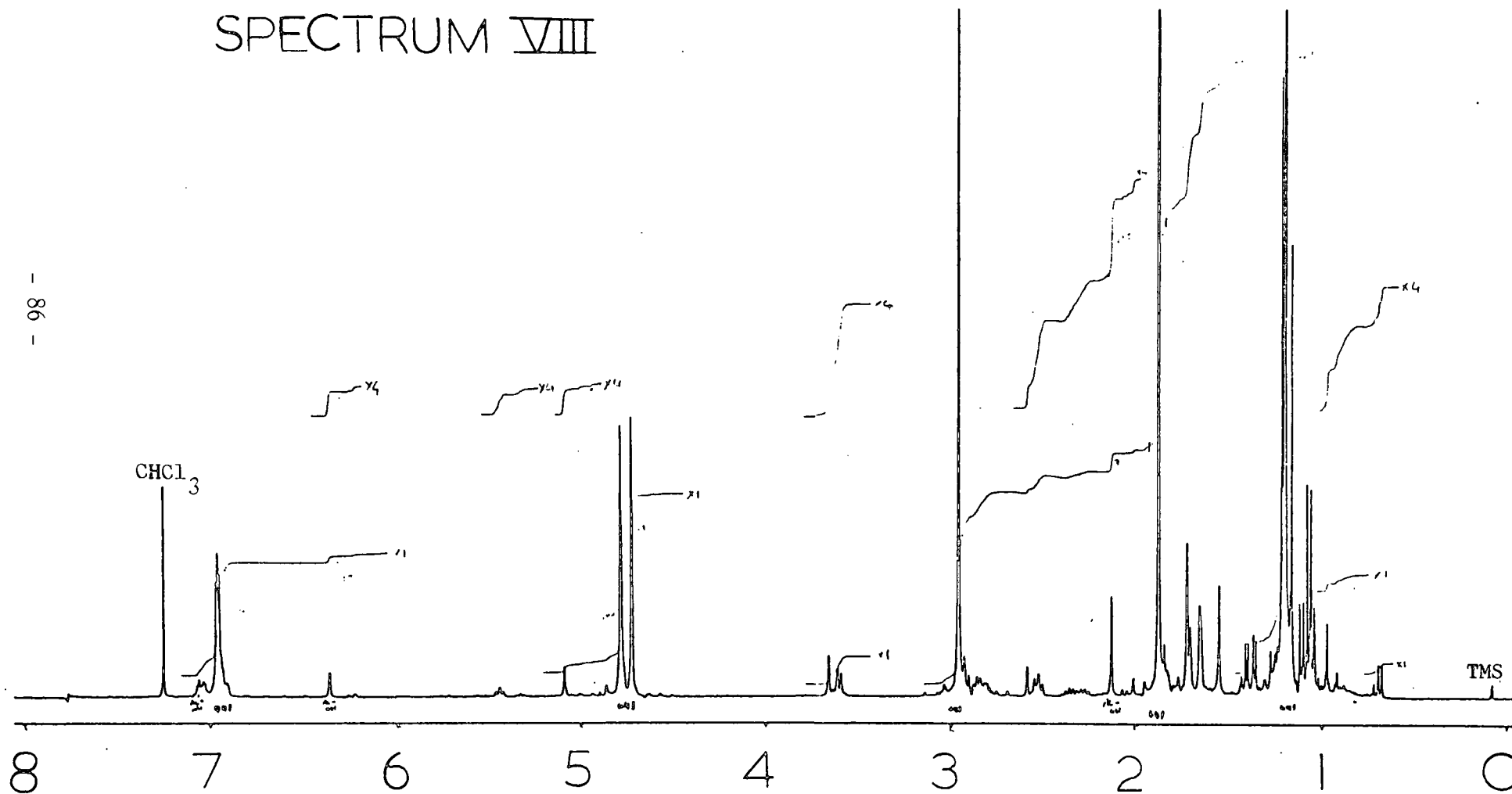
SPECTRUM VII



- 85 -

The Isomer Ratio Calculation Spectrum for the Reaction of 3,3-Dimethylbut-1-ene and the 2-Fluoromethyl Compound (120)

