Durham E-Theses

A study of the thermolyses of polyfluoroaryl-prop-2-ynyl ethers in inert solvents and with alkenes

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A Study of the Thermolyses of Polyfluoroaryl-Prop-2-ynyl

Ethers in Inert Solvents and with Alkenes

By

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(Graduate Society)

Undertaken to obtain an M.Sc. (part-time) at the University of Durham,

Department of Chemistry from October 1981 until October 1983

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

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_6 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·

followed by anti-Markownikov adduct formation, ionisation by loss

of F^- 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^+.

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.G. Morpeth

C O N T E N T S

The Claisen and Cope Rearrangements: Scope, Mechanism and Stereo-
chemistry

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 rearrange-
ment 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)[1] (Scheme 1).

$$CH_3-C=CHCO_2C_2H_5 \quad\longrightarrow\quad CH_3-C-CHCO_2C_2H_5$$

(1)   (2)
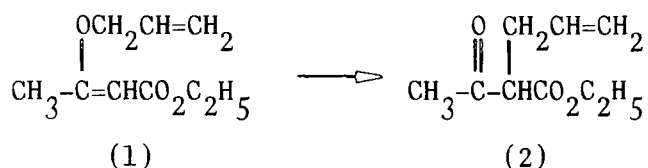
Scheme 1

The Claisen rearrangement is better known for the rearrange-
ment of allyl phenyl ethers to ortho allyl phenols as illustrated
by (3) and (4)[2] (Scheme 2). When the ortho position is

(3)   (4)
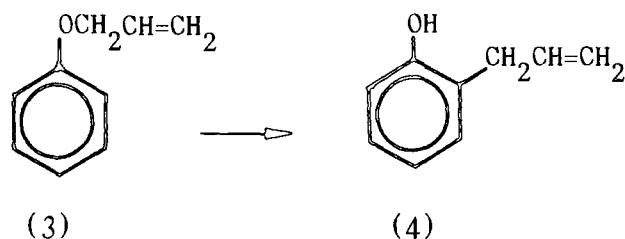
Scheme 2

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[3] to yield the para-allyl phenol

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

$$OCHR^2CH=CHR^1 \qquad R^2CH \qquad OH$$

(7)   (8)   (9)

(11)   (10)
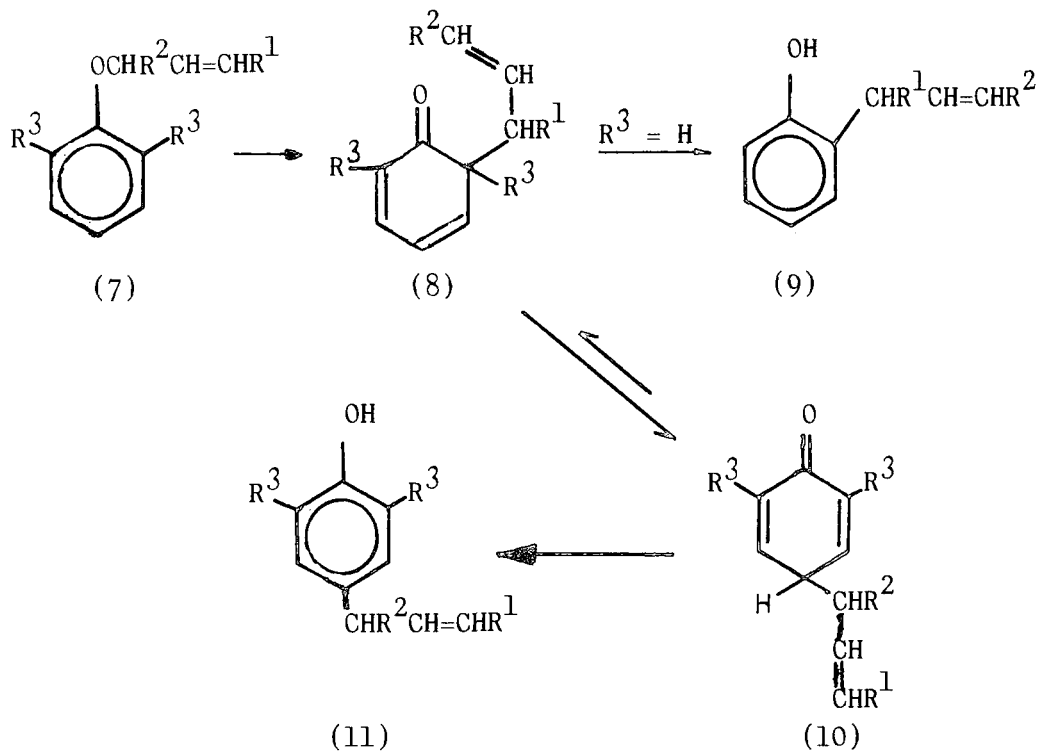
Scheme 3

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 γ-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 re-
arrangement 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).

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,[13] 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[14,15] 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[16]; or cinnamyl 4-methyl-phenyl ether and allyl-4-amino phenyl ether.[17] The conclusions drawn during this period suggested that the rearrangement was best explained by a cyclic mechanism[4] (Scheme 4), in which the cleavage of the carbon-
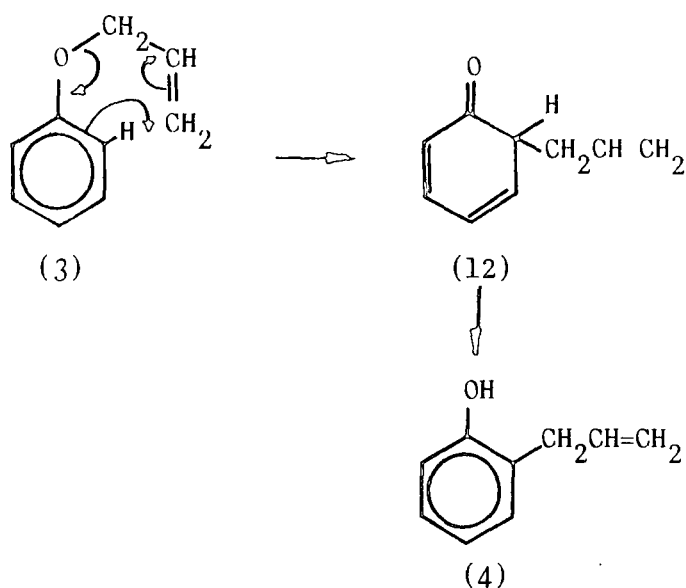
Scheme 4

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

enolisation was rate determining.[18]

The rearrangement to the para-position was also shown to be first order[19] 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.[4]

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[20,21] first postulated, and later isolated the intermediate ortho-dienone, via a maleic anhydride adduct. Curtin et al.[22-24] 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.[25-28] were able to show, using a γ-^{14}C labelled compound, that both the ortho- and para-Claisen transformations required an intermediate cyclohexadienone. Finally Alexander and Kluiber[29] 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).

OCH(CH$_3$)-CH=CH(CH$_3$)

(13)

OH
CH(CH$_3$)CH=CH(CH$_3$)

(14)

OC(CH$_3$)HCH=CH(CH$_3$)
CH$_3$ CH$_3$

(15)

OH
H$_3$C   CH$_3$

HC(CH$_3$)CH=CH(CH$_3$)
(16)

Scheme 5

- 4 -
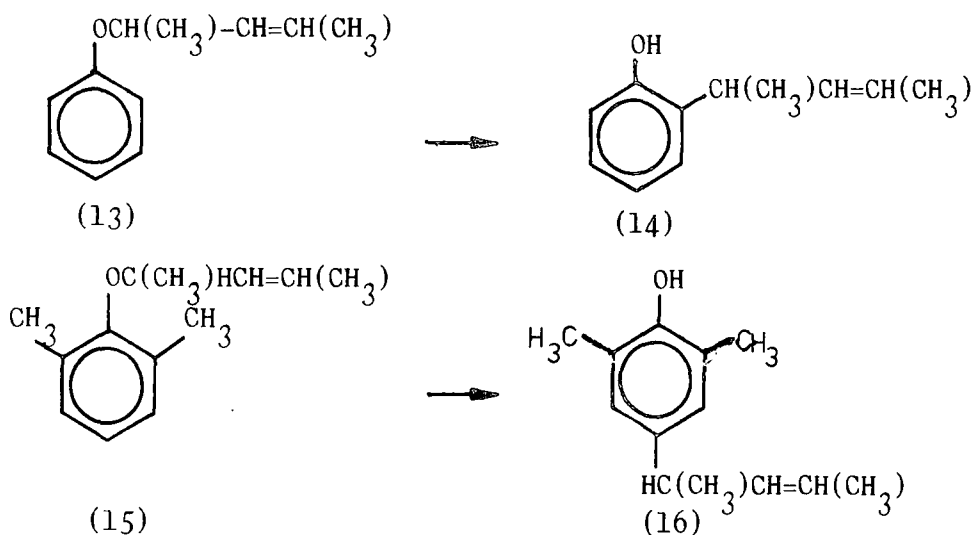
Despite the work during the 1950's the rearrangement was still categorised as a 'No Mechanism' reaction[11] until 1965 when the Claisen rearrangement and other transformations of that type were defined by Woodward and Hoffmann as examples of sigmatropic rearrangements.[30]

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 σ-bond in a π-framework, the reaction is accomplished by a shift in the π-bonds.

$$\underset{\substack{|\\ n}}{\overset{\substack{G\\|}}{C-(C=C-C)}} \longrightarrow \underset{\substack{|\\ n}}{\overset{\substack{G\\|}}{(C=C-C)-C}}$$
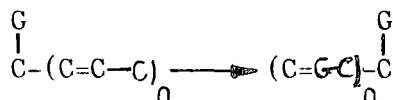
Fig. 1. General Example of a Sigmatropic Transformation

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

Mechanistically the concerted nature of a sigmatropic re-arrangement 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 π-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 π-electron systems to positions 3,3 producing the changes illustrated (Figure 2). In the transition state the Highest Occupied Molecular

- 5 -
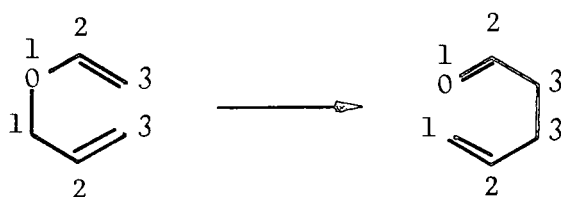
Claisen Rearrangement of allyl vinyl ethers
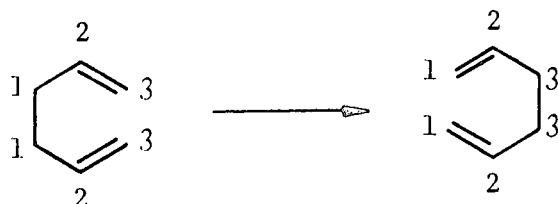
Cope Rearrangement of 1,5-hexadienes

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 π-framework

the length of the chain dictates the phase of the terminal carbons.

The symmetry of the HOMO in $(C-G-C)_n-C$ alternates regularly and so the

HOMO varies according to the number of carbons involved in the

rearrangement (Figure 3).
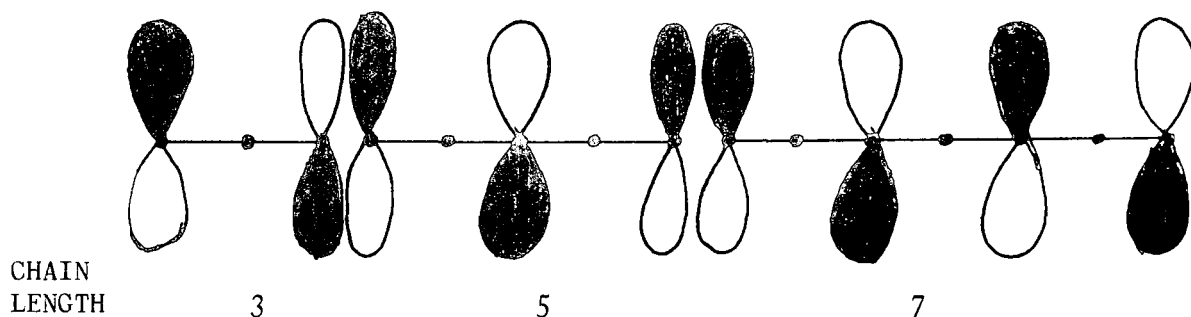
CHAIN
LENGTH   3   5   7

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 π-framework, (b) overlap through two lobes on the migrating carbon.

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

SUPRAFACIAL   ANTARAFACIAL
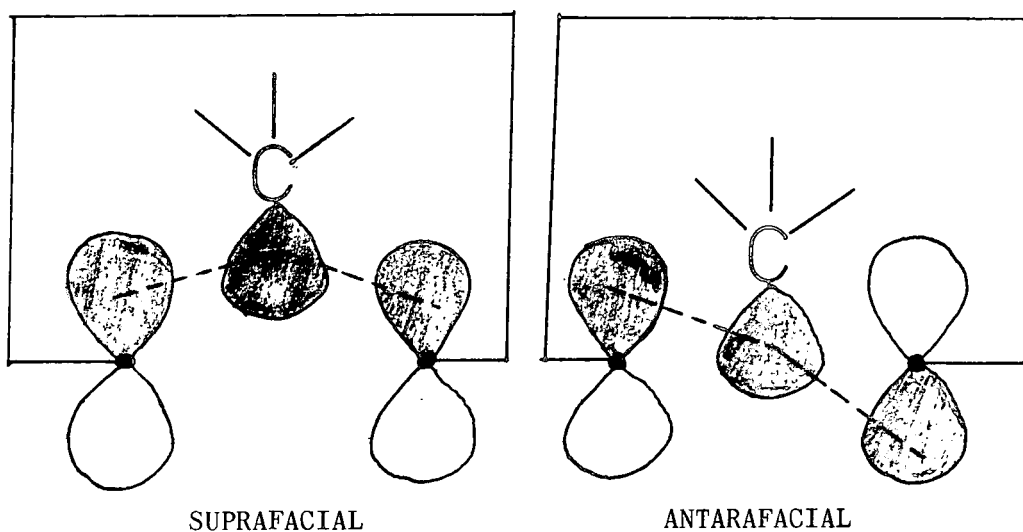
Fig. 4. Carbon Migration Single Lobe Overlap

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

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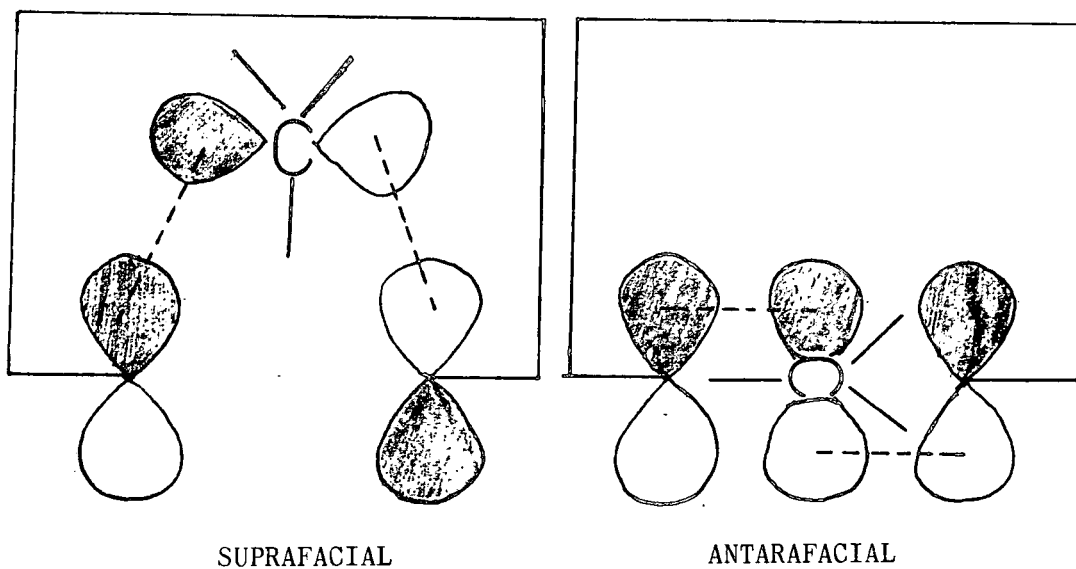
Fig. 5. Carbon Migration Overlap with Two P-Lobes

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 $i + j = 4n$[9] 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 π-electron system over the 3 carbons of the allyl group under

Hückel Orbital Theory.[31] These can be described by three molecular

orbitals ψ_1, ψ_2 and ψ_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.
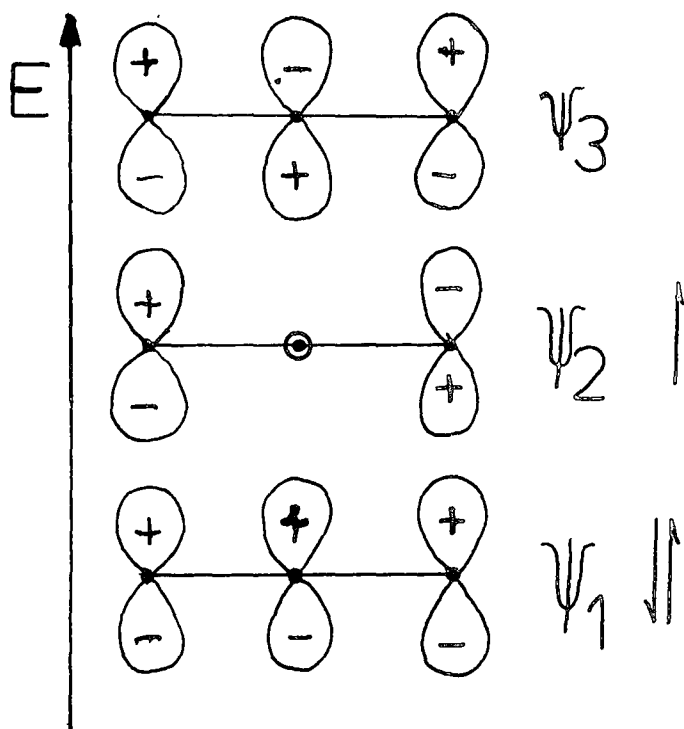
Fig. 6. Molecular Orbitals of the Allyl Group

In the allyl radical, which has three electrons as shown (Figure 6), the HOMO is represented by ψ_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 ψ_2 the [3,3] rearrangement is allowed (Figure 7).
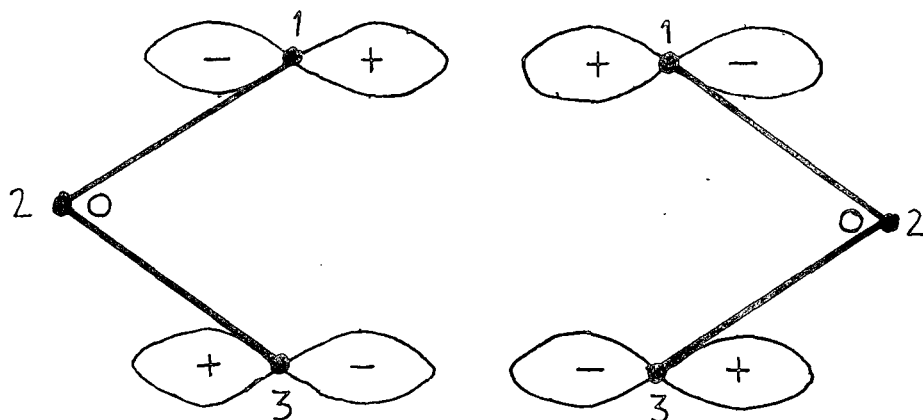
Fig. 7. ψ_2 Orbital Symmetry Allows [3,3] Transformation

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.[9] 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.[30]

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 ψ_4 (Figure 8).[32]

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-
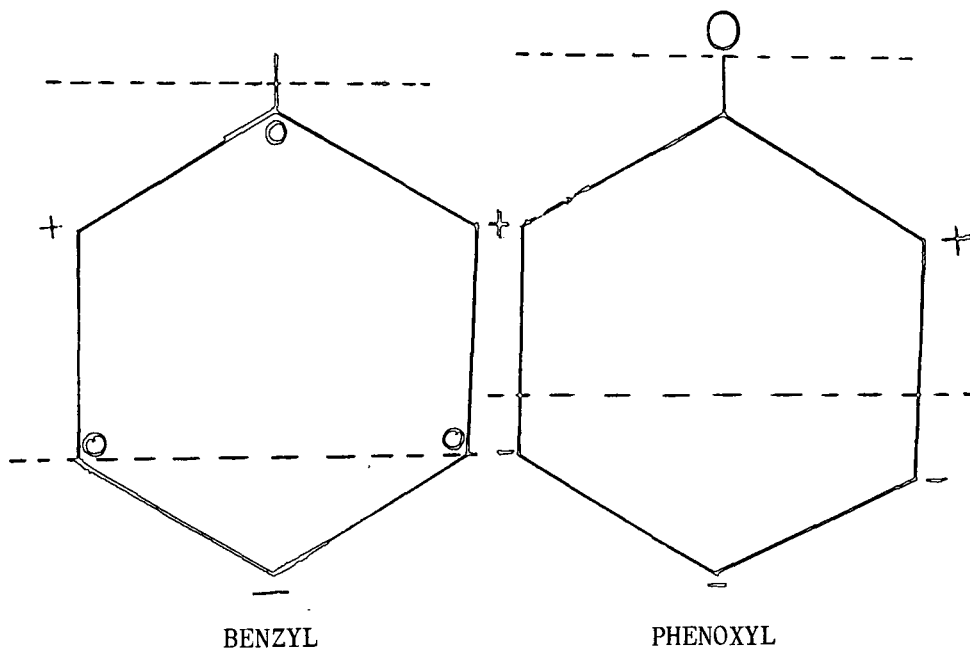
BENZYL   PHENOXYL

Fig. 8. ψ_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 ψ_2 (Figure 7) and the phenoxy radical by ψ_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).
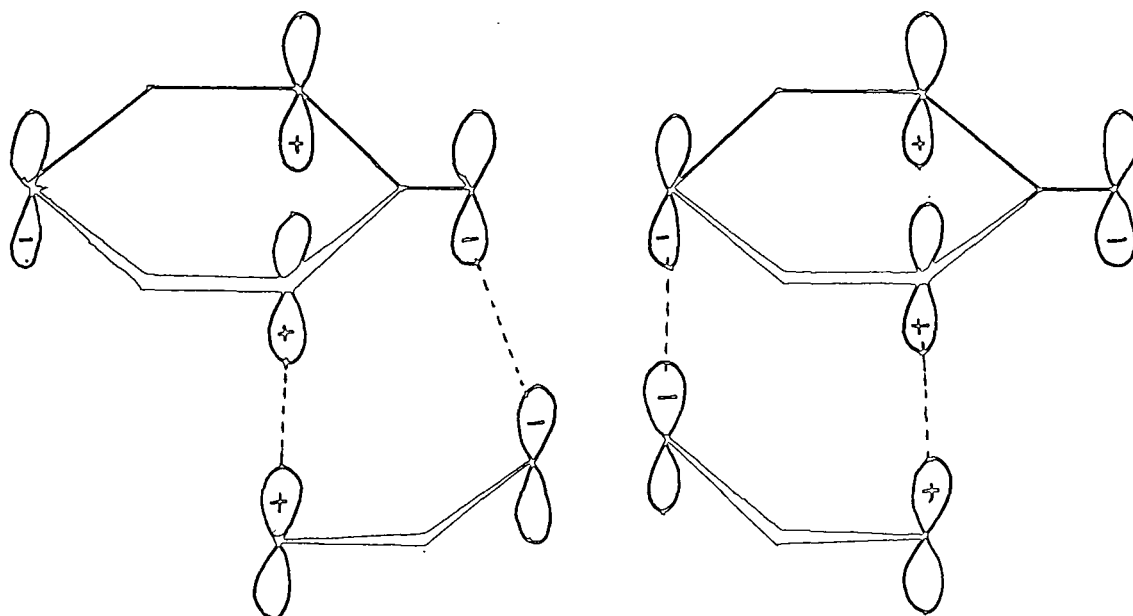
Fig. 9.   Phase Relationships giving Thermally Allowed
          Migrations of the Allyl Group to both Ortho- and Para-
          Positions

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 σ-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.[9]

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

(17)   (18)
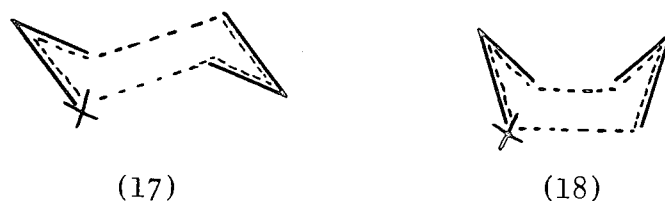
Fig. 10.   Two Possible Geometries of Cyclic Transition
State in [3,3] Suprafacial Migrations (X = O,C)

the chair (17) is strongly favoured.[6] 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-dimethyl-hexa-1,5-diene,[33] 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).

(19)   (20)   (21)
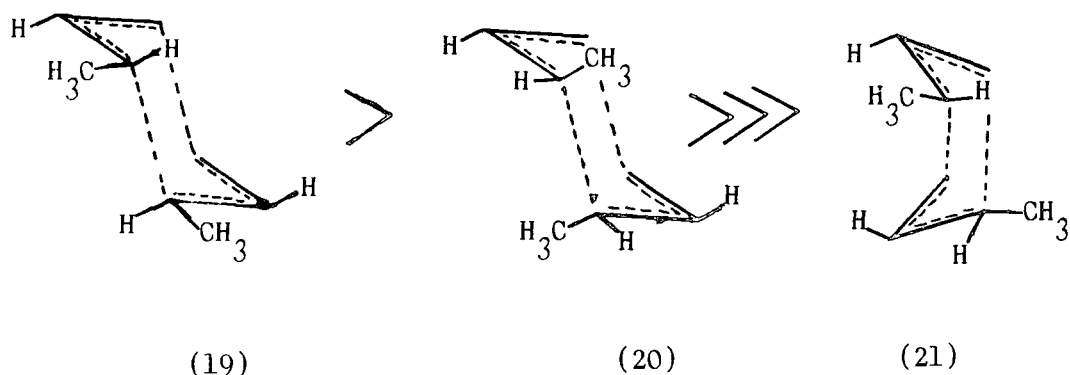
Scheme 6

A similar order of favourability to Scheme 6 is observed in the amino Claisen rearrangement.[34] Concerted [3,3] sigmatropic transformations are stereoselective[6] and this has been demonstrated using optically active molecules for both the aromatic,[35] and amino[34] Claisen rearrangements and Cope transformations.[36]

When the chair-like transition state geometry cannot be achieved, the rearrangements proceed via a boat configuration and there are a number of examples in the literature, including a number of bicyclic derivatives in which the unsaturated linkages are part of the ring system,[37] or in the Cope rearrangements of divinyl cyclopropanes and cyclobutanes.[38]

The Claisen and Cope rearrangements can be seen, therefore, as stereoselective [3,3] sigmatropic shifts which pass through a cyclic transition state usually having the preferred chair-like configuration (19), but which may also adopt the boat-like arrangement (20), when steric constraints demand it.

1.7. The Abnormal and Ortho-Ortho Claisen Rearrangements

There exists two other types of aromatic Claisen rearrangements which must be briefly discussed. The first of these is the abnormal

- 12 -

Claisen rearrangement, the original example of which was reported

by Lauer and Filbert.[39] They observed that γ-ethyl-allyl phenyl

ether (22) underwent a Claisen rearrangement to yield 2-(α,γ-dimethyl

allyl)phenol (24) – not the expected 2-(α-ethyl-allyl)phenol (23).

Later work showed that (23) was also present[40] (Scheme 7). The

(22)   (23)   (24)
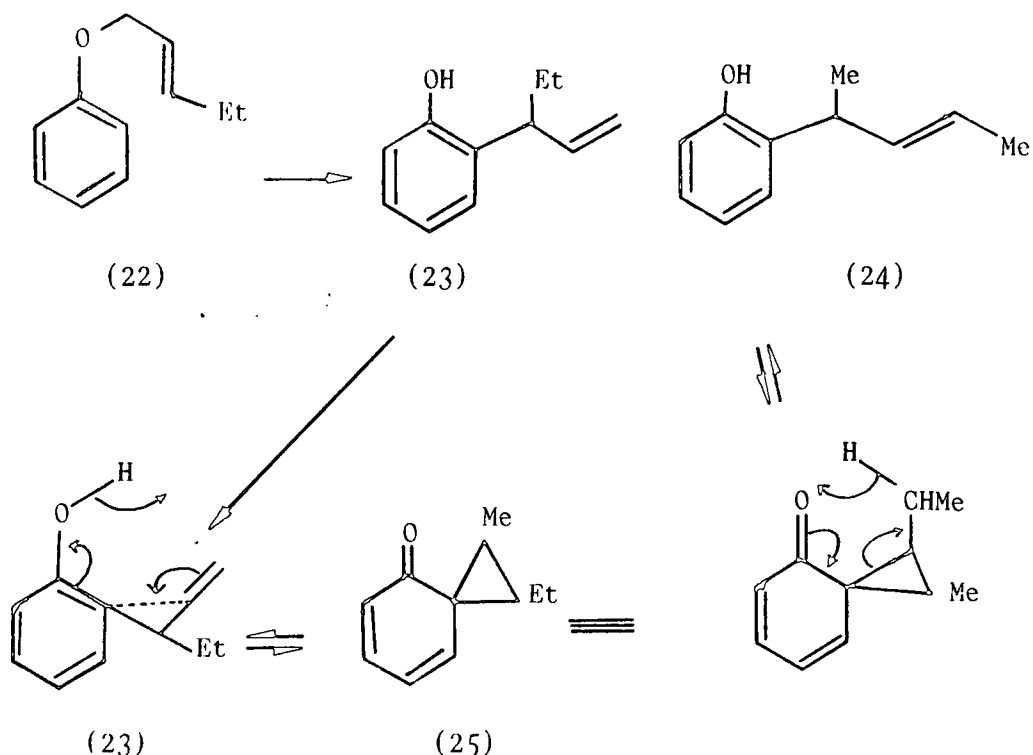
(23)   (25)

Scheme 7

abnormal product is formed from the expected product[40] via two [1,5]

homo-dienyl shifts. Equilibria of the type (23)⇌(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.[41] 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 σ-allenylphenol (27) is able to

further rearrange by a [1,5]-H shift followed by electrocyclisation to

give the observed chromene (29).[41] The ortho-ortho Claisen

(26)   (27)   (28)   (29)
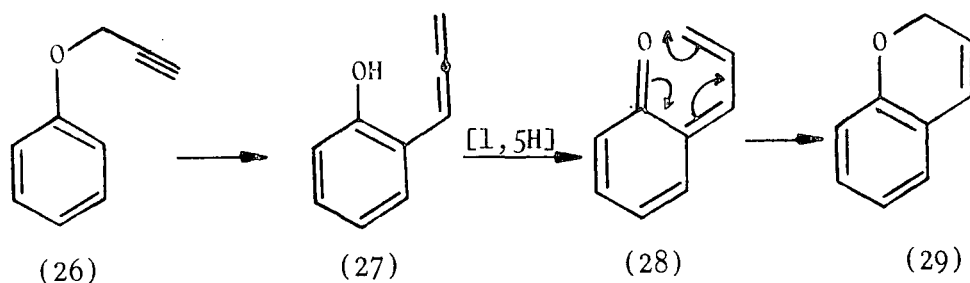
Scheme 8

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

If the rearrangement followed a concerted pathway through the π-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 π-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.[42] (Scheme 9).

The rearrangement was used to account for the distribution of radioactivity between α and γ carbons observed when 2,4,6-trimethyl-phenyl allyl ether having γ ^{14}C (30) was heated. The radioactive distribution was accounted for by the occurrence of an ortho-ortho rearrangement (31⇌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.
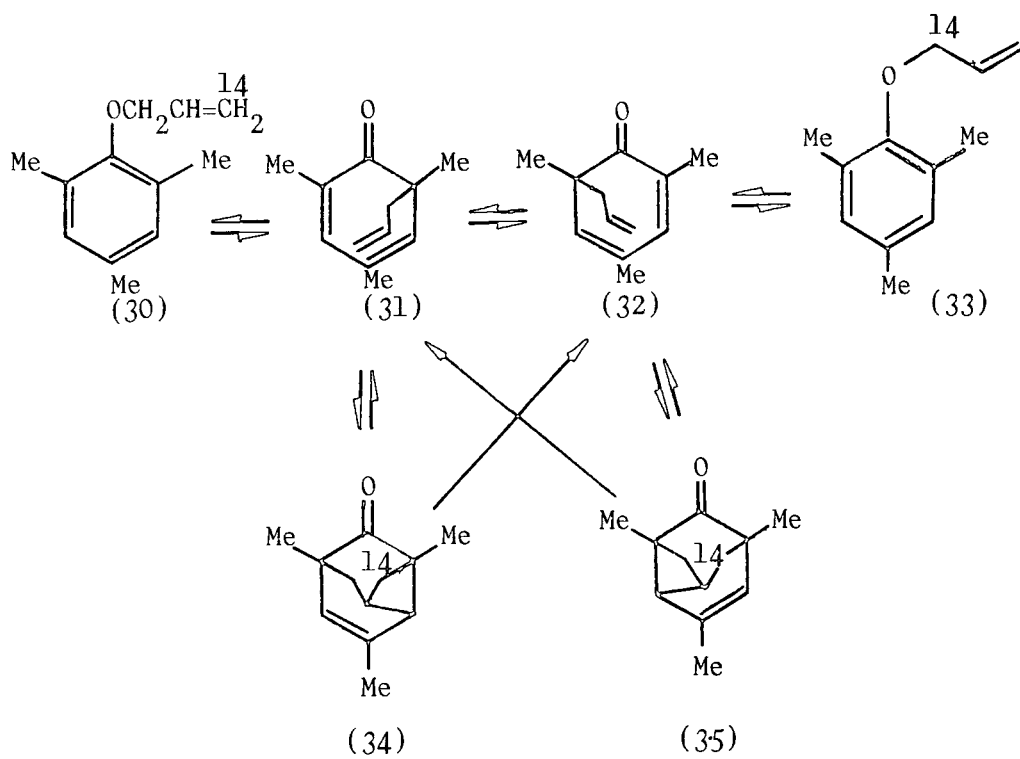
Scheme 9

Claisen Rearrangements Observed in Aryl Prop-2-enyl 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.[42] 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[43] examined the thermolysis of 2,6-dimethylphenylprop-2-ynyl ether (36) and obtained adduct (38) (Scheme 10).
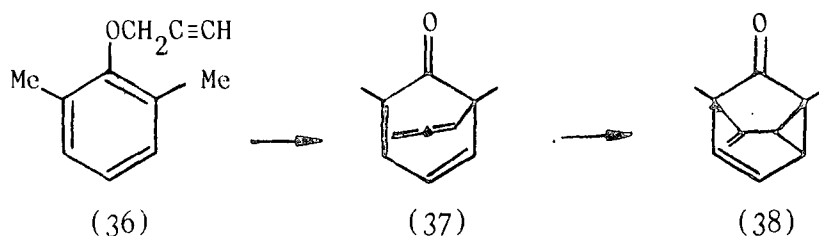
Scheme 10

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[44] also postulated the internal Diels-Alder

addition to account for the products formed when pentafluorophenyl

prop-2-enyl ether (39), and $[2,3,3-{}^2H_3]$prop-2-enyl ether (40) were

pyrolysed at 480° through a quartz tube packed with glass wool.

Pentafluorophenylprop-2-enyl ether (39) did not dehydro-

fluorinate on pyrolysis, as was expected, but instead isomerized

to the bicyclic compound (42), via the Claisen intermediate ortho-

dienone (41) (Scheme 11).

(39)   (41)   (42)
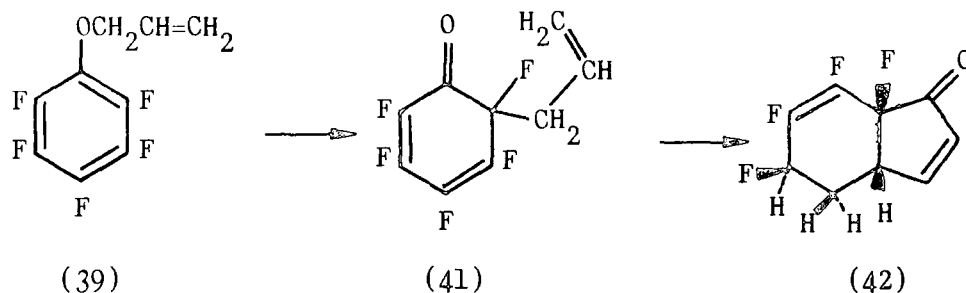
Scheme 11

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).

(39)   (43)   (44)   (42)
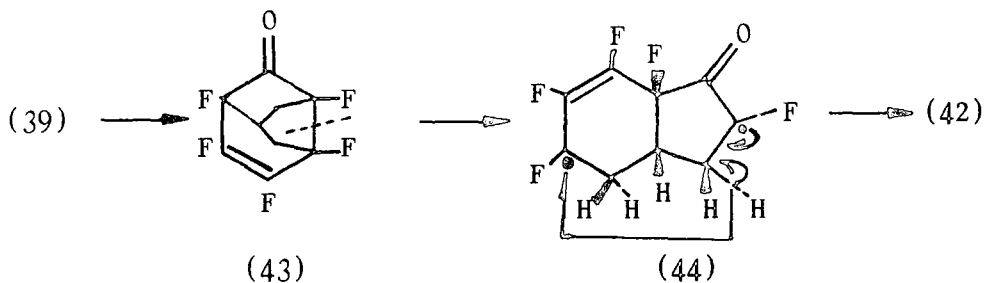
Scheme 12

The described reaction sequence required that the hydrogen

atoms on C_3 and C_5 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

- 17 -

the reaction sequence in Scheme 13.
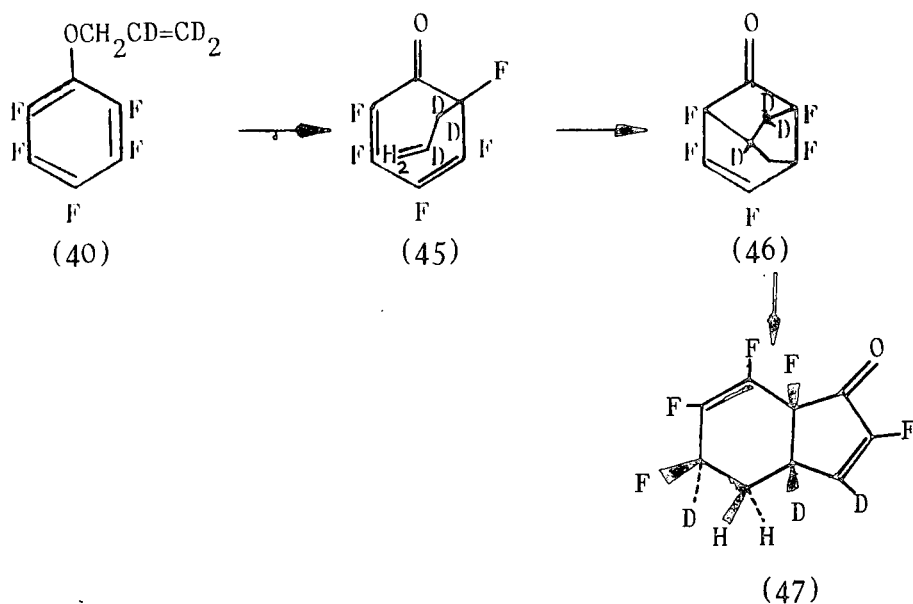
Scheme 13

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).
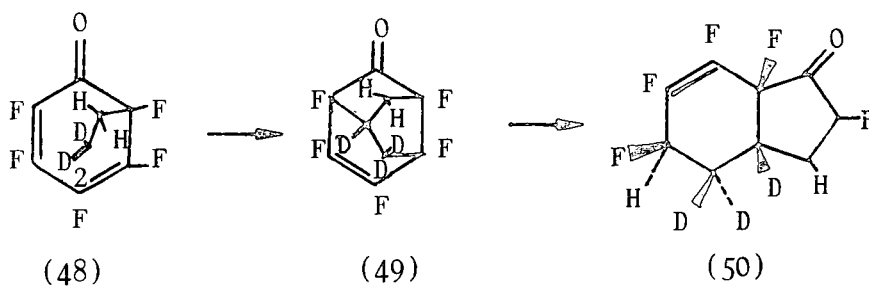
Scheme 14

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.[42] (Scheme 15).

$$(40) \longrightarrow (45) \longrightarrow (51a) \longrightarrow (48)$$

Scheme 15

- 18 -
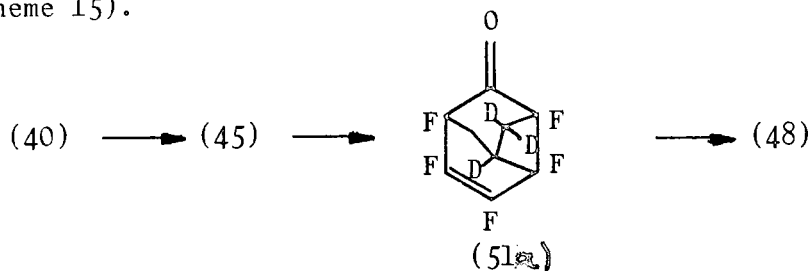
In a later paper, Brooke and Hall[45] showed how it was possible

for the internal Diels-Alder adduct (51) to cleave in two ways:

(a) Cleavage leading to the initially formed Claisen re-

arrangement 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).
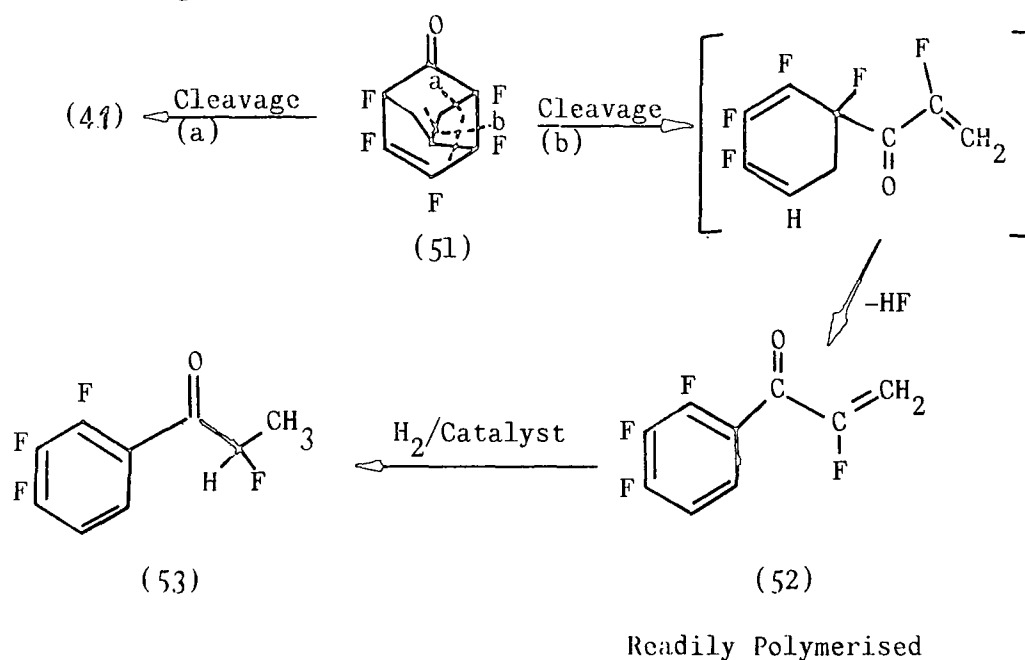
Scheme 16

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

(51a) (56) (54)

(58) (57) (55)
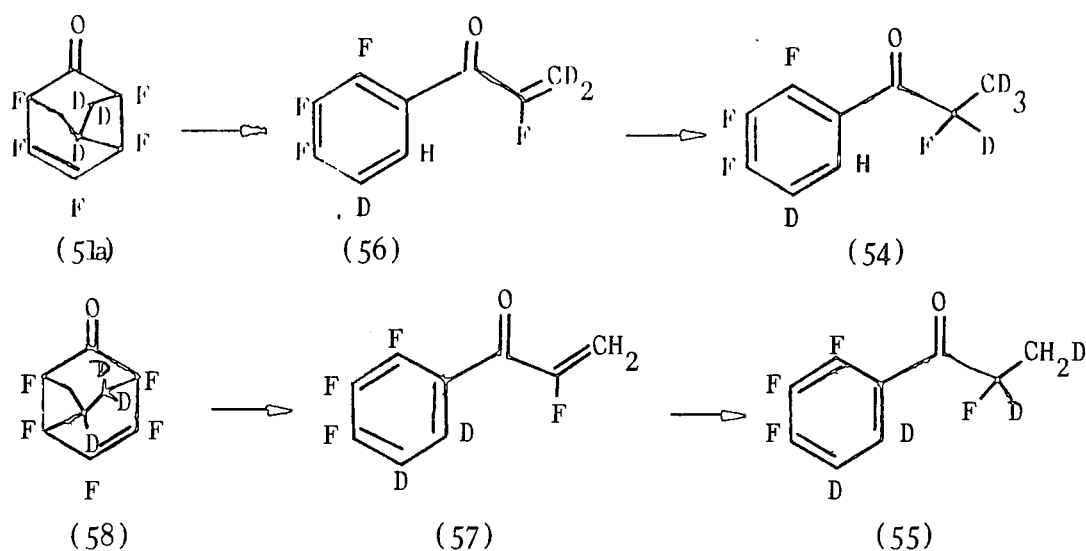
Scheme 17

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[42,43] (cf. Section 2.2)

Schmid et al.[46] 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

(59)   → $\xrightarrow[\text{Decane}]{230^\circ}$ (60)   +   (61)

(62)

(63)

(64) R = CH$_3$
(65) R = Br

(66) R = Br

(67) R^1 = Cl; R^2 = H
(68) R^1 = Br; R^2 = H

(69) R^1 = Cl; R^2 = H
(70) R^1 = Br; R^2 = H

(71)