SPECTRUM VIII



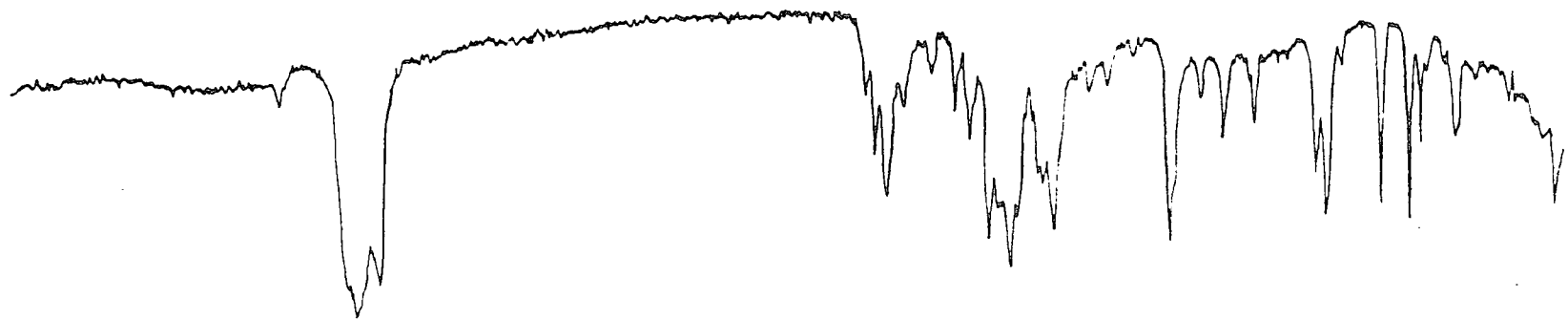
APPENDIX III

Infra-red analyses of the alkenes (137 - 140) and of 2,3,5,6-tetrafluoro-4-pyridyl prop-2-ynyl ether (131)

- Spectrum I: 2-(2-methylbut-1-enyl)-4,5,6,7,8,9-hexafluoro-naphtho[2,1-b]furan (137), nujol mull.
- Spectrum II: 2-(2,3,3-trimethylbut-1-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (138), nujol mull.
- Spectrum III: 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan (139), nujol mull.
- Spectrum IV: 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexafluoronaphtho[1,2-b]furan (140), liquid film.
- Spectrum V: 2,3,5,6-tetrafluoro-4-pyridyl prop-2-ynyl ether (131), liquid film.