Scheme 18

- 21 -

Scheme 19

(a) [3,3] Sigmatropic Shift.   (e₁) Radical Rearrangement/
                                          Recombination.
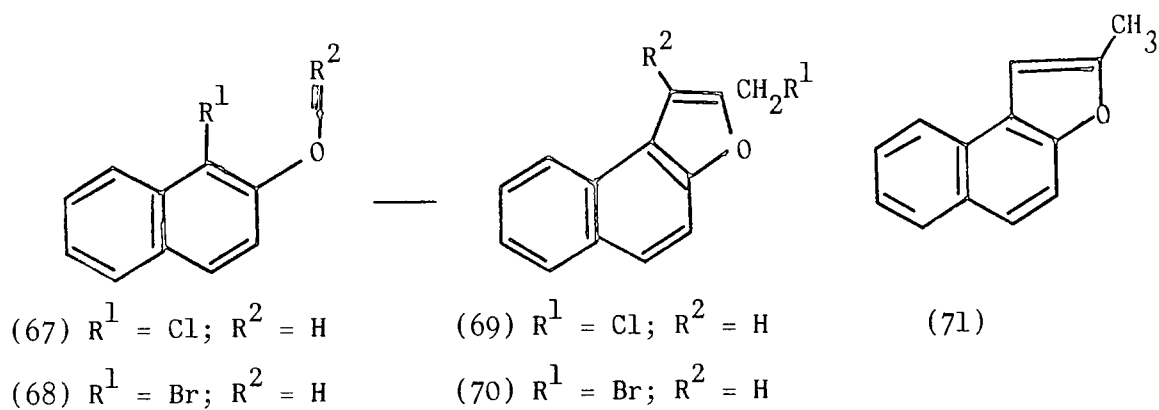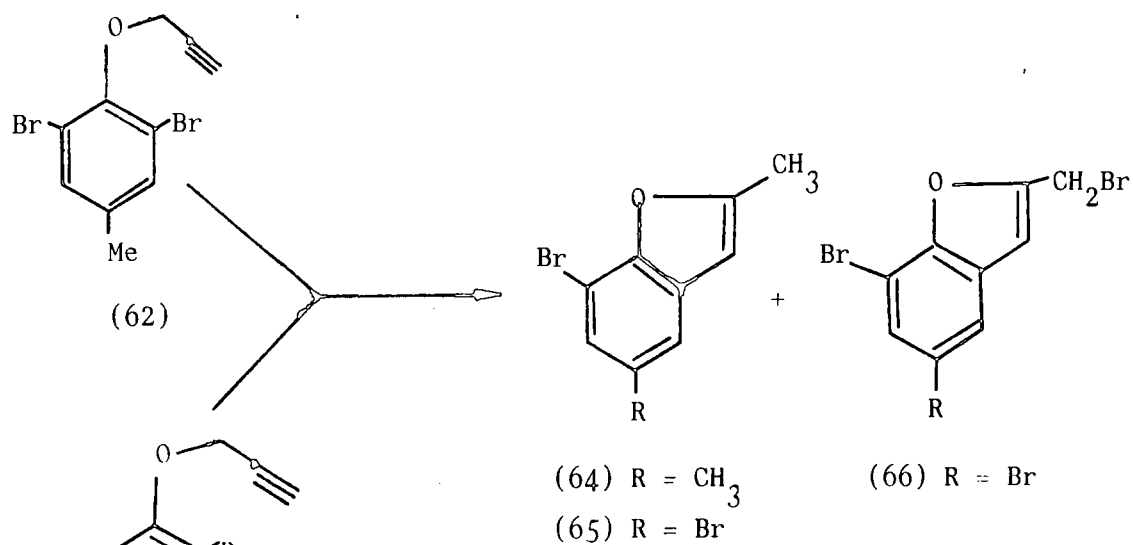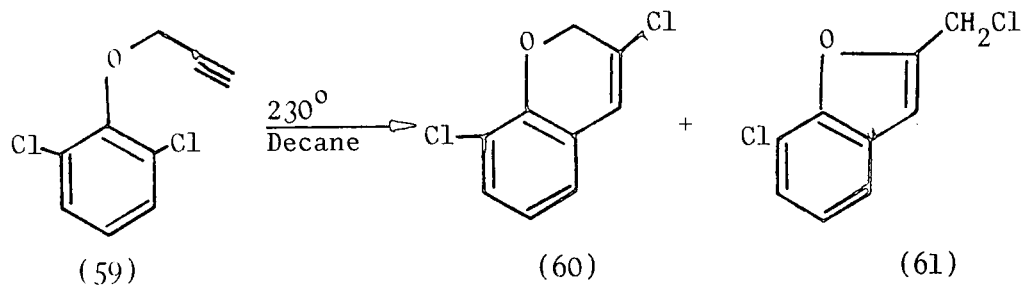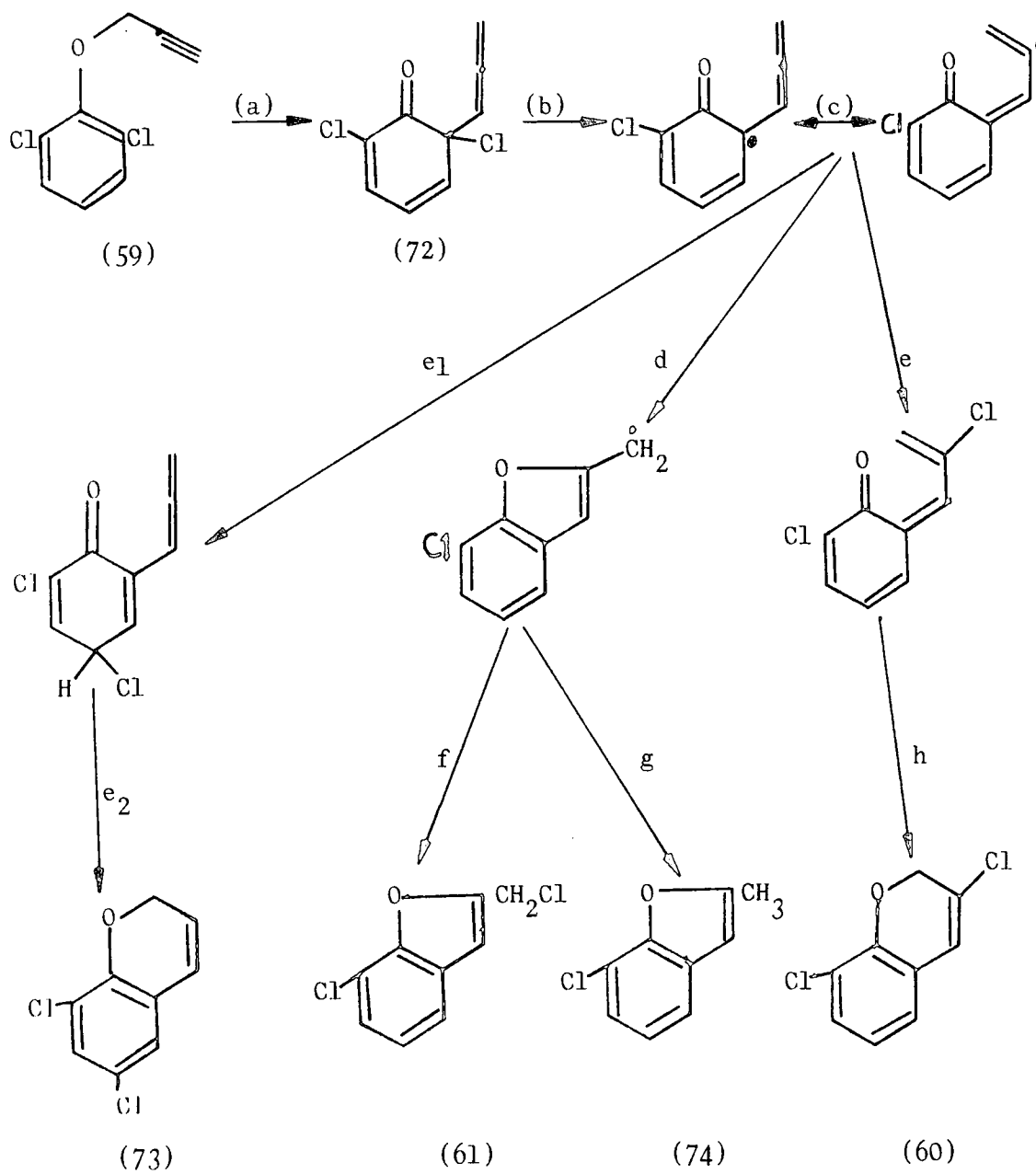
(b) Homolysis of C-Cl.   (e₂) Radical Recombination/Ring
                                          Closure.

(c) Resonance Stabilization.   (f) Radical Recombination.

(d) Ring Closure.   (g) Hydrogen Abstraction.

(e) Radical Recombination.   (h) Cyclisation.

[3,3] sigmatropic shift to the 6-allenyl-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.[47] 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).
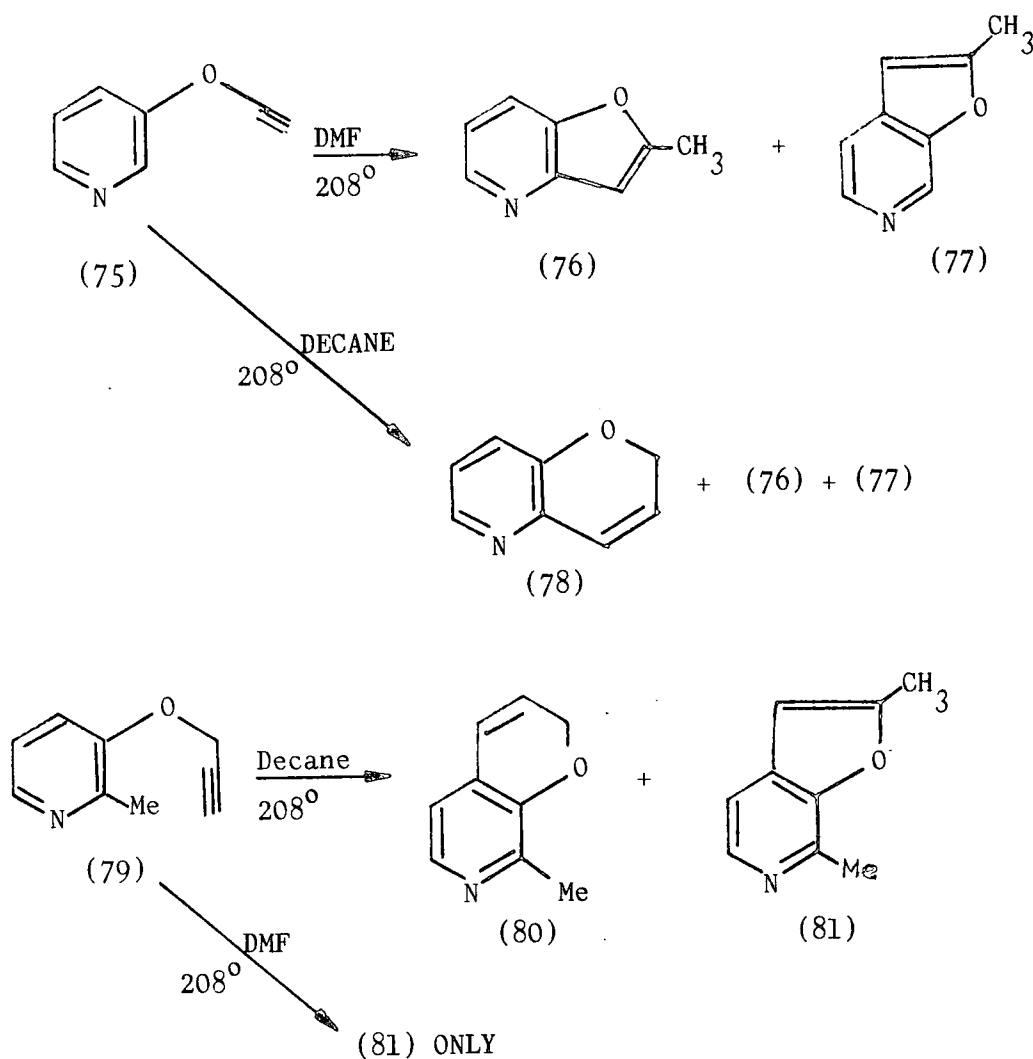
Scheme 20

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).[47]

(82)   DMF/DECANE   (84)

(83)   DMF/DECANE   (85)
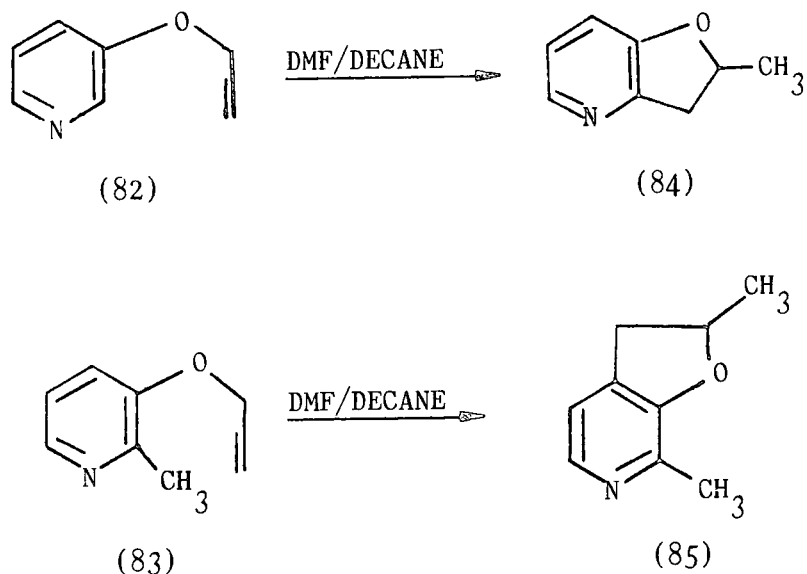
Scheme 21

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).

(86)   DECANE 200-235   (87)

SULPHOLANE   (88)

Scheme 22

- 24 -

Scheme 23

(98) (99) (105) (106)

Δ [3s3s] (b) [H·]

(a)

(100) (100)

CYCLISATION

[H·]

(101) (103)

RING CLOSURE

[H·]

[Cl·]

(102) (104)
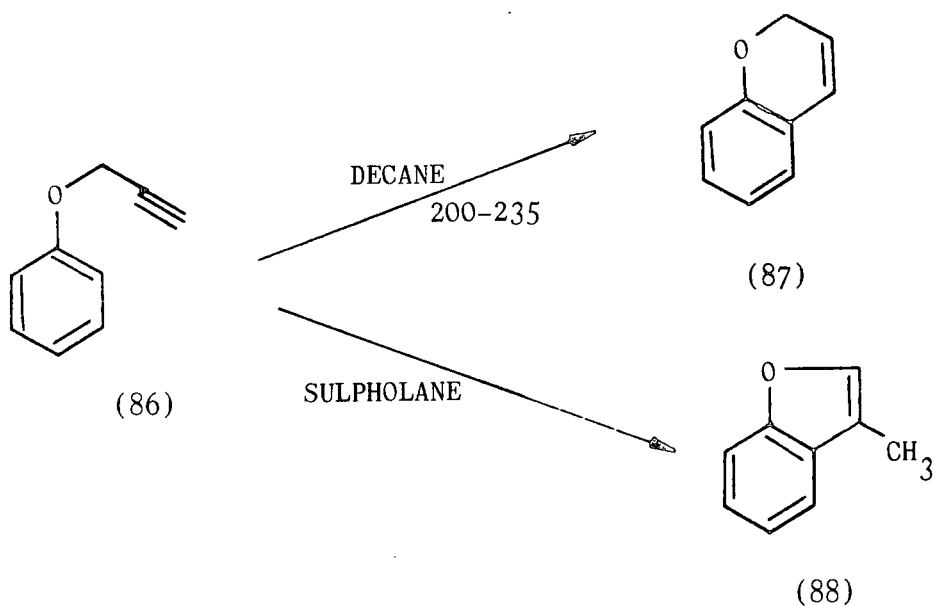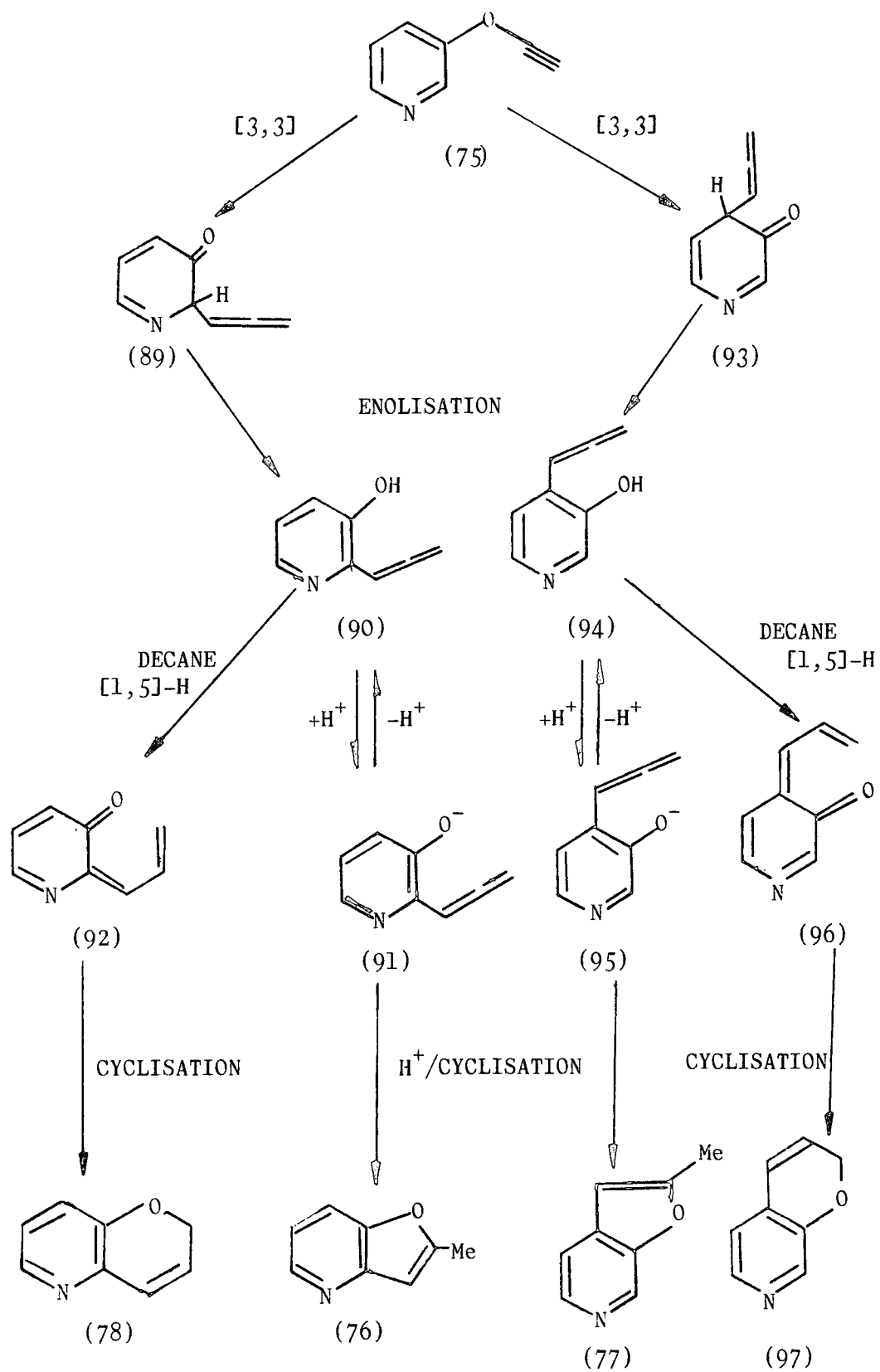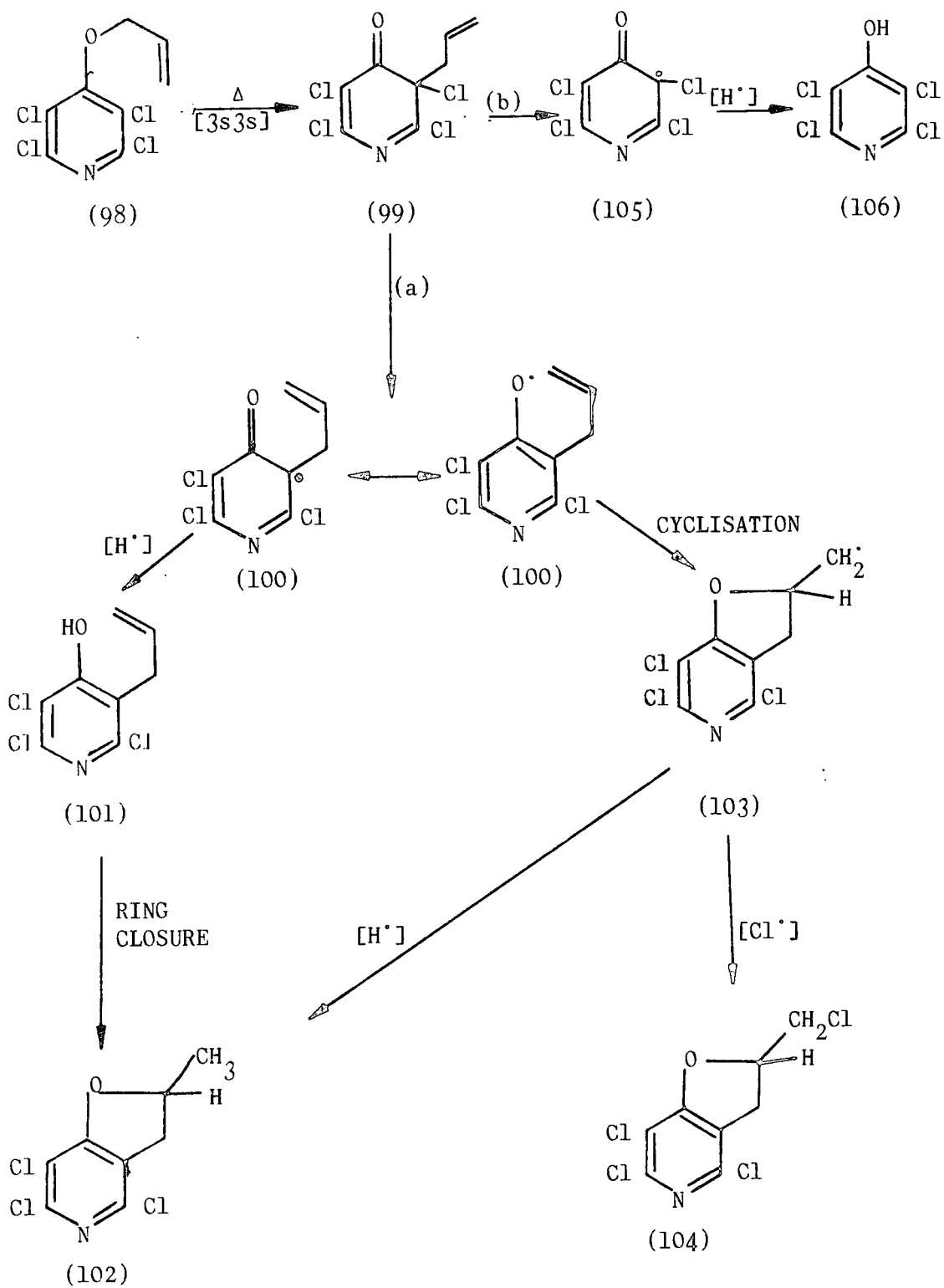
(a) Homolytic Cleavage C–Cl

(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[47] (Scheme 23).

Iddon et al.[48] 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 re-arrangements in these fully substituted compounds. The reactions were undertaken at high temperature in sulpholane. 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.[46]

Brooke and co-workers[49] investigated the behaviour of the tetra-fluoropyridyl 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).