2.5 3.0 4.0 5.0 Microns 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40

SPECTRUM I



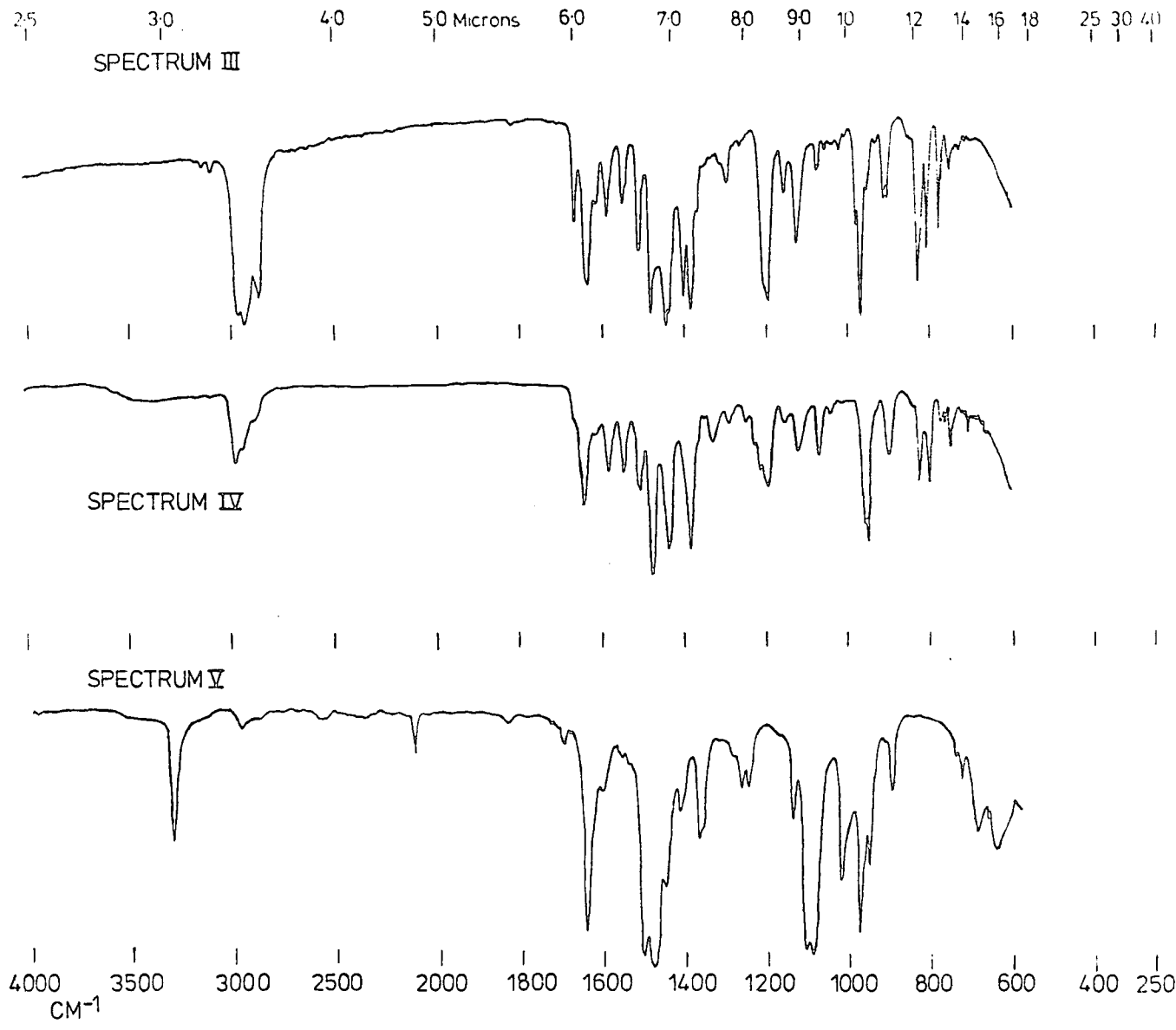
- 88 -



SPECTRUM II



4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250  
CM<sup>-1</sup>



## APPENDIX IV

### COLLOQUIA AND CONFERENCES

(A) Durham University Chemistry Department Colloquia.  
(Asterisk denotes lectures which I attended.)

#### 1981

- 14 October\* Prof. E. Kluk (Katowice): 'Chemiluminescence & Photooxidation'.  
28 October Dr. R.J.H. Clark (University College, London): 'Resonance Raman Spectroscopy'.  
6 November<sup>2</sup> Dr. W. Moddeman (Monsanto Labs., St. Louis, Missouri): 'High Energy Materials'.  
18 November\* Prof. M.J. Perkins (Chelsea College): 'Spin Trapping and Nitroxide Radicals'.  
25 November\* Dr. M. Baird (Newcastle): 'Intramolecular Reactions of Carbenes and Carbenoids'.  
2 December Dr. G. Beamson (Durham): 'Photoelectron Spectroscopy in a Strong Magnetic Field'.  
30 November Dr. B.T. Heaton (Kent): 'N.M.R. Studies of Carbonyl Clusters'.

#### 1982

- 20 January Dr. M.R. Bryce (Durham): 'Organic Metals'.  
27 January\* Dr. D.L.H. Williams (Durham): 'Nitrosation and Nitrosoamines'.  
3 February Dr. D. Parker (Durham): 'Modern Methods of Determining Enantiomeric Purity'.  
10 February Dr. D. Pethrick (Strathclyde): 'Conformation of Small and Large Molecules'.  
17 February Prof. D.T. Clark (Durham): 'Studies of Surfaces by ESCA'.  
24 February\* Dr. L. Field (Oxford): 'Application of N.M.R. to Biosynthetic Studies on Penicillin'.  
3 March\* Dr. P. Bamfield (I.C.I. Organics): 'Computer Aided Design in Synthetic Organic Chemistry'.  
17 March Prof. R.J. Haines (Cambridge/Natal): 'Clustering Around Ru, Fe and Rh'.