(105)   (106)   (107)

(107) H_2O (108)
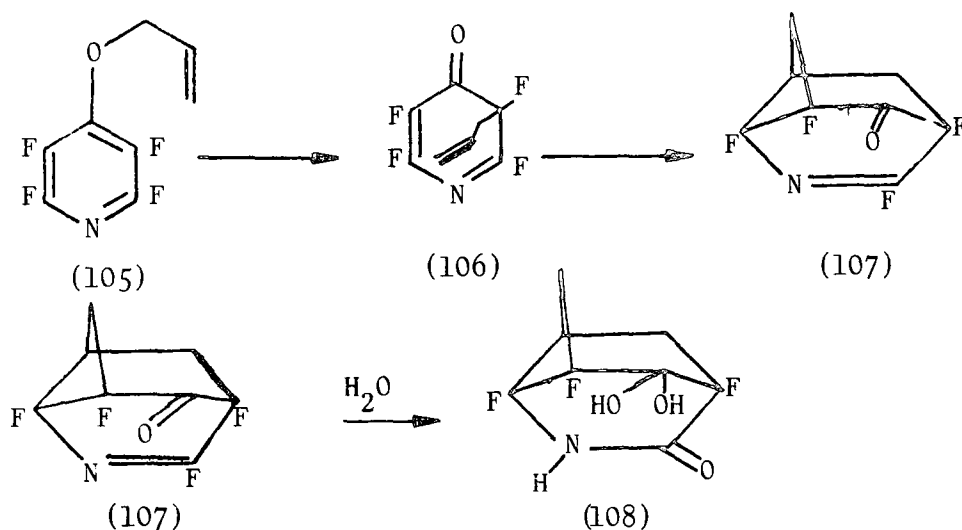
Scheme 25

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.[49]

(109)   (110)   (111)
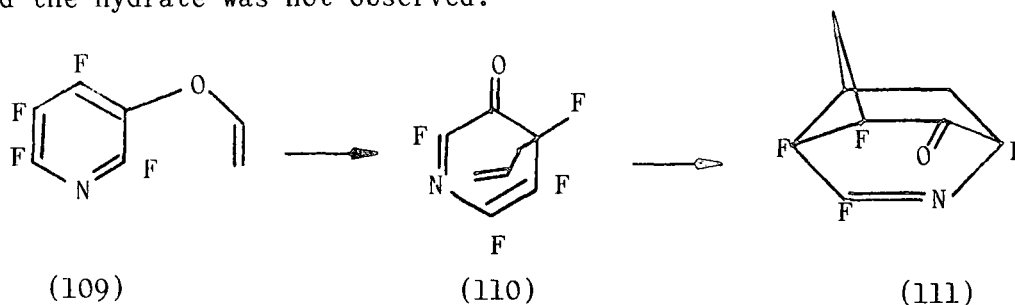
Scheme 26

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 pentafluoro-

phenyl-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.$^{-1}$, 116 kcal.mol.$^{-1}$

respectively[50]) which would make the homolytic cleavage of C-Cl,

postulated by Schmid et al., and Iddon et al.,[46,48] somewhat easier

than the homolytic cleavage of C-F. Furthermore, the two bond lengths

of C-Cl and C-F (1.766Å, 1.317Å respectively[50]) 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-ynyl ether, and heptafluoro-2-naphthyl-prop-2-ynyl ethers, which

when thermolysed do give rise to recognisable electrocyclisation

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 pentafluoro-

phenyl 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[44] (Scheme 27). However the vapour phase
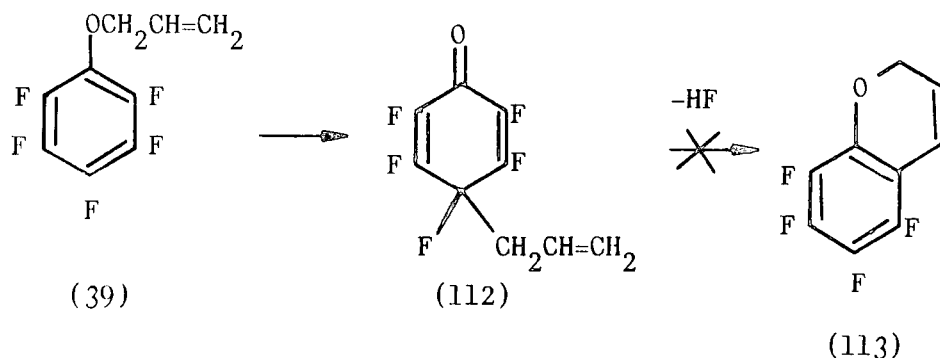
Scheme 27

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[51] (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[44] (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[43] (Scheme 10, Section 2.2).
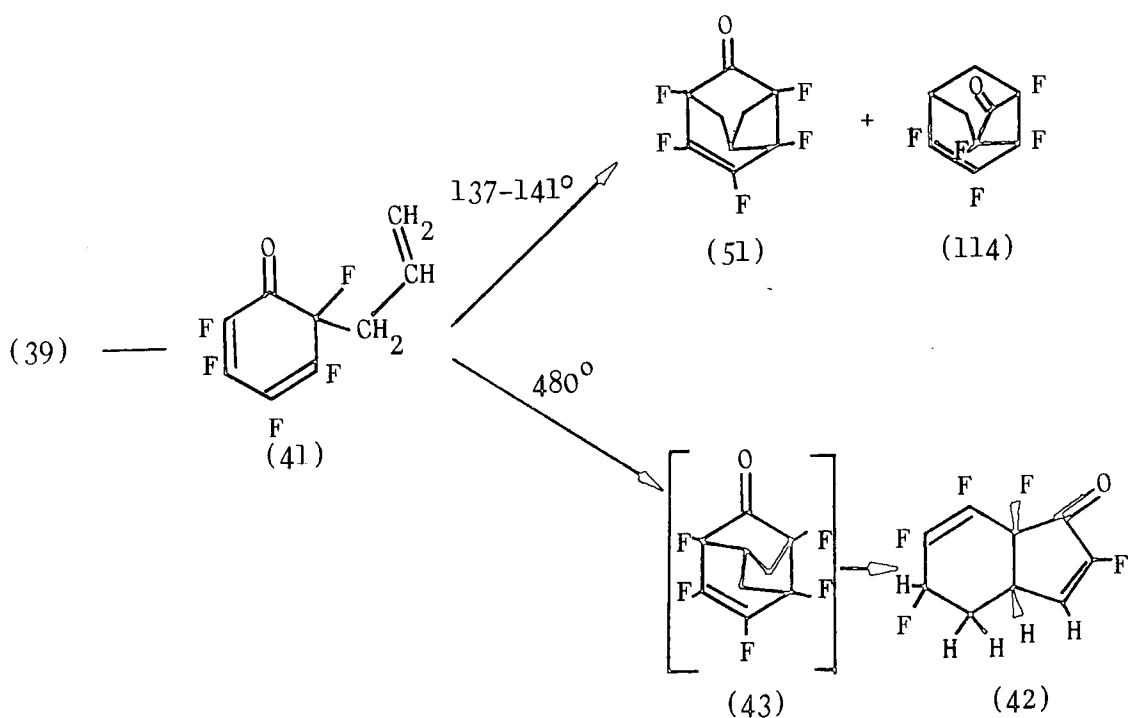
Scheme 28

When pentafluorophenyl prop-2-ynyl ether (115) was distilled

through a silica tube packed with quartz wool at 370°, 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.[52]
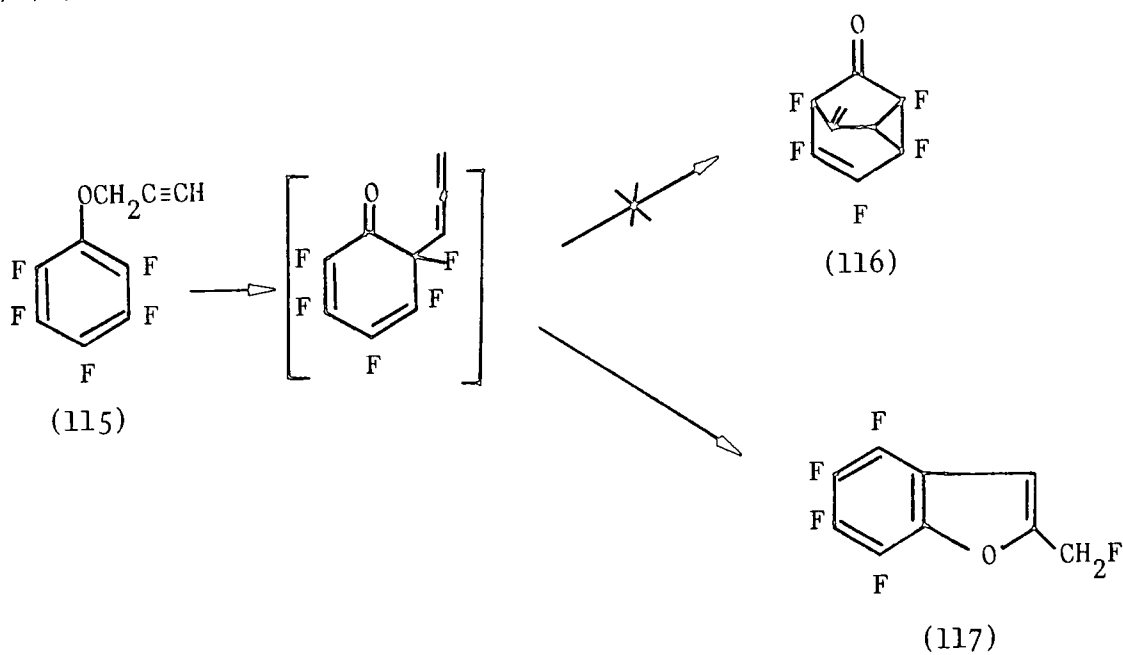
Scheme 29

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-tetrafluoro-

benzo(b]furan (119) (Scheme 30).
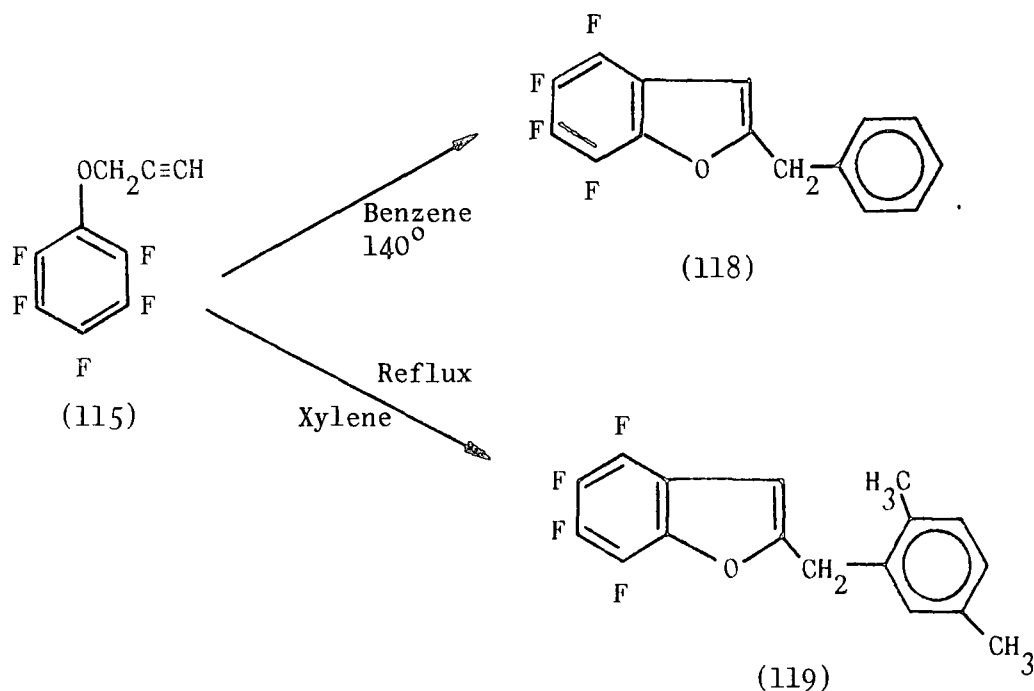
Scheme 30

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-hexa-

fluoronaphtho[2,1-b]furan (121) and (122) (Scheme 31).[52]

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.[46] 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)

(120)

BENZENE

(121)

XYLENE

(122)
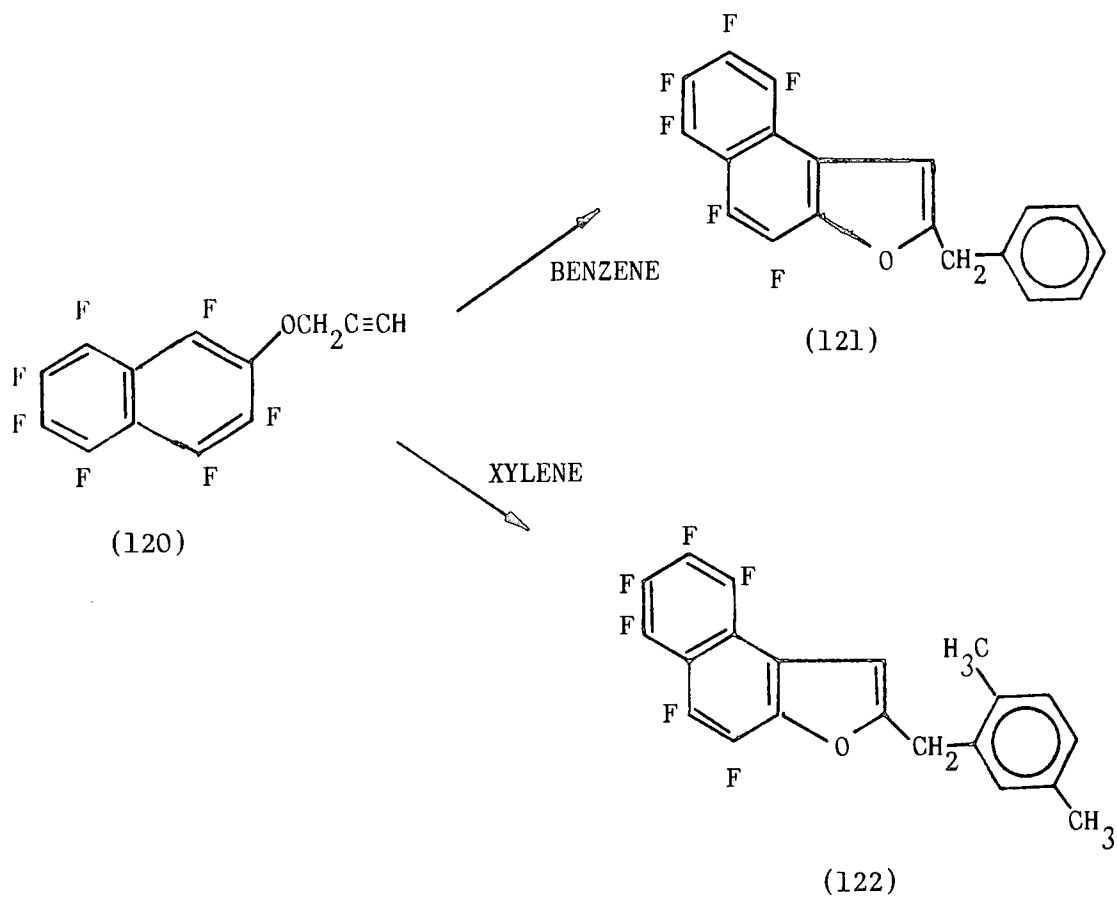
Scheme 31

produced 2-chloro(bromo)methylnaphtho[2,1-b]furan (69,70) and 2-methyl-naphtho[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).

(59)   (72)   RESONANCE

(60)

(61)
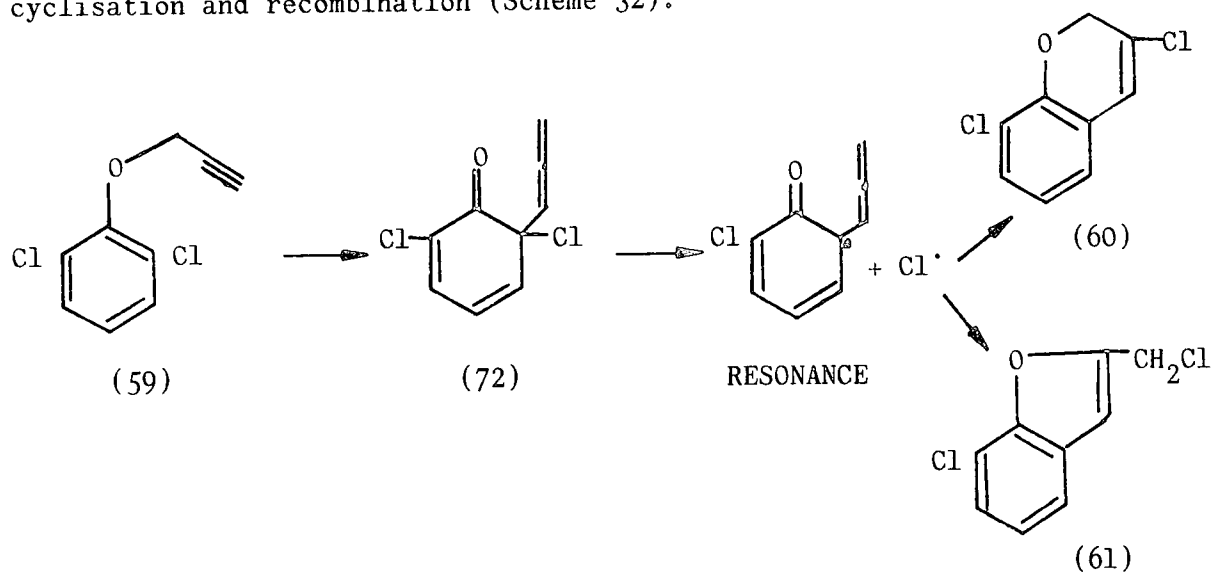
Scheme 32

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°. 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).

(115)   RESONANCE

BENZENE

XYLENE

(118)

(119)
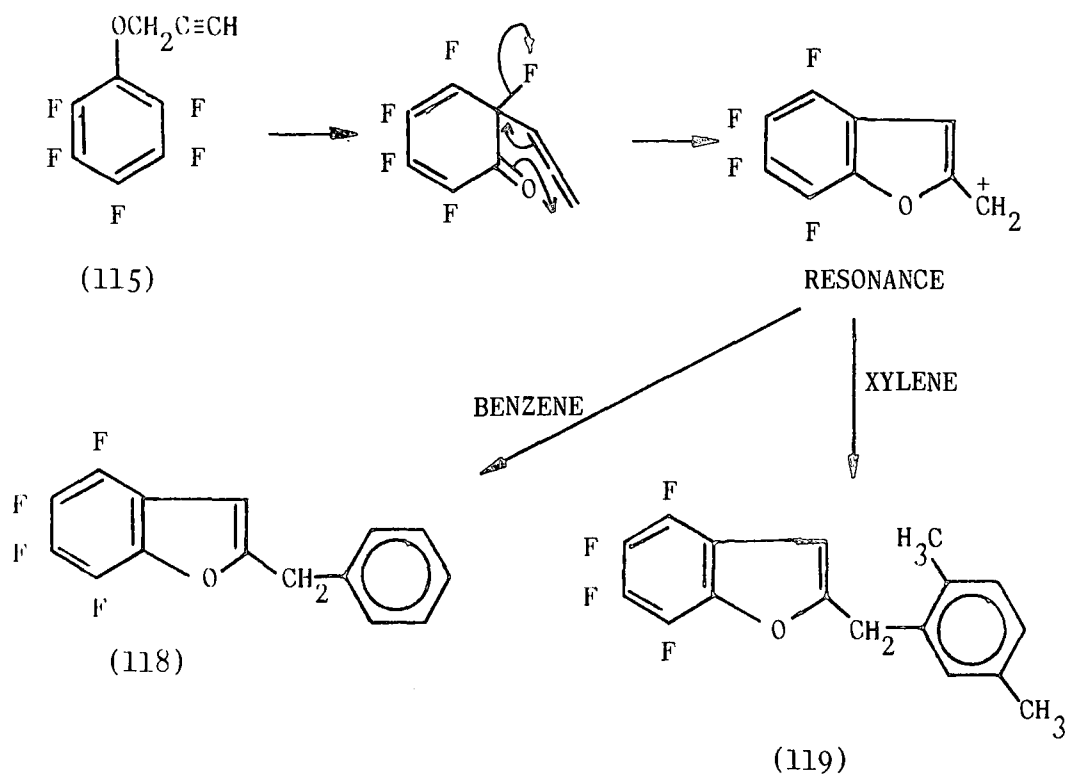
Scheme 33

A series of aromatic solvents: isopropylbenzene, nitrobenzene, benzylidyne 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.[53,54]

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-hexafluoro-

naphtho[2,1-b]furan-2-yl)methane (124), no fluoromethyl compound

analogous to (117) was isolated (Scheme 34).
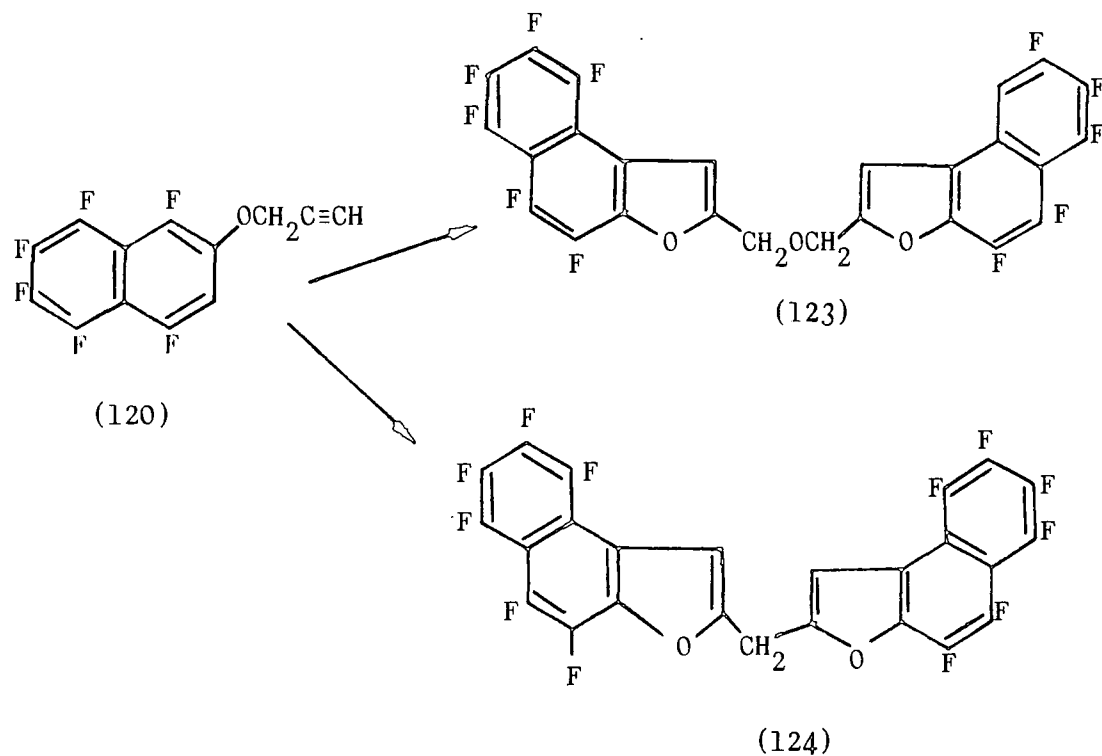
Scheme 34

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

- 34 -

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-hexa-
fluoronaphtho[2,1-b]furan (126) (2%) (Scheme 35).[53,54]

$$(120) \longrightarrow (125) + (126) + (123) + (124)$$
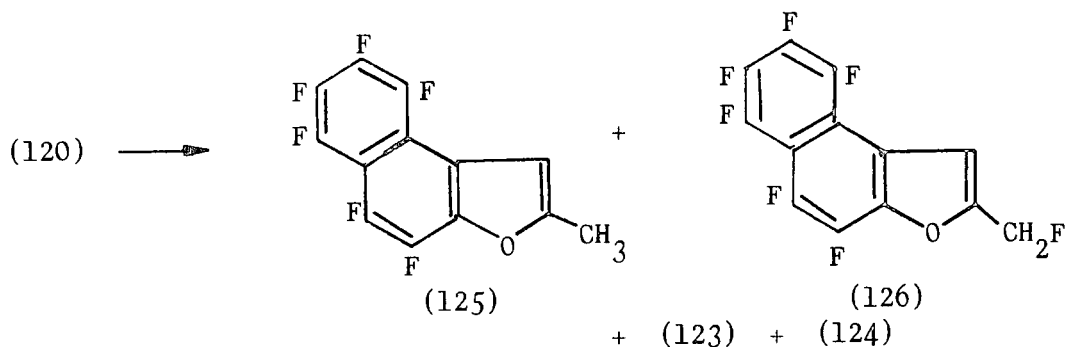
Scheme 35

The absence of the 2-fluoromethyl derivative (126) as a product
in the thermal reaction of ether (120) in 1,1,2-trichlorotrifluoro-
ethane was surprising in view of the observations made by Schmid et al.
in their work with orthohalophenyl prop-2-ynyl ethers (67), (68)[46]
(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).[53]
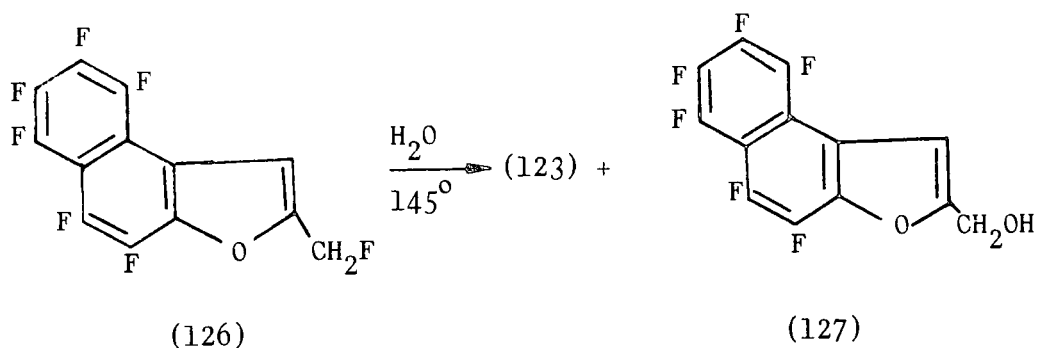
Scheme 36

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[53] 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-Trichloro-trifluoroethane

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[46]), and anhydrous 1,1,2-trichloro-trifluoroethane. 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).

(123)

(120)

(124)

(126)
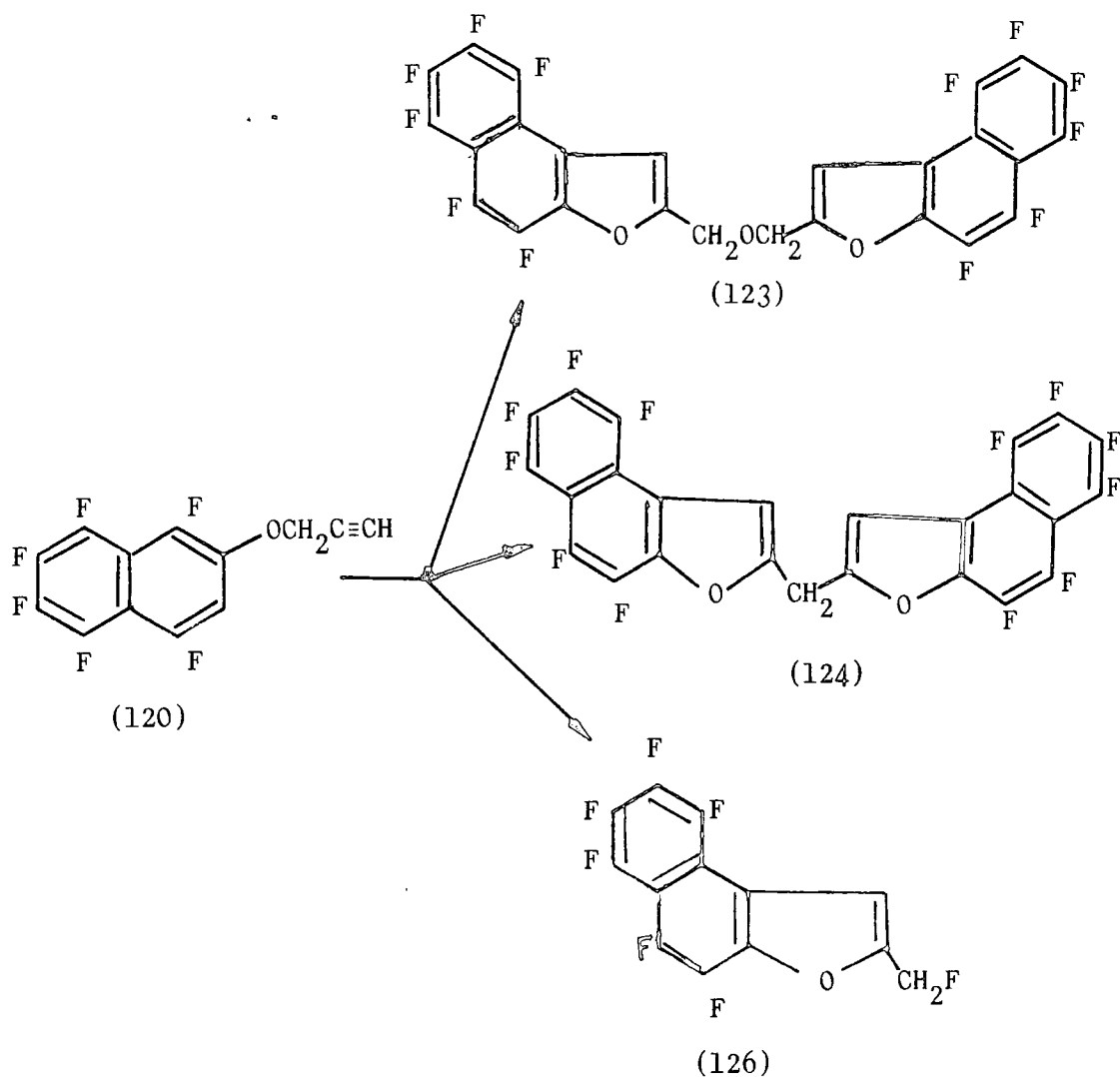
Scheme 37

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),[46] 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-tetrafluoro-benzo[b]furan-2-yl methyl)ether (128) (approximately 20%) (Scheme 38).
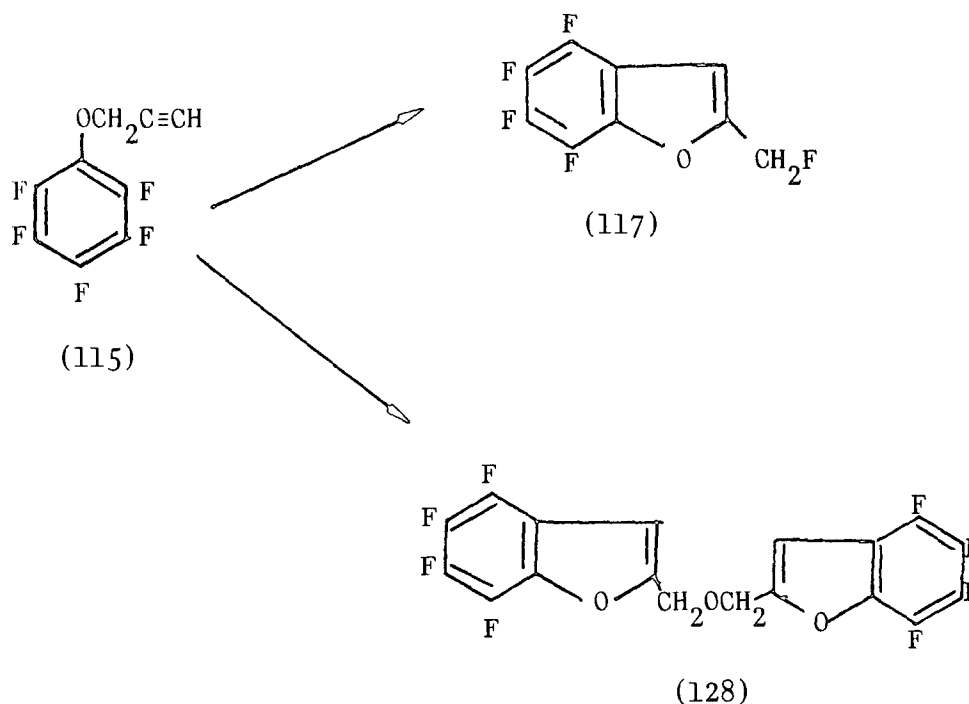
Scheme 38

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)[55] under
thermolysis conditions in various solvents. Initially these
compounds were prepared by reacting 2,3,5,6-tetrafluoro-4-hydroxy-
pyridine (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).

(129)   (131)

(130)   (132)
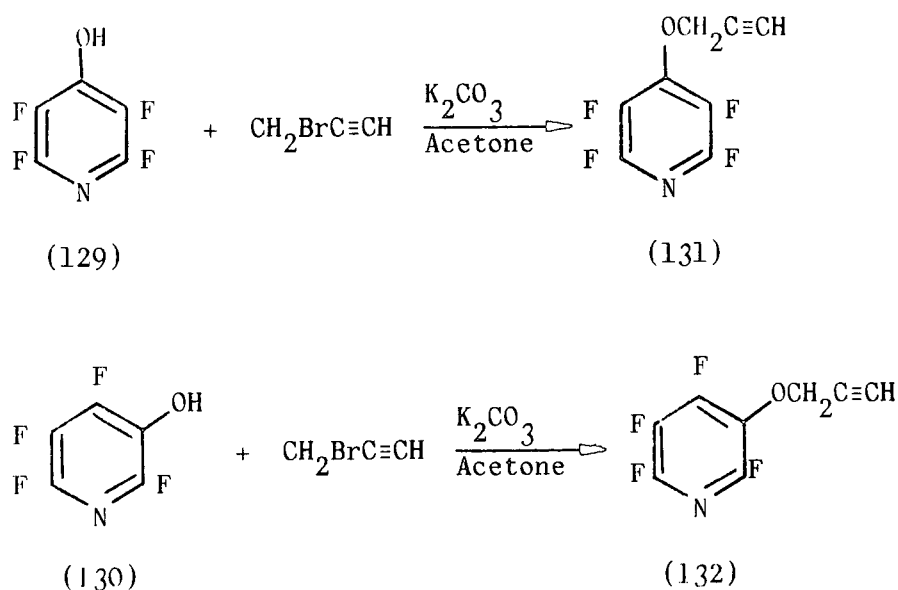
Scheme 39

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 ^{19}F n.m.r. of which showed it
to contain mainly unreacted starting material (δ_F CDCl$_3$ 92.8 p.p.m.,
and 164.5 p.p.m. above CFCl$_3$), but there were four other signals one
of which was a triplet at 213.4 p.p.m. due to a -CH$_2$F presumably of
compound (133) (Scheme 40).
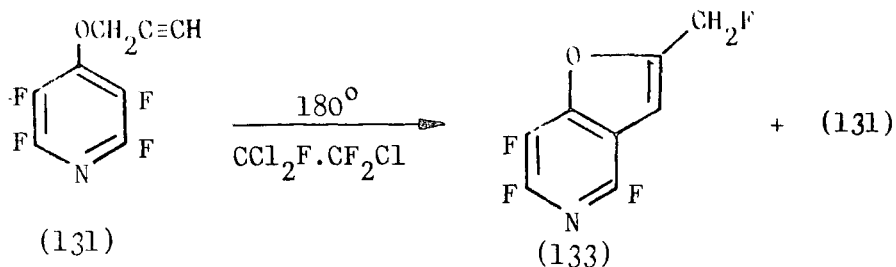
Scheme 40

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

- 40 -
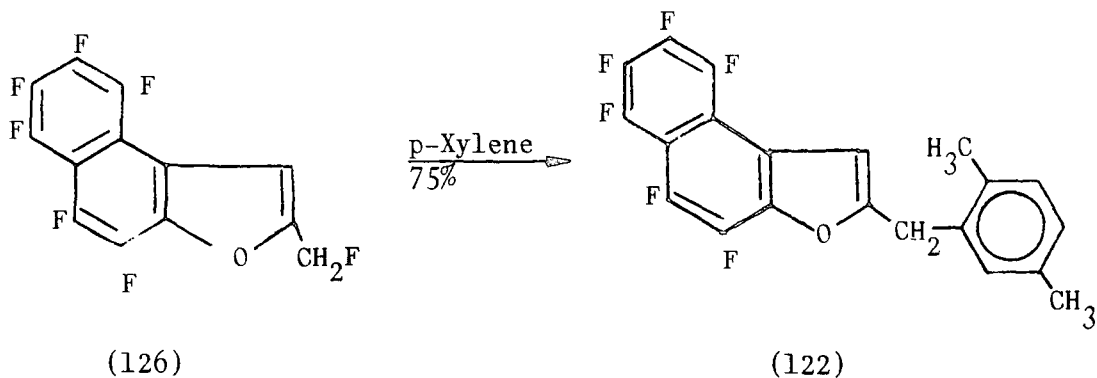
The result clearly indicated by the formation of the

substitution product (122) that 2-fluoromethyl-4,5,6,7,8,9-hexa-

fluoronaphtho[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 CH_2-F bond (homolytic

or heterolytic), which occurs readily at 140° or 150° (Scheme 42).
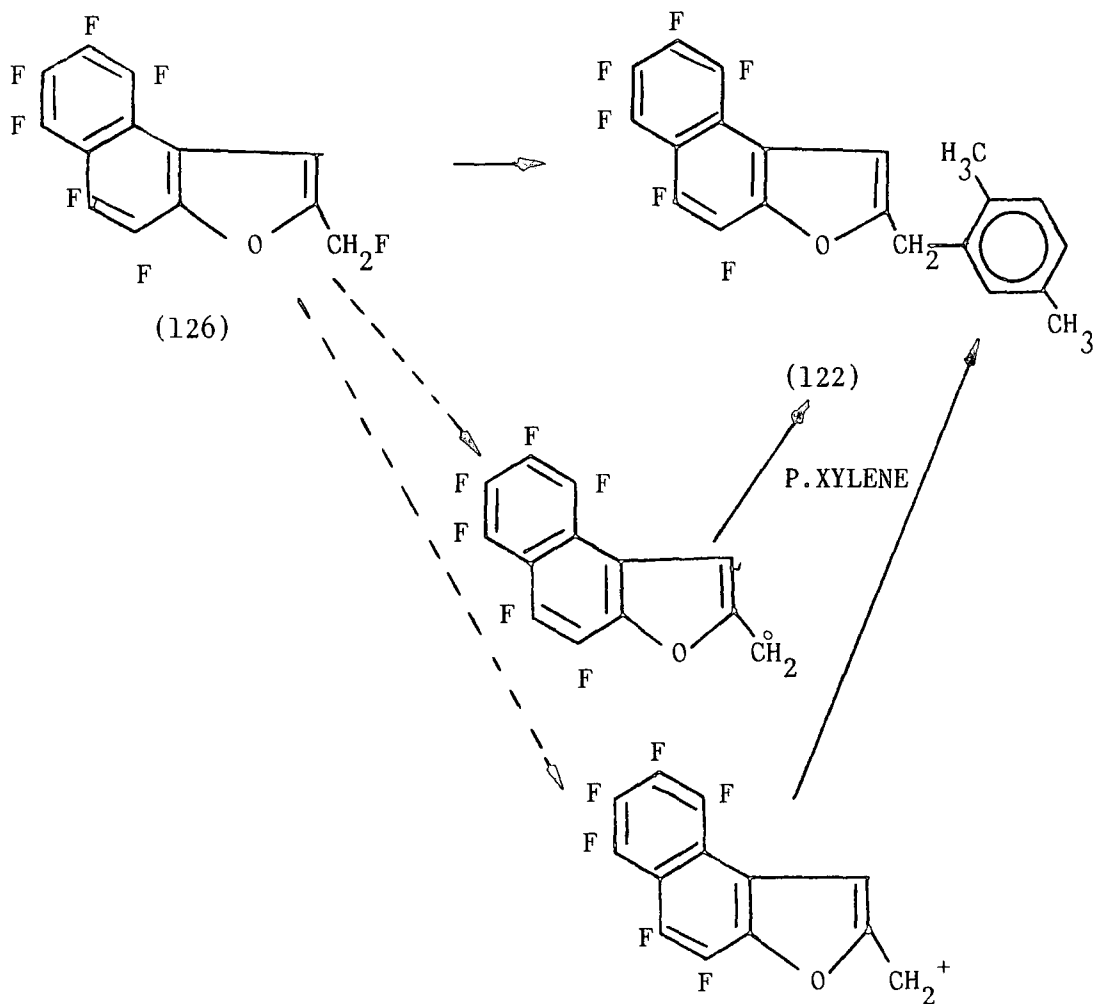
Scheme 42

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 $LiAlH_4$), 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 $CCl_4:CHCl_3$ 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-hexa-

fluoronaphtho[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 ^{19}F n.m.r. analysis by comparison with known samples.[56]

(b) In 1,1,2-Trichlorotrifluoroethane

The ether (120) (1.64 g.) and 1,1,2-trichlorotrifluoroethane

(40 ml.) (freshly distilled from P_2O_5), 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 ^{1}H n.m.r. analysis against known samples.[56]

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

CCl_4:$CHCl_3$ 7:3 as the developing solvent.

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

The ether (115) (2.83 g.) and 1,1,2-trichlorotrifluoroethane (30 ml.),

(freshly distilled from P_2O_5), were sealed in a nickel Carius tube

under nitrogen and heated at 150° 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 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-tetra-

fluorobenzo[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.[56]

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. ≡ 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 $MgSO_4$, 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%). δ_H (CDCl$_3$) 2.73 (multiplet $\equiv$ C-H) and 5.16 (multiplet OCH$_2$); δ_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$_2$O$_5$), 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., ^{1}H and [19]F n.m.r. as 2-(2,5-dimethyl-benzyl)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., ^{1}H and [19]F n.m.r. analyses of known samples.[56]

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:[52,54] (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° 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.

(120)

(134)

(135)

−F· →

+F·

(126)

+F⁻

(136)

RESONANCE

(120) ⟶ (134) $\xrightarrow{-F^-}$

Scheme 43

- 46 -
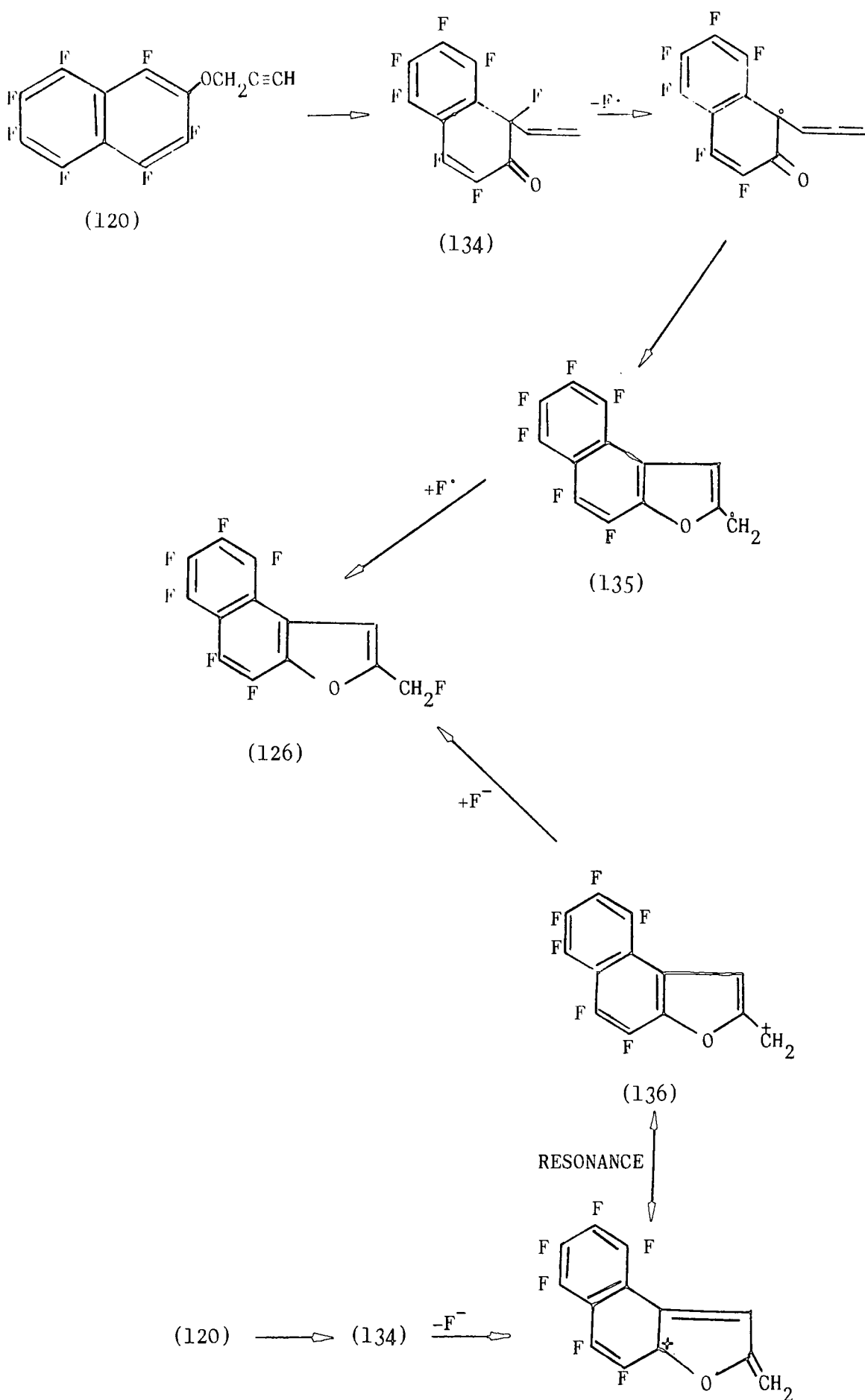
4.2. Thermolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether in the Presence of (Z)-But-2-ene

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 [1]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

(120)   (137)
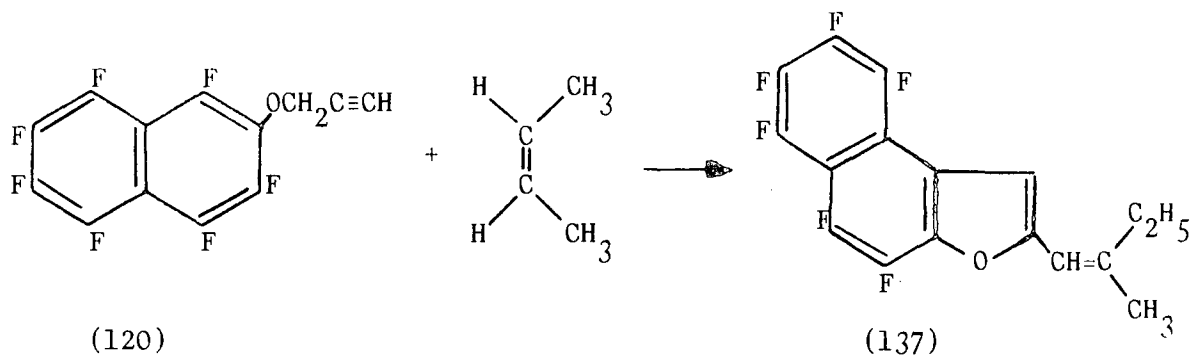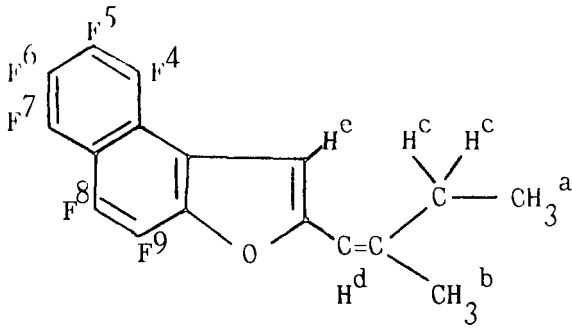
Scheme 44

by ^{1}H and [19]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 $C_{17}H_{10}F_6O$ (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· or R^fCH_2· adduct formation, then ionisation to yield a carbocation which could then rearrange (Scheme 45). No adduct was

(137)

M.pt.	83-84°	
M^+	344	
C	59.00% requires 59.3%	
H	3.00% requires 2.9%	
		REL. INT.
H^a	1.13 - 1.17δ (t-C$\underline{H}_3$)	3
H^b	2.15δ (d-C$\underline{H}_3$)	3
H^c	2.25 - 2.32δ (q C$\underline{H}_2^c$-CH$_3^a$)	2
H^d	6.26δ (sext.vinylic =C$\underline{H}$-)	1
H^e	7.07 - 7.09δ (dd 3-furanyl C$\underline{H}$)	1
F^4, F^7	145 - 146 (b.m)	2
F^8	151 - 152 (b.m) peri J_{F-F} 66.5 Hz	1
F^5, F^6, F^9	158 - 159 (b.m)	3

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

$R^f-CH_2^+$ + (H)(CH$_3$)C=C(H)(CH$_3$) $\longrightarrow$ $R^fCH_2-C(H)(CH_3)-\overset{+}{C}H-CH_3$

[1,2]H

$R^f-CH_2-\overset{+}{C}(C_2H_5)(CH_3)$

[1,2]H

$R^f-\text{CH}\ \text{C}(CH_2CH_3)(CH_3)$

(145)

$R^f-CH_2-C(H)(CH_3)-\overset{+}{C}H(CH_3)$

$-F^-$

$R^fCH_2^\circ$

$\longrightarrow$ $R^f-CH_2C(H)(CH_3)-C(H)(CH_3)\cdot$ $\xrightarrow{F\cdot}$ $R^fCH_2-C(H)(CH_3)-C(F)(H)(CH_3)$

(H)(H)C=C(H$_3$C)(CH$_3$)

$R^fCH_2\cdot$

$F\cdot$ + (H)(H)C=C(H$_3$C)(CH$_3$) $\longrightarrow$ $F-C(H)(CH_3)-C(H)(CH_3)\cdot$

Scheme 45

- 49 -
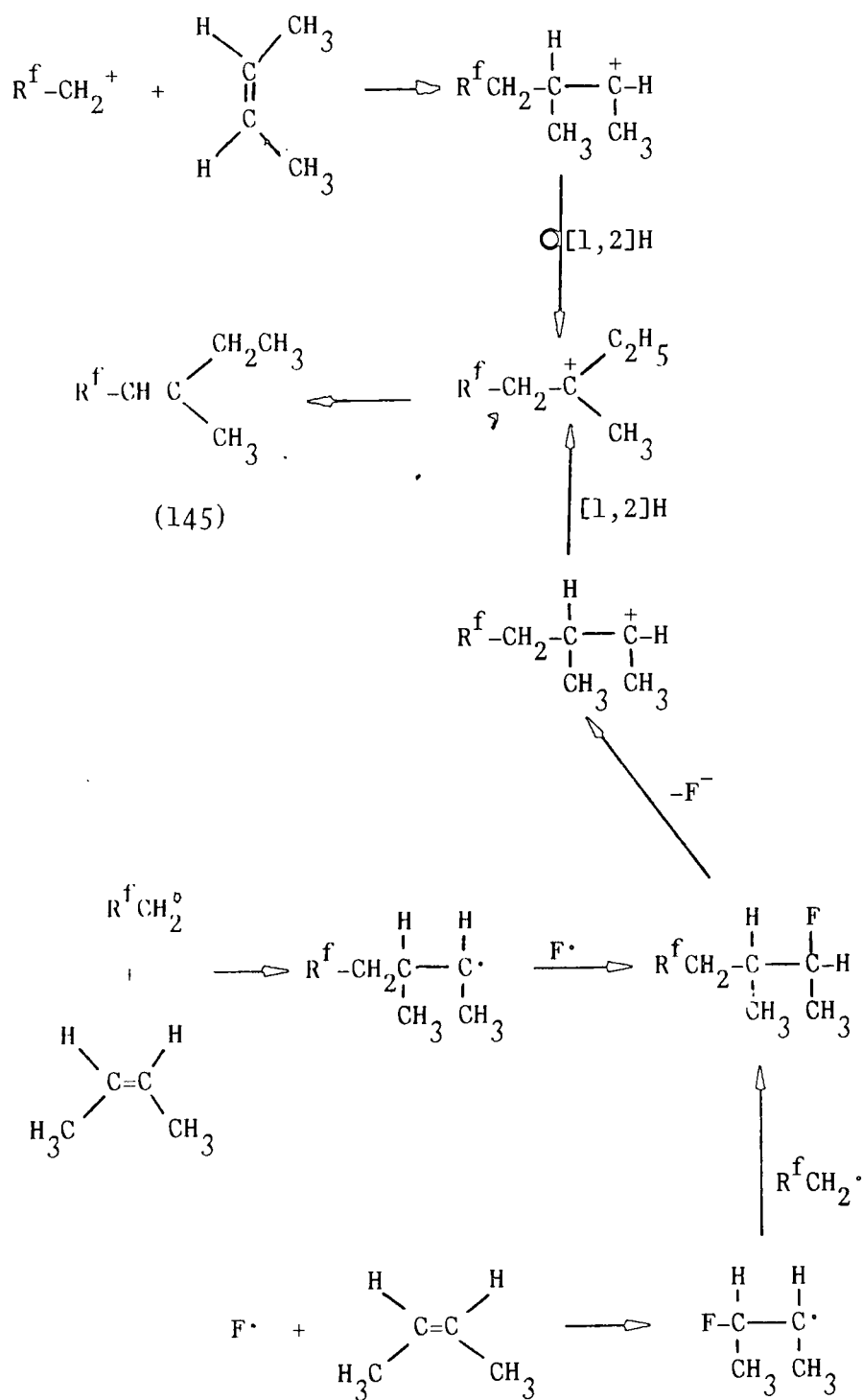
observed, and the reaction only served to illustrate the viability of the reaction of heptafluoro-2-naphthyl prop-2-ynyl ether (120) with alkenes leading to substitution products. Finally note should be made that during the work undertaken to isolate alkene (137) a degradation product 4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan-2-yl aldehyde was observed, 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 (Δ 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}H and [19]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_{F-F} coupling constant in the [19]F n.m.r. spectrum of each compound, and the chemical shifts