- 7 April\* Dr. A. Pensak (Dupont, U.S.A.): 'Computer Aided Synthesis'.
- 5 May\* Dr. G. Tennant (Edinburgh): 'The Aromatic Nitro Group in Heterocyclic Reactions'.
- 7 May Dr. C.D. Garner (Manchester): 'Molybdenum Centres in Enzymes'.
- 26 May Dr. A. Welch (Edinburgh): 'Conformation and Distortion in Carbometalloboranes'.
- 14 June\* Prof. C.M.J. Stirling (University College of Wales, Bangor): 'How Much Does Strain Affect Reactivity?'.
- 28 June\* Prof. D.J. Burton (University of Iowa, U.S.A.): 'Some Aspects of the Chemistry of Fluorinated Phosphonium Salts and their Phosphonates'.
- 2 July\* Prof. H.F. Koch (Ithaca College, University of Cornell, U.S.A.): 'Proton Transfer to and Elimination Reactions from Localized and Delocalized Carbanions'.
- 13 September\* Prof. R. Neidlein (University of Heidelberg): 'New Aspects and Results of Bridged Annulene Chemistry'.
- 27 September Dr. W.K. Ford (Xerox Research Centre, Webster, New York): 'The Dependence of the Electronic Structures of Polymers on their Molecular Architecture'.
- 13 October\* Dr. W.J. Feast (University of Durham): 'Approaches to the Synthesis of Conjugated Polymers'.
- 14 October\* Prof. H. Suhr (University of Tübingen): 'Preparative Chemistry in Non-Equilibrium Plasmas'.
- 27 October Dr. C.E. Housecroft (Oxford High School and Notre Dame University): 'Bonding Capabilities of Butterfly-Shaped  $Fe_4$  Units: Implications for C-H Bond Activation in Hydrocarbon Complexes'.
- 28 October\* Prof. M.F. Lappert, F.R.S. (University of Sussex): 'Approaches to Asymmetric Synthesis and Catalysis using Electron-rich Olefins and some of their Metal Complexes'.
- 15 November Dr. G. Bertrand (University of Toulouse): 'Curtius Rearrangement in Organometallic Series. A Route for New Hybridised Species'.
- 24 November Prof. G.G. Roberts (Applied Physics Department): 'Langmuir-Blodgett Films'.
- 24 November Prof. F.R. Hartley (RMCS, Shrivenham): 'Supported Metal Complex Hydroformylation Catalysts: a Novel Approach Using  $\gamma$ -radiation'.

- 2 December\* Dr. G.M. Brooke (University of Durham): 'The Fate of the Ortho-Fluorine in 3,3-Sigmatropic Reactions Involving Polyfluoro-aryl and -heteroaryl Systems'.
- 8 December Dr. G. Woolley (Trent Polytechnic): 'Bonds in Transition Metal-Cluster Compounds'.
- 1983
- 12 January Dr. D.C. Sherrington (University of Strathclyde): 'Polymer-Supported Phase Transfer Catalysts'.
- 9 February\* Dr. P. Moore (University of Warwick): 'Mechanistic Studies in Solution by Stopped Flow F.T. N.M.R. and High Pressure N.M.R. Line Broadening'.
- 21 February Dr. R. Lynden-Bell (University of Cambridge): 'Molecular Motion in the Cubic Phase of NaCN'.
- 2 March\* Dr. D. Bloor (Queen Mary College, University of London): 'The Solid-State Chemistry of Diacetylene Monomers and Polymers'.
- 8 March Prof. D.C. Bradley, F.R.S. (Queen Mary College, University of London): 'Recent Developments in Organo-Imido-Transition Metal Chemistry'.
- 9 March\* Dr. D.M.J. Lilley (University of Dundee): 'DNA, Sequence, Symmetry, Structure and Supercooling'.
- 11 March Prof. H.G. Viehe (University of Louvain): 'Oxidations on Sulphur'.
- 16 March\* Dr. I. Gosney (University of Edinburgh): 'New Extrusion Reactions: Organic Synthesis in a Hot Tube'.
- 25 March Prof. F.G. Baglin (University of Nevada): 'Interaction Induced Raman Spectroscopy in Supercritical Ethane'.
- 21 April Prof. J. Passmore (University of New Brunswick): 'Novel Selenium-Iodine Cations'.
- 4 May\* Prof. P.H. Plesch (University of Keele): 'Binary Ionization Equilibria Between Two Ions and Two Molecules. What Ostwald Never Thought Of'.
- 10 May\* Prof. K. Burger (University of Munich): 'New Reaction Pathways from Trifluoromethyl-Substituted Heterodienes to Partially Fluorinated Heterocyclic Compounds'.
- 11 May\* Dr. N. Isaacs (University of Reading): 'The Application of High Pressures to the Theory and Practice of Organic Chemistry'.
- 13 May Dr. R. de Kock (Calvin College, Grand Rapids, Michigan/Free University, Amsterdam): 'Electronic Structural Calculations on Organometallic Cobalt Cluster Molecules: Implications for Metal Surfaces'.
- 13 May Dr. T.B. Marder (UCLA/University of Bristol): 'The Chemistry of Metal-Carbon and Metal-Metal Multiple Bonds'.