F

F

F

F

F

F

CH=C

C(CH₃)₃

CH₃

(138)

F

F

F

OCH₂C≡CH

+

H₃C   CH₃

H₃C   CH₃

F

F

F

F

O

CH₂-C

CH₂

C—CH₃

H₃C   CH₃

(139)

F

F

F

F

F

OCH₂C≡CH

F

F

F

F

(142)

H₂C

C

CH₃

CH₂-C

CH₃

CH₃

O

F

F

F

F

F
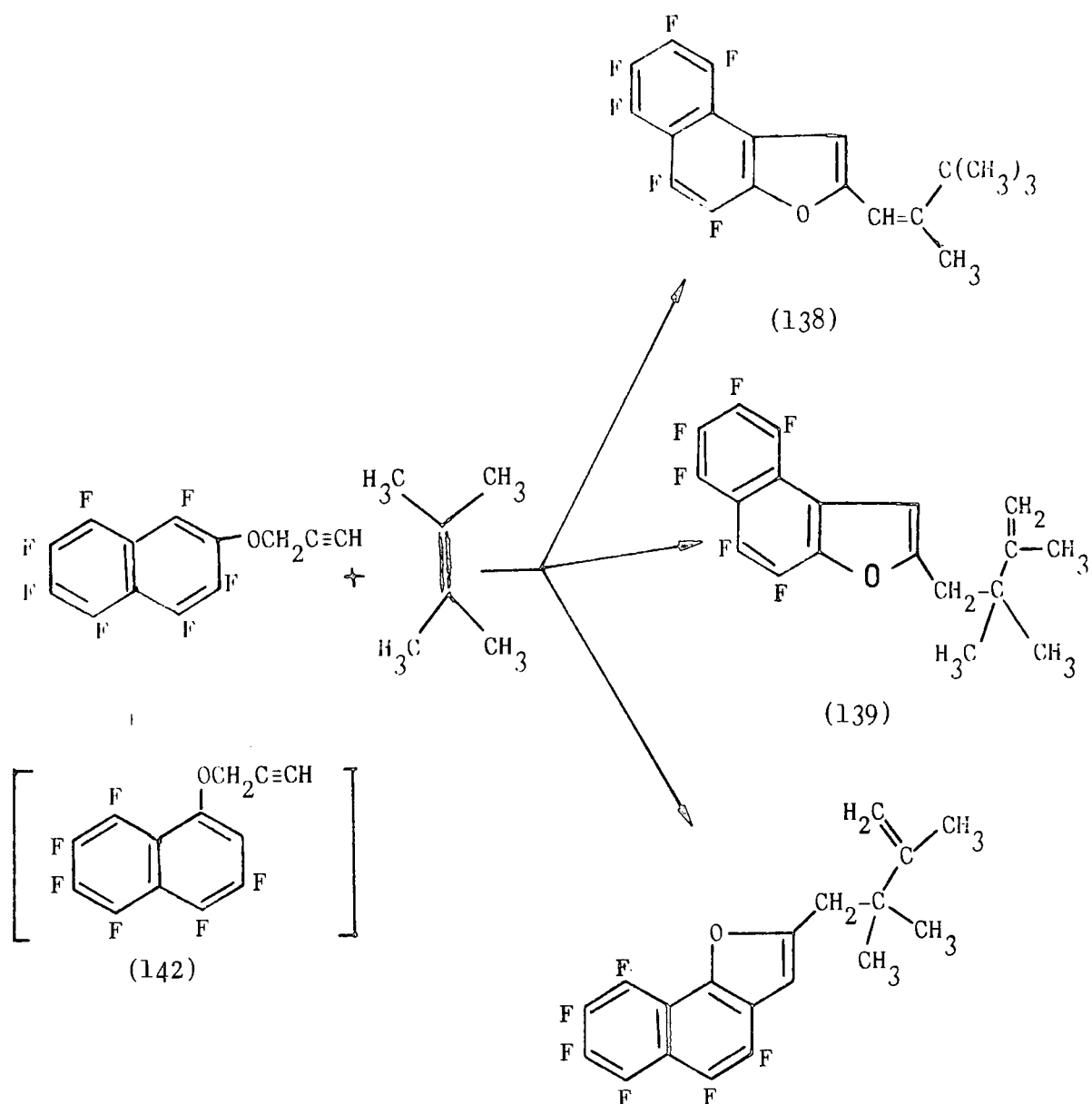
[(140) Due to presence of α-ether in (120)]
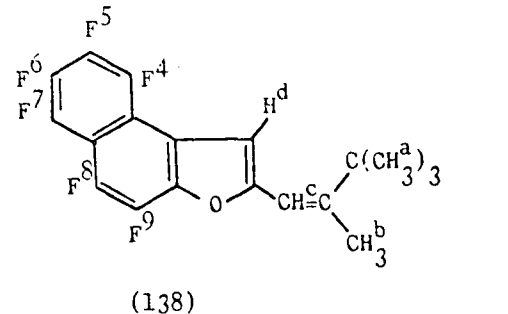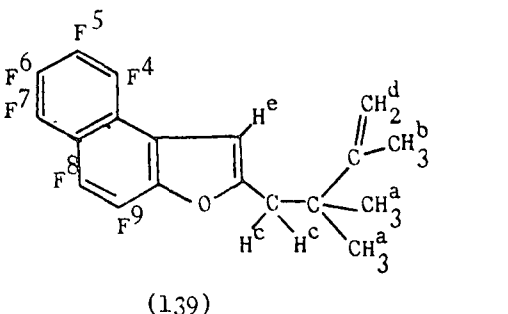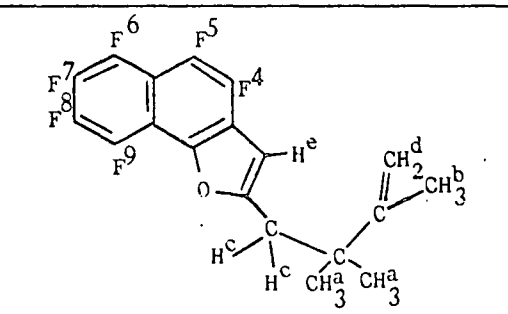
Scheme 46

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

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

by either F· or R^f-CH_2· (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 re-arrangements are well known for reactions proceeding via carbocations. When considering radical rearrangements, Sharp stated[57] '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.[57,58,59] 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 ^{1}H 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^f 4,5,6,7,8,9 hexafluoronaphtho[2,1-b]furan.
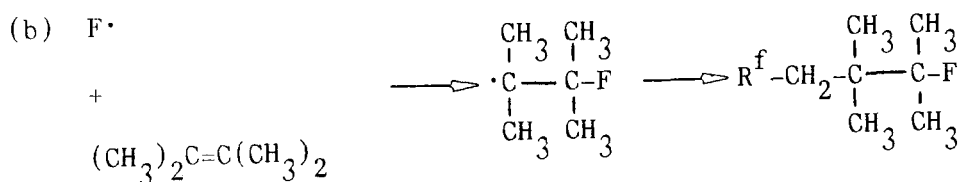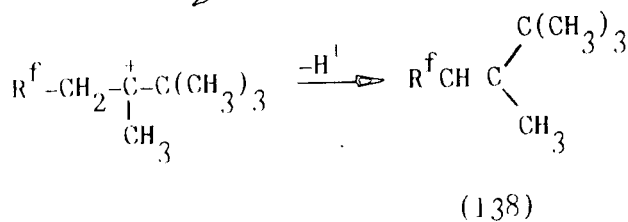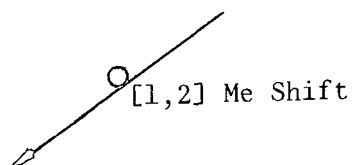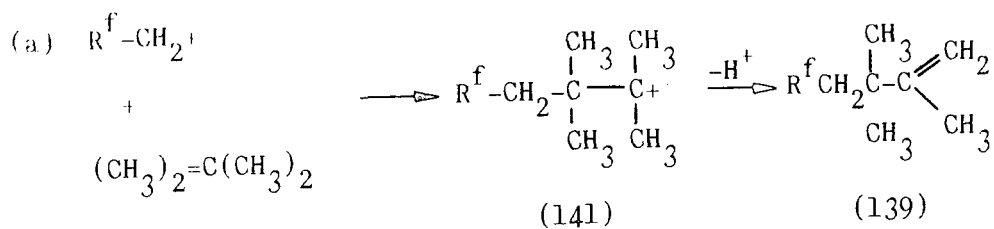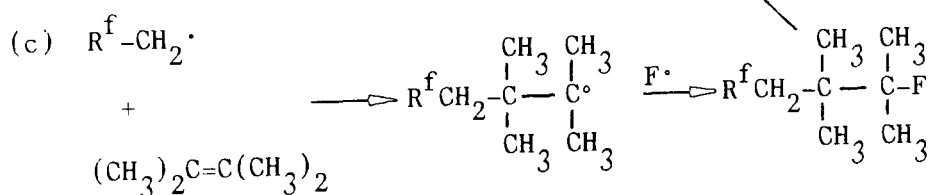
(a) $R^f-CH_2^+$

   +

   $(CH_3)_2=C(CH_3)_2$

$\longrightarrow R^f-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}+$ $\overset{-H^+}{\longrightarrow}$ $R^fCH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-C\overset{\displaystyle CH_2}{\diagdown}$

                        (141)   (139)

[1,2] Me Shift

$R^f-CH_2-\overset{+}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-C(CH_3)_3$ $\overset{-H^+}{\longrightarrow}$ $R^fCH\ C\overset{\displaystyle C(CH_3)_3}{\diagup}\underset{\displaystyle CH_3}{\diagdown}$

                                              (138)

(b) F·

   +

   $(CH_3)_2C=C(CH_3)_2$

$\longrightarrow \cdot\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-F$ $\longrightarrow R^f-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-F$

$-F^-$

As above $\longleftarrow$ (141)

$-F^-$

(c) $R^f-CH_2\cdot$

   +

   $(CH_3)_2C=C(CH_3)_2$

$\longrightarrow R^fCH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\circ$ $\overset{F\cdot}{\longrightarrow} R^fCH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-F$

Scheme 47

- 54 -

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).[60]

$$(CH_3)_3C-CH=CH_2 \quad \xrightarrow[H^+]{ACID} \quad (CH_3)_2C=C(CH_3)_2$$

$$+H^+ \Big\downarrow \qquad\qquad\qquad \Big\uparrow -H^+$$

$$(CH_3)_2\overset{+}{-C-CH-CH_3} \quad \longrightarrow \quad (CH_3)_2\overset{+}{C-CH(CH_3)_2}$$
$$\underset{CH_3}{\big|}$$
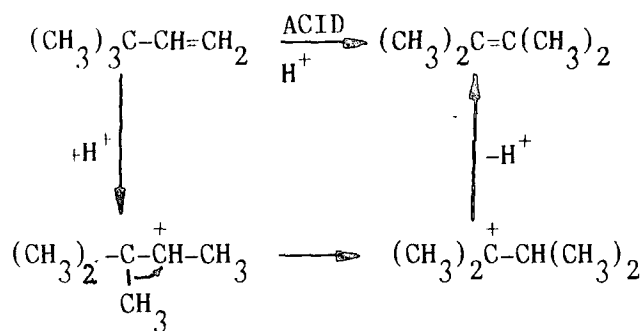
Scheme 48

When 3,3-dimethylbut-1-ene was chlorinated, as a probe for

Wagner-Meerwein rearrangements,[61] 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,[62] 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).

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow{\ Br_2\ } (CH_3)_3C-\overset{\overset{Br}{|}}{C}H-CH_2Br$$

Normal Product

+

$$\begin{array}{c} BrH_2C \\ \\ BrH_2C \end{array} C=C \begin{array}{c} CH_2Br \\ \\ CH_2Br \end{array}$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH-CH_2 \\ \qquad \qquad \overset{|}{Br}$$

Several Steps
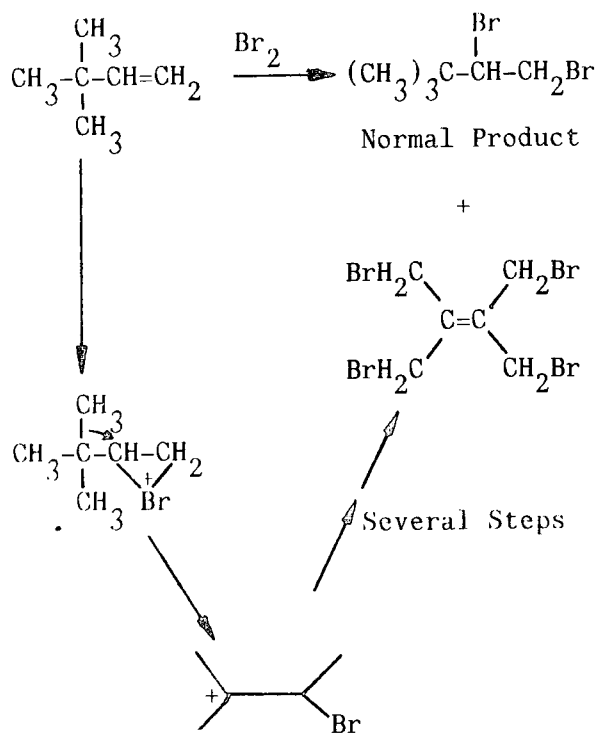
Scheme 49

Pocker and Stevens[63] 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[64] examined the addition of iodine azide to a number of alkenes. Regiospecific addition was observed and accounted for by a bridging iodium 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[64] believed this was due to steric

factors (Scheme 50). Hassner et al.[65] recorded similar behaviour

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-C=CH_2 \xrightarrow{IN_3} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}\underset{\overset{\displaystyle I}{\diagup}}{\overset{\displaystyle +}{\diagdown}}CH_2 \longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle I}{|}}{C}}-\overset{}{\underset{\underset{\displaystyle N_3}{|}}{C}}H_2$$
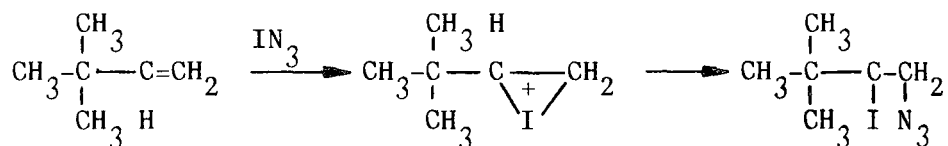
Scheme 50

when examining the addition of iodine isocyanate to 3,3-dimethyl-
but-1-ene, which yielded (3,3-dimethyl-2-iodo)butyl isocyanate.

Diner and Lown[66] 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[67] gave no rearrangement products,

whilst the reaction of CF_3I and CCl_3Br with 3,3-dimethylbut-1-ene[68]

gave the Markownikov products: 1,1,1-trifluoro-3-iodo-4,4-dimethyl-

pentane, and 1,1,1-trichloro-3-bromo-4,4-dimethylpentane (Scheme 51).

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH=CH_2 + CF_3I \longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle I}{|}}{C}}-CH_2CF_3$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH=CH_2 + CCl_3Br \longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_2CCl_3$$
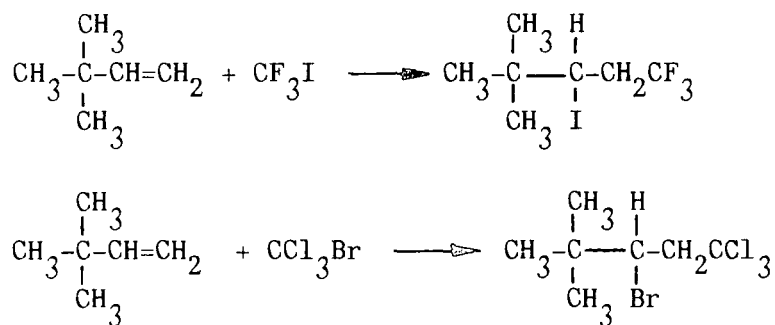
Scheme 51

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 ^{1}H n.m.r.: 2-(2,3,3-trimethylbut-1-enyl)-

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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-

naphtho[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).
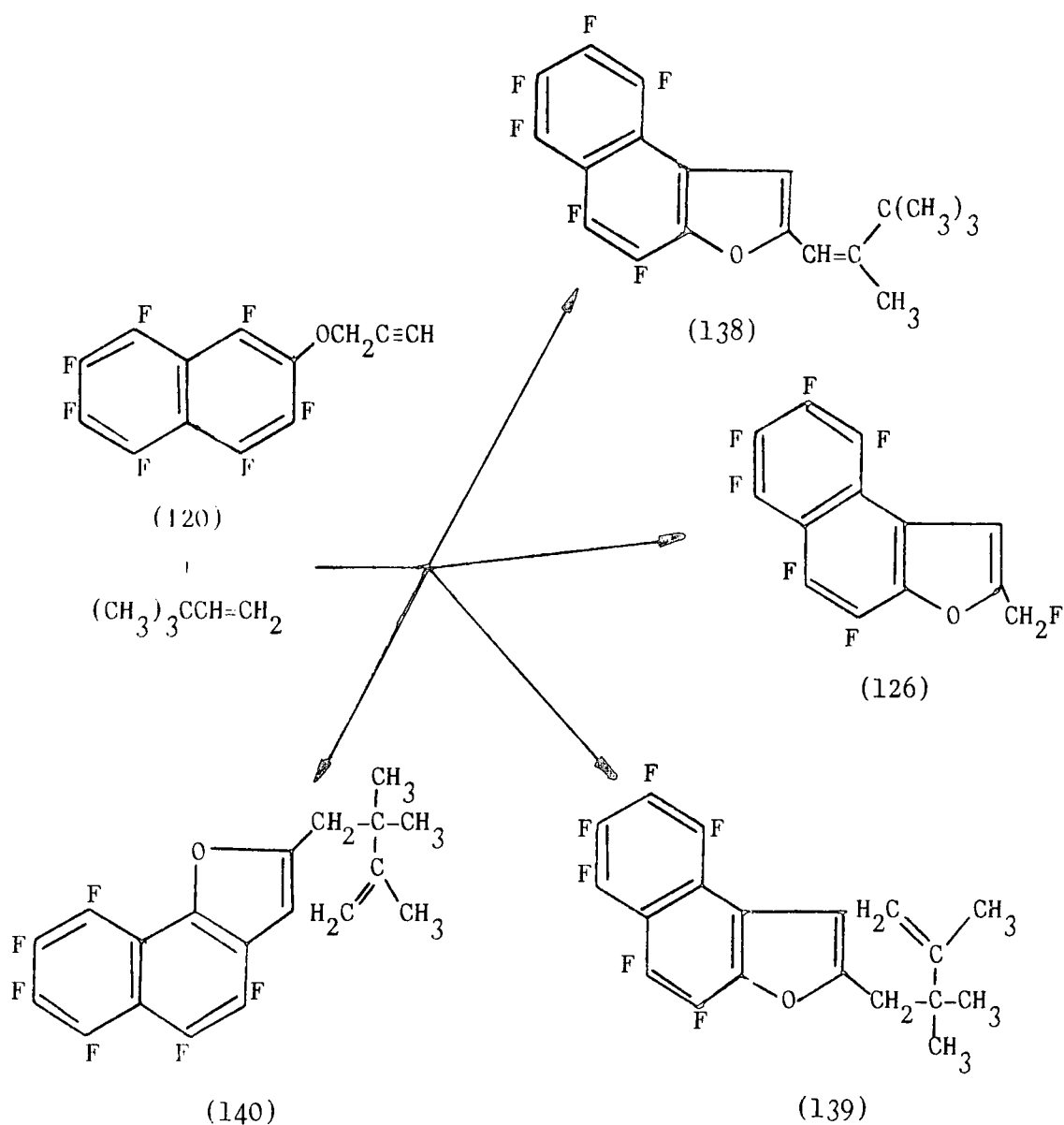
Scheme 52

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°, 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 <u>same</u> 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 <u>and</u> 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· 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 ^{1}H 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}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 qualities 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° 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).

(126)

+

$(CH_3)_2C=C(CH_3)_2$

OR

$(CH_3)_3C-CH=CH_2$

(138)

(126) ∿ 50%

(139)
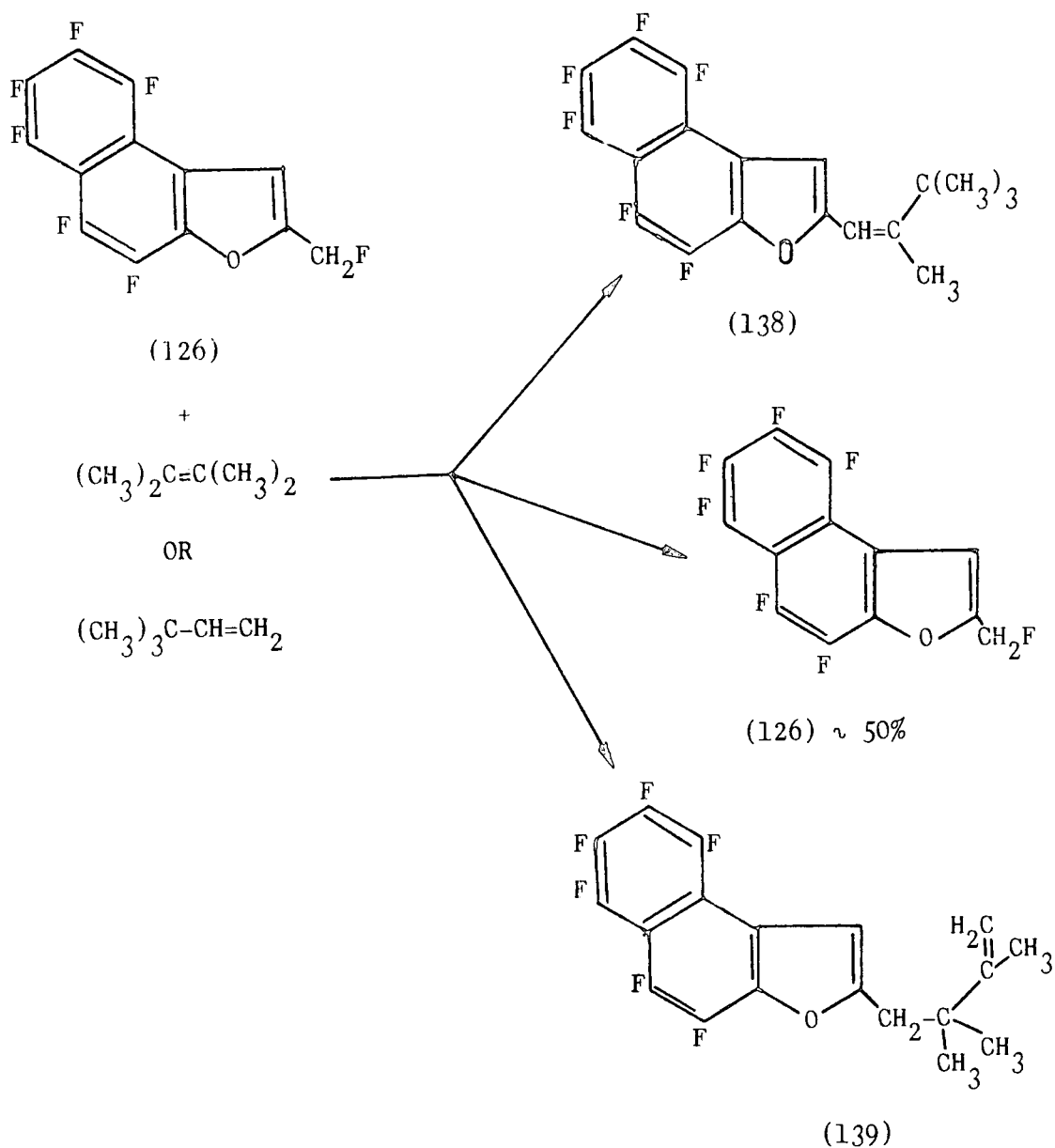
Scheme 53

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)[69]
Alkene	$(CH_3)_2C=C(CH_3)_2$	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

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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-hexa-
fluoronaphtho[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}H n.m.r. spectra
observed in the reactions of both (120) and (126) with 3,3-dimethyl-
but-1-ene were identical in almost every detail, whilst the ^{1}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-Hepta-
fluoro-2-naphthyl Prop-2-ynyl Ether and 2-Fluoromethyl-
4,5,6,7,8,9-hexafluoronaphtho[2,1-b]furan with 2,3-Dimethyl-
but-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· or R^fCH_2· (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 (138) and (139)

should not have been among the five possible products which could

arise via an initial Markownikov addition (Scheme 54). When, however,

Scheme 54

- 65 -
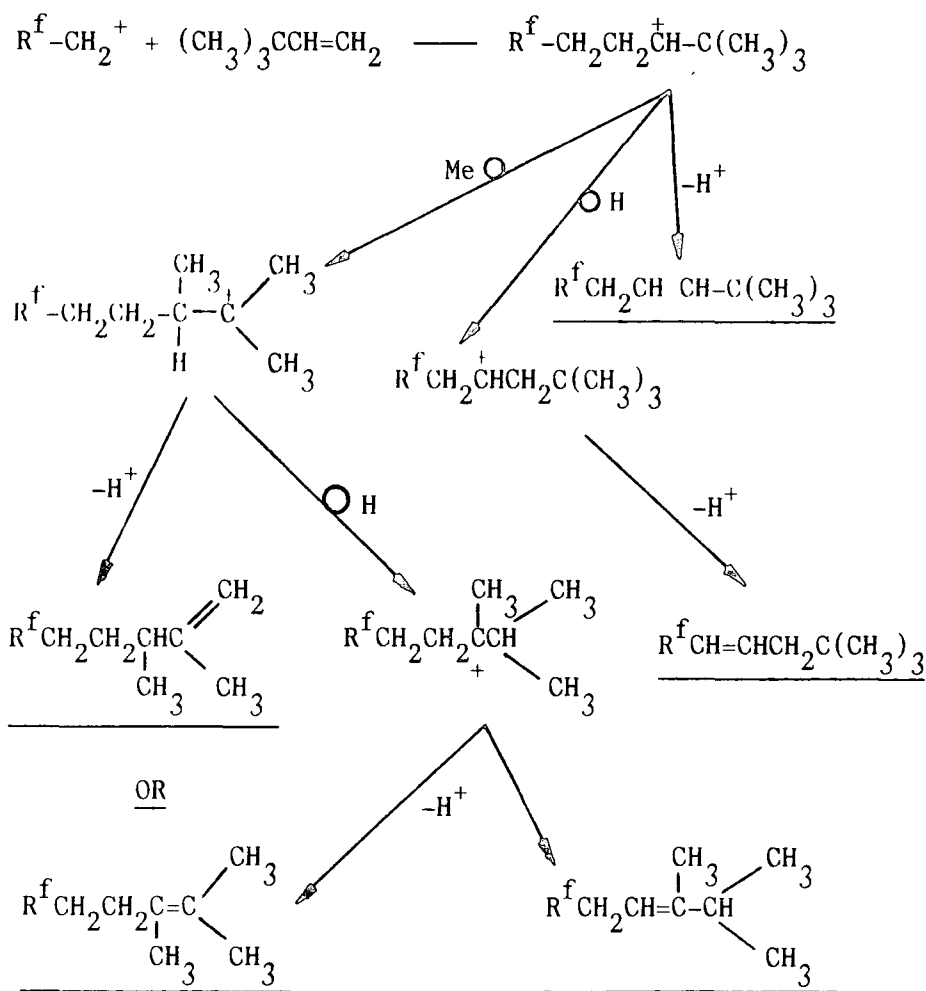
anti-Markownikov addition of R^f = 4,5,6,7,8,9-hexafluoronaphtho[2,1-b]-furan $R^fCH_2^{\cdot}$ (136) was considered the formation of the actual products (138) and (139) was easily rationalized (Scheme 55).

$$R^f-CH_2^{\cdot} \quad + \quad (CH_3)_3CCH{=}CH_2 \quad \longrightarrow \quad R^f-CH_2-CH{\Big\langle}{\overset{\overset{\textstyle \cdot}{CH_2}}{C(CH_3)_3}}$$

(143)

$$\Big\downarrow \overset{O}{\underset{H}{\parallel}}$$

$$R^f-CH_2-\overset{+}{\underset{}{C}}{\Big\langle}{\overset{CH_3}{\underset{C(CH_3)_3}{}}}$$

$$R^f-CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{+}{\underset{}{C}}{\Big\langle}{\overset{CH_3}{\underset{CH_3}{}}} \quad \underset{\overset{O}{\underset{Me}{}}}{\rightleftarrows}$$

(141)

$$\Big\downarrow -H^+ \qquad\qquad\qquad \Big\downarrow -H^+$$

(139)   (138)
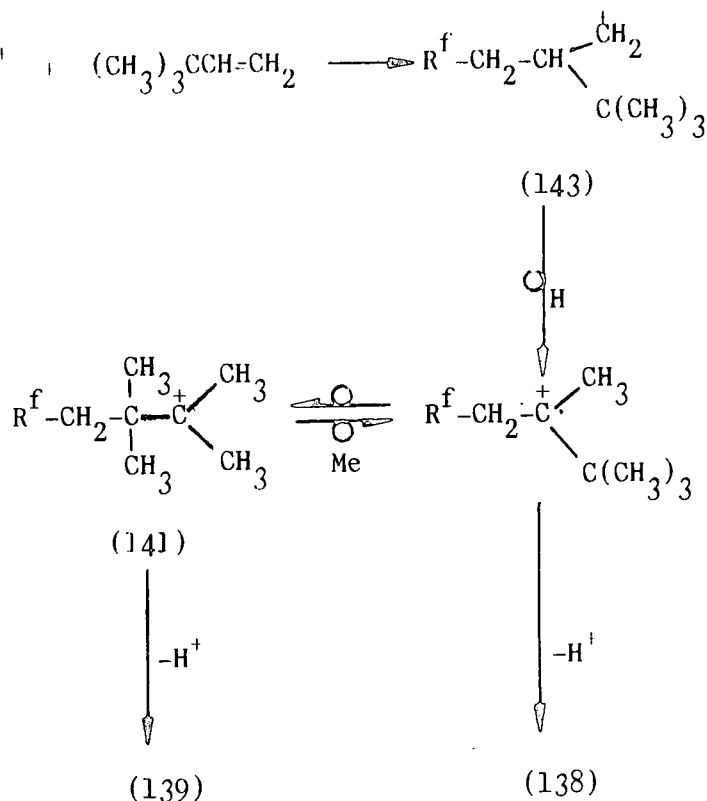
Scheme 55

If the initial attacking species is a radical, the $F^{\cdot}$ must add first followed by $R^f-CH_2^{\cdot}$ to give the anti-Markownikov adduct which then ionizes to yield the two alkenes (138) and (139) (Scheme 56). If

$$F^{\cdot} \quad + \quad (CH_3)_3C-CH{=}CH_2 \quad \longrightarrow \quad FCH_2-\overset{\textstyle \cdot}{C}H-C(CH_3)_3$$

$$\Big\downarrow R^fCH_2^{\cdot}$$

$$\overset{H_2CR^f}{\underset{|}{}}$$

(Scheme 55) (138) + (139) $\longleftarrow$ $FCH_2-CH-C(CH_3)_3$

(144)
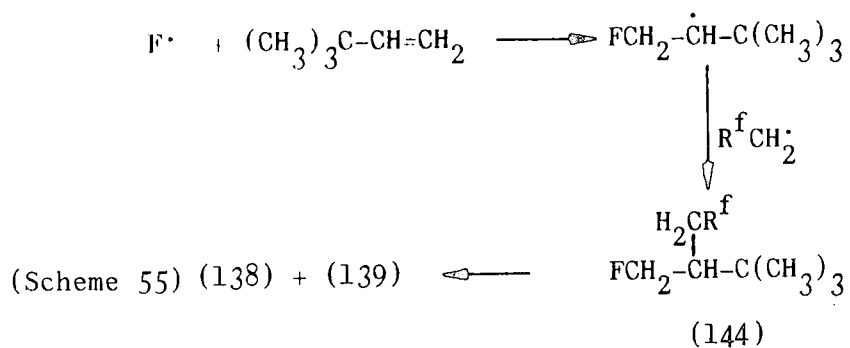
Scheme 56

$R^fCH_2^{\cdot}$ (135) were to add first then the same problems, observed when carbocation attack on 3,3-dimethylbut-1-ene was considered, would arise (Scheme 57).

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(a) Markownikov addition.

$$R^f CH_2^{\cdot} \;+\; (CH_3)_3CCH\!=\!CH_2 \longrightarrow R^f\!-\!CH_2CH_2\!-\!\overset{\cdot}{\underset{H}{C}}\!-\!C(CH_3)_3$$

$$\Big\downarrow F^{\cdot}$$

$$R^f CH_2CH_2\overset{+}{C}HC(CH_3)_3 \;\xleftarrow{\;-F^-\;}\; R^f\!-\!CH_2CH_2\!-\!\overset{F}{\underset{H}{C}}\!-\!C(CH_3)_3$$

$$\Big\downarrow$$

(Scheme 54)

(b) anti-Markownikov addition

$$R^f\!-\!CH_2^{\cdot} \;+\; (CH_3)_3CCH\!=\!CH_2 \longrightarrow R^f\!-\!CH_2\!-\!\overset{H}{\underset{C(CH_3)_3}{C}}\!-\!\overset{\circ}{C}H_2$$

$$\Big\downarrow F^{\cdot}$$

$$\text{(Scheme 55)} \xleftarrow{} \text{(143)} \xleftarrow{\;-F^-\;} R^f\!-\!CH_2CH\!\!\begin{array}{c} ^{CH_2F} \\ _{C(CH_3)_3} \end{array}$$
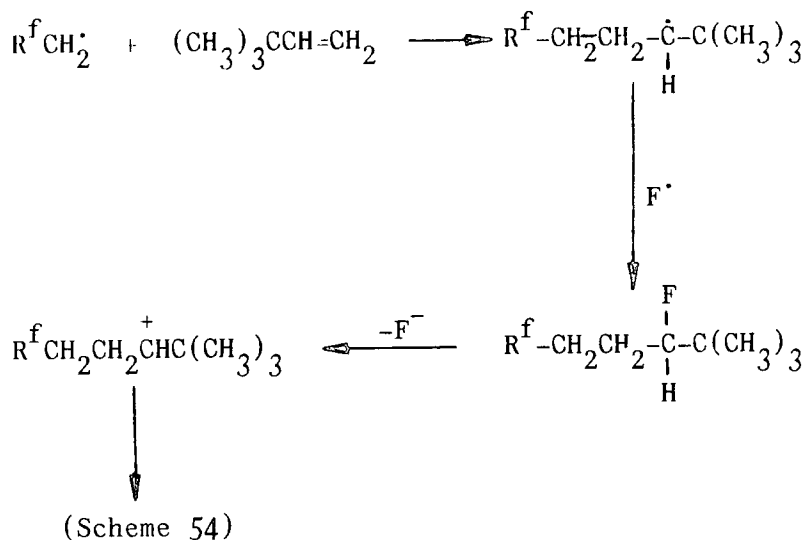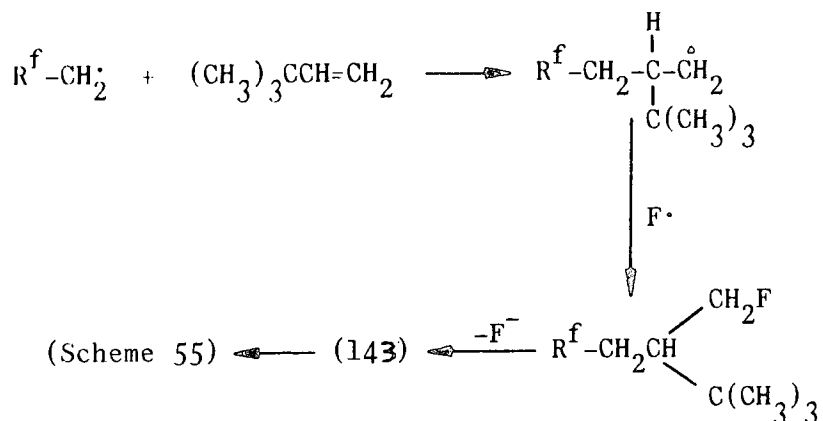
Scheme 57

In the preceding paragraphs and schemes there has been an emphasis on the need for anti-Markownikov addition, whether it be to produce either a carbocation or an adduct. One interesting example of this was found in the literature: the addition of $CH_3OCH_2^+$ cation to 3,3-dimethylbut-1-ene which gave rise to both Markownikov and anti-Markownikov addition products (Scheme 58).[70] These results are surprising as there would seem to be no possibility of bridging similar to that observed when addition to 3,3-dimethylbut-1-ene involved halogenonium ions, where anti-Markownikov products are formed (see Scheme 50). It is possible however to invoke a transition state for

$$Cl \quad CH_2OCH_3$$
$$(CH_3)_3C-CH-CH_2 \xrightarrow{KOH} (CH_3)_3CCH=CHCH_2OCH_3$$

$$(CH_3)_3CCH=CH_2$$

$$+$$

$$Cl-CH_2OCH_3 \xrightarrow{ZnCl_2}$$

$$(CH_3)_3C-CH-CH_2Cl \xrightarrow{KOH} (CH_3)C-C=CH_2$$
$$\qquad\quad CH_2OCH_3 \qquad\qquad\qquad CH_2OCH_3$$
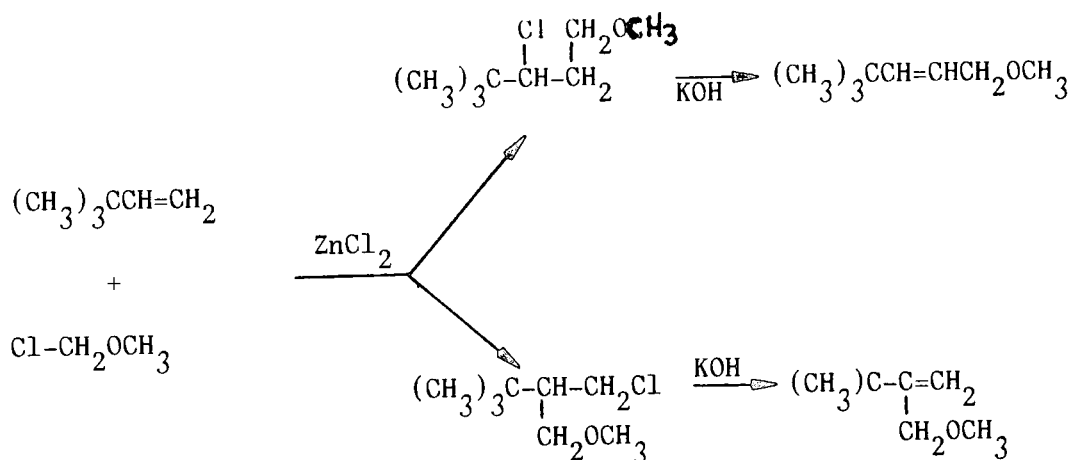
Scheme 58

the reaction, illustrated in Scheme 58, which could be seen as a form of bridging intermediate[71] (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

$$(CH_3)_3CCH=CH_2$$

$$+$$

$$Cl-CH_2OCH_3$$

$$\longrightarrow$$

$$\begin{array}{c} H \\ | \quad + \\ (CH_3)_3C-C-CH_2 \\ | \quad O \\ H_2C-O-CH_3 \end{array}$$

STABILISATION

$$(CH_3)_3C-CH-CH_2Cl$$
$$\qquad\quad CH_2OCH_3$$
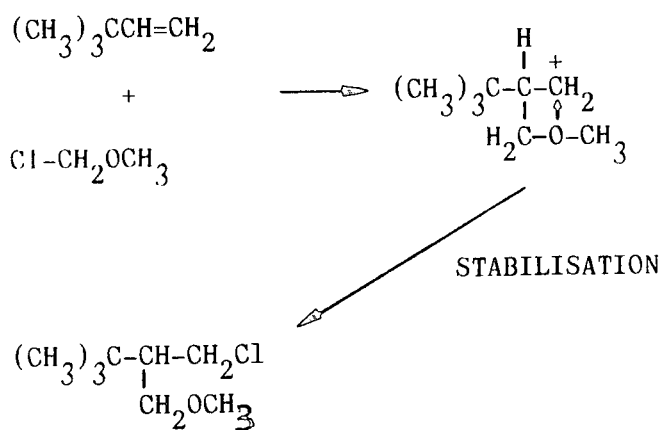
Anti-Markownikov addition

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

(145: Stabilisation of Charge)
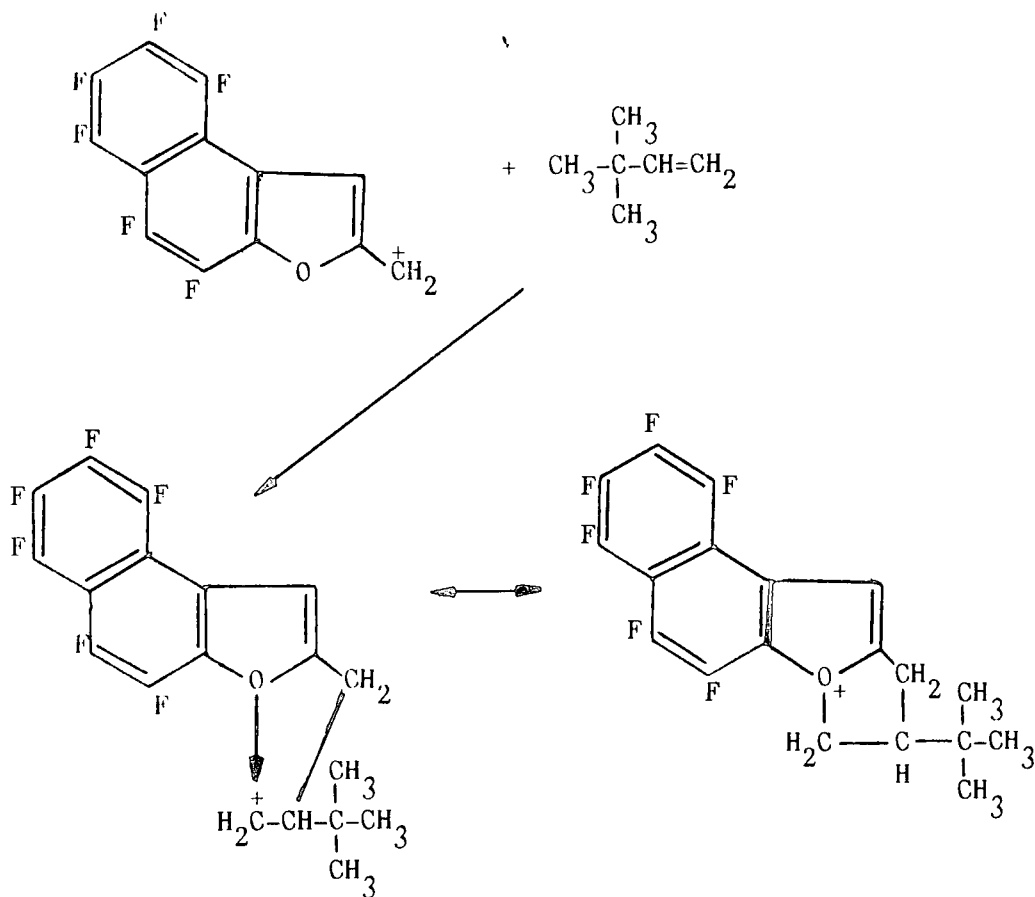
Scheme 60

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,[57-59] 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· 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);

- 69 -

if a radical mechanism is invoked then there can be initial attack by either F· or R^fCH_2· (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,[70] 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· 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 intra-molecular 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-dimethyl-but-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° 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 ^{1}H 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-hexa-fluoronaphtho[2,1-b]furan (137) was isolated. M.pt. 83-84°; (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.; δ_H CDCl$_3$ 1.17 - 1.13 (t. C$\underline{H}_2$-C$\underline{H}_3$), 2.15 (s. -C$\underline{H}_3$), 2.32 - 2.25 (q. -C$\underline{H}_2$-CH$_3$), 6.26 (s. vinylic C$\underline{H}$), 7.07 - 7.09 (t. 3-furanyl C$\underline{H}$); δ_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. ≡
7.8 g.) were sealed in a nickel lined Carius tube and heated at 150°
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° (Found: C, 61.53; H, 3.81; $C_{19}H_{14}F_6O$
requires C, 61.30; H, 3.76%); M^+ 372 a.m.u.; δ_H CDCl$_3$ 1.19 (s.
3 x C$\underline{H}_3$), 2.13 (d. C$\underline{H}_3$), 6.38 (s. vinylic C$\underline{H}$), 7.12 (t. 3-furanyl C$\underline{H}$);
δ_F CDCl$_3$ 145 - 146.5 (b.m.), 150.9(m), 158.2 - 158.9 (b.m.) (p.p.m.
upfield from internal CFCl$_3$) in the ratio 2:1:3 respectively;
single peri J_{F-F} 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° (Found: C, 61.17; H, 3.82; $C_{19}H_{14}F_6O$
requires C, 61.30; H, 3.76%), M^+ 372 a.m.u.; δ_H CDCl$_3$ 1.19 (s.
2 x C$\underline{H}_3$), 1.86 (d of d C$\underline{H}_3$), 2.95 (s. -C$\underline{H}_2$-), 4.72, 4.77 (d. = C$\underline{H}_2$),
6.96 (t. 3-furanyl C$\underline{H}$); δ_F CDCl$_3$ 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$_3$) in the ratio 2:1:3 respectively; single peri J_{F-F} 50 Hz.
The slowest of the faster moving components was 2-(2,2,3-trimethyl-
but-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; $C_{19}H_{14}F_6O$ requires
C, 61.30; H, 3.76%); M^+ 372 a.m.u.; δ_H CDCl$_3$ 1.19 (s. 2 x C$\underline{H}_3$),
1.88 (d of d C$\underline{H}_3$), 2.96 (s. -C$\underline{H}_2$-), 4.69, 4.75 (d. = C$\underline{H}_2$), 6.66

(s. 3-furanyl CH); δ_F 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

CFCl$_3$) in the ratio 1:2:1:2 respectively; single peri J$_{F-F}$ 68 Hz.

Determination of Isomer Ratios

Two further experiments were undertaken to calculate yields of

materials and determine (as calculated by [1]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. ≡ 7.09 g.) were thermolysed. The main products

(0.894 g., 45%) were collected and the mixture analysed by [1]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. ≡ 7.09 g.) were thermolysed. The main products (2.78 g., 54%)

were collected and the mixture analysed by [1]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. ≡

7.8 g.) were sealed in a nickel lined Carius tube and heated at 150°

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]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}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° 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. ≡

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}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. ≡ 7.09 g.) were sealed in a nickel lined Carius tube

and heated at 150° 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[72] of silica using 30/40 petroleum ether as an eluant.

One main fraction of faster moving components (0.325, 58%) was

obtained, ^{1}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}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. ≡ 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[72] 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 [1]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. ≡ 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[72] column of silica with 30/40 petroleum ether. The mixture was analysed by [1]H n.m.r. and the isomer ratios of (138)

and (13ϕ) 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.[69]

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 cm.$^{-1}$ (2.5 -

                         50 microns).

N.m.r.:   Varian EM360 nuclear magnetic resonance

                         spectrometer (^{1}H 60 MHz, ^{19}F 56.46 MHz).