- 16 May\* Prof. R.J. Lagow (University of Texas): 'The Chemistry of Polylithium Organic Compounds: An Unusual Class of Matter'.
- 18 May\* Dr. D.M. Adams (University of Leicester): 'Spectroscopy at Very High Pressures'.
- 25 May\* Dr. J.M. Vernon (University of York): 'New Heterocyclic Chemistry Involving Lead Tetra-acetate'.
- 15 June Dr. A. Pietrzykowski (Technical University of Warsaw/ University of Strathclyde): 'Synthesis, Structure and Properties of Aluminoxanes'.
- 22 June Dr. D.W.H. Rankin (University of Edinburgh): 'Floppy Molecules - The Influence of Phase on Structure'.
- 5 July\* Professor J. Miller (University of Campinas, Brazil): 'Reactivity in Nucleophilic Substitution Reactions'.

(B) Durham University Chemical Society Lectures

1981

- 22 October\* Dr. P.J. Corish (Dunlop): 'What Would Life be Like Without Rubber'.
- 29 October\* Miss J.M. Cronyn (Durham): 'Chemistry in Archaeology'.
- 12 November\* Prof. A.I. Scott (Edinburgh): 'An Organic Chemist's View of Life Through the N.M.R. Tube'.
- 19 November\* Prof. B.L. Shaw (Leeds): 'Big Rings and Metal-Carbon Bond Formation'.
- 3 December Dr. W.O. Ord (Northumbria Water Authority): 'The Role of the Scientist in a Regional Water Authority'.

1982

- 28 January Prof. I. Fells (Newcastle): 'Balancing the Energy Equations'.
- 11 February Dr. D.W. Turner (Oxford): 'Photoelectrons in a Strong Magnetic Field'.
- 18 February\* Prof. R.K. Harris (East Anglia): 'N.M.R. in the 1980's'.
- 25 February\* Prof. R.O.C. Norman (York): 'Turning Points and Challenges for the Organic Chemist'.
- 4 March Dr. R. Whyman (I.C.I. Runcorn): 'Making Metal Clusters Work'.
- 14 October\* Mr. F. Shenton (County Analyst, Durham): 'There is Death in the Pot'.

- 28 October\* Prof. M.F. Lappert, F.R.S. (University of Sussex):  
'The Chemistry of Some Unusual Subvalent Compounds  
of the Main Group IV and V Elements'.
- 4 November\* Dr. D.H. Williams (University of Cambridge): 'Studies on  
the Structures and Modes of Action of Antibiotics'.
- 11 November\* Dr. J. Cramp (I.C.I. Ltd.): 'Lasers in Industry'.
- 25 November\* Dr. D.H. Richards, P.E.R.M.E. (Ministry of Defence):  
'Terminally Functional Polymers, their Synthesis and  
Uses'.

1983

- 27 January\* Prof. D.W.A. Sharp (University of Glasgow): 'Some  
Redox Reactions in Fluorine Chemistry'.
- 3 February\* Dr. R. Manning (Department of Zoology, University  
of Durham): 'Molecular Mechanisms of Hormone  
Action'.
- 10 February\* Sir Geoffrey Allen, F.R.S. (Unilever Ltd.): 'U.K. Research  
Ltd.'.
- 17 February\* R.S.C. Centenary Lecture, Prof. A.G. MacDiarmid  
(University of Pennsylvania): 'Metallic Covalent  
Polymers:  $(SN)_x$  and  $(CH)_x$  and their Derivatives'.
- 3 March\* Prof. A.C.T. North (University of Leeds): 'The Use of  
a Computer Display System in Studying Molecular  
Structures and Interactions'.

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