                         Brüker WX90E nuclear magnetic resonance

                         spectrometer modified for Fourier

                         transform pulsed operation (^{1}H 90 MHz,

                         ^{19}F 84.68 MHz).

                         Brüker WH360 nuclear magnetic resonance

                         spectrometer (^{1}H 360 MHz).

Mass spectroscopy: AEI MS9 mass spectrometer with data system.

Elemental analysis: Perkin-Elmer 240 C,H,N elemental analyser.
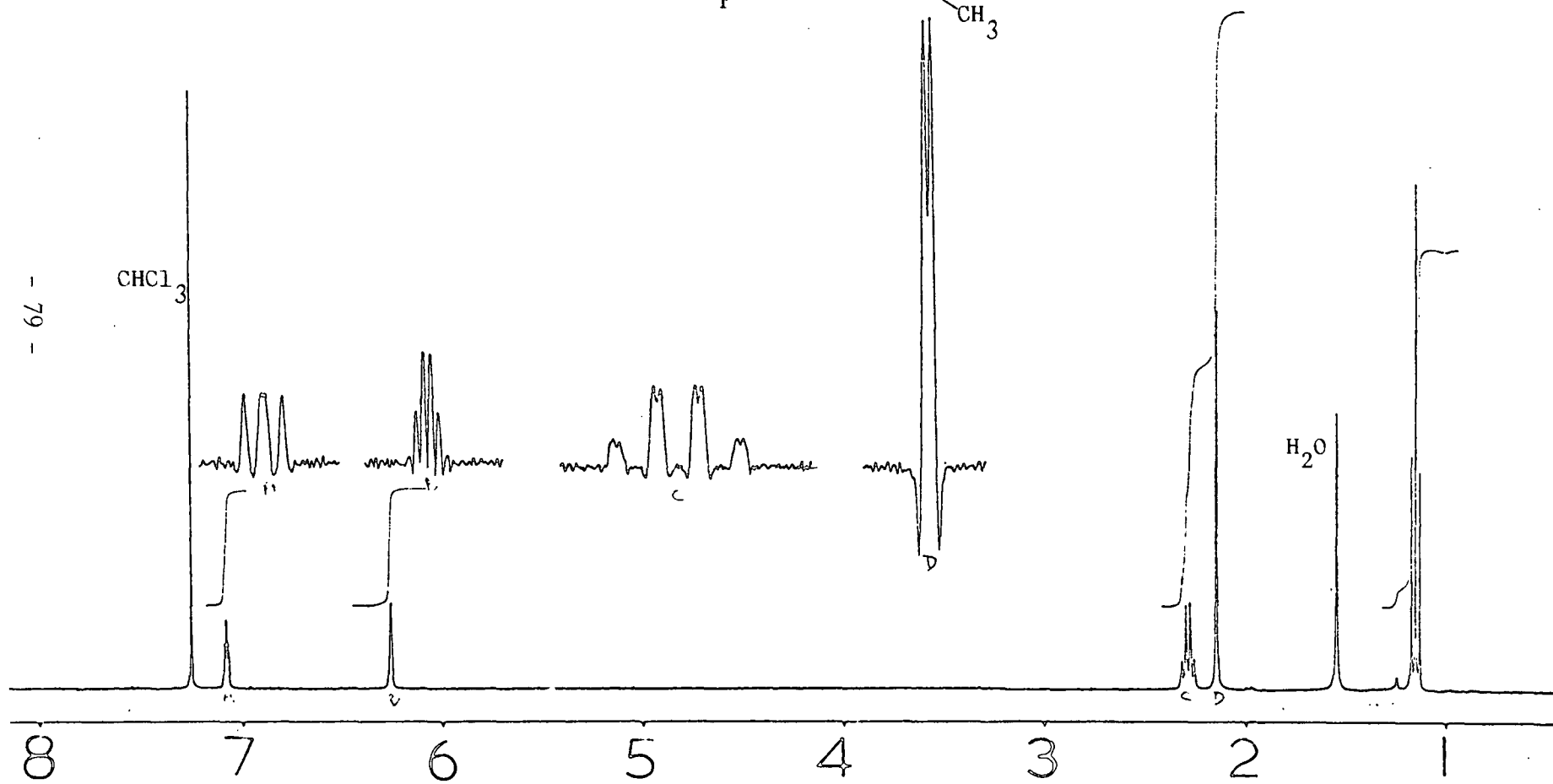
Proton n.m.r. spectra used in the identification of the alkenes

(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-hexa-

fluoronaphtho[2,1-b]furan (138).

Spectrum III: 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexa-

fluoronaphtho[1,2-b]furan (140).

Spectrum IV: 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexa-

fluoronaphtho[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

CHCl$_3$

H$_2$O

SPECTRUM II

C(CH₃)₃ → $C(CH_3)_3$

CH=C

CH₃ → CH_3

F F F F F F (structure labels)

CHCl₃ → $CHCl_3$

H₂O → H_2O

8   7   6   5   4   3   2   1

SPECTRUM III

CHCl$_3$

H$_2$O

SPECTRUM IV

SPECTRUM V

CHCl₃

8   7   6   5   4   3   2   1

SPECTRUM VI

CHCl$_3$

8   7   6   5   4   3   2   1

The Isomer Ratio Calculation Spectrum for the Reaction of 2,3-Dimethylbut-2-ene and the 2-Fluoromethyl Compound (126)

SPECTRUM VII

CHCl$_3$

TMS

SPECTRUM VIII

CHCl₃

TMS

8   7   6   5   4   3   2   1   0
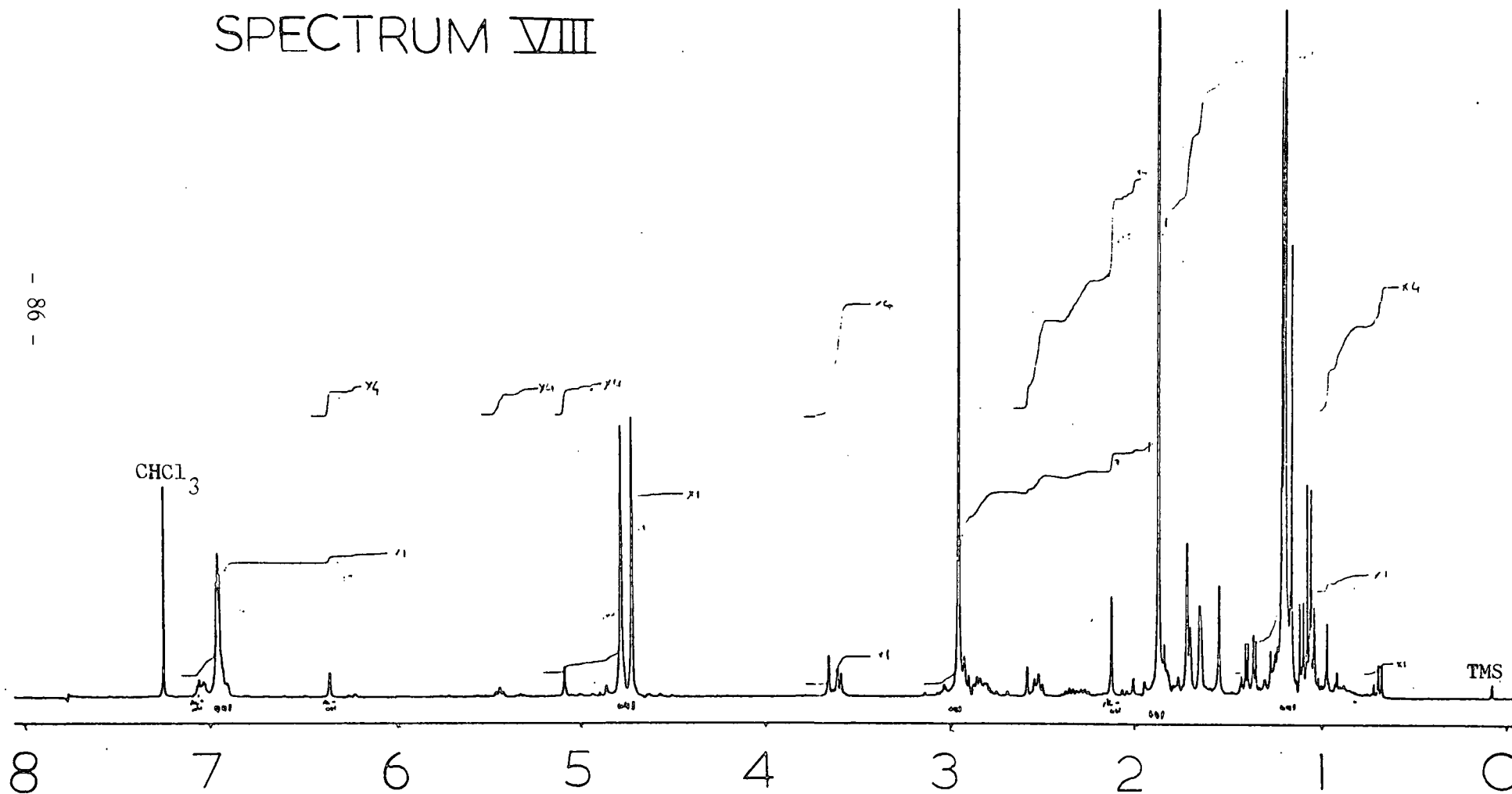
Infra-red analyses of the alkenes (137 - 140) and of 2,3,5,6-
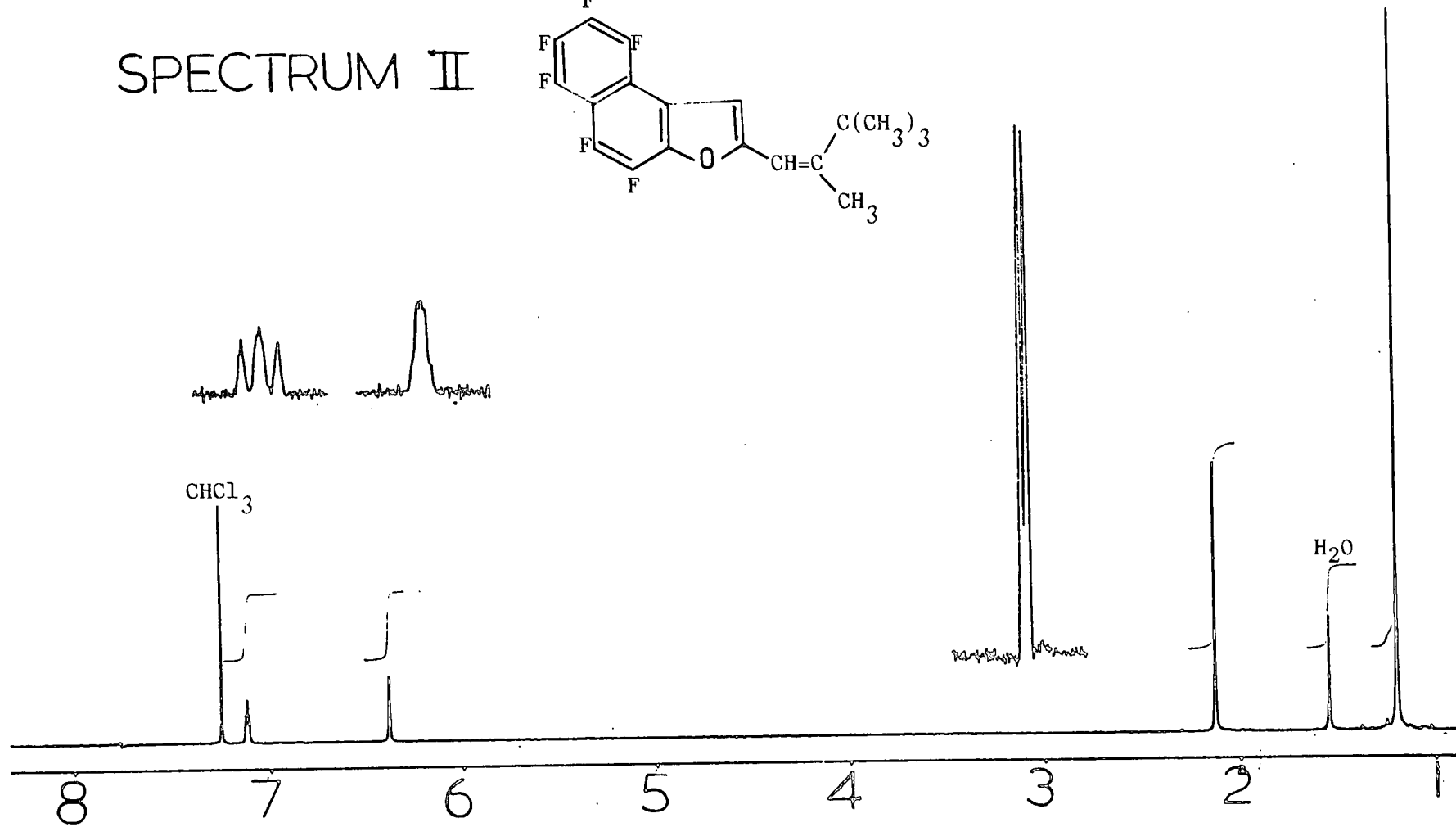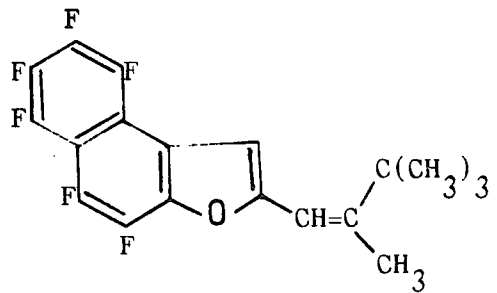tetrafluoro-4-pyridyl prop-2-ynyl ether (131)

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-hexa-
fluoronaphtho[2,1-b]furan (138), nujol mull.

Spectrum III: 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexa-
fluoronaphtho[2,1-b]furan (139), nujol mull.

Spectrum IV: 2-(2,2,3-trimethylbut-3-enyl)-4,5,6,7,8,9-hexa-
fluoronaphtho[1,2-b]furan (140), liquid film.
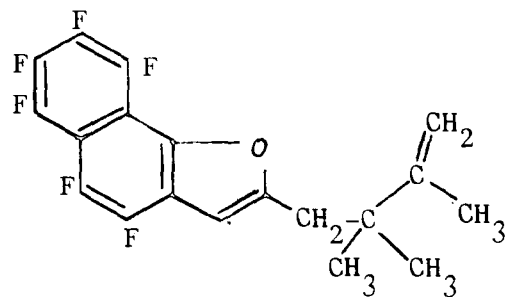
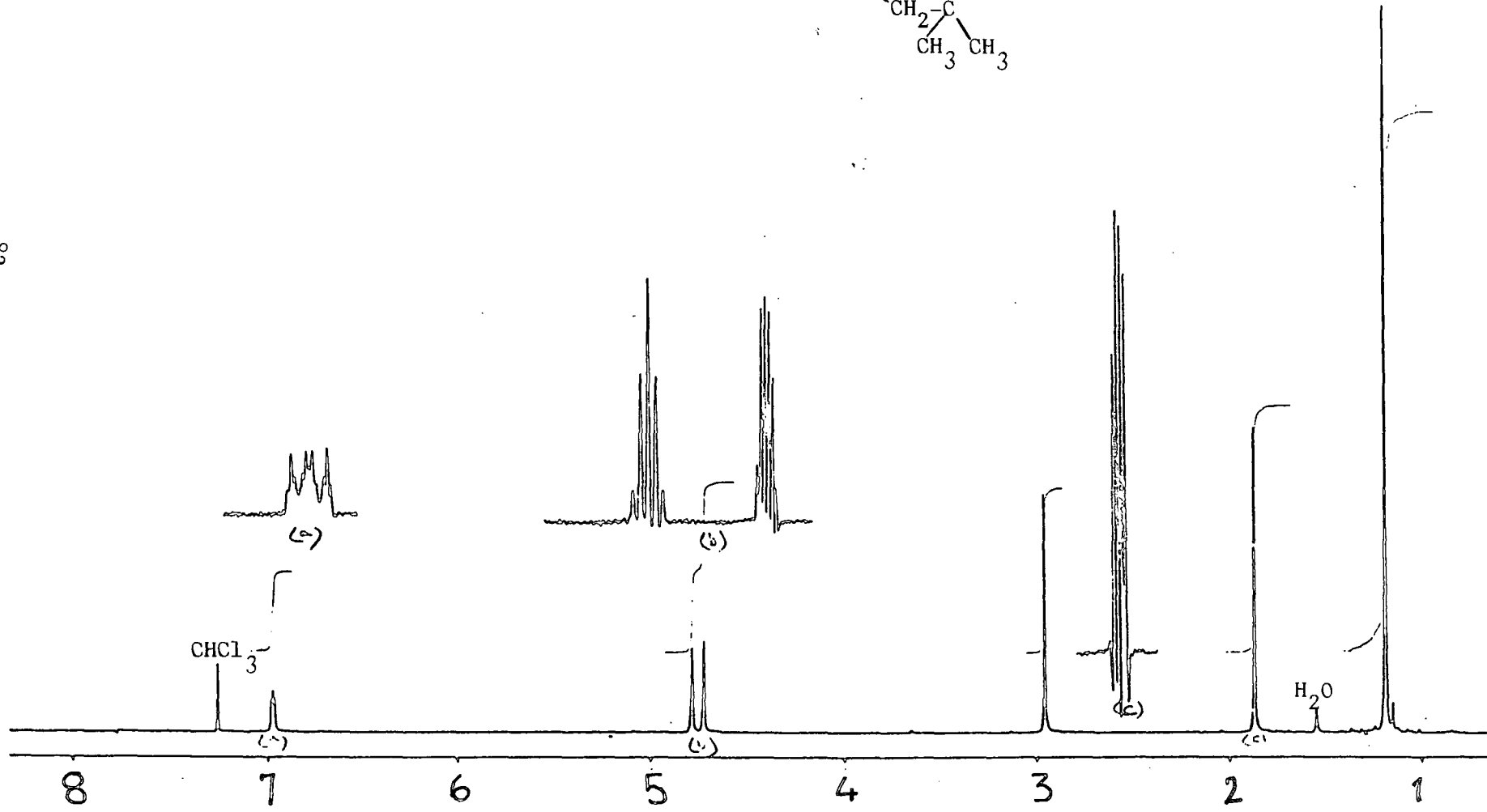Spectrum V: 2,3,5,6-tetrafluoro-4-pyridyl prop-2-ynyl ether
(131), liquid film.

SPECTRUM I

SPECTRUM II

SPECTRUM III

SPECTRUM IV

SPECTRUM V

2·5   3·0   4·0   5·0 Microns   6·0   7·0   8·0   9·0   10   12   14   16   18   25   30   40
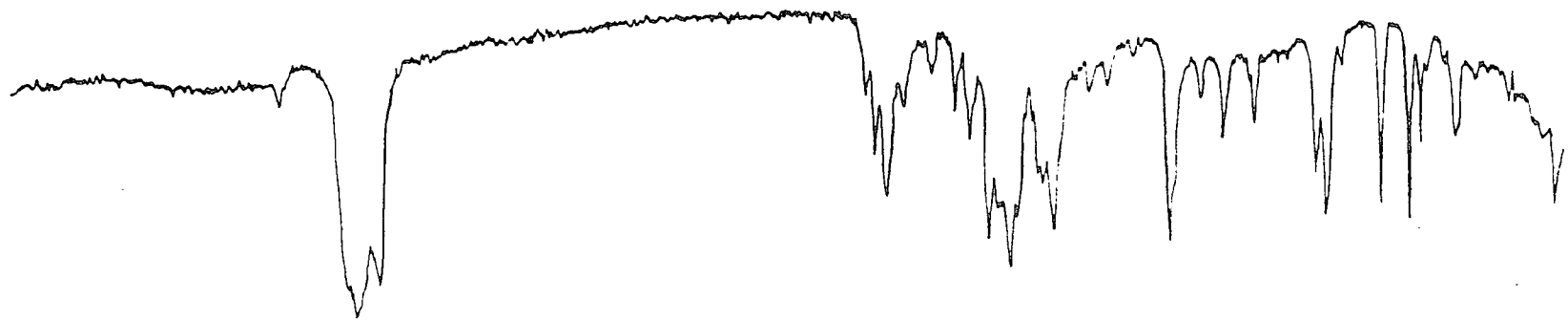
4000   3500   3000   2500   2000   1800   1600   1400   1200   1000   800   600   400   250
CM⁻¹

- 68 -
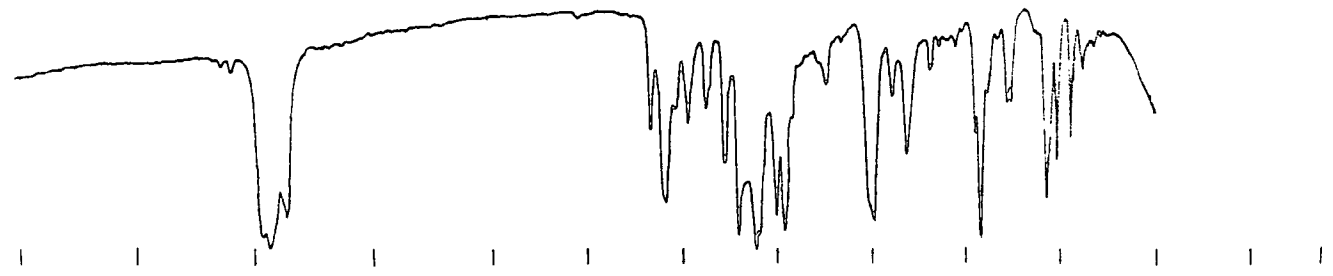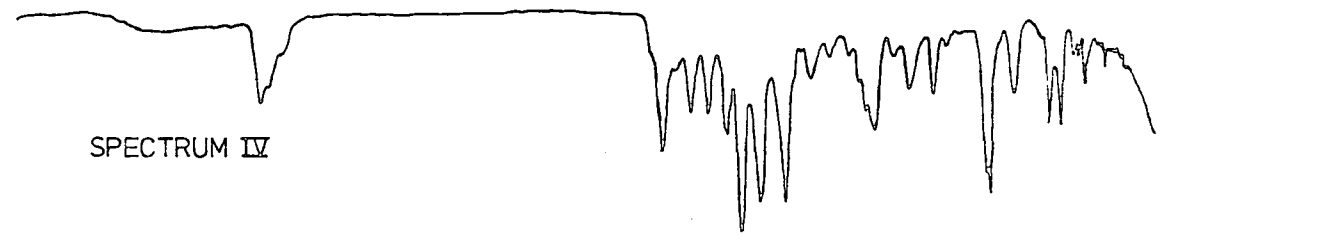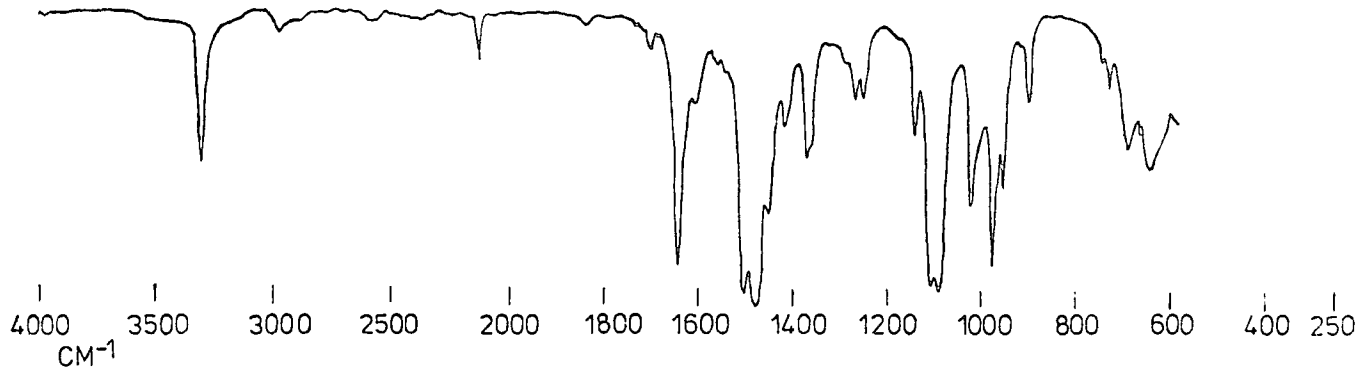
APPENDIX IV

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*   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 γ-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. 'ine 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 Supracritical 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. Pietrzykȯwski (Technical University of Warsaw/ University of Strathclyde): 'Synthesis, Structure and Properties of Alumin⁻xanes'.
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

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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'.

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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'.

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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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